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Present State of Knowledge of the Upper Atmosphere: An Assessment Report

Processes That Control Ozone and Other Climatically Important Trace Gases

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Processes That Control Ozone and Other Climatically Important Trace Gases

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PREFACE

This report is based primarily on material contained in the comprehensive assessment document titled "Atmospheric Ozone 1985: Assessment of Our Understanding of the Processes Controlling its Present Distribution and Change" WMO Global Ozone Research and Monitoring Project Report No. 16, that was coordinated by the National Aeronautics and Space Administration (NASA) and co-sponsored by NASA and two other U.S. agencies, the Federal Aviation Administration (FAA) and the National Oceanic and Atmospheric Administration (NOAA); three international agencies, the World Meteorological Organization (WMO), the United Nations Environment Program (UNEP), and the Commission of the European Communities (CEC); and Bundesministerium fur Forschung und Technologie (BMFT) of the Federal Republic of Germany. Approximately 150 scientists from Australia, Belgium, Brazil, Canada, the Federal Republic of Germany, France, Italy, Japan, Norway, the United Kingdom, and the United States of America contributed toward this assessment. While, for the most part, references have been deleted in this report, they may be obtained by referring to the appropriate sections of this larger document.

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EXECUTIVE SUMMARY

There is now compelling observational evidence indicating increases in the concentrations of gases which control atmospheric ozone. These gases, which include the chlorofluorocarbons (CFCs) 11 and 12, methyl chloroform, methane, nitrous oxide, and carbon monoxide, are the precursors to the hydrogen, nitrogen and chlorine oxides which catalyze the destruction of ozone in the stratosphere. The reaction cycles of the hydrogen, nitrogen, and chlorine oxides are highly coupled, and interfere with one another. Models of the system which include projected continuation of the observed increases in all of these gases show little effect on the ozone column (less than 3%) in the next 70 years unless the chlorofluorocarbon release rate increases by more than 1.5% per year. For example, after 70 years a 10% ozone depletion is calculated for a CFC growth rate of 3% per year. However, even when predicted changes in the ozone column are small, a significant vertical and latitudinal redistribution of ozone is predicted which affects stratospheric structure. Since many of these precursor gases have very long atmospheric lifetimes, ozone changes that take place will persist for several tens to hundreds of years.

A crucial question is to assess the extent of changes in global ozone that have already taken place. The search for global ozone trends involves looking for small secular changes amidst large natural variations that occur on many time scales. Statistical methods must be used on the data which are available from relatively few stations. In general, analyses for the trends in the total column of ozone show no statistically significant trend since 1970 in agreement with model predictions for the same period when the changes in all of the trace gases are taken into account. Because abnormally low

total ozone values were observed in 1983, one analysis ending in that year showed a downward trend. Values of total ozone have risen again in 1984 such that the trend apparently disappears. Total ozone measurements in 1985 and 1986 should make it apparent whether a trend has begun or whether 1983 was simply an anomalous year possibly due to the El Chichon volcanic eruption and/or the large El Nino that took place during this period. Trend estimates have also been made for the altitude profile of ozone from the network of stations observing using the Umkehr method. Fewer Umkehr stations exist than those that observe total ozone. Umkehr measurements are made difficult because of the need to eliminate aerosol effects, such as those from volcanic eruptions, on the derived ozone amounts. After adjusting the ozone measurements for the aerosol contribution, an estimate of the ozone trend in the middle and upper stratosphere gives a 2 to 3% decrease for the period 1970 to 1980. This is consistent with the predictions of photochemical models which give similar changes in ozone at this level.

Important new observational evidence on ozone changes has recently been identified. Springtime Antarctic column ozone amounts have been seen to decrease by approximately 40% since the mid-1970's. At present, no mechanism has been determined to explain this change. It is not possible to say with assurance what the implications of these observations are for future global ozone change.

There are now observations of increases in the gases predicted to affect ozone, and there are observations indicating that ozone has changed significantly on a regional and global scale. The question still remains concerning our ability to predict future concentrations of ozone and other atmospheric species. To do this we rely on mathematical models which are constructed to represent the crucial physics and chemistry of the atmospheric

system. Both one- and two-dimensional models are used for this purpose. The ultimate goal of these models is predictive capability, but the primary test of the models is their ability to simulate the features of the present atmosphere which we are now observing in some detail with our measurements program. In general, the models predict the distribution of trace gases quite well. However, close examination of the intercomparison of models and measurements reveal several disturbing detailed disagreements. Some of these disagreements are as follows: modeled ozone concentrations are typically 30-50% lower than measured ozone concentrations in the upper stratosphere; recent OH profile data are lower than current model predictions; and HNO_3 observations are not consistent with model predictions at high altitudes and high latitudes in winter. These disagreements limit our confidence in the predictive capability of these models. In the end, however, our predictive capability will be tested by measuring the changes taking place in the atmosphere. This will require careful measurement of critical species to be carried out over long time periods.

The observed increases in the chlorofluorocarbons, in methane and in nitrous oxide also have direct implications for the Earth's radiative balance through the so-called greenhouse effect. These gases absorb infrared radiation in a part of the spectrum which is otherwise transparent. Presently, changes in trace gases (other than carbon dioxide) are thought to be contributing an amount that is about equal to that of carbon dioxide changes in greenhouse warming of the surface and lower atmosphere. The cumulative effect of the increase in all trace gases for the period 1850-1980 is a predicted equilibrium warming (neglecting the oceans' heat capacity) in the range 0.7 to 2 K. Present estimates indicate that the greenhouse warming predicted to occur during the next 50 years should be about twice that which

has occurred during the previous 130 years. Thus, problems of ozone change and climate change should be considered together. It is also apparent that what has been previously thought of as the carbon dioxide-climate problem should more properly be thought of as the trace gas-chemistry-climate problem.

In summary, what was once mainly based on theoretical predictions is now being confirmed by observations. The composition of the atmosphere is changing due to a variety of influences of both natural and human origin. These changes have implications for a variety of problems and in particular demonstrate the close connections among the studies of global tropospheric and stratospheric chemistry, trace gases and climate. We must realize that a global scale experiment on the atmosphere of planet Earth is being conducted by humankind without our fully understanding the consequences.

I. INTRODUCTION

For more than a decade scientists have postulated that man-made
pollutants could cause harmful effects by reducing the amount of stratospheric
ozone. In recognition of the importance of understanding such atmospheric
perturbations, Congress directed NASA in June 1975 to "develop and carry out a
comprehensive program of research, technology, and monitoring of the phenomena
of the upper atmosphere so as to provide for an understanding of and to
maintain the chemical and physical integrity of the Earth's upper
atmosphere." Responding to this Congressional mandate, NASA implemented a
long-range upper atmospheric science program aimed at developing an organized,
solid body of knowledge of upper atmospheric processes while providing, in the
near term, assessments of potential effects of human activities on the
atmosphere.

Unlike some other more localized environmental issues, e.g. acid
deposition, ozone layer modification is a global phenomenon which affects the
well-being of every country in the world. Many nations around the world have
actively demonstrated their commitment to understand the processes which
control atmospheric ozone and its susceptibility to change because of human
activities by funding research which should reduce the uncertainties that
currently exist concerning the magnitude of predicted ozone modification for
different concentrations of atmospheric pollutants. In order to achieve this
required greater level of understanding national and international scientific
agencies have implemented research programs aimed at developing a
comprehensive knowledge of atmospheric processes.

Many governments around the world, including that of the United States
have recognized that the use of chlorofluorocarbons (CFC's) constitutes a
potential threat to the stability of the ozone layer, and have taken a series

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of individual actions to regulate the use of these substances. However, there has been no coordinated international approach to safeguard the ozone layer. It was recognized by several nations, including the United States, that effective protection of the ozone layer requires a coordinated international approach to regulating substances that are thought to modify atmospheric ozone. Consequently, the United Nations Environment Program (UNEP) Governing Council, at its ninth session in 1981, decided to initiate work aimed at the elaboration of a global framework convention for the protection of the ozone layer. It was decided to establish an Ad Hoc Working Group of Legal and Technical Experts nominated by interested governments and intergovernmental organizations. Representatives from about twenty different countries, including the United States, met in Stockholm, Sweden in January 1982 to initiate formal discussions on the desirability of a global framework ozone convention which would (a) harmonize regulatory control actions on ozone-modifying substances at the international level, (b) increase coordination of ozone related research, and (c) increase the exchange of information on all scientific, economic, technical, and legal issues relevant to the ozone issue. After a series of meetings of the Ad Hoc Working Group of Legal and Technical Experts, a Convention for the Protection of the Ozone Layer was adopted by twenty-one nations, including the United States, at a Diplomatic Conference held in Vienna, Austria, in March 1985. Since that time four more nations have signed the convention. At the thirteenth UNEP Governing Council meeting held in May, 1985, a schedule was adopted for the possible completion of a protocol to regulate chlorofluorocarbons. Since the convention specifically states that all measures taken under this convention should be based on relevant scientific and technical considerations, and that nations should collaborate on scientific assessments, the need for a comprehensive

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evaluation by the international scientific community of all facets of the ozone issue is clear.

Therefore, in order to provide governments around the world with the best scientific information currently available on whether any human activities represent a substantial threat to the ozone layer, several scientific agencies agreed to co-sponsor a peer reviewed international assessment of our current state of knowledge. This international assessment, which was coordinated by NASA, is much more comprehensive than any previous assessment. It discusses, among other topics, the physical, chemical, and radiative processes which control the spatial and temporal distribution of ozone in the troposphere and stratosphere; the magnitude of natural and industrial sources of substances capable of modifying atmospheric ozone; observations of the composition and structure of the stratosphere; the predicted magnitude of ozone perturbations for a variety of emission scenarios involving a number of substances changing both individually and together; the predicted climate change for similar trace gas scenarios employed to predict ozone perturbations; and the ozone and temperature data used to detect the presence or absence of a long-term trend. Previous assessments have tended to be narrower both in scope and in the degree of international participation.

This comprehensive assessment was co-sponsored by three US agencies, i.e. the National Aeronautics and Space Administration (NASA), the Federal Aviation Administration (FAA), and the National Oceanic and Atmospheric Administration (NOAA); three international agencies, i.e. the World Meteorological Organization (WMO), the United Nations Environment Program (UNEP), and the Commission of the European Communities (CEC); and Bundesministerium fur Forschung und Technologie (BMFT) of the Federal Republic of Germany. This assessment titled "Atmospheric Ozone: Assessment of Our Understanding of the

Processes Controlling its Present Distribution and Change," WMO Global Ozone Research and Monitoring Project Report #16, will hereafter be referred to as WMO (1986). Approximately 150 scientists from Australia, Belgium, Brazil, Canada, the Federal Republic of Germany, France, Italy, Japan, Norway, the United Kingdom, and the United States of America contributed towards this assessment.

The WMO (1986) assessment built upon previous national and international assessments, in particular the most recent comprehensive report, "The Stratosphere 1981: Theory and Measurements" WMO Global Ozone Research and Monitoring Project Report #11, which was prepared in 1981 and was co-sponsored by the same three U.S. scientific agencies, (NASA, FAA, and NOAA) and by one international scientific agency, WMO. The rationale for the scope of the present assessment report was based on information gained at a scientific workshop entitled "Current Issues in Our Understanding of the Stratosphere and the Future of the Ozone Layer" which was held in Feldafing, Federal Republic of Germany in June 1984 with international participation, co-sponsored by NASA, FAA, WMO, and BMFT. The assessment activities officially began in the fall of 1984 when leading scientists were selected as chairpersons, and each charged with the responsibility to produce a specific chapter in the assessment report. At a meeting held in November, 1984, the timetable for the assessment was established and key atmospheric scientists who could make valuable contributions were identified and invited to participate in chapter working groups. The participants were chosen for their expertise and re-presented a cross section of the international scientific community. The assessment was developed through a series of small focused workshops, i.e. chapter by chapter, each addressing a specific scientific issue. Considerable care was taken to ensure that those aspects of the issue which involved more

than one chapter were carefully coordinated. Over 30 small working meetings were held between November, 1984, and May, 1985, to prepare draft chapters which were then critically peer-reviewed at a workshop held at Les Diablerets, Switzerland July 7-14, 1985. The 32 participants who attended the meeting included 19 chapter chairpersons, 8 senior reviewers from the atmospheric scientific community, and 5 sponsoring agency representatives. Based on the reviews, the chapters were then finalized in November/December 1985.

This present NASA report is the fifth ozone assessment report submitted to Congress and the concerned regulatory agencies. It has been written by a small group of NASA scientists, was peer reviewed, and was based upon the WMO (1986) assessment. Each of these reports, with the exception of the first, has been submitted in response to NASA's obligations under the Clean Air Act Amendments of 1977 which state that NASA is required to report both to the EPA and to the Congress on the result of its programs relating to the stratosphere and mesosphere. The first of the NASA ozone assessment reports which was produced in September 1977 was much narrower in scope than the present report and focussed on an evaluation of the effects of chlorofluorocarbon (CFC) releases on stratospheric ozone. That evaluation was based upon a report which resulted from a scientific workshop sponsored by NASA in January 1977. The first report in response to the requirement of the Clean Air Act was due on January 1, 1980, with subsequent reports due on a 2-year interval. To provide the broadbase necessary for the first two reports, NASA organized workshops in June 1979 and May 1981. These workshop reports were entitled, "The Stratosphere: Present and Future," NASA Reference Publication 1049, and "The Stratosphere: Theory and Measurements." WMO Report #11. The latter

workshop was co-sponsored by the World Meteorological Organization and by the Federal Aviation Administration and the National Oceanic and Atmospheric Administration.

While the 1980 and 1982 NASA assessments were based on the scientific findings of major workshops, it was felt for the 1984 assessment that yet another major workshop was unjustified given that there had been no recent dramatic changes in our understanding of the key physical and chemical processes. Consequently, the 1984 assessment was written by a small group of NASA scientists without organizing such a major workshop and was peer reviewed by eminent scientists drawn from the scientific community outside of NASA. The report was based on published articles, preprints, a series of small workshops, and the recent international United Nations Environment Program- Coordinating Committee on the Ozone Layer (UNEP CCOL) assessment.

II. SCIENTIFIC SUMMARY

As our knowledge of the physical and chemical processes controlling atmospheric composition and structure improves, there continues to be concern that the total column and vertical distribution of atmospheric ozone, the temperature structure, and climate, will be modified by changes in the atmospheric concentrations of several trace substances, specifically chlorofluorocarbons (CFC's), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and the nitrogen oxides (NO_x). It is now well recognized that the chemical effects of these trace substances on atmospheric ozone are strongly coupled and should not be considered in isolation. The effects of these trace gases on ozone are not additive, whereas their direct radiative effects on atmospheric temperature are approximately additive.

The major conclusions of the present assessment are presented in four sections: (A) Atmospheric Observations: Source Gases and Reactive Intermediates, (B) Chemical/Dynamical Model Predictions of Ozone Change, (C) Observations of Ozone and Temperature Trends, and (D) Photochemical/-Radiative Effects: Changes in Climate.

A. <u>Atmospheric Observations: Source Gases and Reactive Intermediates</u>

(1) There is now compelling evidence that the composition of the atmosphere is changing on a global scale. The atmospheric concentrations of $CFCl_3$, CF_2Cl_2, CH_3CCl_3, CCl_4, N_2O, CO, CO_2, and CH_4, are currently increasing at annual rates of approximately 5%, 5%, 7%, 1%, 0.2%, 1-2%, 0.5% and 1%, respectively. These changes reflect in part the metabolism of the biosphere and in part a broad range of human activities. Reliable prediction of future trends in the atmospheric concentrations of these gases is impossible without fully understanding the factors (physical, chemical, biological, economic, social, political) which control their fluxes.

(2) The atmospheric residence times of gases such as $CFCl_3$, CF_2Cl_2, and N_2O are known to be long, i.e. approximately 75, 110, and 150 years, respectively. Consequently, we must be aware that if there is either a change in atmospheric ozone or climate caused by increasing atmospheric concentrations of these gases the recovery of the system will take centuries because of their long atmospheric residence times.

(3) The hydroxyl radical, OH, is important in the troposphere where it controls the residence time of some of the gases which can affect stratospheric chemistry and the radiative heating of the surface-troposphere . system. Among these gases are the hydrogen-containing halocarbons (e.g. CH_3Cl, CH_3CCl_3, CHF_2Cl), CO, CH_4, and non-methane hydrocarbons. Because the reactions of CO and CH_4 with OH control both the loss rate of OH as well as

the loss rate for CO and CH_4, the observation of increasing atmospheric concentrations of CO and CH_4 with time is indirect evidence that the OH concentration may be decreasing with time. Thus the capacity of the troposphere to remove many gases may be decreasing. The recovery time for the perturbed tropospheric CO-OH-CH_4 cycle might take several decades because of the nonlinear interactions among these gases.

(4) All the key radicals predicted to be important in controlling atmospheric ozone (O, OH, HO_2, NO, NO_2, Cl, and ClO) have been observed in the stratosphere. However, it should be noted that the data base is rather limited, and that while the observed abundances are generally consistent with current theory to within a factor of 2 or so, the measurements are not adequate for critically testing the photochemical models. In particular:

a. the most recent profile data for OH are lower than most of the earlier data and current model predictions, and the recent in-situ HO_2 data are significantly higher (by a factor of 2 at 34 km and an order of magnitude below 25 km) than predicted, indicating a serious problem with either the measurements or our current understanding of HO_x chemistry.

b. while there is an extensive data base for both NO and NO_2 it is not of adequate accuracy to test the theoretical predictions of the NO/NO_2 ratio or of the diurnal variations of these species.

c. the observed and predicted concentrations of ClO are within a factor of 2 at 28 km, with better agreement above. The observed diurnal variation of ClO is in reasonable agreement with model predictions, but does show a somewhat slower morning rise than expected.

(5) The presence of the temporary reservoir species $ClONO_2$, N_2O_5, and HO_2NO_2 in the stratosphere has been definitively established by recent observations. Quantification of these observations will provide vital data

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needed to test our understanding of stratospheric photochemistry. However, there are still no observations of HOCl or H_2O_2.

(6) Our current understanding of the distribution of the reservoir species HNO_3 is not totally satisfactory. Although observations of HNO_3 near the concentration peak at low and mid-latitudes are in reasonable agreement with models, the observations are not consistent with model predictions at high latitudes in winter, and above 30 km in the photochemically controlled region of the stratosphere.

(7) The predicted increase in the HF column is confirmed by observation. However, the ground-based observations of the column content of HCl do not show the predicted upward trend with time. The interpretation of the HCl measurements is difficult because of the large short term variability in its tropospheric concentrations and because of the variable injection of potentially large amounts of volcanic HCl into the stratosphere.

(8) The most important recent development in our knowledge of O_x, HO_x, and NO_x in the stratosphere has been the release of several large satellite data sets (the LIMS, SAMS, and SBUV/TOMS instruments on the Nimbus 7 satellite, the SAGE instrument on the AEM-2 satellite, and the SME complement of instruments). They have greatly improved our knowledge of the spatial and temporal distributions of O_3, H_2O, CH_4, N_2O, NO_2, and HNO_3 on a global scale. In particular, these data sets have been used to:

a. reconfirm that air is transported upward and poleward from the tropics, consistent with the Brewer-Dobson hypothesis for H_2O.

b. show that the total hydrogen budget of the stratosphere, principally $H_2O+2xCH_4$, is relatively constant with values ranging from 6 to 7 ppmv.

c. determine the total concentration for odd nitrogen in the stratosphere yielding values of 20-25 ppbv depending somewhat on the inferred concentrations of unmeasured species.

d. show that the thermospheric source of total odd nitrogen to the stratosphere may be significant on a local, but not a global scale.

e. verify the ground-based observations of the British Antarctic Survey that there has been an approximately 40% decrease in total column ozone over Antarctica during the spring period since the mid-1970's.

f. show the spatial structure and contribute to the understanding of the dynamical and photochemical processes responsible for regional phenomena such as the NO_2 (Noxon) cliff at high latitudes in winter.

g. infer atmospheric parameters not directly measured, e.g. global OH distributions, and information on the magnitude of the horizontal diffusion coefficients appropriate for use in two dimensional models.

(9) There is an inconsistency between measured and modeled ozone concentrations above 35 km. Model results are typically 30-50% lower than measured ozone concentrations. This discrepancy is particularly troubling given that it occurs in the photochemically controlled region of the stratosphere. Furthermore, if the observed ozone concentrations are used in radiative models of the upper stratosphere the predicted temperatures are higher than measured. Consequently, there appears to be a problem with the photochemistry, radiative transfer, or ozone observations in the upper stratosphere.

B. Chemical/Dynamical Model Predictions of Ozone Change

(10) Both one and two-dimensional models are now being used as predictive tools for possible future states of the atmosphere. One-

dimensional models are still used to examine the first-order impact of widely varying assumptions concerning inputs to the atmosphere. Two-dimensional models that can predict the latitudinal and seasonal dependence of changes have now been put on a much firmer theoretical foundation than was the case at the time of the previous assessment reports.

(11) Recent theoretical work on atmospheric dynamics has made much clearer the proper physical basis for parameterizing planetary-scale, three-dimensional motions in lower dimensional photochemical models. In particular, our appreciation of the intimate interaction between the zonally-averaged transport circulation and atmospheric wave motions has clarified the need for internally consistent advective transport and diffusion in two-dimensional models. There has also been an increased appreciation that specialized observational programs are required to increase our understanding of dynamical processes that occur on small spatial and temporal scales so that we may better parameterize their effects in models of global transport. This has motivated large aircraft programs to study mechanisms of stratosphere-troposphere exchange as well as ground-based studies of gravity waves and turbulence using radar and lidar techniques.

(12) There have been no major changes in our fundamental concept of stratospheric photochemistry. It is still viewed as a highly coupled oxygen/hydrogen/nitrogen/chlorine system. No new catalytic cycles, or radical or reservoir species, have been identified. There have, however, been a number of small changes in rate constants for several important reactions, (e.g. $O+ClO$, $OH+HCl$, $OH+HNO_3$, and HO_2+NO_2+M) which have led to refinements in predictions of ozone depletion and in the comparison of observed and computed distributions of trace gases. There is currently an increased effort to

evaluate whether slow homogeneous or heterogeneous reactions between temporary reservoir species such as $ClONO_2$ and H_2O or HCl are important.

(13) The variation in solar spectral irradiance is well determined for the 27-day solar rotation period but not for the 11-year solar cycle. Variations in the solar ultraviolet radiation at wavelengths that dissociate molecular oxygen, ozone, and other trace gases can produce secular changes in ozone. Determinations of the nature of long term variations in solar spectral irradiance are needed so that we may distinguish solar-induced ozone trends from ozone variations that may occur as a result of human activities.

(14) For the hypothetical case of continuing release of CFC's 11 and 12 at the 1980 release rates ($309 \times 10^6 kg/yr$ and $433 \times 10^6 kg/yr$ respectively) and with the concentrations of CO_2, CH_4 and N_2O fixed at today's levels, a decrease in the ozone column of 4.9 to 7.0% is calculated using one-dimensional models without radiative feedback, and a decrease of 6.1 to 9.4% is calculated using one-dimensional models with radiative feedback. These models all used the same chemical input parameters.

(15) Two-dimensional models give a similar range of results for the global average column ozone change as the one-dimensional models for the case of CFC-only release. One modeling group which uses identical chemical inputs to their 1- and 2-D models found significantly higher global average ozone reduction (-8.5%) in their 2-D model than in their 1-D model (-5.3%) for the standard CFC-only case. The two-dimensional models predict a significant latitudinal variation in the ozone column decrease. More depletion is predicted near the poles than at the equator with the ratio ranging from 2:1 to 4:1 depending upon the model transport formulation. Seasonal effects are predicted but are somewhat less pronounced than the latitudinal effects. In the upper stratosphere significant ozone decreases are predicted at all

latitudes for all seasons. In the lower stratosphere the predictions show an increase in ozone below about 25 km within approximately 40 degrees of the equator. From there to the poles, ozone decreases are predicted at all altitudes.

(16) Both one and two-dimensional models exhibit significant differences in their distributions of the odd-nitrogen species. The cause(s) of these differences among models are currently unresolved. These are important because of the role of the odd-nitrogen species in interfering with the chlorine catalytic cycle for ozone destruction and because of the important catalytic role of the odd-nitrogen species themselves in controlling O_3.

(17) One-dimensional models predict nonlinearity in ozone depletion with respect to chlorine addition such that the change in the ozone column per unit of added chlorine increases with the chlorine amount. There is, however, considerable discrepancy among models in the degree of this nonlinearity, partly due to the corresponding differences in calculated odd-nitrogen concentrations. The two-dimensional model tested for this effect showed little nonlinearity over the range tested (less than 25 ppbv of odd chlorine).

(18) Predictions of ozone change from the combined effects of changes in CFC's, N_2O, CH_4, and CO_2 demonstrate that their effects are not additive. For instance, one model with temperature feedback predicted the following column ozone changes for a series of isolated scenarios: (i) increase of total chlorine to 8 ppbv (this corresponds to 80-100% of the modelled steady state Cl_x for the present CFC flux), -5.7%; (ii) doubling of CH_4, +2.9%; (iii) 1.2 times N_2O, -1.7%; (iv) doubling of CO_2, + 3.5%; the same model predicted the following column ozone changes for combinations of the isolated scenarios: (v) 8 ppbv Cl_x + 2 x CH_4 + 1.2 x N_2O, - 2.8%; (vi) 8 pppv Cl_x + 2 x CH_4 + 1.2 x N_2O + 2 x CO_2, +0.2%. The calculated change in ozone at 40 km remains large

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for all of these cases (e.g. -35 to - 55% for 8 ppbv Cl_x + 2 x CH_4 + 1.2 x N_2O + 2 x CO_2).

(19) Time-dependent scenarios were run in a one-dimensional model assuming atmospheric CO_2, CH_4, and N_2O concentration growth rates of 0.5%, 1.0% and 0.2% per year respectively, in conjunction with CFC emission growth rates of 1.0%, 1.5% and 3% per year. The ozone column changes were calculated to be <3% over the next 70 years for CFC emission increases of ≤1.5% per year, but with a CFC growth rate of 3% per year, the predicted ozone depletion is 10% after 70 years and rapidly increasing. In this case, the CFC effects were temporarily masked by other gases but eventually chlorine dominated ozone loss.

(20) Uncertainty propagation calculations for chemical reaction rates, photodissociation cross sections and solar flux, but not for model formulation or transport parameters, yielded probability distributions for column ozone changes which were asymmetric with a long tail toward large perturbations. The one sigma width of these distributions was comparable to, but less than, the magnitude of the predicted ozone perturbation for perturbations of less than 10% (-6.2 ± 5.5% in one model for the present flux of CFC's only, and -7.7 ± 5.8% in another with 14 ppbv added Cl_x + 2xCH_4 + 1.2xN_2O).

C. <u>Observations of Ozone and Temperature Trends</u>

(21) Statistical analyses for trends in total column ozone using data from the Dobson spectrophotometer network for the period 1970-1983 give mixed results (e.g. -0.17%/decade ± 0.55%/decade and -1.10%/decade ± 0.47%/decade). Some reasons for these disparate results include differences in accounting for solar cycle effects, area weighting of the data, and variations due to

volcanic eruptions and El-Nino (which may have been responsible for the abnormally low 1983 ozone values).

(22) Recent evidence from a single Dobson spectrophotometer instrument at Halley Bay has indicated a considerable decrease (~40%) in Antarctic ozone during the spring period since 1957 with most of the decrease occurring since the mid 1970's. Satellite measurements using both the TOMS and SBUV instruments have verified this trend over Antarctica since 1979 and have demonstrated the spatial and temporal variations in this feature. Similar ozone variations are not observed over the Arctic. It is not yet evident whether the behavior in Antarctic ozone is an early warning of future changes in global ozone or whether it will always be confined to the Antarctic due to the special geophysical conditions that exist there. While it has been suggested that these Antarctic ozone decreases are caused by increasing concentrations of chlorine in the stratosphere no credible mechanism has been demonstrated since models using present chemical schemes are unable to simulate this effect.

(23) Trend estimates from 13 ozone balloonsonde stations indicate statistically significant positive trends in the lower troposphere and negative trends in the lower stratosphere. The interpretation of these trends, however, is clouded by uncertainties in instrument behavior and the lack of a global network of stations. The tropospheric trend is of potential importance in interpreting total ozone trends (as much as 15% of the ozone column can be in the troposphere, depending on latitude). It is also important to the radiative balance of the atmosphere (surface temperature is more sensitive to tropospheric ozone than to stratospheric ozone).

(24) Global ozone trend estimates from 13 Umkehr stations indicate statistically significant trends in the middle to upper stratosphere

(~30-40 km) of the order of -0.2 to -0.3% per year over the period 1970-1980, with little trend at lower altitudes. This is in substantive agreement with results from one-dimensional models and corresponds to the altitude of the maximum predicted effect of ozone depletion from chlorine. The observational results are sensitive to the inclusion of a term accounting for stratospheric aerosol effects on the measurements and on the spatial distribution of the sites.

(25) The large cooling in upper stratospheric temperatures reported for the early 1970's now appears to have been caused by a change in the rocketsonde temperature measurement system. Considering only data subsequent to the change in rocketsonde measurement systems, there is a suggestion of a temperature decrease in the upper stratosphere that is consistent with results from one-dimensional numerical models. However, since the trend in lower stratospheric rocketsonde temperature is not observed in the radiosonde temperatures at the same altitudes, we must await a more complete analysis utilizing all available data.

(26) Increases in tropical lower stratospheric temperatures have been noted following the eruptions of El Chichon in March 1982 and of Agung in March 1963. No tropospheric cooling nor any unambiguous effect on atmospheric ozone has been associated with the El Chichon eruption, although low values of total ozone have been reported subsequent to the eruption. It should be noted that the El-Chichon eruption occurred during a pronounced El-Nino event. Consequently, separation of the effects of these two phenomena is difficult.

D. Photochemical/Radiative Effects: Changes in Climate

(27) The question of the impact of human activities on the greenhouse effect has broadened in scope from the CO_2-climate problem to the trace gas-

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climate problem. Some of the important non-CO_2 greenhouse gases are $CFCl_3$, CF_2Cl_2, CH_4, N_2O, O_3, and stratospheric H_2O.

(28) Trace gases, other than CO_2, are now predicted to be adding to the atmospheric greenhouse effect by an amount comparable to the effect of CO_2. The rate of increase of the total greenhouse forcing is now 3-10 times greater than the mean rate for the period 1850-1980. The cumulative effect of the increase in all trace gases for the period 1850-1980 is a predicted equilibrium warming in the range of 0.7 to 2 K; however, only about one-half of this warming is predicted to have occurred as of the present time because of the oceans' thermal inertia. This estimate of the greenhouse warming that should have occurred is not inconsistent with what is inferred from surface temperature records. Present estimates indicate that the greenhouse warming predicted to occur during the next 50 years should be about twice that which has occurred during the previous 130 years.

(29) In any given scenario for increases in greenhouse gases (including CO_2), the predicted stratospheric cooling is significantly larger (by factors ranging from 2 to 10 depending on altitude) than the predicted surface warming. It should be noted that the addition of CFC's to the atmosphere, through their induced catalytic ozone destruction, have a potentially large stratospheric cooling effect, as large as that caused by a CO_2 increase. This complicates the identification of the increased CO_2 greenhouse effect through stratospheric temperature trends.

(30) In addition to their direct radiative effect, many of the trace gases have indirect effects on climate. For example, addition of such trace gases as CH_4, CO, and NO_x can alter tropospheric O_3, which is a radiatively active gas. Within the troposphere, the indirect climate effects can be as large as the direct climate effect. Thus, the trace gas-climate problem is

really a trace gas-chemistry-climate problem. The evolution of our knowledge in this area has followed naturally from out initial concerns for the individual effects of CO_2 and O_3 changes on climate.

(31) Changes in lower stratospheric ozone and/or tropospheric climate would be expected to result in changed tropical tropopause temperatures. It is also believed that changes in tropical tropopause temperatures will lead to altered stratospheric water vapor concentrations which would affect stratospheric photochemistry and also tropospheric climate. Evaluating this effect depends critically upon the mechanism of stratosphere-troposphere exchange through the tropical tropopause.

(32) Perhaps the greatest uncertainty in the trace gas-climate problem is in identifying the effects of clouds in either amplifying or suppressing the predicted greenhouse warming.

In summary it should be noted that during the past several years we have significantly advanced our understanding, but this has made the complexities of the ozone problem more apparent. There is now compelling evidence that the trace gases affecting ozone are increasing on a global scale. While most of the key stratospheric constituents have been observed and are in general agreement with predictions using photochemical models, detailed disagreement between observations and predictions limits our confidence in the predictive capability of these models. Significant changes in ozone have already been observed, e.g. (a) depletion in the upper stratosphere consistent with the expected changes from the increasing Cl_x content of the atmosphere, and (b) unexpected large depletions (~40%) in total ozone in the Antarctic in Spring which are not consistent with current theory.

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The trace gases that affect stratospheric photochemistry are the same as those that either act as greenhouse gases themselves or through chemistry lead to changes in greenhouse gases. It is thought that appreciable greenhouse warming has already occurred and that the rate of warming will accelerate in the future.

Given what we know about the ozone and trace gas-chemistry-climate problems we should recognize that we are conducting one giant experiment on a global scale by increasing the concentrations of trace gases in the atmosphere without knowing the environmental consequences.

