

NASA
RP
1049
c.1

NASA Reference Publication 1049

LOAN COPY: RETURN TO
AFWL TECHNICAL LIBRARY
KIRTLAND AFB, N. M.



The Stratosphere: Present and Future

DECEMBER 1979

NASA

The NASA logo, consisting of the word "NASA" in a bold, sans-serif font.

ERRATA

for

THE STRATOSPHERE: PRESENT AND FUTURE

NASA Reference Publication 1049

Dated December 1979

Goddard Space Flight Center

Corrections
inserted
9 June 80
dew

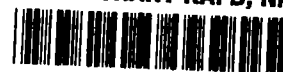
Note the following changes:

1. pp. 65-81. In some copies, these pages are not in correct order.
2. p. 86. The units in the table of CFM production are 10^9 g, not tg.
3. pp. 146-7. Data for NO and NO₂ incorrectly attributed to Chaloner et al. (1978) are in fact a repetition of the data of Drummond and Jarnot (1978).
4. p. 148. The correct reference for the third line of HCl data is Eyre and Roscoe (1977).
5. p. 161. In figure 4-11, BLOXAM should be BLAMONT.
6. pp. 168 and 185. In the discussion of CO, reference should be made to the data down to 45 km by Waters et al. (1976). Waters, J. W., W. J. Wilson, and F. I. Shimabukuro, Microwave measurement of mesospheric carbon monoxide, *Science*, 191, 1174-5, 1976.
7. pp. 296-7. Random errors for the chemiluminescent sensor are $\pm 5\%$ (not $\pm 8\%$) and apply above 20 km (not 1 km).
8. p. 431. E. Hilsenrath was Co-Chairman of the group on Meteorology of the Stratosphere.
9. p. 117. The mixing ratio is in ppmv, not ppm.

April 30, 1980

NASA Reference Publication 1049

TECH LIBRARY KAFB, NM



0063274

The Stratosphere: Present and Future

Edited by

Robert D. Hudson and Edith I. Reed
NASA Goddard Space Flight Center



National Aeronautics
and Space Administration

**Scientific and Technical
Information Branch**

1979



PREFACE

In September 1977, the National Aeronautics and Space Administration published a report entitled *Chlorofluoromethanes and the Stratosphere* (NASA Reference Publication 1010, Robert D. Hudson, Editor) which was transmitted to the Environmental Protection Agency and the United States Congress. Under the provisions of the Clean Air Act Amendment of 1977, the National Aeronautics and Space Administration is required to report both to the Environmental Protection Agency and to the Congress on its assessment of the current state of knowledge of the stratosphere and mesosphere. These reports are to be prepared bi-annually starting in January 1980. This report is the first in that series.

In order to prepare this report, the Goddard Space Flight Center organized a workshop at Harpers Ferry, West Virginia during the week of June 4, 1979. The workshop was centered around seven working groups. A Laboratory Measurements Working Group, chaired by Dr. W.B. DeMore of the Jet Propulsion Laboratory; a Models Working Group chaired by Dr. D. Stroebel of the Naval Research Laboratory; a Budget Working Group chaired by Dr. R. Cicerone of the Scripps Institute of Oceanography; a Radicals Working Group chaired by Dr. J. Anderson, Harvard University; a Meteorology Working Group chaired by Dr. M. Geller, University of Miami; a Trends Working Group chaired by Dr. J. London, University of Colorado; and a Predictions Working Group chaired by Dr. R. Stolarski of the Goddard Space Flight Center. The overall Chairman for the Workshop was Dr. R.D. Hudson of the Goddard Space Flight Center. Dr. L. Rex Megill, Utah State University was the Vice-chairman and Mrs. Edith Reed of the Goddard Space Flight Center was the Co-Chairman.

Each working group was further subdivided and prominent scientists active and expert in stratospheric and mesospheric studies were asked to prepare position papers to cover selected topics of research. In addition to preparing position papers, modeling groups were approached to run their models using a standard set of input data supplied by the Goddard Space Flight Center and to predict the impact on the stratosphere of specific natural and anthropogenic perturbations. Specific output data, as well as predicted ozone changes, were requested in order that realistic model comparisons could be made.

Over 90 scientists representing most of the institutions engaged in upper atmospheric research in the United States, Canada and Europe attended the Workshop. A complete list of the position paper authors and the participants with working group assignments is given in the Appendix. Each working group prepared a summary document and these have been assembled into this report. Thus, this report should represent current knowledge as of June 1979.

Goddard Space Flight Center and the National Aeronautics and Space Administration wish to express their thanks to the working group chairmen, the position paper authors, and the participants for the time and effort that they contributed to the preparation of this report.



CONTENTS

	Page
PREFACE	iii
CHAPTER 1 — LABORATORY MEASUREMENTS	1
<u>KINETIC AND PHOTOCHEMICAL DATA FOR MODELING</u>	1
INTRODUCTION	1
DISCUSSION	1
NO _x and O(¹ D) Reactions	3
HO _x Reactions	3
Halogen Chemistry	4
Methane Oxidation	6
SO _x Reactions	6
Third-Order Reactions	7
Photochemical Processes	8
SUMMARY OF DATA RECOMMENDATIONS	8
Basis of the Recommendations	8
Format	8
Error Estimates	9
Units	9
Bimolecular Rate Constants (Table 1-2 and Notes)	10
Third Order Reactions (Table 1-3 and Notes)	21
Photochemical Reactions (Tables 1-4 through 1-31 and Notes)	23
<u>DATA RELATED TO IONS AND AEROSOLS</u>	43
HETEROGENEOUS PHENOMENA	43
Introduction	43
Formation Process	43
Effects of Aerosols	44
ATMOSPHERIC ION CHEMISTRY	46
Introduction	46
Mesospheric Positive-Ion Chemistry	47
Mesospheric Negative-Ion Chemistry	47
Stratospheric Positive-Ion Chemistry	50
Stratospheric Negative-Ion Chemistry	50
Summary	50
Recommendations	52
<u>DATA FOR INFRARED AND ULTRAVIOLET PHENOMENA</u>	53
INFRARED SPECTROSCOPY	53
Currently Available Data	53
Spectral Requirements	53
Current Capabilities	55

CONTENTS (Continued)

	Page
ULTRAVIOLET FLUXES AND CROSS SECTIONS	55
Overview	55
Solar Fluxes and O ₂ Absorption	56
Solar Flux Variability, O ₃ Absorption	59
CHAPTER 2 — MODELS	65
<u>INTRODUCTION</u>	65
<u>RADIATION AND ONE-DIMENSIONAL RADIATIVE-CONVECTIVE MODELS</u>	65
CURRENT CAPABILITIES AND LIMITATIONS	65
Specified Lapse Rate	66
Relative Humidity	66
Clouds	66
Aerosols	67
MODEL VERIFICATION	67
Comparison with Other Models	67
Comparison with Observations	67
<u>CHEMISTRY MODELS</u>	68
PHOTOCHEMICAL MODELS	68
AEROSOL MODELS	69
<u>SIMPLIFIED TRANSPORT MODELS</u>	70
ONE-DIMENSIONAL DIFFUSION MODELS	70
TWO-DIMENSIONAL DYNAMICAL MODELS	71
Eulerian-Mean Models	71
Lagrangian-Mean Approaches	72
<u>THREE-DIMENSIONAL DYNAMICAL MODELS</u>	73
QUASI-GEOSTROPHIC MODELS OF THE STRATOSPHERE	73
Dynamics	73
Radiation	75
Summary	77
THREE-DIMENSIONAL PRIMITIVE EQUATIONS MODELING	77
Modeling of Various Physical and Dynamical Processes	78
Modeling Approaches and Efforts	79
Model Improvements Required	80
CHAPTER 3 — BUDGETS	83
<u>INTRODUCTION</u>	83
<u>HALOCARBONS</u>	83
SOURCES	83
Natural Sources of Halocarbons	83
Industrial Sources of Halocarbons	85

CONTENTS (Continued)

	Page
TROPOSPHERIC ORGANIC HALOGEN BURDEN	87
Tropospheric Concentration of CCl ₃ F	88
Concentrations of Other Fluorocarbons	92
REMOVAL MECHANISMS FOR CHLOROCARBONS IN THE TROPOSPHERE	93
ESTIMATION OF THE CCl ₃ F TROPOSPHERIC LIFETIME	93
Lifetime for CCl ₂ F ₂	94
<u>NITROUS OXIDE</u>	95
INTRODUCTION	95
ATMOSPHERIC DISTRIBUTION	95
SINKS FOR ATMOSPHERIC N ₂ O	97
SOURCES OF N ₂ O AND MAN-MADE PERTURBATIONS	99
ISSUES	102
<u>STRATOSPHERIC NO_x BUDGET</u>	103
SOURCES AND SINKS	103
COMPARISON WITH MEASUREMENTS	107
<u>CO₂ BUDGET</u>	107
<u>STRATOSPHERIC WATER VAPOR</u>	113
INTRODUCTION	113
HISTORICAL DEVELOPMENTS	113
RECENT OBSERVATIONS	115
DISCUSSION	115
H ₂ O BUDGET	121
<u>HYDROCARBONS AND HYDROGEN</u>	123
METHANE	123
Sources and Sinks	123
Tropospheric Distribution	126
Stratospheric Distribution	126
NONMETHANE HYDROCARBONS	129
HYDROGEN	130
<u>STRATOSPHERIC SULFUR</u>	130
INTRODUCTION	130
TROPOSPHERIC SOURCES AND SINKS	130
TRANSPORT BETWEEN THE TROPOSPHERE AND STRATOSPHERE	132
AEROSOL FORMATION	133
REMOVAL FROM THE STRATOSPHERE	133

CONTENTS (Continued)

	Page
CONCENTRATIONS OF STRATOSPHERIC SULFUR	133
Sulfides and Mercaptans	133
Carbon Disulfide and Carbonyl Sulfide	133
Sulfur Dioxide	134
COMPOSITION OF STRATOSPHERIC AEROSOLS	134
CHEMICAL REACTIONS OF STRATOSPHERIC SULFUR	134
Sulfides and Mercaptans	134
Carbon Disulfide	134
Carbonyl Sulfide	137
Sulfur Dioxide	137
Sulfate Aerosol	137
CHEMICAL SUMMARY	137
Stratospheric Implications of Sulfur Chemistry	137
SUMMARY	139
<u>STRATOSPHERIC PARTICLES</u>	139
SIZE DISTRIBUTION	139
COMPOSITION	139
MASS CONCENTRATIONS	141
NUMBER CONCENTRATIONS	141
SOURCES	142
<u>SUMMARY</u>	142
CHAPTER 4 — RADICALS, RESERVOIRS, AND IONS	143
<u>NEUTRAL SPECIES</u>	143
INTRODUCTION	143
TABULATION OF DATA	144
Atomic Oxygen	144
O ₂ (¹ Δ)	151
O ₂ (b ¹ Σ)	151
Atomic Hydrogen	152
OH	152
HO ₂	155
H ₂ O	155
H ₂ O ₂	155
Atomic Nitrogen	157
NO	157
NO ₂	159
NO ₃	160
N ₂ O ₅	161
NH ₃	161

CONTENTS (Continued)

	Page
HNO ₂	162
HO ₂ NO ₂	162
HNO ₃	162
Atomic Chlorine	162
ClO	164
HCl	166
ClNO ₃	167
HOCl	167
SO ₂	167
COS	168
CO	168
CH ₃ OH	169
H ₂ CO	169
C ₂ H ₂ , C ₂ H ₆	169
COMPARISON WITH THEORETICAL MODELS	169
O(³ P)	169
OH, HO ₂	171
Total NO _x	171
NO	171
NO ₂	171
HNO ₃	171
HNO ₃ /NO ₂ Ratio	175
N ₂ O ₅	175
Cl, ClO	175
Cl/ClO Ratio	177
HCl	177
ClONO ₂	179
Total ClO _x	179
HF	180
HBr	180
Sulfur Constituents	180
EMERGING PROBLEMS AND PROJECTIONS OF FUTURE RESEARCH	183
Problems Remaining From NASA RP-1010	183
Problems Which Have Emerged	184
<u>ENERGETIC FLUXES AND IONS</u>	185
IONIZING SOURCES	185
Overview	185
Magnetospheric Electrons and Bremsstrahlung X-Rays	186
Solar Cosmic Rays	188
Concluding Remarks	188
STRATOSPHERIC IONS	188
Positive Ions	189
Negative Ions	191
Ion Recombination	192
Summary	192

CONTENTS (Continued)

	Page
ATMOSPHERIC EFFECTS OF IONIZING SOURCES	193
Production of NO and HO _x	193
Effects on O ₃ and NO Densities	193
Lightning	195
Conclusions and Recommendations	197
CHAPTER 5 — METEOROLOGY OF THE STRATOSPHERE	199
INTRODUCTION	199
STRATOSPHERIC MEASUREMENTS AND DATA ANALYSIS	200
INTRODUCTION	200
STRATOSPHERIC MEASUREMENTS	200
Background	200
Ground Based Measurements of Temperature and Wind	200
Ground Based Measurements of Total Ozone and Its Vertical Distribution	206
Aircraft Measurements	209
Satellite Characteristics	209
Satellite Measurements of Temperature	211
Satellite Measurements of Ozone	211
DATA ORGANIZATION AND ANALYSIS OF STRATOSPHERIC FIELDS	215
Background	215
Standard Atmospheres	215
Empirical Models	215
Subjective Synoptic Analysis	216
Objective Synoptic Analysis	216
STRATOSPHERIC CIRCULATION	220
INTRODUCTION	220
TYPES OF MOTION	220
GENERAL CIRCULATION OF THE STRATOSPHERE	222
Background	222
Mean Zonal Wind	222
Heat, Momentum and Energy Budgets	224
Contrast Between the Hemispheres	227
Final Remarks	227
QUASI-BIENNIAL AND SEMI-ANNUAL OSCILLATION	228
Background	228
The Quasi-Biennial Oscillation	228
Semi-Annual Oscillation	230
SUDDEN WARMINGS	233
Background	233
Frequency of Warmings and Circulation Reversals	235

CONTENTS (Continued)

	Page
Energy and Forcing from the Troposphere	235
Roles of Waves 1 and 2	238
Low-Latitude Cooling	240
Tropospheric Condition for Circulation Reversal	240
Final Remarks	240
SHORT-PERIOD MOTIONS	240
Background	240
Atmospheric Tides	241
Gravity Waves; Turbulence	242
Synoptic-Scale Instabilities	243
OZONE CONTROL BY DYNAMICS AND CHEMISTRY	245
Background	245
Physical Mechanisms	245
Modeling of Transport and the Ozone Distribution	249
Final Remarks	260
SOLAR-STRATOSPHERIC RELATIONS	261
Background	261
Possible Mechanisms	261
Evidence of Solar-Related Stratospheric Variations	261
Final Remarks	266
<u>STRATOSPHERIC TROPOSPHERIC INTERACTIONS</u>	266
INTRODUCTION	266
MASS EXCHANGE PROCESSES	266
Background	266
Definition of the Tropopause	266
Exchange by Lagrangian Mean Motions	268
Exchange by Extratropical Cyclonic and Jet Stream Systems	269
Exchange by Convective Cloud Systems	270
Discussion of Mass Exchange	270
Final Remarks	273
DYNAMICAL COUPLING	274
Background	274
Mechanisms	274
RADIATIVE COUPLING	275
Background	275
Radiative Properties of Ozone	275
Radiative Properties of Aerosols	276
Radiative Properties of Carbon Dioxide	277
Radiative Properties of Water Vapor	277
Radiative Effects on Wave-Mean Flow Interactions	278
Final Remarks	278
ELECTRICAL COUPLING	278
<u>SUMMARY AND FUTURE NEEDS</u>	278

CONTENTS (Continued)

	Page
CHAPTER 6 — LONG PERIOD CHANGES IN STRATOSPHERIC PARAMETERS	281
<u>INTRODUCTION</u>	281
<u>AVAILABLE OBSERVATIONS FOR TREND ANALYSES</u>	282
TOTAL OZONE	282
Ground Based Observations	282
Satellite Observations	282
VERTICAL DISTRIBUTION OF OZONE	284
Balloon-Borne Ozonesondes	284
Umkehr Observations	284
Rocketsondes	284
Satellite Observations	285
<u>MEASUREMENT ERRORS FOR TREND DETERMINATION</u>	285
TOTAL OZONE MEASUREMENT ERRORS	286
Dobson Spectrophotometer Total Ozone Measurement Errors	286
M-83 Ozonometer Total Ozone Measurement Errors	288
Satellite BUV Experiment Total Ozone Measurement Errors	288
Infrared Sounding Total Ozone Measurement Errors	291
ERRORS IN OZONE PROFILE MEASUREMENT METHODS	291
Balloon Ozoneprobe Observation Errors	291
Umkehr Observation Measurement Errors	293
Rocket Ozoneprobe Measurement Errors	295
BUV Ozone Profile Measurement Errors	297
<u>OBSERVED TRENDS IN OZONE</u>	299
TRENDS FROM GROUND BASED OBSERVATIONS	299
TRENDS FROM SATELLITE OBSERVATIONS	301
TRENDS FROM VERTICAL PROFILE DATA	303
Balloon Ozoneprobe and Umkehr Observations	303
Observed Ozone Variations from Rocket Data	304
Observed Ozone Profile Variations from Satellite Data	307
<u>LONG-TERM VARIATIONS OF OTHER PARAMETERS</u>	309
TEMPERATURE VARIATIONS	309
TRENDS IN TRACE SPECIES	309
CF ₂ Cl ₂ and CFCl ₃	314
CCl ₄	314
CH ₃ CCl ₃	314
N ₂ O	314
CH ₄	315
CO ₂	315
Sulfur Compounds	315
Discussion	317
WATER VAPOR TRENDS	317

CONTENTS (Continued)

	Page
<u>TREND DETECTABILITY — TOTAL OZONE</u>	319
FORMULATION OF THE PROBLEM	319
STATISTICAL ESTIMATION ERRORS	321
INSTRUMENT ERRORS	322
SPATIAL SAMPLING ERRORS	323
LONG-TERM NATURAL TRENDS	323
OTHER ANTHROPOGENIC TRENDS	323
ESTIMATING THRESHOLDS OF TREND DETECTABILITY	324
TREND DETECTION — VERTICAL DISTRIBUTION	327
<u>SUMMARY</u>	330
<u>RECOMMENDATIONS</u>	331
 CHAPTER 7 — MODEL PREDICTIONS	 333
<u>INTRODUCTION</u>	333
<u>CURRENT UNDERSTANDING OF STRATOSPHERIC CHEMISTRY</u>	335
RECENT DEVELOPMENTS	335
<u>MODELING OF THE PRESENT STRATOSPHERE</u>	338
TRACE SPECIES	338
PREDICTED OZONE ABUNDANCE	339
<u>PERTURBATIONS</u>	339
GROUND-LEVEL HALOCARBON RELEASES	339
Chlorofluoromethane Effects	339
Other Chlorine Perturbations	343
Bromine and Fluorine Perturbations	344
NITROGEN CYCLE CHANGES AND NITROUS OXIDE (N ₂ O)	345
EFFECTS OF CHANGES IN CO ₂	345
PERTURBATIONS INDUCED BY CHANGES IN TROPOSPHERIC OH	346
HIGH-ALTITUDE AIRCRAFT OPERATIONS	346
ROCKET EXHAUSTS AND BY-PRODUCTS	350
ATMOSPHERIC NUCLEAR EXPLOSIONS	350
Nuclear Tests	350
Potential Nuclear War	351
NATURAL EVENTS AND VARIATIONS	351
Solar-Proton Events	351
Volcanic Eruptions	352
Solar UV Variability	352

CONTENTS (Continued)

	Page
COUPLED PERTURBATIONS	354
<u>UNCERTAINTIES</u>	355
UNCERTAINTIES IN MODEL INPUT PARAMETERS	355
UNCERTAINTIES DUE TO MODEL CONSTRUCTION.....	356
Uncertainties Due to Diurnal, Latitudinal, and Seasonal Variations	359
Uncertainties Due to Missing Chemistry	360
Uncertainties Due to Treatment of Radiative Transfer	361
Feedbacks	361
CONCLUSION	362
REFERENCES.....	363
APPENDIX — STRATOSPHERE WORKSHOP PARTICIPANTS AND CONTRIBUTORS	429
BIBLIOGRAPHIC DATA SHEET	

CHAPTER 1

LABORATORY MEASUREMENTS

KINETIC AND PHOTOCHEMICAL DATA FOR MODELING

INTRODUCTION

The kinetic and photochemical data in this chapter is an update of the publication JPL 79-27, *Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling*, by DeMore et al. (1979). The foregoing publication should be consulted for a more comprehensive discussion and evaluation of the laboratory data base that was used to arrive at the present recommendations.

The JPL 79-27 publication was prepared by the NASA Panel for Data Evaluation, which is an on-going working group charged with the responsibility of producing an updated tabulation of laboratory data related to the stratosphere, at intervals of approximately nine months. Their first evaluation appeared in NASA RP-1010, *Chlorofluoromethanes and the Stratosphere*, edited by Hudson (1977). The tabulations presented in this chapter represent the third evaluation of that working group.

In addition to kinetic and photochemical data, the present chapter contains sections on the following topics as they relate to the stratosphere: heterogeneous chemistry, ionic processes, and infrared spectroscopy. No attempt is made to tabulate all laboratory data for these areas; rather, they are discussed in more general terms and references to available literature are given.

DISCUSSION

In recent years, considerable progress has been made in the laboratory measurement of rate constants and cross sections for use in stratospheric modeling, and in many respects, these rates are the best-founded part of stratospheric science. Nevertheless, a number of major problems remain, ranging from small (but not insignificant) differences in results for a given parameter obtained by different laboratories, to the possibility that major factors have not been properly incorporated in the chemical schemes. Indeed, there are discrepancies in the comparison of the measurements with predictions in the stratosphere that suggest at least the possibility that the models are not complete. There are also cases involving laboratory simulations of selected aspects of stratospheric photochemistry which do not seem to be compatible with the rate constants which have been measured independently (usually on an absolute, direct basis). Some of the difficulties may stem from the need to study reactions under conditions similar to those under which the results are to be applied. It has long been recognized that rate constants and cross sections used for stratospheric temperatures should be measured at those same temperatures wherever possible because of the uncertainties attached to long temperature extrapolations. Similarly, it is becoming apparent that other conditions such as total pressure must often be taken into account because some presumably bimolecular reactions may in fact occur by more complex mechanisms. Partial pressures of other gases, such as water vapor or oxygen, may occasionally affect reaction rates.

It is the general consensus of the Laboratory Measurement Group that *tuning* of rate constants to fit stratospheric observations is inadvisable, since no matter how uncertain the laboratory measurements may be, they are probably more reliable than the deductions based on stratospheric measurements. The combined errors arising from both model and measurement ambiguities are expected to be greater than those of the laboratory measurements. Thus, artificial adjustment of rate constants may obscure important evidence which could otherwise be inferred from the existence of a discrepancy between prediction and observation.

In subsequent paragraphs of this chapter, recent developments in the different reaction categories are discussed and several specific problem areas are outlined. These should not be taken as a statement of priorities for further study since the definition of importance depends somewhat on the objective in mind. For example, some reactions may be relatively unimportant (as determined by a sensitivity analysis) in terms of the overall effect on the total ozone column density, but may be the most important factor in setting the ratios of certain species in the atmosphere. Since such ratio measurements are important for testing the accuracy of photochemical models, the corresponding rate constants need to be known precisely. In some cases, additional study is suggested because the experimental data do not seem to yield rate constant parameters consistent with theory or previous experience on similar reactions. It must be stressed that anomalies in rate constants frequently suggest the presence of error.

From the standpoint of CFM-induced ozone depletion, there are approximately 16 rate constants and 8 photolysis parameters to which the predictions are particularly sensitive. These processes are listed in table 1-1 in order of descending effect.

Table 1-1
The Most Important Rate Constant and Photolysis Parameters
for Prediction of Ozone Depletion by CFMs

Rate Constants	Photolysis
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$ $\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{NO} + \text{NO}$ $\quad \quad \quad \rightarrow \text{N}_2 + \text{O}_2$ $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ $\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O}(^3\text{P}) + \text{M}$ $\text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}$ $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ $\text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}$ $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ $\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$ $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ $\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{OH}$ $\text{ClO} + \text{NO} \rightarrow \text{NO}_2 + \text{Cl}$ $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	$\text{O}_2, \lambda > 200 \text{ nm}$ Solar flux, $\lambda < 320 \text{ nm}$ N_2O cross sections $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D})$ O_3 cross sections HNO_3 cross sections ClONO_2 cross sections NO_2 cross sections

NO_x and O(¹D) Reactions

In general, the kinetic data base for NO_x reactions is relatively good. The chemistry of N atoms is not too well defined, but these reactions are only of secondary importance in a consideration of stratospheric chemistry. Independent confirmation of the temperature dependence for the important reaction O₃ + NO is needed. Direct mechanistic information is needed for the reaction OH + HNO₃; its unusually low preexponential factor suggests the possibility of a more complex reaction than simple H-atom abstraction, or possibly other problems.

There are only five reactions involving O(¹D) that are important when considering the chemistry of the upper atmosphere. These are the reactions with N₂ and O₂ (the dominant quenching species), with N₂O (the only source of stratospheric NO), with H₂O (the principal source of OH), and with CF₂O (the principal removal mechanism for CF₂O). The very important branching ratio for the reaction of O(¹D) with N₂O requires further study. Recently reported results are significantly different from earlier results, and indicate a source of NO greater than previously believed. Further studies are needed to confirm the recently reported quenching components in the interaction of O(¹D) with N₂O, H₂O, and CH₄.

There are almost no data on the reactions of HO₂NO₂. Studies of HO₂NO₂ reactions with reactive atmospheric species are needed to understand its role in atmospheric chemistry.

HO_x Reactions

Since the original report (NASA RP-1010), kinetic studies have clarified many areas of uncertainty which existed at that time. Many problems, however, still remain. Very few reactions are known to better than 20% at room temperature, no temperature dependence data are available for several reactions, Arrhenius parameters are unusual for some reactions, and, for some key reactions, results are conflicting.

This latter group contains the reactions

- OH + HO₂ → H₂O + O₂
- HO₂ + HO₂ → H₂O₂ + O₂
- HO₂ + O₃ → OH + 2O₂

which have been and still are *the* major problem of HO_x chemistry. Complex-formation between HO₂ and water vapor (at millibar pressures) has interfered in several HO₂ + HO₂ studies, but is now fairly well characterized. For this reaction, there is preliminary evidence for a very strong negative temperature dependence (E/R = -1245 K), as well as possible pressure dependence. As a further complication, the temperature dependence has been shown to change with pressure. The rate constant recommended here, however, is both pressure and temperature independent because the apparent dependencies are preliminary, unpublished, and not fully understood. Users of the tables presented in this chapter will undoubtedly want to use these temperature and pressure dependencies in calculations. They are cautioned, however, to be careful to include *both* effects and not to exceed the range of values actually encompassed by the data. For example, use of the temperature dependence without the corresponding pressure dependence will lead to anomalously high rate constants at low pressures. The overworked cliché *caveat emptor* has never been more valid than it is here.

The reaction OH + HO₂ also exhibits a possible pressure dependence, based on the discrepancies between low pressure and atmospheric pressure studies. Clearly, a detailed study is needed of the pressure dependence of this reaction by a direct technique.

There is reasonable agreement among the various studies on $\text{HO}_2 + \text{O}_3$, although some discrepancies need to be resolved. In addition, this reaction has unusual Arrhenius parameters, and further experimental and theoretical work is needed to confirm these findings. Curiously, the unusual Arrhenius parameters for this reaction, coupled with the surprisingly strong negative temperature dependence for the $\text{HO}_2 + \text{HO}_2$ reaction, yields a rate constant ratio in excellent agreement with actual measurements of that ratio (see JPL 79-27 and DeMore, 1979). The recent DeMore study is a simplified simulation of a clean, wet atmosphere. Thus, if steady-state O_3 levels in that study are not explained by recommended rate constants, it is probable that the actual atmosphere will also remain unexplained. The recommendations given in this chapter are consistent with DeMore's results, except that a high value (1 to 2×10^{-10}) of $k(\text{OH} + \text{HO}_2)$ is needed. Currently, this reaction is, as it has been in all prior reports, a major uncertainty in stratospheric chemistry.

There are several other HO_x reactions worthy of general note. One is $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ which (except under clean, ideal conditions) exhibits a pressure dependence in non-inert gases, doubling the rate constant at atmospheric pressure. Thus, the recommendation contains a multiplicative factor of $1 + P_{\text{atm}}$ where P_{atm} is the pressure in atmospheres.

The reactions of H_2O_2 with O and OH exhibit unusual Arrhenius behavior, both in absolute value and relative to one another. In view of the difficulties in working with H_2O_2 and the problems mentioned in the Notes in JPL 79-27, additional investigations are needed. A recent room-temperature study of $\text{OH} + \text{H}_2\text{O}_2$ (Harris and Pitts, 1979) agrees very well with the present recommendation, but provides no temperature dependence clarification.

The reaction $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ presents an interesting contrast to the typical situation, viz, the temperature dependence below 300 K is in better agreement than either the temperature dependence above 300 K or the room temperature rate constant. Values of k (298 K) reported by various investigators vary over a wider range than desirable, especially in view of the excellent E/R agreement between these studies. An unexplained anomaly concerning this reaction is revealed in the recent Zahniser and Howard study (Howard, private communication, 1979), yielding a curved Arrhenius plot agreeing with the other studies on E/R below 300 K but showing a significant increase above that temperature. A limited temperature range study by DeMore (1975) agrees very well with their apparent E/R in the overlapped temperature range. However, caution must be used here since the DeMore study was relative to $\text{OH} + \text{CO}$ and it is not entirely clear what the correct temperature behavior of that reference reaction is under his conditions.

Recommendations for some other reactions have been confirmed by recent studies. For the most part, conclusions expressed in JPL 79-27 are unchanged in this report.

Halogen Chemistry

Since the NASA RP-1010 evaluation, there have been many changes in the recommended values for halogen rate coefficients. However, most of the modifications in the important ClO_x rate coefficients, i.e., for the reactions $\text{Cl} + \text{O}_3$, $\text{O} + \text{ClO}$, $\text{Cl} + \text{CH}_4$, $\text{OH} + \text{HCl}$ etc., have been at best relatively minor (less than 10% change in k at stratospheric temperatures), and as such will not significantly affect the output of the photochemical modeling calculations. Some of the most important changes in the ClO_x data base are that experimental data have now become available for $k(\text{Cl} + \text{H}_2\text{CO})$, $k(\text{OH} + \text{ClO})$ and $k(\text{HO}_2 + \text{ClO})$. Inclusion of the $\text{Cl} + \text{H}_2\text{CO}$ reaction has neither seriously affected the predicted photochemical partitioning of ClO_x , nor the predicted ozone perturbation by ClO_x . The $\text{OH} + \text{ClO}$ reaction has only been studied at 298 K, and the product distribution is not quantitatively understood. An upper limit of 35% of the total reaction has been placed on the channel producing $\text{HCl} + \text{O}_2$. However, even if only a few percent of the overall reaction produced $\text{HCl} + \text{O}_2$, it would still be of atmospheric importance. Although the HCl channel would seem to require the reaction to proceed rapidly (approximately $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) via a four-center complex, it

cannot be ruled out. One channel of the $\text{ClO} + \text{ClO}$ and $\text{BrO} + \text{BrO}$ reactions proceeds rapidly by an apparent four-center intermediate. Consequently, additional studies of this reaction are required, with emphasis on the temperature dependence of both the overall rate coefficient and the rate coefficients of the individual reaction channels. The experimental values for $k(\text{ClO} + \text{HO}_2)$ at 298 K are significantly greater (by a factor of 30) than the earlier estimate. In addition, Howard et al. (private communication, 1979) report nonlinear Arrhenius behavior for this reaction, suggesting the possibility of a complex reaction mechanism with one or more sets of reaction products. At present, experimental studies are being performed in order to provide detailed mechanistic information on this reaction. As in the case of the $\text{OH} + \text{ClO}$ reaction, even if only a few percent of the total reaction produces HCl , the $\text{HO}_2 + \text{ClO}$ reaction would be of significant atmospheric importance. Consequently, additional studies of the temperature dependence of this rate coefficient and identification of the reaction products are needed.

Reactions where the rate coefficients have been significantly revised include $k(\text{Cl} + \text{HO}_2)$, $k(\text{Cl} + \text{H}_2\text{O}_2)$, and $k(\text{OH} + \text{CH}_3\text{CCl}_3)$. The last of these has a significant impact on understanding the atmospheric lifetime of CH_3CCl_3 .

There are several other areas in which further studies are required. For example, there is reason to suspect that the reaction $\text{ClO} + \text{NO}_2 + \text{M}$ yields both ClONO_2 and possible isomers such as ClOONO as reported by Chang et al. (1979). This possibility is suggested by the fact that the reaction $\text{Cl} + \text{NO}_2 + \text{M}$ yields both ClNO_2 and ClONO as noted by Niki et al. (1978a). The possibility of multiple pathways for other reactions, particularly the fluorine and bromine analogues of the above, needs consideration.

Two recommendations are made for $\text{ClO} + \text{NO}_2 + \text{M}$ (see table 1-3). The first corresponds to the measured disappearance rate constant for the reactants, and assumes that only ClONO_2 is formed. The second corresponds to the results from the pyrolysis of ClONO_2 and must (assuming a correct equilibrium constant) correspond to formation of only ClONO_2 . If the discrepancy is indeed a result of isomer formation, the total disappearance of ClO and NO_2 in this reaction must be obtained by adding rate constants for each of the pathways at any temperature and pressure. The atmospheric fate of the isomers must also be considered. Consequently, identification of the primary products (as a function of T and P) is required, in addition to further studies of the temperature and pressure dependence of this reaction. More information is required on the detailed degradation mechanisms of species such as CH_3CCl_3 and C_2Cl_4 , to determine whether stable chlorinated compounds other than HCl are formed in the degradation process.

Whereas most of the important ClO_x rate coefficients are quite well established, this is not the case in the BrO_x system. Although many of the BrO_x reactions have been studied since NASA RP-1010, all reactions (except the $\text{NO} + \text{BrO}$ and $\text{Br} + \text{O}_3$ reactions) should be re-examined. The key reactions requiring further examination are: $\text{ClO} + \text{BrO}$, $\text{Br} + \text{HO}_2$, $\text{OH} + \text{HBr}$, $\text{OH} + \text{BrO}$, and $\text{BrO} + \text{NO}_2 + \text{M}$. Reactions such as $\text{Br} + \text{H}_2\text{CO}$ may also be important. In each case, emphasis must be placed not only on determining the pressure and temperature dependence of the rate coefficients, but also on understanding the reaction mechanism, i.e., the relative importance of the reaction channels. There is recent evidence of a synergistic effect between ClO_x and BrO_x leading to an efficient catalytic destruction of ozone through the $\text{BrO} + \text{ClO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2$ reaction.

Although the rate coefficient data base for FO_x reactions is rather poor, it is difficult to identify those reactions which need better understanding in relation to the distribution of fluorine-containing species in the stratosphere. In addition, it is generally assumed that the catalytic efficiency of FO_x for destroying ozone is low, due to both the rapid formation of HF and the unreactivity of this species.

Methane Oxidation

A simplified and therefore incomplete scheme describing the oxidation of methane in the stratosphere is shown in figure 1-1. Most of the reactions shown are evaluated in this chapter. Information on these reactions has been increasing rapidly since the appearance of the NASA RP-1010 evaluation. The recommended values for the rate coefficients of all these reactions have undergone modification, and new reactions have been added. The kinetics of CH_3O and CH_3O_2 radicals have been growing especially rapidly, but the present data base is still relatively poor. This should improve as the result of more laboratory experiments involving direct monitoring of the radical species.

A characteristic of many of the reactions involved in methane oxidation is the possibility of multiple reaction channels. Accordingly, there is a need for mechanistic information to complement the growing data base for rate coefficients. In addition, there may be a significant pressure dependence for some of these reactions, especially those involving the larger free radicals such as CH_3O and CH_3O_2 . Also, there is no assurance that reaction channel ratios for a particular reaction will remain constant for varying pressure or temperature. All of these features emphasize the need for continuing mechanistic, temperature, and pressure studies.

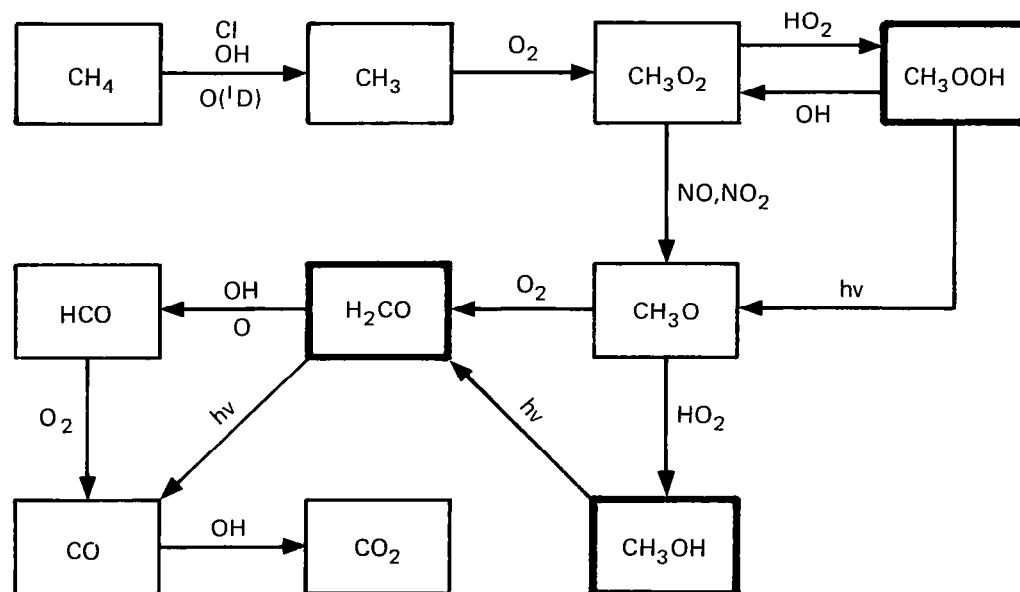


Figure 1-1. Methane oxidation.

SO_x Reactions

The reactions evaluated are for the oxidation of a few simple sulfides which have been observed in the atmosphere and are considered important in the global sulfur cycle.

The reactions of known mechanistic simplicity are characterized by fairly low uncertainties in the Arrhenius parameters. These typically involve simple atom abstraction by either O or OH . For others, however, the

possibility of alternate addition channels has been suggested. Unfortunately, direct mechanistic observations to either support or oppose these hypotheses are lacking, and uncertainties in the rate constants reflect the lack of data. Since it appears that in the 200 to 300 K temperature region, no one reaction path dominates, there is a strong need for quantitative mechanistic measurement as a function of temperature. For the reactions $O + H_2S$, $OH + OCS$, and $OH + CS_2$, these studies should be accompanied by accurate rate constant determinations.

The production of SH as a product in at least two, and possibly four, of the processes opens yet another area of reaction uncertainty. There is at present a paucity of information on the atmospheric fate of the SH radical. Speculation is possible about the fate in the presence of O_2 or O_3 and the similarity (or lack of similarity) of its reactions to those of OH, but there is little direct information upon which to base any conclusions. For this reason, laboratory studies of SH kinetics are also recommended. The reaction of OH with SO_2 is believed to be a primary step in atmospheric aerosol formation, and subsequent reactions of HSO_3 need to be studied.

Third-Order Reactions

The present evaluation uses a somewhat different approach for the presentation of third-order rate constants than NASA RP-1010, which employed either curve-fitted analytical expressions (as for $ClONO_2$ and HNO_3 formation) or otherwise gave only the limiting low-pressure rate constants in the Arrhenius form. Here, the low-pressure rate constants are given in the form:

$$k_o(T) = k_o^{300} (T/300)^{-n} \text{ cm}^6 \text{ s}^{-1} \quad (1)$$

(where the value is suitable for air as the third body), together with the recommended value of n . Where pressure fall-off corrections are necessary, an additional entry gives the limiting high pressure rate constant in a similar form:

$$k_\infty(T) = k_\infty^{300} (T/300)^{-m} \text{ cm}^3 \text{ s}^{-1}. \quad (2)$$

To obtain the effective second-order rate constant for a given condition of temperature and pressure (altitude), the following formula is used: (See JPL 79-27 for a detailed discussion.)

$$k(z) = k(M,T) = \left(\frac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)} \right) 0.6 \left\{ 1 + [\log_{10} (k_o(T)[M]/k_\infty(T))]^2 \right\}^{-1} \quad (3)$$

The number 0.6 which appears in this formula has been changed from the value 0.8 which appears in JPL 79-27. This small change better accommodates the data and is more consistent with theory.

This expression allows the computation of $k(z)$ from the tabulated values of k_o and k_∞ . From the discussion in the Appendix of JPL 79-27 and references cited, it is clear that this formula is an oversimplification of the complex formulae of unimolecular rate theory. As presented, it appears to be a good representation of the sparse amount of relevant data. The adjective *good* is obviously a subjective one, and if the reaction of interest is highly sensitive for a particular calculation, precise and accurate data taken under appropriate conditions must be obtained.

In the case of the important reaction, $HO + NO_2 \xrightarrow{N_2} HNO_3$, the recommended expression fits the pressure and temperature data exactly, within the precision with which they have been obtained.

The representation presented here is a good way to supply information to stratospheric models for many reactions for which the data base is sparse (or even non-existent), and may serve as an indicator of those reactions which deserve high laboratory priorities. One of the best uses of a theoretically based codification-and-extrapolation technique is to indicate where time and effort are *not* necessary.

Photochemical Processes

A number of problem areas remain in UV cross-section measurements, as well as in the determination of quantum yields and identities of products for several photochemical processes.

There is a large discrepancy between the theoretical calculations of HOCl absorption cross sections (which indicate negligible absorption beyond 300 nm) and the experimental results; the reason for this is not known. More experiments should be carried out, if possible, using an HOCl source other than gas-phase hydrolysis of Cl_2O . The recommendation is to adopt the experimental results which indicate that HOCl will photodissociate quite rapidly in the stratosphere (lifetime of about one hour).

The quantum yields for production of $\text{O}(^1\text{D})$ in the photolysis of ozone as a function of wavelength are now reasonably well established, but there are still conflicting laboratory results on the extent of $\text{O}(^3\text{P})$ formation from photolysis at shorter wavelengths in the Hartley band.

There are conflicting reports on the identity of the primary photodissociation products of ClONO_2 , and further work is necessary. Also, the products of BrONO_2 photolysis should be determined and the UV spectra of FONO_2 and of HOBr characterized. In fact, the identity of HOBr in the gas phase is yet to be established. The quantum yields for photodissociation and the identity of the products in the photolysis of N_2O_5 , CF_2O and CFCIO are yet to be determined.

SUMMARY OF DATA RECOMMENDATIONS

Basis of the Recommendations

As in the NASA RP-1010 report, the recommended rate constants and cross sections are based wherever possible on laboratory measurements, and in general only published data are considered. (Occasional exceptions are made when preprints of articles submitted for publication are available to the panel.) However, the panel does consider the question of consistency of data with expectations based on theory, and in cases where a discrepancy appears to exist, this fact is taken into account. The major use of theoretical extrapolation of data is in connection with three-body reactions in which the required pressure dependences are sometimes unavailable from laboratory measurements and can be estimated by use of appropriate theoretical treatment. In the case of a few important rate constants for which no experimental data are available (for example, $\text{OH} + \text{HOCl} \rightarrow \text{H}_2\text{O} + \text{ClO}$), the panel has provided estimates of rate constant parameters based on analogy to similar reactions for which data are available.

Format

The rate constant tabulations for second-order reactions in table 1-2 give the following information:

- Reaction stoichiometry and products (if known).
- Arrhenius A-factor defined by the equation $k = Ae^{-E/RT}$.
- Temperature dependence and associated uncertainty (*activation temperature*, $E/R \pm \Delta E/R$).
- Rate constant at 298 K.
- Uncertainty factor at 298 K.

Rate constant recommendations which have been changed since the previous panel evaluation, JPL 79-27, or for which there is other new information are indicated by an asterisk, and new entries to the table which were not on the previous list are designated by a dagger. Both of these reaction types are accompanied by a note at the end of the table, explaining the basis for the new evaluation. *Only those reactions for which the recommendation has changed, or which are new entries, are annotated*—the reader is requested to consult the previous tabulation (JPL 79-27) to obtain the complete explanatory notes for the entries in this table.

Rate constant parameters for third-order reactions are listed in table 1-3. Where necessary for atmospheric applications, pressure fall-off parameters are given and may be used as previously discussed.

Photochemical cross sections of species of stratospheric interest are also presented in tabular form. Table 1-4 is a summary list of photochemical processes which are important in the stratosphere. Table 1-5 gives recommended reliability factors for some of the more important reactions. Except as noted, these factors refer to total dissociation rate regardless of product identity. For completeness, all previous entries are reproduced in tables 1-6 to 1-31.

Error Estimates

In the previous evaluation (NASA RP-1010), rate constant uncertainties were expressed in the form of $\Delta \log k(230 \text{ K})$, i.e. upper and lower bounds (corresponding approximately to one standard deviation) of the rate constant at 230 K could be obtained by multiplying or dividing the central value by the factor:

$$f = 10^{(\Delta \log k)} \quad (4)$$

However, that approach had drawbacks in certain cases, particularly where the rate constant was measured only at room temperature, or was known with much greater accuracy at room temperature than at other temperatures. Also, that approach gave no information as to the uncertainty at other temperatures.

In the present report, a somewhat different method of error estimation is used. Uncertainty factors, f_{298} , are given for the rate constant at 298 K, and these are analogous to the previous factors given at 230 K. A satisfactory estimate of the uncertainty at temperatures below 298 K may be obtained from the following expression:

$$f_t = f_{298} \exp \left\{ \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right\} \quad (5)$$

Units

The rate constants are given in units of concentration expressed as molecules per cubic centimeter and time in seconds. Thus, for first-, second-, and third-order reactions the units of k are s^{-1} , $\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$, and $\text{cm}^6 \text{ molecule}^{-2} \text{s}^{-1}$, respectively.

The absorption cross sections are defined by the following expression of Beer's Law:

$$I = I_0 \exp(-\sigma n l), \quad (6)$$

where: I_0 , I are the incident and transmitted light intensity, respectively; σ is the absorption cross section in $\text{cm}^2 \text{ molecule}^{-1}$; n is the concentration in molecule cm^{-3} ; and l is the pathlength in cm.

Table 1-2
Summary of Recommended Rate Constants

Reaction	A-Factor	E/R $\pm \Delta$ (E/R)	k(298K)	Uncertainty Factor (298K)	Notes
$O + O_2 \xrightarrow{M} O_3$	(See Table 1-3)	2218 $\pm$ 150	8.8×10^{-15}	1.15	1
$O + O_3 \rightarrow O_2 + O_2$	1.5×10^{-11}	1450 $\pm$ 200	1.8×10^{-14}	1.2	1
$O_3 + NO \xrightarrow{M} NO_2 + O_2$	2.3×10^{-12}				1
$OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 1-3)	⁺⁰ 0 -150	9.3×10^{-12}	1.1	1
$O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}	—	$< 3.0 \times 10^{-17}$	—	2
$^{\dagger}O + HNO_3 \rightarrow OH + NO_3$	—	—	1.0×10^{-15}	5.0	3
$^{\dagger}O + HO_2NO_2 \rightarrow$ products	—	—	8.9×10^{-17}	1.25	1
$N + O_2 \rightarrow NO + O$	4.4×10^{-12}	3220 $\pm$ 340			1
$N + NO \rightarrow N_2 + O$	3.4×10^{-11}	0 $\pm$ 100	3.4×10^{-11}	1.4	1
$OH + HNO_3 \rightarrow$ products	8.5×10^{-14}	0 $\pm$ 100	8.5×10^{-14}	1.25	1
$^{\dagger}OH + HO_2NO_2 \rightarrow$ products			5.0×10^{-13}	10.0	4
$N + NO_2 \rightarrow N_2O + O$	2.1×10^{-11}	800 $\pm$ 350	1.4×10^{-12}	1.25	1
$N + O_3 \rightarrow NO + O_2$	—	—	$< 1.0 \times 10^{-15}$	—	1
$NO_2 + O_3 \xrightarrow{M} NO_3 + O_2$	1.2×10^{-13}	2450 $\pm$ 140	3.2×10^{-17}	1.15	1
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 1-3)				1
$^{\dagger}NO + NO_3 \rightarrow 2NO_2$	—	—			5
$*O(^1D) + N_2O \rightarrow N_2 + O_2$	4.8×10^{-11}	0 $\pm$ 50	2.0×10^{-11}	3.0	6
$*O(^1D) + N_2O \rightarrow NO + NO$	6.2×10^{-11}	0 $\pm$ 50	4.8×10^{-11}	1.5	6
$O(^1D) + H_2O \rightarrow OH + OH$	2.3×10^{-10}	0 $\pm$ 50	6.2×10^{-11}	1.5	6
$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.3×10^{-10}	0 $\pm$ 50	2.3×10^{-10}	1.3	6
$O(^1D) + CH_4 \rightarrow H_2 + CH_2O$	1.4×10^{-11}	0 $\pm$ 50	1.3×10^{-10}	1.3	6
			1.4×10^{-11}	1.3	6

*Indicates a change from the previous Panel evaluation (JPL 79-27) or a change in the note.

[†]Indicates a new entry that was not in the previous evaluation.

Table 1-2 (Continued)

Reaction	A-Factor	E/R $\pm \Delta$ (E/R)	k(298K)	Uncertainty Factor (298K)	Notes
$O(^1D) + H_2 \rightarrow OH + H$	9.9×10^{-11}	0 ± 50	9.9×10^{-11}	1.3	6
$O(^1D) + N_2 \rightarrow O + N_2$	2.0×10^{-11}	$-(107 \pm 50)$	2.9×10^{-11}	1.3	6
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(See Table 1-3)				6
$O(^1D) + O_2 \rightarrow O + O_2$	2.9×10^{-11}	$-(67 \pm 50)$	3.6×10^{-11}	1.3	6
$O(^1D) + O_3 \rightarrow O_2 + O_2$	1.2×10^{-10}	0 ± 50	1.2×10^{-10}	1.3	6
$O(^1D) + O_3 \rightarrow O_2 + O + O$	1.2×10^{-10}	0 ± 50	1.2×10^{-10}	1.3	6
$O(^1D) + HCl \rightarrow OH + Cl$	1.4×10^{-10}	0 ± 50	1.4×10^{-10}	1.3	6
$O(^1D) + CFCl_3 \rightarrow \text{products}$	2.2×10^{-10}	0 ± 50	2.2×10^{-10}	1.3	6
$O(^1D) + CF_2Cl_2 \rightarrow \text{products}$	1.4×10^{-10}	0 ± 50	1.4×10^{-10}	1.3	6
$O(^1D) + CCl_2O \rightarrow \text{products}$	3.6×10^{-10}	0 ± 50	3.6×10^{-10}	1.4	6
$O(^1D) + CFClO \rightarrow \text{products}$	1.9×10^{-10}	0 ± 50	1.9×10^{-10}	1.4	6
$O(^1D) + CF_2O \rightarrow \text{products}$	2.3×10^{-10}	0 ± 50	2.3×10^{-10}	1.4	6
$O(^1D) + NH_3 \rightarrow OH + NH_2$	2.5×10^{-10}	0 ± 50	2.5×10^{-10}	1.3	6
$O(^1D) + CO_2 \rightarrow O + CO_2$	6.8×10^{-11}	$-(117 \pm 50)$	1.0×10^{-10}	1.3	6
$O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0 ± 150	1.0×10^{-11}	1.6	1
$O + N_2O_5 \rightarrow \text{products}$	—	—	$< 3.0 \times 10^{-16}$	—	1
$O_3 + HNO_2 \rightarrow O_2 + HNO_3$	—	—	$< 5.0 \times 10^{-19}$	—	1
$*OH + HO_2 \rightarrow H_2O + O_2$	4.0×10^{-11}	0 ± 250	4.0×10^{-11}	2.0	7
$*HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.5×10^{-12}	$0 + 0, -1245$	2.5×10^{-12}	2.0	8
$*NO + HO_2 \rightarrow NO_2 + OH$	4.3×10^{-12}	$-(200 \pm 200)$	8.4×10^{-12}	1.2	9
$*HO_2 + O_3 \rightarrow OH + 2O_2$	1.1×10^{-14}	$580 + 500$ $- 100$	1.6×10^{-15}	1.4	10

*Indicates a change from the previous Panel evaluation (JPL 79-27) or a change in the note.

†Indicates a new entry that was not in the previous evaluation.

Table 1-2 (Continued)

Reaction	A-Factor	E/R $\pm \Delta$ (E/R)	k (298K)	Uncertainty Factor (298K)	Notes
*OH + O ₃ → HO ₂ + O ₂	1.6 × 10 ⁻¹²	940 ± 300	6.8 × 10 ⁻¹⁴	1.25	11
O + OH → O ₂ + H	4.0 × 10 ⁻¹¹	0 ± 300	4.0 × 10 ⁻¹¹	1.5	1
O + HO ₂ → OH + O ₂	3.5 × 10 ⁻¹¹	0 ± 350	3.5 × 10 ⁻¹¹	1.5	1
O + H ₂ O ₂ → OH + HO ₂	2.8 × 10 ⁻¹²	2125 ± 400	2.2 × 10 ⁻¹⁵	1.4	1
H + O ₂ $\xrightarrow{M}$ HO ₂	(See Table 1-3)				1
*H + O ₃ → OH + O ₂	1.4 × 10 ⁻¹⁰	470 ± 200	2.9 × 10 ⁻¹¹	1.25	12
OH + OH → H ₂ O + O	1.0 × 10 ⁻¹¹	500 ± 400	1.9 × 10 ⁻¹²	1.25	1
OH + OH $\xrightarrow{M}$ H ₂ O ₂	(See Table 1-3)				1
*OH + H ₂ O ₂ → H ₂ O + HO ₂	1.0 × 10 ⁻¹¹	750 ± 350	8.1 × 10 ⁻¹³	2.0	13
OH + CO → CO ₂ + H	1.35 × 10 ⁻¹³ (1 + P _{atm})	0 ± 200	1.35 × 10 ⁻¹³ (1 + P _{atm})	1.25	1
OH + CH ₄ → CH ₃ + H ₂ O	2.4 × 10 ⁻¹²	1710 ± 200	7.7 × 10 ⁻¹⁵	1.2	1
OH + H ₂ → H ₂ O + H	1.2 × 10 ⁻¹¹	2200 ± 200	7.5 × 10 ⁻¹⁵	1.2	1
Cl + O ₃ → ClO + O ₂	2.8 × 10 ⁻¹¹	257 ± 100	1.2 × 10 ⁻¹¹	1.15	1
O + ClO → Cl + O ₂	7.7 × 10 ⁻¹¹	130 ± 130	5.0 × 10 ⁻¹¹	1.2	1
NO + ClO → NO ₂ + Cl	7.8 × 10 ⁻¹²	-(250 ± 100)	1.8 × 10 ⁻¹¹	1.25	1
OH + HCl → H ₂ O + Cl	2.8 × 10 ⁻¹²	425 ± 100	6.6 × 10 ⁻¹³	1.15	
OH + HOCl → H ₂ O + ClO	3.0 × 10 ⁻¹²	800 ± 500	2.0 × 10 ⁻¹³	10.0	1
Cl + CH ₄ → HCl + CH ₃	9.9 × 10 ⁻¹²	1359 ± 150	1.0 × 10 ⁻¹³	1.15	1
Cl + HO ₂ → HCl + O ₂	4.5 × 10 ⁻¹¹	0 ± 250	4.5 × 10 ⁻¹¹	1.6	1
ClO + NO ₂ $\xrightarrow{M}$ ClONO ₂	(See Table 1-3)				
O + ClONO ₂ → products	3.0 × 10 ⁻¹²	808 ± 200	2.0 × 10 ⁻¹³	1.5	1

*Indicates a change from the previous Panel evaluation (JPL 79-27) or a change in the note.

†Indicates a new entry that was not in the previous evaluation.

Table 1-2 (Continued)

Reaction	A-Factor	E/R $\pm \Delta$ (E/R)	k(298K)	Uncertainty Factor (298K)	Notes
OH + ClONO ₂ → products	1.2 × 10 ⁻¹²	333 ± 200	3.9 × 10 ⁻¹³	1.5	1
Cl + ClONO ₂ → products	1.7 × 10 ⁻¹²	607 ± 388	2.2 × 10 ⁻¹³	2.0	1
O + HCl → OH + Cl	1.14 × 10 ⁻¹¹	3370 ± 350	1.4 × 10 ⁻¹⁶	2.0	1
O + HOC1 → OH + ClO	1.0 × 10 ⁻¹¹	2200 ± 800	6.0 × 10 ⁻¹⁵	10.0	1
*Cl + H ₂ → HCl + H	3.5 × 10 ⁻¹¹	2290 ± 200	1.6 × 10 ⁻¹⁴	1.5	29
*Cl + H ₂ O ₂ → HCl + HO ₂	1.1 × 10 ⁻¹¹	980 ± 500	4.0 × 10 ⁻¹³	1.5	14
Cl + HNO ₃ → HCl + NO ₃	≤ 1.0 × 10 ⁻¹¹	+ 2500, 2170 - 500	≤ 7.0 × 10 ⁻¹⁵	+2.0, -300	1
Cl + H ₂ CO → HCl + HCO	9.2 × 10 ⁻¹¹	68 ± 100	7.3 × 10 ⁻¹¹	1.15	1
Cl + CH ₃ Cl → CH ₂ Cl + HCl	3.4 × 10 ⁻¹¹	1256 ± 200	4.9 × 10 ⁻¹³	1.2	1
Cl + NO $\xrightarrow{M}$ NOCl	(See Table 1-3)				
Cl + ClNO → NO + Cl ₂	3.0 × 10 ⁻¹¹	0 + 500, -250	3.0 × 10 ⁻¹¹	2.0	1
Cl + O ₂ $\xrightarrow{M}$ ClOO	(See Table 1-3)				—
ClOO $\xrightarrow{M}$ Cl + O ₂	2.7 × 10 ⁻⁹	2650 ± 800	3.7 × 10 ⁻¹³	7.0	1
*Cl + ClOO → Cl ₂ + O ₂	1.0 × 10 ⁻¹⁰	0 ± 250	1.0 × 10 ⁻¹⁰	3.0	29
Cl + ClOO → ClO + ClO	5.0 × 10 ⁻¹²	0 ± 250	5.0 × 10 ⁻¹²	3.0	1
*ClO + HO ₂ → HOCl + O ₂	—	—	5.2 × 10 ⁻¹²	1.5	15
†ClO + OH → products	—	—	9.1 × 10 ⁻¹²	1.4	16
ClO + CH ₄ → products	≤ 1.0 × 10 ⁻¹²	≥ 3700	≤ 4.0 × 10 ⁻¹⁸	—	1
ClO + H ₂ → products	≤ 1.0 × 10 ⁻¹²	≥ 4800	≤ 1.0 × 10 ⁻¹⁹	—	1
ClO + CO → products	≤ 1.0 × 10 ⁻¹²	≥ 3700	≤ 4.0 × 10 ⁻¹⁸	—	1
ClO + N ₂ O → products	≤ 1.0 × 10 ⁻¹²	≥ 4260	≤ 6.0 × 10 ⁻¹⁹	—	1

*Indicates a change from the previous Panel evaluation (JPL 79-27) or a change in the note.

†Indicates a new entry that was not in the previous evaluation.

Table 1-2 (Continued)

Reaction	A-Factor	E/R $\pm \Delta$ (E/R)	k(298K)	Uncertainty Factor (298K)	Notes
ClO + BrO $\rightarrow$ Br + OClO	6.7×10^{-12}	0 ± 250	6.7×10^{-12}	1.5	1
ClO + BrO $\rightarrow$ Br + Cl + O ₂	6.7×10^{-12}	0 ± 250	6.7×10^{-12}	1.5	1
ClO + ClO $\rightarrow$ Cl + ClOO	—	—	—	—	1
ClO + ClO $\rightarrow$ Cl ₂ + O ₂	—	—	—	—	1
ClO + ClO $\xrightarrow{M}$ Cl ₂ + O ₂	—	—	—	—	1
ClO + O ₃ $\rightarrow$ ClOO + O ₂	1.0×10^{-12}	≥ 4000	$< 1.0 \times 10^{-18}$	—	1
ClO + O ₃ $\rightarrow$ OClO + O ₂	1.0×10^{-12}	≥ 4000	$< 1.0 \times 10^{-18}$	—	1
Cl + OClO $\rightarrow$ ClO + ClO	5.9×10^{-11}	0 ± 250	5.9×10^{-11}	1.25	1
NO + OClO $\rightarrow$ NO ₂ + ClO	2.5×10^{-12}	600 ± 300	3.4×10^{-13}	1.5	1
O + OClO $\rightarrow$ ClO + O ₂	2.5×10^{-11}	1166 ± 300	5.0×10^{-13}	1.5	1
OH + CH ₃ Cl $\rightarrow$ CH ₂ Cl + H ₂ O	2.2×10^{-12}	1142 ± 200	4.8×10^{-14}	1.25	1
OH + CH ₂ Cl ₂ $\rightarrow$ CHCl ₂ + H ₂ O	5.5×10^{-12}	1094 ± 200	1.4×10^{-13}	1.25	1
OH + CHCl ₃ $\rightarrow$ CCl ₃ + H ₂ O	4.7×10^{-12}	1134 ± 200	1.0×10^{-13}	1.25	1
OH + CHFCl ₂ $\rightarrow$ CFCl ₂ + H ₂ O	1.5×10^{-12}	1184 ± 200	2.8×10^{-14}	1.3	1
OH + CHF ₂ Cl $\rightarrow$ CF ₂ Cl + H ₂ O	1.2×10^{-12}	1666 ± 200	4.5×10^{-15}	1.25	1
OH + CH ₂ ClF $\rightarrow$ CHClF + H ₂ O	3.5×10^{-12}	1322 ± 150	4.0×10^{-14}	1.25	1
*OH + CH ₃ CCl ₃ $\rightarrow$ CH ₂ CCl ₃ + H ₂ O	5.4×10^{-12}	1820 ± 200	1.2×10^{-14}	1.3	17
OH + C ₂ Cl ₄ $\rightarrow$ products	9.4×10^{-12}	1199 ± 200	1.7×10^{-13}	1.25	1
OH + C ₂ HCl ₃ $\rightarrow$ products	5.0×10^{-13}	$-(445 \pm 200)$	2.2×10^{-12}	1.25	1
OH + CFCl ₃ $\rightarrow$ products	1.0×10^{-12}	> 3650	$< 5.0 \times 10^{-18}$	—	1
OH + CF ₂ Cl ₂ $\rightarrow$ products	1.0×10^{-12}	> 3560	$< 6.5 \times 10^{-18}$	—	1

* Indicates a change from the previous Panel evaluation (JPL 79-27) or a change in the note.

† Indicates a new entry that was not in the previous evaluation.

Table 1-2 (Continued)

Reaction	A-Factor	E/R $\pm \Delta$ (E/R)	k(298K)	Uncertainty Factor (298K)	Notes
$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	1.4×10^{-11}	755 ± 200	1.12×10^{-12}	1.2	1
$\text{O} + \text{BrO} \rightarrow \text{Br} + \text{O}_2$	3.0×10^{-11}	0 ± 250	3.0×10^{-11}	3.0	1
$\text{BrO} + \text{NO} \rightarrow \text{NO}_2 + \text{Br}$	8.7×10^{-12}	$-(265 \pm 130)$	2.1×10^{-11}	1.15	1
$\text{BrO} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrONO}_2$	(See Table 1-3)				
$*\text{BrO} + \text{BrO} \rightarrow 2 \text{Br} + \text{O}_2$	1.0×10^{-12}	$-(244 \pm 150)$	2.3×10^{-12}	1.25	30
$*\text{BrO} + \text{BrO} \rightarrow \text{Br}_2 + \text{O}_2$	1.8×10^{-13}	$-(244 \pm 150)$	4.0×10^{-13}	1.25	30
$\text{BrO} + \text{O}_3 \rightarrow \text{Br} + 2 \text{O}_2$	1.0×10^{-12}	> 1600	$< 5.0 \times 10^{-15}$	+3; - ?	1
$\text{Br} + \text{H}_2\text{O}_2 \rightarrow \text{HBr} + \text{HO}_2$	2.0×10^{-12}	> 1400	$< 2.0 \times 10^{-14}$	+2; - 50	1
$\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$	2.0×10^{-11}	0 ± 250	2.0×10^{-11}	3.0	1
$\text{OH} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$	8.5×10^{-12}	0 ± 250	8.5×10^{-12}	2.0	1
$\text{O} + \text{HBr} \rightarrow \text{OH} + \text{Br}$	7.6×10^{-12}	1571 ± 300	3.9×10^{-14}	1.5	1
$*\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2$	—	—	5.0×10^{-12}	5.0	18
$\dagger \text{BrO} + \text{OH} \rightarrow \text{products}$	—	—	9.0×10^{-12}	5.0	19
$\text{OH} + \text{CH}_3\text{Br} \rightarrow \text{CH}_2\text{Br} + \text{H}_2\text{O}$	7.9×10^{-13}	889 ± 200	3.8×10^{-14}	1.25	1
$\text{F} + \text{O}_3 \rightarrow \text{FO} + \text{O}_2$	2.8×10^{-11}	226 ± 200	1.3×10^{-11}	2.0	1
$\text{F} + \text{O}_2 \xrightarrow{\text{M}} \text{FO}_2$	(See Table 1-3)				1
$\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$	2.0×10^{-10}	620 ± 250	2.5×10^{-11}	1.5	1
$\text{F} + \text{CH}_4 \rightarrow \text{HF} + \text{CH}_3$	3.0×10^{-10}	400 ± 300	8.0×10^{-11}	2.0	1
$\text{F} + \text{H}_2\text{O} \rightarrow \text{HF} + \text{OH}$	2.2×10^{-11}	200 ± 200	1.1×10^{-11}	5.0	1
$\text{O} + \text{FO} \rightarrow \text{F} + \text{O}_2$	5.0×10^{-11}	0 ± 250	5.0×10^{-11}	3.0	1
$\text{NO} + \text{FO} \rightarrow \text{NO}_2 + \text{F}$	2.0×10^{-11}	0 ± 250	2.0×10^{-11}	3.0	1

*Indicates a change from the previous Panel evaluation (JPL 79-27) or a change in the note.

 $\dagger$ Indicates a new entry that was not in the previous evaluation.

Table 1-2 (Continued)

Reaction	A-Factor	E/R $\pm \Delta$ (E/R)	k (298K)	Uncertainty Factor (298K)	Notes
FO + FO $\rightarrow$ 2 F + O ₂	1.5 $\times 10^{-11}$	0 $\pm$ 250	1.5 $\times 10^{-11}$	3.0	1
FO + O ₃ $\rightarrow$ F + 2 O ₂	—	—	—	—	1
FO + O ₃ $\rightarrow$ FO ₂ + O ₂	—	—	—	—	1
O + FO ₂ $\rightarrow$ FO + O ₂	5.0 $\times 10^{-11}$	0 $\pm$ 250	5.0 $\times 10^{-11}$	5.0	1
O(¹ D) + HF $\rightarrow$ OH + F	1.0 $\times 10^{-10}$	0 $\pm$ 100	1.0 $\times 10^{-10}$	3.0	1
CH ₃ + O ₂ $\xrightarrow{M}$ CH ₃ O ₂	(See Table 1-3)				1
[†] CH ₃ + O $\rightarrow$ H ₂ CO + H	1.0 $\times 10^{-10}$	0 $\pm$ 250	1.0 $\times 10^{-10}$	1.4	20
*CH ₃ O ₂ + NO $\rightarrow$ CH ₃ O + NO ₂	7.0 $\times 10^{-12}$	0 $\pm$ 500	7.0 $\times 10^{-12}$	3.0	21
CH ₃ O ₂ + NO ₂ $\xrightarrow{M}$ CH ₃ O ₂ NO ₂	(See Table 1-3)				1
*CH ₃ O ₂ + HO ₂ $\rightarrow$ CH ₃ OOH + O ₂	—	—	6.0 $\times 10^{-12}$	3.0	22
*CH ₃ O + O ₂ $\rightarrow$ H ₂ CO + HO ₂	5.0 $\times 10^{-13}$	2000 $\pm$ 750	6.1 $\times 10^{-16}$	2.0	23
*OH + H ₂ CO $\rightarrow$ HCO + H ₂ O	1.0 $\times 10^{-11}$	0 $\pm$ 200	1.0 $\times 10^{-11}$	1.25	24
*O + H ₂ CO $\rightarrow$ products	3.2 $\times 10^{-11}$	1550 $\pm$ 250	1.6 $\times 10^{-13}$	1.25	25
HCO + O ₂ $\rightarrow$ CO + HO ₂	5.0 $\times 10^{-12}$	0 $\pm$ 250	5.0 $\times 10^{-12}$	1.4	1
*OH + CH ₃ OOH $\rightarrow$ products	1.0 $\times 10^{-11}$	750 $\pm$ 350	8.0 $\times 10^{-13}$	5.0	26
*O + H ₂ S $\rightarrow$ OH + SH	2.6 $\times 10^{-11}$	2170 $\pm$ 750	1.8 $\times 10^{-14}$	2.0	27
O + OCS $\rightarrow$ CO + SO	2.1 $\times 10^{-11}$	2200 $\pm$ 150	1.3 $\times 10^{-14}$	1.12	1
O + CS ₂ $\rightarrow$ CS + SO	3.1 $\times 10^{-11}$	640 $\pm$ 150	3.6 $\times 10^{-12}$	1.12	1
OH + H ₂ S $\rightarrow$ SH + H ₂ O	1.1 $\times 10^{-11}$	220 $\pm$ 220	5.3 $\times 10^{-12}$	1.25	1
*OH + OCS $\rightarrow$ products	—	—	5.6 $\times 10^{-14}$	2.0	28
*OH + CS ₂ $\rightarrow$ products	—	—	1.9 $\times 10^{-13}$	2.0	28

*Indicates a change from the previous Panel evaluation (JPL 79-27) or a change in the note.

[†]Indicates a new entry that was not in the previous evaluation.

Notes for Table 1-2

- 1 These entries have not been changed since the previous evaluation (JPL 79-27). Notes giving the basis for these recommendations may be found in this reference.
- 2 Accepts the upper limit reported by Chapman and Wayne (1974).
- 3 Preliminary value of Trevor, Chang, Barker, Chang, (private communication, 1979).
- 4 Estimated by analogy with the reaction $\text{OH} + \text{H}_2\text{O}_2$. This value is consistent with the upper limit of 3×10^{-10} reported by Graham, Winer, and Pitts (1978a).
- 5 Value reported by Graham and Johnston (1978).
- 6 Reactions of $\text{O}(^1\text{D})$. The recommendations adopt the time-resolved $\text{O}(^1\text{D})$ emission measurements at the National Oceanic and Atmospheric Administration (NOAA) Laboratories for the reactions with N_2O , H_2O , CH_4 , H_2 , N_2 , O_2 , O_3 , HCl , CFCl_3 , CF_2Cl_2 , NH_3 , and CO_2 (Streit et al., 1976; Davidson et al., 1977a; and Davidson et al., 1978).

Rate constants for all the above reactions (except the reactions with HCl) have also been measured at the Cambridge Laboratory by Heidner and Husain (1973); Heidner, Husain, and Wiesenfeld (1973); and Fletcher and Husain (1976a, 1976b). These results were based on time resolved $\text{O}(^1\text{D})$ resonance absorption measurements. Data analysis uses the modified Lambert-Beer law $I_t/I_o = \exp(-\sigma(nl)\gamma)$ where $\gamma = 0.41$.

The analysis of the latter results is less straightforward than that of the time resolved emission measurements because an independent calibration of the value of γ is required. Additionally, the results from the NOAA Laboratories for H_2O , CH_4 , N_2 , O_2 , O_3 , and CO_2 have been confirmed very recently by a completely independent technique, (Amimoto et al., 1978, 1979), although in this same study, the value for N_2O is 40% higher than the result from the NOAA Laboratory. These same studies report significant quenching components in the reactions with N_2O , H_2O , and CH_4 . Further studies are needed to confirm this result. New studies of $\text{O}(^1\text{D})$ reactions with O_2 and H_2O have been reported by Lee and Slinger (1978 and 1979). These values are in good agreement with the results recommended here.

The branching ratio for the reaction of $\text{O}(^1\text{D})$ with N_2O to give $\text{N}_2 + \text{O}_2$ or $\text{NO} + \text{NO}$ is an average of the values reported by Davidson et al. (1979); Pirkle et al. (1977); and the very recent result of Marx et al. (1979). This latest result is significantly different from the earlier results. Further study is needed.

The branching ratio for reaction of $\text{O}(^1\text{D})$ with CH_4 to give $\text{OH} + \text{CH}_3$ or $\text{H}_2 + \text{CH}_2\text{O}$ is from Lin and DeMore (1973). The branching ratio for reaction of $\text{O}(^1\text{D})$ with O_3 to give $\text{O}_2 + \text{O}_2$ or $\text{O}_2 + \text{O} + \text{O}$ is from Davenport et al. (1974).

For the reactions of $\text{O}(^1\text{D})$ with CCl_2O , CFCIO and CF_2O , rate constants are reported only by the Cambridge Laboratory by Fletcher and Husain (1978). Thus, for consistency, the recommended values for these rate constants were derived using a scaling procedure. This procedure preserves the relative placement of these rate constants among the set of Cambridge Laboratory data but employs an average ratio (0.50) of the NOAA to Cambridge Laboratory rate constants for those reactions studied by both groups. These reactions have been studied only at 298 K. Based on consideration of similar $\text{O}(^1\text{D})$ reactions, it is assumed that E/R equals zero, and therefore the value shown for the A-factor has been set equal to $k(298 \text{ K})$.

The chlorocarbon rate constants are for total disappearance of $O(^1D)$ and probably include physical quenching. Lower limits have been reported for the fraction of the total rate of disappearance of $O(^1D)$ proceeding through the reactive channel forming ClO for $CFCl_3$ (≥ 0.39) and CF_2Cl_2 (≥ 0.49) by Gillespie et al. (1977). It is not possible to give corresponding values for the reaction $O(^1D)$ with CCl_2O and $CFCIO$.

There are significant changes from the recommendations given in NASA RP-1010 for the values of the rate constants for the reactions of $O(^1D)$ with CF_2Cl_2 , CCl_2O , $CFCIO$, and CF_2O , since the studies upon which the present recommendations are based did not exist at the time of the previous evaluation. There are changes in the values recommended for each of the reactive channels with N_2O based on new measurements of the branching ratio.

Because there are two disparate sets of data and that the recommendations are based primarily on one of these, the error limits cited (1σ) are somewhat larger than reported in the NOAA studies.

- 7 The recommended value is derived from the upper limit of Chang and Kaufman (1978), the measurement of Hack et al. (1978), and the ratio measurement (relative to $OH + H_2O_2$) by Burrows et al. (1977), and is within the experimental accuracy of all three studies, although it is not compatible with the value of 1 to 2×10^{-10} derived from rate constant ratios in steady state O_3 photolysis experiments by DeMore and Tschuikow-Roux (1974) and DeMore (1979).
- 8 This is the room temperature value of Hamilton and Lii (1977) and Cox (1978). Both studies found the rate constant to be sensitive to the presence of water vapor (at the millibar level). There is preliminary evidence in the Cox study for a very strong negative temperature dependence ($E/R = -1245$ K), although the data are very limited. However, there is evidence that the strong temperature dependence is not present at lower pressures. Thus, for the time being, $E/R = 0$, with a lower uncertainty bound of -1245 K is recommended. Preliminary evidence of a pressure dependence by Burrows et al. (1978) and Cox (1978), would, if confirmed, require a further change in the recommendation. Recent measurements of the relevant rate-constant ratios in a study by DeMore (1979) are consistent with both the water vapor and temperature effects cited by Cox.
- 9 The recommendation is based on Zahniser and Howard (private communication) and Leu (1979), and the room temperature determinations of Margitan and Anderson (1978) and Kaufman and Riemann (1978), and the ratio determination by Burrows et al. (1978) relative to $OH + H_2O_2$. The agreement is excellent.
- 10 Recent rate-constant ratio measurements by DeMore (1979) are consistent with the previous recommendation for this reaction.
- 11 A recent determination by Zahniser and Howard (private communication, 1979) is in excellent agreement with the recommendation below room temperature. Their measured rate constants also agree very well with the recommended values at higher temperatures, although their data indicates a curved Arrhenius plot over the entire temperature range.
- 12 Recent results by Finlayson-Pitts and Kleindienst (1979) agree well with the present recommendation although their results indicate a second reaction channel to give $HO_2 + O$ ($\sim 25\%$). Confirmation is needed.
- 13 Harris and Pitts (1979) confirm the room temperature recommendation. However, preliminary data by Keyser (private communication, 1979) is about a factor of two higher. This reaction clearly requires additional work, especially on the temperature dependence.

- 14 This revised value is based on the Arrhenius expression reported by Keyser (private communication, 1979). The A-factor reported by Michael et al. (1977) is considerably lower than expected from theoretical considerations and may possibly be attributed to decomposition of H_2O_2 at temperatures above 300 K. The data of Michael et al. at and below 300 K are in good agreement with the Arrhenius expression reported by Keyser. More data are required before the Arrhenius parameters can be considered to be well-established.
- 15 The preferred value at 298 K was obtained by taking a simple mean of the results reported by Howard et al. (private communication, 1979); Birks and Leck (private communication, 1979); and Reimann and Kaufman (1978). No recommendation is given for the temperature dependence of this reaction. Howard et al. have reported that the reaction exhibits nonlinear Arrhenius behavior, with the rate constant increasing as temperature decreases. The magnitude of the temperature dependence below 300 K is similar to that reported by Cox et al. (1978) for $\text{HO}_2 + \text{HO}_2$.
- 16 Value reported by Leu and Lin (1979). A lower limit of 0.65 was determined for $k_1(\text{OH} + \text{ClO} \rightarrow \text{HO}_2 + \text{Cl}) / k(\text{OH} + \text{ClO} \rightarrow \text{products})$ at 298 K. The actual value of k_1/k may possibly be unity.
- 17 This evaluation is based on the recent data of Kurylo (private communication, 1979) and Kaufman (private communication, 1979). The results are in excellent agreement. The earlier results of Howard and Evanson (1976); Watson et al. (1977), Chang and Kaufman (1977), and Clyne and Holt (1979) are rejected in favor of the recent results. The CH_3CCl_3 used in the early studies may have been contaminated.
- 18 Value chosen to be consistent with $k(\text{ClO} + \text{HO}_2)$.
- 19 Value chosen to be consistent with $k(\text{ClO} + \text{OH})$.
- 20 The recommendation is based on the results of Washida and Bayes (1976) obtained over the temperature range 259 to 341 K. This reaction is probably only important in the vicinity of the stratopause.
- 21 The value for $k(298 \text{ K})$ is the average of those reported by Plumb et al. (1979), $k = (8 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; and by Cox and Tyndall (1979), $k = (6.5 \pm 2.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Preliminary data of Sander and Watson (private communication, 1979) supports the recommendation.
- 22 The room-temperature value is that of Cox and Tyndall (1979), who report $(6.5 \pm 1.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This study also reports a large negative E/R value over the temperature range 274 to 338 K. This is similar to that found by this group for $\text{HO}_2 + \text{HO}_2$. This requires independent verification. No recommendations for A or E/R are suggested at the present time.
- 23 The recommended A-factor and E/R are those determined by Barker et al. (1977), who measured the ratio $k(\text{CH}_3\text{O} + \text{O}_2) / k(\text{CH}_3\text{O} + \text{NO}_2 + \text{M})$ from 396 to 424 K. Recent results on this same system have been reported by Batt (1979). Although these new results yield a higher A-factor and somewhat higher E/R, they are consistent with the results of Barker et al. over the limited temperature range studied. The $k(298 \text{ K})$ value is calculated from the recommended A-factor and E/R. The factor of two uncertainty in $k(298 \text{ K})$ encompasses the higher value calculated from the higher A-factor and E/R from the study of Batt. Further work over a wider temperature range is needed.
- 24 The value for $k(298 \text{ K})$ is the average of those determined by Atkinson and Pitts (1978) and Stief et al. (1979), both using the flash photolysis-resonance fluorescence technique. The value of $(1.4 \pm 0.35) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Morris and Niki (1971) agrees within the stated uncertainty. There are two relative values which are not in agreement with the recommendations. The value of Niki et al. (1978b) relative to $\text{OH} + \text{C}_2\text{H}_4$ is higher $(1.4 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ while the value of Smith (1978)

relative to $\text{OH} + \text{OH}$ is lower ($6.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The latter data are also at variance with the negligible temperature dependence observed in the two flash photolysis studies. Although Atkinson and Pitts assign a small energy barrier ($E/R = 90 \pm 150$), their data at 356 K and 426 K and that of Stief et al. at 228 K, 257 K and 362 K are all within 10% of the $k(298 \text{ K})$ value. Thus, the combined data set suggest $E/R = 0$. The abstraction reaction given is probably the major channel; other channels may contribute (Horowitz et al., 1978).

