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Fluorocarbons and the Environment

Report of Federal
Task Force on
Inadvertent
Modification of
the Stratosphere
(IMOS)
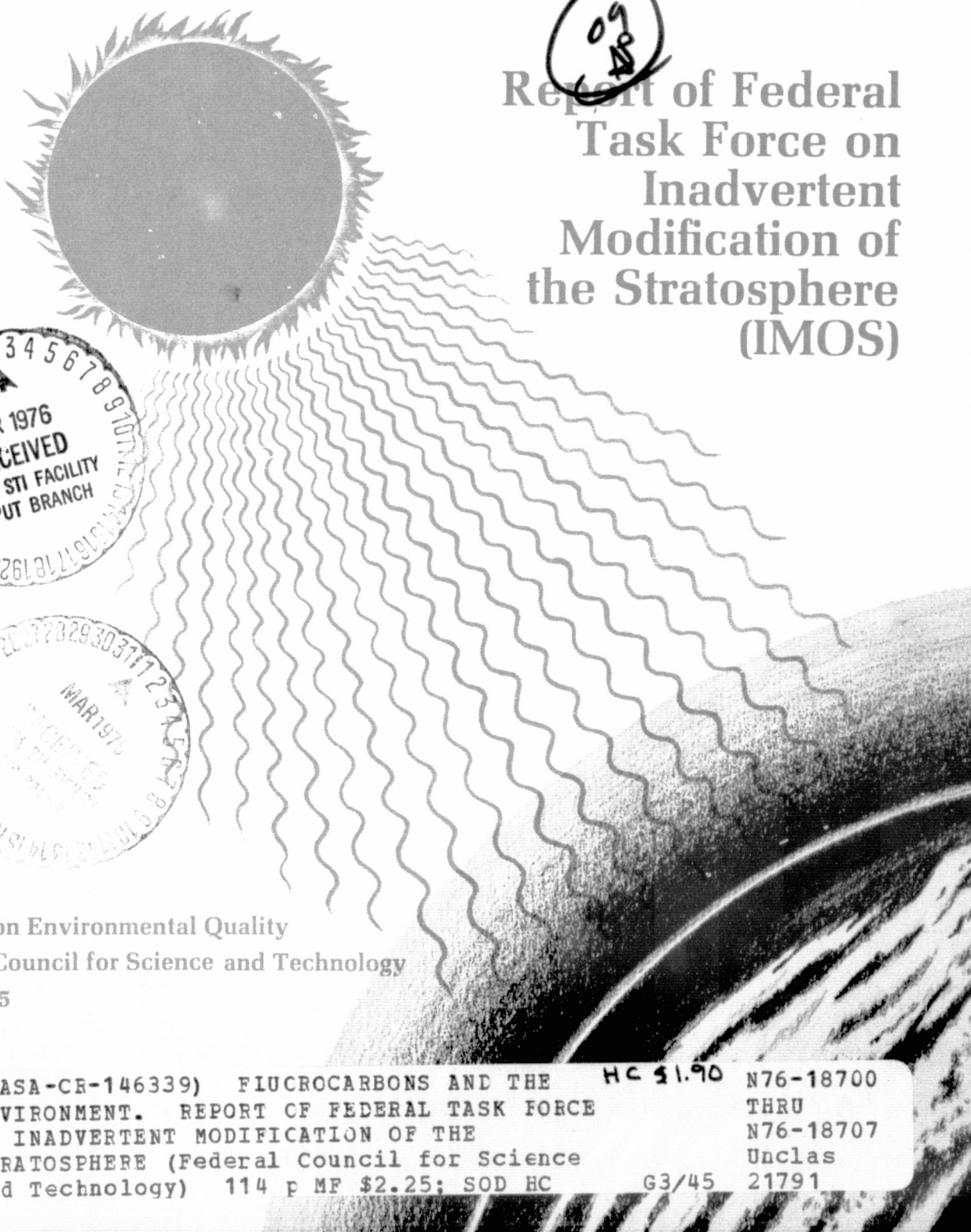
Council on Environmental Quality
Federal Council for Science and Technology
June 1975

The first scientific report expressing concern over possible significant reductions in stratospheric ozone from fluorocarbon releases to the environment was published in June 1974, just 1 year ago. Since that time various scientific, legislative, and other private and public bodies have expressed similar concern.

In January 1975 the Council on Environmental Quality (CEQ) and the Federal Council for Science and Technology (FCST) jointly created the Federal Interagency Task Force on Inadvertent Modification of the Stratosphere (IMOS). This ad hoc group includes the major Federal bodies with relevant research or regulatory responsibilities: the Departments of Agriculture; Commerce; Defense; Health, Education, and Welfare; Justice; State; Transportation; and the Consumer Product Safety Commission; Energy Research and Development Administration; Environmental Protection Agency; National Aeronautics and Space Administration; National Science Foundation; and Interdepartmental Committee for Atmospheric Sciences (ICAS).

The area of study for the group, as reflected in its title, is all potential sources of stratospheric modifications from human activities. Its initial charge, however, was to conduct an intensive study of the fluorocarbon-ozone question within several months, culminating in this report.

The task force has concluded that fluorocarbons released to the environment are a legitimate cause for concern. It also has concluded 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 to the atmosphere.

The National Academy of Sciences is currently conducting an in-depth scientific study of man-made impacts on the stratosphere and will report in less than a year. If the National Academy of Sciences confirms the current task force assessment, the task force recommends that the Federal regulatory agencies initiate rulemaking procedures for implementing regulations to restrict fluorocarbon uses. Such restrictions could reasonably be effective by January 1978—a date that, given the concern expressed now, should allow time for consideration of further research results and for the affected industries and consumers to initiate adjustments.

Other conclusions and recommendations of the task force relate to the expected effects of any reduction in the average ozone concentration in the stratosphere; the need for labeling of aerosol products containing fluorocarbons; the present Federal authorities under which various regulatory actions could be initiated; the need for toxic substances control legislation; the need for international cooperation; and the Federal research program for addressing the scientific and socio-economic issues.

We believe that the report represents a balanced, objective view of current understanding of the problem, and we heartily endorse the conclusions reached by the task force.

This report resulted from many contributions from individual task force members, but represents the collective assessment and recommendations of the group as a whole and has the full knowledge and concurrence of the agencies and groups they represent. It is anticipated that the research and policy actions recommended in this report will be pursued by these agencies.
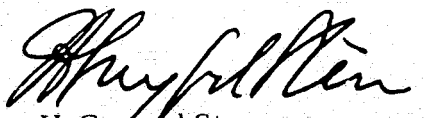
The report is not intended to provide the final answers on this subject. New scientific findings and economic analyses are appearing every day.[1] The information given here is believed current as of May 15, 1975. The program of future intensive study by the Federal agencies, industry, the National Academy of Sciences, and other groups will serve to update understanding of the stratosphere, of effects of stratospheric change, and of economic and social issues. These findings will be crucial in determining the precise course of action to be followed in regard to fluorocarbon production and use.
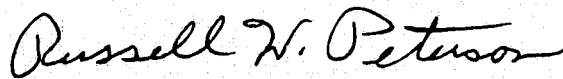
This analysis of the relationship of fluorocarbons to stratospheric ozone reduction is presented in the general context of other possible chemicals that could behave similarly. Although fluorocarbons by comparison seem to warrant the concern expressed in this report, the IMOS task force has not attempted to reach any conclusions at this time about any other possible man-made sources of stratospheric change. These other possible sources will be subjects for further studies by the task force upon the completion of this report.

Other related matters that are not being addressed by this task force include alleged disadvantages of fluorocarbons or fluorocarbon products that do not pertain to the stratosphere—e.g., any direct health or safety hazards to the individual user of aerosol products, cost considerations, or disposal problems.

The report consists of an executive summary, which is an abstract of the whole report; a conclusions and Federal actions section addressing the magnitude and nature of the potential problem and the proposed Federal program of action; and more detailed sections treating the scientific findings concerning the stratospheric, agricultural and biological effects of ozone reduction, human health effects, and industrial and economic considerations. The stratospheric effects section (III) is based on a more detailed report by the Interdepartmental Committee for Atmospheric Sciences (*The Possible Impact of Fluorocarbons and Halocarbons on Ozone*, Report No. 18a), which is available through the Executive Secretary of ICAS, Room 312, National Science Foundation, 1800 G Street N.W., Washington, D.C. 20550.

We hope this report will be widely read not only by the scientific community, but also by the general public.

H. Guyford Stever
Chairman, Federal Council for
   Science and Technology

Russell W. Peterson
Chairman, Council on
   Environmental Quality

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[1] For example, preliminary results of studies by the Department of Commerce were received too late for analysis by the task force or for incorporation into this report. Additional data are also expected to be received from Arthur D. Little, Inc., for the Environmental Protection Agency.

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Acknowledgments

Contents

I.

Executive Summary

One year ago the first scientific paper was published that postulated serious damage to the earth's ozone shield in the stratosphere as a result of the use on earth, and release to the atmosphere, of certain man-made fluorocarbon compounds,[1] used widely as refrigerants, as propellants for aerosol products, and for other uses. Calculations reported in that paper led the authors to believe that fluorocarbons-11 and -12 (F-11 and F-12), developed and valued largely because of their useful chemical properties, apparently are not destroyed in chemical reactions in the lower atmosphere but slowly diffuse upward into the upper atmosphere. Upon reaching the stratosphere,[2] they are decomposed by ultraviolet (UV) radiation from the sun, with the resulting release of free chlorine atoms. The free chlorine atoms then act to decrease gradually the average concentration of ozone by means of catalytic chain reactions. These chlorine chain reactions are postulated to be three times more effective in reducing ozone than the similar processes of ozone destruction by nitrogen oxides (on a molecule for molecule basis), which have been of recent concern in conjunction with the effects of emissions from aircraft operating in or near the stratosphere.

Ozone is a form of oxygen that exists in minor quantities in the atmosphere; it is concentrated primarily in the stratosphere, where it is maintained in a dynamic equilibrium by natural processes through which it is continually being formed and destroyed. The principal reason why fluorocarbon releases to the atmosphere are considered to be of such potential importance is that a reduction in the average long-term concentration of ozone would result in an increase in the amount of harmful UV radiation reaching the earth's surface. In addition to postulated human health effects (such as increased incidence of skin cancer), it is feared that the growth and development of certain plant and animal species might be altered and that the balance of delicate ecosystems might be disturbed. Concern has also been expressed that significant changes in the stratosphere could affect the earth's climate.

The Interagency Task Force on Inadvertent Modification of the Stratosphere has conducted a 5-month intensive study of these matters. The general conclusions of the report are highlighted below; the conclusions and Federal actions are presented in more detail in Section II of the report and are drawn from the information presented in Sections III through VII.

STRATOSPHERIC EFFECTS

Although the theory of possible ozone reduction by F-11 and F-12 cannot presently be supported by direct atmospheric measurements, the matter has been carefully studied independently by many scientists. Thus far, the validity of the theory and the predicted amounts of ozone reduction have not been seriously challenged. More research is required and will be undertaken, but there seems to be legitimate cause for serious concern.

Fluorocarbons are produced in large quantities. World production of F-11 and F-12 (ex-

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[1] The term fluorocarbons, more specifically chlorofluorocarbons, or "Freons" (one of their trade names) refers to chlorofluoromethanes ($CF_x Cl_y H_z$) and other chlorofluoroalkanes. In this report, the terms "fluorocarbon-11 and fluorocarbon-12" refer to $CFCl_3$ and CF_2Cl_2, respectively, produced by any of the various manufacturers.

[2] The stratosphere starts between 8 km (26,000 ft) and 16 km (52,000 ft) above sea level, depending upon latitude, and continues up to approximately 50 km (160,000 ft).

cluding the U.S.S.R. and Eastern European countries) was 1.7 billion pounds in 1973, which represented an 11% growth over the 1972 production. Approximately 50% of that world production and use occurs in the U.S. Almost all are ultimately released to the atmosphere—sooner in the case of aerosols than in the case of refrigerants, which are released principally through leakage and at the time of recharging or eventual disposal of refrigeration and air-conditioning systems.

These fluorocarbons are found in the atmosphere in concentrations that seem consistent with the total world release to date. It is expected that a significant fraction of the total fluorocarbon release eventually reaches the stratosphere through atmospheric circulation and upward diffusion, and recent measurements have detected the presence of F-11 in the stratosphere. There are no known significant natural "sinks" (mechanisms for removal) for their destruction other than stratospheric processes.

Several scientists have independently calculated possible reductions in ozone concentration to date and expectations of future reductions based on alternate patterns of future release to the atmosphere. Despite varying assumptions, the findings of these scientists agree within about a factor of two. The best estimates are that past fluorocarbon releases to the atmosphere may have resulted in a reduction to date of between about 0.5 and 1% and possibly as large as 2% in the natural equilibrium ozone level. It is believed that even if no more F-11 or F-12 were released, the average ozone concentration in the stratosphere would continue to decrease and eventually undergo as much as a 1.3% to 3% reduction because of the delayed effects of past releases of fluorocarbons. An important aspect of the theoretical reduction of ozone by fluorocarbons is its projected decrease for about a decade after cessation of releases to the atmosphere, with very slow subsequent recovery to normal values taking place over as much as a century or more.

Other current calculations predict an eventual reduction of about 7% in the equilibrium ozone concentration, presuming a continuation of fluorocarbon release at the 1972 rate.

The validity of these calculations could be questioned if: (1) major unexpected natural sinks for chlorine atoms were discovered, or (2) large amounts of chlorine from natural sources were measured in the stratosphere, of such magnitude that would overwhelm the amounts attributed to man-made compounds and that were outside the range of present understanding of the dynamics of the stratosphere.

There are uncertainties in predicted values of reduction in ozone levels because of the uncertainties in estimated rates of mixing and transport in the stratosphere and in estimates of the chemical reaction rates for several reactions. The degree of uncertainty introduced from these estimates, however, does not seem to be sufficient, even under the best of circumstances, to eliminate the concern about past and future releases of fluorocarbons.

Ideally, the proof or rejection of the model calculations could be found in measurements of the change in the equilibrium ozone concentration in the stratosphere over time. However, there are natural variations in ozone concentration from day to day, between seasons, from year to year, and at different latitudes that are larger than those that could be attributed to fluorocarbon releases to date. A 5 to 10% average decrease, persisting and measured for several years, would be required before a change could be attributed to human activity with any reasonable statistical reliability. Ozone levels in the northern hemisphere seem to have increased by about 5 to 10% during the period 1955-1970. The ozone concentration, however, has been on the decline since 1970 (approximately 1 to 2%). These fluctuations probably represent primarily natural variations, possibly related to solar activity.

Although human-induced reductions in stratospheric ozone levels may be quite small when compared to natural fluctuations, these reductions may be of considerable significance because the average ozone concentration is affected; therefore, the cumulative exposure to UV-B radiation[3] over time would be increased.

Carbon tetrachloride (CCl_4) also has been measured in the troposphere in significant quantities and is a potential source of free

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[3] UV-B radiation is UV radiation at wavelengths from 280 to 320 nm (nm = nanometer = 10^{-9} meters).

chlorine in the stratosphere. It is suspected to have caused a 0.5 to 2% decrease to date in the equilibrium level of ozone. The extent to which its presence has arisen from natural or man-made sources (or both) has yet to be determined, however, and restrictions upon its use are believed to have resulted in recent substantial decreases in the amounts released to the atmosphere. Nonetheless, it may be of stratospheric concern, and will require additional study. Other man-made chemicals may be of concern with respect to possible reduction of stratospheric ozone. However, most appear at this time not to be as important, either because they are expected to be removed more rapidly in the lower atmosphere or because they are produced and released in substantially lesser amounts. These chemicals will be the subjects of further study.

CLIMATIC EFFECTS OF OZONE REDUCTION

Some scientists postulate that changes in stratospheric ozone levels would cause changes in temperature, wind patterns, precipitation, and other weather elements. The nature and extent of these changes and their effects on the earth's climate, however, cannot be predicted on the basis of present knowledge.

BIOLOGICAL AND HEALTH EFFECTS OF OZONE REDUCTION

There is persuasive, although not absolutely conclusive, clinical and epidemiological evidence of a direct link between solar radiation and the historically observed incidence of several generally non-fatal (non-melanoma) types of skin cancer in humans, as described in more detail in Section V. (The death rate in the U.S. from these types of cancer is estimated to be about 1% of the non-melanoma cases.) There is, for example, an observed doubling of non-melanoma skin cancers with each 8° to 11° decrease in latitude, which is presumed to relate to the correlated increase in UV radiation reaching the earth with decrease in latitude. Estimates based upon observed

changes in incidence of skin cancer with variations in latitude for each percent reduction in average ozone concentration range from 2,100 to 15,000 (6,000 median) new cases of non-melanoma skin cancer per year among light-skinned individuals in the U.S. at steady state. (The National Cancer Institute estimates the current incidence of non-melanoma skin cancers in the U.S. to be about 300,000 cases per year.)

This clinical and epidemiological evidence is strongly supported by the unequivocal induction of skin cancers in animals exposed to increased UV radiation.

There is some evidence, although much less conclusive, to support a correlation between UV-B radiation and melanoma, a considerably more frequently fatal form of skin cancer (median survival time of 7 years). Other expected health effects include greater incidence of sunburning in populations at risk and earlier onset of skin aging. Additional possible effects that have been less studied are eye damage and excessive synthesis of vitamin D in the skin.

Because of the sensitivity of other living organisms to UV-B radiation, any increase in the cumulative dosage of this radiation might be of considerable biological and agricultural significance.

Possible biological and agricultural effects, for which more investigation is required before any definite conclusions can be made, include changes in physiological, biochemical, anatomical, and growth characteristics of certain plant and animal species; health effects on livestock; disturbances in the balance of aquatic and terrestrial ecosystems; and changes in the stability and effectiveness of agricultural chemicals. Any significant climatic changes resulting from reduction in stratospheric ozone levels might be expected to have some agricultural effects, such as reduction of the yield of some crops, especially in areas where production of a crop is marginal.

THE FLUOROCARBON INDUSTRY

Fluorocarbons are produced by six companies in the U.S. and by at least 48 companies in more than 23 other nations. U.S. production has been doubling about every 6 years, with an

annual increase of between 10 and 20%. However, there are indications that the rapid growth may be slowing in the U.S. There are no known plans for new construction to expand production in the next 3 years. In 1974 total aerosol sales (not restricted to those using fluorocarbon propellants) were reported by industry to have decreased about 5 to 10% from 1973 sales of 3 billion units, compared with a growth rate of 10.5% in 1972. It is expected that future expansion of fluorocarbon production to meet market demands would be greater in other parts of the world than in the U.S. (again, presuming the absence of any regulation) because other countries are farther from market saturation.

Approximately one-half of U.S. fluorocarbon production is used in aerosol propellants. Fluorocarbons constitute the propellant in 50 to 60% of the aerosol units sold. By far the largest amounts of fluorocarbons used in aerosols (more than 90%) are for personal products, especially hair care products, deodorants, and antiperspirants, as opposed to household products, most of which contain propellants other than fluorocarbons.

About 28% of U.S. fluorocarbon production is used as refrigerants in residential and commercial air conditioning and refrigeration, food storage and display, and automobile air conditioning. Estimates are that F-11, F-12, and F-22 ($CHClF_2$) constitute about 92% of U.S. refrigerants.

Fluorocarbons are also used as agents in the production of foams, and as solvents and fire extinguishers.

The problem of finding adequate substitutes for fluorocarbons is easier in the case of propellants than refrigerants. Acceptable alternate propellants are available for many aerosol applications; for others, no alternate propellants are known to be suitable, especially in personal products where a fine, well controlled spray is desirable. Non-propellant packaging can be used for many products now utilizing the aerosol, however, and may be less expensive for the consumer. Numerous deodorants and antiperspirants in non-aerosol packaging have been marketed successfully for many years; hair care products are also available with manual atomizers. Improvements in mechanical pumping devices, currently believed to be under investigation by industry, could make such products more widely accepted.

It has been reported by industry representatives that no suitable alternatives are presently known for the majority of refrigeration uses employing F-11 and F-12. It has been suggested that F-22 and other fluorocarbons that might not pose as significant a stratospheric hazard as F-11 and F-12 (because of their anticipated greater chemical reactivity in the lower atmosphere) could be used as alternative refrigerants. Although F-22 does not have properties that would allow it to be used as a propellant in aerosol products, it now constitutes about 30% of the refrigeration market. F-22 probably cannot be substituted in new equipment presently designed for use of F-11 and F-12 without substantial and costly design changes. This possibility should be further investigated, however. It is expected that greater problems would be encountered in switching to presently known non-fluorocarbon refrigerants (e.g., ammonia) because of toxic and other hazardous properties. Substitution of other refrigerants for F-11 and F-12 could not generally be made in existing equipment because the equipment is designed and constructed for the properties of specific compounds.

Development of chemical substitutes for each fluorocarbon use would in nearly all cases be a long and costly process. It is hoped, however, that this will not be necessary—that if restrictions on fluorocarbons are required, substitute delivery systems could be used for most aerosol products presently using fluorocarbon propellants, and that the refrigeration problem might be partially solved through reduction of leakage and recovery of the fluorocarbons for recycling at the time of eventual disposal. Some preliminary study indicates that there may be a potential for controlling a significant portion of the emissions from refrigeration systems during their operation with only relatively minor modifications of existing technology. These matters demand intensive additional study as to technological possibilities and economic feasibility.

Present data do not permit precise judgment on the number of workers and dollar value of business that might be affected by restrictions on fluorocarbon production or use, especially

because any future development of alternatives cannot be predicted. Any restrictions would result in some adverse impacts, which would vary in severity for different occupations and different companies. Industry estimates that more than 1 million jobs may be associated with the use of fluorocarbons (of which 4,000 are associated with fluorocarbon production). The fraction of these 1 million workers who would be affected by restrictions upon fluorocarbon uses would depend upon the nature of the restrictions. It is not probable, for example, that persons associated with refrigeration and air-conditioning sales would be significantly affected by any restrictions likely to be considered. Industry representatives also estimate that the refrigeration and air-conditioning industry as a whole accounts for about $5.5 billion of the gross national product and that aerosol products containing fluorocarbon propellants account for about an additional $2 billion.

Detailed studies of substitution possibilities and of various socio-economic impacts of regulation are currently underway and are expected to be taken into account by the regulatory agencies in determining the exact nature of any regulations and timetables that might be considered.

FEDERAL AUTHORITIES AND RECOMMENDED FEDERAL ACTIONS

Products that release fluorocarbons ultimately reaching the stratosphere can be divided into four categories according to how they may be regulated.

Fluorocarbons that are used as propellants in foods, drugs, and cosmetic products can be regulated by the Food and Drug Administration. These same compounds used to propel pesticide products can be regulated by the Environmental Protection Agency. Any other product (except automobiles) produced for distribution to, or use by, consumers can be regulated by the Consumer Product Safety Commission.

There is, however, no Federal authority governing any of the other fluorocarbon uses such as automobile air conditioning, industrial and commercial applications for air conditioning and refrigeration, and uses as a foaming agent or fire retardant. The proposed Toxic Substances Control Act now pending before Congress would provide for effective control of all uses of fluorocarbons if required and, in addition, would provide a regulatory base for control of a wide variety of potentially harmful substances with broad environmental consequences. This is the preferred approach in lieu of narrower specific legislation for fluorocarbons. The task force urges rapid passage of this legislation to fill these important gaps in the applicable Federal Authorities.

The task force has concluded that fluorocarbon releases to the environment are a legitimate cause for concern. Moreover, 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 to the atmosphere.

The National Academy of Sciences is currently conducting an in-depth scientific study of man-made impacts on the stratosphere and will report in less than a year. If the National Academy of Sciences confirms the current task force assessment, it is recommended that the Federal regulatory agencies initiate rulemaking procedures for implementing regulations to restrict fluorocarbon uses. Such restrictions could reasonably be effective by January 1978—a date that, given the concern expressed now, should allow time for consideration of further research results and for the affected industries and consumers to initiate adjustments.

In order to reduce the chance of unduly penalizing producers and marketers of aerosol products that do not use F-11 and F-12, the task force recommends that the regulatory agencies proceed immediately with consideration of a requirement that all aerosol products using fluorocarbons be labeled to indicate their fluorocarbon content.

International cooperation is strongly urged, inasmuch as the U.S. produces and uses only about one-half of the world-wide fluorocarbons, and effects on stratospheric ozone from ground release transcend national boundaries.

The State Department will initiate and coordinate a program of international exchange of information, cooperative research, and proposals for international action to help implement uniform policy actions on a worldwide basis. U.S. concern will be expressed and coordination will be initiated in the Organization for Economic Cooperation and Development (OECD), other international organizations, and through bilateral channels.

RESEARCH PROGRAMS

Much relevant research on the fluorocarbon question has already been conducted or is currently in progress through basic research programs in the atmospheric sciences and through applied research such as the recent Climatic Impact Assessment Program.

In addition to Federally sponsored research, the chemical industries affected are also conducting research programs. The research supported by 19 fluorocarbon producers around the world will amount to about a $3.75 to $5 million program over 3 years, which might be increased upon consideration of further research proposals. The program will emphasize measuring and monitoring chlorine levels in the stratosphere, modeling atmospheric dynamics, and determining critical rates of reaction. It will also include other studies relevant to determining the validity of the theories of ozone reduction. The program is coordinated through a Fluorocarbons Technical Panel under the auspices of the Manufacturing Chemists Association.

The National Aeronautics and Space Administration (NASA) has accepted lead agency responsibility for the development and testing of instruments and measuring systems for the sampling of trace atmospheric constituents and is chairing an interagency subcommittee of the Interdepartmental Committee for Atmospheric Sciences (ICAS) to develop an expanded program in these areas. Ozone monitoring is conducted by the National Oceanic and Atmospheric Administration (NOAA) and NASA. Other atmospheric research will be conducted by NOAA; NASA; the Departments of Defense and Transportation; Energy Research and Development Administration; Environmental Protection Agency; and the National Science Foundation and will be coordinated through ICAS. This research includes refining critical rates of reaction, searching for additional sinks for chlorine, studying the total chlorine burden of the stratosphere and its sources, monitoring fluorocarbons and other trace gases in the troposphere and stratosphere, and modeling the atmosphere. The entire program amounts to about $14 million in FY 1975, and funds are being sought to continue and expand this effort in future years.

Research on the agricultural, biological, and human health effects of ozone reduction will be conducted by the U.S. Department of Agriculture, the National Institute of Environmental Health Sciences, and the National Cancer Institute. This includes research on effects of increased UV radiation on agricultural crops, timber, natural vegetation, livestock, insects, and aquatic and terrestrial ecosystems; studies of biological mechanisms for resisting UV radiation and alleviating stress; models of effects of potential climatic changes; development of instrumentation for simulating natural UV-B radiation; analyses of the causes and incidence of skin cancer; and toxicological studies of the relationship between UV radiation and various types of skin cancer.

The regulatory agencies will conduct further studies of the socio-economic impacts of any restrictions on fluorocarbons. Sections II and VI indicate the nature of such studies.

II.
Conclusions and Federal Actions

In June 1974 the first scientific paper was published raising the issue of possible harmful effects from discharges of fluorocarbon gases, principally $CFCl_3$ (fluorocarbon-11) and CF_2Cl_2 (fluorocarbon-12), into the atmosphere. Since that time numerous other scientific groups have reported on this issue.

The Interagency Task Force on Inadvertent Modification of the Stratosphere (IMOS) has investigated this subject and found that:

(1) Fluorocarbons are produced in large quantities; ultimately almost all are released into the atmosphere.
  (a) Approximately 13.8 billion pounds of fluorocarbons-11 and -12 (F-11 and F-12) have been produced to date in the world (exclusive of the U.S.S.R. and Eastern European countries).
  (b) 1.7 billion pounds of this total were produced in 1973.
  (c) Total U.S. production has been doubling about every 5 to 7 years since the early 1950's; worldwide production (exclusive of the U.S.S.R. and Eastern European countries) in 1973 was 11% over 1972 production.
  (d) Approximately 50% of the world production and use of these fluorocarbons (exclusive of the U.S.S.R. and Eastern European countries) occurs in the U.S.

(2) F-11 and F-12 are not appreciably chemically decomposed in the lower atmosphere.
  (a) They are virtually inert chemically in the troposphere.

  (b) They have very low solubility in water and therefore are not washed out of the atmosphere by precipitation.
  (c) They are found in the atmosphere in concentrations that seem to be consistent with the total world release to date.

(3) No significant natural "sinks" other than stratospheric processes are known to exist for fluorocarbons in the environment.
  (a) The amount of fluorocarbons contained in the oceans, in soil, in subsurface ground water, and frozen in the polar ice caps is probably insignificant when compared with the atmospheric content.

(4) A significant fraction of the fluorocarbons is expected eventually to move by atmospheric circulation and diffusion up into the stratosphere.
  (a) Recent measurements have detected the presence of F-11 in the stratosphere.
  (b) It is estimated that it would take several years for a significant fraction of the total volume of fluorocarbons discharged in a given year to reach the stratosphere.

(5) In the stratosphere above 25 km (about 80,000 ft), fluorocarbons are expected to:
  (a) Be reactive due to dissociation by UV radiation from the sun which penetrates only as far as the stratosphere.

(b) Yield chlorine atoms (Cl) and a fluorocarbon radical.

(c) Dissociate within days to months depending upon the altitude.

(6) Although it has yet to be confirmed by direct stratospheric measurements, it is assumed that the fluorocarbon radical will probably dissociate until all of the chlorine atoms are released. Cl may react catalytically with either an oxygen atom (O) or ozone (O$_3$) before forming less reactive hydrogen chloride (HCl) and diffusing downward to the troposphere.

(a) Under these conditions the chlorine atoms (Cl) or as the free radical ClO for at least several days, and in this interval would be expected to react with thousands of oxygen atoms or ozone molecules.

(7) Ozone is a minor, but extremely important, constituent gas in the stratosphere.

(a) It is generated by the splitting of a normal oxygen molecule (O$_2$) by ultraviolet (UV) solar radiation and subsequent combination of the liberated oxygen atoms with another oxygen molecule to form ozone.

(b) The rate of formation of ozone is believed to depend almost exclusively upon the amount of incoming UV solar radiation and is therefore virtually independent of human influence.

(8) Ozone is maintained in the stratosphere in a dynamic equilibrium; i.e., there is an approximate balancing of the rate of ozone formation with that of ozone destruction.

(a) The naturally occurring ozone-destroying reactions include the interaction of ozone with oxygen atoms (O), with nitrogen oxides (NO$_x$), with hydrogen species (H, OH, HO$_2$) and possibly other natural stratospheric components. The rate of loss to the troposphere by transport into the stratosphere is much smaller than the rate of loss by chemical reaction.

(b) Most of the ozone in the atmosphere resides in the stratosphere.

(c) The concentration of ozone between the earth and the sun at mid-latitudes fluctuates daily on the average of 10% in the winter and 5% in the summer and 25% between seasons.

(d) The total ozone equilibrium concentration of the stratosphere also varies considerably with latitude; ozone occurs in greater amounts over the polar regions than at lower latitudes.

(9) Because of the large natural variations in ozone content, a 5 to 10% average decrease, persisting and measured for several years, would be required before a change could be attributed to human activity with any reasonable statistical reliability.

(a) Total ozone levels in the northern hemisphere seem to have increased by about 5 to 10% during the period 1955-1970. The ozone concentration has been on the decline since 1970 (approximately 1 to 2%). These fluctuations probably represent primarily natural variations, possibly related to solar activity.

(10) It is expected that any release to the atmosphere of man-made chemicals that reach the stratosphere and react to destroy ozone would create additional decreases in the stratospheric ozone content over and above those caused naturally.

(11) Carbon tetrachloride (CCl$_4$) has been measured in the troposphere and stratosphere. The extent to which its presence has arisen from natural or man-made sources (or both) has yet to be determined. Past restrictions upon the use of carbon tetrachloride as a solvent have resulted in substantially decreased man-made releases to the environment in recent years. Because carbon tetrachloride may also be of

stratospheric concern, it will require additional study.

(12) Other man-made chemicals such as methyl chloroform, perchloroethylene, and other halogenated compounds may also be of environmental concern with respect to possible reduction of stratospheric ozone. However, most appear at this time not to be as important, either because:
   (a) They are expected to be removed rapidly in the lower atmosphere, or
   (b) They are produced and released to the atmosphere in substantially lesser amounts.

(13) Although there are some uncertainties in the calculations, the best estimates are that fluorocarbon production and release to the environment to date may:
   (a) Have resulted in a current reduction in average ozone concentration estimated to be most likely between 0.5 and 1% and possibly as large as 2%.
   (b) Eventually result in as much as a 1.3 to 3% reduction in the equilibrium ozone concentration.

(14) Because of slow diffusion of fluorocarbons into the stratosphere, any changes in ozone from fluorocarbon release would be delayed.
   (a) Even if no additional fluorocarbons were released after a certain date, further reduction of average ozone concentration would continue, reaching a maximum in about a decade or more later.
   (b) It is expected that reduced levels of ozone would last to some extent for as much as a century or more after cessation of fluorocarbon releases.

(15) Current model calculations predict that if release of fluorocarbons were to continue at the 1972 rate, a maximum reduction of about 7% in the equilibrium ozone concentration would be expected after several decades.

EFFECTS OF OZONE REDUCTION

(1) Stratospheric ozone screens UV-B radiation in sunlight from the earth's surface.
   (a) UV-B radiation has a wavelength range of 280 to 320 nanometers (1 nm = 10^{-9} meters).
   (b) An approximately 1.4 to 2.5% (median of 2%) increase in UV-B radiation at the earth's surface at mid-latitudes would occur for each 1% reduction in stratospheric ozone concentration. This relationship holds true for small percentage changes in ozone concentration. For larger reductions of ozone, it is expected that the associated increase in UV-B radiation reaching the earth's surface would be disproportionately greater.

Any significant decrease in the stratospheric ozone layer resulting in increased UV-B radiation reaching the earth would cause environmental effects that are predominantly harmful.

(1) There is persuasive, although not absolutely conclusive, clinical and epidemiological evidence of a direct correlation between solar radiation and the historically observed incidence of several generally non-fatal (non-melanoma) skin cancers in humans. (The death rate in the U.S. is estimated to be about 1% of the non-melanoma cases.) This is strongly supported by the unequivocal induction of skin cancers in animals exposed to increased UV radiation.
   (a) There is, for example, an observed doubling of non-melanoma skin cancers with each 8° to 11° decrease in latitude, which is presumed to relate to the correlated increase in UV radiation reaching the earth with decrease in latitude.
   (b) Based upon the estimated relationship between ozone concentration in the stratosphere and

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UV radiation reaching the earth's surface, and between UV radiation and the incidence of non-melanoma skin cancers, an increase of approximately 2% (range 0.7 to 5%) in the incidence of non-melanoma skin cancers in the U.S. is predicted for a 1% reduction in average ozone concentration (with a disproportionately greater increase in cancer for higher percentages of reduction in ozone levels).

(c) The National Cancer Institute estimates the current incidence of non-melanoma skin cancers in the U.S. to be about 300,000 cases per year.

(d) Calculations based upon observed changes in incidence of skin cancer with variations with latitude for each percent ozone reduction range from 2,100 to 15,000 (6,000 median) additional cases of non-melanoma skin cancer per year in light-skinned individuals in the United States at steady state.

(2) There is some evidence, although much less conclusive, to support a similar correlation between UV-B radiation and melanoma—a much less common, but considerably more frequently fatal, form of skin cancer (median survival time of 7 years).

(3) Other expected health effects include greater incidence of sunburning in population at risk and earlier onset of skin aging.

(4) Other possible effects that have been less studied are eye damage and excessive synthesis of vitamin D in the skin.

(5) Possible biological and agricultural effects, for which more investigation is required before any definite conclusions can be made, include:

(a) Changes in physiological, biochemical, anatomical, and growth characteristics of certain plant species sensitive to UV-B radiation, including some food crops.

(b) Disturbances in aquatic and terrestrial ecosystems.

(c) Effects on the behavior of insects, including those beneficial to agriculture.

(d) Effects on the stability and effectiveness of agricultural chemicals.

(e) Effects on livestock, e.g., increases in certain types of cancer.

(f) Reduction in the yield of some crops, especially in areas of marginal agricultural production, as the result of any significant climatic changes resulting from reduction of stratospheric ozone levels.

(6) Some scientists postulate that changes in stratospheric ozone levels would cause changes in temperature, wind patterns, precipitation, and other weather elements. The nature and extent of these changes and their effects on the earth's climate, however, cannot be predicted on the basis of present knowledge.

ASSESSMENT OF VALIDITY OF STRATOSPHERIC MODELS

In investigating efforts to quantitatively model the stratosphere, the task force found that considerable knowledge already exists. This is due, in part, to the Climatic Impact Assessment Program (CIAP), supported in the past several years by the Department of Transportation for the study of possible environmental effects from the emissions of aircraft flying in or near the stratosphere. The fact that current models are consistent with the behavior of currently measurable chemical

species and reactions suggests that characterizations by the models of other as yet unmeasured reactions are likely to be reasonably predictive.

Therefore, unless future measurements are found to be totally inconsistent with predicted values, there would be no reason to challenge the basic validity of the stratospheric models. For example, a contraindication would be the discovery of natural sources of chlorine in the stratosphere grossly in excess of the amount that could otherwise be accounted for by current understanding.

Calculations of possible reduction in stratospheric ozone by F-11 and F-12 have been made independently by several scientists. Despite varying assumptions and parameters, the findings of these experts agree within a factor of two—an agreement that is somewhat better than the uncertainty in each of the calculations.

The greatest uncertainties in the calculations are believed to arise in the parameters characterizing the rate of diffusion and transport of materials in the atmosphere and in rates of certain stratospheric chemical reactions important for the theory of ozone reduction, such as:

$$OH + HO_2 \rightarrow H_2O + O_2$$
$$Cl + HO_2 \rightarrow HCl + O_2$$
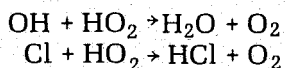
There is some uncertainty in the exact amount of reduction of average ozone concentration expected, based on the model predictions. It is not expected, however, that further refinements in the calculations will affect the conclusions of the task force because, even at the most optimistic end of the currently reported range of uncertainty, there is still a basis for concern about possible stratospheric alterations from past and future releases of fluorocarbons to the atmosphere.

In evaluating the validity of present understanding of the mechanism by which ozone could be decreased by fluorocarbons, the need for direct Cl or ClO stratospheric measurements has been identified as the most crucial. Typically, in complex chemical reactions, it is impossible to measure directly the concentration and reaction of all relevant chemical species. Their presence must be inferred from what is known about the measurable entities. In the case of possible fluorocarbon atmospheric effects, unless there is something fundamentally in error with current understanding of the stratosphere, the question does not become whether or not Cl or ClO exists in the stratosphere, but rather what range of concentrations could be present, given uncertainties in the inputs to the model. A direct measurement of Cl or ClO (not as yet accomplished in the stratosphere) would, however, remove any need to infer their existence from a model.

ASSESSMENT OF VALIDITY OF EXPECTED EFFECTS OF OZONE REDUCTION

Although any changes in the average ozone concentration that might be caused by fluorocarbons may be less than present natural fluctuations, any significant decrease in average ozone level would result in an increase in the cumulative exposure to UV-B radiation and is of potential biological and agricultural importance.

The incidence of skin cancer in humans is believed to be a function of the amount of exposure to UV-B radiation of the population at risk. The greater the exposure, the greater the risk. The precision of estimates of projected increases in skin cancer or other malignancies for incremental increases in UV-B exposure is limited, however, by the relatively poor records on the incidence of skin cancer. Changes in average ozone concentration may also affect other animals and plants adversely because of the sensitivity to UV radiation of proteins, nucleic acids, and other cell constituents in living organisms. Natural products and synthetic agricultural chemicals may also be altered in their effectiveness.

Because of the short time frame in which biological studies were conducted on increased UV-B radiation under CIAP and because of the difficulties of UV-B simulation and measurement, most presently available results are only preliminary. Considerably more research is needed to determine baseline data on present UV-B levels reaching the earth's surface and the biological impact of increased UV-B radiation before definitive statements can be made of the nature and magnitude of any changes that may occur.

Furthermore, most biological experiments on effects of UV-B radiation on plants have been based upon a simulation of 35 to 50% reduction in average ozone concentration. The magnitude of effects at much lower doses cannot presently be assessed because the effects are not known to be linear and because simulation of field conditions in the laboratory is very difficult. In particular, further study is required to assess the impact on plants of reduction in average ozone levels on the order of 10% or less.

The task force would also be concerned if there were a potentially significant climatic impact from alterations in stratospheric ozone. It is not possible at present, however, to predict the exact nature, magnitude, or significance of such a change.

Despite uncertainties concerning the actual amount of decrease in average ozone levels that might occur or the exact nature and magnitude of the resulting effects, the task force concludes that the prospects of a reduction in the equilibrium ozone concentration in the stratosphere from present and future releases of F-11 and F-12 and other atmospheric pollutants may represent a potentially serious problem of long-range consequences that would warrant increased attention on a national and international basis.

CONSIDERATIONS IN REACHING A DECISION

Most well recognized hazards until recent years have been characterized by direct and immediate or almost immediate effects (e.g., food poisoning, unshielded machinery in the workplace, faulty automobile equipment). The inherent risks for these types of hazards are usually measurable directly at the first indication of a problem, and actions can be taken quickly to alleviate the risk. The decision whether to regulate or modify the risk largely depends on whether or not an unacceptable effect has occurred.

Lately, however, many hazards, particularly those related to the environment, have been identified for which the effects are not immediately apparent. Cancer induced by chemicals in the environment is one example; the fluorocarbon-ozone question described in this report is another.

For this latter form of hazard, the harmful effects occur far removed in time and space from their cause. In the case of cancer induced by chemical agents in the environment, or the fluorocarbon-ozone question, the time delay is typically on the order of tens of years. The existence of a long time lag between causes and effects requires that decisions about the possible control of such hazards be made on a somewhat different basis from those acute hazards whose effects can be directly and immediately observed or simulated.

First, the decisionmaker is faced with the fact that the level of current public concern may not always be an accurate measure of the degree of acceptable risk, especially in cases where the effects are not immediately apparent and are not expected to occur until some time in the future.

Second, questions of equity are raised in regard to hazards with latent effects, as the group deriving the benefits is not the same as that accepting the risk. In this case, those using products containing fluorocarbons are only in part those that may in 10 to 40 years time bear the maximum risk from their use. They are almost completely different from those potentially affected 100 years from now.

Third, the latency implies that by the time effects become measurable, a large impact may have already resulted. In this case, in view of the large natural fluctuations in total ozone concentrations, it would take a rather large and long-term effect on the average level (e.g., a 5 to 10% decrease persisting and measured for several years) before it could be confidently concluded, with reasonable statistical reliability, that the average ozone level had changed. (Further evidence would be required that the change was the result of fluorocarbon release.)

Fourth, the decisionmaker is faced with the reality that even if further exposures and releases of the chemicals were totally eliminated, the effects would be likely to continue for many years.

In an attempt to judge what is an acceptable level of risk, as soon as there is reasonable assurance that the predicted effects will indeed occur, the decisionmaker must take into account the equity factors and treat the potential future effects as if they were occurring today. If the hazard poses potentially serious effects, the decisionmaker may not be able to

wait for the measurement of the effects. Great caution has to be exercised in reacting to relatively ·unsupported hypotheses. On the other hand, when presented with well founded scientific theory, confirmed by statistically reasonable experimental evidence, it may be necessary to act.

It is in this context, therefore, that following an assessment of the likelihood of potential adverse impacts of fluorocarbons on the environment, the task force has come to the following conclusions and recommendations.

TIMETABLE FOR ACTION

The task force has concluded that fluorocarbon releases to the environment are a legitimate cause for concern. Moreover, unless new scientific evidence is found to remove the cause for concern, it would seem necessary to restrict uses of F-11 and F-12 to replacement of fluids in existing refrigeration and air-conditioning equipment and to closed recycled systems or other uses not involving release to the atmosphere.

The National Academy of Sciences is currently conducting an in-d· ِth scientific study of man-made impacts on the stratosphere and will report its findings in less than a year. If the National Academy of Sciences study confirms the current task force assessment, it is recommended that the Federal regulatory agencies initiate rulemaking procedures for implementing regulations to restrict fluorocarbon uses. Such restrictions could reasonably be effective by January 1978—a date that, given the concern expressed now, should allow time for consideration of further research results and for the affected industries and consumers to initiate adjustments.