III. THE PROBLEM

Stratospheric composition is determined by a complex set of processes. The system is driven by solar ultraviolet radiation and depends critically on the nature of some of the molecules released at ground level and transported slowly to the stratosphere by atmospheric motions. The molecule ozone, O_3, is central to the problem of stratospheric composition. Ozone alone strongly absorbs ultraviolet radiation from the Sun at wavelengths between 240 and 320 nm. This radiation, if allowed to reach the ground in significant amounts, could have serious effects on human health, agricultural productivity and fisheries. The total amount of ozone in the vertical atmospheric column which is responsible for the nearly complete removal of this radiation would, if reduced to sea level pressure and temperature, be approximately three-tenths of a centimeter in thickness. It is never present at more than about 10 parts per million by volume in the stratosphere and remote regions of the troposphere.

The ozone layer has a continuous distribution with a peak concentration in the lower stratosphere between about 20 and 25 kilometers altitude. Figure 1
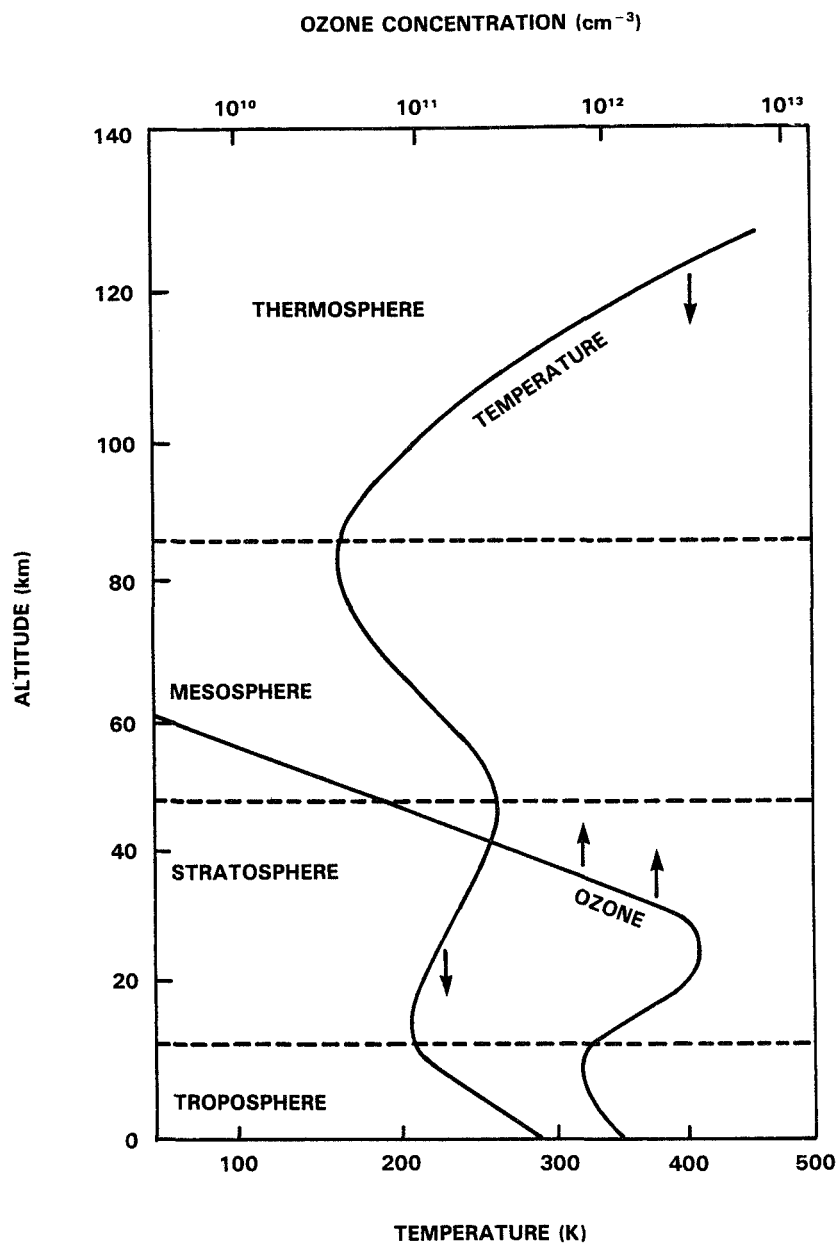
Figure 1. Temperature profile and ozone distribution in the atmosphere.

illustrates the standard definitions of the troposphere, stratosphere and mesosphere in terms of the profile of temperature with altitude and shows an average ozone distribution. The troposphere is heated from below by solar radiation absorbed at the surface and as such it has the potential to be unstable with rapid convective vertical motions such as in cumulus clouds. The stratosphere, on the other hand, is heated from above by the absorption of ultraviolet radiation between 200 and 320 nm by ozone and is very stable with respect to vertical mixing. Because ozone provides the main heat source for the stratosphere its vertical distribution plays the primary role in determining the temperature structure and the consequent motions of the stratosphere. Ozone is thus critical in determining connections between the stratosphere and tropospheric weather and climate. These climatic interactions between the stratosphere and troposphere can take place by means of both radiative and dynamical coupling. A reduction in stratospheric O_3 modifies the surface temperature via two competing radiative processes. Less stratospheric O_3 implies less absorption of solar radiation in the stratosphere, allowing more solar radiation to reach the surface. This effect alone warms the surface. Less stratospheric absorption of solar radiation, however, reduces the downward emission of infrared radiation from the stratosphere to the troposphere. This effect alone cools the surface. For a uniform reduction of stratospheric O_3, these two effects almost cancel each other, although predictions normally give a small cooling of the troposphere. These radiative effects depend on the altitudes of ozone reduction as well as changes in column amounts of ozone, however. Ozone changes in the lower stratosphere and upper troposphere are found to be more effective than changes in other regions of the atmosphere in causing surface temperature change. Latitudinal variations are also important. If decreases

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are spatially uniform, the change in the radiative fluxes into the troposphere will be greater at high latitudes than in the tropics. Finally, the effects of changes in O_3 on the solar radiation and infrared radiation into the troposphere will have different effects at different tropospheric altitudes. For instance, given a uniform O_3 decrease, the downward solar flux into the troposphere is increased, leading to increased heating of the ground and the lowest layers of the troposphere. This uniform O_3 decrease also decreases the downward longwave radiative flux into the troposphere which decreases the heating in the high troposphere. These two effects superpose to decrease the tropospheric stability.

If the distribution of radiatively active trace constituents in the stratosphere (e.g. carbon dioxide and ozone) changes, then the distribution of heating and cooling rates will change, which will in turn alter the stratospheric temperature distribution. The change in the temperature distribution can be accompanied by changes in the wave motions in the stratosphere which may even extend downward into the troposphere, and perhaps change the zonally averaged motions as well. Thus, one has a rather complicated geophysical system in which the radiative, chemical, and dynamic effects are all interrelated.

Ultraviolet solar radiation produces ozone in the atmosphere. Wavelengths of less than 242 nm possess sufficient energy to dissociate molecular oxygen, O_2, into its component O atoms. These O atoms in turn react rapidly with O_2 to form ozone, O_3. The O_3 formed can subsequently absorb ultraviolet radiation in the 200-320 nm wavelength region, dissociating into an O atom and an O_2 molecule. Ozone is also dissociated, by visible and near infrared radiation, although to a much lesser extent. These processes form a long chain in which the oxygen atom alternately attaches itself to an O_2 to form O_3

and then is detached, until finally, the O atom and an O_3 molecule react to reform two O_2 molecules.

According to this very simple model, the ozone concentration is controlled by its production and loss rates. The ratio of the frequency of the ozone loss to production rate is directly dependent on the effective length of the chain (catalytic efficiency) and thus, the O_3 concentration depends directly on the chain length.

There exist chemical processes which can shorten this chain. Among these are the catalytic processes of the nitrogen, chlorine and hydrogen oxides (NO_x, ClO_x, HO_x). These processes have the same net effect as the direct reaction of O and O_3. For example, the simplest catalytic cycle involving ClO_x is the two-reaction set:

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

$$\text{Net} \quad O + O_3 \rightarrow O_2 + O_2$$

for NO_x:

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$

$$\text{Net} \quad O + O_3 \rightarrow O_2 + O_2$$
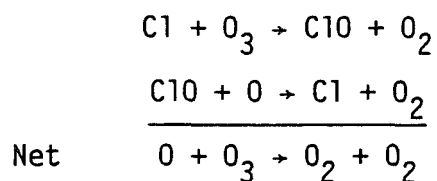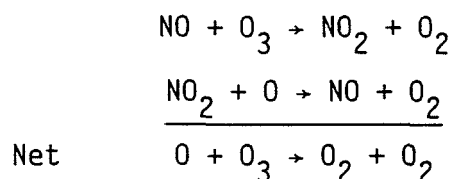
These sets (or cycles) are catalytic because, at the end, the Cl atom or NO molecule is again available to continue converting O and O_3 back to O_2.

The significance of the catalytic cycles is that small amounts of the catalytic species can affect ozone in a substantial manner. We have already seen that parts per million of ozone are important in determining the

temperature structure of the stratosphere and its stability, and in determining the amount of UV radiation which reaches the ground. We now find that an even smaller amount of the catalytic oxides (in the part per billion range) are significant in controlling the amount of ozone.

The sources of these catalytic oxides are primarily at the surface of the Earth (an exception is the downward flux of NO_x from the thermosphere during the polar night). The oxides themselves, HO_x, NO_x, and ClO_x, can be converted by interaction with one another into chemically inactive "reservoir" species such as nitric acid vapor, HNO_3, and hydrochloric acid vapor, HCl, which are soluble in water and can be rapidly rained out in the troposphere. Thus direct release of catalytically active HO_x, NO_x, or ClO_x near the ground does not affect stratospheric ozone. However, these chain reactants can be released in the stratosphere after being carried upward chemically bound in source molecules such as methyl chloride, (CH_3Cl), nitrous oxide, (N_2O), CFC 11 and 12 ($CFCl_3$ and CF_2Cl_2), methane (CH_4), and others which are insoluble and relatively unreactive. They have long residence times in the troposphere and are slowly transported to the stratosphere where they are broken down by ultraviolet solar radiation and other reactive species (e.g. the hydroxyl radical, OH) providing sources of HO_x, NO_x, and ClO_x. It should be noted that the addition of HO_x, NO_x or ClO_x to the stratosphere will enhance ozone destruction due to these species alone but will, in addition, interfere with ozone destruction which would have been taking place through the other cycles. A critically important species in this context is the hydroxyl radical, OH, which in addition to being part of the HO_x catalytic cycle, plays a crucial role in both the NO_x and ClO_x cycles. By reaction with NO_2, OH participates in the formation of the major NO_x reservoir, HNO_3. It plays the opposite role with ClO_x, reacting with the major reservoir, HCl, to release Cl

atoms. Thus, reactions which affect the OH concentrations tend to have opposite effects on the catalytic efficiency for ozone loss by NO_x and ClO_x.

Many mechanisms have been suggested by which human activities can alter the ozone concentrations in the atmosphere. Concern was first directed towards the effects of H_2O and NO_x generated in the stratosphere by the hot exhaust of supersonic transports. More recently the possible effects of the release of NO_x in the upper troposphere and lower stratosphere by subsonic aircraft have been calculated to lead to an increase in ozone. The increased production and utilization of nitrogen fertilizers has also become of concern. Any increase in the nitrogen fixation rate must eventually lead to an increase in the return rate of nitrogen to the atmosphere some of it in the form of N_2O, thus leading to an increase in stratospheric NO_x. N_2O has also been shown to be produced in combustion and its atmospheric concentration is now observed to be increasing with time. Such a perturbation would have a very long time scale since the residence time of N_2O in the atmosphere is more than a hundred years. Attention has also been focused on the industrially produced CFC's 11 and 12 and methyl chloroform, CH_3CCl_3. The CFC's also have long atmospheric residence times (50-100 years). The carbon cycle appears to be undergoing change as evidenced by increasing atmospheric concentrations of carbon dioxide, CO_2, methane, CH_4, and probably of carbon monoxide, CO. In contrast to the troposphere where the so-called greenhouse effect of CO_2 is expected to increase the temperature, the effect of CO_2 in the stratosphere will be a temperature decrease as CO_2 is the main infrared radiator which cools the stratosphere. The stratospheric temperature decrease will, because of the temperature dependences of chemical reaction rates, lead to an increase in ozone in the middle and upper stratosphere.

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The overall picture which has emerged is that the amount of ozone in the atmosphere is maintained by a dynamic balance between production from solar ultraviolet radiation and destruction by catalytic compounds controlled by industrial activities and by the metabolism of the biosphere which is being modified by human activities. Because of the strong interaction amongst the catalytic cycles, a broad view of the state of the atmosphere-biosphere system must be taken.

Similarly, the problem of radiative balance and possible surface warming is influenced by the direct radiative effect of many of the same gases (i.e. N_2O, CH_4, CFC's, CCl_4, CH_3CCl_3 and ozone itself). Unlike the ozone problem where interferences are common, these gases additively contribute to surface temperature changes. Each has absorption bands in regions of the infrared spectrum that are normally transparent allowing heat radiated from the Earth to escape to space. Increases in their concentrations allow more of this radiation to be absorbed in the atmosphere and to be radiated back toward Earth warming both the lower atmosphere and the surface. The problems of ozone and radiative balance are further intertwined by the fact that the primary destruction mechanism for many of these gases is through their transport to the stratosphere where ultraviolet radiation that has not been absorbed by ozone is available to break down these gases directly or to produce reactive molecules which indirectly cause their breakdown. Thus the residence times of these gases and their eventual concentrations are tied to stratospheric photochemistry. Although the absolute increases in the atmospheric concentrations of N_2O, CH_4 and the CFC's are much smaller than of CO_2, the regions of the spectrum in which they absorb are more transparent so that each molecule has more effect.

IV. THE SCIENTIFIC APPROACH

The scientific method involves an interplay between theory and observation: theoretical predictions are made and observations are taken that either confirm or refute the theoretical concepts. As our theoretical understanding evolves, different observations are required to test these changing theoretical concepts. It is by the continual interplay between theory and observation that science moves forward.

The application of the scientific method proceeds quite differently in the geophysical sciences than in the laboratory physical sciences, however. In the laboratory, one seeks to carry out controlled experiments such that theoretically predicted parameters may be measured thus verifying the theory. In the geophysical sciences, it is most difficult, and in some cases impossible, to carry out controlled experiments. Thus a different application of the scientific method is called for, that involves the construction of mathematical models of geophysical systems and the comparison between geophysical data and the model results,

Our application of these concepts to stratospheric predictions requires that our models of the present day stratosphere be verified by comparison against analysis of observations of the present day stratosphere. Inputs to these models include chemical reaction rates and absorption cross sections which must be measured in the laboratory, and solar spectral irradiance which must be measured at the top of the atmosphere. Certain parameterizations of processes not calculated in a self-consistent fashion must also be put into these models. For instance, vertical eddy diffusion profiles and tropospheric constituent rainout rates must be put into a one-dimensional model. An eddy diffusion tensor field must be put into two-dimensional models. Three-dimensional models require inputs of subgrid processes such as those from

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gravity waves and turbulent diffusion. Once the models have been tested against observations, one has some confidence in our ability to predict future states of the stratosphere correctly using these models. Different types of data may be required to test different models. For instance, measurements of diurnal constituent variations are quite useful for checking the chemistry in one-dimensional models at high altitudes where transport effects may be neglected. Data should be averaged globally and temporally through the year to compare against profiles produced by one-dimensional models and averaged zonally as a function of time of year for comparison with two-dimensional models. Since three-dimensional models produce results at various geographical points at all model times, there are a variety of ways in which the models can be compared to observations.

In some cases, models are checked against other models instead of observations. This situation results from the need to use varied levels of model complexity for various aspects of the problem. For instance, testing the predictions of a very complex photochemical scheme against that of a simple scheme can be accomplished for many purposes by a one-dimensional photochemical model, but three-dimensional general circulation models may be required to test the formulation of transport processes that are used in such a one-dimensional model.

As can be seen from the preceding discussion, the development of our understanding of the workings of the present day stratosphere and our ability to predict future stratospheric states will come from pursuing a balanced strategy of laboratory measurements, atmospheric measurements, and modeling of the atmosphere. It is also important that good communication exist among scientists using these different approaches so that the knowledge generated in

one of these areas can efficiently be used to further efforts in the other areas.

V. SOURCE GASES AS DRIVERS FOR ATMOSPHERIC CHANGE

During the past few years compelling evidence has been obtained that the compositions of the atmosphere is changing on a global scale. The atmospheric concentration of nitrous oxide (N_2O), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), carbon tetrachloride, (CCl_4), methyl chloroform (CH_3CCl_3), and several chlorofluorocarbons (CFC's), in particular $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), and $C_2Cl_3F_3$ (CFC-113) are all increasing. These changes reflect in part the metabolism of the biosphere and in part a broad range of human activities. These gases play important direct and indirect roles in both tropospheric and stratospheric chemistry, and climate.

Stratospheric ozone is directly affected by changes in the concentrations of the CFC's, N_2O, and CH_4 insofar as these gases are the dominant sources of stratospheric odd-chlorine, odd-nitrogen, and odd-hydrogen species which photochemically control the distribution of ozone. In addition, CH_4 decreases the catalytic efficiency of chlorine by converting atomic chlorine into the inactive form, HCl. CO_2 indirectly influences the abundance of stratospheric ozone by modifying the temperature structure and hence the rates of ozone production and destruction. CO and CH_4 play a major role in controlling the concentrations of ozone and the hydroxyl radical (OH) in the troposphere. The OH radical controls the photochemical lifetimes of H-containing gases (e.g. CH_4, CH_3Cl, CH_3CCl_3) in the troposphere, and hence their fluxes into the stratosphere where they can influence ozone.

All of these source gases are either infrared active and can directly contribute to a change in the thermal balance of the atmosphere, resulting in

an increase in the temperature of the troposphere, or they can affect the concentrations of other gases which are infrared active, and hence indirectly affect the thermal balance of the atmosphere, e.g. CO controls the abundances of both ozone and CH_4 in the troposphere through its control of OH. Both ozone and CH_4 are infrared active.

This section briefly discusses the current atmospheric concentrations, and trends, of the CFC's, CO, CO_2, CH_4, and N_2O. In addition, there will be a brief description of the factors that control the emission of these gases into the atmosphere.

Chlorofluorocarbons

The dominant source of stratospheric odd-chlorine is the photolysis of CFC-11, CFC-12, CCl_4, and the reactions of CH_3Cl, and CH_3CCl_3 with OH radicals. There are also, however, a large number of other CFC's that act as sources of stratospheric odd-chlorine and whose atmospheric concentrations are currently increasing. In general, the CFC's are of industrial origin with the exception of CH_3Cl. CFC's are used in a wide variety of industrial applications such as aerosol propellants, refrigerants, solvents, and foam blowing agents. The atmospheric concentrations of CFC-11, CFC-12, CH_3CCl_3, and CCl_4 as of late 1985 were 230 pptv, 400 pptv, 130 pptv, and 125 pptv, respectively, and are observed to be increasing at annual rates of about 5% for CFC's-11 and 12, 7% for CH_3CCl_3, and 1% for CCl_4 (Figure 2). The data base for the other halocarbons is much sparser.

The lifetimes of the fully halogenated CFC's are quite long because there are no known tropospheric removal mechanisms. This is in contrast to H-containing halocarbons, which have a much shorter lifetime due to their reactivity with OH radicals in the troposphere. Based on data from the
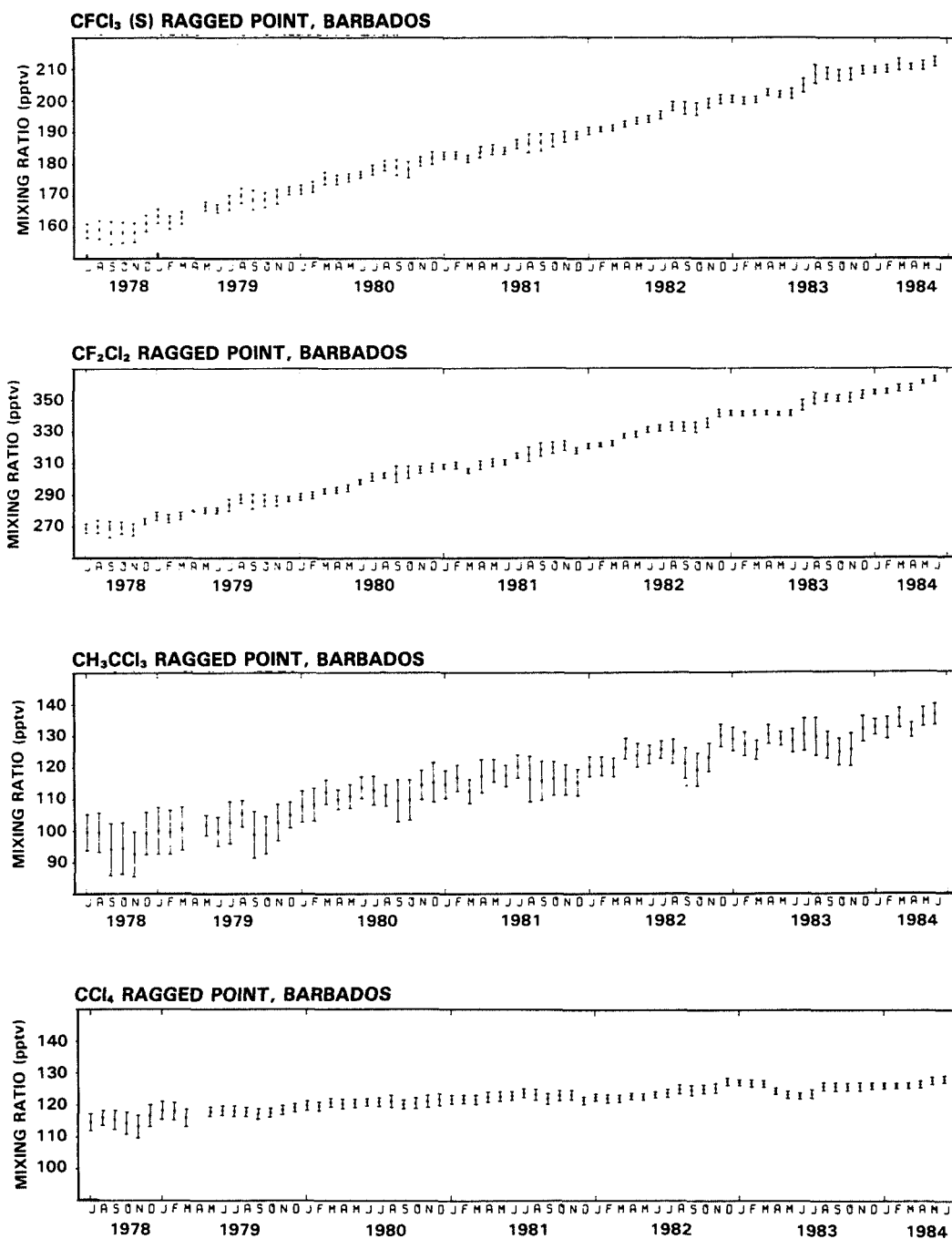
Figure 2. Monthly-mean mixing ratios and monthly variances of CFC-11, CFC-12, CH₃CCl₃ and CCl₄ measured 4-times-daily on a gas chromatograph at the Ragged Point, Barbados ALE/GAGE station during the first six years of the ALE/GAGE network.

Atmospheric Lifetime Experiment (ALE) the lifetimes of CFC-11, CFC-12, CCl_4, and CH_3CCl_3 are approximately 75 years, 110 years, 50 years, and 6.5 years, respectively.

True global production data are not available for any of the CFC's. CFC's 11 and 12 are the only compounds for which data covering a large fraction of the market are published, and for which emission estimates are routinely made. However, even for CFC's 11 and 12, there are no reliable production or emission figures from the Eastern Bloc countries.

The ALE measurements indicate an increase in the atmospheric concentration of CFC-11 consistent with the Chemical Manufacturers Association (CMA) release estimates, but to explain the observed increase in the atmospheric concentration of CFC-12 a substantial additional source is required. Insufficient information is available about possible releases from the USSR and Eastern Europe. For CCl_4 and CH_3CCl_3 the reported sources and atmospheric inventory are consistent.

Accurate long-term projections of future CFC's emissions are vitally important for calculating possible future changes in atmospheric structure and composition. As stratospheric modeling matures during the next few years, the biggest uncertainty in making future predictions will probably be the uncertainty in formulating the scenarios for future changes in CH_4, N_2O, CO_2, and the CFC's. Projections for the CFC's are difficult because they must incorporate changes in population, GNP, regional development and technology. However, several such projections have recently been performed. Projected estimates for the long-term growth (through the year 2075) range from 0.6 to 3.0% per year for CFC's 11 and 12. This range is consistent with the scenarios used in the model predictions that will be discussed later in this report.

Carbon Monoxide (CO), Carbon Dioxide (CO_2), and Methane (CH_4):

The atmospheric concentrations of CO, CO_2, and CH_4 are all increasing on a global scale, and all exhibit seasonal variability which is largest at high latitudes in the Northern Hemisphere. In addition, there is evidence that some of the recent variability in CO_2 and CH_4 is associated with the El Nino-Southern Oscillation (ENSO) phenomenon. The global distribution and seasonal variability of CO_2 (Figure 3) and CH_4 (Figure 4) have been recently synthesized from several thousand air samples collected by the NOAA/GMCC network.

The atmospheric concentrations of CO are higher in the Northern Hemisphere than in the Southern Hemisphere, and higher in the winter than in the summer. These observations are consistent with industrial source regions in the Northern Hemisphere with the dominant atmospheric removal mechanism being reaction with OH radicals. The dominant sources of CO are combustion (including biomass burning) and hydrocarbon oxidation. The atmospheric lifetime of CO is short (the average lifetime is 0.4 years, with a lifetime in the tropics of only 0.1 years), allowing the concentration of CO to vary considerably in both time and space, making it difficult to accurately determine a long-term trend. The magnitude of the annual trend in CO appears to be between 1 and 2% increase in the Northern Hemisphere, and 0.5 to 1% increase in the Southern Hemisphere.

The records of atmospheric CO_2 concentrations are the best of any gas. They are precise, long and detailed at different latitudes. The current global mean concentration of CO_2 is 344 ppmv and is increasing at an approximate annual rate of 0.5%. The major cause of the long-term increase in atmospheric CO_2 is the combustion of fossil fuels. However, the importance of large scale land use changes has still to be established. Quantitative
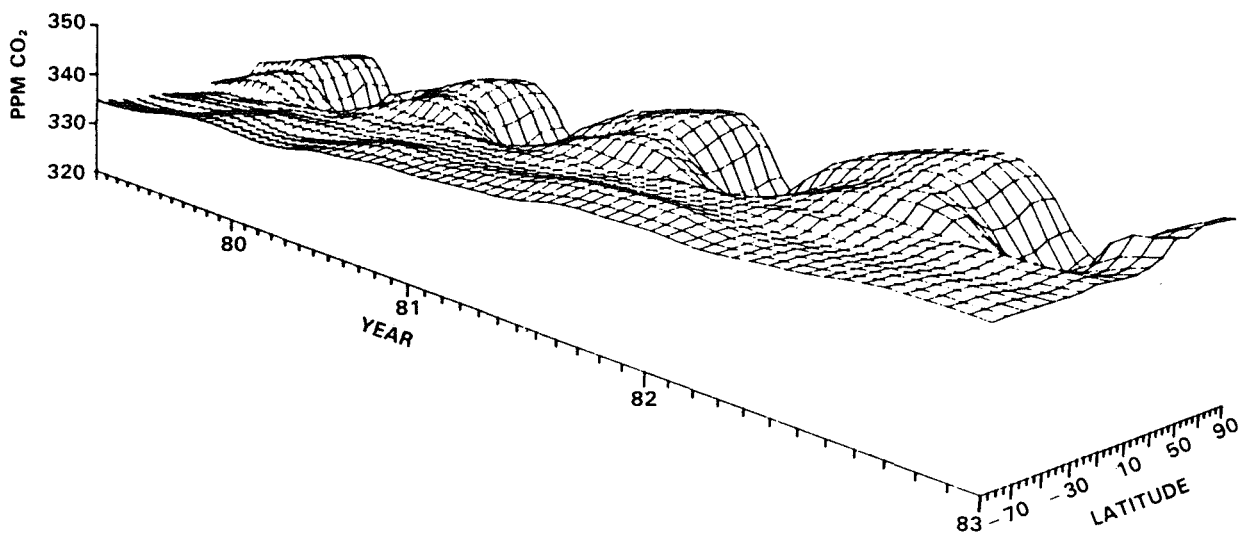
Figure 3. A three-dimensional perspective of the "pulse-of-the-planet," the variation of the global atmospheric CO_2 concentration in latitude and time based on flask measurements for 1979-1982. This zonally averaged surface has a resolution of 20 days and 10° in latitude and was synthesized from results of ~10,000 individual flask samples returned from 15 remote sea-level sites of the NOAA/GMCC sampling network
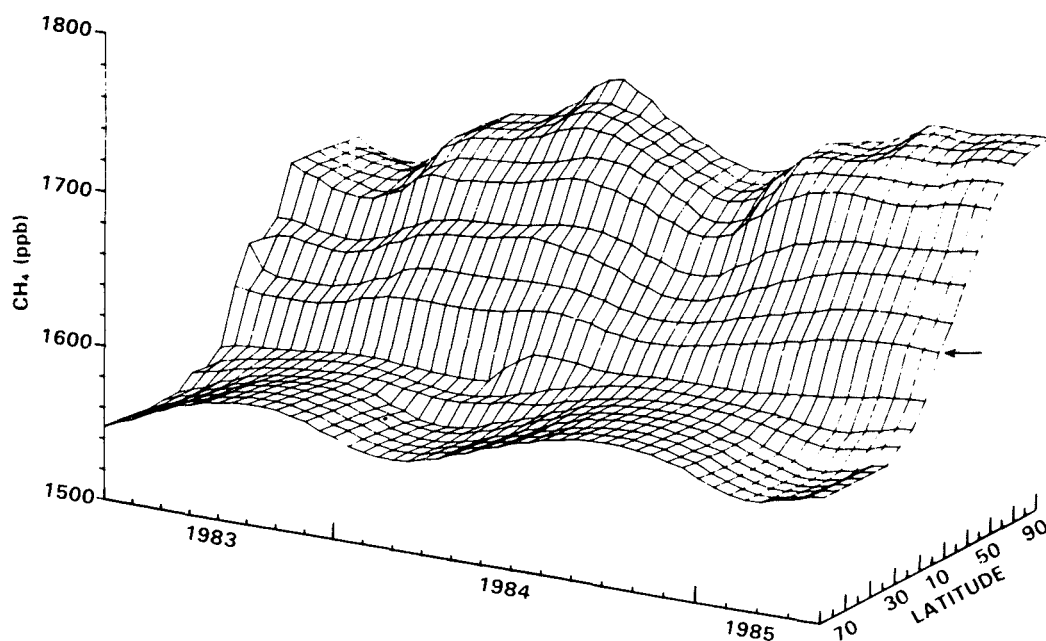
Figure 4. Zonally averaged global distribution of CH_4 in the lower troposphere for the two-year period 5/83-4/85. Surface constructed from biweekly flask samples from 17 sites of the GMCC/OGC/CSIRO global network, 76°N to 90°S. Arrow indicates equator, resolution is 10° in latitude, 14 days in time.

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understanding of the CO_2 trends requires knowledge of the role of the oceans. The observed CO_2 seasonal variability is dominated by the seasonal cycles of photosynthesis and respiration in northern mid-latitudes. It is interesting to note that the amplitude of the seasonal cycle has increased over the last three decades.

The world-wide average atmospheric concentration of CH_4 as of late 1985 was 1.65 ppmv, and for the last decade or so has been increasing at an average annual rate of about 1% (Figure 5). In addition, ice-core data indicate that the atmospheric concentration of CH_4 may have steadily increased over the last several hundred years from a value of approximately 0.7 ppmv.

CH_4 is produced in anaerobic environments. The major natural sources for atmospheric CH_4 are currently thought to be natural wetlands (including wet tundra and sedge, floodplains, peatlands, and associated open water areas), rice paddies, and enteric fermentation in ruminants, with considerable uncertainty as to the importance of termites and biomass burning. Recent studies of the carbon and hydrogen isotopic composition of CH_4 (i.e. the ratios of ^{12}C to ^{13}C, ^{12}C to ^{14}C and D to H) have suggested that presently unexplored biological sources must release CH_4 enriched in C-13 or that there is an error in the kinetic isotope effect for OH with $^{12}CH_4$ versus $^{13}CH_4$. The major removal mechanism for atmospheric CH_4 is reaction with the OH radicals. Model calculations indicate an atmospheric lifetime of approximately 11 years.