- 25 The recommended values for A , E/R and $k(298 \text{ K})$ are the averages of those determined by Klemm (1979) using flash photolysis-resonance fluorescence (250 to 498 K); by Klemm et al. (1979) using discharge flow-resonance fluorescence (298 to 748 K); and Chang and Barker (1979) using discharge flow-mass spectrometry (296 to 437 K). All three studies are in good agreement. The $k(298 \text{ K})$ value is also consistent with the results of Niki et al. (1969), Herron and Penzhorn (1969), and Mack and Thrush (1973). Although the mechanism for $\text{O} + \text{H}_2\text{CO}$ has been considered to be the abstraction reaction yielding $\text{OH} + \text{HCO}$, Chang and Barker suggest that an addition channel yielding $\text{H} + \text{HCO}_2$ may be occurring to the extent of 30% of the total reaction. This conclusion is based on an observation of CO_2 as a product of the reaction under conditions where reactions such as $\text{O} + \text{HCO} \rightarrow \text{H} + \text{CO}_2$ and $\text{O} + \text{HCO} \rightarrow \text{OH} + \text{CO}$ apparently do not occur. This interesting suggestion needs independent confirmation.
- 26 This estimate is based on an assumed similarity to $\text{OH} + \text{H}_2\text{O}_2$ and $\text{OH} + \text{CH}_3\text{OH}$. The $k(298 \text{ K})$ values for these two reactions are reported to be very similar: $k(\text{OH} + \text{H}_2\text{O}_2) = 8.1 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (this evaluation) and $k(\text{OH} + \text{CH}_3\text{OH}) = 9.5 \times 10^{-13} \text{ molecule}^{-1} \text{ s}^{-1}$ (Campbell et al., 1976). In the absence of temperature-dependent data for $\text{OH} + \text{CH}_3\text{OH}$, the A -factor and E/R values are assumed to be the same as those for $\text{OH} + \text{H}_2\text{O}_2$. The latter values are somewhat uncertain at present. The reaction products are not specified since, using the above analogies to CH_3OH and H_2O_2 , abstraction of H from either end of the molecule may be equally probable.
- 27 This recommendation accepts the recent determination by Singleton et al. (1979). The uncertainty factor in $k(298 \text{ K})$ was chosen to encompass the values of $k(298 \text{ K})$ determined by Hollinden et al. (1970); Whytock et al. (1976); and Slagle et al. (1978). The E/R value is that of the Singleton study as confirmed by the higher temperature data of Whytock et al., and the measurements of Slagle et al. It should be emphasized that the Singleton determination did not extend below 298 K. The only existing data below 298 K appear to indicate a dramatic change in E/R in this temperature region. Thus $\Delta E/R$ was set to account for these observations. Such a nonlinearity in the Arrhenius plot might indicate a change in reaction mechanism from abstraction (as written) to addition. An addition channel has been proposed for $\text{O} + \text{H}_2\text{S}$ by Slagle et al. (1978) as well as by Singleton et al., and addition products from this reaction have been seen in a matrix (Smardzewski and Lin, 1977). Further kinetic study is recommended in the 200 to 300 K range. Direct mechanistic information is needed.
- 28 The uncertainty factor in $k(298 \text{ K})$ has been increased to reflect the complexity of the kinetic analysis used to derive $k(298 \text{ K})$. This increase does not permit overlap of $k(298 \text{ K})$ from both literature studies. Further study is still needed to establish the validity of the interpretation upon which the present recommendation is based. Measurements at both the temperature dependence of k and the mechanism of the reaction are essential. If suggestions regarding a possible addition mechanism are correct, the reaction may have a negative temperature dependence.
- 29 Corrected for typographical errors in JPL 79-27.
- 30 Rate constant given in JPL 79-27 has been lowered by a factor of two to be consistent with our definition $-d[\text{radical}]/dt = 2k[\text{radical}]^2$.

Table 1-3
Rate Constants for Third Order Reactions
The Values Quoted are Suitable for Air as Third Body, M

Reaction	Low Pressure Limit $k_0(T) = k_0^{300} (T/300)^{-n}$		High Pressure Limit $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		Notes
	k_0^{300}	n	k_∞^{300}	m	
$\text{HO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{HO}_2\text{NO}_2$	$(2.1 \pm 0.4) (-31)$	5.0 ± 2.0	$(6.5 \pm 3.3) (-12)$	5.0 ± 2.0	1
$\text{OH} + \text{NO}_2 \xrightarrow{\text{M}} \text{HNO}_3$	$(2.6 \pm 0.3) (-30)$	2.9 ± 0.7	$(2.4 \pm 1.2) (-11)$	1.3 ± 1.0	
$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClONO}_2$	$(1.6 \pm 0.2) (-31)$	3.4 ± 0.3	$(1.5 \pm 0.7) (-11)$	1.9 ± 1.0	
(Two recommendations)	$(3.5 \pm 1.7) (-32)$	3.8 ± 1.0	$(1.5 \pm 0.7) (-11)$	1.9 ± 1.0	
$\text{CH}_3 + \text{O}_2 \xrightarrow{\text{M}} \text{CH}_3\text{O}_2$	$(2.2 \pm 1.1) (-31)$	2.2 ± 1.0	$(2.0 \pm 1.0) (-12)$	1.7 ± 1.0	2
$\text{O} + \text{O}_2 \xrightarrow{\text{M}} \text{O}_3$	$(6.2 \pm 0.9) (-34)$	2.0 ± 0.5	— —	—	
$\text{O} (^1\text{D}) + \text{N}_2 \xrightarrow{\text{M}} \text{N}_2\text{O}$	$(3.5 \pm 3.0) (-37)$	$0.45^{+2.0}_{-0.45}$	— —	—	3
$\text{Cl} + \text{NO} \xrightarrow{\text{M}} \text{ClNO}$	$(9.0 \pm 2.0) (-32)$	1.8 ± 0.5	— —	—	
$\text{Cl} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClONO}_2$ (ClONO)	$(1.6 \pm 1.0) (-30)$	1.9 ± 1.0	$(3.0 \pm 1.5) (-11)$	1.0 ± 1.0	
$\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{ClOO}$	$(2.0 \pm 1.0) (-33)$	$1.3^{+2.0}_{-1.3}$	— —	—	
$\text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HO}_2$	$(5.5 \pm 0.5) (-32)$	1.4 ± 0.5	— —	—	4
$\text{OH} + \text{NO} \xrightarrow{\text{M}} \text{HONO}$	$(6.7 \pm 1.2) (-31)$	3.3 ± 1.0	$(3.0 \pm 1.5) (-11)$	1.0 ± 1.0	
$\text{F} + \text{O}_2 \xrightarrow{\text{M}} \text{FO}_2$	$(1.1 \pm 0.3) (-32)$	1.7 ± 1.0	— —	—	
$\text{OH} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$	$(2.5 \pm 1.3) (-31)$	$0.8^{+2.0}_{-0.8}$	$(3.0 \pm 1.5) (-11)$	1.0 ± 1.0	
$\text{CH}_3\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_3\text{O}_2\text{NO}_2$	$(2.0 \pm 1.5) (-30)$	4.0 ± 2.0	$(0.5 \pm 3.3) (-12)$	4.0 ± 2.0	5
$\text{F} + \text{NO} \xrightarrow{\text{M}} \text{FNO}$	$(6.6 \pm 3.3) (-32)$	$1.0^{+2.0}_{-1.0}$	— —	—	
$\text{FO} + \text{NO}_2 \xrightarrow{\text{M}} \text{FNO}_3$	$(8.3 \pm 6.0) (-31)$	$0.7^{+3.0}_{-0.7}$	$(2.0 \pm 1.0) (-11)$	1.5 ± 1.5	
$\text{F} + \text{NO}_2 \xrightarrow{\text{M}} \text{FNO}_2$ (FONO)	$(1.3 \pm 0.7) (-30)$	$1.7^{+2.0}_{-1.7}$	$(3.0 \pm 1.5) (-11)$	1.0 ± 1.0	
$\text{BrO} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrNO}_3$	Use $2 \times k(\text{ClO} + \text{NO}_2 + \text{M})$				6
$\text{NO}_2 + \text{NO}_3 \xrightarrow{\text{M}} \text{N}_2\text{O}_5$	$(1.4 \pm 0.7) (-30)$	2.8 ± 1.0	$(9.0 \pm 4.5) (-13)$	$-0.7 \pm$	
$\text{O} + \text{NO} \xrightarrow{\text{M}} \text{NO}_2$	$(1.2 \pm 0.3) (-31)$	1.8 ± 0.5	$(3.0 \pm 1.0) (-11)$	-0.3 ± 1.0	
$\text{O} + \text{NO}_2 \xrightarrow{\text{M}} \text{NO}_3$	$(9.0 \pm 1.0) (-32)$	2.0 ± 1.0	$(2.2 \pm 0.3) (-11)$	0.0 ± 1.0	
$\text{OH} + \text{SO}_2 \xrightarrow{\text{M}} \text{HOSO}_2$	$(3.0 \pm 1.5) (-31)$	2.9 ± 1.0	$(2.0 \pm 1.5) (-12)$	0.0 ± 1.0	

Note: $k(z) = k(\text{M}, T) = \left(\frac{k_0(T) [\text{M}]}{1 + k_0(T) [\text{M}] / k_\infty(T)} \right)^{0.6} \left\{ 1 + \left[\log_{10} (k_0(T) [\text{M}] / k_\infty(T)) \right]^2 \right\}^{-1}$

Notes for Table 1-3. See JPL 79-27 and the earlier part of this chapter for more detailed discussions.

- 1 Basis for the recommendations discussed in text.
- 2 Error limits reduced based on private communication from: O. Klais, P.C. Anderson and M.J. Kurylo. These authors also report a formula for air as a third body.
- 3 Measured rate constant is now understood to be the result of simultaneous production of ClNO_2 and ClONO . (Niki et al., 1978a; Chang et al., 1979).
- 4 Error limit on temperature-dependence of k_o reduced based on reevaluation of data.
- 5 Provisional data, S. Sander and R. Watson (private communication, 1979).
- 6 Private communications: P. Connell and H.S. Johnston; D. Albritton, F. Fehsenfeld and A. Viggiano.
- 7 These recommendations taken from the evaluations performed by Jurgen Troe of the CODATA panel as communicated by R. T. Watson.

Table 1-4
Photochemical Reactions of Stratospheric Interest

$O_2 + h\nu \rightarrow O + O$	$^{\dagger}HF + h\nu \rightarrow H + F$
$O_3 + h\nu \rightarrow O + O_2$	$^*HOCl + h\nu \rightarrow OH + Cl$
$^*O_3 + h\nu \rightarrow O(^1D) + O_2$	$^{\dagger}HClO_4 + h\nu \rightarrow \text{products}$
$NO + h\nu \rightarrow N + O$	$ClNO + h\nu \rightarrow Cl + NO$
$NO_2 + h\nu \rightarrow NO + O$	$ClNO_2 + h\nu \rightarrow \text{products}$
$^*NO_3 + h\nu \rightarrow NO + O_2$	$ClONO + h\nu \rightarrow \text{products}$
$NO_3 + h\nu \rightarrow NO_2 + O$	$ClONO_2 + h\nu \rightarrow \text{products}$
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	$Cl_2 + h\nu \rightarrow Cl + Cl$
$N_2O_5 + h\nu \rightarrow \text{products}$	$Cl_2O + h\nu \rightarrow Cl + ClO$
$NH_3 + h\nu \rightarrow NH_2 + H$	$CCl_4 + h\nu \rightarrow \text{products}$
$HO_2 + h\nu \rightarrow \text{products}$	$CCl_3F + h\nu \rightarrow \text{products}$
$H_2O + h\nu \rightarrow H + OH$	$CCl_2F_2 + h\nu \rightarrow \text{products}$
$H_2O_2 + h\nu \rightarrow OH + OH$	$CClF_3 + h\nu \rightarrow \text{products}$
$HNO_2 + h\nu \rightarrow OH + NO$	$CHCl_2F + h\nu \rightarrow \text{products}$
$HNO_3 + h\nu \rightarrow OH + NO_2$	$CHClF_2 + h\nu \rightarrow \text{products}$
$^{\dagger}HNO_4 + h\nu \rightarrow \text{products}$	$CH_2ClF + h\nu \rightarrow \text{products}$
$SO_2 + h\nu \rightarrow SO + O$	$CH_3Cl + h\nu \rightarrow \text{products}$
$H_2S + h\nu \rightarrow HS + H$	$CCl_2FCClF_2 + h\nu \rightarrow \text{products}$
$CO + h\nu \rightarrow C + O$	$CClF_2CClF_2 + h\nu \rightarrow \text{products}$
$CO_2 + h\nu \rightarrow CO + O$	$CClF_2CF_3 + h\nu \rightarrow \text{products}$
$CH_4 + h\nu \rightarrow \text{products}$	$CH_3CCl_3 + h\nu \rightarrow \text{products}$
$^*H_2CO + h\nu \rightarrow \text{products}$	$CCl_2O + h\nu \rightarrow \text{products}$
$^*ClO + h\nu \rightarrow Cl + O$	$CClFO + h\nu \rightarrow \text{products}$
$ClO_2 + h\nu \rightarrow \text{products}$	$CF_2O + h\nu \rightarrow \text{products}$
$OCIO + h\nu \rightarrow O + ClO$	$^*CH_3OOH + h\nu \rightarrow \text{products}$
$ClO_3 + h\nu \rightarrow \text{products}$	$^*COS + h\nu \rightarrow CO + S$
$HCl + h\nu \rightarrow H + Cl$	$BrONO_2 + h\nu \rightarrow \text{products}$

† New entry.

* New data or comment. These changes or additions are explained in the notes following the tables. For completeness, all tables of cross sections from JPL 79-27 are reproduced in the present report. For discussion of the origin of these tables, see JPL 79-27.

Table 1-5
Reliability Estimates for Photochemical Rates

Species		Uncertainty Factor
O ₂	Schumann-Runge bands	1.4
O ₂	Continua	1.15
O ₃		1.12
O ₃	→ O(¹ D); (T)	1.4
NO ₂	(T)	1.25
NO ₃		2.0
NO ₃	→ { NO + O ₂ NO ₂ + O (T)	3.0
N ₂ O		1.2
N ₂ O ₅		2.0
HO ₂		2.0
H ₂ O ₂		1.4
HNO ₂		1.4
HNO ₃		1.15
H ₂ CO	→ { H + HCO H ₂ + CO (T)	1.4
HCl		1.12
HOCl		1.4
ClONO ₂	(T)	1.25
CCl ₄		1.1
CCl ₃ F		1.05
CCl ₂ F ₂	(T)	1.15
CH ₃ Cl		1.1
CF ₂ O		2.0
CH ₃ OOH		1.4
COS		1.25
BrONO ₂		1.4

Note: (T) Signifies temperature dependent

Table 1-6
Mathematical Expression for $O(^1D)$ Quantum Yield, φ ,
in the Photolysis of O_3

$$\varphi(\lambda, T) = A(\tau) \arctan \left[B(\tau) (\lambda - \lambda_0(\tau)) \right] + C(\tau)$$

Where: $\tau = T - 230$ is a temperature function with T given in Kelvin, λ is expressed in nm, and arctan in radians.

The coefficients $A(\tau)$, $B(\tau)$, $\lambda_0(\tau)$ and $C(\tau)$ are expressed as interpolation polynomials of the third order:

$$A(\tau) = 0.369 + 2.85 \times 10^{-4} \tau + 1.28 \times 10^{-5} \tau^2 + 2.57 \times 10^{-8} \tau^3$$

$$B(\tau) = -0.575 + 5.59 \times 10^{-3} \tau - 1.439 \times 10^{-5} \tau^2 - 3.27 \times 10^{-8} \tau^3$$

$$\lambda_0(\tau) = 308.20 + 4.4871 \times 10^{-2} \tau + 6.9380 \times 10^{-5} \tau^2 - 2.5452 \times 10^{-6} \tau^3$$

$$C(\tau) = 0.518 + 9.87 \times 10^{-4} \tau - 3.94 \times 10^{-5} \tau^2 + 3.91 \times 10^{-7} \tau^3.$$

In the limits where $\varphi(\lambda, T) > 1$, the quantum yield is set $\varphi = 1$, and similarly for $\varphi(\lambda, T) < 0$, the quantum yield is set $\varphi = 0$.

Table 1-7
Quantum Yields for NO_2 Photolysis

λ , nm	Φ	λ , nm	Φ	λ , nm	Φ
375	0.73	389	0.74	400	0.65
376	0.75	390	0.74	401	0.62
377	0.86	391	0.81	402	0.57
378	0.74	392	0.73	403	0.50
379	0.83	393	0.78	404	0.40
380	0.81	394	0.83	405	0.32
381	0.73	394.5	0.78	406	0.30
382	0.65	395	0.81	407	0.23
383	0.62	395.5	0.75	408	0.18
384	0.66	396	0.78	409	0.17
385	0.70	396.5	0.81	410	0.14
386	0.74	397	0.77	411	0.10
387	0.69	398	0.72	415	0.067
388	0.76	399	0.70	420	0.023

Table 1-8
Absorption Cross Sections of NO₂

λ (nm)	$\sigma(\text{cm}^2)$		λ (nm)	$\sigma(\text{cm}^2)$	
	235 K	298 K		235 K	298 K
185	—	2.60 (-19)	300	1.09 (-19)	1.17 (-19)
190	—	2.93 (-19)	305	1.67 (-19)	1.66 (-19)
195	—	2.42 (-19)	310	1.83 (-19)	1.76 (-19)
200	—	2.50 (-19)	315	2.19 (-19)	2.25 (-19)
205	—	3.75 (-19)	320	2.35 (-19)	2.54 (-19)
210	—	3.85 (-19)	325	2.54 (-19)	2.79 (-19)
215	—	4.02 (-19)	330	2.91 (-19)	2.99 (-19)
220	—	3.96 (-19)	335	3.14 (-19)	3.45 (-19)
225	—	3.24 (-19)	340	3.23 (-19)	3.88 (-19)
230	—	2.43 (-19)	345	3.43 (-19)	4.07 (-19)
235	—	1.48 (-19)	350	3.11 (-19)	4.10 (-19)
240	—	6.70 (-20)	355	4.37 (-19)	5.13 (-19)
245	—	4.35 (-20)	360	3.90 (-19)	4.51 (-19)
250	—	2.83 (-20)	365	5.37 (-19)	5.78 (-19)
255	—	1.45 (-20)	370	4.87 (-19)	5.42 (-19)
260	—	1.90 (-20)	375	5.00 (-19)	5.35 (-19)
265	—	2.05 (-20)	380	5.93 (-19)	5.99 (-19)
270	—	3.13 (-20)	385	5.79 (-19)	5.94 (-19)
275	—	4.02 (-20)	390	5.49 (-19)	6.00 (-19)
280	—	5.54 (-20)	395	5.62 (-19)	5.89 (-19)
285	—	6.99 (-20)	400	6.66 (-19)	6.76 (-19)
290	6.77 (-20)	8.18 (-20)	405	5.96 (-19)	6.32 (-19)
295	8.52 (-20)	9.67 (-20)	410	5.32 (-19)	5.77 (-19)

Note: Numbers in parenthesis signify powers of 10
(e.g., 6.77 (-20) = 6.77×10^{-20})

Table 1-9
Absorption Cross Sections of NO₃

λ (nm)	$10^{19}\sigma$ (cm ²)	λ (nm)	$10^{19}\sigma$ (cm ²)	λ (nm)	$10^{19}\sigma$ (cm ²)
400	0.0	500	9.8	600	24.5
402	0.1	502	9.1	602	28.4
404	0.2	504	10.5	604	40.0
406	0.3	506	11.9	606	33.8
408	0.3	508	10.6	608	15.9
410	0.6	510	13.0	610	13.5
412	0.3	512	16.1	612	16.9
414	0.7	514	14.1	614	22.4
416	0.3	516	14.0	616	17.4
418	0.6	518	12.1	618	18.3
420	0.9	520	14.4	620	24.7
422	0.8	522	17.2	622	76.1
424	1.2	524	15.0	624	116.6
426	0.9	526	13.7	626	70.0
428	1.2	528	17.9	628	68.9
430	1.2	530	20.9	630	64.1
432	1.4	532	18.1	632	32.7
434	1.7	534	17.7	634	13.2
436	2.1	536	23.2	636	12.3
438	1.8	538	21.1	638	17.6
440	1.9	540	18.1	640	9.8
442	2.0	542	16.8	642	6.8
444	2.1	544	13.9	644	7.1
446	2.3	546	20.4	646	5.6
448	2.8	548	27.5	648	4.8
450	2.7	550	22.4	650	3.2
452	3.1	552	21.6	652	3.9
454	3.4	554	24.5	654	5.7
456	3.2	556	29.5	656	8.9
458	3.7	558	31.7	658	16.8
460	3.9	560	32.3	660	51.2
462	3.5	562	26.8	662	170.8
464	4.1	564	24.8	664	115.4
466	4.5	566	25.8	666	48.6
468	5.0	568	25.7	668	17.5
470	4.9	570	25.3	670	7.5
472	5.4	572	24.8	672	5.7
474	5.6	574	25.5	674	3.6
476	6.4	576	29.2	676	3.1
478	6.6	578	30.3	678	5.5
480	6.4	580	29.9	680	4.9
482	6.3	582	31.0	682	2.5
484	6.2	584	24.7	684	0.9
486	7.4	586	27.5	686	0.3
488	8.0	588	44.8	688	0.4
490	9.3	590	56.7	690	0.1
492	8.9	592	48.3	692	0.0
494	8.8	594	39.2	694	0.1
496	10.4	596	41.6	696	0.4
498	10.8	598	35.4	698	0.4

Table 1-10
Mathematical Expression for Absorption Cross Sections
of N_2O as a Function of Temperature

$$\ln \sigma(\lambda, T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4 \\ + (T-300) \exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$$

Where: T: temperature, Kelvin λ : nm

$$\begin{aligned} A_1 &= 68.21023 & B_1 &= 123.4014 \\ A_2 &= -4.071805 & B_2 &= -2.116255 \\ A_3 &= 4.301146 \times 10^{-2} & B_3 &= 1.111572 \times 10^{-2} \\ A_4 &= -1.777846 \times 10^{-4} & B_4 &= -1.881058 \times 10^{-5} \\ A_5 &= 2.520672 \times 10^{-7} \end{aligned}$$

Range: 173 to 240 nm; 194 to 302K

Table 1-11
Absorption Cross Sections of N_2O_5

λ (nm)	σ (cm ²)	λ (nm)	σ (cm ²)	λ (nm)	σ (cm ²)
206	6.6 (-18)	246	4.3 (-19)	286	7.8 (-20)
208	5.9 (-18)	248	3.8 (-19)	288	7.1 (-20)
210	5.2 (-18)	250	3.5 (-19)	290	6.3 (-20)
212	4.4 (-18)	252	3.0 (-19)	292	5.7 (-20)
214	3.7 (-18)	254	2.72 (-19)	294	4.9 (-20)
216	3.0 (-18)	256	2.55 (-19)	296	4.4 (-20)
218	2.48 (-18)	258	2.33 (-19)	298	3.8 (-20)
220	2.06 (-18)	260	2.12 (-19)	300	3.2 (-20)
222	1.71 (-18)	262	1.97 (-19)	302	2.7 (-20)
224	1.41 (-18)	264	1.86 (-19)	304	2.4 (-20)
226	1.23 (-18)	266	1.7 (-19)	306	2.1 (-20)
228	1.06 (-18)	268	1.64 (-19)	308	1.8 (-20)
230	9.3 (-19)	270	1.52 (-19)	310	1.5 (-20)
232	8.4 (-19)	272	1.42 (-19)	320	7.5 (-21)
234	7.5 (-19)	274	1.31 (-19)	330	4.0 (-21)
236	6.9 (-19)	276	1.2 (-19)	340	2.7 (-21)
238	6.3 (-19)	278	1.15 (-19)	350	1.8 (-21)
240	5.7 (-19)	280	1.07 (-19)	360	1.0 (-21)
242	5.3 (-19)	282	9.9 (-20)	370	4.7 (-22)
244	4.7 (-19)	284	8.9 (-20)	380	1.3 (-22)

Note: Numbers in parentheses signify powers of 10 (e.g., 6.6 (-18) = 6.6×10^{-18})

Table 1-12
Absorption Cross Sections
of H₂O₂ Vapor

λ (nm)	$10^{20}\sigma$ (cm ²)
210	37.3
220	27.0
230	19.2
240	13.2
250	9.0
260	5.6
270	3.5
280	2.1
290	1.2
300	0.71
310	0.42
320	0.24
330	0.15
340	0.09
350	0.05

Table 1-13
Absorption Cross Sections of HONO

λ (nm)	$10^{20}\sigma$ (cm ²)	λ (nm)	$10^{20}\sigma$ (cm ²)	λ (nm)	$10^{20}\sigma$ (cm ²)
310	0.0	339	16.3	368	45.0
311	0.0	340	10.5	369	29.3
312	0.2	341	8.70	370	11.9
313	0.42	342	33.5	371	9.46
314	0.46	343	20.1	372	8.85
315	0.42	344	10.2	373	7.44
316	0.3	345	8.54	374	4.77
317	0.46	346	8.32	375	2.7
318	3.6	347	8.20	376	1.9
319	6.10	348	7.49	377	1.5
320	2.1	349	7.13	378	1.9
321	4.27	350	6.83	379	5.8
322	4.01	351	17.4	380	7.78
323	3.93	352	11.4	381	11.4
324	4.01	353	37.1	382	14.0
325	4.04	354	49.6	383	17.2
326	3.13	355	24.6	384	19.9
327	4.12	356	11.9	385	19.0
328	7.55	357	9.35	386	11.9
329	6.64	358	7.78	387	5.65
330	7.29	359	7.29	388	3.2
331	8.70	360	6.83	389	1.9
332	13.8	361	6.90	390	1.2
333	5.91	362	7.32	391	0.5
334	5.91	363	9.00	392	0.0
335	6.45	364	12.1	393	0.0
336	5.91	365	13.3	394	0.0
337	4.58	366	21.3	395	0.0
338	19.1	367	35.2	396	0.0

Table 1-14
Absorption Cross Sections of HO_2NO_2

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	1610	240	68	290	10.9
195	960	245	58	295	8.2
200	640	250	51	300	6.2
205	430	255	45	305	5.0
210	290	260	40	310	4.2
215	200	265	35	315	3.6
220	154	270	28	320	3.0
225	123	275	23	325	2.6
230	99	280	18	330	2.2
235	82	285	14		

Table 1-15
Cross Sections and Quantum Yields for the
Photolysis of H_2CO

λ (nm)	$10^{20}\sigma$ (cm^2)	ϕ_1	ϕ_2
280	2.4	0.63	0.37
290	3.2	0.73	0.27
300	3.3	0.77	0.23
310	3.1	0.76	0.24
320	2.4	0.63	0.37
330	2.4	0.31	0.64
340	2.0	0	0.67
350	0.8	0	0.40
360	0.2	0	0.14

Table 1-16
Absorption Cross Sections of ClO_3

λ (nm)	$10^{18}\sigma$ (cm^2)	λ (nm)	$10^{18}\sigma$ (cm^2)
200	5.3	280	4.6
210	5.0	290	4.3
220	4.8	300	4.0
230	4.3	310	3.2
240	3.5	320	2.5
250	3.7	330	1.8
260	4.3	340	1.1
270	4.5	350	0.76

Table 1-17
Absorption Cross Sections of HOCl

λ (nm)	$10^{20}\sigma$ (cm ²)	λ (nm)	$10^{20}\sigma$ (cm ²)
200	5.2	330	3.7
210	6.1	340	2.4
220	11.0	350	1.4
230	18.6	360	0.8
240	22.3	370	0.45
250	18.0	380	0.24
260	10.8	390	0.15
270	6.2	400	0.05
280	4.8	410	0.04
290	5.3	420	
300	6.1		
310	6.2		
320	5.0		

Table 1-18
Absorption Cross Sections of HClO₄

λ (nm)	$10^{20}\sigma$ (cm ²)	λ (nm)	$10^{20}\sigma$ (cm ²)
190	405	240	1.4
195	230	245	0.78
200	130	250	0.40
205	78	255	0.21
210	45	260	0.12
215	25	265	0.06
220	14	270	0.03
225	8.0	275	0.02
230	4.4	280	0.01
235	2.5		

Table 1-19
Absorption Cross Sections of ClNO

λ (nm)	σ (cm ²)
190	5.27 (-17)
200	6.97 (-17)
210	3.18 (-17)
220	1.17 (-17)
230	3.77 (-18)
240	1.34 (-18)
260	1.80 (-19)
280	1.03 (-20)
300	9.49 (-20)
320	1.21 (-19)
340	1.37 (-19)
360	1.22 (-19)
380	8.32 (-20)
400	5.14 (-20)

Note: Numbers in parentheses signify powers of 10 (e.g., 5.27 (-17) = 5.27×10^{-17})

Table 1-20
Absorption Cross Sections of ClNO₂

λ (nm)	σ (cm ²)	λ (nm)	σ (cm ²)
190	2.69 (-17)	300	1.54 (-19)
200	4.55 (-18)	310	1.32 (-19)
210	3.39 (-18)	320	1.02 (-19)
220	3.42 (-18)	330	7.11 (-20)
230	2.36 (-18)	340	4.81 (-20)
240	1.40 (-18)	350	3.06 (-20)
250	9.85 (-19)	360	1.82 (-20)
260	6.37 (-19)	370	1.07 (-20)
270	3.73 (-19)	380	0.62 (-20)
280	2.31 (-19)	390	0.38 (-20)
290	1.80 (-19)	400	0.21 (-20)

Note: Numbers in parentheses signify powers of 10 (e.g., 2.69 (-17) = 2.69×10^{-17})

Table 1-21
Absorption Cross Sections of ClONO at 231 K

λ (nm)	$10^{20}\sigma$ (cm ²)	λ (nm)	$10^{20}\sigma$ (cm ²)
235	215.0	320	80.3
240	176.0	325	75.4
245	137.0	330	58.7
250	106.0	335	57.7
255	65.0	340	43.7
260	64.6	345	35.7
265	69.3	350	26.9
270	90.3	355	22.9
275	110.0	360	16.1
280	132.0	365	11.3
285	144.0	370	9.0
290	144.0	375	6.9
295	142.0	380	4.1
300	129.0	385	3.3
305	114.0	390	2.2
310	105.0	395	1.5
315	98.1	400	0.6

Table 1-22
Absorption Cross Sections of ClONO₂

λ (nm)	$10^{20} \sigma \text{ (cm}^2\text{)}$			λ (nm)	$10^{20} \sigma \text{ (cm}^2\text{)}$		
	227K	243K	296K		227K	243K	296K
190	555	—	589	325	0.463	0.502	0.655
195	358	—	381	330	0.353	0.381	0.514
200	293	—	307	335	0.283	0.307	0.397
205	293	—	299	340	0.246	0.255	0.323
210	330	—	329	345	0.214	0.223	0.285
215	362	—	360	350	0.198	0.205	0.246
220	348	—	344	355	0.182	0.183	0.218
225	282	—	286	360	0.170	0.173	0.208
230	206	—	210	365	0.155	0.159	0.178
235	141	—	149	370	0.142	0.140	0.162
240	98.5	—	106	375	0.128	0.130	0.139
245	70.6	—	77.0	380	0.113	0.114	0.122
250	52.6	50.9	57.7	385	0.098	0.100	0.108
255	39.8	39.1	44.7	390	0.090	0.083	0.090
260	30.7	30.1	34.6	395	0.069	0.070	0.077
265	23.3	23.1	26.9	400	0.056	0.058	0.064
270	18.3	18.0	21.5	405	—	—	0.055
275	13.9	13.5	16.1	410	—	—	0.044
280	10.4	9.98	11.9	415	—	—	0.035
285	7.50	7.33	8.80	420	—	—	0.027
290	5.45	5.36	6.36	425	—	—	0.020
295	3.74	3.83	4.56	430	—	—	0.016
300	2.51	2.61	3.30	435	—	—	0.013
305	1.80	1.89	2.38	440	—	—	0.009
310	1.28	1.35	1.69	445	—	—	0.007
315	0.892	0.954	1.23	450	—	—	0.005
320	0.630	0.681	0.895				

Table 1-23
Absorption Cross Sections of CCl_3F

λ (nm)	$10^{20} \sigma \text{ (cm}^2\text{)}$			
	213K	232K	252K	298K
186.0	—	—	—	243.0
187.8	—	—	—	217.0
189.6	—	—	—	186.0
191.4	161.0	161.0	164.0	159.0
193.2	137.0	137.0	141.0	133.0
195.1	110.0	110.0	114.0	111.0
197.0	88.5	88.5	91.3	90.3
199.0	69.1	69.1	72.1	73.0
201.0	53.1	54.3	56.6	57.3
203.0	40.2	41.1	43.0	45.2
205.1	28.6	30.0	31.7	33.3
207.3	19.8	21.1	22.6	23.9
209.4	13.3	14.2	15.2	16.8
211.6	8.5	9.1	9.9	11.5
213.9	—	5.7	6.4	7.6
216.2	—	3.4	3.9	5.0
218.6	—	2.0	2.3	3.1
221.0	—	—	—	2.0
223.5	—	—	—	1.2
226.0	—	—	—	0.8

Table 1-24
Absorption Cross Sections of CCl_2F_2

λ (nm)	$10^{20}\sigma_{296}$ (cm^2)
186.0	106.0
187.8	85.4
189.6	64.6
191.4	48.7
193.2	35.3
195.1	24.5
197.0	16.6
199.0	10.8
201.0	6.87
203.0	4.36
205.1	2.59
207.3	1.50
209.4	0.89
211.6	0.51
213.9	0.29
216.2	0.17
218.6	0.095
221.0	0.05
223.5	< 0.05
226.0	< 0.05

$$\sigma_T = \sigma_{296} \exp [3.6 \times 10^{-4}(\lambda - 184.9)(T - 296)]$$

Where: σ_{296} : cross section at 296K
 λ : nm
T : temperature, Kelvin

Table 1-25
Absorption Cross Sections of CClF_3
and $\text{CCl}_2\text{FCClF}_2$

λ (nm)	$10^{20}\sigma$ (cm ²)	
	CClF_3	$\text{CCl}_2\text{FCClF}_2$
184.6	0.36	116.0
186.0	0.31	105.0
187.8	0.23	85.0
189.6	0.168	68.9
191.4	0.126	53.8
193.2	0.090	41.0
195.1	0.064	30.0
197.0	0.041	21.3
199.0	0.026	14.9
201.0	0.017	10.4
203.0	0.012	7.0
205.1	—	4.7
207.3	—	3.2
209.4	—	2.05
211.6	—	1.26
213.9	—	0.78
216.2	—	0.47
218.6	—	0.29
221.0	—	0.18
223.5	—	0.11

Table 1-26
Absorption Cross Sections of $\text{CClF}_2\text{CClF}_2$
and CClF_2CF_3

λ (nm)	$10^{20} \sigma \text{ (cm}^2\text{)}$	
	$\text{CClF}_2\text{CClF}_2$	CClF_2CF_3
186.0	10.0	0.61
187.8	7.91	0.49
189.6	5.97	0.36
191.4	4.44	0.27
193.2	3.13	0.20
195.1	2.52	0.14
197.0	1.54	0.093
199.0	1.00	0.066
201.0	0.67	—
203.0	0.44	—
205.1	0.30	—
207.3	0.18	—
209.4	0.11	—
211.6	0.063	—
213.9	0.043	—
216.2	—	—
218.6	—	—

Table 1-27
Absorption Cross Sections of CH_3CCl_3

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
186.0	325.0	205.1	80.5
187.8	284.0	207.3	63.9
189.6	246.0	209.4	51.1
191.4	215.0	211.6	39.4
193.2	189.0	213.9	28.1
195.1	168.0	216.2	19.6
197.0	148.0	218.6	12.5
199.0	128.0	221.0	8.3
201.0	111.0	223.5	5.1
203.0	95.4	226.0	2.9

Table 1-28
Absorption Cross Sections of CCl_2O , CClFO , and CF_2O

λ (nm)	$10^{20}\sigma$ (cm^2)		
	CCl_2O	CClFO	CF_2O
184.9	204.0		4.7
186.0	189.0	15.6	5.5
187.8	137.0	14.0	5.2
189.6	117.0	13.4	4.5
191.4	93.7	12.9	4.0
193.2	69.7	12.7	3.3
195.1	52.5	12.5	2.8
197.0	41.0	12.4	2.3
199.0	31.8	12.3	1.9
201.0	25.0	12.0	1.4
203.0	20.4	11.7	1.1
205.1	16.9	11.2	0.86
207.3	15.1	10.5	0.65
209.4	13.4	9.7	0.48
211.6	12.2	9.0	0.36
213.9	11.7	7.9	0.26
216.2	11.6	6.9	0.21
218.6	11.9	5.8	0.15
221.0	12.3	4.8	0.12
223.5	12.8	4.0	0.10
226.0	13.2	3.1	0.08

Table 1-29
Absorption Cross Sections of CH_3OOH

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
210	37.5	260	3.8	310	0.34
220	22.0	270	2.5	320	0.19
230	13.8	280	1.5	330	0.11
240	8.8	290	0.90	340	0.06
250	5.8	300	0.58	350	0.04

Table 1-30
Absorption Cross Sections of OCS

λ (nm)	$10^{20}\sigma$ (cm^2)		
	232K	251K	296K
186.0	9.8	10.6	13.8
187.8	5.6	6.6	9.8
189.6	2.0	2.5	3.4
191.4	1.0	1.3	1.5
193.2	0.9	1.1	1.2
195.1	1.2	1.5	1.4
197.0	1.9	2.1	2.0
199.0	2.7	2.9	2.8
201.0	3.7	4.0	4.1
203.0	5.2	5.4	5.3
205.1	7.0	7.2	7.2
207.3	9.3	9.9	9.6
209.4	12.0	12.1	12.2
211.6	16.0	16.1	16.1
213.9	19.9	20.1	20.8
216.2	22.8	23.1	23.2
218.6	24.5	24.9	25.1
221.0	26.7	26.9	27.0
223.5	29.1	29.5	30.6
226.0	27.3	28.0	28.3

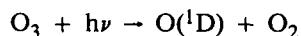
Table 1-31
Absorption Cross Sections of BrONO₂

λ (nm)	σ (cm ²)	λ (nm)	σ (cm ²)
186	1.5 (-17)	280	2.9 (-19)
190	1.3 (-17)	285	2.7 (-19)
195	1.0 (-17)	290	2.4 (-19)
200	7.2 (-18)	295	2.2 (-19)
205	4.3 (-18)	300	1.9 (-19)
210	3.2 (-18)	305	1.8 (-19)
215	2.7 (-18)	310	1.5 (-19)
220	2.4 (-18)	315	1.4 (-19)
225	2.1 (-18)	320	1.2 (-19)
230	1.9 (-18)	325	1.1 (-19)
235	1.7 (-18)	330	1.0 (-19)
240	1.3 (-18)	335	9.5 (-20)
245	1.0 (-18)	340	8.7 (-20)
250	7.8 (-19)	345	8.5 (-20)
255	6.1 (-19)	350	7.7 (-20)
260	4.8 (-19)	360	6.2 (-20)
265	3.9 (-19)	370	4.9 (-20)
270	3.4 (-19)	380	4.0 (-20)
275	3.1 (-19)	390	2.8 (-20)

Note: Numbers in parentheses signify powers of 10 (e.g.,
1.5 (-17) = 1.5×10^{-17})

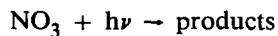
Notes for Tables 1-4 Through 1-31 Photochemical Reactions

(Only those tables which have been changed since JPL 79-27 are discussed here. For the background material on the other tables, see JPL 79-27.)

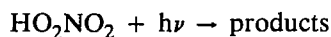


The results of recent laser studies by Brock and Watson (private communication, 1979) are in good agreement with the recommendation given in table 1-6.

The recommended value for the quantum yield for O(¹D) production at wavelengths shorter than 300 nm is unity, as reported by Amimoto et al. (1978) and by Kajimoto and Cvetanovic (1979). The results of Fairchild et al. (1978) as well as those of Sparks et al. (1979) indicate, however, that the quantum yield at those wavelengths is about 0.9. This question requires further study.



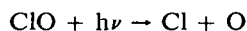
The preferred values, listed in table 1-9, are taken from the work of Graham and Johnston (1978). These are the values which were recommended in the original report (NASA RP-1010). The second evaluation (JPL 79-29) recommended instead the results of Wayne et al. (1978), but these later results have now been withdrawn. However, Wayne (private communication, 1978) has now an absolute NO₃ cross section measurement at 662 nm which indicates that Graham and Johnson's (1978) values should be multiplied by approximately 0.7. The NO₃ spectrum requires further study.



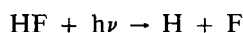
Two groups have investigated the UV spectrum of HO_2NO_2 : Graham et al. (1978b) and Cox and Patrick (1979). Only the former reports cross section values in the critical wavelength region for atmospheric photodissociation beyond 290 nm. The results of Graham et al., which provide the basis of this recommendation, are listed in table 1-14. The two sets of results are in reasonable agreement between 205 and 260 nm, but at 195 nm the cross-section value obtained by Graham et al. is more than twice the value reported by Cox and Patrick. Additional studies of the HO_2NO_2 spectrum would be desirable.



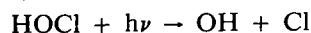
Moortgat and Warneck (1979) have reinvestigated the photolysis of H_2CO . Their results together with earlier studies have been reviewed by Cox (1979). The recommended values listed in table 1-15 are taken from this review.



There are new measurements of ClO absorption cross sections in the 270 to 350 nm region by Jourdain et al. (1978). Photo-decomposition accounts for at most two or three percent of the total destruction rate of ClO in the stratosphere (see JPL publication 79-27), which occurs predominantly by reaction with oxygen atoms and nitric oxide.

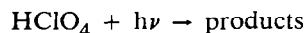


The ultraviolet absorption spectrum of HF has been studied by Safary et al. (1951). The onset of absorption occurs beyond 170 nm, so that photodissociation of HF will be unimportant in the stratosphere.

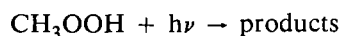


Knauth et al. (1979) have recently measured absorption cross sections of HOCl using essentially the same technique as Molina and Molina (1978) except for a higher temperature, which allowed them to obtain a more accurate value for the equilibrium constant K_{eq} for the $\text{H}_2\text{O} - \text{Cl}_2\text{O} - \text{HOCl}$ system. The cross section values from Molina and Molina's measurements, recalculated using the new K_{eq} are in excellent agreement with the results of Knauth et al. The recommended values, taken from this later work, are presented in table 1-17.

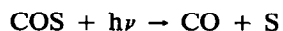
Molina et al. (1979a), by monitoring directly OH radicals produced by laser photolysis of HOCl, obtain an absorption cross section value of $\sim 6 \times 10^{-20} \text{ cm}^2$ around 310 nm, again in excellent agreement with the data of Knauth et al. (1979). In contrast, the theoretical predictions of Jaffe and Langhoff (1978) indicate negligible absorption at those wavelengths. The reason is not known, although it should be pointed out that no precedent exists to validate the theoretical approach for this particular type of problem.



The UV spectrum of HClO_4 has been studied by Molina et al. (1979b), and their results are listed in table 1-18.



Arguello and Molina (1979) have measured the absorption cross sections of CH_3OOH . Their results are listed in table 1-29.



The results of Klemm et al. (1975) indicate that oxygen atoms are not formed in the photodissociation of COS; CO and S are the only products.

DATA RELATED TO IONS AND AEROSOLS

The contents of this section are devoted to laboratory measurements which are of interest to stratospheric research, but which are not generally included in the photochemical models used for the study of ozone. For these areas, the purpose is to refer to current reviews and compilations as sources of data and to indicate the kinds of measurements that are still needed.

HETEROGENEOUS PHENOMENA

Introduction

A relatively persistent aerosol layer is known to exist in the stratosphere over the altitude range extending from approximately 17 to 40 km. This layer is characterized by wide variations in number density with longitude and latitude and often displays stratification with altitude. See reviews by Castleman (1974) and Farlow et al. (1979), and Chapter 3 of this report.

Laboratory work is needed to elucidate the processes leading to aerosol formation, to describe the interactions of aerosols and ions, and to define the extent that aerosol surfaces may catalyze reactions involving stratospheric trace species. Unlike the situation existing in the field of homogeneous chemistry, heterogeneous chemistry is a developing science where interpretation of results is often difficult even under well-controlled laboratory conditions. Much of our current understanding of these processes is based on theoretical considerations.

Formation Process

Stratospheric aerosols appear to be generated *in situ* via the reactions of sulfur bearing gases, possibly from SO₂ and/or COS. The initial phase of new particle formation involves the interaction of numerous precursors until a critical size is reached. This involves tens of elementary reaction steps which are not well identified and are difficult to quantify, even in the laboratory. This "prenucleation critical size embryo" may then be enlarged by heteromolecular processes, involving more than one gaseous species participating in the formation of the particle.

Little is known about the generation of the prenucleation embryos subsequent to the primary steps whereby the sulfur compounds are oxidized. In the case of SO₂, it is likely that it will react with H₂O to form an H₂O · SO₂ adduct, followed by rearrangement to H₂SO₄ (Holland and Castleman, 1978; Castleman et al., 1975). Where HSO₃ is oxidized to HSO₃ via OH, the further addition of O₂ leading to the formation of HSO₅ is a plausible step; subsequent clustering with H₂O may perhaps lead to aerosol formation as suggested by Davis et al. (1979). Friend and Vosta have presented some circumstantial evidence to suggest that hydrated free radical species may be important in aerosol formation. In the case of the nitrosyl compounds which have been tentatively identified as components of the stratospheric aerosol layer, even less is known about their formation mechanisms; reactions involving NO₂, SO₂, SO₃, and H₂O have been invoked to explain field observations (Farlow et al., 1978). Clearly there is an urgent need for laboratory studies in this area.

The initial phase of formation has been theoretically described in terms of individual cluster species forming a liquid drop (Zettlemoyer, 1969; Mason, 1961; Heicklen, 1976); however, there is conflicting evidence as to the

validity of this liquid drop formalism (Heicklen, 1976; Castleman, 1979a, Zettlemoyer, 1977). Recent experimental work using high pressure mass spectrometry (Castleman, 1979), the expansion of proton hydrates in beams composed of water vapor (Searcy and Fenn, 1974; Burke, 1978), and neutral clusters indicate that the small clusters may be relatively ordered, not disordered as assumed in liquid drop theory. Nevertheless such theories have been useful in estimating conditions under which stratospheric aerosols might form and grow (Hamill et al., 1977b and references therein), and have suggested the likelihood of the incorporation of some HNO_3 into the primary aerosol particles (Kiang et al., 1975).

A second mechanism for initiating new particle formation has been proposed by Ferguson, private communication, (1977). As a result of a change in the effective ionization potentials and electron affinities of cluster species involving positive and negative ions, in principle, a size range can be reached where the particles would not be neutralized upon collision, but would lead to the formation of a small electrolytic droplet constituting a new condensed phase and could grow by further condensation. There is an experimental observation of Fe^+ and FeOH^+ and their hydrates associated with noctilucent clouds near the mesopause (Goldberg and Witt, 1977).

It is clear that in order to adequately formulate a theory for heteromolecular nucleation in particular, and to gain more insight into the entire field of aerosol formation, more attention must be paid to the structure of small clusters, the influence of these structures on the energy barrier, and the kinetics of clustering reactions. Promising theoretical approaches to nucleation can be expected to be based on molecular dynamic and Monte Carlo techniques since these methods offer the possibility of describing the molecular properties of small clusters and taking into account the many configurations possible as the clusters develop and grow.

In addition to changes resulting from continual condensation of vapor, particle sizes may also be altered by the coagulation of discrete entities of the condensed phase. The problem has been formulated by Chandrasekhar (1943) for the general case where size distribution is evolving as a result of random collisions among particles. Under some conditions, the collision kernel is directly related to the Boltzmann constant, gas viscosity, and absolute temperature (Hidy and Brock, 1971). Friedlander and co-workers (1966) show that, although number concentration and hence mean particle size vary during coagulation, the *shape distribution* is time independent, leading to the concept of a self-preserving aerosol size distribution. Even if aerosols are initially produced with a nearly uniform particle size, Lindauer and Castleman (1971) have shown that a polydispersed size distribution approaching a log-normal form will ultimately develop.

Effects of Aerosols

Potentially important chemical and physical effects include charge exchange between ions and aerosols, the production of trace species, and surface catalysis. It is of interest to note the total surface area of stratospheric aerosols is estimated to be $0.4 \times 10^6 \text{ km}^2$ and that a given gas phase molecule suffers a collision with a stratospheric aerosol surface about every 10^4 seconds (Castleman et al., 1975a).

The effect of aerosols on stratospheric ion densities is expected to be small. Keefe et al. (1959) show that to a good approximation aerosols maintain a Boltzmann charge distribution. Under stratospheric conditions, with about 10^3 ion pairs/ cm^3 it appears that ion destruction due to charge exchange processes involving aerosols is about a factor of 10 less than destruction due to ion recombination, except when the aerosol concentration is increased following periods of intense volcanic activity.

There is one situation where stratospheric aerosols have been thought to play a role in the production of trace species, namely the production of HCl from the interaction of H_2SO_4 with NaCl (Castleman et al., 1975b). Calculations show that the reaction is exothermic and the quantity of HCl so produced is likely to be limited

by the quantity of NaCl, potentially from sea salt, which may be deposited in the stratosphere following major storms in equatorial regions. However, the kinetics of the reactions are not known under the low temperature conditions prevailing in the stratosphere and laboratory studies of this reaction are needed.

There are three possible ways in which aerosol surfaces may play a role in affecting the gas phase concentration of chemically reactive species. These include the destruction of reactive intermediates such as free radicals which would be normally important in gas phase reactions, a catalytic influence on reactions between stable gas phase constituents, and the stabilization of a product molecule in the condensed state which might otherwise readily dissociate in the gas phase.

Quantitatively, very little is known about catalytic reaction mechanisms or rates which might be important in the upper atmosphere. Therefore, in order to assess which ones warrant attention, model calculations were made where it was assumed that one species is absorbed and others react with it upon each collision (Castleman et al., 1975a). By comparing these rates to known homogeneous ones involving the same species, a crude prediction was made regarding what species might have potentially important surface controlled chemistry. Admittedly this does not provide an unequivocal assessment of the importance, or lack thereof for the species under consideration, but it gives a way of screening and establishing priorities for laboratory investigation. Table 1-32 is a list of reactants, possible products, and an estimate of the maximum possible ratio of heterogeneous to homogeneous rates.

Table 1-32
Comparison of Surface and Gas-Phase Reaction Rates*

Reactants	Products	Ratio, Surface to Gas-Phase Reaction Rate
$\text{N}_2\text{O}_5, \text{H}_2\text{O}$	2HNO_3	$>10^3$
NO_2, O_3	NO_3, O_2	~ 10
$\text{CH}_3\text{O}_2, \text{NO}$	$\text{CH}_3\text{O}, \text{NO}_2$	~ 1
O_3, O	2O_2	200
NO, O_3	NO_2, O_2	~ 10
$\text{HO}_2 \cdot, \text{O}_3$	$\text{OH} \cdot, \text{O}_2$	5.3×10^{-2}
$\text{OH} \cdot, \text{O}_3$	$\text{HO}_2 \cdot, \text{O}_2$	1×10^{-3}
$\text{CH}_3\text{O} \cdot, \text{O}_2$	$\text{CH}_2\text{O} \cdot, \text{HO}_2 \cdot$	1.6×10^{-5}
$\text{Cl} \cdot, \text{O}_3$	$\text{ClO} \cdot, \text{O}_2$	1×10^{-6}
$\text{O} \cdot, \text{O}_2$	O_3	2.5×10^{-7}
$\text{CH}_3 \cdot, \text{O}_2$	$\text{CH}_3\text{O}_2 \cdot$	5.8×10^{-8}
$\text{H} \cdot, \text{O}_2$	$\text{HO}_2 \cdot$	1.7×10^{-10}

*Maximum surface reaction rate based on kinetic theory for collision rates, and assuming unit reaction probability upon collision.

Much of the stratospheric aerosol is believed to be composed of H_2SO_4 which is characteristically non-catalytic for many systems. Yet, since sulfuric acid aerosols contain H_2O , reaction with N_2O_5 might be important and deserves attention in this context. Olzyna et al. (1979) have shown that ozone destruction is not important on sulfuric acid surfaces. Therefore, this marginally important case may be omitted from further consideration unless substantial metallic oxide aerosols are found; in which case, they may play a small role. Ferguson (1978) suggests the possible importance of ozone reactions with metal atoms which might be a source of oxide aerosols.

As far as the possible importance of surface reactions is concerned, three other contenders are: the reaction of ClO with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ to produce HCl (Martin et al., 1978); ClONO_2 with H_2O giving rise to HOCl (Birks, private communication, 1979); and sulfur dioxide with H_2O_2 . Based on laboratory measurements, there is some evidence that the first occurs to a small extent. Estimates by Martin et al. (1978) suggest that the inclusion of this reaction in models could decrease by a few percent the estimated Cl/HCl ratios existing in the stratosphere. Laboratory studies are needed to assess the importance of surface reactions of H_2O_2 (Cadle et al., 1975).

Finally, a consideration of the potential importance of stratospheric heterogeneous reactions on the behavior of the fluorocarbons has failed to provide any evidence in support of such a mechanism. Ausloos et al. (1977) have demonstrated that unexpectedly large surface photochemical effects can result on certain surfaces, notably certain sands, leading to the destruction of some fluorocarbon compounds and N_2O . The mechanisms and significance of these catalytic processes are not well known, but even if they do occur, the quantity of potentially active surface material is far too low to be of importance in the stratosphere.

ATMOSPHERIC ION CHEMISTRY

Introduction

Over the past decade, considerable progress has been made toward a quantitative understanding of the ion chemistry of the Earth's atmosphere. The present status has recently been reviewed in detail by Ferguson (1979a) and Ferguson et al. (1979). Laboratory techniques are presently available to provide the kinetic data required to model atmospheric ion chemistry and many, if not most, of the critical reaction rate constants have been determined. A compilation and critical evaluation of these results has been provided by Ferguson (1973) and, in addition, the ion-neutral reactions measured in flow-tube reactors through 1977 have been compiled by Albritton (1978). For the most part, the laboratory techniques used for these determinations can be considered standard, with the most notable new development in the techniques used to study low-energy ion reactions of atmospheric interest being the selected-ion flow tube of Adams and Smith (1976).

In general, there is good agreement between laboratory measurements. The previous disagreement concerning binary ion-ion recombination coefficients now seems to be resolved in favor of the somewhat lower values measured by Smith et al. (1978). Perhaps the two most notable disagreements are those involving the heat of formation of CO_3^- (see Moseley et al., 1976; and Dotan et al., 1977) and the dissociative recombination of NO^+ (see Torr and Torr, 1978). It should be noted that these disagreements are small and do not involve options that significantly alter the ion reaction schemes that have been devised for the atmosphere. Rather, their significance lies in the detailed understanding of the systematic differences that can exist between the interpreted results of diverse experimental techniques.

The degree to which the directly measured atmospheric ion compositions can be predicted by models using laboratory results is, at present, the most important gauge of the completeness of the chemical reaction schemes, and the correctness of the laboratory measurements of the relevant rate constant data. The current status of this comparison for the mesosphere and stratosphere is reviewed in the following sections.

Mesospheric Positive-Ion Chemistry

Numerous *in situ* measurements of the D-region positive-ion composition (see e.g. Goldberg and Aiken, 1971; Narcisi et al., 1972; Arnold and Krankowsky, 1974; Zbinden et al., 1975) have indicated that the dominant ions of the E-region O_2^+ and NO^+ , are replaced by the water cluster ions, $H_3O^+ \cdot nH_2O$, in the D-region. The reaction scheme that has been devised to explain this conversion is shown in figure 1-2. The conversion of NO^+ to the hydronium ions by this scheme has been modeled by Reid (1977), and the association-reaction sequence seems to offer an adequately efficient mechanism. Certain of the thermochemical values assumed by Reid (1977) have been confirmed by later laboratory measurements (Turner and Conway, 1976; Johnsen et al., 1975; and Fehsenfeld and Albritton, 1979). In addition, some of the key ions in this reaction sequence have been observed *in situ* (Arnold and Krankowsky, 1974).

Because the reactions that convert NO^+ to $H_3O^+ \cdot nH_2O$ involve very weakly bound cluster ions of NO^+ as intermediaries, this conversion is extremely sensitive to temperature. The D-region positive-ion composition is expected to manifest strong seasonal, latitudinal, and even irregular variations as a result of variations in atmospheric temperature. Moreover, electron-ion recombination coefficients for these weakly bound ions, thus far unmeasured in the laboratory, may be considerably larger than those for the unclustered NO^+ and O_2^+ ions. This may explain, at least in part, the strong variations in the electron density that are observed at about 80 km (Arnold and Krankowsky, 1977; Reid, 1977).

Mesospheric Negative-Ion Chemistry

The D-region negative-ion chemistry has been derived predominantly from laboratory studies. This is in contrast to the positive-ion chemistry, which was deduced to explain the *in situ* measurements. The negative-ion chemistry is shown in figure 1-3. This chemistry is initiated by the attachment of electrons to O_2 to form O_2^- . The relatively unstable O_2^- ions undergo a series of ion-molecule reactions with the D-region minor molecular neutral constituents to form progressively more stable ions. In competition with this progression, reactions involving minor neutral constituents, principally atomic oxygen, lead back to the release of the electrons. Eventually, the sequence of reactions lead to terminal ions, e.g. NO_3^- and HCO_3^- , which are sufficiently stable to resist attack by the atomic species.

The rate limiting step in the production of the terminal negative ions, and thus in the loss of electrons by attachment, is the conversion of CO_3^- to NO_2^- by reaction with NO. This is due to the small rate constant for the reaction and the low concentration of nitric oxide. As a consequence, the ion chemistry of figure 1-3 predicts a low negative-ion concentration in the D-region, depending strongly on the concentration of minor neutral species such as O, O_3 , NO, and H.

Figure 1-3 does not include the effects of molecules clustering to the negative ions. At the relatively low D-region temperatures, all of the negative ions are subject to clustering to the atmospheric neutral molecules N_2 , O_2 and CO_2 . Clustering of these molecules to CO_3^- may somewhat alleviate the CO_3^- bottleneck if it inhibits the reaction of CO_3^- with O relative to that with NO. With the improved ability to study individual cluster ions that now exist, more extensive studies of the effects of clustering on chemical reactivity are being undertaken.

The first *in situ* measurements of the D-region negative-ion composition were made by Narcisi et al. (1971) and Arnold et al. (1971). There are sizable differences between these results, as well as areas of disagreement between these profiles and that predicted from the ion chemistry. Narcisi and co-workers observe ions that correspond to $NO_3^- \cdot nH_2O$ ($n = 1$ to 5) as the dominant negative ion below 90 km, which is in accord with the predictions drawn from the laboratory-derived chemical schemes. However, ions identified as O^- and O_2^- were observed above 90 km, which is not in accord with the chemical scheme outlined in figure 1-3. On the other hand, Arnold and co-workers found a rather sharp upper boundary to the D-region negative ions, which is in accord with predictions, but they identified the dominant masses as CO_3^- , Cl^- , and HCO_3^- , with the $NO_3^- \cdot nH_2O$ sequence not observed.

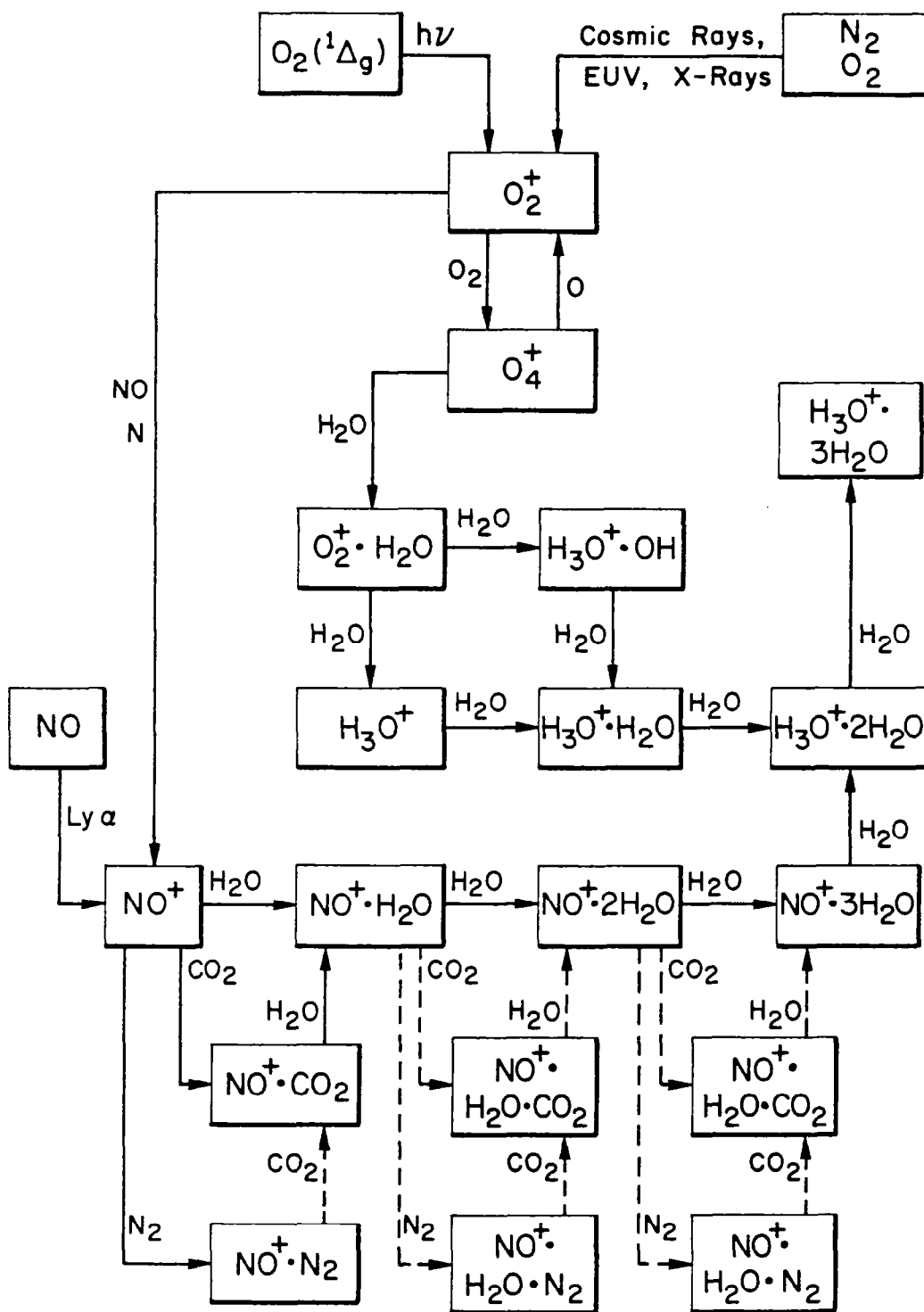


Figure 1-2. Mesospheric positive-ion chemistry.

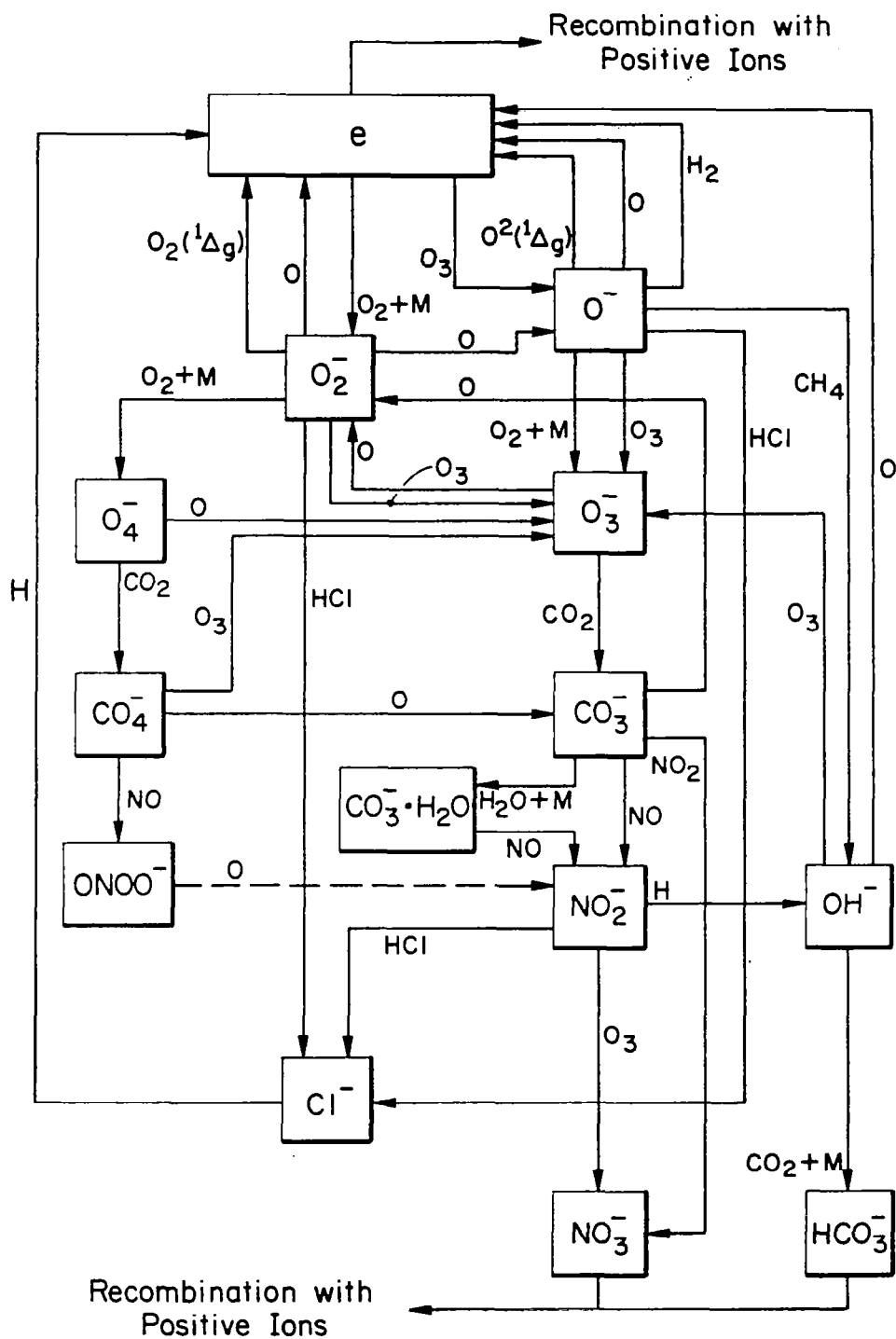


Figure 1-3. Mesospheric negative-ion chemistry.

Stratospheric Positive-Ion Chemistry

The positive-ion reaction scheme for the stratosphere is shown in figure 1-4. Galactic cosmic rays are the primary source of ionization in the stratosphere. An ion production rate of $10 \text{ ion pairs cm}^{-3}\text{s}^{-1}$ is fairly typical (Cole and Pierce, 1965). The ambient concentration of positive ions is determined by the recombination rate with negative ions and yields a concentration of about $5 \times 10^3 \text{ cm}^{-3}$ (Cole and Pierce, 1965; Paltridge, 1965, 1966).

In the ion chemistry the conversion of the primary ions N_2^+ and O_2^+ to the hydronium ions, $\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$, is quite efficient and there seems to be no alternative to their production in the stratosphere. The $\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$ ions are observed to be the dominant ions above 40 km in the stratosphere (Arnold et al., 1977). Below 40 km other ions are observed to become the dominant ions (Arnold et al., 1977; Arijs et al., 1978; Arnold et al., 1978). These non-hydronium ions have recently been interpreted (Ferguson, 1978; and Liu and Reid, 1979) as being protonated sodium hydroxide ions. Sodium is produced by meteor ablation near 90 km. It is argued that this sodium will settle through the stratosphere and be incorporated as NaOH below 40 km. The exceedingly large proton affinity of NaOH (Kearle, 1977) ensures that the reaction with $\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$ is highly exothermic and likely to occur with nearly unit efficiency.

Stratospheric Negative-Ion Chemistry

The negative-ion reaction scheme as deduced from laboratory measurements is indicated in figure 1-5. The shaded boxes and dashed lines represent points of considerable uncertainty, which is associated with the increasing importance of three-body association reactions to form cluster ions. Although the presence of these cluster ions make the exact reaction paths uncertain, there is little question that these paths will lead eventually through NO_3^- . Both HNO_3 and N_2O_5 provide effective NO_3^- production routes (Fehsenfeld et al., 1975; Davidson et al., 1977b). It has been shown that HNO_3 exothermically displaces H_2O in hydrated negative ions (Fehsenfeld et al., 1975); therefore, the agent of NO_3^- formation can enter the cluster.

NO_3^- is not considered the terminal ion of the stratospheric negative-ion chemistry. It has recently been found (Viggiano et al., 1979) that $\text{NO}_3^- \cdot n\text{HNO}_3$, $n = 0, 1, 2$, reacts rapidly with H_2SO_4 . Consequently, this neutral species is capable of establishing HSO_4^- as the terminal stratospheric negative ion. That this does occur in the stratosphere is indicated from the first mass sampling of stratospheric negative ions (Arnold and Henschen, 1978). In this balloon-borne mass-spectrometric measurement, ions identifiable as $\text{HSO}_4^- \cdot \text{HNO}_3$; $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4$; $\text{HSO}_4^- \cdot 2\text{HNO}_3$; $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HNO}_3$; $\text{HSO}_4^- \cdot 3\text{HNO}_3$; and $\text{HSO}_4^- \cdot 2\text{H}_2\text{SO}_4$ were observed.

Summary

As a more comprehensive understanding of the ion chemistry is achieved, the measured ion composition can be used to obtain information concerning the neutral composition of the stratosphere and mesosphere. In this context, Arnold and Krankowsky (1977) have determined the mesospheric water vapor concentration from their D-region positive-ion composition measurements. In the same fashion, the stratospheric positive ion composition (Arnold et al., 1978; Arijs et al., 1978) has been used to establish a lower limit on the stratospheric concentration of NaOH (Ferguson, 1978) and an upper limit for CH_3OH (Fehsenfeld et al., 1978). Furthermore, the stratospheric negative-ion composition observed by Arnold and Henschen (1978) has been used to set a rather precise value for the stratospheric H_2SO_4 concentration (Viggiano et al., 1979). The potential utility of the stratospheric and tropospheric ion composition measurements as sensitive probes of atmospheric composition is quite apparent.

One area in which ion chemistry has arisen from time to time as a potentially significant atmospheric factor is as a source or sink of atmospheric neutrals. Ion reactions have been proposed as a sink for ozone in the

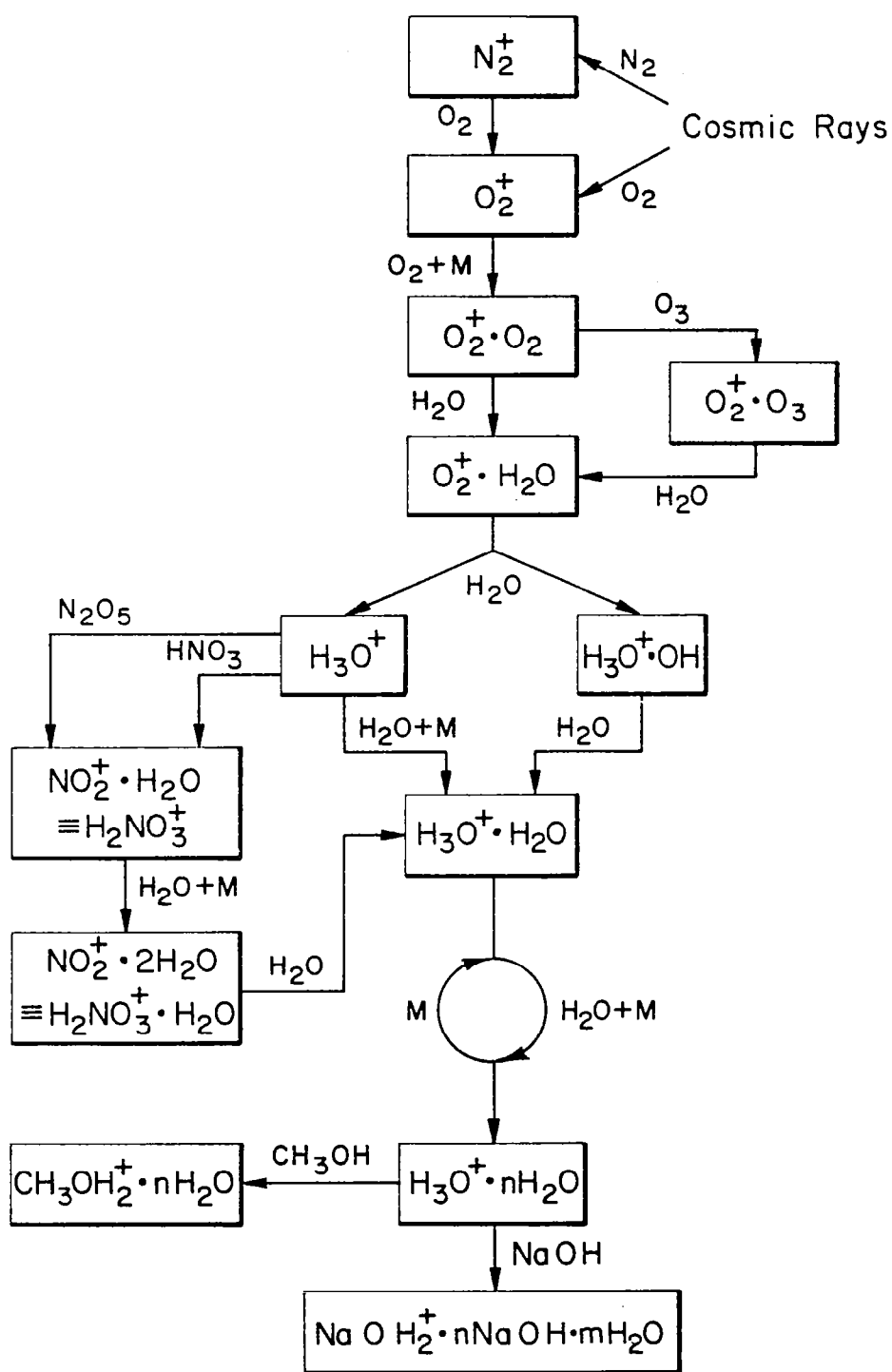


Figure 1-4. Stratospheric positive-ion chemistry.

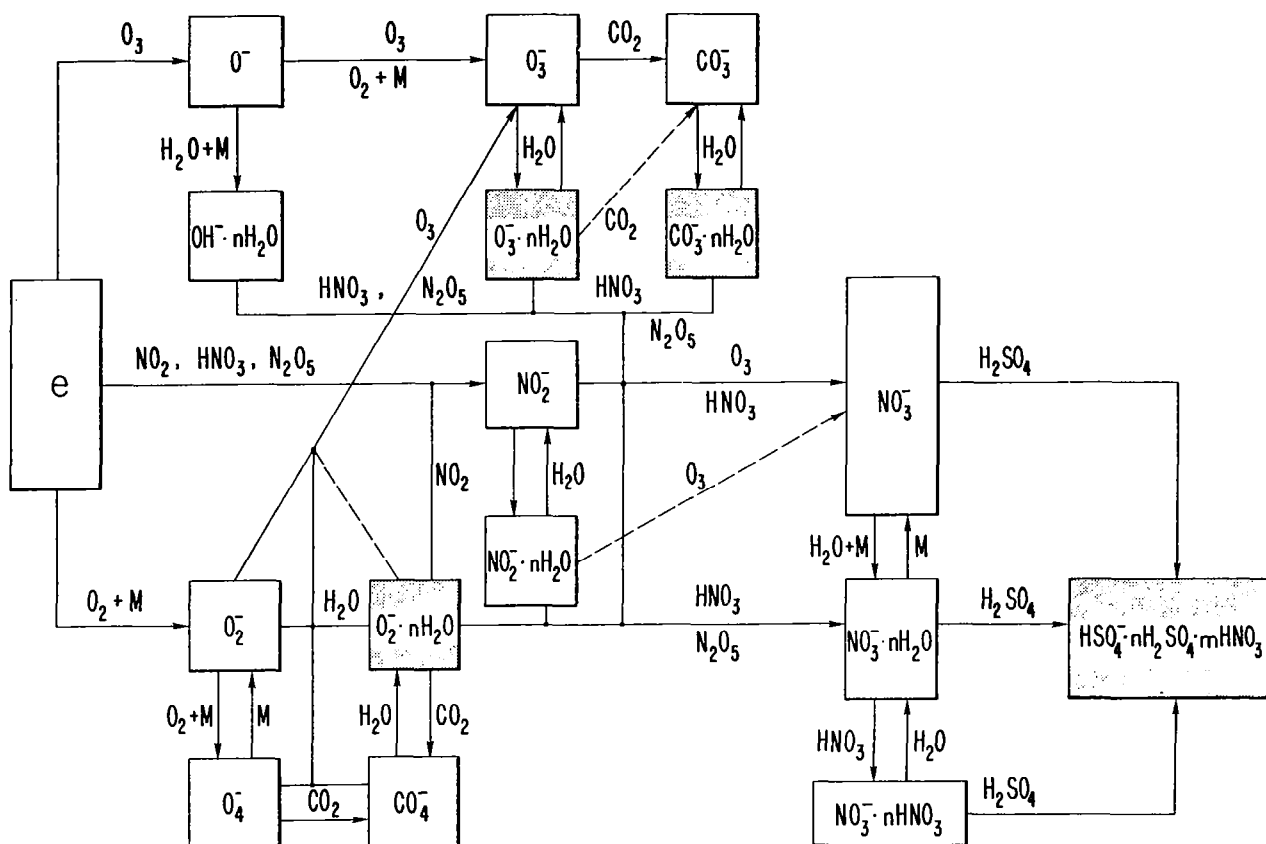


Figure 1-5. Stratospheric negative-ion chemistry.

stratosphere and for N_2O , CFCl_3 , and CF_2Cl_2 in the troposphere. In these cases, however, the reactivity of atmospheric ions with these species is not sufficient to provide an efficient removal mechanism (Fehsenfeld et al., 1976a; Fehsenfeld et al., 1976b; Fehsenfeld and Albritton, 1977). Nevertheless, ion reactions, particularly in catalytic cycles, may be capable of directly altering the neutral composition by providing an effective surface on which neutral reactions may occur.

Recommendations

- Reaction rate data are needed at high pressures ($[M] \geq 10^{18} \text{ cm}^{-3}$) and low temperatures.
- The effect of clustering on ion reactivities and the reaction mechanisms of clustered ions should be studied using selected-ion techniques, where possible.
- The thermochemical values necessary to judge the degree of ion clustering prior to recombination and the stability of those ions is needed.
- The evolution of the products of ion-ion recombination, especially involving very stable ions such as NaOH_2^+ and HSO_4^- , should be understood.

- The ion chemistry of neutrals such as NaOH, H₂SO₄, and ClONO₂ should be investigated.
- Possible schemes for ion-catalyzed neutral conversion should be investigated, by considering reactions between the terminal positive and negative ions and atmospheric trace neutral molecules.

DATA FOR INFRARED AND ULTRAVIOLET PHENOMENA

INFRARED SPECTROSCOPY

Species of interest to the study of stratospheric processes are listed in table 4-2 of Chapter 4. Except for the atoms and the hydrogen molecule, these species have active infrared absorption bands, and infrared instruments of various types can be employed to detect and quantitatively measure the abundance of many of them.

Accurate spectral data are of critical importance to the utilization of infrared techniques for remote, quantitative measurements of stratospheric species. The ability of the infrared techniques to accomplish highly accurate, remote measurements with adequate spatial and temporal resolution and coverage justifies the investment in relevant infrared spectroscopy.

Currently Available Data

The infrared spectrum of the Earth's atmosphere is dominated by numerous spectral features due to the more common gases: H₂O, CO₂, CH₄, CO, N₂O, O₃ and O₂. An extensive compilation of infrared spectral data for these molecules was compiled several years ago by McClatchey et al. (1973), at the Air Force Cambridge Research Laboratory, and a recent update of this compilation has been described by Rothman (1978). The updated data primarily concern certain parameters for H₂O, CO₂, CH₄, and includes an extension to shorter infrared wavelengths, where numerous O₂ lines exist. The compilation includes the following data for each molecule and its isotopes: line center frequency, line strength, air-broadened linewidth, lower state energy, and quantum identification of the transition. Lines whose strengths fall below a certain cutoff value are excluded. Recently, an initial compilation of spectral parameters for other trace gases has been assembled, under the sponsorship of the Air Force Geophysical Laboratory (Rothman et al., 1978). The new molecules include NO, SO₂, NO₂, and NH₃.

The compilations of spectral parameters just mentioned are extremely valuable for unraveling the meaning of an atmospheric spectrum in the infrared, for assessing which spectral regions are most desirable for detecting the existence of other trace gases in the atmosphere, and for accurately calculating the contributions of the various infrared-active molecules to the so-called greenhouse effect. However, much of the spectral data can only be considered approximate, even for the more common trace gases listed in these compilations. This is especially true of the line broadening parameters. Certain overtone and combination bands of these gases are not represented in the compilations, even though they are observable in long-path stratospheric spectra and require identification. However, the compilations are always useful, even if only as a first approximation in some cases, and the organizers involved in the compilations update their material when new data becomes available. The continuation of this program is important.

Spectral Requirements

Until recently, no large effort has existed in the application of high-resolution infrared measurement techniques to the understanding of stratospheric photochemistry. Thus, it is not surprising that the data for most of the constituents of interest are not in any of the major atmospheric absorption compilations. However, a great deal of these data do now exist at various institutions—data which can be used at least for identification

of these species. Data which can be used to obtain a measurement with 20% accuracy or better at stratospheric temperature are yet to be obtained for many of these species (e.g., ClONO_2 , CH_3CCl_3 , HO_2 , CFCl_3).

