ornl

ORNL/TM-9817

OAK RIDGE
NATIONAL
LABORATORY

MARTIN MARIETTA

Environmental Effects of Chlorofluorocarbons: Will Restrictions Be Needed?

A. M. Perry

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A06; Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-9817
Distribution Category
UC-11 and UC-95d

Energy Division

ENVIRONMENTAL EFFECTS OF CHLOROFLUOROCARBONS: WILL RESTRICTIONS BE NEEDED?

A. M. Perry

Date Published: October 1986

Research sponsored by the
Office of Buildings and Community Systems
U.S. Department of Energy

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

FOREWORD

The work described in this report was undertaken initially to provide some guidance in the planning of research and development activities at the Oak Ridge National Laboratory directed towards improvement of refrigeration and air conditioning equipment. The work was mostly completed more than a year ago. In the interim, comments have been recieved from several reviewers, both within and outside the Oak Ridge National Laboratory, and a number of important developments have occurred in the assessment of environmental impacts of chlorofluorocarbons (CFCs). In particular, there has been some further upward revision in the calculated magnitude of ozone depletion for various CFCs, as obtained by the principal modeling groups. Also a major new report, "Atmospheric Ozone 1985: Assessment of Our Understanding of the Processes Controlling its Present Distribution and Change" (WMO, 1986) (also referred to as the International Ozone Assessment) has become available in final draft form and is in publication at present. As a result of these developments and reviewers comments, numerous changes have been required in details of the presentation and some errors have been detected and corrected. However, the conclusions reached in this study remain substantially the same. I realize that they may be somewhat controversial, and indeed that they anticipate (but may not be consistent with) a determination on the need for further regulation that is to be made by the United States Environmental Protection Agency in November 1987. Let the argument presented here speak for itself.

A. M. Perry

CONTENTS

FOREWORD iii

LIST OF TABLES vii

LIST OF FIGURES ix

ACKNOWLEDGMENTS xiii

SUMMARY xv

ABSTRACT xvii

1. INTRODUCTION 1-1
   1.1 THE OZONE SHIELD 1-1
   1.2 THE GREENHOUSE EFFECT 1-2

2. SCOPE OF THE STUDY 2-1
   2.1 COMPOUNDS CONSIDERED 2-1
   2.2 EFFECTS CONSIDERED 2-3
   2.3 APPROACH USED IN THIS STUDY 2-3
   2.4 UNITS OF MEASURE 2-3

3. HISTORICAL PRODUCTION AND RELEASE OF CHLOROCARBONS 3-1

4. HISTORY OF PROJECTED OZONE DEPLETION 4-1
   4.1 EFFECTS OF CHLOROCARBONS 4-1
   4.2 EFFECTS OF OTHER TRACE GASES 4-2

5. NATURAL VARIATIONS IN ATMOSPHERIC OZONE CONCENTRATIONS 5-1

6. EFFECTS OF OZONE DEPLETION AND INCREASED UV RADIATION 6-1
   6.1 UV RADIATION AND BIOLOGICAL RESPONSE FUNCTIONS 6-1
   6.2 EFFECTS OF UV ON HUMAN BEINGS 6-4

6.3 EFFECTS OF UV ON PLANTS 6-9
6.4 EFFECTS OF UV ON DOMESTIC ANIMALS 6-9
6.5 EFFECTS OF UV ON MARINE BIOTA 6-9
6.6 HOW MUCH OZONE DEPLETION IS TOO MUCH? 6-10

7. SCENARIOS FOR FUTURE RELEASE OF CHLOROCARBONS 7-1

8. PROCEDURE FOR ESTIMATING OZONE DEPLETION 8-1

9. RESULTS 9-1

10. THE GREENHOUSE EFFECT 10-1

11. CONCLUSIONS 11-1

12. BIBLIOGRAPHY 12-1

LIST OF TABLES

Table | Page

1. Compounds considered in this study and their estimated worldwide release rates in 1983 2-1

2. Some trace gases and their approximate 1985 concentrations and rates of increase 2-2

3. Comparison of relative mixing ratio values as given by Wuebbles, MacCracken, and Luther and as calculated with Eq. 3 8-2

4. Approximate dates for reaching half of asymptotic values 9-2

5. Relative ozone destruction efficiency of various chlorocarbon compounds 9-12

6. Estimated surface temperature change (°C) resulting from increased CFM concentrations 10-2

7. Increase in average surface temperature per unit increase in concentration of CFC-11 and CFC-12 10-3

8. Temperature sensitivities of some halocarbons and hydrocarbons [ΔT(°C)/ppbv] 10-9

LIST OF FIGURES

Figure

1. Annual worldwide releases of chlorofluoromethanes 3-1

2. Annual worldwide releases of selected chlorocarbons 3-2

3. Ratio of annual release to annual production for chlorofluorocarbons CFC-11 and CFC-12 3-3

4. Estimated total column ozone reduction due to chlorocarbons as a function of the year in which the estimate was made, for the standard scenario with constant emissions at approximately 1975 release rates 4-2

5. Calculated values of the change in steady-state ozone concentration as a function of altitude for continuous releases of CFCs alone at 1980 rates 4-3

6. Vertical ozone distribution, U.S. Standard Atmosphere, latitude 45°N 4-4

7. The combined effect of several gases on the change in total column ozone 4-5

8. Zonally averaged total ozone as a function of latitude and season 5-1

9. Zonally averaged ozone concentration versus latitude and altitude for a standard March 22 5-2

10. Seasonal variation in zonally averaged total ozone for three different latitudes 5-3

11. Time–longitude variations of total ozone during June 1969 5-4

12. The relative intensity of sunlight (solar elevation of 60°C) reaching the surface of the earth for different amounts of stratospheric ozone 6-2

13. Ratio of uv fluxes at the surface for two different ozone densities and ratio of response functions versus wavelength 6-3

14. Product of uv spectrum at the surface and uv response functions versus wavelength 6-4

15. Annual uv measurements by latitude, 1974 and 1978 6-5

16. Annual age-adjusted incidence rates (1970 U.S. standard) for basal- and squamous-cell skin cancer (1977–1978) and all other cancers (1973–1976) by latitude in the U.S. white population 6-6

17. Annual age-adjusted incidence rates for basal- and squamous-cell cancers among white females and males for two surveys, 1977–1978 and 1971–1972, according to one year's uv measurements at selected areas of the United States 6-7

18. Annual age-adjusted incidence rates for skin melanoma among white females and males, according to one-year's uv measurements at selected sites of the United States 6-8

19. CFC emission scenarios 7-3

20. One hypothetical basis for projecting CFC emissions 7-4

21. CFC emission scenarios with remedial actions (evasion scenarios) 7-5

22. CFC emission scenarios with remedial actions (market penetration scenarios) 7-7

23. Tropospheric mixing ratios for CFC-11 and CFC-12 for the case of constant emissions at 1980 rates 8-2

24. Relative ozone depletion for Wuebbles' Case II, illustrating nonlinear response 8-5

25. Relative ozone depletion versus relative weighted CFC masses in the troposphere for Wuebbles' Cases I, II, IV, V, and VIII ($0 \leq M_{rel} \leq 3$) 8-6

26. Relative ozone depletion versus relative tropospheric CFC mass ($0 \leq M_{rel} \leq 5$) 8-7

27. Tropospheric inventories of CFC-11 and CFC-12 for scenarios 1–3 9-1

28. Tropospheric mixing ratios of CFC-11 and CFC-12 for scenarios 1–3 9-2

29. Weighted, combined, and normalized tropospheric inventories of CFC-11 and CFC-12 for scenarios 1–5 9-3

30. Relative ozone depletion, scenarios 1–5 9-4

31. Relative ozone depletion for the evasion scenarios 9-7

32. Maximum relative ozone depletion for the evasion scenarios versus time when emission reduction begins, following 3%/year growth in emissions prior to that year 9-8

33. Relative ozone depletion for certain market penetration scenarios with 3%/year initial growth in emissions 9-9

34. Maximum relative ozone depletion for the market penetration scenarios versus the time when the market share of substitutes reaches 1% 9-10

35. Increase in global annual surface temperature due to increasing concentrations of CFC-11 and CFC-12 versus time for scenarios 1–4 and 4a, expressed as a fraction of the doubling ΔT for CO_2 10-5

36. Comparison of relative temperature rise versus time due to CFMs with that due to CO_2 10-7

37. CO_2 concentrations versus time for the CO_2 scenarios shown in Fig. 36 10-8

38. Increase in global annual average surface temperature versus time for the CFC evasion scenarios 10-10

39. Correlation between relative temperature rise, $\tau = \Delta T/(\Delta T_2)_{CO_2}$, and relative ozone depletion 10-11

40. Correlation between relative temperature rise and absolute ozone depletion for 5, 7, and 9% steady-state ozone depletion for scenario 1 10-12

ACKNOWLEDGMENTS

I deeply appreciate the careful reviews and thoughtful comments on earlier drafts of this report that were provided by several persons both within and outside the Oak Ridge National Laboratory. In particular, I wish to acknowledge the assistance of Donald J. Wuebbles of Lawrence Livermore National Laboratory, of Stephen Seidel and several of his colleagues at the U.S. Environmental Protection Agency, and of Elizabeth Festa Gormley and members of the Fluorocarbon Program Panel, all of whom provided helpful comments and criticisms. However, I am aware that none of these people will approve of this report in its entirety, and any remaining errors are entirely my responsibility.

The encouragement and patience of William Fulkerson and Robert Minturn during the performance of this study are greatly appreciated and gratefully acknowledged.

SUMMARY

Certain chlorocarbons (CLCs), including the chlorofluoromethanes CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2), are extremely valuable for refrigeration and air-conditioning and are very useful as industrial solvents and as foaming agents in the manufacture of plastic foams. They are also widely used as aerosol propellants. These compounds sooner or later find their way into the atmosphere, where it is thought they will cause a reduction in the concentration of stratospheric ozone and an increase in the average surface temperature of the earth. This report provides estimates of ozone depletion and surface warming for various scenarios for future emissions of eight important chlorocarbons: CFC-11, CFC-12, CFC-22 (CHF_2Cl), CFC-113 ($CFCl_2CF_2Cl$), CFC-114 (CF_2ClCF_2Cl), CFC-115 (CF_2ClCF_3), CCl_4, and methyl chloroform (CH_3CCl_3). Although the combined rate of emission of these eight compounds varies among the scenarios, their relative emission rates are, for simplicity, assumed to remain in the same proportions as at present.

A simple method was devised for estimating the reduction of total column ozone by interpolation of published results obtained with more elaborate models of atmospheric chemistry and physics. It appears that relative ozone depletion and relative surface temperature change for various scenarios can be estimated more reliably than can the absolute values of these quantities for any given scenario. Therefore, in this report, the ozone depletion estimates are normalized to the asymptotic, steady-state depletion for a reference scenario having constant CLC emissions at current rates. The estimates of surface temperature change are expressed in terms of the change to be expected for a doubling of the atmospheric carbon dioxide (CO_2) concentration.

Present estimates for the steady-state ozone depletion in the reference scenario (constant CLC emissions at present rates) appear to be in the range of 5–10% of total column ozone, although the preferred estimate continues to change with improved models and reaction rate data. Consideration of the effect of ozone density on the intensity of ultraviolet (uv) radiation at the earth's surface and consideration of the effects of increased uv intensity on people, on terrestrial plants and animals, and on marine biota suggest that a change of this magnitude may be "acceptable." The steady-state ozone depletion in the reference scenario was therefore adopted as a rough measure of acceptable change. Ozone depletion several times greater than this is presumed to be unacceptable.

The scenarios considered, in addition to the reference scenario, included growth of CLC emissions at rates of 3–5%/year up to emission rates a few times higher than present rates. Also included were scenarios in which CLC emissions, having grown to higher levels, subsequently declined at various rates and starting at various times. These so-called "transition" scenarios are illustrative of the changing CLC emissions as substitutions or emission controls are introduced and gradually become effective.

The depletion of total column ozone does not vary linearly with atmospheric burden of CLCs but increases somewhat more rapidly with increasing burden. Thus a twofold increase in CLC emissions, relative to the reference scenario (i.e., constant emissions at present rates) (according to the model employed here), would increase the steady-state ozone depletion by a factor of 2.6; a

threefold increase, by a factor of nearly 5; and a fivefold increase, by a factor of 10. The surface temperature sensitivity is also nonlinear, but the sensitivity decreases with increasing CLC concentrations owing to saturation of the infrared (ir) absorption lines.

The reference scenario appears to present no imminent environmental hazards, and forced reduction of emissions below current levels does not appear to be justified. However, growth in annual CLC emissions seems likely and would lead eventually to disturbingly large effects, e.g., ozone depletion several times greater than the steady-state depletion for the reference scenario and a contribution to surface warming comparable to that from doubling of CO_2. For a growth rate of 3%/year or more, this situation would happen by about the middle of the coming century or sooner. But if such growth can be slowed and then reversed, starting within a few decades, the maximum ozone depletion and the maximum surface temperature change can be kept within acceptable limits, that is, ozone depletion comparable to steady-state depletion in the reference scenario and temperature effect small compared to that expected from doubling CO_2. Depending on the initial growth rate in CLC emissions (e.g., 3–5%/year) and on the rapidity with which substitutions or effective emission controls could be introduced, it appears that the time when such actions would begin to be effective should come within the next few decades, for example, within 15 to 30 years or so.

In summary, the reduction of CLC emissions below present levels does not appear to be necessary—certainly not in the near future. Some growth in emissions is permissible, but not for very long. Continued emissions at a few times current rates are probably unacceptable. If growth in emissions over the next few years averages 3%/year or more, actions to slow and then reverse that growth would need to become effective within about 15–30 years and emission rates would eventually have to be reduced again to levels comparable to or less than the present ones.

ABSTRACT

This report describes a method that has been devised for estimating ozone depletion for various assumptions regarding the future release of chlorocarbons (CLCs) to the atmosphere. The method is calibrated against published results obtained with more elaborate models of atmospheric chemistry. The method is applied for various scenarios for future CLC emissions, with and without emission controls. Estimates are also made of the climatic effects of CLC emissions, as represented by the average surface temperature of the earth. It is concluded that current rates of emission present no immediate danger to the earth and its inhabitants and would not do so for many decades. However, growth in CLC emissions at 3%/year or more, as seems likely, would eventually lead to unacceptable changes both in total ozone density and in surface temperature. Although no corrective action appears necessary at present, given the long times needed to develop and introduce substitutes or to implement effective emission controls, such actions may be necessary within the next one to three decades.

1. INTRODUCTION

Several fully halogenated carbon compounds, notably chlorofluoromethanes (CFMs), have proven extremely useful for refrigeration and air-conditioning. In addition to having desirable thermodynamic properties, they are mostly nonflammable, nontoxic, noncorrosive, and stable. They are ideal for the purpose. These compounds have also proven useful as industrial solvents, as aerosol propellants, as blowing agents in the manufacture of plastic foams, and as fire extinguishers. In general, they have appeared to be environmentally benign, a blessing in these days when so many products of contemporary technology seem to have unwanted and harmful side effects. In recent years, however, two concerns have emerged regarding possible adverse effects of these halocarbons, namely (1) their potential impact on the earth's ozone shield [which limits the intensity of biologically damaging ultraviolet (uv) light at the earth's surface] and (2) their possible contribution to climate change through the so-called "greenhouse effect."

1.1 THE OZONE SHIELD

Ozone (triatomic oxygen, O_3) is an unstable, highly reactive form of oxygen that is normally present in the atmosphere in concentrations ranging from <0.1 ppm at low altitudes to ~10 ppm in the middle stratosphere, with an overall average of ~0.4 ppm. The entire amount of ozone in the atmosphere, if collected in a single layer near the surface (at standard temperature and pressure), would form a layer only about 3 mm thick. However, this relatively tiny amount of ozone absorbs most of the uv radiation in sunlight incident at the top of the atmosphere, shielding plants and animals at the earth's surface from uv-induced damage that would otherwise occur. Of course, these plants and animals have evolved under the protection of this filter. Therefore, it is not surprising that they are subject to damage by uv intensities much higher than normal. Thus the possibility of impairment of the filter over a relatively short period of time must be viewed with some concern.

Ozone is formed, primarily in the stratosphere, by reaction of diatomic oxygen, O_2, with atomic oxygen. The atomic oxygen is formed high in the atmosphere by photolysis of O_2 by incident uv light. Ozone is removed by recombination with atomic oxygen,

$$O + O_3 \rightarrow 2O_2\,(\text{net}) \quad ,$$

or by recombining with itself,

$$O_3 + O_3 \rightarrow 3O_2\,(\text{net}) \quad .$$

These net reactions are catalyzed by several sequences of reactions involving odd hydrogen (H, HO, HO_2, H_2O_2), odd nitrogen (NO, NO_2, NO_3, N_2O_5, HNO_3, HO_2NO_2), odd chlorine (Cl, ClO, HCl, $ClONO_2$), and others. At present, a large fraction (e.g., around 70%) of the ozone-loss reactions involve odd nitrogen. However, Molina and Rowland (1974) pointed out that increasing production

of CLCs and their release to the atmosphere would enhance the contribution of the odd-chlorine catalytic cycles to the destruction of ozone and hence to a reduction in its concentration and to an increase in uv radiation at the surface. (See also Stolarski and Cicerone 1974, Wofsy and McElroy 1974, and Rowland and Molina 1975.)

1.2 THE GREENHOUSE EFFECT

The principal constituents of the earth's atmosphere, diatomic nitrogen and oxygen, are nearly transparent to incident solar radiation and to the infrared (ir) heat radiation that is emitted by the warmed earth. Some minor constituents of the atmosphere, notably water vapor and CO_2, are strong absorbers of ir radiation, which they then reradiate, partly backward toward the earth and partly outward again toward space. This absorption and reradiation of ir radiant energy, along with the processes of convection and evaporation/condensation of moisture, keep the surface and lower atmosphere at a temperature some 35°C warmer, on the average, than would prevail in the absence of these ir-absorbing gases. Since the use of fossil fuels (coal, oil, and gas) is leading to a significant increase in CO_2 concentration in the atmosphere, concern has been expressed for some years regarding the possibly harmful effects of increasing the temperature of the earth. More recently, it has been recognized that a number of other trace gases whose concentrations may be altered by human activities can also contribute significantly to this "greenhouse effect." These other gases include nitrous oxide (N_2O), methane (CH_4), and the chlorofluoromethanes $CFCl_3$ (CFC-11) and CF_2Cl_2 (CFC-12). Others may contribute also, but these are thought to be the likely principal contributors other than CO_2. Taken together, their combined contributions to future warming of the earth may be comparable to that of CO_2.

The purpose of this report is to review evidence concerning these potential effects, to estimate the magnitudes of ozone reduction and surface temperature increase for various scenarios for the future release of CLCs to the atmosphere, and to inquire whether or when some restrictions on future emissions may be justified.

Because the atmospheric lifetimes of the compounds considered here are long, they become rather uniformly distributed around the world. Their effects are global in extent, without regard to their points of origin. Thus, as is the case with CO_2, it is the combined worldwide emissions that matter and that are considered in this report.

It should be pointed out that this subject has been very extensively reviewed by the National Academy of Sciences/National Research Council (NAS/NRC) in a series of reports from 1975 to 1984 (NRC 1975, 1976a, 1976b, 1977, 1979a, 1979b, 1982, 1984). Major reviews have also been published by the National Aeronautics and Space Administration and the World Meteorological Organization (Hudson and Reed 1979; Hudson et al. 1982). (A new report sponsored by these and several other organizations is scheduled to be published in 1986, WMO 1986.) In addition, a very extensive body of literature has accumulated in scientific journals. These sources have been drawn on heavily in the preparation of this report. Our purpose has been to apply the insights and information gathered from this literature in considering these questions: Does it seem likely that the prospect of future environmental changes will be sufficiently alarming to occasion a major effort to reduce future CLC releases to the atmosphere, and, if so, when?

2. SCOPE OF THE STUDY

2.1 COMPOUNDS CONSIDERED

The halocarbons considered directly or indirectly in this study are listed in Table 1, along with estimates of the 1983 annual, worldwide release rates of these compounds to the atmosphere.

Table 1. Compounds considered in this study and their estimated worldwide release rates in 1983

Compound	Name	Release rate (10^6 kg/year)[a]
$CFCl_3$	CFC-11 (F-11)	265
CF_2Cl_2	CFC-12 (F-12)	412
CCl_4	Carbon tetrachloride	131
CHF_2Cl	CFC-22 (F-22)	72
$CFCl_2CF_2Cl$	CFC-113 (F-113)	97
CF_2ClCF_2Cl	CFC-114 (F-114)	18
CF_2ClCF_3	CFC-115 (F-115)	4.5
CH_3CCl_3	Methyl chloroform	455

[a]*Source:* Wuebbles, MacCracken, and Luther (1984). Based largely on estimates by the Chemical Manufacturers Association (CMA 1982) for CFC-11 and CFC-12 and on estimates by the Organization for Economic Cooperation and Development (OECD 1981) for the other compounds.

The first two compounds listed in Table 1 appear to be the most important ones, and most of the following analysis and discussion will be focused on these two. However, the effects of the other compounds will be considered. With the exception of CFC-22 and methyl chloroform, these are fully halogenated compounds, having neither hydrogen atoms nor double bonds. At normal ambient temperatures, these compounds are either gases or volatile liquids, and a major fraction of the volume produced each year soon finds its way into the atmosphere. The fully halogenated compounds have no known tropospheric sinks. Thus, they become almost uniformly distributed throughout the troposphere, whence they are carried into the stratosphere in the slow exchange of air between these two major regions of the atmosphere. High in the stratosphere, these compounds are broken down by uv light (photodissociation). The free chlorine released in this way can react with ozone in the stratosphere, augmenting the loss side of the production/destruction balance and

thus reducing the ozone concentration.* The chlorine so produced forms the basis for several catalytic cycles, the principal one of which is

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2 \\ ClO + O \rightarrow Cl + O_2 \\ \hline O + O_3 \rightarrow 2O_2 \text{ (net)} \end{array}$$

Thus the chlorine is soon regenerated following its reaction with ozone and is available to destroy another ozone molecule. In this way, the destruction of many thousands of ozone molecules can be caused by a single chlorine atom before the chlorine is finally removed by transport back to the troposphere, where it is washed out (as HCl).

The compounds that contain hydrogen (e.g., CHF_2Cl and CH_3CCl_3) and compounds with double bonds (none of which is listed in Table 1) react with the HO (hydroxyl) radical in the troposphere, and their atmospheric lifetimes are much shorter than those of the fully halogenated compounds. Only a fraction (usually small) of these compounds reaches the stratosphere and undergoes photolysis with the release of chlorine. Thus, CHF_2Cl (CFC-22) should be far less damaging to the ozone shield (for a given rate of emission to the atmosphere) than CFC-11 or CFC-12 and might be considered as a substitute for them. We shall return to this point later.

Table 2 lists some trace gases that will be of interest in this study (including those listed in Table 1) and gives their present concentrations and their current rates of increase.

*Fluorine in these compounds is more tightly bound to the carbon atom than the chlorine is and, when released, is much less reactive with O_3. In addition, HF is more stable in the atmosphere than is HCl, thus sequestering fluorine more effectively.

Table 2. Some trace gases and their approximate 1985 concentrations and rates of increase[a]

Compound	Present concentrations	Rate of increase
CO_2	345 ppmv	1.5 ppm/year (0.4%/year)
N_2O	0.3 ppmv	~0.2%/year (?)
CH_4	1.7 ppmv	~1%/year (?)
CFC-11	210 pptv	9 ppt/year (4%/year)
CFC-12	380 pptv	18 ppt/year (5%/year)
CCl_4	161 pptv	3 ppt/year (2%/year)
CFC-22	44 pptv	3 ppt/year (7%/year)
CFC-113	32 pptv	3 ppt/year (9%/year)
CFC-114	10 pptv	0.6 ppt/year (6%/year)
CFC-115	2.3 pptv	0.2 ppt/year (7%/year)
CH_3CCl_3	139 pptv	6 ppt/year (5%/year)

[a]Note that these figures do not agree exactly with those given in other references [e.g., Prinn et al. (1983a), Ramanathan et al. (1985)], but the differences are generally small and inconsequential for our purposes.

Source: Based on Wuebbles, MacCracken, and Luther (1984).

2.2 EFFECTS CONSIDERED

The principal effects considered are those discussed in the Introduction, that is, ozone depletion and the greenhouse effect. We will draw attention also to the question of changes in the temperature structure of the stratosphere.

2.3 APPROACH USED IN THIS STUDY

A very simple one-box model of the atmosphere was adopted to estimate the tropospheric concentrations of CFC-11 and CFC-12, and a simple correlation was used to translate these tropospheric concentrations into estimates of total ozone depletion. The approach used relies on calibrating these simple prescriptions against published computations for CLC concentrations and ozone depletion. The details are presented in Sect. 8.

2.4 UNITS OF MEASURE

Because estimates of the absolute magnitudes of ozone depletion and of global warming are still subject to appreciable uncertainties, we have chosen to present ozone depletion for various CLC release scenarios in terms of the asymptotic (steady-state) depletion for a standard, reference scenario having continued, constant emissions of CLCs at present rates, since this is the quantity most often reported in the literature. Similarly, we report the effect of CLCs on global-average surface temperature in terms of the temperature change that would be induced by a doubling of CO_2 concentration, that is, the so-called "doubling ΔT" of CO_2. Both of these quantities—the steady-state ozone reduction for the standard scenario and the doubling ΔT of CO_2—are still rather uncertain quantities; but it seems likely that estimates of the *relative* ozone depletion for various scenarios and the *relative* greenhouse effect for various trace gases will remain more nearly the same, as research continues, than will the absolute magnitudes of any of these quantities.

3. HISTORICAL PRODUCTION AND RELEASE OF CHLOROCARBONS

Wuebbles, MacCracken, and Luther (1984) have summarized the record of historical releases of CLCs, as estimated mainly by the Chemical Manufacturers Association (CMA 1982) for CFC-11 and CFC-12 and by the Organization for Economic Cooperation and Development (OECD 1981) for the other compounds listed in Table 1. The record for CFC-11 and CFC-12 is reproduced in Fig. 1.* From 1960 to 1973, emissions of CFC-11 grew at an average compound rate of about 15%/year, while CFC-12 emissions increased at about 11%/year. Since the mid-1970s, however, emissions of these compounds have remained roughly constant, primarily as a result of the decrease

*Data given in a more recent CMA report (CMA 1985) lie slightly below those shown in Fig. 1. The later report includes only production and sales figures reported by twenty cooperating companies, representing most production outside the Soviet Bloc and China, while the earlier report includes estimates for those countries; these estimates are not considered to be very reliable, and information has not been available to update them for later years.

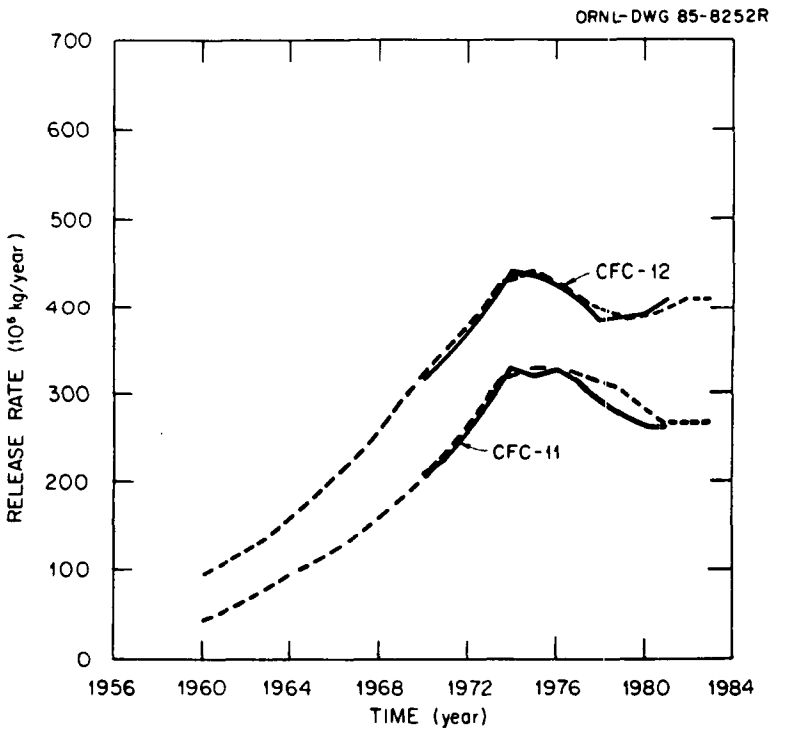


Fig. 1. Annual worldwide releases of chlorofluoromethanes. Dashed curves after Wuebbles, MacCracken, and Luther (1984); solid curves after Chemical Manufacturers Association (CMA 1982).

in the use of CLCs as aerosol propellants. However, a resumption of growth in the mid-1980s is to be expected, as will be discussed in Sect. 7, "Scenarios for Future Release of Chlorocarbons." Figure 2, also based on Wuebbles, MacCracken, and Luther (1984), shows historical releases of some of the other compounds listed in Table 1.

The release rates estimated by the Chemical Manufacturers Association for CFC-11 and CFC-12 were obtained by estimating production in all producing countries (including the Soviet bloc), estimating the fraction of annual production that was used in each application (i.e., refrigeration, automotive air conditioners, foaming agents, aerosol propellants, etc.), and estimating the average time delay before release to the atmosphere in each application (i.e., short for aerosols and manufacture of open-cell plastic foams, somewhat longer for closed-cell foams and auto air conditioners, and longer still for home refrigerators, etc.). The ratio of annual release to annual production in each year, as estimated by the CMA (CMA 1982), is shown in Fig. 3. Although these release figures cannot be considered to be precise, it appears that an amount equal to about 90% of annual production has been released to the atmosphere (including, of course, contributions from production in prior years). Cumulative release divided by cumulative production is about 0.88 for CFC-11 and 0.92 for CFC-12. Of course, these ratios could be modified in future years.

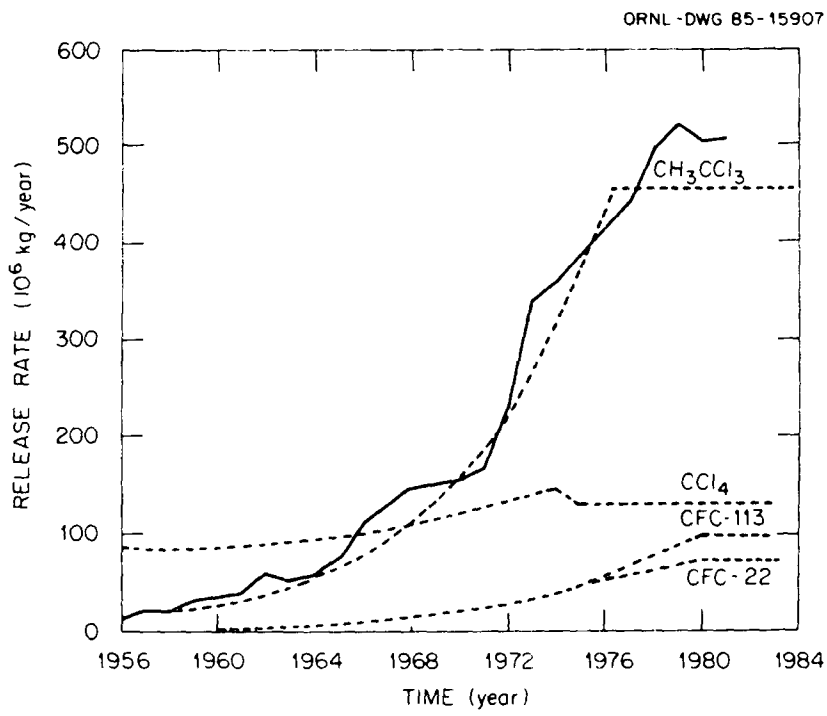


Fig. 2. Annual worldwide releases of selected chlorocarbons. Dashed curves after Wuebbles, MacCracken, and Luther (1984); solid curve after Prinn et al. (1983b).