Projections of the concentrations of atmospheric CH_4 and CO into the future are difficult because the origins of the current increases in these gases are not known. The atmospheric concentrations of these two gases are chemically coupled and both control the atmospheric concentrations of the OH radical. Consequently, the increase in atmospheric CH_4 may be due to
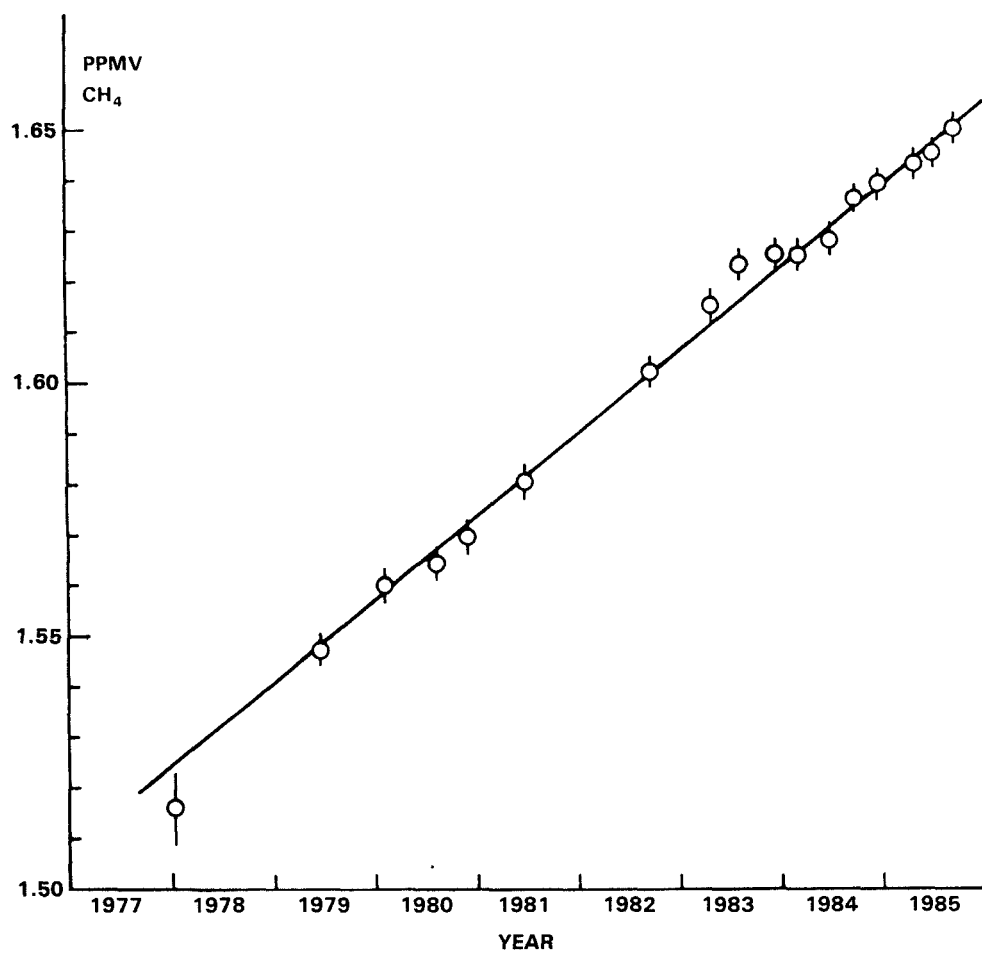
Figure 5. Globally averaged concentrations of CH$_4$ from 1977 to 1985 (Rowland)

increased source strengths, or due to decreased atmospheric removal rates caused by a decrease in the atmospheric concentration of OH.

Nitrous Oxide:

The dominant source of stratospheric odd nitrogen is the reaction of $O(^1D)$ atoms with N_2O to form NO. The current atmospheric concentration of N_2O is 304 ± 2 ppbv, with very little geographic or seasonal variability, and this concentration is increasing at an annual rate of 0.2%. It should be noted that there is some evidence that the annual rates of increase are larger in the Northern Hemisphere (0.25-0.7%) than in the Southern Hemisphere (0.1-0.2%). The rate of increase in atmospheric N_2O, in conjunction with the estimate of a 150 year lifetime, implies that the source strength is currently 30% greater than the sink strength. Consequently if the emission rates of N_2O continue at their present level the atmospheric abundance of N_2O would eventually increase to about 400 ppbv. A major natural source of atmospheric N_2O is thought to be nitrification in aerobic soils and waters. However, there are two significant sources of N_2O which can be ascribed to human activity, i.e. combustion and the use of nitrogeneous fertilizers that would artificially enhance biogenic emissions of N_2O. Consequently, there are reasons to believe that the strengths of the combustion and intensive agricultural sources of N_2O will continue to increase.

VI. ATMOSPHERIC CHEMISTRY

During the past decade considerable progress has been made in the laboratory measurements of rate constants, cross sections, primary quantum yields and product distributions for use in atmospheric modeling, both tropospheric and stratospheric. There is now a better data base for these

reactions, including those exhibiting unexpected temperature and pressure dependence of rate coefficients, but our understanding of the chemical reaction mechanisms is still inadequate. A number of problems remain, ranging from small differences in results for a given parameter obtained by different laboratories to the possibility that major processes have not been incorporated into the photochemical models. Since the previous assessment report of 2 years ago progress has continued at a steady pace, although it has been less spectacular than during earlier periods, reflecting the improved quality of the reaction data base. There have been no major changes in our concept of stratospheric chemistry, but rather there has been a series of minor, yet still important, modifications to some rate constants. Perhaps the most significant changes in recent years have been in our improved understanding of the kinetic and photochemical behavior of OH, HO_2, $ClONO_2$, N_2O_5 and HO_2NO_2 species, and revision of the O_2 absorption cross sections which are needed to calculate the attenuation of solar UV flux in the wavelength region 175 to 220 nm.

The following discussion will emphasize the uncertainty in those processes which are not well defined, and for which the ozone perturbation calculations are sensitive, rather than discussing the large majority of processes for which the present data base is thought to be well established. Although there are still significant gaps in our knowledge of atmospheric chemistry the data base has steadily improved over the past years. Increased emphasis is currently being placed on analysis of reaction products rather than relying solely on measuring the disappearance of reactants. This is particularly important for those reactions which have more than one product channel. Investigations of reaction mechanisms over the full range of atmospheric temperatures and pressures are important, since extrapolation of

results to outside the range where measurements were taken is sometimes unreliable. The partial pressures of other gases such as water vapor or oxygen may occasionally affect reaction rates, particularly for tropospheric reactions.

Tropospheric Chemistry

Processes which control the trace gas composition of the troposphere need to be understood for investigation of many problems in stratospheric chemistry. The troposphere serves as a source region for a large number of gases that play important roles in the photochemistry of the stratosphere. Since the concentrations of several of these gases are controlled by chemical sources and sinks in the troposphere, global changes in the chemical composition of the troposphere may alter the fluxes of these species to the stratosphere. The most important sink for many of these species, e.g. CH_3Cl, CH_3CCl_3 etc., is reaction with OH. Any large-scale changes in tropospheric OH concentration may, therefore, affect fluxes of some source gases to the stratosphere. Furthermore, tropospheric ozone contributes to the total ozone column and plays a significant role in the energy balance of the atmosphere. The chemistry of the global troposphere is complex with both homogeneous and heterogeneous (dry and wet scavenging) processes playing important roles. The homogeneous gas phase chemistry is governed by coupling between the carbon/nitrogen/hydrogen/oxygen systems and can be considered to be more complex than the chemistry of the stratosphere due to the presence of higher molecular weight hydrocarbons, longer photochemical lifetimes, higher total pressures, etc. Significant progress continues to be made in understanding the coupling between the different chemical families, as well as the details of the hydrocarbon oxidation mechanisms and the reactions of HO_2 which play a

vital role in controlling tropospheric OH and ozone concentrations. These are important developments because of the observed increases in atmospheric CH_4 and CO concentrations. Reaction of OH with CO is the dominant process for controlling OH concentrations in the troposphere, yet this important reaction is still not fully understood. Our current understanding of heterogeneous processes is at best qualitative and represents an important void in our understanding of key tropospheric chemical processes.

Reactions involving sulfur compounds are generally considered to be unimportant in the homogeneous chemistry of the global clean troposphere but are quite significant in perturbed regions such as urban areas or volcanic plumes, leading to the formation of sulfate aerosols.

Stratospheric Chemistry

There are some distinct differences between the chemistry of the lower (<30 km) and upper (30-50 km) stratosphere. The chemistry of both regions is quite complex, with significant coupling between the HO_x, NO_x and ClO_x families as shown in Figures 6-8. Extensive recent research has emphasized the importance of temporary reservoir species such as $ClONO_2$, N_2O_5 and HO_2NO_2 which act to lessen the efficiency of NO_x and ClO_x species in destroying ozone in the lower stratosphere. It is within this region of the stratosphere that both dynamics and photochemistry play key roles in controlling the trace gas distributions. In contrast, due to the rapid photodissociation of the polyatomic molecules, the key chemical processes above 30 km all involve atoms and small molecules. In this region of the atmosphere the concentrations are determined predominantly by photochemistry, rather than transport. However, the budgets of the chemical families is dependent upon the transport of their precursors into this region of the atmosphere.
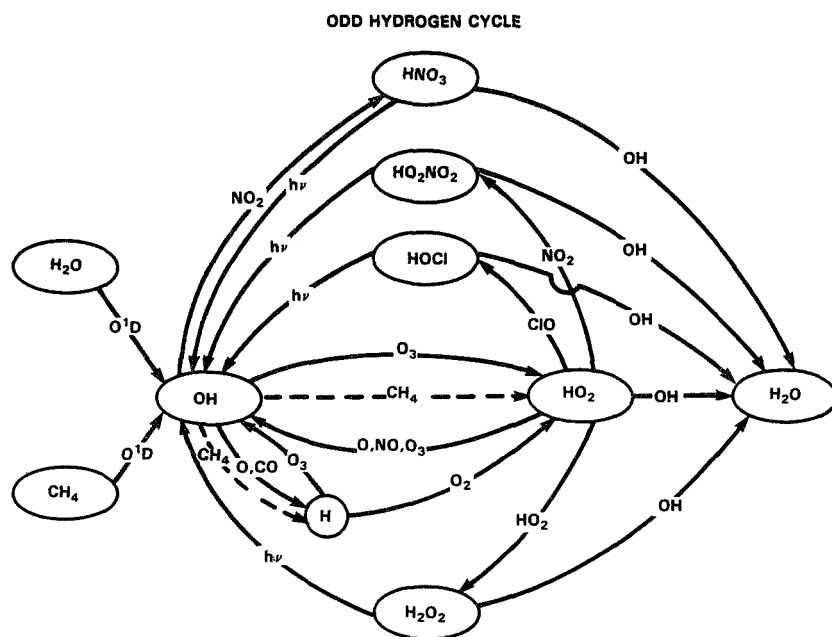
Figure 6. Schematic of the Odd-Hydrogen Cycle.
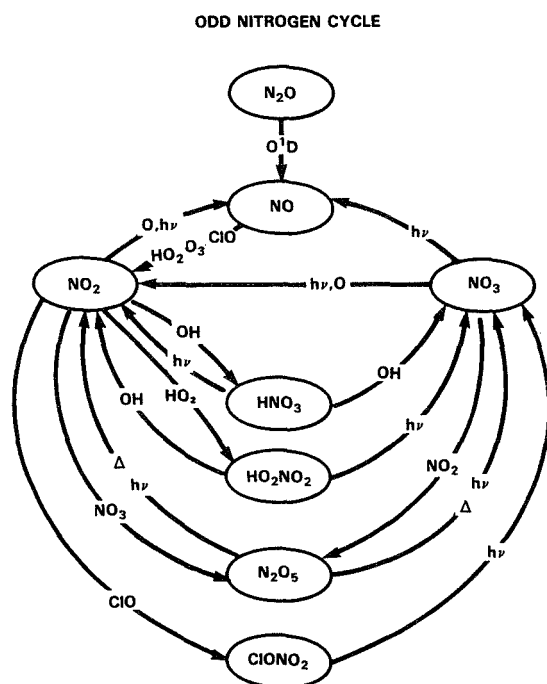
Figure 7. Schematic of the Odd-Nitrogen Cycle. **Figure 8.** Schematic of the Odd-Chlorine Cycle.
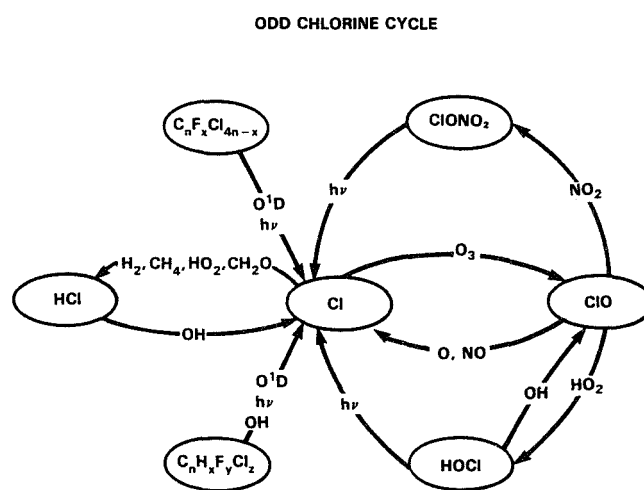
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The current state of understanding of chemical and photochemical processes for individual chemical "families" is discussed separately below, although it should be recognized that there is strong coupling between them. Indeed, it has been changes in our understanding of the inter-family coupling that have resulted in most of the major changes in calculated ozone depletions over the past decade.

Odd-Oxygen Reactions (O_x)

The chemistry of the basic $O(^3P)$, $O(^1D)$, O_2 and O_3 system is well established, and there have been no recent changes in recommended rate coefficients. There is some interest in the roles of excited states of O_3 or O_2, but at present there is no evidence that such states have important effects on the overall chemistry of the stratosphere.

UV radiation at wavelengths between 100 and 240 nm is absorbed by both O_2 and O_3 and between 240 and 320 nm by ozone alone. O_2 and O_3 control the penetration of solar UV radiation into the atmosphere and therefore determine atmospheric transmissivity in these spectral regions. In the O_2 Herzberg continuum ($\lambda < 242$ nm) the absorption cross section data used in earlier atmospheric studies were based on laboratory measurements made at high pressures and extrapolated to low pressures for stratospheric applications. Using these values to calculate the penetration of solar radiation into the stratosphere resulted in an inconsistency with in-situ observations. At the time of the previous assessment report, new laboratory and in-situ atmospheric data between 200 and 225 nm indicated lower O_2 cross sections which improved the agreement between in-situ observations and calculations of the penetration of UV solar flux. These results have now been confirmed by independent laboratory measurements and also have been supported by new in-situ

observations. This is important for the rate of odd oxygen production in the stratosphere and for other molecules such as N_2O, CCl_4, CF_2Cl_2 and $CFCl_3$, which are photodissociated in the 200±20 nm region.

Odd-Hydrogen Reactions (HOx)

The rate coefficients for reactions which control the abundance and partitioning between the odd hydrogen radicals (OH and HO_2) are required with high accuracy because of the central role that they play in controlling the catalytic efficiencies of both the NO_x and ClO_x cycles, as well as their direct role in catalyzing loss of ozone. Changes in the recommended rate constants for the reactions of OH with HNO_3 and HO_2NO_2 were previously responsible for significant revisions of calculated ozone changes. Earlier work indicated unexpected pressure and temperature dependence of reactions involving the HO_x radicals. Since the previous assessment report there have been further refinements in the data base for reactions of HO_2 with H, O, OH, and HO_2 which have included better characterization of the dependence of the rate constants on pressure, temperature and water vapor concentration. Additional studies of the temperature and pressure dependence of the $OH+HO_2$ reaction are needed because of this reaction's important role in HO_x destruction. There has been only one direct temperature dependence study of the HO_2+O_3 reaction, and it indicates a surprisingly low pre-exponential Arrhenius factor; more studies of this rate are needed.

Odd-Nitrogen Chemistry (NO_x)

Over the past several years the kinetics data base for this class of reactions has been significantly improved with new data for the reactions $OH+HNO_3$, $OH+HO_2NO_2$ and HO_2+NO_2+M. For the $OH+HNO_3$ reaction a small pressure

dependence has been confirmed and the negative temperature dependence is now firmly established. For the equally important $OH+HO_2NO_2$ reaction conflicting results have been reported for the temperature dependence, and the reaction products have not been determined. The temperature dependence of the absorption cross sections of HNO_3 and HO_2NO_2 should be determined. Moreover, the products of photodissociation of HO_2NO_2 are not established. The possibility of a minor channel in the photolysis of N_2O to give $NO+N$ should be examined, since if this were to occur to the extent of 1% it would provide a source of NO equal to that of the $O(^1D)+N_2O$ source.

Processes involving NO_3 and N_2O_5 are being studied. Rates of some key NO_3 reactions have recently been reported. Temperature dependent cross sections for N_2O_5 have been reported, but there is still controversy concerning quantum yields for the various product channels. These species do not play a major direct role in controlling the ozone concentration, but do affect the odd nitrogen partitioning and are very important in and near the polar night.

Odd-Chlorine Reactions (ClO_x)

The overall kinetics data base for ClO_x reactions has improved significantly in recent years. There has been a significant revision in our understanding of HOCl and $ClONO_2$ chemistry and of the rates of several ClO_x radical-radical reactions. Although the measured rate constants for important reactions such as $Cl+O_3$, $NO+ClO$, and $Cl+CH_4$ have not changed substantially since 1977, there have recently been revisions in the measured rate constants for OH+HCl (20% increase) and O+ClO (15% decrease) due to intensive reinvestigations of these key reactions. These revisions which were tentative at the time of the previous assessment report have now been confirmed. These

changes have opposing effects on ozone depletion. Recent studies of the OH+ClO reaction have indicated that formation of HCl is negligible, but due to the complexity of the methods involved, the value of the HCl yield cannot be considered to be firmly established, and additional studies of this product yield as a function of temperature are needed. New studies of the reaction $HCl+ClONO_2$ have shown that earlier preliminary results included significant heterogeneous components. The new reduced upper limit to the rate constant for the homogeneous reaction precludes it from having any significant effect in atmospheric chemistry.

Hydrocarbon Chemistry

The observed increase in atmospheric methane concentrations underlines the need to understand its chemistry in the atmosphere. In the stratosphere, the reaction $Cl + CH_4 \rightarrow HCl + CH_3$ constitutes the main loss process for active chlorine. The dominant sink of methane is, however, its reaction with OH, leading to water vapor and CO_2 formation. The subsequent reactions in the methane oxidation chain (Figure 9), which involve CH_3O_2 as the key intermediate, are becoming better known. However, more information is needed about the reaction $CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$ (most important in the troposphere) and about reactions of CH_3O, especially with O_2, at stratospheric temperatures. Also additional information is needed on the temperature dependence of the reaction OH + CO as a function of pressure. Uncertainties in reaction kinetics and mechanisms exist for other hydrocarbons such as C_2H_6, C_3H_8 and C_2H_2, which are useful as tracers to test the transport and chemistry used in models. Ethane and propane oxidation leads to the formation of peroxyacetylnitrate (PAN), which is a reservoir for active odd nitrogen in the troposphere and lower stratosphere.
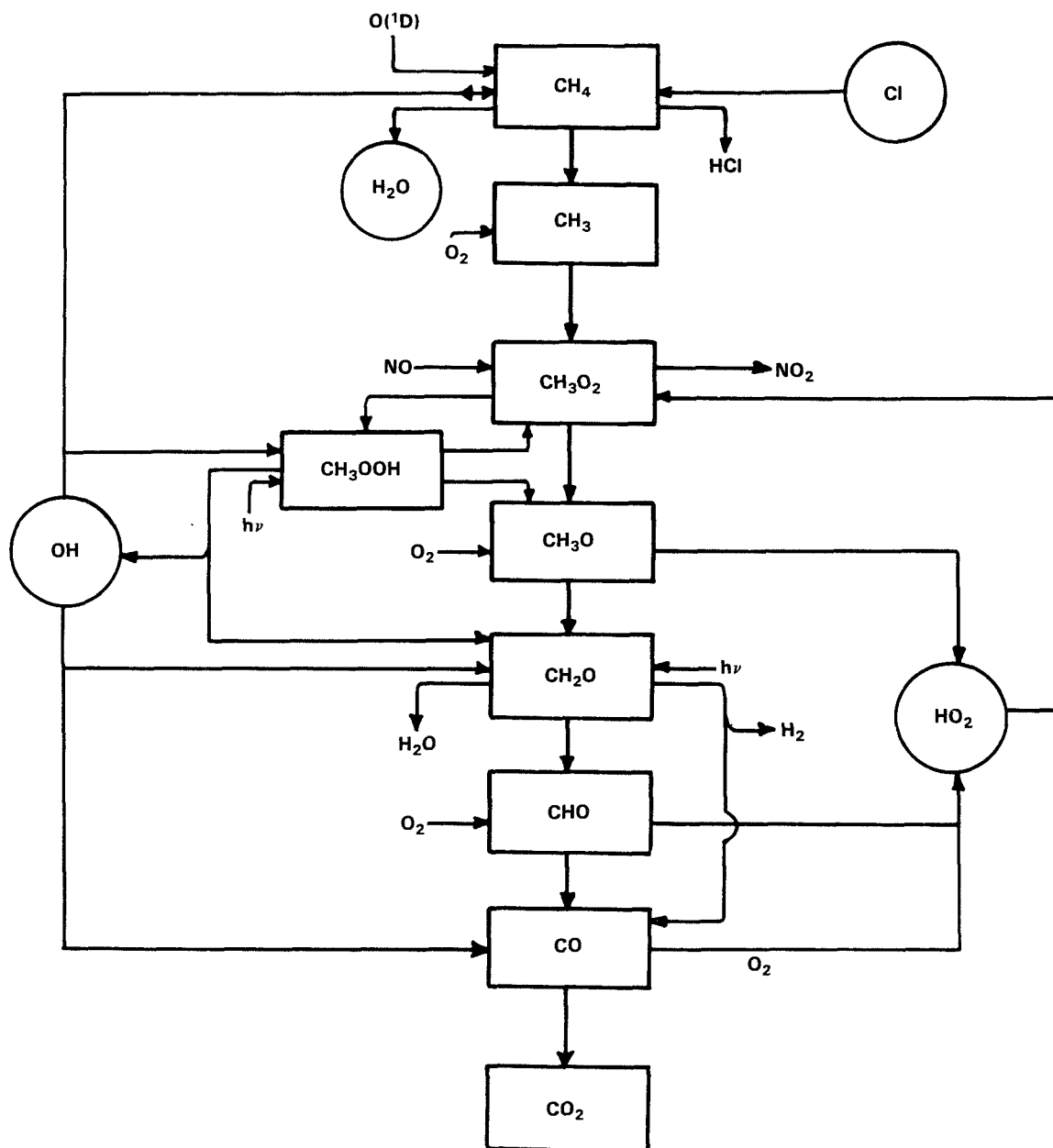
Figure 9. Atmospheric Methane Oxidation Scheme.

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Sulfur Chemistry

Reactions of sulfur compounds are relatively unimportant in stratospheric gas phase chemistry, except possibly in the case of massive injections of sulfur, such as the recent El Chichon eruption. Until recently it was thought that such large injections of sulfur into the stratosphere, primarily in the form of SO_2, might lead to large reductions in ambient OH concentrations, which would have important effects on NO_x and ClO_x chemistry. Recent laboratory data support the suggestion that SO_2 oxidation proceeds via a process catalyzed by HO_x, thus having only a slight impact on the OH concentration consistent with recent observations of the rate of SO_2 oxidation following the El Chichon eruption. The conversion of SO_2 into sulfate aerosols can obviously impact the Earth's radiation budget.

VII. RADIATION AND DYNAMICS

All models of stratospheric ozone must include some formulations of chemical, radiative, and dynamical processes. The previous section discussed the present understanding of atmospheric chemistry. This section will discuss the present understanding of radiation and dynamics so that the treatment of these processes in assessment models will be better appreciated.

Radiative Processes

Solar radiation incident on the Earth and its atmosphere provides the ultimate driving force for all the chemical and dynamical processes addressed in these assessments. Solar radiation provides the energetic input to the planet, and terrestrial (or longwave) radiation provides the means by which the planet radiates energy to space. This energy input and loss to space is balanced on the planetary scale, but is not necessarily in balance locally and

as a function of time. Thus, at any particular point and time there can be a non-zero net heating (positive or negative). Radiative heating forces motions in the Earth's atmosphere, and the resulting motions change the atmospheric temperature structure which in turn affects the net radiation. An important point to appreciate is that atmospheric radiative and dynamical processes are inextricably coupled (as is chemistry).

Solar Radiation

Since the last assessment there has been a substantial increase in our knowledge of the 175 nm $<\lambda<320$ nm solar spectral irradiance which is important for stratospheric modeling. This has been a result of recent analysis from both the SBUV instrument on the Nimbus 7 satellite and data from the SME satellite. In particular, we know more about the 27-day solar rotation variation over this part of the solar spectrum, but our knowledge of its variations over the 11-year solar cycle remains inadequate. It is important that secular variations in those parts of the solar ultraviolet spectrum that dissociate molecular oxygen (<242 nm), O_3 and other trace gases that play a role in the photochemistry of the stratosphere (<330 nm) be understood since the effects of changing solar radiation may produce changes in ozone that could be confused with those resulting from human activities. WMO 1986 gives a new reference solar spectrum which is recommended for use in stratospheric modeling, and is based on recent satellite and rocket measurements. Measurements over most parts of the solar spectrum are thought to be accurate to 5-10%, with the visible part of the spectrum being accurate to 3%.

The 175 nm $<\lambda<210$ nm portion of the solar spectrum has been seen to vary by as much as 5-7% over a solar rotation with this variation decreasing to 1% or less for $\lambda>260$ nm. Using this type of data together with their association

with features observed on the face of the Sun, models have been developed that suggest that the 210 nm $<\lambda<250$ nm solar radiation varies by about 10% over a solar cycle. Such modeling is useful, but carefully calibrated observations are needed over a solar cycle before there can be confidence in these results.

Other factors in modeling solar radiation include Rayleigh scattering and molecular oxygen dissociation by absorption in the Herzberg continuum ($\lambda<242$ nm). In the last assessment it was stated that atmospheric measurements indicated Herzberg continuum cross sections that were lower than those commonly used. Recent laboratory measurements have confirmed this. Knowledge of the O_3 cross sections appear to be adequate for modeling purposes although it is desirable that the temperature dependence of the Hartley absorption ($\lambda<308$ nm) cross sections be included in models and better measurements of the cross sections in the Huggins bands ($\lambda<360$ nm) be obtained. Calculation of solar heating rates in the stratosphere is straightforward if one knows the incident solar radiation, the absorption cross sections of O_3, the Rayleigh scattering cross section, and the vertical distribution of O_3 everywhere. This has been calculated by several investigators. However, it is the difference between solar heating and longwave cooling that is required for dynamical studies. This net heating is often a small difference between two large values, so that small errors in either the solar or longwave calculations can have a substantial impact. There are several calculations of this net heating in progress using internally consistent data (simultaneous measurements of temperature and O_3) that have not yet appeared in the refereed literature. Determination of the net global heating will be a valuable check on the consistency of measured O_3 values and our radiative formulations.

Terrestrial Radiation

In the absence of motions, the thermal structure of the atmosphere is determined solely by the balance between absorption of solar radiation and cooling by infrared emission. Dynamics however induces large departures from this simple balance. The proper treatment of radiative processes is needed to model the temperature correctly, and many of the chemical reaction rates show a strong temperature dependence. Also, refined methods for calculating infrared emission are needed for proper radiative damping of atmospheric wave motions. The major difficulties in properly calculating longwave radiation are the accuracy of line-by-line calculations, the accuracy and completeness of spectroscopic data, and the availability and accuracy of band models. Line-by-line radiative calculations are too computationally intensive to be used in either dynamics or in coupled photochemical-radiative models, but they are used as "benchmarks" for parameterized radiation algorithms. Even line-by-line calculations do not resolve the structure of each rotational line, so inaccuracies are introduced by the line parameterizations in the line-by-line models and are carried forward in the simpler models approximating the line-by-line calculations. Such uncertainties are not the limiting factor in atmospheric heating rate calculations. Of course, laboratory spectroscopy measurements provide the necessary inputs to all these calculations, so we should inquire into their accuracy. CO_2 transmittances are known to better than 10%, and H_2O transmittances are also well known. O_3 transmittances are the least well known, but this is not critical since O_3 infrared cooling rates are less than one-third of the CO_2 cooling rates over most of the stratosphere.

It would be quite valuable to obtain broadband-transmission measurements under stratospheric conditions since they would provide constraints on the

line-by-line calculations upon which further calculations are based. Better spectroscopic measurements for CH_4, N_2O, HNO_3, CFC-11, and CFC-12 are also desired. Even though their contribution is small in the present-day atmosphere, such data is needed for better climate predictions.

Computing longwave cooling rates is relatively straightforward near stratopause levels but becomes increasingly difficult as one descends into the lower stratosphere due to pressure broadening leading to increased line overlap. Also aerosols become more important there, and there is no clear dominance of the net cooling rate by any single contribution since it is determined by many small heating and cooling contributions. There is also the complicating effects of cloud albedo. It has been suggested that cirrus effects are very significant in affecting heating and cooling rates in this region. While background aerosols do not affect stratospheric cooling rates very significantly, they do have substantial effects after major volcanic eruptions such as El Chichon.

Dynamical Processes

During the past few years, the correct physical basis for parameterizing three-dimensional atmospheric motions in lower dimensional photochemical models has become much clearer. In particular, the intimate connection between zonally averaged transport circulations and atmospheric wave motions has become better understood. Understanding how the observed structure of the atmosphere is maintained tells us a great deal about how atmospheric transport takes place. For instance, if atmospheric motions were neglected in a model of the atmosphere, both the modeled temperature structure and the atmospheric composition would be very different from what is observed. For instance, Figures 10a and 10b shows a comparison of a "radiative-convective" (hereafter

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"RADIATIVE-CONVECTIVE" TEMPERATURE FOR 15 JANUARY
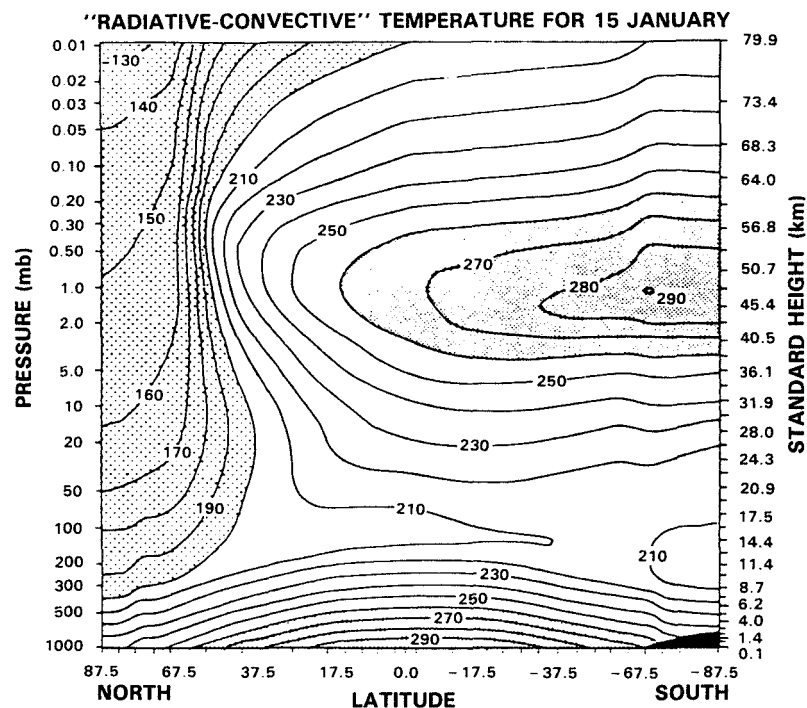
Figure 10a. Time-dependent "radiatively-determined" temperature T_r for 15 January. The surface temperatures are prescribed at their seasonally-varying observed values. Cloudiness, and ozone below 35 km, are prescribed at annual-mean values; ozone above 35 km is allowed to "float," in response to temperature variations, towards a crude photochemical equilibrium. Details of the water vapour prescription are relatively standard.

ZONAL MEAN TEMPERATURE (K) JANUARY
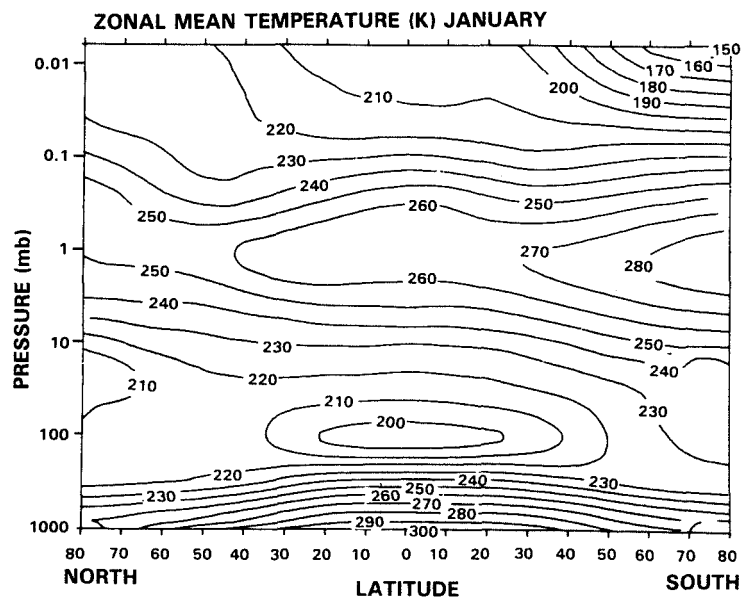
Figure 10b. Cross section of measured zonal mean temperature (K) for the average over 5 years of the monthly means for January. The data are from the combined SCR/PMR retrieval made at Oxford University for 1973 and 1975 to 1978.

referred to as RC) model of the January atmosphere and observations. One sees the following major differences in these RC temperatures and observations. The RC summer stratopause temperatures are close to radiative equilibrium and the exact magnitude of the departure is uncertain. The RC winter stratopause temperatures are too cold by about 90 K. The sense of the polar mesopause temperatures are reversed with the winter temperatures being too cold by about 100 K and the summer temperatures being too warm by about 65 K. The RC tropical tropopause is too warm by about 20 K. Noting that with RC balance there is no vertical and meridional motion, one concludes that it is these motions that are responsible for the differences between RC equilibrium and observations. These motions are pictured schematically in Figure 11. It is also these motions that are responsible for the advective transport in photochemical models.