As needs arise for measurements of trace molecules which are not on this list, it is almost always the case that a laboratory spectroscopic study must be undertaken to produce the data of necessary accuracy to be useful in a stratospheric measurement.

At this point it is useful to insert a few remarks on molecular parameters to help point out the spectral data and infrared instrumentation requirements for optimum measurement capability. Radiation at frequency ν passing through the atmosphere is absorbed according to the expression

$$I = I_0 \exp [-\alpha(\nu, z)], \quad (7)$$

where $\alpha(\nu, z)$ is the absorption coefficient at frequency ν and position z along the path. If the absorption is due to a single nearby absorption line, $\alpha(\nu, z)$ can be expressed as

$$\alpha(\nu, z) = N(Z) S(T) f(\nu - \nu', p), \quad (8)$$

Where $N(Z)$ is the number density of absorber molecules at position Z , $S(T)$ is the line strength, and $f(\nu - \nu', p)$ is the line shape function for the absorber at pressure p and temperature T . The strength of the line centered at frequency ν' , is

$$S = (\nu' / \nu_0) S_\nu^0 L g [\exp(-E''/kT)] [(1 - \exp(-\nu/kT)) F/Q_r] \quad (9)$$

where ν_0 is the molecule's vibration-rotation band center, S_ν^0 is the band strength at temperature T , L is the "rigid rotor" rotational transition probability, g and E are the statistical weight and the energy of the lower energy level, respectively, k is Boltzmann's constant, Q_r is the rotational partition function (which is a function of T), and F is a factor which accounts for vibration-rotation interactions.

The absorption line shape is influenced by collision broadening and Doppler effects. The Doppler half-width is proportional to the transition frequency, and to $(T/M)^{1/2}$, where T is the temperature and M is the molecular absorber's mass. If the absorption line width is dominated by collision broadening, then $f(\nu - \nu', p)$ assume a Lorentz shape. The half-width in this case is proportional to $p/(T)^{1/2}$ in most cases. At stratospheric altitudes, the pressure is low enough such that Doppler broadening becomes important, and the altitude at which this occurs depends on the absorption-line frequency, and on the molecular mass and temperature. Doppler broadening is important at all stratospheric altitudes for, e.g., HF , HCl , CH_4 , and H_2O lines in the 3000 cm^{-1} region and at higher frequencies. In this case, the Doppler limiting linewidths are almost 0.01 cm^{-1} for the light molecules. In the 1000 cm^{-1} region (where many of the heavier molecules have absorption bands), Doppler limiting linewidths are much smaller, e.g., 0.001 cm^{-1} . These linewidths are typical at altitudes above 30 km in the stratosphere.

If possible, laboratory spectroscopic measurements should be carried out with high spectral resolution instruments capable of resolving the absorption lines under Doppler limited conditions. The infrared instruments used for measurements should also have high spectral resolution, for the optimum performance (in terms of sensitivity and selectivity) is obtained when the spectral resolution matches the linewidths. In some cases where heavier molecules are involved, the density of lines within a band is so large that the lines are blended even under Doppler-limited conditions. This produces a band which does not ordinarily have spectral features as sharp as Doppler-limited linewidths, which implies that instruments with lower spectral resolution may be just as effective in detection and measurement of these species.

Current Capabilities

A great deal of spectral information for various trace species is now being generated by various groups with Fourier Transform infrared spectrometers (FTIR) whose spectral resolutions are between 0.01 cm^{-1} and 0.05 cm^{-1} , and by a smaller number of groups with tunable diode lasers (which can yield 0.001 cm^{-1} spectra). The FTIR instruments produce high-quality spectra over large spectral regions. This data is adequate for several existing infrared measurement instruments which have comparable resolution. (See, for example, Murcray, 1978.) For application to measurement programs in which higher resolution instruments are used (e.g., laser heterodyne radiometers, with resolution of about 0.001 cm^{-1}), this data is useful for determining optimum wavelength regions for measurement of a specific trace species. Further spectroscopic measurements with higher spectral resolution are required. This can be accomplished with various lead salt diode laser systems, or with a combination of diode and discretely tunable gas lasers. (Many gas laser frequencies are known with extremely high accuracy, and these can be used as benchmarks.) This type of work was recently done for the chlorine monoxide (ClO) fundamental near 845 cm^{-1} (Margolis et al., 1978; Rogowski et al., 1978); and for the $2\nu_g$ band of nitric acid (HNO_3) near 890 cm^{-1} (Brockman et al., 1977); and is presently being carried out for the H_2O_2 band near 1350 cm^{-1} (Hillman private communication, 1978), and for the ClONO_2 ν_3 and ν_4 bands near 800 cm^{-1} . Work is ongoing with these types of instruments and techniques at several institutions, with plans to produce accurate, high resolution spectra for each of the species of interest (with the exception of O_2 and H_2) for which the data is incomplete or of unacceptable quality for the stratospheric measurements application.

Much of the spectral data which now exists for stratospheric trace species is applicable only to a narrow set of measurement conditions. Further analyses of these and additional laboratory spectra are required to generate the kind of data which can be inserted into compilations for eventual use by a large community of workers. Although this often requires additional manpower and funding, the potential benefits of this investment are considerable.

ULTRAVIOLET FLUXES AND CROSS SECTIONS

The primary influence of the Sun in the middle atmosphere is due to the ultraviolet fluxes absorbed by molecular oxygen and ozone. Nearly all radiation of wavelengths less than 100 nm is absorbed by nitrogen and oxygen in the thermosphere and is, therefore, not considered here. The X-rays of wavelengths of less than 1 nm and energetic particle radiations can penetrate into the atmosphere below 100 km and are considered in Chapter 4.

Overview

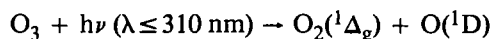
The radiation of wavelengths less than 242 nm is absorbed by molecular oxygen and leads to its photodissociation. The principal photodissociation continuum (Schumann-Runge continuum) at $\lambda < 175\text{ nm}$ results in a complete absorption of the solar radiation in the thermosphere. However, an important solar line, Lyman- α at 121.6 nm , situated in a so-called atmospheric window where the O_2 absorption cross section is only of the order of 10^{-20} cm^2 , is absorbed in the mesosphere.

The second important spectral range for molecular oxygen, between 200 nm and 175 nm , is related to the O_2 Schumann-Runge band system which includes 18 bands, (2-0) to (19-0), subject to the predissociation process. In this spectral region, the mean absorption cross sections are a function of the temperature and number of O_2 absorbing molecules. This absorption, which is essentially a mesospheric process, also plays a role in various stratospheric photodissociations.

From 200 to 242 nm , the O_2 absorption, which is related to the Herzberg continuum with low absorption cross section (from 10^{-24} to 10^{-23} cm^2) occurs in the stratosphere. In addition, the ozone absorption must be

introduced since this spectral region belongs to the spectral range of the O_3 Hartley band. In the mesosphere, the O_2 absorption is practically negligible since the total number of ozone molecules is very small even for low solar zenith angles, but the simultaneous absorption by O_2 and O_3 must be considered in the stratosphere.

For the Hartley band the limit near 310 nm must be determined with precision, since the photodissociation process in the Hartley band, which is



leads to the production of $O(^1D)$ atoms responsible, particularly below 50 km, for the production of OH from H_2O , CH_4 and H_2 , and also of NO from N_2O .

At $\lambda > 310$ nm, the O_3 Huggins bands correspond to the limit of its ultraviolet absorption. The spectral range between 310 nm and 400 nm corresponds also to various limits of the absorption spectrum of H_2O_2 , H_2CO , NO_2 , N_2O_5 , HNO_2 , HNO_3 , $ClONO_2$, $HOCl$, etc.

In the visible region (410 – 850 nm), the Chappuis bands lead to the O_3 photodissociation in the lower part of the atmosphere, troposphere and lower stratosphere.

At $\lambda > 300$ nm, various effects such as the Rayleigh scattering and the albedo must be introduced. In particular, they play a role on the photodissociation rates of O_3 , ratio $n(O)/n(O_3)$, of NO_2 , ratio $n(NO_2)/n(NO)$, and on the absolute concentration of the other constituents absorbing in that spectral region.

Thus, the photodissociation problem is related to a knowledge of the solar flux and its possible variations in certain spectral regions, the exact determination of the vertical distribution of the atmospheric optical depth of O_2 and O_3 , the measurement of the absorption cross sections and photodissociation quantum yields for each constituent, and the introduction of the atmospheric conditions related to the radiation scattering and albedo.

Solar Fluxes and O_2 Absorption

The absorption cross section in the Herzberg continuum is known with an accuracy which is not greater than 25% (figure 1-6). At $\lambda > 230$ nm the O_2 cross section is not known with sufficient precision; but since the ozone absorption is maximum in this part of the ultraviolet spectrum, the numerical error is reduced for the value of the total O_2 photodissociation rate. Table 1-33 shows the variation of the mean absorption cross section based on the experimental data of Ditchburn and Young (1962), Ogawa (1971), Hasson and Nicholls (1971) and Shardanand and Rao (1977) and increasing from about 10^{-24} cm² at 240 nm to 1.5×10^{-23} cm² at 200 nm; this last value involves the 0-0 and 0-1 Schumann-Runge band absorption. The resulting $j_\infty(O_2)$ from identical energy spectral ranges (500 cm⁻¹) shows a rapid increase from 240 nm to 230 nm (table 1-33) and also a decrease at $\lambda > 210$ nm. The problem of the solar flux values will be discussed shortly.

The Lyman- α absorption occurs in the wing of an O_2 band and is subject to a temperature effect (Carver et al., 1977). Its absorption cross section is a function of the temperature and of the O_2 optical depth. Figure 1-7 shows how the absorption cross section varies from 10^{-20} cm² to 7×10^{-21} cm² at $T = 190$ K (mesospheric temperature) for optical depths between 0 and 9. Lyman- α plays a role in the mesospheric photodissociation rate of several constituents, but particularly of H_2O , CH_4 and CO_2 . It is responsible for the NO ionization in the mesosphere.

The problem of the O_2 photodissociation in the Schumann-Runge band spectral range, and also of its atmospheric absorption has not yet reached its final solution. After various applications of the first experimental results to the atmosphere (Hudson et al., 1979; Kockarts, 1971, 1976; Hudson and Mahle, 1972; Fang et al., 1974; Park, 1974; Muramatsu, 1975; Shimazaki et al., 1977), new experimental and theoretical results

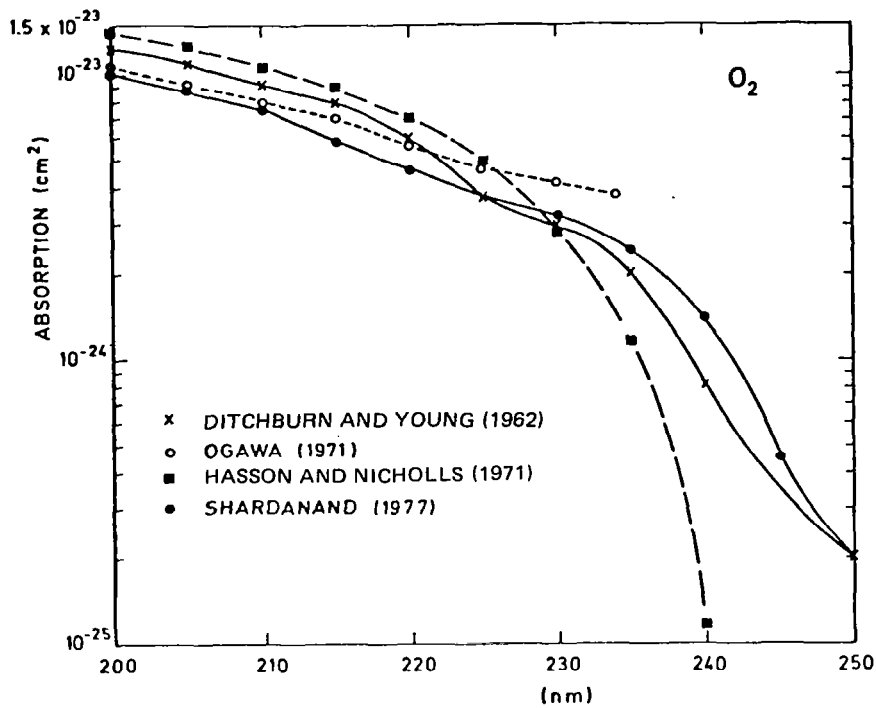


Figure 1-6. Experimental data on O_2 absorption cross sections in the Herzberg continuum.

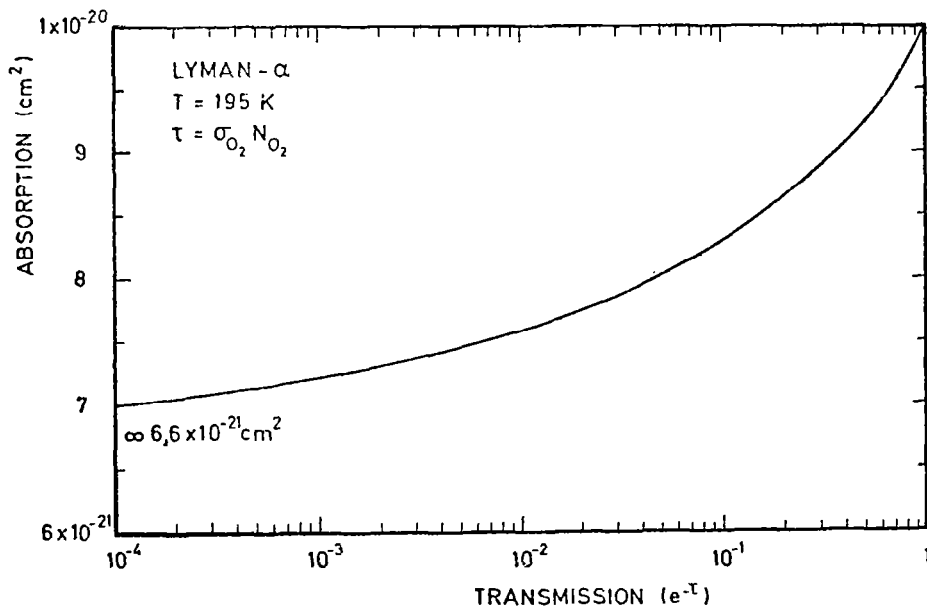


Figure 1-7. Experimental variation of the Lyman-alpha absorption cross section (cm^2) with the optical depth in molecular oxygen, $N(O_2)$ (cm^2).

Table 1-33

Mean value of solar flux (q , photons $\text{cm}^{-2} \text{sec}^{-1}$); mean cross section (σ , cm^2 for 500 cm^{-1}) and O_2 photodissociation coefficients (j , sec^{-1}) at the top of the earth's atmosphere in the spectral range of the O_2 Herzberg continuum ($\lambda(\text{nm})$ = average wavelength in nm of the spectral range, $\pm 250 \text{ cm}^{-1}$).

$\lambda(\text{nm})$	q_{∞}	σ_{O_2}	j_{∞}
201.0	1.44×10^{12}	1.50×10^{-23}	2.16×10^{-11}
203.0	1.80	1.25	2.25
205.1	2.08	1.00	2.08
207.2	2.45	9.80×10^{-24}	2.40
209.4	5.09	9.20	4.68
211.6	7.12	8.50	6.05
213.9	9.23	7.85	7.25
216.2	8.42	7.05	5.94
218.6	1.20×10^{13}	6.15	7.38
220.9	1.22	5.50	6.71
223.4	1.77	4.75	8.41
225.9	1.60	4.05	6.48
228.6	1.96	3.35	6.57
231.2	1.97	2.70	5.32
233.9	1.70	2.20	3.74
236.7	2.00	1.65	3.30
239.5	1.77	1.20	2.12
242.4	1/2 (2.58)	0.75	9.80×10^{-12}

(Lewis et al., 1978; Frederick and Hudson, 1979; Nicolet and Peetermans, 1979) show that still more attention should be given to the accuracy problem.

There is general agreement on the molecular constants used for the O₂ Schumann-Runge bands (*cf* Fang et al., 1974) as known from experimental data obtained by Ackerman and Biauume (1970b) and by Brix and Herzberg (1954), and analyzed for the fine structure of the upper level $^3\Sigma^+ \nu' \geq_g$ by Bergman and Wofsy (1972). Additional measurements with still higher resolution would be useful. But precise oscillator strengths and linewidths associated with exact line positions are an absolute necessity for accurate determination of the photodissociation processes, particularly in the mesosphere. From a comparative analysis (Nicolet and Peetermans, 1979) of the various parameters involved in the atmospheric O₂ absorption, it can be concluded that there is no important direct effect of the Schumann-Runge band absorption on the total J₂ value in the stratosphere. Simplified formulas for computing the O₂ mean optical depth for the Schumann-Runge bands are also given in that paper. They can be applied to stratospheric problems without any restriction, but they may require several improvements for mesospheric applications when the physical parameters are known with better accuracy. Nitric oxide requires a specific analysis (Cieslik, Nicolet, 1973; Cieslik, 1977, 1978; Frederick and Hudson, 1979b; Nicolet and Cieslik, 1979). See table 1-34.

Solar Flux Variability, O₃ Absorption

In the wavelength range of $\lambda > 175$ nm, which is involved in mesospheric, stratospheric and tropospheric photodissociation processes, it has not yet been possible to identify solar flux variations associated with specific solar activity phenomena.

First, fluctuations of the solar constant $S = 137 \pm 1$ mW cm⁻² have not been established by direct measurements; only a few of atmospheric phenomena have been associated with the bi-annual variation of 6.6% in flux due to the variations of the Earth-to-Sun distance variation. Only Lyman- α at 121.6 nm shows a clear evidence of an association of its intensity with solar activity controlled by identified chromospheric plagues. It is not possible to examine here all rocket or satellite measurements made since 1949 (see Friedman, 1960; Weeks, 1967; Prinz, 1974; Vidal-Madjar, 1975, 1977). It is clear that a more precise absolute calibration of the total Lyman- α line flux is still required; on the other hand, the profile measurements (Tousey, 1963; Bruner and Parker, 1969; Bruner and Rense, 1969; Lemaire et al., 1978; Artzner, 1978) indicate that the global profile is a variable average profile whose form is determined by various solar features between the center and the limb which are influenced by solar activity.

Thus, a mean value of 3×10^{11} photons cm⁻²sec⁻¹ (see, for example, Thomas and Anderson, 1976) for the Lyman- α solar flux at the mean Earth-to-Sun distance is almost a conventional value, although the accuracy cannot be better than $\pm 25\%$. If we write

$$q_{\infty}(\text{Lyman-}\alpha) = (3 \pm 1) \times 10^{11} \text{ photons cm}^{-2}\text{sec}^{-1}$$

we may consider 2×10^{11} photons cm⁻²sec⁻¹ as a minimum working value and 4×10^{11} photons cm⁻²sec⁻¹ as an acceptable maximum value corresponding to quiet Sun and active solar conditions, respectively. There is, therefore, a variation of a factor of the order of 2 over an average solar cycle. As far as the variations of the Lyman- α intensity associated with short-term fluctuations (27 days, for example) are concerned, it seems reasonable to use as an indication the preliminary empirical relations established by Vidal-Madjar (1975).

We consider that the Lyman- α flux variations with solar activity represent the maximum possible differences that can occur in the solar flux at $\lambda > 100$ nm. Furthermore, there is no astrophysical result leading to such possibilities at $\lambda > 175$ nm, except for a few emission lines of relatively low intensity related to solar plagues.

Table 1-34
 Solar flux (q_{∞} photons $\text{cm}^{-2} \text{sec}^{-1}$), mean absorption cross section (σ_{MAX} cm^2) at $T = 230 \text{ K}$, and O_2 photodissociation coefficients (j , sec^{-1}) at the top of the Earth's atmosphere in the spectral range of the O_2 Schumann-Runge bands.

O_2 BAND	q_{∞}	σ_{MAX}	j_{∞}
19-0	1.58×10^{10}	7.52×10^{-20}	1.19×10^{-9}
18-0	2.23	1.41×10^{-19}	3.14
17-0	2.80	1.71	4.79
16-0	3.66	1.64	6.00
15-0	5.18	1.44	7.46
14-0	6.60	1.28	8.45
13-0	8.79	9.91×10^{-20}	8.71
12-0	1.03×10^{11}	7.14	7.35
11-0	1.43	4.91	7.02
10-0	2.07	3.17	6.56
9-0	2.09	2.02	4.22
8-0	2.56	1.16	2.97
7-0	3.96	6.06×10^{-21}	2.40
6-0	4.63	2.86	1.32
5-0	6.38	1.16	7.40×10^{-10}
4-0	7.16	4.05×10^{-22}	2.90
3-0	1.14×10^{12}	1.29	1.47
2-0	1.54	3.88×10^{-23}	5.98×10^{-11}

However, a recent review by Heath and Thekaekara (1977) describes various observational results obtained between 1964 and 1975 which would indicate a variation of a factor of the order of 2 at 200 nm and not less than $\pm 10\%$ at 300 nm. On the other hand, Simon (1978) and Delaboudiniere et al. (1978) do not reach the conclusion that there is any such variability during the 11 year cycle. In fact, if we examine the observational results obtained in the ultraviolet region from the first rocket measurements to the last observational results, we can see that there is a systematic decrease in the observed values of this solar ultraviolet flux. Furthermore, if we consider only the more recent observational data in the spectral range of the O₂ Schumann-Runge band system (Rottman, 1974; Simon, 1975; Samain and Simon, 1976; Heroux and Swirbalus, 1976; Brueckner et al., 1976), it is clear that the estimated precision in the flux measurement is of the order of $\pm 20\%$. Thus, any mean value adopted for this spectral region reflects the lack of accuracy resulting from the dubious character of absolute calibrations, and also from the limited precision due to various uncertainties in laboratory and atmospheric measurements in this spectral region. Consequently, it must be said that any solar activity effect leading to a possible variation of the solar flux cannot yet be distinguished from differences between observers. There is no clear indication leading to a perfect choice for mean or specific values of the solar flux in this spectral region leading to the O₂ photodissociation. The adopted numerical values given in table 1-34 should be accepted as provisional values, since the accuracy cannot be given and the precision cannot be better than $\pm 25\%$. They indicate, however, an increase in the solar flux from 175 nm to 200 nm of the order of a factor of 10 for identical spectral ranges ($\Delta\nu = 500 \text{ cm}^{-1}$) and of about a factor of 100 from (19-0) to (2-0) band ranges. Nevertheless, it is not excluded that a systematic error of 50% could exist in a particular domain of this spectral region. In any case, reference must be made to the observational results (Brueckner et al., 1976) on the variation of the solar flux in the spectral range of the Schumann-Runge bands due to solar activity (about 5%).

In the region of the O₂ Herzberg continuum, $200 \text{ nm} < \lambda < 242 \text{ nm}$, several atmospheric measurements have been made (see Simon, 1978). The values adopted here are based essentially on data published by Broadfoot (1972) and Simon (1975) and have been given in table 1-33 with the related O₂ absorption cross sections for 500 cm^{-1} spectral ranges. More observations are needed to improve the accuracy of the adopted values, even if it seems that the precision is better than at $\lambda < 200 \text{ nm}$.

In the spectral region covered by the Hartley band from 242 nm to 310 nm, we have also adopted rocket data by Broadfoot (1972) with the values obtained by balloon measurements (Simon, 1975) at $\lambda > 284 \text{ nm}$ in order to avoid certain discrepancies between various observational data particularly in the spectral region 200-300 nm (see DeLuisi, 1975; Simon, 1978). The adopted results (Nicolet, 1975) are given in table 1-35 with the corresponding O₃ cross sections and photodissociation rates.

Finally, in the ultraviolet region, corresponding to the Huggins bands, it is necessary to introduce in the numerical values a smooth transition from about 300 nm, in the range of the spectral limit of observational data obtained by Broadfoot (1972), to 400 nm where the solar flux data obtained by Arvesen et al. (1969) can be accepted if the published values are reduced to a lower solar constant value (Nicolet, 1975). Such data for $\Delta\lambda = 5 \text{ nm}$ are given in table 1-36. New measurements of the solar flux between 300 nm and 400 nm would be useful in helping to improve the accuracy of absolute values.

Finally, the solar flux which is adopted in the visible region corresponds to the numerical values adjusted to the present value of the solar constant (Nicolet, 1975) and deduced also from observational data published by Arvesen et al. (1969). They are given in table 1-37 with the corresponding values of the O₃ photodissociation rates corresponding to the Chappuis bands. Since the experimental cross sections of the O₃ visible band are certainly good and are not subject to a temperature effect, the total photodissociation rate J_3 (Chappuis) = $3.4 \times 10^{-4} \text{ sec}^{-1}$ seems to be accurate; the total error ($< \pm 10\%$) corresponds to the accuracies of the solar flux observations and of the experimental O₃ absorption cross sections. In the region of the O₃ Huggins bands, where the temperature effect on the absorption cross section value is significant, new solar observations and laboratory measurements are certainly needed.

Table 1-35

Solar flux (q , photons $\text{cm}^{-2}\text{sec}^{-1}$), average cross section (σ , cm^2 for 500 cm^{-1}) and O_3 photodissociation coefficients (j , sec^{-1}) at the top of the Earth's atmosphere in the spectral ranges of the O_2 Herzberg continuum and O_3 Hartley band.

$\lambda(\text{nm})$	q_∞	σ_{O_3}	j_∞	$\lambda(\text{nm})$	q_∞	σ_{O_3}	j_∞
201.0	1.44×10^{12}	3.26×10^{-19}	4.69×10^{-7}	245.4	2.35×10^{13}	1.00×10^{-17}	2.35×10^{-4}
203.0	1.80	3.26	5.87	248.5	2.38	1.07	2.55
205.1	2.08	3.51	7.30	251.6	2.28	1.11	2.53
207.2	2.45	4.11	1.01×10^{-6}	254.7	3.24	1.12	3.63
209.4	5.09	4.84	2.46	258.0	5.83	1.11	6.47
211.6	7.12	6.26	4.46	261.4	4.89	1.03	5.04
213.9	9.23	8.57	7.91	264.9	1.19×10^{14}	9.43×10^{-18}	1.12×10^{-3}
216.2	8.42	1.17×10^{-18}	9.85	268.4	1.29	8.23	1.06
218.6	1.20×10^{13}	1.52	1.82×10^{-5}	272.1	1.17	6.81	7.97×10^{-4}
220.9	1.22	1.97	2.40	275.9	1.11	5.31	5.89
223.4	1.77	2.55	4.51	279.7	7.85×10^{13}	3.99	3.13
225.9	1.60	3.24	5.18	283.7	1.50×10^{14}	2.84	4.26
228.6	1.96	4.00	7.84	287.7	2.12	1.92	4.07
231.2	1.97	4.83	9.52	291.9	3.56	1.14	4.06
233.9	1.70	5.79	9.84	296.3	3.33	6.60	2.20
236.7	2.00	6.86	1.37×10^{-4}	300.7	3.08	3.69	1.14
239.5	1.77	7.97	1.41	305.3	4.39	1.97	8.65×10^{-5}
242.4	2.58	9.00	2.32				

Table 1-36

Solar flux (q , photons $\text{cm}^{-2} \text{sec}^{-1}$) with average cross section (σ , cm^2 for $\Delta\lambda = 5 \text{ nm}$) and O_3 photodissociation coefficient (j , sec^{-1}) in the spectral range of the O_3 Huggins bands, at the top of the Earth's atmosphere.

$\lambda(\text{nm})$	q_{∞}	σ_{O_3}	j_{∞}
310.0	4.95×10^{14}	1.05×10^{-19}	5.20×10^{-5}
315.0	5.83	5.23×10^{-20}	3.05
320.0	6.22	2.91	1.81
325.0	6.96	1.50	1.04
330.0	8.61	7.78×10^{-21}	6.70×10^{-6}
335.0	8.15	3.72	3.03
340.0	8.94	1.71	1.53
345.0	8.44	7.46×10^{-22}	6.30×10^{-7}
350.0	8.69	2.66	2.31
355.0	9.14	1.09	9.96×10^{-8}
360.0	8.23	5.49×10^{-23}	4.52
365.0	1.07×10^{15}		
370.0	1.08		
375.0	9.72		
380.0	1.11		
385.0	8.98		
390.0	1.18		
395.0	9.34		
400.0	1.69		
405.0	1.70		

Table 1-37

Solar flux (q photons $\text{cm}^{-2}\text{sec}^{-1}$) with average cross section (σ , cm^2 for $\Delta\lambda = 5 \text{ nm}$) and O_3 photodissociation coefficient (j , sec^{-1}) in the spectral range of the Chappuis bands.

$\lambda(\text{nm})$	q_{∞}	$j_{\infty}(\text{O}_3)$	$\lambda(\text{nm})$	q_{∞}	$j_{\infty}(\text{O}_3)$
400	1.69		630	2.62	8.99×10^{-6}
405	1.70		635	2.62	8.31
410	1.84	5.35×10^{-8}	640	2.63	7.21
415	1.97	6.19	645	2.60	6.79
420	1.95	7.78	650	2.55	6.17
425	1.81	1.18×10^{-7}	655	2.48	5.46
430	1.67	1.14	660	2.57	5.19
435	1.98	1.71	665	2.61	4.83
440	2.02	2.25	670	2.61	4.36
445	2.18	3.25	675	2.62	4.03
450	2.36	4.04	680	2.62	3.72
455	2.31	4.90	685	2.57	3.21
460	2.39	8.53	690	2.52	2.82
465	2.38	8.76	695	2.60	2.65
470	2.39	9.70	700	2.58	2.37
475	2.44	1.19×10^{-6}	705	2.52	2.12
480	2.51	1.78	710	2.51	1.93
485	2.30	1.94	715	2.48	1.73
490	2.39	1.98	720	2.45	1.54
495	2.48	2.25	725	2.48	1.41
500	2.40	2.93	730	2.45	1.29
505	2.46	3.99	735	2.44	1.16
510	2.49	3.93	740	2.39	1.07
515	2.32	3.71	745	2.40	1.01
520	2.39	4.25	750	2.41	9.04×10^{-7}
525	2.42	5.01	755	2.40	7.80
530	2.55	6.50	760	2.38	6.95
535	2.51	6.88	765	2.34	6.46
540	2.49	7.17	770	2.32	6.26
545	2.55	7.83	775	2.30	6.44
550	2.53	8.02	780	2.33	6.64
555	2.54	8.53	785	2.34	2.90
560	2.50	9.70	790	2.29	5.04
565	2.57	1.11×10^{-5}	795	2.29	4.17
570	2.58	1.20	800	2.27	3.70
575	2.67	1.27	805	2.27	3.97
580	2.67	1.21	810	2.20	4.18
585	2.70	1.17	815	2.22	4.11
590	2.62	1.16	820	2.18	3.71
595	2.69	1.24	825	2.20	3.34
600	2.63	1.29	830	2.14	3.04
605	2.68	1.30	835	2.14	3.00
610	2.66	1.21	840	2.13	2.98
615	2.59	1.10	845	2.09	2.97
620	2.69	1.05	850	2.05	2.97
625	2.61	9.40×10^{-6}			

CHAPTER 2

MODELS

INTRODUCTION

Atmospheric phenomena are extremely complex and because of this, it is impossible to achieve an accurate description of all physical, chemical, and dynamical processes in a single comprehensive computer simulation. Thus, the atmospheric scientist must select the phenomena of most interest, hypothesize on those processes that exercise the most control, and construct an appropriate model which may be either analytic or numerical. Although, by necessity, the model is a simplified representation of the real atmosphere, if the premises upon which it is based prove correct, it can provide an accurate description of the selected phenomena.

Confidence in atmospheric models is generally gained by a comparison of model predictions with observational data. However, the cause-and-effect relationship contained in a model is not always apparent or discernable in observational data. It is quite possible for a model to omit relevant physical processes and still predict effects fortuitously in agreement with observational data. Similarly, a model can fail to predict observed phenomena because it is too restrictive in the number of processes it incorporates.

The most rational approach for studying stratospheric phenomena is to rely upon a hierarchy of models that individually assess the chemical, dynamical, physical, and radiative processes of the stratosphere. Once a firm understanding of individual processes and confidence in the correctness of simple models are gained, then the construction of more complex models can be undertaken.

A variety of models used in the study of stratospheric phenomena are examined in the following paragraphs. Each type of model is important in its own right, and has made a significant contribution to the knowledge of stratospheric processes. Particular models allow in-depth study of selected processes and the possibility of developing suitable parameterizations of these processes. Specific attention is given to three important processes: chemistry, radiative transfer, and motions. All of these processes depend on solar radiation and it is appropriate to begin the discussion with models of the Earth's radiation balance and vertical temperature structure.

RADIATION AND ONE-DIMENSIONAL RADIATIVE-CONVECTIVE MODELS

One-dimensional radiative-convective models play a limited, but useful, role in stratospheric studies, primarily by providing estimates of the direct radiative effect of changes in stratospheric composition on global temperatures. Such estimates have limited significance because they exclude important feedbacks in the atmosphere. However, these models are needed to develop and test parameterizations for the multidimensional models.

CURRENT CAPABILITIES AND LIMITATIONS

One-dimensional radiative-convective (1-D RC) models are used to compute the vertical temperature profile of the atmosphere under certain assumptions concerning the physical processes that determine the profile. In these models, the atmosphere is assumed to be in radiative equilibrium (a balance between radiative heatings and coolings), except at altitudes where the resulting temperature permits processes other than radiation (such as small-scale convection or large-scale dynamics) to contribute significantly to the vertical transfer of energy.

For climate studies, a rapid and accurate method is essential to calculate temperature changes due to infrared radiative heating and cooling in the atmosphere. The available radiative transfer techniques and spectroscopic data on atmospheric gases, by McClatchey et al. (1973), are adequate for stratospheric radiative transfer calculations. In a realistic atmosphere, the basic problems encountered are the inseparable processes of scattering and absorption due to cloud and aerosol particles, and of absorption by atmospheric gases as discussed by Goody (1964). The main difficulties are: (1) integration over frequency is underestimated by the usual band-model techniques for gaseous absorption which do not allow for multiple scattering, and (2) direct line-by-line integration is too time consuming for practical use. Recently, Lacis et al. (1979) have developed an approximate method, called the correlated k-distribution method, to handle the frequency integration. This approximate treatment is remarkably accurate when compared to line-by-line calculations for the $9.6\mu\text{m}$ ozone band (one of the most complex atmospheric band systems), while the commonly used pressure-scaling and Curtis-Godson approximations fail to yield accurate results (Walshaw and Rodgers, 1963). Furthermore, the k-distribution method is several orders of magnitude faster than line-by-line calculations.

Specified Lapse Rate

The procedure used by Manabe and Strickler (1964) and Manabe and Wetherald (1967) to parameterize the vertical transport of heat by atmospheric motions was to limit the computed temperature gradient to a preassigned maximum (6.5 K/km) wherever the radiative equilibrium profile exceeded that limit. This procedure is called a *convective adjustment*, although the empirical maximum lapse rate incorporates effects of large scale dynamics and condensation as well as convection. Most 1-D RC models developed in the last 15 years essentially have followed the method of Manabe and Strickler (1964).

The prime difficulty with this empirical approach is that it does not indicate how the lapse rate may change as the climate changes. Therefore, it is necessary to discuss other physical procedures for specifying the lapse rate, even though these may have only limited domains of applicability.

Relative Humidity

Water (in the form of both vapor and clouds) is the primary atmospheric constituent determining the surface temperature of the Earth. Cloud cover is the prime factor in determining the planetary albedo, and thus the effective temperature. The *greenhouse* effect (by which the surface temperature is increased above the effective temperature), is determined mainly by water vapor which defines the infrared (8 to $14\mu\text{m}$) *window*. Other gases perturb this basic picture, primarily by absorbing the *window* region. In the stratosphere where there is very little water vapor, O_3 and CO_2 primarily determine the temperature structure. However, changes in the stratospheric water vapor abundance have a great impact on surface temperature.

Manabe and Wetherald (1967) assumed that the relative humidity would remain fixed for a perturbation of other radiative constituents. The corresponding change in the amount of water vapor resulted in a positive feedback effect of a factor of approximately 1.8 (i.e., the percent change in H_2O is 1.8 times the percent change in other constituents) compared to the case of fixed absolute humidity. More elaborate radiative calculations by Wang et al. (1976) confirm this, with a slightly smaller feedback factor of approximately 1.6. Most 1-D RC models use the assumption of fixed relative humidity, because it appears more plausible than fixed absolute humidity. Recent work by Sarachik (1979) lends considerable support to the case for approximately constant relative humidity.

Clouds

The radiative effects of specified clouds were included in the early 1-D RC models by Manabe and Wetherald (1967) and others. Most clouds cause a reduction in surface temperature, because their reflection of solar radiation has a larger effect than their blanketing of thermal radiation.

However, cirrus clouds at their normal altitudes (approximately 12 to 20 km) cause a strong *greenhouse* effect at both high and low latitudes (Lacis et al. 1979).

In general, current 1-D RC models do not predict cloud altitude, or the possible feedback effect caused by a change of cloud altitude with a change of climate. However, the models have shown that the assumptions about cloud altitude do strongly influence the model results as reported by Wang et al. (1976). The models also show that the cloud-base altitude, and perturbations of the altitude, are equally important.

Aerosols

Radiative effects of aerosols can be considered similar to the effects of clouds; i.e., there are competing effects in the solar and thermal parts of the frequency spectrum. Current 1-D RC models permit an accurate assessment of the direct radiative effects of aerosols, provided that the physical properties of aerosols are known. This climatic forcing by aerosols depends substantially on the composition, size distribution and altitude distribution of the aerosol, as well as on the amount of the aerosol. Furthermore, the radiative forcing due to aerosols produced by volcanic explosions provides an excellent opportunity for testing climate modeling capabilities (Hansen et al., 1978). One very useful strategy for investigating the global climatic system is to perform detailed observations and analyses of the next large volcanic explosion. The observations should include global monitoring of the spread, growth, and decay of the aerosol, sampling of the aerosol properties *in situ*, and accurate global monitoring of the climate response. These data would permit testing of global climate models and aid in-depth analyses of radiative, chemical, and dynamical processes essential for obtaining an improved understanding of the physical mechanisms and interactions involved.

MODEL VERIFICATION

Several procedures can be employed for verification of 1-D RC models, although ultimately, all of these are based on comparison with observations.

Comparison with Other Models

The first test of 1-D models is a comparison with other models, usually with more sophisticated multi-dimensional models. In general, this can be expected to lead to a similarity in the results of the different models, if the processes included in the more sophisticated models are parameterized in the simpler models. Thus, the procedure is basically a cross-check, since all the models must be compared to observations. Recent model comparisons by Coakley (1979) and others indicate that different models are in rather close agreement when the same processes are taken into account.

Comparison with Observations

The 1-D models offer a reasonably good method of reproducing the mean atmospheric temperature profile, as shown in detail by Manabe and Strickler (1964). However, since there is a certain amount of tuning in the models (such as the 6.5 K/km specified tropospheric lapse rate), additional comparison with observations are crucial. This is especially true if the models are to be relied upon for predicting the effect of atmospheric perturbations.

Recently, Hansen et al. (1978) argued that the temperature perturbation caused by the aerosols produced after a large volcanic explosion can provide an excellent test case for verifying the ability to model radiative perturbations. The best documented large explosion to date (Mt. Agung in 1963), provides some encouraging evidence in this regard as shown in figure 2-1. However, Hansen et al. caution overinterpretation of this

single test, particularly because of the lack of sufficient data on: (1) aerosol properties, (2) the observed temperature changes, (3) other factors which affected the temperature, and (4) the effect of many model simplifications. NASA is currently developing plans for a more comprehensive study of the next large volcanic eruption.

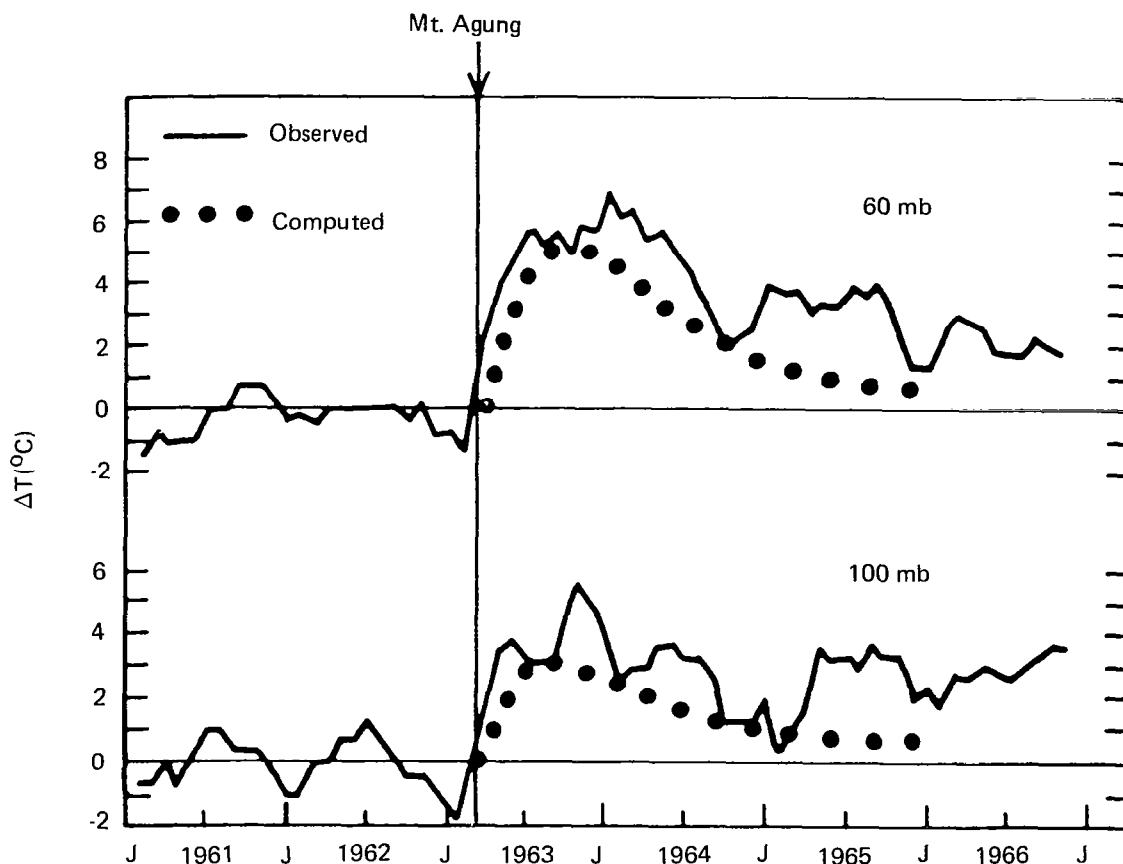


Figure 2-1. Observed stratospheric temperatures over Australia and computed temperatures after the eruption of Mount Agung (Adapted from Hansen et al., 1978).

CHEMISTRY MODELS

PHOTOCHEMICAL MODELS

Incorporation of chemistry into a model (whether a simple 1-D diffusion model or a complex 3-D primitive equation model) is straightforward in principle. Representation of gas-phase chemical reactions by production-and-loss terms in the continuity equation is an accurate description. The difficulties and deficiencies in a chemical model are related to: (1) accurate rate coefficients for atmospheric conditions (2) inclusion of all important species, (3) dissociation rates and quantum yields for photochemical processes (4) proper temporal (diurnal) averaging for long-time integrations, (5) surface sources and sinks and (6) in the case of 1-D models, proper spatial (latitudinal) averaging. The chemical species included in a model depend on laboratory studies, field measurements, and theoretical insight. It is essential that all important species be included. For example, in initial studies of stratospheric chlorine only Cl, HCl, ClO, Cl_2 , and ClOO were considered, but subsequent study showed that ClONO_2 and HOCl were important reservoir species. Because

some chemical species have chemical lifetimes comparable to transport time constants, the completeness of the chemistry depends on the accuracy of the transport employed in the model.

Calculations based on a chemical model are very sensitive to a number of key reactions. Recent revisions of the rate coefficients for reactions such as $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$, and $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$ have resulted in major changes in predictions by chemical models. In principle, the problem can be solved by suitable laboratory kinetics experiments. However, the laboratory studies are usually carried out under conditions very different from those in the atmosphere. For example, the early measurements of $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$, and $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ were carried out at low pressure. Since these reactions were thought to be binary reactions, the results were expected to be valid up to about 1 atmosphere of pressure. However, it was recently found that these reactions may be more complex than previously assumed, and that pressure dependence is not negligible.

Photodissociation rates (J values) depend on the solar radiation field. At wavelengths shorter than 300 nm, the atmosphere acts as a pure absorber, and the radiative transfer problem is straightforward. For longer wavelengths, the calculation of J values is complicated by multiple scattering. The important molecules that are affected by this complication are ClONO_2 , HOCl , ClO , O_3 , H_2O_2 , NO_2 , and HNO_3 . There are other species (such as NO , OH , and HO_2) that are strongly coupled to the above species, and these will be affected by the way the radiation field is handled. Currently, methods developed by Luther and Gelinas (1976), for example, are adequate for calculation of the multiple-scattering corrections, except at sunrise and sunset.

At sunrise and sunset, the sphericity of the atmosphere cannot be ignored. Since the total time involved is only about one-half hour, an incorrect treatment of sphericity will not seriously affect the predictions of the chemical model. However, sphericity considerations are important for comparison of theory with measurements obtained near sunrise and sunset. A number of important species such as OH , HO_2 , and NO_2 at 40 km have response times on the order of minutes.

The production and loss rates in a chemical calculation have the forms, $J[x]$ or $k[x][y]$, where J is defined above and k is the rate coefficient. The most accurate procedure is to solve the time-dependent continuity equation with the radiation field computed at each time step. Algorithms which overcome the *stiffness* problem (most troublesome at sunrise and sunset), and the *convergence* problem (for long-lived species such as O_3 in the lower stratosphere) are in regular use. A very simple, but acceptably accurate technique for performing diurnal averages of $k[x][y]$ has been reported by Turco and Whitten (1978).

In 1-D models, the latitudinal average ($\langle \rangle$) of $k[x][y]$, is approximated by $\langle k \rangle \langle [x] \rangle \langle [y] \rangle$. The validity of this approximation depends on the nature of the problem. For perturbation studies involving CFMs or N_2O , it is probably acceptable. However, for problems with latitudinal asymmetry, proper spatial averaging can only be obtained with a multi-dimensional model. Further details of one-dimensional photochemical models have been discussed in Hudson (1977).

AEROSOL MODELS

Junge et al. (1961) made the first *in situ* measurements of, and constructed the first model for, the stratospheric aerosol layer. Recognition by Pollack et al. (1976c) that these high-altitude particles can influence the climate and by Cadle et al. (1975) that ozone might be affected by surface reactions spurred the development of more sophisticated aerosol models by Kritz (1975), Rosen et al. (1978), and Turco et al. (1979a). Knowledge of the chemical reactions which influence the stratospheric sulfur compounds and the formation of sulfate particles has also advanced through work by Friend et al. (1973), Castlemen et al. (1975a), and Crutzen (1976b). The microphysical processes treated in aerosol models include nucleation (homogeneous, heterogeneous and ion), vapor condensation and evaporation, coagulation (Brownian),

gravitational sedimentation, and convective and diffusive transport. In general, these models can reproduce some of the important features of stratospheric aerosols, the total sulfate mass, the number and size of the particles, and their optical properties, but they cannot generally reproduce conditions following large volcanic eruptions.

Many problems remain unsolved. The composition of natural aerosols is believed by Farlow et al. (1978) to be liquid sulfuric acid with a mixture of numerous sulfates, halogen- and nitrogen-bearing compounds, and insoluble materials such as silicates. The physical and chemical processes responsible for this composition are unknown, and the impact of heterogeneous reactions on ozone abundances is unresolved, although it appears to be small. The major sources of sulfur for the ambient aerosol layer are OCS, SO₂, and CS₂, but the origins of OCS and CS₂ have not been clearly identified (Sze and Ko, 1979a). The mechanism of H₂SO₄ formation from these source gases involves intermediate sulfur radicals (HSO_x) whose properties are undetermined but may be important for initiating aerosol nucleation according to Friend, (private communication). There are also uncertainties in H₂SO₄ vapor pressures, background condensation nuclei concentrations, and the quantity of meteoritic dust and gas reaching the stratosphere. These factors affect aerosol properties and predictions.

Calculations have been made by Turco et al. (1979a, b, c) of man's impact on the aerosol layer due to increased industrial emissions of OCS, high-altitude deposition of soot and SO₂ by SSTs, and injection of aluminum oxide particles by space-shuttle launch motors. The results show that, while large aerosol perturbations are not predicted for any of the emissions studied, aerosol perturbations capable of altering the climate could occur with substantial increases in such emissions. Accordingly, aerosol models are needed to assess the potential influence of anthropogenic activities on terrestrial aerosols and climate.

SIMPLIFIED TRANSPORT MODELS

ONE-DIMENSIONAL DIFFUSION MODELS

The one-dimensional (1-D) vertical diffusion model permits the use of very detailed chemical reaction sets by inclusion of transport in a simplified manner, as an altitude-dependent diffusion coefficient, $K(z)$. This treatment of transport is based on the assumption that the vertical flux, ϕ , of a minor constituent is proportional to the gradient in its time and globally averaged volume mixing ratio, f , and is expressed by the equation:

$$\phi = - KM \frac{\partial f}{\partial z}$$

where M is the bulk atmosphere density and z is the altitude. The appropriate continuity equation for f is then:

$$M \frac{\partial f}{\partial t} - \frac{\partial}{\partial z} (KM \frac{\partial f}{\partial z}) = P - L$$

where P and L are the chemical production and loss rates, respectively. The simplified assumption contained in this equation is that transport always acts to remove gradients in mixing ratios and thus, is down-gradient. This has empirical support in that minor constituents that have long-residence times in the stratosphere are observed to be mixed uniformly with the major gases. Although the neglect of horizontal fluxes cannot be rigorously justified from the physical standpoint, the most important variations of f occur with height and the results of 1-D diffusion models can be interpreted as horizontal averages over the globe. Mahlman (1975), and private communication, (1979) has examined the applicability of 1-D and 2-D diffusion models by comparing the model results to those of a 3-D general circulation model. He concluded that the simplified approaches

produce results consistent to within a factor of 2 over a wide range of conditions, although there are regions where the true circulation does not act to reduce mixing ratio gradients. Alternately, the success of 1-D models in reproducing observations can be cited as empirical evidence that, in many cases, the simple assumptions concerning transport are useful even though they do not constitute a physically correct model of the process.

Empirical determinations of $K(z)$ in the stratosphere are based on observations of a minor gas whose chemistry is presumably well understood. A good example is N_2O which is supplied to the stratosphere by upward transport and lost through dissociation. The altitude-dependence of the mixing ratio may then be used to deduce $K(z)$. The N_2O measurements of Schmeltekopf et al. (1977a) imply a latitude dependent $K(z)$. For 1-D calculations a globally averaged $K(z)$ is required and the profile presented in Hudson (1977) is still considered applicable. Recently Allen and Yung (1979) have derived a profile of $K(z)$ from CO data in the upper stratosphere and mesosphere. Taken with the earlier inferences of Wofsy and McElroy (1973) and Hunten (1975), these imply $K(z)$ values between 1×10^5 and $5 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$ between 50 and 80 km. Throughout the dynamically active troposphere, a large constant value for K on the order of $10^5 \text{ cm}^2 \text{ sec}^{-1}$ is applicable. The stability of the lower stratosphere leads to smaller values (between 10^3 and $10^4 \text{ cm}^2 \text{ sec}^{-1}$).

Although the 1-D diffusion approximation has been used in numerous aeronomic studies, care must be used in interpreting the results. Such models are least applicable when making predictions in cases where large horizontal gradients are involved (for example, NO_x injections along SST corridors). However, as noted by Hudson (1977) and the National Academy of Sciences (1976), the 1-D calculation appears to provide an acceptable level of accuracy when applied to a wide class of globally averaged calculations, particularly when the effects of transport are minor compared to chemistry. Despite its severe limitations, the 1-D diffusion model will probably remain, for sometime, the major tool of chemical aeronomy because of its simplicity compared to the complexity of multi-dimensional models.

TWO-DIMENSIONAL DYNAMICAL MODELS

In an attempt to account for both the latitudinal and vertical structure of the atmosphere, a variety of two-dimensional models have been developed. These models consider only zonally averaged quantities and are classified according to their method of averaging dynamical variables.

Eulerian-Mean Models

The term Eulerian Mean signifies that averaging is performed along latitude circles, at fixed latitude and vertical coordinates. The resulting equations contain *eddy flux divergence* terms that must be either (1) specified in advance, or (2) parameterized in terms of zonal mean quantities. The first approach has the disadvantage of implicitly assuming that departures from zonal symmetry (*eddies* or *waves*) are independent of the structure of the zonal-mean flow, and this is a poor assumption, since it is well known that changes in the mean flow induced by the waves will, in turn, feed back on the waves themselves.

Parameterizations of Eulerian eddy fluxes have mostly followed the approach proposed by Reed and German (1965), who assumed that the local eddy flux of any quantity is related linearly to the mean gradients of that quantity by a positive definite tensor. Arguments of this kind are usually based on some kind of mixing-length hypothesis, and on the assumption that projections of particle trajectories in the meridional plane are straight lines. That such a parameterization sometimes fails was demonstrated by Mahlman (1975), whose 3-D tracer calculations effectively showed that the total implied eddy-flux tensor can often become locally negative. This was recently demonstrated in another way by Matsuno (1979) and also by Plumb (1979). Matsuno showed that for a simple analytical model of a steady, weakly dissipated, stratospheric planetary wave, the projections of the particle paths in the meridional plane are ellipses, and that the tensor relating eddy fluxes to mean gradients is strongly antisymmetric, representing an advective, rather than a diffusive process.

The above arguments indicate only that eddy transport parameterizations by the Reed and German (1965) hypothesis can be inconsistent. This does not mean that successful 2-D transport models cannot be constructed. Such models might be based either on newer, less restricted transport hypotheses, or on a completely empirical engineering approach in which transport coefficients are fitted to produce agreement with real data.

Currently, there exist a number of 2-D transport models empirically based in their construction, e.g., Hidalgo and Crutzen (1977); Louis et al. (1974); Whitten et al. (1977); and Borucki et al. (1979). These models have achieved varying degrees of success when applied to tracers other than those for which the original model was calibrated. Such empirical models show promise of reducing the uncertainties inherent in 1-D models because they allow for meridional variations in trace constituents and overhead Sun angle. There is reason to believe that further progress can be expected in these types of models.

One problem that remains to be resolved is the predictions of perturbations that use empirical transport parameterizations. For many perturbations, there is reason to expect that such models should give useful and reasonable results. But if either subtle balances or large excursions away from the current state must be considered, the confidence in the predictions of these models will decrease markedly. In this context, the more physically based models also result in a decrease in confidence in such situations since they also contain empirically based parameterizations. However, because these models are based on known physical processes, the decrease in confidence should be considerably smaller.

At present, there are no existing 2-D transport models that have demonstrated a more fundamentally correct basis than that in the Reed and German (1965) mixing-length hypothesis. It is useful to outline some of the approaches currently under consideration that may circumvent the difficulties described above.

Mean-Cell 2-D Models

In these models, equations have been solved by Rao-Vupputuri (1973); Harwood and Pyle (1975, 1977); and Turner et al. (1979) for the zonal mean meteorological variables in addition to the tracer variables. These models may show more promise because they contain the possibility, at least, of inducing a meridional circulation that buffers the calculation against the non-physically based eddy-transport parameterization.

Second-Order Closure Approaches

A suggestion was offered by Mahlman and Lee (private communication, 1978) that a 2-D tracer transport model could compute eddy fluxes internally by using the equations of motion to generate specific prognostic equations for the eddy tracer fluxes themselves. Required input parameters are self-consistent sets of zonally averaged meteorological statistics composed of individual variables, variances, and covariances. Such an approach requires closure hypotheses at the level of triple-eddy products. The degree of sensitivity to such higher-order closure uncertainties remains unclear.

Lagrangian-Mean Approaches

A recent theoretical approach to problems of the interaction of waves and mean flows has been to perform averages over specified sets of fluid particles rather than along lines fixed in coordinate space. This is the *generalized Lagrangian-Mean* (GLM) theory set forth by Andrews and McIntyre (1976a; 1978a,b), which has already proved to be a powerful tool in deducing general results concerning the interaction of waves and mean flows. For example, the crucial importance of wave dissipation (or forcing) and wave transience in bringing about mean-flow changes has been clearly demonstrated; this general result is not easily obtainable by the Eulerian-mean approach. The GLM theory also allows a rather general formulation of the *wave-action* concept which, apart from its fundamental physical interest, may also be a useful diagnostic tool in the description of wave propagation in complicated stratospheric mean flows.

Because of its concern with mean particle properties, it is possible that the GLM approach may be a natural tool for the study and interpretation of transports of tracers in the stratosphere. The first attempt to use the theory for this purpose was made by Dunkerton (1978), who exploited the fact that the GLM version of the potential temperature equation contains no eddy-flux terms. After various approximations, he was able to estimate the Lagrangian-mean meridional circulation for the stratosphere and mesosphere at the solstices on the basis of Eulerian-mean heating at those altitudes. This meridional circulation is capable of describing the motion of the center of mass (as viewed in the meridional plane) of a line of tracer particles that originally lay along a circle of latitude. As calculated by Dunkerton, it consists of a single stratospheric cell much like the *Brewer-Dobson* circulation, which had been postulated to explain certain observations of the ozone and water vapor distribution (and which can be regarded as a Lagrangian circulation in some sense). By contrast, the Eulerian-mean circulation consists of two cells, including a wave-induced Ferrel cell in the winter hemisphere.

This qualitative agreement with observation is encouraging, but further improvement in Dunkerton's simple model will require much thought and ingenuity. For example, the Lagrangian-mean heating (rather than the Eulerian-mean heating) should really be used; the differences could be quite significant in the lower stratosphere as shown by Mahlman et al. (1979). It is desirable to relax some of the other assumptions made by Dunkerton as well, which naturally leads to the question of the feasibility of a 2-D Lagrangian-mean numerical model. As yet, no such model has been constructed, but the possibility of such a model, either for simulation or diagnostic purposes, should be considered seriously.

Another approach is to use output from 3-D stratospheric circulation models to construct Lagrangian-mean quantities. This would seem a natural thing to try in view of the insight afforded by the GLM theory in the theoretical studies of Andrews and McIntyre (1978a,b). Numerical experiments by Hsu (private communication, 1979) have shown that the formalism as developed by Andrews and McIntyre may break down in practice when waves approach finite amplitude, because lines of fluid particles become highly convoluted and split into separate segments. At the present time, techniques of adapting the GLM formulation to circumvent this difficulty are being pursued actively by McIntyre (1979) and Mahlman et al. (1979).

THREE-DIMENSIONAL DYNAMICAL MODELS

QUASI-GEOSTROPHIC MODELS OF THE STRATOSPHERE

Between the general circulation models and the eddy-diffusion chemistry models of the stratosphere, there is a multitude of models in which the dynamics are simplified and the chemical and radiative processes are highly parameterized. These models have been developed to focus on particular stratospheric phenomena (such as the quasi-biennial oscillation, or the sudden stratospheric warming), and to provide an inexpensive representation of the general circulation of the stratosphere. They can often sort out the complex dynamical features simulated by general circulation models, as well as provide a test bed for theoretical concepts.

Table 2-1 shows a representative list of stratospheric models. Three categories of assumptions characterize these models: (1) truncated dynamics, (2) parameterized radiative transfer, and (3) simplified chemistry. This section discusses the various schemes employed by the models to simplify calculations and the effect each of these assumptions might have on the transport, production, and loss of ozone. (Note that most of these models do not consider ozone chemistry and its transport.) The major question is: if such transport were to be calculated, how would this transport be affected by the assumptions used in the models, and how accurately might these models assess the impact of pollution-injection into the stratosphere over a long period?

Dynamics

Several approximations are used to simplify the dynamics of the models listed in table 2-1, quasi-geostrophy, spectral truncation, and area limitation. With the exception of the model developed by Clark (1970) (included to provide a historical perspective), the models listed take into account the entire stratosphere.

Table 2-1
Simplified Dynamic Models of the Stratosphere

Model	Dynamics				Radiation		Chemistry		
	Levels	Upper Level (km)	Lower Level (km)	Type	Spectral Components	IR	Insolation	Transport	Reactions
Hartmann and Garcia (1979)	50	100	0	quasi 2-d β -plane quasi-geostrophic	2	Newtonian Cooling (D)	Strobel (1978) Hartmann (1978)	quasi 2-d	Chapman
Ramanathan and Grose (1978)	9	70	0	quasi-geostrophic spectral global	4	Ramanathan (1976)	Ramanathan (1976)	No	No
Schoeberl and Strobel (1978a, 1980)	35	130	16	quasi-geostrophic semispectral global	2	Newtonian Cooling (D)	Strobel (1979)	No	Photochemical Acceleration
Harwood and Pyle (1975, 1977)	23	80	0	quasi-geostrophic empirical global	1	Local Planck Function	Kennedy (1974)	Yes	Chapman HO _x and NO _x
Holton (1975)	33	90	9	primitive semispectral hemispheric	2	Newtonian Cooling (T)	None	No	No
Cunnold et al. (1975)	25	71	0	quasi-geostrophic spectral mirror hemispheres	6	Newtonian Cooling (D)	Lat. dependent	Yes	Chapman HO _x , NO _x
Trenberth (1973a)	17	71	0	quasi-geostrophic spectral hemispheric	4	Newtonian Cooling (T)	None	No	No
Matsuno (1971)	40	100	9	quasi-geostrophic semispectral hemispheric	2	None	None	No	No
Clark (1970)	12	40	0	quasi-geostrophic spectral hemispheric	5	Newtonian Cooling (LG)	Lat. independent	Yes	Chapman

(T) – Trenberth (1973a) (D) – Dickinson (1973b) (LG) – Lindzen and Goody (1965)

Quasi-geostrophy

Rossby waves are the only type of propagating disturbance which exist in a quasi-geostrophic system. Because most of the energy of atmospheric motion resides in Rossby-type disturbances, this assumption provides a good approximation to midlatitude dynamics and a fair approximation to the Hadley circulation near the Equator. The quasi-geostrophic system has the computational advantage of automatically filtering gravity waves.

Atmospheric motion which cannot be correctly simulated by quasi-geostrophic systems includes the class of equatorial waves known to force the quasi-biennial oscillation in the mean wind in the stratosphere (QBO) and the atmospheric tides. However, the role of the QBO or tidal motions in the organized transport of ozone is uncertain.

Spectral Truncation

The transport of ozone appears to be primarily controlled by very large scale waves and the mean circulation in the stratosphere, as indicated by both satellite and ground based observations. As a result, most models consider only the lowest spectral harmonics (planetary waves) to represent the horizontal fields, with diffusion coefficients simulating the mixing by higher harmonics. However, it is not clear that spectral models which include the troposphere can truncate below wavenumber 10 if they are to correctly simulate the general circulation of the upper troposphere and lower stratosphere according to Baer and Alyea (1971) and Mahlman (1975).

As an example, typical spectral forecast models use 20 to 25 harmonics to simulate developing synoptic baroclinic disturbances as reported by Daley et al. (1976).

Area Limitations

Hemispheric, mechanistic and β -plane models exclude large regions of the atmosphere in order to focus on particular phenomena and to increase computational speed. Since hemispheric and β -plane models cannot simulate the pole-to-pole solstitial circulation as reported by Leovy (1964) and Schoeberl and Strobel (1978a), they are inadequate for representing upper stratospheric transport. Mechanistic models usually treat the troposphere as a fixed-boundary condition, with a climatological tropopause temperature or geopotential field specified at some pressure level. These models can treat transport adequately above the troposphere boundary, but must specify constituent fluxes as boundary conditions. Thus, it is difficult, if not impossible, to use these models to evaluate stratospheric-tropospheric interactions.

The level at which the upper boundary is applied is also an area limitation. Most of the models in table 2-1, which calculate the pole-to-pole zonally averaged circulation of the upper stratosphere, under-represent its structure by placing a rigid lid where the meridional velocity maximizes. As a result, the vertical velocities in the polar mesosphere and upper stratosphere are too weak, and the meridional temperature reversal in the mesosphere does not occur. This assumption produces a polar night jet in the mean wind which increases in strength up to the upper boundary and, in turn, affects the planetary wave computations. Schoeberl and Strobel (1978a) find that the zonally averaged circulation can be correctly computed by placing the upper boundary in the 110 to 130 km region. Other procedures, which do not require a boundary condition at such a high altitude, are currently under investigation.

Radiation

Two radiative processes are important in the stratosphere and mesosphere: insolation by ozone and O_2 , and infrared cooling by CO_2 , O_3 , and H_2O , and trace constituents such as N_2O and the chlorofluoromethanes.

Insolation

Several excellent schemes by Lacis and Hansen (1974) and Strobel (1978) accurately treat O_3 and O_2 insolation. Most models include O_3 heating accurately, but few include O_2 heating which according to Strobel (1978) is important only above 80 km. Insolation for the troposphere is often treated in an *ad-hoc* fashion using a Newtonian-type damping approximation. Essentially, a climatological temperature field, T_c , is specified by observations, and then a heating rate is computed using:

$$q = \alpha_o(T_c - T_m)$$

where T_c is a temperature required to reproduce the observed heating rates in the troposphere, α_o is the relaxation time, and T_m is the model temperature. This method is detailed in Cunnold et al. (1975). Clearly, this procedure fixes tropospheric heat sources and prevents any feedback between the stratosphere and troposphere through insolation.

IR Cooling

The most popular procedure for assessing the impact of IR cooling on the stratosphere is, again, the Newtonian cooling approximation,

$$q = \alpha_o T + b$$

where T is temperature and b is the background rate. Most investigators use the rates derived by Dickinson (1973b) for the 1962 standard atmosphere. Unfortunately, the background rates vary considerably with the initial temperature profile, and the α_o values may be in error by 20% or more for disturbances where the temperature varies from 10 to 20 K according to Ramanathan and Grose (1978). This variation is caused by the neglect of radiative exchange in the Newtonian cooling formalism. Other, more elaborate, but still computationally efficient IR models have been developed by Ramanathan (1976) and Fels and Schwarzkopf (1975, 1980) which include exchange, and are currently being installed in some quasi-geostrophic models.

The importance of IR processes has been demonstrated by Dunkerton (1978) who showed how the Brewer-Dobson circulation for ozone is basically a function of the radiative imbalance in the stratosphere. This result is a clear example of how the Lagrangian-mean transport of trace constituents is influenced by external sources of heat and momentum, not by the eddy fluxes. Thus, it appears important that the radiative processes be treated accurately if ozone transport is to be correctly assessed.

Few models listed in table 2-1 explicitly calculate the total photochemical response of ozone in addition to transport. One reason for this is that the photochemical time constant above 40 km is faster than the transport time scale. Thus, within the sharp transition region (40 to 45 km), the time step of the model is dictated by fast photochemistry, so that computational costs increase. Above 50 km, photochemical equilibrium can be assumed.

In models which do not explicitly calculate the transport of O_3 , the dynamic-photochemical-radiative feedback mechanism is often parameterized by a photochemical acceleration which has the same functional form as Newtonian cooling. Values by Blake and Lindzen (1973) for the photochemical acceleration parameter have recently been modified by the inclusion of radiative feedback by Hartmann (1978) and Strobel (1979).

Direct calculation of ozone mixing ratio with quasi-geostrophic models has been made only by Cunnold et al. (1975); and Clark (1970). Even with these models, only a few representative reactions have been used because calculations quickly become too time consuming. Nevertheless, direct calculation is the only realistic technique for assessing the total impact of chemical pollutants on the ozone layer.

Summary

Existing 2-D and 3-D quasi-geostrophic models of the atmosphere have provided considerable information on the dynamics of the stratosphere. Yet, none of these models currently has the capability of realistically forecasting the impact of atmospheric pollutants on ozone. The chief problem areas are:

- Inadequate or inflexible assumptions are used to compute IR processes. Since the Lagrangian-mean motion of constituents in the upper stratosphere appears to depend on heat sources and sinks, these processes must be accurately represented.
- Spectral truncation may be too severe to represent the cross-tropopause mass exchange and lower stratosphere poleward transport by transient eddies. Since the cross-tropopause exchange is the process by which ground-released pollutants reach the stratosphere, it is critical that synoptic disturbances be correctly modeled. Spectral models should contain at least 10 or more zonal and meridional harmonics to represent such exchange or suitable parameterizations should be developed for transport by high wavenumber components.
- Upper boundaries are too low. The upper boundary must be located well above the stratopause to adequately represent the upper stratospheric-mesospheric pole-to-pole circulation.
- Chemistry is poorly represented. More chemical reactions must be considered in the calculation of ozone mixing ratios.

However, all of these problem areas can be resolved, and good predictions can be made at moderate cost with truncated spectral or semispectral models which are within the range of current technology. Furthermore, quasi-geostrophic models have the additional advantages of computational efficiency and simplicity, which allow numerical experiments that can isolate and determine the mechanisms of selected stratospheric phenomena.

THREE-DIMENSIONAL PRIMITIVE EQUATIONS MODELING

In the previous sections, the motivation, methodology, and status of simplified models of the stratosphere have been outlined. Those results present a larger question: at the present time, to what extent is it possible to construct a credible, comprehensive and self-consistent model of the radiation, chemistry, and dynamics of the entire stratospheric system?

It is most important to establish that no such model currently exists, or will exist in the foreseeable future. However, significant progress is occurring in the development and evaluation of models which appear to be sufficient at the present level of knowledge. Even the most comprehensive and sophisticated models still contain important simplifications and idealizations.

It is important that the scientific community continue to develop comprehensive state-of-the-art stratospheric models. At the present time, this state-of-the-art level is defined by the so-called 3-D *primitive equations* general circulation model (GCM). The GCM is usually considered to be an attempt to provide a fully self-consistent numerical model of the atmospheric dynamical system. Since such fully self-consistent models are not currently obtainable, the GCMs tend to differ from models mentioned previously, mainly in their degree of self-consistency and their relative credibility.

Traditionally, GCMs have attempted to incorporate reasonably complete and self-consistent dynamical and radiative transfer calculations (although many significant approximations are made in both). On the other

hand, the ocean temperature, permanent ice caps, and the distribution of radiatively important trace constituents (except water vapor) have usually been incorporated as prescribed quantities. Some of these prescribed quantities are currently being relaxed in various models.

To achieve a fully self-consistent description of the stratosphere, it is necessary that ozone be self-determined in the model. This implies that other trace constituents must be calculated as well. Because of the major chemical uncertainties and the increasing computational burden, some or many of the important trace species must be specified so that they are consistent with available observations.

A stratospheric GCM must include the troposphere as well, since the troposphere supplies significant mechanical energy to the stratosphere. In addition, the transfer of radiative energy and the exchange of mass and trace constituents between the stratosphere and troposphere are important. For such a model to serve also as a climate model in the usual sense, the thermodynamic properties of the surface boundary must be self-consistently determined (i.e., the ocean-surface temperature and ice content must be calculated in the model). To perform this properly in any model remains a most difficult task. Aspects of climatic change in the stratosphere appear to be largely independent of longer-term variations of the lower boundary. Thus, a GCM employing prescribed ocean-surface temperatures and ice caps might serve as an excellent model for climate change in the stratosphere, while being incapable of calculating climatic changes at the Earth's surface.

Modeling of Various Physical and Dynamical Processes

In attempting to model radiation, chemistry, or dynamics in a GCM, the computational difficulties are formidable. Substantial computational simplifications must be made in all three areas. However, at current levels of understanding, such simplifications are reasonable and efficient because substantial uncertainties remain in the physical understanding that are not necessarily reduced by increased computational capacity.

Radiative transfer enters the problem in several ways, the most obvious being the calculation of local temperature changes caused by non-adiabatic heating effects. A complete calculation is very lengthy, because of the requirement to provide integrations over the applicable parts of the electromagnetic spectrum for each radiatively active atmospheric constituent. In addition, the effects of scattering and absorption by particles must be considered. Fortunately, a number of simplified techniques have been developed, e.g. Lacis and Hansen (1974) and Fels and Schwarzkopf (1975, 1980), that can produce accurate calculations (relative to the achievable accuracy) at a small fraction of the cost of more complete calculations.

Chemistry enters the problem mainly because sources and sinks of ozone, a radiatively active gas, must be known. The complete chemistry of ozone requires consideration of a number of other trace constituents, many of whose sources and sinks remain uncertain. Also, much of the chemistry governing the relationships between constituents and groups of constituents is known only approximately.

Even in the presence of these uncertainties, substantial improvements in computational requirements are possible. These can be accomplished through a number of assumptions and approximations, some excellent and some questionable: (1) grouping of constituents into internally coupled chemical families; (2) simplifications in the photodissociation calculations; (3) prescribing or adjusting less important trace constituents (or those with very long time scales); (4) averaging over the diurnal cycle as performed by Kurzeja (1975); and (5) infrequent calculation of slowly varying quantities. Many of these simplifications require parameterizations of other processes.

Complete calculations of the dynamical structure of the atmosphere are overwhelmingly complex. The spectrum of observable motions varies from length scales of a centimeter to the size of the planet itself. Fortunately, observations have indicated that most of the energy of atmospheric motions is contained in the larger scales, i.e., those existing on scales greater than hundreds of kilometers. However, important exceptions occur, particularly in convective clouds, frontal type phenomena, gravity waves, and clear-air turbulence. The most serious exceptions occur in the troposphere. (Most of the energy in the stratosphere is on even larger

spatial scales than in the troposphere.) Hopefully, stratospheric dynamical processes can be properly defined through use of less computational resolution than that required for the troposphere; however, it is not yet clear that this is the case. Proper simulation of trace constituent transfer in the stratosphere, cross-tropopause flux of water vapor, equatorial wave-mean flow interactions, and simulation of the tropospheric long waves and cyclone scale waves that propagate to the stratosphere appear to be significantly sensitive to model spatial resolution. Only careful experimentation and analysis of models employing hierarchies of resolutions can address the question of the minimum spatial resolution required for a given problem. This is an important consideration simply because the computational requirements increase very rapidly with increases in spatial resolution.

Even though most of the energy is contained in the larger scales, a successful dynamical model must take into account unresolved scales and processes through parameterization. Particularly critical in this regard are the parameterization schemes for convection, precipitation, and dissipation. In each case, fully satisfactory methods have yet to be developed. As described in an earlier section, atmospheric transport of trace constituents depends to some degree on these processes. Studies to date suggest that GCM transport results are not sensitive to uncertainties in these types of parameterizations. Further work is required.

Modeling Approaches and Efforts

For a GCM, a reasonably complete description usually implies that the dynamical processes be calculated using the so-called *primitive equations*. In this sense, *primitive equations* means the fluid equations of motion scaled in an energetically consistent manner to eliminate deviations from local hydrostatic equilibrium from the equation set. For the large-scale motions of the atmosphere, it is a superb approximation, and this restriction is used in all known GCMs.

The descriptions of GCMs have not made any reference to the numerical algorithms used to solve the dynamical equations. The various methods available (such as finite difference, spectral transform, pseudo-spectral, and finite element) have all been employed in dynamical problems with varying levels of success. The choice of a particular approach is related to: (1) the character of the problem under emphasis, (2) the computational burden, (3) the coordinate system, and (4) the personal preferences of the investigator. Each approach appears to possess major liabilities when applied to the complete general circulation problem. At this stage, no method appears to possess a clear advantage over all others. It appears that a continued and expanded diversity of approaches in GCM research will enhance longer term progress.

To date, there have been a number of successes in simulating the structure of the stratosphere. Listed below are various phenomena that have been successfully simulated in such models with the first apparent successful simulation listed:

- The reversed meridional temperature gradient in the lower stratosphere by Smagorinsky et al. (1965).
- *Forced from below* energetics of the lower stratosphere by Smagorinsky et al. (1965).
- *Scale filtering* of disturbances with increasing altitude by Manabe and Hunt, (1968).
- Effects of orography by Kasahara et al. (1973) and Manabe and Terpstra (1974).
- Planetary wave structure by Kasahara et al. (1973).
- Equatorial tropopause structure by Manabe and Mahlman (1976).
- Midlatitude warm belt by Manabe and Mahlman (1976).

- Sudden stratospheric warmings by Newson (1974).
- Interhemispheric asymmetries by Manabe and Mahlman (1976).
- Stratospheric tracer structure by Hunt and Manabe (1968).
- Seasonal variation of lower stratospheric temperature by Manabe and Mahlman (1976).
- Cancellation effect between mean cells and eddies by Smagorinsky et al. (1965).
- Realistic stratospheric tropospheric exchange by Mahlman and Moxim (1978).
- Summertime easterly flow by Manabe and Mahlman (1976).
- Identification of Kelvin and mixed Rossby-gravity wave modes by Hayashi (1974) and Tsay (1974).
- Phase relationships between ozone and pressure perturbations by Schlesinger and Mintz (1979).
- Realistic zonal wind intensity in the middle stratosphere by Mahlman et al. (1978).

Model Improvements Required

A number of modeling improvements are required to understand the complete stratospheric system and its potential sensitivity to various natural and anthropogenic perturbations. Although many of the required improvements involve radiative transfer, chemical, oceanic, and cryospheric processes, these areas are not discussed here because they are addressed elsewhere. Listed below are various processes that appear to require considerable attention in terms of self-consistent dynamical modeling:

- Calculation of advection in three dimensions, and its role in interaction with unresolved scales. Local accuracy. Integral constraints.
- Incorporation of the effects of orography on motions of all scales.
- Tropospheric cyclone structure and its variability. Influence on cross-tropopause exchange and structure of the lower stratosphere.
- Planetary scale waves and jet streams and their propagation. Influence of troposphere and stratosphere on structure of planetary scale waves. Influence on cross-tropopause transport.
- Parameterization of sub-scale, dry and moist, vertical transfer processes. Interaction with resolved motions. Their role in cross-tropopause transport, especially in lower latitudes.
- Stratospheric water vapor budget. Effects of *cold trapping*.
- Mechanical dissipation processes and how they are excited in the stratosphere and upper troposphere.
- Self-consistent determination of clouds and their feedbacks to atmospheric structure.
- Naturally induced, stratospheric sudden warmings and coolings, as well as other episodic events.
- The polar-night vortex and its accompanying polar-night jet stream.

- Equatorial waves and their role in the quasi-biennial oscillation and the semiannual oscillation.
- The roles of self-determined ozone in accelerated radiative damping, stratospheric structure, and climatic influence on the troposphere.
- Dynamics of the mesosphere and the role of subplanetary scale motions.
- *In situ* instabilities and their role (if any) in the stratosphere and mesosphere.
- Prescription of physically correct upper boundary conditions.
- Influence of gravity waves and turbulence on stratospheric dynamical and tracer structure.
- Tidal structure and degree of interaction with other motions on various scales.
- Interhemispheric differences in the phenomena listed above.

This list is a formidable one, and strongly suggests that substantial measurement, theoretical, and modeling efforts will be required for an extended period into the future to resolve them. This list is also indicative of the magnitude of atmospheric processes generally neglected in one- and two-dimensional models. Our atmosphere is exceedingly complex to model and will remain a challenge to atmospheric scientists for many years. However, suitably constructed models have been and are continuing to be major tools for investigating the effects of stratospheric pollution.



CHAPTER 3

BUDGETS

INTRODUCTION

This chapter describes the current knowledge of the sources, sinks, and distributions of those atmospheric species that are important in determining the physical and chemical state of the stratosphere. These species are the halocarbons, nitrous oxide, odd-nitrogen, carbon dioxide, water vapor, methane and non-methane hydrocarbons, and sulfur compounds.

HALOCARBONS

SOURCES

The measured tropospheric concentrations for a variety of chlorocarbons at the end of 1977 (Singh et al., 1978; 1979a) and over a 3-year period (Rasmussen, private communication) are given in tables 3-1 and 3-2 respectively. Many of these are produced industrially; some are naturally occurring; most contribute to the halogen content of the stratosphere. The halocarbons found in amounts greater than 50 ppt, CCl_3F , CCl_2F_2 , CCl_4 , CH_3CCl_3 , and CH_3Cl , are considered in more detail in the following sections.

Natural Sources of Halocarbons

All the chlorofluorocarbons identified in the atmosphere are considered to come primarily from man-made sources, and there is little or no evidence to believe otherwise. CF_4 is a molecule whose sources are yet to be characterized, but several anthropogenic sources have been identified (Cicerone, 1979). Currently, the possibility of natural sources cannot be ruled out.

Among the chlorinated (nonfluorinated) species, there is little doubt that the dominant sources are man-made. From time-to-time, suggestions have been made that natural sources of CCl_4 , CHCl_3 , CH_2Cl_2 , and even CH_3CCl_3 may exist. Most of these suggestions have been speculative, and in the course of time have been considerably weakened. In the case of CCl_4 , it now appears that the atmospheric reservoir is largely an accumulation of man-made emissions (Molina and Rowland, 1974; Singh et al., 1976; Galbally, 1976). The possibility of small natural sources of CCl_4 cannot be completely ruled out, although none is known to exist. There is evidence (although scant) that oceans are not such a source. The problem of CHCl_3 and CH_2Cl_2 is comparable to that for CCl_4 . At present the atmospheric burden of CHCl_3 and CH_2Cl_2 is poorly characterized—large man-made sources exist and no natural source has been identified.