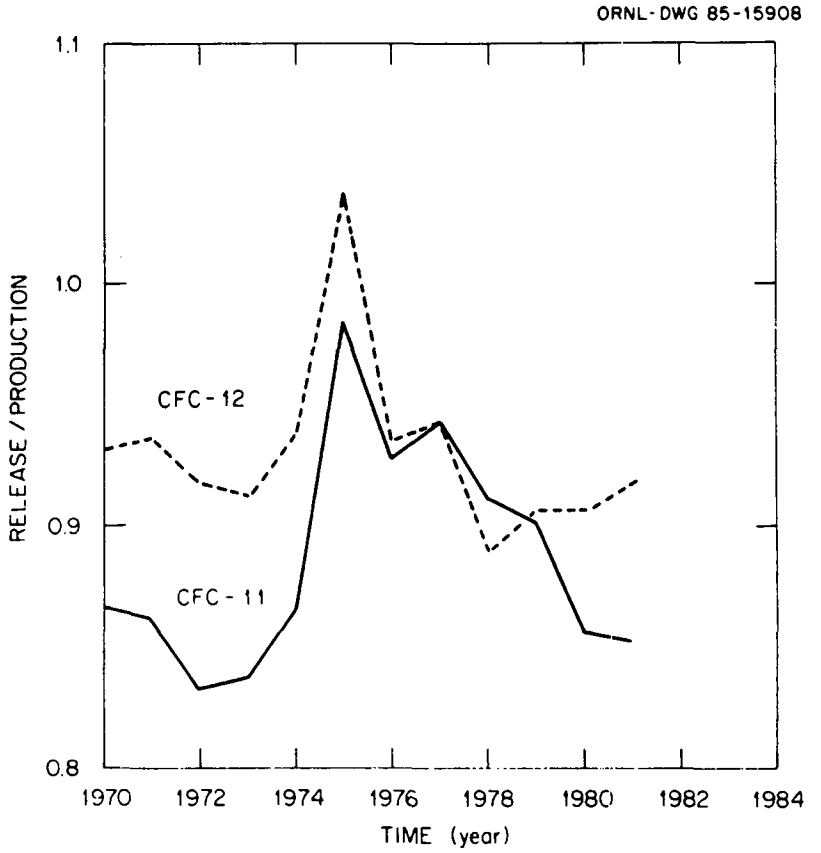


Fig. 3. Ratio of annual release to annual production for chlorofluorocarbons CFC-11 and CFC-12, as estimated by the Chemical Manufacturers Association. [Given in Cunnold et al. (1983a) for CFC-11 and in Cunnold et al. (1983b) for CFC-12.]

4. HISTORY OF PROJECTED OZONE DEPLETION

4.1 EFFECTS OF CHLOROCARBONS

Over the past decade, the prevailing estimates of ozone depletion that would result from continued release of CLCs to the atmosphere have undergone frequent and substantial changes, sometimes upward and sometimes downward. The uncertainty in the estimates at any time has always been understood to be very large. Differences in the estimates obtained by the same investigators at different times and by different investigators at the same times are attributable in part to differences in structure of the atmospheric chemistry models used, but primarily to differences in the set of chemical reactions included in the computations and in the rate constants assigned to these reactions. Interest in the question of stratospheric perturbations has generated a very large research effort over the past ten years or so, resulting in great improvements in the rate-constant data available for the models and in the observations of stratospheric concentration profiles of key species that are used for validating the results of model computations. At present, several dozen chemical species (compounds and radicals) are typically represented in the models, and these species are typically linked by up to 200 different reactions. The inclusion of new reactions or of revised rate data has been responsible for most of the substantial revisions in estimated ozone depletion.

Most of the studies of changes in atmospheric composition have been carried out with one-dimensional (1-D) models (with only the vertical dimension explicitly represented). Such models must allow for transport processes in the atmosphere in a highly simplified manner and, of course, cannot disclose regional differences. Although the simplifications and approximations inherent in the 1-D models have been recognized as a major source of uncertainty in the model predictions, in the main, the results of the 1-D calculations have been confirmed by a few (more costly) two-dimensional (2-D) calculations. Three-dimensional (3-D), general circulation models of the atmosphere can explicitly represent the larger-scale transport processes but, because of computational limitations, cannot yet also accommodate the full range of chemical reactions that are included in the 1- and 2-D models.

For purposes of comparison, it has been customary to consider a standard, reference scenario with constant CLC emissions continued indefinitely at "present" rates (e.g., 1973 rates, 1976 rates, 1980 rates). Since, as can be seen from Fig. 1, the emission rates of the two key compounds CFC-11 and CFC-12 have not changed very much over the past ten years, the calculations for this standard scenario, though done at different times, are roughly comparable.

The range in estimates obtained by various investigators at any given time has usually been narrower than the range of changes that have occurred over the ten-year period. A record of average or typical estimates for ozone depletion for the standard scenario (constant emissions) as a function of the time when the estimates were made is given in Fig. 4. The quantity shown is the percentage reduction in total column ozone that would occur asymptotically, that is, at steady state

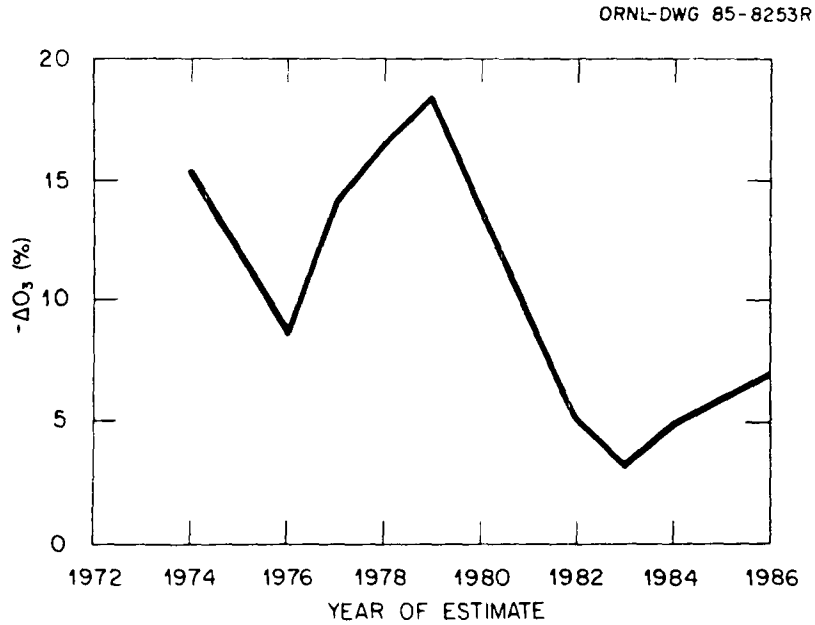


Fig. 4. Estimated total column ozone reduction due to chlorocarbons as a function of the year in which the estimate was made, for the standard scenario, that is, with constant emissions at approximately 1975 release rates. *Sources:* 1974–1983 estimates: NRC (1984); 1984 estimate: Wuebbles (1985a); 1986 estimate: WMO (1986).

(following a long, slow approach to equilibrium) for the case of continued constant emissions at current rates (the standard scenario).

Of greatest interest is the marked reduction in the prevailing estimates of ozone depletion that has occurred since 1979, when the best estimate was that steady-state ozone depletion would be about 18%. By 1983, most estimates were in the range 2–4% (NRC 1984). However, present estimates are again somewhat higher, running generally in the range 5–9% (WMO 1986).

A major reason for the reduction in the estimates since 1979 has been revised information on the rate constants for reactions involving odd-hydrogen species such as HO and HO_2. The effect of these changes is seen primarily in the estimated ozone depletion in the lower stratosphere, where the absolute ozone concentration is highest. The large impact of these changes in the treatment of atmospheric chemistry is shown in Fig. 5 (reproduced from NRC 1984, Figs. 6.1 and 6.2). The large percentage reduction in ozone around the 40-km altitude is relatively unaffected, and this has been a persistent feature of the calculations since the beginning. At lower elevations, however, where there is far more ozone to begin with, what was previously seen as a substantial decrease in ozone concentration is now seen as a modest increase. Interpretation of Figs. 5(*a*) and 5(*b*) may be assisted by reference to Fig. 6, which shows a representative ozone distribution as a function of altitude (U.S. Standard Atmosphere, latitude 45°N).

4.2 EFFECTS OF OTHER TRACE GASES

Recent analyses of the ozone depletion question have made clear that the CLCs are not alone in having an influence on ozone density. (The question of ozone depletion really originated with

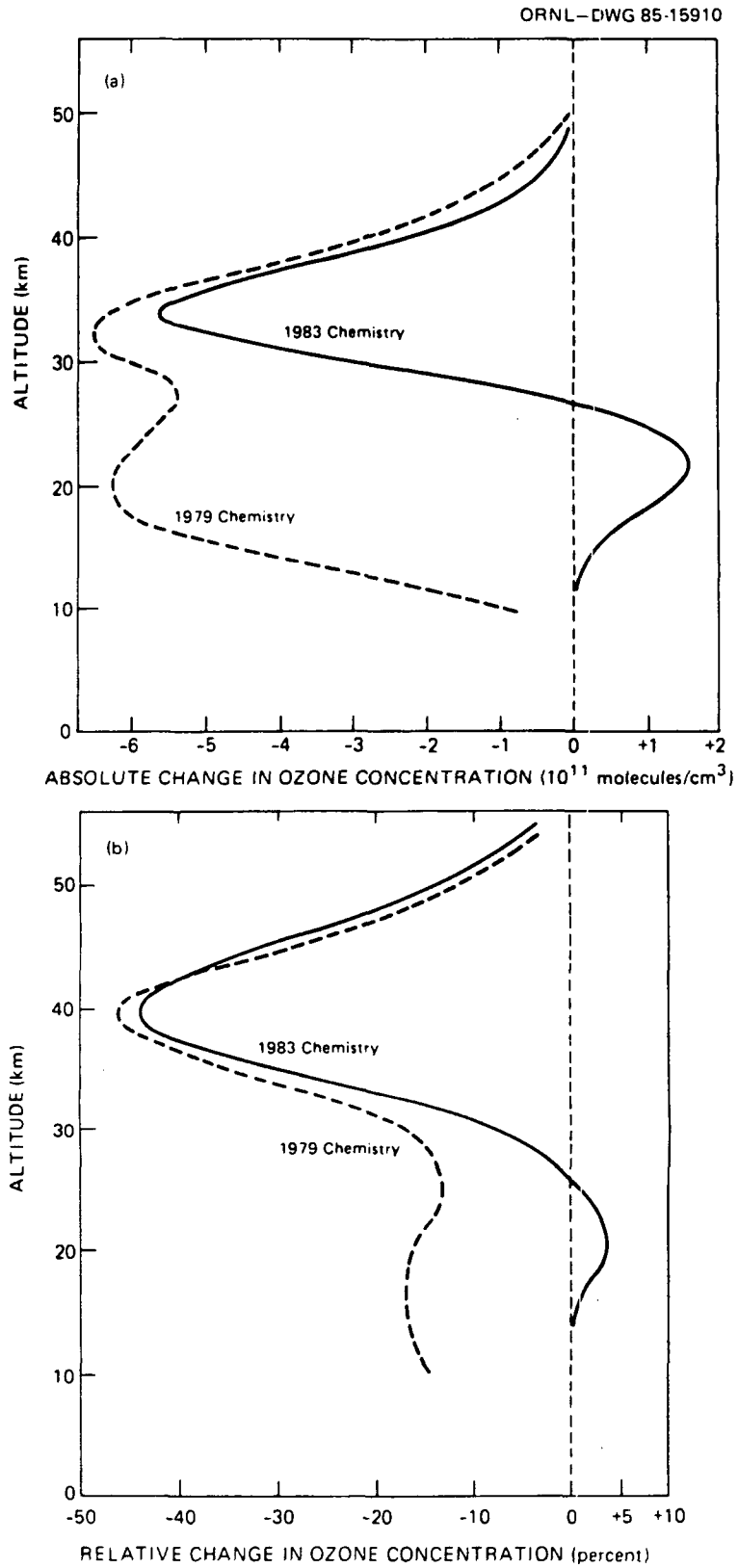


Fig. 5. Calculated values of the change in steady-state ozone concentration as a function of altitude for continuous releases of CFCs alone at 1980 rates. (*a*) Absolute change; (*b*) relative change. *Source:* NRC (1984), Figs. 6-1 and 6-2. Adapted from Turco (1984). (Reproduced with permission from Van Nostrand Reinhold Co.)

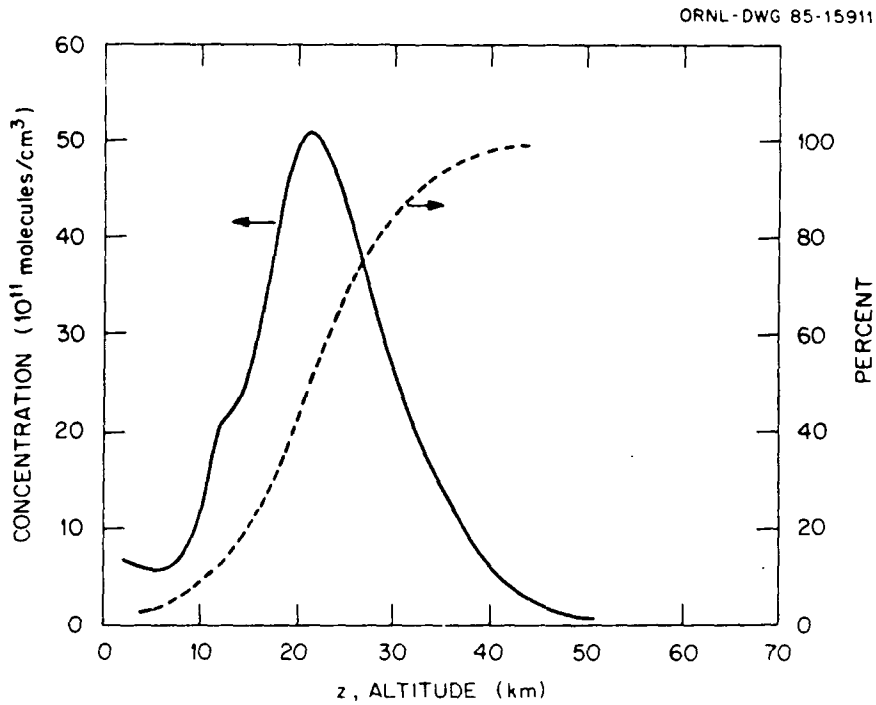


Fig. 6. Vertical ozone distribution, U.S. Standard Atmosphere, latitude 45°N. Solid line: concentration (10^{11} molecules/cm^3) (left scale); dashed curve: percentage of total ozone below altitude z (right scale). *Source:* Adapted from NRC (1984), Fig. 5-13.

concern over the effects of nitrogen oxides from supersonic aircraft, which would operate in the stratosphere, or from the detonation of nuclear weapons. It was only somewhat later that this concern was extended to the effects of chlorine.) It is now generally recognized that the effects of a number of other trace gases should be considered along with those of the CLCs in trying to understand whether continued use of the CLCs may pose a significant environmental threat.

Among the more important of the gases to be considered are the following, all of whose concentrations appear to be changing or to be subject to change by human activities:

CO_2: Increases O_3; increased CO_2 decreases stratospheric temperatures, affecting temperature-dependent rate constants and reducing the importance of certain O_3 loss mechanisms.

N_2O: Decreases O_3; source of the principal natural O_3 destruction cycle; the cycle may be augmented by NO_x from supersonic aircraft if flown above ~17 km or by increased industrial or agricultural production of N_2O.

NO_x: Increases O_3 if injected at lower altitudes, for example, by subsonic aircraft operating in the upper troposphere and lower stratosphere.

CH_4: Increases O_3; CH_4 reacts with chlorine and with HO, in both cases diminishing the chlorine-related destruction of O_3.

Wuebbles, Luther, and Penner (1983) considered the combined effects of these gases (excluding CH_4) and the CLCs listed in Table 1 under reasonable assumptions concerning their future rates of

release to the atmosphere or their concentrations in the troposphere. Their results are summarized in Fig. 7 for the standard CLC emission scenario (continued constant emissions at 1980 levels). Other key assumptions are as follows:

1. Increase in N_2O concentration at 0.2%/year, from 288 ppbv in 1960 to 381 ppbv in 2100.
2. Altitude-dependent NO_x emissions from aircraft, injected between 5 and 21 km, increasing as a function of time until 1990 and constant thereafter [tabulated in Table 1 of Wuebbles, Luther, and Penner (1983)].
3. The CO_2 concentration as a function of time is assumed to be

   $[CO_2] = 280 + 27.4 \exp[0.03318(t - 1958)]$ for $1958 \leq t \leq 1979$

   and

   $[CO_2] = 335 \exp[0.0056(t - 1979)]$ for $1979 \leq t \leq 2100$.
4. No change in CH_4 concentration is assumed. It may be noted that doubling CH_4 concentration in the model atmosphere would increase the total ozone by about 2% (Wuebbles, Luther, and Penner 1983).

The calculations of Wuebbles, Luther, and Penner include all the compounds listed in Table 1 of this report.

More recent calculations by Wuebbles (WMO 1986), reflecting continuing evolution of models and data, show a somewhat smaller effect for CO_2 than is indicated by Fig. 7, but confirm the

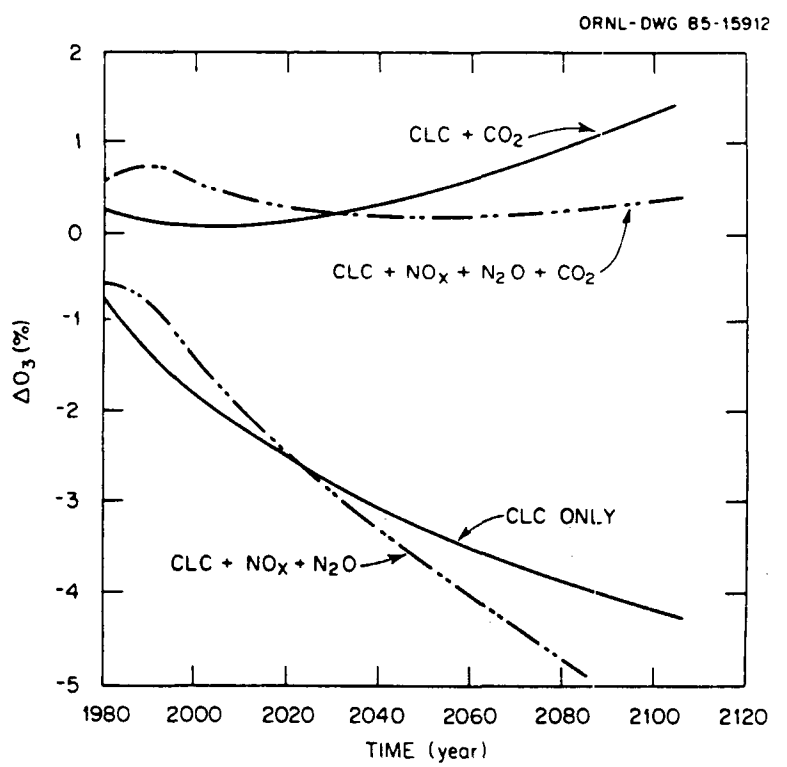


Fig. 7. The combined effect of several gases on the change in total column ozone (1982 chemistry, continued release of CLCs at 1980 rates). *Source:* Wuebbles, Luther, and Penner (1983).

important positive contribution of CH_4. The essential conclusion is the same: the combined effect of other trace gases whose concentrations are changing as a result of human activities can substantially offset the depletion of ozone caused by CFCs in the case of constant emissions at present rates. The precise extent of this offset is impossible to predict, because of large uncertainties regarding the future concentrations of these other trace gases.

5. NATURAL VARIATIONS IN ATMOSPHERIC OZONE CONCENTRATIONS

Ozone concentrations in the atmosphere are by no means uniform. In addition to the well-established systematic variations with altitude, latitude, and season, there are substantial short-term fluctuations in ozone density associated with atmospheric transport processes and arising from the highly nonuniform distribution of ozone production (i.e., predominantly at low latitudes and high altitudes). In considering the consequences of long-term alterations in ozone concentration, it may be worthwhile to bear in mind these substantial natural variations.

Figure 8 shows total column ozone density (integrated over altitude) as a function of latitude and season.* The total ozone density is much higher at high latitudes than near the equator and has

*A similar distribution, resulting from measurements made with the Nimbus 7 total ozone mapping spectrometer, is given by Bowman and Krueger (1985). (1 atm·cm = 1 cm thickness at standard temperature and pressure.)

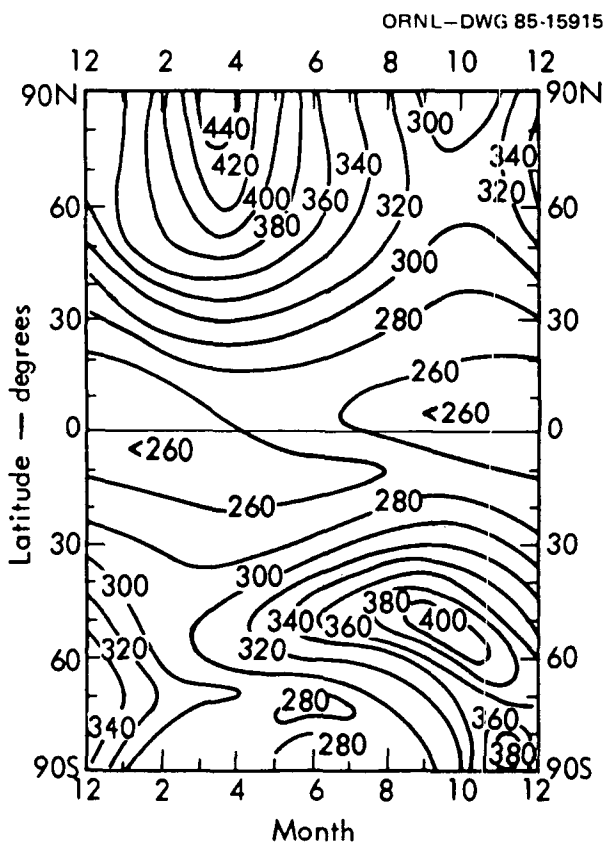


Fig. 8. Zonally averaged total ozone as a function of latitude and season. *Source:* MacCracken and Chang (1975), Fig. A-6, constructed by Dutsch (1971) from data by London (1963) and Sticksel (1970). (Isolines are in 10^{-3} atm·cm.)

an annual peak at about the time of the spring equinox. The patterns are somewhat different in the two hemispheres; the annual maximum in the Southern Hemisphere comes at 50–60°S latitude, while in the Northern Hemisphere the maximum occurs close to the pole.

Figure 9 shows the zonally averaged ozone concentration (i.e., averaged over longitude) versus latitude and altitude for a particular date (March 22). As was already apparent in Fig. 6, the absolute concentration of ozone varies by about an order of magnitude over the lower 20 km of the atmosphere, being nearly ten times higher at 22 km (about 50 mbars) than at 5 km (about 500 mbars). The mixing ratio (mole fraction) varies by more than two orders of magnitude, from about 30 ppbv near the surface to nearly 10 ppm at 33 km.

Figure 10 (adapted from Fig. 8) shows the seasonal variation in zonally averaged total ozone for three different latitudes in the Northern Hemisphere. Both the annual average and the amplitude of the seasonal variation are larger at higher latitudes.

All of these features of the ozone distribution have been established for many years, based mainly on data gathered at some 30 permanently established ozone monitoring stations around the world (but mainly in the Northern Hemisphere and all on land). In recent years, observations from

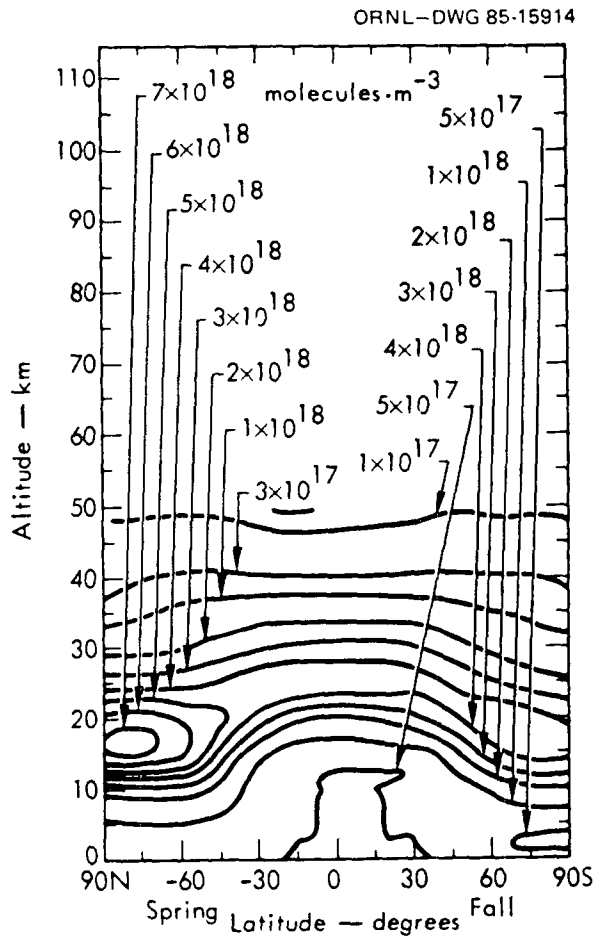


Fig. 9. Zonally averaged ozone concentration versus latitude and altitude for a standard March 22. *Source:* MacCracken and Chang (1975), Fig. A-7.

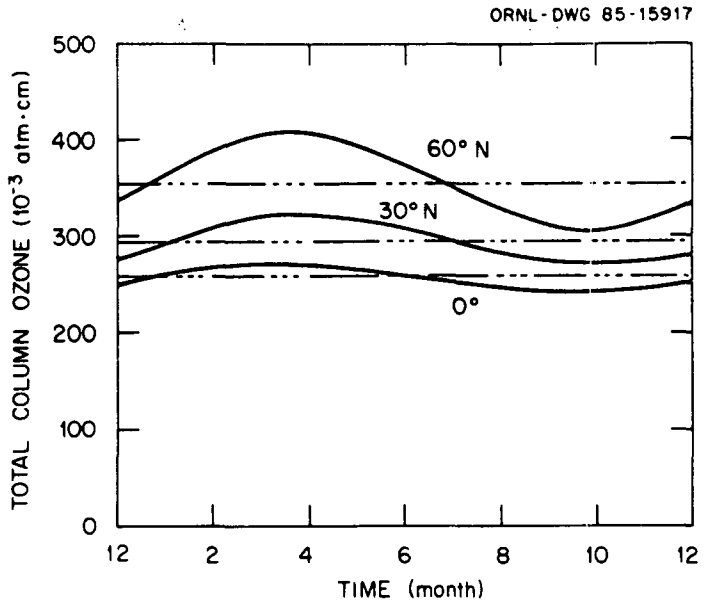


Fig. 10. Seasonal variation in zonally averaged total ozone for three different latitudes. *Source:* Adapted from Fig. 8.

instrumented satellites, based on backscattered uv light and on the atmospheric transmission of ir radiation, have made possible an almost continuous monitoring of total ozone over a major part of the earth's surface. Figure 11 illustrates the kind of detailed data that have become available as a result of this new and powerful tool. It is interesting to note total ozone variations of as much as 35% over a ten-day period (e.g., 60°S, 20°E, June 13 to 23, 1969). Of course, these short-term fluctuations are of less relevance to the present discussion than are the long-term averages.

Of course, the uv intensity at any point on the surface does not depend only on the total ozone column density over that point. Additional large variations in uv intensity are introduced by the higher average insolation at low latitudes and also by the slant angle through which the light must penetrate the atmosphere at high latitudes. All of these factors favor higher uv intensities at low latitudes.

It should be pointed out that 2-D models of atmospheric chemistry, while generally confirming the results of 1-D calculations of Cl-related ozone depletion, do indicate a latitude and seasonal dependence for the percentage reduction in total column ozone, the depletion being larger where O_3 concentrations are already higher, that is, at higher latitudes and in the spring season (Pyle 1980; Borucki et al. 1980).

ORNL–DWG 85-15918

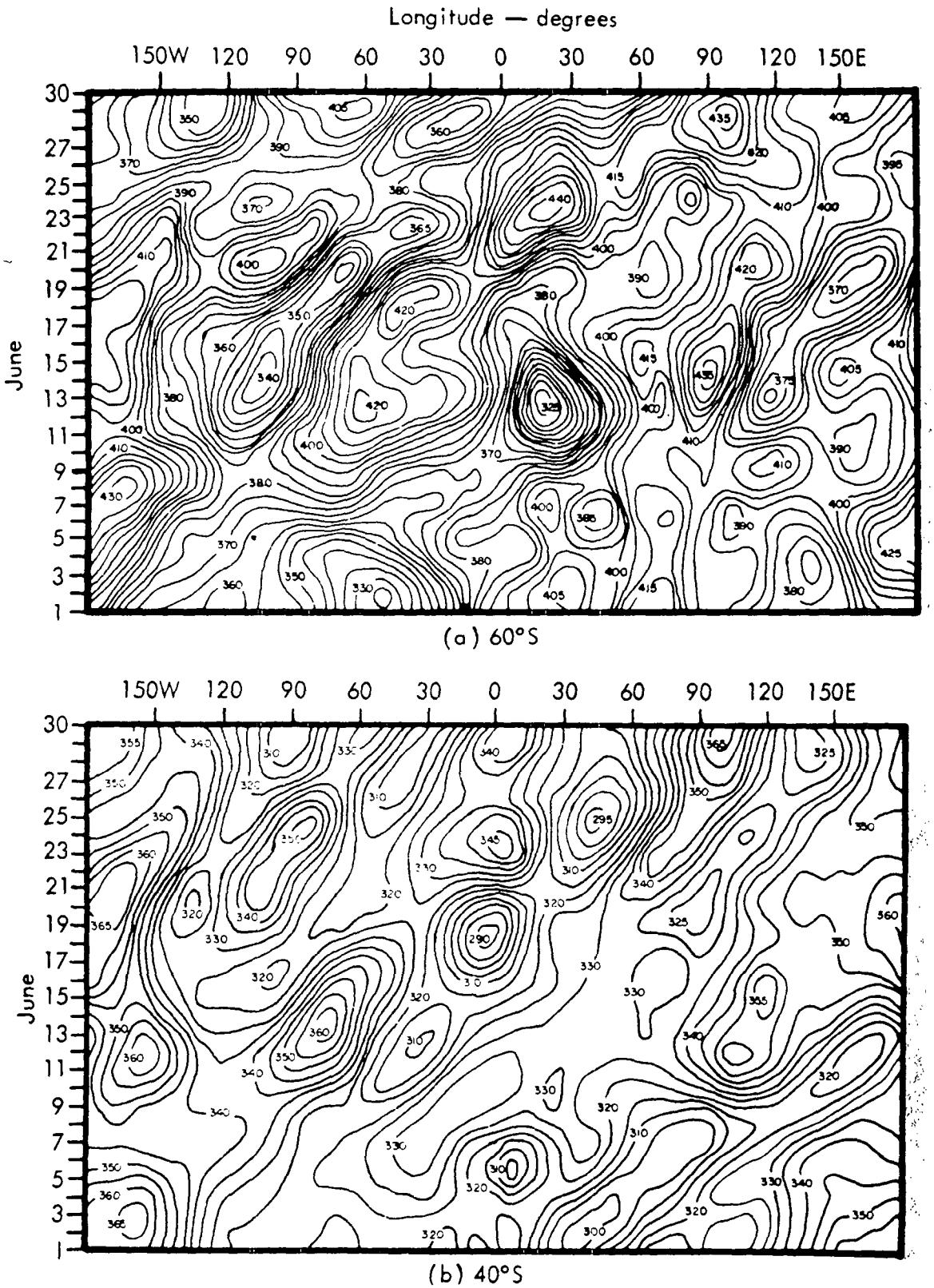


Fig. 11. Time–longitude variations of total ozone during June 1969 [after Reiter and Lovill (1974)]. (Isolines are in 10^{-3} atm·cm.) *Source:* MacCracken and Chang (1975), Fig. A-10.