Note, at this point, that these zonally-averaged transport motions are not forced by the differential solar heating since this differential solar heating is present in the RC state. Theoretical work on atmospheric dynamics has made it apparent that it is the effects of asymmetric motions (or eddies) on the zonal momentum budget that gives rise to the departure from RC equilibrium. These eddies take the form of planetary waves (planetary scale undulations in the flow), gravity waves (propagating buoyancy oscillations) and baroclinic waves in the troposphere. These eddies, in addition to being responsible for the existence of the zonally-averaged transport circulation, also give rise to diffusive mixing of constituents. Thus, the eddy motions and the zonally-averaged transport motions are intimately connected, implying that the advective and diffusive transport of constituents are equally intimately connected. Furthermore, since planetary-scale motions are nearly absent in the summer stratosphere, there must be a similar absence of
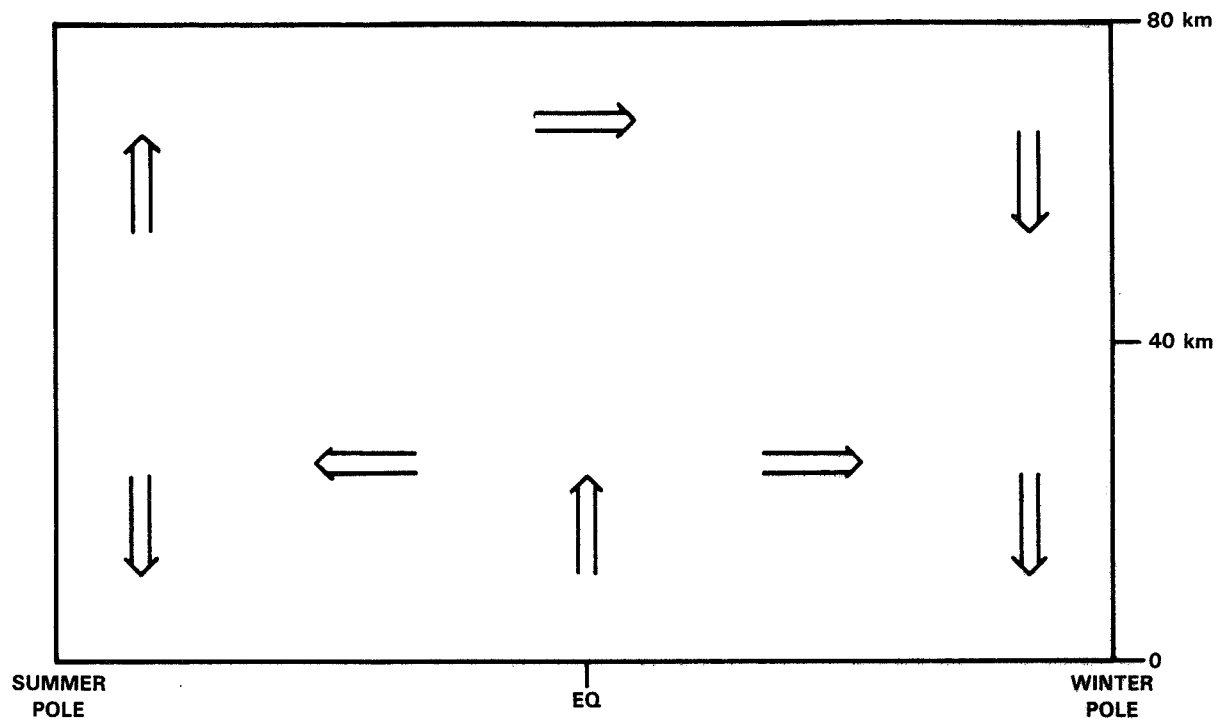
Figure 11. Schematic diagram illustrating the "Transport Circulation" required to reconcile temperatures with radiative equilibrium temperatures.

"diffusion" and reduced advective transport in the summer stratosphere. Since planetary-scale eddies are more weakly forced in the Southern Hemisphere due to smaller landmass, both the zonally-averaged transport and "diffusion" should be less in the Southern Hemisphere than in the Northern Hemisphere.

One concept which has been recently developed is that of "wave breaking" as a major mechanism for transport events.

There has been very recent progress in evaluating advective transport circulations from both general circulation models and atmospheric data, accompanied by attempts to derive diffusion coefficients from these models and data. The temporal and spatial distribution of these diffusion coefficients generally agree with the physical concepts set forth above. These newly derived coefficients and circulations are just beginning to be used in two-dimensional photochemical models.

One difficulty in deriving transport circulations and diffusion coefficients from general circulation models is that these models do not yet give results that agree with observations in several crucial respects. For instance, in all existing general circulation models of the middle atmosphere, the stratospheric winter polar temperatures are too cold. This suggests that both the eddy activity and the zonally-averaged transport circulation are too weak in comparison to the actual atmosphere in these models.

The previous discussion on dynamical processes has dealt almost exclusively with global scale dynamics. There are also relatively small scale phenomena whose cumulative effects can determine the atmospheric global scale structure as well as the large scale constituent distributions. Gravity waves and turbulence can act in this manner. Specialized observational techniques such as radar and lidar are very valuable in observing these phenomena, but

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Another physical process that occurs on small scales but whose cumulative effects determine global structure is stratosphere-troposphere exchange. It is by this process that ozone from the stratosphere provides the troposphere with the means to initiate photochemistry through production of $O(^1D)$. Also, this exchange transports the source gases that originate from the planetary surface, to the stratosphere, where they are the precursors of the HO_x, NO_x,

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The crude morphology of stratosphere-troposphere exchange is illustrated in Figure 11 where there is upward flow in the tropics and downward flow at higher latitudes. This is also the Brewer-Dobson circulation that was deduced from the distribution of water vapor and ozone in the atmosphere. Although this circulation is deduced from the atmosphere's global structure, the stratosphere-troposphere exchange of mass implied by this circulation is not thought to occur in steady global scale circulations but rather as a cumulative result of small scale events.

A crucial clue to the mechanism for upward mass transport in the tropics came from water vapor and temperature profiles measured by instruments on the NASA U-2 research aircraft during the 1980 Panama Experiment. Results obtained during this experiment closely resemble those shown in Figure 12. These profiles showed a tropopause at about 15 km with a water vapor mixing ratio around 5-6 ppmv. Above this level, the water vapor mixing ratio drops to a local minimum of about 4 ppmv at 16 km and then increases again to a local maximum of about 5 ppmv at 17 km. The water vapor mixing ratio then drops to its absolute minimum just below 3 ppmv at about 18.5 km before gradually increasing. Qualitatively speaking, the temperature shows swings
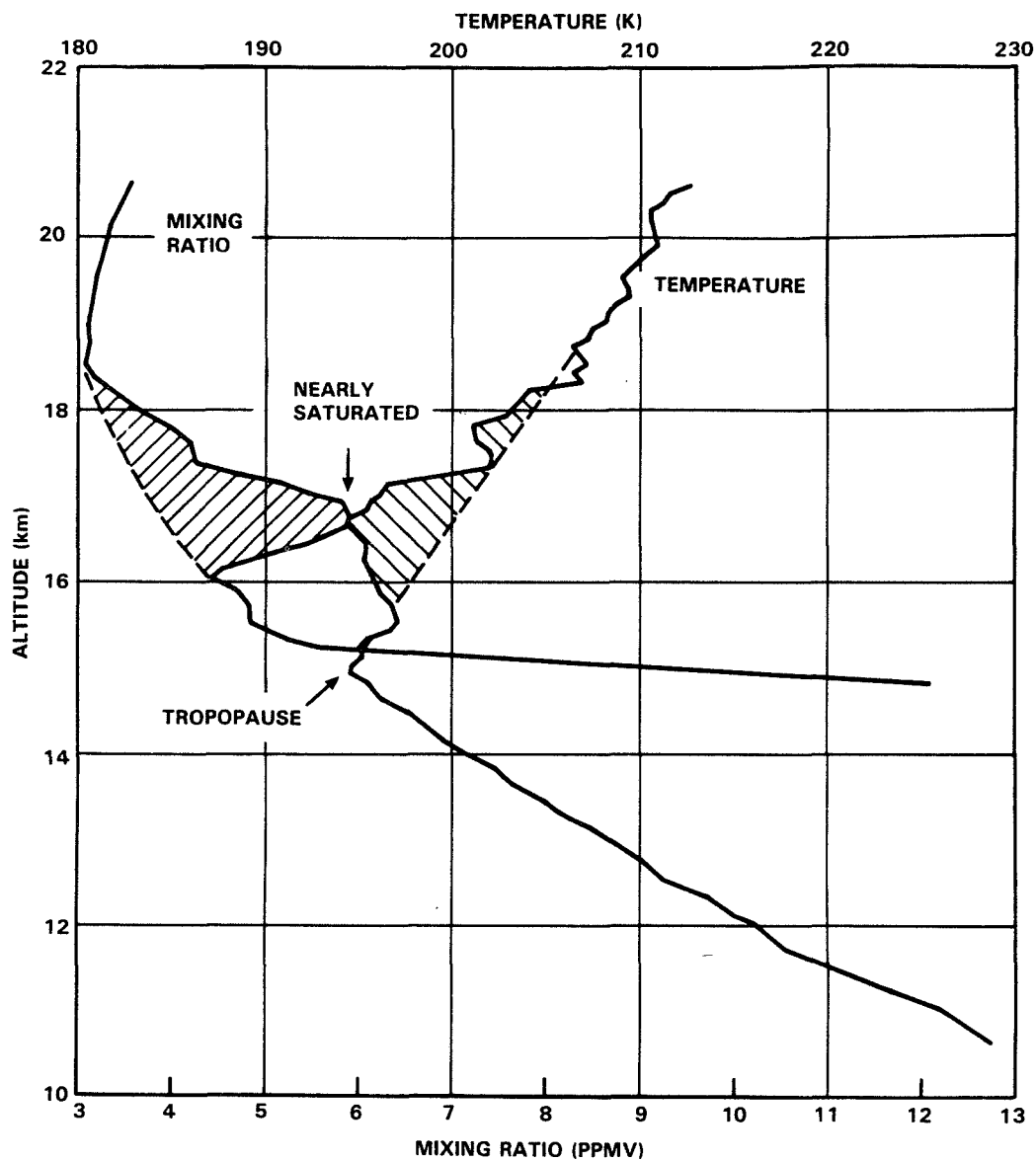
Figure 12. Water vapour mixing ratio and temperature, averaged over 100 m intervals, from U2 aircraft instrumentation at descent to Howard AFB on 11th September 1980. These values of H_2O mixing ratio must be corrected by multiplying them by a factor of 0.88.

out of phase with the water vapor. It is intriguing that the minimum water vapor mixing ratio in this profile is less than that associated with the minimum saturation vapor pressure anywhere in this profile. What is believed to be the case is that virtually all water vapor entering the stratosphere must pass through the coldest tropopause temperatures that occur anywhere on the globe, those in the vicinity of Malaysia. Furthermore, the detailed temperature and water vapor structure in these profiles is strongly influenced by the combination of local cloud microphysical processes and those occurring near Malaysia. Although the discussion here has centered on water vapor, these processes of air entry into the stratosphere are of wider interest for other constituents. Extensive aircraft programs are to be carried out investigating these processes.

The entry of stratospheric air into the troposphere is thought to occur in tropopause folding events that occur in conjunction with tropospheric cyclogenesis. It has also been suggested that such exchange occurs in association with cut-off lows. Aircraft measurement programs have investigated these situations to some extent already, but more extensive aircraft measurement programs are planned.

VIII. MODELS OF STRATOSPHERIC STRUCTURE

The structure of the stratosphere is determined by a complex interplay among radiative, dynamical and chemical processes. Ideally we would like to model this system by including a relatively complete description of all of the relevant processes in a three-dimensional time dependent model. This is not yet possible, both because of limitations in computer resources and limitations in the complete understanding of all of the relevant processes. Thus, the problem of understanding the complete stratosphere is attacked with

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a hierarchy of models which vary in complexity and vary in completeness of description of each of the major aspects of the atmospheric system. Although it is still true that we have primarily dynamical models which have little or no chemistry and primarily chemical models which highly parameterize dynamics as was stated in the 1984 assessment report, there has been a significant narrowing of the gap in that there is an increased effort toward using three-dimensional general circulation model dynamics to perform coupled transport-chemistry studies and to use transport formulations based on either general circulation model results or upon observed three-dimensional dynamics for photochemical simulations. Thus, we are moving toward our goal of having completely integrated models of the entire radiative-dynamical-chemical system, but there is still a long way to go.

One convenient method of classifying stratospheric models is according to their dimensionality. A zero dimensional model considers chemistry in a box, i.e., at single points in the atmosphere decoupled from all other points. Such models (or sub-models) allow a detailed description of the chemical evolution of the system. They generally consider situations in which a chemically dominated system is driven from equilibrium. One example is the diurnal variation of the solar input which can be isolated from the complexity of the overall system so that the problem of diurnal correlation of reacting species can be evaluated. This leads to accurate computation of the modification of the effective diurnal average rate of reaction as compared to that computed from average constituent concentrations. With zero-dimensional models, the impact of changes in rate coefficients or reaction mechanisms on the chemical system are readily evaluated. Of course, care must be taken to apply these models only to chemically dominated regions of the atmosphere. Another use is in the interpretation of atmospheric data in terms of chemical

mechanisms. For instance, the problem of the absolute magnitude of the ozone concentration in the 1 mb region can be attacked by using measured temperature and water vapor together with a zero-dimensional photochemical model to determine whether or not ozone is consistent with the adopted photochemical mechanism. One recent application of a zero dimensional model was to calculate the changing composition of air parcels along trajectories where the initial parcel composition was taken from LIMS and SAMS observations, and the results of these calculations were then checked against the parcel's composition when it intersected a subsequent LIMS observation.

The next level of complexity in atmospheric models is the one-dimensional model which considers variations in the vertical dimension. In this type of model, transport in the vertical dimension is parameterized as Fickian diffusion in which the same diffusion coefficient is used for each chemical species. In general, optimal values for the diffusion coefficient vs. altitude are obtained by fitting the distribution of one or more of the source gases. Recently, however, dynamically based transport formulations have been proposed in which the one-dimensional model vertical diffusion coefficient depends on species and chemical gradients. Although not fully developed and exploited, these techniques may provide a better physical basis for representation of globally averaged transport in one-dimensional models. In one sense, however, one-dimensional models represent the globally and annually averaged stratosphere, in that the diffusion representation of transport attempts to account for globally averaged motions in which all horizontal motions average out. Yet in another sense, the models purport to represent a specific latitude (30° N) and a specific time of year (equinox) in that they use a diurnal march of zenith angles for the Sun appropriate to those conditions. Thus, the photochemical driver is not globally averaged properly,

and the models represent a hybrid situation. One recent application of a one-dimensional model is in modeling the diurnal variation in the vertical column of ClO in comparison with observations. Figure 13 shows this comparison. Note that apart from the faster model rise in ClO in the morning, there is good agreement between the model and observed results. One-dimensional photochemical models are often coupled to one-dimensional radiative-convective models so that changes in ozone can feed back to affect the atmospheric temperature structure through heating by ozone absorption. The one-dimensional radiative-convective models can also be used to look at global climate effects that result from changes in radiatively active trace species. These types of models are used for many of the model predictions that are given in Section X of this report. Temperature dependent chemistry can then modify the ozone perturbations. A feedback which cannot be evaluated in one-dimensional models is that due to dynamical changes which result when changes in the ozone distribution modify the net heating rate causing changes in transport. Despite the above shortcomings, one-dimensional models remain the principal tool with which evaluations are made of possible perturbations of the ozone layer, although the use of two-dimensional models has increased since the 1984 assessment report.

The next level of complexity in the dimensionality of atmospheric models are two-dimensional models. These models attempt to simulate the latitudinal and seasonal variations in atmospheric structure. Some of these models use specified two-dimensional transport dynamics while others seek to model the evolution of the transport by zonally averaged meridional and vertical motions. A characteristic difficulty with such models is how to rationally specify the transport effects of asymmetric motions.
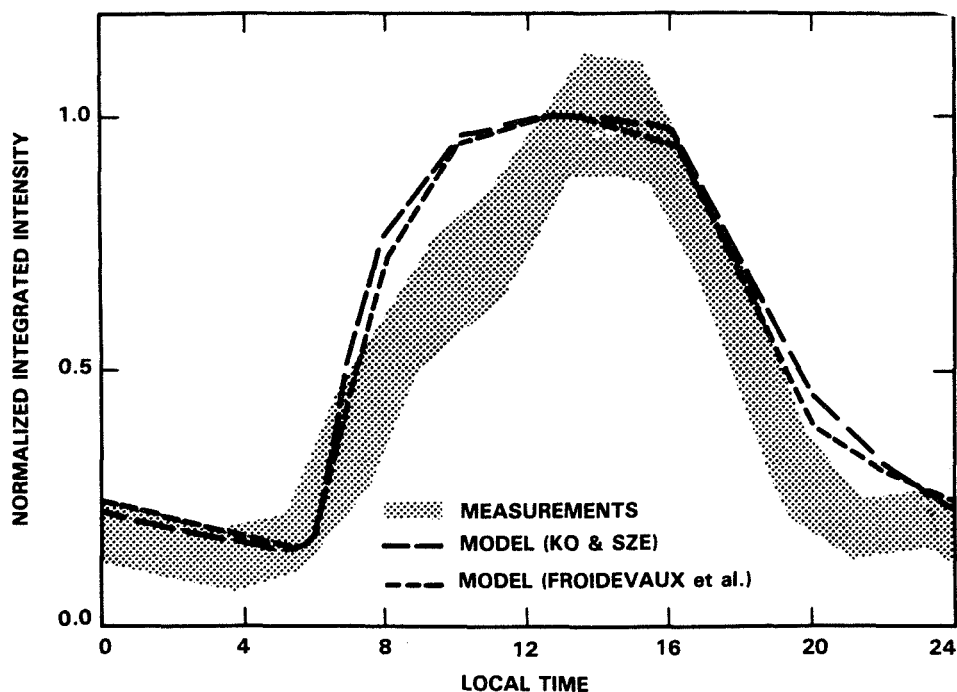
Figure 13. Diurnal variation of ClO measured by ground-based millimeter-wavelength spectroscopy and compared with theoretical predictions. Measurements and predictions have both been normalized to unity at midday. Measurements were binned in two-hour intervals and smoothed; the shaded area represents estimated error limits about the mean. The measurements have been analyzed so that the normalized integrated intensity shown here is proportional to the ClO column density above ~30 km, although a small contribution from lower material is present.

Three different broad classes of two-dimensional photochemical models are presently in use. These are the models in which transport is accomplished by specified diffusion coefficients which are quite large. There are also those two-dimensional models with either specified or internally computed advective circulations with specified small diffusion coefficients, and finally, there are some models in which an effort is being made to use a consistent formulation of the advective and diffusive transports (see Section VIII of this report). Diffusive two-dimensional models (e.g. DuPont) produce quite different latitudinal slopes in constituent concentration isopleths, e.g. N_2O, (Figure 14) which are reflected in quite different vertical profiles of constituent concentrations (see Figure 15).

Two-dimensional models do allow latitudinal and seasonal variations of constituents to be calculated. Thus, these features may be tested against observations for models of present-day conditions. These models also allow predictions of the latitudinal and seasonal effects of constituent scenarios to be made. Many present two-dimensional models include quite complete chemical schemes. In fact, in several cases, the chemical scheme being used in a two-dimensional model is identical to the one being used in a one-dimensional model by the same group.

There are a few very troubling problems with both one- and two-dimensional models that limit the confidence that can be placed in the model predictions of future ozone changes. One is that there is an inconsistency between modelled (using both one- and two-dimensional models) and measured (by both ground-based and satellite instrumentation) ozone abundances above 35 km by as much as 30-50% (Figure 16). It is particularly troubling that this problem occurs in an altitude region in which the ozone concentrations are photochemically controlled. Furthermore, if the observed ozone concentrations
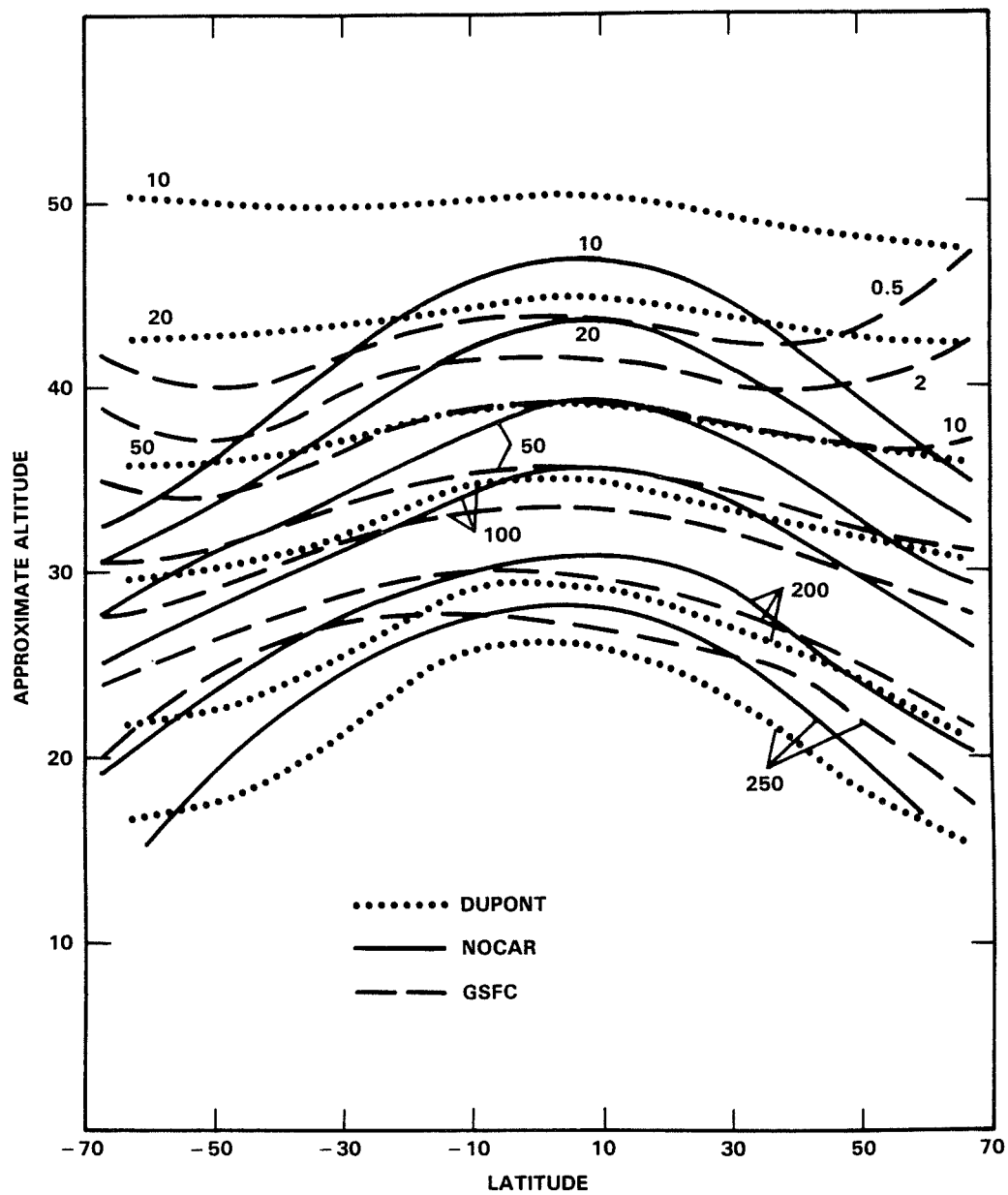
Figure 14. Latitude-height cross-section of the N_2O distribution (ppbv) from three different 2-D models.
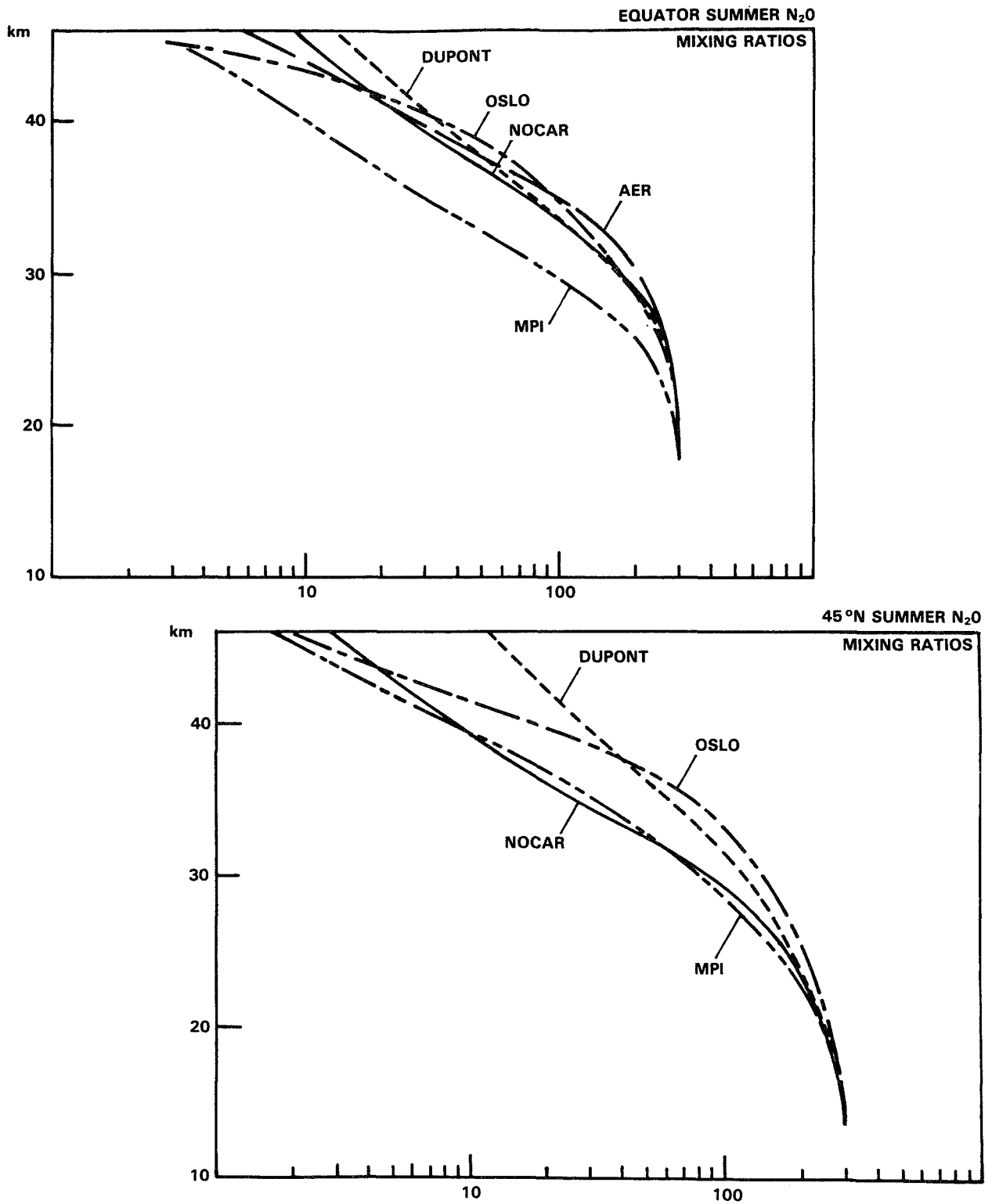
Figure 15. Vertical profiles of N_2O (ppbv) calculated by various models.
    a) Summer, $O°$
    b) Summer, $45°N$
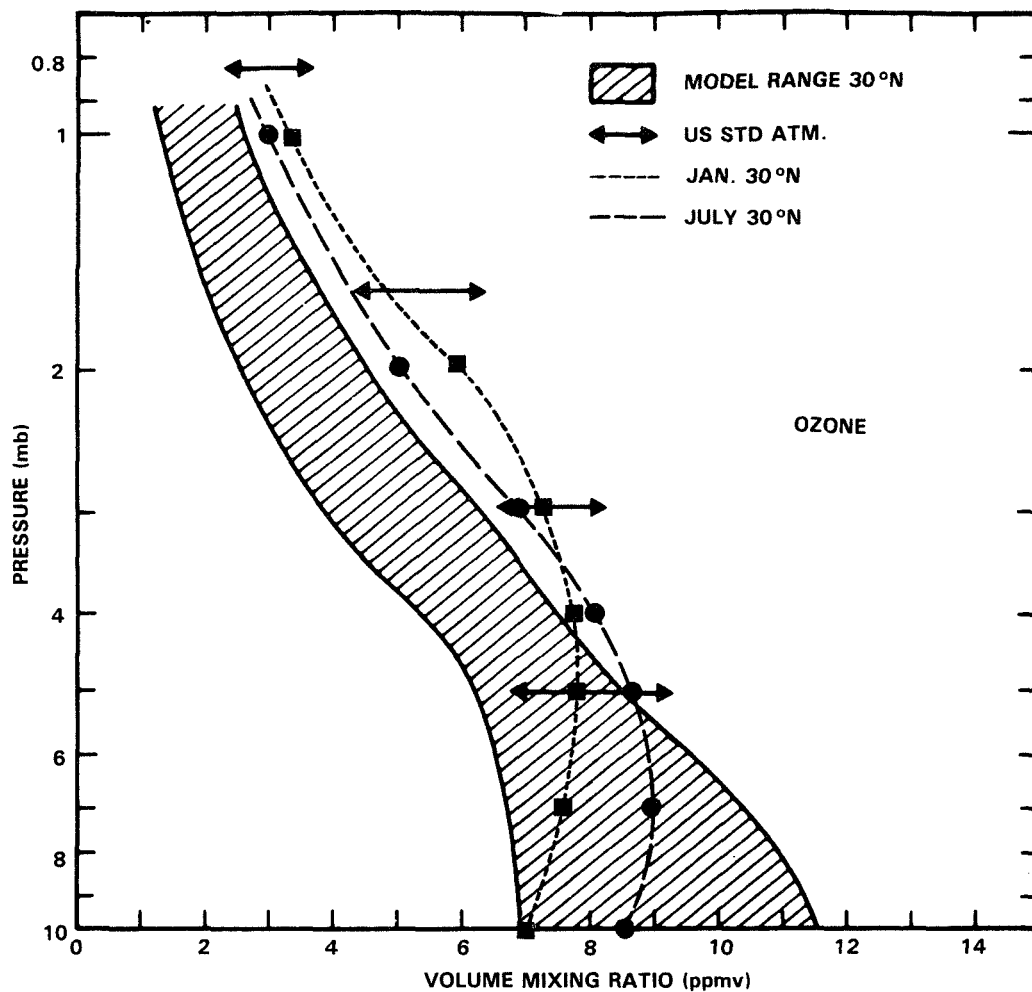
Figure 16. Vertical distribution of the ozone mixing ratio in the upper stratosphere. The shaded area included 2-D model results obtained for winter and summer conditions at 30°N. The O_3 mixing ratio given by the US Standard Atmosphere as well as representative observations at 30°N for January and July are also indicated.

are used in radiative models of the upper stratosphere the predicted temperatures are higher than measured. Another problem is that there are considerable differences in the distributions of odd nitrogen species that are computed by the models of different groups (Figure 17). This is true for both one- and two-dimensional models. This disagreement is understandable for the two-dimensional models given the differences in their formulations of transport, but is very disturbing for the one-dimensional models in which these differences cannot be attributed to differences in transport. One source for these differences in odd nitrogen distributions are the differing treatments for the penetration of solar radiation in the Schumann-Runge bands. However, models with similar radiation schemes still show significant differences in odd nitrogen. We do not presently understand the source of these different odd nitrogen distributions. They are important, however, since nitrogen species interfere with chlorine catalysis of ozone destruction and also because of the important catalytic role of the odd nitrogen species themselves.

Another type of two-dimensional model is aimed at looking at alterations in climate that might result from changed distributions of radiatively active trace constituents. Models of this type have been used to look at the changes in radiative fluxes into the troposphere as a result of ozone decrease. They indicate that if there was a uniform column decrease in O_3, the high latitude cooling would be about four times greater than that at low latitudes. It was also found that fractional decreases in tropospheric ozone would have the same cooling effect as the same fractional decrease in stratospheric ozone even though only about 10% of the total ozone is found in the troposphere.