However, methyl chloride, CH_3Cl has a large atmospheric reservoir. Accumulation over a long time period is not possible because of its short lifetime (2 to 3 years). The data from the Southern Hemisphere is highly limited (Singh et al., 1977), but it appears that the north-south gradient is extremely small. The large reservoir, the uniform distribution, the short lifetime, and the lack of large man-made emissions indirectly point to a natural source. The nature of the source or sources has never been adequately characterized. The two major sources appear to be (1) the oceanic source and (2) the burning of vegetation, but their quantitative contributions are undefined. Preliminary measurements of Lovelock (1975) and Singh et al. (1979a), clearly demonstrate the existence of a natural oceanic source. This source is poorly characterized (Zafirou, 1975), but may turn out to be the dominant source of CH_3Cl . Little work has been done to determine production of CH_3Cl from the burning of vegetation. Simplistic analysis of data and simple models (Cicerone et al., 1975; Yung et al., 1975; and Graedel, 1979) require a source of 3 tg per year of CH_3Cl and no more than 10% of that source is man-made. The evidence that CH_3Cl is indeed a component of the natural atmosphere is strong, but additional research is needed to better characterize its sources.

Table 3-1
Background Concentrations of Halocarbons
at the End of 1977

Compound	Average Concentration* (ppt)†		
	N. Hemisphere Average	S. Hemisphere Average	Global
CCl ₂ F ₂ (FC-12)	230	210	220
CCl ₃ F (FC-11)	133	119	126
CCl ₂ FCClF ₂ (FC-113)	19	18	18
CClF ₂ CClF ₂ (FC-114)	12	10	11
CHCl ₂ F (FC-21)	5	4	4
CCl ₄	122	119	120
CH ₃ CCl ₃	113	75	94
CH ₃ Cl	611	615	613
CH ₃ I	2	2	2
CHCl ₃	14	≤ 3	8
CH ₂ Cl ₂	44	20	32
C ₂ HCl ₃	16	< 3	8
C ₂ Cl ₄	40	12	26

(Adapted from Singh et al.; 1978, 1979a)

*For those species where significant variations within each hemisphere were observed, the average concentration within each hemisphere is the concentration that, when uniformly mixed in the hemisphere, represents the total burden of the species in that hemisphere.

†ppt = 10⁻¹² v/v.

Table 3-2
Atmospheric Halocarbon Concentrations (ppt) (1976-1978)

Compound	Hemisphere	1976	1977	1978
CCl ₂ F ₂	North	230	258	271
	South	217	246	258
	Average	223	252	264
CCl ₃ F	North	134	154	164
	South	127	148	151
	Average	130	151	157
CH ₃ CCl ₃	North	108	108	119
	South	84	91	94
	Average	96	99	106
CCl ₄	North	131	137	137
	South	124	131	135
	Average	127	134	136

(Adapted from Rasmussen; private communication, 1979)

There is no indication that other chlorocarbons (chlorinated ethanes, ethylenes, etc.) have natural sources of any significance. The north-south distributions of these, even though poorly defined, appear to be consistent with man-made sources in the Northern Hemisphere. The knowledge of brominated and iodated halocarbons is considerably poorer than for the chlorinated species. The only two brominated species detected in the atmosphere are CH₃Br and CH₂BrCH₂Br. There is little doubt that the latter is all man-made, but the former appears to also have natural sources. Neither the atmospheric distribution nor the sources of CH₃Br have been studied in detail.

There is some evidence of an oceanic source of CH₃Br, but quantitative data are lacking. The only iodated organic identified in the air is CH₃I and this appears to come primarily from the oceans. The data base is virtually nonexistent—there is some doubt as to the identity of CH₃I, and lack of measurements in ocean water make it impossible to assess its natural sources. It should also be added that because of its very short lifetime (a few days), CH₃I is of little interest for understanding the chemistry of the stratosphere.

Industrial Sources of Halocarbons

Values for the United States production of major halocarbons are available through United States Tariff Commission reports and are believed to be accurate to within $\pm 5\%$, but world production figures are generally less accurate. For the particular cases of CCl₃F (FC-11) and CCl₂F₂ (FC-12), a concerted effort by the major manufacturers has produced accurate ($\pm 5\%$) worldwide production figures (A.D. Little, Inc., 1975; Manufacturing Chemists Association Technical Panel, 1978a, b; McCarthy et al., 1977; CMA, 1979).

Atmospheric release is much more difficult to determine and must be assessed for each material on the basis of use. Assessments of this type have been carried out for the halocarbon industry (Bauer, 1978a; Galbally, 1976; and McConnell and Schiff, 1978). For most compounds, about half of the release was in the United States.

Accurate data for the production and release to the atmosphere of CCl_3F and CCl_2F_2 have been published by McCarthy et al. (1977). Release to the atmosphere is estimated as being close to 85% of the amount produced at any given time; this value was obtained by breaking down sales in terms of end use (refrigeration, aerosols, closed-cell foam, etc.) and combining it with a release pattern for each application. For example, CCl_2F_2 used in domestic refrigerators is released slowly, whereas aerosol propellants are released quickly. Total world release to the atmosphere by the end of 1978 was 3.73 tg of CCl_3F and 5.48 tg of CCl_2F_2 (CMA, 1979). Overall estimates of release to the atmosphere are probably accurate to $\pm 5\%$. World production and release grew exponentially up to about 1973. Since 1973 the release has been nearly constant; recent production has been as follows:

2. p. 86. The units in the table of CFM production are 10^9 g, not tg.

<u>Year</u>	<u>FC-11</u>	<u>FC-12</u>	<u>FC-22</u>
1973	354.3 tg	447.5 tg	78.7 tg
1974	377.6 tg	473.6 tg	90.2 tg
1975	322.5 tg	419.7 tg	76.0 tg
1976	349.9 tg	449.8 tg	94.2 tg
1977	330.7 tg	424.4 tg	101.9 tg
1978	307.9 tg	401.2 tg	

CHF_2Cl (FC-22), $\text{CFCl}_2\text{CF}_2\text{Cl}$ (FC-113), $\text{CF}_2\text{ClCF}_2\text{Cl}$ (FC-114), and $\text{CF}_3\text{CF}_2\text{Cl}$ (FC-115) are produced in small amounts. Of these CHF_2Cl occurs in the largest volume; world production through the end of 1977 for uses other than as an intermediate in the production of other chemicals being 1 tg (Manufacturing Chemists Association, 1978b), approximately 1/10th of the combined CCl_3F and CCl_2F_2 production. World production and release of FC-22 on a year by year basis to the end of 1977 has been reported by Jesson (private communication) as given above.

Currently, CCl_4 is manufactured largely as an intermediate for the production of CCl_3F and CCl_2F_2 . The use of CCl_4 for other purposes (solvent applications, fire extinguishing applications, fumigating agents, etc.) has declined significantly since the 1950s. Values for its production and atmospheric emission through 1976 have been estimated by several groups (Galbally, 1976; Singh et al. 1976; and Parry, 1977) and show considerable scatter. Release of CCl_4 in recent years is only a small fraction of total production and could, therefore, be subject to large errors. Total worldwide production is also somewhat uncertain. The estimates of Galbally assume that the only significant production between 1914 and 1955 was in the United States, United Kingdom, France, and Germany. Estimates for later dates include Japan and other European countries. No data are available for the USSR and China. These emission estimates were obtained by subtracting CCl_4 production used as a feedstock and assuming that 90% of the remainder is lost to the atmosphere. Linear interpolation was used to obtain estimates for those years where no production and usage figures were available. An uncertainty figure of $\pm 30\%$ was given for the final estimates.

Production and release figures for methyl chloroform are given by Neely and Plonka (1978). Industrial production of methyl chloride is not a significant source.

TROPOSPHERIC ORGANIC HALOGEN BURDEN

Table 3-3 provides total tropospheric budgets of organic Cl, Br, I, and F, and indicates the source contributions (Singh et al., 1979a). It is clear that the global average tropospheric Cl concentration (organic) in late 1977 was 2.7 ppb. The possibility that unknown sources of tropospheric chlorine exist cannot be completely dismissed, but measurements of total organic chlorine (Berg and Winchester, 1977) do not support the existence of large unknown Cl sources. Using a 1-D model, it is possible to estimate the contributions of the various chlorocarbons to the background in the upper stratosphere. A current estimate is:

CH ₃ Cl	0.56 ppb
CCl ₄	0.50 ppb
CH ₃ CCl ₃	0.29 ppb
HCl	0.16 ppb
CCl ₃ F	} 0.62 ppb
CCl ₂ F ₂	
Total	2.13 ppb

Of the Cl total of 2.7 ppb, about 77 percent is man-made and the remaining 23 percent appears to be of natural origin.

Table 3-3
Tropospheric Chlorine, Bromine, Iodine and
Fluorine Organic Budgets in 1978
Compiled by Singh and Cicerone (Private Communication)

Species	Budgets			Percentage Source Contributions (%)	
	Northern Hemis- sphere	Southern Hemis- sphere	Global Average	Natural	Man- Made
Cl	2.9 ppb	2.4 ppb	2.7 ppb	23	77
Br	5-30 ppt	---	---	50-90	50-10
I	~2 ppt	<2 ppt	<2 ppt	100	0
F	1.0 ppb	0.9 ppb	1.0 ppb	0	100

The organic bromine and iodine budgets are much more uncertain. Measurements by Singh et al. (1979a) suggest only two brominated species CH₃Br and CH₂BrCH₂Br. Even for these two species the data base is sparse (see table 3-1). A preliminary interpretation suggests an organic Br content of 5 to 30 ppt, of which 50 to 90% may be of natural origin (table 3-3).

There are no obvious significant sources of organic iodine, but loss of iodine-rich materials from the marine aerosol is possible. The only species currently identified is methyl iodide, which is present at a concentration of about 2 to 5 ppt in the marine boundary layer. The tropospheric mean concentration of CH₃I is expected to be much less than 2 ppt. The atmospheric residence time of CH₃I is about 5 days.

The chlorine, bromine, and iodine budgets are contrasted with the budget for fluorine, which shows approximately 1 ppb of fluorine almost entirely attributed to man-made sources. There is a real possibility that other sources of organic bromine and iodine are yet to be identified. Special emphasis should be devoted to the identification of new species and better characterization of those already measured.

Tropospheric Concentration of CCl_3F

There have been extensive measurements of CCl_3F over a period of eight years, mostly at midlatitude locations of the Northern Hemisphere.

Measurements by Singh et al. (1978, 1979a), Rasmussen (private communication 1979), and by Pack et al. (1977) show that local variability is small at remote points in the Southern Hemisphere (i.e., points well removed from sources of release). These measurements may reasonably be assumed to represent background concentrations at their respective locations. Measurements (Singh et al., 1978, 1979a; Rasmussen, private communication, 1979) at relatively remote locations in the Northern Hemisphere suggest that Northern Hemisphere background concentrations are less than 20% above the Southern Hemisphere background. The South/North ratios of approximately 0.5 found by Pack et al. between Capetown (35°S) and Adrigole (51°N) suggest that a significant contribution to the Adrigole measurements is arising from local sources. It appears that with careful selection of a number of locations and repeated measurement over a significant period of time, reliable samplings of background air could be obtained.

The results of an interlaboratory calibration exercise for CCl_3F (Rasmussen, 1978b) involving 16 blind determinations are given in table 3-4. The extremes of the range, for a single standard sample, were 120 and 176 ppt, and, although 8 of the measurements were within 6 ppt of the nominal value (150 ppt), 5 of the measurements were at the 120 ppt extreme (20% below the nominal value). Comparison results for CCl_2F_2 , CH_3CCl_3 and CCl_4 intercalibrations are also given in table 3-4. Here the results were even less satisfactory. The highest CCl_2F_2 value was 45% above the nominal value. The overall scatter was worse for these three compounds than for CCl_3F .

Additionally, comparison of the data in Tables 3-1 and 3-2 shows that Rasmussen finds a global CCl_3F concentration of 151 ppt for 1977, while Singh et al. (1978) finds a value of 126 for the end of 1977. Clearly, both numbers cannot be correct. Although the two observations differ by only 20% the tropospheric lifetimes derived from these values are infinity and 30 years respectively.

A further comparison, which is important to the discussion of interhemispheric gradients which follows, is between Rasmussen data (Table 3-2), and Pack et al. (1977) Southern Hemisphere data for 1976. Pack et al. found 85 to 95 ppt CCl_3F at Capetown in mid 1976 (consistent with many earlier measurements taken at this location over a period of 4 years) while Rasmussen's Southern Hemisphere value for 1976 was 127 ppt.

Figure 3-1 shows the global distribution of many halocarbons for late 1977. For all stable halogenated species (CCl_2F_2 (FC-12), CCl_3F (FC-11), $\text{CCl}_2\text{FCClF}_2$ (FC-113), $\text{CClF}_2\text{CClF}_2$ (FC-114), and CCl_4) the average concentration in the Northern Hemisphere and Southern Hemisphere differs by only 10 to 15% (Singh et al., 1979a). This small North/South difference is also in agreement with the results of Rasmussen (private communication, 1979) and Tyson et al. (1978a). These results appeared to be in conflict with the earlier data obtained by Lovelock et al. (1973) on a voyage of the Shackleton from North to South and back in 1971 and 1972. Cunnold et al. (1978) have pointed out two factors that could make the data compatible: (1) the higher fluorocarbon concentrations over the Atlantic relative to the Pacific because of transport of fluorocarbons released in the United States and Europe, and (2) the fact that exchange between the hemispheres occurs mainly in the upper troposphere. They analyzed the problem on the basis of an 8 box model (4 latitudinally by 2 vertically). They estimate the unpolluted background S/N ratio to be about 0.8, but that it could be as low as 0.5 when proximity to source of locations in the North is taken into account. The corresponding value in the upper troposphere is 0.89, with a midlatitude Southern Hemisphere value in the upper troposphere of 0.94 times the global average.

Table 3-4
Halocarbon Results Returned from Participating Laboratories*

Sample No.	CCl ₂ F ₂ ppt v/v	CCl ₃ F ppt v/v	CH ₃ CCl ₃ ppt v/v	CCl ₄ ppt v/v
1	243 2.8%	145 3.3%	—	—
2	246 1.6%	136 9.3%	97	167
3	223 10.8%	120 20.0%	—	—
4	250 0%	148 1.3%	100	144
5		145 3.3%	—	—
6	227 9.2%	149 0.7%	—	130
7	246 1.6%	150 0%	112	105
8	322 28.8%	176 17.3%	—	—
9	250 0%	120 20.0%	80	120
10	362 44.8%	150 0%	103	108
11	249 0%	141 6.0%	130	71
12		156 4.0%	37	126
13	224 10.4%	124 17.3%	106	122
14		145 3.3%	—	—
15	243 2.8%	123 18.0%	—	—
16	204 18.4%	120 20.0%	30	321

*The % figures are percent difference from the submitted value.

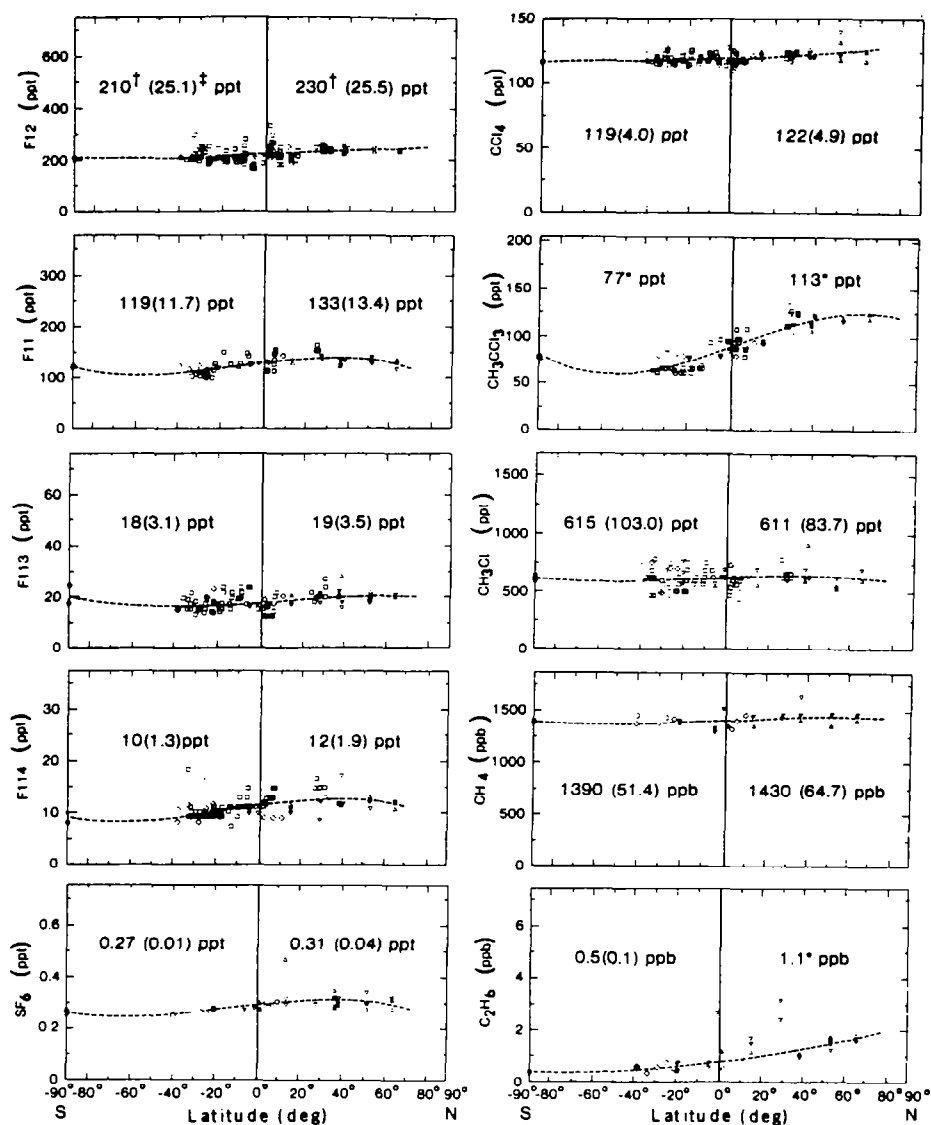


Figure 3-1. Global distributions of atmospheric constituents (Singh et al., 1979a)

Key: ppt = 10^{-12} (volume/volume); ppb = 10^{-9} (volume/volume); (†) is the average concentration in the hemisphere; (‡) is the standard deviation; (*) indicates that for species where a significant gradient within each hemisphere is observed the weighted average concentration is defined to represent the total burden of the species in that hemisphere; ▽, trip 1, stainless steel vessels; △, trip 1, glass vessels; ◇, trip 2, stainless steel vessels; and □, trip 2, in-situ air-sampling and analysis. The dashed line is a third-order polynomial fitted to the data. In most cases, individual hemispheres can be treated as well mixed. In the case of CH₃CCl₃ and C₂H₆, where this is not true, the global profile is well represented by the polynomial $89.71 + 0.818 L + 7.584 \times 10^{-4} L^2 - 7.894 \times 10^{-5} L^3$ for CH₃CCl₃ and $0.769 + 9.926 \times 10^{-3} L + 6.526 \times 10^{-5} L^2 + 5.561 \times 10^{-8} L^3$ for C₂H₆, where L is the latitude (in degrees) and varies from -90° to +64° (NH = 0° to +90°; SH = 0° to -90°).

This analysis provides the most reasonable explanation for the observed distributions. If it is correct, it leads to the conclusion that the Lovelock southern data (lower troposphere) at any given time should correspond to the global mean concentration multiplied by a factor of approximately 0.93, while the Rasmussen southern data (upper troposphere) should correspond to the global mean concentration multiplied by a factor of approximately 0.94. In other words, at any given time, the two sets of data should agree in the Southern Hemisphere, with the Lovelock data being higher than the Rasmussen data in the Northern Hemisphere due both to proximity to sources of release and to the tropospheric circulation patterns. Figure 3-2 shows a Southern value of 85 to 95 ppt for Lovelock for mid-1976; this translates into an approximate global mean of $90/0.93$ or 97 ppt.

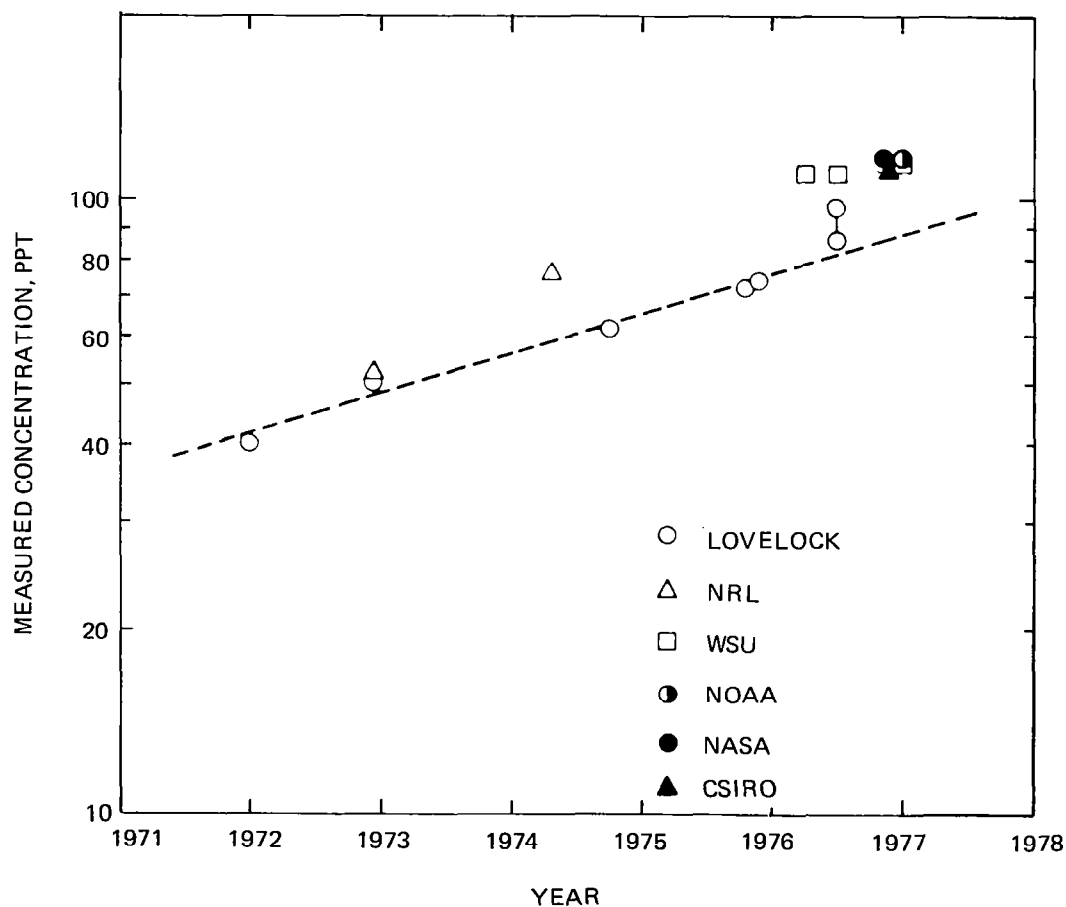


Figure 3-2. Southern Hemisphere CCl_3F concentrations vs time (Meakin et al., 1978).

The straight line is the data of Lovelock (1971-1976), the data point at the end of 1972 represents an interpretation of NRL data by Pack et al. (1977). The other data are: NOAA (Schmeltekopf et al., 1977b), NASA (Inn et al., 1977), WSU (Rasmussen and Krasnec, 1977, and private communication), NRL (Naval Research Laboratory), CSIRO (Fraser and Pearman, 1978).

On the other hand, the Rasmussen Southern Hemisphere data (also shown in figure 3-2) give values of approximately 127 ppt for 1976 leading to a global estimate of 130 ppt.

Assuming the Cunnold et al. (1978) analysis is correct, there is a systematic absolute calibration difference between the Lovelock and Rasmussen groups, with the Rasmussen data being uniformly higher. The Singh et al. (1979a) data lie between the other two sets (see tables 3-1 and 3-2 and figure 3-2).

Concentrations of Other Fluorocarbons

Table 3-2 shows global average concentrations for $\text{CCl}_2\text{FCClF}_2$ (FC-113) at 18 ppt; $\text{CClF}_2\text{CClF}_2$ (FC-114) at 11 ppt; and CHCl_2F (FC-21) at 4 ppt. Based on production, CHClF_2 (FC-22) might be expected to be the most abundant fluorocarbon after FC-11 and FC-12. However, it is subject to attack by OH (limiting its tropospheric lifetime), and in addition, it is difficult to detect by electron capture gas chromatography. No reliable estimates of the atmospheric concentration of FC-22 are available.

Of the three other fluorocarbons which were detected, FC-113 and FC-114 are produced industrially. Presumably their concentrations can be roughly accounted for on the basis of historical release. On the other hand, FC-21 is not produced commercially and total release from industrial sources could account for only 0.03 ppt (Glasgow et al., 1978).

FC-21 has now been detected by a number of groups (Singh, 1978; Cronn, 1978; Rasmussen, 1978a; Bruner, private communication, 1979) and has been unambiguously identified using gas chromatograph mass spectrometry (Crescentini and Bruner, 1979).

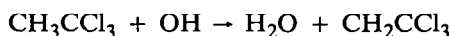
It has been suggested that FC-21 may arise from Teflon out-gassing in the measuring equipment. This seems unlikely on the basis of the following studies: FC-21 is still detected in Teflon-free equipment (Rasmussen, 1978a); no increase in FC-21 is observed when the gas from large amounts of finely divided Teflon is sampled (Rasmussen, 1978a); there is no indication in the manufacture, chemistry, or industrial experience with Teflon that FC-21 is a contaminant (Glasgow et al., 1978).

Ausloos et al. (1977) have observed the formation of CHCl_2F following irradiation of CCl_3F with near-UV light ($300\text{nm} < \lambda < 400\text{nm}$) in the presence of sand. Although the size of this effect in terms of a possible tropospheric sink has not been determined, it could provide evidence for conversion of CCl_3F into CHCl_2F . Thus, if FC-21 is a real atmospheric constituent, it could be a degradation product of FC-11. In any case, at a concentration of 1 ppt the FC-21 present could not represent a significant FC-11 sink.

An alternative suggestion is that FC-21 arises from decomposition of FC-11 on the chromatographic columns, or from degradation of stored FC-11 standards. Either of these explanations would raise questions about the accuracy of current FC-11 measurements.

Tables 3-1 and 3-2 give measured atmospheric concentrations for CCl_4 . Unlike the fluorocarbons, CCl_4 is uniformly distributed, presumably because the growth of emissions over the last decade has been relatively small. Because of uncertainties in the release figures for CCl_4 , it is difficult to determine whether all the current atmospheric burden is of industrial origin. The observation of elevated CCl_4 concentrations in urban areas is evidence for continued industrial emission (Singh et al., 1977), as is the observation of an apparent growth rate of approximately 2% per year in the atmospheric background concentration (Singh et al., 1979a).

CH_3CCl_3 is the only abundant measured industrial halocarbon subject to attack by tropospheric OH at a significant rate:



For this reason, most of the studies of the tropospheric concentration of CH_3CCl_3 have been used as an indirect route to estimating tropospheric OH concentrations.

Singh has attributed the fairly sharp change in the latitude gradient for CH_3CCl_3 between 20°N and 20°S to the high tropospheric OH concentration and temperature in this region. The much larger interhemispheric difference (50% in table 3-1) than is observed for background FC-11 and FC-12 (less than 20%) could suggest a latitude-dependent removal mechanism. However, it must be noted in this regard that the hemispheric difference found by Rasmussen (private communication, 1979) for CH_3CCl_3 is smaller (24% in table 3-2). Current estimates suggest that the tropospheric lifetime of CH_3CCl_3 is approximately 8 years, but the uncertainties in this lifetime are large.

REMOVAL MECHANISMS FOR CHLOROCARBONS IN THE TROPOSPHERE

Removal processes in the troposphere would be significant if their rate approaches or exceeds the overall rate of removal via stratospheric photolysis. However, that removal is a slow process. In the case of CH_3CCl_3 , removal by OH is clearly a process which effectively competes with stratospheric photolysis.

In the case of fully halogenated hydrocarbons, processes of comparable efficiency have not yet been established. The NAS report (1976) identified three removal processes for FC-11 and FC-12 which are believed to warrant more study: (1) solution in surface waters (estimated lower limit on removal time approximately 100 years), (2) ion-molecule reactions (1000 years), and (3) photodissociation in the troposphere (5000 years). As they stand, none of these is likely to present significant competition to stratospheric photolysis.

Singh et al. (1979a) have investigated the possibility that the ocean might act as a sink for CCl_4 . They estimate this sink to be about half as effective as the stratospheric photolysis sink. This leads to residence times in the 25 to 40 year range.

The only sink of possible interest for FC-11 and FC-12, which has been suggested since the NAS report, is decomposition on the surface of sand particles (Ausloos et al., 1977). Irradiation of CCl_4 , CCl_3F , and CCl_2F_2 in the presence of C_2H_6 in vessels containing silica sand results in the formation of products containing chlorine. The formation of these compounds occurs at wavelengths extending to 400 nm, i.e., at wavelengths where the solar radiation penetrates to the Earth's surface. More recently, experiments performed in the presence of oxygen suggest an apparent rate increase of a factor of approximately 40 (Rebbert, 1978). Additionally, earlier work by Lovelock (1976) has suggested that CCl_4 concentrations in the atmosphere are diminished in the vicinity of large bodies of windblown sand; the question of photo- or thermal decomposition of FC-11 and FC-12 on airborne and surface sand (and other surfaces) clearly merits further study. However, no reliable quantitative estimate of the possible size of the effect is available.

ESTIMATION OF THE CCl_3F TROPOSPHERIC LIFETIME

To date, it is not known whether there are processes in the troposphere which destroy CCl_3F at a rate sufficiently fast to compete with photolysis in the stratosphere as a removal process. The existence of such processes might be inferred from calculation of the tropospheric lifetime. There are two approaches to the calculation of this lifetime. One is to estimate the lifetime from determination of the absolute atmospheric burden using the accurate production-and-release data discussed previously. The second is to estimate the lifetime from analysis of the rate of increase of atmospheric concentration with time. The first approach has the advantage of giving large differences in tropospheric lifetime for different burdens (currently the absolute concentration for an infinite lifetime is about 60% greater than the absolute concentration for a 10-year lifetime for CCl_3F), but suffers the disadvantages of being quite sensitive to a number of parameters entering the calculation. The second approach is less sensitive, or even insensitive to these parameters, but results in small growth-rate differences for different tropospheric lifetimes (less than 3% per year between infinite and 10-year lifetimes for CCl_3F and CCl_2F_2).

Whatever the latitude, to allow meaningful estimates of the tropospheric lifetime from absolute burden measurements the following criteria must be satisfied (Meakin et al., 1978): (1) The measurements must represent *background* concentrations at the latitude of measurement (particularly difficult in the Northern Hemisphere because of proximity to the sources of release). (2) The measurements must be accurately calibrated on an *absolute* scale. (3) For comparison with model calculations the measurements must be converted to a global average, using *latitude correction factors* since the background concentration varies as a function of latitude (or a 2-D model must be used).

It is to be noted that calculated concentrations for a particular release scenario are sensitive to the *eddy diffusion scheme* chosen, and that the accuracy of the calculated concentrations also depends on the accuracy of the *release* figures.

The problems of obtaining representative background measurements, accurate calibrations, and latitude distributions have been discussed earlier in this chapter.

Statistics for fluorocarbon release are now believed to be accurate to $\pm 5\%$. This is one of the smaller uncertainties in the problem, but must be accounted for in comparing measurements and theory.

The stratospheric photolytic sink must be properly taken into account. The effectiveness of this sink is quite sensitive to the rate of transport to the stratosphere. For a range of commonly assumed eddy diffusion profiles, Meakin et al. (1978) indicated that calculated lifetime can vary by a factor of 2. The accuracy with which transport of fluorocarbons to the stratosphere must be specified limits the accuracy of tropospheric lifetimes calculated from global burdens.

With 2-D models, it should be possible to empirically describe the transport more realistically. Interhemispheric gradients would be expected to be correctly reproduced as well as seasonal effects. Use of a 2-D model would provide an improved evaluation of tropospheric lifetimes from global burdens. Such models will soon be available.

The combination of these problems in estimating tropospheric lifetime for FC-11 from global burdens, make it unlikely that this approach will prove satisfactory in the immediate future. The current *best estimates* are infinity from the Rasmussen data, approximately 40 years from the Singh data, and approximately 15 to 20 years from the Lovelock data. The estimates based on measurements of Goldan et al. (1979) and Tyson et al. (1978b) would also suggest residence times between 40 and 60 years. The sources of error described above would allow a range of possible lifetimes from 10 years to infinity.

The difficulties associated with determination of tropospheric lifetimes from absolute atmospheric burdens have lead to the examination of other approaches. The most promising of these is to determine lifetimes from temporal trends in concentration (Cunnold et al., 1978). Cunnold et al. estimated that a network of four stations spaced around the globe could establish a 10-year lifetime from 3 years of observations and a 20-year lifetime from observations over a period of 5 years (2σ confidence limits) assuming relatively constant production and release.

A network of four fluorocarbon measuring stations has been established under the auspices of the Manufacturing Chemists Association to acquire long-term fluorocarbon growth-trend data with the specific objective of establishing fluorocarbon tropospheric lifetimes. The network has been operating for one year.

Lifetime for CCl_2F_2

Measured atmospheric concentrations for CCl_2F_2 are given in tables 3-1 and 3-2. Most of the detailed discussion of concentrations and lifetimes has been in terms of CCl_3F since there are a large number of CCl_3F measurements over a long period of time. However, all the considerations in the previous section apply, essentially unchanged, to CCl_2F_2 except that CCl_2F_2 is inherently less reactive than CFCl_3 in the troposphere.

Measurements of Singh (table 3-1) suggest overall residence times of approximately 45 years, and correspond to a tropospheric lifetime of approximately 80 years, and those of Rasmussen (table 3-2) suggest overall residence times of approximately 100 years and corresponds to a tropospheric lifetime of infinity. The tropospheric lifetime of CCl_2F_2 from chemical considerations, is probably greater than that for CCl_3F . When the cumulative uncertainties are included, a range of tropospheric lifetimes between 20 years and infinity can be calculated.

NITROUS OXIDE

INTRODUCTION

Nitrous oxide is thought to originate primarily as a product of microbial metabolism. For many years, it was believed that the gas was formed primarily during denitrification, but recent works (Elkins et al., 1978; Cohen and Gordon, 1978, 1979; Yoshinari, 1976; Bremner and Blackmer, 1978; and Freney et al., 1979) suggest that nitrification (microbial oxidation of NH_4^+ to NO_3^-) may represent an important source, both in aquatic systems and in soils. Moreover, denitrification appears to function as a sink for atmospheric N_2O under selected conditions (Elkins et al., 1978; Kaplan et al., 1978; Elkins, 1979; and Cohen, 1978).

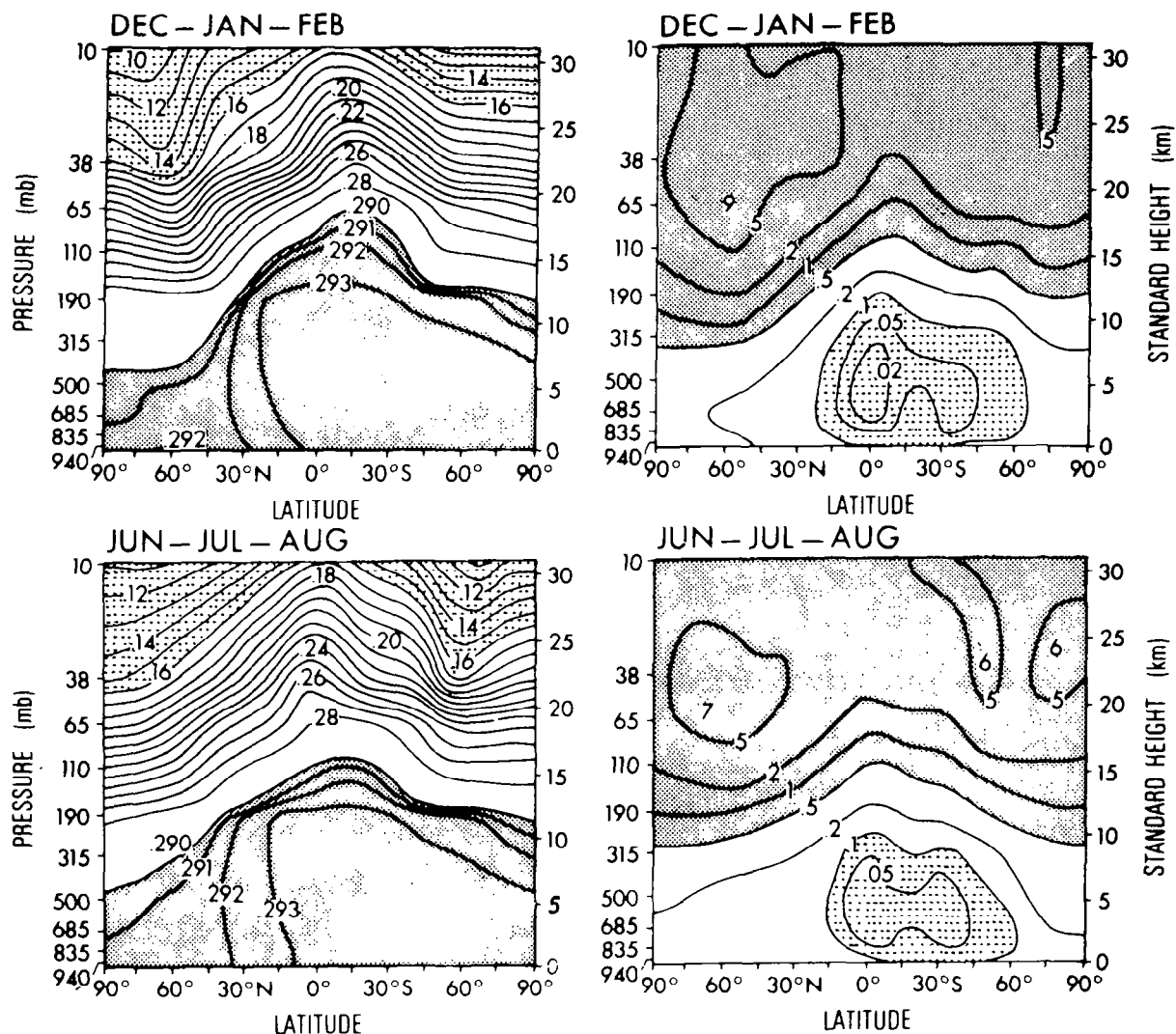
Stratospheric photolysis represents the largest currently established sink for N_2O , accounting for removal of 10 to 20 tg (N) per year. This flux is quite small compared to global rates for fixation or mineralization of nitrogen, and therefore, relatively modest changes in the balance of biospheric nitrogen transformations could effect large changes in the source of atmospheric N_2O (McElroy et al., 1977; and Johnston, 1977). However, the view that nitrification may play a central role in the cycle of N_2O requires revision of earlier concepts concerning the nature and magnitude of the human influence. A number of investigations are currently underway intended to obtain a quantitative understanding of human influences on nitrification and the associated impacts on sources of N_2O to the atmosphere.

The following paragraphs contain a brief summary of current knowledge about the atmospheric distribution, sinks and sources (both natural and anthropogenic) of N_2O .

ATMOSPHERIC DISTRIBUTION

Nitrous oxide is distributed uniformly through the troposphere, and under most conditions, it exhibits extremely small short-term variability (Ehhalt et al., 1975; Pierotti and Rasmussen, 1977a, 1979; Singh et al., 1979b; Pierotti et al., 1978; Cicerone et al., 1978; and Goldan et al., 1978). The mixing ratio is between 290 and 335 ppb by volume. This range of values results from inconsistent calibration standards. The uncertainty interferes with attempts to measure long-term trends, since the implication cannot be avoided that at least some existing calibration procedures are subject to systematic errors. Large fluctuations of the atmospheric concentration of N_2O , reported by earlier investigators appear to result from instrumental effects, although some studies (e.g., Goody, 1969; and Hahn and Junge, 1977) might reflect true variations of regional scale. However, nocturnal increases of N_2O have been unequivocally observed over active soils under stable atmospheric conditions (Matthias et al., 1979).

The uniform concentration observed for N_2O in the atmosphere implies a fairly long lifetime for the gas, and further suggests that its sources and sinks are rather widely dispersed over the globe. According to GCM studies by Levy et al. (1979), the empirical relation between variability and lifetime proposed by Junge (1974) does not apply to N_2O because of the proximity of stratospheric air with low N_2O concentrations. Figure 3-3 shows the calculated global distributions of N_2O (Levy et al., 1979) for a model with a completely uniform source for the gas at the ground, and with stratospheric photolysis assumed to be the only sink. The model predicts slightly lower concentrations at northern midlatitudes than at corresponding southern locations, due



Note: Left-most figures are winter and summer cross sections of zonal mean N_2O mixing ratios. Note smaller contour interval in the dark shaded area. Right-most figures are winter and summer zonal mean cross sections of N_2O longitudinal relative standard deviation (V_λ). $V_\lambda = 100 (\overline{R^{*2}})^{1/2} / \overline{R}$ where $(\overline{\quad})^\lambda$ represents a zonal average and $(\quad)^*$ is a deviation from it. Values of V_λ are not contoured in the surface layer due to resolution limitation.

Figure 3-3. Calculated global distributions of N_2O for a model with a completely uniform source at the ground, and with stratospheric photolysis assumed to be the only sink (adapted from Levy et al., 1979).

to more active mixing of stratospheric air into the northern troposphere. The variability of N_2O in the model (shown on the right-most panels of figure 3-3) is influenced by infrequent events which advect stratospheric air into the troposphere. It is interesting to note that the North/South contrast in the model (about 2 ppb at 40° latitude) agrees remarkably well with data reported earlier by Pierotti and Rasmussen (1977b) and Singh et al. (1979b) (see table 3-5), despite the fact that the concentration differences are so small that the experimenters did not claim to have accurately measured it.

Table 3-5
Observed Interhemispheric Differences of N_2O

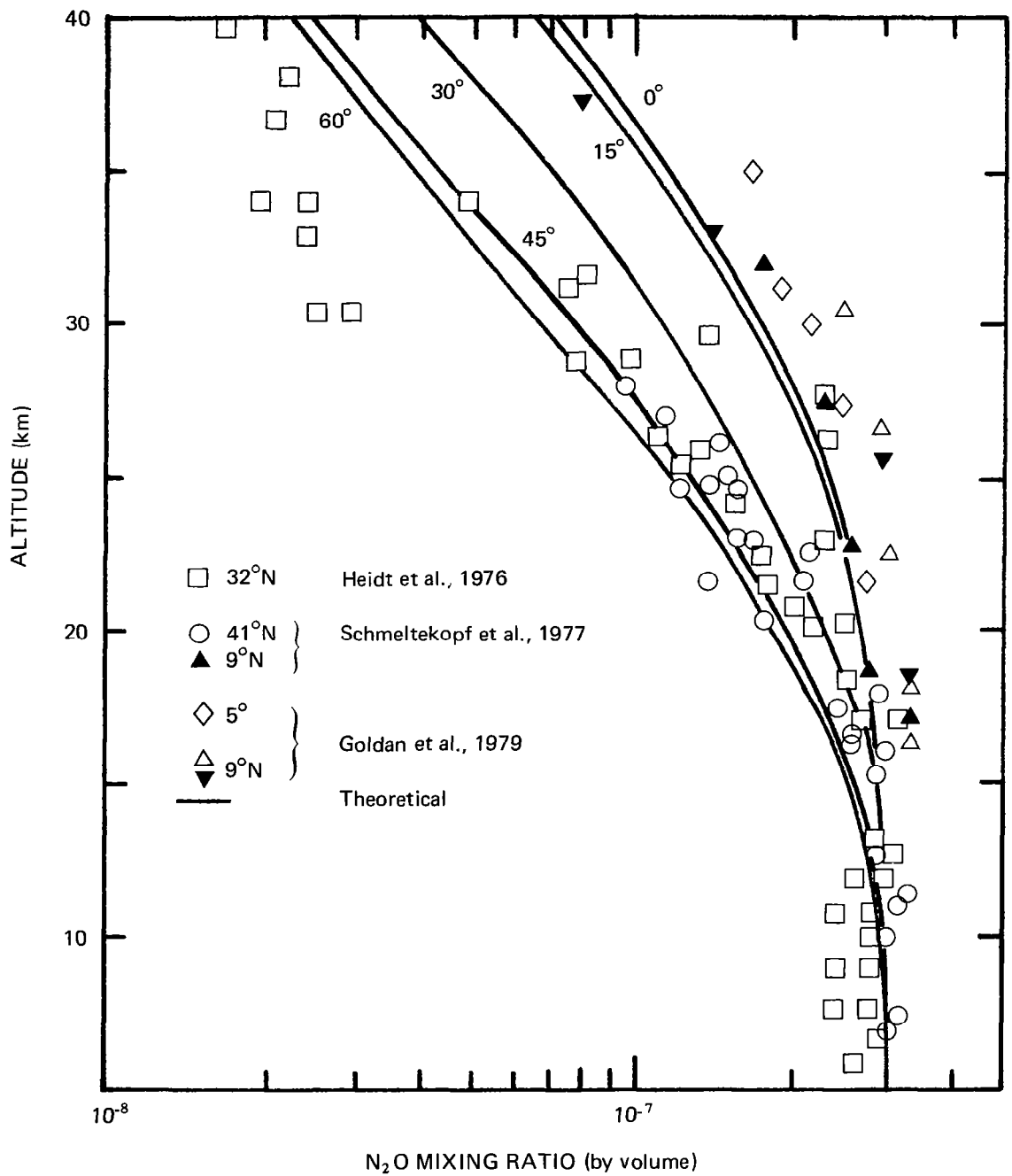
Latitude	Altitude (km)	N_2O (ppbv)	N_2O (North-South) (ppb)	References
47°N	7.7	330	-2	Pierotti & Rasmussen (1977b)
45°S	10.8	332		
4-24°N	0	312	-0.4	Singh et al. (1979b, 1975 data)
4-35°S	0	312.4		
4-24°N	0	311.5	-0.5	Singh et al. (1979b, 1977 data)
4-35°S	0	312		

Mixing ratios of N_2O decline with height in the stratosphere because of photochemical destruction. In the lower stratosphere, the meridional isopleths follow the preferred-mixing surfaces identified from radioactive tracer observations and from potential temperature data, as shown in figure 3-4 (Wofsy, 1978; and Logan et al., 1978). Above about 30 km, the lifetime of N_2O appears to be too short for complete meridional mixing, as manifested by sharp variations in concentrations at mid- and high-latitudes. Atmospheric upwelling in the tropics is apparently more vigorous above 30 km than is represented in the model of Logan et al. (1978). This deviation is not surprising in light of the fact that the data in figure 3-4 represent the first accurate tracer observations in this part of the atmosphere.

SINKS FOR ATMOSPHERIC N_2O

Stratospheric photolysis and reaction with $\text{O}(^1\text{D})$ account for removal of about 10 tg of N_2O (as nitrogen) per year. The distribution of N_2O is now known sufficiently well that a rather accurate calculation of the associated NO_x production rates should be possible. But unfortunately, the distribution of total NO_x is not accurately known, so that it is not clear whether other sources of stratospheric NO_x are globally important.

Surface-catalyzed photodissociation and biological uptake offer potential sinks for atmospheric N_2O . Rebert and Ausloos (1978) reported heterogeneous decomposition of N_2O over various types of sand from Africa. The quantum efficiency for a mercury arc ($\lambda \geq 280\text{nm}$) was rather low, about 10^{-7} molecules per photon, although it could be increased to 10^{-5} molecules per photon by heating the sand prior to the experiment. Pierotti et al. (1978) observed a slight depression (3 ppb, or 1%) of the N_2O concentration in dusty air from West Africa, with rather large reductions for CH_3CCl_3 (10%) and CCl_4 (5%). It seems unlikely that these rather gentle depressions could play a dominant role in removing these gases from the atmosphere (except perhaps for CCl_4), but further work is needed to clearly resolve the question.



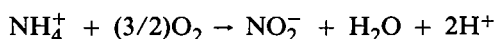
Theoretical profiles were calculated with a 1-D model in combination with the mixing-surface procedure discussed by Logan et al. (1978). The latitude height distributions shown in the figure are very similar to those of Ehhalt et al. (1978a), Tyson et al. (1978a), and Vedder et al. (1978), which are omitted for clarity.

Figure 3-4. Altitude profiles at various latitudes for N₂O.

Biological uptake of N_2O from the atmosphere has been observed in marshes and ponds (Kaplan et al., 1978; and Elkins et al., 1978). These systems are characterized by anoxic sediments underlying shallow water which has been stripped of dissolved inorganic nitrogen, and which is undersaturated in oxygen. It appears that denitrifying organisms may very rapidly consume N_2O under these conditions, so that the water remains depleted in N_2O despite contact with the atmosphere. The examples studied to date represent rather common systems, but their global importance is not clear. Gas exchange rates have not been measured, but are probably slow, as evidenced by the low oxygen concentrations in the water. Further studies are clearly indicated on this question.

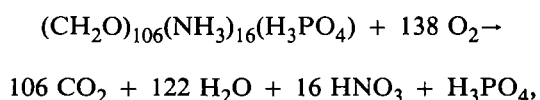
SOURCES OF N_2O AND MAN-MADE PERTURBATIONS

Observations in the oceans, in the Potomac and Delaware Rivers, in freshwater ponds, and in agricultural soils provide direct evidence for a quantitative relation between oxidation of organic material and production of N_2O . Interpretation of these studies and of laboratory experiments suggests that microbial oxidation of ammonia under oxygenated conditions,



may be the mechanism responsible for production of N_2O (Yoshinari, 1976; Hahn and Junge, 1977; Elkins et al., 1978; Cohen and Gordon, 1978, 1979; and Bremner and Blackmer, 1978). Surprisingly, the yield of N_2O observed during nitrification appears to be uniform in many aquatic systems. Fertilization of agricultural soils with ammonium or organic N and disposal of human and animal wastes strongly stimulate nitrification and may lead to globally significant efflux of N_2O to the atmosphere.

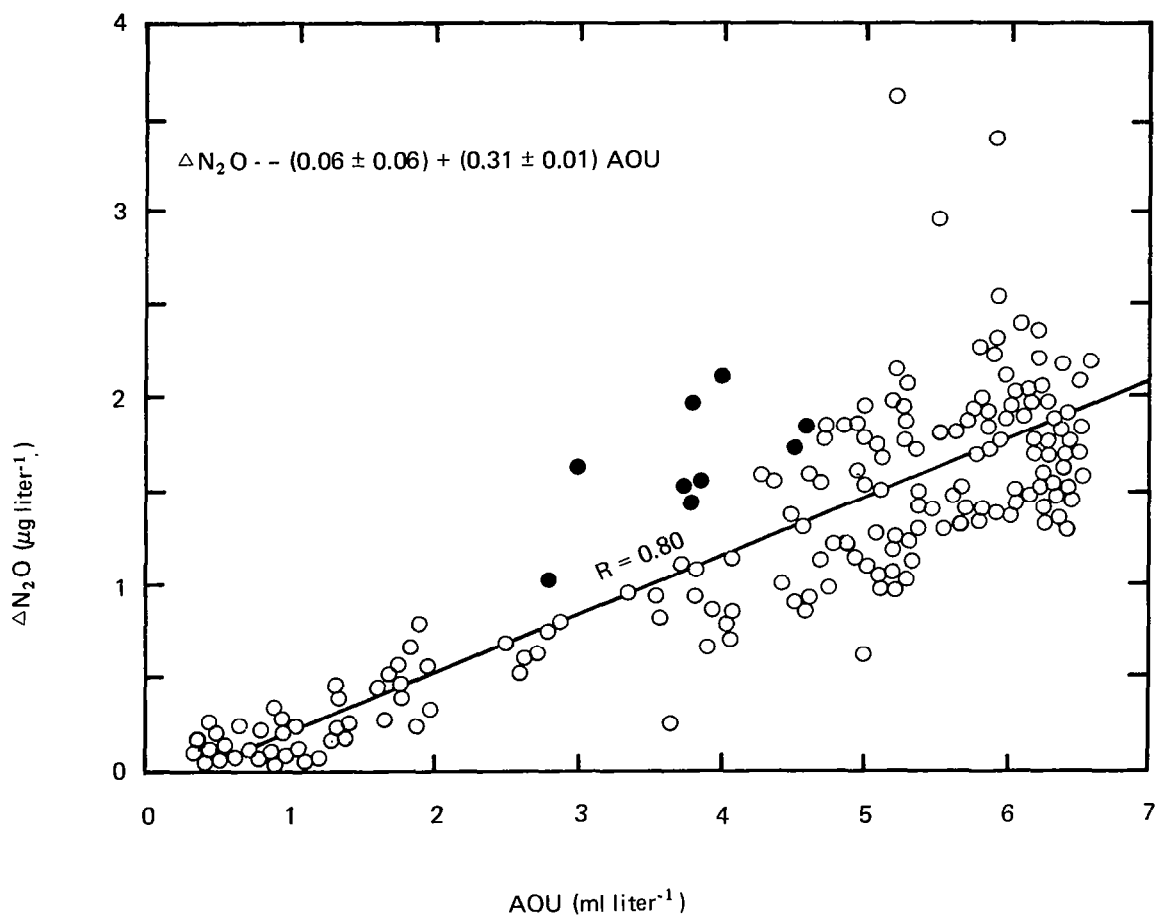
The relationship between the oxidation of organic material and the evolution of N_2O in the oceans is indicated in figures 3-5 and 3-6 (Elkins et al., 1978). The quantity ΔN_2O provides a measure of the net accumulation of N_2O in a water mass since its last contact with the air, and AOU (the apparent oxygen utilization) provides a cumulative record of the net quantity of oxygen consumed over the same period due to oxidation of organic material. If it is assumed that the C:N:P ratios in marine organic material are 106:16:1 (Redfield et al., 1963), and that the stoichiometry of decay is represented by



then the data in figures 3-5 and 3-6 may be used to estimate an average yield of one mole of nitrogen as N_2O for every 350 moles of ammonia oxidized (0.28%).

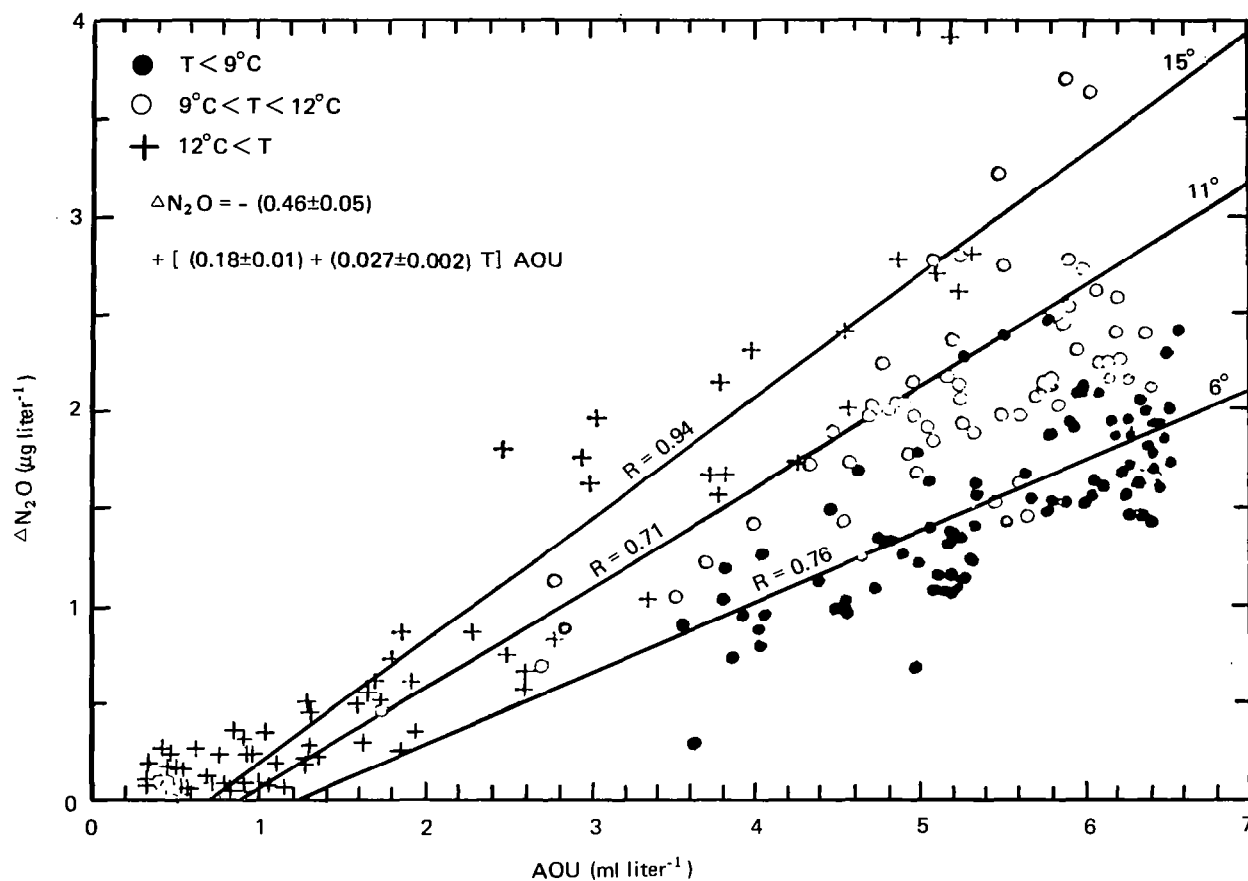
The small yield of N_2O in the oceans is consistent with a *minor* role in marine processes in the global budget for atmospheric N_2O . Even if all nitrogen incorporated into primary organic material were oxidized to NO_3^- , the marine source of N_2O would account for less than 10 tg of nitrogen per year (Elkins et al., 1978; and Cohen and Gordon, 1979). Since much of the nitrogen mineralized in the sea is reused as NH_4^+ , the oceanic source of N_2O is probably very small (less than or equal to 10% of the global source).

Recent data by Weiss (1979) show that the surface waters of the world's oceans are supersaturated with respect to atmospheric N_2O by only 4%. Weiss' experiments measure the surface super-saturation directly using an equilibration chamber, and cover cruise tracks in excess of 60,000 km. Using the thin-film model (Broecker and Peng, 1974; and Liss and Slater, 1974), Weiss estimates a global source of approximately 3 tg N in N_2O per year. However, the applicability of the thin-film model to such small supersaturations is unclear since physical effects may produce small excesses of N_2O .



Note: Most of the data are shown in this figure, except for unusually active regions and $AOU < 0.3$ ml liter⁻¹. The straight line is a least squares fit which yields a rms deviation of $\pm 0.35 \mu g$ liter⁻¹. R is the linear correlation coefficient.

Figure 3-5. N_2O observations from the Central Pacific Ocean expressed as excess N_2O plotted against apparent oxygen utilization (adapted from Elkins et. al., 1978).



Note: The rms deviation of the fit is $\pm 0.3 \mu\text{g liter}$.

Figure 3-6. Results of a least squares fit relating $\Delta\text{N}_2\text{O}$ to AOU (AOU $> 0.3 \text{ ml liter}^{-1}$) and temperature (adapted from Elkins et al., (1978).

The small size of the marine sources lends new emphasis to work on terrestrial sources of N_2O . The disposal of nitrogenous wastes in rivers and estuaries stimulates vigorous production of N_2O . McElroy et al. (1977) using data on the concentration of N_2O , O_2 and inorganic nitrogen species in the Potomac River estuary, estimated a conversion to N_2O of 1 to 5% of the total nitrogen input. If the nitrogen in human and animal wastes were on the average converted to N_2O with such high efficiency, disposal of these wastes could represent a globally significant source of N_2O .

Recently, extensive observations in the Delaware and Potomac estuaries have revealed marked variations of the N_2O production rate. The data suggest that enhanced production of N_2O is triggered by severe oxygen depletion, where concentrations of O_2 in surface waters drop below 2 mg liter^{-1} . There is evidence to suggest that denitrification near the water-sediment interface may be responsible for the enhanced production of N_2O . Consequently, a nonlinear amplification may occur where more severe pollution reduces O_2 levels and increases the fraction of waste nitrogen converted into N_2O . Because of increasing world population, such a nonlinear response could greatly amplify anthropogenic production of N_2O in the future.

Work on fertilized agricultural soils indicate that nitrification may be the dominant source of N_2O in these systems (Bremner and Blackmer, 1978; McKenney and Wade, 1978; and Freney et al., 1979). The fractional yield of N_2O in fertilized soils appears to increase under oxygen stress in a manner analogous to that of the estuaries. The yield of N_2O from nitrification of fertilizer N appears to be similar to oceanic values at low rates of application, (10^{-3} moles N_2O per mole of NH_4^+) increasing rapidly at high rates (Bremner and Blackmer, 1978). McKenney and Wade (1978) observed an exponential increase in the N_2O flux as a function of the application rate of fertilizer at high rates. Where the systems are heavily loaded with reduced nitrogen the aquatic and soil systems both appear to exhibit nonlinear amplification of the N_2O flux in response to increased loading.

Laboratory and field studies of instantaneous N_2O fluxes from soils give values ranging from less than $0.1 \text{ kg-N ha}^{-1} \text{ yr}^{-1}$ ($< 1.4 \times 10^9 \text{ N-atoms cm}^{-2}\text{s}^{-1}$) to larger than $10 \text{ kg-N ha}^{-1} \text{ yr}^{-1}$ ($> 1.4 \times 10^{11} \text{ N-atoms cm}^{-2}\text{s}^{-1}$) (Bremner and Blackmer, 1978). Averaged over the year, the sources of N_2O from agricultural soils appear likely to be globally significant.

A curious feature emerging from the field studies on agricultural soils is the marked small-scale variability observed in the N_2O flux, even where the soil surface appears homogeneous. As a consequence of this variability, it is presently difficult to generalize about the anthropogenic sources of N_2O arising from agricultural activities.

Small quantities of N_2O are produced during chlorination of water containing ammonia or organic nitrogen. Presumably, the reaction involves intermediates in the oxidative chain for N initially in the -3 oxidation state. This phenomenon has been observed in drinking-water plants (Cicerone et al., 1978) and sewage-treatment plants (McElroy et al., 1977). Although unlikely to be a significant global source, the mechanism responsible for generation of N_2O is of interest in view of possible similarities with the nitrification process.

Weiss and Craig (1976) and Pierotti and Rasmussen (1976) observed production of significant quantities of N_2O during combustion of coal and oil. Catalytic converters on automobiles may also be potentially important sources. Estimates for the global contribution of combustion range between 1 and $2 \text{ tg N in } N_2O$ per year. Combustion appears to be a potentially significant source of anthropogenic N_2O .

ISSUES

The magnitudes of the sources and sinks for N_2O remain uncertain, despite considerable advances in our understanding during the last 5 years. The possibility of important unknown sinks cannot be discounted. The locus of important sources and time scales for anthropogenic change are presently understood only in rough outline. The relative importance of nitrification as compared to denitrification is not yet firmly established.

Nonlinear amplification of the N_2O flux from oxygen-stressed environments could result in greatly enhanced anthropogenic sources of N_2O , but the cause of this phenomenon is not presently understood. The mechanism must be clarified in order to make meaningful assessments of future human perturbations.

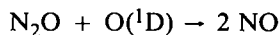
The existence of a long-term trend is a key question. Weiss (1979) reported preliminary results which suggest an increase of approximately 0.5 ppb per year between 1977 and 1979. These data come from remote stations in the Pacific and Antarctica. Goldan and co-workers (1979) reported a similar upward trend from observations in the upper troposphere over Wyoming. In neither case is the data base adequate at the present time to accurately establish the magnitude of the increase. The Weiss data suggest a present flux of 3 tg N in N_2O per year (or a doubling time of approximately 400 years). However, the slow growth rate is not genuinely reassuring since the recovery time of the atmosphere is probably correspondingly slow. Moreover, both biogenic sources (soils, aquatic systems, nitrogenous waste disposal) and combustion sources may grow rapidly, and it is presently unclear at what level such changes could become significant to stratospheric chemistry or tropospheric infrared transmissivity.

Future research on N_2O should emphasize quantitative characterization of sources and elucidation of biogeochemical mechanisms, which control evolution of the gas to the atmosphere. This effort should proceed in parallel with observations of the long-term and seasonal variations of atmospheric N_2O , since changes in the background concentration of N_2O reflect the net effects of man-made and natural perturbations. It should also be remembered that the existence of presently unknown sinks for N_2O could have a major impact on our understanding of the atmospheric cycle of the gas.

STRATOSPHERIC NO_x BUDGET

SOURCES AND SINKS

The major source of stratospheric NO_x is the oxidation of nitrous oxide by $\text{O}(^1\text{D})$ (Nicolet, 1971).

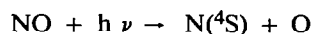


Using the reaction rate constants in this report, a typical 1-D calculation gives a column production rate of $2.3 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$ above the tropopause. Estimates of this source strength by Schmeltekopf et al. (1977b) with extrapolated measured profiles of N_2O and the 2-D model of Crutzen (1975a), found the value to be $4.5 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$. Given the uncertainties in both models, it is not clear that the discrepancy is significant.

The reaction above accounts for only about 10% of the known atmospheric sink of nitrous oxide. Photodissociation in the stratosphere is the dominant sink.

The major sink of NO_x is the downward flow through the tropopause followed by heterogeneous removal processes in the troposphere. A simple 1-D model calculation including only the major source and sink will predict an NO_x mixing ratio of about 32 ppb at 40 km as shown in figure 3-7. The importance of other sources and sinks will be estimated by comparing their effects on the predicted NO_x mixing ratio at 40 km.

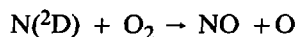
Table 3-6 lists known sources and sinks of NO_x and their effects on the NO_x mixing ratio. Inclusion of the sink



followed by



can significantly reduce the NO_x mixing ratio in the mesosphere (Brasseur and Nicolet, 1973; and Duewer et al., 1977). It is believed that this sink is responsible for the minimum mixing ratio near 70 km. This sink also reduces the mixing ratio of NO_x at 40 km to a value of about 25 ppb when the NO photodissociation rate of Frederick and Hudson (1979a) was used (figure 3-7). If the NO photodissociation rate of Cieslik and Nicolet (1973) is used, this mixing ratio is further reduced to about 18 ppb. It is essential to include this sink in evaluating the effect of a downward NO_x flux from the thermosphere. This source of NO_x is due to the reaction



where $\text{N}(^2\text{D})$ is produced through ionospheric reactions (Frederick and Rusch, 1977):

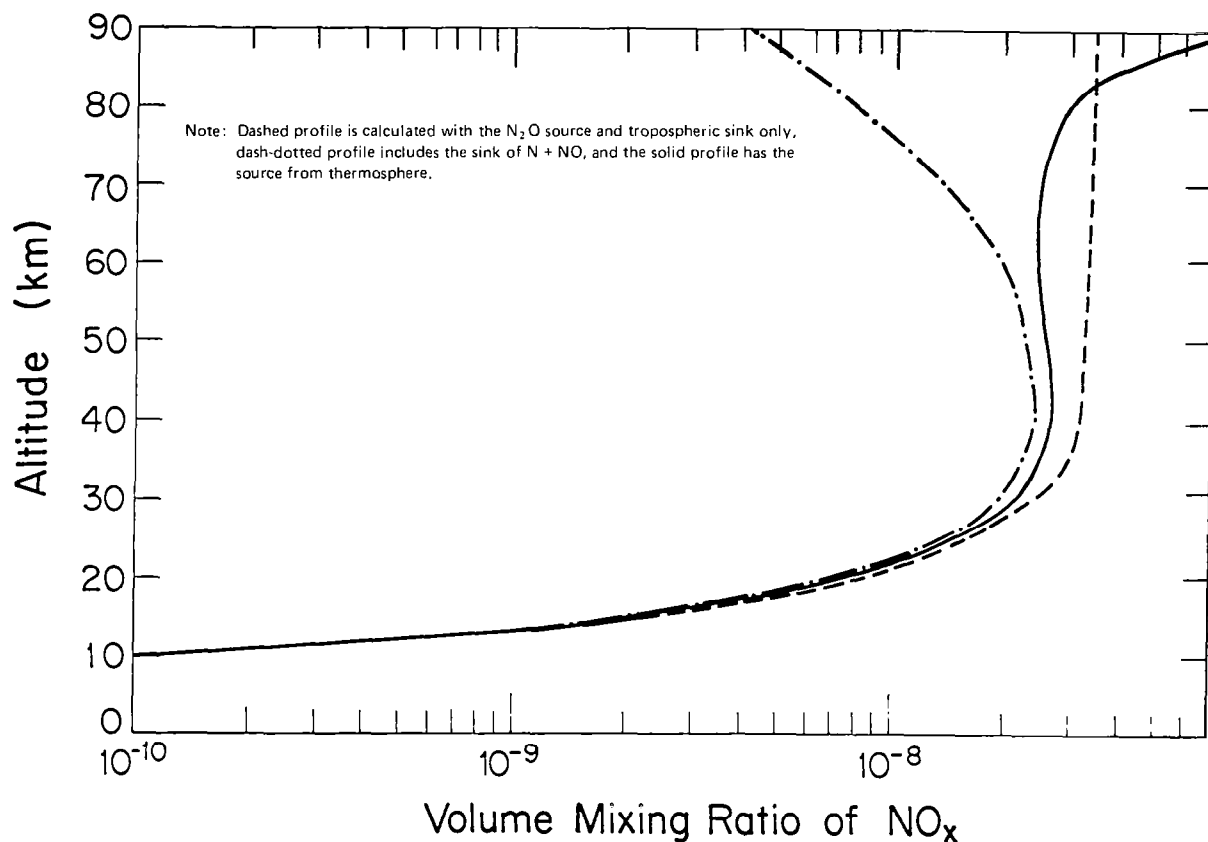
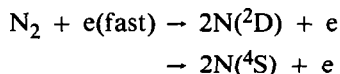
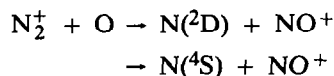
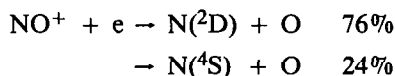


Figure 3-7. Calculated NO_x volume mixing ratio.

Table 3-6
Sources and Sinks of NO_x and Their Effects on NO_x Mixing Ratio*

Sources	Effect on NO_x Mixing Ratio at 40 km
$\text{N}_2\text{O} + \text{O}(^1\text{D})$	---
Ionospheric	+10%
Auroral	?
Cosmic ray	< +1% (but about +5% at 15 km)
Tropospheric intrusion	Negligible
Lightning	?
Volcanic	Negligible
$\text{NH}_3 + \text{OH}$	Negligible
Subsonic transport	Negligible (but about +5% at 15 km)
Solar proton events	Sporadic
Nuclear bombs	Sporadic
Sinks	
Tropospheric	---
$\text{NO} + h\nu$ and $\text{N} + \text{NO}$	-20% (much larger in mesosphere)
Meteoric N and $\text{N} + \text{NO}$	A sink of about $5 \times 10^7 \text{ cm}^{-2}$ near mesopause
Aerosols	Could contain as much as 30% of NO_x in lower stratosphere

*As compared to the NO_x calculated with only N_2O source and tropospheric sink

The branching ratio of the first reaction has been measured by Kley et al. (1977). The downward flux of NO_x at the mesopause is about 1 to $5 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$ (Strobel, 1971; and Cravens et al., 1979). Figure 3-7 also shows the calculated NO_x mixing ratio for 30° latitude at equinoctial condition when the downward flux of $2 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$ is used. This profile should be latitude dependent since both the source and the sink are latitude dependent. At high latitude during the winter, the thermospheric NO_x can be transported into the stratosphere without suffering any significant loss. Furthermore, there could be a large increase of NO_x from the auroral source during the winter. This effect should be investigated with a 2-D or 3-D model. NO_x measurements at high latitudes are needed to resolve this problem. It is important to measure the branching ratios of the second and third reactions, because if $\text{N}(^4\text{S})$ rather than $\text{N}(^2\text{D})$ is the primary product, then the reaction, $\text{N}(^4\text{S}) + \text{NO} \rightarrow \text{N}_2 + \text{O}$ would follow and result in an NO_x sink.

Cosmic rays produce O^+ , N^+ , and N , and thus produce NO_x (Warneck, 1972). However, the production is only about $10^7 \text{ cm}^{-2}\text{s}^{-1}$ in high latitudes (above 60°), and a factor of 5 less in low latitudes. Since most of the NO_x is produced in the lower stratosphere where it is easily transported into the troposphere, the contribution of this source to the NO_x mixing ratio at 40 km is less than 1%. Through similar reactions, solar proton events can produce large amounts of NO at high geomagnetic latitudes (greater or equal to 60° according to Crutzen et al., 1975). The largest event recorded was in August, 1972. As much as $2 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$ of NO was produced at high latitudes, comparable to the source of N_2O oxidation in the midlatitude. The fact that an ozone reduction was observed in the high-latitude upper stratosphere (Heath et al., 1977), supports qualitatively the catalytic ozone destruction by NO_x . However, since then, because of the drastic changes in stratospheric photochemistry (such as addition of chlorine), it is important to make a current evaluation of this problem.

Events like this are rare. Smaller events such as the September 1966 event produce only about $2 \times 10^7 \text{ cm}^{-2}\text{s}^{-1}$. Events of this size happened several times per year during 1958 and 1959, but have been sporadic (less than once per year) since then.

Intrusion of tropospheric NO_x into the stratosphere is unlikely because of the low tropospheric NO_x (less than or equal to 0.5 ppb) that has been measured (Drummond et al., 1977; Noxon, 1975; and McFarland et al., 1979). There is no quantitative estimate of the intrusion of NO_x produced by lightning. Injection of NO_3 by volcanic eruption is also negligible (Lazrus et al., 1979). Efficient scavenging by rain apparently prevents NO_x in the upper troposphere from building up. For the same reason NH_3 in the upper troposphere should be so low that its conversion to NO_x through reaction with OH is negligible also. High-flying subsonic transport aircraft inject NO into the lower stratosphere. Using the projected injection profile for the year 1980 (CIAP, 1974) it can be found that the increase of NO_x at 15 km is about 5%, but is negligibly small above 20 km.

Nuclear bombs produce NO through high-temperature reactions. Two recent papers (Bauer, 1978b; and Chang et al., 1979) have summarized these NO_x inputs into the stratosphere. In 1961 and 1962, the NO_x injected was large, about 1 to 2×10^{34} molecules. There should have been large increases in NO_x at high latitudes in the Northern Hemisphere at that time. Recent nuclear tests inject only about 10^{32} molecules per test, negligible compared to the N_2O source.

Odd-nitrogen species are also produced by high-temperature reactions during atmospheric entry of meteors (Park and Menees, 1978). The production of NO is about $5 \times 10^6 \text{ cm}^{-2}\text{s}^{-1}$ and peaks at an altitude of about 85 km. The production of atomic nitrogen is about $5 \times 10^7 \text{ cm}^{-2}\text{s}^{-1}$ and peaks at 95 km. Since most of the atomic nitrogen produced near this height will recombine with NO rather than reacting with O_2 to form NO , this represents an important sink of NO_x , especially during intensive meteoric showers.

Heterogeneous reactions can affect the stratospheric NO_x abundance in two ways: one is that aerosols can be a reservoir of NO_x , and the other is that NO_x can be removed from the stratosphere by aerosols settling into the troposphere. Although the stratospheric aerosol apparently consists mainly of sulfate (Junge and Manson, 1961; Lazrus et al., 1971), Kiang et al. (1975) have pointed out that in laboratory analyses undertaken at

room temperatures that nitric acid may have evaporated. Recently, Farlow et al. (1978) have tentatively identified nitrogen-sulfur compounds in the stratospheric aerosols and concluded that although the NO_x removed by aerosols settling into the troposphere is small in comparison to the production rate of reaction $\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{NO}$, the aerosol layer may constitute an important reservoir of NO_x in the lower stratosphere.

COMPARISON WITH MEASUREMENTS

Measurements of the various atmospheric nitrogen-containing species show a great deal of variability, particularly in the lower stratosphere. The measured mixing ratios of NO , shown in figure 3-8; NO_2 , shown in figure 3-9; and HNO_3 , shown in figure 3-10, indicate a general increase from the tropopause into the upper stratosphere. Although consistent with model calculations, these values are generally lower by about a factor of 2 than those predicted for the stratosphere. Extensive NO_2 column density measurements by Noxon (1979) in low latitudes (0 to 40°) are consistent with the *in situ* data shown in figure 3-9. But the much lower NO_2 values (by more than a factor of 2) in winter high latitudes indicate there may be either an NO_x sink or an unknown mechanism converting NO_2 to more stable species such as HNO_3 . Most of the upper stratosphere and lower mesosphere measurements indicate a decrease in NO mixing ratio with altitude contrary to the presence of an important thermospheric source. However, the measurements at even higher altitudes (Meira, 1971) are consistent with the models which include the thermospheric source.

In the daytime, most NO_x resides in the form of NO above 40 km. Extensive latitudinal and seasonal measurements of NO between 40 km and 100 km can determine the NO_x mixing ratio, and the importance of the ionospheric and the auroral sources. At night NO_2 and HNO_3 are the dominant NO_x species below 60 km. Simultaneous measurements of NO_2 and HNO_3 at night can also determine the mixing ratio of NO_x . A more detailed discussion of these observations and a comparison with model predictions is found in Chapter 4.

CO₂ BUDGET

As of 1978, the global atmosphere contained 610,000 tg carbon, or a mole fraction of 3.33×10^{-4} . The observations shown in figure 3-11 confirm that the atmospheric inventory is increasing, presently at a rate of about 2×10^{14} moles of carbon per year (1.5 ppm). The rate of increase has also been increasing, roughly doubling since the late 1950s.

Major gaps exist in the knowledge of the biogeochemistry of CO_2 . The preindustrial inventory is uncertain. Most models adopt a value of 290 ppm, about 15% less than the present concentration. If this assumption is wrong, model-based predictions of future trends could be in error.

Another related question concerns the role of the biosphere in the long term storage of carbon. This role is potentially large, especially with respect to the exchange between the atmosphere and the reservoirs of reduced carbon in soil and in forest biomass.

The biospheric reservoir is composed of several parts, each with markedly different exchange times and magnitudes. The terrestrial, non-fossil biosphere contains about 14×10^{17} moles of carbon, of which 90% exchange carbon with the atmosphere on time scales of tens of years or more. The remainder consists of material such as leaves, small branches and roots, litter, etc. Annually, this part of the biosphere introduces, by virtue of photosynthetic and decay activities, the seasonal variation in the atmospheric inventory, amounting to approximately 5×10^{14} moles of CO_2 or about 3 ppm globally, or 5 ppm in the Northern Hemisphere (see figure 3-11). The marine biosphere contains an amount of carbon similar to the terrestrial non-fossil biosphere. Large quantities of organic carbon are also stored as terrestrial organic matter in soil humus (1.6×10^{17} moles) and peat (1.0×10^{17} moles). Each of these reservoirs exchange carbon with the atmosphere at a comparatively slow rate (100 to 1000 years); longer for peat.