6. EFFECTS OF OZONE DEPLETION AND INCREASED UV RADIATION

6.1 UV RADIATION AND BIOLOGICAL RESPONSE FUNCTIONS

The biological effects of uv radiation have been extensively reviewed by the National Research Council in the series of reports already referred to and especially in the last two reports of the series (NRC 1982, 1984). However, a quantitative assessment of the effects remains elusive, and no firm guidelines can yet be identified to suggest how much reduction in total column ozone is "too much."

The radiation of greatest concern lies in the wavelength interval from about 290 to about 320 nm, often referred to as uv-B. Both the transmittance of the atmosphere for uv radiation and the biological effects of uv radiation are very steep functions of wavelength in this range. The intensity of uv light reaching the earth's surface is more than four orders of magnitude less at 290 nm than at 320 nm, while the biological sensitivity (i.e., the damage potential) is some three orders of magnitude greater. This is well illustrated in Fig. 12. Figure 12 shows three curves for the relative intensity of uv light reaching the surface; these correspond to a normal ozone shield density (i.e., a total layer thickness of about 3.4 mm if all the ozone in the atmosphere were spread on the surface at standard atmospheric temperature and pressure), a 53% reduction of total ozone, and complete absence of the ozone shield. Also shown are three sensitivity curves, or response functions: one for human sunburn (erythema), one for damage to DNA, which is believed to be relevant to the frequency of skin cancers, and one for the Robertson–Berger uv meter, an instrument to measure relative uv intensities at different locations.

It is clear from Fig. 12 that the change in uv intensity at the surface that would be caused by a reduction in total column ozone is also a marked function of wavelength. This is further illustrated in Fig. 13, which shows the factor by which the uv intensity would be increased by a 53% reduction in total ozone. Also shown in Fig. 13 is the ratio of the Robertson–Berger meter response to the DNA response (often called the DNA Action Spectrum, but including here a factor for the uv transmittance of human epidermis).

The total response of the measuring instrument or of a biological system is the integral over wavelength of the product of the uv flux times the response function, that is,

$$D = \int \phi(\lambda)\, R(\lambda) d\lambda \ ,$$

where λ is the wavelength of the radiation, $\phi(\lambda)$ is the uv flux intensity, and $R(\lambda)$ is the response function.

The integrand in this expression, the product $\phi(\lambda)\ R(\lambda)$, is plotted in Fig. 14 for two uv spectra (the normal spectrum, with 3.4 atm·mm of ozone, and a perturbed spectrum, with 1.6 atm·mm of ozone) and for two response functions (the DNA Action Spectrum and the Robertson–Berger meter response). (The normalization of these products is arbitrary; our concern

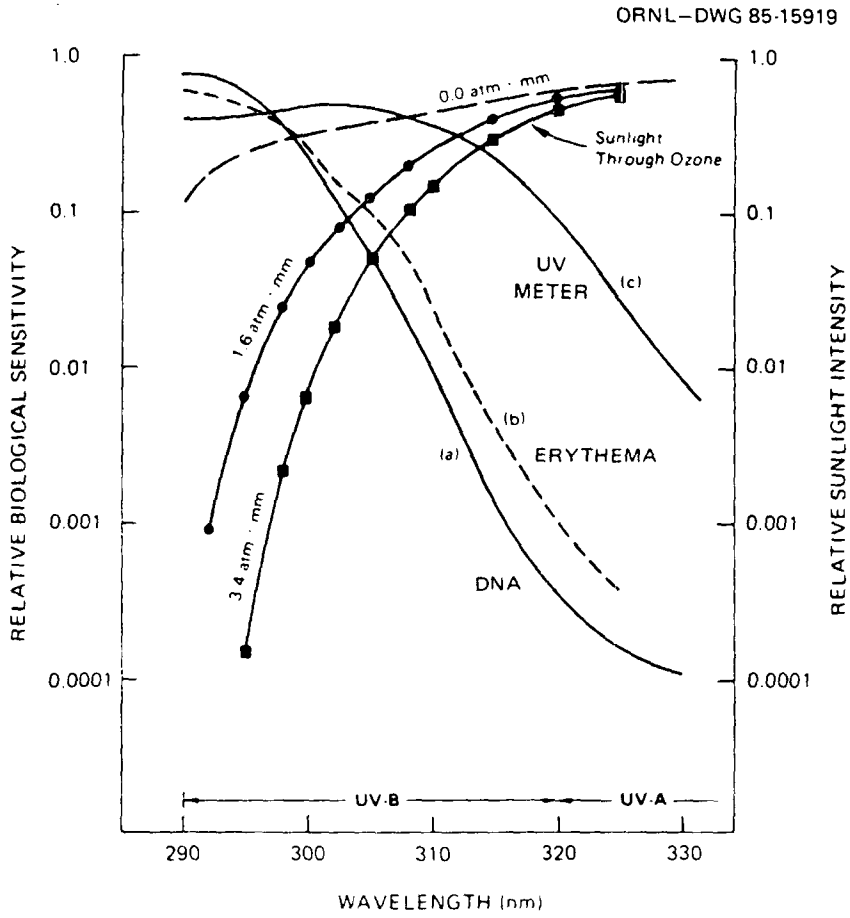


Fig. 12. The relative intensity of sunlight (solar elevation of 60°) reaching the surface of the earth for different amounts of stratospheric ozone (the normal amount is close to 3.4 atm·mm). The shapes of two biological sensitivity curves are also shown: (a) damage to DNA multiplied by the transmission of human epidermis and (b) human erythema, or sunburn. Curve (c) is the response of the Robertson–Berger meter. [*Source:* The three curves of sunlight intensity are from U.S. Congress, Senate (1975); the two biological sensitivity curves are from Setlow (1974) and Scott and Straf (1977); the Robertson–Berger meter curve is from Berger, Roberston, and Davies (1975).] Reproduced from NRC (1982), Fig. 2.2.

will be for the ratios of the integrals with different amounts of atmospheric ozone.) Three points may be noted:

1. The integrands are strongly peaked, indicating the narrow range of wavelengths pertinent to this discussion.

2. For the DNA response, shorter wavelengths are more important than for the Robertson–Berger meter.

3. The ratios of the integrals for the perturbed and normal uv spectra are different for the two response functions; that is, when the DNA response is considered, the response for the perturbed uv spectrum is 3.8 times larger than for the normal uv spectrum, as compared with a ratio of 1.6 when the response of the Robertson–Berger meter is used.

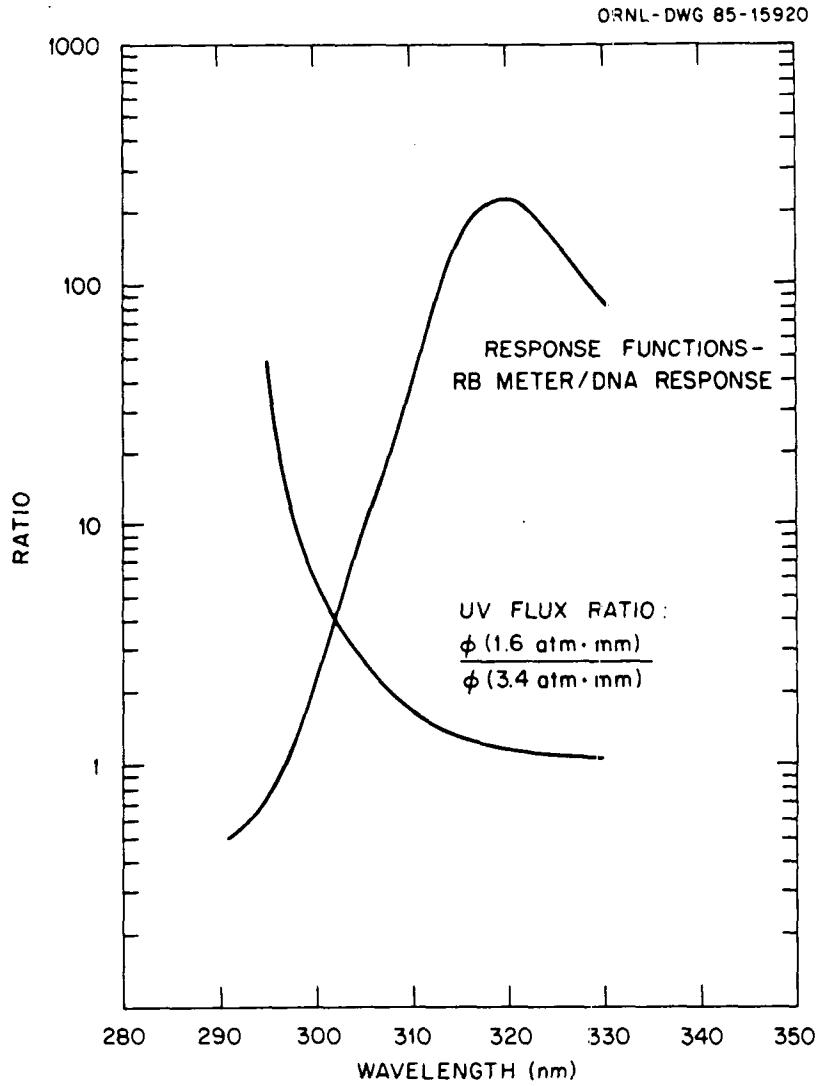


Fig. 13. Ratio of uv fluxes at the surface for two different ozone densities and ratio of response functions versus wavelength. *Source:* Adapted from Fig. 12.

A common rule of thumb has been that a 1% decrease in total column ozone would produce a 2% increase in damaging ultraviolet (duv), but it has been well recognized that the factor [(percentage increase in duv) divided by (percentage decrease in ozone)]—sometimes called the Radiation Amplification Factor (RAF)—depends very much upon the particular response function chosen. Gerstl, Zardecki, and Wiser (1981) showed that the RAF is also a function of latitude and season. For a 10% reduction in total ozone, they found RAF values of 2.1–2.5 for erythema and 2.8–3.0 for DNA. However, the DNA response function used by Gerstl et al. (1981) (essentially that of Setlow 1974) does not include the skin transmission factor that is included in curve a of Fig. 14. It therefore weights the shorter wavelengths (290–300 nm) somewhat more, leading to a larger RAF. Allowance for the skin transmission factor reduces the RAF about 10% (i.e., to about 2.5). We therefore assume in this study that a 10% reduction in ozone would produce a 25%

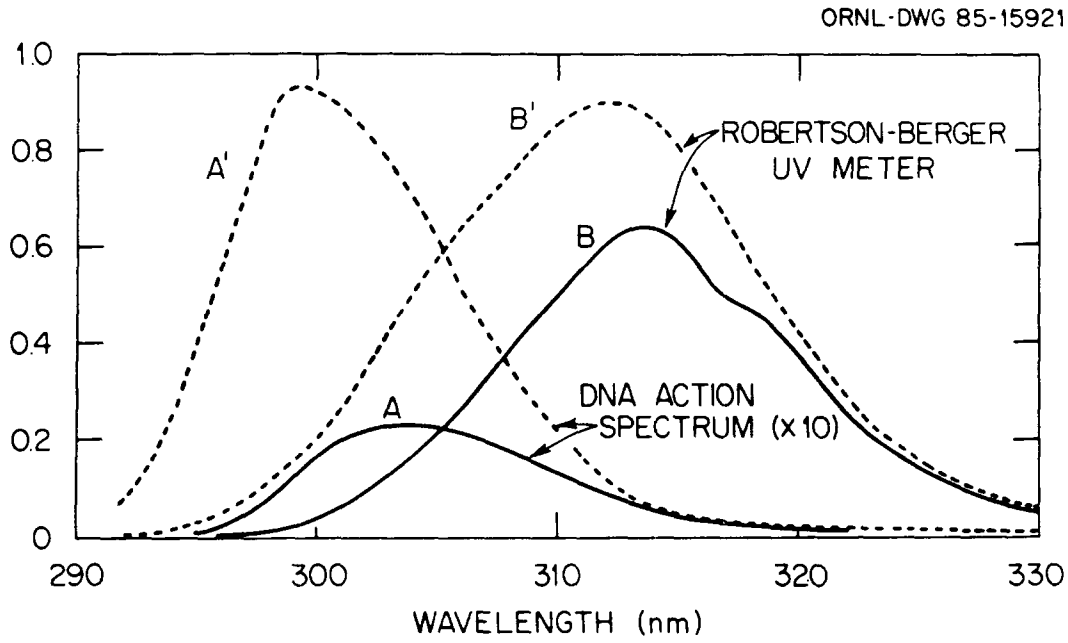


Fig. 14. Product of uv spectrum at the surface and uv response functions versus wavelength. Solid curve: normal spectrum, 3.4 atm·mm O_3; dashed curve: perturbed spectrum, 1.6 atm·mm O_3; A,A′: DNA action spectrum (×10); B,B′: Robertson–Berger uv meter response (units: arbitrary). *Source:* Adapted from Fig. 12.

increase in duv. [It should be noted that the RAF, referring always to the same initial ozone amount, necessarily increases with increasing ozone depletion; that is, for 10% ozone depletion, the RAF is about 2.5; for 20% depletion it is about 2.8 (i.e., 55–60% increase in duv) and for 30% depletion about 3.2 (i.e., 100% increase in duv)].

The following discussion of the biological effects of uv radiation is based mainly on the extensive reviews given by the NRC, especially in their 1982 and 1984 reports. We consider the effects on human beings, on plants, on domestic animals, and on marine biota.

6.2 EFFECTS OF UV ON HUMAN BEINGS

Concern over the possibility of increasing uv intensity is focused mainly on the incidence of skin cancer. These cancers are of three principal types: (1) basal-cell carcinomas, (2) squamous-cell carcinomas, and (3) melanomas.

In the United States, the incidence of nonmelanoma skin cancers is around 200–400/year per 100,000 people and is confined almost entirely to light-skinned people. These carcinomas are rarely fatal (about 1 in 100 cases). The incidence of melanomas is much less, roughly 7/year per 100,000 people, but about one-third of the cases result in fatality. Thus the overall mortality rates for melanomas and for nonmelanoma skin cancers are comparable. Ultraviolet is clearly implicated in the incidence of nonmelanoma skin cancers. Indeed, it is believed that more than 90% of these cancers are caused by exposure to sunlight.

Annual total uv intensity varies more than a factor of 2 over the United States. This is shown in Fig. 15, which shows the total response of a Robertson–Berger uv meter, integrated over one year at representative locations throughout the country. Not counting the Mauna Loa station, the

ORNL–DWG 85-15922

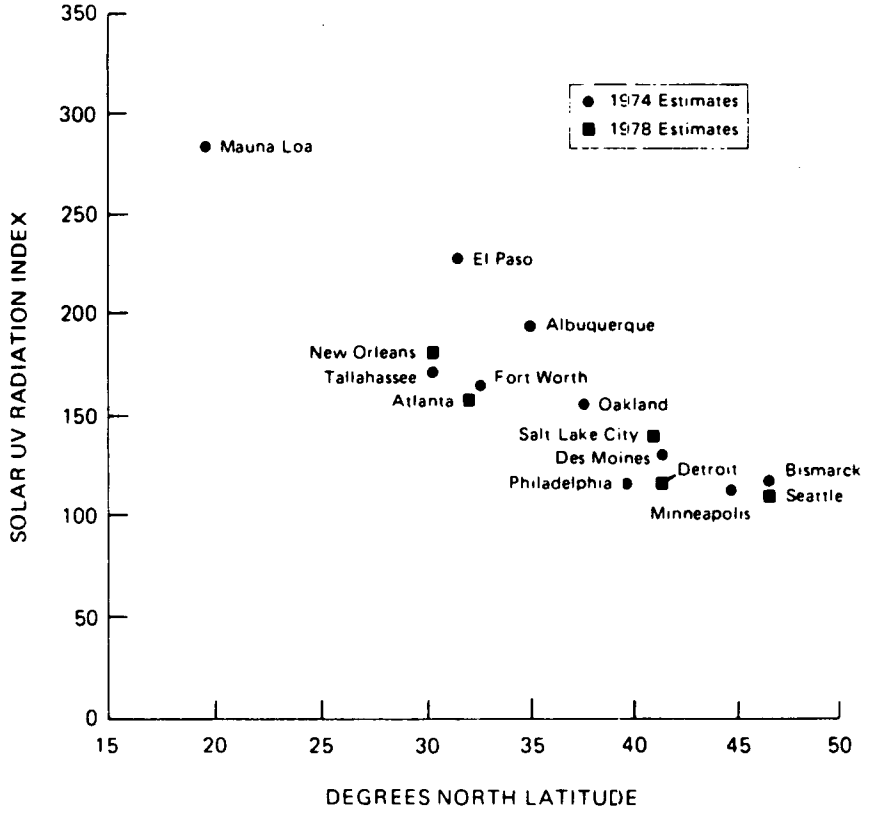


Fig. 15. Annual uv measurements by latitude, 1974 and 1978. The uv radiation index is total Robertson–Berger meter counts over a one-year period multiplied by 10^{-4} (preliminary monthly averages provided by Daniel Berger of Temple University for the 1978 estimates). The meters read uv-B between 290 and 320 nm, as well as some uv-A. [Modified from Scotto, Fears, and Fraumeni (1982).] Reproduced from NRC (1982), Fig. 5.3. (Reproduced with permission from the W. B. Saunders Co.)

range of variation is from about 100 in Seattle to about 225 in El Paso. (The units may be considered to be arbitrary.)

The incidence of nonmelanoma skin cancers is strongly correlated with latitude, as shown in Fig. 16; it varies more than a factor of 2 from north to south. By comparison (Fig. 16), the incidence of all other cancers is essentially independent of latitude.

The NRC has correlated the incidence of basal-cell, squamous-cell, and melanoma skin cancers with uv index (the total annual uv intensity as measured by a Robertson–Berger meter) for white males and for white females in the United States. The correlations are shown in Fig. 17 and 18. Note that the data are fitted to straight lines on a semilog plot, that is, $y = a \exp(bx)$, where y is the incidence of skin cancers and x is the uv index. A characteristic of this particular functional form is that the logarithmic derivative of y with respect to x is proportional to x, that is, $(dy/y) \div (dx/x) = bx$, which, as noted, varies more than a factor of 2 over the coterminous states.

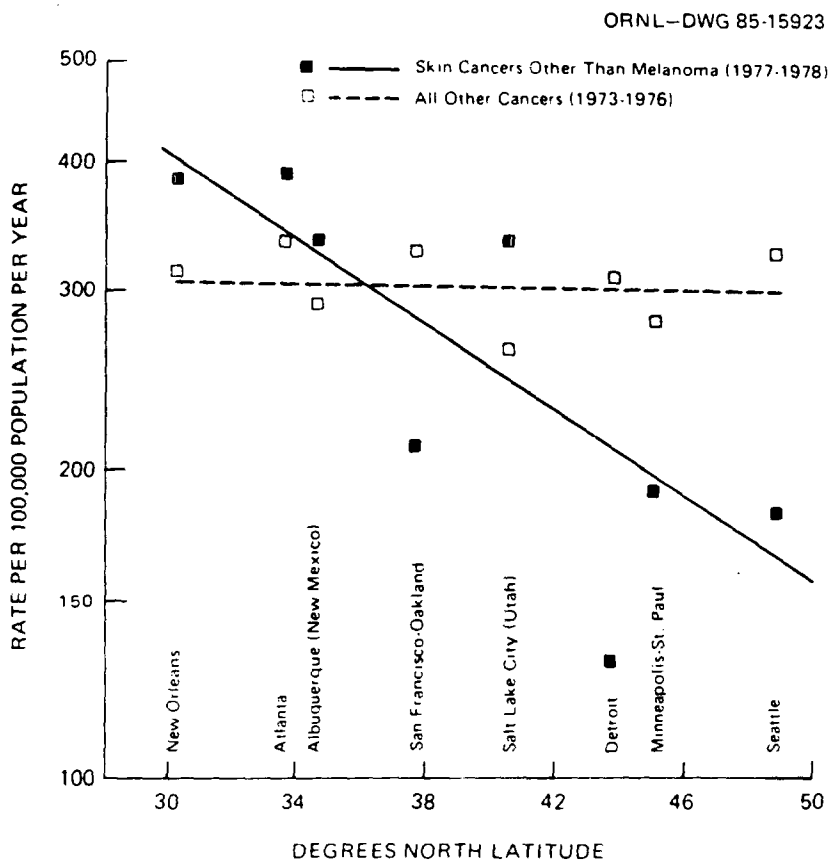
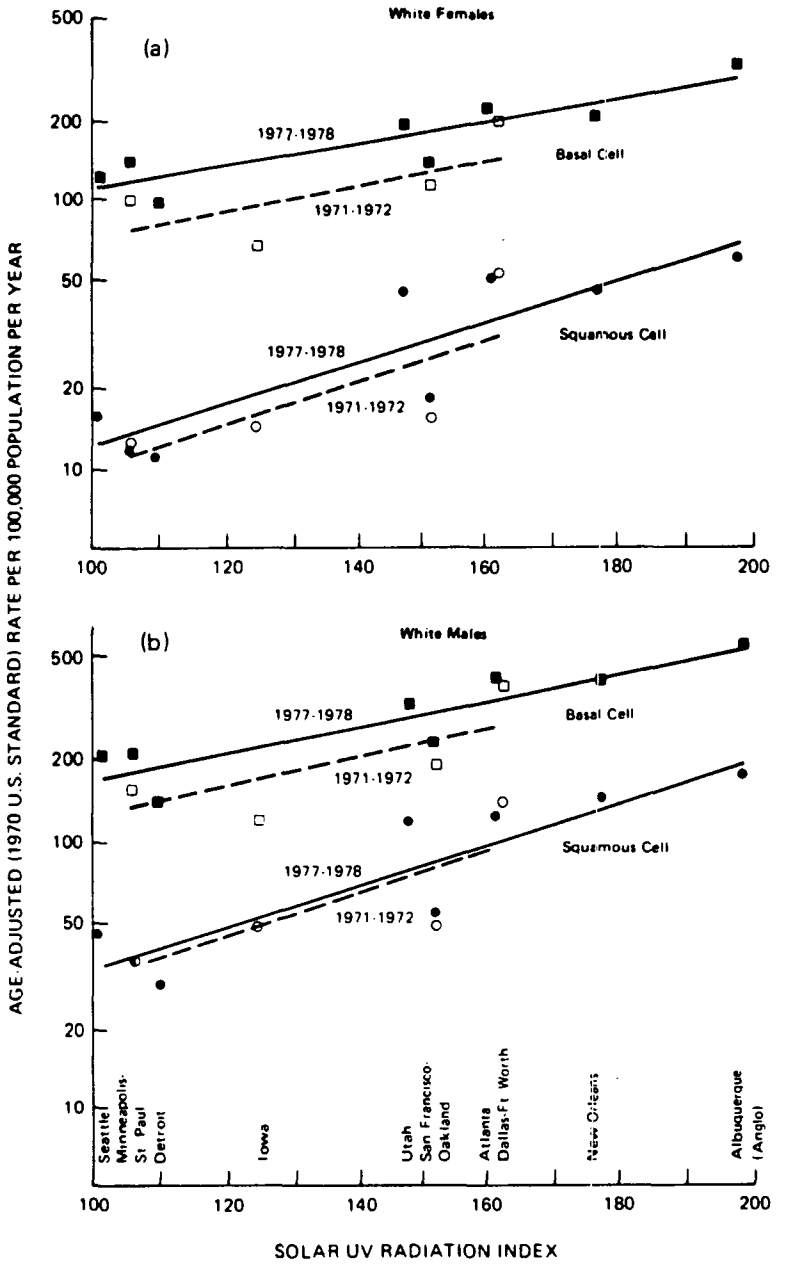


Fig. 16. Annual age-adjusted incidence rates (1970 U.S. standard) for basal- and squamous-cell skin cancer (1977–1978) and all other cancers (1973–1976) by latitude in the U.S. white population [Scotto, Fears, and Fraumeni (1982)]. Reproduced from NRC (1982), Fig. 5.4. (Reproduced with permission from the W. B. Saunders Co.)

There seems to be no theoretical reason for selecting an exponential model for correlating the rather widely scattered data (other than the convenience of making a linear least-squares fit of ln y versus x). It seems to us that the data might almost as well have been fitted by a power-law relation, $y = ax^b$, for which the logarithmic derivative is $(dy/y) \div (dx/x) = b$ (i.e., a constant). Thus the latitude dependence of the sensitivity (here defined as the fractional change in incidence versus the fractional change in uv index) which was noted in the NRC reviews (e.g., NRC 1982) may be open to question.

It is generally believed that the DNA Action Spectrum is a better representation of the effectiveness of uv light in inducing skin cancers than is the response function of the Robertson–Berger meter. As pointed out by the NRC, the ratio of DNA response (i.e., the DNA-weighted uv spectrum) to Robertson–Berger meter response will change differently with latitude than with decreasing ozone concentration. Thus the question of how much the incidence of skin cancers would increase for a given percentage decrease in total column ozone density remains rather elusive. The NRC (NRC 1982) has estimated that, for a 1% decrease in ozone, the incidence of basal-cell carcinomas (currently accounting for about 80% of all skin cancers in the United States)

ORNL–DWG 85-15924



NOTE For each sex and cell type, the model used to fit the data is log incidence = $\alpha + \beta F$, where F is the flux in annual R-B meter counts x 10^{-4}

Fig. 17. Annual age-adjusted incidence rates for basal- and squamous-cell cancers among white females and males for two surveys, 1977–1978 (closed symbols) and 1971–1972 (open symbols), according to one year's uv measurements at selected areas of the United States. The uv radiation index is the total Robertson–Berger meter counts over a one year period multiplied by 10^{-4}. The meters read uv-B between 290 and 320 nm, as well as some uv-A. [Adapted from Scotto, Fears, and Fraumeni (1981).] Reproduced from NRC (1982), Fig. 5.5.

ORNL–DWG 85-15925

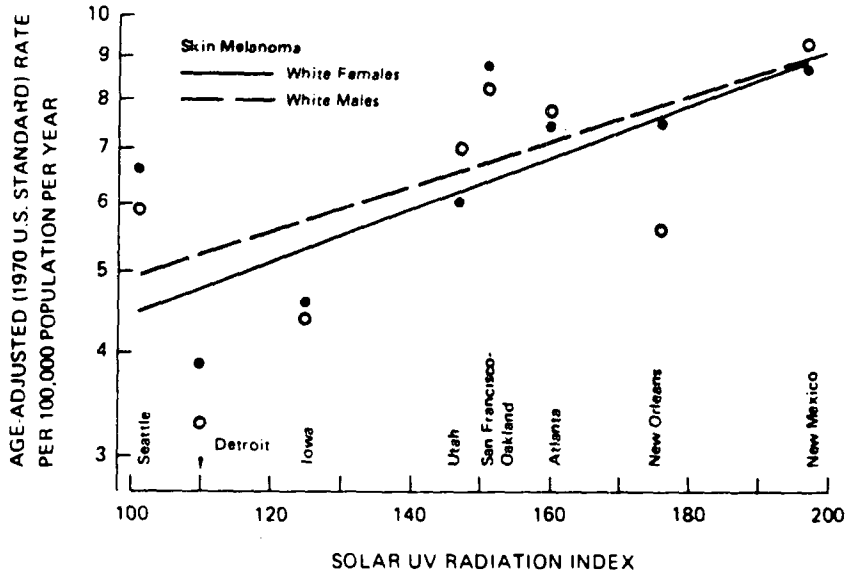


Fig. 18. Annual age-adjusted incidence rates for skin melanoma (SEER data, 1973–1976) among white females (open symbols) and males (closed symbols), according to one-year's uv measurements at selected areas of the United States. The uv radiation index is the total Robertson–Berger meter counts over a one-year period multipled by 10^{-4}. The meters read uv-B between 290 and 320 nm, as well as some uv-A. (J. Scotto, National Cancer Institute, personal communication, 1981.) Reproduced from NRC (1982), Fig. 5.7.

would increase between 2% and 5%, depending on latitude; for squamous-cell carcinomas (<20% of total incidence), the estimates are about twice as large. These estimates were obtained with the help of the exponential model, with its inherent latitude dependence, as noted above.

In view of the difficulty of determining the sensitivity factors more precisely, we assume for purposes of this study a sensitivity factor equal to 4-6; that is, a 1% decrease in total ozone would produce roughly a 5% increase in the incidence of nonmelanoma skin cancers, all other factors being equal.

For melanomas, the situation is much less clear. Although it seems likely that exposure to sunlight is a contributing factor in the incidence of at least some types of melanomas, the evidence is confusing and often conflicting. There is no doubt that the incidence of malignant melanomas has been increasing rapidly worldwide over the past half-century. However, the role of uv radiation is not yet clear and there is no adequate basis, at present, for projecting an increase in incidence of melanomas as a result of decreasing total column ozone density.

There is growing evidence (NRC 1984), primarily from small-animal studies but also from a few observations on human subjects, that exposure to uv radiation can modify the immune response system and may impair the body's ability to react to certain kinds of insults. This raises the possibility that the effects on humans of long-term exposure to uv-B could extend beyond the incidence of skin cancers. However, the implications of the evidence available thus far are still far from clear.

At the end of this discussion of the effects on people which might follow from a reduction in the ozone shield, the fact remains that much depends on individual behavior. As observed by the NRC (NRC 1982), excellent sunscreens are available which can reduce uv intensity at the skin by as much as a factor of 10. Avoidance of exposure to sunlight during a few hours around midday

can also diminish total uv exposure by much larger factors than the factors of increase that might result from any anticipated depletion of ozone.

6.3 EFFECTS OF UV ON PLANTS

It seems clear that uv-B inhibits photosynthesis and damages plants in various ways. However, the damage can be at least partly repaired by uv-A (320–400 nm) and by visible light (400 to 700 nm). Experiments conducted in growth chambers with high intensities of uv-B but with much lower than ambient levels of visible light may, by not providing the opportunity for these repair mechanisms to operate, lead to serious overestimates of the damage to be expected from increased uv-B intensities. Also, some plants appear to have compensating mechanisms for adaptation to higher levels of uv-B, for example, by production of epidermal pigments that absorb uv. Plants of the same species growing under very different ambient uv intensities (e.g., at low altitudes in high latitudes or at high altitudes in the tropics) are found to have very different amounts of these pigments—enough, in general, to produce roughly comparable levels of uv beneath the epidermis. It may be noted that there is a sevenfold variation between the equator and 70° latitude in the total daily dose of uv (weighted by the DNA Action Spectrum) when measured at the time of seasonal solar radiation maximum. The variation in total annual uv dose is even larger.