The Federal Government has a significant stratospheric research program, which resulted in part from a concern over possible effects of supersonic transport flights upon the stratosphere. This major effort will continue, with some shift of emphasis on the chemical reactions of interest, to improve the understanding of the stratosphere and man's impact upon it, and resulting effects of stratospheric changes on man, the biosphere, and climate. It will address the key areas of inquiry that could potentially affect the inter-

pretation of the effects of fluorocarbons or other possible sources of halogens and other chemical species in the stratosphere.

Currently, the Environmental Protection Agency has jurisdiction over pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act as amended. The Food and Drug Administration has authority over aerosol-propelled foods, drugs, and cosmetics under the Federal Food, Drug, and Cosmetic Act. The Consumer Product Safety Commission has authority over all other consumer aerosol products, home air conditioners, home refrigerators, and any other consumer products except automobiles under the Consumer Product Safety Act. There is, however, no Federal authority governing any of the remaining uses of fluorocarbons such as automobile air conditioning, industrial and commercial applications for air conditioning and refrigeration, and uses as a foaming agent or fire retardant. The proposed Toxic Substances Control Act now pending before Congress would provide for effective control of all uses of fluorocarbons, if required, and also would provide a regulatory base for control of a wide variety of potentially harmful substances with broad environmental consequences, including other compounds that may be of stratospheric concern. This is the preferred approach in lieu of narrower specific legislation for fluorocarbons.

The Congress is, therefore, urged to act promptly to enact toxic substances control legislation so that, if necessary, the Federal Government will have sufficient authority to address any potentially serious problems involving such substances.

In order to reduce the chance of unduly penalizing manufacturers of aerosol products that do not employ F-11 and F-12 (approximately 40 to 50% of the market), the task force recommends that the regulatory agencies proceed immediately with consideration of a requirement that all aerosol products using fluorocarbons be labeled to indicate their fluorocarbon content.

CRITICAL RESEARCH AREAS

It is reassuring that an entirely new research program does not have to be initiated, despite the short period of time since the fluorocarbon

issue was identified. A considerable amount of research is already completed or underway. This research has added greatly to the general understanding of the chemistry and physics of the stratosphere and of the potential effects of stratospheric changes. Much research has occurred within the past several years under the auspices of the CIAP, sponsored by the Department of Transportation. This program supported more than $20 million of research directed to both specific and general questions concerned with possible environmental consequences of the emissions from aircraft flying in or near the stratosphere. Other relevant general research has come out of basic research programs in the atmospheric sciences, and some of this has been applied within the past year to address the fluorocarbon-ozone question more specifically. These current Federal research efforts are summarized in other sections of this report.

In addition to this Federal research, it is believed that the affected chemical industries are conducting research programs of their own to study possible alternatives to fluorocarbons. They are supporting measuring and monitoring of chlorine levels in the stratosphere, modeling of atmospheric dynamics, determining rates of critical reactions, and other studies relevant to determining the validity of the theories of ozone reduction. The research supported by 19 fluorocarbon producers around the world will amount to about a $3.75 to $5 million program over 3 years, which might be increased upon the consideration of further research proposals. It is coordinated through a Fluorocarbons Technical Panel under the auspices of the Manufacturing Chemists Association.

Following is a list of the most critical areas for future research that have been identified in this study, along with the plans of the Federal agencies for addressing these needs. Further description of the rationale for identifying this research as critical is included in other chapters of the report.

Atmospheric Sciences

The National Aeronautics and Space Administration (NASA) has accepted lead agency responsibility for the development and testing of instruments and measuring systems for the sampling of trace constituents in the upper atmosphere. An interagency subcommittee of the Interdepartmental Committee for Atmospheric Sciences (ICAS) under the chairmanship of NASA was established in April 1975 to coordinate 'he Federal effort in these areas, including programs conducted by the National Oceanic and Atmospheric Administration (NOAA), NASA, Departments of Defense and Transportation, Energy Research and Development Administration (ERDA), Environmental Protection Agency (EPA), and the National Science Foundation (NSF). The goals of technique and instrumentation development programs are defined by the following priorities identified for work in the next 2 years:

(1) Measurement of chlorine and chlorine oxides in the stratosphere. This is the single most crucial set of measurements for substantiating the photodissociation of the chlorine-bearing compounds and for verifying that there are no quantitatively significant natural "sinks" to remove the chlorine atoms from the stratosphere (other than the expected removal by the formation of hydrogen chloride).

(2) Measurements of F-11 and F-12, CCl_4, OH, and HO_2 radicals, especially at altitudes of 25 to 40 km, along with measurement of certain other gases that may act as tracers to determine air transport to these altitudes. Such measurements can help in the confirmation of various aspects of the models for reduction of average ozone levels such as the relative photochemical reaction rates and vertical transport.

(3) Search for other chlorine-bearing gases in the stratosphere besides those already observed. This is needed both in the modeling of stratospheric chemical reactions and in the interpretation of results of the measurements of chlorine and chlorine oxides.

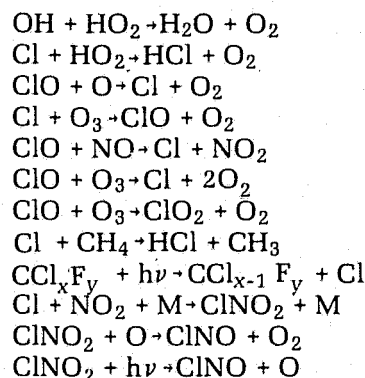(4) The filtering of stratospheric air samples for measurement and com-

parison of radioactive chlorine content. Radioactive chlorine is generated in small amounts in the stratosphere by the impact of cosmic radiation on argon and has a very short half-life (approximately 30 to 60 minutes). Because the radioactive chlorine exists for only a few hours at most, it would be in the form of Cl or ClO. Normal chlorine, which has been in the stratosphere much longer, would be expected to be predominantly in the form of HCl. Thus, if radioactive chlorine behaves no differently from the normal form of chlorine in the collected sample, it would be a positive indication that, in accordance with the theories of average ozone level reduction, ClO is an important intermediate in the stratosphere.

The regular program of monitoring of ozone in the atmosphere from ground-based stations by NOAA and from satellites by NASA will continue to provide information about both the total ozone and ozone concentrations at high altitudes. The monitoring program is not likely to reveal any significant reduction in the average ozone concentration that can be disentangled from natural variations within the decision time+able discussed above. However, it is important for providing information that eventually will be used in assessing the extent of stratospheric changes, and thus in predicting and perhaps alleviating predicted adverse effects from fluorocarbons or possible future threats to stratospheric ozone.

Other areas of critical chemical and physical research and monitoring that will be carried out by the various relevant Federal agencies (NASA; Departments of Commerce, Defense, Transportation; ERDA; EPA; and NSF) and coordinated through ICAS are:

(1) Research to determine the possible presence of sinks for chlorine in the environment besides the tropospheric washout of hydrogen chloride.

(2) Research directed at confirming or improving upon certain rates for chemical reactions crucial to the chlorine destruction of ozone in the

stratosphere. A list of such reactions follows:

$$OH + HO_2 \rightarrow H_2O + O_2$$
$$Cl + HO_2 \rightarrow HCl + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + NO \rightarrow Cl + NO_2$$
$$ClO + O_3 \rightarrow Cl + 2O_2$$
$$ClO + O_3 \rightarrow ClO_2 + O_2$$
$$Cl + CH_4 \rightarrow HCl + CH_3$$
$$CCl_xF_y + h\nu \rightarrow CCl_{x-1}F_y + Cl$$
$$Cl + NO_2 + M \rightarrow ClNO_2 + M$$
$$ClNO_2 + O \rightarrow ClNO + O_2$$
$$ClNO_2 + h\nu \rightarrow ClNO + O$$

(3) Study of the distribution, average residence times, and chemistry of all chlorine-bearing and halogenated compounds to provide clues to their possible contributions to the total amount of stratospheric chlorine, and study of other halogens that might act as catalysts for ozone reduction.

(4) Continued and expanded monitoring of fluorocarbons-11 and -12, carbon tetrachloride, and other trace gases in the troposphere, mainly in clean air ground locations. Development of standards to permit more accurate comparison among the results obtained by different measuring systems.

(5) Continued and expanded modeling of the effects of reduced equilibrium levels of stratospheric ozone on the climate. (Such research, however, should not be expected to produce any quick answers to the possible ozone reduction/climate relationship.)

To carry out the accelerated program, approximately $14 million is being expended in FY 1975. Additional sums are being sought to continue and expand this effort in FY 1976 and beyond.

Agricultural, Biological, and Human Health Effects Research

The U.S. Department of Agriculture (USDA) has formed an *ad hoc* working group on ozone depletion of the stratosphere, with

membership from the Agricultural Research Service and Forest Service for identifying critical research needs in USDA and developing an expanded research effort on the biological and climatic effects of ozone reduction in the stratosphere on agricultural and natural ecosystems. Research priorities will be in the following areas:

(1) Effects of increased UV-B radiation on crop and timber production and natural vegetation. Expansion of critical narrow-band UV studies to examine effects of increased UV-B radiation on critical physiological and biochemical processes. Identification of threshold dosages for UV damage in major plant species. Modeling of possible yield losses of major crops from increased UV-B radiation dosages.

(2) Measurements of UV-B levels at the earth's surface to determine improved baseline data on UV-B penetration into crop, timber, and aquatic ecosystems.

(3) Improved instrumentation for monitoring UV radiation and broadband sources for simulating natural UV-B radiation. This would include improved instrumentation for measuring UV penetration of natural waters in order to evaluate possible effects on aquatic ecosystems.

(4) Effects of increased UV radiation on livestock, insects, and agricultural ecosystems.

(5) Identification of mechanisms of resistance to UV radiation and techniques for alleviating stress, including study of the available photorepair mechanisms in higher organisms.

(6) Study of whether plants and animals exposed to UV radiation are more sensitive to insects and pathogens.

(7) Modeling of the effects of potential climatic changes on agricultural production and total ecosystems.

The most critical research needs in the area of human health effects are the following, which are being addressed under a program of approximately $1 million per year by the National Institute of Environmental Health Sciences and the National Cancer Institute:

(1) Further statistical analyses and studies of the actual number of cases and time incidence of all forms of skin cancer, with correlations with latitude and other indications of the amount of exposure to UV-B radiation.

(2) Further toxicological studies on the relationship between skin cancer, particularly melanoma, and UV radiation, based on varying wavelengths, quantities, and timing of dosages.

Research on Industrial Alternatives and Economic Impacts

Research and testing of alternative aerosol propellants, alternative delivery systems, and alternative refrigerants is the primary responsibility of the affected industries, and it is the understanding of the task force that some of the research is already underway. (Detailed information on such research is proprietary to the individual companies.) The task force strongly urges accelerated study by industry of methods for controlling releases of fluorocarbons to the atmosphere and of harmless alternatives to fluorocarbons for uses for which losses to the atmosphere cannot be prevented.

It will be the responsibility of the regulatory agencies to take the lead in determining:

(1) More detailed qualitative and quantitative data on specific fluorocarbon uses and users. Specific formulation information, production data, safety data, and labeling for fluorocarbon products should be sought under the various Federal authorities.

(2) More detailed analysis of groups of workers and occupations potentially affected by curtailment of fluorocarbon production and analysis of opportunities for retraining in related industrial processes.

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(3) Environmental and economic cost/benefit analyses on alternative fluorocarbons and other chemicals that might be proposed for use in air-conditioning, refrigeration, and other non-aerosol uses.

(4) Similar analyses of technological and economic feasibility of reducing leakage of fluorocarbons from air-conditioning and refrigeration equipment and of recovery of fluorocarbons for recycling before final disposal of such equipment.

(5) Analysis of adjustment costs to industry and workers associated with timetables and alternative levels of restrictions.

IMPACTS OF FEDERAL RESTRICTIONS

If restrictions on fluorocarbon uses are required, it is anticipated that the regulatory agencies will prepare a program environmental impact statement covering environmental and socio-economic impacts for alternative regulatory approaches. In this section, a preliminary outline is made of the expected impacts of any restrictions on fluorocarbon use.

To the Environment

If the theories of ozone reduction are correct, the reduction of ozone concentration below long-term average levels from the use of fluorocarbons (which is presently estimated to be most likely between 0.5 and 1% and possibly as large as 2%) would increase further as a result of the past releases of fluorocarbons to the stratosphere. Even if all fluorocarbon releases were stopped in July 1975 (which is considered impossible to accomplish as well as inadvisable under the circumstances), the reduction according to estimates might still be as large as 3%. The exact amount of additional ozone reduction from releases of fluorocarbons prior to any regulations would depend primarily on the timing and extent of those regulations as well as on production and market developments in the U.S. and other countries. Models showing the expected ozone reduction under varying assumptions are described and illustrated in Section III.

To Affected Industries and Workers

The total retail value of the United States industry related to the production, packaging, and distribution of fluorocarbons, is estimated by Dr. Raymond McCarthy of E. I. du Pont de Nemours & Company to be $8 billion (of which $2 billion is accounted for by aerosols), and the total related employment to be approximately 1 million workers. Of this number, approximately 4,000 workers are directly involved in fluorocarbon production, carried out by six companies in the United States at 15 plants. The fraction of these 1 million workers who would be affected by restrictions upon fluorocarbon uses would depend upon the nature of the restrictions. It is not probable, for example, that persons associated with refrigeration and air-conditioning sales would be significantly affected by any restrictions likely to be considered. The cosmetic industry will obviously continue to manufacture cosmetics. whether or not they are packaged as aerosol products. The impact would be uneven, however, and in some cases severe for certain occupations, for smaller companies, and for companies specializing in processes solely related to fluorocarbon production or applications. Any period until restrictions become effective would provide some opportunity for developing alternatives and easing the impact of the required transition. The degree of the impact will, of course, depend heavily upon the length of time to restriction; if the period is short, only minimal adjustments could be expected. Even under relatively long timetables, however, substitution and a smooth transition are not expected to be possible in all instances. Additional analyses of expected economic impacts are needed and will be undertaken in order to help guide the development of any necessary regulations and to provide indications of how adverse effects might be alleviated.

Although the fluorocarbon-related industries and workers would be impacted by restrictions, most of the effects would probably be of a short-term nature because it

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is expected that alternative chemicals and products eventually would be developed to fill vacated markets.

To the Consumer

Aerosol products were developed and successfully marketed primarily because of their convenience for the consumer, and thus will no doubt be missed by many if no substitute propellants are made available for certain products. There is considerable variation in opinion about the essentiality of various uses of aerosol products and about the likelihood of acceptance of substitute delivery systems. For example, roll-on and cream deodorants already represent a substantial portion of the deodorant market. Non-aerosol hair sprays are also now available on the market. Because personal care items, i.e., deodorants, hairsprays, and antiperspirants, et cetera, account for approximately 90% of the fluorocarbons used in aerosols, it seems that alternative delivery systems may already be available for most aerosol products now using fluorocarbons. Some other aerosol products, however, for which there presently may be no alternative delivery systems with similarly acceptable properties, might be less easily replaced. Also, more evaluation is needed of the safety implications as well as the environmental effects of switching from fluorocarbons to alternative chemicals or delivery systems.

It has been reported by industry representatives that no suitable alternatives are presently known for the majority of refrigeration uses employing F-11 and F-12. It has been suggested by others that F-22 and other fluorocarbons that might not pose as significant a stratospheric hazard as F-11 and F-12 (because of their anticipated greater chemical reactivity in the lower atmosphere) could be used as alternative refrigerants. Although F-22 does not have properties that would allow it to be used as a propellant in aerosol products, it now constitutes about 30% of the refrigeration market. F-22 probably cannot be substituted in new equipment presently designed for use of F-11 and F-12 without substantial and costly design changes. This possibility should be further investigated, however. It is expected that greater problems would be encountered in switching to presently known non-fluorocarbon refrigerants (e.g., ammonia) because of toxic and other hazardous properties. Substitution of other refrigerants for F-11 and F-12 generally could not be made in existing equipment because the equipment is constructed and designed for the properties of specific compounds.

INTERNATIONAL ACTIONS

Inasmuch as the U.S. produces and uses only about one-half of the world-wide fluorocarbons (excluding the U.S.S.R. and Eastern European countries), and any resulting changes in stratospheric ozone from fluorocarbon release could not be restricted to the country of release, the problem described in this report transcends national borders. Furthermore, there is no current Federal authority under which exports of fluorocarbons from the U.S. can be controlled, although it is anticipated that industries based in the United States would take a responsible position in voluntarily cutting back on production for export if regulatory measures are taken in the United States.

Given the conclusions of the collective agencies represented on IMOS and the possible actions, it is particularly important that these conclusions and recommendations be made known to the other countries producing and using fluorocarbons and that concerted international action be sought through appropriate international organizations and bilateral channels.

The State Department will initiate and coordinate this international undertaking. Actions will include, but not be limited to, obtaining directly from individual countries information concerning fluorocarbon production and use; research and policy efforts directed at the fluorocarbon-ozone question; encouragement of and cooperation in non-duplicative research with individual countries or within international organizations; expression of the U.S. concern on this matter in the Organization for Economic Cooperation and Development (OECD) and other organizations, with timely proposals for appropriate action to help bring

about uniform treatment of this problem on a world-wide basis; and similar coordination with the U.S.S.R. and Eastern European countries, perhaps starting with the U.S.S.R. through the mechanism of the U.S.-U.S.S.R. bilateral agreements.

III.

Stratospheric Effects

SUMMARY

Calculations of possible reduction of the ozone column by fluorocarbons-11 and -12 (F-11 and F-12) currently in the atmosphere have been made independently by several scientists. The same calculations with alternate future patterns of releases of F-11 and -12 also predict future reductions. Despite varying assumptions and parameters, the findings of these scientists agree within a factor of about two.

The theoretically calculated global reduction of stratospheric ozone by fluorocarbons in 1975 is between 0.5 and 1% and may be as large as 2%. Even if no more F-11 or -12 were added, the ozone would theoretically continue to decrease and eventually achieve as much as a 1.3 to 3% reduction as a result of past releases of fluorocarbons.

An important aspect of the theoretical reduction of ozone by F-11 and -12 is its projected decrease for about 10 years after cessation of releases to the atmosphere and the very slow subsequent recovery to normal values taking place over many tens of years.

Carbon tetrachloride (CCl_4) is suspected of having also created a reduction in ozone of about 0.5 to 2%. It has been measured in the troposphere in significant quantities. The extent to which these concentrations arise from natural versus man-made sources has yet to be determined. Reductions in the use of carbon tetrachloride as a solvent have resulted in dramatically decreased man-made releases to the environment in recent years. It may still be of stratospheric concern, however, and will require additional study.

The potential is now being explored of chlorine-bearing compounds other than F-11 and -12 and CCl_4 as sources of chlorine in the stratosphere; no definitive predictions similar to those for F-11 and -12 and CCl_4 are available as yet.

There is at present almost no direct evidence supporting the theoretical model predictions of ozone reduction; conversely, there is no evidence against the validity of the predictive models. There are two suggested areas in which the models could most likely be in error:

(1) There may be large natural sources of chlorine in the stratosphere that overwhelm the chlorine produced by photodissociation of man-made F-11 and -12 or other halogenated compounds. Just how such as yet unproved large contributions of natural chlorine would affect the predictions is uncertain.

(2) There may be sinks for chlorine atoms beyond that included in the predictions. Unexpected sinks would decrease, but probably not eliminate, the predicted ozone reduction.

The most clear-cut proof or rejection of the model predictions of ozone reduction due to man-made fluorocarbons should, in principle, be found in a reduction of ozone. But, unfortunately, the natural variability of ozone precludes detection of man-made changes until those changes reach at least 5 to 10% and persist for several years.

Overwhelming evidence points to man-made sources for F-11 and -12; there is still uncertainty whether atmospheric CCl_4 is man-made, natural, or both.

Uncertainties concerning the nature of transport mechanisms of trace constituents in the predictive models do not alter the general estimates of ozone reduction.

F-11 and -12 and CCl_4 present potential problems because of their computed very long average residence times (more than 300 years)

in the troposphere. The only known non-stratospheric sinks are the oceans, air raised to high temperatures as in combustion, and possibly freeze-out on ice or snow. Fluorocarbon destruction by soil microorganisms is being studied at present. None of these tropospheric destruction processes is thought to be significant. This view is supported by an agreement between estimated releases of F-11 and -12 to, and their measured concentrations in the atmosphere. However, it should be noted that the uncertainties of both worldwide release and measurement data possess potential errors of 10 to 25%.

It is not possible at present to associate any specific changes in weather or climate with ozone reductions on the order of 10% or less. Ozone reductions of this magnitude have occurred for short periods in the past. However, the lack of numerical relationships between ozone reduction in the stratosphere and predicted climatic change probably is due to the inexact state of climate modeling. Prolonged small ozone reductions could still produce significant consequences on the weather and climate that cannot now be predicted.

INTRODUCTION

The material contained in this chapter is based on a much more comprehensive report on this subject that was prepared by the Interdepartmental Committee for Atmospheric Sciences (ICAS) for submission to the Chairman, Federal Council for Science and Technology. The reader is encouraged to read this report:

The Possible Impact of Fluorocarbons and Halocarbons on Ozone, ICAS Report 18a, June 1975.

The following background information on stratospheric ozone is excerpted from the National Academy of Sciences report, Climatic Impact Committee, Environmental Impact of Stratospheric Flight: Biological and Climatic Effects of Aircraft Emission in the Stratosphere, pp. 23—26, April 1975. Additional information on the stratosphere is found in Appendix A of that report.

The Natural Stratosphere

The stratosphere is a nearly cloudless and remarkably quiescent region of the earth's atmosphere that is susceptible to contamination. The stratosphere is characterized by a temperature inversion—a region in which the temperature remains constant or increases with height. As a result, the stratosphere is not stirred by the violent vertical motions characteristic of the troposphere below. The regions called the troposphere (the turbulent region of the atmosphere below the stratosphere), the stratosphere, and the mesosphere (the portion of the atmosphere immediately above the stratosphere) are shown in Figure 2. . . Temperature profiles for the atmosphere vary with latitude so that the bottom of the stratosphere is at a considerably higher altitude at the equator than it is, for example, at latitude 70 degrees; the base of the stratosphere is known as the tropopause, and it varies in altitude from about 8 km (26,000 ft) or less at high latitudes to about 16 km (52,000 ft) over the equator.
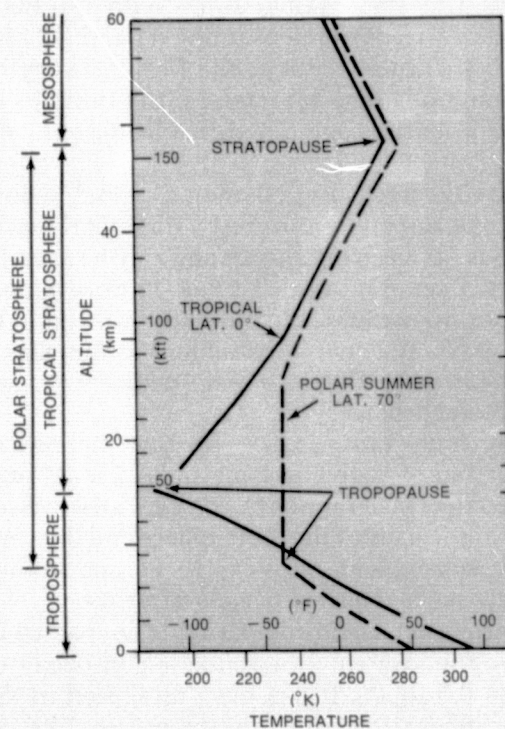
Figure 2. The atmosphere's temperature/altitude profile showing the various regions of the atmosphere.

The special properties of the stratosphere—its temperature inversion and resulting slow vertical mixing—are a consequence in part of the presence of ozone (O_3), which is formed rapidly in the upper stratosphere at altitudes of 30 to 50 km by the photolysis of molecular oxygen (O_2), producing atomic oxygen (O), which in turn recombines with O_2 to form O_3. Below about a 25-km altitude, the ozone concentrations are determined mainly by complicated transport mechanisms that move air toward the poles and downward. These mechanisms are

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responsible for the latitude distribution of ozone and for the paradox that the total amount of ozone overhead is large at high latitudes where its rate of production is small. The absorption of ultraviolet sunlight (of wavelengths 240 to 320 nm) by ozone shields the earth's surface from harmful ultraviolet radiation and heats the upper stratosphere, thereby producing the temperature inversion. Several natural ozone destruction processes balance its photochemical formation. The most important one, only recently identified, is the catalytic decomposition of ozone by nitric oxide (NO) and nitrogen dioxide (NO_2). The two oxides of nitrogen are referred to collectively as NO_x. The natural concentrations of these oxides of nitrogen are not yet accurately known. They are only present in a few parts per billion, but they are recycled during ozone removal (i.e., they act as a catalyst).[1]... Reactive molecular fragments (radicals), which are formed in the photolysis of water vapor in the stratosphere, mainly at levels about 40 km, also destroy ozone catalytically....study has shown, however, that water vapor tends to reduce the concentration of NO_x by partially converting it to nitric acid. This tends to counteract the catalytic destruction of ozone by radicals derived from water vapor. An increase in stratospheric water could cause either an increase or decrease in ozone, depending on the water distribution....The stratosphere also contains numerous other minor constituents including carbon dioxide, methane, hydrogen, carbon monoxide, nitrous oxide, and nitric acid. Many of these are important to the chemical processes that occur within the stratosphere.

OZONE REDUCTION BY STRATOSPHERIC CHLORINE

In addition to the NO_x cycle of ozone destruction, photodissociated atomic chlorine is a free radical that can catalytically cause the removal of stratospheric ozone. It reacts by the cycle of two reactions shown below:

$$Cl + O_3 \rightarrow ClO + O_2 \tag{1}$$
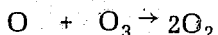$$ClO + O \rightarrow Cl + O_2 \tag{2}$$
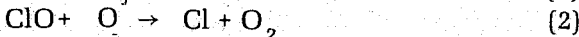
Net result
$$O + O_3 \rightarrow 2O_2$$

Note that in reaction (2) a Cl atom is formed which is then free to return to the chain by combining with more ozone as in reaction (1). One chlorine atom is capable of destroying thousands of ozone molecules. Present information indicates that the ClO_x cycle may be 3 times more efficient in destroying ozone than the NO_x cycle on a molecule for molecule basis.

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[1] Other sources of oxides of nitrogen in the stratosphere are effluents from high-altitude aircraft such as supersonic transports, powerful nuclear explosions, volcanic eruptions, solar proton storms and nitrous oxide (N_2O) from fertilizers.

The natural level of Cl in the stratosphere is not well known, but it is probably low. However, as with artificial NO_x, the addition of artificial ClO_x has the effect of reducing the natural ozone level. Most man-made chlorine-containing compounds are rapidly removed from the lower atmosphere by precipitation and by other weather processes. However, some molecules containing chlorine can survive in the lower atmosphere for many years, and thus can last long enough to reach the stratosphere.

Table III-1 shows the tropospheric average residence times of certain halocarbons based on reactions with OH (hydroxyl radicals) to form water (Cox et al., personal communication, 1975). The table shows that, because of their long average residence times, the most important molecules for possible reduction of ozone in the stratosphere are $CFCl_3$ (F-11), CF_2Cl_2 (F-12), and CCl_4 (carbon tetrachloride).

Table III-1. Average residence times of halocarbons in the troposphere based on reaction with OH radicals[1]
(After Cox et al., personal communication, 1975)

Halocarbon	Average residence times,[2] yr
Chloroform ($CHCl_3$)	0.19
Methylene chloride (CH_2Cl_2)	0.30
Methyl chloride (CH_3Cl)	0.37
1,1,1-trichloroethane (CH_3CCl_3)	1.1
1,1-difluoro-1-chloroethane (CH_3CF_2Cl)..	8
Dichlorodifluoromethane (F-12; CF_2Cl_2)	330 or more
Carbon tetrachloride (CCl_4)	330 or more
Trichlorofluoromethane (F-11; $CFCl_3$)..	1000 or more

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[1] Independent estimates by Yung, McElroy, and Wofsy (personal communication, 1975) suggest that the average residence times for some of the halocarbons may be as much as three times longer than those shown in the table. Wofsy (personal communication, 1975) estimates that the average residence time in the troposphere for F-22 ($CHClF_2$) is about 10 years, based upon room temperature reaction rates with OH.

[2] The time it takes for a substance to reduce to a concentration of 1/e or about one-third of its original value.

These fluorocarbon compounds are essentially inert in the lower atmosphere, a property of some significance for their main technological uses as solvents, aerosol spray propellants, and refrigerants. All such fluorocarbon uses involve eventual release

into the atmosphere and therefore potential transport into the stratosphere.

In the middle stratosphere, above about 25 km, these molecules are able to absorb solar energy in wavelengths of UV radiation (190 to 220 nm) and dissociate to release chlorine atoms. The inert parent molecules thus form the highly reactive chlorine atom that removes ozone by reactions (1) and (2) (*Molina and Rowland*, 1974; *Rowland and Molina*, 1974).

SOURCES OF
STRATOSPHERIC CHLORINE

Natural Sources of Stratospheric Chlorine

Ozone reduction will occur from many gaseous chlorine compounds that act as a source of active Cl in the stratosphere; thus, all possible sources must be considered. Large amounts of sea salt (NaCl) and hydrogen chloride (HCl) are injected into the lower atmosphere by natural events (e.g., sea spray) and man-made processes. However, both substances are effectively removed from the air by precipitation (rain, snow, etc.), impaction on vegetation and other obstacles, and by dry deposition. It is expected that negligible amounts will therefore enter the stratosphere (*Crutzen*, 1974a; *Wofsy and McElroy*, 1974; *Stolarski and Cicerone*, 1974; *Cadle*, 1975). An unknown, but presumably small, amount of F-11 vents from volcanoes (*Stoiber et al.*, 1971). In any case, natural sources of chlorine would be of minor significance to the question of *changing* concentrations of ozone unless:

(1) The amounts were so large that they invalidated the total calculation of the chemical balance of ozone in the stratosphere. The amount of chlorine required to disturb the calculations in this manner is at least ten times the Cl content of the CCl_4 now in the atmosphere (1×10^{-10} CCl_4 by volume).

(2) Rare and unusual natural events, such as catastrophic volcanic activity, introduced overwhelmingly large amounts of chlorine directly into the stratosphere.

Man-Made Sources of Stratospheric Chlorine and Other Halogens

The halogens of interest are a family of four active non-metallic chemical elements: fluorine, chlorine, bromine, and, to a lesser extent, iodine. These elements, because they are so active chemically, must be considered in the context of possible adverse effects on the atmospheric ozone layer. The term "halocarbon" is often used to describe compounds consisting of carbon, one or more of the halogens, and in some cases other elements such as hydrogen. Chlorocarbons and fluorocarbons are subsets of the halocarbons. Fluorocarbons -11 and -12 are also more specifically referred to as chlorofluoromethanes.

Many other man-made chlorinated organic compounds are released to the atmosphere (CH_3CCl_3, $CHCl_3$, $CHClCCl_2$, etc.) (*Rowland and Molina*, 1974); there may be some natural chlorine organics (CH_3Cl) (*Lovelock*, 1974a; *Rasmussen*, personal communication, 1974), but the molecules containing carbon—hydrogen (C—H) bonds or carbon—carbon (C=C) double bonds are also rapidly removed in the troposphere (see Table III-2), and are therefore not likely to be important for stratospheric calculations (*Rowland*, 1974; *Rowland et al.*, 1975). Thus, the most significant stratospheric chlorine compounds are those apparently inert in the troposphere: F-11, F-12, and CCl_4. Comparison of the amount of F-11 ($CFCl_3$) found in the atmosphere with that manufactured to date indicates that the atmospheric average residence time for $CFCl_3$, although uncertain, seems to be very long (see Table III-1); thus, it is essentially inert in the troposphere, as suggested in Table III-1.

Before 1973, only one stratospheric measurement of F-12 was obtained (*Murcray et al.*, 1975).[2] It has recently been shown that $CFCl_3$, CF_2Cl_2, CCl_4, and CH_3CCl_3 are present in the lower stratosphere (Lovelock, 1974a; *Hester*, personal communication, 1974); HCl has also been detected in the stratosphere (see "Measurements of Stratospheric Hydrogen Chloride," later in this section). No measurement has been reported for the chain carriers Cl and ClO.

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[2] Reporting a 1974 analysis of a 1968 balloon flight.

Table III-2. Halogenated hydrocarbon U.S. production in 1972.
(After *McCarthy,* 1974)

Chemical	Production[1]
Total	20,126,644
Carbon tetrachloride	996,687
Chlorinated paraffins, total	63,453
35 to 64% chlorine	40,806
Other	14,647
Chlorodifluoromethane	—
Chloroethane (ethyl chloride)	575,513
Chloroform	234,677
Chloromethane (methyl chloride)	453,533
1,2-dibromoethane (ethylene dibromide)	315,523
Dichlorodifluoromethane	439,224
1,2-dichloroethane (ethylene dichloride)	7,808,938
Dichloromethane (methylene chloride)	471,276
1,2-dichloropropane (propylene dichloride)	—
Iodomethane (methyl iodide)	18
Tetrachloroethylene (perchlorethylene)	734,216
1,1,1-trichlorethane (methyl chloroform)	440,681
Trichloroethylene	426,684
Trichlorofluoromethane	299,583
Vinyl chloride, monomer (chloroethylene)	5,088,511
All other halogenated hydrocarbons	1,722,674

[1] Production in thousands of pounds.

Another potential man-made source of stratospheric chlorine arises from the use of NH_4ClO_4 as fuel oxidant in the proposed U.S. Space Shuttle. About half of the chlorine so used will be released directly into the stratosphere. As the number of future Space Shuttle flights is predicted as about 60 per year, the thorough evaluation of such injections is important.

There are more than a dozen chlorine-containing organic chemicals produced in quantity in the range of 200 million to 8 billion pounds per year (100,000 to 4 million tons). Table III-2 gives the 1972 production of the principal halogenated hydrocarbons. Many of these chemicals, including trichloroethylene, perchloroethylene, methyl chloroform, and methylene chloride, are used in applications such that most of the annual production is lost to the atmosphere as are significant fractions of the annual production of carbon tetrachloride and methyl chloride. The two chlorinated chemicals in large production, ethylene dichloride and vinyl chloride, are not lost in large amounts in usage. However, estimates of ethylene dichloride and vinyl chloride losses through venting, spilling, and various production steps range from 3.0 to 6.3% (*Environmental Protection Agency,* 1974). By taking the estimate of over 5 billion pounds per year for vinyl chloride monomer production, it can be seen that losses can exceed 150 million pounds per year (see Table III-2). On a world-wide basis, it seems that the sum of such losses may approach or even exceed 5 billion pounds per year. Not all of this 5 billion pounds, however, will be capable of reaching the stratosphere.

Necessary initial steps in estimating the potential for ozone reduction by reactions in the stratosphere involving chlorine and other halogenated organic compounds include:

(1) Inventory of halogenated chemicals in large-scale production.

(2) Estimates of losses to atmosphere or water during production or use.

(3) Measurements of tropospheric concentrations.

(4) Determination of average residence times of halogenated substances in the troposphere: (a) kinetics and photochemistry, (b) removal by precipitation or dry deposition.

(5) Identification of reaction products formed.

(6) Search for natural sources of halogenated compounds.

These analyses are being made. The results will allow the development of a key set of long-lived species that can survive for periods sufficient to cross the tropopause into the stratosphere.

MODELING

Predictions of future levels of stratospheric ozone are derived from patterns of future injections of fluorocarbons and mathematical simulation of atmospheric transport and chemistry. These simulations or models vary in their complexity, differing primarily in degree of chemical interactions and assumed horizontal homogeneity. All models include

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processes by which both nature and man create and destroy ozone. Crucial to these processes are the estimates of solar energy absorbed by each of the several constituents (oxygen, ozone, and fluorocarbons) expressed as an "absorption cross section." Almost invariably, the transport is based on the assumption that the amount of each chemical species moves from regions of high concentration toward regions of low concentration. The proportionality factor describing the rapidity of the transport for a given gradient of concentration is termed "the eddy-diffusion coefficient."

Model Results

At least a dozen research groups have made estimates of ozone reduction from the NO_x emitted by supersonic transports, and many groups including some of those modeling the NO_x have also made calculations for ClO_x. Most models allow for variation only in the vertical, but some permit changes in both the north-south and vertical directions; one allows three-dimensional (north-south, east-west, and vertical) variability in the modeling of stratospheric motions. A comparison of the one-dimensional NO_x studies using identical chemistry but different transport has also been made. Comparison has shown that discrepancies among individual studies lie in the choice of values for atmospheric transport, the "eddy-diffusion coefficients" in the one-dimensional models. In general, the agreement among all of these NO_x models suggests that the estimates of ozone reduction expected for a given input of NO_x will vary only by about a factor of two from low to high estimates if the same eddy-diffusion coefficients are used in all calculations. The inclusion of the second and third dimensions in the calculation provides estimates of latitudinal and longitudinal variations, but does not appreciably alter the overall estimates of average ozone reduction. Calculations of ozone reductions from chlorine employ the same types of chemical reactions and transport processes used in the NO_x computations except that fluorocarbons rather than man-made NO_x are added to the system.

Four complete time-dependent, one-dimensional calculations (Wofsy et al., 1975; Crutzen, 1974b; Turco and Whitten, personal communication, 1975; Chang et al., personal communication, 1975) have been reported for the fluorocarbons, plus one two-dimensional calculation (Vupputuri and Boville, 1975). Calculations of the time dependence of relative ozone reduction have also been performed by two groups (Rowland and Molina, 1974; Cicerone et al., 1974), requiring normalization of actual ozone reduction by reference to one of the complete calculations. One comparison (Rowland and Molina, 1974) has been made of the atmospheric residence times and stratospheric delay times for different choices of eddy-diffusion coefficients. All of the various calculations utilize different (although presumably similar) procedures for estimation of solar flux versus altitude, for handling the chemistry, and for general calculation method.

All models use the absorption cross sections of Rowland and Molina (1974) for CF_2Cl_2 and $CFCl_3$ and the recommended chemical and photochemical reaction rate constants from the National Bureau of Standards–Climatic Impact Assessment Program (NBS–CIAP). Probably the most critical reaction rate in the present studies is the rate constant for the reaction $OH + HO_2 \rightarrow H_2O + O_2$. This reaction is important because the chlorine atoms that cause the problem of ozone reduction can be removed from the stratosphere through various reactions that result in the formation of hydrogen chloride (HCl), which could eventually diffuse downward to the troposphere and be removed. However, HCl can react with the hydroxyl radical (OH) to release a chlorine atom which could then re-enter the ozone-reducing chain. It is therefore important to know the concentration of OH in the stratosphere. The NBS–CIAP recommendation for the rate constant for $OH + HO_2 \rightarrow H_2O + O_2$ is a range between 2×10^{-11} (low) and 2×10^{-10} (high) cm^3 molecule^{-1} sec^{-1}. The major effect of the choice of the "high" value for this rate constant is to reduce the average OH concentration, which in turn slows down the rate of return of HCl to the chain reaction sequence through the reaction $OH + HCl \rightarrow Cl + H_2O$. The net effect is a lower ozone reduction than for the low value 2×10^{-11}.

Crutzen (1975) calculated the time history of ozone reduction caused by fluorocarbons in a
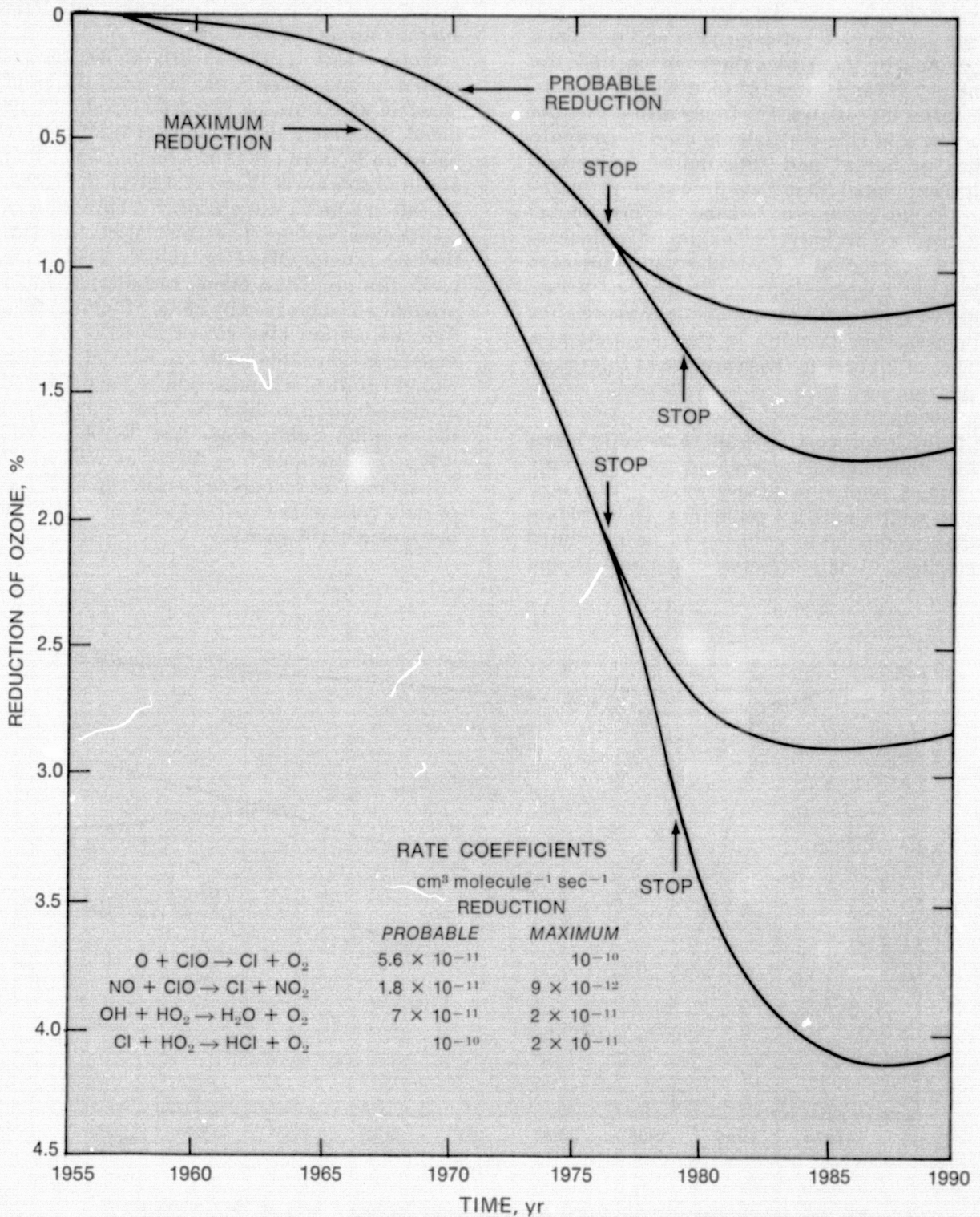
Fig. III-1. Time history of the percentage of ozone reduction due to fluorocarbons. "STOP" denotes the date after which fluorocarbons are no longer released to the atmosphere. Rate constants for certain chemical and photochemical reactions used in each set of calculations are also shown. (After *Crutzen*, 1975)

one-dimensional model assuming a 10% per year growth rate between 1974 and the times indicated by the arrows shown in Fig. III-1, the end of 1975 and the end of 1978. No releases occur after these dates. The figure also shows the two sets of rate coefficients used to compute the "probable" and "maximum" reduction. Crutzen noted that new information might reduce the ozone even beyond the "maximum" reduction. This lower or "maximum" reduction curve represents a 2.5-fold-greater decrease than the "probable" curve. The greatest reduction on each curve occurs about 10 years after the cessation of input. In this calculation, a delay of 3 years in the cessation of fluorocarbon releases leads to an additional ozone reduction of 0.6%

If the lower curve proves to be valid when new information on reaction rate constants becomes available, the 3-year delay will lead to an additional 1.4% reduction. These reductions would be in addition to an estimated reduction to date of between 0.5 and 1% and perhaps as much as 2% below the long-term average ozone levels.