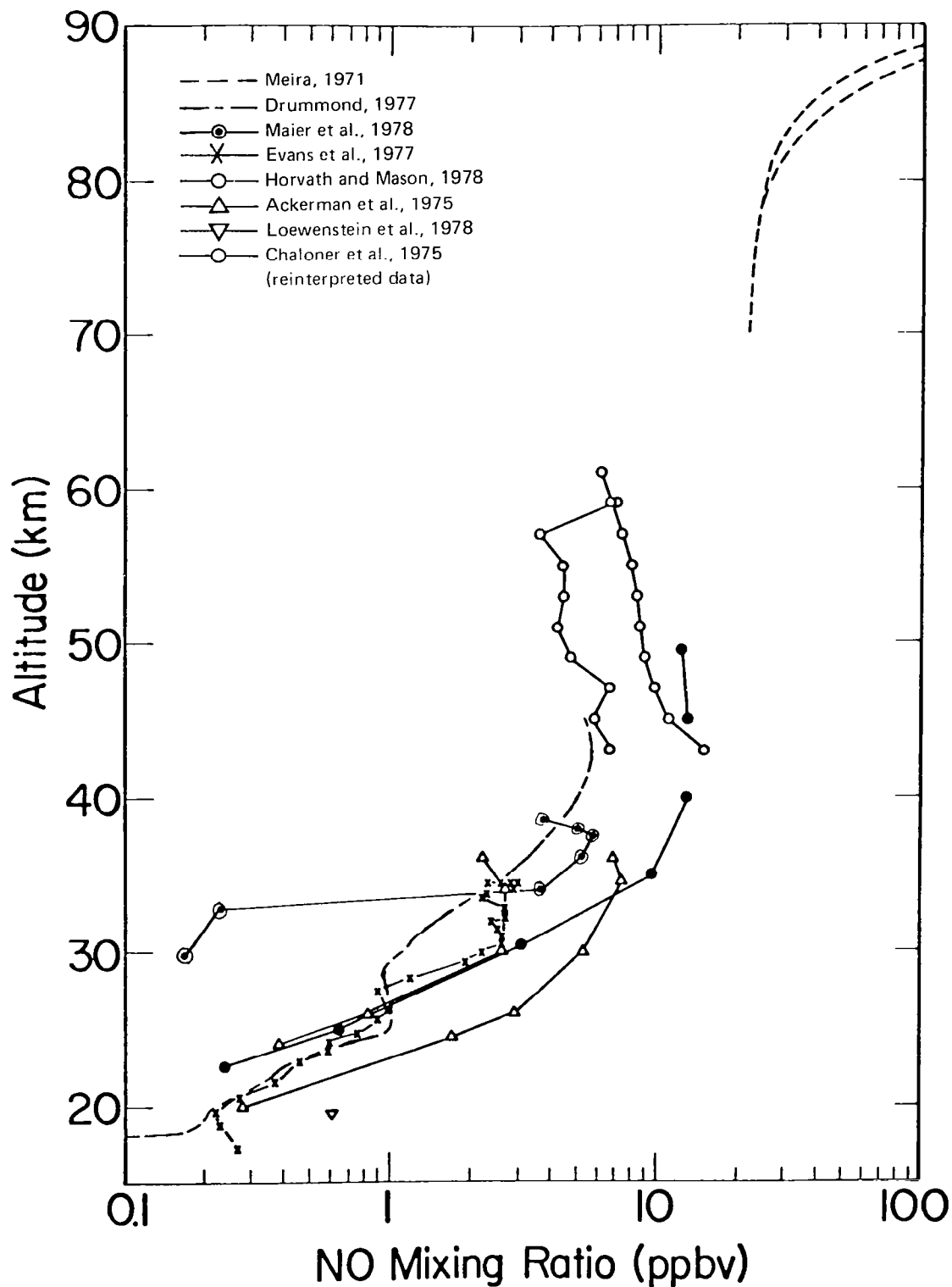
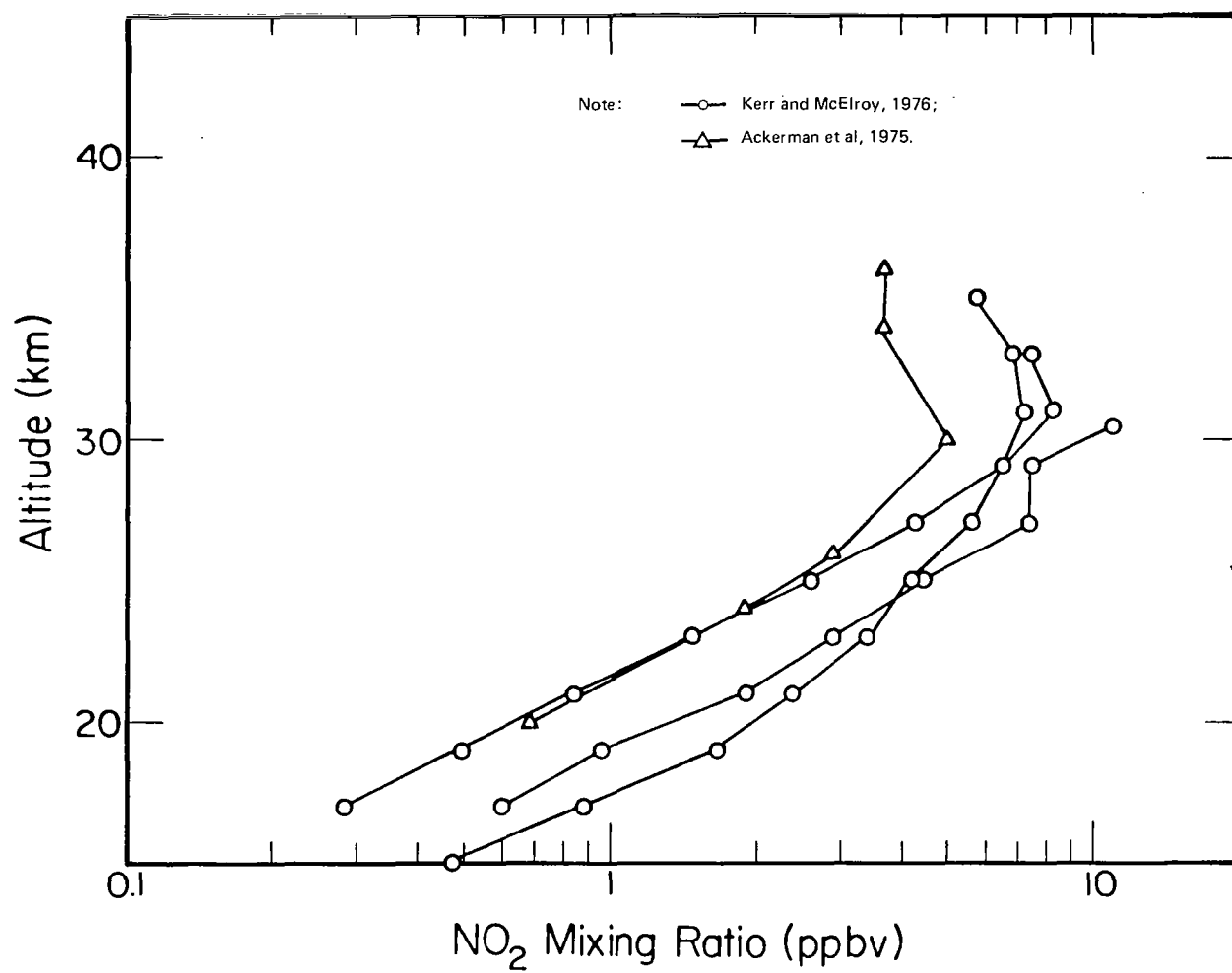
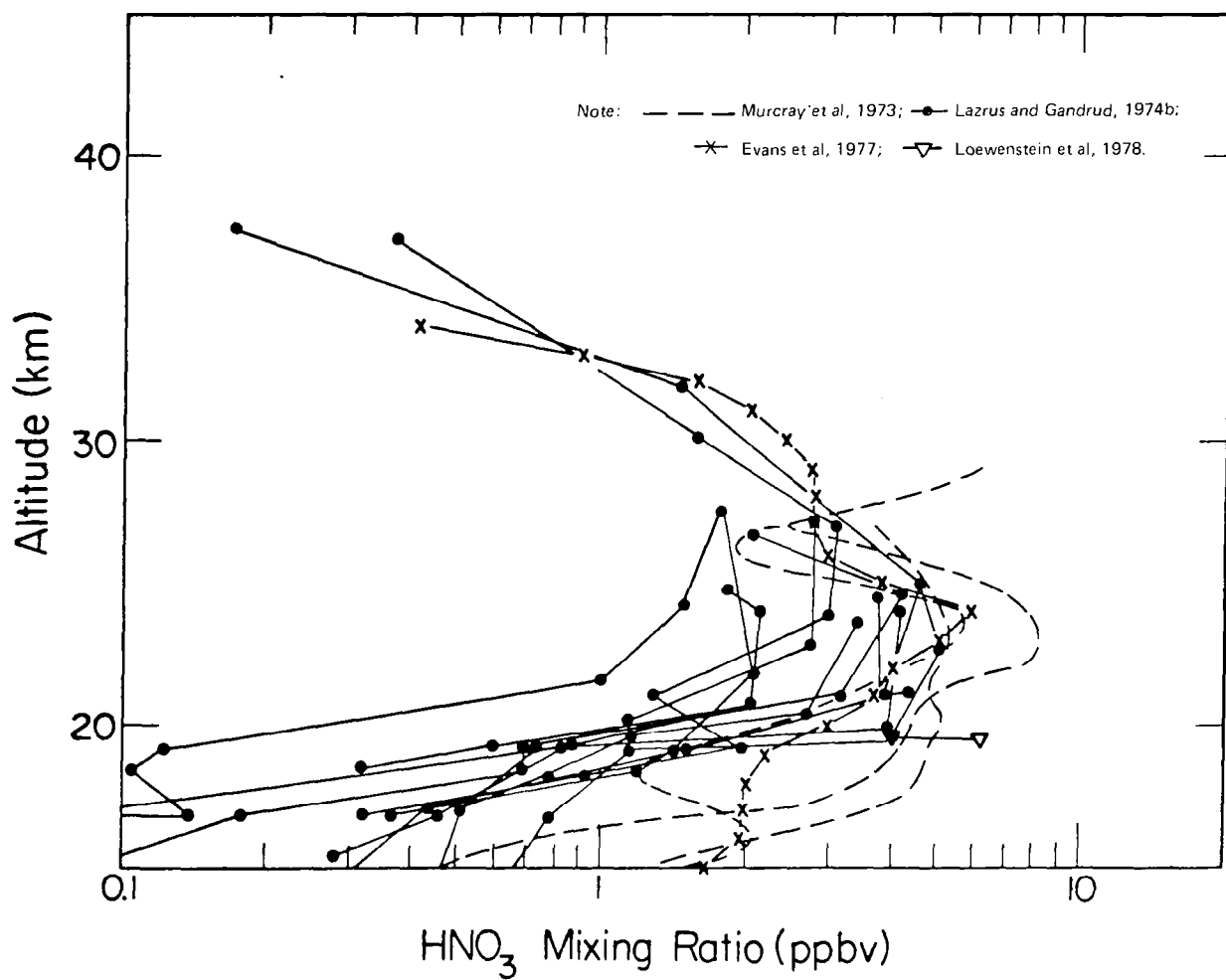


Figure 3-8. Measurements of NO.

Figure 3-9. Measurements of NO₂.

Figure 3-10. Measurements of HNO_3 .

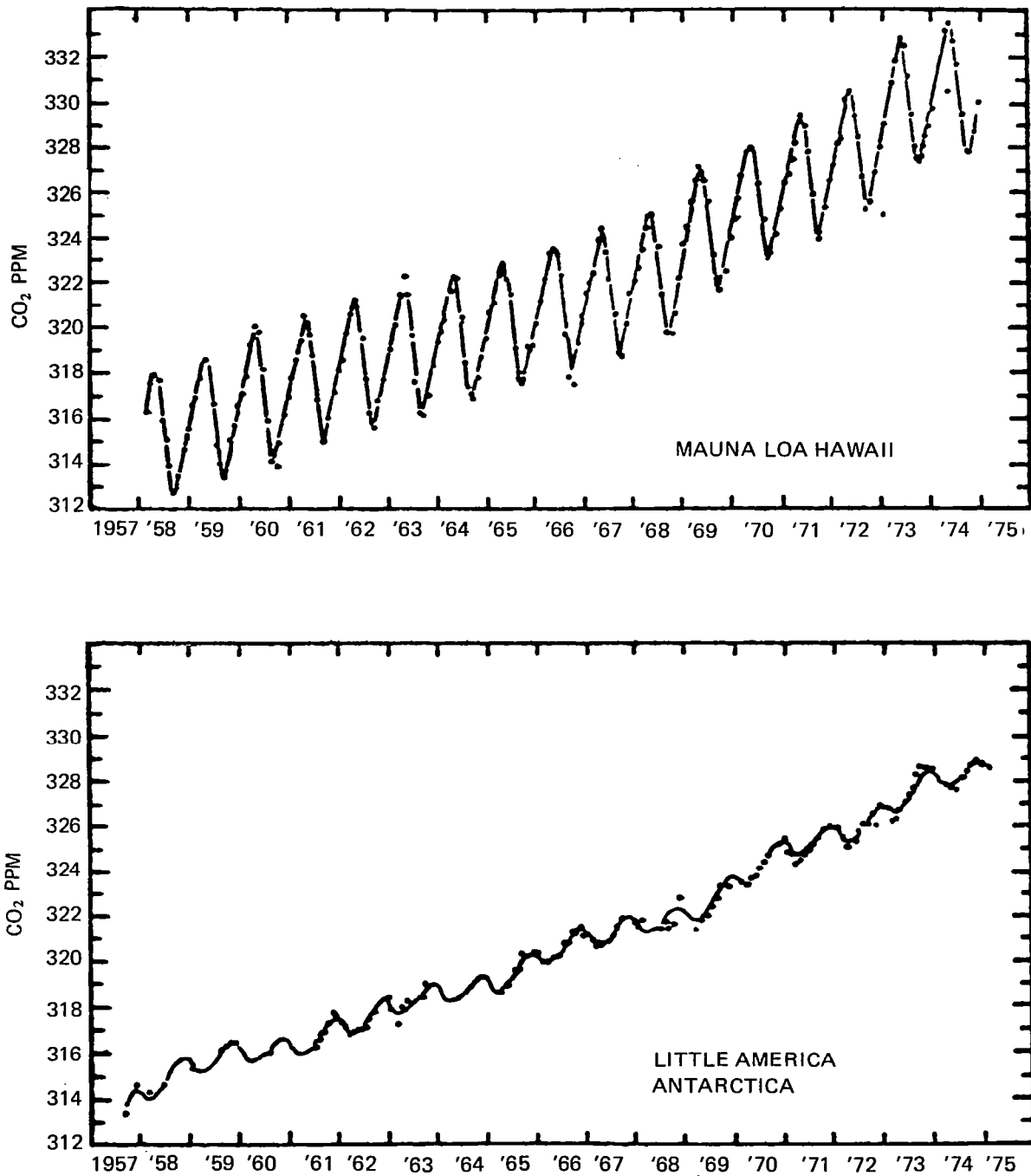


Figure 3-11. The record of the atmospheric concentrations by volume in dry air at the Mauna Loa Observatory, Hawaii, and the South Pole over the period 1958 to 1975 (Keeling et al., 1976a, 1976b).

The ocean represents a major reservoir of inorganic carbon; some 4.8×10^{16} moles reside in the upper 100 meters of the ocean and exchange with the atmosphere on time scales of a few years. An additional 3×10^{18} moles of carbon reside in the bulk of the oceans, but exchange between this reservoir and the atmosphere is very slow (100 to 1000 years). Because of the potential magnitude of this reservoir for taking up atmospheric carbon, the precise evaluation of the exchange time between the upper mixed ocean and mid-ocean is important. Further research is required to fully quantify the detailed mechanisms by which CO_2 is transferred between the atmosphere and oceans. Organic and inorganic ocean sediments contain about 3×10^{21} moles of carbon, but this reservoir is well isolated from the atmosphere, except on the geological (10^8 years) time scale. The principal carbon reservoirs and their exchange rates with the atmosphere are summarized in table 3-7.

Table 3-7
Principal Carbon Reservoirs
and Their Exchange Rates with the Atmosphere*

Reservoir	Inventory (10^{18} g C)	F_{R-A} (10^{16} g C/yr)	F_{A-R} (10^{16} g C/yr)
Atmosphere	0.615		
Perennial biota	1.56	0	0.69
Annual biota	0.075	20.9	0.80
Ocean surface layer	2.46	17.3	8.83
Deep ocean	36.2		

(Adapted from model parameters of Keeling and Bacastow, 1978).

* F_{R-A} and F_{A-R} are fluxes from reservoir to atmosphere and atmosphere to reservoir, respectively.

It has been commonly assumed that the increase in the abundance of atmospheric CO_2 has resulted only from the input of fossil carbon due to combustion of fuels such as oil, coal, or natural gas. Production rates of fossil fuels since industrialization have been estimated by the United Nations, and Keeling (1973) calculated CO_2 production rates from these data. Combustion rates have grown at about 4.3% per year, except for the depression and war periods, with slightly faster rate of increases (4.5%) since 1960 (Rotty, 1977) and a decrease after 1973. There appears to be consistency between the increasing rates of fossil fuel production and the accelerating increase of atmospheric CO_2 levels. If it is assumed that fossil fuel combustion is the major net source of CO_2 to the atmosphere, it can be calculated that about 55% of the carbon released since industrialization has accumulated in the atmosphere. At present, about 5×10^9 tons are released annually, with a total of 150×10^9 tons released since 1850.

Recent works (Bolin, 1977; Woodwell et al., 1978; and Stuvier, 1978) suggest a large value for the cumulative net rate of forest destruction and loss of organic carbon from soils. The magnitude of this biospheric source has been estimated to be in the range of 1 to 10×10^9 tons annually, roughly equal to the fossil fuel source at present, and exceeding it in total CO_2 release up to the present. However, Broecker et al. (1979) argue that current ocean-atmosphere models are consistent with available data and that regrowth of forests cut in the past may have compensated for much of the recent cutting.

It has been commonly assumed that the oceans are the only major sink for anthropogenic CO_2 , and the magnitude of the ocean sink has been calculated from measured transport rates of water to the deep, combined with theoretically deduced values for the average degree of undersaturation of the oceans with respect

to atmospheric CO_2 (cf, Broecker and Peng, 1974). According to these analyses, removal by the oceans can account for slightly less than the quantity of fossil fuel CO_2 which has apparently been removed from the atmosphere. Therefore, the addition to the inventory of a large biospheric source of CO_2 would invalidate global models for the CO_2 budget.

The problem is characterized by a severe lack of pertinent data, e.g., on the historical levels of CO_2 , the actual degree of undersaturation of ocean waters on a global basis, and mechanisms for transferring carbon from the atmosphere to the oceans. Projections of future CO_2 levels depend strongly on resolution of the questions surrounding the biospheric source.

Quantitative predictions are not reliable. The relative importance of terrestrial plants, ocean carbonate sediments and ocean water in the removal of CO_2 from the air are not known. None of the existing models can be shown to be correct in their parameterizations of the circulation of intermediate and deep-ocean waters, which are of critical importance in long-term prediction. The impact of global changes in soils and vegetative covers is poorly understood and the necessary data base does not exist for evaluations to be made. Finally, there is the question (not easily answered) as to whether increases in atmospheric carbon dioxide might produce secondary effects which in themselves could significantly influence the level of atmospheric CO_2 . Examples might include changes in the biospheric flux of CO_2 , alteration of the oceanic circulation, or ocean-atmosphere exchange mechanisms in response to climatic perturbations.

STRATOSPHERIC WATER VAPOR

INTRODUCTION

Documentation of the extreme aridity (approximately 3% relative humidity) of the lower stratosphere and the rapid decrease of mixing ratio with height through the polar tropopause (20-fold in the first kilometer) was begun in 1943 by Dobson et al. (1946). They recognized that this extreme and persistent aridity must be dynamically maintained or it would be destroyed by turbulent diffusion. This led Brewer (1949) to hypothesize a stratospheric circulation in which all air enters through the tropical tropopause where it is freeze-dried to a mass mixing ratio of 2 to 3 ppm. This dry air then spreads poleward and descends through the polar tropopauses, overpowering upward-transport of water vapor by diffusion, which would otherwise be permitted by the much higher temperatures of the polar tropopauses.

HISTORICAL DEVELOPMENTS

For a quarter-century following Brewer's (1949) hypothesis, there was little further progress in understanding the stratospheric water budget. Observations served mainly to confirm the dryness of the stratosphere and the difficulty of obtaining reliable measurements. The intermittent observations of the MRF (British Meteorological Research Flights) and of Mastenbrook (1968, 1971, 1974a) tended to confirm the basic Brewer hypothesis and to suggest a gradual increase in the mixing ratio of the stratosphere from the 1940s through the 1960s, followed by a decline thereafter (see Chapter 6).

During the CIAP program, Newell et al. (1973) explicitly pointed out that if H_2O cannot diffuse upward through the polar tropopause, neither can other trace species. That is, all atmospheric transport from the troposphere to the stratosphere must occur through the tropical tropopause. Wofsy et al. (1972) and Weickman et al. (1975) have pointed out that since CH_4 destruction in the stratosphere exceeds planetary escape of hydrogen approximately 300-fold, the stratosphere must be a *source* of water vapor, returning more to the troposphere than it receives. Ellsaesser (1974) found from existing data analyses that the H_2O mixing ratio of air entering the stratosphere through the tropical tropopause cold trap exceeded that generally found in the lower stratosphere suggesting that there must be a stratospheric sink specific for water vapor. Stanford (1973) and Ellsaesser (1974) independently pointed out that the winter temperatures of the polar

stratospheres, particularly that of Antarctica, typically dropped below that of the tropical tropopause cold trap, and by freezing out ice crystals which could precipitate, might provide a sink for stratospheric water vapor. Since CIAP, three reviews on the subject of water in the stratosphere have been published.

Harries (1976) made a comprehensive review of all the various types of observations. By excluding two somewhat extreme sets of data from the Southern Hemisphere, and some observations which contributed greatly to the rms scatter of the H_2O mixing ratios, he attempted to deduce representative vertical, latitudinal, and temporal variations. He concluded that the considerable uncertainties in the absolute levels of stratospheric mixing ratios preclude anything more than qualitative conclusions concerning the water budget of the stratosphere.

The data summarized by Harries indicated that measured mass mixing ratios generally lie between 0.5 and 5 ppmv for all stratospheric levels up to 40 km. In northern midlatitudes, there is a vertical profile of fairly constant mixing ratio between 13 and 30 km of about 2.5 ± 0.7 ppmv. There is some evidence for a small increase above 30 km to about 2.9 ppmv, but occasionally, as high as 4 to 5 ppmv. Three independent sets of observations show an upward trend of 0.1 to 0.25 ppmv per year which may possibly be related to long-term changes of temperature at the tropical tropopause (see Chapter 6). Observations at fixed levels above single locations in the Northern Hemisphere show marked annual cycles, the amplitudes and phases of which are in fair quantitative agreement.

Penndorf (1978) performed another comprehensive and critical review of stratospheric H_2O measurements. He rejected all soundings reporting mixing ratios exceeding 9 ppmv above 15 km as suffering from contamination. He then summarized the remaining observations by observational technique. In determining a vertical profile, he rejected as invalid Harries' (1976) method of combining, with equal weight, data sets representing from 1 to nearly 100 balloon flights and specific altitude averages containing between 5 and 15 different data sets. From his analysis he concluded that 32 retained data sets strongly support a constant mixing ratio from the tropopause to at least 30 to 35 km with a mean northern midlatitude value (circa 1969-1970) of 2.58 ± 0.6 ppmv. Limited observations suggest a higher mixing ratio above this level. Although 6 data sets indicate an equatorial maximum, any deduction of a latitudinal gradient of mixing ratio from the existing field measurements below 18 km is still controversial. Above 20 km, no conclusions about latitudinal gradients can be drawn since field measurements are nonexistent. Three independent Northern Hemisphere series of measurements indicate that an annual cycle is significant only for altitudes below 20 km, amounting to 10 to 20% at 15 km and decreasing with altitude. At 15 km the maximum occurs in November; it lags with altitude, occurring in April at 20 km. Three independent series of measurements indicate an overall increase from 1954 to about 1973 of about 0.87 ppmv/decade and a steep decrease thereafter of about 1.6 ppmv/decade. (See Chapter 6.)

Robinson (1978) emphasized several features of H_2O soundings. The tropical soundings appear to fall in one of two distributions classified by Kuhn (unpublished work) as *wet* and *dry* days. On the wet days, the mixing ratios (approximately 6 ppmv) correspond to saturation at the ambient tropical tropopause and remain reasonably constant upward in altitude to pressures as much as 60 mb below the tropopause pressure.

On dry days, the mixing ratios (approximately 3 ppmv) are generally less than that corresponding to saturation at the ambient tropical tropopause and are found to extend as much as 100 mb beneath the tropopause in clearly tropospheric air. In Robinson's words, the mixing ratios, ... "suggest that stratospheric air is entering the troposphere in the tropics, but other tracers, particularly ozone, show no evidence of this." Robinson also notes that the freeze-dry mechanism implies a deep or thick cloud extending downward from the tropical tropopause, and points out that this requirement can be reconciled with the observations only if the ascending branch of the Hadley cell is entirely confined to cumulus towers with slow descent at all other locations.

RECENT OBSERVATIONS

Observations of stratospheric H_2O mixing ratios versus latitude are depicted in figure 3-12. With the exception of Mastenbrook's (1968) data, all measurements compiled in figure 3-12 were obtained from aircraft platforms and, due to limitations on ceiling heights, were not necessarily performed high enough over the local tropopause in tropical regions to be free from direct contributions from the underlying troposphere.

Vertical profiles measured since about 1976 from aircraft, balloon and rocket platforms over midlatitudes are compiled in figure 3-13. These soundings agree in showing a minimum mixing ratio near 20 km and an increase above, but disagree strongly with regard to the magnitudes of both the minimum and maximum mixing ratios and the altitude of the latter. Harries et al. (1979), and Farmer et al. (1979) used remote spectroscopic techniques which are less sensitive to local contamination than *in situ* techniques with the implication that the observed increase with altitude is less likely due to contamination. Note that the gradient for all individual profiles of figure 3-13 is notably smaller than that of some of the more extreme earlier measurements discussed in Harries (1976).

Note also that the apparent substantial increase in stratospheric mixing ratio up to 1973 and rapid decline thereafter would, if valid, tend to make any mixing ratio increase with altitude due to CH_4 oxidation more apparent now than at any time since about the beginning of the Mastenbrook series.

Only one measurement (Kley et al., 1979) has been made in tropical regions in recent years.

DISCUSSION

There is still no better explanation of the persistent extreme aridity of the stratosphere than that proposed by Brewer (1949), i.e., all air enters the stratosphere through the cold tropical tropopause where it is freeze-dried. This hypothesis is supported by essentially all available observations. Annual cycles in stratospheric mixing ratios in the Northern Hemisphere vary in the proper sense, and with the expected phase lag with the saturation mixing ratios permitted by the tropical tropopause cold trap, which is warmest in July and coldest in February in both hemispheres. Tropical tropopause heights and temperatures, and stratospheric O_3 and particulates, in turn, vary as would be expected from the Brewer hypothesis and the observed annual shifts and variations in intensity of the intertropical convergence zone and the Hadley cells. There is substantial evidence that H_2O does not diffuse upward through the polar tropopause, the temperature of which would permit mixing ratios approximately one order of magnitude greater than generally observed just 1 km or so higher in the stratosphere.

The Brewer (1949) mechanism, augmented by the proposed stratospheric oxidation of CH_4 would appear to require a downward directed H_2O gradient from levels of more rapid CH_4 oxidation to the tropopause, and an equator-directed gradient so that the return Hadley flux through the polar tropopause could carry more H_2O than the upwelling branch of the Hadley flux. However, nearly all available observational data support gradients of the opposite signs, i.e., directed upward and poleward from the Brewer (1949) tropical tropopause source.

Due to the variations in absolute values of stratospheric H_2O obtained by different instruments, gradients can be inferred only from homogeneous data. Even with this precaution, the available data do not provide unambiguous answers.

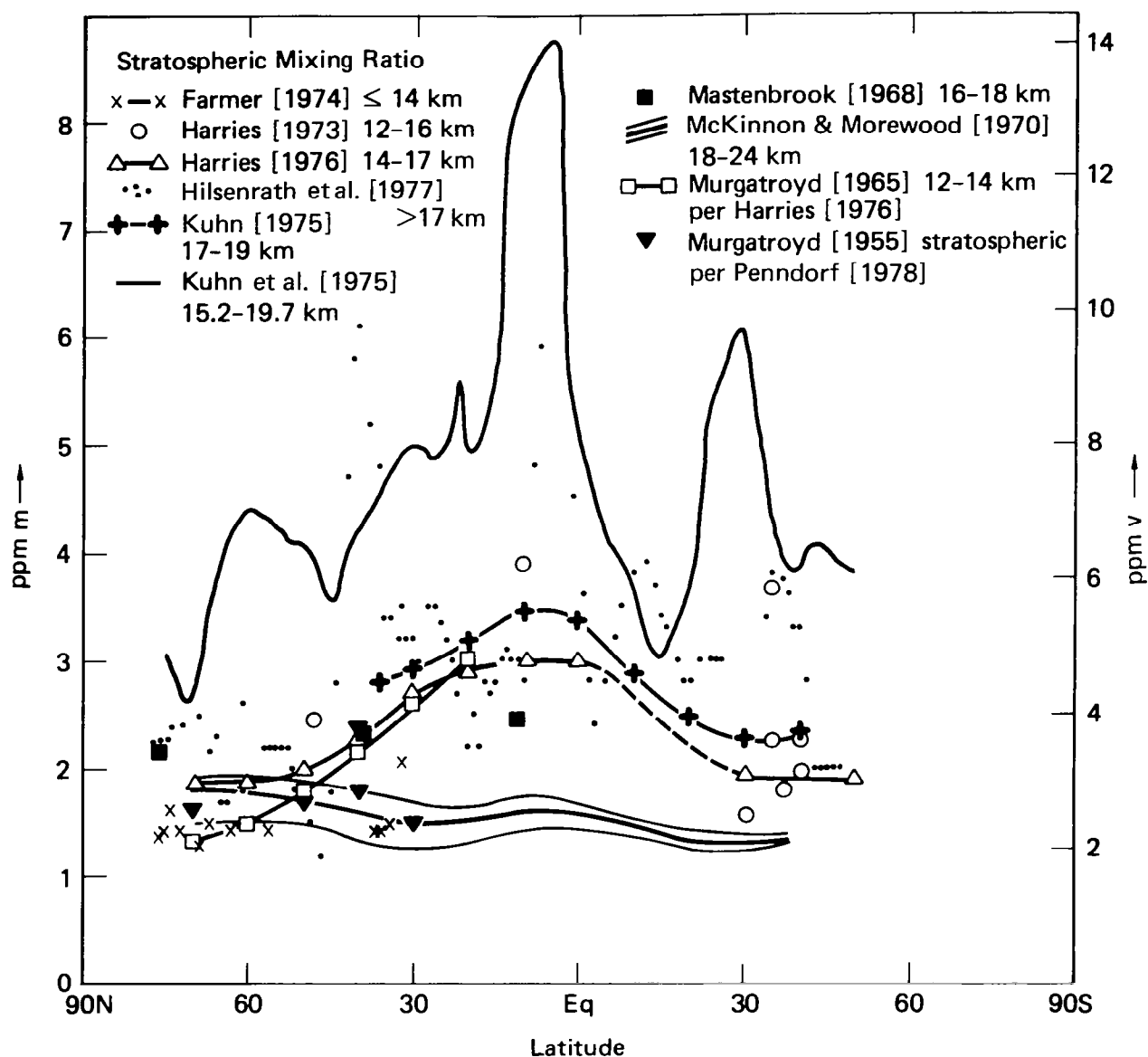


Figure 3-12. Measurements of the latitudinal variation of stratospheric H_2O mixing ratio by several authors, based on measurements from balloons (Mastenbrook only), and aircraft.

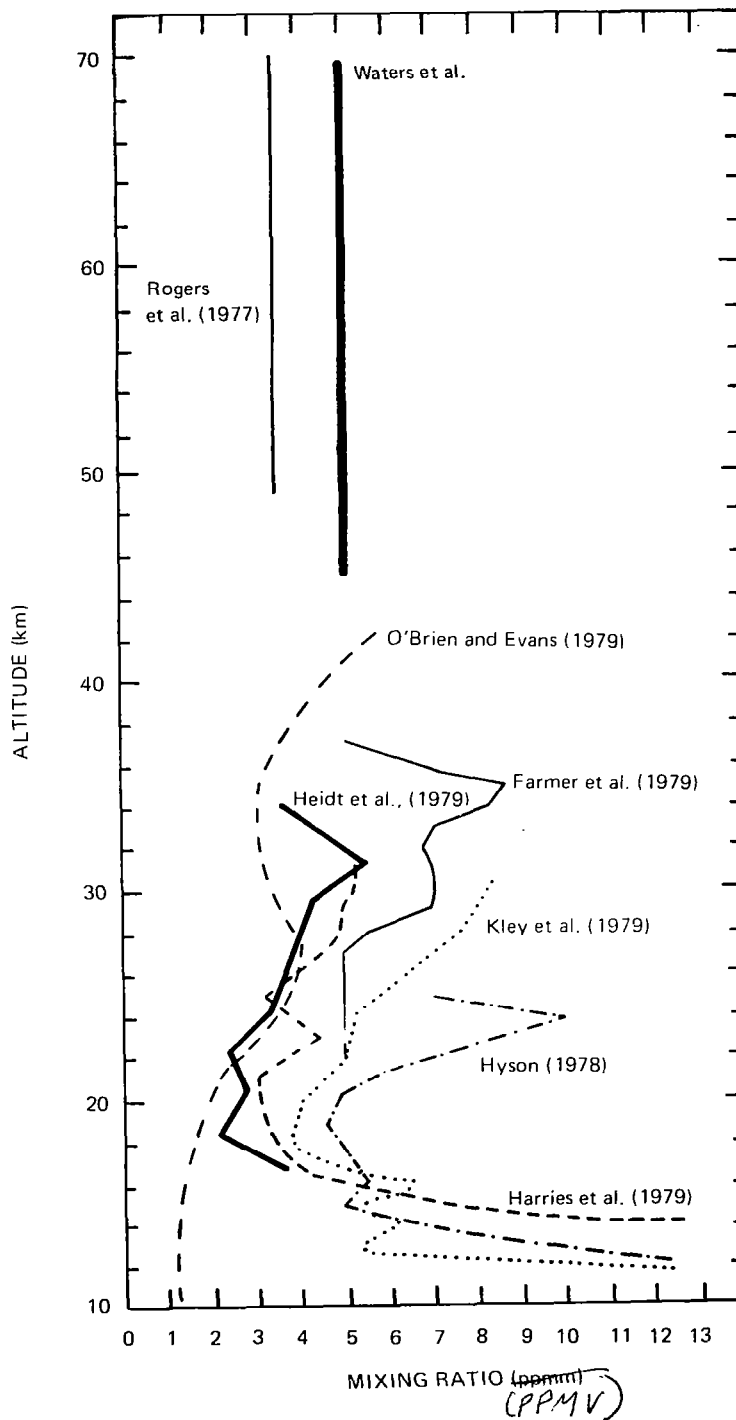


Figure 3-13. Vertical distribution of stratospheric H_2O as measured by several authors since 1976. Names against profiles indicate entry in reference list. See Table 3-8.

Inspection of the data used to compile figure 3-12 shows that some of those obtained over tropical regions might have been influenced by larger mixing ratios from the nearby tropical tropopause. Indeed, of the several data sets represented in figure 3-12, it is those measured at the higher altitudes (e.g. McKinnon and Morewood, 1970; and Mastenbrook, 1968) which yield relatively flatter profiles as a function of latitude: those measurements made at the lower altitudes clearly show the influence of the troposphere. However, this provides no grounds to restrict the search for evidence for a stratospheric sink to examining latitudinal gradients obtained only above 18 km. Air in the upwelling Hadley cell, once above the tropopause (unless it contains visible hydrometeors of an overshooting cumulus cloud), is presumably stratospheric air. Any decrease in mixing ratio above this point would appear to represent a stratospheric process, and be just as indicative of a stratospheric sink as poleward-directed gradients pointing horizontally away from the tropical tropopause source. If this is not true, clearly the process by which the tropical tropopause cold trap operates is not understood.

The observational data on vertical profiles (such as that in figure 3-13) appears less ambiguous.

Mastenbrook's (1968) Trinidad soundings and the Brazil sounding of Kley et al. (1979) show H_2O decreasing through the tropical tropopause to minimum mixing ratios near 19 km (approximately 60 mb and termed the *hygropause* by Kley et al.) of 2.1 and 1.7 ppmm respectively. These mixing ratios would require cold trap temperatures of -83° and -84°C at the tropical tropopause. Even if such low cold trap temperatures prevailed it would leave unexplained the higher mixing ratios generally reported just above the tropical tropopause, and the decrease in mixing ratio from the tropopause upward to the hygropause.

At present, these data must be taken as factual experimental results without a satisfactory theoretical explanation. They seem to require a stratospheric sink for H_2O (i.e., a mechanism other than return Hadley flow for removing H_2O from the stratosphere), or to imply that there are gaps in our understanding of the method of operation of the tropical tropopause cold trap.

The temporal or spatial variability suggested by the data in figures 3-12 and 3-13 is well outside anything that could be expected from the Mastenbrook series. For this reason it would appear the safest choice, at present, to assume that most of the variability among data sets reflects observational difficulties more than variations in stratospheric mixing ratio. Estimates of the observational accuracy of stratospheric H_2O measurements are very nebulous. Estimates culled from reports of the experimenters by Penndorf (1978) are listed in table 3-8.

One proposed stratospheric sink is *freeze-out* over the winter poles as has been put forward by Stanford (1973) and by Ellsaesser (1974). In this case, the mixing ratio lapse rate above the tropopause might be taken as indicative of a sink at some higher level, and the very cold winter poles (particularly Antarctica) might provide such a sink. According to Kochanski's (1955) 1948-1951 mean January cross section for 80°W there is a closed -85°C isotherm centered over the North Pole at approximately 30 km. Similarly the June-July cross section for 140°W (the coldest longitude) synthesized from radiosonde, rocketsonde and SCR data by Labitzke and Van Loon (1972) shows a closed -90°C isotherm centered over the South Pole at approximately 24 km. These correspond to saturation mixing ratios of about 10 ppmm from 22 to 30 km for the Arctic and about 3 ppmm from 16 to 24 km for the Antarctic. A more recent picture of these low winter pole temperatures is given in figure 3-14 from Prabhakara and Rodgers (1976) showing satellite-determined 100- and 50-mb temperatures as a function of latitude and season.

These numbers are barely of the right magnitude for a freeze-dry sink even over Antarctica. And even if winter polar temperatures drop low enough to produce saturation mixing ratios below 3 ppmm, there remain the nagging questions of the small volume of the stratosphere so cooled, the restricted movement of air through this volume due to the reduced meridional mixing and transport enforced by the dynamic stability of the winter polar vortices, and that any precipitated ice crystals must survive falling through several kilometers of warmer air before they can exit the stratosphere. An attempt to quantitatively model such a sink mechanism might be illuminating.

Table 3-8
Typical Uncertainties in the H₂O Measurements Proposed
by Various Investigators

Name	Precision (random error)	Accuracy (systematic error)
Mastenbrook (1968)	-	± 10%
Cluley and Oliver (1978)	± 6%	± 8%
Met-Res. Flight (1955)	-	± 10%
Kley et al. (1979)	± 5%	± 18%
Murcray et al. (1974)		± 20%
McKinnon and Morewood (1970)		± 30%
Ackerman (1974)		± 20%
Farmer (1979)		± 20%
Brewer and Thompson (1972)		± 50%
Kuhn (1973)		± 30%
Harries (1973)		± 20%
Bussoletti and Baluteau (1974)		± 50%
Rogers et al. (1977)		± 60%
O'Brien and Evans (1979)	10%	± 30%
Waters et al. (1977)		± 20%

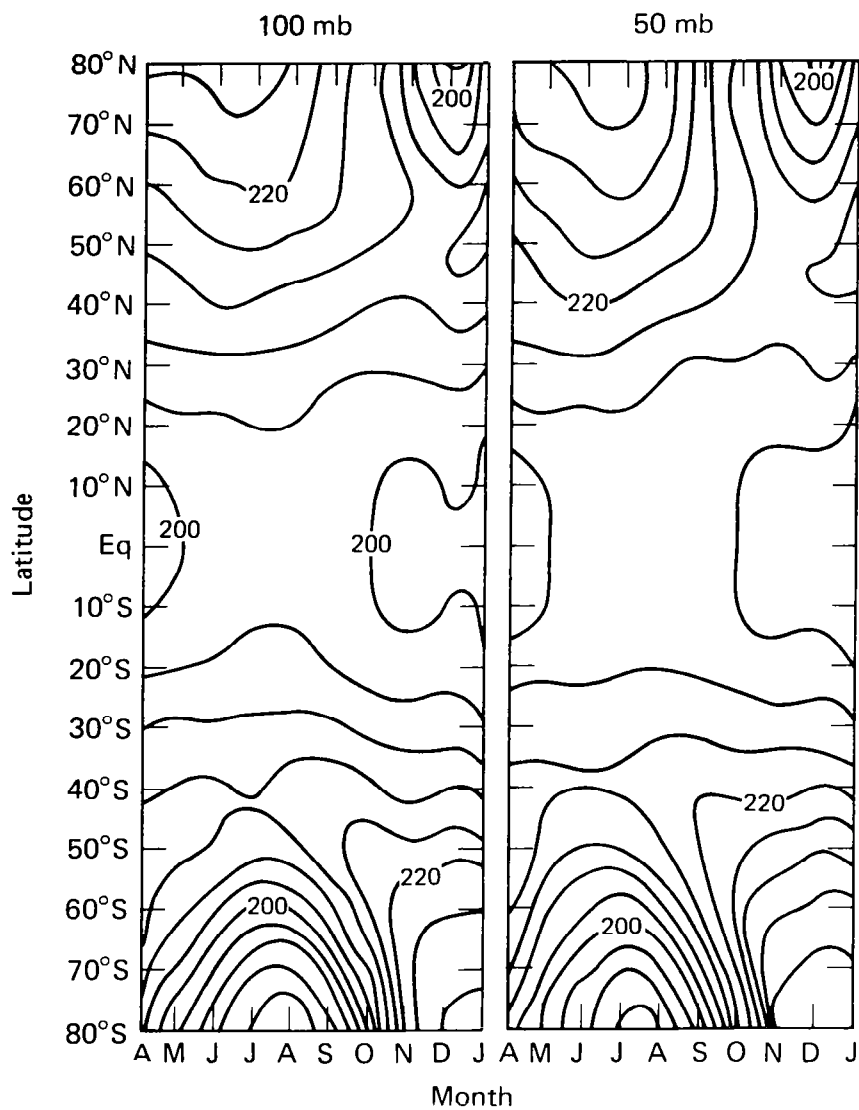


Figure 3-14. Zonal average stratospheric temperature (K) derived from Nimbus-4 IRIS measurements for April 1970 through January 1971 (adapted from Prabhakara and Rodgers, 1976).

Johnston and Solomon (1979) have suggested that cumulus towers could overshoot the tropical tropopause by over 2 km, cooling adiabatically to below -100°C and act as a *cold finger* modification of the *cold trap* mechanism. Mahlman (private communication, 1979) reports that his new 3-D model, because of forced convection, calculates relative humidities at and above the tropical tropopause of only 50 to 60%. Although both these results must be regarded as preliminary, they suggest types of processes to be explored as alternatives to a stratospheric sink for H_2O .

But, in turn, such alternative mechanisms must be given careful scrutiny. Considering the steepness of the tropospheric lapse rate just below the tropical tropopause and of the temperature inversion just above it, it is difficult to see how air parcels once above the tropopause (unless having first arrived there in an overshooting cumulus) could again return to the troposphere without first spending an appreciable lifetime (months) in the stratosphere. Accordingly, it is difficult to understand why the H_2O mixing ratio is observed to decrease for another 2 or 3 km above the tropical tropopause. The faster a convective cell penetrates the tropopause and the farther it overshoots it, the larger will be the hydrometeors it can support, and the greater will be the local temperature deficit or density excess to accelerate it back toward the troposphere. It is not clear whether the temperature difference leads to freeze-drying of entrained stratospheric air, or to evaporation in the stratosphere of hydrometeors shed from a tropospheric cloud.

What does appear clear is that there is a compensating trade-off between latent heat and buoyancy which tends to restrict net transfer of water across the original altitude of neutral buoyancy. Specifically, evaporation of hydrometeors will reduce internal energy or buoyancy, and thus, lower the altitude at which the convection element is at buoyant equilibrium with the environment; conversely, freezing hydrometeors out of stratospheric air increases the altitude of buoyant equilibrium. That is, the more the overshooting convective element evaporates water into stratospheric air, the more likely the total mixing unit is to return to the troposphere; the more it condenses out stratospheric water vapor, the more likely the total mixing unit is to remain in the stratosphere. Thus, it appears difficult to argue that penetrating convection does anything other than continue to bring saturated air to the level of buoyant equilibrium with the environment which cannot be very far removed from the tropical tropopause itself. The contained hydrometeors will quickly adjust the water vapor content to the saturation vapor pressure at the pressure and temperature of buoyant equilibrium, and then precipitate back into the troposphere. Since air at the tropical tropopause is radiatively warmed at about 0.25°C per day, it will slowly ascend as it is replaced by successive convective elements. Given a constant tropopause temperature and pressure, there appears to be no reason why this process should not lead to a constant mixing ratio with height above the tropical tropopause.

H_2O BUDGET

The stratospheric H_2O budget was discussed by Ellsaesser (1974). He proposed that a stratospheric sink was needed to balance the budget and to explain the gradients indicated by the data.

The observed mixing ratios at 60 mb over the tropics appear to require a cold-trap temperature of about -84°C at the tropical tropopause. However, the available data tend to support a tropopause cold-trap temperature of -80°C and a decrease in mixing ratio from the tropical tropopause to 60 mb. This implies either the existence of a sink for H_2O within the stratosphere or a gap in the understanding of the mechanism by which the cold trap operates. Ellsaesser (1974) noted that the limited observational data available appeared to be consistent with an Antarctic winter freeze-dry sink of sufficient magnitude to bring the budget into balance.

It must be noted that the apparent long-term trend in stratospheric H_2O (see Chapter 6), if valid, has been of sufficient magnitude (90% increase from 1954 to 1973 per MRF data) to have an appreciable effect on the H_2O budget and possibly on the radiation of the stratosphere. If such variations are indicative of changes in the general circulation of the atmosphere or the strength of the Hadley flux through the tropical tropopause, they may impact on other stratospheric species as well.

Available data indicate several unresolved questions with regard to stratospheric water vapor such as:

- Are there significant long-period trends in lower stratospheric mixing ratio, suggesting changes in the general circulation of the atmosphere?
- Are there decreases in mixing ratio with height just above the tropical tropopause which suggest a stratospheric sink for H_2O or a lack of understanding of the operation of the tropical tropopause *cold trap*?
- Are there latitudinal gradients in H_2O mixing ratio of the following types?
 - Poleward-directed gradients between the tropical tropopause and the higher level minimum in mixing ratio or hygropause supporting a higher mixing ratio in the ascending air over that of the descending branches of the Hadley current.
 - Equatorial-directed gradients at the hygropause supporting a higher mixing ratio (due to CH_4 oxidation) in the high latitude descending branches of the stratospheric Hadley current than in the low-latitude ascending current.
- Are there increases in mixing ratio with height above the hygropause, and can the increases be fully accounted for by CH_4 oxidation?

To achieve answers to these questions will require observational programs of the following types:

- Continued homogeneous observations from fixed locations to define long-term trends. To accomplish this, it is important that past observational series such as those of Mastenbrook, Hyson, and the MRF be continued, and that new series be initiated at other locations. In this connection, documentation from both past and future data of the year-to-year variations at height and temperature of the tropical tropopause at as many stations as possible would be a valuable endeavor.
- Measurements from aircraft at various stratospheric altitudes to determine latitudinal gradients. Such flights should make simultaneous high-resolution measurements of H_2O , O_3 , temperature, and other parameters. Of most value would be:
 - Flights across the Equator or seasonal position of the ITCZ at 18 km and above.
 - Flights over midsouthern latitudes during September and October when the latitudinal gradient is expected to be a maximum as a result of any Antarctic sink and Hadley cell source.
 - Flights during the winter over the polar caps themselves seeking any evidence of freeze-dry removal of H_2O from the stratosphere.
- Satellites to provide long-period coverage (in both time and space) of H_2O distributions in the stratosphere. The first usable data on global H_2O distributions are just now beginning to emerge from Nimbus-7; strong support should be given to the continuation of similar programs.

It is important to emphasize the need for high accuracy in measuring stratospheric H_2O . To determine the vertical, horizontal, and temporal variations in stratospheric H_2O will require relative accuracy capable of distinguishing changes of $\pm 5\%$, or less. Uncertainty in absolute values must be kept below $\pm 20\%$ in order to resolve the global budget. To resolve the long-term trend will require even greater accuracy: on the order of 1 to 3%. Different scale resolutions are also required. To define H_2O morphology in the region of the

tropopause requires small-scale resolution. For studying global patterns and budgets and comparison with model predictions global coverage is more important than scale resolution.

In addition to measurements, model experiments could help provide answers to these questions. It is believed the following would be productive:

- Design and execute a complete model of stratospheric chemistry without holding H_2O constant to determine rates and patterns of H_2O consumption and production.
- Model winter polar freeze-out to quantitatively estimate the rate of exchange through the polar vortex and the total amount of H_2O that can be removed or the total mass of air which can be freeze-dried per year.
- Model thunderstorm penetrations of the tropical tropopause to determine whether such occurrences transport H_2O upward or downward, and whether they introduce gradients by vertical redistribution of H_2O .
- Study the physics of low-temperature condensation and evaporation of H_2O . (Although homogeneous nucleation may not occur under normal stratospheric conditions, could nacreous cloud particles, once formed, survive a fall to the troposphere?)
- Model penetrative tropical convection from the surface through 100 mb to determine the vertical distribution of H_2O which will result from successive penetrations under expected atmospheric conditions.

HYDROCARBONS AND HYDROGEN

METHANE

Sources and Sinks

The major sources of CH_4 are believed to involve the anaerobic fermentation of organic material due to microbial action (Koyama, 1963) in rice paddy fields, swamps and marshes, tropical rain forests, and tundra, as well as enteric fermentation in mammals. The magnitude of these sources has been studied by Ehhlalt (1974) and Baker-Blocker et al. (1977); the estimated source strengths for each category are listed in table 3-9. The larger area of wetlands and rice paddies, as well as the greater population of livestock in the Northern Hemisphere as compared to the Southern Hemisphere, implies a hemispherically asymmetric source of CH_4 . This asymmetry appears to be borne out in the finding of slightly more CH_4 in the Northern Hemisphere than that of the Southern Hemisphere. Although soils have been shown to act as a sink for CO (Inman et al., 1971) and H_2 (Schmidt, 1974), there is no evidence for a globally significant CH_4 soil sink.

Observations of CH_4 supersaturations of 1.2 to 1.7 in the surface waters of the open ocean (Lamontagne et al., 1974) implies a source of atmospheric CH_4 due to oceanic biological activity. However, estimates of this source (using the stagnant film diffusion model) imply that this source is small, as is the source from the continental shelf and tidal flat regions (see table 3-9).

Table 3-9
Atmospheric CH₄ Budget

Sources	Estimated* Rate (tg CH ₄ yr ⁻¹)**	Reference
A. Biogenic		
Enteric fermentation	100 - 200	Ehhalt (1974)
Paddy fields	280	Ehhalt (1974)
Paddy fields	170 - 350	Baker-Blocker et al. (1977)
Wetlands	130 - 260	Ehhalt (1974)
Wetlands	150	Baker-Blocker et al. (1977)
Freshwater lakes	1 - 25	Ehhalt (1974)
Forest and tundra	1 - 13	Ehhalt (1974)
Oceans	5 - 20	Ehhalt (1974)
Total	400 - 900	
B. Direct Anthropogenic	10 - 50	Ehhalt (1974)
C. Lithospheric		
Volcanic	0.2	Ehhalt (1974)
Cool seeps, earthquakes	20***	Gold (1979)
TOTAL SOURCES	450 - 1000	
Photochemical Sink (CH ₄ + OH)	800	Wofsy (1976)
Photochemical Sink	140 - 220	Crutzen and Fishman (1977)
Photochemical Sink	170 - 260	Chameides (1978)

*Large extrapolations are involved in arriving at these numbers and they should be viewed as order-of-magnitude estimates.

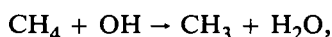
** $\text{tg CH}_4 \text{ yr}^{-1} = 2.4 \times 10^{10} \text{ CH}_4 \text{ molecules cm}^{-2} \text{ s}^{-1}$.

***There is no experimental verification of this source, see text.

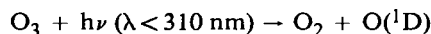
Sources directly related to anthropogenic activities (i.e., mining, industrial processes, automobile exhaust) are small, producing about 15 to 50 tg CH₄ per year (Ehhalt, 1974). However, while direct anthropogenic sources are small, the large emissions due to rice paddy cultivation and enteric fermentation in livestock are indirectly related to man's activities. While the former tend to enhance CH₄ production, the draining of wetlands and clearing of forests by man tends to decrease the source rate, and it is not presently known if the CH₄ source rate is increasing, decreasing, or constant.

The atmospheric source of CH₄ due to lithospheric processes is generally believed to be small. Since CH₄ is unstable at high temperatures relative to CO₂, the CH₄ source from volcanoes (which are characterized by hot gaseous discharges) is only about 0.2 tg CH₄ per year. However, Gold (1979) has proposed a major new source of CH₄ due to cool outgassing of carbon-containing molecules during earthquakes and seeps along fault lines. While the escape of CH₄ in this manner has not been observed, Gold estimates that this source may account for a significant fraction of the atmosphere's CH₄ source. From the rate of deposition of limestone, Gold (1979) estimates an average yearly source of 20 tg CH₄ per year due to this process; however, this source would be highly variable, and in any given year, could be orders of magnitude larger or smaller. Although present data on the C¹⁴H₄ to C¹²H₄ ratio in the atmosphere cannot rule out this source (Ehhalt, 1974), further measurements are needed to establish its existence or nonexistence.

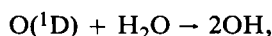
The major sink of atmospheric CH₄ is reaction with tropospheric OH (Levy, 1971):



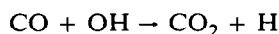
which initiates a long series of reactions known as the methane oxidation chain and ultimately leads to the production of CO, H₂CO, and H₂ (Levy, 1971, 1972; McConnell et al., 1971; and Wofsy et al., 1972). Thus, a determination of the loss rate of CH₄ requires knowledge of the tropospheric OH abundance. OH is initially produced by



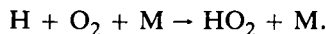
while



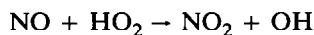
and is converted to HO₂ by reactions in the methane oxidation chain as well as



followed by



The reaction



acts to recycle OH from HO₂ and is a key reaction in the formation of O₃ in the troposphere as well as lower stratosphere. Other sinks for OH involve chain terminating steps such as the heterogeneous removal of HNO₃, CH₃OOH, and H₂O₂. Photochemical models have predicted average, free-tropospheric OH levels of 10⁵ to 10⁶ molecules cm⁻³ (Wofsy, 1976; Crutzen and Fishman, 1977; Chameides, 1978; and Chang et al., 1977), and recent measurements indicate at least qualitative agreement with these predictions (Wang et al., 1975; Davis et al., 1976; Perner et al., 1976; and Philen et al., 1978). Uncertainties in the NO and H₂O levels in the troposphere as well as key rate constants cause uncertainty in the calculated OH abundance, and thus, in the rate of oxidation of CH₄ by OH. It is estimated that the tropospheric OH sink for CH₄ is about 200 to 800 tg CH₄ per year.

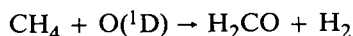
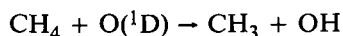
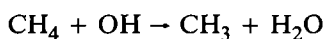
Tropospheric Distribution

Since stratospheric CH_4 originates from the troposphere (where it is injected into the atmosphere by biospheric and lithospheric processes at the Earth's surface), the stratospheric CH_4 abundance is determined by the tropospheric CH_4 concentration. Tropospheric CH_4 is relatively long-lived (a lifetime on the order of 10 years), and is thus well-mixed throughout the troposphere, except near source regions. Observations indicate about 10% less CH_4 in the Southern Hemisphere than in the Northern Hemisphere (Wilkniss et al., 1973; Lamontagne et al., 1974; and Ehhalt, 1978b).

The possibility and implications of temporal variations in atmospheric CH_4 has been the subject of several recent studies (e.g., Sze and Rice, 1976; Chameides et al., 1977; Wang et al., 1976; and Logan et al., 1978). Recent measurements of a CH_4 abundance of 1.65 to 1.70 ppm (Heidt and Krasnec, 1978; Ehhalt, 1978b; Bush et al., 1978; and Fabian et al., 1978); when compared to earlier determinations of about 1.40 ppm (Ehhalt and Heidt, 1973), imply a large increase in CH_4 . However, a re-examination of the earlier measurements indicates that a CH_4 abundance of 1.60 ppm for the early 1970s is more appropriate (L. Heidt and D. Ehhalt, private communication, 1979) implying a small rise in CH_4 over the decade. It is not clear if this apparent increase in the CH_4 abundance, equivalent to the addition of about 150 tg CH_4 to an atmospheric burden of 4000 tg CH_4 is due to a real variation in the CH_4 sources or sinks, or is merely due to statistical or systematic errors in the measurement technique. A long-term program to measure the CH_4 abundance is needed to clarify temporal variability.

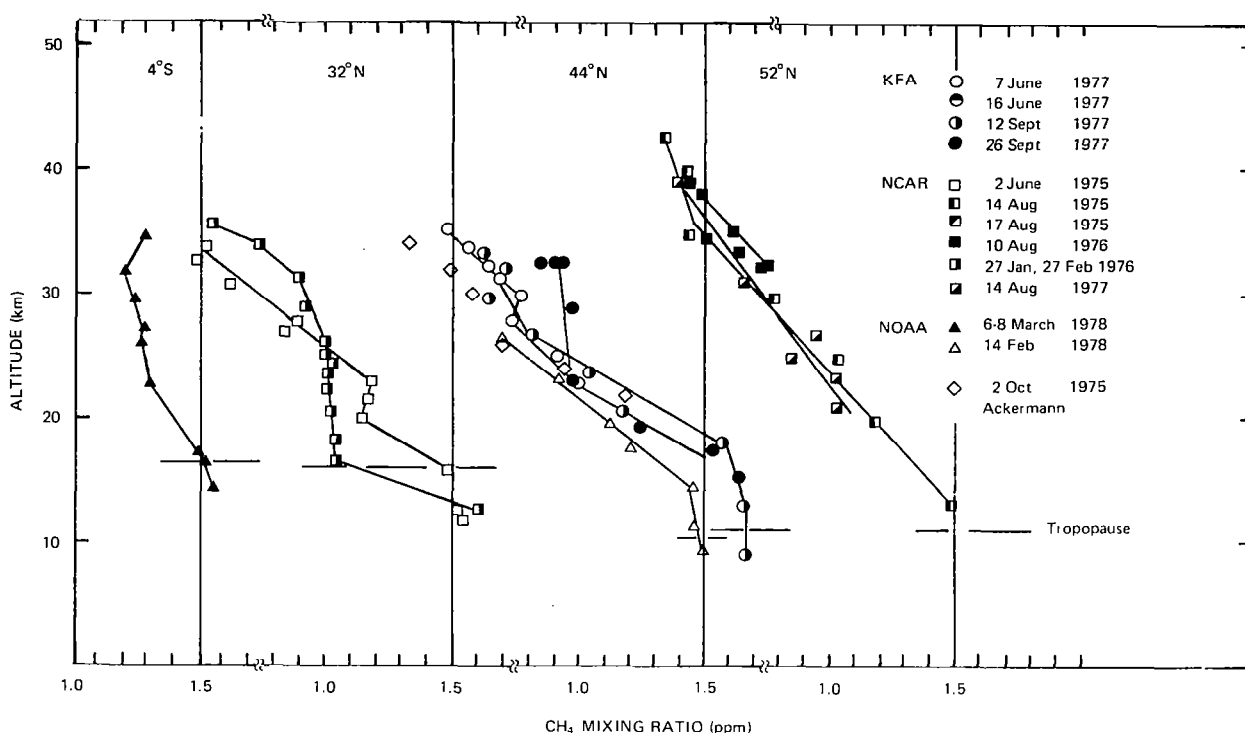
Stratospheric Distribution

The CH_4 not destroyed in the troposphere is injected into the stratosphere where the principal loss processes are:



It is estimated that oxidation in the stratosphere accounts for about 10% of the global CH_4 sink (Ehhalt, 1974; and Wofsy, 1976). The increased intensity of ultraviolet radiation in the stratosphere results in higher concentrations in OH and $\text{O}(^1\text{D})$, which when coupled with the positive altitude gradient in temperature, causes the CH_4 photochemical lifetime to decrease from about 100 years at 10 km, to 3 years at 30 km, and to 0.2 years at 40 km. This decrease in photochemical lifetime, coupled with the slow rate of transport through the tropopause results in a decreasing CH_4 mixing ratio with altitude in the stratosphere and mesosphere.

Figure 3-15 illustrates the most recent observations of CH_4 abundance as a function of altitude at various latitudes. Although all profiles indicate a decrease of CH_4 with altitude, the shape of the profiles vary significantly between latitudes. The tropical profile of Bush et al. (1978) indicate a slow vertical decrease suggesting a relatively strong upward transport. The profiles at 32°N and to some extent at 44°N suggest a complicated transport pattern, with a steep decrease in CH_4 immediately above the tropopause, a layer of fairly constant CH_4 , and above this layer a steep CH_4 decrease. Many more *in situ* profiles (or satellite data) are required before a meridional cross section of the CH_4 mixing ratio can be established, but the present data indicate that there should be quite significant latitudinal variations in the stratosphere.



Note: Data labeled NOAA were published by Bush et al. (1978), those labeled NCAR were communicated by Heidt (1978), those labeled KFA were published by Ehhalt (1978) and Fabian et al. (1979a). The actual tropopause during the flights is indicated by the horizontal line.

Figure 3-15. Vertical profiles of the CH_4 mixing ratio in the stratosphere at various latitudes.

An important product of stratospheric CH_4 degradation is CO, which is also injected into the stratosphere by tropospheric-stratospheric exchange processes. Thus, stratospheric CO levels may be altered by variations in atmospheric CH_4 as well as processes which cause changes in tropospheric CO levels, including anthropogenic activities. Model calculations have revealed that an increase in lower stratospheric CO may lead to an enhancement in O_3 via reactions similar to those associated with photochemical smog (Logan et al., 1978; Butler et al., 1979) and further confirm the importance of the CH_4 -CO system for stratospheric ozone. The gross features of the tropospheric CO distribution are probably reasonably well represented by Seiler's (1974) meridional CO cross section, with an average CO abundance of 0.11 ppm and about 2 to 3 times more CO in the Northern Hemisphere as compared to the Southern Hemisphere. This hemispheric asymmetry has been interpreted to indicate the importance of anthropogenic CO emissions relative to natural sources. Figure 3-16 illustrates the observed stratospheric CO profiles, indicating a sharp decrease in CO above the tropopause followed by a relatively constant mixing ratio with altitude in the upper stratosphere.

Water vapor is also an important product of CH_4 oxidation in the stratosphere as has been discussed in the section on the water vapor budget.

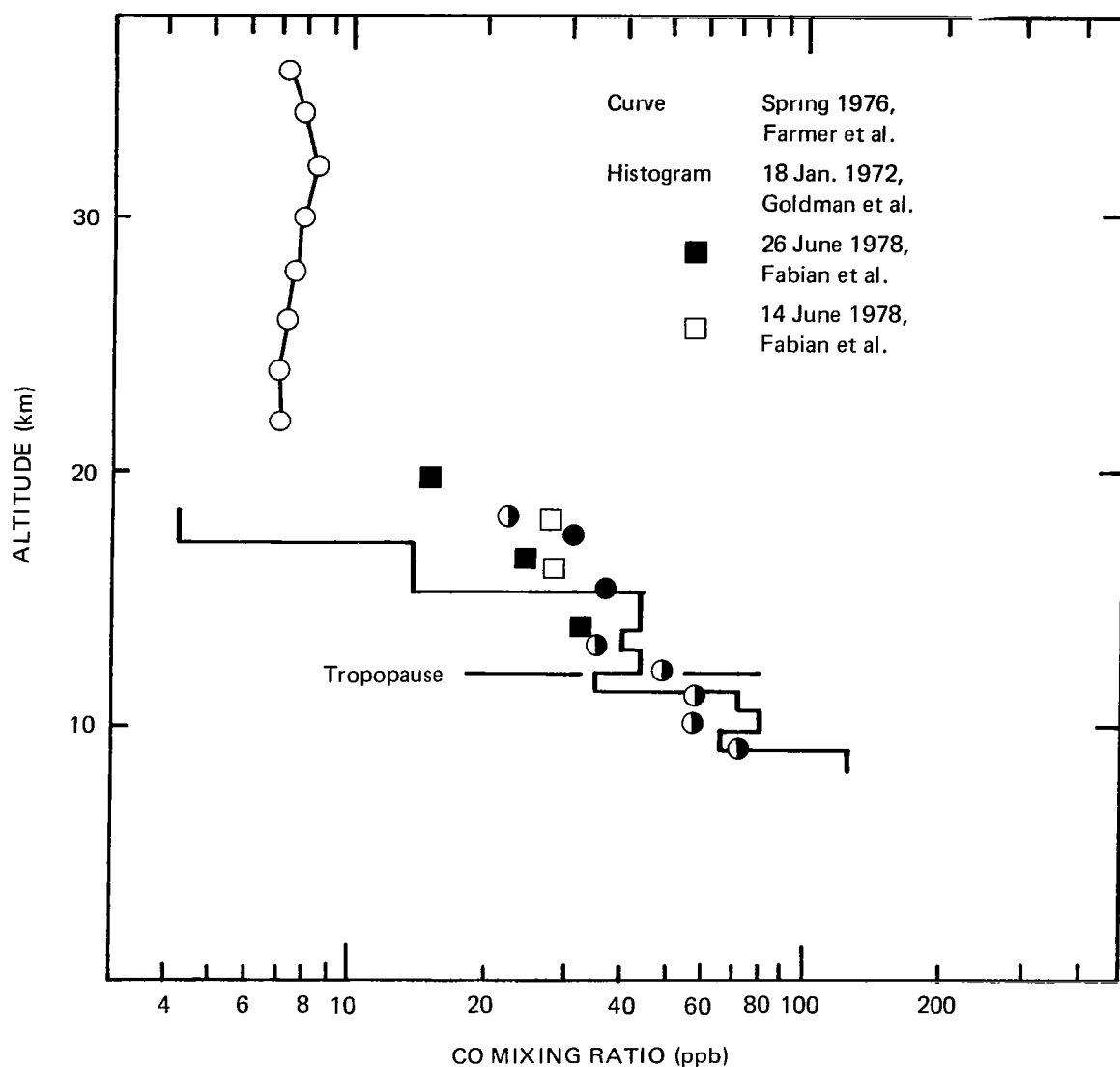


Figure 3-16. Vertical profiles of the CO mixing ratio in the stratosphere. Curve and histogram were measured by balloon-borne IR spectroscopy. Only the lower part of the profiles from cryogenic sampling is shown (Ehhalt, 1978; and Fabian et al., 1979a). The upper samples were partly contaminated. Also included are data from flights in 1978 which have not been published. Other symbols are the same as in Figure 3-15.

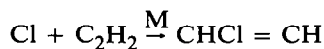
NONMETHANE HYDROCARBONS

The importance of nonmethane hydrocarbons (NMHC) in the stratosphere has not yet been fully determined. Short-lived NMHC (such as propylene) produced in urban areas play a central role in the formation of photochemical smog, and terpenes and pinenes, emitted by vegetation, may produce ozone, haze, and CO in rural, forested areas (Went, 1960; and Zimmerman, 1978). Since the sources of NMHC (like those of CH₄) are located at the Earth's surface, reactive varieties are too short-lived to be transported across the tropopause and directly affect the stratosphere. However, unreactive NMHC (such as C₂H₆, C₂H₂, C₃H₈, C₄H₁₀, and C₅H₁₂) are sufficiently long-lived to have a possibly significant flux into the stratosphere, depending on their source rates at the Earth's surface.

Observations indicate background tropospheric abundance of unreactive NMHC in the range of 0.1 to 1.0 ppb (Cavanaugh et al., 1969; Research Triangle Institute, 1974; Grenda and Goldstein, 1977; Singh et al., 1978; Rasmussen and Robinson, 1977; and Cronn et al., 1977).

Typically, concentrations of 1.0 ppb are found for C₂H₆ and 0.2 ppb for C₂H₂. Somewhat lower concentrations of C₂H₆ and C₂H₂ are found in the Southern Hemisphere relative to the Northern Hemisphere, probably indicating hemispherically asymmetric sources. A comprehensive inventory of C₂H₆ and C₂H₂ sources has not been made, and it is not certain if the major unreactive NMHC sources are of natural or anthropogenic origin. Observations by Grenda and Goldstein (1977) and others indicate that non-negligible C₂H₆ emissions may be associated with gas fields. Significant concentrations of C₂H₆ (0.2 to 0.5 ppb) and C₂H₂ (0.02 to 0.05 ppb) have been observed in the lower stratosphere (Rasmussen and Robinson, 1977; and Cronn and Robinson, 1979) and these observations are in qualitative agreement with 1-D model calculations of the vertical profile of NMHC (Chameides and Cicerone, 1978).

Chameides and Cicerone (1978) studied the photochemistry of these long-lived, unreactive NMHC and attempted to identify their stratospheric photochemical roles and budgets. The major sink for long-lived NMHC are photochemical reactions with OH in the troposphere. In the stratosphere, NMHC are destroyed by H abstraction reactions with Cl, as well as OH. (It is likely that NMHC have oxidation chains similar to that of CH₄ as reported by Demerjian et al., 1974.) Chameides and Cicerone (1978) found that NMHC have a negligible impact upon the stratospheric O₃ system provided their tropospheric abundances are a few ppb or less and the product of the reaction



is photochemically destroyed before removal to the troposphere. If CHCl = CH were stable in the lower stratosphere, C₂H₂ could act as a chain terminator, impeding catalytic removal of stratospheric O₃ by Cl and ClO.

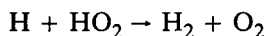
Normalizing to ground-level mixing ratios of 1 ppb for C₂H₆ and 0.1 ppb for C₂H₂, C₃H₈, C₄H₁₀, and C₅H₁₂, 1-D model calculations imply ground-level sources, in molecules cm⁻²s⁻¹, of 2.6×10^9 for C₂H₆, 1.8×10^9 for C₂H₂, 9.3×10^8 for C₃H₈, 1.5×10^9 for C₄H₁₀, and 2.1×10^9 for C₅H₁₂; equivalent to a total unreactive NMHC source due to natural or anthropogenic activities or about 100 tg per year. The corresponding rates of injection into the stratosphere for these assumed ground-level abundances, in molecules cm⁻²s⁻¹, were 1.2×10^8 for C₂H₆, 9×10^6 for C₂H₂, 1.0×10^8 for C₃H₈, 5.6×10^7 for C₄H₁₀, and 3.0×10^7 for C₅H₁₂. Proportionally smaller or larger NMHC source strengths and fluxes are implied by smaller or larger ground-level mixing ratios. However, a complete understanding of the budgets and role of NMHC in the stratosphere will have to await more detailed measurements and laboratory studies.

HYDROGEN

Molecular hydrogen, H_2 , has a tropospheric abundance of about 0.5 ppm with a relatively uniform distribution in the vertical and horizontal (Schmidt, 1974; and Ehhalt et al., 1977). The average H_2 abundance in the Southern Hemisphere is about 0.02 ppm lower than in the Northern Hemisphere.

The tropospheric H_2 budget was reviewed by Schmidt (1974), who estimated an H_2 residence time of 4 to 7 years. Schmidt included sources from anthropogenic activities, photochemistry (H_2CO photolysis in the methane oxidation chain), ocean emissions, and emissions from soils and sinks from photochemistry ($H_2 + OH \rightarrow H + H_2O$), and soil losses. The major processes identified were anthropogenic production and soil losses and the total atmospheric budget comprised a turnover of about 30 to 40 tg per year (or 6 to $9 \times 10^{10} \text{ cm}^{-2}\text{s}^{-1}$). Zimmerman et al. (1978) have proposed an additional source from the oxidation of nonmethane hydrocarbons from vegetation of 10 to 35 tg per year.

Figure 3-17 illustrates H_2 stratospheric profiles at various latitudes taken from Ehhalt et al. (1978) and Fabian et al. (1978). The profiles indicate a relatively constant stratospheric mixing ratio in the vertical and a small latitudinal variation. Stratospheric H_2 is produced from the photolysis of H_2CO , which, in turn, is produced from CH_4 oxidation. Above 40 km,



is also a significant H_2 source as well as a chain terminator for free radicals. The major sinks of stratospheric H_2 are the oxidation of H_2 by OH and OClO. Model calculations indicate that the stratosphere may be a small net source of H_2 , with a column production rate of $7.5 \times 10^9 \text{ cm}^{-2}\text{s}^{-1}$ and loss rate of $4.0 \times 10^9 \text{ cm}^{-2}\text{s}^{-1}$ (Liu, private communication, 1979).

STRATOSPHERIC SULFUR

INTRODUCTION

The sulfur budget of the stratosphere is closely related to that in the troposphere, which is quite uncertain in several respects. As a result, it is not appropriate at this time to construct an overall budget. Instead, this section discusses current knowledge of the specific sources and sinks of the sulfur compounds, their measured concentrations, their chemical processes, and the implications of sulfur compounds for the chemistry of the stratosphere. Such information is required for the eventual construction of a detailed atmospheric sulfur budget.

TROPOSPHERIC SOURCES AND SINKS

Tropospheric sources and sinks, together with appropriate transformation processes, are the items that constitute a sulfur budget. Such budgets have been prepared in recent years by Robinson and Robbins (1968), Kellogg et al. (1972), Friend (1973), Granat et al. (1976) and Rodhe (1978); and some aspects of sulfur budget construction are discussed in detail by Hitchcock et al. (1979). For the purposes of stratospheric sulfur assessment, it is most important to discriminate between major and minor processes, to indicate the areas of major uncertainty, and to identify those aspects of atmospheric sulfur that have not been included at all in sulfur budget assessments.

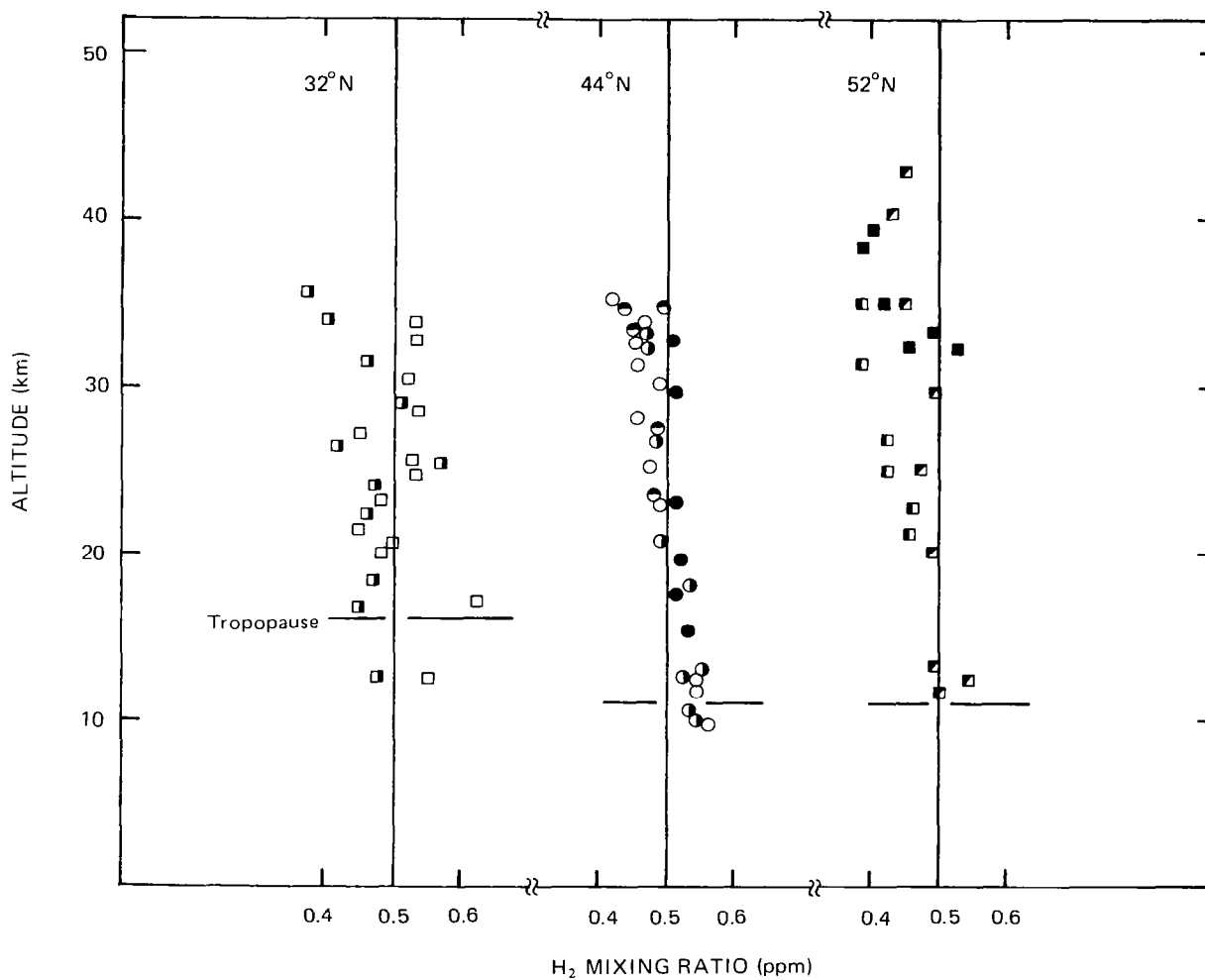


Figure 3-17. Vertical profiles of the H_2 mixing ratio in the stratosphere at various latitudes. Symbols are the same as Figure 3-15.

Hydrogen sulfide appears to be the major naturally generated gaseous sulfur species being produced by biogenic processes in fine-grained anoxic muds (Hitchcock, 1976). Similar processes occur in oceanic surface films, at least in nutrient-rich areas. Lovelock et al. (1972) have proposed that dimethyl sulfide is emitted in quantities comparable to H_2S , a thesis supported to some extent by measurements of dimethyl sulfide in ocean waters (Nguyen et al., 1978) and by atmospheric modeling studies (Graedel, 1979). Other sulfur species may be emitted as well. Sulfur budget studies have generally estimated natural gas-phase emissions by using values that make the budgets balance. The fluxes estimated in this way range from 34 to 92 tg per year, the difference reflecting conflicting results for other budget components.

Volcanoes are the primary natural source of oxygen-containing sulfur compounds, mostly in the form of sulfur dioxide (White and Waring, 1963; Shepherd, 1938; Nordlie, 1971; and Cadle et al., 1978). Various estimates have been made of average annual volcanic emissions of sulfur dioxide, with extremes ranging from 1.5 tg (Kellogg et al., 1972) to 40 tg (Naughton et al., 1975). These estimates are complicated both by the statistical fluctuations in active volcano eruptions and by the temporal emission fluctuations of individual volcanoes (Malinconico, 1979). The more recent flux estimates have clustered nearer the high end of this range, and biogenic and volcanic fluxes of sulfur seem likely to be of similar magnitude. COS, CS_2 , H_2S , and possibly other sulfur compounds are also emitted by volcanoes. The amounts are probably not large, but remain to be accurately assessed.

Sea water contains about 2.65 milligrams of sulfate per gram of water, and sea-salt particles formed by the breaking of bubbles introduce large amounts of sulfate into the atmosphere. However, most of this particulate material very soon returns to the ocean and is not an important source of stratospheric sulfate. Eriksson (1960) estimated that 13 tg per year of sea-salt sulfate passes over the continents. However, data are very sparse and confirmation of this estimate is desirable.

Anthropogenic sources of sulfur compounds emit largely sulfur dioxide with smaller amounts of carbon disulfide, sulfuric acid, carbonyl sulfide, and a number of organic sulfur compounds. The main anthropogenic source of emission to the air is the burning of fossil fuels. Recent estimates for the emission of sulfur are as much as 65 tg per year. The estimates do not yet include fluxes of COS from combustion and other sources (Crutzen, 1976; and Turco et al., 1979c), CS_2 , from a variety of industrial operations (Peyton et al., 1976), or mercaptans and sulfides from pulp mills and other sources (Graedel, 1977). It may be quite important to establish these fluxes accurately, because of the long tropospheric lifetimes of some of the compounds.

Rainout and washout are major mechanisms for the removal of sulfur dioxide and sulfate ions from the troposphere. Estimates of the quantities removed by these means are based on analysis of precipitation and estimates of the total global annual rainfall, usually calculated as *excess sulfate*, (i.e., total sulfate from all sources other than sea salt). The derived removal fluxes have ranged from 106 to 350 tg per year, the most recent estimates being at the low end of this range. A major difficulty in arriving at this estimate is the lack of precipitation chemistry data for many parts of the globe.

The other principal sink for the removal of tropospheric sulfur is dry deposition of sulfur dioxide and sulfate at the Earth's surface as a result of turbulent diffusion and sedimentation. Estimates of this quantity have ranged from 38 to 75 tg per year, not including sea-salt sulfate.

TRANSPORT BETWEEN THE TROPOSPHERE AND STRATOSPHERE

A single, extremely violent volcanic eruption may introduce sufficient sulfur compounds into the stratosphere to exceed (by an order of magnitude or more) that from any other source for a year or two (Cadle and Grams, 1975). If many such eruptions occur during an extended time period, they can appreciably affect the Earth's climate by affecting its radiation balance (Lamb, 1970). Most of this sulfur is converted to impure sulfuric acid by the oxidation and hydration of sulfur dioxide. The dispersion of volcanic sulfur in the stratosphere has been discussed by Lamb (1970), Cadle et al. (1976), and Cadle et al. (1977).

After two or more years have elapsed since a major explosive volcanic eruption, stratospheric sulfur may be dominated by that crossing the tropopause as a result of the atmospheric circulation. Aitken particles, including sulfates and sulfuric acid, which serve as nuclei for the condensation of sulfuric acid vapor, sulfur dioxide, various sulfates (including sulfuric acid, carbonyl sulfide, and carbon disulfide) are probably the major sulfur compounds which reach the stratosphere in this manner. Exchange processes between the troposphere and the stratosphere have been reviewed by Reiter (1975).

Lazrus and Gandrud (1974a) have estimated that 0.14 tg of SO_2 , or of SO_2 precursors would have to enter the stratosphere each year to maintain the sulfur in the stratosphere as sulfuric acid during periods of little explosive volcanic activity.

AEROSOL FORMATION

Various sampling studies and numerical models have provided evidence that stratospheric aerosols are generated *in situ* via the reaction of sulfur bearing gases (Junge et al., 1961; Turco et al., 1979a). An extensive study of the temporal and spatial distribution of the sulfur isotope ratio by Castleman et al. (1973) has borne this out. As a result of elementary modeling calculations and the results of laboratory experiments, Castleman et al. (1975a; 1976/77); Davis et al. (1979); and Moortgat and Junge (1977) have speculated that the stratospheric aerosol layer originates, at least in part, from SO_2 oxidation via OH. Other candidates for the origin of the sulfur component of the aerosol layer are COS (Cadle and Crutzen, 1975) and CS_2 as a precursor to COS (Sze and Ko, 1979a).