According to Teramura (1986), over 200 species of plants have been screened for uv sensitivity and two-thirds of these were found to be sensitive in various degrees. Among the most sensitive are peas, beans, squash, melons, and cabbage. Most of the evidence is based on indoor experiments, subject to the difficulty mentioned above. Only a few field experiments have been done and extensive data are available only for soy bean, which apparently is among the most sensitive plants tested so far. For uv intensities corresponding to a 25% reduction in total column ozone, reductions in soy bean yield up to 20–25% were found. Crop quality (oil and protein content) was also diminished. Yield reduction also depends on other conditions, such as the amount and distribution of rainfall and is less for some cultivars than for others.

The question of possible adaptations and compensating adjustments over long periods of time is an important one but seems still to be largely a matter of speculation.

The effect of increased uv intensity on the unmanaged biosphere is even less clear, although it is expected that interspecies competition would be affected.

On balance, it is not clear that small increases in uv intensity, such as might accompany a few percent decrease in total ozone, would present any significant problems for plants.

6.4 EFFECTS OF UV ON DOMESTIC ANIMALS

There does not appear to be a problem for domestic animals associated with any expectable increase in uv. Ultraviolet light is probably implicated in eye cancer in White-faced Hereford cattle, but the incidence of this disease is low. The NRC appears to discount any threat to animals (NRC 1982).

6.5 EFFECTS OF UV ON MARINE BIOTA

Ultraviolet light is absorbed in seawater mainly by colored matter in the water. This matter is apparently primarily of plant origin and is brought to the sea mainly by rivers. It is more

concentrated near the continental shelves than in the open ocean far from continents; that is, uv absorbtion is strongest in regions of the ocean that are most productive of marine life.

The uv absorption lengths vary greatly from place to place, but a typical value, within a factor of 2 either way, would be on the order of 1 m (for attenuation by a factor *e*).

Ultraviolet effects on phytoplankton would be largely confined to a surface layer on the order of a meter thick; the effects would be small when integrated over the whole layer in which photosynthesis occurs.

It is known that fish larvae (e.g., anchovettes, the larvae of anchovies) are very sensitive to uv and may be seriously or fatally damaged by exposure to above-ambient levels of uv. However, the usual distribution of these organisms is over depths much greater than the uv can penetrate; small variations or adjustments in this distribution would compensate for a significant fractional increase in uv intensity at the surface.

Worrest (1986) pointed out that many aquatic organisms exhibit a threshold tolerance for uv radiation (actually both a dose-rate threshold and a total dose threshold) and that most of these organisms, especially in their larval stages, seem under present conditions to be operating close to those thresholds. Above-threshold doses result in greatly increased mortality. In latitudes where daily uv fluence increases greatly from winter to summer, the larvae of late-spawning species exhibit a correspondingly higher tolerance than those of early-spawning species. Worrest also pointed out that vertical mixing near the surface of the ocean can afford a significant degree of protection. Model calculations show that the extent of that protection (measured in reduced mortality) depends both on the depth of the mixed layer and on the postulated increase in uv intensity. For large increases in uv, mixing can increase mortality by increasing the number of individuals exposed to above-threshold doses (Worrest 1986).

It was estimated that for a 10% reduction in total column ozone about 8% of the annual larval population in the whole water column would be killed by the direct effects of increased uv, with the possibility of additional losses due to indirect effects such as diminished food supply.

It is well recognized, however, that uncertainties related to ecosystem dynamics are much greater than those related to uv effects on individuals. Organisms normally reproduce far beyond the minimum levels required to maintain their populations. Thus, the extent of the potential damage to marine biota arising from some increase in uv intensities is far from clear. There should probably be no great concern for the consequences of a few percent reduction in ozone, that is, up to a 20–30% increase in uv.

6.6 HOW MUCH OZONE DEPLETION IS TOO MUCH?

In summary, we have no clear basis for setting a practical limit on an "acceptable" increase in uv intensity at the earth's surface and hence on the decrease in ozone that might be accepted without alarm. In the absence of any such clear basis, I assume that a reduction of total ozone of 5–10%, giving rise to an increase in uv intensity of some 10–25%, would not produce effects of sufficient magnitude or severity to stimulate an effective campaign for the reduction of CLC emissions. I suggest the following highly tentative guidelines:

- 5% ozone reduction—probably acceptable;
- 10% ozone reduction—possibly acceptable;
- 20% ozone reduction—probably unacceptable; and
- 30% ozone reduction—almost certainly unacceptable.

I concede that these "guidelines" are quite speculative and are likely to be controversial. Nevertheless, they do summarize my present perspective on the question posed in the heading of this section: "How much ozone depletion is too much?" It is my belief that these suggested tentative guidelines are probably on the conservative side. That is, it seems unlikely that a 5% reduction in total ozone (roughly a 12% increase in DNA-weighted uv intensity) will be found to be "unacceptable," while there is a rather higher probability that an ozone reduction greater than 10% (corresponding to roughly a 25% increase in uv), after adaptations and behavioral changes are taken into account, will be found to be "acceptable." However, in this report we shall explore the implications of the assumption that a 5–10% reduction in ozone is acceptable but that a reduction 2–3 times larger is unacceptable.

We should not lose track of a point made earlier, namely, that a 5% reduction in total column ozone, though perhaps not considered serious in terms of uv effects, will apparently still be accompanied by a 40–50% reduction in ozone concentration in the middle-to-upper stratosphere (i.e., in the neighborhood of 40-km altitude). Since the temperature structure of the stratosphere depends very much on the absorption of uv radiation by ozone and since the stratosphere plays a significant, though not completely understood, role in determining climate patterns on earth, one must view with some concern the prospect of large reductions of upper-stratospheric ozone.

7. SCENARIOS FOR FUTURE RELEASE OF CHLOROCARBONS

For purposes of discussion and of comparison among results obtained by different groups and at different times, it has been customary to report the estimated total column ozone depletion at steady state ($t \rightarrow \infty$) for a standard, reference scenario having continued constant releases of the various CLC compounds at "current" rates. Since the emission rates, at least of CFC-11 and CFC-12, have remained roughly constant over the past decade (Fig. 1), these various results may, in fact, be reasonably compared without renormalization.

Of course, there really is no reason to expect CLC releases to remain nearly constant in the future, and certainly not over the long periods of time necessary for achieving equilibrium. On the contrary, while CLC use as an aerosol propellant might reasonably be expected to decline,* other uses such as refrigerants and industrial solvents should surely be expected to increase, at least in the absence of controls. Wuebbles, MacCracken, and Luther (1984) proposed the following three scenarios for future release of CFC-11, CFC-12, and six other CLCs (all releases remaining in the same proportions):

1. constant release at 1980 rates;
2. 3%/year increase from 1983 to 2010; constant release after 2010 at 2.248 times the 1983 rates; and
3. 3%/year decrease from 1983 to 2010; constant release after 2010 at 0.445 times the 1983 rates.

These scenarios were not intended as forecasts but were suggested to promote uniformity and facilitate comparisons among studies. Nevertheless, I have adopted them (numbers 1, 2, and 5 respectively of the scenario list below) and have considered several others as well, with two considerations in mind:

1. In the absence of controls, future CLC releases may well rise to levels greater than 2.25 times present rates.
2. After some period of increasing CLC releases, it may be decided to cut down on CLC releases. We wished to explore the possible efficacy of various "evasion" scenarios, representing possible future restrictions on the use (or release) of CLCs. Because of the very long atmospheric lifetimes of CFC-11 and CFC-12, a reversal of growth even several decades from now might be expected to reduce significantly the maximum atmospheric concentrations of these compounds.

In each of the scenarios, only two compounds are considered explicitly: CFC-11 and CFC-12. However, as will be explained in Sect. 8, the contributions of other compounds are implicitly included as a result of the procedure adopted for estimating the depletion of ozone. It is assumed in all scenarios that CLC emissions vary with time in proportion to their relative 1980 emission rates.

*After decreasing by 50% or more from 1976 to 1982, CFC use for aerosols appears to have leveled off and may be slightly increasing again (CMA 1985). Certainly the CFCs can be more easily substituted for in this application than in other major applications (NRC 1979a); future trends are difficult to foresee.

The following scenarios are considered in this study:

1. The "standard," reference scenario: constant emissions at 1980 rates, continuing into the indefinite future. (This is the central scenario of Wuebbles, MacCracken, and Luther 1984.)
2. A 3%/year increase in emissions from 1983 to 2010; constant emissions thereafter at 2.248 times the 1980 rates. (This is the "high" scenario of Wuebbles, MacCracken, and Luther 1984.)
3. A 3%/year increase in emissions from 1983 to 2033; then constant emissions at 4.48 times the 1980 rates. (This just doubles the steady-state emission rates of case 2.)
4. A 3%/year increase in emissions from 1983 to 2000, a 5%/year increase from 2000 to 2020, and then constant emissions at 4.527 times the 1980 rates. (This reaches the same level as case 3 but does so sooner. It conforms closely over the next few decades to a hypothetical scenario for future CLC releases that may be derived from recent trends, as will be explained later.)

4a. The same as scenario 4 to 2020; then a decrease at 2%/year for $t > 2020$. (This is a first example of a "remedial" or "evasion" scenario.)

5. A 3%/year decrease in emissions from 1983 to 2010; then constant emissions at 0.445 times the 1980 rates. (This is the low case of Wuebbles, MacCracken, and Luther 1984.)

These scenarios are displayed in Fig. 19, normalized to a value of unity for the 1980 release rates, that is, 0.265 Tg/year* for CFC-11 and 0.412 Tg/year for CFC-12 (Wuebbles, MacCracken, and Luther 1984). Note: Emissions are assumed to be constant from 1980 to 1983. Calculations were initialized in 1980 using tropospheric mixing ratios given by Wuebbles, MacCracken, and Luther (1984).

It should be noted that in scenarios 2, 3, and 4, growth in CLC emissions ceases abruptly at times not very far in the future (e.g., 2010, 2020) and at levels not very far above present levels (e.g., 2.25 and 4.5 times the present release rates). It is entirely possible that at least the production and use of these extremely useful compounds (if not their actual release to the atmosphere) would continue to grow to much higher levels. Thus, these scenarios (e.g., 3 and 4) are by no means the highest that might reasonably be considered. However, if these prove to be potentially troublesome, we would need to look no further to conclude that some remedial actions might be required.

The hypothetical situation referred to in scenario 4 is based approximately on recent trends and is intended to suggest that roughly constant emissions from the mid-1970s to the early 1980s and a resumption of growth in the 1980s constitute a consistent pattern. Wuebbles, MacCracken, and Luther (1984) point out that, while worldwide use of CLCs as aerosol propellants has declined in recent years, their use for other purposes has continued to increase. They assert, on the basis of data gathered by the Chemical Manufacturers Association, that (in the CMA reporting countries) aerosol use declined from 56% of total CFC production in 1976 to 34% in 1982 (Wuebbles, MacCracken, and Luther 1984, p. 30). Combining these percentages with estimated production for those years suggests the simplified hypothesis that aerosol uses are declining (and might continue to decline) at 10%/year while nonaerosol uses are growing (and might continue to grow) at 5%/year.† This leads to the following expression for recent and future CFC releases, relative to unity in 1982:

*1 Tg = 1 teragram = 10^{12} grams.

†As mentioned in the previous section, the latest CMA report on CFC production and sales (CMA 1985) shows that use of CFCs as aerosol propellants has leveled off (at a much lower level than a decade ago) and may now be increasing slowly. If this trend continues, that would modify the picture only slightly so long as the growth rate for aerosol use is much less than for nonaerosol uses.

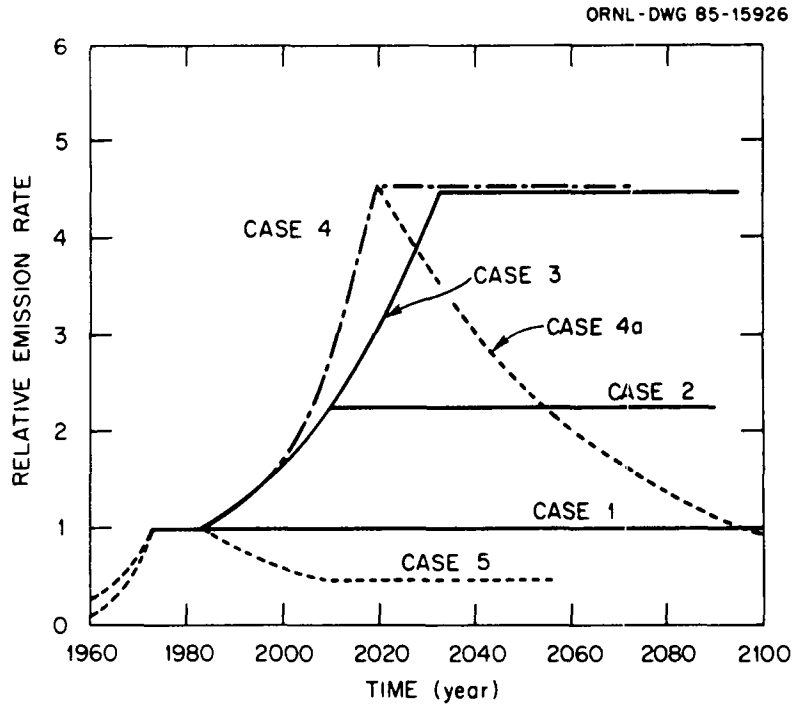


Fig. 19. CFC emission scenarios.

$$y = 1.11\{0.44 \exp[0.05(t - 1976)] + 0.56 \exp[-0.10(t - 1976)]\} .$$

A comparison of this expression with actual releases of CFC-11 plus CFC-12 and with the scenarios for this study, as described above, is given in Fig. 20.

The CFC emission scenarios described above, and in particular scenarios 2–4, which were adopted at the beginning of this study, turn out to be very much in harmony (out to the point where growth abruptly ceases in my scenarios) with emission scenarios developed by several investigators for the U.S. Environmental Protection Agency (EPA). These were presented at an EPA-sponsored workshop, "Protecting the Ozone Layer: Workshop on Demand and Control Technologies," held in Washington, D.C., March 6–7, 1986. These scenarios suggest a probable range of growth rates averaging 2–5%/year over the next half century. The most likely growth rate suggested by these scenarios seems to be around 3%/year (averaged over the next 50 years), with a low (but nonvanishing) probability of growth at 5%/year or more. Thus, my scenarios 3 and 4 may be considered as representative scenarios over the next four or five decades, with scenario 2 on the low side (limited growth). A 5%/year growth scenario will also be considered here, in the context of possible remedial action scenarios.

In addition to scenarios 1–5 above, I considered several highly schematic "remedial-action" scenarios, with reversal of growth starting at various times and with the subsequent decreases proceeding at various rates. The purpose of these scenarios is to examine the dynamics of the substitution process in which techniques and technologies that would result in much lower (or much less harmful) CFC releases to the atmosphere may gradually replace the present processes and practices whose continued use in the future is assumed in the "no-regulation" scenarios presented at

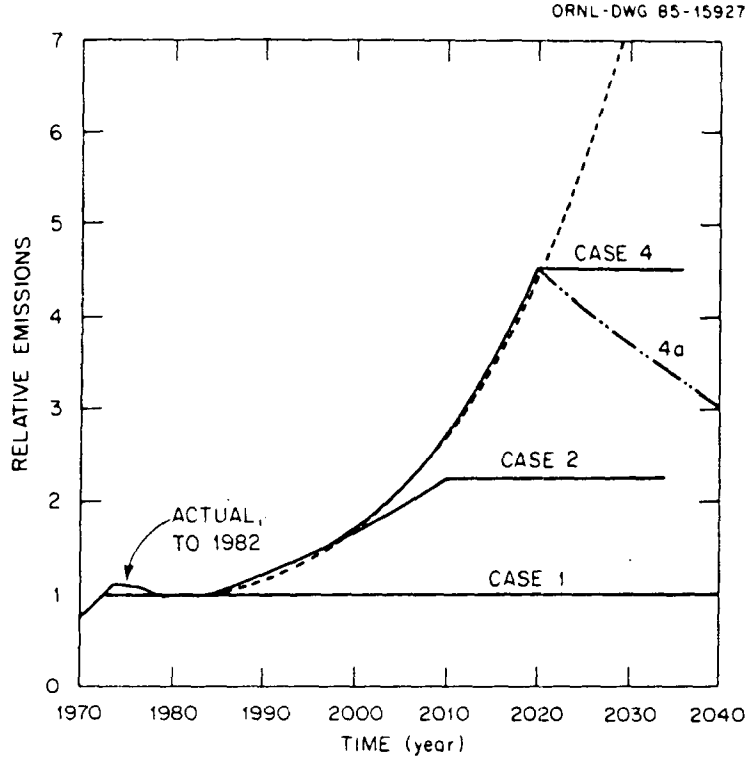


Fig. 20. One hypothetical basis for projecting CFC emissions. Dashed curve follows the expression $y = 1.11\{0.44 \exp[0.05\,(t - 1976)] + 0.56 \exp[-0.10\,(t - 1976)]\}$.

the EPA workshop. The intent here is to consider the effect of actions intermediate between a "do-nothing" policy and a "shut-everything-down-now" policy (which of course is impossible to carry out). In this way perhaps we can get a feeling for the timing and the rapidity of substitutions that might be required in order to limit the environmental impacts of continued CFC emissions.

The remedial-action scenarios considered fall into two groups. In the first group, which I refer to as "evasion" scenarios, a period of sustained growth of emissions at a constant growth rate (e.g., 3%/year) is followed abruptly by a period of declining emissions, with a constant rate of decrease (e.g., −1%/year, −2%/year, −3%/year). In the second group, which I refer to as "market penetration" scenarios, the replacement of the existing technologies (referred to as component A of the market) by substitute, nonpolluting technologies (component B) is described by a logistic function, in a manner to be described below.

The "evasion" scenarios are all keyed to scenarios 2 and 3, with a 3%/year growth rate starting in 1983:

- 3a. Continued 3%/year growth past 2033 (until 2080).
- 3b.1. A 3%/year increase from 1983 to 2030; then a 1%/year decrease starting in 2031.
- 3b.2. A 2%/year decrease starting in 2031.
- 3b.3. A 3%/year decrease starting in 2031.
- 3c.1. A 3%/year increase from 1983 to 2020; then a 1%/year decrease starting in 2021.
- 3c.2. A 2%/year decrease starting in 2021.

- 3c.3. A 3%/year decrease starting in 2021.
- 2a.1. A 3%/year increase from 1983 to 2010; then a 1%/year decrease starting in 2011.
- 2a.2. A 2%/year decrease starting in 2011.
- 2a.3. A 3%/year decrease starting in 2011.
- 2b.2. Follows scenario 2 to 2040; then a 2%/year decrease in emissions starting in 2041.

These scenarios are illustrated in Fig. 21. They will simply serve to illustrate, in a very general way, the reduction in ozone depletion and in climatic warming that would result from moving from a period of growth in CFC emissions to a period of decreasing emissions.

Of course, one would not expect such an abrupt reversal of growth actually to occur; the sharp cusps are to be viewed as simplified approximations to a more gradual transition from growth to decline, which would have to begin 10–15 years before the cusps in these idealized scenarios. It is this (unspecified) earlier date that must be visualized in judging when effective actions might have to begin to limit the maximum concentrations of CLCs in the atmosphere.

In order to represent the dynamics of the substitution process in a little more detail, I have also considered a series of "market penetration" scenarios in which two technologies, or groups of technologies (the established group, component A, and the replacement group, component B) together supply the entire market. The market share, f, of the new component B is described, in the manner of Fisher and Pry (1970), by the logistic equation

$$f(1-f)^{-1} = ke^{b(t-t_0)} \tag{1}$$

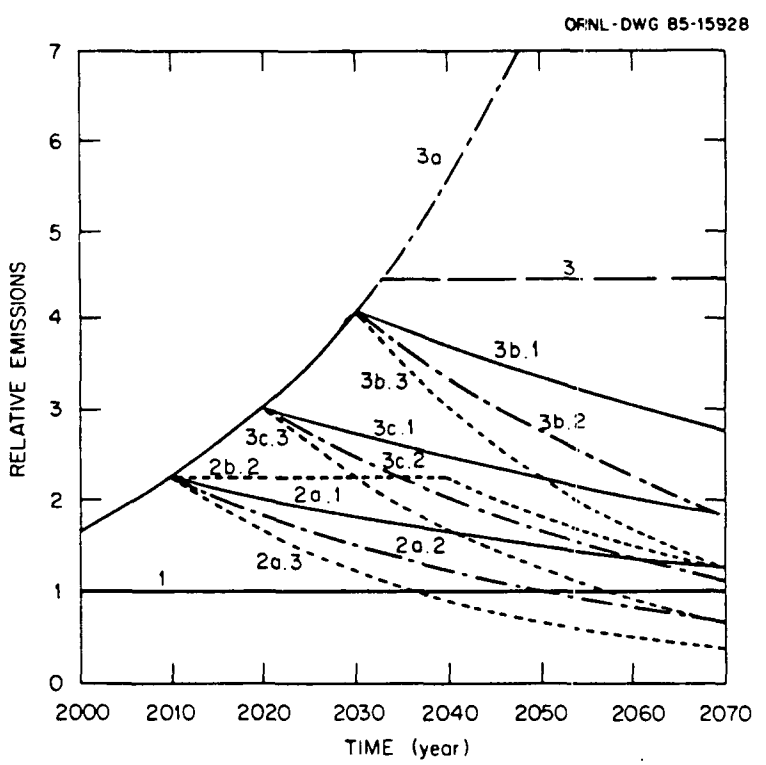


Fig. 21. CFC emission scenarios with remedial actions (evasion scenarios).

If t_0 is chosen as the time when component B attains a market share of 1%, then $k = 0.01/0.99 = 0.0101$. We may characterize the rapidity of the substitution process by noting the time, T, in which the market share of the "nonpolluting" component B increases from 1 to 50%. This is given by

$$T = \ln 99/b = 4.595/b \quad . \tag{2}$$

I assume that the total market, $M = A + B$, is growing at the constant annual rate r, that is, $M = M(t_0) \exp r(t - t_0)$. Thus, the amplitude of component B is given by

$$B(t) = M(t_0)\exp r(t - t_0) \frac{k \exp b(t - t_0)}{1 + k \exp b(t - t_0)} \tag{3}$$

and that of the older component, A, by

$$A(t) = \frac{M(t_0)\exp r(t - t_0)}{1 + k \exp b(t - t_0)} . \tag{4}$$

Equation (4) gives us the CFC emissions as a function of time in the market penetration scenarios. If b is larger than r, the annual CFC emissions, after first going through a peak, will eventually fall to zero (or some arbitrarily small amount).

I have considered such market penetration scenarios with:

r = market growth rate
= 0.02, 0.03, 0.04, 0.05/year (2–5%/year)
b = market penetration parameter
= 0.08, 0.10, 0.12, 0.15, 0.30/year
T = time for B to go from 1 to 50% market share (Eq. 2)
= 57, 46, 38, 31, 23 years
t_0 = time when B reaches 1% market share
= 10, 20, 30, 40, 50 years after 1983.

A small sampling of these scenarios, for 3%/year growth rate in the total market ($r = 0.03$/year), is shown in Fig. 22.

In order for such a formulation to be useful, one must have some feeling for the market penetration rates that might be achievable in practice, whether driven by ordinary market forces or by regulation. The chlorofluorocarbon market is of course very heterogeneous. The aerosol segment of the market (once the dominant segment) can change very rapidly, as experience in the past ten years has shown. The refrigeration and air-conditioning segment of the market is characterized by mature technologies and by equipment with typical lifetimes of ten or twenty years. The plastic foam segment and the electronic component segment of the market have no CFC customers at the retail level, but have a relatively small number of producers with investments in manufacturing facilities that are tied to specific processes. The National Research Council (NRC 1979a, Tables 6.4–6.22) has estimated the times likely to be required for "implementation" and for "full effectiveness" of various alternatives in each CFC application. Implementation times (analogous to the 1% market penetration time, t_0, in the present study) were estimated in most cases to be less than ten years, 10–20 years in a few cases, and more than 20 years, in a very few cases (e.g.,

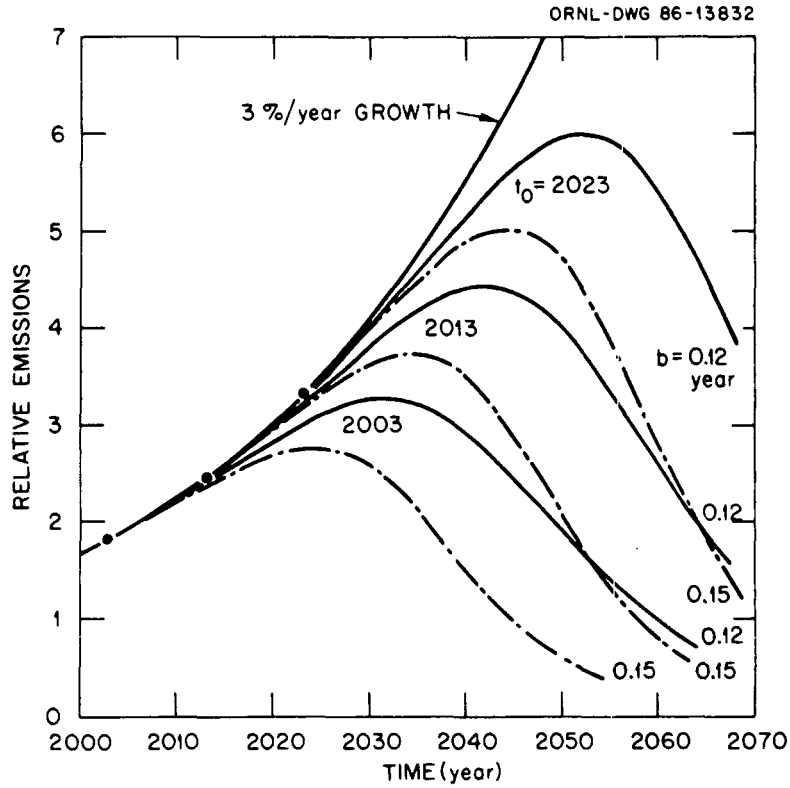


Fig. 22. CFC emission scenarios with remedial actions (market penetration scenarios).

introduction of certain alternative refrigeration cycles). Times to full effectiveness (analogous to >>50% market penetration in this study?) were in many cases estimated to be less than ten years, in some cases ten to twenty years, and in a few as long as thirty years. "Banked" CFCs (stored, for example, in closed-cell plastic foams) may continue to be released for many years; although these may prevent future CFC releases from being reduced to very low levels, they will become relatively unimportant if no further substantial deposits in the bank are being made.

I adopt here what I believe to be a conservative view: that a time lapse of 40 years from 1 to 50% market penetration is likely to be relatively easy to achieve for the aggregate CFC market (measured in terms of nonemitting versus emitting equipment and practices), that 30 years may also be considered a reasonable market penetration time (1 to 50% market share), and that 20 years may be considered to represent a rather tight schedule. Making use of Eq. (2), one can relate these to the market penetration parameter, *b*, as follows:

b (year^{-1})	T(1–50%) (year)
0.10	46
0.12	38
0.15	31
0.20	23

We shall see later what the implications of these choices may be in terms of the required timing of actions to limit atmospheric concentrations of CFCs.

Taken together, these two groups of scenarios—the "evasion" scenarios, with their abrupt change from growth to decline, and the "market-penetration" scenarios, with their gradual transition from growth to decline—will be referred to as "transition" scenarios. They represent various possibilities for the evolution of events following a decision to limit future CFC concentrations, with the actions to implement such a decision spread out over various lengths of time.

8. PROCEDURE FOR ESTIMATING OZONE DEPLETION

Having selected a few scenarios for future growth in the release of CLCs, I needed a procedure for estimating the depletion of atmospheric ozone as a function of time for each scenario. I did not have a computational model of the relevant atmospheric processes, nor was it appropriate for this work to develop or acquire one. I therefore sought a procedure for interpolating or extrapolating published results for somewhat similar scenarios. The procedure adopted is as follows.

A simple, one-box model of the troposphere was adopted and "calibrated" against projected tropospheric mixing ratios for CFC-11 and CFC-12 which were published by Wuebbles, MacCracken, and Luther (1984) for the standard scenario of constant emissions at 1980 rates. These mixing ratios were obtained by Wuebbles, MacCracken, and Luther with the Lawrence Livermore National Laboratory's (LLNL's) 1-D atmospheric chemistry model.

The simple model used here was just the solution of the balance equation

$$\frac{dN}{dt} = S(t) - \alpha N \ , \tag{5}$$

where N is the quantity of a compound in the atmosphere, S is the emission rate at time t, and α is the removal probability per unit time. The solution for an exponentially varying source, $S(t) = S_o e^{\beta t}$, is

$$N(t) = N_o e^{-\alpha t} + \frac{S_o}{(\alpha + \beta)} \left[e^{\beta t} - e^{-\alpha t} \right] , \tag{6}$$

which can be initialized at any time when the concentration is known. This solution can be applied stepwise over intervals of exponential growth (e.g., $\beta = 0.03$/year) or of constant emissions ($\beta = 0$).

Appropriate values of α are found independently for CFC-11 and CFC-12 by fitting the projected mixing ratios, $y(t)$, given by Wuebbles, MacCracken, and Luther (1984) for the case of constant emissions ($\beta = 0$) to expressions of the form

$$y(t) = A\left[1 - e^{-\alpha(t - t_o)}\right] \ . \tag{7}$$

An initial fit yielded values of α equal to 0.013/year and 0.00667/year for CFC-11 and CFC-12, respectively, and these values were used in the simple model to obtain the results given in this report. A subsequent, more careful fitting procedure, undertaken to verify the initial values, gave values of $\alpha = 0.0122$/year and $\alpha = 0.00665$/year for CFC-11 and CFC-12, respectively. Normalized values of the mixing ratios given by Wuebbles, MacCracken, and Luther (1984) are compared in Table 3 and in Fig. 23 with values calculated with the above expression. As may be seen, an excellent fit to Eq. 7 may be obtained, especially over the interval 2050–2100. This is not

Table 3. Comparison of relative mixing ratio values as given by Wuebbles, MacCracken, and Luther (WML) (1984) and as calculated with Eq. 3[a]

Year	CFC-11			CFC-12		
	WML values[b]	Equation 3		WML values[b]	Equation 3	
		$\alpha = 0.0122$[c]	$\alpha = 0.013$[d]		$\alpha = 0.00665$[c]	$\alpha = 0.00667$[d]
2000	0.3601	0.3634	0.3451	0.2085	0.2077	0.2078
2010	0.4350	0.4366	0.4235	0.2592	0.2586	0.2588
2020	0.5005	0.5013	0.4924	0.3067	0.3063	0.3065
2030	0.5583	0.5586	0.5528	0.3512	0.3510	0.3511
2040	0.6097	0.6094	0.6058	0.3928	0.3927	0.3929
2050	0.6546	0.6543	0.6523	0.4319	0.4318	0.4319
2060	0.6940	0.6940	0.6931	0.4684	0.4684	0.4685
2070	0.7291	0.7292	0.7290	0.5026	0.5026	0.5026
2080	0.7604	0.7603	0.7604	0.5346	0.5346	0.5346
2090	0.7878	0.7878	0.7880	0.5645	0.5645	0.5645
2100[e]	0.8122	0.8122	0.8122	0.5925	0.5925	0.5925
00		1.0000	0.9858		1.0000	0.9981

[a]Normalized to 1.0000 for $t = \infty$ for the best fit obtained for each compound.
[b]Wuebbles, MacCracken, and Luther (1984), p. 45, Table 6.
[c]Best fit.
[d]Value used in simple model for computations reported in this study.
[e]An exact fit was imposed at the year 2100, the last year in the WML projection.