Wofsy et al., (1975) clearly show the expected ozone reductions for four different possible scenarios in Fig. III-2. It should be noted, however, that these calculations are based on F-11 and F-12 production rates that are 20 to 30% lower than those given in Section VI, but in which tropospheric F-11 predictions match observations. This calculation also uses the high rate for OH + HO$_2$. If the low rate were used, the predicted ozone reductions would probably be increased by about a factor of two. The calculation also substitutes the new Cl atom reaction rates with O$_3$ and CH$_4$, which would result in a diminution of the predicted ozone reduction to about half that appearing in the original publication. The Wofsy et al., (1975) calculations (Fig. III-2), as well as all others, must be recognized as interim, as revised rate constants expected soon are likely to produce modifications.
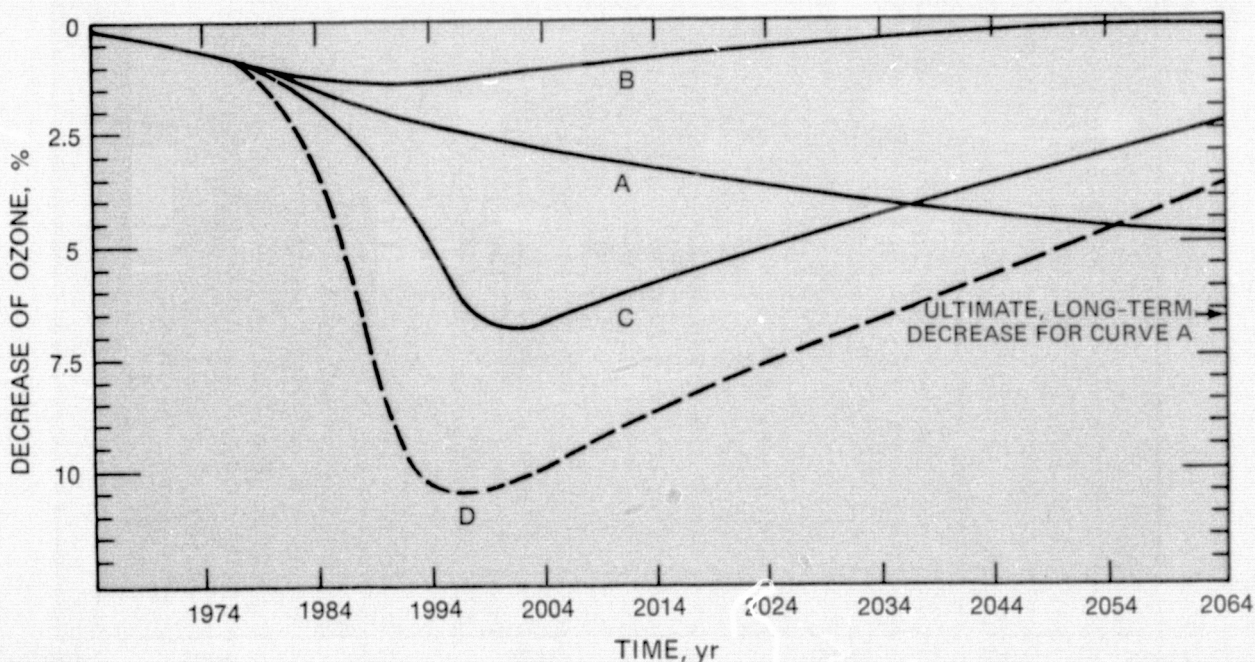
Fig. III-2. Interim reductions in global ozone computed for four models. In 1972, emissions of CF$_2$Cl$_2$ and CFCl$_3$ were assumed to be about 3 x 10^5 and 2 x 10^5 metric tons, respectively. Growth rates for each fluorocarbon are 10% per year (7-year doubling) for models B and C and 22% for model D. Production held constant at the 1972 level for A. Fluorocarbon emissions are assumed to end abruptly in 1978, 1995, and 1987 for models B, C, and D, respectively. The small arrow at the right side of the figure indicates the ultimate amount of ozone reduction that will be reached, according to model A, after many years have passed. (After Wofsy et al., 1975; modified by Wofsy, personal communication, 1975)

Calculations of carbon tetrachloride behavior in the stratosphere have been reported by *Molina and Rowland* (1974). *Crutzen* (personal communication, 1975) estimates an ozone reduction of 0.5 to 2% maximum due to the existing CCl_4 content in the atmosphere. Much of the current production of CCl_4 is used in the production of fluorocarbons, however, and future uses are not expected to result in as much release into the atmosphere as in the past. More study is required of the man-made and natural sources of CCl_4 and its behavior in the atmosphere.

MEASUREMENTS

The Importance of Trace Gas Measurements

In order to make reliable estimates of future large-scale climatic changes, either natural or man-made, it is necessary to rely upon the ability to simulate the physical and chemical processes in the atmosphere. As the full complexity of the atmospheric processes cannot be simulated on a laboratory scale, the most efficient tool is numerical simulation or modeling of such processes with the aid of fast electronic computers. As any model is an idealization of the complex real world, it is important to check its validity against observations. Some models may be more detailed in their treatment of the photochemical processes, others more detailed in their treatment of dynamic processes. A knowledge of the distribution of a number of trace gases is extremely important to test the validity of such models and/or to provide input parameters for them. Information is needed about large numbers of trace gases. There are many important gases formed within the stratosphere by natural processes; the most significant of these gases are O_3, O, NO, NO_2, N_2O_5, HNO_3, HCl, ClO, Cl, and H_2. Some trace gases are or may be deposited directly into the stratosphere by volcanic activity (mainly HCl, HF, and SO_2) or by high-altitude aircraft (NO, NO_2) or rockets (HCl from Space Shuttle). Some important minor gases with low solubility or reactivity in cloud droplets, e.g., N_2O, CH_4, CO, H_2, can diffuse upward into the stratosphere through the cloud and rain filter of the troposphere.

This class of gases also includes some industrial products such as the halogenated hydrocarbons (CF_2Cl_2, $CFCl_3$, CCl_4, CH_3Cl, CH_2Cl_2, $CHCl_3$).

All of these gases differ with respect to their origin and chemistry. Their distribution is modified by large- and small-scale atmospheric wind systems. Consequently, their temporal and spatial distributions provide essential information regarding the photochemical and transport properties of the atmosphere.

Measurements of Stratospheric Fluorocarbon and Carbon Tectrachloride

Many hundreds of measurements of F-11 have been obtained at ground level and in the rest of the troposphere as of May 1975. The results are documented in the ICAS Report No. 18a. Unfortunately, only a few observations of F-12 have been made because of the greater difficulty in its measurement; there are even fewer observations of carbon tetrachloride. The ratio of F-12 to F-11 in clean air locations is about 1.65 to 1.80 to 1. As no universal standard exists for F-11, F-12, or CCl_4, there is still some uncertainty in absolute readings and thus in comparisons of results among different investigators.

Local fluorocarbon sources such as in urban areas produce high local concentrations and unrepresentative ratios of F-12 to F-11 that differ from world-wide averages. In clean areas, there seems to be a seasonal variation of F-11 that may be due to seasonal differences in releases of fluorocarbons to the atmosphere and/or seasonal differences in the intensity of vertical mixing in the troposphere. Weak evidence suggests higher values at ground level north of 50°N than south of that latitude. Hemispheric differences are clear cut, however. In 1974, the northern hemisphere, the primary source of F-11, contained about 100 parts per trillion by volume (pptv) in clean air; the southern hemisphere contained about 60 pptv at Capetown, South Africa (*Lovelock*, 1974a) and 80 pptv in the band 5 to 15°S (*Wilkniss et al.*, 1975). From the limited amount of aircraft data, both the fluorocarbons and carbon tetrachloride concentrations

seem to be fairly uniform with height in the troposphere of the northern hemisphere.

Available data show an unequivocal increase in F-11 concentration with time through 1974, the most recent available information. From the relatively constant F-12 to F-11 ratio, it may be assumed that F-12 had a similar increase with time. The growth rate between 1973 and 1974 seems to be as large or larger than in earlier years. Carbon tetrachloride data are scanty, but in the 1973-1974 interval, the CCl_4 seems to have increased in percentage as much as has the F-11. Additional study of the significance of the CCl_4 concentration and growth is required, taking into consideration those factors given previously.
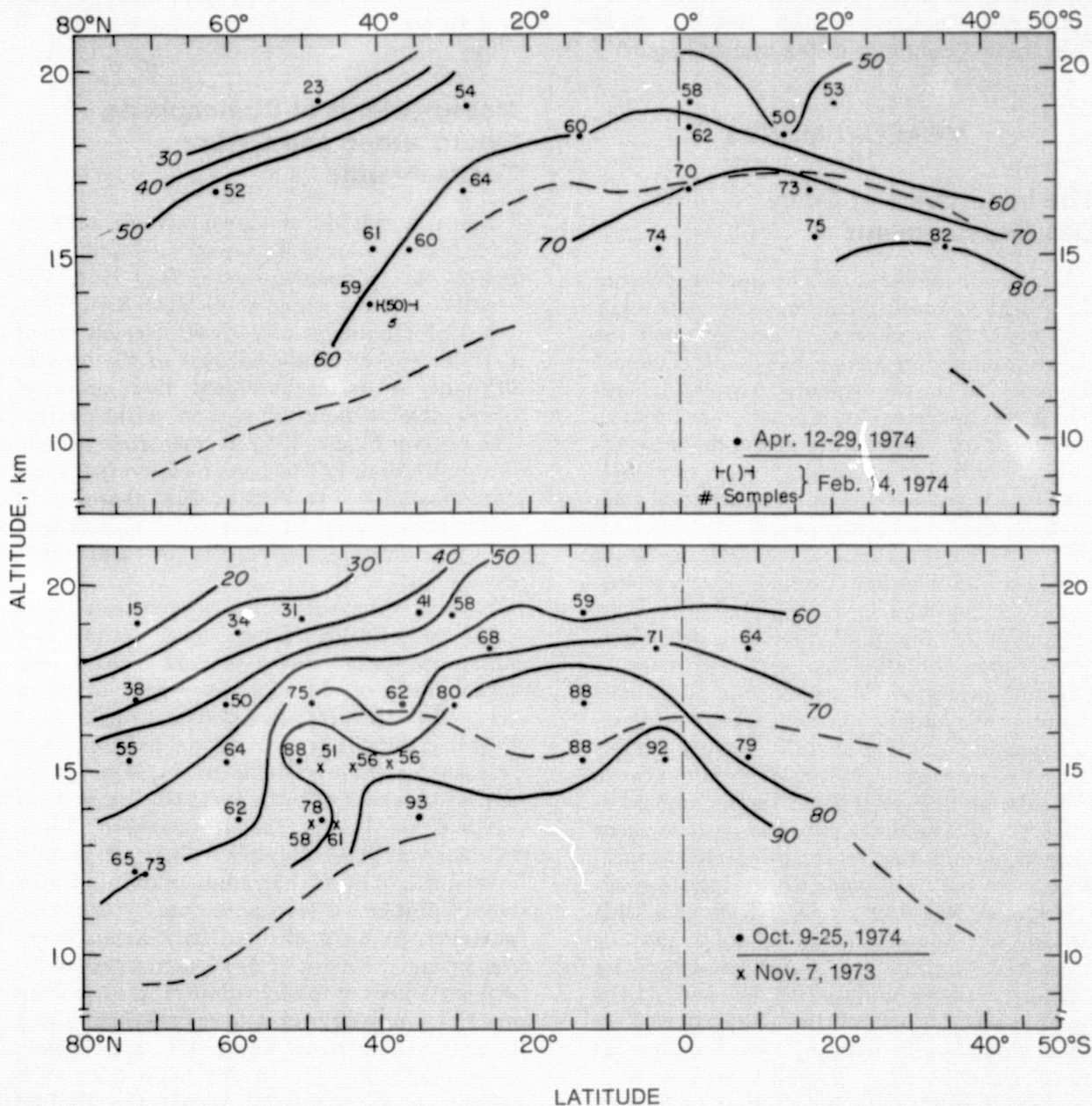
Fig. III-3. Observed atmospheric concentrations of F-11 in parts per trillion by volume. Dashed lines denote the observed average tropopause positions during sampling periods. Solid lines are subjectively drawn between observation points. (After *Krey and Lagomarsino*, 1975)

Measurements of
Stratospheric F-11, F-12, and SF₆

Because of their low concentrations and, until recently, the lack of an urgent justification for their measurement, there are understandably few analyses of fluorocarbons in the stratosphere. Three laboratories have reported stratospheric results up to the present time.

In November 1973, the Health and Safety Laboratory (HASL) of the Atomic Energy Commission (AEC) began measurements of F-11 and SF_6 (sulfur hexafluoride, an industrial product) in the stratosphere as part of a global study of atmospheric diffusion. The stability of these materials and the absence of any known tropospheric sink made them excellent candidates for the diffusion study. The
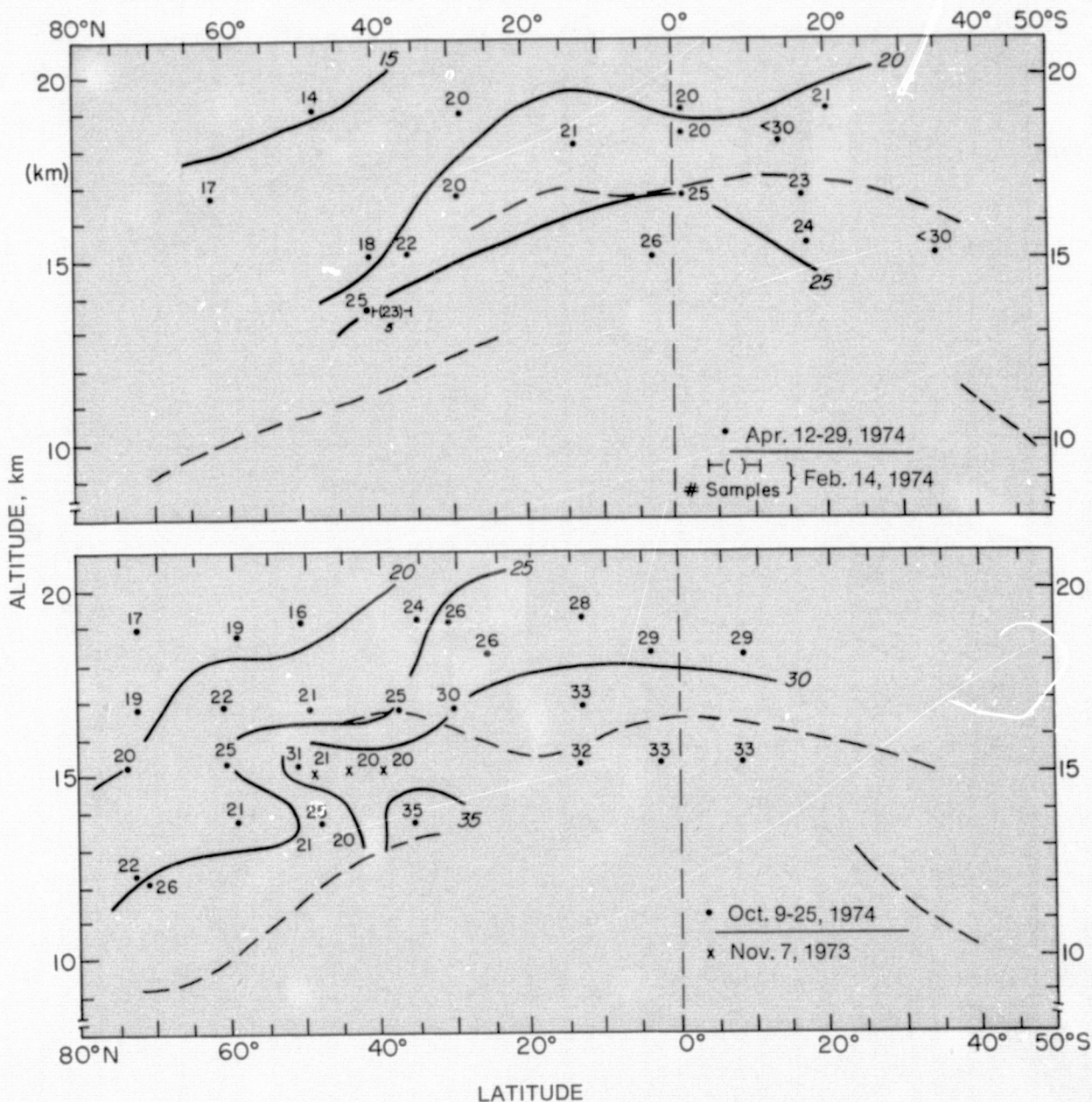
Fig. III-4. Observed atmospheric concentrations of SF_6 in hundred of parts per trillion by volume. Dashed lines denote the observed average tropopause positions during sampling periods. Solid lines are subjectively drawn between observation points. (After *Krey and Lagomarsino*, 1975).

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samples were collected by high-altitude WB-57F aircraft under Project Airstream, which is an on-going HASL investigation of the radioactivity structure and burden of the stratosphere over North and South America.

Hester (personal communication, 1975) analyzed several stratospheric air samples for F-11 and F-12 collected over the western United States in May 1974. These samples

were obtained by the WB-57F aircraft with the identical sampling system used in the HASL study.

Lovelock (1974b) is the third source of halocarbon measurements in the stratosphere. His data are based upon an aircraft flight in June 1974 that barely penetrated into the lower stratosphere over the Irish Sea. The collection system for this flight was an evacuated pre-
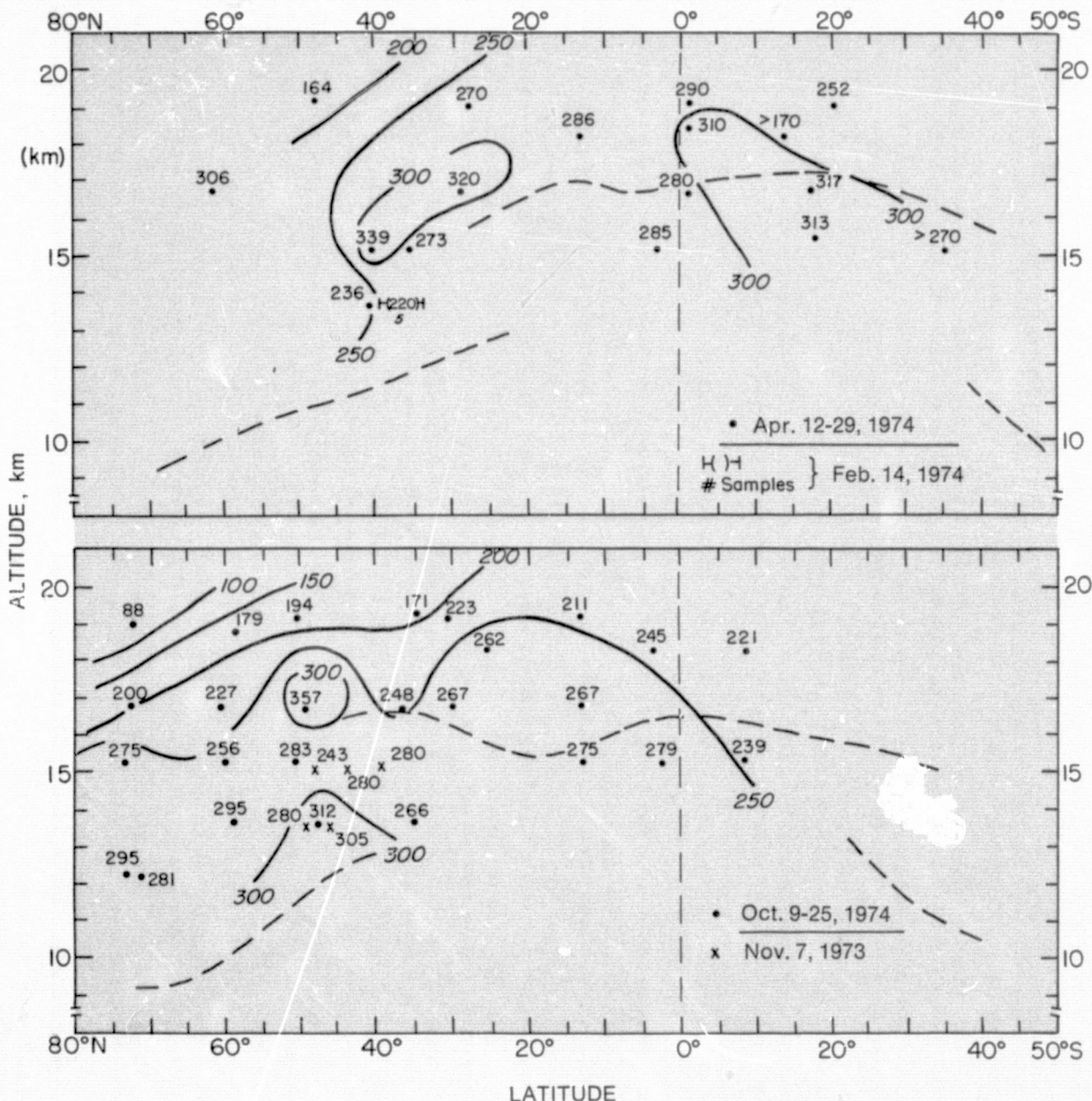

Fig. III-5. Observed atmospheric ratios of F-11 to SF$_6$ derived from Figs. III-3 and III-4. Dashed lines denote the observed average tropopause positions during sampling periods. Solid lines are subjectively drawn between observation points. (After *Krey and Lagomarsino*, 1975)

treated glass flask; this system offers a valuable comparison. The gases detected were $CFCl_3$, CCl_4, and CH_3CCl_3.

Patterns of F-11 and SF_6 from the HASL studies appear in Figs. III-3 and III-4 for the periods April 1974 and October 1974 in both the upper troposphere and lower stratosphere. The downward slope of the isolines of concentration toward the poles is typical of all tracers in the lower stratosphere. As with other tracers, the patterns are highly suggestive of preferential entry into the stratosphere in equatorial latitudes, slightly south of the geographical equator in winter and north in summer. This seasonal variation is consistent with meteorological circulations in the troposphere where air in the lower altitudes converges toward the meteorological equator and rises, with a small portion thought to enter the stratosphere. The lowest concentration in the figure appears at the highest sampling altitudes nearest the poles. This feature also agrees with other tracers; this region possesses air that has been in the troposphere the longest time in the past.

Figure III-5 presents the ratio of F-11 to SF_6. In general, the ratios decrease upward, especially in the high-latitude stratosphere. This variation with altitude has two possible explanations. First, the time history of the two substances may be different; for example, the SF_6 may have been injected into the atmosphere a longer time ago, allowing a more uniform distribution with height than is the case for F-11. As of this writing, the time input history into the air of SF_6 is unknown. Second, the lower ratio of F-11 to SF_6 at higher altitudes may be accounted for by photodissociation of F-11. It is likely that SF_6 is more stable than F-11 in the stratosphere. If the latter explanation for the decreasing ratios with height into the stratosphere is correct, these data constitute the first atmospheric evidence for photodissociation of F-11.

Measurements of Stratospheric Hydrogen Chloride

There are three general approaches for measuring stratospheric HCl either currently in use or under development. The only technique now yielding concentrations entails the capture of HCl from stratospheric air drawn through chemically impregnated filters and subsequent laboratory analysis of the chloride ion. Two highly sensitive infrared spectrophotometers, one utilizing a diffraction grating and the other interferometry, will soon be available for both ground-based and airborne observations. These instruments determine HCl concentration by determining its absorption of solar radiation. A third technique involving surface ionization is currently in the exploratory stage and appears extremely promising.

Based on infrared spectrometry, an upper limit of 0.18 parts per billion by volume (ppbv) HCl above 12 km was reported by *Farmer* (1974) and *Farmer et al.*, (1974) as early as September 1973. This upper limit assumes uniform mixing and therefore does not preclude layers of higher concentration. Farmer also reported observations of infrared absorptions, suggesting an upper limit of 0.8 ppbv for uniform concentration above 16 km. These results are consistent with the measurements obtained by base-impregnated filters (*Lazrus et al.*, 1974) shown in Fig. III-6. Multiplying ppbv HCl by 1.2 converts this unit to parts per billion by mass (ppbm) HCl.

The concentration of HCl in the upper troposphere is low, as seen in Fig. III-6 and confirmed by infrared spectrometry (*Farmer et al.*, 1974). It is likely that these low concentrations of HCl are derived from ground-level sources. The small value in the upper troposphere shows the results of precipitation scavenging. Increasing concentration with altitude in the stratosphere, confirmed by data collected after 1974 by *Lazrus et al.* (1974) probably reflects a source at high altitudes generated by photodissociation of CCl_4, fluorocarbons, and some other chlorine-bearing compounds in accord with model calculations.

Uncertainties in the spectrometric results are introduced by possible absorptions by other species at the HCl line frequencies. Detailed laboratory and theoretical studies are underway to resolve this issue.

The parts of the sampling filter paper that do not collect HCl obtain only sporadic and small concentrations of chlorides. It is possible that the filter paper actually collects much more chloride, but that the latter is converted to HCl on the paper and, being gaseous, is then lost.
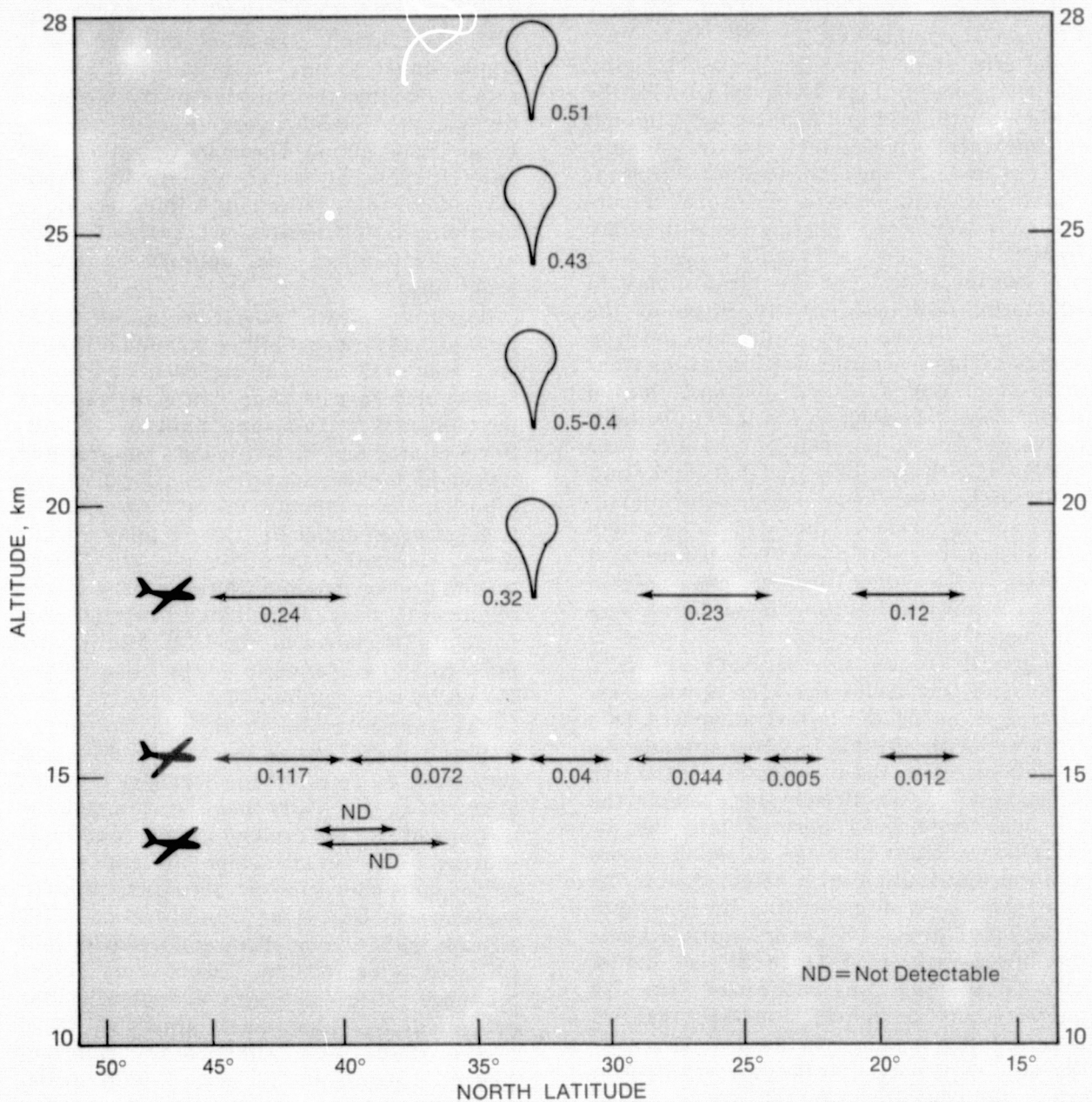
Fig. III-6. Stratospheric measurements of HCl obtained onboard aircraft and balloons by the base-impregnated filter method. (After *Lazrus et al.*, 1974)

Measurements of Stratospheric NO$_x$

During the past 3 years, there have been many measurements of NO$_x$ and O$_3$ concentrations. The results of these measurements show considerable variability in the NO concentration over both short (hours) and long (year) time scales; observed variations are greater than can be explained by instrument uncertainty. Insufficient data are available to determine whether there are seasonal or latitudinal effects. One-dimensional models are incapable of accounting for such variability. Nevertheless, model predictions that represent average values on a global basis are not inconsistent with these measurements.

Perhaps of more significance is the fact that the models are compatible with the relative amounts of observed NO, NO_2, HNO_3, and O_3, indicating the internal consistency of the models and lending credibility to predictions of the effect of increasing the NO_x burden on the O_3 budget, again on a global average basis.

Measurement of Cosmogenic Chlorine

Young et al. (1970) have measured chlorines-38 and -39 on filter papers at 18.2 km. These radioisotopes originate from the cosmic ray bombardment of atmospheric argon and possess 37- and 55-minute radioactive half-lives, respectively; 30% or more of the ambient concentration of the two radioisotopes was filtered from the air.

It is thought that ClO in gaseous form will attach to the filter papers. This likelihood will be checked in the laboratory in the near future.

Because of the short half lives of the two chlorine isotopes, their measurements can yield valuable information about the early stages of the chemical transformations of chlorine. Ratios of stable chlorine derived from the fluorocarbons, CCl_4, and other natural halogen gases to chlorines-38 and -39 may be especially important in confirming or rejecting certain parts of the theory used to predict an ozone reduction.

Ozone Today

The ozone shield against excessive UV radiation at ground level is world-wide. In order to obtain the total UV radiation reduction due to ozone, one measures the "total" ozone (ozone contained in a vertical air column of unit cross section corrected to sea level pressure). It is expressed as the apparent depth of pure ozone atmosphere assuming the gas to have a standard density. A typical depth in the mid-latitudes is 0.3 cm. Total ozone depths are observed daily at tens of stations over the globe. Typically, average monthly, seasonal, or annual values are treated in order to minimize the variability. Figure III-7 is an analysis of average annual total ozone values. The numerals on the map are the apparent depth values of ozone multiplied by 1000 to eliminate decimals. Note in the figure that the yearly average distribution of ozone shows a minimum of ozone (as low as less than 240 units) straddling the equator and an increase in total ozone poleward to values of as high as 380.

In addition to the horizontal variation in total ozone, evident in Fig. III-7, there is also a pronounced variation in the vertical distribution of ozone concentration. In general, the height of the maximum ozone concentration rises from about 17 km over the winter hemisphere pole to about 25 km over the equator and then descends to about 22 km over the pole in the summer hemisphere. The result of this pattern is to virtually cut off UV radiation below about 20 km.

OZONE TRENDS

Several previous studies have emphasized the increase in total ozone (hereafter referred to as ozone in this section) that occurred in most regions of the world during the 1960's (*Komhyr et al.*, 1971; *Angell and Korshover*, 1973; *Goldsmith et al.*, 1973; *London and Kelley*, 1974).

Between 1962 and 1970 there was an increase in ozone in all regions of the hemisphere (Table III-3); this increase varied from 1% in Japan to an indicated 8% in European Russia, with an average increase of 4% if each region is weighted equally. The increase is statistically significant at the 5% level in the West Arctic, West Europe, East Europe, European Russia, North America, and India. A significant increase was also noted in the South Tropics, but there was no appreciable change in Australia and Antarctica during this interval; on the average, at Pretoria and Buenos Aires, there was a 2% decrease between 1966 and 1970. Thus, in south temperate and polar latitudes there was, if anything, a statistically insignificant decrease in ozone during this period.

There is clear evidence for a secondary ozone maximum at the Western European stations in 1960. Table III-3 shows that, between 1960 and 1962, there was a 1 to 2% decrease in ozone in West Arctic, European Russia, West Europe, and North America, but a 1 to 2% increase in Japan and India, suggesting that the decrease was confined to more northerly latitudes (there was also a 1% decrease in Antarctica). None of the decreases is statistically significant. Large nuclear explosions that inject debris into the

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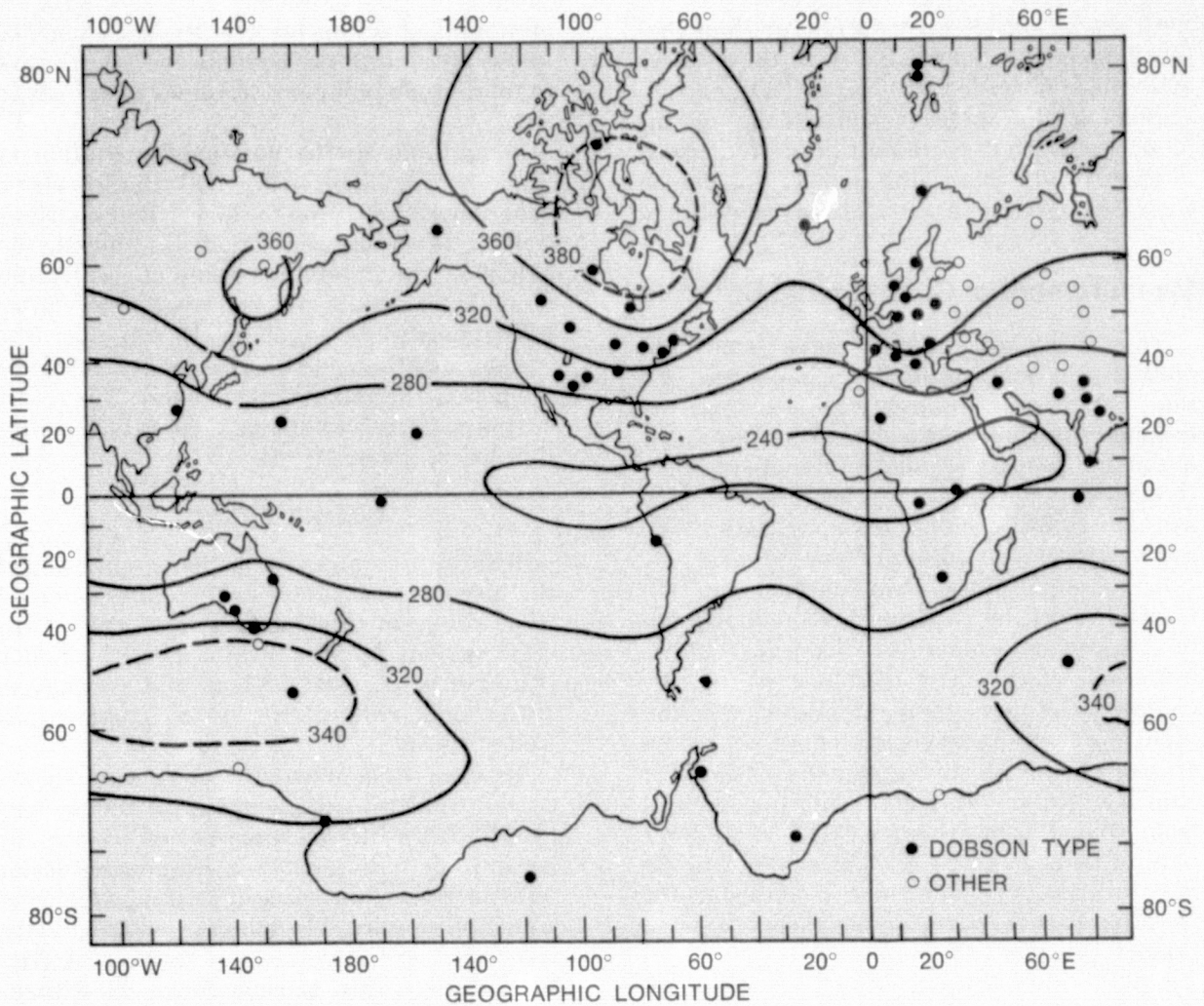
Fig. III-7. Average global distributions of total ozone. The ozone amounts are given in milli-atmosphere-cm. (After *Gebbart et al.*, 1970)

stratosphere are believed also to be a major source of nitrogen oxides. *Johnston et al.* (1973) note that the extensive nuclear testing in the autumn of 1961 and 1962 could account for the above decreases in ozone. As the decrease in ozone began before the nuclear tests, however, this explanation is not completely satisfactory. In West Europe there was a highly significant 7% increase in ozone between 1955 and 1970, a value similar to that for India but twice as large as for European Russia.

Between 1970 and 1972, there was a 1 to 2% decrease in ozone for all regions in the northern and southern hemispheres except Asiatic Russia and the South Tropics, both of which exhibited no change. Thus, there is little doubt that the upward trend in ozone observed in the 1960's has been reversed, at least temporarily.

The left-hand part of Fig. III-8 shows the ozone trend between 1963 and 1974 at five contiguous United States stations, three British stations, and at Mauna Loa, Hawaii, and Huancayo, Peru. Between 1970 and 1974 there has been a decrease in ozone in the contiguous United States, Great Britain, and at Mauna Loa and Huancayo stations. Table III-4 shows that the decrease varies from 2.3% in the United States to 0.7% at Huancayo, with an average of 1.9% if all stations are weighted equally. The decrease in the United States and

Table III-3. Percentage change in total ozone in the given regions (ordered by mean latitude) for the given period intervals. The numbers in parentheses indicate the slightly different period intervals for some regions.
(After *Angell and Korshover,* 1975)

Region	1960-1962	1962-1970	1970-1972	1955-1970
Russian Arctic (72°N)		4	-2	
West Arctic (70°N)	-1	6	-1	
European Russia (51°N)	-2	8	-1	4 (1958-1970)
Asiatic Russia (51°N)		5	0	
East Europe (51°N)		3 (1963-1970)	-2	
West Europe (48°N)	-2	4	-1	7
North America (45°N)	-1	3	-1	
Japan (37°N)	1	1	-1	0 (1958-1970)
India (21°N)	2	4	-1	8
South Tropics (8°S)		3 (1964-1970)	0	
Pretoria-B. Aires (30°S)		-2 (1966-1970)	-1	
Australia (40°S)	0	0	-1	-2 (1957-1970)
Antarctica (78°S)	-1	0 (1962-1968)		

Great Britain is barely significant at the 5% level. In the contiguous United States, and also at Mauna Loa, the approximately 2% decrease almost returns the ozone to its 1963 level. In Great Britain, however, the decrease amounts to only one-third of the increase between 1963 and 1970, and at Huancayo to one-fifth of this increase. (Only the first 4 months of 1974 are available at Huancayo, so the 1974 average is provisional.)

As shown by Table III-4, available evidence indicates that the annual rate of ozone reduction is diminishing, the decrease between 1971 and 1972 averaging 0.7% compared with 0.2% between 1973 and 1974. This trend is consistent in all locales, with the exception of Huancayo where the 1974 data are provisional.

The right-hand part of Fig. III-8 gives a more detailed picture of the recent variation in ozone. This has been accomplished by dealing not with annual means but with seasonal (spring, summer, fall, winter) means, where December-January-February represents winter in the northern hemisphere, etc.

Within the contiguous United States, the seasonal changes in ozone have been small from 1972-1974; the minimum usually associated with the tropical west wind maximum did not materialize in 1973-1974. In Great Britain, on the other hand, there was a fairly large increase in ozone in the summer

Table III-4. Annual percentage change in total ozone for given regions and stations, and the total change between 1970 and 1974. At right is the average change weighted by the number of stations.
(After *Angell and Korshover,* 1975)

Year	United States (5)	Great Britain (3)	Mauna Loa	Huancayo	Average
1970-1971 ...	-0.6	-0.4	-0.3	-0.1	-0.5
1971-1972 ...	-0.9	-0.6	-0.7	-0.2	-0.7
1972-1973 ...	-0.6	-0.5	-0.4	-0.2	-0.5
1973-1974 ...	-0.2	-0.3	0	-0.2	-0.2
Total	-2.3	-1.8	-1.4	-0.7	-1.9

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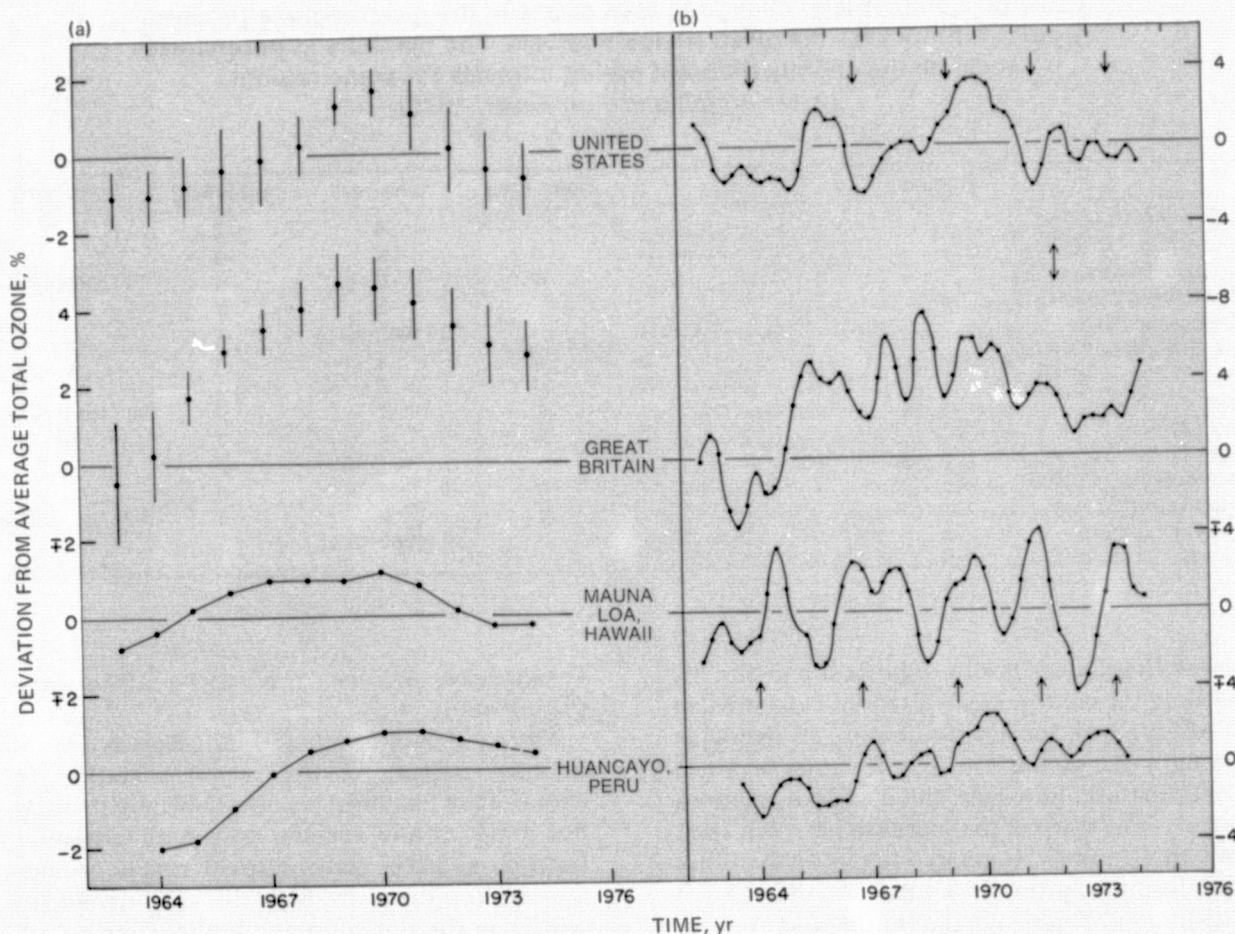
Fig. III-8. (a) Recent trend in total ozone based on five contiguous United States stations; three British stations; and at Mauna Loa, Hawaii; and Huancayo, Peru. (b) 1-2-1 smoothing of four successive seasonal values computed as a percentage deviation from the average for the total length of record. Single-headed arrows indicate the time of quasi-biennial west wind maximum at 50 mb in the tropics. Double-headed arrow indicates the date of an intense solar proton storm. (After *Angell and Korshover*, personal communication, 1975)

and autumn of 1974. The quasi-biennial oscillation is so dominant at Mauna Loa, Hawaii, that it is difficult to delineate other trends. However, Huancayo should be useful for trend analysis because it is in the tropics where ozone variations are generally small, and yet it is also at a latitude where quasi-biennial oscillations are minimal.