REMOVAL FROM THE STRATOSPHERE

The sink for stratospheric sulfur compounds is transport to the tropopause where they are removed by the processes described above. Gases and particles smaller than 1 or 2 micrometers in diameter are transported to the troposphere by descending air (Reiter, 1975). Larger particles and small particles that grow into the larger size range by agglomeration, or by vapor condensation are usually removed by sedimentation.

CONCENTRATIONS OF STRATOSPHERIC SULFUR

Sulfides and Mercaptans

H_2S , the most common of the sulfides, is known to be a component of volcanic gas emissions (Huntingdon, 1973). Therefore, it is likely that volcanic eruptions which penetrate the tropopause inject H_2S into the stratosphere. At present, the fluxes of H_2S from such sources cannot be estimated accurately, but are certainly much less than those of SO_2 .

There is no evidence yet for the existence of organic sulfides in the stratosphere. However, members of this chemical group are ubiquitous in the troposphere, generally at low concentrations. Their lifetimes are on the order of a few days (Graedel, 1978), which appear to preclude their diffusion into the stratosphere.

Carbon Disulfide and Carbonyl Sulfide

Carbonyl sulfide (COS) has only recently been detected in the stratosphere, but appears to be a major component of the stratospheric sulfur cycle except following major volcanic eruptions. It is present in the troposphere at about 500 ppt (Torres et al., 1978). Measurements of COS in air samples obtained above the tropopause by high-flying aircraft indicate concentrations of 14 to 524 ppt (Inn et al., 1979) at different altitudes and seasons.

Carbon disulfide (CS_2) is found in the troposphere at concentrations within the range 70 to 370 ppt (Sandalls and Penkett, 1977) and has a life-time of about half a year (Graedel, 1978). It has not been detected thus far, however.

COS and possibly CS_2 are minor constituents of volcanic emissions (Stoiber et al., 1971) and thus, like H_2S , are expected to enter the stratosphere in volcanic eruptions that penetrate the tropopause. As with H_2S , the fluxes from such processes cannot be accurately estimated at present.

Sulfur Dioxide

SO_2 appears to be a major gas-phase constituent of the stratospheric sulfur cycle. Its concentrations have been measured on only four occasions, but with results that differ very widely. Jaeschke et al. (1976) measured approximately .05 ppb SO_2 at 13 km. Data from two recent balloon flights by Mauersberger and Finstad (1978) give an SO_2 concentration of approximately 10 ppb within an altitude range of 25 to 35 km. These could all be consistent if SO_2 is being produced at higher altitudes by chemical reaction of other sulfur-containing compounds. The balloon observation of Sagawa and Itoh (1977) report SO_2 concentrations at 18 to 30 km of 10 to 30 ppm. These numbers are so much higher than are seen near major tropospheric sources that they seem unlikely to be realistic.

Volcanic plumes generally possess high SO_2 concentrations and volcanic eruptions are thus capable of major modifications in the stratospheric sulfur balance if tropopause penetration occurs.

COMPOSITION OF STRATOSPHERIC AEROSOLS

Aerosol particles in the stratosphere consist largely of volcanic ash for periods of a few months following explosive eruptions; at other times they consist largely of impure sulfuric acid (Cadle and Grams, 1975). In addition to H_2SO_4 , the particles may contain $(\text{NH}_4)_2\text{SO}_4$ (Friend, 1966) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Friend, 1966), nitrosyl sulfuric acid NOHSO_4 (Farlow et al., 1978) and nitrosyl pyrosulfate NOHS_2O_7 (Farlow et al., 1978).

Generally, stratospheric sulfate aerosol concentrations fall in the range 0.1 to 1.5 ng/g of air. Strong latitudinal, altitude, and seasonal variations appear to be present. Figures 3-18 and 3-19 show the most complete sulfate concentration observations made to date, although these may be relevant only to the time and region to which the observations apply.

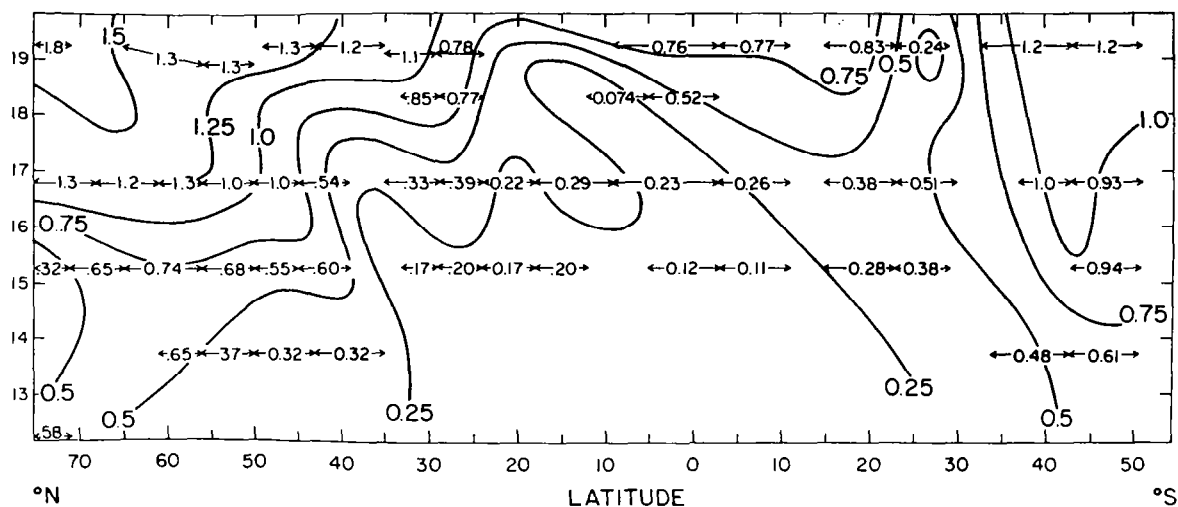
CHEMICAL REACTIONS OF STRATOSPHERIC SULFUR

Sulfides and Mercaptans

The initial reaction of these compounds involve hydrogen atom extraction by OH to give the thiyl (HS) or thioxyl (RSO) radical. The subsequent reactions of these radicals have not been determined with certainty, but the available evidence (Graedel, 1977, 1978; and Thiemens and Schwartz, 1978) suggests that the sulfur in the original compound is converted rapidly to SO_2 by reaction with molecular oxygen.

Carbon Disulfide

Carbon disulfide reacts with the hydroxyl radical. Although the intermediate states are unclear (Sannigrahi et al., 1977; Kurylo, 1978; and White and Gardiner, 1978), the sulfur-containing products have been suggested to be COS and HS (Kurylo and Laufer, 1979). If COS is confirmed as a product, CS_2 will be a global source of COS that may be significant if CS_2 is sufficiently abundant (Sze and Ko, 1979a). Photolysis of CS_2 can occur at wavelengths less than 230 nm to yield, in oxygen, COS and SO_2 (Wood and Heicklen, 1971).



Note: The numbers on the isopleths are grams of $\text{SO}_4 \times 10^{-9}$ per gram of air.

Figure 3-18. Sulfate concentration isopleths through a vertical section of the stratosphere roughly along a meridian (adapted from Lazrus and Gandrud, 1974b).

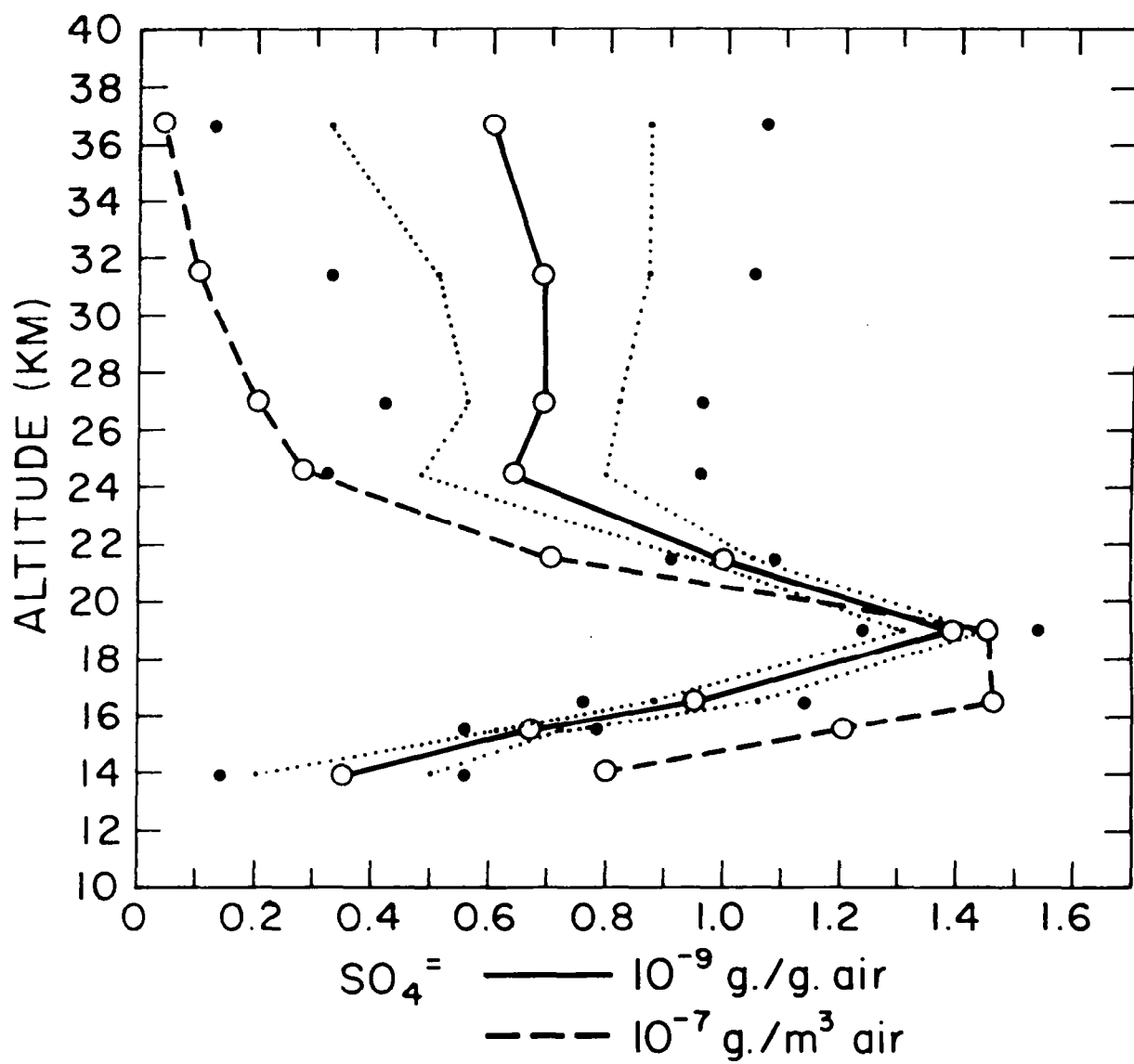


Figure 3-19. Midlatitude profiles of sulfate during 1976 (adapted from Lazrus and Gandrud, 1977).

Carbonyl Sulfide

The hydroxyl radical is a scavenger for COS. Whether addition or abstraction occurs is uncertain (as for CS_2), but SO_2 or other oxygen-containing sulfur compounds are likely products. COS will photolyze at stratospheric wavelengths to produce a free sulfur atom (Donovan, 1969; and Crutzen, 1976) that will promptly form SO (Davis et al., 1972) and then SO_2 (Schofield, 1973).

Sulfur Dioxide

The principal reactions of SO_2 are with the OH and HO_2 radicals. The product in the former case is the HSO_3 radical; its subsequent reactions are not known, but appear certain to lead monotonically to sulfate aerosol (Davis et al., 1979; and Friend et al., 1979). SO_2 reaction with HO_2 produces SO_3 , which combines directly with water vapor to yield sulfuric acid. The conversion of gas-phase sulfur compounds to particulate sulfur compounds has been studied theoretically by Turco et al. (1979a); further research in this difficult field is needed.

Sulfate Aerosol

Reactions of the sulfate anion can take place upon the stratospheric aerosol particles. Chemical studies of the aerosol suggest that ammonia vapor may add to sulfuric acid aerosol to produce ammonium sulfate or ammonium hydrogen sulfate, and that nitrogen dioxide vapor may add to produce nitrosyl sulfate and nitrosyl pyrosulfate. The heterogeneous loss of SO_2 and other stable stratospheric molecules to the stratospheric aerosol has been discussed by Cadle et al. (1975); the processes are potentially significant as loss mechanisms.

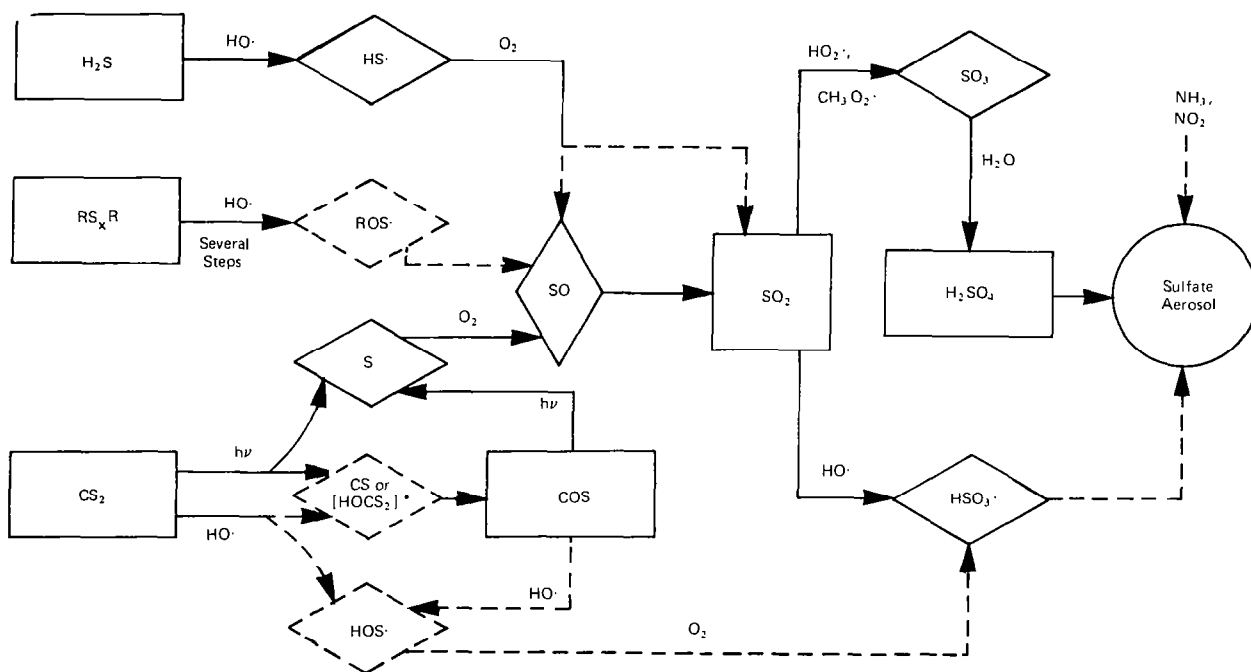
CHEMICAL SUMMARY

The stratospheric chemistry of sulfur is summarized on the schematic flow chart of figure 3-20. Two features deserve comment. The first is that the hydroxyl radical and solar radiation are the significant chain initiators; the second, that the sulfur atoms proceed unremittingly in the direction of increased oxidation state, ending with the +6 state as sulfate aerosol. All species and reactions shown dotted on this figure need confirmation by laboratory experiments; they are important but uncertain parameters in stratospheric sulfur chemistry.

Stratospheric Implications of Sulfur Chemistry

The most important chemical function of stratospheric sulfur compounds appears to be the removal of hydroxyl radicals from the stratospheric odd-hydrogen cycle. This effect, normally small compared to removal of OH by CH_4 and CO, may be particularly important after volcanic injection of sulfur compounds into the stratosphere; Cadle et al. (1978) have calculated that a major depletion of OH may occur following such an event as a result of OH reaction with SO_2 . Reaction of OH with other sulfur compounds would add to this effect.

It appears certain that both NH_3 and NO_2 can be incorporated into sulfate aerosol, and thus lost to stratospheric odd-nitrogen processes. The magnitude of such effects is probably small, but needs to be quantitatively assessed. They could affect the composition, index of refraction, and radiative transfer processes associated with stratospheric aerosols.



Note: Stable stratospheric species are indicated by rectangular boxes, transient species by diamonds. Species or reactions shown by dashed lines are insufficiently confirmed by laboratory data at present to be considered certain.

Figure 3-20. Chemical transformation of sulfur compounds in the stratosphere.

SUMMARY

The sparse data now available do not permit the influences and interactions of stratospheric sulfur compounds to be assessed with any reliability. Fluxes of COS and CS₂ from tropospheric sources including volcanoes, and the tropospheric and stratospheric concentration of SO₂, COS, and CS₂ are perhaps the most significant of the factors that are, at present, either poorly established or undetermined. It is clear that sulfur chemistry can markedly perturb the stratosphere during periods of major volcanic eruptions. The diffusion of tropospheric sulfur compounds into the stratosphere may be great enough to render sulfur chemistry significant at other times as well. The transformation of gaseous sulfur into sulfate aerosol in the stratosphere and the importance of the stratospheric aerosol to global radiation and climate suggest that studies of sulfur in the stratosphere should be promptly and vigorously pursued.

STRATOSPHERIC PARTICLES

SIZE DISTRIBUTION

The size distribution of stratospheric aerosol particles has been reviewed by Cadle and Grams (1975). The concentrations in the stratosphere of Aitken particles (namely those having radii less than 0.1 micrometers) have been determined by several groups using condensation nucleus counters. These methods determine the concentration of essentially all particles greater than a critical size. It depends on the supersaturation employed in the chamber of the counter, but since concentrations of Aitken particles in the stratosphere greatly exceed the concentrations of the larger ones, such methods largely measure the concentrations of Aitken particles. By changing the supersaturation, rough indications of the size distribution within the Aitken size range can be achieved in principle, but to date this has not been particularly successful. So-called mobility techniques have indicated quite varying size distributions for the Aitken particles; distributions that are often bimodal.

Considerably more information is available concerning the concentrations and size distribution of particles exceeding 0.1 micrometer radius than concerning the Aitken particles. These are often plotted as $dN/d\log R$ against the log of the radius or diameter. Often the curves have a slope of about -2 for particles larger than about 0.1 micrometers, and this slope has sometimes been stated to be typical of stratospheric particles. However, numerous measurements have indicated marked departures from the slope of -2 , and at times, the overall curves are multimodal.

COMPOSITION

As a result of the work of Cadle and coworkers (Cadle et al., 1970) stratospheric aerosols are known to contain the elements Si, Na, Cl, Mn, Br, as well as nitrates and sulfates (See table 3-10). A relatively persistent aerosol layer is known to be distributed between approximately 17 and 40 km elevation, but with wide variations in number density existing around the globe; stratification with altitude is also known to be characteristic of the layer (Farlow et al., 1979). Measurements by Junge et al., (1961a), showed the average particle size of stratospheric aerosols to be $\approx 0.3\mu\text{m}$ diameter with sulfate representing the single most abundant chemical component. This fact has been borne out by the work of Friend (1966).

Although early measurements suggested the presence of ammonium ions chemically combined with the sulfate, subsequent work by Manson et al. (1961) indicate that this conclusion must be taken with caution since handling procedures can introduce ammonia as a contaminate in the particles after collection. However, Bigg et al. (1970) have presented morphological evidence suggesting that the percentage of sulfate existing as ammonium sulfate increases somewhat with altitude. More recently, Farlow and coworkers (1978) have acquired tentative evidence that other compounds such as NOHSO₄, NOHS₂O₇, (NH₄)₂S₂O₈ and possibly sodium sulfate, as well as ammonium sulfate, are also important components of the stratospheric aerosol.

Table 3-10
Chemical Composition of Stratospheric Aerosols*

Location/Date	Trace Elements (micromoles m ⁻³ x 10 ⁴)										max% (NH ₄) ₂ SO ₄
	SO ₄ ⁻	Si ⁻	Na	Cl	NO ₃ ⁻	Mn	Br	NH ₄ ⁺	K	NO ₂ ⁻	
18-19km 3°S-11°N July 69	20.	5.0	6.5	3.4	13.	0.02	0.20	0	0	0	0
17-18km 18-32°N July 69	16.	6.4	6.1	2.5	6.0	0	0.35	0	0	0	0
17-19km 34-48°N Dec. 69	31.	39.	7.4	14.	29.	0.35	0.29	8.3	0	0	13.4
7½-12km ** 11-35°N Nov. 69	11.	3.6	7.4	13.	4.7 (3.5)	0.06	0.11	1.7	0	0	7.7

*Data of Cadle et al. (1970) averaged and recalculated.

**Upper tropical troposphere.

Although there is no definite evidence concerning the cation with which sulfate is in chemical composition, the work of Rosen (1971) and Toon and Pollack (1973) suggests the presence of a substantial quantity of sulfuric acid in the stratospheric aerosol. Calculations by Kiang et al. (1973, 1975) indicate that H₂SO₄ might also nucleate with HNO₃; however, whether HNO₃ is actually present in the aerosol or only distributed as a vapor species at similar altitudes is still a controversial subject warranting further study. Regarding the very small (Aitken) particles which may represent those formed most recently, there is virtually no information about their chemical composition.

Even less is known about aerosols at the higher elevations. On the basis of optical observations, some evidence for the occasional existence of aerosols at the stratopause has been presented in the literature (Rossler, 1968; Clemesha and Simonich, 1978; Kent et al., 1971). These higher altitude particles are thought to result from products of meteoritic ablation, formed in the neighborhood of 90 km, and settling through the lower regions of the atmosphere.

There is an urgent need for knowledge of aerosol molecular composition as a function of particle size. Such data require very carefully designed experiments and it is not clear that the problem is amenable to study with existing techniques. Yet, without such data it is difficult to assess proposed mechanisms and models of aerosol formation. The paucity of such data also makes an assessment of potentially important catalytic surface mechanisms rather speculative.

MASS CONCENTRATIONS

Mass concentrations of stratospheric particles have proved to be extremely variable. Measurements by scientists at the National Center for Atmospheric Research, and also by Castleman et al. (1974) have shown that during the period from 1963 to 1973, the concentrations in the vicinity of the peak concentration of the sulfate layer varied from about 0.001 to 0.4 micrograms per cubic meter of ambient air at about 18 kilometers altitude. Multiplying these values by approximately 20 would convert them to concentrations in terms of parts per billion of particulate matter by mass. The reason for the wide variation in concentration is that major volcanic eruptions inject very large amounts of particulate material (especially ash and sulfuric acid) and also extremely large amounts of sulfur dioxide into the stratosphere. In fact, sulfur compounds injected into the atmosphere by volcanoes consist largely of sulfur dioxide. The sulfur dioxide is slowly converted to sulfuric acid droplets over periods of several months, probably by reaction with OH. At the same time, the large particles of ash settle out of the stratosphere. The effect of a single, very large eruption on the concentration of particles in the stratosphere can last for as long as two years. During 1963 to 1973, a number of highly explosive volcanic eruptions occurred, and the eruption clouds penetrated the tropopause. The largest of these was that of Agung in Bali in 1963. Toward the end of the decade, the effects of the volcanic eruptions on the particulate content of the stratosphere disappeared and the lowest values obtained were for that later time. A value of about .01 micrograms per cubic meter of sulfate at the levels of the highest concentration in the sulfate layer might be considered average for the concentration in the absence of a perturbation as a result of volcanic activity.

During the decade 1963 to 1973, perhaps 60% of the time the stratospheric concentration of particles was perturbed as a result of volcanic eruptions. In 1974, an eruption by Fuego in Guatemala took place, which again introduced very large amounts of material into the stratosphere; the effects of this were observed until about 1976. Since that time, the concentrations (judging from lidar measurements) have remained those of the unperturbed atmosphere. Lazrus and Gandrud (1974a) have estimated that 0.14 tg of sulfur dioxide (or of sulfur dioxide precursors) calculated as SO_2 would have to enter the stratosphere each year to maintain the sulfur in the stratosphere during periods of little explosive volcanic activity, based on sulfate concentrations during Spring, 1973. Cadle et al. (1977) estimated that the Agung eruptions in 1963 in Bali introduced about 12 tg of sulfur (calculated as sulfur dioxide) into the stratosphere. The Fuego eruption in Guatemala in 1974 was estimated to have introduced one-fifth this amount of sulfur dioxide. It is important to realize that in order to estimate the effects of such volcanic eruptions on the Earth's radiation balance, the rates of spreading of volcanic debris in the stratosphere and also the rates of conversion of the sulfur dioxide to sulfuric acid must be taken into account. In addition, particle growth and particle sedimentation must be taken into account, and the transport of stratospheric material into the troposphere by means of atmospheric transport processes considered. These factors can be taken into account by means of actual measurement of the concentration of particulate material in the stratosphere, by the measurements of atmospheric turbidity, or by means of modeling.

NUMBER CONCENTRATIONS

The number concentrations of Aitken particles vary from a few hundred near the tropopause to fractions of a particle per cubic centimeter at altitudes above about 20 kilometers. There is much uncertainty concerning the effects of volcanic eruptions on the concentrations of these small particles. The effects of volcanoes on mass concentrations are primarily the result of particles that are larger than 0.1 micrometer radius. Furthermore, the Aitken particles do not exhibit the maxima corresponding to the sulfate layer, as mentioned earlier. The number concentrations of the larger particles may vary to a much greater extent than those of the Aitken particle. In general, the surface mean diameter of the particles is probably in the vicinity of 0.2 micrometers radius. The radius of the particles of mean mass is probably somewhat larger than this, but any such figures are highly uncertain in view of the variability in the estimate of size distribution as has previously been mentioned.

SOURCES

Volcanic sources have already been discussed at length, and the fact has already briefly been mentioned that the sulfur dioxide introduced by volcanoes is probably converted to sulfuric acid primarily by reaction with OH. It might also be pointed out that the reaction of sulfur dioxide with OH when the sulfur dioxide concentrations are high can deplete the affected portions of the stratosphere of OH; this effect has been noted by Cadle et al. (1979). A rate constant of about $3 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ is assumed, and it is also assumed that two OH radicals are involved in the conversion to sulfuric acid. The OH is largely formed by the reaction of $\text{O}(^1\text{D})$ with water to form 2OH, and the rate constant for this reaction is assumed to be $7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Then, assuming a water vapor concentration of 10^{13} cm^{-3} and daytime concentrations of OH to be $5 \times 10^5 \text{ cm}^{-3}$ (in the absence of large quantities of SO_2) and $\text{O}(^1\text{D})$ of 0.5 cm^{-3} , and equating the rates of formation and depletion of OH, the volcanic SO_2 will deplete the stratosphere of OH until the SO_2 concentration drops to 4 ppbm. Of course, this calculation is a considerable oversimplification; for example, it neglects other reactions of OH, but it does demonstrate that volcanic SO_2 can markedly deplete the affected portion of the stratosphere of OH. Conversely, higher values of SO_2 concentrations than 4 ppbm in the equation yield values of OH less than $5 \times 10^5 \text{ cm}^{-3}$. Sources of sulfate aerosol in the stratosphere during periods when there has been little volcanic activity (at least little explosive activity) have been discussed in the section on the stratospheric sulfur budget.

The possibility exists that sulfate aerosol from the troposphere is transported into the stratosphere and influences the stratospheric sulfate budget. The amounts are thought to be negligible but there is little direct evidence on this issue. Figure 3-18 supports this idea since it represents a situation relatively unperturbed by fresh volcanic injections.

SUMMARY

In this chapter we have reviewed available information on the stratospheric budgets of key chemicals and chemical groups. For the chlorofluoromethanes where global emissions are known to within $\pm 5\%$, the amounts that enter the stratosphere annually are uncertain only to the extent that unknown tropospheric removal processes might exist. It is clear that most of the CFMs do reach the stratosphere but the determination of the exact extent of tropospheric removal loss, if any, must await better absolute calibrations and longer term temporal trend data than now available. Of the other key gases in atmospheric chemistry and radiation several are biogenic: CH_4 , N_2O , and possibly certain sulfur-containing gases. For CH_4 virtually no background trend data exist and although reasonable annual budgets have been deduced, they are based on very few field measurements. Nitrous oxide is now thought to be very long-lived in the troposphere so that its principal sinks are stratospheric; one such reaction comprises the principal source of stratospheric NO_x . The relative importance of the oceans, combustion, inland waters, loss from fertilized fields and from animal wastes as atmospheric N_2O sources is not yet clear and the classical view that biogenic N_2O results solely from denitrification (in anerobic environments) is being challenged by recent data on ammonium oxidation as an N_2O source. Global CO_2 levels continue to rise. While we are fortunate to have a 25-year data base, the extent to which the biosphere and the ocean can accommodate ever-increasing amounts of anthropogenic CO_2 is not well determined. The origin of the stratospheric sulfate particles and their exact role in climate control are still not clear and the global sulfur cycle itself needs research to determine the principal species involved in sulfur transfer and the relative contributions of man and nature. Fluxes of sulfur to the stratosphere as COS, CS_2 , and SO_2 are suggested but unmeasured. Mechanisms that control stratospheric water vapor concentrations are now under active study; with the increased accuracy and coverage possible with modern instrumentation, we expect a greatly improved understanding of its distribution and variability to be gained in the next several years.

CHAPTER 4

RADICALS, RESERVOIRS, AND IONS

NEUTRAL SPECIES

INTRODUCTION

This section discusses radicals and reservoirs, herein defined as those molecules chemically formed in the stratosphere. For convenience they are divided into 9 groups as shown in table 4-1. The purpose of this discussion is threefold:

- (1) To review the available library of data on those constituents which are currently believed to be of primary importance to stratospheric ozone photochemistry. In most cases, only the most recent publications by each measurement group are cited so that all previous observations are appraised therein by those authors in terms of recent improvements in experimental technique, improved data coverage, etc.
- (2) To identify emerging problems by comparing calculated and observed concentration profiles of those constituents for which a developing data base exists, such as NO, NO₂, HNO₃, O(³P), Cl, ClO, OH, HO₂, HCl, ClONO₂
- (3) To appraise emerging research objectives in the field of observational stratospheric ozone photochemistry, including those questions which remain unsolved since the writing of NASA RP-1010 and those which have emerged during the past two years of research.

The group preparing this section was particularly concerned with the problem of achieving a compromise between completeness in the coverage of data sources and coherence in the comparison between observed and calculated concentration profiles in view of the broad audience which this document must serve. To achieve this compromise it was decided to deal with the data base on four levels. First, a table giving the most recent references for observations of these constituents was constructed which lists the analytical method, date, latitude, solar zenith angle, and season of the observation, the observed concentration or mixing ratio at various altitudes, and any subjective comments of importance to the measurement such as observations made simultaneously with the constituent listed, observation platforms used, etc. Second, the tabulated data were reviewed and those observations which could be compared directly with model calculations were chosen and presented in graphical form. In view of the need to condense an observational data base for an inherently variable natural system given a wide range of latitude, solar zenith angle, season, etc., represented by the observations, a brief overview of the observations for each molecule is given. Third, for those constituents which could be represented by an altitude distribution in the stratosphere, graphs were prepared representing the *range* of available observations and the *mean* of those observations. The danger of oversimplification exists in the determination of this mean, and care was taken to represent as completely as possible the logic applied to the condensation. Considerable guidance was taken from the models discussed in Chapter 7 to determine this mean only when a meaningful correlation could be made with the calculated profiles. For example, only when small variations within a range of solar zenith angles were predicted by the models was a mean of the observations which fell within that range of solar zenith angles determined. Emphasis was given in this section to a comparison between experimental uncertainties and the observed range of concentrations. Finally, those profiles representing the range and mean of the observations were overlaid with current model calculations for the appropriate latitude, season and solar zenith angles.

Table 4-1
Neutral Species of Interest

Group 1	O(³ P), O(¹ D), O ₂ (¹ Δ), O ₂ (¹ Σ), O ₃
Group 2	H, OH, HO ₂ , H ₂ , H ₂ O, H ₂ O ₂
Group 3	N, NO, NO ₂ , NO ₃ , N ₂ O ₅
Group 4	NH ₃ , HNO, HONO, HONO ₂ , HO ₂ NO ₂
Group 5	Cl, ClO, ClO, ClO ₂ , ClO ₃ , HCl, HOCl, ClONO ₂
Group 6	Br, BrO, OBrO, BrO ₂ , HBr, HOBr, BrONO ₂
Group 7	F, FO, HF, FOH, FONO ₂
Group 8	S, SO, SO ₂ , SO ₄ , HS, H ₂ S, COS, CS ₂
Group 9	CO, CH ₂ O, CH ₃ O ₂ , CH ₃ OH, CH ₃ , CH ₃ O, CHO, CH ₃ OOH, CH ₃ ONO, CH ₃ ONO ₂ , C ₂ H ₅ , HCOOH, CH ₃ CHO, C ₂ H ₅ ONO, C ₂ H ₂ O ₂ , OC ₂ H ₂ O.

TABULATION OF DATA

The purpose of table 4-2 is to review, in condensed form, the available literature on those constituents involved directly in chemical exchange processes in the stratosphere that have a demonstrated relationship to the photochemistry of ozone. This choice reflects our current perceptions of stratospheric photochemistry rather than a representation of current analytical methods. A collation of the available data was significantly more complex for this document than for NASA RP-1010 two years ago, emphasizing the rapid expansion in our observational knowledge of stratospheric photochemistry resulting from the proliferation of new techniques. The expanded data base has begun to test many of the hypotheses which form the basis of chemical models used to predict changes in the total column concentration of stratospheric ozone.

Atomic Oxygen

Atomic oxygen, in its ³P ground state, has been observed on six occasions *in situ* through the middle and upper stratosphere by the parachute drop resonance fluorescence technique using the 130.4 nm triplet to induce fluorescence, as described in Anderson (1975, 1976, and 1979). The method provides vertical resolution on the order of 0.2 km throughout the stratosphere. These data (figure 4-1) reveal significant local structure below ~32 km except in the October 1977 and November 1978 observations.

A simultaneous, *in situ* observation of O(³P) and O₃ was made on December 2, 1977 using the above technique for O(³P) and a modified Dasibi instrument (see Robbins and Carnes, 1977) for the measurement of O₃ by ultraviolet absorption at 253.7 nm; the results are displayed in figure 4-2. Figure 4-3 presents the observed ratio, [O(³P)]/[O₃], obtained from that flight, a quantity which will be used to check the calculated steady state ratio in the later section, Comparison with Theoretical Models. The atomic oxygen-ozone ratio will receive careful attention as a more detailed consideration of the rate limiting processes governing the destruction of odd oxygen is attempted since O(³P) is involved in virtually every rate limiting O_x loss process above 30 km.

Table 4-2. Available Data on Radicals and Reservoirs

[illegible]

Table 4-2. Available Data on Radicals and Reservoirs (continued)

Molecule	Investigator*	Method or Technique	Season	Date	Solar Zenith	Latitude/Location	Observed Values					State Accuracy	Comments
							Column at 5 Jp	Column at 10 Jp	Column at 20 Jp	Column at 30 Jp	Altitude (km)		
NO	Meylin (1978)	Absorption Spectroscopy at 5 Jp	Summer	1978		Vares	3.1(15)	3.1(15)	3.6(15)	3.9(15)	48°N		Column amounts above 12 km aircraft platform
			Winter	1978		Sunset	2.7(15)	3.0(15)	4.0(15)	4.1(15)	48°N		Column amounts above 11 km aircraft platform
	Gard et al (1979)	Absorption Spectroscopy at 5 Jp	Winter	Nov 1976		Sunset	5.0(5)	4.0(5)	20°N	20°N	60°N		
			Summer			Sunset	5.1(5)	5.5(15)	5.1(5)	7.1(5) pm	4.5(15)	3.5(15)	
	Lerner (1974)	Absorption Spectroscopy at 5 Jp											Column amounts above aircraft platform
	Horsfield and Gaston (1978)	Chemiluminescence	Spring	9 Apr 1975		38°N							Rocket-borne. Corrected data from previously published results.
			Spring	10 Mar 1976		48°N							
	Hales et al (1977)	Chemiluminescence	Fall	13 Nov 1973		35°N 106°W							Data for three other flights are available
			Spring	16 May 1975		31°N							Details unimie variation
	(1974)		Spring	16 Mar 1975		31°N							Errors due to sampling given values that comparison with NO ₂ and HNO ₃ data to give total NO _x . Also, see (1978) for more recent data than that listed in this table
			Summer	22 Jul 1974		48°N							Comparison with 1973 data show significant difference above 20 km.
	Akiyama et al (1978)	Near IR absorption	Spring	13 May 1975		44°N							Balloon-borne; depends
			Winter	1 Dec 1977									
	McLaren et al (1979)	Chemiluminescence	Summer	14 Jun 1975		44°N							
			Summer	14 Jun 1975		44°N							
	Cordery et al (1978)	Pressure- modulated radiometer at 5 Jp											
	Burkhardt et al (1975)	In situ laser excitation fluorescence	Fall	19 Oct 1973		37°N							
	Pate et al (1974)	Spin flip magnetic resonance with photo- acoustic detection at 5 Jp											
	Meyer et al (1978)	In situ photoacoustic spectrometer	Spring	Apr 1977	50°	32°N							
	Anderson (1978)	In situ laser excitation fluorescence	Fall	20 Sep 1977	41°	32°N							
	Horsfield and Gaston (1978)	Chemiluminescence	Summer	27 Jun 1976		40°26'N							
	Lowenstein et al (1978)	Chemiluminescence	Spring	1976		45°N							
			Summer	1976		45°N							
	Drummond and Horsfield (1978)	IR emission radiometer	Fall	1976		45°N							
			Summer	Jun 1975		44°N							

Table 4-2. Available Data on Radicals and Reservoirs (continued)

Molecule	Investigator*	Method or Technique	Season	Date	Solar Zenith	Latitude/Location	Observed Values						Stated Accuracy	Comments
NO ₂	Mankin (1978)	Absorption Spectroscopy at 6.3 μ	Summer	1978	Sunrise or Sunset	Various	4°N 2.9(15)	11°N 3.5(15)	24° 4.1(15)	32°N 5.1(5)	44°N 6.2(15)			NO (nitrogen oxide) measured simultaneously Aircraft platform Column amounts above 12 km
	Gratz et al. (1977) Lind (1978)	Absorption Spectroscopy at 6.3 μ	Fall	1976	Sunrise or Sunset	Various	50°S 3(15)	40°S 2.8(15)	20°S 2.4(15)	20°N 2.1(5am) 1.6(15pm)	70°N 1.9(15am) 1.7(5(15)			Balloon and aircraft platforms Column above 11 km versus latitude
	Asserman et al. (1975)	Absorption Spectroscopy at 6.3 μ	Spring	May 1979				20 km 3.1 km	34 km 13.5(4(8)	26 km 20.7(8)	34 km 19.7(4(8)	36 km 6.7(3(8)		Balloon platform
	Nakamura et al. (1975) Murray et al. (1974)	Absorption Spectroscopy at 6.3 μ					16 km 3 ppb	22 km 2 ppb	24 km 2.4 ppb	26 km 2.4 ppb	27 km 2.4 ppb	28 km 2.4 ppb		Balloon platform. Concordance at 16 km Different analysis of Murray's data
	Chabot et al. (1975)	Pressure Broadened Radiometer at 6.3 μ			Day Night		20 km 0.9 ppb	25 km 0.9 ppb	35 km 2.0 ppb	40 km 4.0 ppb	40 km 1.0 ppb			Balloon platform
	Harnes (1976)	Submillimeter Spectroscopy	Summer	1974	45°	44°N			2.9 $\pm$ 1 ppb	12 $\pm$ 4 ppb	18 $\pm$ 5 ppb			Balloon platform Column amounts above
	Goldman et al. (1978)	Near UV Spectroscopy	Winter	Feb. 1977	63° 80°	35°N		20-24 km 1.4 ppb	24-28 km 1.3 ppb	26-33 km 0.3 ppb	32-34 km 10.1 ppb	34-36 km 12.8 ppb	36-40 km 10.5 ppb	Balloon platform Column amounts above
	Harrison (1979)	Near UV Spectroscopy	Winter	1978	Sunset Sunrise	44°S		2.9(15) km 1.1(15) km						Column amounts above Christchurch N. Zealand
	Nolan et al. (1979) Nolan (1979)	Near UV Spectroscopy	Spring Winter	From 1974 to 1979	Sunset Sunrise Night	55°S to 60°N					4(1.4) km ²		20%	For typical peak sunset column amounts 40°N July-March max ~4(13) cm ² , center of mass ~30 km April-May min ~1(14) cm ² , center of mass ~35 km Error in center of mass ~3 to 4 km Column amounts above Fritz Peak for all seasons Column amounts by latitude from surface and aircraft
	Kerr and McIlroy (1976)	Near UV Spectroscopy	July Aug.	1974 1975	Sunset Sunrise	69°N to 51°N		20 km 1.5 ppb	25 km 6.0 ppb	30 km 8.0 ppb	35 km 9.0 ppb			Balloon platform Column amounts and center of mass Column amounts above ground: 31°N summer 7(15) cm ² 55°N winter 3(15) cm ²
	Kulkarni (1975)	Near UV Spectroscopy	Spring Fall	Varies 1974			0.6 km Average	3.2 km 8.1 ppb	4.3 km 12.5 ppb	5.9 km 5.9 ppb	7 ppb	8.1 km 10.4 ppb	10.14 km 3.9 ppb	Data seems to be unrealistically high
NO ₃	Blamont et al. (1975)	Near UV Spectroscopy	Summer	1973	Morning Evening	44°N		15 km 3.2 day 2.2 night	15 km 4.5 night	15 km 4.5 night				Data seems to be unrealistically high Column absorption interpreted in terms of 2 concentrations
	Filshie (1978)	In situ 1 k. from Paramagnetic fluorescence	Summer	Aug 1976	Morning	15°N					15 km 5(5) cm ²		3X	32 km. Center of three Balloon measurements cryogenic sampling
	Drummond and (1978)	Instrument IR radiometer sun modulated radiometer	Summer	June 1975	Night/Day	44°N		20 km (6-10)	25 km (2.0-4)	30 km 4.5(4)	35 km 4.5(4)	45 km 2(4)		Column amounts above ground Upper limit 4(13) cm ² (private communication)
	Nolan et al. (1975)	Visible Spectroscopy	Spring	Jun 1978 Mar 1979	Night	40°N								Column amounts above ground. Moon as source.
N ₂ O ₅	Davies (1974)	Visible Spectroscopy	Spring	1974	Night	42°N								Column amounts above ground. Moon as source.
	Farns et al. (1978)	Emission radiometer at 8.1 μ	Summer	Aug 1977		31°N				2(4)				Column amount measured theoretical profile for shape yields quoted mixing ratio
	Murray et al. (1978)	Emission Spectrometer at 8.1 μ	Winter	Feb 1978 24 Feb 1979		54°N 40°N								Aircraft platform at 18 km. Column amount in vertical <1(15) cm ²

Table 4-2. Available Data on Radicals and Reservoirs (continued)

Molecule	Investigator*	Method or Technique	Season	Date	Solar Zenith	Latitude/Location	Observed Values										Stated Accuracy	Comments
							15 km	20 km	25 km	30 km	35 km	40 km	45 km	50 km	55 km	60 km		
HNO ₃	Murphy (1973)	IR Emission	Various	Various		32° 64°	5(-10)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)		
	Blair (1979)	IR Emission	Summer	1976		31°	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)	1(-9)		Upper limit latitude summer profile
HOCl	Lewis (1974)	Filter Collection				Survey												
	Harries (1978)	IR Emission				40°	1(10)	4 to 5(-9)	5 to 6(-9)	2 to 4(-9)	0 to 1(-9)							
HO ₂ NO ₂	Girard (1977)	IR Emission				42°	50°S	40°S	20°S	40°N	60°N							Column above 11 km
	Murphy (1979)	IR Emission (780 cm ⁻¹)	Spring	May		64°	2(-15)	2(-15)	6(-15)	8(-15)	4(-15)							Upper limit is 0.4 ppb
Cl	Anderson et al. (1979)	In situ Resonance Fluorescence	Summer	28 Jul 1976	16° 55°	32°N												0.0 measured simultaneously
	Anderson et al. (1979)	In situ Resonance Fluorescence	Summer	28 Jul 1976	16° 55°	32°	0.22	0.17	0.54	0.10	1.1	1.1	0.14	0.12	0.12	0.12		Various altitudes measured simultaneously
ClO	Anderson et al. (1979)	In situ Resonance Fluorescence	Summer	28 Jul 1976	16° 55°	32°	0.05	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15		Various altitudes measured simultaneously
	Anderson et al. (1979)	In situ Resonance Fluorescence	Summer	28 Jul 1976	16° 55°	32°	0.05	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15		OH HO ₂ NO ₂ measured simultaneously
ClO ₂	Menzies (1979)	Laser Heterodyne Radiometry	Fall	20 Sep 1978	90° (sunset)	32°N												OH HO ₂ NO ₂ measured simultaneously
	Waters et al. (1979)	Microcavity Radiometry	Spring	10 Mar 1977 to 15 Jun 1977	36°N to 53°N	36°N to 53°N												OH HO ₂ NO ₂ measured simultaneously
ClO ₃	Waters et al. (1979)	Microcavity Radiometry	Spring	10 Mar 1977 to 15 Jun 1977	36°N to 53°N	36°N to 53°N												OH HO ₂ NO ₂ measured simultaneously
	Waters et al. (1979)	Microcavity Radiometry	Summer	26 Jun 1977 to 27 Jun 1977	41°N to 54°N	41°N to 54°N												OH HO ₂ NO ₂ measured simultaneously
ClONO ₂	Waters et al. (1979)	Microcavity Radiometry	Summer	26 Jun 1977 to 27 Jun 1977	41°N to 54°N	41°N to 54°N												OH HO ₂ NO ₂ measured simultaneously
	Waters et al. (1979)	Microcavity Radiometry	Summer	1 Aug 1977	17°N to 43°N	17°N to 43°N												OH HO ₂ NO ₂ measured simultaneously
HOCl	Farrar (1979)	IR Spectroscopy	Spring	May 1979	32°S	32°S												OH HO ₂ NO ₂ measured simultaneously
	Farrar (1979)	IR Spectroscopy	Spring	May 1979	32°S	32°S												OH HO ₂ NO ₂ measured simultaneously
HO ₂	Raper (1976)	Absorption	Spring	1975	30°S	30°S												OH HO ₂ NO ₂ measured simultaneously
	Raper (1976)	Absorption	Spring	1976	30°S	30°S												OH HO ₂ NO ₂ measured simultaneously
HO ₂	Williams (1976)	IR Absorption	Winter	Dec 1975	32°	32°												OH HO ₂ NO ₂ measured simultaneously
	Williams (1976)	IR Absorption	Winter	Dec 1975	32°	32°												OH HO ₂ NO ₂ measured simultaneously
HO ₂	Eyre et al. (1977)	Passive Mediated Radiometer	Spring	Mar 1977	32°	32°												OH HO ₂ NO ₂ measured simultaneously
	Eyre et al. (1977)	Passive Mediated Radiometer	Spring	Mar 1977	32°	32°												OH HO ₂ NO ₂ measured simultaneously
HO ₂	Ackerman (1976)	IR Absorption	Various	1976	42°	42°												OH HO ₂ NO ₂ measured simultaneously
	Ackerman (1976)	IR Absorption	Various	1976	42°	42°												OH HO ₂ NO ₂ measured simultaneously
HO ₂	Lewis (1977)	Filter Collection	Various	Various		Various												OH HO ₂ NO ₂ measured simultaneously
	Lewis (1977)	Filter Collection	Various	Various		Various												OH HO ₂ NO ₂ measured simultaneously

Raper

Table 4-2. Available Data on Radicals and Reservoirs (continued)

Molecule	Investigations*	Method or Technique	Season	Date	Solar Zenith	Latitude/Location	Observed Values							Stated Accuracy	Comments
							10 km	15 km	20 km	25 km	30 km	35 km	40 km		
HF	Farmer (1979)	IR absorption	Fall	1977		30°S			3(-11)	6(-11)	1(-10)	1(-10)			Above 28 km.
	Zander (1977)	IR absorption									3(-10)				
	Mroz (1977)	Filter collection							6(-11)	8(-11)	1(-10)	1(-10)			
Br	None available														
BrO	None available														
HBr	Larus (1979)	Filter collection	Various			32°		1.5(-7)	1.5(-7)	6(-6)	4(-6)	5(-6)		See text.	
SO ₂	Jaesske (1976)	Chemiluminescence	Spring	27 Mar 1976		54°	0.5 ppb	0.5 ppb							
H ₂ S	None available														
COS	Inti et al (1979)	G.C. Flame Photometric detection	Winter	18 Feb 1978		36°N		40(-5), 5(-3) ppt	26(-4), 4(-3) ppt						
			Spring	12 Mar 1978		32°N					13(-8), 17(-8) ppt				
			Spring	5 May 1978		38°		25(-6), 17(-5) ppt							
CS ₂	None available														
HS	None available														
CO	Farmer et al (1979)	IR absorption	Spring	18 May 1976					10 ppb	10 ppb	10 ppb			±50% at 30 km ±20% at 20 km	
	Goldman et al. (1973)		Winter	18 Jan 1972			80 ppb	2(-)							
	Fabian et al (1979)	IR absorption	Summer	12 Sept 1977	43°N			28 ppb	10 ppb						
			Summer	14 Jun 1978	43°N										
			Summer	26 Jun 1978	43°N			25 ppb							
	Pratt and Falconer (1979)						44 ppb								
CH ₃ OH	Arnold et al (1979)	Positive-ion mass spectrometer													Upper limit based on identification of positive ion mass spectrometer
NH ₃	Murphy (1979)	IR absorption	all	Oct 1978		42°									
H ₂ CO	Farmer (1979)	IR absorption	Summer			40									
C ₂ H ₂	Cram and Robinson (1979)	Sampling	Spring	Apr 1977	17°N, 123°W		Upper troposphere 1.5(-9), 0.7(-9)								
C ₂ H ₄	Cram and Robinson (1979)	Sampling	Summer	July 1977	9°N, 80°W										
C ₂ H ₆	Cram and Robinson (1979)	Sampling	Spring	Apr 1977	17°N, 123°W										
C ₂ H ₄	Cram and Robinson (1979)	Sampling	Summer	July 1977	9°N, 80°W										

*Most recent results for each investigator group

Note: Numbers in parentheses signify powers of 10 (e.g., 3(-7) = 3 × 10⁻⁷)

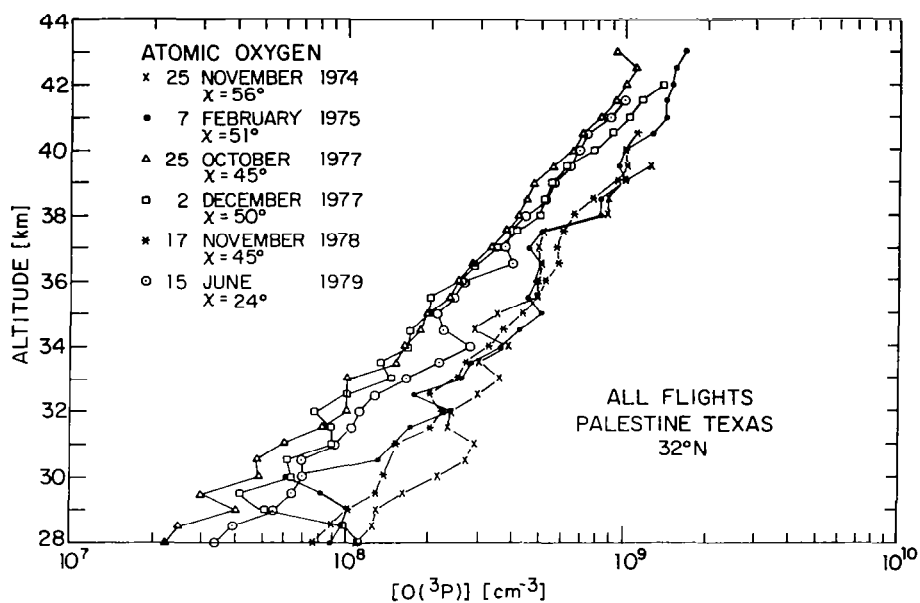


Figure 4-1. Shown are profiles of $O(^3P)$ measured by *in situ* resonance fluorescence.

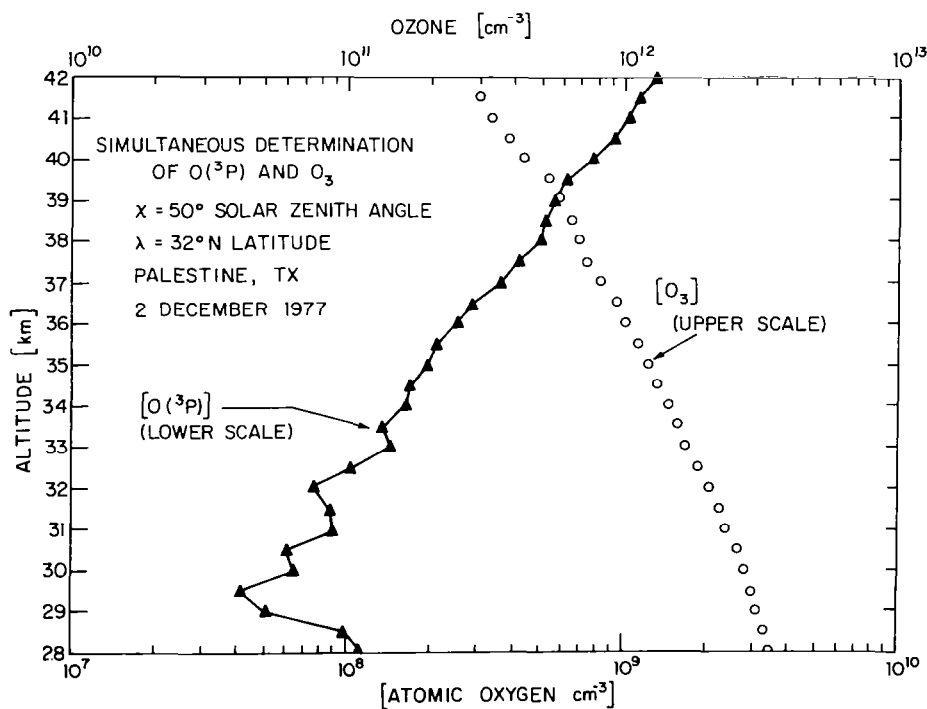


Figure 4-2. Results of the simultaneous *in situ* atomic oxygen-ozone ratio measured within the same cubic meter during parachute controlled descent.

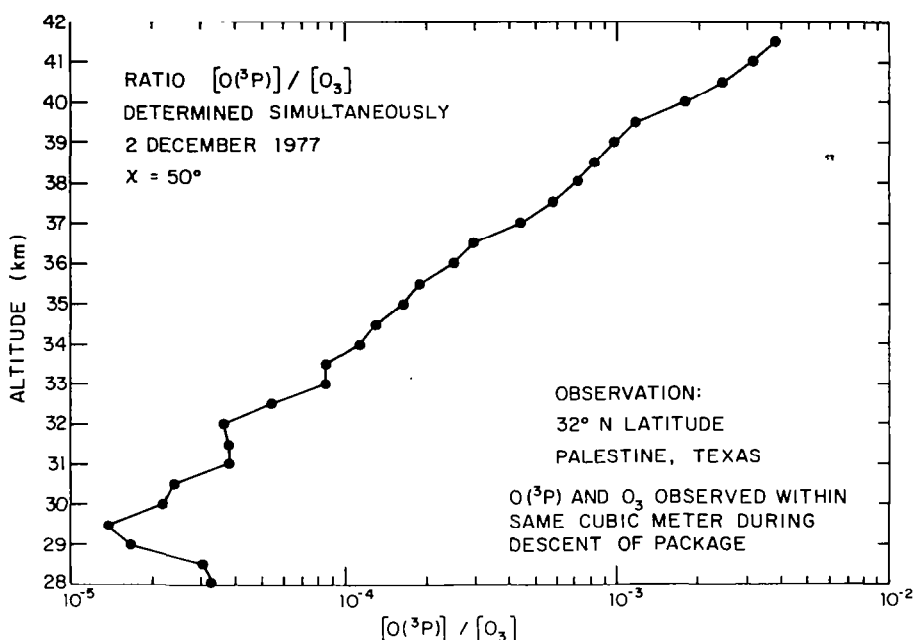


Figure 4-3. Observed $[O(^3P)] / [O_3]$ ratio determined from simultaneous *in situ* observations of atomic oxygen and ozone.

$O_2(^1\Delta)$

Numerous rocket measurements of the infrared atmospheric system of $O_2(^1\Delta)$ have been made and interpreted in terms of $O_2(^1\Delta)$ concentrations. Most of these are mesospheric and auroral studies. Only a few are applicable to the lower levels of the stratosphere. Two rocket measurements of the day airglow in the $1.27\mu m$ band with a rocket photometer are given in the table (Evans and Llewellyn, 1970). They are in essential agreement. Aircraft measurements (Noxon, 1968) and balloon measurements (Evans and Llewellyn, 1969) of the integrated dayglow intensity are in agreement with these rocket measurements. Below 30 km new balloon ascent measurements would be required to obtain good estimates of $O_2(^1\Delta)$ concentrations. New measurement techniques such as photoionization mass spectrometry could be applied. $O_2(^1\Delta)$ is produced by ozone photolysis and resonance phosphorescence, is quenched by molecular species, and is reasonably simple to model. A summary of the observed profiles is shown in figure 4-4.

$O_2(b^1\Sigma)$

Although there have been numerous measurements in the airglow and aurora of the atmospheric system of $O_2(b^1\Sigma^+ - X^3\Sigma^-_g)$, there are few measurements applicable to the stratosphere. The results of the only relevant rocket measurement by Wallace and Hunten (1968) are shown in table 4-2. These have a large radiative transfer correction; hence the concentrations of $O_2(b^1\Sigma)$ below 50 km are quite uncertain. Balloon ascent measurements would be required to obtain better estimates. The main production processes are $O(^1D)$ transfer and resonance fluorescence. Due to self absorption in the atmosphere, the measurement of $O_2(b^1\Sigma)$ concentrations at lower levels by optical techniques is difficult.

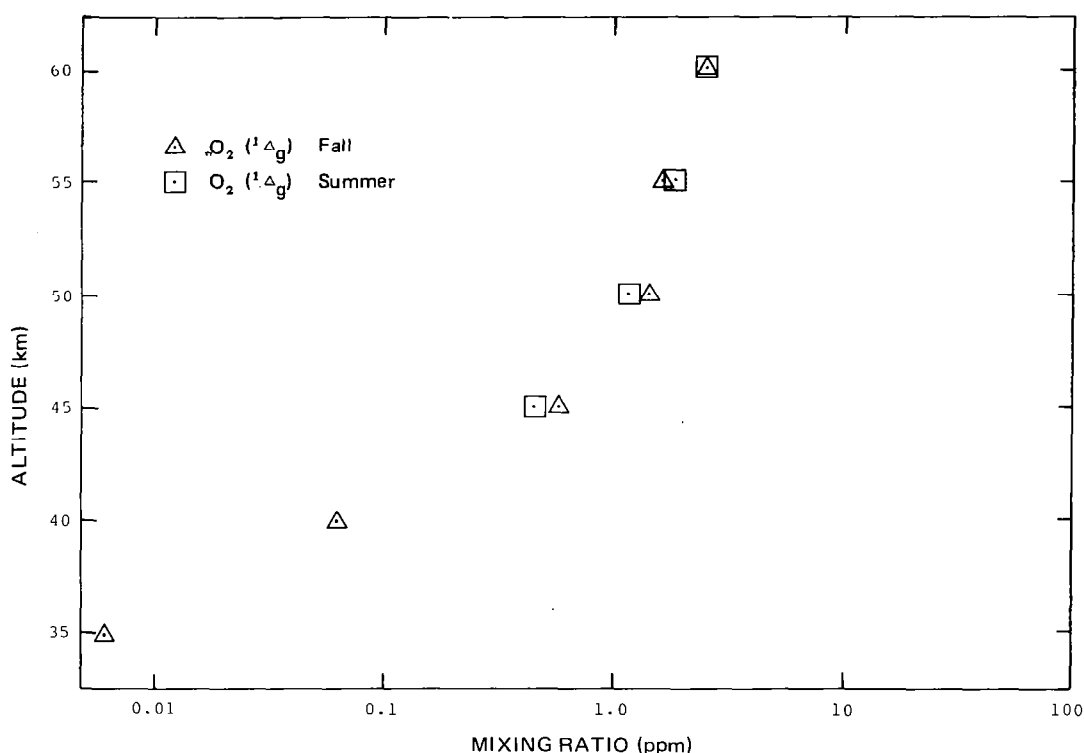


Figure 4-4. Shown are profiles of $O_2 (^1\Delta_g)$. The uncertainty estimate is $\pm 20\%$. (Evans and Llewellyn, 1970)

Atomic Hydrogen

As noted in table 4-2, no observations of any kind are presently available for atomic hydrogen. Although a sensitive *in situ* analytical method exists for its detection, the predicted midday concentration ranges from 120 cm^{-3} in the lower stratosphere to $\sim 1 \times 10^5 \text{ cm}^{-3}$ in the upper stratosphere, the latter of which is approximately equivalent to the detection threshold of current methods.

OH

The OH radical has been observed in the stratosphere by three techniques. A rocket-borne high resolution (0.06 nm), polarized scanning spectrophotometer was used to observe solar induced fluorescence (Anderson, 1971a,b) at 309 nm from which the altitude distribution between 45 and 70 km was inferred by differentiation with height of the vertical column emission rate. These results were extended downward to $\sim 28 \text{ km}$ using a parachute drop, *in situ* resonance fluorescence technique (see Anderson, 1976, 1979). Burnett and Burnett (1979) report the results of several hundred observations of the total atmospheric column of OH at 40°N using high resolution absorption spectroscopy with the Sun as the source. They have been able to study both the diurnal and seasonal changes in total column abundance.

In the troposphere, Davis et al. (1976), Perner et al. (1976) and Wang et al. (1975) have measured the radical from aircraft and at ground level. Those measurements demonstrate that the total column concentration of

OH observed from the ground by Burnett and Burnett is unaffected by the tropospheric contribution and is thus dominated by the stratospheric and mesospheric distribution. As will be discussed in a later section of this chapter the integrated column from the mean of the rocket and balloon *in situ* measurements above 30 km and the mean of the total column concentrations of OH observed from the ground both fall within the range $4 - 9 \times 10^{13} \text{ cm}^{-2}$ and both exhibit variability in excess of the stated accuracy of the technique.

In Situ Appraisal

Figure 4-5 displays the *in situ* observations of OH in terms of volume mixing ratio with the two late afternoon observations (January 12, 1976, April 26, 1977) made at a solar zenith angle of 80° corrected to 41° for comparison with the observations of July 14, 1977 and September 20, 1977 and the midday model calculations discussed in Chapter 7. This requires an upward adjustment in those $\chi = 80^\circ$ profiles of a factor of two based on the solar zenith angle dependence of OH determined by the diurnal models. Observed structure in the OH profiles of a factor of two exceeds significantly the precision of the observations ($\pm 15\%$) as well as the accuracy of the measurement ($\pm 35\%$). For a discussion of experimental uncertainty see Anderson (1976). The appearance of local structure in the observed profiles, as in the case of the atomic oxygen data, is not an uncommon feature even with the somewhat limited vertical resolution ($\pm 2 \text{ km}$).

No *in situ* observations are available in the important region below 25 km which represents a serious gap in our observational knowledge.

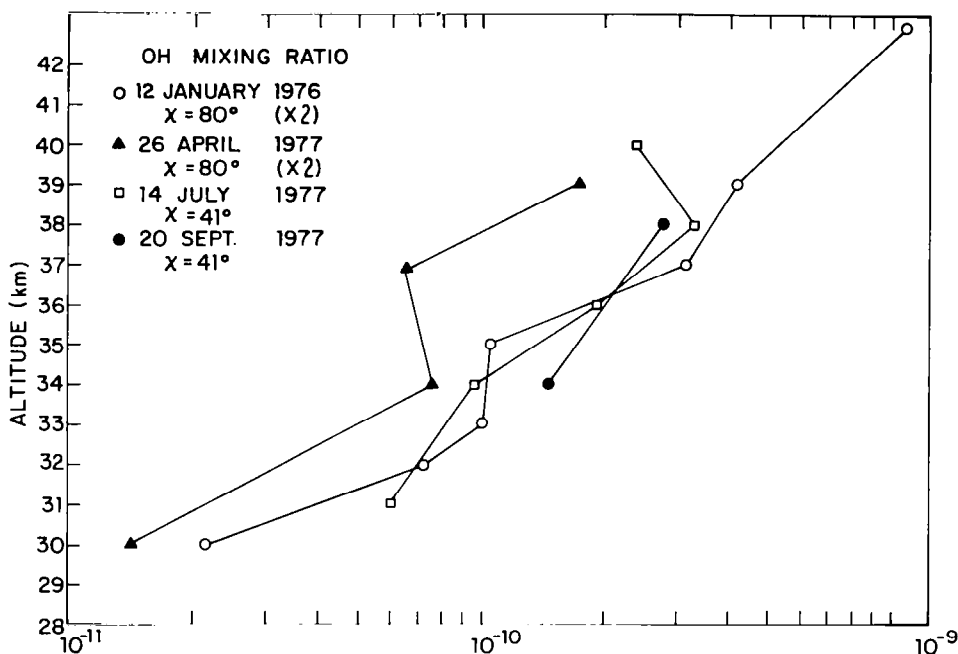


Figure 4-5. The observed midday OH mixing ratio from 4 balloon flights. Two $\chi = 80^\circ$ sets have been scaled up by 2 (suggested by a diurnal model) to compare with midday measurements.

Total Column Appraisal

Apart from creating and maintaining an operational multi-element interferometer, the Burnett technique faces the problem that the background solar spectrum is not a flat continuum but exhibits structure. Even so, the limiting uncertainty is set by statistical noise which corresponds to $\sim 2 \times 10^{13} \text{ cm}^{-2}$ for a single one-hour measurement. By averaging, the Burnetts have presented a convincing argument that the uncertainty can be reduced to about $1 \times 10^{13} \text{ cm}^{-2}$. They present their data in four seasonal means of the total vertical column as a function of solar zenith angle. In the summer, when $\chi < 40^\circ$, the data reveal a curious morning/afternoon asymmetry not seen at larger χ . In only an hour or two, centered on noon, the abundance drops by about 30% as indicated in figure 4-6. This appears to be a real atmospheric phenomenon but is not understood as yet. The derived OH column does depend upon the temperature assumed for the altitude at which the bulk of OH is located. Some of the variability observed in the OH column may therefore reflect changes in temperature.

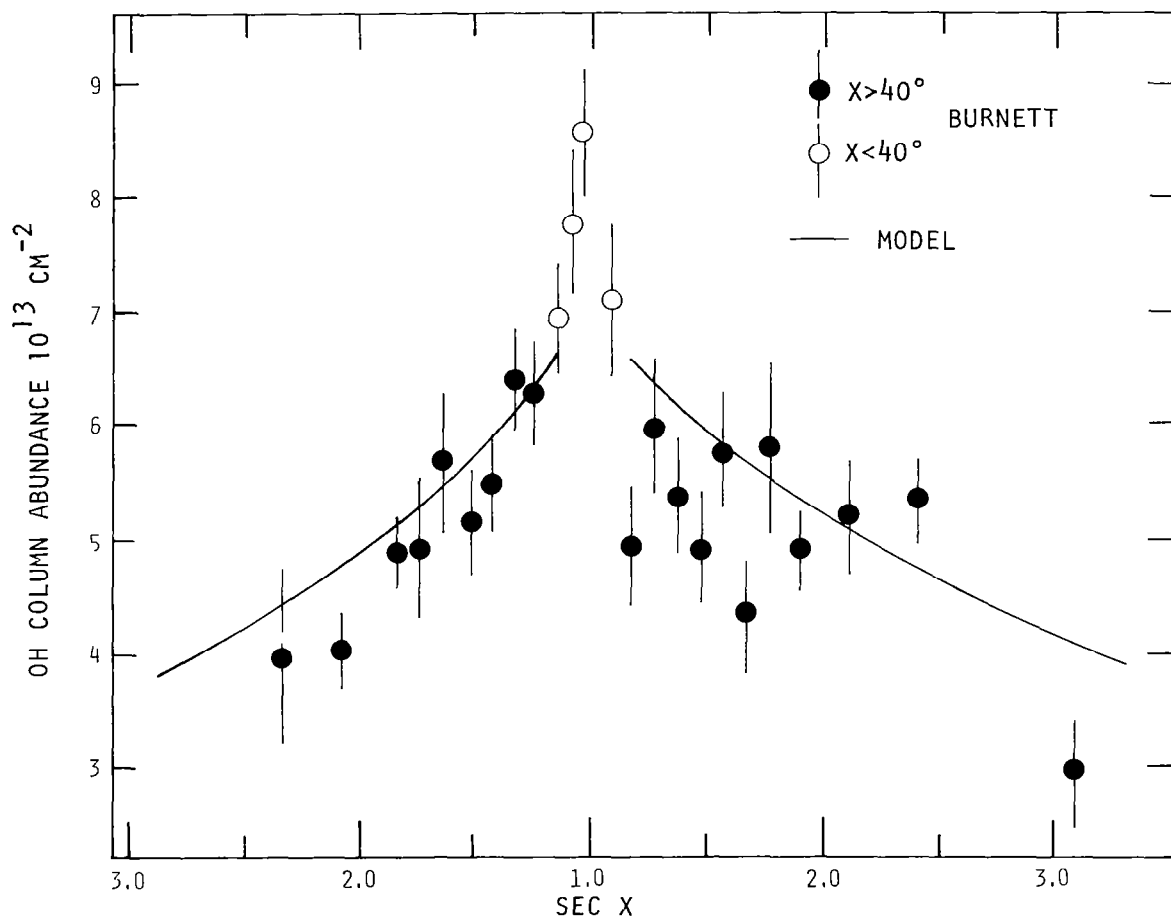


Figure 4-6. The preliminary mean set of OH column abundance (Burnett) versus secant X . The summer measurements exhibit a noon period asymmetry center $X < 40^\circ$. The solid line is a rough estimate for an equinox model derived from Logan et al.

Diurnal Variation

The Burnett measurements show a fairly good correlation with the solar zenith angle, particularly in the morning. Both the column measurements lend support to the correction of a factor of 2 in the *in situ* OH measurements obtained at $\chi = 80^\circ$.

Seasonal Variation

The Burnett measurements extend over several years and show there to be a small spring maximum and fall minimum. The departures from a mean diurnal curve fitting all measurements as a function of χ show an excess of 15% in spring and a deficit less than this in the fall. Logan et al. (1978) indicate that $[\text{OH}]$ is proportional to $[\text{H}_2\text{O}]^{1/2}$; the Burnett measurements thus suggest a rather small seasonal change in stratospheric water vapor (at least above ~ 40 km) near 40°N .

HO₂

Three *in situ*, midlatitude, midday observations of HO₂ in the Earth's stratosphere, using a chemical conversion - resonance fluorescence technique, are available (Anderson et al., 1979) which encompass the altitude interval 27-39 km. The mean of the observed HO₂ volume mixing ratio (see table 4-2 and figure 4-7) at 37, 35, 33, 31, and 29 km are respectively 4.7×10^{-10} , 2.6×10^{-10} , 3.9×10^{-10} , 2.1×10^{-10} , and 1.1×10^{-10} with an experimental uncertainty of $\pm 35\%$. Significant variability is observed among the three observations. Since HO₂ is rate limiting in the closure of the HO_x catalytic cycles which recombine O_x, the HO₂ observations provide a comparison between the rate of odd oxygen production by O₂ photolysis and the rate of HO_x catalyzed destruction demonstrating that hydrogen-oxygen free radicals account directly for a fractional destruction of O_x equal to 0.15, 0.10, 0.20, 0.13, and 0.10 respectively at 37, 35, 33, 31, and 29 km given current formulations of stratospheric chemistry. A graphical comparison between $2k_2[\text{HO}_2][\text{O}(^3\text{P})]$ and $2J_{\text{O}_2}[\text{O}_2]$ is shown in figure 4-8.

H₂O

In figure 4-9, the left-most shaded area is from Harries' 1976 review and represents the rms limits to the mean calculated in that paper from sources quoted therein. The right-most shaded area indicates the bounds of several post-1976 measurements which are currently available. Clearly, an increase with height is strongly indicated by this data set. Much of the data is just being submitted for publication. No value judgment other than authors' own claims to good accuracy can be made at this stage. Some evidence (Kley et al., 1979) indicates that the vertical profile of H₂O may change with season at the same site. Further, other results (Heidt et al., private communication) may indicate that measurements at different latitudes show a dependence of profile shape on latitude. It should also be noted that evidence for a maximum of ~ 8 ppmv was found at both 30°N and 30°S by Farmer et al. (1979 and private communication) in measurements spaced one year apart using the same instrument.

H₂O₂

H₂O₂, hydrogen peroxide, is a moderately strong infrared absorber with a band in the 1250 cm^{-1} region. Sunset solar spectra covering this region were obtained during a balloon flight made October 27, 1979 by Murcray et al. (1979), at a resolution of 0.01 cm^{-1} . Examination of these spectra fails to show any absorption that can be attributed to H₂O₂. If H₂O₂ were present at a mixing ratio of 5×10^{-10} at 20 km, the absorptions would be observable. Thus, an upper limit of this amount can be placed on this specie on the basis of these data.

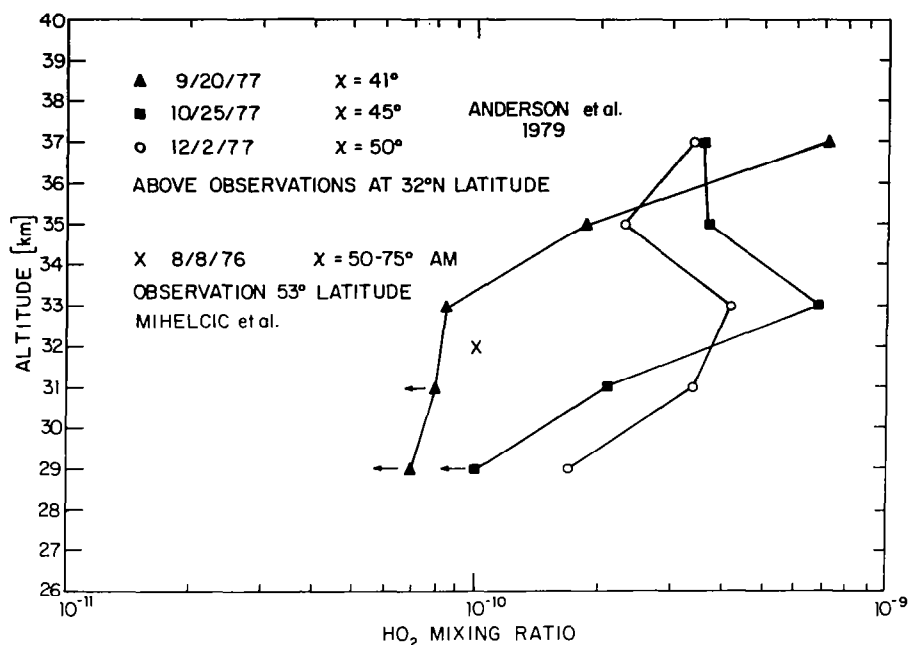


Figure 4-7. The observed midday HO_2 mixing ratio from three Anderson balloon flights (chemical conversion to OH followed by resonance fluorescence) and one Mihelcic experiment (cryogenic sampling with EPR analysis).

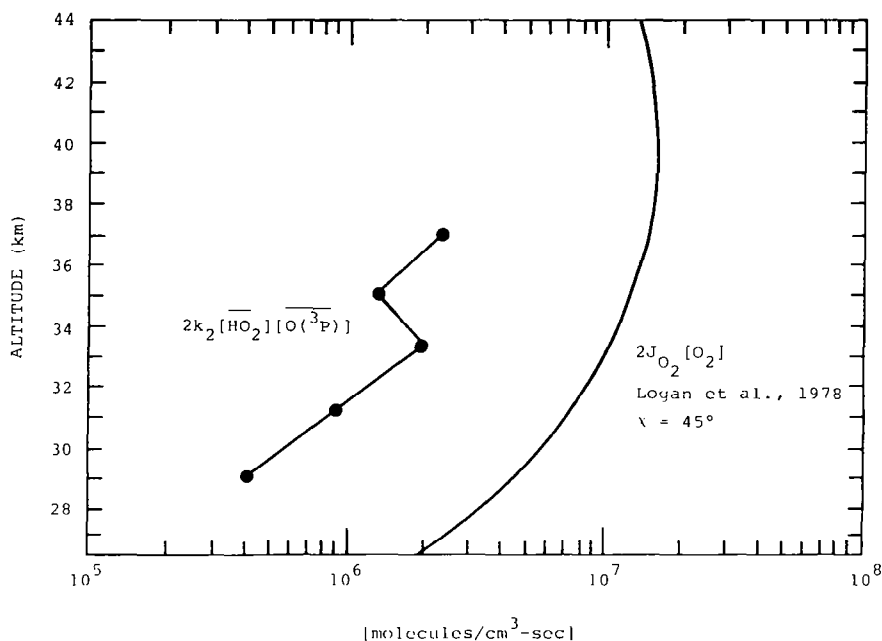


Figure 4-8. The odd oxygen destruction rate determined from measurements by Anderson is compared with the production rate by O_2 photolysis.

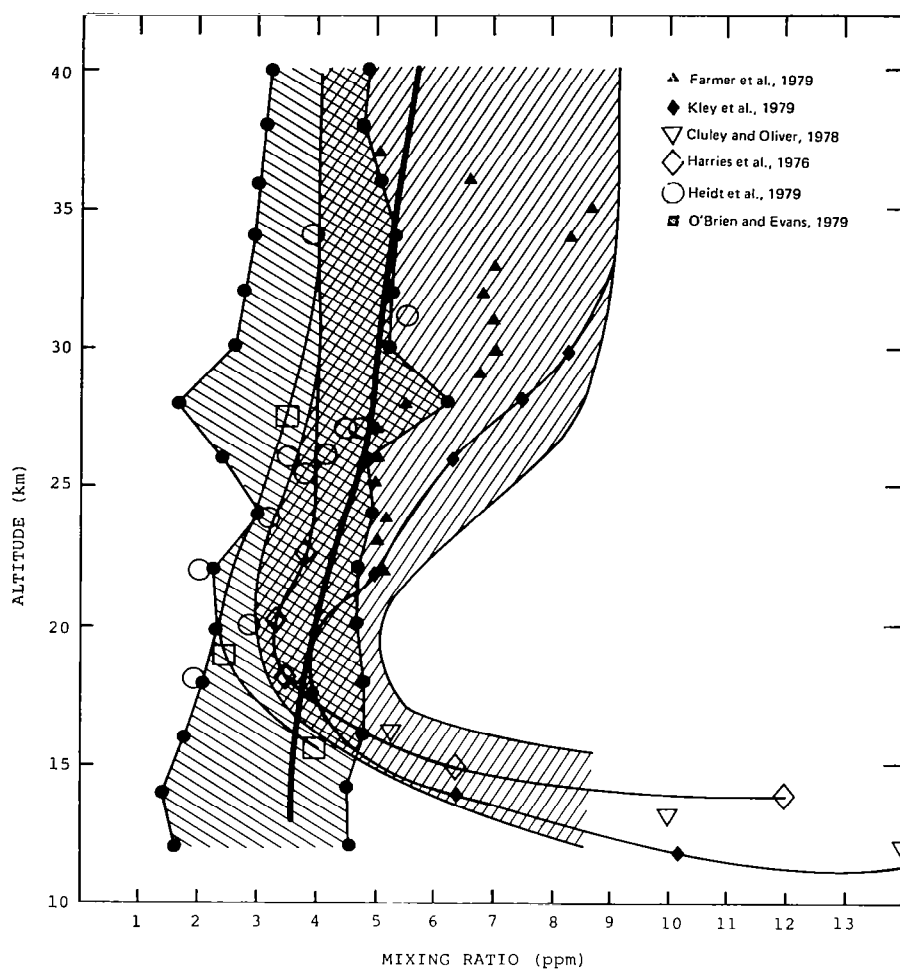


Figure 4-9. Water vapor mixing ratio profiles measured by several groups. The shaded region bounded by shaded circles shows the rms limits of measurements up to 1976. The second shaded area gives the limits including more recent data. The heavy dark line is the current mean value.

Atomic Nitrogen

Atomic nitrogen has not been measured in the stratosphere. Although it is amenable to *in situ* atomic resonance fluorescence methods, the low densities expected imply a formidable experimental problem. The uncertainty in calculated values is principally due to calculations of the J-value for NO.