The situation is the same as that mentioned in the previous report in that there has been no published work in the past 2 years that has integrated

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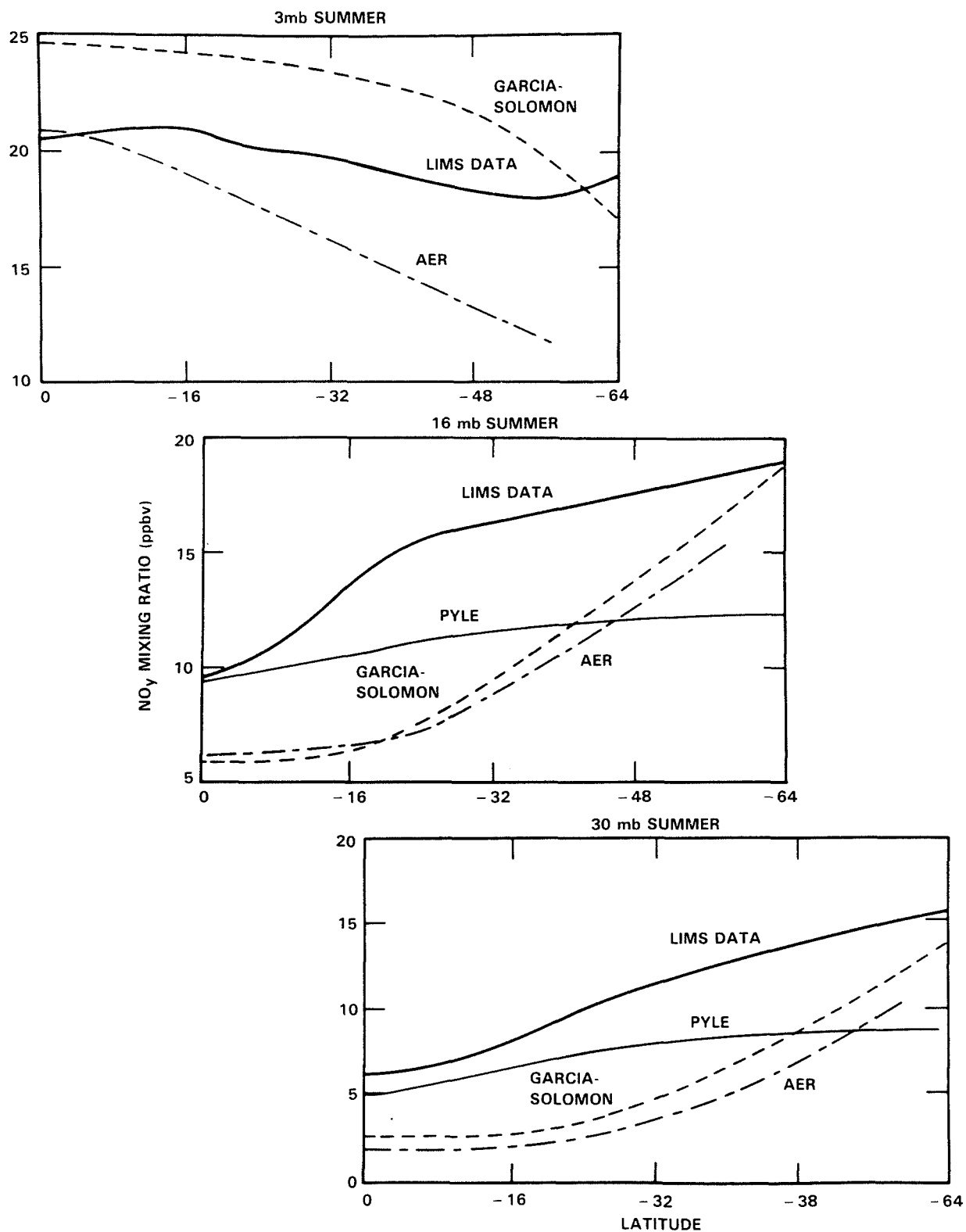
Figure 17. Latitudinal gradients in NO$_Y$ observed by LIMS, and calculated in various 2-D models, at the 3 mb, 16 mb, and 30 mb levels.

realistic chemistry into a three-dimensional general circulation model. Several efforts to do off-line transport-chemistry with general circulation models have been presented at scientific meetings or are in progress, however. These include climatological simulations, simulations of constituent changes during stratospheric warmings and forecasts of constituent change from observed initial conditions. One problem in performing realistic transport-chemistry simulations with general circulation models is that there is clear evidence that present general circulation models do not produce enough eddy activity and hence a vigorous enough zonally-averaged transport circulation compared to observations. Thus, we would expect these models to underestimate both the advective and diffusive transport of constituents.

IX. ATMOSPHERIC OBSERVATIONS AND INTERPRETATION: OXYGEN, HYDROGEN, NITROGEN, AND HALOGEN SPECIES

Understanding the chemical composition and future behavior of the stratosphere cannot be achieved through laboratory simulation experiments because of the scale and complexity of atmospheric phenomena. The atmosphere is a complex chemical system with photochemical lifetimes of species ranging from nanoseconds to years, strongly influenced by dynamical and radiative processes. Consequently, at present and for the foreseeable future, heavy reliance must be placed on theoretical models. However, these models must be checked against atmospheric observations at every opportunity. A wide variety of in-situ and remote sensing techniques are now being used to determine the atmospheric concentrations of a large number of chemical species at a limited number of geographical locations from ground, aircraft, balloon and rocket platforms. This type of data predominantly tests the radiative and chemical aspects of the models. A major advance in the last few years has been the demonstration of a capability to make global measurements of temperature and

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the concentrations of several species from satellites. Such new measurements are required to test the coupling of dynamics, chemistry and radiation in the multidimensional models. In the longer term, future field and satellite programs will be needed to overcome our greatest limitation, which is a shortage of data. At present, the available measurements are inadequate for a complete test of the theoretical models.

In order to model quantitatively the roles of hydrogen-, nitrogen-, and chlorine-containing species in controlling the distribution of atmospheric ozone it is vital to measure and understand their total budgets. In addition, it is essential to understand the photochemical partitioning between the active and inactive species within each family. The key chemical constituents of importance in understanding the spatial and temporal distribution of atmospheric ozone include the source gases (H_2O, CH_4, N_2O, and the halogenated alkanes) and the active and inactive inorganic species from the oxygen ($O(^3P)$, $O(^1D)$, and O_3), hydrogen (H, OH, HO_2, and H_2O_2), nitrogen N, NO, NO_2, NO_3, N_2O_5, $ClONO_2$, HNO_3 and HO_2NO_2), and chlorine (Cl, ClO, HOCl, HCl, and $ClONO_2$) families. Active species are defined as being those species which directly participate in the catalytic cycles which destroy odd oxygen, i.e. OH and HO_2 (HO_x), NO and NO_2 (NO_x), and Cl and ClO (ClO_x). It should be noted that NO_x plays the major role in controlling ozone throughout most of the stratosphere in today's atmosphere (Figure 18). However, even if the emission rates of the CFC's do not increase but remain constant at the present level, ClO_x will play an increasingly important, even dominant, role in controlling ozone in the middle and upper stratosphere as the concentration of ClO_x approaches its steady state value.

We now have at least some measurements of most key species, including the temporary reservoir species $ClONO_2$, N_2O_5, and HO_2NO_2. While many of these
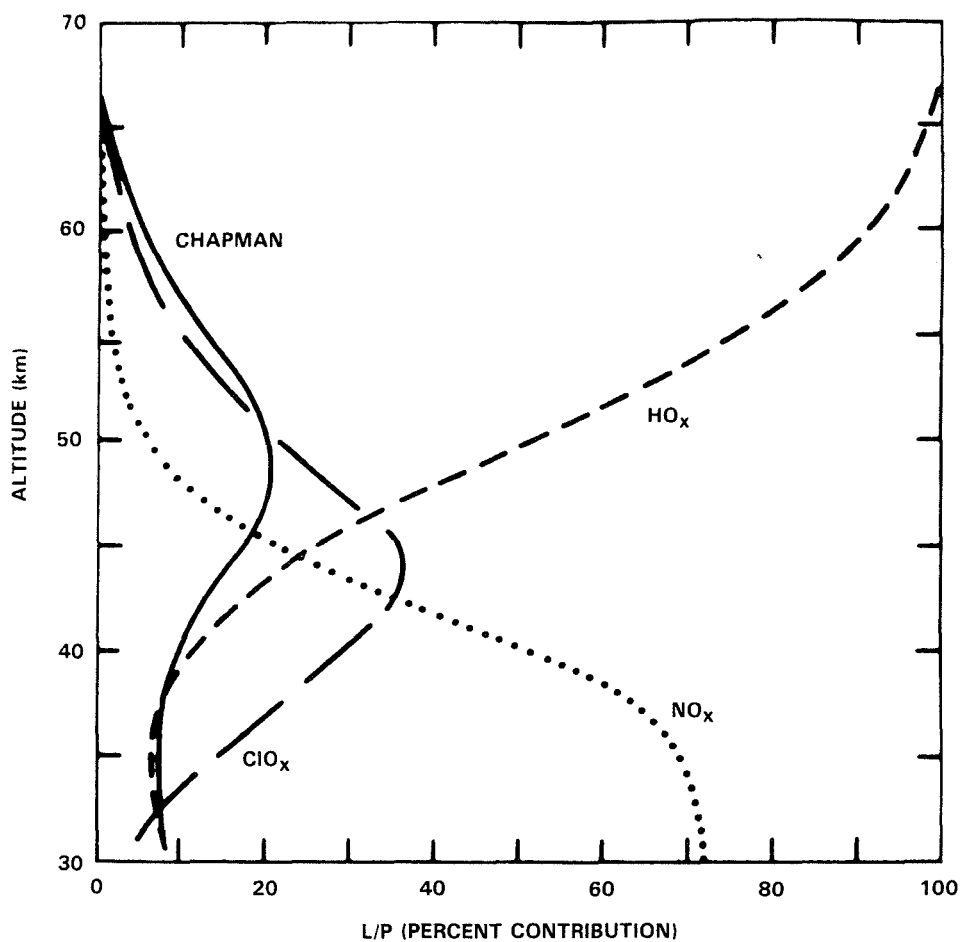
Figure 18. Ratio (in percent) of the odd oxygen loss rate due to the Chapman, HO_X, NO_X, ClO_X mechanisms to the odd oxygen production rate (based on mid-latitude diurnal average calculation with the Caltech 1-D model JPL 1985 recommended photochemical data). L and P are the O_X loss and production rates respectively.

observations have been isolated measurements of a single species, they have provided a valuable yet limited test of our knowledge of atmospheric photochemistry. However, it is now well recognized that the simultaneous measurement of several photochemically coupled species in the same air mass is necessary for the required critical test of photochemical theory; such tests are not possible from isolated measurements of single species. While there have been only a limited number of such simultaneous measurements to date, there is currently a growing emphasis to implement such a measurement strategy.

A major limitation in our ability to critically compare atmospheric observations with theoretical predictions at the time of writing previous assessment reports was our lack of knowledge of the accuracy and precision of the atmospheric chemical composition measurements. Differences between measurements of the same species made at different times and places could be ascribed either to atmospheric variability or to measurement inaccuracies. Consequently, a major effort has been expended during the last few years to determine the accuracy and precision of atmospheric chemical composition measurements by conducting a series of international intercomparison balloon campaigns where chemical constituents were measured using a variety of observational techniques simultaneously in time and space. The intercomparison campaigns performed to date include:

(a) a series of three campaigns to measure ozone, employing both in-situ and remote sensing balloon and rocket-borne instruments.

(b) two campaigns utilizing remote sensing balloon-borne instruments (13 on the first, and 18 on the second), using eight different techniques including grating spectrometers, radiometers, and Fourier transform interferometers, to measure several key atmospheric constituents including

HNO_3, NO_2, NO, HCl, HF, O_3, H_2O, CH_4, and OH. These sensors covered the visible, infrared, far infrared, and microwave regions of the electromagnetic spectrum in both absorption and emission.

(c) in-situ cryogenic grab sampling techniques to measure the source gases such as CH_4, N_2O, and CFC's (including $CFCl_3$ and CF_2Cl_2).

(d) three campaigns employing in-situ and remote sensing balloon-borne instruments to measure water vapor.

The data from these intercomparison campaigns is currently in the final stages of analysis. The results have shown that some of our current measurements, such as those for O_3, are accurate to better than 10%. Others are accurate to no better than a factor of two, e.g. those for NO_2.

Within the last few years, several newly developed in-situ and remote sensing techniques have been demonstrated for species for which there had been inadequate measurements, e.g. OH. In addition, some existing techniques have been improved which will result in greater sensitivity for a number of species, e.g. ClO and O_3 by balloon-borne microwave emission. This newly developed and improved instrumentation is required to measure nearly all key atmospheric species over a significant altitude range with the accuracy and precision sufficient to critically test our understanding of atmospheric photochemistry. Techniques that have been demonstrated within the last four years include:

(a) Two balloon-borne far-infrared emission interferometers for remote sensing detection of OH;

(b) Balloon-borne laser induced fluorescence systems for in-situ and range resolved detection of OH;

(c) A balloon-borne laser diode absorption system for in-situ detection of NO and NO_2;

(d) A shuttle-borne high resolution infrared absorption interferometer (ATMOS) for detection of a wide range of chemical constituents including several of the temporary reservoir species, e.g. $ClONO_2$, N_2O_5, and HO_2NO_2.

(e) A ground-based microwave emission system for remote detection of species including ClO, HO_2, and O_3.

(f) A balloon-borne cryogenic matrix isolation technique for in-situ detection of HO_2 and NO_2.

(g) Ground-based lidar systems for remote detection of O_3 and temperature.

As stated earlier, the single greatest advance during the last four years has been the analysis, validation and release of data obtained by instruments flown on the Nimbus 7, Applications Explorer Mission II (AEM-2), and Solar Mesospheric Explorer satellites. These data include seven months of Limb Infrared Monitor of the Stratosphere (LIMS) (HNO_3, NO_2, O_3, H_2O, temperature); four years of Stratospheric and Mesospheric Sounder (SAMS) (CH_4, N_2O, temperature), six years of Solar Backscatter Ultraviolet/Total Ozone Monitoring System (SBUV/TOMS) (O_3 column and vertical distribution, and solar flux); three years of Stratospheric Aerosol and Gas Experiment (SAGE) (O_3, NO_2, aerosols); and Solar Mesospheric Explorer (SME) (O_3, NO_2, aerosols, solar flux). In addition, five years of polar stratospheric aerosol data are available from the SAM II experiment. These data have now been processed and archived at the National Space Science Data Center in Greenbelt, Maryland, U.S.A.

In the following section of the report the observations of trace species will be compared to predictions of the present day atmosphere from one- and two-dimensional photochemical models. The observations will be discussed by chemical family.

Oxygen Containing Species

The oxygen species of interest in the stratosphere are ground state atomic oxygen $O(^3P)$, excited-state atomic oxygen $O(^1D)$, excited molecular oxygen $O_2(^1\Delta)$ and ozone O_3. There exist only six profiles of $O(^3P)$, but numerous profiles of $O_2(^1\Delta)$ in the upper stratosphere and mesosphere. $O(^1D)$ has not been measured in the stratosphere because of its low concentration. The relevant comparison for $O(^3P)$ measurements is the ratio $O(^3P)/O_3$. Comparisons of the measured ratios with those predicted by models show good agreement; however, the data base is very limited and, therefore, not adequate to critically test these models.

Another potential test of stratospheric photochemical theory is the calculation of the ozone concentration in the primarily photochemical region above about 35 km altitude, where the models give values 30-50% below the best experimental data (Figure (16). This discrepancy has now been confirmed by careful tests in which satellite and in-situ data sets have been used to evaluate the chemical loss rates, production rates and ozone concentration with consistent temperature measurements. Its resolution is essential to improving our confidence in model calculations.

Solar proton events have been the classical test of ozone perturbation by catalytic chemistry. Simulations of the perturbation of ozone by NO_x chemistry in the upper stratosphere following the August 1972 event provided a significant success for model calculations. Recently, particle events which penetrated only as far as the mesosphere, and should produce effects on O_3 through HO_x chemistry, have been examined and indeed found to produce the expected short-term effect. There remain, however, some inconsistencies in the magnitude of the effects when compared to models.

Satellite ozone measurements were strongly affected by the high aerosol concentrations after the El Chichon volcanic eruption. After subtraction of the aerosol interference on the measurements there appears to be a decrease in atmospheric ozone. These data are still preliminary and subject to further tests and examination. It is not clear what the predicted effect on ozone of such a large volcanic cloud should be. We need to consider the chemistry of the injected chlorine, sulfur and water vapor as well as surface chemistry, and heating due to aerosol absorption and scattering of the incident solar radiation. This problem needs more study, but may be too complex in the short term to provide definitive model tests.

Recent studies of the variability of both ozone and temperature in the upper stratosphere have led to the conclusion that most of the variability is dynamically driven, but a small 27-day solar variability component can be obtained after subtracting out the meteorological component. Detailed studies of the meteorological O_3-T variability continue to be undertaken in an attempt to test the temperature coefficient of the controlling photochemistry. These studies are shedding much light on the detailed variations which occur in the atmosphere, and will have to be examined in future models, but they have yet to provide a critical test of the chemistry.

Finally, the Antarctic total ozone column measurements discussed later in the trends section show a strong decrease over the last two decades during the spring. These appear to be due to some special mechanism operating in the cold Antarctic polar night and/or polar twilight. Elucidation of the mechanism will provide an important test of our ability to model at least some aspects of lower stratospheric chemistry. It is not obvious, at the moment, what impact the answers will have on predicted global ozone decreases.

Hydrogen Containing Species

Although the odd-hydrogen species play a vital role in stratospheric chemistry, our current knowledge of the atmospheric concentrations of the key species OH, HO_2, and H_2O_2 is woefully inadequate. The available observations for both OH and HO_2 do little more than demonstrate the existence of these radicals in the stratosphere and are insufficient to provide a critical test of theory. In addition, there are still no definitive measurements of H_2O_2.

There has been only one new published profile of OH, using a balloon-borne laser radar system, during the last four years and this is lower than most of the earlier in-situ resonance fluorescence data (which are somewhat scattered and of low precision), and also lower than predicted by either one- or two-dimensional models (Figure 19a). However, given the experimental precision, the fact that only O_3 was measured simultaneously, and the wide range of values predicted by the models, it is difficult to say that the discrepancy is serious. There are still no measurements of OH below 28 km which is a serious gap in our knowledge. There are now seven years of quasi-continuous column measurements of OH (approximately half of the signal is due to OH in the mesosphere) which show a long-term trend, seasonal, diurnal, and spatial variability, and response to volcanic eruptions and a solar eclipse. While the total column content of OH is in general agreement with model predictions, most features of the data await a theoretical interpretation.

Data from the LIMS instrument has been used to derive global OH fields from the measured HNO_3/NO_2 ratio, and by using the production and loss approach with fixed temperature, H_2O, O_3, and HNO_3 (Figure 19b). However, while this is extremely valuable given the dearth of OH data, and encouraging given that the results are consistent with two-dimensional model predictions, it must be remembered that we do not fully understand the quality of the LIMS

HYDROXYL PROFILE
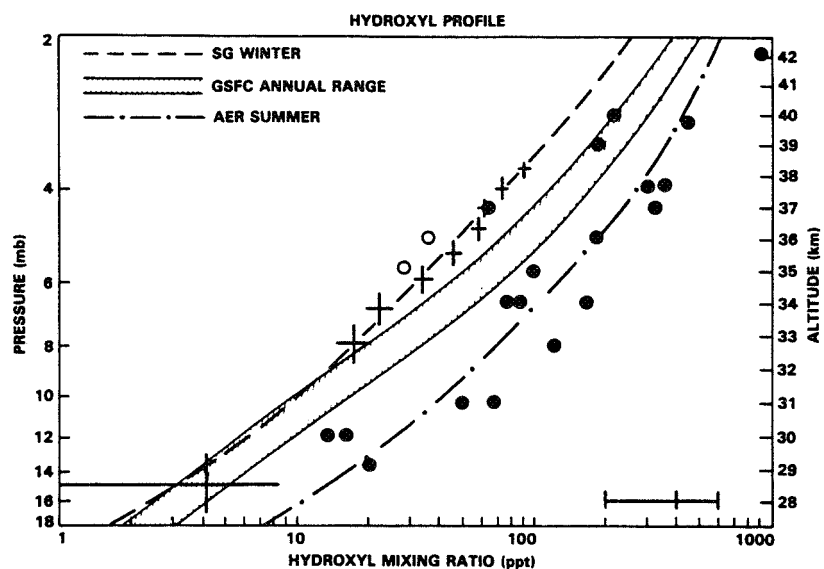
Figure 19a. OH concentration versus altitude. The circles represent all stratospheric OH measurements prior to 1983: filled circles were obtained using lamps to excite fluorescence and have typical uncertainties of ±30%; open circles and crosses are results from two different flights of a balloon-borne LIDAR system. The height of the crosses represents the altitude range of the measurements; the width of the crosses present the precision (1σ). The bar at the bottom of the figure represents the accuracy estimates for all the points. Also shown are representative results from several current 2-D models. The seasonal range shown for the GSFC model is typical for models of this type.

HYDROXYL PROFILE
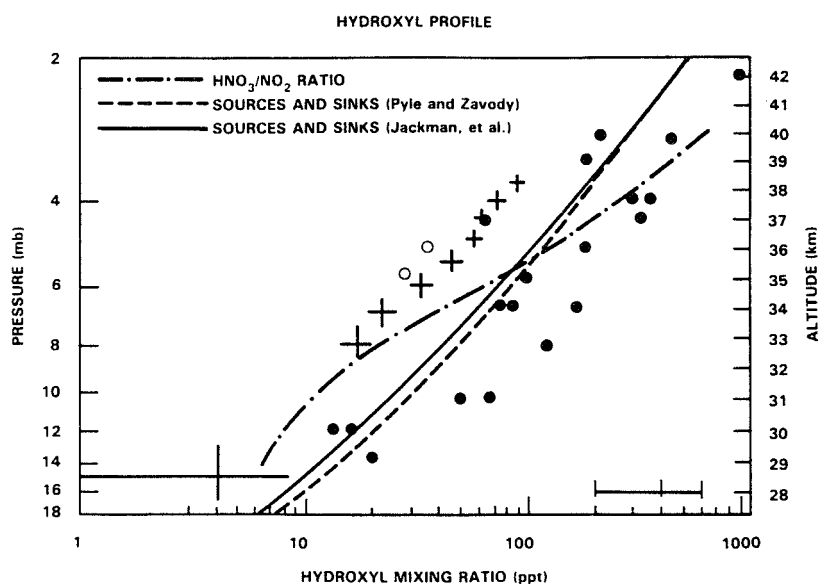
Figure 19b. Data as in Figure 19a. The - . -, - - -, -----, lines represent the OH profiles inferred by Pyle and Zavody from the HNO₃/NO₂ ratio; by Pyle and Zavody from the sources and sinks; and by Jackman et al. from the sources and sinks.

HNO$_3$ data above 35 km, and the observed HNO$_3$ profile above 30 km is still not adequately simulated by the theoretical models.

There have been recent measurements of HO$_2$ between 16 and 34 km, and between 35 and 60 km using in-situ balloon-borne cryogenic grab sampling and ground-based mm wave emission techniques, respectively. This data complements the earlier data which covered the altitude range 30 to 35 km. While there is only a small overlap in the altitude range of the two reported data sets, the mm emission data is not consistent with the high concentrations of HO$_2$ below 35 km that have been observed by all of the in-situ measurements. The in-situ HO$_2$ data is significantly higher (a factor of two at 34 km and an order of magnitude at and below 25 km) than predicted from theory, indicating a serious problem with either the measurements or our current understanding of both the total odd hydrogen budget and the partitioning between OH and HO$_2$ (Figure 20). In addition, if the HO$_2$ concentrations are as high as reported from the in-situ studies then we should have observed high concentrations of species such as H$_2$O$_2$ and HO$_2$NO$_2$.

Major improvements have occurred in our knowledge of the spatial and temporal distributions of stratospheric and mesospheric H$_2$O and CH$_4$. While most of these improvements have come from satellite observations, significant new information has also been obtained from balloon in-situ and ground-based measurements, particularly for H$_2$O. Clear evidence has been obtained for the existence of a hygropause, a region of minimum H$_2$O mixing ratios, just above the tropopause. Structure in the vertical profiles for both H$_2$O and CH$_4$ species, but especially for H$_2$O, has been observed as a result of the improved vertical resolution (~0.5 km) of the in-situ measurements. Also measurements both by in-situ and remote methods have extended the data throughout the mesosphere.
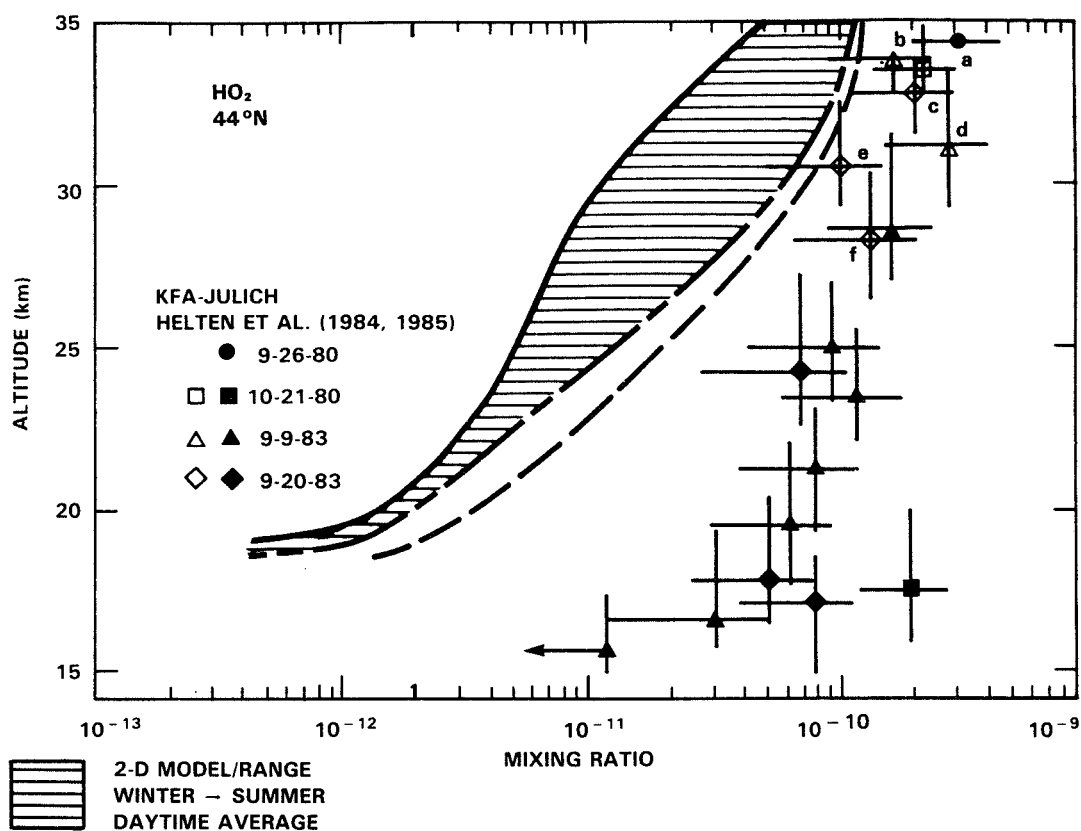
Figure 20. In situ observations of HO₂, employing the matrix isolation technique. The samples were collected during several balloon flights at local time between sunrise and approximately noontime. Data for observations made within 3 hours after sunrise are plotted with open symbols, because they should be adjusted due to the rather strong diurnal variation of HO₂ within this time period. The zenith angle for these samples are as follows: a: 88.1-78.1; b: 62.3-53.3; c: 95.8-83.9; d: 55.0-46.6; e: 86.8-77.2; f: 80.7-70.5. The dashed line represents a typical altitude profile for HO₂ calculated by Prather.

Observations by the LIMS instrument on Nimbus 7 over the period October 1978 to May 1979 have revealed nearly global distributions (64° S to 84° N) of H_2O from 100 to 1 mb (16 to 50 km) for the first time. The key results of the observations are: (a) the zonal means show a region of low mixing ratio (~3 ppmv) at ~60 mb (~22 km) extending over low latitudes (the hygropause region); (b) the mixing ratio generally increased poleward and upwards in tropical regions reaching a maximum value of ~6 ppmv; (c) the variability in mean zonal mixing ratios is small except in high latitude winter; (d) the longitudinal variability in mixing ratio is 0.5 ppmv in the tropics, and ranges from 1 to 1.5 ppmv at mid-to-high latitudes; and (e) there is a considerable structure at low latitudes.

The SAMS instrument on Nimbus 7 has provided nearly global observations (50° S to 70° N) of CH_4 from October 1978 to June 1983 from 20 to 0.3 mb (27 to 55 km). The data show: (a) a low latitude, low stratospheric maximum, with mixing ratios generally decreasing polewards and upwards; (b) gradients in the vertical distribution exhibit a wide range depending on latitude and season; (c) significant seasonal changes with a marked asymmetry between the equinoxes each year; (d) little interannual variability; and (e) significant structure at low latitudes.

The satellite data set for H_2O and CH_4 have clearly demonstrated that air is transported upward and poleward from the tropics. The transport of dry air in this fashion is consistent with the Brewer-Dobson hypothesis. The combination of these data sets has demonstrated that the total hydrogen budget of the stratosphere, principally H_2O + 2 x CH_4, is relatively constant at values ranging from 6 to 7 ppmv (H_2 is assumed to be constant and ~0.5 ppmv). The satellite data also shows enhanced H_2O levels in the lower stratosphere at high latitudes ($>50^O$) in the winter, indicating that not

all the H_2O in the stratosphere can be explained by exchange in the tropics or CH_4 oxidation. Simulation of the observed variability in the spatial and temporal distribution of CH_4 and H_2O utilizing multidimensional models present a major challenge to the modelling community.

Nitrogen Containing Species

The odd-nitrogen species considered to be important in the chemistry of the stratosphere are N, NO, NO_2, NO_3, N_2O_5, HNO_3, HO_2NO_2, and $ClONO_2$. All of these species, except N, have either been measured or at least detected. HCN has also been detected but is not thought to be important in the photochemistry of the stratosphere. The recent observations of N_2O_5, HO_2NO_2, and $ClONO_2$ are extremely important as they will allow vital tests of certain facets of stratospheric photochemistry, i.e. the coupling between the odd-nitrogen, odd-hydrogen, and odd-chlorine families in the lower stratosphere. As stated earlier, the availability of satellite data for NO_2, HNO_3, and N_2O has been a major achievement allowing us to quantify our knowledge of the temporal and spatial variability of these species.

There is a large balloon-borne data base for NO, NO_2, and HNO_3. This data exhibits considerable scatter, and it is difficult to determine changes in the vertical distribution with either season or latitude. It is still not totally clear whether the scatter is due to atmospheric variability or to experimental inaccuracies. Recent intercomparisons of balloon-borne techniques for each of these species has augmented and greatly added to the value of the existing data, and has led to an improved knowledge of the detailed profiles of these species at mid-latitudes. However, it should be noted that there are still some unresolved issues regarding data accuracy,

particularly between the remote sensing techniques for NO_2, and between the in-situ chemiluminescence instruments for NO in the mid-stratosphere.

Direct measurements of the NO to NO_2 ratio are also available from balloon-borne instruments, and while consistent with theoretical predictions, they are not really of adequate accuracy to critically constrain them.

Data on diurnal variations of NO_2 from balloons and satellites, while of considerable use, are not yet sufficiently accurate nor temporally detailed to definitively test photochemical theory. Ground-based, balloon, aircraft, and satellite data have all been used to address the variability of NO_2 at high latitude in winter in much more detail than previously possible. These data have greatly quantified our understanding of the distribution of N_2O_5 and its role in the Noxon "cliff` phenomena. Balloon data have shown that the cliff region of "missing" NO_2 occurs at altitudes from about 15-30 km. Theoretical studies have revealed that the Noxon "cliff" is primarily due to meridional transport processes and combined photochemical effects in the presence of large-scale waves in the vicinity of the polar night region.

Satellite observations of NO_2 in the polar night region have quantified our knowledge of thermospheric sources of odd-nitrogen to the stratosphere. They demonstrate that while thermospheric odd-nitrogen can be transported down to the upper stratosphere, and may be important on a local scale, it is probably unimportant to the global budget.

NO_3 has been observed both by ground-based and balloon-borne instrumentation, revealing an inconsistency with photochemical theory over much of the annual cycle.

While the data for HNO_3 in the low and mid-stratosphere is in good agreement with the theoretical models, our understanding at both high altitudes (above the main layer) and at high latitudes, has been shown to be

incomplete. In the latter case, the existence of an additional polar source of HNO_3 has been suggested. Studies of the latitudinal variation of HNO_3, both from aircraft and satellite observations, have led to some important insights into transport processes, showing in some detail how advection and dispersion compete in tropical latitudes.

The combination of available balloon and satellite data for NO, NO_2, and HNO_3 has greatly improved our knowledge of total odd-nitrogen. This information is particularly important both because it enables us to better understand the budget of the family as a whole, and because odd-nitrogen plays a major role in model predictions of ozone perturbations. It is important to emphasize that the odd-nitrogen derived from the data is in marked disagreement with two dimensional model predictions below about 30 km (Figure (17). On the other hand these same models seem to predict the odd-nitrogen concentrations above 30 km quite well. This suggests that boundary conditions or low-altitude sources of odd-nitrogen are not properly treated in the models.

The availability of improved data for N_2O has greatly enhanced our understanding of stratospheric transport processes. Satellite observations of N_2O have shown that tropical circulation patterns are likely to be strongly linked to the semiannual oscillation. Further, balloon data for N_2O at higher vertical resolution than that obtained by the satellites has shown that vertical variability exists systematically, and on very fine spatial scales. These are beginning to be understood theoretically, and there is some evidence that the variance associated with stratospheric warming events seems to play a significant role in this phenomenon.

Chlorine Containing Species

The odd-chlorine species of importance are Cl and ClO (radical species), HOCl and $ClONO_2$, (temporary reservoir species), and HCl (sink species).