One of the several periodicities in ozone is an approximately 2-year cycle, a periodicity even more marked in the east-to-west winds in the equatorial lower stratosphere. This quasi-biennial cycle is indicated by the arrows on the right side of Fig. III-8, the dates of the strongest winds from the west in the tropics. The ozone minimum in 1972–1973 at United States and British stations may be related to the large solar flare (solar proton event) observed in August 1972 (double-headed arrow).

In summary, the increase in ozone noted during the 1960's in most regions of the northern hemisphere stopped by 1970; between 1970 and 1972 there was a 1 to 2% ozone reduction in all global regions except Asiatic Russia and the South Tropics, where there was no change. There was a significant 2% reduction in ozone in the United States and Great Britain between 1970 and 1974, bringing the value almost down to its 1963 level in the United States, but not nearly to this level in Great Britain or at Huancayo, Peru. The annual rate of ozone reduction

has diminished, however, with a value one-fourth as large between 1973 and 1974 as between 1971 and 1972. The reason for the change of rate is uncertain, but probably reflects the superpositions of several of the periodicities in ozone.

The detection of man-made influences on the amount of total ozone is made difficult by the natural, large-amplitude fluctuations that occur on various time scales. For example, for a typical mid-latitude station such as Arosa, Switzerland, the daily variations in ozone average almost 10% in winter and 5% in summer; the variations are much greater at higher latitudes. In addition, there is an approximately 25% annual variation and 2% quasi-biennial variation. There are also natural long-term trends (some possibly connected to the 11-year solar cycle), with ozone variations on the order of 5% in a decade.

Model predictions of ozone in the next few years indicate reductions of a few percent or less, depending on the assumed pattern of fluorocarbon injection and model assumptions. Being smaller, in general, than most of the natural fluctuations of ozone, one may logically ask the reasons for concern over such small changes:

(1) Large day-to-day changes are due to moving wind systems transporting ozone-rich or poor air from one area to another; hemispheric or globally averaged values would have a substantially smaller short-term variability.

(2) Large seasonal variations represent a natural cyclic behavior, which is part of normal climate and climate variability. Changes in ozone that disrupt or enhance the normal periodicities may alter the climate and climate fluctuations. The few percent of predicted changes are on the same order as the amplitude of the biennial and only slightly smaller than the uncertain 11-year solar cycle.

Methods for Measuring Fluorocarbons and Other Halocarbons

Complementary methods of analysis exist for fluorocarbons and other halocarbons that will allow the monitoring of these compounds in ambient air samples. The present methods are more than sensitive enough to measure the levels of both F-11 and F-12 in tropospheric and lower stratospheric samples, and should be sensitive enough to measure fluorocarbon concentrations in samples taken from the higher stratosphere.

To measure the concentrations of fluorocarbon air pollutants, three basic techniques are used:

(1) *Gas chromatography utilizing an electron-capture detection system (GCECD).* Because of its low cost and high sensitivity, this is the most widely used method of analysis for fluorocarbons, and will probably continue to be. There are, however, gaps in GCECD system capabilities that should be filled by the other instrumentation discussed.

(2) *Gas chromatography followed by a mass spectrometer with a single ion detector (GCMS).* This system offers more sensitivity to the total spectrum of halocarbons than does GCECD and should find wide use in the analysis of halogenated hydrocarbons that are not easily measured by electron capture.

(3) *Long-path infrared spectroscopy (LPIRS).* This system offers the capability of real-time, continuous measurements and will be most useful in the examination of the chemistry of fluorocarbons and other halocarbons.

The advantages and disadvantages of each system are discussed in detail in ICAS Report No. 18a.

Methods for Measuring Chlorine and Its Compounds in the Stratosphere

Because of the large natural variations in ozone concentrations, man-made changes are difficult to observe and probably would reveal no harmful effects of pollutants until the effects had become serious. Thus, it seems more practical to monitor the pollutants themselves or products of their reactions with ozone. Such measurements might provide advance warnings of potential environmental problems.

When atomic chlorine reacts with ozone, one of the major products is ClO, which in turn can react with atomic oxygen to regenerate the atomic chlorine. Atomic chlorine can also react with methane and hydrogen to produce hydrogen chloride. To determine the effects of chlorine-containing compounds on stratospheric ozone, it is desirable to measure HCl and ClO or Cl. Although concepts do exist that appear promising, at present the task of measuring ClO is not easy because:

(1) There are no standard "off the shelf" instruments available for the measurement of trace chlorine gases.

(2) Concentrations predicted by stratospheric models are smaller than measurable by current laboratory techniques (mass spectrometer, interferometers, et cetera).

(3) Measuring equipment must operate unattended on aircraft, rockets, and balloons under less than ideal conditions.

At present, the concentrations of Cl and ClO can be obtained only theoretically. Calculations indicate that stratospheric Cl will be found in concentrations of 3×10^{-13} to 3×10^{-12} concentration by volume (v/v) (10^5 to 10^6 molecules per ambient cm^3), and ClO in concentrations of 3×10^{-11} v/v (10^7 molecules per ambient cm^3), all at 30 km.

There are three possible methods used to measure chlorine gases:

(1) Analysis of air filters.

(2) Spectrometry.

(3) Resonance-fluorescence scattering.

Air-filtration and spectroscopic techniques are currently available to measure HCl; however, it seems that Cl and ClO can best be measured by resonance-fluorescence techniques. Although this third method is sensitive and lends itself to routine use, a great deal of development is required.

Stratospheric Sampling Platforms

Several types of platforms, from commercial jets to satellites, are capable of making atmospheric measurements. However, for direct measurements in the altitude range of from 25 to 40 km (82,000 to 131,000 ft), the choice is essentially limited to balloons because they are the only existing vehicles that can reach those altitudes carrying large payloads and remain longer than a few seconds. To provide spatial and temporal coverage for studying the distribution of stratospheric constituents, balloons, carrying payloads of thousands of pounds, could be launched periodically at several, widely separated sites to various altitudes up to 40 km.

Because sampling over specific points on earth may not provide sufficient detail about the distribution of concentrations, aircraft, although limited in altitude, may have to be considered to supplement balloon data for three-dimensional contiguous coverage. Two aircraft capable of making measurements up to 21 km, the WB-57F and the U-2, are immediately available for making such measurements.

Questions have frequently been raised concerning the validity of data on minor atmospheric constituents sampled in the vicinity of the balloon. Recently, several flights were designed to address this criticism in the case of NO measurements. Results showed, at least in the case of NO, that the balloon and its payload do not affect the measurements. (The maximum altitude tested was 30 km.)

Stratospheric research aircraft available for immediate use are two U-2 planes located at the NASA Ames Research Center, California; two WB-57F planes operated from the NASA Johnson Space Center (JSC), Texas; and a joint DOT/AEC-sponsored WB-57F plane flown by NASA out of JSC. Although all of these aircraft are operated at near capacity, some residual hours could be made available for equipment development and test and some limited sampling profiles could be operated from the home bases.

Methods for Measuring Ozone

The ozone in a column (total ozone) is conventionally measured by a Dobson spectrophotometer (or an equivalent instrument in the Soviet Union). Such measurements undoubtedly will continue so that a limited number of locations can monitor trends in total ozone. However, the likelihood of detecting

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changes in total ozone attributable to fluorocarbons is poor in the presence of the marked natural variability in ozone. Model calculations of ozone reduction as a consequence of fluorocarbons indicate that the decrease will be more marked above the ozone concentration maximum or above about 25 km in altitude. In some calculations, there may be an increase in ozone below the maximum ozone concentration. Thus, to detect trends possibly due to fluorocarbons, emphasis should be directed toward ozone measurements at high altitudes rather than the total ozone.

Several important requirements that should be met by measurement systems to qualify them for detecting long-term trends in ozone concentration above the maximum are: sensitivity to changes in ozone concentration at the upper levels, accuracy of the data-evaluation method, good stability and precision of measurement, long lifetime, and economy of operation.

From research involving measurement of the vertical distribution of atmospheric ozone, there have evolved five practical measurement techniques:

(1) Umkehr (Götz et al., 1934; Mateer and Dütsch, 1964).

(2) ROCOZ (rocket ozone; Krueger et al., 1973).

(3) BUV (backscattering ultraviolet satellite experiment; Heath et al., 1973).

(4) LRIR (limb radiance inversion radiometer satellite experiment; Gille et al., 1973).

(5) Balloon-borne ozonesondes.

All of these techniques are capable of detecting ozone-concentration trends above the ozone maximum to an altitude of 45 to 50 km. The Umkehr and satellite techniques are in the remote-sensing category and require sophisticated mathematical inversion methods for inferring ozone profiles. The rocket and balloon techniques are in the category of direct sampling and have a higher vertical spatial resolution capability than remote-sensing techniques. Each of these techniques is discussed in ICAS Report No.

18a, which also contains an assessment of the capabilities and shortcomings of each technique.

ASSESSMENT OF POSSIBLE CLIMATIC EFFECTS RESULTING FROM LARGE DECREASES OF STRATOSPHERIC OZONE

The possibility of large reductions in stratospheric ozone leads to the speculation that changes in the earth's climate could also result. Such a conjecture is reasonable because ozone is a radiatively important gas in the atmosphere. It is the dominant gas controlling the absorption, and thus the thermal structure, of the stratosphere.

The possible response of the climate to a reduction and redistribution of the ozone column is enormously complicated because the climate of the earth is controlled by a large variety of physical processes that sometimes compete with one another and at other times become mutually reinforcing. Some of these processes involve long-term interactions with the ocean and the earth's ice (cryosphere). Other processes can be moderated or amplified through the effects of clouds in the atmosphere (e.g., Smagorinsky, 1974; Schneider and Dickinson, 1974). At present, the ability to formulate reliable numerical models of these processes and their implications for climatic change is still in its infancy (Manabe and Bryan, 1969; Manabe, 1974). More simplified models of climatic effects do exist, however, and provide the possibility of examining first-order responses to various climate-perturbing mechanisms (Budyko, 1969; Sellers, 1969, 1973; Kurihara, 1970; Faegre, 1972; MacCracken, 1973; Schneider and Gal-Chen, 1973; Gal-Chen and Schneider, 1974; Held and Suavez, 1974). These models help to determine whether a given climate-perturbing mechanism is insignificantly small or potentially significant. In many cases, a simplified model is sufficient to demonstrate that a hypothesized effect is too small to lead to any measurable response by the climatic system. However, in cases where a significant climatic response is indicated by a simplified model, a more cautious interpretation should be taken. In such cases, a reasonable inference would be

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that a climatic response may be possible, but that the nature of such a response cannot be reliably predicted. The possibility of climatic changes resulting from large decreases in the amount of ozone and changes in its distribution seems to fall in this category.

One of the simplest possible models of climate is that provided by the vertical one-dimensional models of radiative-convective equilibrium (*Manabe and Wetherald*, 1967). In these models, the equilibrium vertical temperature is assumed to be only a function of the incoming solar radiation; an assigned distribution of absorbing gases and aerosols (e.g., carbon dioxide, ozone, cloudiness, and dust); and an assumption that the vertical gradient of temperature be stable enough to inhibit convective processes.

At present, there appear to be no calculations of radiative-convective equilibrium that have utilized the type of fluorocarbon-induced ozone changes indicated by the simplified photochemical/transport models. However, three unpublished calculations have been performed at the Geophysical Fluid Dynamics Laboratory (NOAA), Langley Research Center (NASA), and the National Center for Atmospheric Research for the related problem of, and assumed factor-of-two reduction of ozone everywhere in the vertical column. These crude calculations indicate a possible temperature decrease of about 5° to 10°Celsius in the middle and upper stratosphere. Such changes, if valid, are large. Much lower temperature changes (about 0.5°C) in the troposphere are indicated. It must again be emphasized that such models are drastically simplified and may not be interpreted as a meaningful prediction of the actual climatic response.

However, it does seem reasonable to infer that temperature decreases by as much as 10°C in the upper stratosphere would result in observable alterations of the general circulation of that part of the atmosphere. The possibility that an altered circulation in the upper stratosphere would lead to an observable change in the tropospheric climate should be considered as totally speculative at this time. That possibility cannot be excluded; but at present, the nature and degree of the actual climate response expected must be considered as unknown.

INDUSTRY RESEARCH PROGRAM

The Fluorocarbons Technical Panel, supported by 19 fluorocarbon manufacturers throughout the world and administered by the Manufacturing Chemists Association, has had an active program of atmospheric research for several years. Since the question of the effect of fluorocarbons on ozone was raised in 1974, this industrial research effort has been redirected and enlarged to address this matter. Industry has reported that they are planning to spend between 3.75 and 5 million dollars over the next 3 years, with the possibility of this amount increasing considerably as more pertinent studies are reviewed.

Distribution of Chlorine-Containing Compounds in the Atmosphere

The fluorocarbon industry is supporting atmospheric sampling programs directed at understanding the rate of accumulation and pattern of distribution of fluorocarbons and other chlorine-containing compounds, both man-made and natural, in the atmosphere. These programs include measurements in the troposphere and in the stratosphere.

Chemistry of Chlorine-Containing Compounds in the Stratosphere

Analytical experiments are being supported that are needed to provide the basis for development of various techniques for measuring concentration of chlorine and ClO in the stratosphere; such measurements are believed crucial in assessing the validity of the theory of ozone reduction by fluorocarbons. Planned research includes measurement of the altitude dependence of chlorine atoms using a resonance-fluorescence technique similar to one previously used in determination of atomic oxygen. If preliminary work proves successful, the Fluorocarbons Technical Panel expects to support balloon or rocket ascents into the stratosphere to make measurements of those critical species.

Support is also being given to measurements of the reaction rates of critical species, especially the ClO radical, designed to further elucidate the chlorine chemistry in the stratosphere and particularly to determine

whether the chlorine atoms might undergo reactions leading to stable, harmless substances.

Ozone Concentration in the Stratosphere

To gain a better understanding of the amounts and importance of ozone in the atmosphere and the patterns of ozone variations, assessments are being made of the data resulting from Federally supported monitoring of the ozone concentration in the atmosphere.

Modeling of Atmospheric Processes

The Fluorocarbons Technical Panel expects to form a panel of several qualified atmospheric modelers to offer comments on the scope and depth of the technical program as presently conceived. This panel of modelers will conduct analyses of the assumptions and data used in the several current models that have been used to predict ozone reduction, and evaluate new data (e.g., from stratospheric sampling and rate reaction experiments) as they become available.

FEDERAL STRATOSPHERIC RESEARCH EFFORTS

Plan for a Coordinated Federal Research Program

Since October 1974, the ICAS has been acting as a coordinator for the member Federal agencies involved in the stratospheric research efforts pertaining to the fluorocarbon-ozone question. ICAS discussions focused on the search for adequate instrumentation with which to conduct measurements of trace constituents in the upper atmosphere. As a result of these discussions, the Chairman of the Federal Council for Science and Technology requested, with the concurrence of the Administrator of the National Aeronautics and Space Administration (NASA), that NASA accept lead agency responsibility to coordinate Federal efforts to develop necessary new approaches.

Under NASA's chairmanship, ICAS formed a subcommittee, with other member agencies the Departments of Commerce, Transportation, and Defense; the Environmental Protection Agency; the Energy Research and Development Administration; and the National Science Foundation. The objective of this working group is to evolve a detailed plan for development and testing of instruments and measuring systems.

This plan, now being formulated, will initiate measurements of trace constituents that have been identified as significant and others that may subsequently be identified as such, and will also provide for the development and testing of the instruments used to make such measurements.

The ICAS Panel on Inadvertent Modification of Weather and Climate has subsequently been charged with the formulation of a more general plan for subsequent research programs and atmospheric monitoring efforts. This research and monitoring plan is heavily dependent on results of the instrument development work; for example, whether the first practical instrument to measure stratospheric chlorine is one that is ground-based or one that is operated from a balloon, aircraft, or rocket is significant. The plan will be revised frequently as necessitated by future progress in the instrument development field.

Planned Federal Program for Addressing Critical Research Needs in the Atmospheric Sciences

A research and measurement program on the fluorocarbon-ozone question will consist of three phases:

(1) Field Measurements. Process of determining physical or chemical characteristics of the stratosphere by the use of in situ or remote-sensing devices. This phase includes development of instruments and platforms to perform these tasks.

(2) Laboratory Experiments. Laboratory simulation of atmospheric chemical and photochemical reactions and measurements of the results.

(3) Theoretical Studies. Development and use of modeling programs for describing stratospheric processes; interpretation of field measurements.

These three phases are discussed in detail in the subsequent paragraphs.

FIELD MEASUREMENTS

There is an urgent requirement to measure the concentration of certain stratospheric trace constituents needed by the models and that result from the predicted chemical and photochemical theory. Examples of the former are such radicals as OH and HO_2. The chlorine products of fluorocarbon photodissociation, especially ClO, are particularly important.

This work is the most significant because it involves the real atmosphere; it is the most costly and also the most difficult because of the need to detect trace constituents often using unmanned platforms in the high atmosphere. The Federal research program will support all reasonable ideas on instruments capable of making measurements of the trace constituents. Direct, in situ, as well as optical measurements should be undertaken. The time history of ozone concentration in the upper altitudes where the predicted changes due to fluorocarbons are most marked should be observed by ground-based and satellite techniques. The program should also include the search for other natural and man-made chlorine-bearing compounds in both the troposphere and stratosphere which may be participating with the fluorocarbons in ozone destruction. Advice on which chlorine compounds to seek will evolve from studies conducted in the laboratory and from theory. Other tracers, such as sulfur hexafluoride and carbon dioxide, should be measured along with the two fluorocarbons to provide guidance for calculations on vertical mixing. A program of gas standards is essential, as several groups are likely to be making many of the measurements of the trace constituents.

LABORATORY EXPERIMENTS

In the case of some reactions (e.g., $OH + HO_2 \rightarrow H_2O + O_2$ and $Cl + HO_2 \rightarrow HCl + O_2$; the models have shown that there is a need for more or better rate-constant data. A list of such reactions follows:

$$OH + HO_2 \rightarrow H_2O + O_2$$
$$Cl + HO_2 \rightarrow HCl + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + NO \rightarrow Cl + NO_2$$
$$ClO + O_3 \rightarrow Cl + 2O_2$$
$$ClO + O_3 \rightarrow ClO_2 + O_2$$
$$Cl + CH_4 \rightarrow HCl + CH_3$$
$$CCl_xF_y + h\nu \rightarrow CCl_{x-1}F_y + Cl$$
$$Cl + NO_2 + M \rightarrow ClNO_2 + M$$
$$ClNO_2 + O \rightarrow ClNO + O_2$$
$$ClNO_2 + h\nu \rightarrow ClNO + O$$
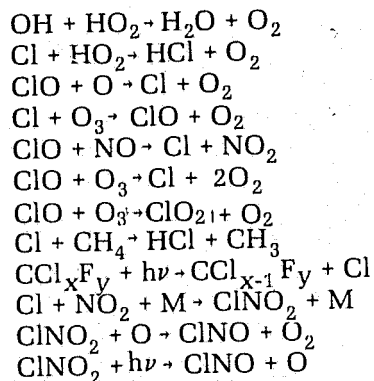
There are many other reactions for which the rate data are not well known or are usually estimated. Laboratory programs must continue to reduce uncertainties in these areas. Laboratory experiments can also provide leads for several field measurements including chlorine-bearing gases that may enter the stratosphere in significant amounts and end of chain compounds that would act as sinks for the chlorine.

THEORETICAL STUDIES

The results from the first two phases of the program will be fed into models of atmospheric transport and chemistry to predict ozone decreases caused by fluorocarbons. This work must continue because, to a great degree, it is a forerunner of the other phases. In addition, general circulation models that attempt to predict the possible climatic consequences of decreases in ozone in the stratosphere should be accelerated at several institutions.

The models predicting ozone decrease by fluorocarbons require a knowledge of vertical transport in the atmosphere, especially in the stratosphere. Based on better information derived from the measurement of inert tracers, the theoretical modeling should produce improved forecasts of ozone decreases.

The insertion of fluorocarbons and other relevant halocarbons and oxides of nitrogen must be known in order to predict their conse-

quences on the ozone layer. These input data, much of it obtained from industrial records, should be sought globally.

Summary of Critical Gap Areas

The previous discussion states the most critical areas for research in the atmospheric sciences. Current Federal research programs that for the most part consider many of these needs are described below. Several notable gaps exist, some institutional and some imposed by technological limitations:

(1) Instruments and subsequent field programs must be developed to measure chlorine oxides and radicals such as OH and HO_2.

(2) Specific difficult rate reaction determinations must be undertaken by competent laboratories.

(3) More attention must be directed toward establishing the intensity of vertical mixing above about 20 km.

Current Research Efforts

This discussion of current Federal stratospheric research related to the fluorocarbon-ozone question involves only the directly related programs; far more supporting work is in progress. The direct aspects of the research encompass specialized types of information required to predict the consequences of fluorocarbons on the ozone layer, the evidence of change in ozone concentration, and the atmospheric effects of ozone reduction including transport and transformation of relevant compounds in the atmosphere, chemical and photochemical reactions that form and destroy ozone, measurement of ozone and related substances, and atmospheric effects of ozone reduction in the stratosphere. The designation of programs as relevant to the fluorocarbon-ozone question was made by the agencies reporting this information to the ICAS working group conducting the survey. The concept of what is relevant is changing rapidly as the problem becomes better understood.

The work reported was in progress or firmly committed on or before May 1, 1975. The dollar amounts given are for FY 1975 funds. These are followed by some qualitative projections

of the level of effort in FY 1976. Data for FY 1976, however, are greatly dependent upon as-yet-incomplete actions by the Legislative and Executive branches regarding the budget for that year.

Dollar amounts should not be construed as representing entirely new dedicated efforts to attack the potential problems associated with the postulated ozone reduction by fluorocarbons. They are primarily the result of the fortuitous coexistence of such programs as the NASA investigations of the possible atmospheric effects of the Space Shuttle, the Department of Transportation's Climatic Impact Assessment Program, and the basic stratospheric research efforts of many Federal agencies. The lack of dedicated funds should not be viewed as indicative of indifference by the Federal agencies. The potential fluorocarbon threat surfaced well into the FY 1975 and FY 1976 budget cycles.

The task force recommends, and the agencies are committed to, seeking funding for FY 1977 and beyond sufficient to meet the additional research needs identified in this report and those that may be subsequently identified.

DEPARTMENT OF COMMERCE (DOC)

National Oceanic and Atmospheric Administration (NOAA)

NOAA operates a network to monitor total ozone via Dobson spectrophotometers at seven U.S. stations plus two others. These data plus data for the rest of the world, including those from satellites, are analyzed to detect trends and cycles and to better understand the causes for ozone variations. At all four of its world-wide benchmark stations NOAA routinely collects air samples, which are analyzed for fluorocarbon-11 and carbon tetrachloride. A NOAA research laboratory is developing instruments capable of directly and indirectly measuring trace constituents needed to predict ozone reduction caused by fluorocarbons and other substances and is also conducting experiments to determine selected chemical rate reactions. As part of NOAA's major effort in climate modeling, the possible climatic effects of reduced stratospheric ozone

are being simulated in model atmospheres. One-and two-dimensional models of atmospheric dynamics and chemistry are being pursued by NOAA to help in forecasting potential ozone reduction by fluorocarbons and other gases. NOAA provides substantial indirect support through its measurement, analysis, and model work. As of this writing, NOAA plans a modest increase in funding for FY 1976.

NOAA Stratospheric Research: FY 1975

Field Measurements	$400,000
Laboratory Experiments	100,000
Theoretical Studies	500,000
Total	$1,000,000

National Bureau of Standards (NBS)

NBS archives and evaluates information on the chemical and photochemical reaction-rate constants derived from both its own work and others, which it then supplies to those predicting changes in ozone due to fluorocarbons and other substances. NBS also conducts laboratory experiments to determine the rate and photochemical coefficients for selected reactions. Present indications are that funding for FY 1976 will be lower.

NBS Stratospheric Research: FY 1975

Field Measurements	0
Laboratory Experiments	$125,000
Theoretical Studies	0
Total	$125,000

DOC Stratospheric Research: FY 1975

	NOAA	NBS
Field Measurements	$400,000	0
Laboratory Experiments	100,000	$125,000
Theoretical Studies	500,000	0
Total	$1,000,000	$125,000
Department Total	$1,125,000	

DEPARTMENT OF DEFENSE (DOD)

The DOD conducts a strong basic program of stratospheric research as well as specific applied projects related to its missions. There is no authorization that would require the DOD to support research on the question of ozone reduction as a consequence of fluorocarbons. However, to the extent possible within existing operational and fiscal constraints, DOD will help the required research programs because the postulated adverse effects of ozone reduction would, if they did occur, impact military operations and other military programs in many serious ways. Many programs within the research elements of the Military Services, e.g., numerical modeling and sampling in the stratosphere, will generate information that can be applied by the appropriate agencies to solving the fluorocarbon–ozone question. In general, this support can and will be produced at no cost, or at best incremental costs on existing and planned efforts.

Army

The Army statospheric research program is primarily motivated by a military need to be able to predict the performance of Ballistic Missile Defense Systems in a nuclear-disturbed environment and to provide techniques for the detection, guidance, and control of Anti-Ballistic Missile interceptors. Its principal elements are to:

(1) Determine theoretically and experimentally the normal stratospheric composition and its variability.

(2) Develop a chemical, kinetic, and thermodynamic model to predict the concentration of stratospheric constituents.

(3) Determine the effects of nuclear-burst pheonomena on atmospheric constitutents.

(4) Describe the nuclear-disturbed atmosphere.

The program consists of theoretical modeling and laboratory and in situ measurements to develop stratospheric models for both the neutral and disturbed environments. Laboratory and upper-atmosphere equipment are developed, tested, and evaluated. Rocket and balloon-borne instrumentation are utilized. Solar measurements are made at various

times, heights, and locations and are correlated to other constituents. Ozone concentrations have been determined as a function of altitude, season, latitude, diurnal phase, and during special events such as solar eclipse and aurora. The experimental program includes the operation of spectrometers and the development and testing of ozonesondes that will become a regular part of the Meteorological Rocket Network by FY 1978. Budget actions for FY 1976 are incomplete at the time of publication of this report; preliminary indications are that funds for the work described above will be reduced by about 50%.

Army Stratospheric Research: FY 1975

Field Measurements $476,000
Laboratory Experiments 139,000
Theoretical Studies 118,000

    Total .... $733,000[3]

Navy

The Navy has historically conducted a broad program of basic research on the atmosphere; the scope of these projects spreads from the ocean-atmosphere interface into outer space. Significant attention is devoted to the stratosphere to determine possible adverse effects of Navy aircraft and missile systems on that vital stratum; the Navy scientific program also provides for studies of the stratosphere to assess the possibilities of events adversely affecting Naval communications and detection and control systems.

Applicable portions of the Navy research program consist of aircraft and balloon-borne sampling of the atmosphere to determine the concentrations of carbon tetrachloride, water vapor, ozone, and particulates (dust); analysis of rain water and ocean water to determine whether or not fluorocarbons are present; development and test of improved stratospheric water vapor sensors; laboratory effort to attempt to synthesize fluorocarbons that resist photodecomposition; and theoretical studies for understanding the kinetics of fluorocarbon reactions. Present plans for FY 1976 call for continuation of efforts at about

the same level of funding as applied in FY 1975.

Navy Stratospheric Research: FY 1975

Field Measurements $76,000
Laboratory Experiments 64,000
Theoretical Studies 22,000

    Total $162,000

Air Force

The Air Force is required by law to provide an environmental impact assessment of its stratospheric operations. The objectives of the stratospheric research program described here are to supply the Air Force with stratospheric environmental standards and criteria, environmental monitoring and instrumentation technologies, and to provide models for environmental impact assessments, especially for high-altitude advanced aircraft and missiles.

With the FY 1975 level of funding, instrumentation development and initial measurement programs will be conducted to determine gaseous and aerosol composition and concentrations, UV penetration, and transport parameters. Chemical processes that lead to removal of pollutants by aerosol formation and photo-absorption cross-sections will be measured in the laboratory, and a theoretical assessment of stratospheric chemical reactions will be performed. A one-dimensional photochemical transport model that will include pollutant sources will be calculated for various latitudes. A radiative transport model will be initiated. A test model of a three-dimensional global atmospheric circulation model will be constructed for both normal and perturbed conditions.

If the budget request for FY 1976 research in this area is approved, there will be a modest increase in the amount of funds devoted to it.

Air Force Stratospheric Research: FY 1975

Field Measurements $345,000
Laboratory Experiments 0
Theoretical Studies 37,000

    Total .... $382,000[4]

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[3] Does not include civil service salaries.

[4] Does not include civil service salaries.

DOD Stratospheric Research: FY 1975

	ARMY	NAVY	AIR FORCE
Field Measurements	$476,000	$76,000	$345,000
Laboratory Experiments	139,000	64,000	0
Theoretical Studies	118,000	22,000	37,000
Total	$733,000	$162,000	$382,000
Department Total	$1,277,000		

DEPARTMENT OF TRANSPORTATION (DOT)

A Climatic Impact Assessment Program (CIAP) was conducted to assess the environmental and meteorological effects of the projected world high-altitude aircraft fleet, including subsonic and supersonic vehicles. The CIAP addressed the complex interactions between the engine emissions exhausted into the upper atmosphere, the natural composition of the stratosphere, and the dynamic processes of the atmosphere. It examined the effects of projected changes in the upper atmosphere upon climate close to the earth's surface.

The CIAP field measurements program included observations from the ground, stratospheric aircraft, and satellites for the measurement of the altitude distribution of atmospheric trace constituents such as ozone, water vapor, hydrogen chloride, and nitrogen oxides. Some observations of stratospheric transport were also made. The CIAP laboratory experiments included determination of chemical reaction coefficients under stratospheric conditions of pressure and temperature, and of coefficients of absorption and radiation in the UV spectra important for the evaluation of NO_x effects on ozone.

Theoretical studies conducted during the CIAP consisted of changes in the stratosphere resulting from the introduction of nitrogen oxides at various altitudes at which aircraft may operate in the stratosphere. A hierarchy of models of differing complexity was used in the studies; about eight one-dimensional (altitude, only) models were employed; four models were used to study effects in two dimensions (altitude and latitude); three three-dimensional models (altitude, latitude, and longitude) were employed; and two models were used to examine small-scale effects in aircraft wakes. The variety of models was necessary to permit examinations emphasizing the hydrodynamics by the more complicated and expensive three-dimensional models, as well as examinations of the detailed chemistry (sometimes profoundly influenced by air transport) and of the radiation transfer by the less expensive one- and two-dimensional models.

CIAP modeling of the troposphere, usually (but not in every case), coupled with the stratosphere, examined climatic change consequences of stratospheric pollution, which affects the radiation controlling the troposphere.

The CIAP formally ended on December 31, 1974. Its report of findings has subsequently been published and released. The monographs that were composed as a part of the program in 1974 are currently in publication and will serve as a major source of information in dealing with the fluorocarbon-ozone question. Selected activities have continued into the remainder of FY 1975, especially in the areas of stratospheric monitoring and laboratory experiments.

A High-Altitude Pollution Program is being formulated by the Federal Aviation Administration; the planned funding will be slightly lower than that expended in FY 1975.

DOT Stratospheric Research: FY 1975

Field Measurements	$1,388,000
Laboratory Experiments	493,000
Theoretical Studies	900,000
Total	$2,781,000

ENVIRONMENTAL PROTECTION AGENCY (EPA)

With the FY 1975 level of funding, the EPA will conduct photo-oxidation studies of halocarbons in the laboratory. Simulations of

tropospheric reaction conditions will use radiation of wavelengths down to 300 nm, whereas stratospheric simulations will use wavelengths down to 190 nm. Reactive intermediates and products will be measured. Direct attack of chlorine on ozone will be observed. Mechanisms will be deduced and chemical and photochemical reaction rates will be measured. Halocarbons, halogen acids, and related compounds will be measured in the laboratory and field using gas chromatography, infrared spectroscopy, and mass spectroscopy. The combination of laboratory and field measurements will yield an integrated picture of the atmospheric chemical and photochemical transformation and transport processes.

With the budget process incomplete, indications are that in FY 1976 the funding for this area will be somewhat greater than indicated for FY 1975.

EPA Stratospheric Research: FY 1975

Field Measurements	$115,000
Laboratory Experiments	175,000
Theoretical Studies	0
Total	$290,000

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION (ERDA)

ERDA's involvement with the fluorocarbon-ozone question is and will continue to be through its support of basic science and stratospheric research, including the use of fluorocarbons and other stable constituents as tracers of atmospheric motion. For example, the article that initially drew attention to the fluorocarbon-ozone question was based on work conducted under an ERDA contract for basic radiochemical research. Measurements of fluorocarbons-11 and -12, carbon tetrachloride, and sulfur hexafluoride have been added to the high-altitude radioactivity sampling program conducted with balloons and aircraft. Filters from these flights are also shared with other government laboratories for analyses of additional stable constituents including hydrogen chloride, chlorine, and bromine.

It is anticipated that funding for FY 1976 programs relating to the fluorocarbon-ozone question will continue at approximately the same level.

ERDA Stratospheric Research: FY 1975

Field Measurements	$198,000
Laboratory Measurements	0
Theroretical Studies	$84,000
Total	$282,000

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION (NASA)

Four NASA program offices participate in the overall stratospheric research program: (1) The Office of Manned Space Flight (OMSF) emphasizing the Space Shuttle environmental effects, (2) The Office of Applications (OA) emphasizing the stratosphere in applying space technology to the earth's environment, (3) The Office of Aeronautics and Space Technology (OAST) emphasizing pollution from aircraft engines, and (4) The Office of Space Science (OSS) emphasizing fundamental physics and chemistry of the stratosphere. The OSS has the major role in managing the Agency's overall stratospheric program.

The NASA program is structured in the three phases of field measurements, laboratory experiments, and theoretical studies (including modeling of the perturbations of the natural stratosphere).

(1) *Field Measurements.* Program emphasis is aimed toward the measurement of ambient stratospheric concentrations of chlorine species. Also, high priority is assigned to means of measurement of O and OH, and development of other advanced instrumentation.

(2) *Laboratory Experiments.* Program objective is to understand how chlorine compounds affect the chemistry and physics of the stratosphere. The emphasis is on key chemical reactions involving chlorine and ozone.

(3) *Theoretical Studies: Modeling.* Program objective is to develop one-dimensional, two-dimensional, and three-dimensional models that accurately simulate stratospheric conditions through a combined effort by NASA centers and at universities.

As a result of legislation pending before the Congress, there is considerable uncertainty concerning funds for these programs in FY 1976. It is anticipated that funds in at least the amounts shown for FY 1975 will be available for similar efforts in FY 1976.

NASA Stratospheric Research: FY 1975

Field Measurements $4,354,000
Laboratory Experiments 1,609,000
Theoretical Studies 913,000

Total .... $6,876,000[5]

NATIONAL SCIENCE FOUNDATION (NSF)

The effort of the NSF with regard to stratospheric research is centered around the general understanding of the stratospheric environment. For many years theoretical, laboratory, and field work have been supported to achieve this understanding. As a result, modeling projects that include both chemistry and circulation are well underway. Recent events have affected the nature of the proposals arriving at the NSF so that at present many grantees are working directly on this problem. This includes modeling, observations, laboratory research, and the development of new techniques of measuring important constituents. Indications are that there will be a modest increase in funding for these projects in FY 1976.

NSF Stratospheric Research: FY 1975

Field Measurements $738,000
Laboratory Experiments 274,000
Theoretical Studies 596,000

Total .... $1,608,000[5]

Total Federal Stratospheric Research Related to the Fluorocarbon–Ozone Issue: FY 1975

Agency	Amount
DOC	$1,125,000
DOD	1,277,000
DOT	2,781,000
EPA	290,000
ERDA	282,000
NASA	6,876,000
NSF	1,608,000
Total	$14,239,000

[5] Does not include civil service salaries.

Summary of Research by Function

Field Measurements $7,926,000
Laboratory Experiments $2,938,000
Theoretical Studies $3,375,000

REFERENCES

Angell, J.L., and Korshover, J. (1973). "Quasi-biennial and Long-Term Fluctuations in Total Ozone," *Mon. Weather Rev.*, Vol. 101, pp. 426-443.

Angell, J.L., and Korshover, J. (1975). "Global Analysis of Recent Total Ozone Fluctuations" (submitted to the *Mon. Weather Rev.*).

Budyko, M.I. (1969). "The Effect of Solar Radiation Variations on the Climate of the Earth," *Tellus*, Vol. 21, pp. 611-619.

Cadle, R. (1975). "Volcanic Emissions of Halides and Sulfur Compounds to the Troposphere and Stratosphere," *J. Geophys. Res.*, Vol. 80, pp. 1650-1652.

Cicerone, R.J., Stolarski, R.S., and Walters, S. (1974). "Stratospheric Ozone Destruction by Manmade Chlorofluoromethanes," *Science*, Vol. 185, pp. 1165-1167.

Crutzen, P. (1974a). "A Review of Upper Atmospheric Photochemistry," *Can. J. Chem.*, Vol. 52, pp. 1569-1581.

_____ (1974b). "Estimates of Possible Future Ozone Reductions From Continued Use of Fluoro-chloromethanes," *Geophys. Res. Letters*, Vol. 1, pp. 205-220.

_____ (1975). Testimony before the Committee on Aeronautical and Space Sciences of the U.S. Senate. Updated for the New York Assembly Standing Committee on Environmental Conservation of the Environmental Impact of Chlorofluoromethanes.

Environmental Protection Agency. (1974). *Preliminary Assessment of the Environmental Problems Associated With Vinyl Chloride and Polyvinyl Chloride (Appendices)*. Report of the Vinyl Chloride Task Force.

Faegre, A. (1972). "An Intransitive Model of the Earth-Atmosphere Ocean System," *J. Appl. Meteor.*, Vol. 11, pp. 4-6.

Farmer, C.B. (1974). "Infrared Measurements of Stratospheric Composition," *Can. J. Chem.*, Vol. 52, pp. 1544-1599.

Farmer, C.B., Raper, O.F., Toth, R.A., and Schindler, R.A., (1974). *Proceedings of the Third Conference of the Climatic Impact Assessment Program* (A.J. Broderick and T.M. Hards, eds.), pp. 234-245.

Gal-Chen, T., and Schneider, S.H. (1974). *Proceedings of the Third Conference on the Climatic Impact Assessment Program* (A.J. Broderick and T.M. Hards, eds.), pp. 450-456.

Gebhart, R., Bojkov, R., and London, J. (1970). "Stratospheric Ozone: A Comparison of Observed and Computed Models," *Contributions to Atmospheric Physics*, Vol. 43, pp. 209-227.

Gille, J.C., Russell, J.M., Bailey, P.L., and House, F.B. (1973). *Proceedings of the Technical Conference on Observations and Measurements of Atmospheric Pollution*, Finland.

Goldsmith, P., Tuck, A.F., Foot, J.S., Simmons, E.L., and Newson, R.L. (1973). "Nitrogen Oxides, Nuclear Weapon Testing, Concorde and Stratospheric Ozone," *Nature*, Vol. 244, pp. 545-551.

Götz, F.W.P., Meetham, A.R., and Dobson, G.M.B. (1934). "The Vertical Distributions of Ozone in the Atmosphere," *Proc. Roy. Soc. London*, Vol. A145, pp. 416-446.

Heath, D.F., Mateer, C.L., and Kreuger, A.J. (1973). The *Nimbus-4 Backscatter Ultraviolet (BUV) Atmospheric Ozone Experiment-2-years' Operation,* GSFC Report No. X-651-73-64, NASA Goddard Space Flight Center, Greenbelt, Md., 24 pp.

Held, I.M., and Suavez, M.J. (1974). "Simple Albedo Feedback Models of the Icecaps," *Tellus*, Vol. 26, pp. 613-629.

Johnston, H.S., Whitten, G., and Birks, J. (1973). "The Effect of Nuclear Explosions on Stratospheric Nitric Oxide and Ozone," *J. Geophys. Res.*, Vol. 78, pp. 6107-6135.

Komhyr, W.D., Barrett, E.W., Slocum, G., and Weickman, H.K. (1971). "Atmospheric Ozone Increase During the 1960's," *Nature*, Vol. 232, pp. 390-391.

Krey, P.W., and Lagomarsino, R.J. (1975). "Stratospheric Concentrations of SF_6 and CCl_3F. Health and Safety Laboratory," *Environmental Quarterly*, HASL-294.

Krueger, A.J., Heath, D.F., and Mateer, C.L. (1973). "Variations in the Stratospheric Ozone Field Inferred from Nimbus Satellite Observations," *Pure and Applied Geophysics*, Vol. 106, pp. 1254-1263.

Kurihara, Y. (1970). "A Statistical-Dynamical Model of the General Circulation of the Atmosphere," *J. Atmos. Sci.*, Vol. 27, pp. 847-870.

Lazrus, A.B., Gandrud, B., Sedlacek, W., and Woodward, R. (1974). Presentation at meeting of American Geophysical Union, San Francisco.

London, J., and Kelley, J. (1974). "Global Trends in Atmospheric Ozone," *Science*, Vol. 184, pp. 987-989.

Lovelock, J. (1974a). "Atmospheric Halocarbons and Stratospheric Ozone," *Nature*, Vol. 252, p. 292.

——————— (1974b). "Fluorocarbons in the Environment," in "Fluorocarbons—Impact on Health and Environment," *Proceedings of the Hearings Before the Subcommittee on Public Health and Environment, of the Committee on Interstate and Foreign Commerce, House of Representatives, Ninety-Third Congress,* pp. 455-463.

MacCracken, M.C. (1973). *Proceedings of the Second Conference on the Climatic Impact Assessment Program,* (A.J. Broderick, ed.), pp. 298-320.

Manabe, S. (1974). The International Study Conference on the Physical Basis of Climate and Climate Modeling, WMO-Joint-GARP Organizing Committee, Stockholm, July-August.

Manabe, S., and Bryan, K. (1969). "Climate Calculations with a Combined Ocean-Atmosphere Model," *J. Atmos. Sci.*, Vol. 26, pp. 786-789.

Manabe, S., and Wetherald, R.T. (1967). "Thermal Equilibrium of the Atmosphere With a Given Distribution of Relative Humidity," *J. Atmos. Sci.*, Vol. 24, pp. 241-259.

Mateer, C.L., and Dütsch, H.U. (1964). Manuscript. National Center for Atmospheric Research, 105 pp.

McCarthy, R.L. (1974). "Fluorocarbons in the Environment," Presented at American Geophysical Union Meeting, San Francisco, by Frank Bower, Data from U.S. Tariff Commission reports.

Molina, M.J., and Rowland, F.S. (1974). "Stratospheric Sink for Chlorofluoromenthanes—Chlorine Atom-Catalysed Destruction of Ozone," *Nature*, Vol. 249, pp. 810-812.

Murcray, D.G., Bonomo, F.S., Brooks, J.N., Goldman, A., Murcray, F.H., and Williams, W.J. (1975). "Detection of Fluorocarbons in the Stratosphere," *Geophys. Res. Letters*, Vol. 2, pp. 109-112.

Rowland, F.S. (1974). "Aerosol Sprays and the Ozone Shield," *New Scientist*, Vol. 64, pp. 717-720.

Rowland, F.S., and Molina, M.J. (1974). AEC Report No. 1974-1, Revised and appearing in *Rev. Geophys. and Space Phys.*, 1975.

Rowland, F.S., Molina, M.J., Milstein, R., and Chou, C.C. (1975) Manuscript in preparation.

Schneider, S.H., and Dickinson, R.E. (1974). "Climate Modeling," *Rev. Geophys. and Space Phys.*, Vol. 12, pp. 447-493.

Sellers, W.D. (1969). "A Global Climatic Model Based on the Energy Balance of the Earth-Atmospheric System," *J. Appl. Meteor.*, Vol. 8, pp. 392-400.

Sellers, W.D. (1973). "A New Global Climatic Model," *J. Appl. Meteor.*, Vol. 12, pp. 241-254.

Smagorinsky, J. (1974). *Weather Modification,* (W. Hess, ed.), John Wiley, N.Y.

Stolarski, R.S., and Cicerone, R.J. (1974), "Stratospheric Chlorine: Possible Sink for Ozone," *Can. J. Chem.*, Vol. 52, pp. 1610-1615.

Stoiber, R.E., Leggett, D.C., Jenkins, T.F., Murrmann, R.P., and Rose, W.T., Jr. (1971). "Organic Compounds in Volcanic Gas from Santiaguito Volcano, Guatemala," *Geol. Soc. Am. Bull.*, Vol. 82, pp. 2299-2302.

Vupputuri, R., and Boville, B.W. (1975). Paper presented at the 4th Climatic Impact Assessment Program, Cambridge, Mass.