NO

In situ and remote techniques to measure NO have included chemiluminescence, Ridley et al. (1973) and Ridley and Howlett (1974), atmospheric absorption of solar infrared radiation, Girard et al. (1973) and Toth et al. (1973), and atmospheric infrared NO emission, Chaloner et al. (1975). Also employed have been spin flip laser photoacoustic detection, Patel et al. (1974), photoionization mass spectrometry, Aikin and Maier

(1978), and NO gamma band resonance fluorescence, Anderson et al. (1978). A rocket-borne chemiluminescent detector for the upper stratosphere and lower mesosphere measurements has been developed by Mason and Horvath (1976). The solar infrared radiation absorption technique has been used at 1876 cm^{-1} in the R and Q branches of the 1-0 fundamental, Toth et al. (1973). A detailed description of the technique is given by Farmer (1974). The absorption features are weak at this wavenumber. Uncertainties arise from inaccuracies in line strength parameters and difficulties in the process of deconvolution as well as the weak line strength. Because of the long tangent path the technique emphasizes NO densities at 90° solar zenith angle when NO is being rapidly converted to NO_2 at sunset and created from NO_2 at sunrise. The method has also been employed at 1890 to 1914 cm^{-1} , Fontanella et al. (1975).

Problems associated with measurements at the terminator can be overcome by observing NO in emission rather than absorption. It provides useful diurnal information. Nitric oxide has been detected at 1876 cm^{-1} using a pressure modulated radiometer (Chaloner et al., 1975, 1978). Height profiles are obtained by scanning the horizon. Deconvolution contributes to the uncertainty of this measurement. The addition of the pressure modulated NO cell reduces uncertainty but careful laboratory calibration is still required. The measurement is along an integrated path so that only averages over large areas are possible. A thorough discussion of the method and results appears in Drummond and Jarrot (1978).

To date, the majority of NO measurements have been obtained utilizing the chemiluminescent technique. In this technique, NO is detected by observing the fluorescence of NO_2^* produced by the reaction of NO with O_3 . In a sense the method is non-specific, since other compounds also fluoresce after reaction with O_3 . However, in the stratosphere, the abundance of such compounds is thought to be extremely low. Various instruments have been flown on balloons and rockets. The technique is potentially very precise but attention should be directed towards problems in absolute calibration. Also, sampling problems are particularly troublesome with balloon-borne instruments. Errors in past measurements have probably been less than a factor of 1.8 (Ridley, private communication). The technique has been used to provide altitude profiles and to provide diurnal behavior of NO.

The laser photoacoustic technique has been used to provide measurements of the diurnal variation of NO. However, because of the complexity of the technique, it has not been used extensively.

Photoionization mass spectrometers have been used to detect NO. The technique employs selective ionization of gases using a krypton lamp with lines at 123.6 nm and 116.5 nm and detection of the resulting ions. As with most *in situ* techniques, uncertainties arise from the inlet system.

In the gamma-band method, NO is detected by observation of the γ -band radiation from NO excited by a resonance lamp. In the experiment, a pod containing the lamp and detector is dropped by parachute. Sampling should not be a problem with this method. Calibration uncertainties yield an accuracy of approximately $\pm 35\%$.

Figure 4-10 illustrates data taken at northern midlatitudes and is representative of midlatitude fall mixing ratios. There is considerable spread in the data with a factor of 5 or more variability in NO over most altitudes. Some of this variation must be attributed to experimental errors such as uncertainties in calibration and modeling of the deconvolution process. As noted above, earlier values measured by Ridley et al. (1974, 1975) may have been too low due to sampling problems. Photoionization mass spectrometer data (Maier et al., 1978) from a flight in April 1977 exhibits a steep gradient below 35 km . The global distribution of nitric oxide can be obtained from a pressure modulated radiometer on a satellite. Such an instrument is on Nimbus-7 and data should be available soon. Intercomparison of satellite and *in situ* NO measurements has been accomplished using the instrument on Nimbus-7 and the chemiluminescent technique.

The only available data on latitudinal variations of NO come from aircraft carrying chemiluminescent detectors for measurements in the 18 to 21 km altitude region. In the 30° to 45° latitude zone summer values are

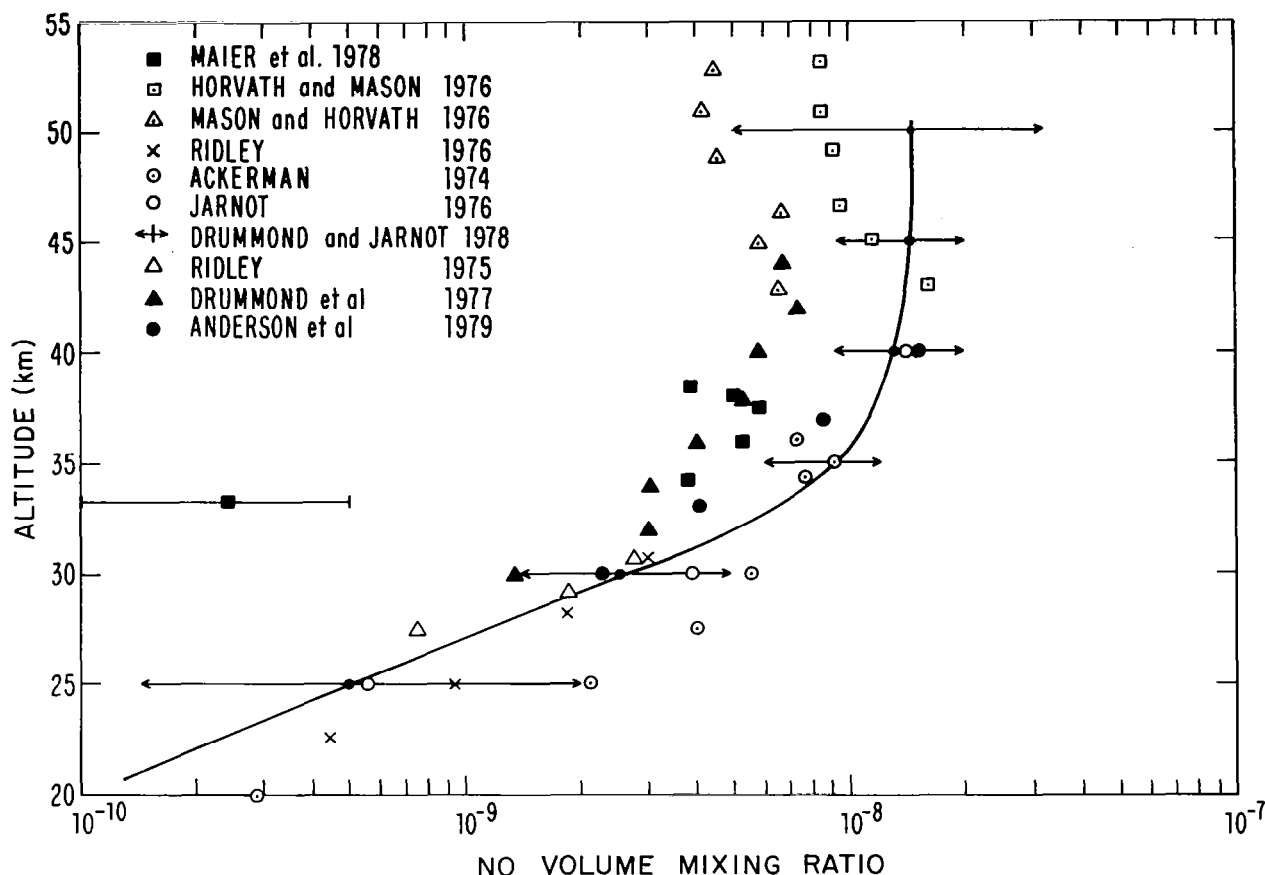


Figure 4-10. Nitrogen oxide mixing ratio profiles for northern midlatitudes measured by chemiluminescence, photoionization mass spectroscopy, and IR absorption and emission.

two to three times greater than winter. Between the Equator and approximately 50°N, data obtained during summer and fall exhibit only small changes, Loewenstein and Savage (1975). For latitudes greater than approximately 50°N there is an increase of nearly a factor of three (Loewenstein et al., 1978).

Few studies of the diurnal variation of NO have been made. However, the rapid decrease at sunset and increase at sunrise has been observed (Patel, 1974, and Ridley et al., 1974). The general features of the diurnal variation have also been seen (Ridley et al., 1977, and Burkhardt et al., 1975).

To date there has been no intercomparison of the various techniques reported. This remains a valid goal. However, there have been laboratory comparisons made of the photoionization and chemiluminescent methods.

NO₂

A limited number of altitude profiles of NO₂ have been measured using spectroscopic techniques in the near UV, IR and submillimeter regions. The altitude profiles obtained from balloons using long path length solar absorption suffer from the inaccuracies and errors of the kind discussed briefly for NO. For these types of measurements, we note that the deconvolved data apply to a χ of order 90°, which is typical of late afternoon

NO₂ amounts. Below 26 km the NO₂ amounts measured are more typical of nighttime NO₂ densities, due to the conversion of NO to NO₂. In the visible spectrometric/photometric techniques, which measure the absorption due to NO₂ in zenith sky light during the sunset or sunrise period, the deconvolution of the data is not as straightforward as for absorption spectroscopy of direct sunlight. Accordingly, the information obtained is not as detailed; the method provides column abundances with errors ~ 20 to 30% and also the height ± 3 to 6 km of the center of mass of the column. Emission measurements have been made in the submillimeter region and in the 6.3 μ m region. The latter experiment utilized a pressure modulated radiometer. The inaccuracies specific to this technique have been discussed in the section for NO. The emission methods, however, enable the diurnal behavior of NO₂ to be mapped throughout the day. To date, the only *in situ* measurement of NO₂ has been made using cryogenic sampling with paramagnetic resonance detection. Details of the various measurement methods are listed in table 4-2.

Column amounts of NO₂ have been obtained from the ground and from aircraft platforms using both emission and absorption spectrometry. To date, the most extensive set of measurements of NO₂ have been made by measuring the absorption of NO₂ in zenith sky light (Noxon et al., 1979). As noted above, the method allows an estimate of the stratospheric columnar amount of NO₂ and its center of mass to be made. The most readily apparent feature of the measurements is the variability of NO₂. However, the number of measurements made is sufficiently extensive that certain latitudinal and seasonal features emerge. The latitudinal behavior of columnar NO₂ suggested by these measurements is that lower amounts of NO₂, by about a factor of two, occur at equatorial regions, compared to midlatitude regions. Also, the center of mass of the column appears to be lower in the equatorial regions. The principal seasonal features inferred are (a) the summer maximum of NO₂ at midlatitudes and (b) the winter "cliff" around 50° latitude in both hemispheres. The "cliff" is a steep decline of column NO₂ that occurs over a few degrees of latitude in winter around 50° when there is a strong polar vortex. The drop in sunset NO₂ may be as large as a factor of five or so. Another important feature of the Noxon et al. (1979) measurements is the diurnal behavior of NO₂ which is not in total agreement with earlier results (Brewer et al., 1974). Generally, more NO₂ is observed at evening than at sunrise. In addition, using the Moon as a source, NO₂ is observed to increase after sunset and then subsequently decrease. The detailed altitude profiles of Kerr and McElroy (1976) from balloons using direct solar absorption measurements also show more NO₂ at sunset than at sunrise. Drummond and Jarnot (1978) have discussed in considerable detail the day-night comparison obtained using a pressure modulated radiometer. A summary of the altitude profiles in the latitude range of 40-50°N is shown in figure 4-11. Given the accuracy of the various techniques and the variability established by Noxon's more extensive column data set, the altitude profiles inferred from the measurements appear to be in reasonable accord.

An intercomparison problem may exist. The measurements of the groups using the near UV region of the spectrum and similar techniques, both spectroscopy and spectrophotometry (table 4-2), tend to measure NO₂ amounts which are lower by up to a factor of two. It is not clear whether this is a serious quantitative problem that needs to be resolved, or whether it is just indicative of a combination of inaccuracy and variability. In this regard it should be noted that measurements of column NO₂ Mankin (1978) using IR and Noxon et al. (1979), using visible wavelengths above the same location and same day agree to within 20%.

For the NO₂ measurements a more extensive intercalibration of techniques is required.

NO₃

NO₃ has been detected in the stratosphere using ground-based visible absorption spectroscopy and spectrophotometry with the Moon as a light source (table 4-2). Currently there is no latitudinal information. Noxon et al. (1978) and Noxon (private communication) have obtained some seasonal information on NO₃ column abundances above Fritz Peak (40°N). The amounts of NO₃ observed in March and April are $\sim 10^{14}$ cm⁻² but by July the column amount of NO₃ is below the detection threshold of 0.4×10^{14} cm⁻².

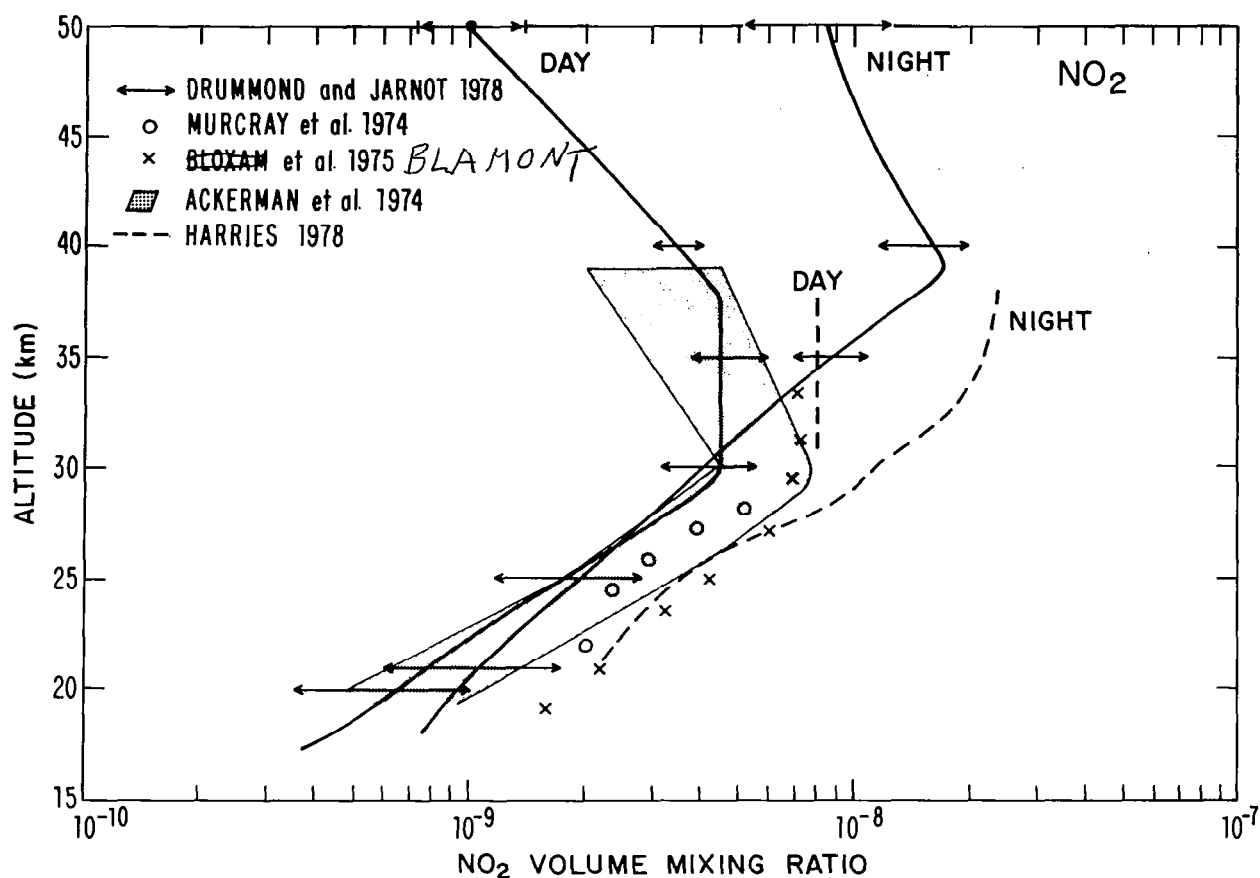


Figure 4-11. Nitrogen dioxide mixing ratio profiles

A problem arises in the determination of absolute amounts of NO_3 since there appears to be a factor of 1.3 uncertainty in the absorption cross sections of NO_3 . Noxon et al. (1978) use the higher cross sections of Graham and Johnston (1978). Use of the Wayne et al. (1978) cross sections would yield NO_3 amounts higher than those quoted.

N_2O_5

Stratospheric N_2O_5 has been searched for in emission in the $8.1\mu\text{m}$ region of the spectrum. Evans et al. (1978), using a radiometer, have a tentative detection of N_2O_5 a few hours after sunrise. They obtain 2 ppbv at 30 km. Murcray (1978 and private communication) has looked for N_2O_5 on several occasions but has set upper limits of $< 1.2 \times 10^{15} \text{ cm}^{-2}$ above 18 km before dawn in February 1979 in California and also Cold Lake, Alberta in February 1978.

NH_3

Ammonia has been measured in the troposphere by means of absorption features present in infrared solar spectra obtained from the ground (Murcray et al., 1978). Examination of infrared solar spectra obtained from balloon altitudes fails to show any absorptions due to NH_3 , corresponding to an upper limit of 0.2 ppb at 20 km.

HNO₂

Nitrous acid has a number of absorption bands in the infrared including one in the window between 1000 cm⁻¹ and 800 cm⁻¹. This band is stronger than the 895 cm⁻¹ HNO₃ band and occurs in a region of little overlap with other absorbers. Emission spectra obtained at an altitude of 40 km looking down at 3.5° covering this spectral region have been examined for any indication of emission by HNO₂ and no evidence of any such emission was found. It is estimated that if HNO₂ were present in the atmosphere at a mixing ratio of 10⁻¹⁰ at 26 km, it would be detectable in such spectra (Murcray, 1979).

HO₂NO₂

This compound has a strong absorption feature around 800 cm⁻¹. Atmospheric emission spectra obtained at 40 km looking at a depression angle of 3.5° have been examined for any indication of a feature which can be assigned to this molecule. No indication of such a feature is present. This yields the upper limit of 0.4 ppb as given in table 4-2 (Murcray, 1979).

HNO₃

Nitric acid profile and column measurements have been made by filter paper absorption (Lazrus and Gandrud, 1974b) by IR and submillimeter emission (Murcray et al., 1975a, Harries et al., 1974, Evans et al., 1976c, 1978), and by infrared absorption (Fontanella et al., 1975). Since HNO₃ is a relatively long-lived species, dynamics play a significant role in its distribution, both with latitude and altitude. Thus, the altitude profiles which have been presented in the literature show large variations which are associated with motion rather than any measurement error. The effect of transport must be taken into account in comparing experimental profile with model calculations. The effect of transport is illustrated by comparing a profile obtained at 33°N with one from 51°N as given in figure 4-12. The lowering in altitude of the peak of the mixing ratio is believed to be the result of the lower tropopause present at the high latitude. This effect also accounts in part for the variation in column data with latitude observed by Murcray et al. (1975a) since the lowering of the peak results in a greater column density. It should be pointed out, however, that this is not a totally satisfactory explanation for these observations, since at the higher latitudes the aircraft penetrates the layer and this should result in a decrease in column density at the higher latitude which is not observed.

Seasonal variability is not firmly established. However, the latitude survey data (Murcray et al., 1975a) appear to indicate lower HNO₃ amounts in summer than in winter, and Alaska profiles obtained in the fall seem to be higher than those obtained in the spring (figure 4-13).

The data obtained with the various techniques are in reasonable agreement. However, the filter data appear to be consistently lower than the infrared techniques, and the reason for the disagreement should be determined.

Atomic Chlorine

To date atomic chlorine has been measured only by *in situ* resonance fluorescence using its ²D_{5/2} - ²P_{3/2} transition at 118.9 nm (Anderson et al. 1977). The measurements were performed using apparatus mounted in an aerodynamically shaped pod lowered through the stratosphere at a controlled rate (~40 to 100 m/s) by a stabilized parachute released from a balloon near 44 km. The atmospheric flow passes unrestricted through a hollow detection chamber in the pod which (a) isolates the detector from the photon beam which induces the fluorescence and from the stratospheric radiation environment and (b) contains the flow so that the controlled chemical conversion used for measurements can be carried out. The resonant photon beam which induces fluorescence in atomic chlorine is formed by collimating the output from a low pressure microwave plasma discharge of helium and molecular chlorine. Resonance fluorescence from the interacting chlorine is detected by a cesium iodide cathode photomultiplier. A background count rate from the photomultiplier in

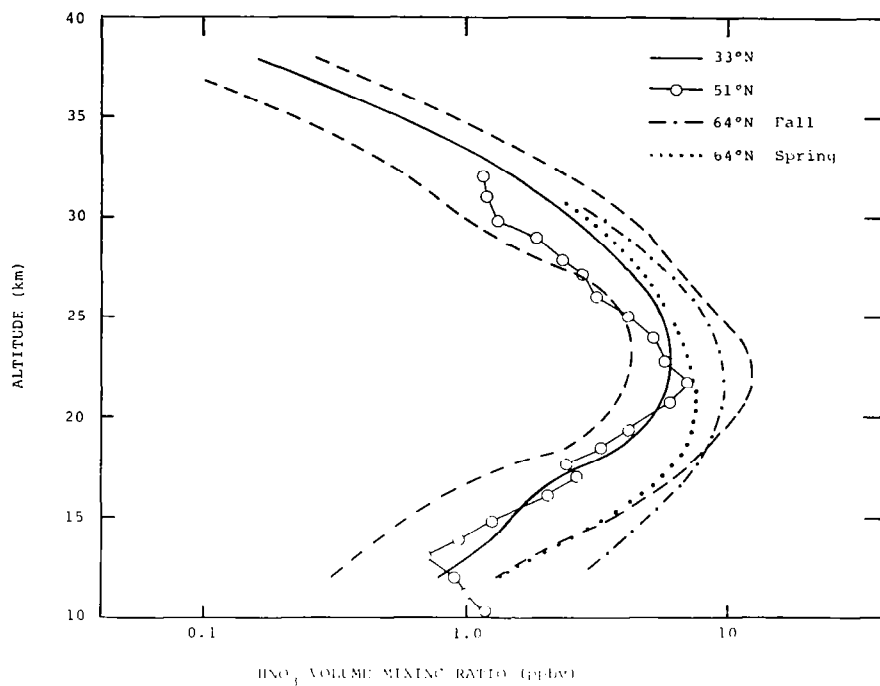


Figure 4-12. Shown are nitric acid mixing ratio profiles measured by IR and submillimeter emission, IR absorption, and filter paper absorption.

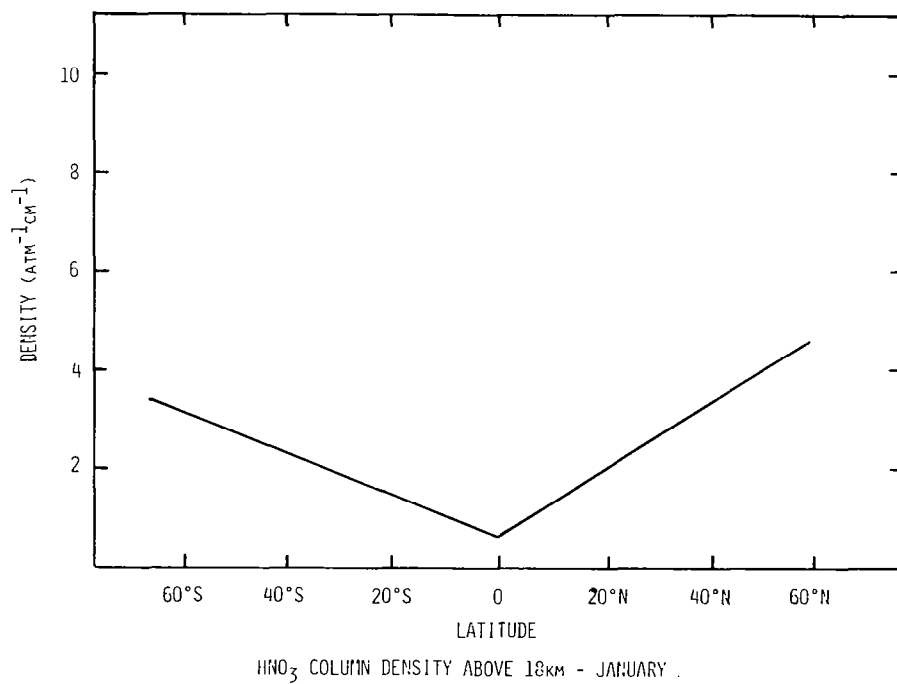


Figure 4-13. Illustrated is the nitric acid column density above 18 km versus latitude. (Murcray et al., 1975)

the absence of Cl is determined periodically during the descent through the stratosphere by adding a controlled flow of C_2H_6 into the detection chamber which reacts rapidly with atomic chlorine to eliminate it from the chamber.

Measurements of atomic chlorine have been made from Palestine, Texas, near local noon on July 28 and December 8, 1976. Results of these measurements are shown in table 4-2 and figure 4-14. A third measurement of atomic chlorine made on 2 October 1976 reported earlier (Anderson et al., 1977) is not included here because on that flight, an O_2 absorption cell used as a filter in the measuring apparatus was subsequently found (Anderson et al., 1979) to have stabilized at a pressure a factor of ten below its nominal design value.

ClO

Stratospheric ClO has been measured by the same *in situ* resonance fluorescence techniques used for measuring Cl (Anderson et al., 1977, 1979) and remotely by laser heterodyne radiometry (Menzies, 1979) from a balloon. A tentative detection of stratospheric ClO has been obtained from aircraft-based microwave radiometry (Waters et al., 1979).

For the *in situ* resonance fluorescence measurements the atmospheric ClO is first converted to Cl by adding NO to the atmospheric flow prior to its entry into the detection chamber. Fluorescence from the resulting Cl is then detected as described above for the atomic chlorine measurement. Ten balloon flights, in which the apparatus to measure ClO functioned as designed have been reported to date (Anderson et al., 1979 and private communication); all were from Palestine, Texas, and most occurred near local noon. Atomic chlorine was simultaneously measured on flights on July 28, 1976 and December 8, 1976; certain of several other species (OH, O_3 , NO, HO_2 , O) were measured on the other flights. The results for ClO are shown in table 4-2 and figure 4-15.

For the laser heterodyne radiometer measurement of stratosphere ClO, a CO_2 laser local oscillator was used in a balloon-borne radiometer to observe the $R(13/2)\Omega = 3/2$ vibration-rotation line of ^{35}ClO in the sunset absorption spectrum. This measurement was also performed from Palestine, Texas, on 20 September 1978. An absorption feature, most pronounced at an observation path having 33.8 km tangent height, was detected at a frequency within ~ 15 MHz of the laboratory value for the ClO line. The agreement between the observed and laboratory ClO line frequency is within the expected laboratory uncertainty and, after investigating potential absorption by other species, the observed absorption line was concluded to be due to ClO. The profile retrieved from the laser heterodyne radiometer measurement is given in table 4-2 and figure 4-15.

Stratospheric emission from three millimeter-wavelength ^{35}ClO rotational transitions has been searched for with aircraft-based microwave radiometers by Waters et al. (1979). The $J = 9/2 - 7/2$ transition at 167 GHz was searched for on five flights occurring between May 30 and June 15, 1977 and between latitudes 36° and 53° ; the $J = 13/2 - 11/2$ transition at 241 GHz on flights on 26 and 27 June 1977 between 41° and 54° N; and the $J = 15/2 - 13/2$ transition at 278 GHz on August 1, 1977 between 37° and 43° N. Data for all three transitions were taken during midday. The millimeter-wavelength data suggest the presence of ClO in the stratosphere but its detection by these techniques is not definitive. The most sensitive millimeter-wavelength result was obtained from the 278 GHz observation (made over the Pacific, west of San Francisco). This result indicates that, at the time and place of the measurement, there was (a) more than ten times less stratospheric ClO than measured two weeks later by the *in situ* resonance fluorescence technique from Palestine, Texas; (b) more than two times less than measured on 20 September 1978 by the laser heterodyne radiometry technique; and (c) $\sim 30\%$ less than the mid-range of current model predictions (comparison with model predictions is discussed further in a later section). The stated uncertainty in the microwave radiometry results is $\sim \pm 30\%$, which includes the effect of uncertainty in the stratospheric temperature profile. From the aircraft platform where the microwave measurements were made, the vertical resolution which can be achieved is only ~ 10 km, $\sim 10\times$ coarser than results from the other two techniques mentioned above; the spectral characteristics of the instrument made it sensitive to ClO between altitudes of approximately 25 and 45 km.

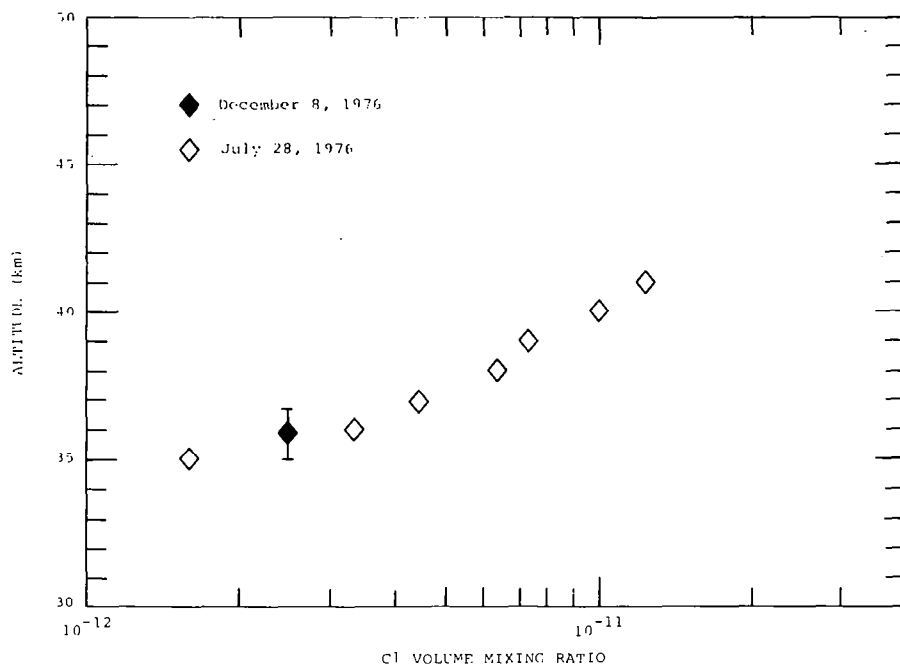


Figure 4-14. Shown are chlorine mixing ratio profiles measured by resonance fluorescence near noon at 32°N . Accuracy is $\pm 35\%$. (Anderson et al., 1977, 1979).

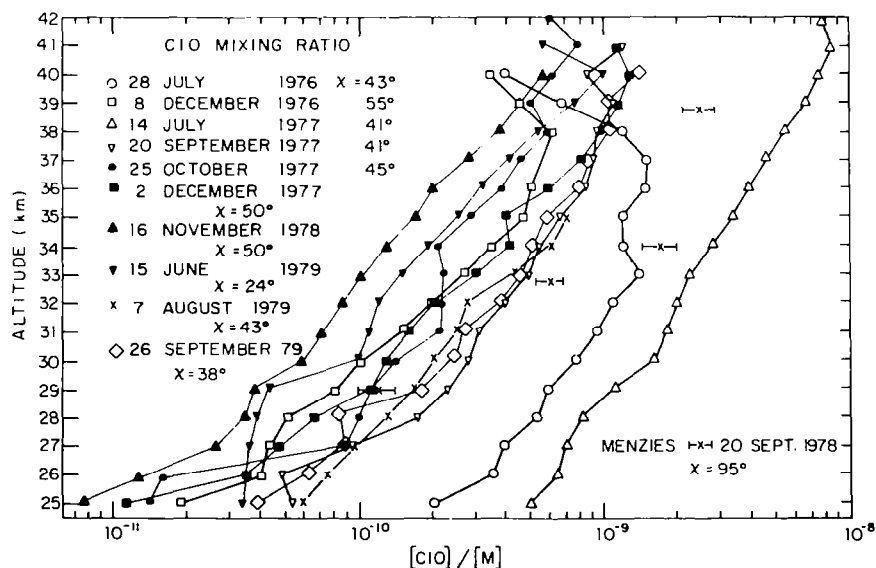


Figure 4-15. Shown are chlorine oxide mixing ratio profiles measured by chemical conversion to chlorine with subsequent resonance fluorescence detection (Anderson et al., 1979) and by laser heterodyne detection of IR absorption (Menzies, 1979).

HCl

Stratospheric HCl concentrations have been measured by three different techniques: By high resolution spectroscopy in absorption (viewing the Sun near the limb), (Farmer et al., 1976, Raper et al., 1977, Williams et al., 1976, Ackerman et al., 1976); by pressure modulated radiometry, again in absorption (Eyre and Roscoe, 1977); and by an *in situ* method using a filter collection technique followed by wet chemical analysis, (Lazrus et al., 1977). The latter method is not specific to HCl but determines *total acid chlorine* in the atmospheric sample and thus should yield an upper bound to the HCl concentration values.

Figure 4-16 illustrates the results. The spectroscopic results show an apparently high degree of consistency, but it should be noted that conservative estimates of the uncertainties associated with them (including all sources of error) are $\pm 30\%$ at intermediate altitudes, increasing to $\pm 50\%$ at the extremes of the profile. The data of Lazrus et al. fall well below the spectroscopic values above 25 km, the opposite of what would be expected if the two techniques were mutually consistent. Problems with uncertainty in the details of the CH_4 spectrum and the degree to which CH_4 lines contaminate the HCl features may have caused overestimation of the HCl abundances in the case of the radiometer measurements (Eyre and Roscoe, 1977). Considerations of the mechanisms involved in the formation and recycling of HCl, together with the known characteristics of other analogous species, suggest that HCl might be expected to exhibit a significant degree of variability in the vertical. No evidence for such variability has been seen in the rather limited data available to date, and this may well be the result of the rather large-scale averaging characteristic of the optical methods. This should be borne in mind when making comparison between this suggested mean profile and model predictions.

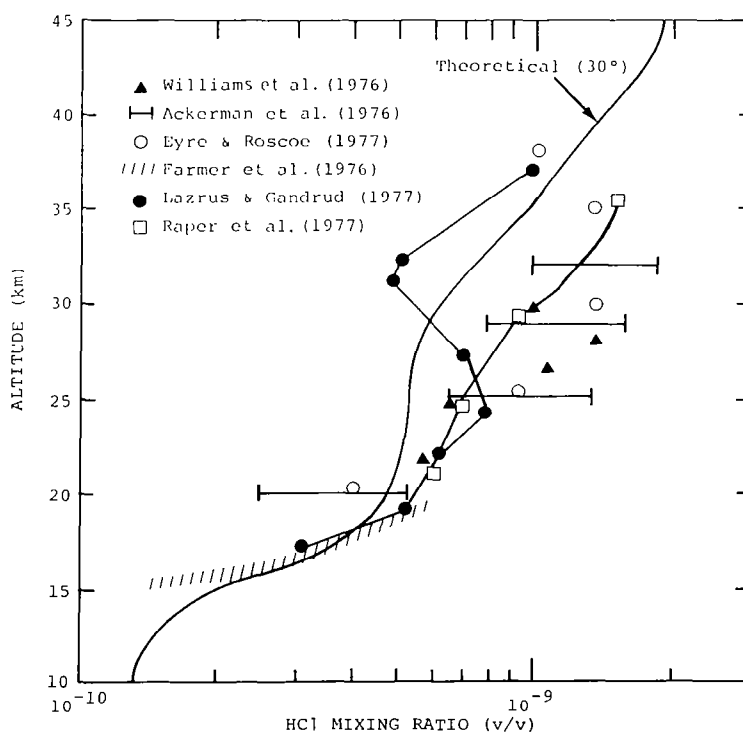


Figure 4-16. Illustrated are hydrochloric acid mixing ratio profiles measured by IR absorption and trapping on base-impregnated filters.

ClNO_3

Early calculations of the possible perturbations of the ozone layer resulting from the use of fluorocarbons were based on the assumption that HCl was the predominant sink for the chlorine. In 1976 Rowland et al. suggested that ClNO_3 might also be an important stratospheric sink. Model calculations based on the available laboratory data confirmed a significant role for ClNO_3 in stratospheric chemistry. Recent revisions in some of the rates reduce the predicted amount of ClNO_3 expected to be present; however it still appears to be a significant sink.

Attempts to measure chlorine nitrate have been made using two techniques, infrared spectroscopy and base-impregnated filters. Chlorine nitrate is a relatively strong infrared absorber with intense bands occurring in the 780 cm^{-1} and 1292 cm^{-1} region (Graham et al., 1977). Murcray et al. (1977) examined infrared solar spectra obtained during a balloon flight in 1975 covering the 780 cm^{-1} region and estimated an upper limit for its mixing ratio of 2 ppbv at 30 km decreasing to 4×10^{-11} at 15 km. Data covering the 1292 cm^{-1} region were obtained during a balloon flight made March 4, 1977 (Murcray et al., 1978). Examination of the spectra obtained during the flight resulted in a tentative identification of ClNO_3 in these spectra with a resulting mixing ratio of 2 ppbv at 26 km. Spectra covering this region at much higher resolution were obtained during a balloon flight made October 27, 1978. The identification of the ClNO_3 is confirmed in these spectra and the results have been used to determine the mixing ratio profile given in table 4-2.

The results obtained by the infrared techniques differ considerably from those obtained by the base-impregnated filter techniques (Lazrus et al., 1977). Lazrus has shown that these filters respond not only to HCl but also to ClNO_3 . Thus, his measurements represent the sum of both HCl and ClNO_3 ; however, when his results are compared with the infrared data for HCl they indicate much less HCl than observed by the remote sensing technique. This presents a problem in attempting to interpret his results in terms of ClNO_3 . If one accepts his measurement as representing an upper limit for ClNO_3 there is serious disagreement between the ClNO_3 results. The uncertainty in the results obtained with both methods is large, but not large enough to bring the results into agreement.

HOCl

Laboratory infrared spectra of the 3600 cm^{-1} and 1240 cm^{-1} bands of HOCl have recently been recorded by Sams et al. (1979) and Wells et al. (1979). While this work provides accurate frequencies for the individual transitions in the two regions, knowledge of their intensities is rendered very uncertain by the difficulties associated with measurement of the quantity of absorber in the sample cell. The high resolution balloon spectra of both Murcray et al. and Farmer et al. are potentially able to provide information on stratospheric HOCl; at the time of this writing no features due to HOCl have been positively identified in the spectra, and the current uncertainty in the line intensity values does not allow a reliable upper limit for this important species to be quoted. It is to be hoped that additional quantitative laboratory data will be made available in the near future.

SO_2

Lower stratospheric SO_2 data were reported by Jaeschke et al. (1976) using a method based on the chemiluminescence effect which occurs during oxidation of sulfite with potassium permanganate in aqueous solution. The measured SO_2 mixing ratio profile appears to be remarkably constant with a mixing ratio of about .05 ppb, see figure 4-34.

COS

Carbonyl sulfide (COS) was detected by Inn et al. (1979), and mixing ratio measurements are reported (see table 4-2 and figure 4-35) for altitudes of 15.2 to 31.2 km. A large volume, cryogenic sampling system mounted on board a U-2 aircraft has been used for lower stratospheric measurements and a balloon platform for measurement at 31.2 km. The gaseous sample was analyzed for sulfur compounds by gas chromatograph-flame photometric detection methods.

CO

Data on stratospheric CO are summarized in figure 4-17 and table 4-2. Two profiles obtained by infrared spectroscopy are included. The older measurement of Goldman et al. (1973) reaches only into the lower stratosphere. Recent data by Farmer et al. (1979) are the only valid data above 20 km. Cryogenic sampling and subsequent gas chromatograph analysis in the laboratory by Fabian et al. (1979a) are also given in the table and figure. This technique is sensitive to CO production due to O₃ interaction with hydrocarbons absorbed on the inner walls of the inlet line. It is felt that this effect is minimal below 20 km where the O₃ concentration is reduced.

6. pp. 168 and 185. In the discussion of CO, reference should be made to the data down to 45 km by Waters et al. (1976). Waters, J. W., W. J. Wilson, and F. I. Shimabukuro, Microwave measurement of mesospheric carbon monoxide, *Science*, 191, 1174-5, 1976.

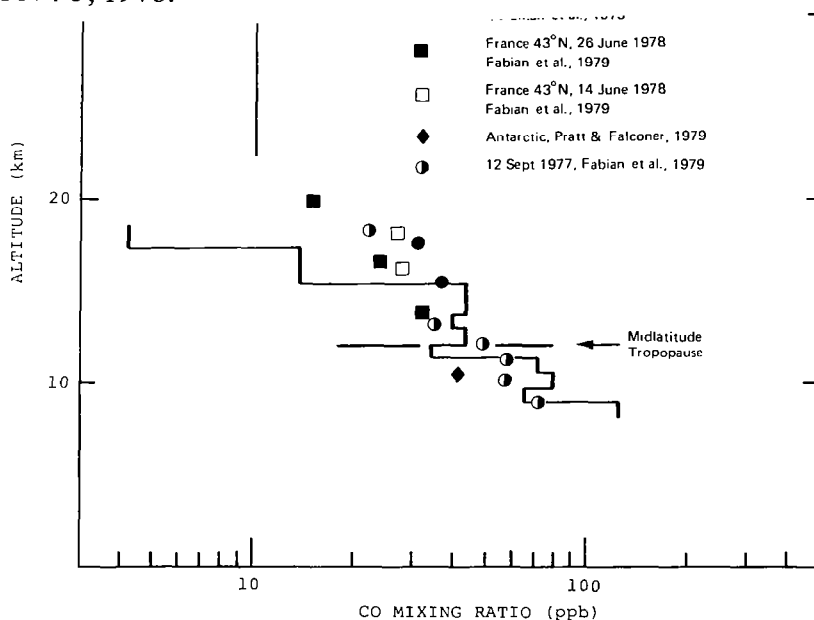


Figure 4-17. Carbon monoxide mixing ratio profiles are shown. Measurements were obtained by IR spectroscopy and gas chromatography of cryogenic samples.

CH₃OH

Only an upper limit estimate of 1×10^{-11} mixing ratio is available for this species. This upper limit is based on an analysis of positive ion composition measurements. This conclusion is based on the failure to observe the ion CH₃OH₂⁺ which is formed as the result of proton transfer between H₃O⁺ • (H₂O)_n and CH₃OH, (Arnold et al., 1977; Ferguson, 1978; Fehsenfeld et al., 1978).

H₂CO

The moderately strong bands of H₂CO in the near infrared at 2700 cm⁻¹ lie in the range of balloon spectra recorded at midlatitudes (Farmer et al., 1979). Since laboratory spectra of these bands have been analyzed recently by Brown (1979) it is possible to search the high resolution stratospheric spectra for features of H₂CO. The spectral region is contaminated by lines of several of the more abundant stratospheric gases (principally CH₄ and O₃ so that a very careful reconstruction of the spectrum is necessary before an unequivocal identification of H₂CO can be made. At the time of writing it can be stated, however, that if H₂CO were present in the stratosphere at altitudes in the 26 to 30 km region with a mixing ratio in excess of 5×10^{-10} (by volume) it would be clearly visible in the spectra. It is expected that this value will be refined, or a positive identification made, from further analysis of the higher resolution observational data being acquired currently.

C₂H₂, C₂H₆

Vertical profiles of acetylene and ethane have been obtained from analysis of mid and low latitude air samples (Cronn and Robinson, 1979). The values drop off precipitously in the first 3 km above the tropopause; low latitude upper tropospheric values are appreciably less than for midlatitudes.

COMPARISON WITH THEORETICAL MODELS

An important aspect of validation of numerical model representations of the physical and chemical processes believed to be occurring in the stratosphere is the comparison of computed values with data available from the measurements. In the following sections, the results of one-dimensional models (those used for the predictions in Chapter 7) are shown in the plots as a range of values, reflecting differences between models (e.g. global mean versus midlatitude average) plus uncertainties in some of the chemistry used in the calculations. Results for two- and three-dimensional models were unavailable at the time of the meeting.

O(³P)

A comparison between model calculated distributions and the mean of the six *in situ* observations from figure 4-1 are shown in figure 4-18, indicating agreement well within the cited accuracy of the observations, $\pm 30\%$. The excellent agreement may be fortuitous because, with the exception of the data of December 2, 1977, ozone was not simultaneously observed, and the calculations use model-generated ozone distributions that are more appropriate for a climatological mean. A detailed comparison between atomic oxygen and ozone is available for one simultaneous *in situ* observation, however, which is displayed in figure 4-19 comparing the [O(³P)]/[O₃] ratio observed on December 2, 1977 with the calculated ratio for the appropriate solar zenith angle by Logan et al. (1978). The [O(³P)]/[O₃] ratio is a particularly fundamental quantity and must be defined with significantly better precision than that indicated in figure 4-19 since O(³P) is the rate limiting odd oxygen constituent in the major gas phase catalytic cycles throughout much of the stratosphere.

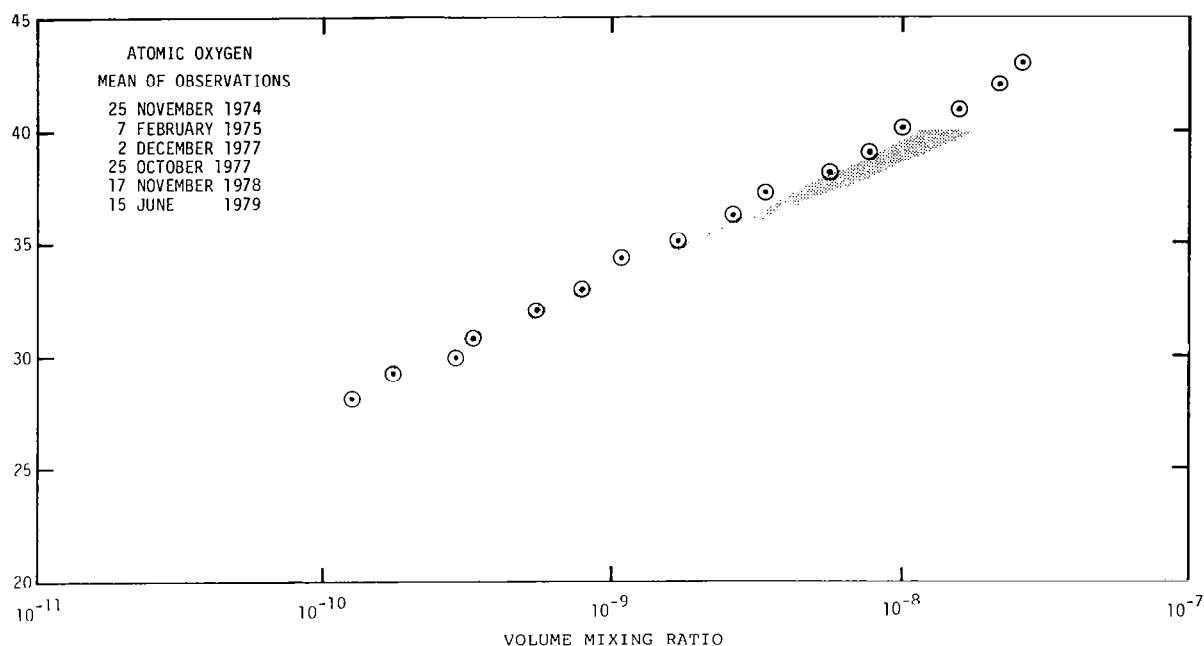


Figure 4-18. The mean of observations ($\odot$) and the range of 1-D model values (shaded) for $O(^3P)$.

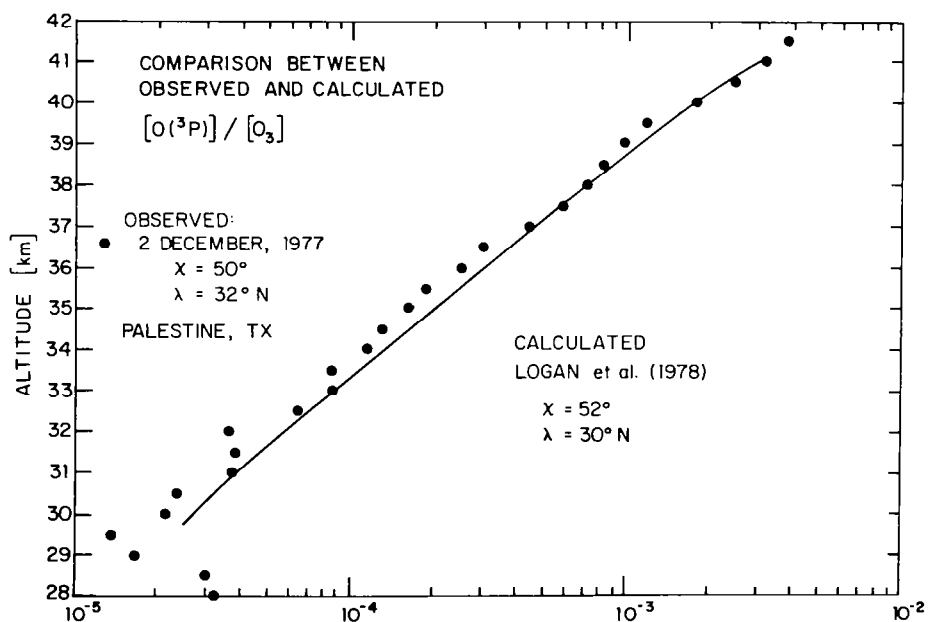


Figure 4-19. Comparison between the observed simultaneous *in situ* $[O(^3P)] / [O_3]$ ratio and the calculated quantity at the appropriate solar zenith angle.

OH, HO₂

There does not appear to be any significant disagreement between theoretical calculations and the few available measurements of the distributions of OH and HO₂ in the stratosphere (see figures 4-20 and 4-21). However, data is available only between 30 and 40 km. Also, a problem in comparing with these data is that the variability of the structure for both species exceeds measurement precision, suggesting that the different air masses being measured have significantly different time histories. Concurrent measurements of various species (OH, HO₂, O₃, H₂O, etc.) are desired in the future to study this variability. Studies of the HO₂/OH ratio and the (HO₂ + OH)/H₂O ratio are also of particular importance.

Comparison of the total OH column as calculated by current 1-D models with the observations of Burnett et al. (1979) do not indicate any significant differences. However, seasonal and diurnal variation effects need further examination.

Total NO_x

The theoretical models are presently calculating up to approximately a factor of two or more NO_x (NO + NO₂ + HNO₃) than is being measured. See figure 4-22. It should be noted that *in situ* measurements of all three species are not available with the same technique.

It appears that the cause for the large difference is due to the model predicting too much N₂O in the stratosphere; N₂O being the primary source for NO_x in the stratosphere. The N₂O content in the one-dimensional models used in this comparison results to a large extent from the choice of vertical transport coefficient, K_z, used in the calculations. The transport coefficients used have been based on fitting the methane, CH₄, and nitrous oxide, N₂O, profiles plus the chlorofluoromethanes. Current models are capable of fitting the methane profile, but are not able to fit the N₂O, CF₂Cl₂, and CFCl₃ profiles without adjusting the transport used in the lower stratosphere. Doing this, however, would destroy agreement between the modeled and observed CH₄ profile. In addition to the vertical transport, the distribution of methane is determined by the OH content. Thus, changing the transport coefficient would require that some mechanism be found for reducing the OH concentration in the 20 to 30 km region of the stratosphere. At present, this is unresolved, and the one-dimensional models calculate too much total NO_x.

NO

The average of measurements shown in figure 4-23 is for midlatitudes near local noon. When compared to model calculated noon profiles, we find significant differences above 30 km with the maximum difference occurring in the upper stratosphere where NO is the dominant NO_x species. The difference between models and observations is probably not conclusive due to the large spread in the various measurements.

NO₂

A comparison is shown in figure 4-24 between the model calculated range of distributions for NO₂ and that measured near sunset near the fall equinox at 40 to 50°N. The models correspond more to 30°N equinox conditions which leads to uncertainty regarding the differences found in the lower stratosphere.

HNO₃

When compared to available data (figure 4-25), it is clear that current models predict too much HNO₃ in the stratosphere. This may be at least partially explained, especially at altitudes below 25 km, by the high total NO_x being calculated by current models. However, this does not appear to be sufficient to explain the entire difference above 25 km. Above 30 km, the difference may be due to an incorrect treatment of photolysis.

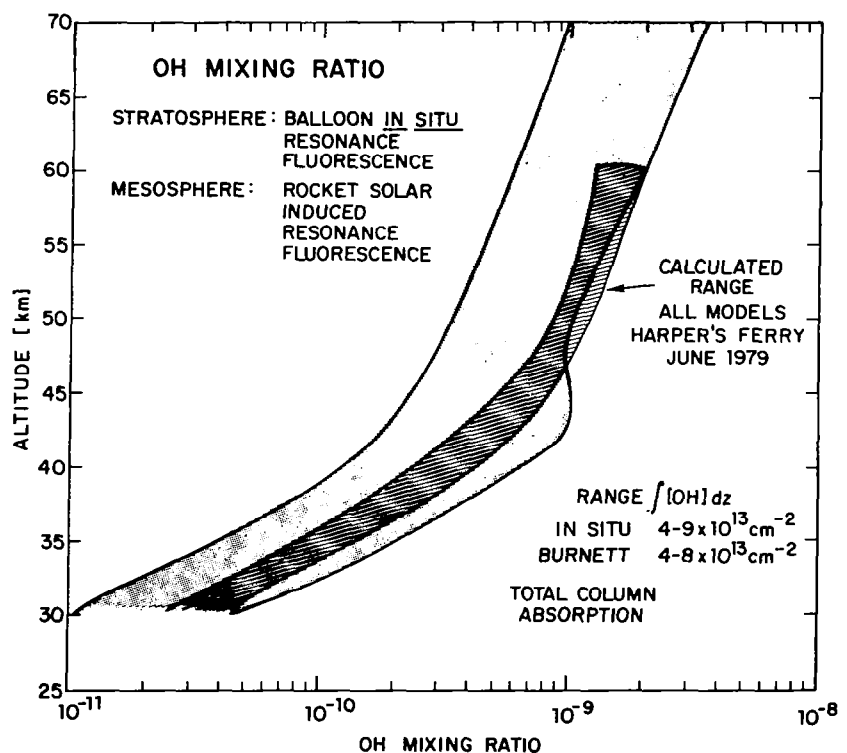
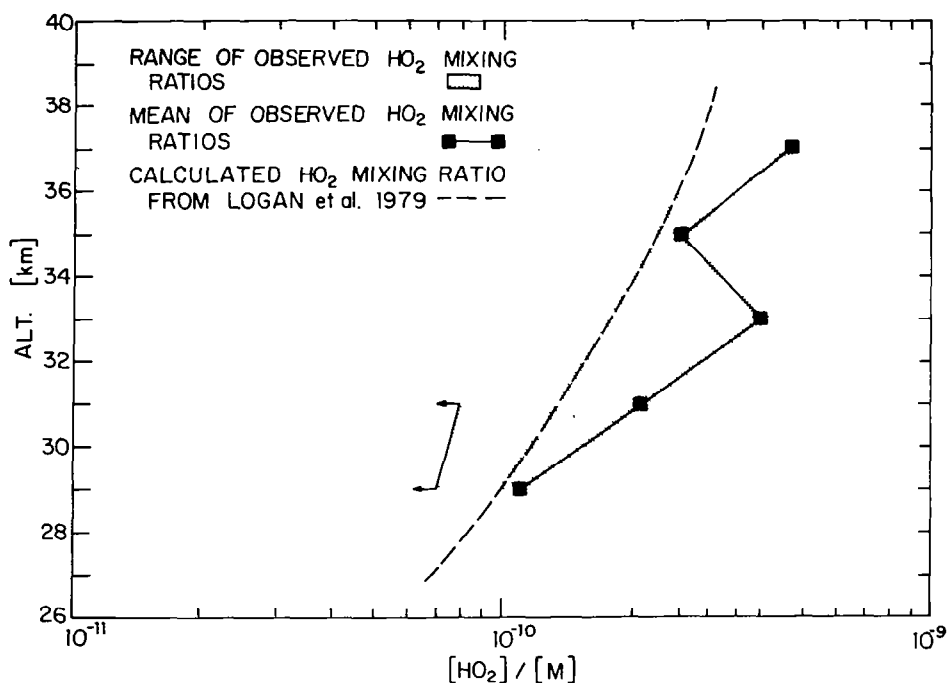


Figure 4-20. The mean of observations and the range of 1-D models for OH.

Figure 4-21. The mean and range of measured HO_2 compared with the range in model predictions.

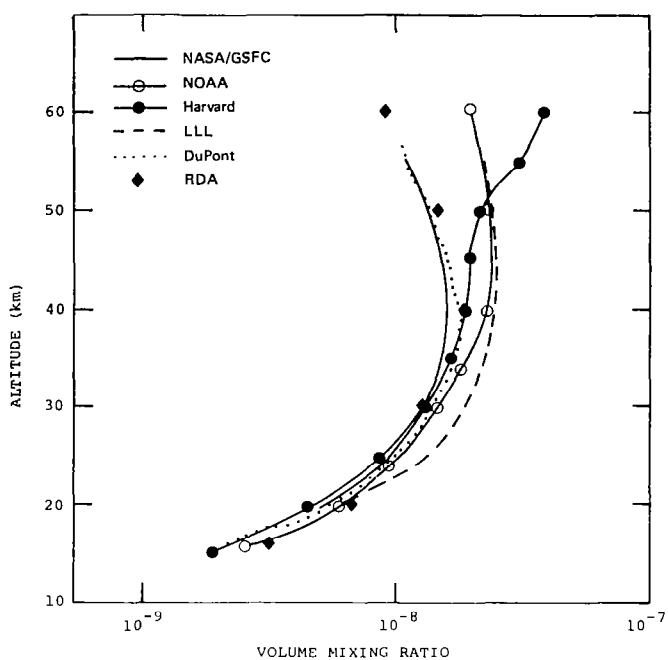


Figure 4-22. The range of total NO_x profile predictions for several 1-D models is presented.

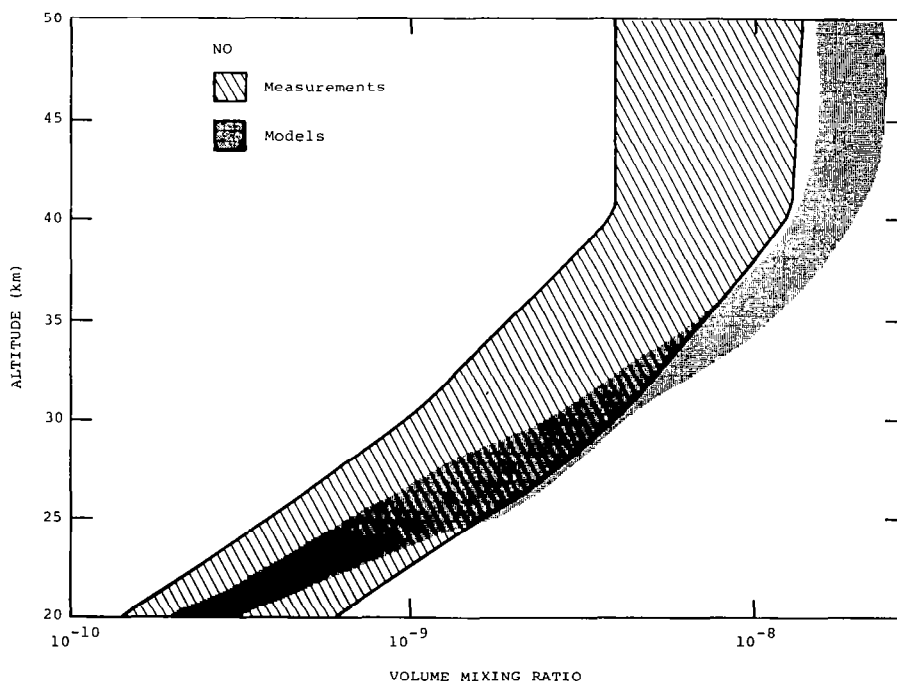


Figure 4-23. The observed range and the range of predictions by 1-D models are illustrated for NO.

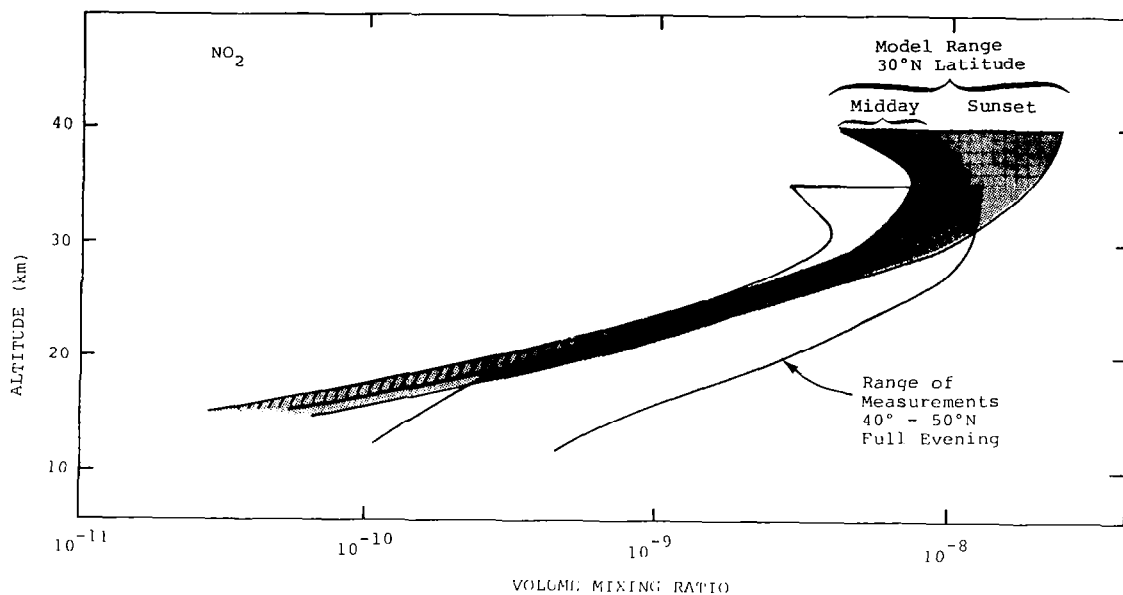


Figure 4-24. Shown is the range of measurements and the 1-D model range for NO_2 .

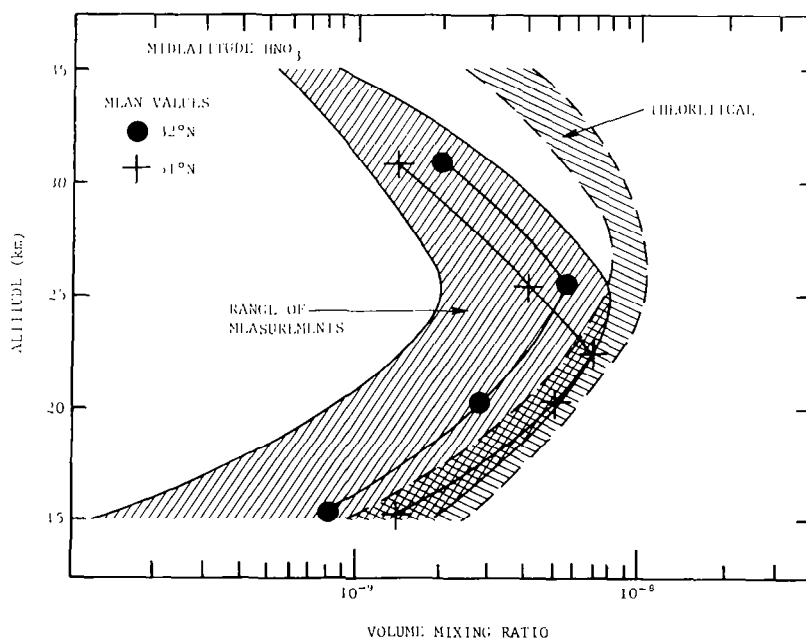


Figure 4-25. The range of measurements (at 32°) and the mean of measurements (32°N and 51°N) for HNO_3 compared with the range of 1-D model values.

HNO₃/NO₂ Ratio

Models currently calculate this ratio to be much higher than found by available measurements (not taken with the same instrument, however). One possible explanation would be for a sink to be found for OH in the lower stratosphere to reduce the OH concentration currently being calculated. Results are summarized graphically in figure 4-26.

N₂O₅

One-dimensional models currently calculate an N₂O₅ concentration of ~2.5 ppb near sunrise as compared to the one measurement of 2 ppb found a few hours before sunrise by Evans et al. (1978). Until further measurements are made, the comparison is inconclusive.

Cl, ClO

Figure 4-27 compares model predictions and measurements of Cl and ClO. The model predictions shown apply to 32°N, where all reported measurements to date have been made, and midday equinox (fall or spring) solar zenith angles. Variations of the predicted Cl and ClO profiles with season are small on the scale shown and very small compared to the range of measured profiles. The indicated range of calculated profiles encompasses the results of various groups and chemical models and is discussed further in Chapter 7.

For ClO the resonance fluorescence measurements, with the exception of the July 14, 1977 measurement, are within a factor of about 2 of the predicted ClO abundances near the mixing ratio profile peak. The September through December measurements show a significantly sharper decrease in ClO at altitudes below the mixing ratio peak than is predicted. The July measurements give more ClO than the September through December measurements. The July 14, 1977 measurement gives 6 × more ClO than predicted near the mixing ratio peak, which exceeds the total chlorine mixing ratio believed to be present in the stratosphere. The laser heterodyne radiometer measurement also shows more than 2 × more ClO than predicted near the mixing ratio peak and sharper decrease in ClO at lower altitudes than is predicted; it also gives approximately 3 × more ClO than the resonance fluorescence measurements performed at the same time one year earlier. The millimeter-wavelength results imply slightly less ClO than the mid range of model predictions and substantially less ClO than the July resonance fluorescence and the September 20, 1978 laser heterodyne results. A broader data base is needed to explain the difference in these results, as well as the overall large (> 10 ×) variation in the ClO profiles which is observed by resonance fluorescence but which is not predicted by models.

Because of the implication of the July 14, 1977 resonance fluorescence ClO measurement on our understanding of stratospheric chemistry, Anderson et al. (1979) have given its analysis special attention. After careful examination they have concluded the large ClO values are not due to instrument malfunctions and, using simultaneous measurements of other species, have concluded it implies either:

- ClO was injected into the observed region prior to the measurement in a time which is short compared with the chemical response time of odd oxygen or
- The reaction $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$ is not rate limiting in the closure of the chlorine catalytic cycle or
- There exists an odd oxygen production term proportional to ClO_x and competitive with direct O_2 photolysis in the middle and upper atmosphere.

At present it is uncertain which, if any, of these explanations is correct.

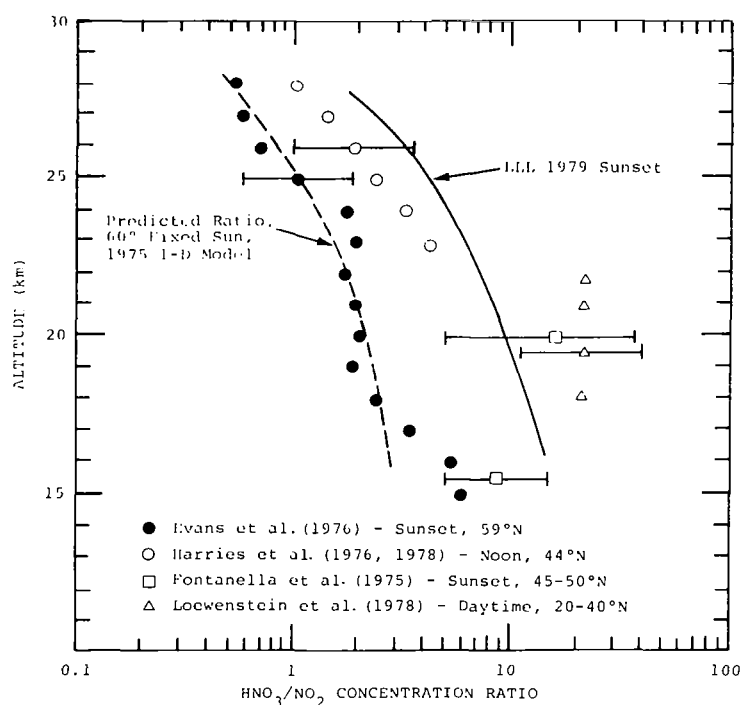


Figure 4-26. The ratio of HNO_3 to NO_2 for a variety of latitudes and local times is compared with results from 1-D models.

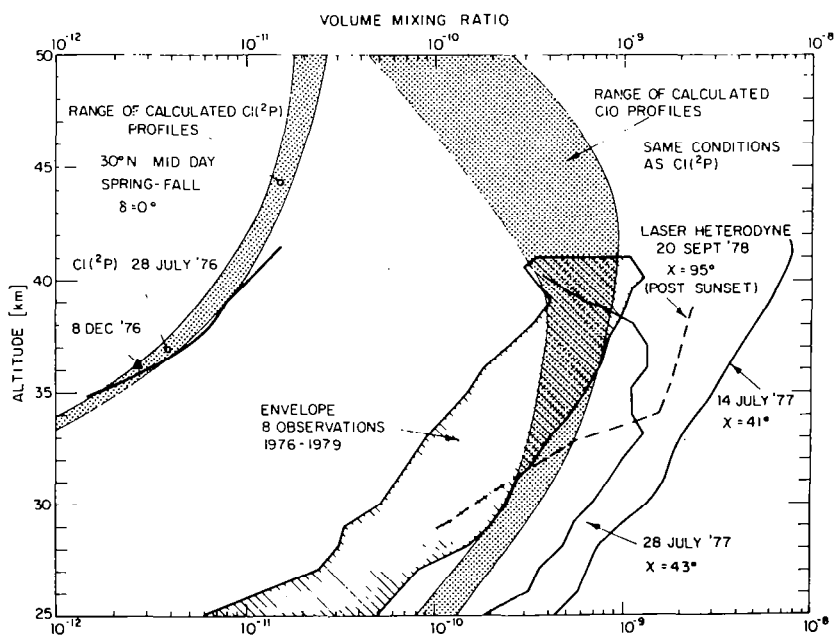


Figure 4-27. Comparison between observed and calculated ranges of atomic chlorine and chlorine monoxide.

The differences between theoretical calculations and observations in the ClO gradient below 35 km also requires attention. However, at present, speculations for explaining this range from the possibility of a missing chemical reaction or an incorrect rate constant in present theory to a possibility of its being an artifact of the transport parameterization in current models. A comparison between the mean of the observed ClO, excluding the July 14, 1977 observation which is not representative of "typical" midlatitude conditions, and the band of model calculated ClO is shown in figure 4-28.

Cl/ClO Ratio

The Cl/ClO ratio from the July 28, 1976 resonance fluorescence measurements has been examined by Anderson et al. (1979) and agrees to within measurement uncertainty with calculations. Figure 4-29 compares the measured and calculated Cl/ClO ratio. It is difficult at present to make any conclusions regarding this comparison because of the experimental uncertainties and the limited amount of data, however it does appear that models are not correctly predicting the slope of the ratio versus altitude.

HCl

Except for a possible difference (as large as 30 to 40% when compared with the IR spectra data; much larger if compared to the better of the radiometer data) above 30 km there does not appear to be any large disagreement between the measured data and the theoretical calculations of HCl (see figure 4-30). Also, the uncertainty in the data in this range is such as to probably encompass the areas of disagreement.

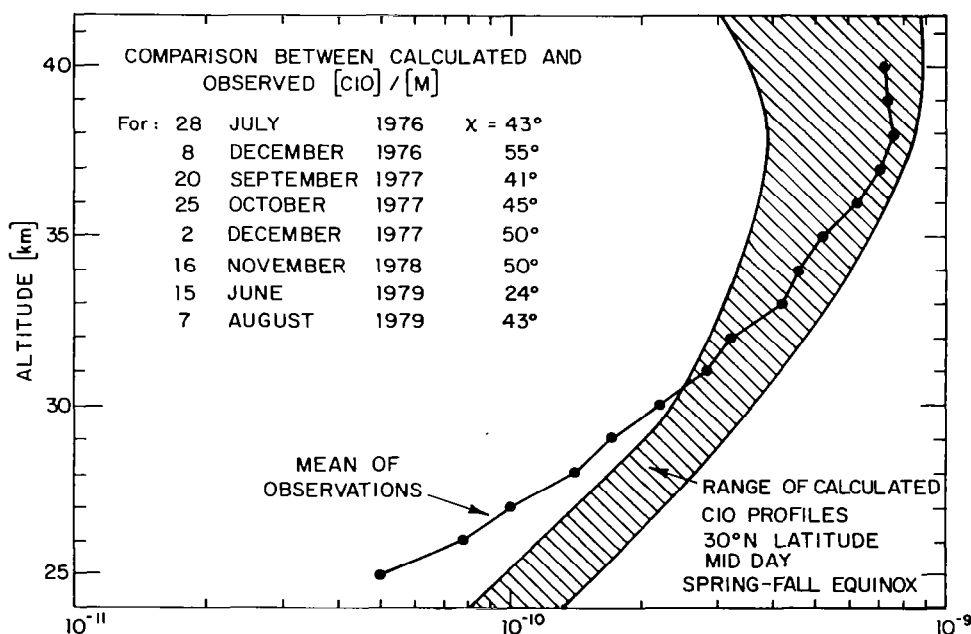


Figure 4-28. Comparison between the mean of the midday *in situ* resonance fluorescence observations and the range of calculated ClO distributions.

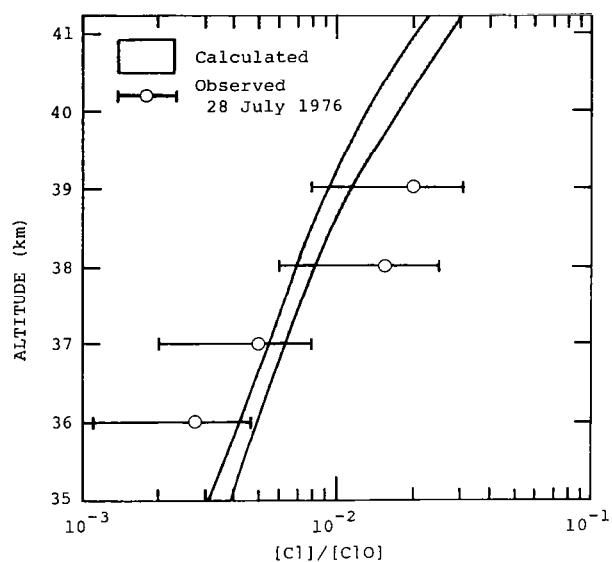


Figure 4-29. Shown is a comparison of the Cl/ClO ratio from 1-D models with a measurement by Anderson.

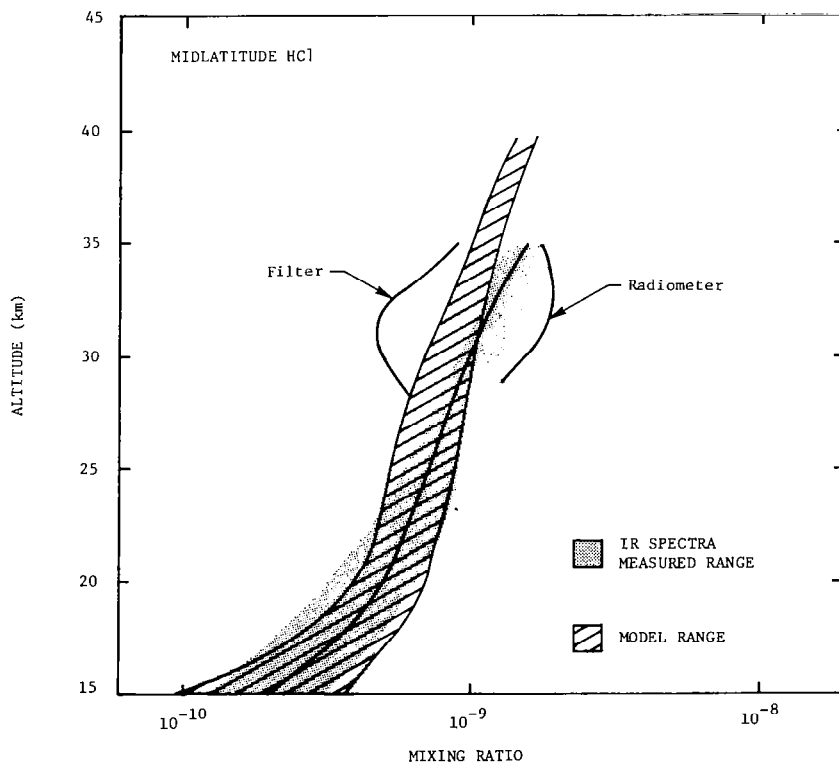


Figure 4-30. Midlatitude HCl range of measurements and model predictions are shown.

ClONO₂

As shown in figure 4-31, there is excellent agreement with the data given by Murcray (1979), for the upper limit of the range in present model uncertainty. This excellent agreement is obtained if the fast production rate for ClONO₂ is used in the calculations, whereas there is a factor of 2 difference if the slower production rate is used (see Chapter 1 discussion regarding the rate of production of ClONO₂). Until further data are available, it is difficult to make any conclusive statements regarding this specie. However, the limited amount of data available do not indicate any gross discrepancies between theory and observations.

Total ClO_x

There now exist a limited number of measurements for Cl, ClO, HCl, and ClONO₂ in the stratosphere. Except for three measurements of ClO taken in summer (Anderson, 1979; Menzies, 1979) there does not appear to be any large discrepancy in the total amount of ClO_x predicted and that observed. However, the summer measurements of ClO are so large as to require much more total ClO_x than capable of being produced by present estimates from known sources.

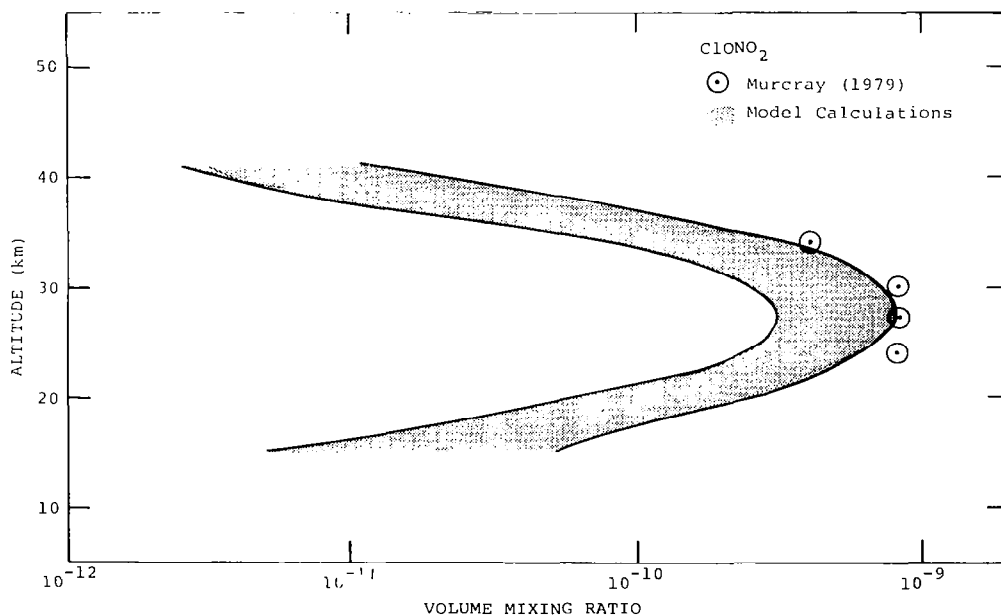


Figure 4-31. The range of model prediction and the observations of Murcray are shown for ClONO₂.

HF

Measurements of HF in the stratosphere have been made from spectroscopic observations of the R1 line of the 1-0 fundamental at 4040 cm^{-1} . Farmer et al. (1977, 1979) obtained a profile covering the 20 to 40 km region at 30° latitude; Zander et al. (1977) determined a total column abundance value above 28 km at northern midlatitudes; and Buijs (private communication) has obtained a vertical profile at 64° . In addition to these, *in situ* sampling using the filter collection/wet chemistry method have been reported by Mroz et al. (1977). The combined data are shown in figure 4-32. Intercomparison of the results is made difficult by the fact that the available measurements are made under very different conditions. The Zander value refers to the apparent volume mixing ratio obtained if the observed column total is assumed to be uniformly mixed. It provides a useful guide to the trend expected at altitudes above the highest reached by the other observers. The two infrared profiles (Farmer et al., Buijs et al.) diverge with increasing altitude, but this difference is reduced if the results are adjusted to take into account the approximately 5 km difference in the tropopause altitude at the latitude of two sets of data. The *in situ* data of Mroz et al., on the other hand, while in agreement with the spectroscopic results (within the stated errors) over much of the common altitude range, nevertheless show a considerably different altitude gradient. This, again, may be related to the fact that the filter technique records total acidic fluoride in the samples collected, rather than HF specifically.

HBr

Hydrogen bromide has been measured by Lazrus et al. (1979) using the acid filter technique. The data obtained by these investigators is given in table 4-2 and shown in figure 4-33.

Sulfur Constituents

The status of current model agreement, or disagreement, with atmospheric measurements of sulfur compounds is difficult to assess. Only one reliable measurement of SO_2 above the planetary boundary layer is available (Jaeschke et al., 1976). For COS the situation is better; an initial stratospheric height profile has been measured by Inn et al. (1979), and numerous low-altitude observations have verified its ubiquitous tropospheric distribution (Maroulis et al., 1977). Regarding CS_2 , however, just one preliminary, highly-uncertain measurement exists at Harwell, England (Sandalls and Penkett, 1976). Nevertheless, Turco et al. (1979c) and Sze and Ko (1979b) have calculated SO_2 , COS, and CS_2 profiles (which are compared to data in figures 4-34 and 4-35). Considering the meager data base, the agreement between theory and experiment seems reasonable.