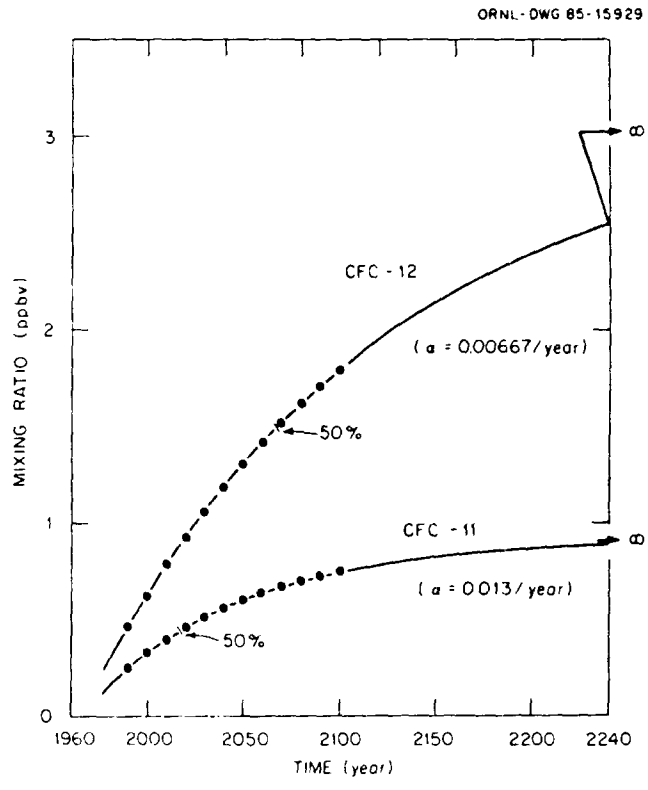


Fig. 23. Tropospheric mixing ratios for CFC-11 and CFC-12 for the case of constant emissions at 1980 rates. Each curve represents the prediction of a simple one-box model with α determined by fit to the data of Wuebbles, MacCracken, and Luther (1984) (the points). Tics on the curves indicate where they reach 50% of the asymptotic values.

surprising, since, for the simple case of constant emissions, the results obtained with the detailed LLNL model should be very nearly of the form of Eq. 7, despite the fact that the real situation (as approximated by the LLNL model) is rather more complicated than the simple model represented by Eq. 5 (e.g., with recirculation of gases between the stratosphere and the troposphere). The sole purpose of this fitting procedure is to obtain appropriate values of α for CFC-11 and CFC-12 for use in the simple model to obtain tropospheric inventories for our various scenarios. The other parameters of the fit, t_o and A, do not appear explicitly in applications of the simple model, being replaced by appropriate values of S_o and the stepwise initial times for various segments of each scenario. Only the derived values of α for CFC-11 and CFC-12 are carried over to the calculations for the scenarios considered in this study.

It may be noted that the values of α determined in this way imply atmospheric lifetimes somewhat longer than those listed in Table 4 of Wuebbles (1983) but perhaps more in keeping with those suggested by the Atmospheric Lifetime Experiment (ALE) (Prinn et al. 1983a; Cunnold et al. 1983a, 1983b). These differences arise in part because of differences in the diffusion parameters used in the various calculations. In any case, the lifetimes are not yet very well known. The essential point is that, with the values of α used here, our simple model reproduces very well the CFC-11 and CFC-12 concentrations projected by the LLNL model (Wuebbles, MacCracken, and Luther 1984).

The depletion of stratospheric ozone will, of course, not depend directly on the tropospheric CLC mixing ratios but on the odd chlorine (CL_x) concentrations in the stratosphere, for which the tropospheric CLC concentrations merely provide the source. To establish a link between the tropospheric CLC concentrations and stratospheric ozone reduction, we make further use of the Livermore work, as follows.

Wuebbles and Chang (1982) estimated the relative effectiveness of the various CLCs for destroying stratospheric ozone (as reported in Wuebbles 1983). The values given are per unit of mass of compound emitted, that is, the emission rate, not per unit of mass retained in the atmosphere. Thus the relative efficiencies quoted by Wuebbles (1983) apply only at equilibrium; at short times (e.g., over the next several decades), short-lived compounds will be relatively more effective, compared to longer-lived compounds such as CFC-11 and CFC-12, than would be indicated by the asymptotic relative efficiencies estimated by Wuebbles and Chang (1982). At equilibrium, for the case of constant emissions, the tropospheric inventories are directly proportional to the emission rates and inversely proportional to the loss coefficients, α_i, that is,

$$N_i(\infty) = S_i/\alpha_i \quad .$$

Thus, relative ozone destruction efficiencies per unit of inventory can be deduced from Wuebbles' and Chang's (1982) efficiencies per unit of source strength,

$$\gamma_i = \epsilon_i(\alpha_i/\alpha_{11}) \quad ,$$

where γ_i is the relative efficiency per unit of inventory ($\equiv$1.00 for CFC-11); ϵ_i is the relative (asymptotic) efficiency per unit of source strength given by Wuebbles and Chang (1982) ($\equiv$1.00 for CFC-11); and α_i is the loss coefficient for compound i ($\equiv$0.013/year for CFC-11). With α = 0.00667/year and ϵ = 0.86 (Wuebbles 1983) for CFC-12, we find γ_{12} = 0.44.

We calculate the tropospheric inventories of CFC-11 and CFC-12 (from Eq. 6) and obtain the weighted, combined total tropospheric CLC inventory, $M \equiv m$(CFC-11) + 0.44 m(CFC-12),

which we then *normalize* to a value of 1.00 for the standard scenario (constant emissions) at $t \rightarrow \infty$, that is, the steady-state value. This normalization procedure has three distinct purposes:

1. It allows for the fact that estimates of ozone depletion, obtained with the best available models, have been changing greatly from year to year. I thought it more likely that the *relative* ozone depletions for the various scenarios would remain valid, with further refinements in data and models, than that the estimated absolute value for any scenario (e.g., the standard scenario) would remain unchanged.

2. It allows, in an approximate way (as will be seen later), for the apparent neglect in this work of contributions from other CLCs (e.g., CCl_4, CFC-113, CH_3CCl_3, CFC-22, etc.), which, together, if emissions of the various CLCs remain in the same relative proportions, may contribute roughly half as much to ozone depletion as do CFC-11 and CFC-12 together (Wuebbles 1983). Including the other compounds in this way may slightly distort the time dependence of the ozone depletion (the shape of the approach to equilibrium) but will not affect relative steady-state values for scenarios (such as those considered here) for which it is assumed that emissions of the various compounds remain in the same proportions, even though they change in absolute magnitude. Numerical experiments with up to six compounds (including CLC-11 and CLC-12) suggest that this distortion is not too serious.

3. It allows, in an approximate way, for consideration of nonlinearities in the response of ozone to CLC emissions.

Wuebbles (1983) presents results for ozone depletion as a function of time (out to the year 2100) for 18 different scenarios for future CLC releases; in all of these, the *relative* releases of the eight compounds considered remained unchanged. Three of these scenarios (II, V, VIII) had constant emissions (at one level or another) after the year 2000. These three cases are

- VIII—Constant emissions at 1980 rates.
- V—A 3%/year growth in emissions until 2000; then constant emissions at 1.822 times the 1980 rates.
- II—A 7%/year growth in emissions until 2000; then constant emissions at 4.055 times the 1980 rates.

Two other scenarios represented continued exponential growth from 1980 at 7%/year (case I) or 3%/year (case IV). The nonlinear response of the system is manifest in the fact that the calculated ozone reductions (i.e., percentage depletion of total column ozone) at long times are not proportional to the emission rates. This nonlinearity is illustrated in Fig. 24, which shows that for case II (for example) the total ozone depletion after 2075 exceeds the asymptotic ozone depletion in case VIII (the standard scenario) by a factor greater than the ratio of their steady-state emission rates (indicated by S_{II}/S_{VIII}). The nonlinear response is also stressed by Prather, McElroy, and Wofsy (1984) and is apparent again in calculations summarized in WMO (1986).

To establish a link between ozone depletion and tropospheric CLC inventories, as calculated with the simple one-box model, I calculated the tropospheric inventories for CFC-11 and CFC-12 for Wuebbles' cases VIII, V, II, IV, and I (Wuebbles 1983), using the emission rates given in Wuebbles' Table 4 and values of α equal to the reciprocal of the atmospheric lifetimes given in Wuebbles' Table 4. [These differ from the emission rates given by Wuebbles, MacCracken, and Luther (1984) and from the α's deduced from their time-dependent tropospheric mixing ratios, as described above]. I then calculated

$$M_j(t) \equiv m_{11,j} + 0.44\ m_{12,j} \quad ,$$

where $m_{11,j}$ and $m_{12,j}$ are the calculated tropospheric inventories of CFC-11 and CFC-12, respectively, for case j ($j \equiv$ VIII, V, II, etc.) and 0.44 is the relative efficiency of CFC-12 for destroying ozone (per unit of mass in the troposphere, as described earlier). I then calculated relative combined inventories,

$$M_{\mathrm{rel},j}(t) \equiv \frac{M_j(t)}{M_{\mathrm{VIII}}(t=\infty)} \quad ,$$

where $M_{\mathrm{VIII}}(t = \infty)$ is the asymptotic, steady-state value for case VIII, the standard scenario with constant emission rates. I then obtained, from Wuebbles' Table 3 (Wuebbles 1983, p. 1437), relative ozone depletions for each scenario,

$$(\Delta O_3)_{\mathrm{rel},j}(t) \equiv \frac{(\Delta O_3)_j(t)}{(\Delta O_3)_{\mathrm{VIII}}(t=\infty)} \quad ,$$

that is, normalized to the steady-state depletion for case VIII. (Note that Wuebbles gives the steady-state depletion only for case VIII; for all other cases, ozone depletions are given only out to the year 2100.) I then plotted $(\Delta O_3)_{\mathrm{rel},j}(t)$ versus $M_{\mathrm{rel},j}(t)$ for cases VIII, V, II, IV, and I. This

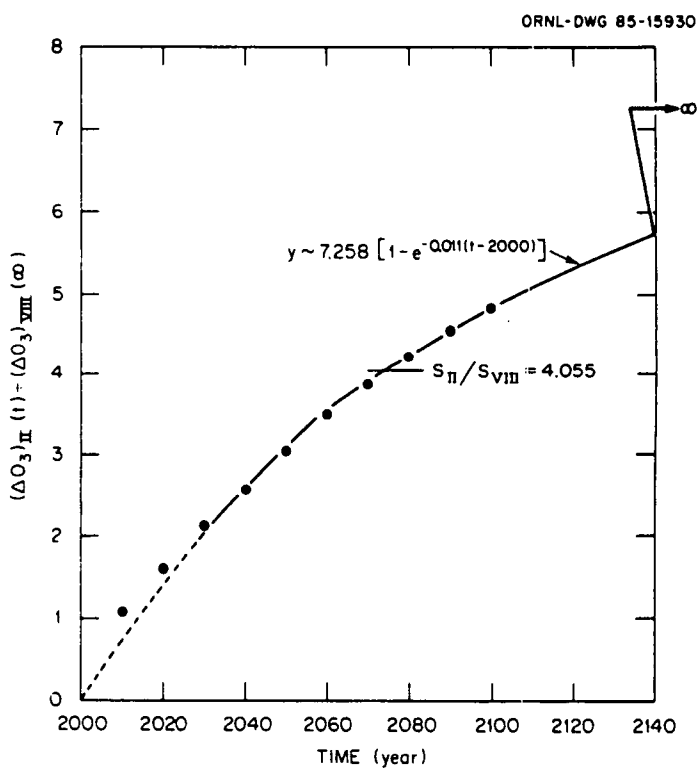


Fig. 24. Relative ozone depletion for Wuebbles' Case II (Wuebbles 1983), illustrating nonlinear response. Points are Wuebbles' data. Ordinate is normalized to 1.00 for the asymptotic ozone depletion for Wuebbles' Case VIII, the standard scenario with constant emissions at 1980 rates.

plot is shown in Fig. 25 and in Fig. 26 (plotted to a different scale). It may be noted that the correlation is remarkably good for all the cases except case I, which has continued exponential growth at 7%/year. The deviation of ΔO_3 for case I from the pattern established by the other cases is perhaps to be expected since, for this continued rapid growth, the stratospheric concentrations of the CLCs lag further behind the tropospheric concentrations. I therefore adopt the correlation between relative ozone depletion, $(\Delta O_3)_{rel,f}(t)$, and relative tropospheric inventory (weighted by relative ozone-destroying efficiency), $M_{rel,f}(t)$, that is established by cases VIII, V, II, and IV. This correlation is well approximated by the third-order polynominal,

$$y = ax + bx^2 + cx^3 \quad , \tag{8}$$

where

$y = (\Delta O_3)_{rel}$,
$x = M_{rel}$,
$a = 0.648$,
$b = 0.370$,
$c = -0.018$.

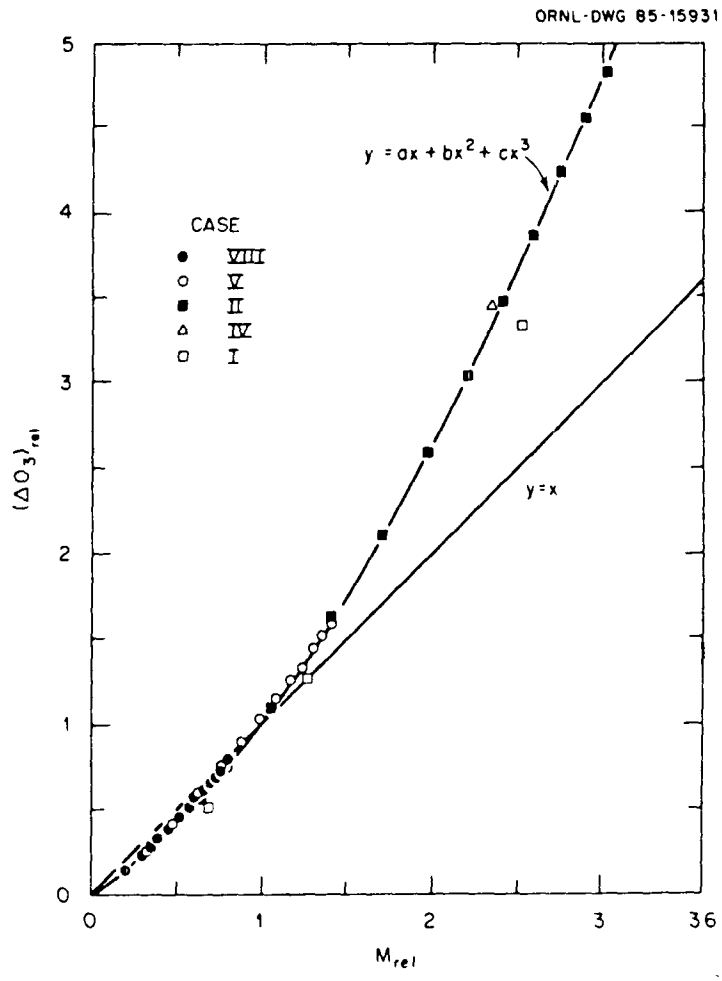


Fig. 25. Relative ozone depletion versus relative weighted CFC masses in the troposphere for Wuebbles' Cases I, II, IV, V, and VIII ($0 \leq M_{rel} \leq 3$). (After Wuebbles 1983.) The curve follows the expression $y = ax + bx^2 + cx^3$, with coefficients given in the text.

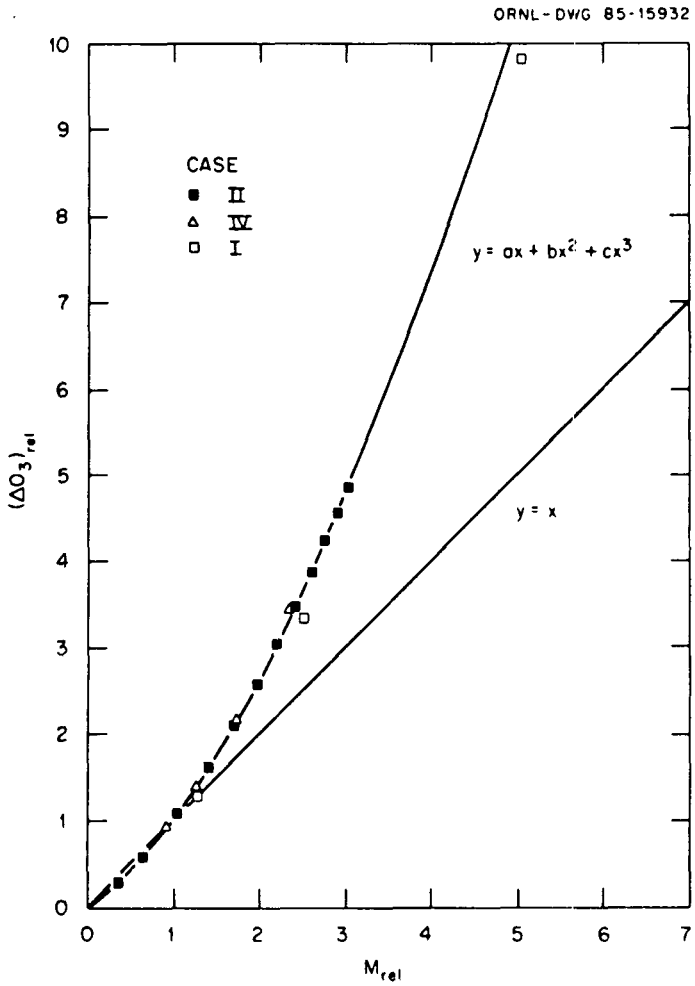


Fig. 26. Relative ozone depletion versus relative tropospheric CFC mass ($0 \leq M_{rel} \leq 5$). The curve follows the expression $y = ax + bx^2 + cx^3$, with the same coefficients as in Fig. 25.

This expression passes through the points (0,0) and (1,1) and provides a reasonable fit to the correlation over the range $x \leq 5$, $y \leq 10$.

Note that only CFC-11 and CFC-12 were explicitly considered in obtaining this correlation. However, Wuebbles' ozone depletion calculations considered all of the eight compounds previously enumerated. Thus the contributions of the other six compounds are *implicitly* included in this correlation. The excellent correlation shown in Figs. 25 and 26 was not necessarily to be expected; however, it is gratifying and useful.*

In applying this correlation to the various scenarios considered in this study, I normalized $M_{rel}(t)$ to a value of 1.00 at $t = \infty$ for the case of constant emissions defined in Sect. 7 [and by Wuebbles, MacCracken, and Luther (1984)]. This standard scenario is not quite identical to case

*It should be noted that, for cases with constant emissions at different rates, the tropospheric inventories and hence M_{rel} at steady state are proportional to the relative emission rates (relative to the present rates, represented by scenario 1). Thus, Figs. 25 and 26 also give the steady-state ozone depletion for cases with constant emissions at various multiples of the present rates. For example, for constant emissions (continued indefinitely) at three times the present rates, $M_{rel} = 3$ (at steady state) and $(\Delta O_3)_{rel} = 4.8$.

VIII of Wuebbles 1983: The atmospheric lifetimes are somewhat different, and the relative emission rates of CFC-11 and CFC-12 are also somewhat different. However, I wished to refer all ozone depletion values to the steady-state value for our standard (constant-emissions) scenario (Wuebbles, MacCracken, and Luther 1984). In order to do that and to use the correlation of ΔO_3 with M, as described above, it was necessary also to normalize the masses, $M_{rel}(t)$, to unity for our standard scenario at steady state ($t \rightarrow \infty$).

It may be noted that the main thing accomplished by use of this correlation is to represent the nonlinearity of the response of ozone depletion to increasing concentrations of CFCs in the atmosphere. The simplest such correlation would be a linear response, that is, $(\Delta O_3)_{rel} = M_{rel}$. The cubic expression used in this study allows for some departure from simple proportionality. But the degree of nonlinearity in ozone depletion versus CFC concentrations is quite different in calculations performed with different models (WMO 1986), and hence must still be regarded as quite uncertain. Furthermore, the notion that the relative ozone depletion for various scenarios will be invariant to changes in the estimated steady-state depletion for scenario 1 is probably not correct; that is, model and data changes may produce changes in the expected nonlinearity of the response. Thus, the results obtained with the simple model described here can only be viewed as approximations to those that would be obtained with a particular atmospheric chemistry model, namely the LLNL 1-D model as reported by Wuebbles (1983).

To recapitulate, the procedure for estimating the ozone depletion for the various scenarios considered in this study was as follows:

- Calculate m_{11} and m_{12}, using the simple one-box model, with α's deduced from the mixing ratios given by Wuebbles, MacCracken, and Luther (1984).
- Calculate $M_j(t) = m_{11} + 0.44\, m_{12}$.
- Calculate $M_{rel,j}(t) = M_j(t) \div M_1(\infty)$.
- Calculate $(\Delta O_3)_{rel,j}(t)$ from the third-order polynomial $y = ax + bx^2 + cx^3$, with values of a, b, and c as given above.

9. RESULTS

Results of these computations are displayed in the following several figures. Figure 27 shows the tropospheric inventories of CFC-11 and CFC-12, in teragrams (10^{12} g), for scenarios 1–3. Figure 28 shows the corresponding tropospheric mixing ratios in parts per billion, by volume. These scenarios have steady-state emission rates in the proportions 1, 2.248, and 4.482, and, because of the structure of the simple one-box model, the asymptotic mixing ratios of the three scenarios are also in these proportions. An important aspect of these results, which is known from other investigations, is the long time needed for the tropospheric mixing ratios to approach equilibrium levels, a consequence of the long atmospheric lifetimes of these compounds. The dates when the mixing ratios would reach half of their asymptotic values are indicated in Table 4.

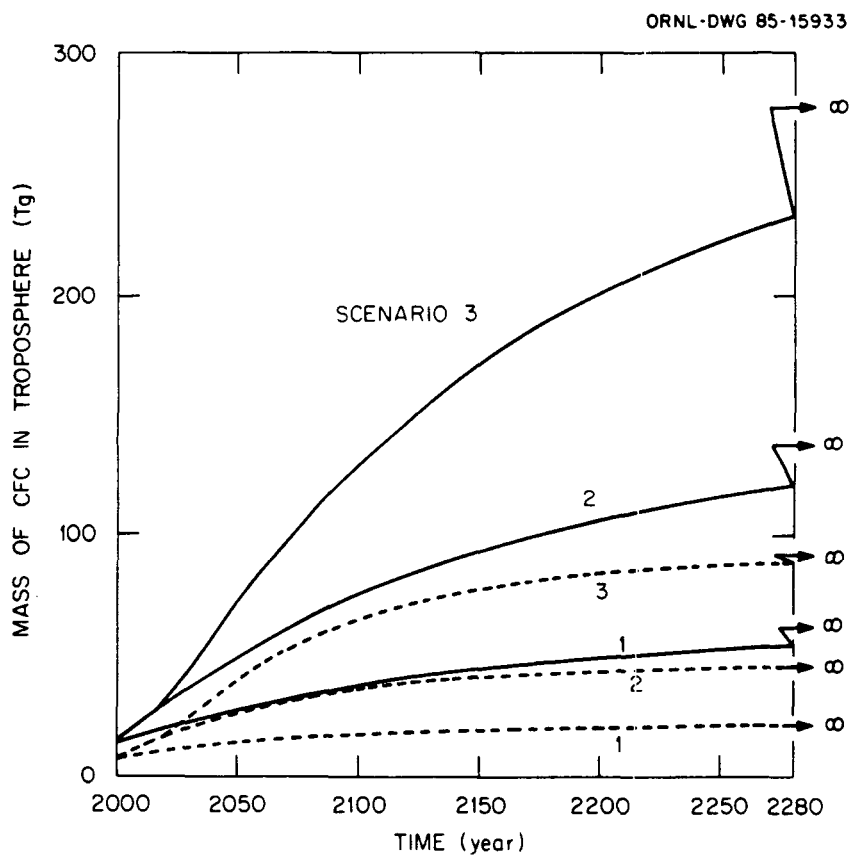


Fig. 27. Tropospheric inventories of CFC-11 and CFC-12 for scenarios 1–3. Solid curves: CFC-12 [1980 inventory = 5.9 Tg (5.9 × 10^{12} g)]; dashed curves: CFC-11 (1980 inventory = 3.6 Tg).

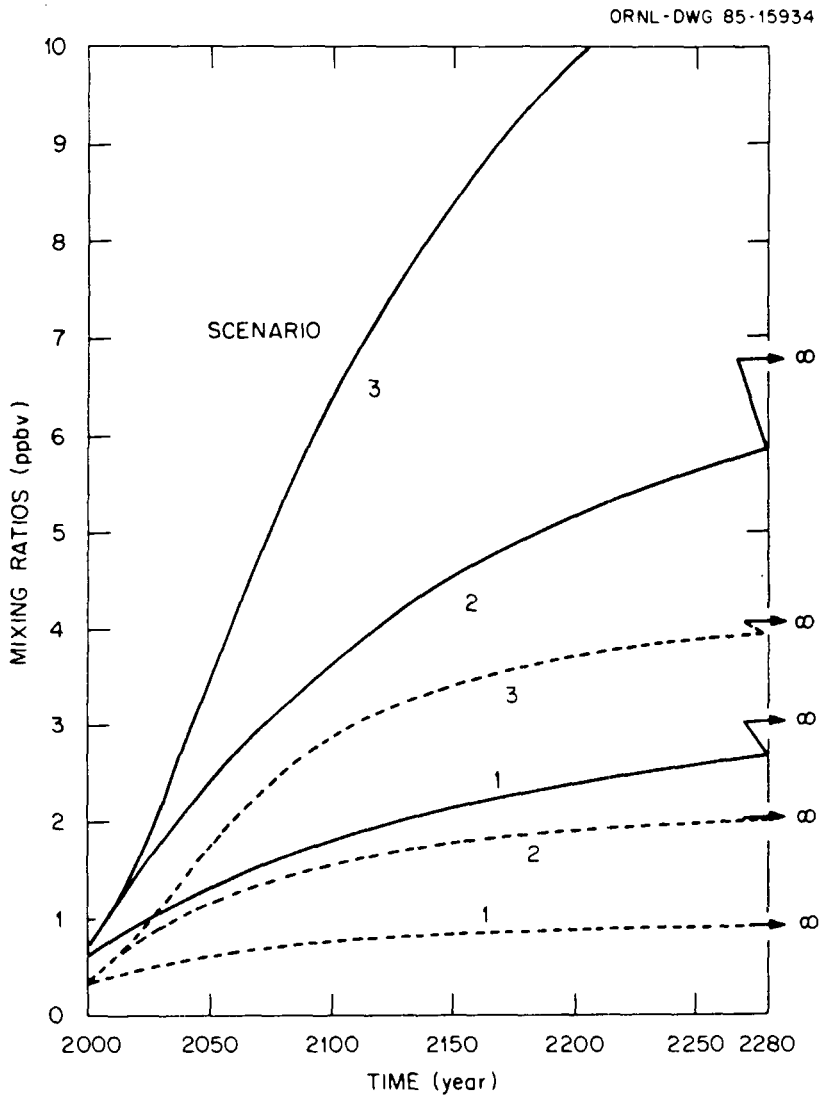


Fig. 28. Tropospheric mixing ratios of CFC-11 and CFC-12 for scenarios 1–3. Solid curves: CFC-12 (1980 mixing ratio, ~0.29 ppbv); dashed curves: CFC-11 (1980 mixing ratio, ~0.16 ppbv).

Table 4. Approximate dates for reaching half of asymptotic values

Scenario	Tropospheric mixing ratios		M_{rel}	$(\Delta O_3)_{rel}$
	CFC-11	CFC-12		
1	2020	2068	2045	2067
2	2039	2088	2065	2095
3	2060	2108	2085	2120

Also shown in Table 4 are the times when M_{rel} (the weighted, combined tropospheric inventory) and $(\Delta O_3)_{rel}$ (the normalized, relative ozone depletion) reach half of their asymptotic values. CFC-12 takes longer than CFC-11 because of its longer atmospheric lifetime; $(\Delta O_3)_{rel}$ takes longer than M_{rel} because of the nonlinearity discussed in the previous section. The dates are later for scenarios 2 and 3 than for scenario 1 because of the growth period (ending respectively in 2010 and 2033) that precedes the period of constant emissions.

It should be noted that the rate of approach to equilibrium depends on the atmospheric lifetimes of the important compounds. The lifetimes used here (77 years for CFC-11, 150 years for CFC-12) are significantly longer than those given by Wuebbles (1983) owing partly to changes in the vertical diffusion coefficients employed in the LLNL model (Wuebbles 1985b). If the shorter lifetimes should ultimately prove to be more nearly correct, then the approach to equilibrium would be more rapid than is indicated by Table 4. In addition, the results reported here are based on the time-dependent behavior of only two compounds (CFC-11 and CFC-12) as compared with eight in Wuebbles (1983). Compounds with much shorter lifetimes (e.g., CFC-22 and methylchloroform), though having a much smaller asymptotic effect than CFC-11 and CFC-12 in these scenarios, approach equilibrium more rapidly and speed up the early growth in ozone depletion. However, by comparison with the results of Wuebbles (1983), it appears that this latter effect (eight compounds explicitly considered versus two) advances the date of reaching 50% of the asymptotic ΔO_3 by only about ten years.

Figure 29 shows the normalized combined tropospheric inventory, M_{rel} for scenarios 1–5, while Fig. 30 shows the relative total column ozone depletion, computed from M_{rel} by use of Eq. 8 in Sect. 8.

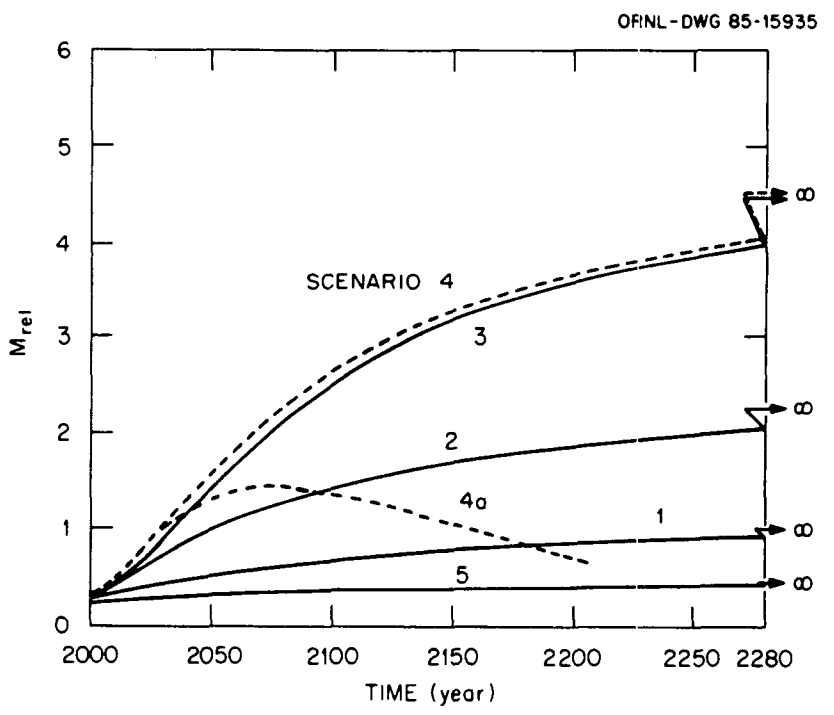


Fig. 29. Weighted, combined, and normalized tropospheric inventory of CFC-11 and CFC-12 for scenarios 1–5. Normalization is to a value of 1.00 for the asymptotic inventory in scenario 1.