Wilkniss, P.W., Swinnerton, J.W., Lamontagne, R.A., and Bressan, D.J. (1975). "Trichlorofluoromethane in the Troposphere, Distribution and Increase, 1971 to 1974," *Science*, Vol. 187, pp. 832-833.

Wofsy, S.C., and McElroy, M.B. (1974). "HO_x, NO_x, and ClO_x: Their Role in Atmospheric Chemistry," *Can. J. Chem.*, Vol. 52, pp. 1582-1591.

Wofsy, S.C., McElroy, M.B., and Sze, N.D. (1975). "Freon Consumption Implications for Atmospheric Ozone," *Science*, Vol. 187, pp. 1165-1167.

Young, J.A., Thomas, C.W., Wogman, N.A., and Perkins, R.W. (1970). "Cosmogenic Radionuclide Production Rates in the Atmosphere," *J. Geophys. Res.*, Vol. 75, pp. 2385-2390.

IV.

Biological Effects of Ozone Reduction

INTRODUCTION

Studies of biological and climatic effects of ozone reduction in the stratosphere were undertaken by the Federal Government in 1972, during the Climatic Impact Assessment Program (CIAP), under the sponsorship of the Department of Transportation (DOT), with program direction by the U.S. Department of Agriculture (USDA). Since the inception of that program, approximately $1 million has been spent to determine the possible biological effects of increased UV radiation and climatic changes at the earth's surface caused by increases in supersonic transport (SST) flights. Results of these studies will help to determine the potential effects of further ozone reduction in the stratosphere as a consequence of the increased use of fluorocarbons and other atmospheric contaminants. Because of the extreme sensitivity of living organisms to increased UV irradiation in the 280- to 320-nm region and to small changes in the climate, any perturbation of the ozone layer could be of considerable biological and agricultural significance, and have long-range consequences for man and the biosphere.

This section of this report presents current knowledge regarding the effects of increased UV radiation on the biosphere, describes some of the ongoing research, and examines critical research areas that should be investigated as a follow-up to the CIAP effort. Some mention is also made of the potential climatic effects of ozone reduction on agriculture and the biosphere.

For a more detailed discussion of biological and climatic effects of ozone reduction, the reader is referred to the following documents:

- National Academy of Sciences-National Academy of Engineering (NAS-NAE) Report, entitled *Biological Impacts of Increased Intensities of Solar Ultraviolet Radiation*, published in 1973.

- National Academy of Sciences Report, entitled *Environmental Impact of Stratospheric Flight: Biological and Climatic Effects of Aircraft Emission in the Stratosphere*, published in April 1975.

- CIAP Report of Findings, entitled *The Effects of Stratospheric Pollution by Aircraft*, published by the DOT in 1974.

- DOT CIAP Monograph 5, entitled *Impacts of Climatic Change on the Biosphere*, 1974 draft.

BIOLOGICAL EFFECTS OF INCREASED UV-B RADIATION

The Problem

Without sunlight, life on earth would not exist. However, too much sunlight can be injurious to living organisms for, in addition to providing visible radiation in the range of 400 to 700 nanometers (1 nm = 10^{-9} m) and long-wave energy in the form of infrared radiation, sunlight also contains an appreciable amount of short-wave energy in the UV region.

Biologists divide the UV part of the spectrum into three wavelength regions:

(1) UV-A: 320 to 400 nm.

(2) UV-B: 280 to 320 nm.

(3) UV-C: less than 280 nm.

The UV-B region is also known as the erythemal region because this wavelength range causes sunburn or reddening of the skin known as erythema. It is the region most sensitive to changes in stratospheric ozone content and is of the greatest biological significance in the natural ecosystem.

Ozone is a strong absorber of solar radiation in the UV region. Because of this property, the ozone layer in the stratosphere is essential in protecting life on earth from the damaging UV rays of the sun. Without this protective shield of ozone, life on earth, as we know it, would not have developed. This ozone shield begins at about 320 nm and becomes increasingly effective at shorter wavelengths, with the cutoff at about 290 nm.

A slight decrease in ozone content of the stratosphere opens the ozone window and allows shorter wavelengths of UV radiation to pass through. The biological implications of such a shift may be profound, as the effectiveness of UV radiation increases greatly as the wavelength becomes shorter. Thus, even slight shifts in spectral composition can have an adverse effect on biological systems. Whether or not present-day organisms can handle an additional burden of UV radiation is a significant question.

Although there is some disagreement among investigators as to the amount of increase in UV-B radiation to be expected from a decrease in stratospheric ozone level for small changes, e.g., less than about 10%, an approximately 2% increase in UV-B radiation at the earth's surface is expected to occur with a 1% reduction in stratospheric ozone at mid-latitudes. At larger reductions, the relative effects would be disproportionately greater.

Molecular and Cellular Responses to Increased UV-B Radiation

UV ABSORPTION

Protective UV-absorbing materials occur in all types of organisms. These materials include waxy coatings or hair-like growths on the leaves of plants, and hair, feathers, scales, and shells on animals. Pigments also serve this purpose in both animals and plants. Melanin is the most common example of a protective pigment in man and other animals. Flavonoids and other phenolic compounds, which are found in the outer layer of cells in leaves, serve this function in many plants because they are highly absorbent in the UV region (Caldwell, 1971; Brabham and Biggs, 1974). The absence of these protective pigments results in susceptibility to UV injury (Biggs and Campbell, 1974; Caldwell, 1968, 1971).

UV PENETRATION TO SENSITIVE SITES WITHIN THE CELL

Relatively little research involving UV penetration of the various substances composing cell walls and membranes has been accomplished. Studies of UV penetration into human skin, which have probably received more attention than all other organisms, show a wide variation, depending upon the amount of melanin or skin pigmentation. Transmission of UV radiation through light skin is about 18% at 300 nm. Considerably more baseline data are needed to determine the amount of natural UV-B radiation reaching the earth's surface before a definitive picture of UV penetration into biological targets and the total ecosystem can be elucidated.

EFFECTS ON NUCLEIC ACIDS AND PROTEINS

The most important and sensitive sites of UV injury in plant and animal cells are the nucleic acids, DNA and RNA. These compounds absorb strongly in the UV region, with a maximum absorbtion at 260 nm, and absorbed energy must either be dissipated or expended in chemical alteration of the absorbing molecule. Because of their vital role in the storage, transmission, and expression of genetic information, any alteration of DNA or RNA by increased UV radiation could have far-reaching and drastic results (Murphy, 1974; Billen and Fletcher, 1974).

Most of the information regarding UV effects on nucleic acids has been obtained in studies on microorganisms and indicates both irreversible and photoreversible injury. Several repair systems have been shown, including a reversal by radiation in the near UV or blue light area. A dark repair system has also been found in bacteria. Present indirect evidence suggests the existence of a photorepair system in higher plants as well,

although the nature of this system is unknown.

Another sensitive target for UV injury in living organisms consists of proteins. These important molecules make up enzymes and are structural constituents of cells. Because they absorb strongly in the 280-nm region, any increase in UV radiation from stratospheric ozone reduction could have an adverse impact on these vital constituents. Inactivation of enzyme systems has been shown in the laboratory under increased UV conditions for such enzymes as trypsin, ribonuclease, and aldolase (Setlow and Doyle, 1957). As a consequence of increased UV radiation, entire integrated systems could be disrupted because of enzyme inactivation or membrane damage.

EFFECTS ON CHROMOSOMAL MAKEUP AND MUTATION RATES

Most early work on UV effects on chromosomes was performed at 254 nm. Early evidence with corn (Stadler and Uber, 1942) showed injury at 254, 297, and 302 nm. Campbell (1974a,b) found chromosomal damage in Wandering Jew (Tradescantia) at UV-B wavelengths of 290 to 320 nm. Therefore, the possibility that UV-B irradiation can induce increased chromosomal mutation must also be considered.

EFFECTS ON OTHER CONSTITUENTS IN THE CELL

The impact of UV on chemical systems other than nucleic acids and proteins is not well documented. Carns and Christiansen (1974) demonstrated degradation of a solution of abscisic acid, an important plant hormone, by radiation with a source containing UV-B and UV-C radiation. Photodegradation of xanthophylls and other carotenoids at wavelengths of 280 to 320 nm has also been shown. Adverse effects of UV irradiation have also been observed on chloroplasts, mitochondria, and other important organelles.

Response of Organisms to Increased UV-B Radiation

Although some biological phenomena resulting from the photochemical impact of UV irradiation are considered beneficial to certain organisms (e.g., the synthesis of vitamin D in human skin, or insect visual response), most biological responses are detrimental (Blum, 1959; Allison, 1960; Anderson and Skinner, 1961; Billen and Fletcher, 1974; Epstein et al., 1974). These responses range from death to more subtle responses such as an increase in chromosomal abnormalities (Stadler and Uber, 1942; Chu, 1965; Campbell, 1974b), increased mutation rate (Campbell, 1974a), or the reduction in photosynthetic activity (Sisson and Caldwell, 1974). The key question raised from research studies to date (Caldwell, 1974; Antonovics, 1974; Nachtwey, 1974) is: Can organisms avoid, tolerate, or evolve resistance to greater-than-normal UV-B irradiation?

The effects on biological systems of UV-A (320 to 400 nm) and UV-C (less than 280 nm) radiation are well documented (Caldwell, 1968, 1971; Nilsen, 1971). However, until the CIAP research was conducted to determine the potential biological and climatic implications of ozone reduction in the stratosphere, relatively little attention was given to the effects of UV-B irradiation on living organisms other than man. Efforts made by Nachtwey (1974) and other workers to link photobiological studies at 254 nm with UV-B radiation were inconclusive.

Any changes in the average ozone concentration possibly caused by fluorocarbons could be of considerable biological and agricultural significance because of the sensitivity of nucleic acids (believed to be the carriers of genetic information), proteins, and other cell constituents to increased UV irradiation in this region (Setlow and Doyle, 1957; Murphy, 1974). This is true even though these changes may be less than the present daily or seasonal fluctuations and may cause only small changes in the total energy flux in the UV-B region.

During the CIAP, biological studies on increased UV-B radiation were conducted on a wide range of organisms, including agricultural and native plant species, marine phytoplankton, insects, and marine invertebrates (Bartholic and Halsey, 1974; Caldwell et al., 1974; Carns et al., 1974; Lorenzen, 1974; Sisson and Caldwell, 1974; Ambler et al., 1974; Krizek, 1974; Biggs and Campbell, 1974; Brabham and Biggs, 1974;

Carns and Christensen, 1974; Calkins, 1974a,b,c; Hsiao and Hsiao, 1974; Hsiao et al., 1974). Results of these studies indicate that:

(1) Organisms differ greatly in their sensitivity to UV-B irradiation depending upon their stage of development, age, size, anatomical composition, environmental condition, and geographic location.

(2) Living organisms withstand the damaging effects of UV-B radiation primarily in four ways: (a) protective substances, (b) behavioral adaptation to avoid the sunlight, (c) photoreactivation or photoprotective mechanisms, and (d) dark repair mechanisms.

(3) Many organisms have developed one or more of these adaptations to endure present levels of UV-B irradiation, but have little reserve capacity to tolerate higher levels of UV-B irradiation or to repair damage.

(4) Many organisms are sensitive to present UV-B radiation levels reaching the earth's surface, and would become even more vulnerable to increased UV exposure.

Because of the short time span during which biological experiments have been conducted under the CIAP and because of the technical difficulties of UV simulation and measurement, most results are preliminary. Much more research is needed, therefore, before unequivocal statements can be made regarding the impacts of fluorocarbons on the biosphere.

As many of the UV-radiation studies have been based on a 35 to 50% reduction in ozone level, much more research must be conducted to determine the biological effects of ozone reduction at levels of 10% or less. No time estimates can be given for completion of these studies.

Response of Plants to Increased UV-B Radiation

STATE OF THE ART

Since 1972, studies of the effects of increased UV-B radiation on plant growth and development have involved a wide range of horticultural and agronomic species as well as some native species. Certain crops such as peanut, wheat, milo, and fescue are fairly resistant to increased UV-B radiation; others such as lettuce, pea, tomato, cotton, and radish are sensitive to increased UV-B radiation.

The extent of UV-B damage depends a great deal on the size and anatomical composition of the plant, the amount of available visible light for photorepair, and other environmental factors. In general, seedlings are much more sensitive to UV exposure than are mature plants, and reproductive organs are more sensitive than vegetative structures. Plants grown under low-intensity visible light are more sensitive to UV radiation than those grown under high-intensity visible light.

Under experimental conditions in the growth chamber, greenhouse, and solarium where, during the CIAP, the amount of UV-B radiation was increased to simulate an upper level of 35 to 50% ozone reduction in the stratosphere, many adverse biological responses were observed in native plants and crop species. Despite the existence of photorepair mechanisms, subtle changes in leaf anatomy, disruptions in photosynthesis, and decreases in dry matter accumulation were observed in about half of the species studied.

Under field conditions, where the amount of visible light available for photorepair is high and natural variability is great, it has not been possible to reach definitive conclusions as to the significance of damage observed. However, major changes in photosynthesis and other plant processes were evident in certain species as a result of increased UV-B radiation. Thus, the biological implications may be far-reaching and may require further investigation to determine long-range effects and potential genetic changes.

ONGOING RESEARCH

Research on the biological and agricultural effects of enhanced UV-B radiation on plants has been conducted principally at three locations:

(1) Beltsville, Maryland, where current research at the USDA Agricultural Research Center involves broad- and narrow-band UV radiation studies,

The narrow-band studies will enable investigators to determine exact wavelengths and irradiances capable of inflicting UV damage.

(2) *Gainesville, Florida*, where ongoing research at the University of Florida involves the ultra-structural, photosynthetic, and chemical impacts of UV irradiation.

(3) *Logan, Utah*, where current work at Utah State University includes the ultra-structural, photosynthetic, and chemical impacts of UV irradiation as well as an examination of its genetic effects.

Anatomical, physiological, and biochemical studies on the effects of increases in UV radiation are being studied at all three locations. The studies are supported to great extent under a reimbursable agreement with the USDA and the DOT.

CRITICAL RESEARCH NEEDS

In view of the potentially adverse effects of ozone reduction in the stratosphere and the attendant increase in UV-B radiation reaching the earth's surface, there is an urgent need for increased research in order to:

(1) Determine the effects of increased UV-B radiation on crop and timber production and natural vegetation. This should include an expansion of critical narrow-band UV studies to determine the effects of enhanced UV radiation on critical physiological and biochemical processes, identification of threshold dosages for UV damage in major species, modeling of possible losses in yields of major crops from increased UV radiation, and measurements of UV-B penetration into crop and timber ecosystems.

(2) Develop improved instrumentation for monitoring UV radiation with greater sensitivity in the UV-B region and improved projected increases in UV-B radiation.

(3) Identify physiological and anatomical criteria for resistance to UV radiation

and techniques for alleviating UV stress. These studies should include a detailed examination of the photorepair process in higher plants.

(4) Determine whether or not crop and timber plants exposed to increased UV radiation are more susceptible to attack by insects and disease.

(5) Develop improved models of the effects of possible climatic changes on agricultural production and total ecosystems.

Response of Animals to Increased UV-B Radiation

STATE OF THE ART AND ONGOING RESEARCH

The effects of increased UV-B radiation on animals other than man generally have received little attention, as it has been assumed that the UV-B radiation is usually absorbed by the outer covering of most animals. Hair, feathers, scales, shells, and normal pigments protect many animals from solar radiation, and presumably will continue to provide some degree of protection from probable increased levels of UV radiation (*Porter and Norris*, 1968; *VanBrunt et al.*, 1964; *NAS-NAE*, 1973; *Caldwell*, 1974). Some animals may already be at their UV-B tolerance limit, and further increases may produce harmful effects in animals that at present show no damage.

There are three major ways in which UV irradiation can affect farm animal production:

(1) *Infectious disease.* A disease of cattle known as pinkeye causes serious economic annual loss in cattle. Although this disease is caused by a bacterium, *Moraxella bovis* (*M. bovis*), UV radiation increases its effects by making the disease more severe and by affecting greater numbers of cattle. Cattle with previous ocular disease and chronic eye lesions are also more likely to develop squamous cell carcinomas.

(2) *Carcinogenesis.* The most common type of skin cancer in domestic

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animals is the ocular squamous cell carcinoma of cattle known as "cancer eye" (*Anderson and Skinner*, 1961; *MacDonald*, 1974). This cancer occurs on the eyelids and eyeballs of cattle and accounts for more than 90% of the slaughterhouse condemnations attributed to skin cancer. Squamous cell carcinomas are particularly common in areas of the skin in which there is a deficiency of melanin (brown pigment), which explains in part why the incidence of cancer eye in white-faced Herefords is higher than in breeds of cattle in which melanin is more abundant. The incidence of cancer eye in these white-faced cattle has been found to be highly correlated with geographic location; the parts of the country exposed to high natural sunlight have the highest incidence. Squamous cell carcinomas are also found in other animals including Ayrshire cattle, Angora goats, sheep, and horses. In most cases, these carcinomas are found in parts of the body lacking melanin, e.g., eyelids, genitals, or skin near brand marks.

(3) *Photosensitization.* Domestic animals suffer from photosensitization (sensitivity to light) when in a hypersensitive condition caused by ingestion of a photodynamic agent and subsequent exposure to UV radiation. The photodynamic agent may be ingested by the animal or an inactive compound may become active during normal metabolism. Wide varieties of plants contain sensitizing agents during part or all of their growth cycle. The most common plants of this type in the U.S. are rye, buckwheat, clover, alfalfa, and weeds such as St. John's wort. Drugs (phenothiazine) and microorganisms (*Leptospira*), for example, are sensitizing agents. Phenothiazine is commonly used to treat parasitic infestation, and its use under conditions of increased solar UV radiation may present serious problems.

Unlike humans, most animals will not expose themselves to full sunlight unless they have a way of preventing light in excessive amounts from reaching sensitive tissues. Most marine species hide in crevices in rocks, burrows, or in deep water during the day and come out at night to browse. Most wild animals on land are nocturnal in habit, and thus generally avoid sunlight except in the shade of a forest where some may be active during the day. Domestic animals on farms, however, are vulnerable to increased UV-B radiation because protective cover is often lacking. If UV radiation were increased without a corresponding change in photoperiod, amount of visible light, or heat, many domestic animals probably would be injured because they lack cues of increased UV-B radiation.

RESEARCH NEEDS

The current incidence of cancer eye in cattle should be investigated to determine whether:

(1) Time of onset of the disease and the geographic location can be correlated with the level of natural solar radiation and total lifetime UV dosage.

(2) Long-term irradiation of cattle, with increased levels of UV-B radiation, would result in increased incidence of cancer eye as well as its appearance at an earlier age. A reduction of 1 to 2 years in lifespan could have a sizable impact on agricultural production and could necessitate the screening and selection of more resistant breeds of cattle.

Although somewhat less urgent, research is also needed on photosensitization to:

(1) Establish the nature of the photodynamic agent.

(2) Determine animal tissues affected by photosensitization.

(3) Examine the influence of UV-irradiated plant material on feeding behavior by animals and the resultant reactions of the products of irradiation on various tissues in cattle,

sheep, swine, and other animals.

Because of the anatomical and physiological implications associated with photosensitivity and its relation to a wide variety of animal diseases, both infectious and metabolic, the results of some or all of this research could be applicable to man.

Response of Insects to Increased UV-B Radiation

STATE OF THE ART

UV-B radiation is within the visual spectrum of many insects, and thus can affect their behavior in many ways. Although there is a great deal of scientific literature dealing with insect vision and behavioral responses to UV radiation of 250 to 400 nm, most of the available information has not been analyzed in sufficient detail to permit a quantitative interpretation of the relative importance of UV irradiation, as compared with other environmental factors that affect insect behavior.

Much information is available on the effects of the germicidal region (254 nm) of UV radiation on the growth and development of insects. The effects of UV-B wavelengths have not been investigated thoroughly because of the lack of adequate instrumentation to simulate the radiation range.

Preliminary experiments conducted in northern Utah show that increased UV-B radiation did not have an adverse effect on pollination behavior under test conditions. Physiological sensitivity to UV-B radiation varies widely among insect species and depends on the exact life stage of the organism (Hsiao et al., 1974). Only the larvae of certain insects, e.g., the Mexican bean beetle and the Colorado potato beetle, were found from laboratory experiments to be strongly sensitive to continuous irradiation with large UV-B doses (Hsiao and Hsiao, 1974).

It is possible that an increase in solar UV irradiation on the earth's surface and the climatic changes that accompany it could affect an insect population either directly or indirectly by acting through other components of the ecosystem. Relevant research on the effects of increased UV irradiation on various components of the ecosystem must be analyzed before any predictions can be made regarding the impact on insect populations.

ONGOING RESEARCH

Agricultural Research Service (ARS). Work at Gainesville, Florida, is proceeding on the morphology, cytology, and physiology of insect sensors. Emphasis has been on the infrared spectrum, although some work with UV sensing has also been performed. Work with UV light traps is proceeding, as are basic studies on physical and chemical factors affecting insect biorhythms. These studies include light responses, and some UV work, but not in the UV-B radiation region. Comparative sensory reception and host recognition studies are being pursued, which could be adapted to studies of the effects of UV-B radiation.

DOT. The DOT has funded preliminary research on the effects of elevated UV-B irradiation on insects.

CRITICAL RESEARCH NEEDS

Insect behavior and the susceptibility of plants to invasion by pathogens or attack by insect pests could be altered significantly by changes in climatic conditions and increases in UV-B radiation reaching the earth's surface. Therefore, research is needed to determine the effects of:

(1) Increased UV-B irradiation on the physiology and behavior of beneficial and non-beneficial insects.

(2) Increased UV-B irradiation on host plant susceptibility to pests.

(3) UV-A and UV-B irradiation on the responses of male insects to pheromones.

(4) UV-B irradiation on insect vision, chemical perception, visual cue indications and production, and flight orientation to host plants.

Effects of Increased UV-B Radiation at the Community Level

Because of the difficulties in simulating increases in UV-B radiation on a large scale, it has not been possible to irradiate an entire ecosystem. Consequently, extrapolation of

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findings at levels of cells and organisms is beyond the scope of the present data base. Nevertheless, some discussion of the implications of increased UV-B exposure at the community level is necessary.

Although the potential effect of increased solar irradiance on man, especially in the form of skin cancer, has attracted much attention, the possible impacts of increased UV irradiation on organisms in aquatic and terrestrial ecosystems (both agricultural and non-agricultural) ultimately may be of much greater concern because they may affect large populations.

EFFECTS ON AQUATIC ECOSYSTEMS

Preliminary investigations involving the carbon dioxide incorporation (photosynthesis) of phytoplankton, the basic organisms in the food chain of marine ecosystems, show a statistically significant increase when solar UV-B radiation is removed by absorbing filters, compared with organisms exposed to a normal solar radiation spectrum. These experiments, which were conducted in coastal waters near Seattle, Washington, by Lorenzen (1974), show that present-day levels of UV-B radiation suppress the photosynthesis of naturally occurring marine phytoplankton populations. Other experiments conducted by Lorenzen off the coast of Africa suggest that photosynthesis of plankton may be inhibited by as much as 60% under increased UV-B radiation.

Studies show that UV radiation can penetrate considerable distances through water. For example, Lenoble (1957) reported that 75% of the UV radiation at 318.5 nm was transmitted to a depth of 1 m in natural waters off the coast of Corsica and 43% at 321 nm off the coast of Brittany. Additional studies are required to determine the exact magnitude of UV effects on marine ecosystems. Improved instrumentation must be developed for measuring UV penetration of natural waters in order to evaluate these effects.

Freshwater organisms exhibit a wide range of sensitivity to UV-B irradiation presently reaching the earth's surface. Some organisms may already be at their UV-B irradiation tolerance limit; they also may be maintaining population levels only because of the dynamic balance between reproduction and mortality,

resulting in part from UV-B radiation. Observations suggest that increased levels of solar UV-B radiation may modify freshwater ecosystems and reduce the efficiency of natural water purification. An assessment of the true impact of such modification on humans depends on the nature of the freshwater organisms, the body of water under study, and the quality of water considered tolerable for human consumption (Calkins, 1974a,b,c).

Damaging effects of solar irradiance have been reported for trout in shallow ponds (Allison, 1960; Hoffer and Fromm, 1965). It seems likely, therefore, that an increase in UV-B irradiation could provide an additional burden to these and other organisms in breeding ponds and other shallow bodies of water.

Caldwell (1974) noted that most organisms function in competitive situations in their natural ecosystems. With only mild additional stress imposed by increased UV-B exposure, they could be placed at a competitive disadvantage. Although this may not immediately affect the growth and development of the organism directly, it could change its probabilities for success in its interactions with other organisms in the ecosystem.

EFFECTS ON TERRESTRIAL ECOSYSTEMS

The effects of increased UV-B irradiation on terrestrial ecosystems cannot be predicted accurately. However, if one were to extrapolate from growth chamber, greenhouse, and solarium studies in which almost half of the native and cultivated species showed a significant decrease in biomass, similar effects on vegetation could be expected on a global basis.

Various physiological disorders of crops and forest vegetation have been ascribed to high levels of solar irradiation, especially at high altitudes. These include chlorosis (yellowing) in Engelmann spruce (Ronco 1970, 1972), sunscald in certain vegetables, and other disorders reviewed by Caldwell (1968, 1971) and Nilsen (1971). In most cases, however, a direct cause-and-effect relationship between UV radiation and plant damage has not been established. The impact of elevated UV-B irradiation on tree species is also generally unknown.

Effects of Increased UV-B Radiation on Agricultural Chemicals

STATE OF THE ART

In addition to direct effects on plants and animals, an increase in UV-B radiation and a shift in UV wavelength could also have profound effects on the natural and synthetic chemicals used in agriculture.

Agricultural chemicals are widely dissipated in the environment and exposed to many natural processes including attack by sunlight. Inorganic compounds are generally quite resistant to the action of sunlight. Thus, fertilizers and some of the older inorganic pesticides should not be adversely affected by any increase in UV-B radiation. Since the 1940's, however, there has been a significant increase in the production of synthetic organic compounds. Many of these, e.g., herbicides, insecticides, and fungicides, are derived from benzene, which absorbs strongly in the 250- to 260-nm region of the UV spectrum, with a dropoff toward 300 nm. Thus, these compounds would be subjected to increased photochemical reactions under increased UV radiation. Photochemical products may have altered toxicity, biological activity, or capacity to undergo degradation (*Plimmer*, 1969, 1971, 1972). There are many polymers that also may be affected (*Barker*, 1968).

Secondary processes (photosensitization) that involve absorption of light by a molecular species that does not react, but which brings about a reaction in a nonabsorbing species, may also cause photochemical changes in the ecosystem. The process of photosensitization may be common in the environment, as natural waters contain numerous sensitizer molecules. Photo-oxidation, caused by reaction of molecules with oxygen in the presence of light, is another common phenomenon that may be responsible for increased degradation of organic molecules.

ONGOING RESEARCH

At the Beltsville Agricultural Research Center and at other locations, research is continuing on the influence of natural sunlight and artificial sources of UV radiation on the photochemistry of pesticides and other important organic compounds used in agriculture. This information is potentially valuable in the development of future strategies of pesticide use and in maintenance of pesticide efficacy.

A study of photochemical reactions initially requires that the products be identified and that their rates of formation be determined. Rates and products depend on wavelength, duration and intensity of radiation, and solvent. At shorter wavelengths, photodecomposition is generally more rapid and extensive. At longer wavelengths, there may be no measurable reaction. In many cases, both laboratory and field studies are conducted to determine the stability of organic compounds under UV irradiation.

Recent areas of investigation have included the sensitized photolysis of amitrole (3-aminotriazole), the photo-oxidation of DDT and DDE, the photolysis of butralin (4-tert-butyl-N-sec-butyl-2,6-dinitroaniline), photolysis of the chlorinated dioxins, and sensitized photolysis of 2, 4-dichlorophenol. During the last year, there has been an effort to develop protocols for the Environmental Protection Agency to furnish a standardized procedure for permitting estimation and prediction of photoalteration. Such a procedure is necessary for the registration of a pesticide, as it is a factor in determining its potential hazard and efficacy. Laboratory evaluation of these protocols is essential.

CRITICAL RESEARCH NEEDS

The successful utilization of presently available pesticides and alternative pest control methods such as microbial agents, insect juvenile hormones, pheromones, and chemosterilants may be adversely affected if the residual activity of these substances is greatly reduced by increased UV irradiation.

If chemicals are to be used effectively in agriculture under an increased UV environment, it is important to:

(1) Define optimum conditions for their effective use.

(2) Identify compounds that may be destroyed by UV-B radiation.

(3) Find and evaluate methods of protection against UV-B radiation, including improvements in formulation techniques. Some progress has been

made in the pyrethroid field by incorporation of new substructures in the molecule.

Development of reliable information on the hazard and toxicology of photoproducts is limited by:

(1) Partial knowledge of their chemical nature.

(2) Lack of standardized procedures for investigation of photochemical reactions.

(3) Lack of information regarding the macro- and micro-environments to which pesticides are exposed in the field.

If pesticides are to be effectively used, it is essential to obtain information on the intensity and distribution of solar energy, effects of adsorption on soil, dust, or foliar surfaces; and the effects of sensitizers.

Effects of Climatic Changes on Agriculture and the Biosphere

Modeling studies conducted during the CIAP indicate that ozone reduction in the stratosphere may cause a slight decrease in average global temperature as well as changes in wind and rainfall. The magnitude of these effects on agricultural crops and the total ecosystem cannot be predicted with certainty.

Productivity changes resulting from shifts in climate were evaluated for selected agricultural crops during the CIAP. If average temperatures were lowered by 1° to 3°C over the Great Plains and agriculturally similar areas, planting and maturation dates of most wheat varieties, corn, and sorghum hybrids would be delayed by 1 to 2 weeks. The combined effects of delayed planting and maturing would mean that the effective growing season could be shortened by as much as 1 month. It would, therefore, be necessary to change to shorter season varieties or to a shorter season crop.

For non-marginal areas, certain crops such as wheat, corn, and sorghum would benefit from some cooling trends; however, in marginal areas, for example in parts of Canada and the U.S.S.R. where the growing season is short, yields of agricultural crops would be reduced. Warm-weather crops such as rice and cotton would experience decreased yields with decreases in temperature. Modeling studies for soybeans, rice, and cotton are summarized in *DOT CIAP Monograph 5, 1974.*

No quantitative assessment has been made of the effect of climatic change on the production of cattle, swine, and poultry. The NAS Report (*Climatic Impact Committee, 1975*) indicates that dairy milk production might be increased by cooler temperatures. However, these calculations do not include the possible influence of cold stress that dairy cattle could experience during winter or any other interactions that could influence heat balance in these animals. A decrease in rainfall would also curtail productivity of rangelands, and thus the carrying capacity for grazing animals. Lower temperatures would also have an adverse effect on timber production.

According to the NAS Report (*Climatic Impact Committee, 1975*), a 10% reduction in ozone level or an increase of $\pm 0.1\,\mu g$ m-3 in stratospheric particles would produce long-term global surface temperature changes of no more than a few tenths of a degree Celsius, and global rainfall would be altered by no more than $\pm 5\%$. Temperature changes in higher latitudes in the northern hemisphere could reach values several times those estimated on a global basis (i.e., about 1°C). On a local basis, precipitation could also be disturbed by as much as $\pm 10\%$. With increased cooling in higher latitudes, one could also expect great annual variability in weather conditions, with all of the implied ramifications for crop production.

REFERENCES

Allison, L. N. (1960). "Sunburning Fingerling Lake Trout With Light and the Effect of a Niacin-Fortified Diet," *Prog. Fish-Culturist,* Vol. 22, pp. 114-116.

Ambler, J. E., Krizek, D. T., and Semeniuk, P. (1974). "Influence of UV-B Radiation on Early Seedling Growth and Translocation of ^{65}Zn From Cotyledons in Cotton," *Impacts of Climatic Change on the Biosphere,* DOT CIAP Monograph 5.

Anderson, D. E., and Skinner, P. E. (1961). "Studies on Bovine Ocular Squamous Carcinoma ('Cancer Eye'). XI. Effects of Sunlight," *J. Animal Sci.,* Vol. 20, pp. 474-477.

Antonovics, J. (1974). "Predicting Evolutionary Response of Natural Populations to Increased UV Radiation,"

Impacts of Climatic Change on the Biosphere, DOT CIAP Monograph 5.

Barker, R. E. (1968). "The Availability of Solar Radiation Below 290 nm and Its Importance in Photo-modifications of Polymers," *Photochemistry and Photobiology*, Vol. 7, pp. 275-295.

Bartholic, J., and Halsey, L. (1974). "Response of Vegetables to Natural UV Irradiation," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Biggs, R. H., and Campbell, W. F. (1974). "Effects of UV Radiation on Other Molecular and Cellular Systems," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Billen, D., and Fletcher, M. M. (1974). "Comparison of the Germicidal and Erythemal Activity of Sunlight," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Blum, H. F. (1959). *Carcinogenesis by Ultraviolet Light*, Princeton University Press, Princeton, N.J.

Brabham, D., and Biggs, R. H. (1974). "Optical Properties," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Caldwell, M. M. (1968). Solar Ultraviolet Radiation as an Ecological Factor for Alpine Plants," *Ecol. Monogr.*, Vol. 38, pp. 243-268.

Caldwell, M. M. (1971). "Solar Ultraviolet Radiation and the Growth and Development of Higher Plants," *Photophysiology*, Vol. 6, pp. 131-177.

Caldwell, M. M. (1974). "CIAP Monograph 5: Impacts of Climatic Change in the Biosphere," in Grobecker, A. J., Coronoti, S. C., and Cannon, R. H., Jr., *CIAP Report of Findings: The Effects of Stratospheric Pollution by Aircraft*, pp. 1-80.

Caldwell, M. M., Sisson, W., and Jahn, A. (1974). "Plant Growth Response to Elevated UV Irradiation Under Field Conditions," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Calkins, J. (1974a). "Penetration of UV Radiation into Aquatic Ecosystems," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

————— (1974b). "Effect of UV-B Radiation on Aquatic Invertebrate Organisms," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

————— (1974c). "Preliminary Assessment of UV Irradiation Effects on Aquatic Micro-Organisms and Their Ecosystems," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Campbell, W. F. (1974a). "Effects of Enhanced UV Radiation (280-320 nm) on *Tradescantia inflorescenses*," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

————— (1974b). "UV-induced Ultrastructural and Chomosomal Changes in Plant Cells," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Carns, H. R., Hart, R. H., Carlson, G. E., Klueter, H. H., and Liu, R. C. (1974). "Importance of UV-B Radiation on Economically Important Crops," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Carns, H. R., and Christiansen, M.N. (1974). "Influence of UV-B Radiation on Abscission," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Chu, E. H. Y. (1965). "Effects of Ultraviolet Radiation on Mammalian Cells. 1. Induction of Chromosome Aberrations," *Mutation Res.*, Vol. 2, pp. 75-94.

Climatic Impact Committee. (1975). *Environmental Impact of Stratospheric Flight: Biological and Climatic Effects of Aircraft Emissions in the Stratosphere*, National Academy of Sciences, Washington, D. C., 348 pp.

DOT CIAP Monograph 5 (1974). *Impacts of Climatic Change on the Biosphere*, Department of Transportation, Washington, D. C.

Environmental Studies Board. (1973). *Biological Impacts of Increased Intensities of Solar Ultraviolet Radiation*, National Academy of Sciences-National Academy of Engineering, Washington, D.C., 46 pp.

Epstein, J. H., Urbach, F., Lee, J. A., Forbes, P. D., and Scotto, J. (1974). "Chronic Detrimental Effects of UV Radiation," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Hoffer, J. R., and Fromm, P. D. (1965). "Biomicrosopic, Gross, and Microscopic Observations of Corneal Lesions in the Lake Trout, *Salvelinus namaycush*," *J. Fish. Res. Bd. Canada*, Vol. 22, pp. 761-766.

Hsiao, C., and Hsiao, T. H. (1974). "Effects of Elevated UV-B Radiation on Insects," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Hsiao, C., Cromroy, H. L., and Agee, H. R. (1974). "Effects of UV Radiation on Insects," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Krizek, D. T. (1974). "Influence of Ultraviolet Radiation on Germination and Early Seedling Growth," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Lenoble, J. (1975). "Penetration of Ultraviolet Radiation into the Oceans," *Proc. 2nd Intl. Cong. Photobiol.* (Turin), Vol. 44, p. 2.

Lorenzen, C. J. (1974). "Whole Plant Response–Aquatic Plants," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

MacDonald, E. J. (1974). "Association Between Cancer Eye and Sunlight," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Murphy, T. M. (1974). "Effects of UV-B Radiation on Nucleic Acids," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Nachtwey, S. (1974). "Linking Photobiological Studies at 254 nm with UV-B," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

National Academy of Sciences-National Academy of Engineering, *Biological Impacts of Increased Intensities of Solar Ultraviolet Radiation*, Washington, D.C., 1973.

Nilsen, K. N. (1971). "Plant Responses to Near Ultraviolet Light," *HortScience*, Vol. 6, pp. 26-29.

Plimmer, J. R., (1969). "Photochemistry of Halogenated Herbicides," *Residue Reviews*, Vol. 31, pp. 47-74.

Plimmer, J. R. (1971). "Photochemistry of Pesticides: A Discussion of Some Environmental Factors," *Pesticide Chemistry*, Vol. 6, pp. 47-76.

Plimmer, J. R. (1972). *Photochemistry of Pesticides: Principles in Degradation of Synthetic Organic Molecules in the Biosphere*, pp. 279-290, National Academy of Sciences, Washington, D. C.

Porter, W. P., and Norris, K. S. (1968). "Lizard Reflectivity Change and Its Effect on Light Transmission Through

Body Wall," *Science*, Vol. 163, pp. 482-484.

Ronco, F. (1970). "Chlorosis of Planted Engelmann Spruce Seedlings Unrelated to Nitrogen Content," *Can. J. Bot.*, Vol. 48, pp. 851-853.

Ronco, F. (1972). *Solarization—A High Elevation Problem* Paper Presented at the Annual Meeting of the Western Reforestation Coordination Committee in Seattle, Washington, December 1972.

Setlow, R. B., and Doyle, B. (1957). "The Action of Monochromatic Light on Proteins," *Biochim. Biophys. Acta*, Vol. 24, pp. 27-41.

Sisson, W., and Caldwell, M. M. (1974). "Effects on Enhanced UV Radiation (280-320 nm) on Higher Plant Photosynthesis," *Impacts of Climatic Change on the Biosphere*, DOT CIAP Monograph 5.

Stadler, L. J., and Uber, F. M. (1942). "Genetic Effects of Ultraviolet Radiation in Maize," *Genetics*, Vol. 27, pp. 84-118.

VanBrunt, E. E., Shepherd, J., Wall, J. R., Ganong, W. F., and Clegg, M. T. (1964). "Penetration of Light Into the Brain of Mammals," *Ann. N. Y. Acad. Sci.*, Vol. 117, pp. 217-227.

V.

Human Health Effects of Ozone Reduction

INTRODUCTION

Modification of the stratosphere, such as a reduction in its equilibrium ozone content, could produce direct and indirect effects on human health. The direct hazard to humans would be caused by an increase in the cumulative amount of UV radiation reaching the earth's surface in the range of 285 to 340 nm, encompassing the UV-B or erythemal wavelength region of 280 to 320 nm. Exposing the susceptible human population to an increased total UV dosage of shorter wavelengths could increase skin cancer incidence. Although effects would be delayed by decades, for each 1% decrease in ozone the expected increase in skin cancer incidence would be on the order of 2%. Indirect effects could be significant; however, they are too speculative to be considered here. This section, therefore, contains a discussion of direct health effects only.

For a discussion of the indirect effects of ozone reduction, the reader is referred to:

- National Academy of Sciences (NAS) Report, entitled *Environmental Impact of Stratospheric Flight: Biological and Climatic Effects of Aircraft Emissions in the Stratosphere*, published in April 1975.

- CIAP Report of Findings, entitled *The Effects of Stratospheric Pollution by Aircraft*, published by the Department of Transportation in 1974.

- DOT CIAP Monograph 5, entitled *Impacts of Climatic Change on the Biosphere* (1974 draft).

HUMAN HEALTH EFFECTS

Most living organisms possess adaptive mechanisms that protect them in varying degrees when perturbations occur in the environment. Some of these mechanisms are behavioral and some are internal. The internal process is referred to as "homeostasis." When the external perturbation is small, the change may be within the ability of the organism to function normally. In some cases, minor or major damage is sustained that can be repaired and is therefore consistent with life. In other cases, acute or long-standing damage can lead to serious permanent incapacities or even death.

The human health effects of exposure to the sun are well known; they include sunburn and suntan, skin cancer, synthesis of vitamin D, premature aging and other structural changes of the skin, varying degrees of eye damage, and some effects that are more generalized and less studied. The effects vary with the geographical location of residence, occupation, recreational pattern, behavioral characteristics, skin color, and a variety of other external and internal conditions. These effects are discussed in some detail below.

Effects on the Skin

SUNBURN AND SUNTAN

The most common response of humans to moderate levels of UV radiation is sunburn (known as erythema solare). Within 1 to 6 hours following exposure, a reddening develops that may progress to inflammation, blistering, and peeling. The shorter wavelengths of UV-B radiation that reach the
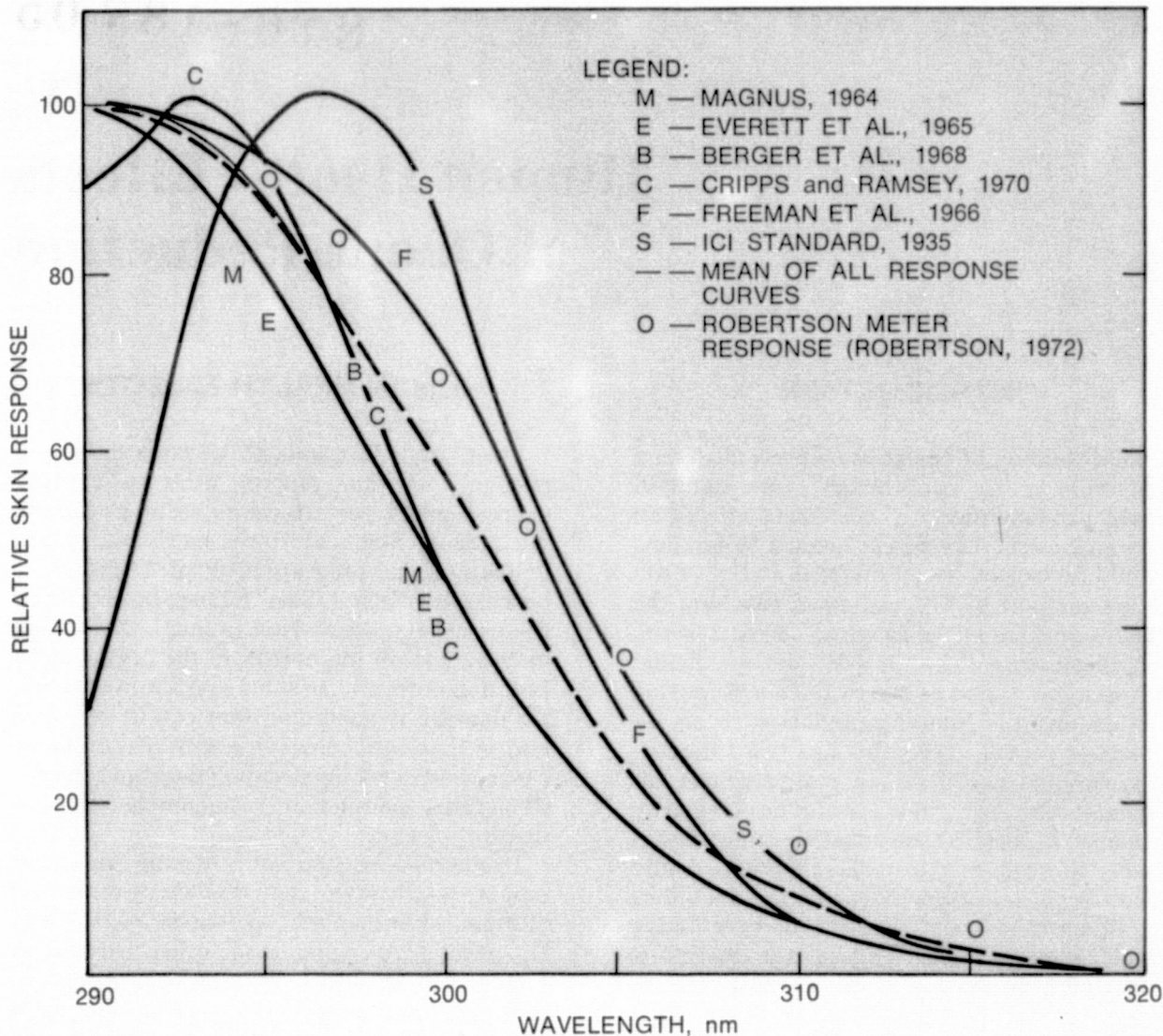
Fig. V-1. Action spectra for minimal erythema of human skin. (After *Robertson*, 1972)

earth burn the skin more easily; however, the longer wavelengths, between 320 and 400 nm, increase the sunburn (*Willis et al.*, 1972).