While there are only three measurements of the vertical distribution of Cl over a limited altitude range, there is a relatively large data base for ClO, with the majority of the measurements being made with the balloon-borne in-situ resonance fluorescence and ground-based millimeter wave emission techniques. Additional data have been obtained using two remote sensing balloon-borne instruments; one which sensed the millimeter wave emission; the other using infrared laser heterodyne absorption techniques. The mean of the resonance fluorescence data and the ground-based mm data are in good agreement. However, there is one substantive difference between the two data sets and that is the degree of variability observed in ClO concentrations. The in-situ resonance fluorescence data indicates significant variability in the ClO concentration profiles. With the exception of the two apparently anomalous profiles in July 1976 and July 1977, the vertical profiles span a range of approximately a factor of 4 between 25 and 40 km (Figure 21). In contrast, the ground-based mm wave data, which has been obtained between January 1980 and December 1984, with observations taken at 20, 32, and 42° N in winter and summer, shows less than a ±20% variation about the mean above 30 km. While some of this difference may be ascribed to a lower reported precision in the in-situ data this is clearly not the complete explanation. Theoretical models predict a variability in ClO that is consistent with the ground-based data, but not with the in-situ data. However, we should remember that the in-situ measurements are made within a few minutes with high vertical resolution (less than 1 km), whereas the ground-based measurements take several hours and are averaged vertically over approximately 7 km. The mean

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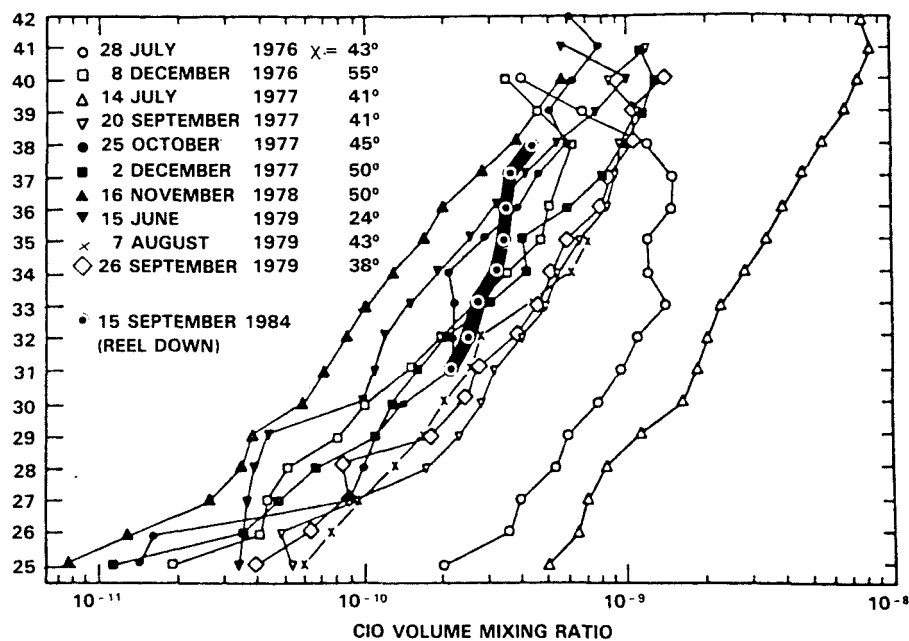**Figure 21.** Comparison of the average reel down ClO profile of 15 September 1984 with earlier "fast" parachute drop profiles measured by *in situ* resonance fluorescence. Concentrations from the reel down measurement have been converted to mixing ratios using the 9176 U.S. Standard Atmosphere.
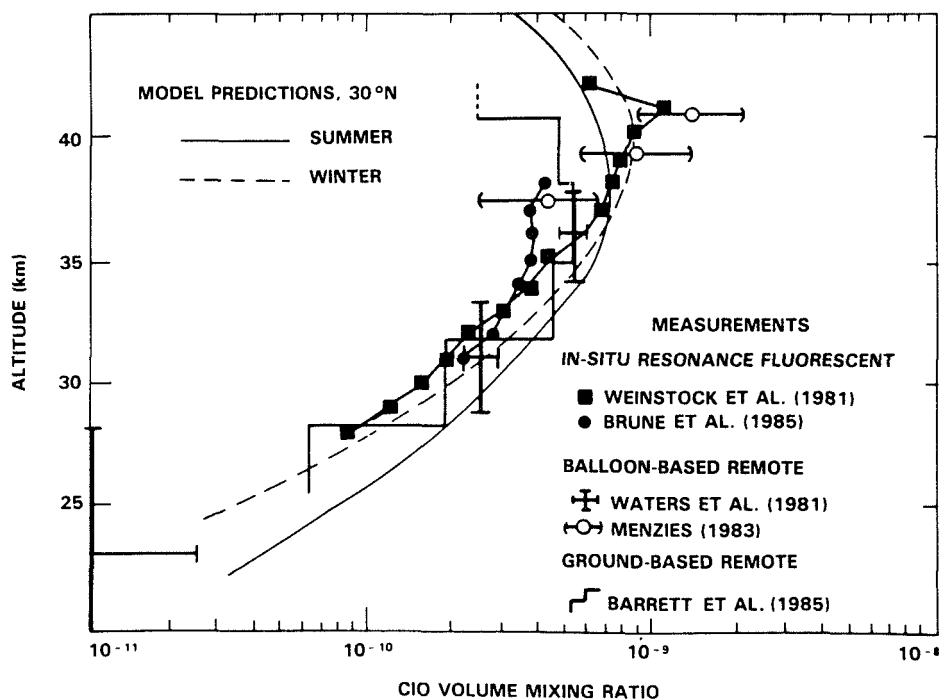

Figure 22. ClO vertical profiles from measurements and theoretical models. See text for details.

of the in-situ and ground-based data agrees with one- and two-dimensional model predictions to within a factor of two at 25 km and better at higher altitudes (Figure 22). The ClO data from the balloon-borne millimeter emission instrument are in good agreement with the other measurements, as are the reevaluated balloon-borne infrared laser heterodyne data. The diurnal variability of ClO has been measured by using both the ground-based and balloon-borne millimeter wave techniques and is in reasonable agreement with model predictions, although the observations indicate a somewhat slower rise than theoretically expected (Figure 13). The existing ClO data base is not yet adequate to establish seasonal and latitudinal variations or long-term increases which are all predicted by theoretical models.

The few measurements of Cl in the upper stratosphere (40 km) are limited yet consistent with the observations of ClO and the photochemical partitioning between Cl and ClO. The measurements of ethane (C_2H_6) in the lower stratosphere are an indicator of atomic chlorine concentrations (the major stratospheric loss process for C_2H_6 is its reaction with Cl) and are reasonably consistent with the ClO measurements and the theoretical predictions of Cl.

Direct evidence for the presence of $ClONO_2$ in the stratosphere has now been obtained with balloon-based infrared absorption measurements being made in a second spectral region. The vertical distribution determined from these observations is in reasonable agreement with model calculations. In addition, $ClONO_2$ has been observed during the recent space shuttle flight of the ATMOS instrument (a high resolution infrared interferometer used in the absorption mode). These direct observations are supported by the observed diurnal behavior of ClO which is thought to be due to the formation and destruction of $ClONO_2$.

There have been no observations to date of HOCl.

Several different remote sensing techniques for HCl were carefully intercompared during a series of balloon intercomparisons (BIC) carried out in 1982 and 1983. The vertical concentration profile of HCl can now be measured to 15% accuracy with confidence. These observations complement the earlier measurements of the vertical distribution of HCl which were largely made using remote sensing spectroscopic techniques. The earlier measurements had a significant amount of scatter which could have been due to either atmospheric variability or measurement inaccuracies. As the cause of the scatter in the observations was, and still is, unknown it was difficult to meaningfully compare them to model calculations. It should be noted, however, that the mean HCl profile obtained from the BIC campaigns is quite similar to the mean of the earlier data and has been compared to the results of a two-dimensional model. The observations and theory agree very well at both 20 and 40 km, but the predicted HCl is lower by a factor of two at 30 km (Figure 23). However, the discrepancy cannot be considered to be very significant at present, considering the lack of data on HCl variability and on simultaneous observations for HCl, ClONO$_2$, and ClO.

Total column measurements of HCl from the surface (including the tropospheric component) can be determined with a precision approaching 5%. Significant spatial and temporal variability in the column amount of HCl in the stratosphere (observed from an aircraft platform) has been established. Column values for the total HCl seen from the surface show even greater temporal variability. The expected trend in stratospheric HCl has not yet been observed and has presumably been masked by this variability, some of which may have been due to recent volcanic eruptions such as El Chichon. It
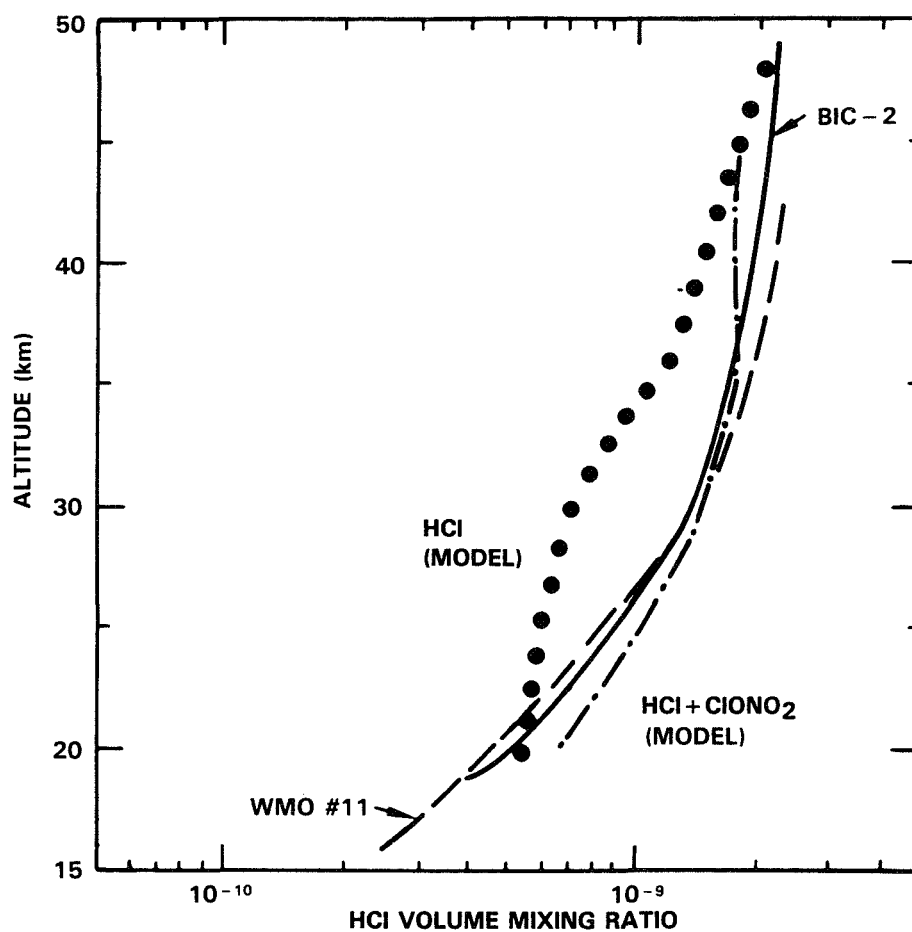
Figure 23. The weighted mean profile of measurements taken during BIC-2 of the vertical distribution of HCl reproduced as HCl mixing ratio by volume (———) compared with the mean profile of the last assessment (---), and the model prediction of Ko and Sze for HCl (•••) and for HCl + ClONO₂ (·——·——).

should be noted that the observed long-term trend of HF is compatible with theoretical predictions.

There have been very few measurements of the total amount of chlorine in the stratosphere. However, the few measurements that do exist appear to be consistent with calculations.

The data base for the vertical profiles of the halocarbon source gases has expanded over the last few years. There is now general agreement between calculated and observed profiles for these gases. Some differences remain but these are most likely due to imperfections in the modeling of transport processes. The least satisfactory agreement occurs with CH_3Cl, a species removed predominantly by reaction with OH. However, CH_3Cl is among the halocarbons presenting the greatest measurement difficulty.

X. MODEL PREDICTIONS OF OZONE CHANGE

One of the primary reasons for the scientific study of the upper atmosphere concerns possible long-term changes in the total column content and the vertical distribution of ozone. In much the same way that measurements of the composition of the present-day atmosphere allow us to test the ability of our theoretical models to describe the mechanisms that control the distribution of the chemical constituents, long-term measurements of the change (or lack of change) in key parameters, e.g. ozone, provides a partial test of the model's ability to predict the response of the atmosphere to changing conditions.

Our goal is to understand how the atmosphere will respond to the variety of changing conditions that have occurred and will continue to occur. The first step in attempting to understand the atmospheric response to changing conditions is to consider the idealized case of an individual perturbation.

These individual perturbations determined from model computations assume one particular aspect of the model is changing the atmosphere from its present state (e.g. chlorofluorocarbon release) while all others are held constant. The model is then usually integrated until a steady state is reached and the ozone concentration is compared to a similar calculation that is performed without the perturbing influence. A major difference between this and previous reports is the increased emphasis on two-dimensional models. This change derives from a combination of factors including increased computational facilities, the improved theoretical foundation of two-dimensional transport (see Sections VII, VIII), increased availability of latitude-dependent data to test models, and the increased realization of the importance of latitudinal and seasonal effects. A benefit in using two-dimensional models is the improved ease of interpretation of model-measurement intercomparisons because of the greater degree of specificity in the model prediction. One-dimensional model-measurement intercomparisons have always been confounded by difficulties in interpreting model results as to whether they are local, global or some combination of the two.

A further difference from previous reports is the emphasis on realistic time-dependent scenarios for both the past and future emissions of the entire suite of important trace gases, especially CFC-11, CFC-12, N_2O, CH_4 and CO_2. These have been made with one-dimensional models which are computationally fast and can be run for many simulated years with varying combinations of input.

In order to compare the results for the complex scenarios to previous evaluations we begin by considering individual isolated perturbations. Because of the small changes discussed in Section VI in some reaction rate coefficients, the predicted changes in the total column of ozone at steady-

state due to continued release of CFC's 11 and 12 at 1980 rates have increased since the last report. Table 1 contains the one-dimensional results reported by the various modeling groups participating in the comprehensive assessment (WMO, 1986) report. The numbers shown without parentheses are for calculations without the radiative-temperature feedback while the ones in parentheses include this feedback. For the idealized case of continuing release of CFC's 11 and 12 at the 1980 release rate ($309x10^6$kg/yr and $433x10^6$kg/yr, respectively), a decrease in the ozone column of 4.9 to 7.0% is calculated without radiative-temperature feedback and a decrease of 6.1 to 9.4% is calculated with radiative-temperature feedback. Each model uses the chemistry as updated by JPL Publication 85-37 and which is given in the Appendix to the WMO, 1986 Report. The differences among models represent differences in assumptions about treatment of other physical and chemical processes, in particular transport parameters, diurnal averaging procedures and photodissociation cross sections.

Rows 2 through 7 of Table 1 show the results obtained using one-dimensional models for a sequence of isolated perturbations. Row 2 shows results for the calculated change in ozone column when total chlorine, Cl_x, is increased from just over 1 ppbv to 8 ppbv without regard to the source of the chlorine. The wide variation among these numbers indicates a wider variation in model sensitivity to chlorine than would be expected. One of the major factors in this discrepancy is the difference among the models in the calculated distribution of the odd-nitrogen species. These odd-nitrogen species are important both because of their role in interfering with the chlorine catalytic cycle and their direct role in catalyzing ozone destruction. Resolution of these major discrepancies is required to put the predictions on firmer ground.

Table 1. Change in Total Ozone from Representative Models for Steady State
Scenarios. Numbers in Parenthesis Refer to Calculated Changes When
Including Temperature Feedback

		% Change in Total Column Ozone					
		LLNL (Wuebbles)	Harvard (Prather)	AER (Sze)	DuPont (Owens)	IAS (Brasseur)	MPIC (Bruehl)
(1)	CFC 1980 Flux only	-7.0 (-7.2)	-5.3	-5.3	-4.9 (-6.1)	(-7.9)	(-9.4)
(2)	8 ppbv Cl_x only	-5.1 (-5.7)	-2.9	-4.6		(-4.1)	(-9.1)
(3)	2 x CH_4	+2.0 (+2.9)	+0.3	+0.9	+1.7	(+1.6)	(+1.4)
(4)	1.2 x N_2O	-2.1 (-1.7)	-2.6	-1.8	-2.3	(-1.1)	(-1.2)
(5)	2 x CO	+1.1 (+1.1)	+0.3	+0.6	+0.8		(+0.8)
(6)	2 x CO_2	(+3.5)		(+2.6)	(+2.8)	(+3.1)	(+1.2)
(7)	NO_x, injection 17 km, 1000 molec. $cm^{-3}s^{-1}$	-1.8 (-1.3)				(-1.4)	
(8)	8 ppbv Cl_x + 2 x CH_4 + 1.2 x N_2O	-3.4 (-2.8)	-3.0	-3.3	-3.1	(-2.3)	(-6.0)
(9)	8 ppbv Cl_x + 2 x CH_4 +1.2 x N_2O + 2 x CO_2	(+0.2)			(-1.4)	(0.0)	(-5.2)
(10)	15 ppbv Cl_x only	-12.2 (-12.4)	-17.8	-15.		(-8.8)	(-22.0)
(11)	15 ppbv Cl_x + 2 x CH_4 +1.2 x N_2O	-7.8 (-7.2)	-8.2	-8.8	-7.2	(-5.6)	(-13.7)
(12)	15 ppbv Cl_x + 2 x CH_4 + 1.2 x N_2O + 2 x CO_2	(-4.6)				(-3.5)	(-13.6)

Relative to atmosphere with about 1.3 ppb background Cl_x and with no CFC (SOA)

This is further illustrated in Table 2 (from WMO, 1986) where perturbations of the ozone column for changes in Cl_x of approximately 7 ppbv and 14 ppbv are considered. The sensitivity given in column 5 is the ozone change in percent divided by the chlorine change in ppbv. With a 7 ppbv Cl_x change the sensitivity among one-dimensional models varies from 0.41%/ppbv to 1.30%/ppbv. Some of this variance, but not the major portion, is due to inclusion or omission of radiative-temperature feedback. With a change in Cl_x of ~14 ppbv the sensitivity ranges from 0.68%/ppbv to 1.67%/ppbv. The two-dimensional models give numbers in the middle of the range. The sixth column gives the linearity, L, defined as the sensitivity at a ClX change of ~14 ppbv divided by the sensitivity at a ClX change of ~7 ppbv. These numbers vary from 1.03, or almost perfectly linear, to 3.1, or very nonlinear. Again these numbers are presumably partially explained by the differing odd-nitrogen amounts calculated in the models, but it is not at all clear that it is entirely due to this cause. Going one step further, the odd-nitrogen differences appear to be due, in part, to varying treatments of the penetration of solar ultraviolet radiation in the complex Schumann-Runge Band region. Again, the differences appear to be only partially explained and resolution of the problem is fundamental to a full understanding of the model results.

The last 5 rows of Table 1 show results for various combinations of steady-state perturbations. The importance of interference terms is clearly demonstrated here by adding up individual perturbation results and comparing to the combined perturbation result. For example, the Livermore model (column 1), including radiative-temperature feedback gives +0.2% column ozone change for simultaneously increasing ClX to 8 ppbv, doubling CO_2 and CH_4, and multiplying N_2O by 1.2. The individual perturbations give -5.7%, +3.5%,

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Table 2. Comparison of 1-D and 2-D Model (Global Average) Results with Respect to Sensitivity S and Linearity L, Where Cl_x is the Only Perturbation. Sensitivity is Percentage Ozone Reduction Divided by ppb Cl_x Increase. Linearity is $S(14)/S(7)$, which is 1.00 if the Ozone Reduction is Directly Proportional to Cl_x Increase.

Cl_x/ppb			% Ozone Decrease	Sensitivity -%/ppb	Linearity = S(14)/S(7)	Model
Initial	Final	Increase				
1.3	8.2	6.9	8.5	1.23		2D
1.3	15.5	14.2	18.	1.27	1.03	AER
1.	8.	7.	4.6	0.66		1-D
1.	15.	14.	15.	1.07	1.63	AER
		7.	5.1	0.73		1-D
		14.	12.2	0.87	1.20	LLNL
		7.	2.9	0.41		1-D
		14.	17.8	1.27	3.10	Harvard
1.1	8.1	7.	9.1	1.30		1-D
-2.5	8.1	5.6	7.4	1.32		
2.5	14.8	12.3	20.6	1.67	1.27	MPIC
1.0	7.5	6.5	4.1	0.63		1-D
1.0	14.0	13.0	8.8	0.68	1.08	IAS
2.7	9.5	6.8	7.2	1.06		2-D MPIC

+2.9%, and -1.7%, respectively summing these would give -1.0%. The effect is more pronounced for the 15 ppbv ClX case which gives -4.6% in the combined calculation while the individual components add to -7.7%. Thus the individual components are not additive.

The calculated change in ozone at about 40 km altitude remains large for all of these cases. Table 3 shows a number of results for some of the same steady-state runs reported in Table 1. Note, for example, that for the case of 8 ppbv ClX, doubled CO_2 and CH_4 and $1.2xN_2O$ the ozone change at 40 km ranges from -35 to -55%. This is the same case that gave no change in the column or slight increase in two of the models.

As discussed earlier in Section VIII, two-dimensional models have been recently put on a much firmer theoretical foundation. A number of differences in formulation still exist among the groups constructing such models. However, the combination of improved theoretical understanding and two-dimensional satellite measurements of a half-dozen key species promise to help sort out the key differences within the next few years. The two-dimensional models consider latitude and altitude as their coordinates and are able to model seasonal variations explicitly as the Sun angle and transport parameters are varied.

Two-dimensional models predict a significant latitudinal variation in the sensitivity of the ozone column to chlorine increases. More depletion is predicted near the poles than at the equator with the ratio ranging from 2/1 to 4/1 depending on the model transport formulation. This is illustrated in Figure 24 which shows the latitude response of two different models to an increase in chlorine of about 7 ppbv for the month of April. Figure 25 shows both the seasonal and latitudinal effect for the same scenario as calculated

Table 3. Change in Ozone at 40 km for Steady State Scenarios Containing Cl_x Perturbations. Numbers in Parenthesis Refer to Calculated Changes Including Temperature Feedback. Row Numbers are Keyed to those in Table 1.

		LLNL (Wuebbles)	% Change in Ozone at 40 km Harvard (Prather)	AER (Sze)	DuPont (Owens)	IAS (Brasseur)	MPIC (Bruehl)
(1)	CFC 1980 Flux only	-63 (-56)	-64	-62	-62 (-57)	(-81)	(-59)
(2)	8 ppbv Cl_x only	-55 (-50)	-57	-56		(-67)	(-57)
(8)	8 ppbv Cl_x + 2 x CH_4 +1.2 x N_2O	-50 (-45)	-50	-49	-58	(-62)	(-50)
(9)	8 ppbv Cl_x + 2 x CH_4 + 1.2 x N_2O + 2 x CO_2	(-35)			(-49)	(-55)	(-45)
(10)	15 ppbv Cl_x only	-74 (-68)	-78	-77		(-83)	(-76)
(11)	15 ppbv Cl_x + 2 x CH_4 + 1.2 x N_2O	-69 (-64)	-73	-64	-74	(-81)	(-71)
(12)	15 ppbv Cl_x + 2 x CH_4 + 1.2 x N_2O + 2 x CO_2	(-58)				(-78)	(-67)

Relative to atmosphere with about 1.3 ppb background Cl_x and with no CFC (SOA)
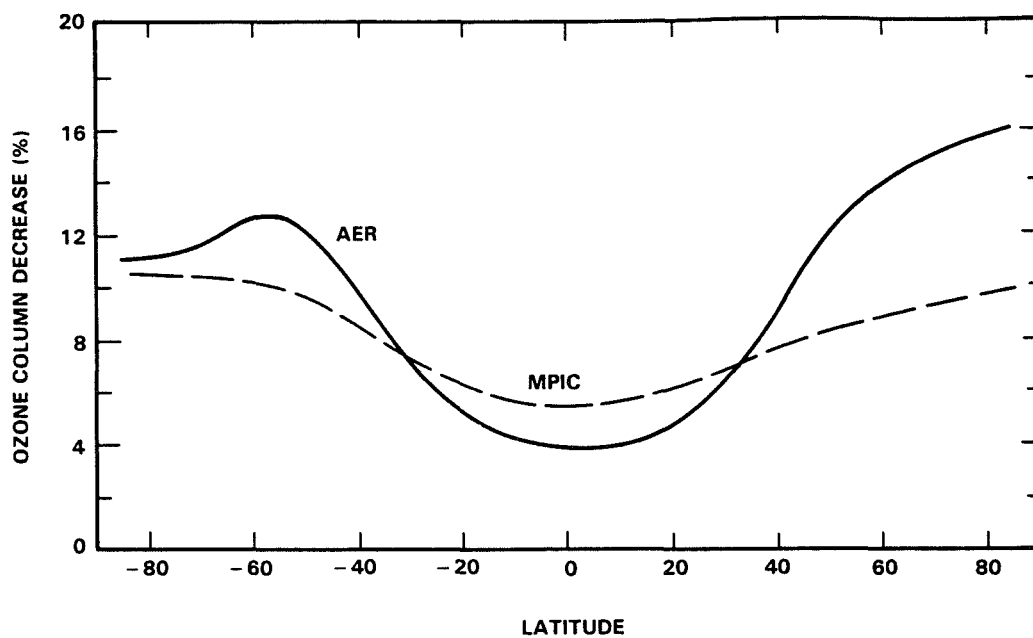
Figure 24. The effect of type of atmospheric dynamics used in two-dimensional models on the latitudinal variation of calculated ozone-column reduction (April). the increase of Cl_x is about 7 ppbv in each case.
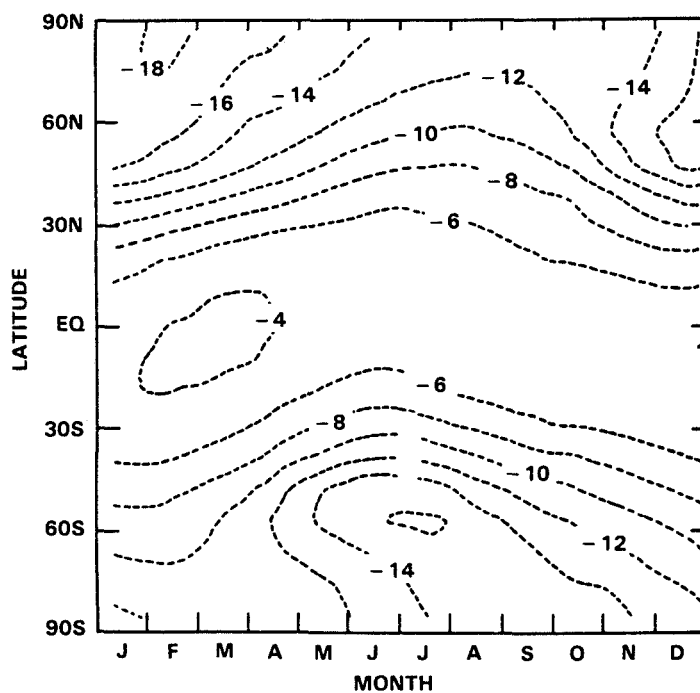

Figure 25. Calculated steady-state percentage change of the ozone column relative to a reference atmosphere with 1.3 ppbv Cl_X as a function of latitude and season for the 1980 fluorocarbon emission giving 8.2 ppbv Cl_X or an increase of 6.9 ppbv Cl_X.

in the AER model. Note that a significant seasonal effect is present but it is less than the latitudinal effect.

The altitude dependence of the predicted perturbation for the chlorine-only case is shown in Figure 26. As in one-dimensional models large depletions are predicted in the upper stratosphere centered at approximately 40 km (Figure 27). The primary variation of the column ozone change with latitude arises because of the large latitude dependence of the ozone change in the lower stratosphere. Below 25 km, within ~40° of the equator a region of ozone increase is predicted. The primary cause of this is the so-called self-healing effect in which ozone depletion at higher altitudes allows more ultraviolet radiation from the Sun to penetrate to lower altitudes. This radiation increases the formation rate of ozone from molecular oxygen dissociation. This effect competes with increased catalytic loss due to the chlorine increase and with all of the subsequent interference effects among the other catalytic cycles. The net effect is an ozone increase at low latitudes in the lower stratosphere and an ozone decrease at all altitudes poleward of ~40° degrees latitude. The magnitudes of the low latitude increase and the high latitude decrease in the lower stratosphere are sensitive to the transport formulation and are responsible for the latitudinal behavior of the column ozone decrease as was shown in Figure 26. The comparable one-dimensional model calculation is shown in Figure 27. An ozone increase is predicted for this case from 10 to 25 km but its magnitude is never more than a few percent. The above results are important to the interpretation of any measured trends (or lack of trends) in ozone as a function of altitude. Because of the strong latitude dependence in the lower stratosphere, with a change in sign at approximately 40°, the one-dimensional results cannot be taken as representative of what to expect at mid-latitude
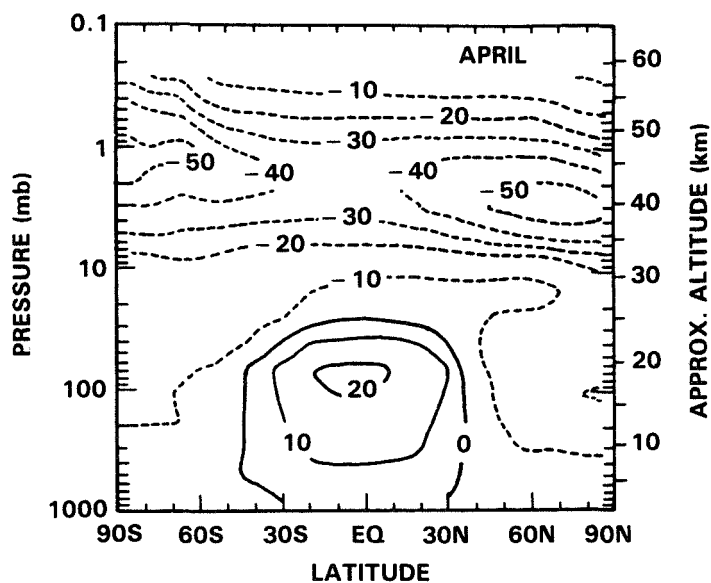
Figure 26. Calculated steady-state local percentage zone change for the month of April as a function of latitude and altitude — for fluorocarbon emission giving 8.2 ppbv Cl_X relative to reference atmosphere with 1.3 ppbv Cl_X, or an increase of 6.9 ppbv.
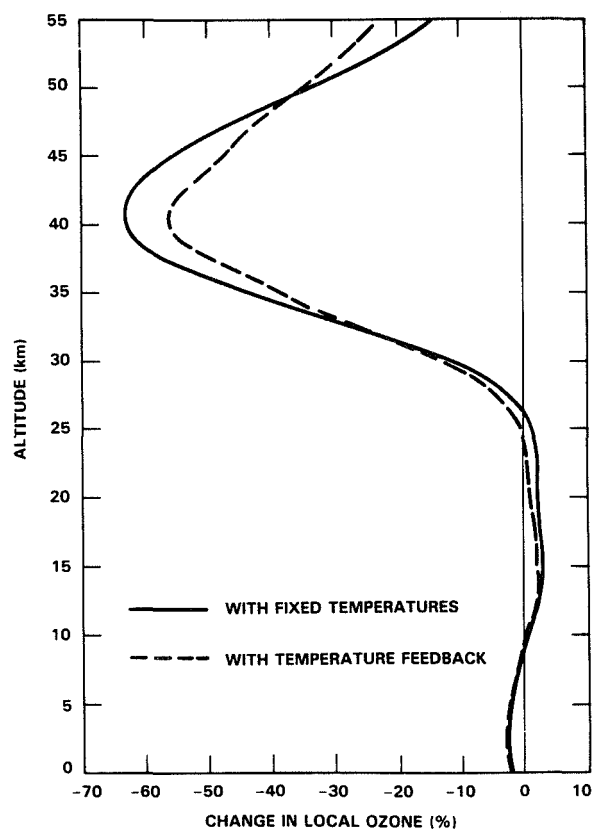

Figure 27. Calculated percentage change in local ozone at steady state for constant CFC-11 and CFC-12 fluxes at 1980 rates relative to the atmosphere with no CFC (LLNL one dimensional model).

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stations. Because the mid-latitudes are at the transition from positive to negative predictions they are not ideally suited to testing this particular model prediction. A further caveat is that the two-dimensional models have only been run thus far for idealized repeating seasonal cycles equivalent to steady-state one-dimensional runs. The trend predictions for past and near future changes in ozone due to all influences have yet to be made in two dimensions.