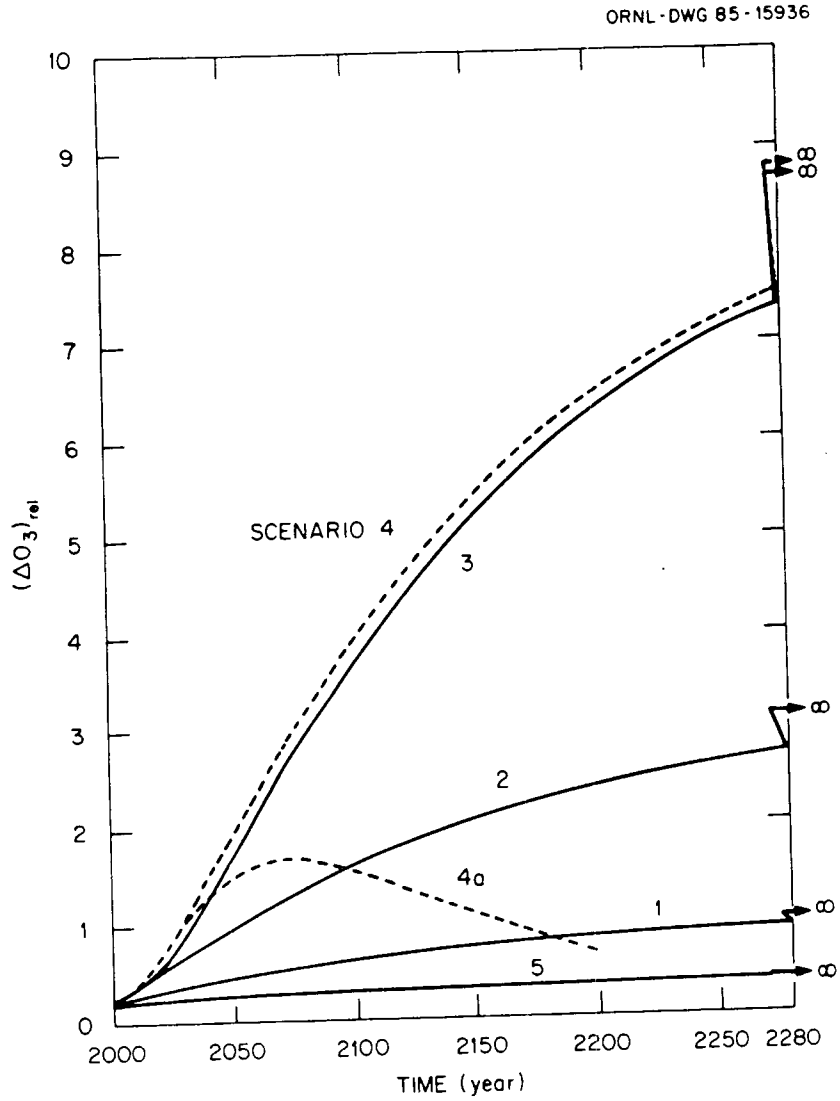


Fig. 30. Relative ozone depletion, scenarios 1–5. Normalization is to a value of 1.00 for the asymptotic ozone depletion in scenario 1. The curves follow the expression $(\Delta O_3)_{rel} = ax + bx^2 + cx^3$, where $x = M_{rel}$ (Fig. 29) and the coefficients are given in the text.

The estimates of ozone depletion presented in Fig. 30 include only the effects of the CLCs; that is, the possible contributions of other trace gases are not included. It was suggested in Sect. 4, on the basis of calculations by Wuebbles, Luther, and Penner (1983), that the combined effect of the CLCs, nitrogen oxides, and CO_2 might be close to zero or slightly positive for the standard CLC scenario (case 1 of Fig. 30). More recent calculations by various investigators (WMO 1986), now including the effect of methane, continue to show a substantial offsetting of the CFC-induced ozone depletion for this case. The magnitude of this offset is quite uncertain, in part because the concentrations of the other gases cannot be reliably predicted. (Neither, of course, can the CFC concentrations be reliably predicted; but they are indirectly specified in these scenarios, thereby removing that uncertainty as an issue for a given scenario.) Nevertheless, the overall ozone change associated with scenario 1 is likely to be smaller than that due to the CFCs alone and may even be positive.

For the higher scenarios in Fig. 30 (e.g., scenarios 3 and 4, with constant emissions at 4½ times the present rates), the indicated ozone depletions are much greater than for scenario 1. In these cases, too, there may be some compensation by other gases, and indeed the positive effect of some of them (e.g., methane) at a given concentration, may be greater at the higher CFC concentrations than at the steady-state CFC concentrations of scenario 1 (see WMO 1986, Tables 13-2, 13-4). Nevertheless, it is strongly suggested by these calculations, as of course it already was by the calculations of Wuebbles (1983) on which the present results are based, that annual CFC emissions at a few times present rates are likely to cause ozone reductions several times greater than the steady-state depletion in scenario 1. According to the tentative guidelines suggested in Sect. 6, such reductions would be unacceptable and in anticipation of their occurrence some preventive actions would become necessary.

Of course, it is not reasonable to suppose that CLC emissions would remain constant for decades at a time, let alone for centuries, as is assumed for these scenarios. Thus the scenarios are merely illustrative of the effects to be expected from various levels of emissions. In this connection, scenario 4a may be of interest as an indication of the effect of a future reversal of a near-term upward trend in emissions, for example, a growth phase reaching 4.5 times current emissions in 2020, followed by a 2%/year decrease, continued indefinitely. By 2020, ozone depletion would have reached only 7.8% of the asymptotic value for scenario 4 (constant emissions after 2020 at 4.5 times the current emission rates) but would have reached 69% of the asymptotic ozone depletion for scenario 1 (constant emissions throughout at present rates). In scenario 4a, despite the continuing 2%/year decrease in emissions after 2020, there is a large "overshoot" in ozone depletion to a level 2.4 times higher than the 2020 level; this maximum level is reached in about 2075. (Even if the CLC emissions were reduced abruptly to zero, there would still be a substantial overshoot in ozone depletion (NRC 1976a) although the overshoot in that particular case is not disclosed by the simple one-box model). Still, the maximum relative ozone depletion of 1.68 for scenario 4a (i.e., 1.68 times the asymptotic value for scenario 1) is far less than the value of almost 9 that would eventually be reached in scenario 4 or that would be reached much sooner if emissions continued to increase past 2020.

Many other scenarios could be considered for limiting the maximum ozone depletion after a period of unrestricted growth, and some of these possibilities will be discussed below.

It should be pointed out that the nonlinear response of $(\Delta O_3)_{rel}$ to increasing tropospheric CLC concentrations could not continue indefinitely in the same direction, that is, $(\Delta O_3)_{rel} > M_{rel}$; the maximum possible ozone reduction is 100%, whereas the atmospheric burdens of CFC-11, CFC-12, and other CLCs could, in principle, become very much larger than are indicated for the scenarios considered here. Thus the effect must eventually saturate, and extrapolation much beyond the range "calibrated" against the calculations of Wuebbles (1983) is not warranted.

It should also be remembered that, even if total column ozone (which determines uv intensities at the surface) is reduced only a few percent, much larger percentage reductions in ozone will occur in the middle and upper stratosphere, for example, around 40 km (see Fig. 5). An estimate of 40–50% reduction in local ozone concentration at 40 km for the standard reference case (scenario 1) has been a constant feature of all previous analyses of this question, even as estimates of total ozone reduction were undergoing major revisions (mainly because of changes in calculated atmospheric chemistry at lower altitudes). Such large reductions in local ozone concentration would significantly alter the temperature structure of the stratosphere, with effects on climate that are not yet clear.

As discussed in Sect. 6, we do not have firm guidelines for deciding how much reduction in total column ozone might be acceptable, in the sense that the costs are commensurate with the

benefits. It seems reasonable to suppose that, if scenario 1 would indeed lead to an asymptotic ozone depletion on the order of 5–7%, with some compensation from other trace gases, and in view of the very long time constants involved, there is not likely to be any universal agreement on measures to reduce CFC emissions in the near future. On the other hand, it seems clear from the results already presented that continued growth in emissions at, say, 3%/year or more would lead in a few decades to a level of ozone depletion, or the prospect of future depletion, that would call for control of emissions.

At some point, then, a reversal in the growth of CLC emissions would be required. The emissions, having reached a level substantially above the present level, would have to fall back gradually to levels more nearly comparable to (or even less than) the present levels of emission. I have considered a few highly idealized scenarios in which CFC emissions, after increasing at 3%/year for a few decades, begin to decrease at rates of 1%, 2%, or 3%/year, starting in the years 2031, 2021, or 2011 (i.e., the 3%/year increase stops in 2030, 2020, or 2010). These scenarios were illustrated in Fig. 21. The rates of decline were chosen somewhat arbitrarily, in the belief that they represent a reasonable range. (Also, rates of decline faster than −3%/year bring only marginal further reductions in maximum ozone depletion.) It may be noted that the cusp-shaped curves illustrated in Fig. 21 are highly schematic approximations to the smoother curves that presumably would characterize the actual phaseout of one technology being replaced by another. Thus the replacement process would actually have to begin some years before the cusps in Fig. 21.

The corresponding ozone depletions for the evasion scenarios, calculated in the same way as before, are shown in Fig. 31. For all these scenarios, ranging from a 3%/year decrease starting in 2010 to a 1%/year decrease starting in 2030, the maximum relative ozone depletion falls approximately in the range of 0.6 to about 2 (relative to the asymptotic ozone depletion for the standard scenario).

As was true of the results presented in Fig. 30, Fig. 31 represents only the contribution of the CLCs, not augmented or diminished by those of other trace gases. However, the results of Wuebbles, Luther, and Penner (1983), as reproduced here in Fig. 7, and the more recent results presented in the International Ozone Assessment Report (WMO 1986), suggest that the combined effect of the other trace gases may approximately cancel the expected reduction due to CLCs in the standard scenario. Since the units are relative ones (again, 1.00 = the asymptotic value for case 1), one may subtract from the curves of Fig. 31 the values shown for case 1 as a rough measure of the offset attributable to the other trace gases. An acceptable case is perhaps one in which this difference [i.e., $(\Delta O_3)_{rel,j}(t) - (\Delta O_3)_{rel,1}(t)$] does not exceed unity, as is true, for example, of cases 3b.3 and 3c.1 in Fig. 31. This leads to the further criterion that if the maximum relative ozone depletion, $(\Delta o_3)_{rel}$, calculated without taking account of the compensating effect of other trace gases, lies in the range from about 1 to 2, that is,

$$\approx 1 < \max(\Delta O_3)_{rel} < \approx 2 \ ,$$

then the scenario probably represents an acceptable transition from CFC-emitting technologies and practices to nonemitting ones. (Of course, max $(\Delta O_3)_{rel} < 1$ is also all right; the bounds relate to uncertainty in the criterion, and don't imply that smaller ozone depletion would be unacceptable!) For example, if the steady-state ozone depletion for scenario 1 (the one with constant emissions at 1980 rates that is used as a reference throughout this discussion) turns out to be 5% and that depletion turns out to be largely canceled by the effects of other trace gases, then scenario 1 and any other scenario for which the calculated $(\Delta O_3)_{rel}$ is less than one would be acceptable. Indeed, according to the tentative guidelines suggested in Sect. 6, any scenario with $(\Delta O_3)_{rel}$ less than about two would be acceptable from the standpoint of ozone depletion.

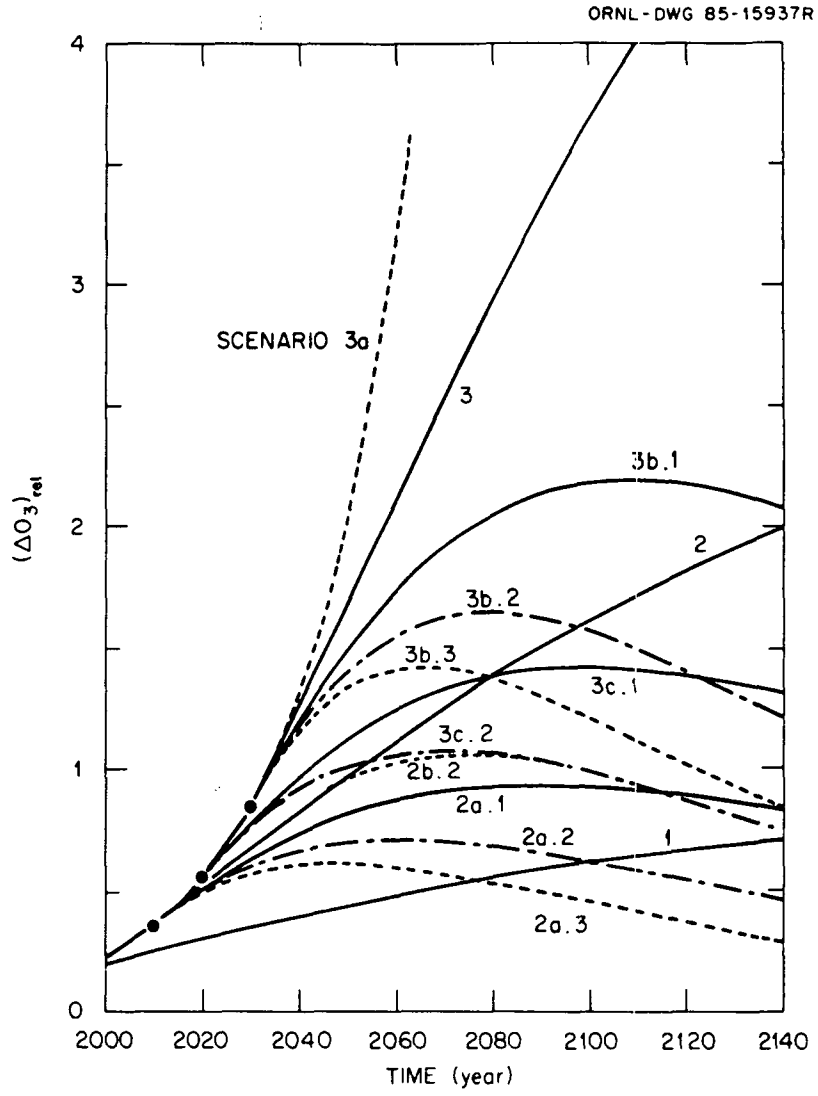


Fig. 31. Relative ozone depletion for the evasion scenarios.

On the other hand, if the steady-state ozone depletion for scenario 1 turns out to be closer to 10% and is only partly compensated by the other trace gases, then the lower bound, $(\Delta O_3)_{rel} \leq 1$, would apply in evaluating the various transition scenarios. In the following discussion, use will be made of this criterion (i.e., that the calculated maximum relative ozone depletion should not exceed one or two). However, if further research shows that the steady-state ozone reduction for case 1 would actually be much larger than 5–7% after all, or if the much larger percentage ozone reduction in the middle and upper stratosphere proves to be very important climatically, then this acceptability criterion would have to be reconsidered.

The possibilities for limiting the maximum ozone depletion by taking action to reduce CLC emissions, as represented schematically by the above "evasion" scenarios, are summarized in Fig. 32, in which the eventual maximum values of $(\Delta O_3)_{rel}$ (corresponding to the peaks in the curves of Fig. 31) are shown as a function of the year in which the emission reduction starts and as a function of the rate of reduction. For example, a decrease of 2%/year in annual emissions, starting in the year 2020 (following a 3%/year increase in emissions for 1983 to 2020), would limit the

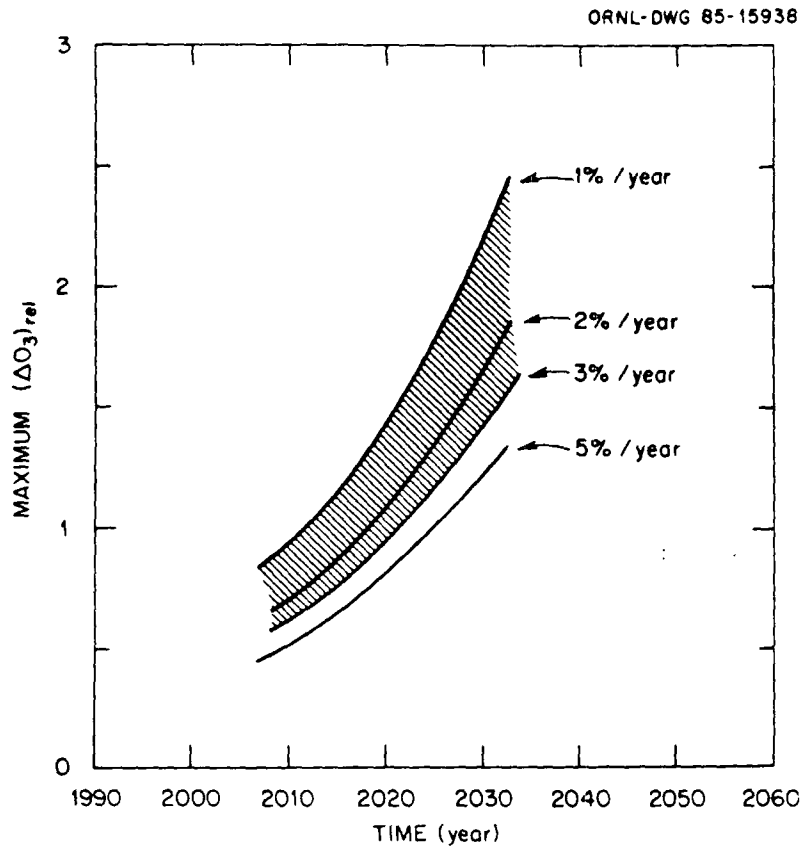


Fig. 32. Maximum relative ozone depletion for the evasion scenarios versus time when emission reduction begins, following 3%/year growth in emissions prior to that year. The figures attached to each curve equal the rate of change (reduction) in emissions starting in the given year.

maximum ozone depletion to about the same value as the steady-state depletion in scenario 1, here considered to be acceptable. (Note that this maximum would not actually be reached until about 2070, a half-century after beginning the decrease in emissions and that during that half-century the ozone depletion would have doubled.)

The cusp-like evasion scenarios considered above illustrate in a general way the effect of actions to initiate a decrease in CFC emissions following a period of sustained growth in emissions. They show the marked reduction in eventual ozone depletion that can be accomplished by actions begun even several decades in the future. They also illustrate the large overshoot in ozone depletion that will occur after remedial actions have begun and the long time period required before the ozone density, having reached a minimum (i.e., maximum depletion), actually starts to increase again. However, they are ambiguous with respect to the question of timing of remedial actions, which would have to begin some time before the abrupt change from growth to decline that characterizes these evasion scenarios. For this reason, the market penetration scenarios were introduced (see discussion in Sect. 7). A few of these were illustrated in Fig. 22. Ozone depletion in these scenarios is shown in Fig. 33, in comparison with scenario 3a, the case of uninterrupted 3%/year growth in emissions.

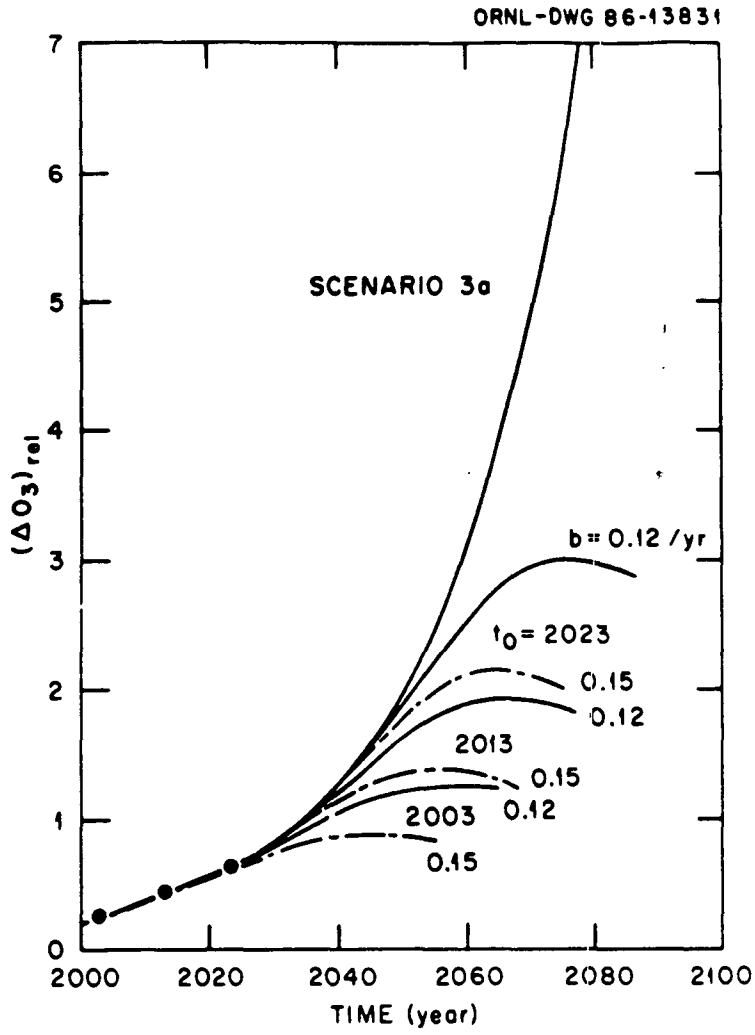


Fig. 33. Relative ozone depletion for certain market penetration scenarios with 3%/year initial growth in emissions. Also shown is scenario 3a with continued 3%/year growth rate.

For a much larger series of market penetration scenarios, maximum ozone depletion (corresponding to the peaks of the curves in Fig. 33) is plotted in Fig. 34, as a function of the time t_0 when the market share of the new, nonemitting technologies and practices reaches 1%. For the cases represented in Fig. 34, the growth rate in CFC emissions, prior to the time t_0, ranges from 2%/year to 5%/year, with a growth rate of 3–4%/year being thought most likely (Sect. 7). Also represented are values of the market penetration parameter, b, ranging from 0.1 to 0.2/year [i.e., market penetration times (1 to 50% market share) from 46 years to 23 years (see Sect. 7)]. [Note that Fig. 34 does not show $(\Delta O_3)_{rel}$ versus time for any scenario; rather, it shows the maximum $(\Delta O_3)_{rel}$ versus the time when remedial actions effectively begins. That maximum, as is apparent in Fig. 33, would not be reached until several decades after the time t_0. Each curve in Fig. 34 represents a series of scenarios having different values of t_0 but the same initial growth rate prior to t_0 and the same market penetration time, $T = \ln 99/b$.]

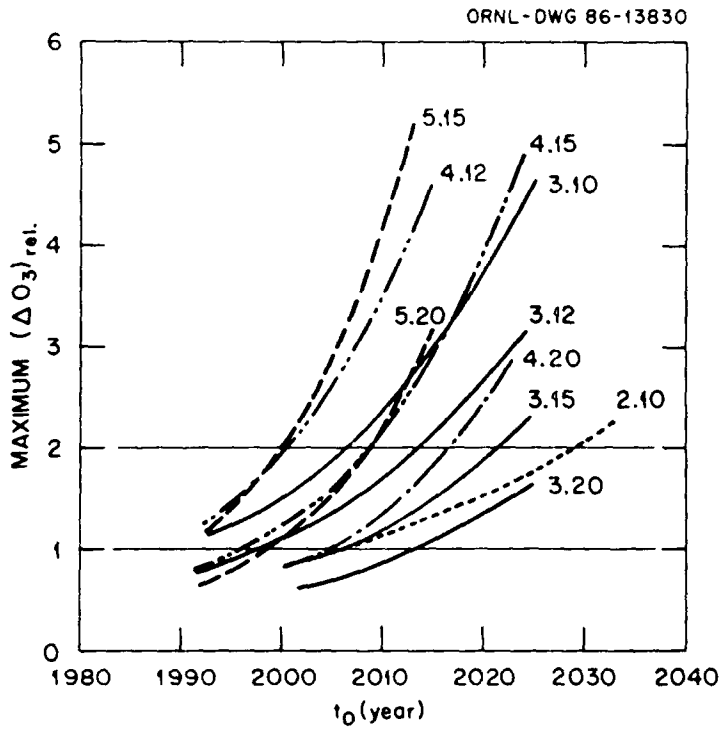


Fig. 34. Maximum relative ozone depletion for the market penetration scenarios versus the time when the market share of substitutes reaches 1%. Labels on the curves indicate initial growth rate prior to t_0 and the market penetration parameter b. For example, 3.15 means 3%/year initial growth rate and b = 0.15/year.

Consider for example the mid-range scenarios having initial growth rate of 3%/year and market penetration parameter b = 0.15/year (T = 31 years), represented by the curve labeled 3.15 in Fig. 34. For this series of scenarios (identical except for t_0), Fig. 34 shows that a time t_0 = 2005 would result in a maximum $(\Delta O_3)_{rel}$ of 1, and t_0 = 2022 leads to a maximum $(\Delta O_3)_{rel}$ of 2. On the other hand, for an initial growth rate of 5%/year things get out of hand much more quickly: limiting max $(\Delta O_3)_{rel}$ to 2 requires $t_0 \sim 2000$. It is clear from Fig. 34 that lower growth rates and shorter market penetration times allow growth in emissions to continue longer before remedial actions must begin to be effective. Too long a delay could only be compensated for by shortening the market penetration time, which might prove to be costly. For example, if 5%/year growth should continue until 2010, a market penetration time of 31 years (b = 0.15/year) would lead to an eventual maximum relative ozone depletion of more than 4, which is here considered to be unacceptable. It would require a much shorter market penetration time, that is, about 23 years (b = 0.20/year) to get the maximum $(\Delta O_3)_{rel}$ down to about 2, and there would be very little chance of getting it down to 1.

As shown by these examples, Fig. 34 can be used to evaluate a broad spectrum of possible future CFC emission scenarios and implementation times for remedial actions. My own conclusion is that for growth rates of 3 or 4%/year and for reasonable market penetration times of about 30 to 40 years ($b \sim$ 0.15–0.12/year; see discussion in Sect. 7), effective actions to replace present CFC-emitting technologies and practices, even if begun 20 to 30 years from now, could limit the eventual

maximum ozone depletion to acceptable levels. But higher growth rates (e.g., 5 to 7%/year) would present us with a more urgent situation and could not be allowed to continue very long.

I am well aware that this sort of argument is not very rigorous, and indeed several reviewers of a draft of this report took rather strong exception to it. There are large remaining uncertainties in the degree of ozone depletion that would actually be caused by a given concentration of CFC compounds in the atmosphere, in the effects of that depletion should it occur, and hence in the amount of depletion that could be regarded as acceptable, in the extent of compensation by other trace gases of Cl-induced ozone depletion (as well as exacerbation of other effects), and in the times and rates at which substitutes could be introduced in various segments of the CFC market. The criteria suggested above and the calculations for the various emission scenarios are presented here in quantitative terms. Yet the essential rationale is perhaps best appreciated in qualitative terms. The reasoning, stripped of qualifying remarks, goes as follows:

1. Continued CFC emissions at present rates (scenario 1) would not produce an unacceptable reduction in total column ozone—not for many decades and probably never.

2. Any schedule of CFC emissions that depletes ozone no more than scenario 1 is acceptable.

3. Continued CFC emissions at rates much higher than present rates would produce ozone reductions several times greater than scenario 1 and that is probably unacceptable. Sustained growth in emissions from current levels to much higher levels would do the same thing. At growth rates of a few percent per year, it would only take a few decades to reach emission levels that would be unacceptable if continued for a long time.

4. In between, there is a range of ozone depletion, somewhat larger perhaps than for scenario 1 but not much larger, that may be found to be acceptable.

5. Because of the long time constants of the processes involved (i.e., the long atmospheric lifetimes of the principal CFC compounds), ozone depletion over periods of several decades depends more on long-term total emissions than on short-term variations in annual emissions. Thus, annual CFC emissions could safely be allowed to grow, even to rates several times greater than at present, provided that they were brought back soon enough to something roughly comparable to present rates.

This report is an attempt to present an initial, semiquantitative elaboration of these general observations. It is certainly not the last word on the subject, but it may perhaps be regarded as an early effort to explore the ground between no action and precipitate action concerning the ozone-depletion problem.

The analysis thus far has been based on the simplifying assumption that the relative emissions of the eight CLCs considered would remain in the same proportions as at present. However, substitution of one CLC for another may serve to reduce the amount of chlorine remaining in the atmosphere without actually reducing the total mass of CLCs produced. For example, CFC-22 (CHF_2Cl), because it reacts with hydroxyl radical in the troposphere, has a shorter atmospheric lifetime than CFC-11 or CFC-12 and a much smaller effect on stratospheric ozone. Wuebbles and Chang (1982) (quoted in Wuebbles 1983) have estimated the relative ozone destruction efficiency of these compounds, per unit of mass of the compound emitted into the atmosphere. Their results, taken from Table 4 of Wuebbles (1983), are reproduced here in Table 5.

Table 5. Relative ozone destruction efficiency of various chlorocarbon compounds

Compound	Molecular weight	Chlorine weight fraction	Relative efficiency	
			(*a*)	(*b*)
CCl_4	153.8	0.922	1.11	0.93
CFC-11	137.4	0.774	1.00	1.00
CFC-12	120.9	0.587	0.86	1.13
CFC-113	187.4	0.568	0.80	1.09
CFC-114	170.9	0.415	0.60	1.12
CFC-115	154.5	0.230	0.32	1.08
CH_3CCl_3	133.4	0.798	0.15	0.15
CFC-22	86.5	0.410	0.05	0.09

[a]Relative efficiency for destroying ozone per unit of mass of the compound released to the atmosphere, normalized to unity for CFC-11 (from Wuebbles 1983, Table 4).

[b]Relative efficiency per chlorine atom released, also normalized to unity for CFC-11.

It will be noted that some compounds have a lower potential for destroying ozone simply because they contain less chlorine, while others (in the lower group in Table 5) have a much smaller effect on ozone because of their removal by reactions (with hydroxyl) in the troposphere. Of course, these compounds are not all interchangeable in their various applications because they have different physical, chemical, and thermodynamic properties. Nevertheless, over a period of time and with some process or equipment modifications, some substitution of the less-destructive for the more-destructive compounds should be possible.

10. THE GREENHOUSE EFFECT

The temperatures of the earth's surface and lower atmosphere are controlled in part by minor gaseous constituents of the atmosphere that absorb infrared (ir) radiation, mainly from the surface. The most important of these so-called greenhouse gases are water vapor and CO_2, but other trace gases also influence the transfer of ir radiation within the atmosphere. Among these are ozone,* nitrous oxide, methane, and the chlorofluorocarbons. The concentrations of all of these trace gases appear to be changing, or are subject to change, as a result of human activities and the magnitudes of the prospective changes are sufficient to cause significant changes in temperature and climate. Although most attention has been focused on CO_2 as a "greenhouse gas," the combined effects of N_2O, CH_4, and the CLCs may be comparable in magnitude to that of CO_2 alone (Seidel and Keyes 1983; Chamberlain et al. 1982; Ramanathan et al. 1985).