Individuals vary greatly in their tendency to sunburn. In one study, about 13% of the population developed sunburn without tanning, 20% tanned without excessive burning, and 67% sunburned and then tanned (*Schulze*, 1956). Genetic factors are involved to a great extent in this tendency to burn or to tan. For example, persons of Celtic heritage and those with a variety of metabolic conditions such as albinism, phenylketonuria, acute porphyria

and xeroderma pigmentosum are photosensitive and tend to sunburn.

The spectrum of UV radiation that causes sunburn has been determined in the laboratory by several investigators under a variety of conditions (*Robertson and Urbach*, 1974). Some of these "erythemal spectra" are shown in Fig. V-1. The measurements are affected by age, sex, anatomic location of the sunburn, time elapsed until measurement, degree of pigmentation in the skin, and the degree of tanning to which the individual is capable.

A typical spectrum of solar UV radiation

that reaches the earth is presented in Fig. V-2. The extent to which the incident UV radiation tends toward shorter wavelengths depends upon many things, the most significant of which are the ozone content of the stratosphere, the latitude, altitude, solar attitude (angle of the sun), and weather conditions in the lower atmosphere.

When the two types of spectra shown in Figs V-1 and V-2 are combined, the curves of Fig. V-3 are obtained. This figure shows that radiation with wavelengths between 295 and 310 nm causes the erythemal response.

The amount of total UV-B radiation that reaches earth in nine cities of the U.S., from about 30° to 47° latitude, is shown in Fig. V-4

(Machta et al., 1975). The daily amount varies not only with the ozone content of the stratosphere, but also with such variables as cloudiness, air turbidity, air mass, and the proportion of radiation reflected from the ground (ground albedo). There are smaller latitudinal differences during the summer months than during the year as a whole. Discounting important differences caused by cloudiness, air turbidity, air mass, and ground albedo, the incident total UV-B radiation at earth level is greater at lower latitudes within the range shown.

The relationship of erythemal dosage to average stratospheric ozone concentration is shown in Fig. V-5 (Schulze, 1973). For a 10%
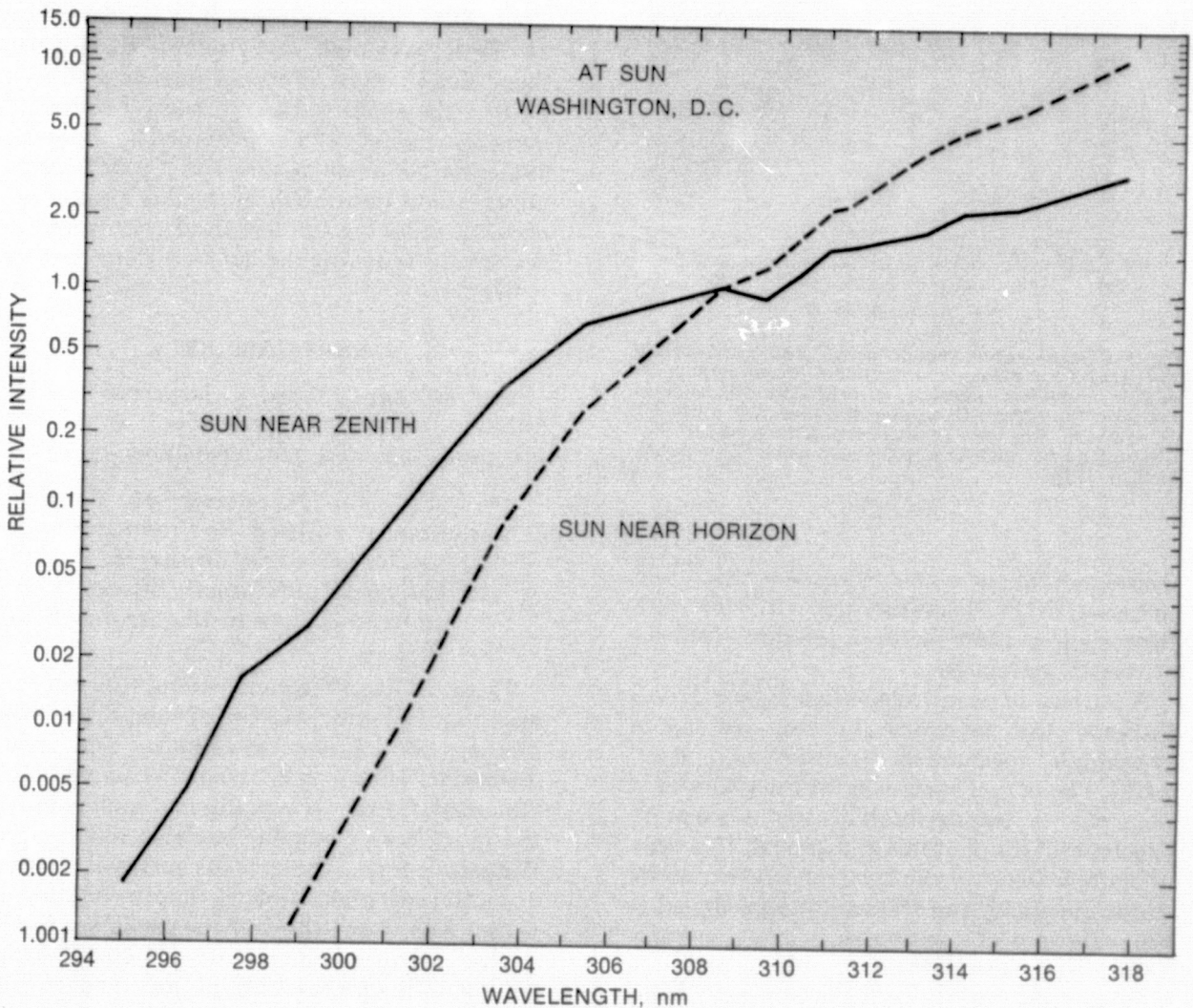

Fig. V-2. Solar radiation reaching the earth at Washington, D.C., at two times of the day. (After Machta et al., 1975)
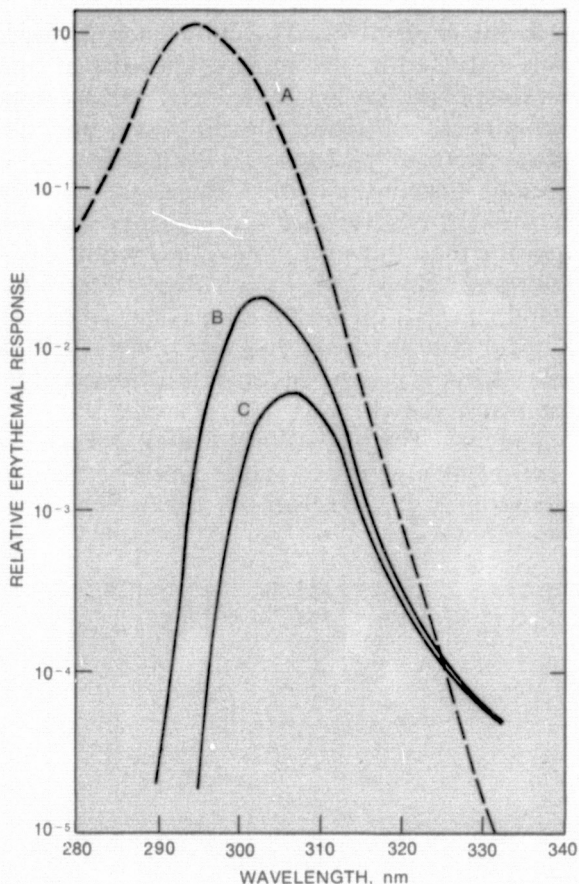
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Fig. V-3. Relative erythemal efficiency of solar radiation at the ground for different atmospheric ozone content. A: relative erythemal response; B: erythemal efficiency of radiation, O_3, 0.20 cm; C: erythemal efficiency of radiation, O_3, 0.40 cm. Standard atmosphere, solar elevation 60°. (Reprinted from NAS Report: *Climatic Impact Committee,* 1975, p. 173)

decrement, about a 20% increase (or two-fold increase) in UV-B is estimated, while for a 40% decrement a 120% increase (or three-fold increase) is estimated.

A variety of chemicals, when ingested, will increase the tendency to sunburn by a phototoxic mechanism (*Harber and Baer,* 1972). The action spectrum for the phototoxic response is approximately the absorption spectrum of the phototoxic chemical. This type of photosensitivity can occur on first exposure to the chemical, and the reaction produced is typically that of a sunburn.

Some chemicals can also produce photoallergic reactions (*Harber and Baer,* 1972). However, the peak of the action spectrum for this type of response occurs at

wavelengths of about 315 nm or greater. Because of this, the photoallergic reactions are of less relevance to the present consideration. A variety of skin disorders can develop because of the photoallergy.

The ozone in the stratosphere represents the initial and most important filter for the more hazardous, shorter UV wavelengths. The tendency of some individuals to tan, however, also provides a natural filtering mechanism that can be enhanced by the use of sun-screen and tanning preparations. For some heavily tanned individuals, repeated exposure to sunlight over a period of years may still cause keratoses (callous-like thickening of the skin), skin cancers, and other structural changes of the skin.

Behavioral and physical methods for preventing an excess of exposure are available, although many people do not use them. For example, clothing such as a hat can protect the scalp, ears, and neck. Additional margins of safety can be provided by avoiding exposure between 10 a.m. and 2 p.m. (during which about two-thirds of the day's radiation occurs), reducing the length of time spent in the sun, or reducing the length of time periods while wet.

SKIN CANCER

This section is based in large part on the following document. The reader is referred to this publication for greater details.

- National Academy of Sciences Report, entitled *Environmental Impact of Stratospheric Flight: Biological and Climatic Effects of Aircraft Emissions in the Stratosphere,* 1975.

There are two different general types of disease that fall under the broad category of skin cancer: malignant melanoma and non-melanoma (basal cell or squamous cell carcinomas). Of the two, malignant melanoma is the much less common, but also much more dangerous form. The average survival time for a victim of melanoma is approximately 7 years. About one-third of the cases are fatal.

The more common non-melanoma skin cancer, although rarely fatal (an estimated 1% mortality rate among cases), often is disfiguring. Its treatment can be expensive and ul-

Data from Temple SUV counts and conversion factor of 2.8 counts/J m^{-2} from regression with ARL data at Bismarck, Oct. 1973—Feb. 1974. (Average daily tenths of cloudiness plotted.)

ANNUAL TOTALS
(Oct. 1973–Sept. 1974)
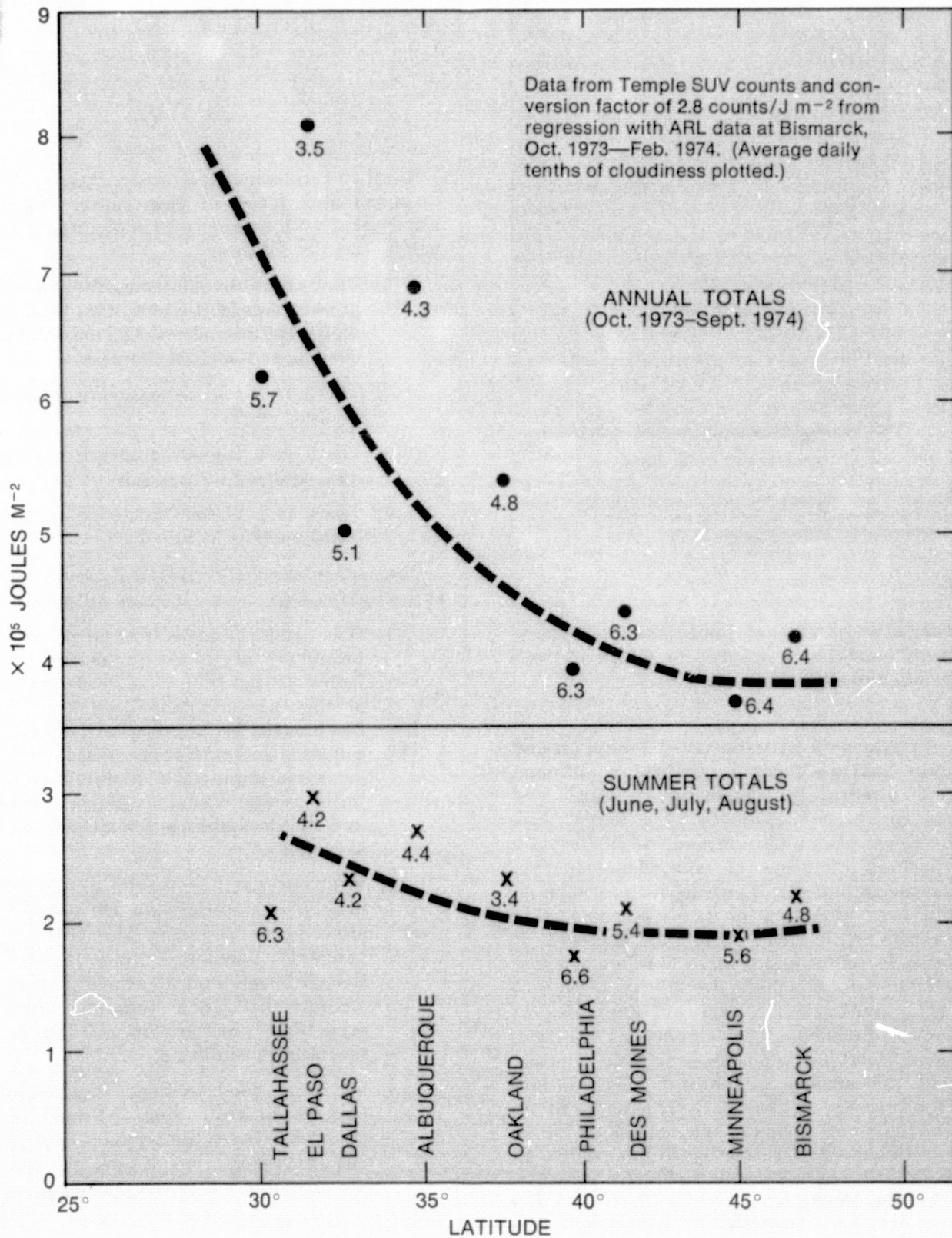
SUMMER TOTALS
(June, July, August)

Fig. V-4. Variation in UV-B radiation with latitude for nine cities in the United States.
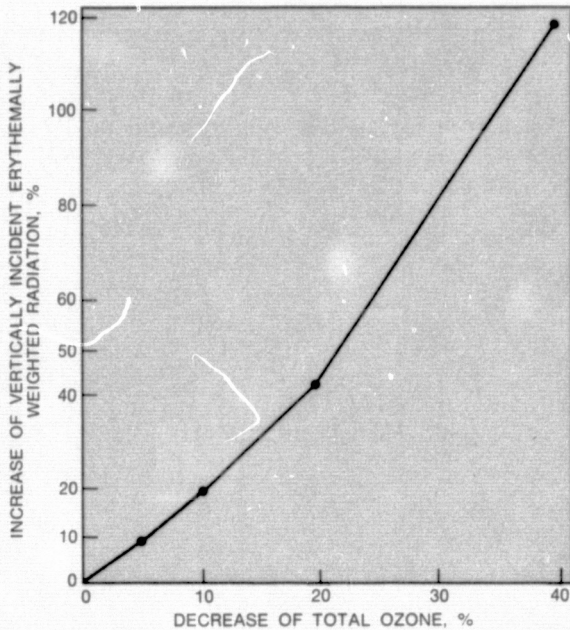
Fig. V-5. Percentage of change in dose of vertically incident erythemally weighted radiation vs percentage of change in ozone column. (After *Schulze*, 1973)

timately the disease limits one's activities, particularly with respect to additional exposures to sunlight.

Relationship Between UV-B Radiation and Skin Cancer—There is persuasive, although not absolutely conclusive, clinical and epidemiological evidence of a direct link between solar radiation and the historically observed incidence of non-melanoma skin cancer in humans. There is, for example, an observed doubling of non-melanoma skin cancers with each 8° to 11° decrease in latitude, which is presumed to relate to a correlated reduction in the average ozone concentration with latitude. There are other relevant factors including local cloudiness, lifestyle, hours of outdoor exposure, genetic differences, and the amount of natural pigmentation. However, the incidence of skin cancer and the mortality rate owing to skin cancer are better correlated with the intensity of solar radiation than with any other environmental variable. This conclusion is strongly supported by the unequivocal induction of skin cancers in animals exposed to UV-B radiation.

There is some evidence, although much less conclusive, to support a correlation between UV-B radiation and melanoma. The following are brief summaries of the evidence supporting an association between solar UV radiation in the range of 295 to 320 nm and skin cancer in light-skinned individuals.[1]

Basal and squamous cell carcinomas are the most common forms of skin cancer. Their association with exposure to sunlight can be summarized as follows:

(1) They occur almost exclusively on exposed areas of the body that receive high light intensities, e.g., nose, ears, cheeks, and back of the neck.

(2) There is a higher incidence among outdoor workers.

(3) There is a higher incidence among light-skinned individuals.

(4) There is a higher incidence at low latitudes (Fig. V-6).

Their association with the UV-B component of sunlight can be summarized as follows:

(1) Wavelengths known to be effective in producing erythema (sunburn) are below 320 nm (Fig. V-1). Injury of the skin by the sun is most likely the principal factor in inducing skin cancer. Sunburn and skin cancer arise in the same tissue, and individuals who sunburn easily have a higher than average probability for developing skin cancer.

(2) In numerous experimental studies on mice, wavelengths below 320 nm were effective in inducing skin cancer. Longer UV wavelengths were ineffective, although a recent experiment indicates that such radiation may accentuate the effects of shorter wavelength radiation.

(3) There is good evidence that skin cancer arises from UV-induced changes in DNA, the carrier of genetic information in living cells. Wavelengths below 310 nm are hun-

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[1] NAS Report, pp. 37-41.
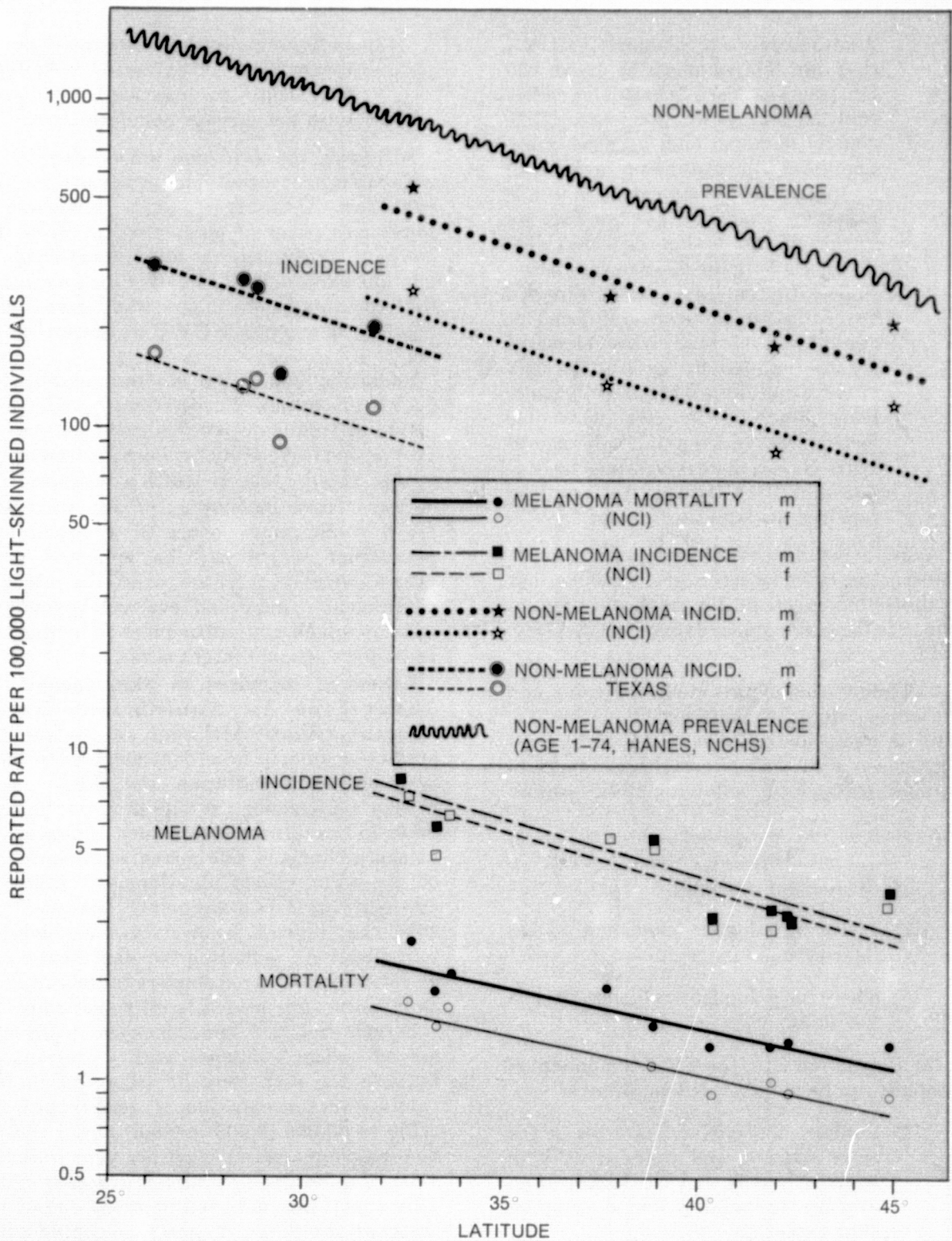
Fig. V-6. Reported skin cancer rates among light-skinned individuals as a function of latitude. (After *Mason and McKay*, 1974 (melanoma mortality); *National Cancer Institute* (NCI), 1974 (melanoma incidence); *Scotto et al.*, 1974 (non-melanoma skin cancer incidence); *Macdonald*, 1974 (non-melanoma skin cancer incidence, Texas); and *McDowell*, personal communication, 1975 (prevalence of non-melanoma skin cancer based on preliminary data from the Health and Nutrition Examination Survey of the National Center for Health Statistics. (Reprinted from NAS Report: *Climatic Impact Committee*, 1975)

dreds of times more damaging to DNA than are the wavelengths above 330 nm (see Fig. V-7). Ultraviolet radiation is mutagenic (i.e., can cause genetic damage) and, because many chemical carcinogens are also mutagens, it is expected that UV radiation would be carcinogenic by virtue of its action on DNA. Individuals with the disease xeroderma pigmentosum are extraordinarily susceptible to skin cancer induced by sunlight (in one study a prevalence of greater than 50% by age 10). The cells of these individuals are defective in at least one of several molecular mechanisms that repair UV damage to DNA. Hence, there is a strong implication that DNA damage not properly repaired leads to skin cancer.

Available evidence indicates that the spectral sensitivity for skin cancer is similar either to the action spectrum for erythema production or to the spectrum for damaging DNA (Fig. V-7).

Malignant melanoma is much more rare than the skin carcinomas mentioned above, but it is fatal in about one-third of the cases. Its occurrence is also associated with exposure to sunlight through the following observations:

(1) It occurs on exposed areas of the body, but not exclusively those that receive the highest intensity.

(2) There is a higher incidence among light-skinned individuals.

(3) There is a higher incidence at low latitudes.

Its association with the UV-B component of sunlight can be summarized as follows:

(1) Sunburn and melanoma arise in the same tissues, and individuals who sunburn easily have a higher than average probability for developing skin cancer.

(2) Although UV irradiation alone does not give rise to melanomas in mice, irradiation of a chemically induced benign pigmented lesion does.

(3) Individuals with xeroderma pigmentosum have an extraordinarily high prevalence of melanoma compared with the average population.

Although the evidence associating UV-B with malignant melanomas is not as strong as for non-melanomas (e.g., melanomas sometimes occur on unexposed parts of the body), it is believed that the only action spectra that can prudently be used for any quantitative estimate of the potential hazard arising from an increase in UV-B are those given in Fig. V-7.

Radiation and other environmentally induced cancers are characterized by a latency period of from approximately 15 to 40 years. This period is the delay between the time of exposure and the time at which symptoms first appear. Thus, the impact of any increased UV-B radiation exposure of a susceptible population would not be apparent until decades after the increase occurred and would continue at an increased level well beyond the time at which any subsequent reductions in radiation exposure might occur.

Estimated Increases in Skin Cancer for Reductions in Equilibrium Ozone Concentrations—Although experimental studies on animals have demonstrated the link between UV-B radiation and skin cancer, human epidemiological data provide the best basis for quantitative estimates of cancer incidence in humans. The current understanding of the skin cancer development from an epidemiological standpoint, however, is somewhat limited. Answers to many important questions, including the identification of as yet unidentified parameters contributing to skin cancer, are needed to refine estimates.

Estimates based upon changes in the observed cancer incidence with variations in latitude for each percent reduction in the equilibrium concentration of ozone range from 2,100 to 15,000 (6,000 median) new cases of non-melanoma skin cancer per year in light-skinned individuals in the U.S. at steady state. This conclusion is based upon the following assumptions (Urbach, personal communication, 1975):

(1) A 1.4 to 2.5% (2% median) increase in UV-B radiation will occur at the earth's surface for a 1% reduction in

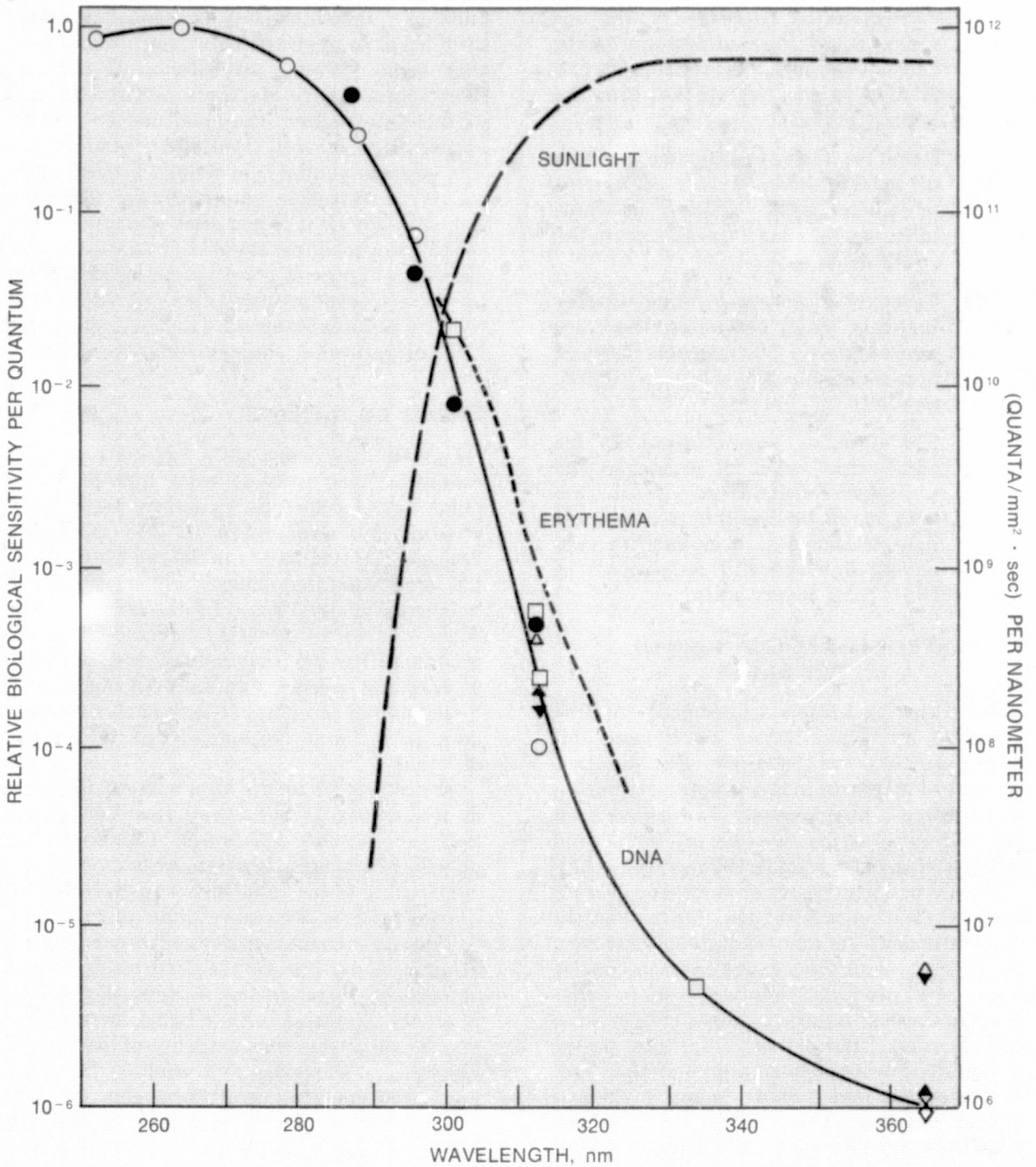Fig. V-7. The solid curve represents the action spectrum for affecting DNA; the dashed curve is the long-wavelength part of a recent erythemal action spectrum normalized to the DNA spectrum at 297 nm. The sun's spectrum at the earth's surface was calculated by Green for Gainesville, Florida, for 2.3 mm O_3 and a zenith angle of 25°. (Reprinted from NAS Report: *Climatic Impact Committee*, 1975)

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the equilibrium ozone concentration of the stratosphere.

(2) For each 1% rise in UV-B radiation, a corresponding increase in the incidence of non-melanoma skin cancers can range from 0.5 to 2% (1% median) at steady state (i.e., after the latency period).

(3) Items (1) and (2) combined lead to a 0.7 to 5% (2% median) increase in non-melanoma skin cancers at mid-latitudes for each 1% reduction in the equilibrium ozone level.

(4) Based upon recent National Cancer Institute (NCI) estimates, there are approximately 300,000 new cases of non-melanoma skin cancer in the U.S. annually.

(5) Therefore, a 1% reduction in the equilibrium level of ozone in the stratosphere might lead to from 2,100 to 15,000 (6,000 median) new cases of non-melanoma skin cancer per year among light-skinned individuals in the U.S. at steady state.

STRUCTURAL CHANGES OF THE SKIN

Possible structural changes include atrophy, wrinkling, areas of hyper- and hypopigmentation, yellow discoloration because of increases in abnormal elastic tissue and dilation of blood vessels. These have been referred to as aging, weathering, or actinic changes (caused by short UV wavelengths). There are no quantitative data on prematurely aged skin so that it is not possible to quantify its relationship to solar radiation. However, for every patient who develops skin cancer, there are probably hundreds more who develop these structural changes (Silverstone and Gordon, 1966), which are not easily treated. The weather-beaten sailor, fisherman, or farmer may take it in stride, but it can be a serious psychological problem for a woman who, because of excessive exposure, may look 70 when she is actually 50, and even may create an employment problem for many men and women in their middle years. Significant increase in UV radiation could make this a much more common occurrence.

SYNTHESIS OF VITAMIN D

Vitamin D production, usually considered a beneficial aspect of sunlight, enhances calcium uptake in the intestine and deposition of mineral in the bone. However, it is known that large excesses of vitamin D can be detrimental in several situations. On the basis of this information, the Food and Drug Administration recently limited the amount of this vitamin available as a daily food supplement in vitamin preparations (Federal Register, 1973). It is a matter of controversy whether or not an excess of UV radiation could cause the synthesis of sufficient vitamin D in the skin to produce symptoms of vitamin D toxicity in individuals who ingest large quantities of natural or supplemented vitamin D.

Effects on the Eyes

Human experience with exposure to UV radiation from welding arcs, high-pressure pulse lamps, and reflection from snow have adequately demonstrated the potential dangers of UV radiation to the eye. Most of the UV irradiation that enters the eye is absorbed by the cornea and some by the lens, making these parts especially susceptible to photokeratitis of the cornea and perhaps cataracts. Because UV radiation is not sensed by the visual receptors of the eye, it can cause damage without the knowledge of the individual.

Photokeratitis occurs after a latent period of 30 minutes to 24 hours and most commonly between 6 and 12 hours. Conjunctivitis develops first and is often accompanied by sunburning of the facial skin and eyelids. Unlike the tanning response of the skin, tolerance to subsequent exposure does not occur. The individual has a sensation of particles in the eye as well as experiencing varying degrees of photophobia (sensitivity to light), lacrimation (excessive or abnormal secretion of tears), and blepharospasm (excessive winking from involuntary contraction of the eyelid muscle). These effects usually disappear within 48 hours and rarely result in permanent damage.

Cataracts may develop on exposure to UV radiation. A common feature of cataract formation appears to be swelling of the lens, which occurs with ionizing and microwave radiation, several chemicals, and in a

hereditary condition (Kinoshita, 1974). Whether or not this, in fact, occurs with exposure to UV radiation remains to be determined.

Ongoing Research

The National Cancer Institute is the principal agency sponsoring investigations upon the relationship between UV-B radiation and skin cancer. It has been responsible for both laboratory experimental work and for collecting epidemiological information on the incidence of skin cancer. Currently, UV exposure data from many locations are being collected; information on the incidence of melanoma skin cancer is being collected by the Surveillance Epidemiology and End-Result Reporting (SEER) group.

Further experimental research into the health effects of UV radiation is being conducted by the National Institute of Environmental Health Sciences and will be continued.

The National Center for Health Statistics is collecting data on melanoma mortality.

Because much of this information is being collected as part of larger programs, it is difficult to define precisely the level of effort. It is, however, on the order of $1 million per year.

Research Needs

Research is needed to refine the skin cancer incidence and mortality predictions for exposure to increased UV-B radiation. Such research should consist of:

(1) Obtaining more epidemiological data on the prevalence of both non-melanoma and melanoma skin cancers, particularly at low and middle latitudes where the highest incidences are expected.

(2) Correlating incidence data with information on variation in the form of UV-B exposure, skin phenotype, sex, occupation, and personal behavioral characteristics.

(3) Measuring UV-B and total sunlight exposure at many more locations world-wide, particularly at latitudes below 20° and higher than 55°, to ob-

tain better correlations of natural erythemal exposure with human skin cancer incidence.

(4) Improving UV-B monitors. For example, improvements should include the ability to filter out longer wavelengths, to withstand temperature changes, and to make direct recordings of the data on magnetic tape.

(5) Exposing hairless mice to UV-B radiation that is varied by filtration through ozone to refine the relationship between skin cancer incidence and the amount of UV-B radiation.

(6) Determining the carcinogenic activity of different wavelengths of UV radiation in mice in order to develop an action spectrum.

(7) Obtaining an animal model to study malignant melanoma induced by UV-B radiation.

REFERENCES

Berger, D., Urbach, F. and Davies, R. E. (1968). "The Action Spectrum of Erythema Induced by Ultraviolet Radiation," *Proceedings of the 13th Congr. Int. Dermatol.*, pp. 1112-1117, Munich, Springer Verlag, Berlin.

Climatic Impact Committee. (1975). *Environmental Impact of Stratospheric Flight: Biological and Climatic Effects of Aircraft Emissions in the Stratosphere*, National Academy of Sciences, Washington, D.C.

Cripps, D. J., and Ramsey, C. A. (1970). "Ultraviolet Action Spectrum With a Prism-Grating Monochrometer," *Brit. J. Derm.*, Vol. 82, pp. 584-592.

Everett, M. A., Olson, R. L., and Sayre, R. M. (1965). "Ultraviolet Erythema," *Arch. Derm.*, Vol. 92, pp. 713-719.

Federal Register. (1973). Part II, pp. 20723-20725.

Freeman, R. D., Owens, D. W., Knox, J. M. and Hudson, H. T. (1966). "Relative Energy Requirements for an Erythemal Response of the Skin to Monochromatic Wavelengths of Ultraviolet Present in the Solar System," *J. Invest. Derm.*, Vol. 47, pp. 586-592.

Harber, L. C., and Baer, R. I. (1972). "Pathogenic Mechanisms of Drug-Induced Photosensitivity," *J. Invest. Derm.*, Vol. 58, pp. 327-342.

International Commission on Illumination (ICI). (1935). "Standard Erythemal Action Curve," *C.R.*, Vol. 9, pp. 596-625.

Kinoshita, J. H. (1974). "Mechanisms Initiating Cataract Formation," *Invest. Ophth.* Vol. 13, pp. 713-724.

Macdonald, E. J. (1974). *A Statement on Skin Cancer Incidence and Sun Exposure* (manuscript).

Machta, L., Cocton, G., Hass, W., and Komhyr, W. (1975). "Erythemal Ultraviolet Solar Radiation and Environmental Factors," *Proceedings of the 4th Climatic Impact Assessment Program (CIAP)*, Cambridge, Mass., Department of Transportation.

Magnus, I. A. (1964). "Studies with a Monochrometer in the Common Ideopathic Photodermatoses," *Brit. J. Derm.*, Vol. 76, pp. 245-264.

Mason, T. J., and McKay, F. W. (1974). *U.S. Cancer Mortality by County: 1950—1969*, DHEW Pub. No. (NIH) 74-615, Washington, D.C.

National Cancer Institute. (1974). *The Third National Cancer Survey Advanced Three Year Report: 1969-1971 Incidence*. Preprint.

Robertson, D. F. (1972). *Solar Ultraviolet Radiation in Relation to Human Sunburn and Skin Cancer*, Ph.D. Thesis, University of Queensland, Australia.

Robertson, D. F., and Urbach, F. (1974). "Erythemal Effects on the Skin," *Impacts of Climatic Change on the Biosphere*, Chapter 7.2.1., DOT CIAP Monograph 5, Washington, D.C.

Schulze, R. (1956). Quoted in Van Ham, E.W., and Herzog, W.P. (1973). "The Design of Sunscreen Preparations," *Drug Design*, Vol. 4, pp. 193-235, Academic Press, N.Y.

Schulze, R. (1973). quoted in CIAP Report of Findings, *The Effects of Stratospheric Pollution by Aircraft*, Final Report, DOT-TST-75-50.

Scotto, J., Kopf, A. W., and Urbach, F. (1974). "Non-melanoma Skin Cancer Among Caucasians in Four Areas of the United States," *Cancer*, Vol. 34, pp. 1333-1338.

Silverstone, H., and Gordon, D. (1966). "Regional Studies in Skin Cancer: 2nd report: Wet Tropical and Sub-Tropical Coasts of Queensland," *Med. J. Australia*, Vol. 2, pp. 733-740.

Willis, I., Kligman, A., and Epstein, J. H. (1972). "Effects of Long Ultraviolet Rays on Human Skin: Photoprotective or Photoaugmentative?," *J. Invest. Derm.*, Vol. 59, pp. 416-420.

VI.

The Fluorocarbon Industry

INTRODUCTION

This section presents an overview of the history, production, and uses of fluorocarbons, the extent of leakage to the atmosphere, and the possibilities for developing or expanding the use of substitute products. Some data are also included on the economic value and the work force related to fluorocarbon production and applications, but the analysis is incomplete regarding the possible economic impacts that would result from any curtailment of production or use.

Urgently needed additional study of these matters is currently underway. Representatives of industrial and trade organizations have been extremely helpful to the task force by supplying data for this section. Because the potential problem of stratospheric ozone reduction was identified so recently, and because the fluorocarbon market is so diverse, all information that would help to provide a greater understanding of the present and future production and use of fluorocarbons and of the strategies for minimizing economic disruption is not yet available.

Subjects that require more complete and detailed analyses include:

(1) Specific fluorocarbon uses and users.

(2) Workers and occupations potentially affected by curtailment of fluorocarbon production, and opportunities for retraining and reassignment in related industrial processes.

(3) Possibilities for reducing leakage of fluorocarbons from refrigeration and air-conditioning equipment and for recovery of fluorocarbons for recy-

cling before final disposal of such equipment.

(4) Probable advantages and disadvantages of various alternatives to fluorocarbon use and production, and marketing strategies and costs associated with these alternatives.

(5) Adjustment costs to industry and workers associated with timetables and alternative levels of restrictions.

These are factors that would necessarily receive explicit consideration by the regulatory agencies in the process of developing any specific restrictions, if restrictions are found to be necessary.

HISTORY OF FLUOROCARBONS

Fluorocarbons first came into use as refrigerants in the early 1930's. These products, which were nonflammable and had low toxicity and chemical reactivity, were prime substitutes for materials previously used as refrigerants because they evaporated rapidly and were liquefied quickly when compressed. The use of fluorocarbons in aerosols began during World War II after researchers at the U.S. Department of Agriculture found that the dispersal of insecticides as fine aerosols greatly increased their effectiveness. When low-pressure valves and nozzles were developed, fluorocarbons-11 and -12 (F-11 and F-12)[1] became standard propellants for dis-

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[1] The numbering system for fluorocarbons is one used by U.S. industry which, by a complex set of rules, indicates the number of each type of atom in the compound.

pensing aerosols; since 1955 the rate of production of these two compounds has increased progressively. Halogen derivatives of several homologous series of organic compounds were synthesized and evaluated to meet the expanding needs for propellants, refrigerants, and solvents.

PHYSICAL AND CHEMICAL PROPERTIES

Almost all possible combinations of carbon, hydrogen, fluorine, and chlorine have been prepared for the lower organic compound (aliphatic) series. The physical characteristics of some of the more common fluorocarbons are presented in Tables VI-1 and VI-2. In general, these substances are clear, colorless, highly volatile liquids; their vapors have a mild, somewhat ethereal odor. They are nonflammable, and have high density; low viscosity, surface tension, and toxicity; and good stability.

Fluorocarbons do not react with most metals below 200°C or with most acids or oxidizing agents. They react with highly reactive metals under extreme circumstances, and F-11 reacts with concentrated sulfuric acid and sulfur trioxide at room temperature. Otherwise, they are substantially inert to chemical reactions on earth and in the lower atmosphere.

The hydrolysis rate for these substances is low when compared with other halogenated compounds; within the fluorocarbon group there is considerable variation in the hydrolysis rate. With water, at atmospheric pressure, the rate of hydrolysis is too low to be measured by most analytical methods. When catalyzed by the presence of steel, hydrolysis rates remain quite low, but are detectable; at higher temperatures and saturation pressures, the rates are increased as shown in Table VI-3. The significance of this to the issue of ozone reduction is that the rate of hydrolysis in the atmosphere will be too low to be a mode of degradation of the compounds in the troposphere.

Table VI-1. Physical properties of selected fluorocarbons: methane series.
(After *Shepherd,* 1961)

Property	F-11	F-12	F-21	F-22	F-30
Chemical formula	CCl_3F	CCl_2F_2	$CHCl_2F$	$CHClF_2$	CH_2Cl_2
Molecular weight	137.4	120.9	102.9	86.5	84.9
Boiling point, °F	74.8	-21.6	48.1	-41.4	105.2
Freezing point, °F	-168	-252	-211	-256	-142
Vapor pressure, psig					
At 70°F	[1]13.4	70.2	8.4	122.5	[1]7.1
At 130°F	24.3	181.0	50.5	300	9.0
Liquid density, g/cm₃					
At 70°F	1.485	1.325	1.323	1.209	1.325
At 130°F	1.403	1.191	1.193	1.064	—
Vapor density at boiling point, g/1	5.86	6.26	4.57	4.83	3.30
Heat of vaporization at boiling point, Btu/lb	78.31	71.94	104.2	100.7	141.7
Liquid viscosity, centipoise					
At 70°F	0.439	0.262	0.351	0.238	[2]0.441
At 130°F	0.336	0.227	0.286	0.211	—
Liquid thermal conductivity at 70°F, (Btu)(ft)/(ft₂)(hr)(°F)	0.063	0.051	0.072	0.063	[2]0.059
Surface tension at 77°F, dynes/cm	19	9	19	9	[2]28
Solubility of water at 70°F, wt %	0.009	0.008	0.13	0.12	[3]0.17
Flammable limits, vol % in air	None	None	None	None	None
Toxicity: Underwriters' Laboratories, Inc. rating system	5A	6	[4](5)	5A	4-5

[1] In pounds per square inch absolute.
[2] At 68°F.
[3] At 77°F.
[4] Much less than 4, slightly more than 5.