Time-dependent scenarios have been run in several one-dimensional models. Figure 28 shows the results for several scenarios from one of these models run from the present to 100 years in the future. The three solid lines refer to cases in which the CH_4 concentration was increased at a rate of 1%/yr, N_2O at 0.25%/yr and CO_2 according to a DOE projected scenario. The three curves refer to differing assumptions concerning the future course of CFC emissions. All three start with the 1980 emission rates, then differ, one remaining constant at that emission rate, one rising at 1.5%/yr and one rising at 3%/yr. The dashed curve has CFC emissions, as well as the concentrations of CH_4 and N_2O constant. The ozone column changes were calculated to be < 3% over the next 70 years for CFC increases of ≤1.5%/yr, but with a CFC growth rate of 3%/yr the predicted ozone depletion is 10% after 70 years and rapidly increasing. In this case the fluorocarbon effects were temporarily masked by other gases but eventually chlorine dominates ozone loss. Figure 29 shows the same calculation for the case of 1.5%/yr increase in CFC emissions for three different models, illustrating model-to-model variations. Figure 30 shows the altitude distribution of the predicted change for the same scenario (1.5%/yr increase in CFC's). Again the lesson from the two-dimensional runs implies caution in interpreting the expected lower-stratospheric trend at mid-latitudes.
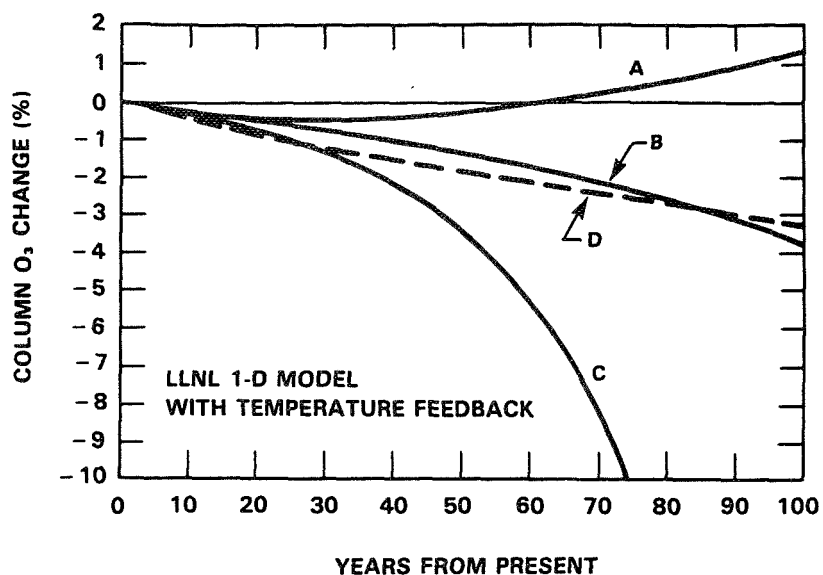
Figure 28. Calculated changes in ozone column with time for time-dependent scenarios: A (CFC flux continues at 1980 level, CH_4 increased 1% per yr, N_2O increases 0.25% per yr, and CO_2 increases according to the DOE scenario); D (same as A but without increases in CH_4 and N_2O); B (CFC emissions begin at 1980 rates and increase at 1.5% per yr, other trace gases change as with A); C (same as B except CFC emissions increase at 3% per yr).
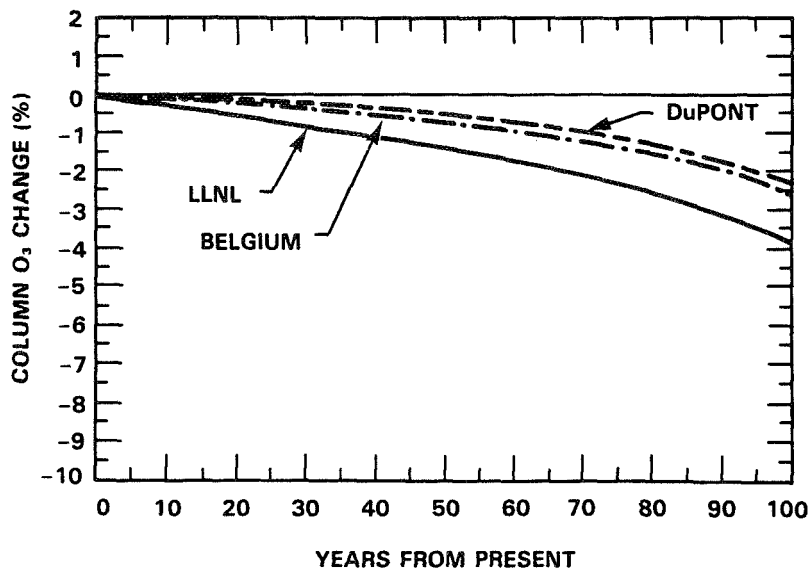
Figure 29. Calculated (by three different 1-D models) change in ozone column as a function of time for scenario B in Figure 28 (CFC emissions begin at 1980 rates and grow 1.5% per yr compounded, CH_4 increases at 1% per yr, N_2O increases at 0.25% per yr, and CO_2 increases according to the DOE scenario).

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Figure 30. Calculated percentage change in local ozone at selected times (5 to 100 years) for scenario B of Figure 28 (CFC emissions begin at 1980 rates and increase at 1.5% per yr, CH_4 increases at 1% per yr, N_2O increases at 0.25% per yr, and CO_2 increases according to the DOE scenario).

Figure 31. Monte Carlo calculated ozone-column-change distribution functions for CFC fluxes, at 1.0 times the 1985 CFC flux (Stolarski and Douglass model).

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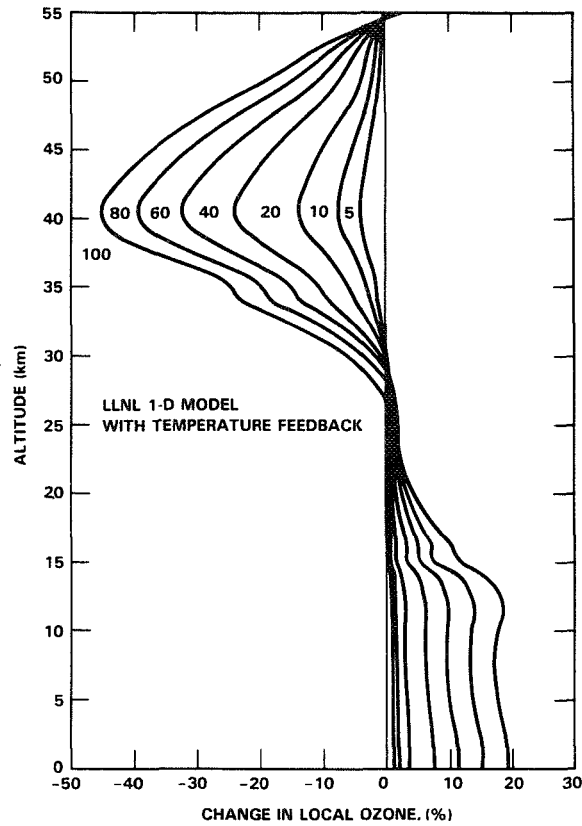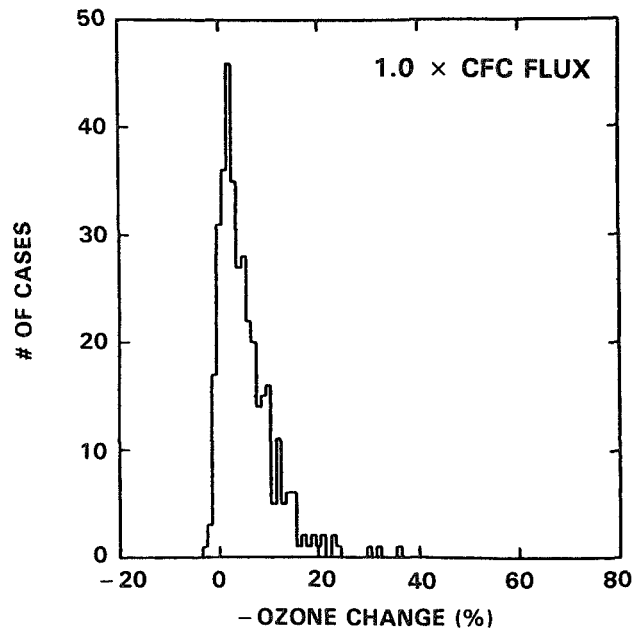Uncertainties are always difficult to evaluate. Models have both known and unknown deficiencies in their formulation. Undiscovered processes may be found at any time. This is the reason for the need for continued comparison of models to field measurements as described in Section IX. The hope is to reduce the possibility that unknown processes exist by a thorough and complete testing of the whole model as well as of each of its parts. One type of uncertainty can and has been evaluated, the propagation of estimated input uncertainties through a one-dimensional model. Such calculations for uncertainties in chemical reaction rates, photodissociation cross sections and solar flux, but not for model formulation or transport parameters, yielded probability distributions for column ozone depletions which exhibited a long tail toward large ozone perturbations as is shown in Figure 31. The one-sigma width of these distributions was comparable to, but less than, the magnitude of the predicted ozone perturbation for perturbations of less than 10% (-6.2±5.5% in one model for the 1980 flux of CFC's only, and -7.7±5.8% in another with 14 ppbv added $ClX + 2xCH_4 + 1.2xN_2O$).

XI. OZONE AND TEMPERATURE TRENDS

In this Section, the evidence for observed trends in ozone is discussed. We also note that ozone and temperature are very closely coupled through radiative, dynamical and photochemical processes. Thus, changes in either ozone or temperature should be accompanied by changes in the other. Therefore, a complete study should examine the consistency between the trends in both parameters compared with the results from a fully coupled predictive model. To date, these fully coupled scenario predictions have only been performed using one-dimensional models. Two-dimensional models have only been used to examine isolated perturbations (e.g., CO_2 only or CFC only), to date.

Total Column Ozone

Statistical analyses for the global trend in total column ozone using data from the Dobson spectrophotometer network do not show a statistically significant trend during the 11-year period 1970-1980. However, different groups using the Dobson network data for the period 1970-1983 have reported quite different results. One study reported that there was no statistically significant trend, i.e. -0.17%/decade ± 0.55%/decade, while another study reported that the trend was statistically significant, i.e., -1.10%/decade ±0.47%/decade (the uncertainties represent the 1σ confidence limits). In each case the data were adjusted for both instrument intervention and solar cycle effects. In the latter study it was reported that the negative trends were primarily the result of abnormally low total ozone values in the Northern Hemisphere during early 1983, and that the reason for the disagreement between the different results may be due to the different methods of area weighting of the data. It should be noted that there is no evidence that the trends in total ozone at some latitudes are greater than the trends at other latitudes. There is, however, a suggestion of a regional effect which is indicated by a greater positive trend at all North American stations than at all Indian stations. The reasons for this are not clear. As stated earlier the global ozone data shows a strong minimum in late 1982 and early 1983. It has been suggested that this "ozone hole" is related to the El Chichon eruption in April 1982 or to the very large El Nino event of 1982-83. The ozone values appear to be returning to their previous levels now. It should be mentioned that the existence of this "ozone hole" does not seem to be caused by the volcanic aerosol from El Chichon in an instrumental sense. Furthermore, examination of the total ozone record over North America and Europe from the late 1950's through 1983 indicates that the 1982-83 results do

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not appear remarkable, in that similar major perturbations occur at not infrequent intervals.

Recent evidence from a single Dobson spectrophotometer instrument at Halley Bay (76° S) has indicated a considerable decrease (>40%) in Antarctic ozone during the spring period since 1957 with most of the decrease occurring since the mid-1970's (see Figure 32). Another Dobson instrument at Argentine Islands (64° S) has registered lesser but still significant changes in the last several years. Satellite measurements using the TOMS and SBUV instruments on Nimbus 7 have both verified this trend over Antarctica since 1979 and have demonstrated the spatial and temporal variations of this feature (see Figure 33 on the inside back cover, for example). Such large ozone variations are not observed over the Arctic. It is not yet evident whether the behavior in Antarctic ozone is an early warning of future changes in global ozone or whether it will always remain confined to the Antarctic due to the special geophysical conditions (polar night, cold temperatures, and stable polar vortex) that exist there. While it has been suggested that these Antarctic ozone decreases are caused by increasing concentrations of chlorine in the stratosphere no credible mechanism has been demonstrated since models using present chemical schemes are unable to simulate this effect. This possibly suggests missing chemistry in existing models. Simulating these observations presents a major challenge.

Ozone Profiles

Trend estimates from 13 ozonesonde stations indicate statistically significant positive trends in the lower troposphere and negative trends in the lower stratosphere. The interpretation of these trends is clouded by uncertainties in instrument behavior because these data have been subjected to
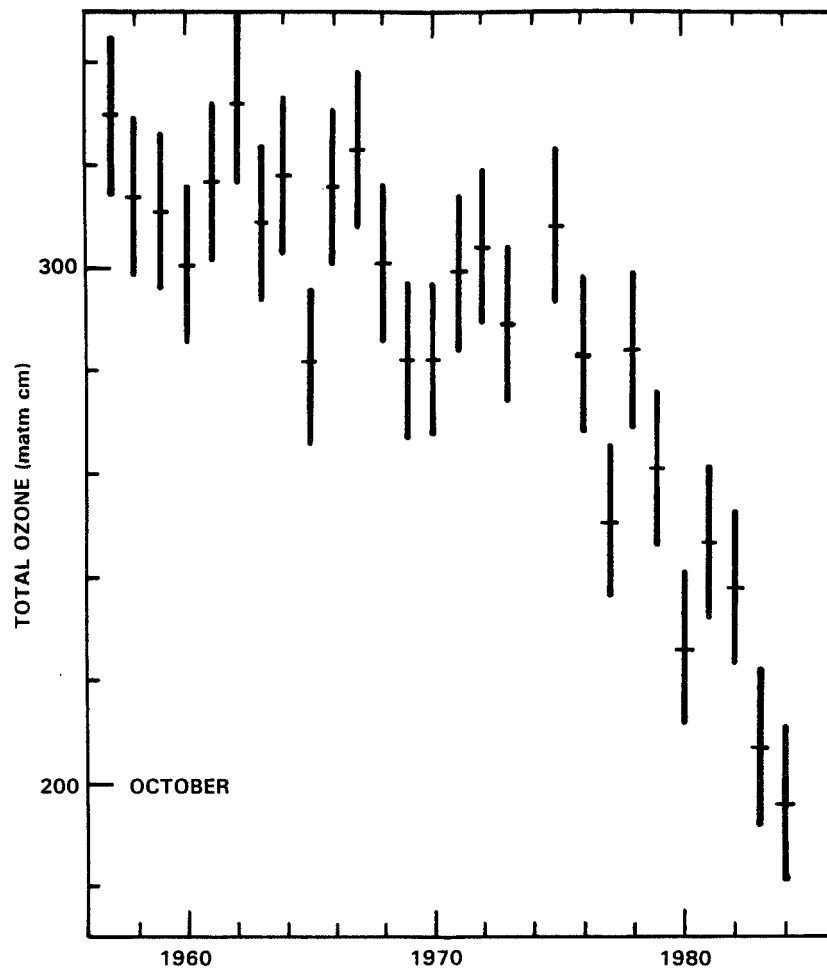
Figure 32. Monthly means of total ozone at Halley Bay for October of the years 1957 through 1984.

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quite large correction factors, the cause(s) of which are unclear. There is also added uncertainty in the tropospheric ozone trend resulting from the limited network of ozonesonde stations and whether the tropospheric ozone increase is due to local pollution effects or whether it is symptomatic of a more general atmospheric behavior.

Perhaps the most important result on global ozone trends comes from trend estimates from 13 Umkehr stations that indicate statistically significant trends in the middle to upper stratosphere (~30-40 km) of the order -0.2 to -0.3% per year over the period 1970-1980, with little trend at lower levels. This is in substantive agreement with results from one-dimensional models (see Figure 34). There are three points to be raised with respect to these Umkehr analysis results. The first is that these results, including the sign, are very sensitive to the inclusion of a stratospheric aerosol impact and that aerosol data from only a single station were used in this analysis. That is to say, the aerosol concentrations over Mauna Loa were assumed to exist globally. The second point is whether or not the data from the 13 Umkehr stations are representative of a global result. This has been examined by seeing whether satellite ozone data from the SBUV instrument at the Umkehr station locations gave trends that were representative of the zonally-averaged trends. In general, the individual "station" trends were not representative of the trends for the zonally-averaged ozone, but the trend obtained from averaging all the stations was found to be quite close to the global trend. Finally, the trend results, as indicated in Figure 34, do not appear to be sensitive to the inclusion of a term representing the solar cycle variation.

An SBUV-2 measurement program is now operational on the NOAA satellite system. These measurements are restricted to daytime only measurements of total ozone and vertical ozone profiles above the ozone concentration
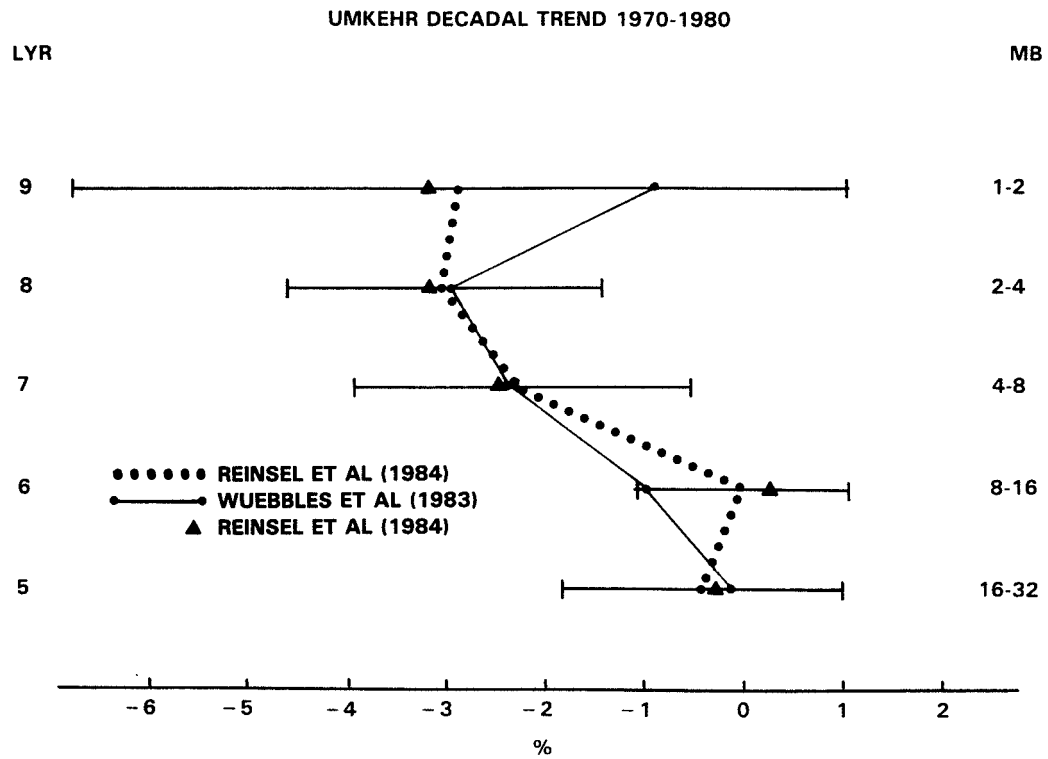
Figure 34. Umkehr decadal trend 1970-1980. Units: percent per decade.

maximum. The SBUV-2 instruments include an onboard calibration lamp intended to assist in tracking any instrument-related drift in the measurements. Also, the Shuttle-borne SBUV (SSBUV) instrument will be flown regularly as an additional check for possible instrument drift. If this system operates to its specifications it will be able to detect a global ozone change of about 1.5% per decade at the 95% confidence level. This is considerably better accuracy than the magnitude of the change that is predicted to occur in the upper stratosphere so that such a change should be readily detectable. In addition, NOAA has implemented a ground-based ozone validation program for these measurements.

Stratospheric Temperatures

Increases in tropical lower stratospheric temperatures have been noted following the eruptions of El Chichon in March 1982 and of Agung in March 1963. No tropospheric cooling can be clearly associated with the El Chichon eruption. This situation is complicated by the fact that a major El Nino occurred shortly after the El Chichon eruption and is known to have had a major effect on tropospheric climate.

Several studies have sought to observe the 1.5 K decrease in upper stratospheric temperatures that has been predicted to occur from 1970-1980 by fully-coupled one-dimensional models. It was thought that such a temperature decrease had been seen in analyses of rocketsonde temperatures. Recently, however, a comparison between rocketsonde and radiosonde measured lower stratospheric temperatures over the same altitude region showed substantial differences. The disagreement between these two measurements has indicated that there was a previously uncompensated change in the rocketsonde measurement system that was used before the early 1970's (the Arcasonde

system) and that used after this time (the Loki-datasonde system). There have been efforts to look at the upper stratosphere temperatures after the changeover to the latter system, and some have suggested that a temperature decrease similar to that which is predicted is seen. However, if one examines the lower stratosphere temperature trends from both rocketsonde and radiosonde measurements, one sees that there is disagreement and that the year-to-year variability is much greater than that in the upper stratosphere. Thus, the existence of a decreasing trend in upper stratospheric temperature is open to serious question, and we must await a complete analysis utilizing all available data.

As was stated earlier in this chapter, any trend in ozone should be accompanied by a predictable temperature trend due to the strongly coupled nature of the system. Hence, it is particularly troubling that although an ozone trend detection system has been implemented to detect the predicted decadal ozone variations, no similar system has been implemented for stratospheric temperatures. Indeed our current ability to make accurate measurements of stratospheric temperatures is totally inadequate. This is a serious shortcoming given that our understanding of both chemical and dynamical processes depends upon knowledge of stratospheric temperatures and limits our ability to verify model predictions of ozone change.

XII. TRACE GAS EFFECTS AND CLIMATE

It is now generally recognized that anomalies in radiative forcings induced by trace gases of anthropogenic origin can become the dominant factor governing climate change on decadal to longer time scales. The most familiar example of this is the CO_2 problem in which combustion and land use practices are producing a secular increase in atmospheric CO_2 concentrations such that

its concentrations may be expected to double by the middle of the next century. There has also been concern about whether ozone changes produced by human activities will have an appreciable effect on the Earth's climate. The ozone problem is fundamentally different from the CO_2 tropospheric climate problem in that the ozone problem involves climate-chemistry interactions rather than being a predominantly radiative problem. The ozone-climate problem involves effects of various source gases on atmospheric photochemistry resulting in changes in the radiatively active gas, ozone. Our present broader concern for other trace gas effects on climate (e.g., CH_4 and N_2O) has grown out of these two initial concerns about the effects of CO_2 and O_3 changes on climate.

In the following discussion, we will briefly review how some of these trace gas effects on climate came to the attention of the scientific community. First, there was the finding that the greenhouse effects of many polyatomic trace gases (e.g., CFC's) were greater than that of CO_2 on a molecule per molecule basis. To cite one example, the addition of one molecule of $CFCl_3$ (CFC-11) or CF_2Cl_2 (CFC-12) to the atmosphere was calculated to have the same surface warming effect as that due to an addition of 10^4 molecules of CO_2. Subsequently, it was uncovered that perturbations in stratospheric ozone can have perceptible effects on tropospheric climate through radiative-dynamical interactions between the stratosphere and troposphere. Furthermore, tropospheric ozone has been shown to be very effective in enhancing the greenhouse effect. Over the years, other gases (CH_4, N_2O, to cite a few) were added to the list of important greenhouse gases, and the list is still growing. Finally, it has been established that if the present rates of growth in the concentrations of various trace gases continue unabated for the next several decades, the surface warming due to

trace gases could surpass the observed temperature changes of the past century. In such estimates, the combined effect of increases in trace gas amounts (other than CO_2) was comparable to the greenhouse effect of CO_2 increase.

Observed Temperature Trends

The most frequently used index of climate change is the observed trend in surface-air temperature over the land areas of the globe. Figure 35 shows a record of these globally averaged land-area temperatures from 1850 to the early 1980's. What is seen in this record is an extreme swing in these temperatures of less than 1.5 K, with the temperatures for 1850 to about 1885 being the coldest, on the average, with a slow rise in these temperatures to about 1940, a sharper fall in these temperatures to about 1970, and a rapid rise in these temperatures from 1970 to the present time. The exact cause for these variations in the globally averaged land-area temperature are not well known. Of course, these global temperature changes are also accomplished by regional changes in temperature and precipitation that are both larger and smaller than the global changes.

Greenhouse Theory

Much of the discussion in this chapter refers to the greenhouse effect and to the atmospheric "window" region of the atmosphere's absorption spectrum. Figure 36 illustrates the greenhouse effect. On a global average, the Earth-atmosphere system intercepts about 236 W m^{-2} of solar energy. With a mean surface temperature of 288 K, the surface emits about 390 W M^{-2} of terrestrial radiation but due to atmospheric absorption only 236 W m^{-2} of terrestrial radiation leaves the top of the Earth's atmosphere so that the
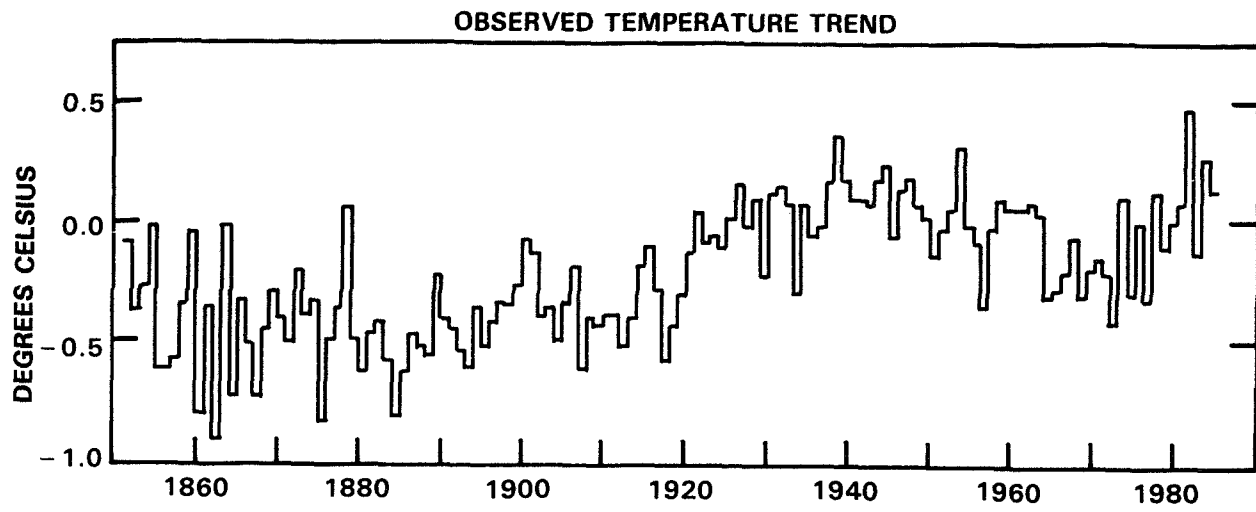
Figure 35. Observed surface-air temperature trends for land masses of the Northern Hemisphere.

GLOBAL ENERGY BALANCE AND THE GREENHOUSE EFFECT

REFERENCE ATMOSPHERE
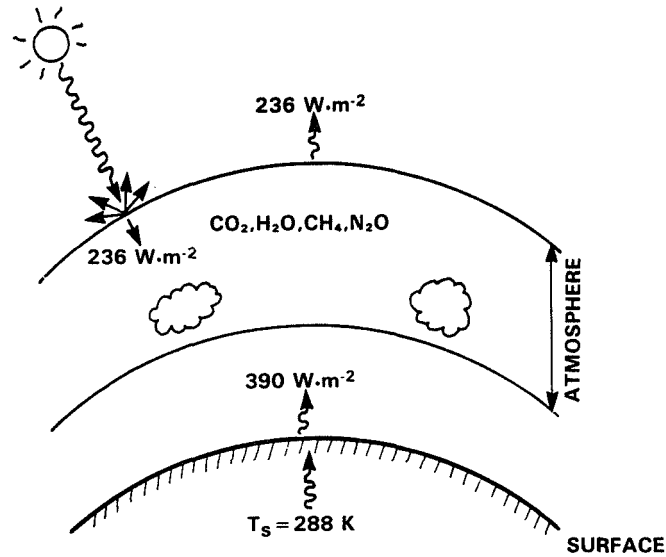
Figure 36. Global energy balance and the greenhouse effect.

TRACE GASES WITH ABSORPTION IN THE ATMOSPHERIC "WINDOW"

Figure 37. Spectral locations of the absorption features of various trace gases. The spectral region between 7 to 13 μm is referred to as the atmospheric "window."

entire Earth-atmosphere system is in radiative balance. About 90% of the atmospheric absorption is from H_2O, CO_2, and clouds in the Earth's atmosphere, and the remaining 10% of the absorption is due to atmospheric O_3, CH_4, and N_2O. If extra atmospheric absorption is introduced into this syste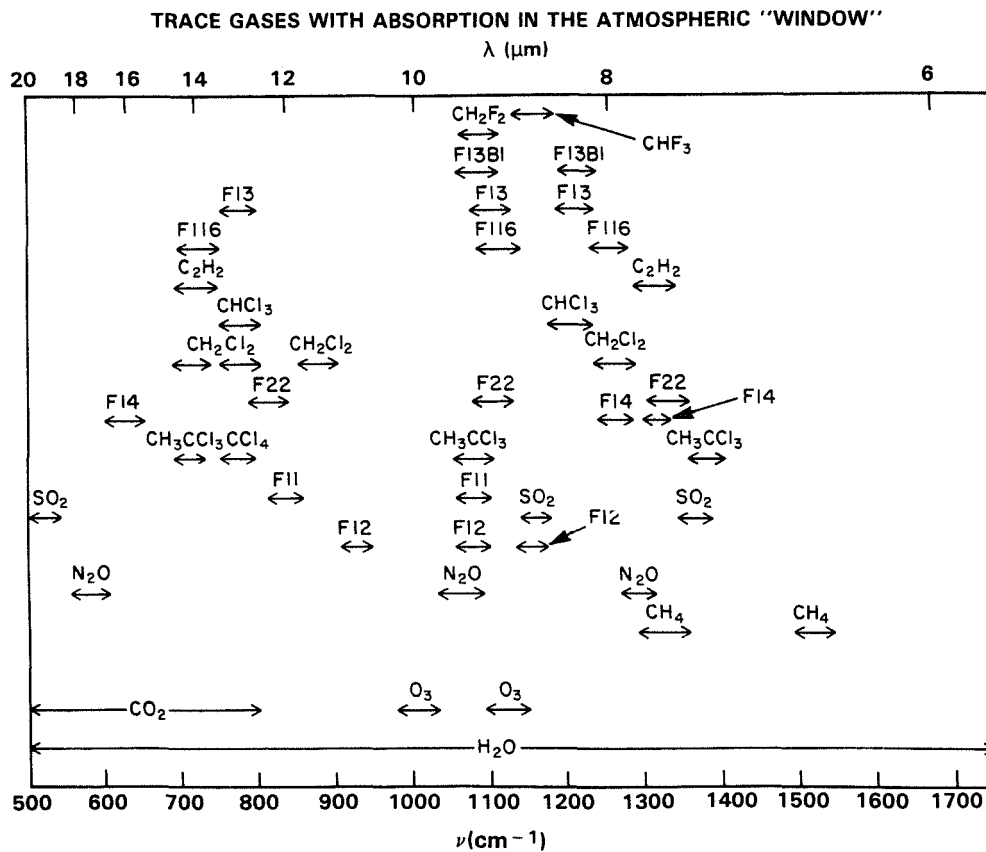m, the Earth's surface temperature must increase so that the same 236 W m^{-2} leaves the Earth-atmosphere system thus maintaining the radiative balance of the system.

A particularly important part of the atmospheric absorption spectrum for the greenhouse effect is the atmospheric "window" region from 7-13 μm. This is the spectral region through which approximately 70-90% of the surface and cloud emitted terrestrial radiation escapes to space. If there is a sizeable increase in the atmospheric concentration of a gas with strong absorption features in this atmospheric "window" region, this will tend to cause a warming of the Earth's surface by the greenhouse effect. Figure 37 illustrates many of the atmospheric trace gases with absorption features in the atmospheric "window."

Gases that absorb solar radiation may also add to the effective greenhouse effect if most of this absorption takes place in the lower half of the troposphere due to the efficient thermal coupling of the lower troposphere-surface system. If, however, most of the solar absorption takes place in the stratosphere, a surface cooling should result since this is reducing the amount of solar energy that is available to be absorbed by the surface-troposphere system.

Mechanisms by which Trace Gases Alter Climate

Some of the ways in which the addition of trace gases to the Earth's atmosphere can affect the climate are as follows:

(1) direct addition of radiatively active gases to the atmosphere (greenhouse or absorbing),

(2) addition of chemically active gases to the atmosphere which play a chemical role in altering the concentration of a radiatively active gas (e.g., CO and NO have negligible direct radiative effects, but they can chemically lead to alterations in the concentrations of CH_4 and O_3 which are radiatively active),

(3) addition of a gas that is both radiatively and chemically active (e.g., CH_4),

(4) addition of a gas that influences stratospheric ozone chemistry thereby affecting leading to changed stratospheric ozone distributions. The radiative role of the changed stratospheric ozone can lead to an altered radiative forcing of the atmosphere,

(5) addition of a radiatively active gas that affects ozone photochemistry by producing changes in stratospheric temperatures and hence ozone photochemistry reaction rates (e.g., CO_2 effect on O_3).

(6) addition of a trace gas that leads to changes in stratospheric temperatures and dynamics which then feedback on tropospheric climate,

(7) climate-chemistry interactions (e.g., tropospheric temperature increases leading to increased H_2O leading to increased OH which alters the concentration of other radiatively active trace gases through chemistry).

Effects of CFC's

The addition of CFC's affect climate in two different ways. CFC's are very efficient greenhouse gases. The addition of one molecule each of CFC-11 and CFC-12 gives a greenhouse warming of more than 10^4 molecules of CO_2. This is because of several factors. The CFC's have stronger IR band strengths than

CO_2. The absorption of terrestrial radiation by CFC's increases linearly in relation to their concentration in the atmosphere rather than logarithmically as is the case with CO_2 since parts of the CO_2 absorption spectrum are already nearly saturated. CFC's have strong absorption features in the atmospheric "window" region.