The potential contribution of the CLCs to the overall greenhouse effect has been investigated by several authors whose conclusions were reviewed by Ramanathan (1982). Ramanathan's summary of the available estimates is reproduced in Table 6. The various estimates are, in fact, a bit difficult to compare because different approximations were used. The differences are related, among other things, to the treatment of various feedback effects; that is, the anticipated temperature rise, resulting from the change in trace-gas concentration, will itself cause changes in other parameters of the problem (e.g., water vapor content, clouds, surface albedo, etc.), and these effects are treated differently in different computations or are not taken into account at all.

From the papers referred to in Table 6 and other sources, I have prepared Table 7, which identifies the individual contributions of CFC-11 and CFC-12. The upper part of Table 7 lists calculated values of the average global surface temperature increase per unit increase in mixing ratio of the two principal CLCs considered in this study (measured in parts per billion by volume). The line labeled "Sum × 2" contains the same numbers as Table 6. Also shown is the ratio of the temperature response per part-per-billion increase in CFC-12 to that for CFC-11. Most studies indicate a value of about 1.2.

Differences in the estimates shown in Table 7 can arise from differences in modeling assumptions, some of which (i.e., feedback effects) should have a similar effect on the temperature sensitivity for various trace gases; that is, the ratio of the temperature changes induced by changes in concentration of the CFMs and of CO_2 may be more reliably calculated than the absolute magnitude of the temperature changes for a given gas. For this reason, in the lower part of Table 7, we express the temperature change per part-per-billion (by volume) increase in CFC-11 or CFC-12 in units of $(\Delta T_2)_{CO_2}$, the temperature change associated with a twofold increase in CO_2 concentration. This "doubling ΔT" for CO_2 is not yet well determined, partly because of remaining

*Most of the total column ozone is in the stratosphere, and it is there that most of the absorption of incident uv light takes place. However, because of pressure broadening of the ir absorption lines, the tropospheric ozone is more important as a greenhouse gas.

Table 6. Estimated surface temperature change (°C) resulting from increased CFM concentrations[a]

Model	FCA[b]	FCT[c]	Empirical[d]
Ramanathan (1975)	0.56	0.9	0.9
Reck and Fry (1978)	0.6–0.76		
Goddard Institute for Space Studies:			
Wang et al. (1976)	0.38	0.56	
Wang, Pinto, and Yung (1980)		0.69	
Hansen et al. (1981)		0.50	
Lacis et al. (1981)		0.65	
Karol et al. (1981)	0.8		
Chamberlain et al. (1982)			1.42

[a]$CFCl_3$ and CF_2Cl_2 are each increased from 0 to 2 ppbv.

[b]1-D radiative-convective model with fixed relative humidity and with fixed cloud-top altitude.

[c]Same as (*b*), except for fixed cloud-top temperature (rather than altitude).

[d]Estimated from an empirical expression for the surface temperature sensitivity parameter dT/dF, the change in surface temperature per unit change in downward long-wave radiation flux at the surface (Chamberlain et al., 1982) or outward flux at the top of the atmosphere (Ramanathan).

Source: Ramanathan (1982).

uncertainties regarding feedback effects. It seems expedient, therefore, to measure the possible future greenhouse effect of the CFMs in terms of the doubling ΔT for CO_2.

The expression given by Lacis et al. (1981) (column d of Table 7) is

$$\begin{aligned}\Delta T(°C) = {} & 0.57[CH_4]^{0.5} + 2.8[N_2O]^{0.6} - 0.057[CH_4][N_2O] \\ & + 0.15[CFCl_3] + 0.18[CF_2Cl_2] \\ & + 2.5 \ln [1 + 0.005\ \Delta CO_2 + 10^{-5}(\Delta CO_2)^2] \quad ,\end{aligned}$$

where

$[CH_4]$ = the methane concentration (in ppmv),
$[N_2O]$ = the nitrous oxide concentration (in ppmv),
$[CFCl_3]$ = the CFC-11 concentration (in ppbv),
$[CF_2Cl_2]$ = the CFC-12 concentration (in ppbv),
ΔCO_2 = the increase in CO_2 concentration (in ppmv) relative to a reference concentration of 300 ppmv.

This expression fits the results of numerous 1-D radiation–convection model calculations to better than 5% of the calculated ΔT for $[CH_4] < 5$ ppm, $[NO_2] < 1$ ppm, $\Delta CO_2 < 300$ ppm, $[CFCl_3] <$

Table 7. Increase in average surface temperature per unit increase in concentration of CFC-11 and CFC-12

	Ramanathan (1975)		Reck and Fry (1978)	Lacis et al. (1981)	Chamberlain et al. (1982)	Seidel and Keyes (1983)		Ramanathan et al. (1985)
	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)	(*h*)
				ΔT(°C)/ppbv				
CFC-11	0.180	0.207	0.16	0.15	0.25	0.161	0.209	0.13
CFC-12	0.215	0.247	0.14	0.18	0.47	0.194	0.251	0.15
Sum	0.395	0.454	0.30	0.33	0.72	0.355	0.46	0.28
Sum × 2	0.79	0.91	0.60	0.66	1.44	0.71	0.92	0.56
CFC-12/CFC-11	1.20	1.20	0.88	1.20	1.9	1.20	1.20	1.15
				$\frac{\Delta T(°C)/ppbv^{i}}{(\Delta T_2)_{CO_2}}$				
CFC-11				0.049		0.054	0.070	0.074
CFC-12				0.059		0.065	0.084	0.085
Average[j]				0.056		0.061	0.079	0.082

[a]FCT (fixed cloud-top temperature); no feedbacks.

[b]Increased by 15% to allow for feedbacks.

[c]FCA (fixed cloud-top altitude); no feedback; includes effects of aerosol particles.

[d]FCT. Model gives $(\Delta T_2)_{CO_2} = 3.06$ (the temperature rise for CO_2 doubling).

[e]Based on empirical estimates of sensitivity parameter dT/dF (see note *d*, Table 6).

[f]Seidel and Keyes (1983), based on an expression furnished by Lacis (Goddard Institute for Space Studies) that is similar but not identical to the expression of Lacis et al. (1981); values listed correspond to present concentrations of all other trace gases; value assumed for $(\Delta T_2)_{CO_2}$ is 3.0°C.

[g]Seidel and Keyes (1983); for $\Delta CO_2 = 300$ ppm; $\Delta CH_4 = 3$ ppm and $\Delta NO_2 = 0.3$ ppm; $(\Delta T_2)_{CO_2} = 3.0$°C.

[h]FCA; no ice-albedo feedback.

[i]$(\Delta T/\text{ppbv}) \div (\Delta T_2)_{CO_2}$ is the temperature change per part-per-billion (by volume) increase for CFC-11 or CFC-12 relative to the temperature change associated with a doubling of the CO_2 concentration.

[j]Average = 1/3(value for CFC-11) + 2/3(value for CFC-12).

2 ppb, and $[CF_2Cl_2] < 2$ ppb. In this expression, the effect of the CFMs is linear and is independent of changes in concentrations of the other trace gases.*

An expression given by Seidel and Keyes (1983), as obtained from Lacis at the Goddard Institute for Space Studies, is

$$
\begin{aligned}
F = {} & 2.6 \times 10^{-5} (\Delta CO_2)(1 + 0.0022\Delta CO_2)^{-0.6} \\
& - 5.88 \times 10^{-3}\tau + 3.685 \times 10^{-4}\tau^2 \\
& - 4.172 \times 10^{-7} (\Delta CO_2)\tau + 1.197 \times 10^{-3} (\Delta CH_4)^{0.5} \\
& + 5.88 \times 10^{-3}(\Delta N_2O)^{0.6} - 1.197 \times 10^{-4} (\Delta CH_4)(\Delta N_2O) \\
& + 3.15 \times 10^{-4} [CFCl_3] + 3.78 \times 10^{-4} [CF_2Cl_2] \\
& + \text{terms involving insolation and volcanic aerosols .}
\end{aligned}
$$

In this expression, in addition to terms already defined,

F = downward long-wave radiation flux at the surface (in cal/cm^2-min),
$\tau = \Delta T \div (\Delta T_2)_{CO_2}$,
ΔCH_4 = the change in CH_4 concentration from a reference value of 1.6 ppmv,
ΔN_2O = the change in N_2O concentration from a reference value of 0.3 ppmv, and
ΔCO_2 = the change in CO_2 concentration relative to a reference concentration of 293 ppmv.

The temperature change that restores equilibrium following a change in concentration in one or more of the trace gases is obtained by setting $F = 0$ and solving for τ. Because of the quadratic term in the temperature change and the cross term involving ΔCO_2 and τ, this expression is not quite linear in CFM concentration, and the temperature effect of the CFMs is not independent of the concentrations of the other gases. Column *f* of Table 7 was obtained with ΔCO_2, ΔCH_4, and ΔN_2O all equal to zero, while column *g* was obtained with $\Delta CO_2 = 300$ ppm, $\Delta CH_4 = 3$ ppm, and $\Delta N_2O = 0.3$ ppm. For the latter conditions, the weighted average sensitivity to increasing CFM concentration is $\tau = 0.079$ ($\sim$0.08) per part per billion by volume. This is the sensitivity value used here to approximate the greenhouse effect of the CFMs for the various scenarios considered in this study; it is applied to the combined total mixing ratio for CFC-11 and CFC-12. It may be noted that essentially the same relative sensitivity value ($\tau = 0.08$/ppbv) is implied by the results of Ramanathan et al. (1985). Using the weighted-average sensitivity indicated in the last line of Table 7 (i.e., one-third of the sensitivity for CFC-11 plus two-thirds of the sensitivity for CFC-12) implies that CFC-12 is twice as abundant as CFC-11 in the troposphere. This is approximately the case, so long as their emission rates remain in the same proportions as at present, as is assumed for all the scenarios. In fact, because of the longer atmospheric lifetime of CFC-12, its mixing ratio increases somewhat more than that of CFC-11; its relative abundance increases from about two times that of CFC-11 in the near term to a little more than three times that of CFC-11 in the long term. Because the sensitivities of CFC-11 and CFC-12 are thought to be nearly the same, the weighted average is not very sensitive to changes in the ratio of concentrations,

*The possible greenhouse effect of CFM-induced changes in ozone concentration is discussed later in this section.

varying only a few percent as the concentration ratio (CFC-12/CFC-11) ranges from zero to infinity.

The last expression above (Seidel and Keyes 1983) suggests that the temperature sensitivity to increasing CFM concentrations becomes slightly larger as the CFM concentration increases, but this is merely an artifact of the fitting to results of a large number of 1-D radiation–convection calculations for various combinations of trace gases. Ramanathan (1975) states that the optically thin approximation (i.e., no saturation of ir absorption bands) should remain approximately correct for CFC-11 and CFC-12 concentrations less than about 5 ppbv each. For higher concentrations, the sensitivity would decrease. In none of the scenarios considered in this study does the CFC-11 concentration exceed 5 ppbv. However, the CFC-12 concentration does exceed 5 ppbv in scenarios 3 and 4, though only after the latter part of the next century. For these scenarios, the contribution of the CFMs to the greenhouse effect is probably overestimated in the later years.

The calculated increases in global average temperature for each scenario (relative to the doubling ΔT of CO_2) are presented in Fig. 35.* For the standard scenario (case 1), with constant

*Note that these are equilibrium temperature increases for the concentrations that prevail in each year; no allowance has been made for the lags associated with the enormous heat capacity of the oceans.

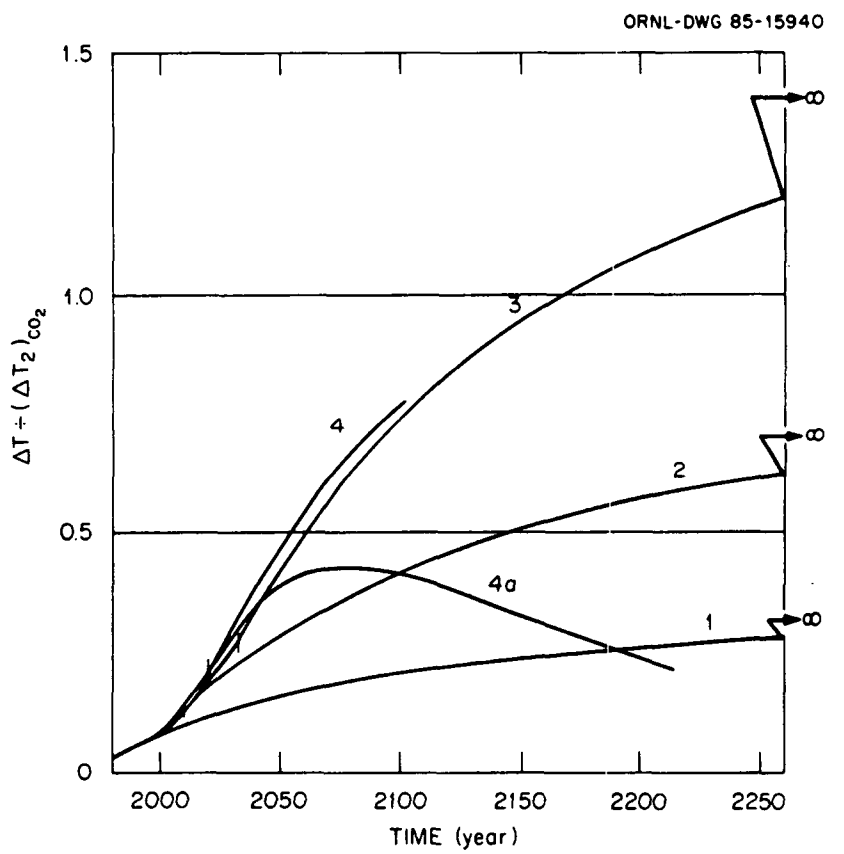


Fig. 35. Increase in global annual average surface temperature due to increasing concentrations of CFC-11 and CFC-12 versus time for scenarios 1–4 and 4a, expressed as a fraction of the doubling ΔT for CO_2.

emissions, the temperature increase attributable to CFC-11 and CFC-12 approaches one-third the doubling ΔT of CO_2. However, the approach to this asymptotic value is very slow, as in the case of ozone reduction. By the latter part of the coming century, when CO_2 may, in fact, have doubled, the CFM effect (for case 1) would be only about 15–20% as large. This is not quite negligible; and, if it began to appear that some restrictions on CO_2 emissions might be needed, pressures would arise to moderate also the effects of the other greenhouse gases, including the CFMs. Thus the standard scenario would seem to be a marginal case. If climate change due to increasing concentrations of CO_2 (and of other trace gases) becomes a sufficiently serious source of concern to require some restriction on emissions, the CFMs, even in this scenario, would probably come under attack. This is especially true since the atmospheric lifetimes of the CFMs, though long, are not as long as that of CO_2 (i.e., roughly a century as compared to a millenium). Thus a somewhat faster response would be expected from reduction in CFM emissions than from reduction in CO_2 emissions.

For scenarios 3 and 4, the estimated temperature rise is clearly much more rapid than for the standard scenario and, indeed, is perhaps half as large as that to be expected from future increases in CO_2. This is illustrated in Fig. 36, in which a comparison is made between temperature rise due to increases in CO_2 concentration for several CO_2 growth scenarios and the temperature rise due to CFMs in our cases 1–4. The CO_2 scenarios shown in Fig. 36 are taken from an earlier study (Perry 1984) and are selected to cover a range of key parameters characterizing the possible future emissions of CO_2. These parameters are

α_0: The initial post-1980 growth rate in annual CO_2 emissions (units: %/year).

p_{max}: The maximum annual CO_2 emission rate (units: 10^9 metric tons of carbon/year).

Q_∞: The ultimate cumulative total carbon release, related to the combined resources of oil, gas, and coal that will eventually be used (units: 10^9 tons of carbon).

$(CO_2)_{max}$: The maximum atmospheric concentration of CO_2 (units: ppmv), as calculated with the carbon cycle model of Killough and Emanuel, Model 3b (Killough and Emanuel 1981; Perry 1984).

The CO_2 concentrations associated with these CO_2 emission scenarios are shown in Fig. 37.

As may be seen from Fig. 36, the principal parameter governing the temperature increase due to CO_2 over the next few decades is the initial post-1980 growth rate, α_0. Although it is not possible to forecast future CO_2 emissions precisely, it presently appears that growth rates of 1–2%/year over the next few decades are more likely than higher growth rates of, say, 3–4%/year or more (Perry 1982; Edmonds et al. 1984). For the lower growth rates, the temperature increases due to CO_2 cluster around a line that may be approximated by the expression

$$\tau = \Delta T/(\Delta T_2)_{CO_2} \approx 0.13 + 0.01(t-1980), \ (2000 \leq t \leq 2060) ,$$

while the temperature rise due to CFMs in scenario 3, after about 2040, is roughly half as large. Thus, if global warming associated with increased concentrations of the ir-absorbing trace gases becomes a problem, the CFMs could be a significant part of that problem, and pressures to reduce emissions of CFMs could become comparable to pressures to reduce CO_2 emissions.

In short, the greenhouse effect, like the ozone reduction problem, could well put a cap on future growth in CFM emissions.

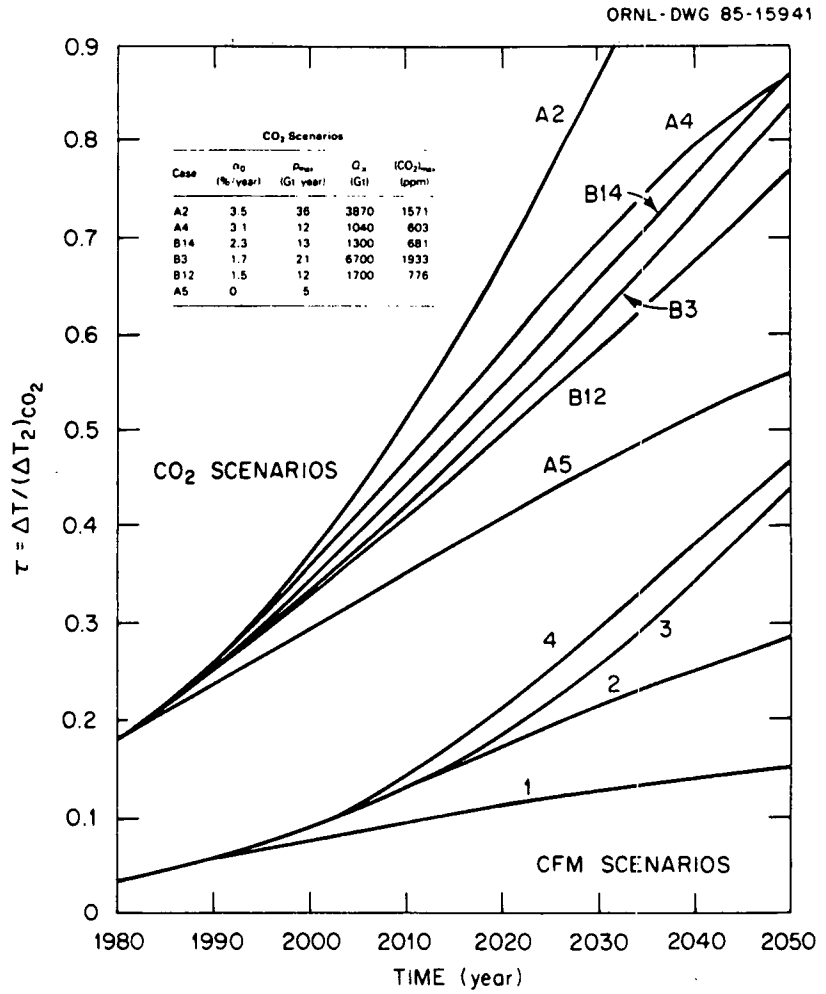


Fig. 36. Comparison of relative temperature rise versus time due to CFMs with that due to CO_2. For the CO_2 scenarios (from Perry 1984), α_0 is the initial, post-1980 growth rate in annual CO_2 emissions, p_{max} is the maximum annual CO_2 emission rate (in 10^{15} g of carbon/year), Q_∞ is the ultimate cumulative total post-1980 CO_2 release (in 10^{15} g of carbon), and $(CO_2)_{max}$ is the maximum attained CO_2 concentration (in ppm).

It should be noted that nothing has been said thus far about the possible greenhouse effect of CLCs other than CFC-11 and CFC-12. However, these two appear to be the main contributors and probably will remain so (Wuebbles 1983; Ramanathan et al. 1985). Other compounds either are released to the atmosphere in much smaller amounts (e.g., CFC-113, CFC-114, CFC-115) or have much shorter atmospheric lifetimes and hence lower concentrations (e.g., CFC-22, CH_3CCl_3). In addition, it appears that most of the other CLCs are not stronger ir absorbers than CFC-11 and CFC-12. Among the compounds whose temperature sensitivities (i.e., ΔT/ppbv) have been estimated by one or more of the authors represented in Table 7 are (in addition to CFC-11 and CFC-12): CCl_4, CF_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, CH_4, C_2H_4, and CH_3CCl_3. Table 8 offers a comparison of estimated temperature sensitivities for these compounds. It may be noted that most of the compounds are estimated to have lower sensitivities (°C/ppb) than CFC-11 and CFC-12, either because their ir absorption bands are not as strong or because they fall in a wavelength range

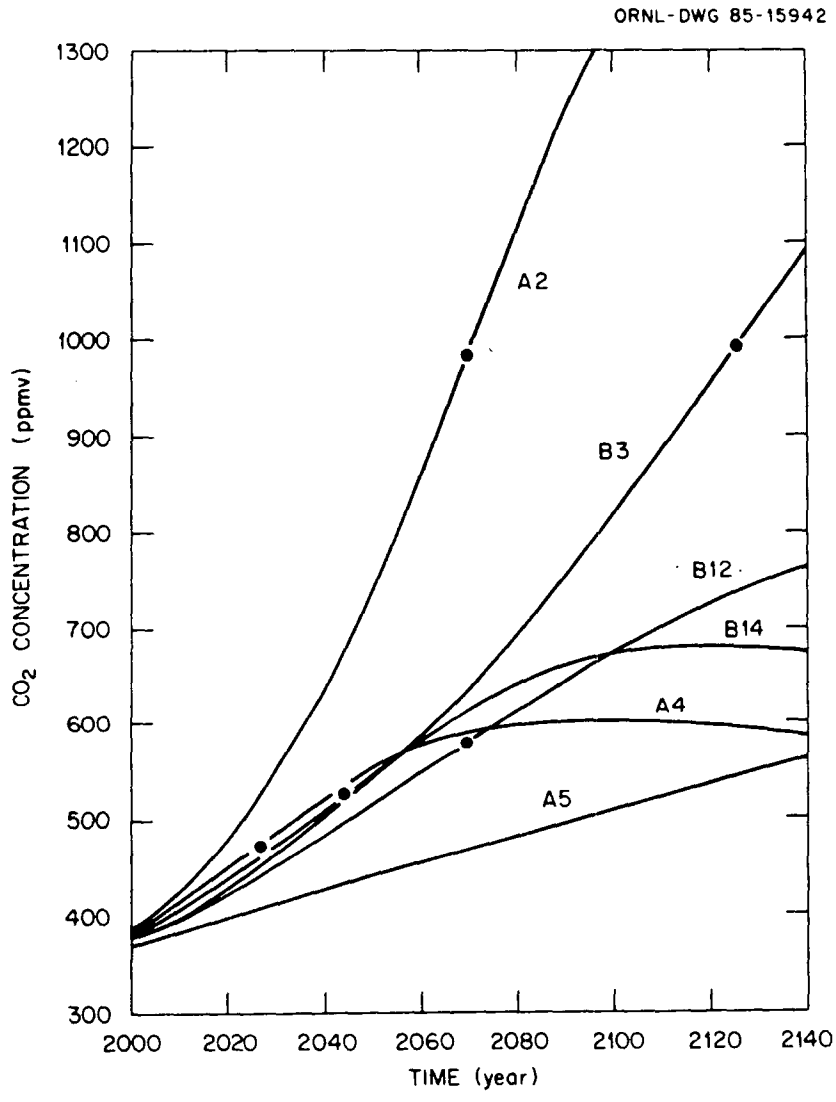


Fig. 37. CO_2 concentrations versus time for the CO_2 scenarios shown in Fig. 36. Dots on curves indicate the times when maximum annual CO_2 emissions, p_{max} occur.

already covered by another strong absorber such as water vapor or CO_2. The large disagreement for C_2H_4 is unexplained.

Since ozone is an important greenhouse gas and since it is depleted by increasing CFM concentrations, we must consider to what degree the ozone reduction may offset the temperature increase due to the CFMs. Wang, Pinto, and Yung (1980) estimated that the steady-state (asymptotic) temperature increase due to CFMs alone, for the standard scenario (with constant CFM emissions), would be about 0.64°C (fixed cloud-top temperatures, with ice-albedo feedback). They also estimated for this case that the cooling associated with reduced ozone concentrations would be about 0.4°C, leaving a net warming of 0.24°C due to CFMs with the ozone feedback effect included. However, their calculations for this case indicate a steady-state ozone reduction of 18% of total column ozone and show especially high sensitivity of surface temperature to ozone

Table 8. Temperature sensitivities of some halocarbons and hydrocarbons [ΔT(°C)/ppbv]

Compound	Ramanathan (1975)[a]	Wang et al. (1976)[a]	Reck and Fry (1978)	Wang, Pinto, and Yung (1980)[b]	Chamberlain et al. (1982)	Ramanathan et al. (1985)[c]
$CFCl_3$	0.21	0.14	0.19	0.23[d]	0.24	0.13
CF_2Cl_2	0.25		0.15		0.47	0.15
CCl_4	0.14				0.14	0.07
CF_4				0.07	0.06	0.05
CHF_2Cl						0.05
$CHCl_3$	0.104					0.06
CH_2Cl_2	0.052					0.02
CH_3Cl	0.013				0.006	
CH_4		0.00018[e]				0.0002[f]
C_2H_4		0.005			1.8	
CH_3CCl_3						0.01

[a]Fixed cloud-top temperature.
[b]Fixed cloud-top temperature, with ice-albedo feedback.
[c]Fixed cloud-top altitude; no ice-albedo feedback.
[d]Average for CFC-11 and CFC-12.
[e]Average over increase from 1.6 to 3.2 ppm.
[f]Average over increase from 1.6 to 2.0 ppm.

depletion in the neighborhood of the tropopause. It is in this region (and in the lower stratosphere, up to about 30 km) that recent revisions in the atmospheric chemistry calculations have most modified the earlier estimates of ozone depletion. These revisions, as noted earlier in Sect. 4, have sharply reduced the estimates of total ozone depletion, from about 18% to perhaps 5–7% for the standard scenario, with most of the adjustment occurring below 30 km. Indeed, the 1979 prediction of a large ozone depletion is now replaced by a prediction of a modest increase in ozone concentration in this altitude range. Ramanathan and Dickinson (1979) also point out the strong dependence of surface temperature change on the altitude dependence of the ozone perturbation. They found that a reduction in ozone concentration at any altitude tends to warm the surface and lower atmosphere because of an increase in solar radiation reaching those regions. However, reduction in stratospheric ozone cools the stratosphere, and reduction at any altitude reduces the trapping of longwave radiation emitted from the surface–troposphere system; both effects reduce the downward emission of longwave radiation, thus tending to cool the surface. While the surface warming due to increased solar radiation is independent of the altitude of the ozone perturbation (reduction), the surface cooling due to decreased longwave radiation from above diminishes with increasing altitude of the perturbation. Thus, for a reduction in ozone in the middle or upper stratosphere, the shortwave effect dominates, and a net warming of the surface occurs. For an ozone reduction in the lower stratosphere or troposphere, the longwave effect dominates, and a net cooling occurs. Thus, as pointed out by Ramanathan et al. (1985), both the large, CFM-induced depletion of ozone at higher altitudes and the now-anticipated small increase in ozone at lower altitudes contribute to a warming of the surface and lower atmosphere. The amount of this

warming is estimated to be perhaps 20–25% as large as that of the CFMs themselves. However, because it is the net result of two larger components of opposite sign (i.e., the solar radiation and the longwave radiation effects), the net effect is quite uncertain and is neglected in the present work.

In summary, the estimated greenhouse effect of the CFMs, relative to that of CO_2, is as shown in Figs. 35 and 36 for the various scenarios considered in this study. For the standard scenario (case 1), the effect appears to be marginal. For the growth scenarios, and especially for cases 3 and 4, the effect is a significant fraction of that to be expected from CO_2. Thus, in these scenarios, pressures for reduction of CO_2 emissions would almost certainly be accompanied by pressures to reduce CFM emissions.

We next consider the greenhouse effect of the evasion scenarios, previously considered in connection with the issue of ozone depletion. These are shown in Fig. 38. In all of these cases, the maximum temperature rise ranges from about 0.3 to about 0.5 times the CO_2 doubling ΔT, and these temperatures occur in the time period 2070 to 2100, when the CO_2 concentration, if not controlled, may have reached 600 ppm (i.e., roughly twice the concentration in 1900). Again, this is not a negligible contribution. Thus the evasion scenarios considered here (or their equivalents in more gradual and more realistic transitions), even if successful from the point of view of ozone depletion, might be considered barely acceptable, or unacceptable, from the point of view of global climate change.

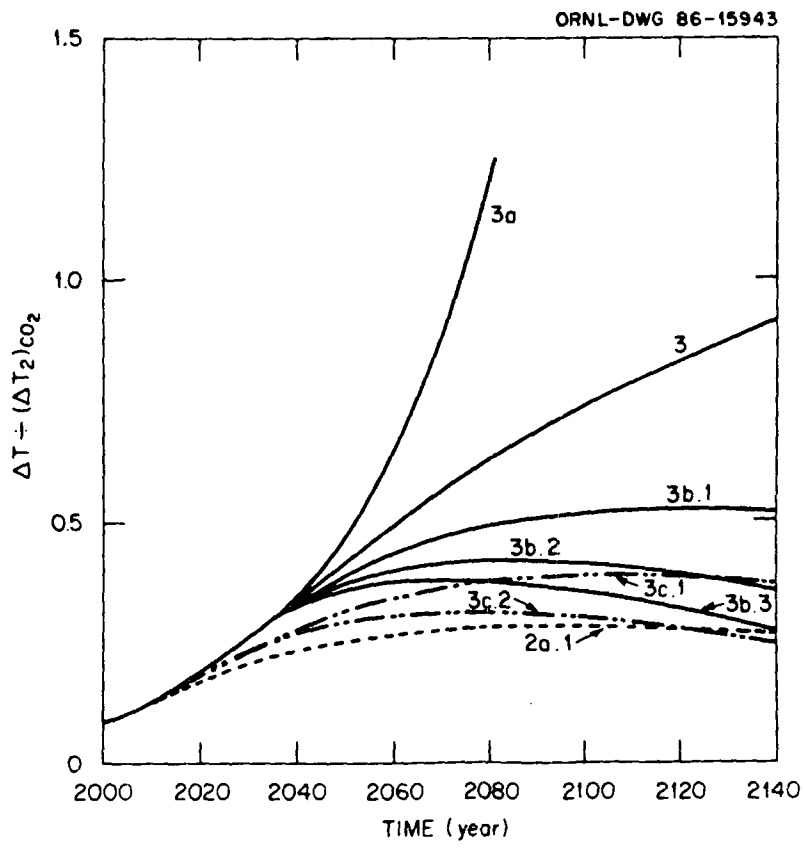


Fig. 38. Increase in global annual average surface temperature versus time for the CFC evasion scenarios.