Table VI-2. Physical properties of selected fluorocarbons: ethane series.
(After *Shepherd*, 1961)

Property	F-114	F-114a	F-142b	F-152a	F-160
Chemical formula	$CClF_2CClF_2$	CCl_2FCF_3	CH_3CClF_2	CH_3CHF_2	CH_3CH_2Cl
Molecular weight	170.9	170.9	100.5	66.1	64.5
Boiling point, °F	38.4	37.8	15.1	-11.2	12.2
Freezing point, °F	-137	ca. -76	-204	-179	-139
Vapor pressure, psig					
At 70°F	12.9	13.4	29.1	61.7	5.0
At 130°F	58.8	60.6	97.2	176	41.3
Liquid density, g/cm_3					
At 70°F	1.468	1.478	1.119	0.911	0.920
At 130°F	1.360	1.371	1.028	0.813	—
Heat of vaporization at boiling point, Btu/lb	59.0	58.2	96.0	141	—
Liquid viscosity, centipoise					
At 70°F	0.386	0.463	0.330	0.243	—
At 130°F	0.296	0.347	0.250	0.186	—
Solubility of water at 70°F, wt %	0.008	0.006	0.054	0.17	—
Flammability limit, vol % in air	Nonflammable	Nonflammable	9.0 to 14.8	5.1 to 19.1	3.7 to 12.0
Toxicity: Underwriters' Laboratories, Inc. rating system	6	[1]6	[1]5A	[1]6	4

[1] Probable.

Fluorocarbons are non-polar liquids; as such, they are found to be good solvents for non-polar substances and poor solvents for highly polar substances such as water. Therefore, fluorocarbons will not dissolve in atmospheric precipitation. The usefulness of fluorocarbons as solvents for polar substances varies from poor for highly fluorinated compounds such as F-12 and F-114 to fairly good for those that contain less fluorine such as F-113. The miscibility of most of the halocarbons permits the formation of solvents with selective properties for specific needs. With some combinations, azeotropes are formed; with other combinations, two phases may result. The solvent properties of various fluorocarbons are compared in Table VI-4 using the results of kauri-butanol tests in which a high number indicates a good solvent.

Table VI-3. Hydrolysis rates in water, grams/liter of water (yr).
(After *du Pont de Nemours* & *Company,* 1974)

Compound	1-atm pressure (85°F)		Saturation pressure (122°F), with steel
	Water alone	With steel	
CH_3Cl	[1]	[1]	110
CH_2Cl_2	[1]	[1]	55
F-113	<0.005	[3]ca. 50	40
F-11	<0.005	[3]ca. 10	28
F-12	<0.005	0.8	10
F-21	<0.01	5.2	9
F-114	<0.005	1.4	3
F-22	<0.01	0.1	[1]
F-502	<[2] 0.01	[2] 0.1	

[1] Not measured.
[2] Estimated.
[3] Observed rates vary.

Table VI-4. Solubility relationships.
(After *du Pont de Nemours* & *Company,* 1974)

Product	Solubility of water at 32°F (0°C), wt %	Oil solutions	Kauri-butanol No.
F-11	0.0036	Miscible	60
F-12	0.0026	Miscible	18
F-21	0.055	Miscible	102
F-22	0.060	[1]	25
F-113	0.0036	Miscible	32
F-114	0.0026	[1]	12
F-502	0.022	[1]	14 (est.)

[1] Two liquid phases at low temperatures.

TOXICOLOGICAL PROPERTIES

Because of their relatively low toxicities and chemical inertness, fluorocarbons are commonly used under pressure for a variety of purposes including the self-administration of certain drugs and as propellants for household and personal products. In spite of their low toxicities, under certain conditions the physical properties of the fluorocarbons have been contributors to severe injury and death which occurred following intentional exposure, from heat-induced explosions, or from pyrolysis products formed in the presence of water. Other hazards that have been alleged or proved to be associated with the use of fluorocarbons under certain conditions include skin irritation, skin freezing, eye irritation or damage, and heart and lung effects. It is not within the scope of this task force to study these aspects of aerosol use or to determine the validity of any other issues that do not relate to the stratosphere. Such matters are under study by the appropriate regulatory agencies.

METHODS OF MANUFACTURE

The most commonly used method for the manufacture of fluorocarbons is the successive replacement of the chlorine atoms of the chlorocarbon by fluorine using anhydrous hydrogen fluoride with partially fluorinated antimony pentachloride as a catalyst. A schematic diagram of this multi-staged process is presented as Fig. VI-1. By changing the conditions of temperature, pressure, and fluorine concentration, the degree of fluorination can be varied. Methods of continuous operation with automatic controls have been developed, and the reaction can be conducted in either liquid or vapor phases. The desired organic product is withdrawn as a vapor from the reflux condenser. The byproduct of this reaction is an extremely pure grade of anhydrous hydrogen chloride (HCl), which is important in several industrial operations; e.g., E.I. du Pont de Nemours & Company uses it in the manufacture of neoprene and ethyl chloride and the recovery of chlorine. The fluorocarbon products, purified by distillation and by scrubbing through water and a slightly

alkaline solution, are dried by passage in the liquid phase through beds of silica gel, alumina gel, or synthetic zeolites.
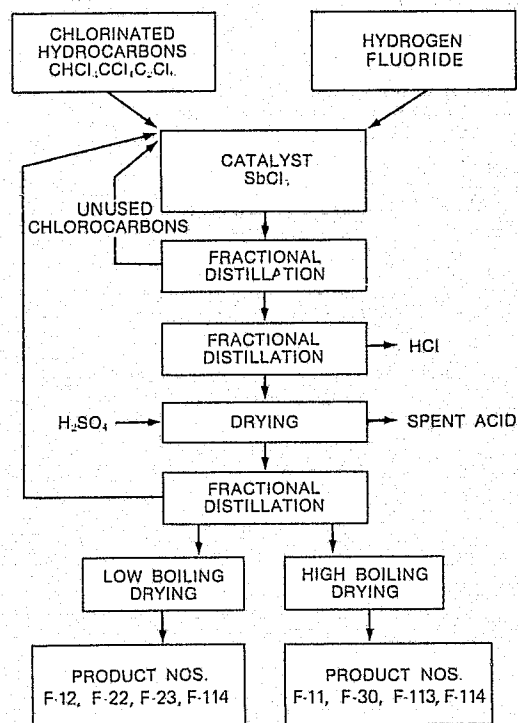
Fig. VI-1. Method for manufacturing fluorocarbons from chlorocarbons. (After *Anon*, 1965; *Hamilton*, 1962)

PRODUCTION

Fluorocarbons are produced by six companies in the U.S. and at least 48 companies in more than 23 nations. A partial list of the foreign companies and producers is presented in Table VI-5. The U.S. companies, locations of their production facilities, trade names of their products, total plant capacities of each company, and types of fluorocarbons produced by each are presented in Table VI-6. Annual U.S. production of selected fluorocarbons during 1958-1973 and total world production of F-11 and F-12 are presented in Table VI-7, which shows that U. S. production of F-11 and F-12 has been doubling about every 6 years, with an annual increase of between 10 and 20%.

Table VI-5. World-wide fluorocarbon producers[1]

Country	Company	Trade name
United States	E.I. du Pont de Nemours & Company	Freon
	Allied Chemical Corporation	Genetron
	Kaiser Aluminum and Chemical Company	Kaiser
	Pennwalt Chemical Co.	Isotron
	Racon, Inc.	Racon
	Union Carbide Corporation	Ucon
Argentina	Ducilo S.A.	Freon
	Fluoder S.A.	Algeon
	I.R.A., S.A.	Frateon
Australia	Australian Fluorine Chemicals Pty., Ltd.	Isceon
	Pacific Chemical Industries Pty., Ltd.	Forane [2]Frigen
Belgium	Akzo Chemie	—
Brazil	du Pont do Brasil S.A.— Industrias Quimicas	Freon
	Hoechst do Brasil Quimica e Farmaceutica S.A.	Frigen
Canada	du Pont of Canada, Ltd.	Freon
	Allied Chemical (Canada), Ltd.	Genetron
Czechoslovakia	Slovek Pro Chemickov A Hutni Vyobu, Ustinad Cabem	Ledon
England	du Pont Co., Ltd.	Freon
	Imperial Chemical Industries, Ltd.	Arcton
	I.S.C. Chemicals, Ltd.	Isceon
France	Produits Chimiques Pechiney— Ugine-Kuhlman	Forane
	Rhone-Progil	Flugene
Greece	Chemical Industries of Northern Greece	—
East Germany	V.E.B. Chemiewerk Nunchritz	Frigedohn
West Germany	Chemische Fabrik von Heyden AG	Heydogen
	Farbwerke Hoechst AG	Frigen
	Kali-Chemie Pharma GmbH	Kaltron
	E.I. du Pont de Nemours & Company, Deutschland	Freon
India	Everest Refrigerants, Ltd.	Everkalt
	Navin Fluorine Industries	Mafron
Italy	Montecatini-Edison	Edifrene Algofrene
Israel	Koor Chemicals	
	Makhetsim-Darom	—
	Romat-Horar	—
Japan	Mitsui Fluorochemicals Co., Ltd.	Freon
	Daikin Kogyo Co., Ltd.	Daiflon
	Asahi Glass Co., Ltd.	Asahiflon
	Showa Denko K.K.	—
Mexico	Halocarburos S.A.	Freon
	Quimobasicos	Genetron

[1] Compiled from information supplied by the U.S. Commerce Department and the U.S. Consumer Product Safety Commission, 1975
[2] Manufactured by P.C.I., but sold at Farbwerke Hoechst as Frigen.

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Table VI-5. World-wide fluorocarbon producers—Continued

Country	Company	Trade name
Netherlands	du Pont de Nemours (Nederland) N.V.	Freon
	AKZO Chemie N.V.	FCC
Rumania	Not known (State authority)	—
Russia	Not known (State authority)	Eskimon
South Africa	African Explosives & Chemical Industries, Ltd.	Arcton
Spain	Ugine .nica de Halogenos, S.A.	Forane
	Kali-Chemie Iberia S.A.	Kaltron
	Electroquimica de Flix S.A.	Frigen
Sweden	Henning Stenbeck AB	—
Switzerland	du Pont de Nemours Int'l. SA	Freon
	Pluss-Stauffer	—

Table VI-6. Fluorocarbon producers, plant locations, and capacities, trade names, and compounds produced. (After *Chemical Marketing Reporter*, 1973; data also from U.S. Tariff Commission, 1972)

Producer	Plant location	Trade name	Total plant capacity (1973)[1]	Compounds produced
Allied Chemical Corporation	Baton Rouge, La. Danville, Ill. Elizabeth, N.J. El Segundo, Ca.	Genetron	310	F-11, F-12, F-22 F-113, F-114, F-152
E.I. du Pont de Nemours & Company	Antioch, Ca. Carney's Point, N.J. Corpus Christi, Tex. East Chicago, Ind. Louisville, Ky. Montague, Mich.	Freon	500	F-11, F-12, F-22 F-113, F-114, F-13B1, F-152a
Kaiser Aluminum and Chemical Company	Gramercy, La.	Kaiser	50	F-11, F-12, F-22
Pennwalt Chemical Corporation	Calvert City, Ky. Thorofare, N.J.	Isotron	115	F-11, F-12, F-22
Racon, Inc.	Wichita, Ka.	Raycon	20	F-11, F-12, F-22
Union Carbide Corporation	Institute, W. Va.	Ucon	200	F-11, F-12

[1] Production in millions of pounds.

Table VI-7. Production[1] of fluorocarbons: 1958-1973[2]

Year	[3]F-22	F-114	[3]F-142	F-11 U.S.	F-11 World Total	F-12 U.S.	F-12 World Total
1958				51	51	131	131
1959				60	60	157	157
1960				72	89	166	191
1961				91	114	173	208
1962	22	11		124	158	207	258
1963	36	12		140	184	217	284
1964	43	13		148	206	228	315
1965	50	22		170	246	271	385
1966	56	17		170	268	286	432
1967	59	[3]22		182	307	310	497
1968	55	[3]17		204	364	326	565
1969	71			239	435	368	661
1970	73			244	478	375	725
1971	80		0.2	258	532	390	801
1972	80			300	628	439	931
1973				325	690	487	1034
Totals					4810		7575
McCarthy estimated totals					5400		8400

[1] Production in millions of pounds.
[2] Data from U.S. Tariff Commission, 1961-1973, also from *Stanford Research Institute*, 1973, *McCarthy*, 1974; du Pont de Nemours & Compan,, personal communication, 1975.
[3] Sales.

Total world production of fluorocarbons is increasing, although the relative amounts contributed annually by the U.S. to world production are progressively decreasing.

FUTURE PLANS FOR EXPANSION

There are indications that the rapid growth in fluorocarbon production might be slowing in the U.S. No plans are known for increasing construction to expand production during the next 3 years. One company, which does not expect the 10% annual increase to continue (du Pont de Nemours & Company, 1974), forecasts a 5 to 6% growth in market demands for fluorocarbons in the next several years (in the absence of any regulation), but is not certain whether industry will meet that demand. The company indicates that it will attempt to obtain needed production from present facilities and expects that minor modifications in one plant will allow sufficient increases in production capacity if required by market needs.

In 1974 total aerosol sales in the U.S. (not restricted to those using fluorocarbon propellants) decreased about 5 to 10% from 1973 sales of 3 billion units (du Pont de Nemours & Company, 1974). This compares to a growth rate of 10.5% in 1972 and 27% from 1968 to 1973 (Chemical Specialties Manufacturing Association, 1974). Whether this was the result of any changing consumer preferences or consumer concerns about various aspects of aerosol usage, as opposed to the general economic slump or a natural slowing of market expansion following past growth, is not immediately apparent.

It is expected that expansion of fluorocarbon production to meet market demands in the next several years would be greater in other parts of the world than in the U.S., presuming the absence of any regulatory actions, because other countries are farther away from market saturation. For example, annual world production (excluding the U.S.S.R. and Eastern European countries) of aerosol products has been estimated as about 6 billion units, with approximately one-half of that amount occurring

Table VI-8. Estimated world use of aerosols: 1970-1974[1]
(Syracuse University Research Corp., 1974)

	1970	1971	1972	[2]1973	[2]1974
U.S., Canada	2756	2695	2983	3105	3185
Western Europe	1425	1600	1620	1750	1850
Other[3]	507	550	597	645	765
Total	4688	4845	5200	5500	5800

[1] In millions of pounds.
[2] Estimates from *Chemical Marketing Reporter*, 1974
[3] Does not include U.S.S.R. or Eastern European countries.

in the U.S. In 1973 the U.S. aerosol market increased only about 4%, while a 21% increase was reported for the United Kingdom. According to the *Chemical Marketing Reporter* (1974), future market increases will be overseas (not considering any regulatory actions), with a total annual global use near 10 billion units (see Table VI-8 for estimated world use of aerosols during 1970-1974).

USES

Fluorocarbons are used as original and replacement charges in refrigeration and air-conditioning equipment; as propellants in aerosols; as foaming agents, cleaning fluids, solvents, and heat exchange agents; and for other purposes. The properties of selected fluorocarbons, their availability in commercial quantities, and purposes for which they are used are demonstrated by the following description of products produced by E.I. du Pont de Nemours & Company (Table VI-9). The use of this information is not to be considered as an endorsement of the du Pont Freon products. It is assumed that compounds identified by the same fluorocarbon numbers, but produced by other manufacturers, can be used for similar purposes as the Freons.

Table VI-9. Products produced by E.I. du Pont de Nemours & Company
(Reprinted verbatim from booklet)

Du Pont Halon 1301 Fire Extinguishing Agent—Bromotrifluoromethane CBrF$_3$: B.P. -72.0°F (-57.8°C) at 760 mm. Pressure -199 psig at 70°F (21.1°C). USE: As a low-toxicity fire extinguishing agent which is much more effective than other liquefied-compressed-gas type agents and leaves no harmful residues. CONTAINERS: 10-, 28- and 150-lb. cylinders and 2,000-lb. tanks.

Freon® 11 Refrigerant, Propellant, Blowing Agent and Solvent—Trichlorofluoromethane—CCL$_3$F: B.P. 74.9°F (23.8°C) at 760 mm. USE: As a refrigerant in industrial and commercial air-conditioning systems; also in industrial process water and brine cooling to -40°F (-40°C) employing single or multistage centrifugal compressors of 100 tons refrigeration capacity and larger. As brine refrigerant in indirect low-temperature systems to -150°F (-101.1°C). As solvent for cleaning up a refrigeration unit which has experienced a burnout in the hermetic motor. As blowing agent for rigid and resilient polymeric foams. Solutions of Freon® 11 and Freon® 12 are used as propellants for a wide variety of aerosol products; can be tailored to individual

pressure requirements from 1-70 psig at 70°F (21.1°C). CONTAINERS: 100-, 200- and 650-lb. drums, 2,200-lb. tanks, tank trailers and tank cars.

Freon® 11 B Blowing Agent—Trichlorofluoromethane Formulation—CCl$_3$F: Freon® 11 to which has been added an inhibitor that virtually eliminates stability problems caused by an acid-forming reaction between the trichlorofluoromethane and hydroxyl groups of polyol components. (U.S. Patent 3,183,192) USE: As blowing agent for rigid and resilient polymeric foams. CONTAINERS: 100-, 200- and 650-lb. drums, 2,200-lb. tanks, tank trailers and tank cars.

Freon® 11 S Propellant—Trichlorofluoromethane Formulation—CCl$_3$F: This product is a formulation of Freon® 11 containing 0.3 wt. % of nitromethane (U.S. Patent 3,085,116) The stabilizer serves to inhibit the free-radical reaction of trichlorofluoromethane with ethanol and other alcohols. USE: As a propellant for aerosol hair sprays and other aerosol products containing alcohols.

CONTAINERS: 100-, 200- and 650-lb. drums, 2,200-lb. tanks, tank trailers and tank cars.

Freon® 12 Refrigerant, Propellant and Blowing Agent—Dichlorodifluoromethane—CCl₂F₂: B.P. -21.6°F (-29.8°C) at 760 mm pressure—70 psig at 70°F (21.1°C). USE: As a refrigerant in both direct and indirect industrial, commercial, household and automotive air-conditioning systems; also in household refrigerators, ice cream cabinets, frozen food cabinets, food locker plants, water coolers, etc., employing reciprocating compressors ranging in size from fractional to 800 horsepower. Freon® 12 is also used in household refrigerating systems, ice cream and frozen food cabinets employing rotary-vane compressors. Freon® 12 is used in industrial process water, and brine cooling to -110°F (-78.9°C) employing multistage centrifugal compressors in cascade of 100 tons refrigeration capacity and larger. Freon® 12 is used as a propellant for high-pressure aerosols such as those containing insecticides. Also for surface-coating products such as metallic and pigmented paints and lacquers. Solutions of Freon® 12 with other Freon® products are used as aerosol propellants for a wide variety of products; also as low-temperature solvents. As a blowing agent for rigid and resilient polymeric foams; available in pressure-flow cylinders for frothed polymeric and other foams. As a leak-detecting agent. CONTAINERS: Dispos-A-Can® container in 12- (two per carton), 30- and 50-lb. sizes, 145-lb returnable cylinders and 2000-lb. returnable tanks, tank trailers and tank cars.

Freon® 13 Refrigerant—Chlorotrifluoromethane—CClF₃: B.P. -114.6°F (-81.4°C) at 760 mm. Pressure—457 psig at 70°F (21.1°C). USE: As a refrigerant in both direct and indirect industrial very-low-temperature cascade systems ranging in size from fractional to 100 horsepower, employing reciprocating or rotary compressors; aircraft environmental test chambers; shrink fit, toughening and hardening of metals; pharmaceutical processing. CONTAINERS: 9-, 23- and 80-lb. cylinders.

Freon® 13B1 Refrigerant—Bromotrifluoromethane CBrF₃: B.P. -72.0°F (-57.8°C) at 760 mm. Pressure—199 psig at 70°F (21.1°C). USE: As a refrigerant in both direct and indirect industrial low-temperature cascade or multiple compression systems ranging in size from fractional to 100 horsepower, employing reciprocating or rotary compressors; aircraft environmental test chambers; shrink fit, toughening and hardening of metals; pharmaceutical processing. CONTAINERS: 10-, 28- and 150-lb. cylinders and 2,000-lb. tanks.

Freon® 14 Propellant and Refrigerant Gas—Tetrafluoromethane—CF₄: B.P. -198.3°F (-128.0°C) at 760 mm. Critical temperature -50.2°F (-45.7°C). Critical pressure—543 psia. USE: As a regrigerant in extremely low-temperature cascade systems for environmental testing, metal conditioning, pharmaceutical processing, freezing and storage of biological products and other cryogenic applications. As an inert propellant gas to operate satellite guidance and stabilization rockets. CONTAINERS: (Approximate weights) 5-, 15- and 70-lb. cylinders as a compressed gas.

Freon® 21 Refrigerant, Solvent and Propellant—Dichlorofluoromethane CBrF₃: B.P. -72.0°F (-57.8°C) at 760 mm. Pressure—8.4 psig at 70°F (21.1°C). USE: As a refrigerant for centrifugal machines. As a solvent where its relatively high kauri-butanol number is desirable. Solutions with Freon® 12 are useful in aerosol products requiring special solvent qualities in the propellant. CONTAINERS: 10-, 25- and 150-lb. cylinders, 2000-lb. tanks and tank trailers.

Freon® 22 Refrigerant, Polymer Intermediate, Propellant and Solvent—Chlorodifluoromethane—CHClF₂: B.P. -41.4°F (-40.8°C) at 760 mm. Pressure—121.4 psig at 70°F (21.1°C). USE: As a refrigerant in room and central residential air-conditioning systems and heat pumps employing reciprocating of rotary compressors; also in industrial and commercial low-temperature refrigerating systems employing reciprocating and centrifugal compressors. Solutions of Freon® 22 with Freon® 11 and Freon® 12 are used as propellants for aerosol products requiring special solvent and pressure qualities. Chemical intermediate for polymer manufacture. CONTAINERS: Dispos-A-Can® container in 10- (two per carton), 25- and 50-lb. sizes, 125-lb. returnable cylinders and 1750-lb. returnable tanks, tank trailers and tank cars.

Freon® 23 Refrigerant—Trifluoromethane—CHF₃: B.P. -115.7°F (-82.0°C). Pressure—609 psig at 70°F (21.1°C). USE: As a refrigerant for very-low-temperature applications similar to those described under Freon® 13. CONTAINERS: 5-, 20-, and 70-lb. cylinders.

Freon® 113 Refrigerant, Propellant, Blowing Agent and Polymer Intermediate—Trichlorotrifluoroethane—CCl₂FCClF₂: B.P. 117.6°F (47.6°C) at 760 mm. USE: As a refrigerant in industrial and commercial air-conditioning systems; also in industrial process water and brine cooling to 0°F (-17.8°C) employing four or more stage centrifugal compressors of 25 tons capacity and larger. Freon® 113 is used with other Freon® compounds as a propellant for aerosol products. As blowing agent for rigid and resilient polymeric foams. As a chemical intermediate for polymer manufacture. CONTAINERS: 100-, 200- and 690-lb. drums, 2200-lb. tanks, tank trailers and tank cars.

Freon® 114 Refrigerant, Propellant, Blowing Agent and Dielectric Fluid—Dichlorotetrafluoroethane—CClF₂CClF₂: B.P. 38.8°F (3.8°C) at 760 mm. Pressure—13 psig at 70°F (21.1°C). USE: As a refrigerant in fractional horsepower household units and drinking water coolers employing rotary compressors; also in industrial and commercial air-conditioning systems and in industrial process water and brine cooling to-70°F (-56.7°C) employing multistage centrifugal compressors of 100 tons capacity and larger. As a high-stability heat transfer medium. Solutions of Freon® 114 and Freon® 12 are used as propellants for aerosol products where active ingredients require extreme stability-cosmetics for example; provide pressures from 13 to 70 psig at 70°F (21.1°C). As blowing agent for rigid and resilient polymeric foams. As a dielectric fluid having extremely high strength—about 130 KV per in. at 760 mm. CONTAINERS: 25- and 150-lb. cylinders, 2200-lb. tanks, tank trailers and tank cars.

Freon® Food Propellant 115 and Freon® 115 Refrigerant and Freon® 115 Dielectric—Chloropentafluoroethane—$CClF_2CF_3$: B.P. –37.7°F (–38.7°C) at 760 mm. Pressure—103 psig at 70°F (21.1°C). USES: Food grade: Accepted as a safe food additive by United States Food and Drug Administration. 21 CFR 121.1181. It is tasteless, odorless, colorless and nonflammable. Can be used as a propelling and aerating agent for dessert toppings, whipped cream, salad dressing, spices and other food products. May be used in conjunction with other food propellants, such as Freon® food propellant C-318, nitrous oxide, carbon dioxide, and nitrogen. Refrigerant grade: As a refrigerant having a capacity between those of Freon® 12 and Freon® 22; can be used with both reciprocating and rotary compressors and in a wide variety of applications; has a lower discharge-gas temperature than either Freon® 12 or Freon® 22. CONTAINERS: 11- and 135-lb. cylinders, 1800-lb. tanks.

Freon® 116 Dielectric Gas—Hexafluoroethane—CF_3CF_3: B.P. –108.8°F (–78.2°C) at 760 mm. Pressure—440 psig at 70°F (21.1°C). USE: As a dielectric and coolant gas where its high dielectric strength—about 70 KV per in. at 760 mm. USE: As a dielectric and coolant gas where its high dielectric strength and effective heat transfer characteristics result in increased capacity of the electrical equipment; applicable at high pressures; suitable for use at both very high and very low temperatures; one of the most stable of all organic compounds. CONTAINERS: 18-, 26-, and 95-lb. cylinders, 1750-lb. tanks.

Freon® 116/Nitrous Oxide (90/10 Wt. %). USE: Same as for Freon® 116 Dielectric Gas. CONTAINERS: 25- and 90-lb. cylinders.

Freon® 500 Refrigerant—73.8/26.2 Wt. % CCl_2F_2/CH_3—CHF_2: B.P.—28.0°F/(33.3°C) at 760 mm. Pressure—86 psig at 70°F (21.1°C). This is an azeotrope of Freon® 12 and 1,1-Difluoroethane (R 152a) refrigerants. USE: As a refrigerant in direct and indirect industrial and commercial refrigeration and air-conditioning systems employing reciprocating compressors varying in size from fractional to several hundred horsepower. Freon® 500 has been used primarily when electrical service is 50 rather than the standard 60 cycles per second or in equipment modified for its use somewhat higher capacity is needed than can be obtained from Freon® 12 alone. CONTAINERS: Dispos-A-Can® container in 10-(two per carton), 25- and 50-lb. sizes, 125-lb. returnable cylinders.

Freon® 502 Refrigerant—48.8/51.2 Wt. % $CHClF_2/CClF_2CF_3$: B.P. –49.8°F (–45.4°C) at 760 mm. Pressure—137 psig at 70°F (21.1°C). This is an azeotrope of Freon® 22 and Freon® 115 refrigerants. USE: As a refrigerant in food display cases, food storage and processing, ice makers, home freezers, low-temperature environmental refrigeration, and heat pumps. Freon® 502 is a high-capacity refrigerant with distinctly lower discharge-gas temperatures in reciprocating and rotary compressors. CONTAINERS: Dispos-A-Can® container in 10- (two per carton), 25- and 50-lb. sizes, 125-lb. returnable cylinder and 1750-lb. returnable tanks.

Freon® 503 Refrigerant—40/60 Wt. % $CHF_3/CClF_3$: B.P. 127.6°F (–88.7°C) at 760 mm. Critical temperature 67°F (19.4°C). Critical pressure—627.4 psia. This is an azeotrope of Freon® 23 and Freon® 13 refrigerants. USE: As a refrigerant for very low temperature applications similar to those described under Freon® 13. For the same applications, Freon® 503 normally provides more compressor capacity than Freon® 13. CONTAINERS: 5-, 9-, 20- and 70-lb. cylinders, 1500-lb. tanks.

FREON® SOLVENT PRODUCTS

Freon® MF Solvent—Trichlorofluoromethane—CCl_3F: B.P. 74.9°F (23.8°C) at 760 mm; F.P. -168°F (–111°C). USE: As a cleaner for hermetic motor compressors; vapor degreasing liquid for oxygen and other low-temperature storage and transfer tanks, etc. In blends as a cleaner for motion picture and television film, lithographic plates, typewriters, etc. As a flash point retarder for flammable solvents. As a simulation fluid for testing rocket systems and as a hydrostatic test fluid. Also used as an inert, non-corrosive brine and low-temperature heat transfer fluid such as in the cold treatment of brazed stainless steels. CONTAINERS: 5-, 20- and 55-gal. nonreturnable drums, tank trailers and tank cars.

Freon® Precision Cleaning Agent—Trichlorotrifluoro-ethane—CCl_2FCClF_2: B.P. 117.6°F (47.6°C) at 760 mm; F.P. –31°F (–35°C). Residue content not more than 1 ppm by weight (soluble plus insoluble). USE: As a solvent of exceptionally high purity for use in critical cleaning applications, such as in clean rooms, missiles, space vehicles, guidance systems, etc. CONTAINERS: 5-, 30- and 55-gal. drums, tank trailers, and tank cars.

Freon® TA Solvent—Freon® TF/Acetone Azeotrope; This composition (U.S. Patent 2,999,815) has a B.P. of 110.5° (43.6°C) at 760 mm. USE: A nonflammable solvent for removing organic contaminants and particulate matter from molded plastic and elastomeric parts, electronic components and films. Suitable for vapor degreasing as well as other cleaning techniques, such as dip, spray or flush. CONTAINERS: 5-, 20- and 55-gal. drums, tank trailers and tank cars.

Freon® TE Solvent—Freon® TF/SDA-30 Ethanol Azeotrope: This composition has a B.P. of 112.3°F (44.6°C) at 760 mm. USE: A nonflammable solvent for removing organic contaminants such as rosin-type solder flux from printed circuit boards and other electronic assemblies. Suitable for vapor degreasing as well as other cleaning techniques such as dip, spray or flush. CONTAINERS: 5-, 20- and 55-gal. drums, tank trailers and tank cars.

Freon® T-E 35 Solvent—Blend of Freon® TF and SDA-30 Ethanol: Initial B.P. 119°F (48.3°C) at 760 mm.

Freon® TF Solvent—Trichlorotrifluoroethane—CCl_2FCClF_2: B.P. 117.6°F (47.6°C) at 760 mm; F.P. –31°F (–35°C). USE: As a solvent; for cold immersion cleaning, as a vapor degreasing solvent, for ultrasonic or combination

ultrasonic-vapor-degreasing cleaning. Used as a cleaner for mechanical and electrical controls, instruments and gauges, motors and generators, electrical and electronic equipment and assemblies, motion picture film, television and magnetic tapes, printed circuits. As a flash point retardant in blends. As a simulation fluid for testing rocket systems and as a hydrostatic test fluid. Also used as an inert liquid medium for chemical processing and in extraction processes. CONTAINERS: 5-, 20- and 55-gal. non-returnable drums, tank trailers and tank cars.

Freon® TMC Solvent—Freon® TF/Methylene Chloride Azeotrope: This composition (U.S. Patent 2,999,817) has a B.P. of 97.2°F (36.2°C) at 760 mm. USE: As a solvent for removing organic contaminants including rosin-type flux from printed circuit board assemblies, computer parts, electrical relays, guidance components and metal parts. Suitable for vapor degreasing as well as other cleaning techniques such as dip, spray or flush. CONTAINERS: 5-, 20- and 55-gal. drums, tank trailers and tank cars.

Freon® T-P 35 Solvent—Blend of Freon® TF and Anydrous Isopropanol: This composition (U.S. Patent 3,085,116) has an initial B.P. of 120°F (48.9°C) at 760 mm.

Freon® T-WD 602 Solvent—Freon® TF/Water Dispersion: (U.S. Patent 3,336,232) Initial B.P. 112°F (44.4°C) at 760 mm. USE: Simultaneously removes water and oil soluble contaminants from business machines in maintenance cleaning operations and from semi-conductor devices, glass substrates and plated parts in precision cleaning operations. CONTAINERS: 5- and 55-gal. drums and tank trailers.

FREON® SPECIALTY PRODUCTS

Freon® E Series—F(CFCF₂O)ₙCHFCF₃—The E number equals n and n equals 1 through 9
$$Freon® \ E \ Series—F(CFCF_2O)_n CHFCF_3$$
with side group CF_3

B.P. 105.4°F (40.8°C) for Freon® E 1 up to 554.0°F (290.0°C) for Freon® E 9 at 760 mm. USE: Stable liquids for heat transfer with remarkably broad liquid ranges.

Freon® HV-3 High Volatility Coolant: Freon® MF blend, B.P. 74.9°F. USE: As a coolant for drilling and machining. Exceptional cooling power plus lubricity provide close tolerances, smooth finishes, faster machining and prolonged tool life. Complete volatility minimizes contamination and need for subsequent cleaning. CONTAINERS: 5- and 55-gal. drums, tank trailers and tank cars.

Freon® T-B 1 High-Volatility Coolant: Freon® TF/2-butoxyethanol blend (U.S. Patent 3,129,182) has a B.P. of 117.6°F. USE: As a coolant for drilling and machining. Operates on the same principles as Freon®HV-2. Higher boiling point provides slower evaporation rate for warm weather conditions. CONTAINERS: 5- and 55-gal. drums, tank trailers and tank cars.

Freon® T-DA 5: Make-up solution for Freon® Solvent Drying System described above. CONTAINERS: 5-, 20- and 55-gal. drums, tank trailers and tank cars.

Freon® T-DA 35 Solvent: Drying solution for use in Freon® Solvent Drying System (U.S. Patents 3,397,150 and 3,386,181). System provides fast spot-free drying at low temperature (117°F). It is based on the principle of water displacement, and special handling equipment is required. CONTAINERS: 5-, 20- and 55-gal. drums, tank trailers and tank cars.

FREON® PRODUCTS, MISCELLANEOUS PRODUCTS

1,1,1-Chlorodifluoroethane—CH₃CClF₂: B.P. 14.4°F (-9.8°C) at 760 mm. Pressure—29 psig at 70°F (21.1°C). USE: As a mixture with Freon® 11 and Freon® 12 to produce aerosol propellants having various solvent, density and pressure characteristics. As a chemical and polymer intermediate. CONTAINERS: 8-, 20- and 120-lb. cylinders, 1650-lb. tanks.

1,1-Difluoroethane—Ethylidene Fluoride—CH₃CHF₂: B.P. -13.0°F (-24.0°C) at 760 mm. Pressure—63 psig at 70°F (21.1°C). USE: As a refrigerant, aerosol propellant and chemical intermediate. CONTAINERS: 16- and 95-lb. cylinders, 1300-lb. tanks, tank trailers and tank cars.

Freon® C-51-12 Fluorocarbon—Perfluorodimethyl-cyclobutane—C₆F₁₂ (cyclic): B.P. 113.0°F (45.0°C) at 760 mm. F.P. -26.0°F (-32.0°C) USE: Stable fluid for heat transfer and electrical insulation.

Fluorocarbon 114B2—Dibromotetrafluoroethane—CBrF₂CBrF₂: B.P. 117.1°F (47.3°C) at 760 mm. Liquid Density—2.18 g/cc at 70°F (21.1°C). USE: As a thrust vector control fluid. CONTAINERS: 17-, 85- and 250-lb. drums, tank trailers.

Hexafluoroacetone—CF₃COCF₃: B.P. -18.4°F (-28.0°C) at 760 mm. F.P. -200.0°F (-129.0°C). USE: Chemical intermediate.

Hexafluoroisopropanol—HFIP—(CF₃)₂CHOH: B.P. 136.8°F (58.2°C) at 760 mm. F.P. 26°F (-3.4°C). USE: Chemical intermediate and solvent for polyamides and polyesters.

Vinyl Fluoride—CH₂=CHF: BP -97.5°F (-72.0°C) at 760 mm. Pressure—350 psig at 70°F (21.1°C). USE: As a chemical and polymer intermediate. CONTAINERS: 50-lb. cylinders.

Vinylidene Fluoride—1,1-Difluoroethylene—CH₂=CF₂: B.P. -122.3°F (-85.7°C) at 760 mm. Pressure—515 psig at 70°F (21.1°C). USE: As a chemical and polymer intermediate. CONTAINERS: 58-lb. cylinders and 1,050 lb. tanks.

Table VI-10. Broad end uses of fluorocarbon production[1] [2]: 1972

Compound	[3]Sales	Production	Aerosol propellents	Refrigerants	Solvents	Foaming agents	Fire-fighting agents
F-11	285	300	215	19	5	50	
F-12	415	439	220	132		45	
F-22	80	80		80			
F-113		[4]50			50		
F-114		[4]20	20	10			
F-115 .... }	[4]10	0.6		5			
F-13B1 ...... }				0.2			4

[1] Production in millions of pounds.
[2] Data from U.S. Tariff Commission Reports, 1972; also from *du Pont de Nemours & Company* (personal communication, 1975).
[3] Sales 5% less than production because of inventory buildups.
[4] Estimated figures based on footnote [2].

Amounts of fluorocarbons produced in the U.S. in 1972 for broad end-use purposes are given in Table VI-10. As information on production and sales was insufficient for a firm determination, production figures for F-113, F-114, F-115, and F-13B1 must be considered marginal. For a relative evaluation, the percentage values in Table VI-11, calculated from Table VI-10, were compared with similar factors presented by the *Chemical Marketing Reporter* (1973). Minor quantitative differences in the two sets of values are attributed to the exclusion of plastics in the Table VI-10 data.

More recent data on fluorocarbon uses in 1973 are given in Table VI-12, developed from industry data by Arthur D. Little, Inc., as preliminary findings from a study being performed under contract to the Environmental Protection Agency. The major discrepancy between Tables VI-10 and VI-12 is in the relative amounts of F-11 and F-12 used as foaming agents.

Table VI-11. Uses of fluorocarbon production[1]: 1972

Use	From *Chemical Marketing Reporter*, 1973 [1]800	From Table VI-10 [1]890
Propellants	50%	51%
Refrigerants	28%	27%
Plastics	10%	
Solvents	5%	6%
Foaming agents, etc.	7%	11%
Inventory buildups		5%
	100%	100%

[1] Production in millions of pounds.

Table VI-12. Industry estimates of U.S. domestic consumption of fluorocarbons by major use category: 1973. (After *Arthur D. Little, Inc.*, personal communications, 1975)

Fluorocarbon	Production[1]
Aerosol	
F-11	267
F-12	240
F-114	20
Foam	
F-11	75
F-12 (for frothing specifically)	3
Refrigerants	
F-12	180
F-11	10
F-22	95
Plastics	
F-22	25
Miscellaneous	
F-113: 60 x 10^{5} lb/yr, almost exclusively for solvent uses.	
F-22: Virtually none used for aerosols.	

[1] Production in millions of pounds.

Aerosol Propellants

The data presented in Tables VI-10 and VI-12 indicate that about 50 to 58% of total U.S. production of fluorocarbons is utilized as propellants for aerosols, and that of this amount, probably more than 95% consists of F-11 and F-12. Fluorocarbons constitute the propellant in 50 to 60% of the aerosol units sold and are about 75% by weight of the propellant market (du Pont de Nemours & Company, personal communication, 1975). Aerosol use constitutes controlled release of substances from containers that are charged below 55 psia and fitted with suitable pressure valves and nozzles. The solubility of the charge in the contained material, the type of material to be dispensed, and the structure of the valve and nozzle determine the pattern of the aerosol release. Uses for aerosols in the U.S. from 1970 to 1974, excluding food uses, is shown in Table VI-13.

Approximately 3 billion units of aerosol products were marketed in the U.S. in 1973. The distribution of this production wi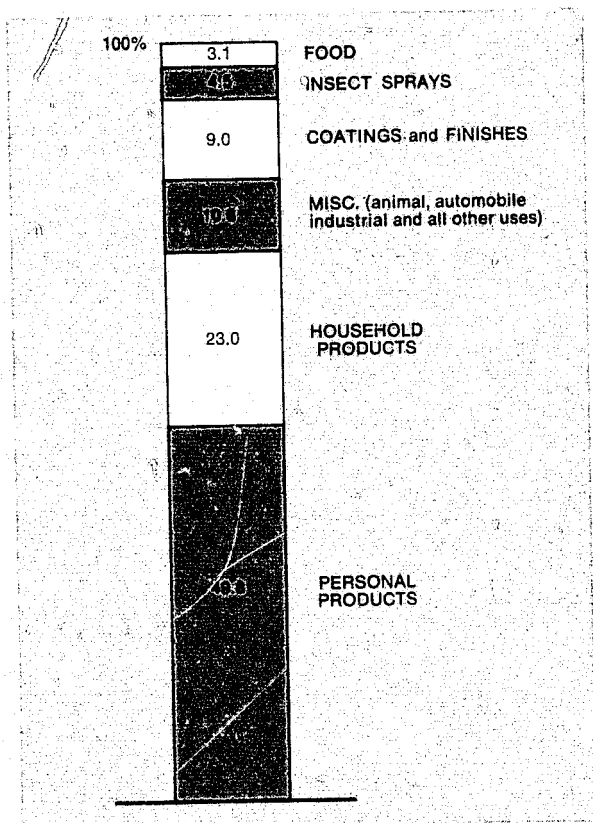thin six general categories, including food, is presented in Fig. VI-2 (du Pont de Nemours & Company, personal communications, 1975). The annual survey conducted by the Chemical Specialties Manufacturers Association (1974) shows an estimate of 2.9 billion aerosol units filled in 1973. This estimate was based on responses received from 14 U.S. manufacturers reporting that they had produced and sold 2.9 billion metal containers for food and non-food products in 1973. The number of glass containers used during 1973 has been estimated as 190 million. Reports from 10 U.S. valve manufacturers indicated that they had sold 3.1 billion valves for food and non-food products during the same period. Inquiries were also sent to 268 companies with aerosol product filling lines in the U.S. Responses from 100 companies reported filling a total of 1.835 billion containers for food and non-food products.

Table VI-14 provides some comparative data on distribution of aerosol uses in the U.S. and several other countries, with the data given in terms of units consumed per thousand capita per year. Note that the data in Table VI-

Table VI-13. U.S. non-food end uses of aerosols[1] (After *Chemical Specialties Manufacturers Association,* 1974; personal communication, 1975)

Use	1970	1972	1973	1974
Household				
Cleaners and laundry	355	370	385	400
Room deodorants	160	180	183	187
Waxes and polishes	85	100	105	110
Other	30	50	52	53
Personal				
Perfumes and deodorants	625	650	710	740
Medicines	65	65	70	70
Hair spray	490	460	460	460
Shave creams	150	165	180	185
Other	50	63	75	80
Miscellaneous				
Insecticides	120	135	140	145
Industrial	90	120	130	145
Paint and varnish	230	250	255	260
Automotive	50	80	85	90
Other	22	35	40	45

[1] Data in millions of units.

100%

3.1	FOOD	
4.0	INSECT SPRAYS	
9.0	COATINGS and FINISHES	
10.0	MISC. (animal, automobile industrial and all other uses)	
23.0	HOUSEHOLD PRODUCTS	
	PERSONAL PRODUCTS	

CONTRIBUTION OF MAJOR PRODUCT GROUPS
TO THE ADJUSTED TOTAL PRODUCTION

Fig. VI-2. Distribution of aerosol products marketed in the United States in 1973. (After *du Pont de Nemours & Company*, personal communication, 1975)

14 refer to total aerosol usage, including the 40 to 50% of aerosol products that do not use fluorocarbons as propellants. By far the largest amounts of fluorocarbons used in aerosol products are for personal products, especially hair care, deodorants, and anitperspirants. Most household products use propellants other than fluorocarbons. Although precise information as to the distribution of fluorocarbon propellants among different aerosol products was not available at the time of publication of this report, Table VI-15 gives some preliminary estimates from the Authur D. Little, Inc., study of fluorocarbon propellant "losses" (i.e., amounts released to the atmosphere) by aerosol product type. According to Table VI-15, 93% of fluorocarbon releases to the atmosphere from propellants are from personal products.

Refrigerants

Available information indicates that about 28% of U.S. production of fluorocarbons is used as refrigerants (see Tables VI-10 and VI-12). Fluorocarbons-11, -12, and -22 are estimated to account for about 92% of refrigerants in the U.S. (*IMOS Task Force*, 1975). The most frequently used (56% of U.S. refrigeration) is F-12, used as the refrigerant in centrifugal compressors in large building systems. F-22 (30% of U.S. refrigeration) is used in residential and commercial air conditioning and refrigeration and in food storage and display where lower temperatures are required.

Low toxicity, chemical stability and solubilities, nonflammability, and good dielectric and thermodynamic properties of fluorocarbons make them suitable for refrigeration use. These properties permit incorporating the motor and compressor of refrigeration systems into single, efficient, compact, hermetically sealed units.