The addition of CFC's to the atmosphere are predicted to modify the vertical distribution of ozone. In looking at the effects of altered stratospheric ozone on tropospheric climate, it must be remembered that a reduction in stratospheric ozone affects the surface temperature in two ways. Less stratospheric ozone implies that more solar radiation will reach the surface-lower troposphere system which will tend to warm the climate, but less stratospheric ozone will lead to cooler stratospheric temperatures which will lead to less downwelling infrared radiation to the surface-lower troposphere system. This latter effect will tend to cool the climate. The net effect is much smaller than either of the two effects taken alone. Furthermore, the sign of the net effect depends on the altitudes where the ozone change takes place. For ozone changes at high stratospheric altitude the first effect, the increase in solar radiation, will dominate. At lower stratospheric altitudes, the second effect, the decrease in downwelling radiation, will dominate. For a given change in ozone at a given altitude, changes at lower stratospheric levels are thought to affect surface temperatures the most. Also, ozone changes in the tropics have more effect on tropospheric temperature than do changes in middle and high latitudes due to the warmer surface temperatures and colder tropopause temperatures in the tropics, both of which tend to maximize the greenhouse effect of ozone.

Climate Models

Several different types of mathematical models are used for climate simulations. There are the simple energy balance models in which the surface temperature change is taken to be proportional to the perturbation radiative heating of the surface/troposphere system. This proportionality constant is taken to reflect the feedback of the system. There are radiative-convective models (RCM's) which determine the equilibrium vertical temperature distribution for atmospheric columns and their underlying surface for given insolation and prescribed atmospheric composition and surface albedo. An RCM includes submodels for the transfer of solar and longwave radiation; the turbulent heat transfer between the Earth's surface and the atmosphere, the vertical redistribution of heat within the atmosphere by dry or moist convection, the atmospheric water vapor content and cloud amount. There are also general circulation climate models (GCM's) which attempt to explicitly model all the physical processes that are resolvable given the spatial resolution of the GCM and to parameterize processes that take place on smaller spatial scales than can be resolved. Only GCM's that contain some representation of the oceans' thermal inertia can be used to predict the actual time evolution of the climate.

Feedbacks

Given a change in atmospheric trace gas concentrations, it is conceptually straightforward to estimate the resulting change in the radiative forcing of the surface/troposphere system. It is more difficult to calculate the resulting surface temperature change; however, because of uncertainties in climate feedbacks. Some of the feedbacks that have been estimated include the following: changes in water vapor content that accompany the direct trace gas

warming or cooling; changes in the temperature lapse rate; changes in cloud temperature; changes in cloud cover; changes in cloud optical depth; and changes in surface albedo. Some of these feedbacks are relatively well understood. For instance, the water vapor feedback is quite well understood since it merely involves knowing how the atmospheric water vapor content depends on temperature. On the other hand, cloud feedbacks are probably the least understood in that even the sign of the feedback is uncertain.

Thermal Inertia of the Oceans

The world's oceans can take a decade to as much as a century to equilibrate with the changes in radiative heating induced by trace gases. As a result the estimated equilibrium surface temperature, computed by ignoring the huge ocean inertia, will lag the time history of trace gas increases by several decades. The influence of the oceans in delaying the warming is an active area of research. Current model calculations suggest that as a result of the oceans inertia we have currently realized only half of the predicted equilibrium surface warming.

Assessments of Past Trace Gas Climate Effects

Taking into account our best estimates of the concentrations of CO_2, CFC's-11 and 12, CH_4, N_2O, stratospheric H_2O, and O_3 over the period from 1850 to the present time, the following conclusions are reached:

(1) Non-CO_2 greenhouse gases are now adding to the greenhouse effect by an amount at least comparable to the effect of CO_2. This is a fundamental change from the situation during the period 1850-1960.

(2) The rate of increase of the total greenhouse forcing is now 3-10 times greater than was the mean rate for the period 1850-1960, due to both the

increase in the growth rate for CO_2 and the recent growth in other trace gases.

(3) The cumulative change in surface temperature (with zero feedbacks) for the period 1850-1980 is about 0.56 K; CO_2 increase contributes 0.4 K, and the other trace gases contribute the balance of 0.16 K. Models with feedbacks included give an equilibrium surface-air temperature change ranging from 0.7 to 2 K, reflecting an uncertainty in the range of surface equilibrium temperature changes of about a factor of three.

(4) Taking into account the thermal inertia of the world's oceans, these surface equilibrium temperature changes are not inconsistent with observations that indicate that a surface warming of about 0.6 K has occurred between 1850 and 1980.

(5) The computed stratospheric cooling for the period 1850-1980 is slightly under 1 K between 25-30 km and about 3 K between 35-40 km. These calculations do not include the effects of CFC-induced O_3 change which can amplify the cooling due to CO_2 increase by about 20%.

Greenhouse Forcing Projected into the Next Century

Projecting the greenhouse warming due to the addition of trace gases into the atmosphere requires the assumption of a scenario for the increase of trace gas concentrations in the Earth's atmosphere. Uncertainties in the trace gas scenario introduces uncertainties in the projections. One scenario for the increase in trace gases is shown in Table 4. Figure 38 shows the results for the cumulative surface warming calculated for this trace gas scenario. These results were obtained from a radiative-convective model whose equilibrium climate sensitivity is roughly half of that of GCM's. The surface warming is for steady-state equilibrium conditions and has been plotted in terms of both

Table 4. Estimates of the Abundance of Trace Chemicals in the Global Atmosphere of Years 1980 and 2030.

Source: Ramanathan, Cicerone, Singh and Kiel (1985)

Chemical Group	Chemical Formula	Dominant Source*	Dominant Sink*	Estimated Average Residence Time (τⱼ) (years)	Year 1980 Global Average Mixing Ratio (ppb)†	Year 2030 probable global average concentration (ppb)*** Probable Value	Possible Range	REMARKS
Carbon Dioxide	CO_2	N.A	O	2	339×10^3	450×10^3	--	Combustion and fertilizer sources
Nitrogen Compounds	N_2O	N.A	S(UV)	120	300	375	350 - 450	Concentration variable and poorly characterized
	NH_3	N.A	T	0.01	<1	<1	--	Concentration variable and poorly characterized
	$(NO+NO_2)$	N.A	T(OH)	0.001	0.05	0.05	0.05 - 0.1	
Sulfur Compounds	CSO	N.A	T(O,OH)?	1(?)	0.52	0.52	--	Sources and sinks largely unknown
	CS_2	N.A	T	1(?)	<0.005	<0.005	--	Sources uncharacterized
	SO_2	A(?)	T(OH)	0.001	0.1	0.1	0.1 - 0.2	Given the short lifetime the global presence of SO_2 is unexplained
	H_2S	N	T(OH)	0.001	<0.05	<0.5	--	
Fully Fluorinated Species	CF_4(F14)	A	—	>500	0.07	0.24	0.2 - 0.31	Aluminum industry a major source
	C_2F_6(F116)	A	—	>500	0.004	0.02	0.01 - 0.04	Aluminum industry a major source
	SF_6	A	—	>500	0.001	0.003	0.002 - 0.05	
Chlorofluoro-carbons	$CClF_3$(F13)	A	S(UV,I)	400	0.007	0.06	0.1	All chlorofluorocarbons are of exclusive man-made origin. A number of regulatory actions are pending. The nature of regulations and their effectiveness would greatly affect the growth of these chemicals over the next 50 years.
	CCl_2F_2(F12)	A	S(UV)	110	0.28	1.8	3.5	
	$CHClF_2$(F22)	A	T(OH)	20	0.06	0.9	1.9	
	CCl_3F(F11)	A	S(UV)	65	0.18	1.1	2.0	
	CF_3CF_2Cl(F115)	A	S(UV)	380	0.005	0.04	0.1	
	$CClF_2CClF_2$(F114)	A	S(UV)	180	0.015	0.14	0.3	
	CCl_2FCClF_2(F113)	A	S(UV)	90	0.025	0.17	0.3	
Chlorocarbons	CH_3Cl	N(O)	T(OH)	1.5	0.6	0.6	0.7	Dominant natural chlorine carrier of oceanic origin
	CH_2Cl_2	A	T(OH)	0.6	0.03	0.2	0.3	A popular reactive but non-toxic solvent
	$CHCl_3$	A	T(OH)	0.6	0.01	0.03	0.1	Used for manufacture of F22; many secondary sources also exist
	CCl_4	A	S(UV)	25 - 50	0.13	0.3	0.4	Used in manufacture of fluorocarbons; many other applications as well
	CH_2ClCH_2Cl	A	T(OH)	0.4	0.03	0.1	0.3	A major chemical intermediate (global production=10 tg/yr); possibly toxic
	CH_3CCl_3	A	T(OH)	8.0	0.14	1.5	3.7	Non-toxic, largely uncontrolled degreasing solvent
	C_2HCl_3	A	T(OH)	0.02	0.005	0.01	0.005 - 0.02	Possibly toxic, declining markets because of substitution to CH_3CCl_3
	C_2Cl_4	A	T(OH)	0.5	0.3	0.07	0.03 - 0.2	Possibly toxic, moderate growth due to substitution to CH_3CCl_3
Brominated and Iodated species	CH_3Br	N	T(OH)	1.7	0.01	0.01	0.01 - 0.02	Major natural bromine carrier
	$CBrF_3$(F13B1)	A	S(UV)	110	0.001	0.005	0.003 - 0.01	Fire extinguisher
	CH_2BrCH_2Br	A	T(OH)	0.4	0.002	0.002	0.001 - 0.01	Major gasoline additive for lead scavenging; also a fumigant
	CH_3I	N	T(UV)	0.02	0.002	0.002	--	Exclusively of oceanic origin
Hydrocarbons, CO, H_2	CH_4	N	T(OH)	5 - 10	1650	2340	1850 - 3300	A trend showing increase over the last 2 years has been identified
	C_2H_6	N	T(OH)	0.3	0.8	0.8	1.2	Predominantly of auto exhaust origin
	C_2H_4	A	T(OH)	0.3	0.06	0.1	0.16	No trend has been identified to date
	C_2H_8	N.	T(OH)	0.03	0.05	0.05	0.1	No trend has been identified to date
	CO	N.A	T(OH)	0.3	90	115	90 - 160	No trend has been identified to date
	H_2	N.A	T(SL,OH)	2	560	760	560 - 1140	
Ozone	O_3 (Tropospheric)	N	T(UV, SL,O)	0.1 - 0.3	$F(Z)$**	12.5%	--	A small trend appears to exist but data are insufficient
Aldehydes	HCHO	N	T(OH,UV)	0.001	0.2	0.2	--	Secondary products of hydrocarbon oxidation
	CH_3CHO	N	T(OH,UV)	0.001	0.02	0.02	--	1980 concentration estimated from theory

*N - Natural. A - Anthropogenic; O - Oceanic; S - Stratosphere; UV - Ultraviolet Photolysis; T - Troposphere;
OH - Hydroxyl radical removal; I - Ionospheric and extreme UV and electron capture removal; SL - Soil sink.
†These concentrations are integrated averages; for chemicals with lifetimes of 10 years or less, significant latitudinal gradients can be
expected in the troposphere; for chemicals with extremely short lifetimes (0.001-0.3 years) vertical gradients may also be encountered.
**Varies from 25 ppbv at the surface to about 70 ppbv at 9 km. The concentration was increased uniformly by the same percentage from the surface to 9 km.
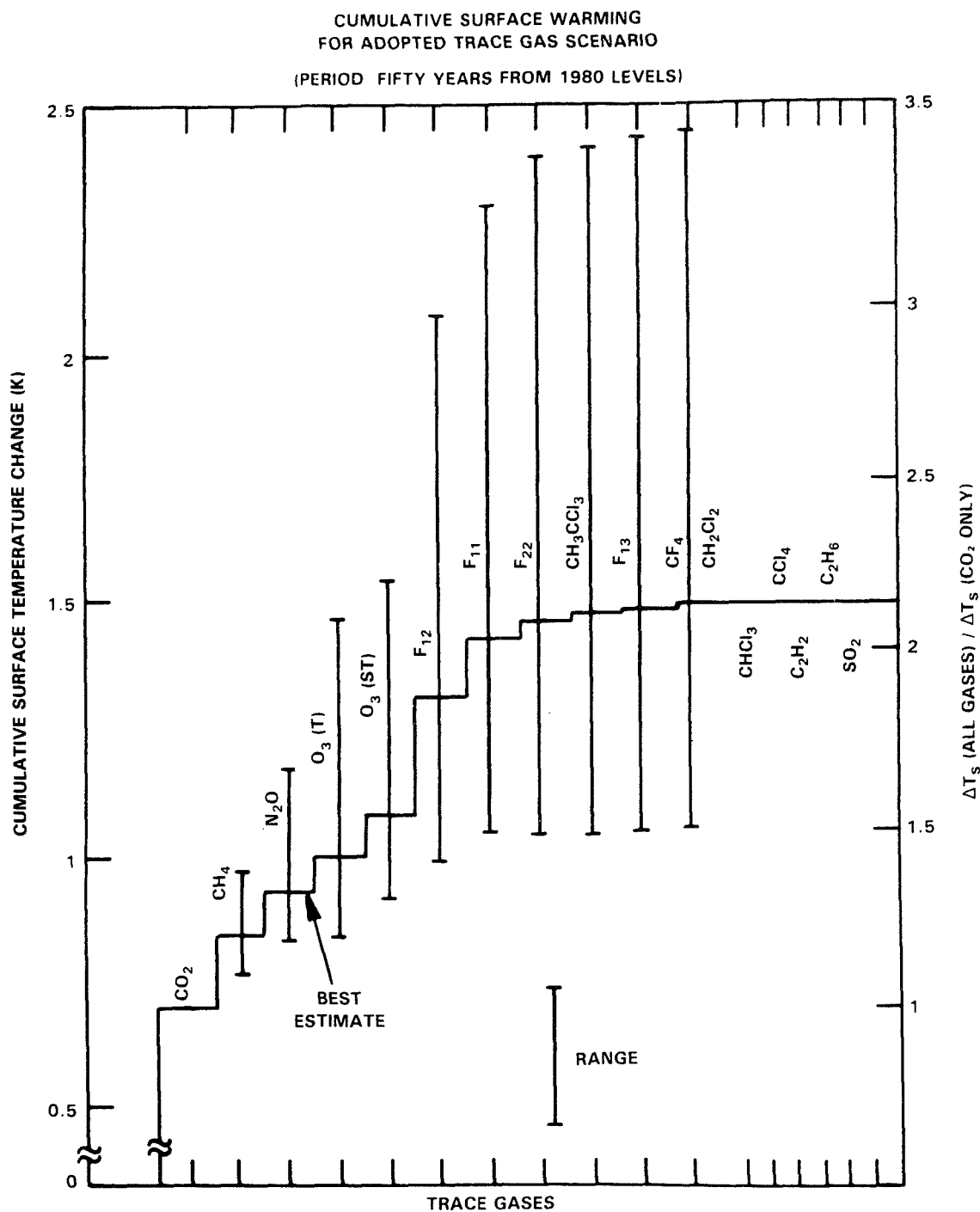***These values are not used in the present assessment.

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CUMULATIVE SURFACE WARMING
FOR ADOPTED TRACE GAS SCENARIO
(PERIOD FIFTY YEARS FROM 1980 LEVELS)

Figure 38. Cumulative equilibrium surface temperature warming due to increases of CO_2 and other trace gases, for the trace gas scenario of Table 4. See Table 4 for the adopted scenario. Surface temperature change is based on a 1-D model including some climate feedbacks, with estimated feedback factor $f \sim 1.5$; ΔT_0 can be obtained by dividing the indicated surface temperature changes by that value of f.

the cumulative temperature change and the ratio of the surface warming to be expected from all of the trace gases to that from CO_2 alone over this same time period. The range shown corresponds to the uncertainty in the projected trace gas scenarios. The cumulative equilibrium surface warming is about 1.5 K and according to current understanding of ocean thermal inertia, roughly half (i.e. 0.75 K) of this warming would be realized by the year 2030. This 0.75 K warming is about the same as the CO_2 equilibrium warming estimate from CO_2 alone over the period from 1850-1980. The non-CO_2 trace gases are estimated to produce an equilibrium surface warming of about 0.8 K over the period from 1980-2030 which is about three times what these other trace gases are estimated to have produced during the period 1850 to 1980. Other trace gas scenarios have shown qualitatively similar results.

Regional Effects

There is general agreement that climate sensitivity is not globally uniform, but that the surface air temperature response is magnified at high latitudes and thus is somewhat muted at low latitude, in comparison to the global mean response. This high latitude enhancement is expected on theoretical grounds because the ice-snow albedo feedback only operates at high latitudes and because the relative stability of the atmosphere there tends to confine the surface warming or cooling to low altitudes.

XIII. FUTURE NEEDS AND RECOMMENDATIONS

In the previous sections, it has been pointed out that there are many areas in which our understanding has advanced very significantly. There are also many areas in which important discrepancies between observations and models exist.

In this final section, we have tried to point out several needs for future research and actions that are needed to build on what we have already learned and to resolve some of the disagreements that exist between theory.

Chemistry

(1) Further laboratory studies of the rates, branching ratios and photodissociation channels of reactions involved in the production of NO_x from N_2O in the stratosphere, are required to reduce the uncertainties in this source term.

(2) Several key reactions involving HO_x species proceed through long-lived intermediates, resulting in complex pressure and temperature behavior, e.g. $OH+CO$, HO_2+O_3, HO_2+OH, etc. These reactions need further study to provide better characterization over the full range of atmospheric conditions.

(3) Uncertainties in the data base for BrO_x and coupled BrO_x-ClO_x catalyzed ozone destruction need to be reduced.

(4) A continued effort is required to identify possible missing chemistry or species of significance in the stratosphere, making use of all state-of-the-art experimental and computational techniques.

Source Gases

(5) Continued development of baseline measurements for CH_4, N_2O, CO_2, and the halocarbons are vital.

(6) Flux measurements of biogenic gases from representative ecosystems, especially for CO, CO_2, CH_4, N_2O, and NO, are needed in conjunction with studies of the underlying biological and geochemical processes which regulate the observed fluxes. In the case of CH_4, isotopic studies promise to elucidate the relative importance of various ecosystems in producing CH_4.

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(7) Studies of source gases in ice cores should elucidate the historical atmospheric concentrations of these gases.

(8) It is essential that the world-wide industrial production figures for all halocarbons be available.

Tropospheric Chemistry

(9) Measurement techniques need to be developed for more of the important tropospheric species.

(10) Further laboratory studies are needed to determine the kinetics and mechanisms of the oxidation of methyl and other organic radical species under the "low NO_x" conditions that characterize the background troposphere.

(11) Measurement programs and modeling efforts are needed to better understand the role of long-range transport of constituents on the chemistry of the troposphere.

(12) Measurement programs are needed to better understand the relative contributions of stratospheric exchange processes and in situ chemistry to tropospheric ozone.

Stratosphere-Troposphere Exchange

(13) While considerable progress has been made in aircraft studies, both of tropical cumulonimbus and extratropical exchange near polar front jet streams, there remains the need to incorporate our understanding of these individual cloud-mass and synoptic-scale events into a global framework. In particular, synthesis of the global scale morphology of the cross-tropopause flux of specific molecules will require considerable thought and work on case studies, satellite data and global meteorological analyses.

(14) Case studies of exchange processes at subtropical jet streams, particularly above their cores, are required.

(15) Studies of exchange processes at polar front jet streams, particularly where the flow is split, are required, to investigate both the extent of mixing and the possibility of return flow to the stratosphere.

(16) Exchange in cut-off lows needs to be studied further, to establish how much of it is reversible.

(17) Studies near tropopause level should be made in cut-off anticyclones, with a view to establishing the tropopause behavior on radiative time scales.

(18) Investigation of exchange processes in connection with the largest (highest reaching) cumulonimbus storms is required, to establish whether or not they are consistent with the height of the hygropause.

(19) The sources of the water vapor between the tropopause and the hygropause need to be established, especially in middle and high latitudes. This will afford valuable insight into the role of large scale, quasi-horizontal processes in cross-tropopause fluxes.

Dynamical Processes

(20) Much of our information on the middle atmosphere circulation is based on satellite observation of temperature alone. Wind and higher-order derived quantities such as potential vorticity are derived from these measurements, together with lower boundary conditions from conventional analyses, using mathematical manipulations such as spatial differentiation which can degrade the signal-to-noise ratio. The availability of direct wind observations from UARS will greatly improve this situation.

(21) The major advantage of satellite measurements is their global coverage and uniformity. One further attribute which needs greater emphasis than it has received in the past is continuity of measurement. This is highly desirable for the establishment of climatologies and absolutely vital for the detection of trends. It is therefore urged that further remote sensing missions be planned to succeed UARS following 1989 and that more emphasis be given to intercalibration of successive satellite measurements.

(22) Ground-based techniques (radars and lidars) have proven to be very useful for dynamical studies, especially for important small-scale motions such as gravity waves. It is desirable that these facilities operate on a more continuous basis and that observations from different sites be coordinated. Equatorial measurements are needed and networks would be very valuable. Lidars and radars should be collocated.

(23) While general circulation modeling of the middle atmosphere is increasingly proving to be a useful tool in studies of the region, such models continue to have major deficiencies. The most serious of these is their pathology in generating winter high-latitude temperatures far below those observed. Theory suggests that this must be due to an underestimate of eddy transport processes. This could be the result of an inadequate representation of planetary wave activity or of the inability of the models to resolve gravity waves. The role of gravity waves in the actual stratospheric momentum budget requires further study.

(24) Our conceptual picture of stratospheric transport processes has changed dramatically in recent years, and the theoretical basis for the parameterization of transport in zonally-averaged models has been made more secure. At the same time, however, the limitations of such models are becoming more apparent. Some of these limitations are obvious, given the

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highly three-dimensional nature of the wintertime flow (especially during active periods in the Northern Hemisphere). Others, such as the inability of zonally-averaged models to be truly interactive in the sense of predicting climate changes, are perhaps less obvious but equally important. Given the present problems of general circulation modeling and the expense of running such models with chemistry included, however, it is not envisaged that fully three-dimensional assessments will be forthcoming in the near future. Three-dimensional transport modeling may depend on a simplified approach; a new theoretical framework is needed to make this a reality.

Radiative Processes

(25) Improved determination of ozone cross sections in the Huggins bands would be valuable, especially for ground-based atmospheric ozone measurements.

(26) Improved determinations are needed of the O_2 absorption cross sections (Schumann-Runge bands and Herzberg continuum) and of the O_3 photodissociation $O(^1D)$ channel).

(27) Better determination of line shapes, line widths, and their temperature dependencies are needed to better determine terrestrial heating rates. Present line-by-line calculations are based on idealized values that have not been verified in many cases.

(28) Better spectroscopic measurements for such gases as N_2O and the CFC's are needed.

(29) Stratospheric measurements relating the O_2 cross section determinations by high resolution measurements of the solar irradiance from 180 to 250 nm are needed.

(30) The continued analysis of satellite data sets for ozone, temperature, solar irradiance, and outgoing terrestrial emission is essential

for developing a complete understanding of radiative processes in the Earth's stratosphere and mesosphere.

(31) A drift-free record of the ultraviolet solar irradiance covering at least the wavelength range 175-400 nm is needed over one or more entire solar cycles.

Atmospheric Observations of HO_x, NO_x, and ClO_x Species

(32) The accuracy and precision of many measurements need to be improved, and an improved measurement strategy needs to be formulated in order to more stringently test photochemical models.

(33) A continuation of the intercomparison of measurement techniques is highly vital.

(34) A network of ground-based observational techniques must be designed and implemented to detect any change in the atmospheric concentrations of reactive species, e.g. ClO and OH.

(35) Precise determinations are needed of the $(O)/(O_3)$ ratio and of the diurnal variation of O_3 in the upper stratosphere and in the mesosphere.

(36) Simultaneous measurements of odd hydrogen containing species are required over a full diurnal cycle to provide a more critical test of the photochemical models (OH, HO_2, H_2O_2, H_2O, in conjunction with temperature, O_3, and NO_x determinations).

(37) Simultaneous measurements of nitrogen containing species over a full diurnal cycle are required to critically test the photochemical models. These ratio measurements should be made in conjunction with appropriate measurements of O_x, HO_x, and ClO_x species.

(38) While we have a reasonable understanding of the diurnal variability of NO_2, a more rigorous test of theory requires more accurate experimental data.

(39) Simultaneous measurements of chlorine-containing species are required to provide a satisfactory test of the photochemical models (Cl, ClO, HCl and $ClONO_2$, preferably coupled with temperature, solar flux, O_3, H_2O, CH_4, and NO_x determinations).

(40) Continued monitoring of stratospheric HCl and HF is needed to establish long-term trends.

(41) There is a need for definitive observations of H_2O_2 and HOCl.

Assessment Models

(42) Continued efforts are needed to develop two- and three-dimensional models with interactive chemistry, dynamics, and radiation.

(43) Better models need to be developed to describe polar phenomena.

(44) Multidimensional models (2- and 3-D) are needed to study climate-chemistry interactions with particular emphasis on modeling the potential climatic effect arising from redistribution of O_3.

(45) Models need to be developed to understand the contribution of volcanic eruptions to changes in stratospheric composition, dynamics, and radiative budget.

(46) The new Monte Carlo method that screens the results against atmospheric observations should be emphasized.

Ozone and Temperature Trends

(47) The present SBUV-2 ozone monitoring program measures daytime values of total column amounts and profiles between 25 and 55 km. A program to

determine unambiguous ozone trends from the Earth's surface to the overlap region with the SBUV-2 profiles under both daytime and nighttime conditions would greatly improve the program to determine ozone trends.

(48) No satisfactory program exists to measure long-term trends in stratospheric temperatures. A long-term satellite and ground-based temperature system needs to be developed that is sufficient to measure the mid-stratosphere temperature trend of 1.5K/decade to the 95% confidence level.

(49) The causes of the measurement biases among SBUV, LIMS, and SAGE need to be determined thereby reducing the absolute error estimates.

(50) The Bass and Paur ozone absorption coefficients need to be implemented in processing the ground-based measurements, and these results compared with satellite observations.

(51) The ground-based ozone profile measurement program should continue to be developed with particular emphasis on the following:

(a) determination of the aerosol impact on Umkehr measurements;

(b) development of a high altitude (~40 km) balloon sampling system with specific attention to the adjustment procedure to match the Dobson total ozone measurements;
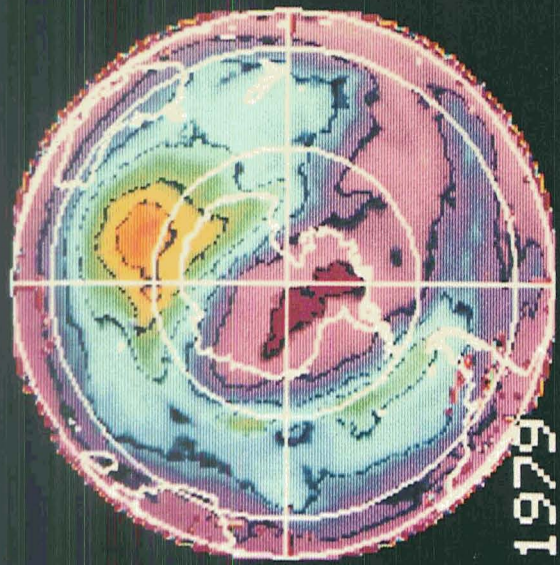
(c) development of a lidar system capable of routine ozone measurements in the troposphere and stratosphere, especially above about 40 km.
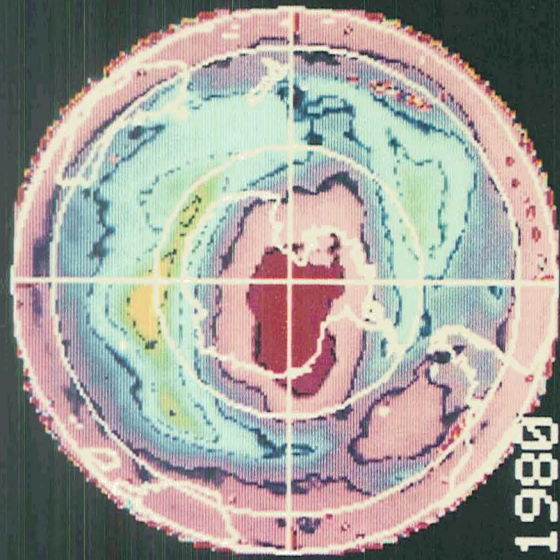

Trace Gas Effects on Climate

(52) Model and in situ observational studies are needed to study the relative importance of transport, chemistry, and the indirect effects of trace gases in governing the long-term trends of tropospheric and stratospheric O_3, CH_4, and stratospheric H_2O to address fundamental issues of the trace gas-climate problem.

(53) Accurate determination of decadal trends in radiative forcings, trace gases, planetary albedo (to determine the effects of aerosols and cloud feedback) and surface-troposphere-stratosphere temperatures are needed. The observational challenges in doing this are formidable but must be overcome to obtain a scientifically credible interpretation of the human impacts on the climate system.
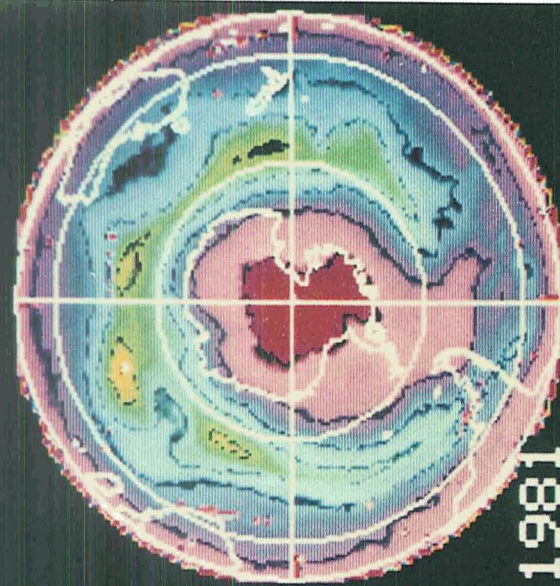
Figure 33. TOMS maps of total ozone shown in Southern Hemisphere polar
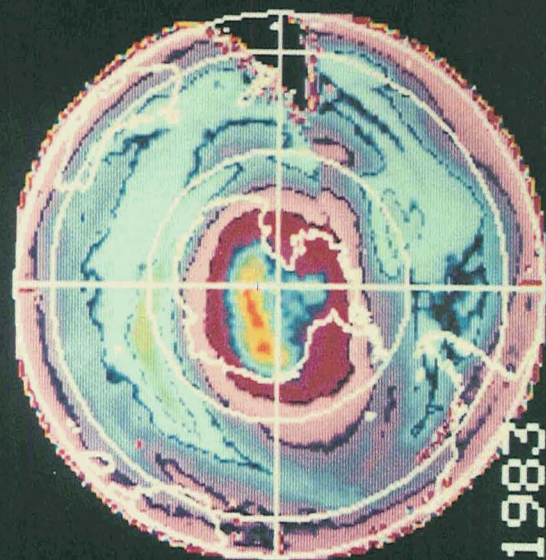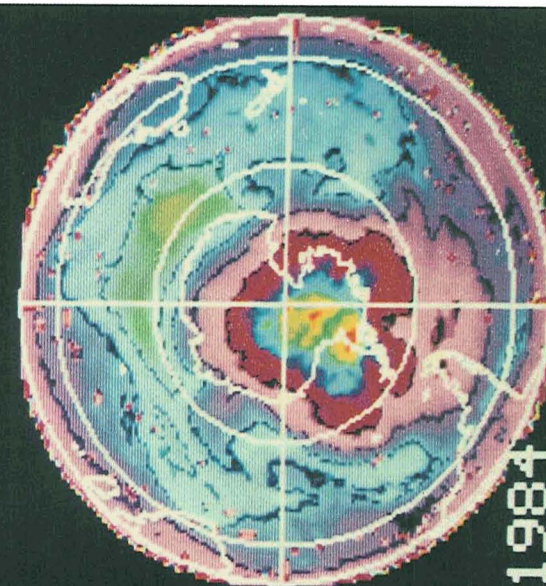projection focussed on Antarctica for October 7 of the years 1979-1984.

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1980

1983

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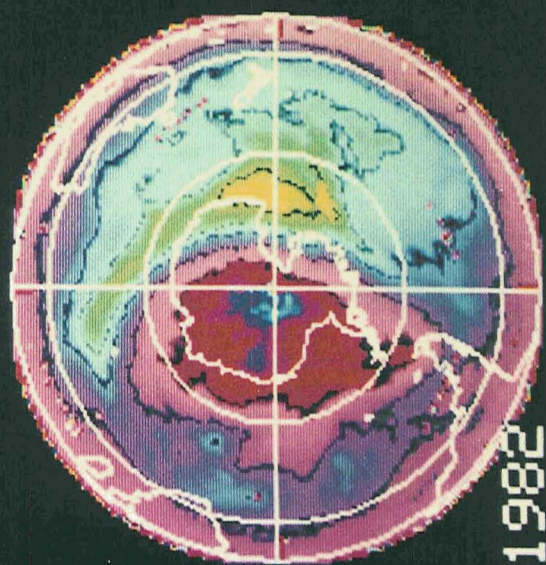
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16. Abstract

This report presents an assessment of the state of knowledge of the upper atmosphere as of January 1986. It discusses the physical, chemical, and radiative processes which control the spatial and temporal distribution of ozone in the atmosphere; the predicted magnitude of ozone perturbations and climate changes for a variety of trace gas scenarios; and the ozone and temperature data used to detect the presence or absence of a long-term trend. This assessment report was written by a small group of NASA scientists, was peer reviewed, and is based primarily on the comprehensive international assessment document entitled "Atmospheric Ozone 1985: Assessment of Our Understanding of the Processes Controlling Its Present Distribution and Change" to be published as the World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 16.

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