A similar conclusion is reached from consideration of the market penetration scenarios described in Sect. 7. Results for these scenarios are summarized in Fig. 39 in the form of a correlation between the temperature parameter $\tau = \Delta T/(\Delta T_2)_{CO_2}$ and the relative ozone depletion, $(\Delta O_3)_{rel}$, both of which depend (in the formulations used to calculate them in this study) only on the tropospheric inventories, M_{11} and M_{12}, or equivalently on the corresponding mixing ratios [CFC-11] and [CFC-12]. The correlation cannot be exact because the proportions of CFC-11 and CFC-12 are different in different scenarios, owing to their different atmospheric lifetimes. However, it is more than adequate for our present purpose. The correlation of τ versus $(\Delta O_3)_{rel}$, shown in Fig. 39, is independent of the absolute value of ozone depletion for these cases, but a correlation of τ with the absolute value itself (i.e., ΔO_3) is not. The correlations corresponding to 5, 7, and 9% for the steady-state ozone depletion in scenario 1 are shown in Fig. 40.

Figure 39 indicates that values of $(\Delta O_3)_{rel}$ of 1 or 2, employed in the acceptability criterion of the previous section, correspond to (equilibrium) temperature increase of about 0.28 to 0.47 (~0.3 to 0.5) times the doubling ΔT of CO_2. As noted above, these are not negligible contributions to the greenhouse effect. If the doubling ΔT of CO_2 turns out to be as much as 4 or 4½°C, the concentrations of CFC-11 and CFC-12 that correspond to $(\Delta O_3)_{rel} = 1$ or 2 (i.e., τ ~0.3 to 0.5) may well be found to be unacceptable, even if they are considered acceptable from the standpoint of total ozone depletion. In short, it is quite possible that consideration of climate impacts of CFC-11 and CFC-12 will be found to be at least as significant as their impact on total ozone, if not more so.

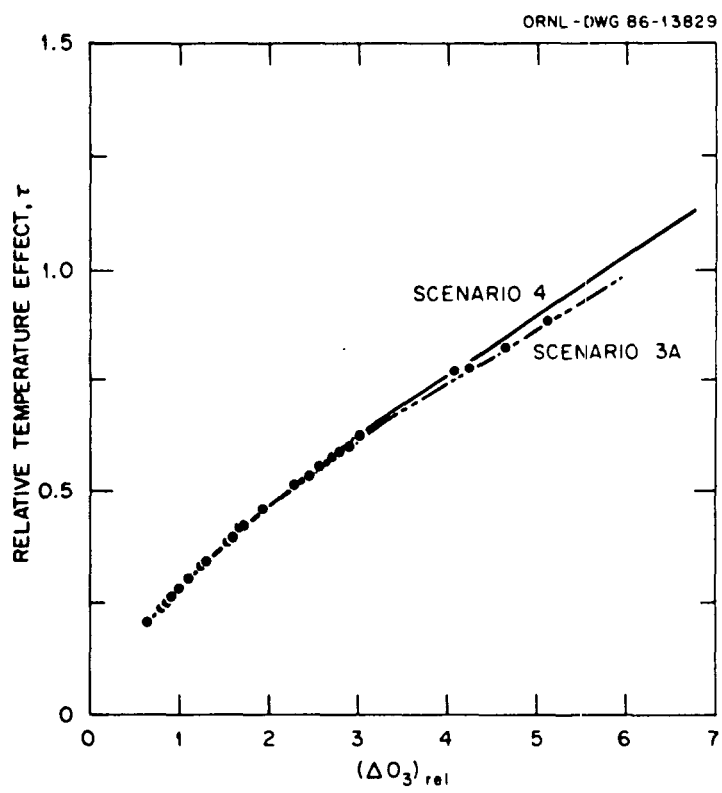


Fig. 39. Correlation between relative temperature rise, $\tau = \Delta T/(\Delta T_2)_{CO_2}$, and relative ozone depletion. Lines are taken from scenarios 3a and 4. Dots are taken from the peaks of the market penetration scenarios.

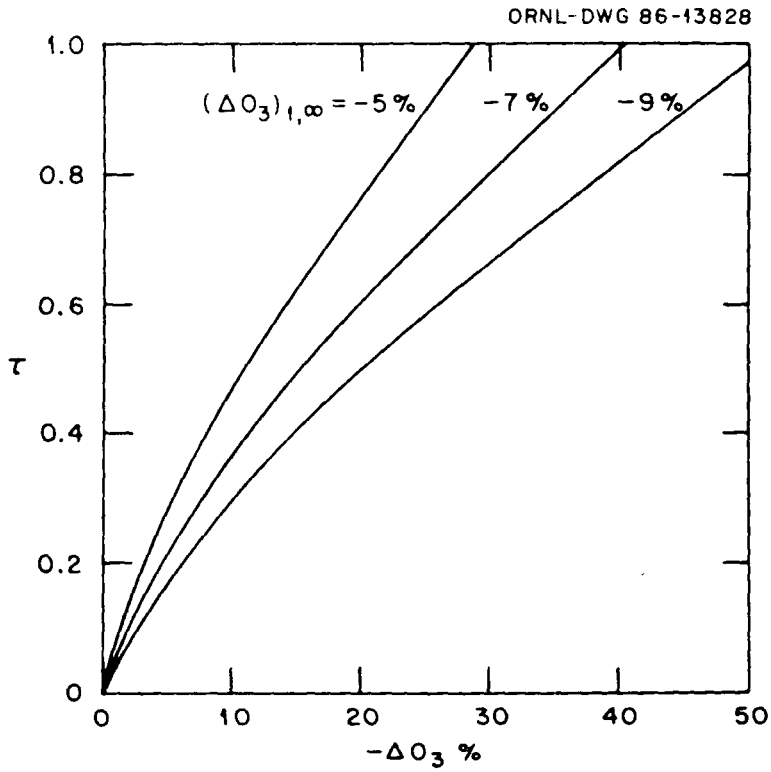


Fig. 40. Correlation between relative temperature rise and absolute ozone depletion for 5, 7, and 9% steady state ozone depletion for scenario 1.

Substitution of CFC-22 for CFC-12, where possible, would significantly reduce the impact of CFCs on climate, as it would their impact on the ozone layer (Sect. 9). According to Ramanathan et al. (1985), a molecule of CFC-22 is only about one-third as effective in contributing to the greenhouse effect as a molecule of CFC-12 (Table 7). Taken together with a factor of about 6 in atmospheric lifetime (WMO 1986, Table 3.3), and a factor of 1.4 in molecular weight, this indicates that for equal annual emission rates (kg/year) CFC-22 would be about (1/3)(1/6)(1.4) = 0.08 times as significant a contributor to the greenhouse effect as CFC-12. On both counts, then—ozone depletion and greenhouse effect—the impact of CFC-22 would be an order of magnitude less than that of CFC-12.

11. CONCLUSIONS

From the foregoing analysis and discussion, I draw the following conclusions. I am aware that some of these may be controversial; nevertheless, they represent my reading of the current situation.

1. With respect to stratospheric ozone depletion, the standard, reference scenario (with constant CLC emissions at current rates) does not appear to me to be a source of immediate concern. The asymptotic ozone depletion due to CLC releases in this scenario is probably sufficiently small (e.g., around 5–10%) and the time required to approach equilibrium sufficiently long that forced reduction of CLC emissions below the current levels would not be justified in the next several decades. The effect would develop very slowly (Fig. 30), requiring many decades to reach one-half of the steady-state ozone depletion and leaving ample time for future corrective action if later evidence should indicate the need for it. Moreover, plausible increases in the concentrations of other trace gases (CO_2, CH_4, NO_x) may reduce the loss of ozone, at least partially offsetting the depletion due to the CLCs (Fig. 7) and possibly even reversing the sign of the ozone change.

2. With respect to the greenhouse effect, the standard scenario would, at steady state, give rise to an effect equal to about one-third that due to doubling the concentration of CO_2 (Fig. 35). Relative to the increasing influence of CO_2 on climate, that of the CFMs in the standard scenario would remain roughly one-fifth as large (Fig. 36). If it should prove necessary to try to limit the increase of the CO_2 concentration because of climatic effects, some attention would undoubtedly be given also to the CFMs.

3. It seems likely, however, that annual worldwide emissions of CLCs will not remain constant but will begin again to increase to rates much higher than the present rates (e.g., Fig. 20). These higher emission rates, if continued, would eventually cause reductions in total column ozone that would probably be unacceptable (Fig. 30). Thus the prospect of future growth in emissions is cause for concern.

4. Even if CLC emissions do increase at modest rates (e.g., 3%–5%/year), measures to restrict such growth may not be necessary immediately. However, growth would probably have to be halted and reversed within a few decades, possibly within the next 15 to 30 years, in order to limit ozone depletion to an acceptable degree (Figs. 21, 22 and 31–34). Neglecting the offsetting effect of other trace gases (Fig. 33), the eventual maximum ozone depletion increases by a factor of about 1.5 for each decade of delay in implementing an effective substitution (or emission control) program following a period of 3%/year growth in CLC emissions and by a factor of about 2 per decade of delay following growth at 5%/year (Fig. 34).

   It should be noted that the optimum (i.e., the lowest-cost) scenario for limiting future CLC emissions has certainly not been determined in this study. Such a determination would require

far more information than is presently available concerning the effects of uv radiation and the time-dependent costs of limiting the emissions. Nevertheless, the transition scenarios summarized in Figs. 32 and 34 do suggest that, even with 3%/year growth in emissions, a delay of 15 to 30 years in arresting and reversing that growth would not preclude keeping the maximum ozone depletion to less than 5% to 10%.

5. There are still substantial uncertainties in the analysis of ozone-depletion effects of CLCs. Some of these could be resolved in a manner that could increase the sense of urgency for regulating CLC emissions. If further research shows greater ozone depletion, for a given CLC release, than is presently estimated; if the atmospheric lifetimes prove to be much shorter than those assumed here, so that the approach to equilibrium is much faster; or if the compensating effects of other trace gases prove to be significantly smaller than indicated here, then actions to restrict further releases of CLCs might be required somewhat sooner than is suggested by Fig. 34.

6. With respect to the greenhouse effect, continued emissions at rates substantially above the present rates would lead to climatic effects that are significant in comparison with those expected from increasing concentrations of CO_2. For example, in scenarios 3 and 4 (Fig. 19), with emissions at about 4½ times the present rates, the greenhouse effect of the CFMs would eventually exceed that due to doubling the CO_2 concentration (Fig. 35); and, during the first half of the coming century, their effect would be one-third to one-half as large as the (increasing) effect of CO_2 (Fig. 36). If restrictions on CO_2 emissions should prove necessary, the same would probably be true of the CFMs, if emissions followed these (or higher) scenarios.

7. The transition scenarios previously considered in connection with ozone depletion would limit the warming effect of the CFMs to one-quarter to one-half that of doubling the CO_2 concentration (Figs. 38 and 39). This is not a negligible effect, and it may be that the greenhouse effect will prove to be as significant as ozone depletion in providing incentives to limit future emissions of CFMs and possibly more so.

8. Even if the reduction of total column ozone is small (as in the standard scenario, scenario 1), there is still expected to be a large relative reduction in ozone density in the upper stratosphere (Fig. 5), which will lead to a significant cooling of that region, augmenting the effect already anticipated from increasing CO_2 concentration. A substantial change in the temperature profile of the stratosphere may have a significant effect on climate. The magnitude and importance of the effect are not clear but deserve further study.

9. Although a discussion of specific measures to limit future emissions of CFMs is beyond the scope of this report, it may be noted that some other CFMs might usefully be substituted for CFC-11 and CFC-12. For example, CFC-22, a possible substitute in some applications, would have a much smaller effect both on ozone depletion and on climate.

12. BIBLIOGRAPHY

Berger, D., D. F. Roberston, and R. E. Davies. 1975. "Field Measurements of Biologically Effective UV Radiation," *Impacts of Climatic Change on the Biosphere, CIAP Monograph 5, Part I: Ultraviolet Radiation Effects*, D. S. Nachtwey, M. M. Caldwell, and R. H. Biggs, eds., U.S. Department of Transportation, Washington, D. C.

Borucki, W. J., et al. 1980. "Stratospheric Ozone Decrease Due to Chlorofluoromethane Photolysis: Predictions of Latitude Dependence," *J. Atmos. Sci.* **37**, 686–697.

Bowman, K. P., and A. J. Krueger. 1985. "A Global Climatology of Total Ozone from the Nimbus 7 Total Ozone Mapping Spectrometer," *J. Geophys. Res.* **90**, 7967–7976.

CMA (Chemical Manufacturers Association). 1982. *World Production and Release of Chlorofluorocarbons 11 and 12 Through 1981*, Report FPP 83-F, Chemical Manufacturers Association, Washington, D.C.

CMA (Chemical Manufacturers Association). 1985. "Production, Sales, and Calculated Release of CFC-11 and CFC-12 through 1984." Letter report, October 1985.

Chamberlain, J. W., et al. 1982. "Climate Effects of Minor Atmospheric Constitutents," in *Carbon Dioxide Review: 1982,* W. C. Clark, ed., Oxford University Press, New York.

Cunnold, D. M., et al. 1983a. "The Atmospheric Lifetime Experiment: 3. Lifetime Methodology and Application to Three Years of $CFCl_3$ Data," *J. Geophys. Res.* **88**, 8379–8400.

Cunnold, D. M., et al. 1983b. "The Atmospheric Lifetime Experiment: 4. Results for CF_2Cl_2 Based on Three Years of Data," *J. Geophys. Res.* **88**, 8401– 8414.

Dütsch, H. N. 1971. "Photochemistry of Atmospheric Ozone," *Advan. in Geophys.* **15**, 219–322.

Edmonds, J. A., et al. 1984. *An Analysis of Possible Future Atmospheric Retention of Fossil Fuel CO_2,* DOE/OR/21400-1 (TR 013), U.S. Department of Energy.

Fisher, J. C., and R. H. Pry. 1970. "A Simple Substitution Model of Technological Change," Technical Information Series Report 70-C-215, General Electric Company, Research and Development Center, Schenectady, New York.

Gerstl, S. A. W., A. Zardecki, and H. L. Wiser. 1981. "Biologically Damaging Radiation Amplified by Ozone Depletions," *Nature* **294**, 352–354.

Hansen, J., et al. 1981. "Climate Impact of Increasing Atmospheric Carbon Dioxide," *Science* **213**, 957–966.

Hudson, R. D., and E. I. Reed. 1979. *The Stratosphere: Present and Future.* NASA R.P. 1049, National Aeronautics and Space Administration, Greenbelt, Md.

Hudson, R. D., et al., eds. 1982. *The Stratosphere 1981: Theory and Measurements*, WMO Global Research and Monitoring Project Report No. 11, World Meteorological Organization, Geneva (available from National Aeronautics and Space Administration, Code 963, Greenbelt, Md. 20771.)

Karol, I., et al. 1981. "Atmospheric Ozone and Global Climate," *Report of U.S./U.S.S.R. Workshop on the Climatic Effects of Increased Atmopsheric Carbon Dioxide*, Leningrad.

Killough, G. G., and W. R. Emanuel. 1981. "A Comparison of Several Models of Carbon Turnover in the Ocean," *Tellus* **33**, 274–290.

Lacis, A., et al. 1981. "Greenhouse Effect of Trace Gases, 1970–1980," *Geophys. Res. Lett.* **8**, 1035–1038.

London, J. 1963. "The Distribution of Ozone in the Northern Hemisphere," *Beitr. Phys. Atmos.* **36**, 254–263.

MacCracken, M. C., and J. S. Chang. 1975. *A Preliminary Study of the Potential Chemical and Climatic Effects of Atmospheric Nuclear Explosions*, UCRL-51653, Lawrence Livermore Laboratory.

Molina, M. J., and F. S. Rowland. 1974. "Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom-Catalyzed Destruction of Ozone." *Nature* **249**, 810–812.

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

NRC (National Research Council). 1976a. *Halocarbons: Environmental Effects of Chlorofluoromethane Release*. National Academy of Sciences, Committee on Impacts of Stratospheric Change, Assembly of Mathematical and Physical Sciences, Washington, D.C.

NRC (National Research Council). 1976b. *Halocarbons: Effects on Stratospheric Ozone*, National Academy of Sciences, Panel on Atmospheric Chemistry, Committee on Impacts of Stratospheric Change, Assembly of Mathematical and Physical Sciences, Washington, D.C.

NRC (National Research Council). 1977. *Response to the Ozone Protection Sections of the Clean Air Act Amendments of 1977: An Interim Report*, National Academy of Sciences, Washington, D.C.

NRC (National Research Council). 1979a. *Protection Against Depletion of Stratospheric Ozone by Chlorofluorocarbons*, National Academy of Sciences, Committee on Impacts of Stratospheric Change, Assembly of Mathematical and Physical Sciences and Committee on Alternatives for the Reduction of Chlorofluorocarbon Emissions, Commission on Sociotechnical Systems, Washington, D.C.

NRC (National Research Council). 1979b. *Stratospheric Ozone Depletion by Halocarbons: Chemistry and Transport*, National Academy of Sciences, Panel on Chemistry and Transport, Committee on Impacts of Stratospheric Change, Assembly of Mathematical and Physical Sciences, Washington, D.C.

NRC (National Research Council). 1982. *Causes and Effects of Stratospheric Ozone Reduction: An Update*, National Academy of Sciences, Committee on Chemistry and Physics of Ozone Depletion and Committee on Biological Effects of Increased Solar Ultraviolet Radiation, Environmental Studies Board, Commission on Natural Resources, Washington, D.C.

NRC (National Research Council). 1984. *Causes and Effects of Changes in Stratospheric Ozone: Update 1983*, National Academy of Sciences, Committee on Causes and Effects of Changes in Stratospheric Ozone: Update 1983, Environmental Studies Board, Commission on Physical Sciences, Mathematics and Resources, Washington, D.C.

OECD (Organization for Economic Cooperation and Development). 1981. *Scenarios for Chlorofluorocarbons*, ENV/CHEM/PJC/81.93, Organization for Economic Cooperation and Development, Paris.

Perry, A. M. 1982. "Carbon Dioxide Production Scenarios," in *Carbon Dioxide Review: 1982*, W. C. Clark, ed., Oxford University Press, New York.

Perry, A. M. 1984. *Atmospheric Retention of Anthropogenic CO_2: Scenario Dependence of the Airborne Fraction*, EPRI/EA-3466, Electric Power Research Institute, Palo Alto, Calif.

Prather, M. J., M. B. McElroy, and S. C. Wofsy. 1984. "Reductions in Ozone at High Concentrations of Stratospheric Halogens," *Nature* **312**, 227–231.

Prinn, R. G., et al. 1983a. "The Atmospheric Lifetime Experiment: 1. Introduction, Instrumentation and Overview," *J. Geophys. Res.* **88**, 8353–8367.

Prinn, R. G., et al. 1983b. "The Atmospheric Lifetime Experiment: 5. Results for CH_3CCl_3 Based on Three Years of Data," *J. Geophys. Res.* **88**, 8415–8426.

Pyle, J. A. 1980. "A Calculation of the Possible Depletion of Ozone by Chlorofluorocarbons Using a Two Dimensional Model," *Pure and Appl. Geophys.* **118**, 355–377.

Ramanathan, V. 1975. "Greenhouse Effect Due to Chlorofluorocarbons: Climatic Implications," *Science* **190**, 50–52.

Ramanathan, V., and R. E. Dickinson. 1979. "The Role of Stratospheric Ozone in the Zonal and Seasonal Radiative Energy Balance of the Earth-Troposphere System," *J. Atmos. Sci.* **36**, 1084–1104.

Ramanathan, V. 1982. "Commentary," in *Carbon Dioxide Review: 1982*, W. C. Clark, ed., Oxford University Press, New York.

Ramanathan, V., et al. 1985. "Trace Gas Trends and Their Potential Role in Climate Change," *J. Geophys. Res.* **90**, 5547–5566.

Reck, R. A., and D. L. Fry. 1978. "The Direct Effects of Chlorofluoromethanes on the Atmospheric Surface Temperature," *Atmos. Env.* **12**, 2501–2503.

Reiter, E. R., and J. E. Lovill. 1974. "Longitudinal Movement of Stratospheric Ozone Waves As Determined by Satellite," *Arch. Meteorol., Geophys. Bioklimatol. Ser. A* **23**, 13–27.

Rowland, F. S., and M. J. Molina. 1975. "Chlorofluoromethane in the Environment," *Rev. Geophys. and Space Phys.* **13**, 1–35.

Scott, E. L., and M. L. Straf. 1977. "Ultraviolet Radiation As a Cause of Cancer," pp. 529–546 in *Origins of Human Cancer, Book A, Incidence of Cancer in Humans*, H. H. Hiatt, J. D. Watson, and J. A. Winsten, eds., Vol. 4 of The Cold Spring Harbor Conferences on Cell Proliferation, The Cold Spring Harbor Laboratory, New York, N.Y.

Scotto, J., T. R. Fears, and J. F. Fraumeni, Jr. 1981. *Incidence of Non-Melanoma Skin Cancer in the United States*, DHHS Publication No. (NIH) 82-2433, National Cancer Institute, Bethesda, Md.

Scotto, J., T. R. Fears, and J. F. Fraumeni, Jr. 1982. "Solar Radiation," pp. 254–276 in *Cancer Epidemiology and Prevention*, D. Schottenfeld and J. F. Fraumeni, Jr., eds., W. B. Saunders Company, Philadelphia, Pa.

Seidel, S., and D. Keyes. 1983. *Can We Delay a Greenhouse Warming?* U.S. Environmental Protection Agency, Washington, D.C.

Setlow, R. B. 1974. "The Wavelengths in Sunlight Effective in Producting Skin Cancer: A Theoretical Analysis," *Proc. Nat. Acad. Sci. USA* **71**, 3363–3366.

Sticksel, P. R. 1970. "The Annual Variation of Total Ozone in the Southern Hemisphere," *Mon. Wea. Rev.* **98**, 787–788.

Stolarski, R. S., and R. J. Cicerone. 1974. "Stratospheric Chlorine: Possible Sink for Ozone," *Can. J. Chem.* **52**, 1610–1615.

Teramura, A. H. 1986. "The Potential Consequences of Ozone Depletion Upon Global Agriculture;" paper presented at the International Conference on Health and Environmental Effects of Ozone Modification and Climate Change, Arlington, Virginia, June 16–20, 1986.

Turco, R. P. 1984. "Stratospheric Ozone Perturbation," Chapter 6 in *Stratospheric Ozone*, R. C. Whitten and S. S. Prasad, eds., Van Nostrand Reinhold, New York, N.Y.

U.S. Congress, Senate. 1975. "Stratospheric Ozone Depletion Hearings Before the Subcomittee on the Upper Atmosphere, Committee on Aeronautical and Space Sciences," Part 1, Appendix 1, Sept. 8, 9, 16, and 17, 94th Congress.

Wang, W., et al. 1976. "Greenhouse Effects Due to Man-Made Perturbations of Trace Gases," *Science* **194**, 685–690.

Wang, W., J. P. Pinto, and Y. L. Yung. 1980. "Climatic Effects Due to Halogenated Compounds in the Earth's Atmosphere," *J. Atmos. Sci.* **37**, 333–338.

Wofsy, S. C., and M. B. McElroy. 1974. "HO_x, NO_x and ClO_x: Their Role in Atmospheric Photochemistry," *Can. J. Chem.* **52**, 1582–1591.

WMO (World Meteorological Organization). 1986. *Atmosphere Ozone 1985: Assessment of Our Understanding of the Processes Controlling its Present Distribution and Change,* WMO, Global Ozone Research and Monitoring Report No. 16. In press.

Worrest, R. C. 1986. "Is there a 'Doomsday' Scenario for the Effect of Enhanced Levels of Solar UV-B Radiation on Worldwide Fisheries?;" paper presented at the International Conference on Health and Environmental Effects of Ozone Modification and Climate Change, Arlington, Virginia, June 16–20, 1986.

Wuebbles, D. J. 1983. "Chlorocarbon Emission Scenarios: Potential Impact on Stratospheric Ozone," *J. Geophys. Res.* **88,** 1433–1443.

Wuebbles, D. J. 1985a. Private communication to A. M. Perry, Jan. 30, 1985.

Wuebbles, D. J. 1985b. Private communication to A. M. Perry, December 1985.

Wuebbles, D. J., and J. S. Chang. 1982. "The Relative Efficiency of a Number of Halocarbons for Destroying Stratospheric Ozone," report, Lawrence Livermore National Laboratory, Livermore, Calif.

Wuebbles, D. J., F. M. Luther, and J. E. Penner. 1983. "Effect of Coupled Anthropogenic Perturbations on Stratospheric Ozone," *J. Geophys. Res.* **88**, 1444–1456.

Wuebbles, D. J., M. C. MacCracken, and F. M. Luther. 1984. *A Proposed Reference Set of Scenarios for Radiatively Active Atmospheric Constitutents*, DOE/NBB-0066 (TR 015), U.S. Department of Energy, Washington, D.C.

ORNL/TM-9817
Distribution Category
UC-11 and UC-95d

Internal Distribution

1. V. D. Baxter
2. T. J. Blasing
3. J. B. Cannon
4. R. S. Carlsmith
5. J. E. Christian
6. C. C. Coutant
7. G. A. Dailey
8. P. D. Fairchild
9. M. P. Farrell
10. W. Fulkerson
11. M. S. Guy
12. V. J. Harley
13. E. L. Hillsman
14. R. B. Honea
15. M. R. Ives
16. M. L. Johnson
17. R. O. Johnson
18. S. V. Kaye
19. J. O. Kolb
20. M. A. Kuliasha
21. R. Lee
22. R. S. Loffman
23. L. N. McCold
24. V. C. Mei
25. W. A. Miller
26. E. A. Nephew

27–46. A. M. Perry

47. S. F. Rayner
48. D. E. Reichle
49. L. W. Rickert
50. C. R. Richmond
51. M. W. Rosenthal
52. R. B. Shelton
53. R. Skeens
54. R. A. Stevens
55. B. T. Tonn
56. R. I. Van Hook, Jr.
57. T. J. Wilbanks
58. H. E. Zittel
59. Central Research Library
60. Document Reference Section

61–62. Laboratory Records

63. Laboratory Records (RC)
64. ORNL Patent Office

External Distribution

65. M. Blatt, Electric Power Research Institute, P.O. Box 10412, Palo Alto, CA 94303
66. J. A. Bledsoe, Vice President Engineering, York International, Central Environmental Systems, York International Corporation, P.O. Box 1592-191B, York, PA 17405-1592
67. A. Braswell, President, Air-Conditioning & Refrigeration Institute, 1501 Wilson Boulevard, 6th Floor, Arlington, VA 22209-2403
68. John Calkins, Department of Radiation Medicine, University of Kentucky, Lexington, KY 40536
69. D. J. Chase, Assistant To The President, Vice President, Public & Governmental Affairs, Lennox Industries, Inc., P.O. Box 809000, Dallas, TX 75380-9000
70. D. M. Dassler, Manager, Advanced Engineering, Snyder General Corporation, Comfortmaker—Snyder General Corporation, Arcoaire—Snyder General Corporation, 401 Randolph Street, Red Bud, IL 62278-1098
71. R. J. Fiskum, Energy Conversion Equipment Branch, U.S. Department of Energy, GF217 Forrestal Building, CE-132, 1000 Independence Avenue, SW, Washington, DC 20585
72. D. Flamm, Vice President, Residential Controls, Honeywell, Inc., 1985 Douglas Drive North, Golden Valley, MN 55422-3992
73. D. F. Foster, President, Air Conditioning Division, Rheem Manufacturing Company, 5600 Old Greenwood Road, Fort Smith, AR 72903
74. S. Malcolm Gillis, Professor, Economics and Public Policy, Department of Economics, Duke University, Durham, NC 27706

75–84. Elizabeth Gormley, Fluorocarbon Program, Chemical Manufacturers Association, 2501 M Street, NW, Washington, DC 20037

85. Theodore Harris, Domestic Policy Council, Room 200, Old Executive Office Building, Washington, DC 20500
86. J. S. Hoffman, U.S. Environmental Protection Agency, 401 M Street, SW, Washington, DC 20460
87. P. Joyner, Electric Power Research Institute, P.O. Box 10412, Palo Alto, CA 94303
88. Fritz R. Kalhammer, Vice President, Electric Power Research Institute, P.O. Box 10412, Palo Alto, CA 94303
89. T. E. Kapus, Building Equipment Division, U.S. Department of Energy, GF 217 Forrestal Building, CE-132, 1000 Independence Avenue, SW, Washington, DC 20585
90. F. A. Koomanoff, Carbon Dioxide Research Division, ER-12, U.S. Department of Energy, Washington, DC 20545
91. A. Lannus, Electric Power Research Institute, P.O. Box 10412, Palo Alto, CA 94303
92. Todd R. LaPorte, Professor, Political Science, Institute of Government Studies, University of California, 109 Moses Hall, Berkeley, CA 94720
93. J. A. Laurmann, Gas Research Institute, 8600 West Bryn Mawr Avenue, Chicago, IL 60631
94. Martin Lessen, Consulting Engineer, 12 Country Club Drive, Rochester, NY 14618
95. M. C. MacCracken, Lawrence Livermore National Laboratory, Livermore, CA 94550
96. R. H. Males, Electric Power Research Institute, P.O. Box 10412, Palo Alto, CA 94303
97. J. P. Millhone, Office of Buildings and Communicty Systems, U.S. Department of Energy, GF231 Forrestal Building, CE-13, 1000 Independence Avenue, SW, Washington, DC 20585
98. Office of Assistant Manager for Energy Research and Development, DOE-ORO, Oak Ridge, TN 37831
99. R. M. Perhac, Electric Power Research Institute, P.O. Box 10412, Palo Alto, CA 94303
100. V. Ramanathan, National Center for Atmospheric Research, Boulder, CO 80307
101. W. R. Reedy, Director, Advanced Technology Engineering, Carrier Corporation, Carrier—United Technologies Corporation, P.O. Box 4808, Carrier Parkway, Syracuse, NY 13221
102. F. S. Rowland, Department of Chemistry, University of California, Irvine, CA 92664
103. M. H. Russell, U.S. Environmental Protection Agency, 401 M Street, SW, Washington, DC 20460
104. J. D. Ryan, Energy Conversion Equipment Branch, U.S. Department of Energy, GF217 Forrestal Building, CE-132, 1000 Independence Avenue, SW, Washington, DC 20585
105. S. R. Seidel, U.S. Environmental Protection Agency, 401 M Street, SW, Washington, DC 20460
106. T. Statt, Energy Conversion Equipment Branch, U.S. Department of Energy, GF217 Forrestal Building, CE-132, 1000 Independence Avenue, SW, Washington, DC 20585
107. A. H. Teramura, Department of Botany, University of Maryland, College Park, MD 20742
108. R. T. Watson, National Aeronautics and Space Administration, Washington, DC 20546
109. C. E. Whittle, Institute for Energy Analysis, Oak Ridge Associated Universities, Oak Ridge, TN 37831
110. E. R. Williams, Office of Environmental Analysis, U.S. Department of Energy, EH-22 Forrestal Building, 1000 Independence Avenue, SW, Washington, DC 20585
111. William H. Williams, Division Manager, AT&T Information Systems, Building 83, Room 1B23, 100 Southgate Parkway, Morristown, NJ 07960
112. J. Wolf, Vice President, Government Affairs, American Standard Corporation, 2020 14th Street, North, Arlington, VA 22201
113. R. C. Worrest, Oregon State University, Corvallis, OR 97331
114. D. J. Wuebbles, Lawrence Livermore National Laboratory, Livermore, CA 94550

115–412. Given distribution as shown in DOE/TIC-4500 under Environmental Control Technology and Earth Sciences and Energy Conservation–Buildings and Community Systems (298 copies, NTIS)

☆U.S. GOVERNMENT PRINTING OFFICE 1986–730-064/40074