Small refrigeration units designed for maintaining localized low temperatures and for single dwelling air-conditioning purposes may be precharged at the factory during fabrication. Larger units for industrial or commercial use are charged after installation. Table VI-16 gives the quantities of F-11, F-12, and F-22 used for these purposes during 1973-1974.

Solvents

Combinations of fluorocarbons consisting predominantly of F-113 are used selectively for cleaning electrical components in fabrication operations requiring high precision, and in the selective extraction of non-polar components from natural products. Characteristics of fluorocarbons that make them desirable for use with electrical components and precision equipment are their dielectric properties, specificity of solvent action without significant swelling effects on plastics, and ability to evaporate without leaving residues. Selective solvent action permits preferential extraction of edible oils from agricultural products; essential oils from fish, coffee, and spices; and active ingredients of perfumes and scents (*Hamilton*, 1962).

Table VI-14. Aerosol consumption[1] and production[2]: 1968 and 1970.
(After *Arthur D. Little, Inc.*, personal communication, 1975)

Country	Total	Insecticides	Paints	Household	Hair spray	Deodorants	Production
1970							
West Germany	6,800	222	238	870	2,720	1,980	389
Great Britain	5,500	432	234	1,470	1,820	576	361
France	4,400	318	99	596	1,690	318	277
Italy	3,100	847	19	394	1,050	414	173
Netherlands	4,400	430	78	1,000	1,290	650	90
Switzerland	8,200	305	168	1,540	3,020	1,930	60
Sweden	3,600	253	101	406	1,320	885	20
Western Europe, average	4,300	420	110	779	1,550	745	Other 250
Total	36,000	2,807	937	6,276	12,910	6,753	1,620
United States	13,000	500	1,100	3,070	2,200	2,000	2,823
1968							
West Germany		222	229	595	1,960	93	NA
Great Britain		398	181	1,186	1,374	226	200
France		310	40	358	1,451	80	[3]267
Italy		795	14	341	928	170	NA
Netherlands		472	32	890	898	315	—
Switzerland		290	100	1,148	2,180	1,148	—
Sweden		375	94	379	775	635	23
Western Europe, average		390	97	505	1,110	309	Other 540
Total		2862	690	4,897	9,556	3,288	1,030
United States		460	1,000	2,900	2,220	1,000	2,290

[1] Comsumption in units per thousand capita.
[2] Production in millions of units.
[3] Includes Belgium, Holland, Switzerland, Spain.

Table VI-15. Estimated fluorocarbon propellant losses by aerosol product type: 1975. (After *Arthur D. Little, Inc.*, personal communication, 1975)

Product	Fluorocarbon loss, %
Personal	
Hair care	44
Deodorant and	
antiperspirant	42
Other	7
Subtotal	93
Household	
Subtotal	3
All others	
Subtotal	4
Total	100

Foaming Agents

F-11, F-12, and F-114 are used as foaming agents in the production of polyurethane, polystyrene, and polyolefin foams. The major fluorocarbon for making foam is F-11. Stabilized formulations are designed to provide long shelf life of premixed systems containing amine catalysts and amine-base polyols. F-12 is used with froth foams, especially the rigid urethane type. F-11 and F-12 are used in polystyrene sheet, which is subsequently thermoformed into packaging containers. Properties of fluorocarbons that make them advantageous as foaming agents include inertness toward the finished product, compatibility with the urethane, low toxicities, favorable heats of vaporization, low boiling points, and nonflammability.

Table VI-16. Fluorocarbons used[1] in U.S. for refrigeration and air conditioning: 1974. (After *du Pont de Nemours & Company*, personal communication, 1975)

Fluorocarbon	Amount used	Prefabricated		After installation	
		Refrigeration	Air conditioning	Refrigeration	Air conditioning
F-11	15		5		10
F-12	150	20	20 (autos)	55	55
F-22	80	10	20	10	40

[1] Millions of pounds.

Fire Fighting

Fluorocarbons are commonly used to control fires in confined areas by terminating the free radical propagation mechanism of the fire (*Hamilton*, 1962). These extinguishing agents are usually used in areas of high value density such as computers, aircraft, spacecraft, tanks, and mines (*Jensen*, 1972).

Miscellaneous Uses

According to E. I. du Pont de Nemours & Company (1974), relatively small amounts of fluorocarbons are used as dielectrics, heat transfer, power, and cutting fluids, and as gases in leak-testing devices, wind tunnels, and bubble chambers.

Other Potential Uses

Use of fluorocarbons as heat-transfer agents as in the Rankine-type engine and power fluids has been suggested (*Callighan*, 1971; *Nobel*, 1972). Selected fluorocarbons have been suggested as substitutes for the perchloro- and trichloroethylenes in dry-cleaning agents (*Drysdale*, 1971; *Lutz et al.*, 1967), but adopting these suggested substitutes has been retarded by the relatively high cost of F-113. Increases in demands for immersion freezing of foods would probably encourage increased production of F-12 (*Buchloz and Pigott*, 1972).

RELEASE INTO THE ATMOSPHERE

Fluorocarbons can be released into the atmosphere at any stage in the processes of production, transportation, storage, use, and disposal. The potential for environmental pollution from fluorocarbons has been discussed briefly by *Korte and Klein* (1971).

Production

Losses during production are usually limited to small mechanical leakage, miscellaneous venting, and the escape of small amounts of hydrogen chloride. *McCarthy* (personal communication, 1973) has estimated that amounts released during production do not exceed 1%. Based on available information, this amount would be no greater than 10 million pounds in the U.S.

Transportation and Storage

Loss during transportation and storage is determined from the difference in the weight of the material loaded and the weight of the material in the receptacle after delivery. The cost of the fluorocarbon product is relatively high, and product billings and receipts are carefully monitored for transportation losses. Portage and storage are conducted under completely closed systems with containers that are designed, tested, and labeled in accordance with Interstate Commerce Commission specifications for pressurized uses. Storage tanks at plants of producers and formulators are designed and operated to meet established specifications for pressure. Established procedures are observed during transfer between transport and storage facilities (*du Pont de Nemours & Company*, personal communication, 1975). Less than 1% is judged to be lost during transportation and storage operations. Annual loss in the U.S. probably does not exceed 10 million pounds.

Losses During Use

The major source for the release of fluorocarbons into the atmosphere results from their use as propellants. Lesser amounts are released from uses as foaming agents, refrigerants, fire extinguishers, and solvents. An annual loss in excess of 650 million pounds may result during use (*McCarthy*, 1974).

PROPELLANTS

It is reasonable to expect that more than 90% of the annual production for propellant gases is released into the atmosphere, or at least 477 million pounds. Loss during charging operations is less than 1% (about 5.3 million pounds) for a total of more than 482 million pounds (*Harmon*, personal communication, 1974).

REFRIGERANTS

Losses from this general use may occur from scrapped, junked, or abandoned prefabricated-type refrigeration units, from recharging or replacing large commercial units, or during fabrication of sealed-type units. Some leakage also occurs gradually in certain units, e.g., in automobile air conditioning, where recharging to replace leakage typically is required about every 3 to 4 years. The Syracuse University Research Corp. (1974) used information from the American Society of Heating, Refrigeration, and Air Conditioning Engineers (*ASHRAE*, 1972a,b; 1973) and reported that about 72 million pounds were released from abandoned refrigeration units, 42 million pounds during the recharging operation, and 1.15 million pounds during fabrication.

Preliminary findings from the study underway by Arthur D. Little, Inc. indicate that there is a strong potential for controlling leakage and recycling the fluorocarbons especially in the case of automobile, commercial, and home air-conditioning uses (*Arthur D. Little, Inc.*, personal communication, 1975).

FOAMING AGENTS

Fluorocarbon use as foaming agents is approximately equal in open and closed cell operations. A loss of 100% (44.5 million pounds of 1972 production) can be assumed with the open cell process; a negligible loss is assumed with the closed cell process.

FIRE EXTINGUISHERS

The 4 million pounds of fluorocarbons produced in 1972 for this purpose will be released into the atmosphere when the extinguishers containing the material are used.

SOLVENTS

Based on the assumption of a recovery efficiency of 80%, 10 million pounds may have escaped into the environment from the 1972 production for solvents.

SUBSTITUTES FOR F-11 and F-12

The major sources of atmospheric contamination are associated with uses of fluorocarbons as propellants and refrigerants. Approximately 80% of all fluorocarbons released to the atmosphere are used either as refrigerant or propellant; more than 85% of these fluorocarbons are F-11 and F-12.

Aerosols

Substitutes for products now in aerosol packaging can be classified into two general categories: alternative propellants and non-aerosol packaging alternatives. For some product classes, substitutes for fluorocarbon propellants would cause a deterioration in product quality. In other cases, product quality would not deteriorate. In fact non-aerosol alternatives may, in some cases, be less expensive to the consumer.

Propellants

Fluorocarbon-propelled aerosols contain the active ingredient dissolved in a solvent and pressurized by a liquefied fluorocarbon. The fluorocarbon is part of the solvent. Fluorocarbon vapor occupies the space above the liquid phase and forces the active ingredient/fluorocarbon solution through a spray nozzle. Upon exit, the pressure on the solution decreases instantaneously, causing immediate vaporization of the fluorocarbon solvent. This results in a bursting of the solu-

tion into a fine-mist pattern. The fluorocarbon solvent rapidly evaporates.

Acceptable alternate propellants are available for many aerosol applications and represent 40 to 50% of the total aerosol market. For other uses, no alternate propellants are presently known to be suitable. Following is a brief analysis of the properties, advantages, and disadvantages of presently known alternatives (du Pont de Nemours & Company, 1975; Steadman and Helper, 1974; and Arthur D. Little, Inc., personal communcation, 1975).

COMPRESSED GASES

Compressed inert gas propellants include nitrogen, carbon dioxide, and nitrous oxide. They are presently used in pressurized food products such as cheese spreads and dessert toppings; in household products such as cleaners, starches, and polishes; and in automotive products such as engine starters and windshield de-icers.

A compressed gas aerosol contains the active ingredient in solution in a relatively nonvolatile solvent, such as alcohol, under pressure of a compressed gas. Nitrogen is nontoxic, inexpensive, and nonflammable. It is essentially insoluble in the active ingredient/solvent portion of the formula. The principal disadvantage is the coarseness of the spray. Fluorocarbon propellants burst from the spray nozzle into fine-mist particles, but as nitrogen is not dissolved in the solvent, the burst effect is reduced. Consequently, the spray pattern normally consists of big droplets of active ingredient, ordinarily in solution in a relatively nonvolatile solution such as alcohol. Typical spray products, such as hair spray and antiperspirants, that now use fluorocarbons are not formulated with nitrogen, not only because of the coarse-spray characteristics but also because the presence of the solvent gives a wet, cold spray that is unpleasant to the skin. Products that are not entirely dependent on the fine-spray characteristics, such as aerosol dusting products, can probably be formulated using nitrogen as a propellant; however, this is only a minor product in terms of quantity produced.

Another disadvantage to compressed gas propellants is that the pressure decreases during use, resulting in undesirable changes in spray characteristics. Also, excessive amounts of unused product remain in the container after the pressure becomes too low to expel it.

Carbon dioxide and nitrous oxide share many of the characteristics of nitrogen, but they do provide greater formulating flexibility because of increased solubility in the active ingredient/solvent concentrate. These more soluble gases can be used for aerosol products that do not require fine sprays or careful control of the discharge. Although the gases have greater solubility than nitrogen, they do not have sufficient solubility to burst the solution. Products such as furniture polish and windshield de-icer can be formulated successfully with these gases. However, the coarse, cold, wet solvent spray makes these propellants unsuitable for typical personal aerosol products such as hair spray and antiperspirants. Industry is investigating alternative formulation approaches to alleviate some of these problems associated with use for personal aerosol products.

In addition to these shortcomings, carbon dioxide can cause serious corrosion within unlined aerosol cans if any water is present in the formulation. This results in pinhole leaks in the can and the escape of propellant. This corrosion problem can be overcome by the use of a non-corrosive metal can.

SOLUBLE LIQUEFIED GASES

Soluble liquefied gas propellants such as vinyl chloride, propane, and butane physically perform much the same as fluorocarbon propellants. Vinyl chloride is no longer an acceptable propellant because of its recently discovered carcinogenic properties; it has been banned by the Food and Drug Administration, Environmental Protection Agency, and Consumer Product Safety Commission. Propane and butane have the advantages of low cost, stability, and low toxicity. However, they are highly flammable under some circumstances and, because of a potential blowtorch effect, should not be used in personal products.

The formulations of most aerosol products are trade secrets. The feasibility of substituting hydrocarbons for fluorocarbon propellants in the hundreds of aerosol products currently on the market is uncertain without a knowledge of each formulation. However, one major producer of aerosol

products has successfully substituted hydrocarbons in all of its aerosol products except those for indoor fogging purposes, in aerosol sprays containing fungicides for ornamental plants, and in dry antiperspirant aerosols (*Mace*, personal communication, 1975). At the present time, hydrocarbons have been substituted as propellants in about 85% of the insecticide aerosols. The recent development of water-based varnishes has prompted investigation into the use of hydrocarbons and nitrogen as propellant for this type of finishing agent.

The hydrocarbons have been used with aqueous products. The resulting active ingredient/propellant solution is nonflammable. Reformulation of products now using fluorocarbon propellants, to enable the substitution of hydrocarbons, could probably not be accomplished in many cases without considerable changes in product characteristics.

Non-aerosol Packaging

Non-propellant packaging can be used in almost all end-use classes now utilizing the aerosol, with varying suitability according to the product. Hand-pumped atomizers have been on the market for many years. Their main disadvantages for general use are larger droplet size and finger fatigue for the user. Pumps are also unsatisfactory where the extended exposure of the product to air would cause decomposition. Non-aerosol delivery systems generally produce a less expensive product, as the consumer does not have to pay for the propellant. Preliminary analysis by *Arthur D. Little, Inc.*, (personal communication, 1975), indicates that products dispensed by atomizers would cost about two-thirds to three-fourths of the price of the corresponding product delivered by a fluorocarbon propellant for the same amount of active ingredient. However, in some cases the product quality would suffer because of the non-aerosol system.

Of the principal classes of aerosol uses now employing fluorocarbon propellants (hair care products, deodorants, and antiperspirants), deodorants and antiperspirants have been marketed successfully for years in non-aerosol delivery systems. Hair care products are now marketed by several different companies with

manual atomizers, but have to date commanded only a small part of the market. Industry is searching for more efficient mechanical pumping devices for these applications.

Refrigerants

Mechanical refrigeration systems using fluorocarbons constitute the great majority of the refrigeration units and include all automotive air conditioners; at least 95% of household refrigerators, freezers, and air conditioners; 90% of building air conditioners, and substantially all transportation mechanical refrigeration (*du Pont de Nemours & Company*, personal communication, 1975).

According to E. I. du Pont de Nemours & Company (personal communication, 1975), no suitable alternatives are presently known for the majority of refrigeration uses employing F-11 and F-12. It is believed that, although industry is searching for and evaluating other candidates including other fluorocarbons, no alternatives with satisfactory thermodynamic properties, environmental stability, and economic feasibility have yet been developed.

OTHER FLUOROCARBONS

It has been suggested that F-22 and other fluorocarbons that might not pose as significant a stratospheric hazard as F-11 and F-12 could be used as alternative refrigerants. Prime candidates would be those that contain more than a single carbon atom and those that contain hydrogen atoms. Such compounds are less stable than F-11 and F-12, and might be removed from the troposphere so rapidly through reaction with the hydroxyl radical (OH) that they would not reach the stratosphere in sufficient quantity to be a problem (*IMOS Task Force*, 1975). Further studies to measure OH in the lower atmosphere and to calculate its rate of reaction with F-22 are needed and will be undertaken. F-22 now constitutes about 30% of the refrigeration market, principally in home air conditioners and commercial freezers. Substitution of F-22 for automobile air-conditioning refrigerants may be difficult and costly, although technically possible with substantial design change. The low operating temperature of F-22 would be difficult to maintain because of the

relatively high operating temperatures of the automotive engine. For other uses, the efficiency of the system would be significantly altered by the introduction of F-22, because F-22 is not readily miscible with the refrigerant lubricant. As with F-22, other fluorocarbons now being used in some types of equipment cannot be used interchangeably in existing equipment without substantial modification or replacement of major components. Redesign of new equipment to use other fluorocarbons may take several years for testing, modification of production facilities, and other steps in the formulation of a new product line (*IMOS Task Force*, 1975).

NON-FLUOROCARBON REFRIGERANTS

It is expected that greater problems would be encountered in switching to non-fluorocarbon compounds used in certain refrigerant applications before the development of fluorocarbons, because of their toxic and other hazardous properties. (There also would be the same problem of not being able to use the compounds in existing systems.) Following is a brief summary of the problems associated with these non-fluorocarbon refrigerants, as provided by E. I. du Pont de Nemours & Company and the Air-Conditioning and Refrigeration Institute (ARI) and based on classification of hazards by the Underwriters' Laboratories, Inc. (*du Pont de Nemours & Company*, personal communication, 1975; *IMOS Task Force*, 1975).

(1) *Ammonia.* Ammonia is toxic to humans, with a threshold limit value (TLV) of 25 parts per million (ppm), as compared with the high TLV of 1000 ppm for fluorocarbons. It also forms an explosive mixture in air at 16% concentration, whereas fluorocarbons are nonexplosive in air and nonflammable. Because of its toxic and explosive properties, ammonia is not suitable for use in units within buildings where human exposure is possible, e.g., houses, stores, offices, hospitals, and especially automobiles where the severe vibrations increase leakage potential. Ammonia is also corrosive. Typical home refrigerator and air-conditioning units are hermetically sealed with the refrigerant in contact with the electrical components; ammonia corrodes such components.

(2) *Sulfur dioxide.* Sulfur dioxide is more toxic than ammonia, with a TLV of 5 ppm. This high toxicity, combined with the possibility of leaks, makes sulfur dioxide completely unsuitable for household, auto, and building air conditioning and refrigeration units. It is highly corrosive, requiring expensive corrosion-resistant construction materials not required by present-day equipment. Its corrosiveness also makes it unsuitable for use in hermetic systems.

(3) *Methyl chloride.* This compound is more toxic than the fluorocarbons with a TLV of 100 ppm. It forms an explosive mixture in air at a 10% concentration. It is highly corrosive, generating hydrochloric acid on contact with moisture, rendering it unsuitable for use in hermetic systems. Because of its toxic and explosive properties, as well as its corrosiveness, it is unsuitable for use in household, auto, and most building units.

(4) *Hydrocarbons.* Ethane has been used in some low-temperature systems. However, since a concentration of only about 2% in air is explosive, this material is, therefore, suitable only under properly controlled conditions.

RECOVERY AND RECYCLING OF FLUOROCARBONS USED AS REFRIGERANTS

Given the various difficulties of developing substitutes for the uses of fluorocarbons as refrigerants, every effort should be made to determine if losses through leakage can be significantly reduced and the fluorocarbons recovered for recycling. Preliminary estimates by *Arthur D. Little, Inc.,* (personal communication, 1975) indicate that a significant portion of the emissions of fluorocarbons from refrigeration systems can be controlled with only relatively minor modifications of existing

technology. Automobile air conditioners, which on the average lose their fluorocarbon charge every 3 to 4 years, have a high potential of recycling at a low cost. Commercial air conditioning and central home air conditioning are also candidates with a high recycling potential. These matters are being studied further, not only in regard to the technological possibilities and economic feasibility, but also to the types of public policies and incentives that would be necessary to recover fluorocarbons at the time of disposal of the containing system, as in the case of junked automobiles and home refrigerators. The environmental impact of such measures, as well as the economic and social costs and benefits, should be compared with the same considerations if substitutes for fluorocarbons instead were developed or utilized.

Substitutes for Other Uses of Fluorocarbons

As of the publication of this report, no information was available regarding the current and future possibilities for alternatives to the uses of fluorocarbons as foaming agents, fire extinguishers, solvents, and other minor applications. These uses represent a small release of fluorocarbons to the atmosphere. In any specific regulations, if such are necessary, special consideration might have to be given to any small, specialized uses for which acceptable substitutes could not be developed.

Development and Marketing of Substitutes

E. I. du Pont de Nemours & Company (personal communication, 1975) has provided an analysis of the steps that should be followed if it becomes necessary to develop and market substitutes for fluorocarbons, in a case where it is possible to use products for which manufacturing technology currently exists:

(1) Evaluate the functionality of the proposed compound in the intended use (aerosol or refrigeration).

(2) Test the compatibility of the candidate compound with materials of construction:

(a) Metals.
(b) Plastics.
(c) Elastomers.

(3) Evaluate the compatibility of the candidate compounds with other chemicals normally present:

(a) Lubricating oils.
(b) Solvents.
(c) Surfactants.
(d) Perfumes.

(4) Evaluate the toxicology.

(5) Evaluate the flammability.

(6) Evaluate the environmental effect.

(7) Build manufacturing plants for additional raw material supply.

(8) Build new or modify existing manufacturing plants.

The du Pont plan provides for these evaluations to be run concurrently so as to be complete in 1 to 2 years at a cost of about $500,000 per product. Other estimates by E. I. du Pont de Nemours & Company are that building of large-volume plants for raw materials would require about 3 years and $100 million, and modifications to existing fluorocarbon plants, if suitable, would span 1 to 2 years, depending on size, and would cost about $10 million per plant on the average. The total timetable for evaluation, raw material plants, and fluorocarbon plant conversion would be about 5 years. The du Pont comparable timetable for developing a completely new substitute, if it should be necessary, covers a total span of 9 to 10 years and total costs between $120 million and $150 million per major, large-volume product.

EFFECTS ON INDUSTRY OF ANY RESTRICTIONS ON FLUOROCARBON PRODUCTION

It is apparent from the previous discussion that development of chemical substitutes for each present fluorocarbon use would be a long and costly process. It is hoped, however, that it will not be necessary —that if restrictions on fluorocarbons are required, substitute

delivery systems could be used for most aerosol products presently using fluorocarbon propellants, and that the refrigeration problem might be partially solved through reduction of leakage and recovery of the fluorocarbons for recycling at the time of eventual disposal. Nevertheless, any restrictions on fluorocarbons would be expected to have some adverse impacts, which would be most severe for certain occupations, for smaller companies, and for companies that specialize in processes that relate exclusively to fluorocarbon production or applications.

Presently available data do not permit a precise judgment on the number of workers and dollar value of business that might be affected by various degrees of reduction of fluorocarbon production. Even if good data were available on all aspects of the large and diverse industries associated with fluorocarbon production and use, it is not known what might occur in the next several years in the way of development of alternatives which would alter the impact. Industry estimates indicate that more than 1 million jobs may be associated with the use of fluorocarbons (Table VI-17). Of this amount, approximately 4,000 persons are identified as involved in the manufacture, sales, and research associated with their production. The fraction of these 1 million workers who would be affected by restrictions upon fluorocarbon use would depend upon the nature of the restrictions; it is not probable, for example, that persons associated with refrigeration and air-conditioning sales would be significantly affected by any restrictions likely to be considered.

Industry representatives also estimate that refrigeration equipment (including air conditioners) accounts for about $5.5 billion of the gross national product and that aerosol products containing fluorocarbon propellants account for about $2 billion of the gross national product (*du Pont de Nemours & Company,* personal communication, 1975).

More detailed studies of the industry, of substitution possibilities, and of various socio-economic impacts of regulation are currently underway and are expected to be taken into account by the regulatory agencies in determining the exact nature and timetables of any regulations to be considered.

Table VI-17. Estimate of the jobs related to fluorocarbon production and use: 1974.
(Compiled by U.S. Department of Commerce from sources listed in footnotes)

Industry category	Jobs
Refrigeration	
Packaged air conditioners, refrigerators, and freezers: manufacturing[1]	150,000
Packaged air conditioners, refrigerators and freezers: sales and service[1]	225,000
Contractors: refrigeration and air conditioning[2]	400,000
Fluorocarbon manufacturers and related suppliers ....,	2,500
Total refrigeration	777,500
Aerosols[3]	
Propellant manufacturers and related suppliers	5,000
Can, valve, and cap manufacturing	9,000
Other ingredients, and loading machinery manufacturing	5,000
Can loading	25,000
Total aerosol manufacturing	44,000
Selling and supporting activity	9,000
Total aerosol manufacturing	53,000
Foaming agents[3]	
Foamed plastic manufacturing	15,000
Raw materials manufacturing	10,000
Foamed product end-use manufacturing	150,000
Total foaming agents	175,000
Solvents	
Employment in plants of major users of fluorocarbon solvent[4]	160,000
Fluorocarbon manufacturing and related suppliers	1,000
Total solvents	161,000
Total jobs related to fluorocarbon manufacture and end use	1,166,500

[1] ARI data for 1972.
[2] ARI estimate of 460,000 people in 1972 adjusted to eliminate heating specialists.
[3] du Pont estimates based on industry contacts.
[4] Bureau of Census data.

REFERENCES

Anon. (1965). "Fluorine Chemical Complex Getting a Big Boost," *Chem. and Eng. News*, Vol. 72, p. 92.

———— (1974a). "Industry and Business," *Chem. and Eng. News*, Vol. 72, p. 8.

———— (1974b). "Fluorocarbon Shortage Easing But Future Hinges on DuPont," *Chemical Marketing Reporter*, p. 3, April.

ASHRAE. (1972a). "Refrigerants," *Handbook of Fundamentals*, Chapt. XIV, ASHRAE, N.Y.

———— (1972b). "Factory Dehydrating, Charging, and Testing," *1972 Guide and Data Book*, Chapt. XXII, p. 248, ASHRAE, N.Y.

———— (1973). "Engineered Refrigeration Systems (Industrial and Commercial)," *ASHRAE Handbook*, Chapt. 24, p. 241, ASHRAE, N.Y.

Buchloz, S. G., and Pigott, G. M. (1972). "Immersion Freezing of Fish in Dichlorodifluoromethane," *J. Food Sci.*, Vol. 37, p. 149.

Callighan, J. A. (1971). "Thermal Stability Data on Six Fluorocarbons," *Heating, Piping, Air Conditioning*, Vol. 43, p. 119.

Chemical Marketing Reporter. (1973). *Chemical Profile Fluorocarbons*, January.

Chemical Marketing Reporter, (1974). *Aerosols Outlook*, p. 27, May.

Chemical Specialties Manufacturers Association (1974). *CSMA Tech. Bull. 168-74*.

Drysdale, J. J. (1971). *Present and Future Applications of Fluorocarbons*, U.S. Nat. Tech. Inform. Serv. AD Report 751424.

DuPont de Nemours, E. I. & Co. (1974). *Freon Products Information*, Tech. Bull. B-2, Rev. April 1974, 5M-A98825.

Hamilton, J.M. (1962). "The Organic Fluorocarbon Industry," *Advances in Fluorine Chemistry*, Vol. 3, p. 117.

IMOS Task Force. (1975). *Transcript of Proceedings*, Washington, D.C., Feb. 27.

Jensen, R. (1972). "Summary," in "Appraisal of Halogenated Fire Extinguishing Agents," *Proceedings Symposium*, National Academy of Sciences, Washington, D.C.

Korte, F., and Klein, W. (1971). "Problems of Environmental Chemistry," *Pharma. International*, Vol. 5, p. 1.

Lutz, G. A., Gross, S. B., Boatman, J. B., Moore, J. P., Darby, R. L., Veazie, W. H., and Butrico, F. A. (1967). "Design of an Overview System for Evaluating the Public Health Hazards of Chemicals in the Environment," Vol. 1. *Test Case Studies*, Battelle Memorial Institute, Nat. Tech. Inform. Serv. CPB 194398.

McCarthy, R. L. (1974). *Fluorocarbons in the Environment*, Presented at Am. Geophysical Union Meeting, San Francisco, by Frank Bower. Data from U.S. Tariff Comission reports.

Nobel, H. L. (1972). *Fluorocarbon Industry Review and Forecast*, Chem. Mark. Res. Assoc. Meeting, May 15.

Shepherd, J., (1961). *Aerosols: Science and Technology*, Interscience Publishers, Inc., N.Y., Lib. Cong. Cat. Card 61-8070.

Stanford Research Institute. (1973). "Fluorinated Hydrocarbon—Salient Statistics," *Chem. Econ. Handbook*, 658.3030B.

Steadman, T. R., and Helper, E. W. (1974). *Use of Chlorofluorocarbons and Chlorocarbons as Aerosol Propellants*, Battelle (Columbus Laboratories, Ohio) Contract Report submitted to CPSC.

Syracuse University Research Corp. (1974). *Environmental Assessment of One and Two Fluorocarbons*, Prepared for Office of Toxic Substances, EPA, September.

VII.
Federal Authorities

INTRODUCTION

The U.S. Department of Justice has analyzed the existing Federal authority for regulation of fluorocarbons and the effectiveness of the various types of regulation. A copy of the memorandum from Wallace H. Johnson, Assistant Attorney General for the Land and Natural Resources Division, stating the opinion of the Justice Department, is included as part of this section.

POTENTIAL REGULATORY AGENCIES

Even if scientific evidence justifies control because of the effects on stratospheric ozone, there now exists no single Federal agency that can regulate all production or uses of fluorocarbons. Jurisdiction over the part of the fluorocarbon production that can be regulated is divided among three Federal agencies:

(1) Consumer Product Safety Commission (CPSC).

(2) Environmental Protection Agency (EPA).

(3) Food and Drug Administration (FDA).

CPSC has the authority to regulate "consumer products," a term that has been defined in the Consumer Product Safety Act to exclude, among other things, foods, drugs, cosmetics, and pesticides, as well as motor vehicle equipment and products not sold to or used by a consumer. CPSC can regulate refrigeration units used in residences or schools, but has no jurisdiction over industrial or commercial refrigerators or air conditioners.

EPA's authority extends to pesticides, as defined in the Federal Insecticide, Fungicide, and Rodenticide Act, as amended,

FDA has the authority to regulate foods, drugs, and cosmetics, extending to the entire packaging of such products, and thus to the propellant in aerosol containers.

There is at present no Federal authority governing any of the industrial or commercial uses of fluorocarbons that might affect stratospheric ozone. Fluorocarbons used for automobile or industrial refrigeration units, foaming agents, and fire retardants are currently free from regulatory authority. The proposed Toxic Substances Control Act would provide effective control of all fluorocarbon uses and would provide a regulatory base for any of a wide variety of other potentially harmful substances with long-range consequences to the environment.

TIMETABLES

In order to effect any proposed restriction, the regulating agency must follow specific established procedures that involve thorough and frequently lengthy considerations.

CPSC

To issue a consumer product safety rule banning a hazardous product, the CPSC must find that an unreasonable risk of injury exists and that no feasible safety standard under the Act would protect the public.

Within 60 days of publishing a proposed consumer product safety rule, the Commission must either declare a consumer product safety rule or withdraw the notice of proceeding. With good reason, the Commission can extend this 60-day period. Opportunity for oral or

written comment by the public must be provided. The Commission must make appropriate findings regarding the nature and degree of the risk of injury involved, economic effects, public need, and other factors specified in the Act. These findings are published as part of the consumer product safety regulation (rule).

Unless the Commission determines that different effective dates are in the public interest, the effective date of a consumer product safety rule cannot exceed 180 days from the date of declaration, with the effective date of a standard at least 30 days after its promulgation. A consumer product safety standard applies only to consumer products manufactured after the effective date. However, the Commission can prohibit a manufacturer from stockpiling any product to which a consumer product safety rule applies to prevent that manufacturer from circumventing the reason for the rule.

EPA

Under the Federal Insecticide, Fungicide, and Rodenticide Act, the Administrator of EPA has the authority to cancel the registration of a pesticide product or to change its classification when its use may present an unreasonable safety hazard to humans and to the environment. To exercise this authority, a notice of intent to cancel the registration or to change the classification must be given. Unless a hearing is requested by a registrant, this action is effective in 30 days from publication of the notice or receipt of the notice by the registrant (whichever is later). If a hearing is requested, unless the Administrator suspends the registration immediately to prevent an imminent hazard, the cancellation or change in classification does not become effective until the proceedings have ended. A registrant with a resulting canceled or suspended product can obtain judicial review in the U.S. Court of Appeals.

FDA

There are two ways in which the FDA can regulate propellants: (1) the agency can issue a regulation that, on safety grounds, bans all foods, drugs, and cosmetics packaged in aerosol dispensers containing such a propellant; or (2) it can institute proceedings against individual aerosol foods, drugs, and cosmetics under the safety provisions of the Act. In either case, the agency can at any time withdraw the banned adulterated products from the market.

The FDA must approve all new drugs, within 180 days of the application, before they can be introduced into interstate commerce.

LABELING

The FDA has power over the labeling of foods, drugs, and cosmetics, as the CPSC has over "consumer products" and EPA over pesticides. The sole purpose of each of these agencies under such authorities is to warn the consumer of any health or safety hazards.

Under the Federal Trade Commission Act, if the failure to disclose information is constituted as unfair or a deceptive practice, the Federal Trade Commission has the authority to require labeling to state the contents or hazards of a given product.

Department of Justice

Washington

June 10, 1975

Mr. Warren Muir
Ms. Carroll Pegler
Chairpersons
Interagency Task Force on Inadvertent
  Modification of the Stratosphere
Council on Environmental Quality
722 Jackson ˥ace, N.W.
Washington, .C. 20006

Dear Mr. Muir and Ms. Pegler:

This is in response to your request for our opinion on the extent of federal statutory authority to regulate fluorocarbons should scientific evidence show that these compounds are hazardous by virtue of their destroying the earth's protective ozone layer in the stratosphere. 1/ We understand that the chief sources of chlorofluorocarbons are aerosal containers and refrigeration units.

The Consumer Product Safety Commission has authority to regulate consumer products, 2/ and may promulgate consumer product safety standards if they are "reasonably necessary to

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1/ The stratosphere is a band of the atmosphere of irregular thickness that lies between 5 and 30 miles from the earth's surface.

2/ "Consumer product" is defined, subject to exceptions including those mentioned below, as:

> any article, or component part thereof, produced
> or distributed (i) for sale to a consumer for
> use in or around a permanent or temporary house-
> hold or residence, a school, in recreation, or
> otherwise, or (ii) for the personal use, consump-
> tion or enjoyment of a consumer, in or around a
> permanent or temporary household or residence, a
> school, in recreation, or otherwise . . . . [15 U.S.C.
> §2052(a)(1)]

prevent or reduce an unreasonable risk of injury associated with such product." 15 U.S.C. §2056. In addition, under 15 U.S.C. §2057, the Commission may ban consumer products if it finds that "no feasible consumer safety standard under this chapter would adequately protect the public from the unreasonable risk of injury associated with such product." The Consumer Product Safety Act, 15 U.S.C. 2051 et seq., however, limits the Commission's jurisdiction in two crucial respects. First, "the Commission has no authority under this chapter to regulate any risk of injury associated with a consumer product if such risk could be eliminated or reduced to a sufficient extent by actions taken under . . . the Clean Air Act." 15 U.S.C. §2080. Second, "consumer product" is defined so as to exclude economic poisons, drugs, cosmetics, and foods. 3/

We will first consider whether the risk of injury associated with the discharge of fluorocarbons into the stratosphere may be "reduced to a sufficient extent" under the Clean Air Act, 42 U.S.C. §1857 et seq. Title I of the Act, "Air Pollution Prevention and Control," established a procedure by which EPA and the states share responsibility for controlling air pollution.

3/ Section 2052(a)(1) of Title 15, U.S.C. excludes from the definition of "consumer product":

    (C) motor vehicles or motor vehicle equipment . . .

    (D) economic poisons (as defined by the Federal Insecticide, Fungicide, and Rodenticide Act);

    (H) drugs, devices, or cosmetics (as such terms are defined in sections 321(g), (h), and (L) of Title 21), or

    (I) Food. The term "food" as used in this subparagraph means all "food", as defined in section 321(f) of Title 21 . . .

21 U.S.C. §321 is the definition section of the Food, Drug, and Cosmetic Act.

Pursuant to Section 109 (42 U.S.C. §1857c-4) the Administrator of the Environmental Protection Agency is authorized to set national ambient air quality standards for each air pollutant for which air quality criteria have been issued under Section 108. Section 108 authorizes the Administrator to publish a list for the purpose of establishing ambient air quality standards for any pollutant which has an adverse effect on public health and welfare and the presence of which in the ambient air results from mobile or stationary sources. 42 U.S.C. §1857c-3(a)(1)(A) and (B). 4/

Once the ambient air quality standards are set, each State, pursuant to Section 110 of the Act (42 U.S.C. 1857c-5), must develop a plan which "provides for implementation, maintenance and enforcement" of the standards in each air quality control region within the State.

Title II authorizes the Environmental Protection Agency to regulate ". . . the emission of any air pollutant from any class or classes of new motor vehicles . . ." [Sec. 202(a)(1)], and ". . . emissions of any air pollutant from any class or classes of aircraft . . ." [Section 231(a)(2)].

Title III, "General" consists of miscellaneous provisions, one of which is entitled "Emergency Powers" (Sec. 303, 42 U.S.C. §1857h-1). The section authorizes the Administrator,

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4/ The Act does not define the term "ambient air," but the Environmental Protection Agency has defined it to be " . . . that portion of the atmosphere, external to buildings, to which the general public has access." 40 C.F.R. 501(e). "Mobile sources" of pollution are not defined, but appear to be motor vehicles or aircraft. See Title II of the Clean Air Act, "Emission Standards for Moving Sources", which regulates only motor vehicles and aircraft. Stationary sources include buildings, structures, facilities, or installations which emit any air pollutant. See Clean Air Act, Section 111, 42 U.S.C. 1857c-6(3).

upon receipt of evidence that a pollution source
or combination of sources (including moving
sources) is presenting an imminent and substantial
endangerment to the health of persons . . .

to file suit to restrain the emission of air pollutants or to
obtain such other relief as may be necessary.

It is the opinion of the Justice Department that the
Clean Air Act does not authorize the Environmental Protection
Agency to regulate the discharge of fluorocarbons into the
stratosphere. First, the Act applies only to stationary sources
and mobile sources, and the latter category seems to include only
motor vehicles and aircraft. Second, the Act is intended to
regulate only that portion of the lower atmosphere that is
associated with the earth's surface. We have noted that ambient
air is defined as that portion of the atmosphere " . . . to which
the general public has access." The same conclusion follows from
the requirement that State plans implement the ambient standards
". . . in each air quality control region (or portion thereof)
within such State." Congress could not have intended State plans
to control the quality of the stratosphere, since it is physically
impossible for any State's plan to have a significant effect on
any part of the stratosphere. In fact, it is probably meaningless
to speak of a part of the stratosphere as being "within" a State.

Title II is intended to regulate emissions from vehicle
and aircraft engines, and therefore does not apply to emissions
of fluorocarbons from accessories such as air conditioners.
Moreover, Title II, like Title I, was probably intended by
Congress to apply to the lower atmosphere only. Evidence of this
is found in section 231(a)(1)(A), which appears to restrict air-
craft standards to those emissions that ". . . affect air quality
in air quality control regions . . ." The legislative history
also supports this conclusion. See A Legislative History of the
Clean Air Act Amendments of 1970, Senate Committee on Public
Works, Ser. No. 93-18, 1974, p. 979 (hereinafter, Legislative
History).

Although Section 303 confers broad authority on the
Administrator to control pollution emergencies, it is reasonable
to construe this authority to be limited to pollution from
stationary or mobile sources. Similarly, it is reasonable to
limit the application of section 303 to pollution of the ambient
air. Thus section 303 is inapplicable for the same reasons that
Title I is inapplicable to the discharge of chlorofluorocarbons

into the stratosphere. In any event, §303 is not a regulatory
mechanism, and in our view, 15 U.S.C. §2080 deprives the
Commission of regulatory authority only where the Environmental
Protection Agency has regulatory authority, as opposed to
emergency authority to act. Moreover, the scope of Section 303
has never been tested. The legislative history indicates that
the Section was intended to provide for immediate action in
the event of "severe air pollution episodes" notwithstanding
any other regulatory, administrative, or judicial remedies in
the Act. Legislative History at 436. Its use for the type of
problem presented by the use of fluorocarbons is questionable.

We have already noted that the Commission's authority
does not extend to foods, drugs, or cosmetics, as defined by
the Food, Drug and Cosmetic Act, nor to economic poisons, as
defined by the Federal Insecticide, Fungicide and Rodenticide Act.

The terms "drug", "food" and "cosmetic" are broadly
defined in the Food, Drug, and Cosmetic Act. The definitions
include not only the dictionary sense of the words, but also
" . . . articles used for . . . components of any such article."
Recent court decisions have construed "component" very broadly
and have held inedible substances associated with foods to be
"food" under the Act. Natick Paperboard Corp., et al. v.
Weinberger, et al. (No. 73-2988-C, D. Mass., March 4, 1975)
(paper food-packaging material is "food" under the Act); United
States v. Articles of Food Consisting of Pottery Labeled Cathy
Rose, 370 F. Supp. 371 (E.D. Mich., 1974) (pottery dinnerware
from which lead may be leached into food is "food" under the Act.) 5/

It is our opinion that whenever fluorocarbons are
used as propellants for any food, drug, or cosmetic, they are
themselves foods, drugs, or cosmetics and thus subject to
regulation by the Food and Drug Administration, and exempt
from regulation by the Commission.

The term "economic poison" is also broadly defined
by the Federal Insecticide, Fungicide, and Rodenticide Act. 6/

5/ Appeal pending in Natick Paperboard Coarp., et al. v.
   Weinberger, et al.

6/ Section 135(a) of Title 7, U.S.C., defines "economic poison" as:

    (1) any substance or mixture of substances
    intended for preventing, destroying . . .
    forms of plant or animal life . . . which
    the Administrator shall declare to be a pest,
    and (2) any substance or mixture of substances
    intended for use as a plant regulator, defoliant,
    or desiccant.

The plain language of the definition suggest that the entire contents of a fluorocarbon-propelled aerosol falls within the definition of economic poison.

This conclusion is supported by the provisions on labeling of economic poisons. Section 135a(5) prohibits the sale, etc., of any economic poison that is "misbranded." "Misbranded" is defined by section 135(z) to mean, inter alia, not bearing an "ingredient statement." Section 135(o) defines "ingredient statement" to be a list of the names and percentages of both the "active ingredients" and the "inert ingredients" of the economic poison. Thus the Act regulates every ingredient of an economic poison, even if the ingredient has no poisonous, defoliating, etc. effect. In fact, the Agency has formally defined "inert ingredient" to include "propellants in aerosol dispensers." 40 C.F.R. 162.103(a).

This is also the holding of the only reported decision construing the meaning of "inert ingredient". United States v. Thirty Dozen Packages of Roach Food. 202 F.271 (D. Md., 1913). In that case, the court was construing section 8 of the Insecticide Act of April 26, 1910, 36 Stat. 333, which was the predecessor statute to the Federal Insecticide, Fungicide, and Rodenticide Act, and which defined "misbranded" in substantially the same way. The court held that Congress intended to require pesticide labels to list all ingredients, whether they were poisonous, non-harmful, or indeed beneficial to insects.

Finally, we note that the Agency has already invoked its authority under the Act to regulate economic poisons solely on the basis of the harmful effects caused by an inert aerosol propellant. On April 26, 1974, the Administrator announced that he was suspending all registrations for pesticide products containing vinyl chloride (an aerosol propellant) meant for use in the home or other enclosed areas. 39 F. R. 14753
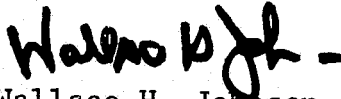
It appears therefore that when fluorocarbons are used as propellants for economic poisons, they are themselves economic poisons, and not subject to regulation by the Consumer Product Safety Commission.

In summary, we find that the authority to regulate products containing fluorocarbons, insofar as the fluorocarbons threaten the ozone of the stratosphere, is divided among three federal agencies. Food, drug and cosmetic products may be regulated

only by the Food and Drug Administration. These would include, for example, deodorants and hairsprays as cosmetics, burn medications as drugs, and dessert toppings as foods. Economic poisons may be regulated only by the Environmental Protection Agency. These would include pesticides and defoliants. Any other "consumer product", as defined by 15 U.S.C. §2052(a)(1) (see footnotes 2, 3, supra) may be regulated by the Commission. These would include such household products as window cleaners and paints. It would also include consumer goods such as refrigerators and air conditioners, but not automotive accessories. Products outside the above-mentioned categories, such as automotive accessories and industrial products, cannot be regulated under any of the statutes examined in this opinion.

This opinion has been read and approved by the Assistant Attorney General in charge of the Antitrust Division. Civil Division has no objection to this opinion.

Sincerely,

Wallace H. Johnson
Assistant Attorney General