Turco et al. have, in addition, determined a global budget for COS which is consistent with COS observations and other geophysical data. One important source of COS may be CS_2 , through its decomposition by OH (Kurylo, 1978; Sze and Ko, 1979a; Turco et al., 1979c). In the atmosphere COS is destroyed primarily by reaction with OH below 25 km (Kurylo, 1978, Sze and Ko, 1979) and by ultraviolet photolysis above 25 km (Crutzen, 1976). SO_2 (some of which is formed by the decomposition of COS and CS_2) reacts in air with OH to produce HSO_3 , whose fate is as yet undetermined but likely leads to the formation of H_2SO_4 . Because hydroxyl radicals play a key role in the sulfur chemical cycle, that cycle is subject to a large degree of uncertainty.

In figure 4-34, the difference in the SO_2 predictions above 25 km arises in part because Turco et al. (1979c) consider sulfur vapor to be recycled from evaporating aerosols above 30 km, initially as H_2SO_4 and, after photolytic decomposition, as SO_2 . Interestingly, their model predicts H_2SO_4 concentrations greater than $10^6/\text{cm}^3$ above 30 km, which is consistent with the recent tentative identification of H_2SO_4 molecules clustered to stratospheric negative ions (Arnold and Henschen, 1978).

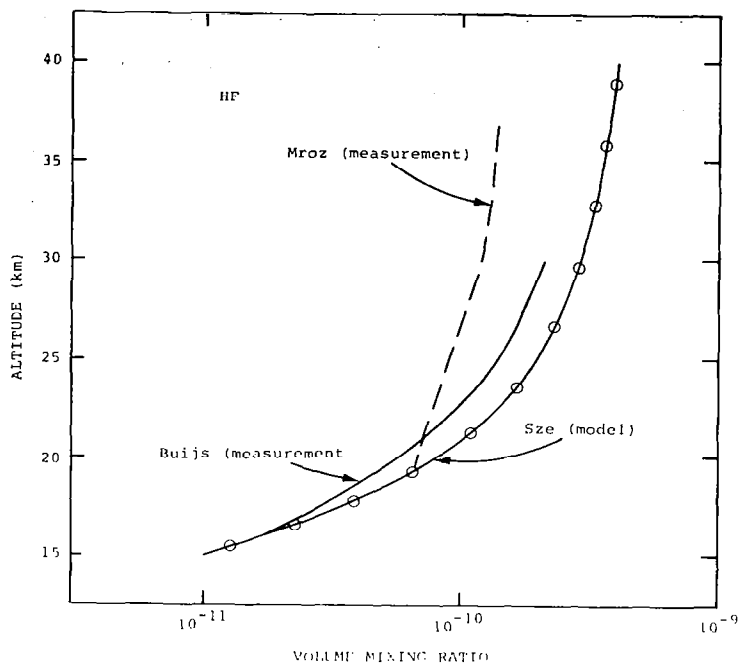


Figure 4-32. Two measured profiles (Mroz and Buijs) and a 1-D model (Sze, 1977) are compared for HF.

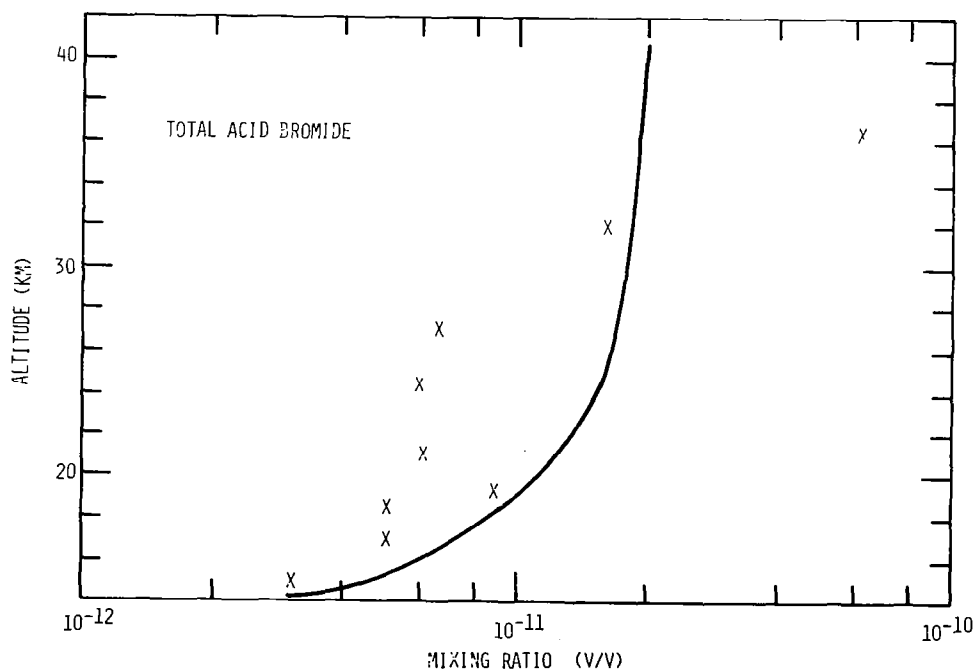


Figure 4-33. Mixing ratio profiles for acidic bromine compounds are shown. Determinations by trapping on base-impregnated filters by Lazrus et al., 1979.

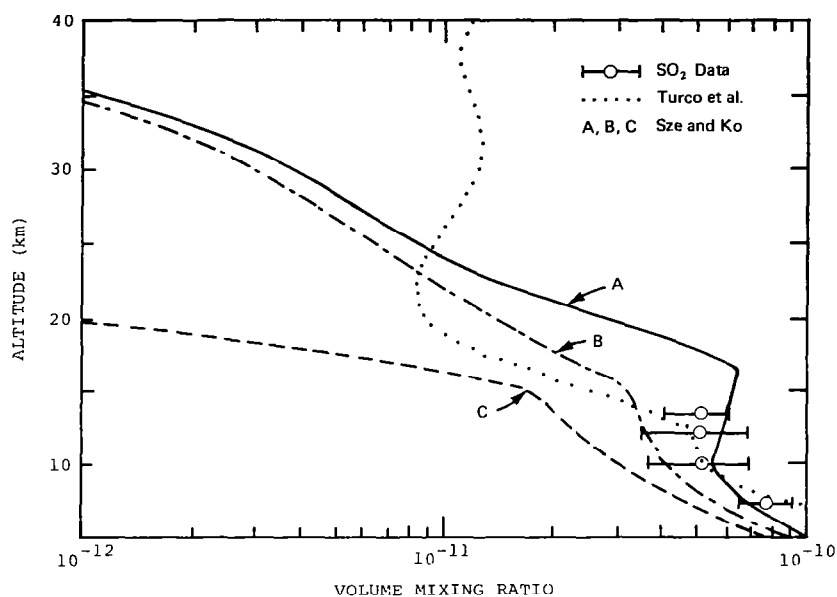


Figure 4-34. SO_2 data (Jaeschke et al., 1976) and results of 1-D models are compared. Curve A is calculated with contribution from both COS and CS_2 . Curve B is calculated with contribution from CS_2 alone and Curve C is calculated with both CS_2 and COS omitted (Sze and Ko, 1979b).

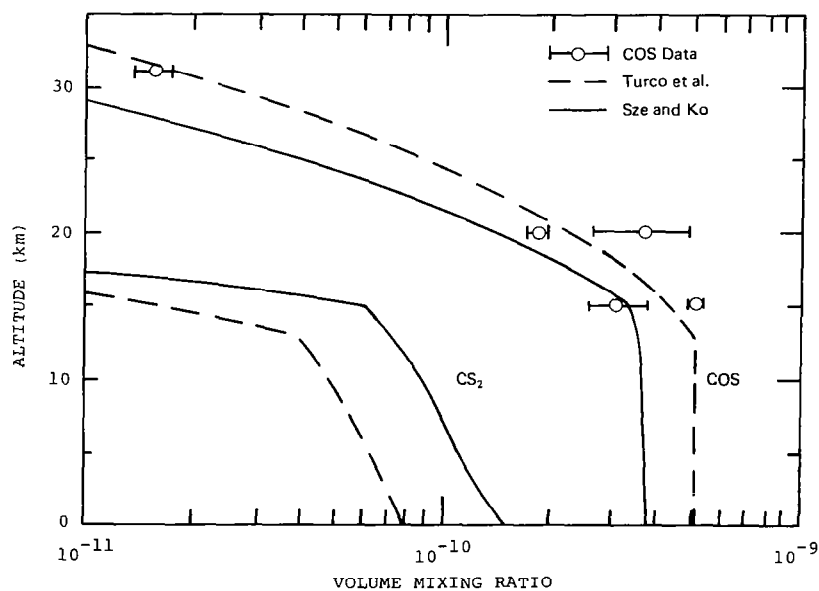


Figure 4-35. COS data (Inn et al., 1979) and 1-D model results are shown.

EMERGING PROBLEMS AND PROJECTIONS OF FUTURE RESEARCH

Problems concerning the observation and interpretation of stratospheric chemically active trace constituents will be treated in the sections which follow by (1) identifying those problems posed in NASA RP-1010 which remain unsolved and, (2) highlighting those aspects of stratospheric chemistry, revealed by data acquired during the past three years, that indicate potential shortcomings in our understanding of the problem.

Problems Remaining From NASA RP-1010

New analytical techniques are urgently needed. Although a complete list of molecules known to be of importance would be prohibitively long, a few species for which new or improved techniques must be developed include:

- Bromine compounds
Br, BrO, BrO₂, OBrO, HOBr, etc.
- Chlorine compounds
HOCl, ClONO₂, ClO₂, OClO, ClO₃
- Total chlorine
- Fluorine compounds
- Sulfur compounds
HS, COS, SO₂, CS₂, SO₃, etc.
- Hydrocarbon oxidation fragments
CH₃O, CH₃O₂, H₂CO, CHO, etc.
- Total odd nitrogen

Eddy diffusion coefficients K_z were derived principally from measurements of the upward diffusion of species such as N₂O, CH₄ and the CFMs. It should be noted that such eddy diffusion coefficients may not be appropriate for downward diffusion of species such as O₃, ClX and NO_x. Measurements of ClX and NO_x may provide important information concerning the removal of molecules chemically produced in the stratosphere.

Carefully selected simultaneous measurements are needed of related species such as NO₂, OH, and HNO₃; Cl, ClO, OH, CH₄ and HCl; OH, HO₂, H₂O, O₃, and O; ClO, HCl, and ClONO₂ to mention a few. These observations provide a much more stringent examination of mechanisms proposed for stratospheric photochemical models.

Although further experimental evidence in the last two years has demonstrated that a clear pattern is present in fall-winter ClO concentrations, there remain cases showing significant departure from an *envelope* of typical ClO profiles. Detection of chlorine monoxide by laser heterodyne solar absorption indicates concentrations well above the *envelope*. This is an important indicator that major mechanistic problems remain with respect to the free radicals of chlorine. The steep gradient in the ClO mixing ratio observed below the peak at ~38 km also remains unexplained.

The diurnal behavior of the NO_x system remains unexplained. The relationship between NO₂, NO₃ and N₂O₅ is poorly understood.

Problems Which Have Emerged

Atmospheric Variability

Fluctuations in the chemical composition of the stratosphere have been observed over a wide range of temporal and spatial scales. Although some of this variability can be rationalized by examination of meteorological records, it can be stated that, in general, characterization of the mechanisms and quantitative importance of these phenomena are not well established. Atmospheric variability is emerging as an important problem in the formulation and interpretation of field experiments. A summary follows of the measurements which establish large fluctuations for a variety of trace gases.

Kley et al. (1979) observed fine structure in the vertical profile of water, which appeared to be positively correlated with the fluctuations observed simultaneously for ozone. The correlation may be interpreted in terms of air parcels advected from various locations, since the stratification of water vapor in the stratosphere is morphologically similar to that of ozone. This explanation has not been tested experimentally, however, and other explanations may be equally plausible.

Burnett and Burnett (1979) observed short-term fluctuations of up to a factor of 2 in the total column OH. Variations of this magnitude are extremely difficult to understand. Short-term enhancements of OH near the mesopause could perhaps be caused by turbulent transports of H, O, and O₃, but there is little evidence to support the existence of such an effect on the total OH column.

One of the most celebrated fluctuations of atmospheric species has been discussed by Anderson et al. (1979). Measurements showed on one occasion very large concentrations of ClO near 40 km. Rather large variations occur seasonally and within a single season. Explanations advanced for these variations (rocket launches, meteoritic deposition) are not presently convincing.

Fluctuations of total column NO₂ (Noxon, 1977, 1979) have been reported, and the concentrations near 30 km of N₂O, CH₄, and CFMs show marked variability (Goldan et al., 1979; Ehhalt, 1978).

In order to characterize the concentration of a trace species in the atmosphere, measurements are required of the mean concentrations throughout the atmosphere, as well as the short-term variance about the mean and the distribution of that variance. Secular trends (seasonal, long-term) are also required. The initial efforts of field programs naturally focus on determination of the mean concentration field. However, the apparent variances of the observed concentrations are quite large. Understanding these fluctuations may be no less important than characterizations of the mean values. The problem is more challenging than the mean problem both for experimental and for theoretical studies. At the present time, it is truly an *emerging* problem, with poorly-understood ramifications.

Other Problems

A major disparity exists between the observed sum of NO_y = NO + NO₂ + HNO₃ and that currently used in the models. This discrepancy depends upon the value used for the rate of dissociation of NO which has recently been examined (Frederick and Hudson, 1979a) and shown to be less than previously used. When account is taken of this, about 2.5 ppb more NO_x is used in the model than exists in the atmosphere with serious implications for the O_x balance in the stratosphere.

The upper limit reported by Murcray for N₂O₅ lies significantly *below* that predicted by current models, yet the molecule remains undetected. The observed diurnal response of NO₂ (a decrease through the night following an initial increase and then a slow increase from dawn to midday resulting from N₂O₅ photolysis) does not consistently appear. There are also major unexplained latitude effects in NO₂ (the Noxon cliff).

The role of excited states of molecular oxygen and other energy pooling processes and the importance of ion-molecule processes in the rate of breaking and reforming the O_2 bond must receive continued attention.

6. pp. 168 and 185. In the discussion of CO, reference should be made to the data down to 45 km by Waters et al. (1976). Waters, J. W., W. J. Wilson, and F. I. Shimabukuro, Microwave measurement of mesospheric carbon monoxide, *Science*, 191, 1174-5, 1976.

The oxidation chains linking halogenated methane to their terminal products need considerable attention in both laboratory measurements and atmospheric observations.

Investigation of the methane oxidation chain should be pursued by measurement of the oxidation products. There is only one valid measurement of CO above 20 km and only an upper limit of the CH_2O mixing ratio. Since little information on the methane oxidation cycle can be gained by measuring CO, techniques need to be developed to measure more precisely other products of methane oxidation. Examples of species are shown in table 4-1 under Group 9.

Tropospheric measurements indicate that ethane, C_2H_6 , is a long-lived species which may enter the stratosphere in quantities as large as 1 ppb. Although this species has little effect as a loss process for chlorine it may influence the OH distribution. The chemical cycles involving the products of methane oxidation and the destruction of low molecular weight hydrocarbons are not well understood and a survey should be taken of all species present in the stratosphere.

The influence of sulfur containing radicals on ozone is poorly understood. There exist almost no measurements of these species. Techniques must be developed to determine the distribution of constituents such as SO_2 . There remains considerable uncertainty on the total chlorine content of the stratosphere. Additional techniques to measure total chlorine and chlorine species will have to be developed.

ENERGETIC FLUXES AND IONS

IONIZING SOURCES

Overview

Middle atmosphere ionization sources are important for a variety of reasons. For example, large variations in the ionizing input may play a role in aerosol formation (Mohnen and Kiang, 1978) and a role in altering the concentrations of minor neutral species (Crutzen et al., 1975; Thorne, 1977; Reagan et al., 1978). Variations in the ionization input can also modulate atmospheric electricity via the influence of conductivity variations on the mapping of electric fields and current flow (Markson, 1978). Thus, for the middle atmosphere at all geomagnetic latitudes, it is important to determine the relative importance of the ionization rates from the various background (quiet-time) energy sources; it is also important to evaluate the atmospheric response to transient solar-geophysical phenomena. This topic has recently been reviewed by Rosenberg and Lanzerotti (1979); this section is largely from that review.

Of particular interest for ionization of the middle atmosphere is the wavelength range from the ultraviolet (UV) through X-rays, electrons >0.01 MeV and protons >0.3 MeV. Higher energy heavy nuclei associated with galactic cosmic rays can also penetrate to the middle atmosphere.

Ionization of the middle atmosphere is controlled, to a degree strongly dependent on altitude and latitude, by direct energy inputs in the form of galactic and solar cosmic rays, solar H Ly α (and solar UV and EUV radiation), non-flare and flare-associated solar X-rays, and magnetospheric electron precipitation with its associated X-ray bremsstrahlung.

Table 4-3 lists the energy sources that contribute to the ionization of the middle atmosphere, together with estimates of the incident energy fluxes. In the table the various sources have been separated according to whether they contribute to the background (quiet-time) ionization levels, or are associated with specific events. Event sources can have durations ranging from a few minutes, as in the case of solar flare X-rays, to several days as in the case of solar cosmic ray events or for the midlatitude precipitation of energetic electrons following a geomagnetic storm (Spjeldvik and Thorne, 1975).

For the quiescent case, solar Ly- α (121.6 nm) ionization of NO dominates between 70 and 85 km with small contributions from cosmic radiation and 0.1 to 1.0 nm X-rays. Between 85 and 120 km, 1.0 – 10.0 nm X-radiation and Ly- β (102.6 nm) are the dominant ionization sources. During solar flares 0.1 – 1.0 nm X-rays dominate the 50 to 90 km altitude region. Only galactic and solar cosmic rays and high energy solar X-rays and X-ray bremsstrahlung can contribute to the ionization of the stratosphere at altitudes below 30-40 km. Table 4-4 (Smith and Gottlieb, 1974) gives X-ray levels for various solar activities.

Galactic cosmic rays represent a continuous ionization source which is a factor of two greater during sunspot minimum than sunspot maximum. Variation with geomagnetic latitude shows a factor of 10 more ionization at the poles than the Equator. Solar cosmic rays are sporadic and associated with major solar flares.

Magnetospheric Electrons and Bremsstrahlung X-Rays

Observations of trapped 100 keV electrons at altitudes of 250-400 km from measurements obtained on a polar-orbiting satellite (Seward, 1973; Paulikas, 1975) show their presence in the auroral zones as well as in regions of trapped fluxes extending to quite low latitudes, including the magnetic anomaly region in the South Atlantic.

At middle latitudes, electron precipitation can be a significant ionization source for the lower ionosphere for both nighttime and daytime conditions (Potemra and Zmuda, 1970; Potemra, 1973; Gough and Collin, 1973; Larsen et al., 1976; and Spjeldvik and Thorne, 1975) and may be responsible for magnetic storm after-effects which are observed on VLF communication signals.

In the auroral zones, considerably higher fluxes of precipitated energetic electrons are routinely encountered. Here ionization produced by substorm electrons will dominate the upper reaches of the middle atmosphere a large fraction of the time. Rates have been calculated by Berger et al. (1974) and Berger and Seltzer (1972).

Even more intense electron precipitation with energies sufficiently high (≥ 200 keV) to perturb daytime HF forward scatter radar of VLF propagation circuits is known to occur during some geomagnetic storms and substorms (Bailey, 1968; Bailey et al., 1970; Rosenberg et al., 1972; Larsen and Thomas, 1974; and Thorne and Larsen, 1976). Such events have been called relativistic electron precipitation (rep) and have yet to be thoroughly investigated.

Energy deposition by electrons or bremsstrahlung X-rays has been speculated as possibly influencing the mechanisms for cirrus cloud formation (Roberts and Olson, 1973a,b) and for thunderstorm generation (Markson, 1978). However, these energy sources have been rejected as an important agent for solar-weather coupling on the basis of energy flux considerations (Johnson and Imhof, 1975; Willis, 1976).

Table 4-3
Ionization Sources for the Middle Atmosphere
(Rosenberg and Lanzerotti, 1979)

BACKGROUND ENERGY SOURCES	
SOURCE	FLUX (ergs cm ⁻² ·sec ⁻¹)
Galactic Cosmic Rays	10 ⁻³ - 10 ⁻²
Cosmic x-rays: Diffuse, 0.1 - 1 nm	4 x 10 ⁻⁹
Solar x-rays: Nonflare, < 1 nm	10 ⁻³ - 10 ⁻¹
1 - 10 nm	10 ⁻¹ - 10 ⁰
Solar H Ly α : Direct	6
Scattered (Nightside)	6 x 10 ⁻³ - 6 x 10 ⁻²
Magnetosphere Electrons: Auroral Zone	10 ⁻¹ - 10 ⁰
Midlatitude	10 ⁻⁴ - 10 ⁻³
EVENT SOURCES	
Solar Cosmic Rays	10 ⁻³ - 10 ⁰ , 50 (8/2/72)
Solar x-rays: Flare, < 1 nm	< 3
1 - 10 nm	< 35
Cosmic x-rays: SCO x-1, 0.1 - 1 nm	4 x 10 ⁻⁷
Magnetosphere Electrons: Auroral Zone	10 ⁰ - 10 ³
Midlatitude	10 ⁻³ - 10 ⁻²

Table 4-4
Solar Irradiance (erg cm⁻²·sec⁻¹)

Wavelength Range, nm	Quiet Sun R ~ 10-40	Active Sun R ~ 100	Slowly Varying Sun	3B Flare
0.2-1	1.24 (-3)	2.32 (-2)	6.16 (-2)	3.10
1-3.0	1.02 (-1)	3.04 (-1)	1.37	27.8
3.0-10.0	2.31 (-1)	3.15 (-1)	4.50 (-1)	6.7

Solar Cosmic Rays

Although the Sun seems to be a more or less continuous emitter of low fluxes of MeV particles, these fluxes have relatively little impact on the ionization of the middle atmosphere. In contrast, the discrete solar flare events that produce large fluxes of > 10 MeV particles can dominate the ionization levels of the polar caps over the entire range of the middle atmosphere for several days at a time. The normal geographical distribution of polar cap radiowave absorption effects (pca) resulting from solar particle bombardment of the atmosphere cover the polar caps down to invariant latitudes of about 65° and 60° .

The ionization rates during average pca events far exceed those from any other source at altitudes below 80-90 km and above 20-30 km. However, it is obviously difficult to typify the ionization situation during these solar particle events. For example, the rates maximize at altitudes varying from 40 to 80 km, depending on the event, indicating that the spectra of individual events can vary widely.

Concluding Remarks

The sources of atmospheric ionization are well defined. However, there is great need to characterize the solar cycle variation as well as fluctuations on much shorter time scales. In the case of solar Lyman alpha and X-ray fluxes, this can be accomplished by continuous solar observations. Such observations should be carried out in conjunction with atmospheric observations. Inclusions of such measurements in the Upper Atmosphere Research Satellite is one way to accomplish this. Electron precipitation is difficult to characterize since electron trapping in the terrestrial magnetic field leads to precipitation with a large range of electron fluxes, energy spectra, and spatial distribution. Satellite measurements of X-ray bremsstrahlung fluxes at different energies as well as ultraviolet and visible radiations can supply some of the needed information. Solar protons have been measured from orbit and atmospheric ionization successfully inferred. Satellite measurements should be supplemented with rocket and balloon campaigns until it is possible to infer ionization rates from satellite data. This is most important for auroral electrons.

STRATOSPHERIC IONS

In situ access to stratospheric ion measurements is very difficult, with balloons being the primary vehicle, and measurement techniques are not easy. Current information is thereby mainly based upon model calculations, with only very few *in situ* experiments.

Based upon laboratory and field measurement, we can derive a sketchy and preliminary picture of the nature of stratospheric ions. However, we cannot yet assess the importance of ions in the atmospheric chemistry of that region. There exists the potential that ions do indeed influence some of the gaseous and particulate trace constituents in the stratosphere.

The free electrons produced by the various ionizing sources discussed earlier in this chapter will, after thermalization, attach to neutral molecules. The positive and negative ions undergo a series of so-called ion-molecule reactions including charge transfer, attachment reactions, switching reactions, proton transfer reactions, clustering reactions, and recombination reactions. Furthermore, there can be ion annihilation reactions resulting in charged aerosol particles or ion-induced aerosol formation reactions that are generally described by a heteromolecular, heterogeneous nucleation theory.

Ion molecule reactions of the first five types have been compiled by D. L. Albritton (1978). With this information, reaction schemes can be designed for the stratosphere as was done, for example, by Mohnen (1971) for positive and negative ions or, more recently, by Ferguson (1979). See Chapter 1. Vertical profiles can be computed as were shown in Reid (1979).

Positive Ions

The first *in situ* mass spectrometric measurements of stratospheric positive ions above 24 km were conducted by Arnold et al. (1977). They revealed the presence of proton hydrates of the form $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ as suggested from model calculations. However, the observed water cluster contained fewer water molecules than expected on theoretical grounds as a result of shock wave induced cluster fragmentation. Arnold et al. (1977) detected some other ion species have masses 29 ± 2 , 42 ± 2 , 60 ± 2 and 80 ± 2 .

Later balloon-borne mass spectrometer measurements at 33-37 km altitudes by Arnold et al. (1978) confirmed their earlier findings and are summarized below:

Mass (amu)	Tentative Identification
55	$\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2 \equiv \text{H}^+ \cdot (\text{H}_2\text{O})_3$
73 ± 1	$\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_3 \equiv \text{H}^+ \cdot (\text{H}_2\text{O})_4$
78 ± 1	$\text{H}^+ \cdot (\text{H}_2\text{O})_2 \cdot \text{N}_1$
91 ± 1	$\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_4 \equiv \text{H}^+ \cdot (\text{H}_2\text{O})_5$
96 ± 1	$\text{H}^+ \cdot (\text{H}_2\text{O})_3 \cdot \text{N}_1$
100 ± 1	$\text{H}^+ \cdot (\text{H}_2\text{O}) \cdot \text{N}_2$
114 ± 2	$\text{H}^+ \cdot (\text{H}_2\text{O})_4 \cdot \text{N}_1$
118 ± 1	$\text{H}^+ \cdot (\text{H}_2\text{O})_2 \cdot \text{N}_2$
136 ± 2	$\text{H}^+ \cdot (\text{H}_2\text{O})_3 \cdot \text{N}_2$
140 ± 2	$\text{H}^+ \cdot (\text{H}_2\text{O}) \cdot \text{N}_3$

Here, N_1 , N_2 and N_3 are unknown molecular species. The overall abundance of these unknown ion species was determined to be 0.43 at 37 km.

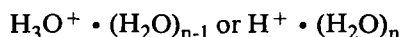
Other groups have, to some extent, confirmed the existence of $\text{H}^+ \cdot (\text{H}_2\text{O})_n$ at stratospheric levels. Arijs et al. (1978) observed at 35 km altitude the following proton hydrates and their abundances:

37 ± 2	1%
55 ± 2	16%
73 ± 2	80%
91 ± 2	3%

They also observed some of the unknown ion species detected by Arnold et al. having masses of 78 ± 2 , 96 ± 2 and 99 ± 2 (Arijs et al. upper mass detection limit is 109 amu). In addition, they detected masses 47 ± 3 , 50 ± 3 and 60 ± 2 . There have been several attempts to identify the unknown ion species. Obviously, they must evolve from $\text{H}^+ \cdot (\text{H}_2\text{O})_n$ via any one of the principal ion-molecule reaction mechanisms listed above, the most likely one being a proton transfer reaction. Ferguson (1978) has speculated that the unknown molecular specie N_1 might be NaOH or KOH, both of which have higher proton affinities than water. For example:

77	$\text{H}^+ \cdot (\text{H}_2\text{O})_2 \cdot \text{N}_1 \equiv \text{H}^+ \cdot (\text{H}_2\text{O})_2 \cdot \text{NaOH}$
99	$\text{H}^+ \cdot (\text{H}_2\text{O}) \cdot \text{N}_2 \equiv \text{H}^+ \cdot \text{H}_2\text{O} \cdot (\text{NaOH})_2$
139	$\text{H}^+ \cdot (\text{H}_2\text{O}) \cdot \text{N}_3 \equiv \text{H}^+ \cdot \text{H}_2\text{O} \cdot (\text{NaOH})_3$

The presence of aerosol particles would, for all practical purposes, exclude the existence of free molecular NaOH at concentration levels high enough to encounter collisional interactions with ions. One can therefore conclude that the above type of ion does not exist at levels below 25 km. With regard to the measured $\text{H}^+ \cdot (\text{H}_2\text{O})_n$ cluster distribution at around 35 km as reported by Arnold et al. and Arijs et al., they agree reasonably well with the abundance calculated by Mohnen (1971) and Fehsenfeld et al. (1976) in that $\text{H}^+ \cdot (\text{H}_2\text{O})_4$ is by far the most abundant cluster at that altitude. Since there are no *in situ* mass spectrometric observations available to date below 25 km, one must fall back on model predictions: It can be assumed with some degree of certainty that for all stratospheric levels, the intermediate ion will be of the form



which is the same. Through collisional interaction during the lifetime of the ion with neutral stratospheric constituents, further transformation might occur, leading to mixed ion clusters of the general type



via proton transfer reactions or any other "ion growth" reaction mechanism. The ion lifetime is governed by the recombination coefficient or the annihilation coefficient. At stratospheric levels, the ion annihilation coefficient is normally smaller than the recombination coefficient (Zikmunda and Mohnen, 1972). The latter has been determined as

$$1.4 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1} \text{ for troposphere, Nolan (1943)}$$

$$1 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1} \text{ at 15 km, Gringel et al. (1978)}$$

$$4.5 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ at 25 km, Gringel et al. (1978)}$$

$$3.5 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ at 30 km, Gringel et al. (1978)}$$

For the observed ion concentrations of 1000 to 10,000 cm^{-3} in the stratosphere, these coefficients yield ion lifetimes on the order of 1000 seconds (Mohnen, 1975).

There is indirect proof that the average reduced stratospheric ion mobility below 30 km is of the order of $1.3 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$. (Riekert, 1971; Morita et al., 1971.) As reported by Young et al. (1970), the mobility of $\text{H}^+ \cdot (\text{H}_2\text{O})_4$ was measured as $2 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$. A value of $1.85 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ was reported by Huertas (1972). Mobility values of $1.3 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ would correspond to ion masses of roughly 350 amu, or far in excess of the proton hydrates predicted at stratospheric altitudes. The sulfuric acid molecule is a prime candidate for ion molecule interactions leading to "prenucleation clusters" (Castleman, 1975). An attempt to predict the ion cluster of the type $\text{H}^+ \cdot (\text{H}_2\text{O})_n \cdot (\text{H}_2\text{SO}_4)_x$ under stratospheric conditions has been made by Chan et al. (1978). Using a modified Thomson theory, it can be shown that preferred or "optimal" cluster combinations exist between H_2O and H_2SO_4 . The real nature of ions can be expected to be more complex in that nitrogen, carbon dioxide, nitric acid, oxides of nitrogen, etc., continuously attach and detach to the more stable "ion core." However, one type of molecule, the chlorofluorocarbons FC-11, FC-12, FC-13, etc., do not seem to participate in any of these ion molecule reactions (Fehsenfeld et al., 1976) or clustering reactions (Kadlecek et al., 1977). Obviously as the temperature reaches extremely low values as it does around the mesopause, cluster formation involving N_2 and CO_2 in addition to water vapor become more likely. Arnold has experimentally confirmed this possibility from a measurement at the summer polar mesopause (Arnold and Joos, 1979).

Negative Ions

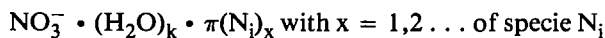
The first and only negative ion measurements from stratospheric levels of 34-37 km have been reported by Arnold and Henschen (1978). They reported the major ion masses with fractional abundance greater than 1% as follows:

Mass numbers and tentative identifications of major negative ions observed at 33-37 km altitude

<i>Mass</i>	<i>Tentative identification</i>
125 ± 2	$\text{NO}_3^- \cdot \text{HNO}_3$
161 ± 2	$\text{R}^- \cdot \text{HNO}_3$
	$\text{NO}_3^- \cdot \text{HNO}_3 \cdot \text{HCl}$
188 ± 2	$\text{NO}_3^- \cdot (\text{HNO}_3)_2$
197 ± 3	$\text{R}^- \cdot \text{HR}$
224 ± 3	$\text{R}^- \cdot (\text{HNO}_3)_2$
	$\text{NO}_3^- \cdot (\text{HNO}_3)_2 \cdot \text{HCl}$
253 ± 3	$\text{NO}_3^- \cdot (\text{HNO}_3)_3$
260 ± 3	$\text{R}^- \cdot \text{HR} \cdot \text{HNO}_3$
289 ± 3	$\text{R}^- \cdot (\text{HNO}_3)_3$
	$\text{NO}_3^- \cdot (\text{HNO}_3)_3 \cdot \text{HCl}$
295 ± 3	$\text{R}^- \cdot (\text{HR})_2$

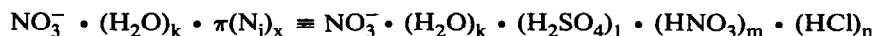
There are obviously two ion sequences, $\text{NO}_3^- \cdot (\text{HNO}_3)_n \cdot (\text{HCl})_m$ with $n = 1, 2, 3$ and $m = 0, 1$, and $\text{R}^- \cdot (\text{HR})_m \cdot (\text{HNO}_3)_n$ with HR having a mass of 98 ± 2 amu and with $m = n \leq 3$. Arnold and Henschen have proposed H_2SO_4 as a possible candidate for mass 98 ± 2 .

The major core ion NO_3^- is predicted to be of importance in the stratosphere and its evolution is relatively well understood (Mohnen, 1971; Fehsenfeld et al., 1975). The complex cluster ion at upper stratospheric levels is expected to be of the form:



Here, $\pi(\text{N}_i)_x \equiv (\text{HNO}_3)_{1,2,3} \cdot (\text{HCl})_{0,1}$

The absence of any water clusters in Arnold and Henschen's (1978) tentative ion identification scheme comes as a surprise. As Fehsenfeld and Ferguson (1974) indicated, their tests showed that weakly bound cluster ions could be detectably broken up with draw-in potentials in the mass spectrometer in excess of 1 volt. On the basis of heteromolecular, heterogeneous nucleation theory, one would expect some water molecules attached to these large prenucleation ion clusters. From a nucleation point of view, the following additional ion identification would be conceivable,



with the numerical values for k , l , m , n according to Arnold and Henschen's measurements:

<i>Observed</i>		<i>Actual</i>
161 ± 2	$k = 0, l = 1, m = 0, n = 0$	160
193 ± 3	$k = 0, l = 1, m = 0, n = 1$	196
260 ± 3	$k = 0, l = 2, m = 0, n = 0$	258
295 ± 3	$k = 0, l = 2, m = 0, n = 1$	294

(Arnold and Henschen (1978) assumed HSO_4^- as the core ion)

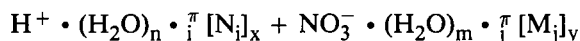
This scheme would allow full interpretation of all the observed mass peaks at that altitude on the basis of well established ion molecule reactions (Fehsenfeld et al., 1976) and hypothesized ion prenucleation processes (Mohnen, 1971, and Chan et al., 1978). However, the key issue for the existence of prenucleation ion clusters is the presence of water molecules in these ions.

There exist no *in situ* measurements for other stratospheric levels. Again, one must resort to model predictions. As the concentration of HNO_3 , H_2SO_4 , HCl , O_3 , N_xO_y , etc., decreases in the stratosphere with decreasing altitude and H_2O increases, one might expect other core ions appearing besides NO_3^- . For example, CO_3^- , O_3^- , CO_4^- and O_2^- ion cores are conceivable.

Complex ion clusters are certain to appear with trace gas molecules constantly attached and detached to these core ions as a result of collisional interactions with the gaseous environment, whereby the degree of clustering is determined by the physical and chemical properties of the neutral gas molecules and the ambient temperature.

Ion Recombination

The general assumption in ion chemistry has been that positive and negative ions will charge, neutralize and decay into neutral fragments. It is conceivable that the recombination reaction between stratospheric ions of the general type



$[\text{N}_i]$ and $[\text{M}_j]$ being stratospheric trace gas constituents with concentration greater than around 10^5 molecules cm^{-3} and x , y the number of molecules clustered to the ion, $x, y = 1, 2, \dots$

does not yield charge neutralization for $x, y \geq 1$ and $m, n \geq 1$. Rather, these postulated recombination reactions lead to metastable "charged" condensation embryos (Mohnen, 1971). Experimental proof for the existence of metastable or stable states is unavailable currently. However, other investigators (i.e., Ferguson, 1978, private communication) are calling attention to the possible existence of large molecular products of ion-ion recombination containing ions of both signs. The presence of metastable and stable clusters does have important implications on initiating aerosol formation, particularly if McMurry's (1977) and Gelbard and Seinfeld's (1979) mechanisms of aerosol formation based on cluster-cluster interactions proves to be dominant.

Summary

There seems to exist a basic understanding of stratospheric ion chemistry based upon extensive laboratory data, so that the observed positive and negative ion spectra can be interpreted. Current instrumentation for

probing the stratosphere needs to be refined to minimize mass uncertainties, to extend the mass range substantially, to sample the ambient ion population at near thermal energy, and to cover, eventually, all stratospheric levels. Clustered protonated hydrates, as expected, are a significant part of the stratospheric positive ion population, while the NO_3^- core ion seems to dominate the negative ion population. The type and degree of clustering depends on the collisional interaction of ions with their neutral environment. This conceivably allows appropriate trace constituents of concentration down to 10^5 molecules cm^{-3} to play a significant role in determining the ion nature, and at the same time renders models into diagnostic rather than predictive tools. The existence of large metastable or stable clusters, neutral or charged, still awaits *in situ* verification. The role of H_2SO_4 in positive and negative ion chemistry needs further investigation.

ATMOSPHERIC EFFECTS OF IONIZING SOURCES

Production of NO and HO_x

Atmospheric ionization events can modify the concentration of neutral species in the stratosphere and mesosphere. In particular ozone is destroyed because of the production of significant quantities of odd nitrogen and hydrogen compounds which react photochemically to destroy ozone.

It was first suggested by Dalgarno (1967) that ionization could lead to modification of the neutral upper atmosphere. Maeda and Aikin (1968) suggested that mesospheric ozone would be modified by production of atomic oxygen during auroral events. Ionization by cosmic radiation and the subsequent ion neutral reactions which lead to the formation of NO was proposed by Warneck (1972), Brasseur and Nicolet (1973) and in more detail by Nicolet (1975a). The production of NO during solar flare proton events has been discussed by Crutzen et al. (1975), Frederick (1976), Reagan (1977), and Reid et al. (1978).

Odd nitrogen is produced by several processes following the creation of the primary ion pair. The quantity of NO generated per ion pair has been estimated. Nicolet (1975a) used 1 NO per ion pair, Crutzen et al. (1975) adopted 1.5 NO molecules per ion pair for the August 4, 1972 polar cap absorption (pca) event. Frederick (1976) assumes 1.27 NO per ion pair. This figure is in agreement with calculated values by Porter et al. (1976). Most recently Fabian et al. (1979b) have adopted a value of 2-2.5 NO molecules per ion pair based on experimental measurements of NO produced during an aurora and their two-dimensional model fit to the August 4, 1972 pca observations. The same ozone data has been fitted with a value of 1.5 molecules/ion pair by Reagan et al. (1978) using a time-dependent photochemical model. Jackman et al. (1979) estimate the upper limit as 2.68 NO/ion pair for 10 KeV electrons. This estimate includes the effect of N_2^+ which is lost in the stratosphere by charge exchange to form O_2^+ . When the contribution from N_2^+ is omitted the upper limit for the stratosphere is 1.5.

Ionization can lead to odd hydrogen through several processes involving water cluster ions. The net production of OH and H depends on the species of negative ion present. It is usually assumed that each ion pair leads to the production of 2 odd hydrogens, Swider and Keneshea (1973). Odd hydrogen influences the O_3 distribution primarily above 50 km; below 50 km odd nitrogen is more important.

Effects on O_3 and NO Densities

The decrease in ozone following the August 4, 1972 solar flare (the largest such event in 25 years) was observed by the Nimbus-4 BUV instrument, Heath et al. (1977). Data for both hemispheres is illustrated in figure 4-36 which plots total ozone above 4 mb as a function of time. The winter hemisphere is normally disturbed by planetary wave propagation. This masks to some extent the influence of proton precipitation. Thus, while ozone recovers within 20 days in the summer hemisphere, the winter hemisphere still exhibits ozone depletion after more than one month.

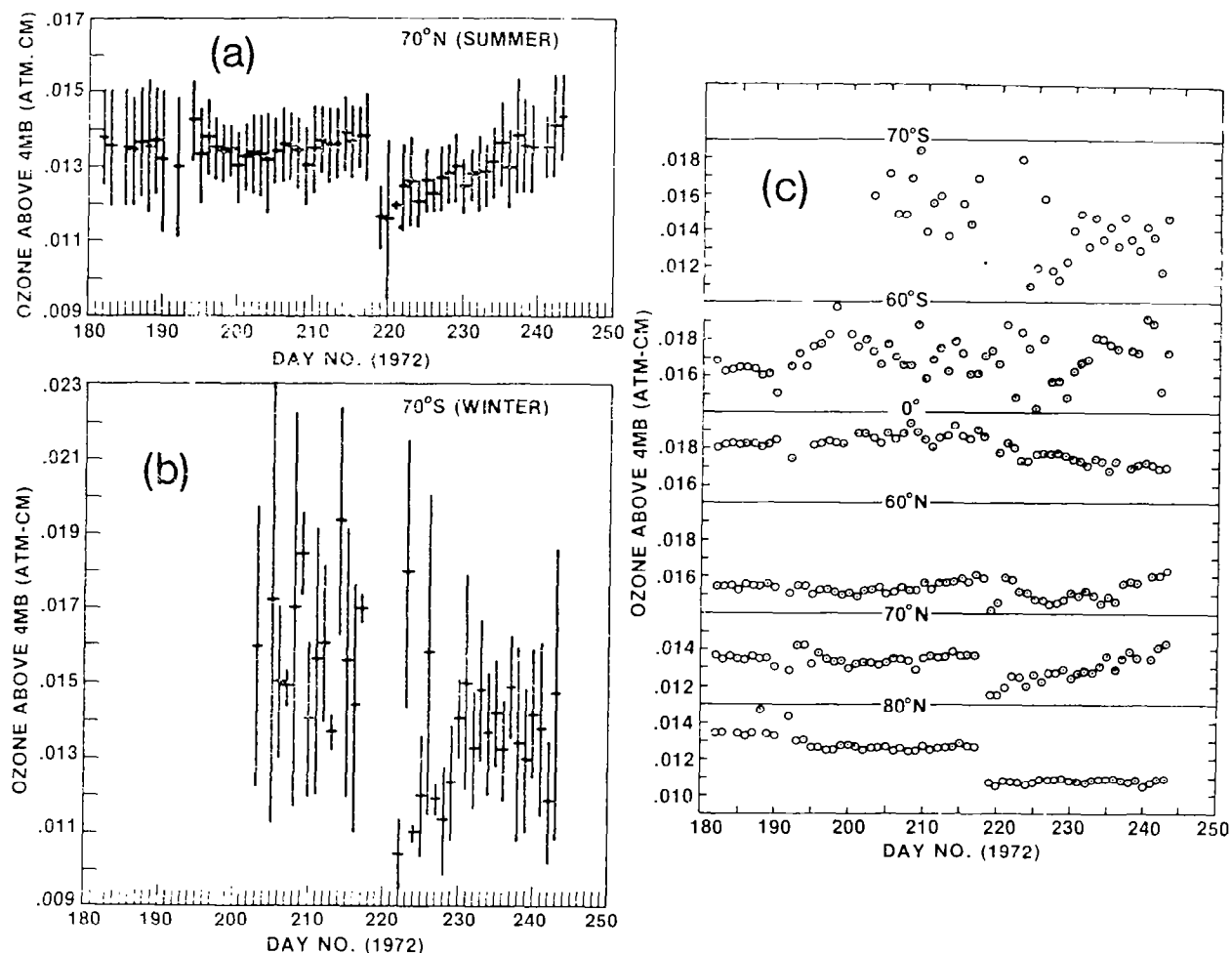


Figure 4-36. Zonally averaged total ozone above the 4-mb level during July-August 1972. The solar proton event occurred on 4 August (day 217). (a) at 70°N, (b) at 70°S, and (c) at 6 latitude bands: 70°S, 60°S, 0°, 60°N, and 80°N. The vertical bars for each data point in (a) and (b) indicate the standard deviations of all data obtained in the latitude band of that day, Maeda and Heath (1978).

Computational comparisons with ozone data are shown in figure 4-37. Part A shows ozone measurements for the November 2, 1969 event by Weeks et al. (1972) and computations by Swider et al. (1978). Part B shows data for the August 4, 1972 event with computations by Reagan et al. (1978) using a time dependent model, but not including eddy diffusion. In Part C, the ozone data for the 1972 event is compared to computations by Fabian et al. (1979b) and by Crutzen et al. (1975), each of which used two different values for the NO production rate. None of the four computations fit the data as well as desired, due both to the paucity of data and to our incomplete understanding of the odd nitrogen and odd hydrogen interactions involved. A better understanding of neutral species changes occurring in the ionization of air is required, together with more accurate measurements of O_3 and other species during a pca. Simultaneous measurement of NO, O_3 , and OH should be attempted.

Other ionizing sources are also important to the middle atmosphere. In the sunlit atmosphere the production of nitric oxide by cosmic radiation dominates NO production by the reaction of $O(^1D)$ with N_2O only below 20 km. Solar flares are characterized by large enhancements in hard X-radiation emitted from the flare region during 10 to 15 minutes. This radiation source will affect ozone only above 50 km and the effect will be limited due to the short duration of the X-ray pulse. Aikin and Maeda (1978) have presented evidence that such an effect occurs based on the Nimbus-4 BUW ozone data.

Energetic electrons are precipitated into the atmosphere largely in the auroral zone and can influence ozone, Maeda and Aikin (1968). The flux and energy spectrum are the determining factors in the altitude region where ozone changes occur. It is usually assumed that the energy spectrum does not contain enough high energy electrons to create significant ionization below 65 km and that the accompanying bremsstrahlung must account for any effect below that altitude. However, Imhof et al. (1977) have presented evidence for higher energy electrons and discussed their implications for O_3 depletion. Calculations of the influence of relativistic electron bremsstrahlung throughout the stratosphere has been carried out by Thorne (1978). Simultaneous measurement of energetic electrons, X-radiation and ozone during an auroral event has been conducted by Hilsenrath et al. (1978). A 25 percent decrease in O_3 above 1 mb is reported. Observations during solar flares and electron precipitation events will be useful in studying the recovery phase of ozone depletion above 50 km.

Lightning

Although the debate on the production of NO from lightning has been ongoing for many years, see for example Reiter and Reiter (1958), Ferguson and Libby (1971), it is only recently that it has been introduced into the problem of the global troposphere NO budget and its relation to the stratosphere, Dubin (1975), Zipf and Dubin (1976a,b), Noxon (1976), Griffing (1977), Chameides et al. (1977) and Chameides (1979). There is great uncertainty concerning formation efficiency for NO, NO_2 , HNO_3 and, N_2O . Calculations as well as measurements during simulated and natural lightning have been used to estimate these efficiencies. Formation of NO_2 has been observed during a lightning storm and the estimated NO_2 production is 10^{17} NO_2 molecules per joule or 60 ev is required for 1 NO_2 molecule with 10^9 joules per lightning stroke. Based on laboratory measurements with a spark chamber Chameides et al. (1977) estimate 6×10^{16} NO molecules per joule. Using shock dissociation of air approximation, Chameides (1979) has calculated the NO molecule/joule yield dependence on input energy in joules/meter. He concludes that lightning accounts for a large fraction of tropospheric nitrogen oxides.

This conclusion is based on an energy dissipation of 10^5 joule meter⁻¹. However, a recent survey of lightning energy estimates by Hill (1979) concludes that an upper limit of only 10^4 joules meter⁻¹ is dissipated per stroke. This limits lightning odd nitrogen production to 10% of the value quoted by Chameides (1979). Recent satellite optical data, Turman (1978) indicates that power and distribution of lightning can be mapped globally. If agreement is reached on the percentage of total power represented by optical power, such satellite experiments can reduce the uncertainty in lightning odd nitrogen production estimates.

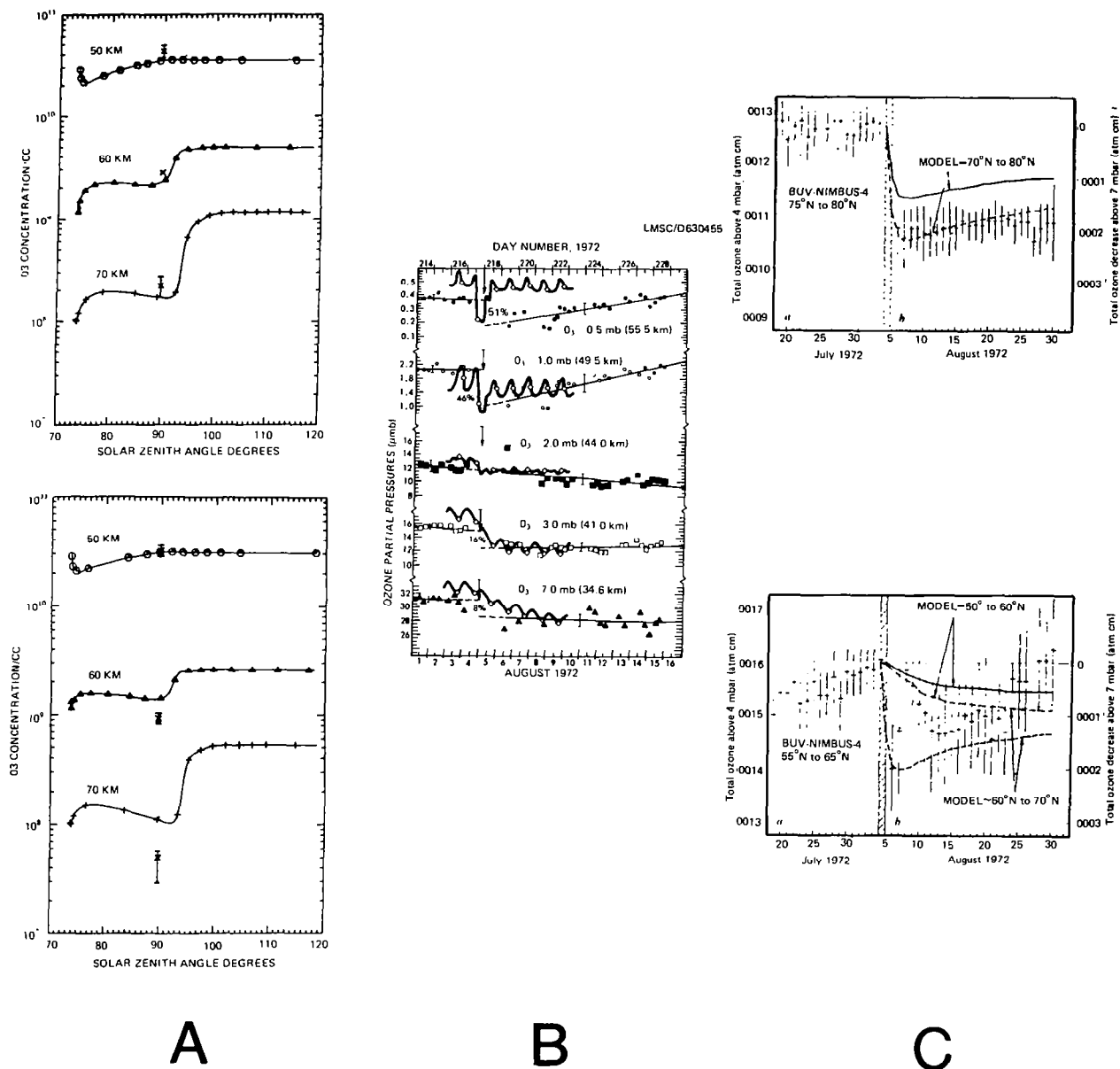


Figure 4-37. Comparisons of computed and actual ozone variations during the pca events of A) 2 November 1969, B and C) 4 August 1972. In part A solid curves represent time-dependent calculations for (1) 2 November and (2) 4 November. X represents experimental data. Part B shows experimental and calculated ozone variations for 4 August 1972, 77°N latitude. Part C shows a comparison of theory and experiment for 4 August 1972 using two values of NO production rate, from Crutzen et al., (1975) and from Fabian et al., (1979b).

The production of N_2 and CO has also been considered by Levine et al. (1979), Griffing (1976), and Green et al. (1973). For CO, it is concluded that if an upper limit of lightning production of 2×10^8 tons is assumed, then lightning represents a significant source of CO. Production of N_2O may be one to two orders of magnitude less but the long lifetime of N_2O allows its transport to the stratosphere.

Conclusions and Recommendations

The types of natural events which give rise to changes in atmospheric composition have been identified and the mechanisms for species production is understood in a qualitative manner. A quantitative understanding is required if the influence of such events on stratospheric ozone is to be properly evaluated. There is uncertainty concerning the amount of odd nitrogen produced by proton impact on the atmosphere. The influence of photochemistry and dynamics on recovery from such events is poorly understood. Better laboratory data on important parameters is required. Future measurements during polar cap absorption events should measure NO and its temporal variations as well as O_3 .

The amount of ionization as a function of time and altitude is needed in order to quantify energetic electron precipitation and solar flare X-ray events. The transient nature of these events can be used to evaluate recovery of the mesosphere and upper stratosphere following such events. Neutral and ionized species measurements in addition to ozone should be carried out during such events.

Since the global lightning distribution can be measured from orbit, Turman (1978), better estimates of global lightning production of odd nitrogen should be possible. Continued experiments and theoretical work on the efficiency for odd nitrogen production are required.

CHAPTER 5

METEOROLOGY OF THE STRATOSPHERE

INTRODUCTION

In the geophysical sciences in general, and in the study of the stratosphere in particular, application of the "scientific method" does not follow the same course as it does in the laboratory sciences. Carefully controlled laboratory experiments cannot be formulated to test against theory. Instead, complementary observational and theoretical studies must be designed to achieve the goals of understanding the present workings of the stratosphere and ultimately of predicting with confidence its future states. In Chapter 2, the techniques for theoretically modeling the stratosphere were presented. This chapter discusses how far past theoretical and observational efforts have taken us toward understanding the workings of the stratosphere.

The first part of this chapter considers the role of stratospheric measurements with an indication of the advantages and shortcomings of various types of data in testing meteorological theories. Then various techniques are discussed for obtaining the geographical and temporal distributions of measured parameters from the collection of discrete measurements that are taken at different locations and times.

Current understanding of the stratospheric general circulation is discussed, emphasizing the physical processes which maintain the observed distribution of meteorological variables in the stratosphere. Since one particularly important stratospheric variable is ozone, a separate discussion is devoted to presenting the status of our understanding of the physical processes that determine the observed distribution of ozone and to what extent present day models are able to simulate these processes. Since the stratosphere is not a static medium, the status of our understanding of the physical processes that lead to the long period oscillations in the stratosphere - the annual cycle, the quasi-biennial oscillation, and the semi-annual oscillation are discussed. In addition to these rather regular variations, irregular changes occur in the form of both major and minor stratospheric warmings. The current understanding of these phenomena is discussed, along with that of short period phenomena such as tides, synoptic scale instabilities, gravity waves, and turbulence.

There is presently considerable controversy about the extent to which solar disturbances affect the structure of the stratosphere. It is important to establish this, since our ability to detect anthropogenically induced stratospheric change depends to some extent on our ability to identify naturally occurring variations, of which solar disturbance effects are but one example. The observational and theoretical evidence for these effects is reviewed.

Finally, the stratosphere cannot be considered in isolation from the atmospheric regions above and below. Thus, a discussion is given of our present understanding of chemical exchange processes, dynamical coupling processes, radiative interactions, and electrical coupling between the troposphere and stratosphere. The goal of this chapter, then, is to indicate how far existing observational and theoretical efforts have progressed toward the understanding of stratospheric processes and toward the ability to use this knowledge to predict future states of the stratosphere. In this connection, gaps in present knowledge are pointed out, and the necessary research areas identified.

STRATOSPHERIC MEASUREMENTS AND DATA ANALYSIS

INTRODUCTION

For the past several decades, stratospheric data have been obtained from ground observing stations (including balloons and rockets). Although there are large quantities of temperature, pressure-height, wind, and ozone data (the meteorological parameters to be discussed in this chapter), they are restricted mostly to land areas of the Northern Hemisphere. Until recently, they have been the basis for the accepted climatology of the stratosphere. Spatial, seasonal, and short term variations of these parameters were first described by balloon observations in the lower stratosphere and by rockets in the upper stratosphere and mesosphere. An initial description of the general circulation was then determined by a compilation of the various ground observations. However, this climatology has not been truly representative of global characteristics.

Satellite observations of the upper atmosphere began nearly a decade ago. These early measurements were used to develop the remote sensing techniques for later global observations. During the past several years, an extensive effort has gone into verifying remotely sensed data so that they may be used to accurately derive global morphologies. Such verifications will be continued by comparison with the ground observing stations. The series of Nimbus satellites is yielding a stratospheric data base of unprecedented size. Some of these data are discussed in this chapter.

The availability of large quantities of data has required new and sophisticated analysis schemes to be developed. These schemes, which are briefly discussed in a following section, draw on traditional numerical analysis techniques such as interpolation, harmonics, and adjustment to first guesses. With the availability of large quantities of satellite data, a 3-dimensional plus time presentation will be required.

STRATOSPHERIC MEASUREMENTS

Background

This section deals with currently active measurement programs which include those that are regularly performed from the ground (balloons, rockets and aircraft) and the on-going satellite programs such as the Nimbus and the NOAA operational satellites. Many individual specialized experiments are conducted worldwide for limited time periods, and have significantly contributed to our knowledge of the stratosphere, but are not included herein because of the limitation of space in this report. A brief history, coverage and advantages of each of the measurement systems are reviewed. The accuracies of the temperatures measured from the balloon, rocket and satellite systems are discussed in this chapter, while accuracies of the ozone measurement are discussed in Chapter 6.

Ground Based Measurements of Temperature and Wind

When considering the data distribution in the stratosphere, it is necessary to distinguish between the lower stratosphere, below about 30 km, and the upper stratosphere from 30 km to about 55 km. The lower region is mainly sampled by rawinsondes (balloonsondes or radiosondes for temperature and wind measurements), while data for the upper region has come from less numerous rocketsonde flights.

Figure 5-1 depicts the distribution of balloonsonde stations throughout the Northern Hemisphere as of July 1978. This map indicates that the coverage over the land areas is rather extensive, but the coverage is achieved with different instrument types. McInturff and Finger (1968) studied the problems posed by various instrument types and showed that the temperature measurements may require adjustments of up to 7°C in order to form a consistent data set. In the Southern Hemisphere extensive areas exist with little or no coverage as can be seen in figure 5-2, and satellite information is required to fill in the gaps. The distribution of pressure levels at which data are available has also been studied. Thomas and Finger (1974) have compiled, from worldwide radiosonde flights, the heights achieved and their sampled frequency. They show that only 45% of the observations reach 70 mb and less than 15% reach 10 mb. The main sources of radiosonde error are listed in the Air Weather Service Technical Report (1955). Seven sources of error, which contribute to a total standard deviation of $\pm 0.36^\circ\text{C}$, are considered. A value two or three times this value is considered applicable for a radiosonde in flight.

With respect to the upper stratosphere, figure 5-3 depicts the current rocketsonde stations of the Northern Hemisphere, and figure 5-4 those of the Eastern and Western Meridional Networks that extend into the Southern Hemisphere. Currently, the United States' sites launch rocketsondes on a 1-3 per week schedule while the other countries launch at a rate of approximately 1 per week. The height range of these instruments is between 20-65 km. As with the radiosonde information, the use of several instrument types necessitates a comparison between types. Results of such comparisons (Finger et al., 1975) have shown that temperatures are generally within 5°C (1 standard deviation) for the U.S., U.K., and French systems, but that significant differences above 50 km (over 20°C in the average values and a 10°C standard deviation) exist between the data from the U.S. and U.S.S.R. systems. The rms wind differences, on the other hand, show a general increase with altitude, but are basically within about 20 m/s.

Within the United States, there have been at least 10 different types of temperature sensors used, all of which have different errors. For a summary up to 1968, Quiroz (1970) and Hoxit and Henry (1972) give an extended discussion of sensors and accuracies. Since 1969 a common rocketsonde instrument type has been used at all U.S. sites, and a common adjustment scheme (Krumins and Lyons, 1972) that is considered reliable up to about 60 km has been applied. Thus, a major source of difficulty in the analysis and interpretation of the data has been alleviated. Naylor (1976) has shown that the temperature uncertainties below 50 km are on the order of 1.0-1.5 K, increasing to 3.6 K at 60 km. Performance of this instrument has been discussed by Miller and Schmidlin (1971) who indicate an overall repeatability to about ± 2 K (2σ).

It should be noted that the measured parameter of the rocketsonde is temperature as a function of height. Pressure is determined by matching the rocket temperature sounding to a balloon sounding in the overlap region, and calculating upward using the hydrostatic equation. Densities are then determined from the equation of state. Errors in the pressure, then, are not independent of the errors in temperature.

In addition to the utilization of these data by the NOAA/National Meteorological Center in synoptic analyses for temperature, height, and wind, the *in situ* soundings serve several other important purposes that are listed below:

- At the present time, the operational (NOAA) satellite temperature soundings are not independent of the *in situ* data. Satellite retrievals currently utilize a regression technique (Quiroz and Gelman, 1972; Smith and Woolf, 1976) and, in practice, it has been found necessary to update the regression coefficients on about a monthly basis using *in situ* data. The accuracy of the satellite retrievals, then, is dependent on the data acquired from the meteorological radiosonde-rocketsonde program.

THE STRATOSPHERE: PRESENT AND FUTURE

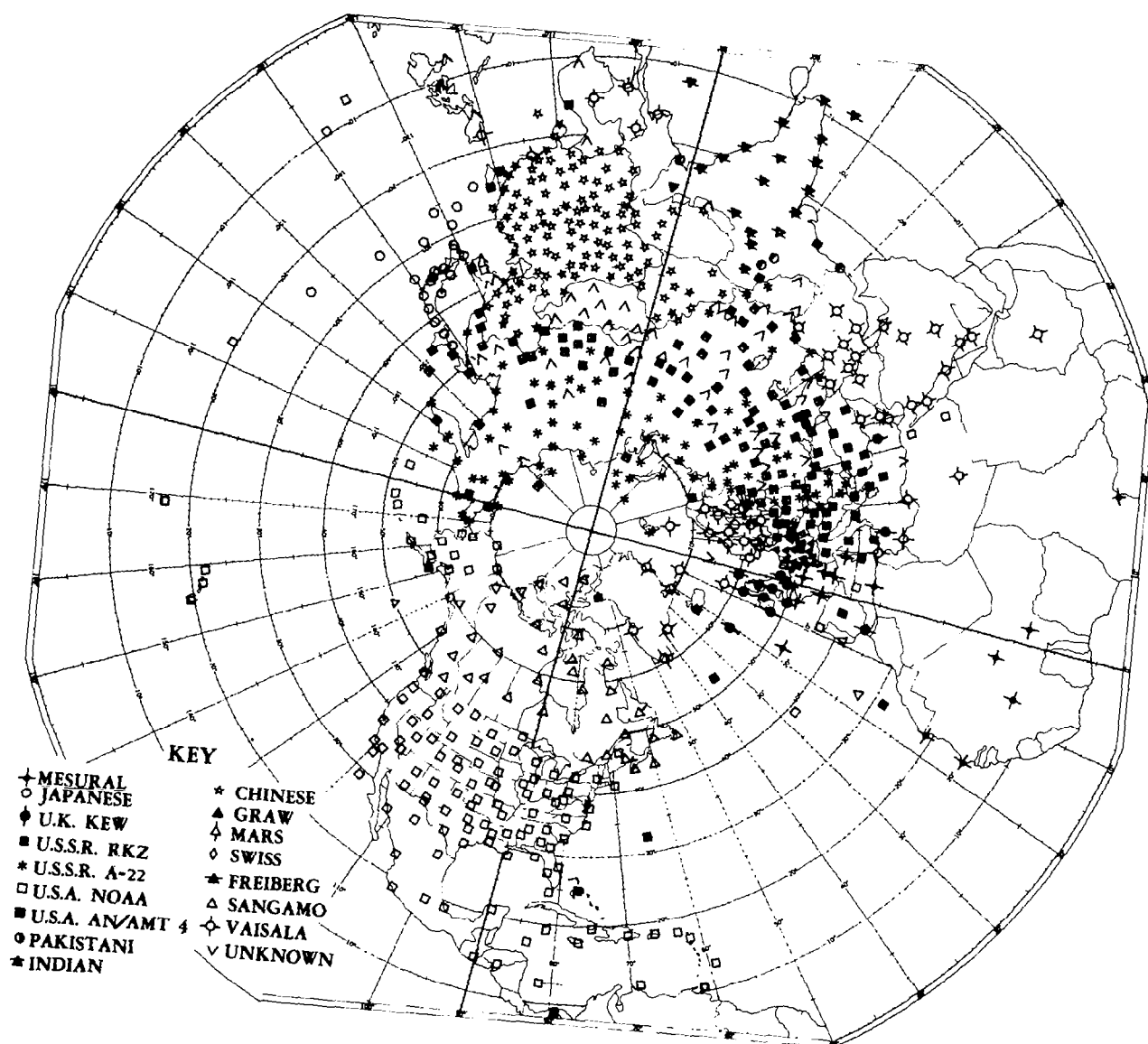


Figure 5-1. Distribution of radiosonde instrument types throughout the Northern Hemisphere, as of July 1978.

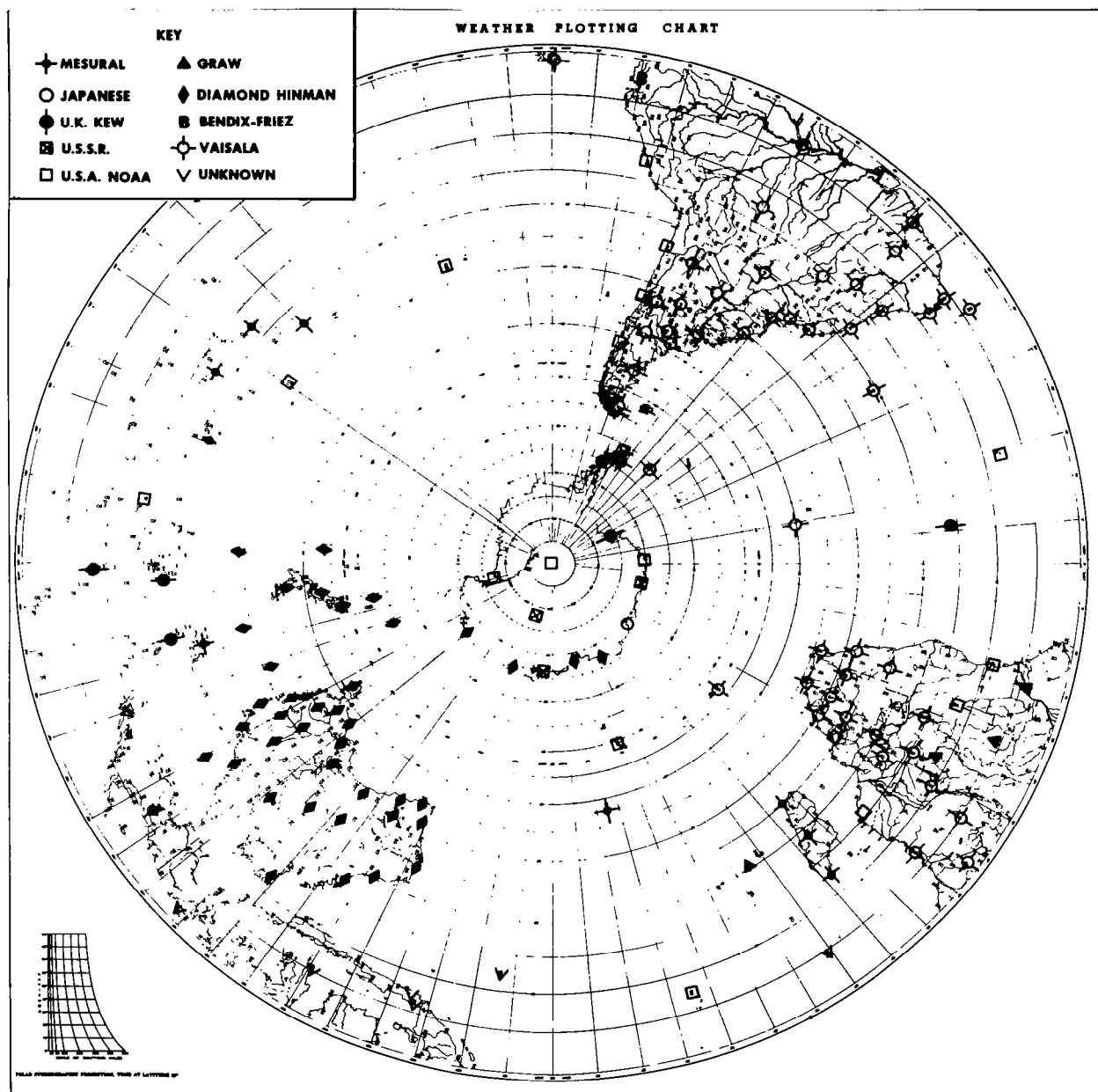


Figure 5-2. Distribution of radiosonde instrument types throughout the Southern Hemisphere as of July 1978.



Figure 5-3. Distribution of meteorological rocketsonde sites in the Northern Hemisphere.

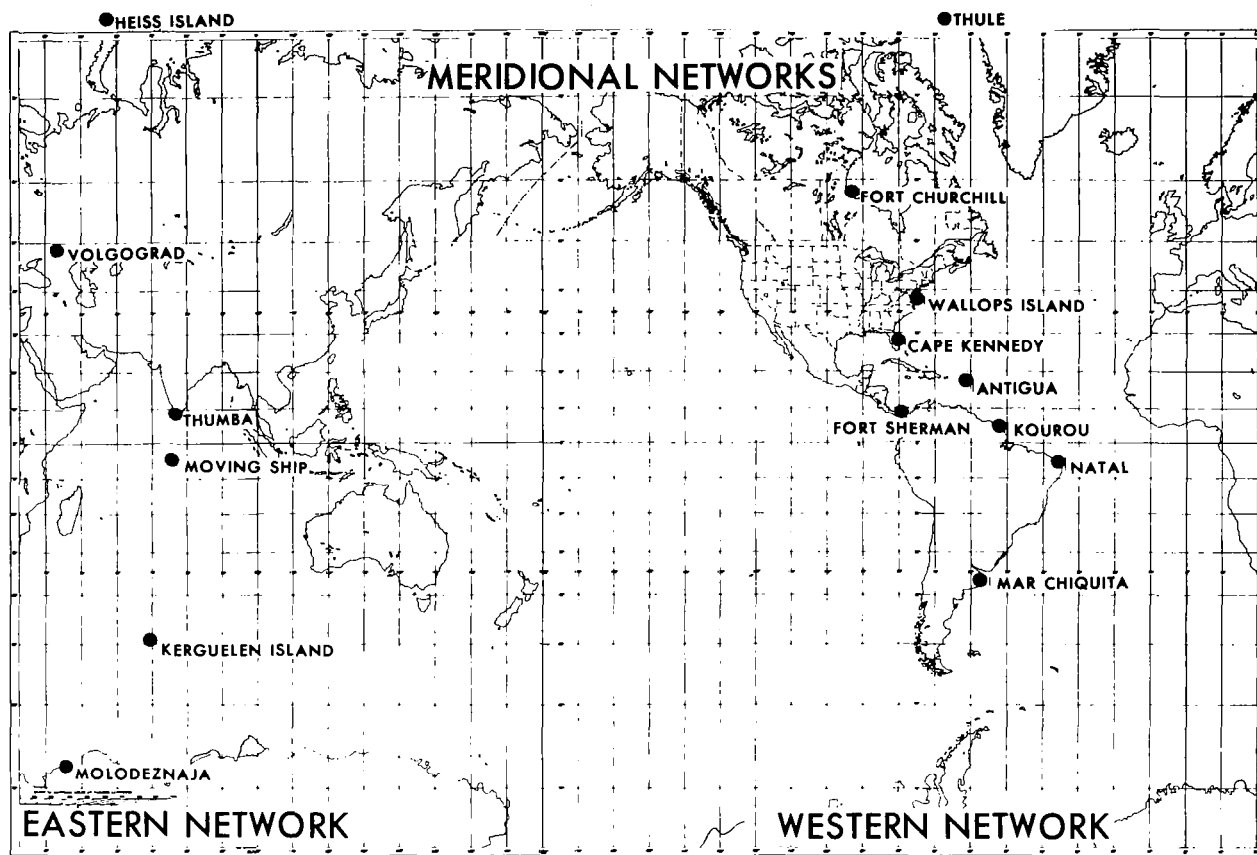


Figure 5-4. Distribution of meteorological rocketsonde sites for the Eastern and Western Meridional Networks.

- The *in situ* horizontal wind information is desirable both as a check on the thermodynamic analyses by comparing measured versus thermal balance winds, and as the major source of reliable wind information in the tropics where the geostrophic wind equation does not apply. *In situ* data has been particularly important in delineating the tropical Kelvin and mixed Rossby-gravity waves (e.g., Wallace, 1973).
- The radiosonde-rocketsonde systems provide considerable information with respect to the small-scale structure in the vertical that is smoothed out in the synoptic analyses, but is essential for investigation of certain problems. Danielson (1968) and Reiter (1972), for example, present cases where the detailed radiosonde observations are critical for delineating the tropopause-folding that results in mass exchange between the troposphere and stratosphere. In a similar vein, Webb (1965) and Miller et al. (1968) have shown that the meteorological rocketsondes can delineate 1 km variations in the vertical which are important for consideration of gravity wave structure in the stratosphere. Figure 5-5 (Miller et al., 1968), for example, shows the smoothed temperature and wind profiles and departure therefrom for several soundings utilizing two different rocketsonde sensors during a U.S.-Japan intercomparison test. Clearly, the detailed structure as evidenced by the two systems is reproducible and is not an artifact of the measurement.

In the past few years, a new generation of sensitive radars utilizing the Doppler technique has been developed that has the potential to provide routine observations of wind, turbulence, and stable atmospheric layers in the troposphere and stratosphere via scattering from clear air irregularities in the radio refractive index. Gage and Balsley (1978) present a broad overview of the measurement capabilities of several Doppler radars operating over a range of frequencies in the VHF (30-300 MHz) and UHF (300-3000 MHz) regions. This study points out that previous radar observations (non-Doppler) do not provide continuous backscatter from all heights in the troposphere. On the contrary, they only outline the strongest echoing regions, where the reflectivity exceeds the minimum detectable reflectivity for the particular radar being used.

Addition of the Doppler capability significantly enhances radar sensitivity and increases the information content that can be retrieved from the radar echoes. Since the atmospheric scatterers are advected with the wind, the echoes are Doppler shifted and easily separated from stationary ground clutter. Moreover, since the radial component of the wind can be determined from the mean Doppler shift, the magnitude of the horizontal wind component can also be deduced, with minor assumptions. Observations made at a sequence of heights at one azimuth and fixed elevation result in a vertical profile of the horizontal wind component at that azimuth (assuming negligible vertical velocity). Vertical profiles obtained in more than one direction (e.g., an orthogonal set or an azimuth scan) can be used to determine the horizontal wind vector as a function of height. Sensitive radars can obtain such data in a few minutes to an hour depending on their processing capabilities and the altitude being probed.

Because of their ability to take data continuously over a period of several days, these radars have the potential to provide scientifically interesting data on gravity waves and on dissipative processes (turbulence). Additional comparisons with other independently obtained data are needed to fully evaluate their capabilities including the possibility that they be able to provide information on vertical transport. Parameters for a number of coherent pulsed radar systems involved in clear air studies are given in table 5-1.

Ground Based Measurements of Total Ozone and Its Vertical Distribution

The ground-based total ozone and vertical distribution techniques have been reviewed in NASA RP-1010 and are discussed in more detail in Chapter 6. One additional item to be noted, however, is that an international comparison of ozone rocketsondes is planned for the fall of 1979 at Wallops Island, Virginia. The participants are to be the United States, Canada, India, Japan, and Australia. As in the case for the groundbased

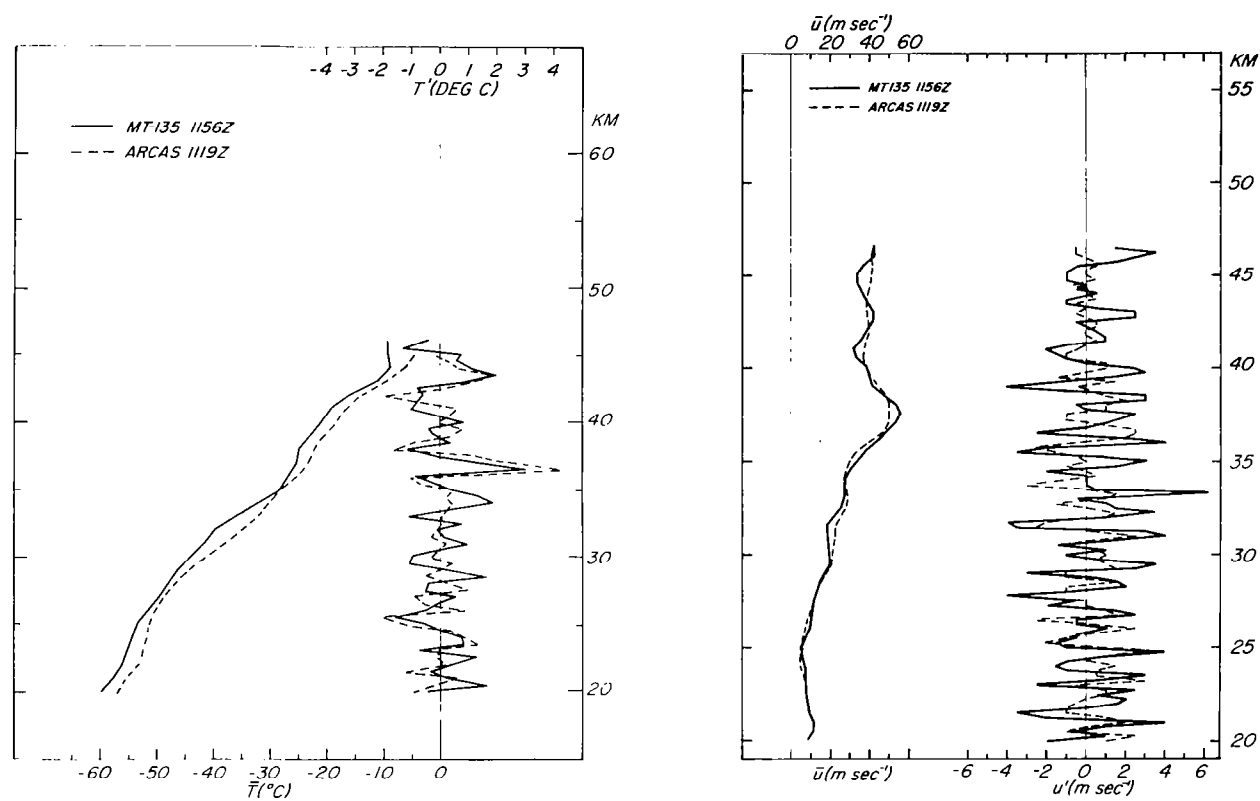


Figure 5-5. Smoothed $\bar{T}$ (left) and $\bar{U}$ (right) profiles and departures therefrom for U.S. Arcasonde and Japanese MT-135 rocketsonde intercomparisons (Miller et al., 1968).

Table 5-1
Parameters for Some Coherent Pulsed Radar Systems Involved in Clear Air Studies (Gage and Balsley, 1978)

Facility	Location	Frequency, MHz	Wavelength, m	Average Power Aperature ($\text{W}\cdot\text{m}^2$)	Beam Width, deg.	Antenna Configuration
Jicamarca	Peru	49.9	6.01	2.0×10^{10}	1.0	Phased Dipole Array
Arecibo	Puerto Rico	430	0.75	7.0×10^9	0.17	Fixed Dish/Steerable Feed
SOUSY	Germany	53.5	5.61	1.3×10^8	10	Phased Yagi Array
Chatanika	Alaska	1290	0.23	2.6×10^7	0.6	Steerable Dish
Millstone	Massachusetts	1290	0.23	2.6×10^7	0.6	Steerable Dish
Sunset	Colorado	40.5	7.36	9.0×10^6	5 x 9	Phased Dipole Array
Platteville	Colorado	49.9	6.01	5.0×10^6	3 x 3	Phased Dipole Array
Wallops	Virginia	430	0.75	3.1×10^6	2.9	Steerable Dish
Poker Flat	Alaska	49.9	6.01	2.5×10^6	3 x 6.5	Phased Dipole Array
Defford	England	2800	0.107	1.9×10^6	0.33	Steerable Dish
NSSL	Oklahoma	2851	0.105	2.6×10^4	0.8	Steerable Dish

meteorological soundings, the utility of the ozone information extends beyond that of synoptic type analysis (e.g., London et al., 1976b), and these are listed below:

- The satellite ozone measuring techniques require comparison data for validation and calibration with special emphasis on the long-term aspects of the latter. A major strength of the ground-based systems is that they can be calibrated and thus serve as standards for long-term satellite measurements.
- The balloon-rocketsonde system provides information on the small-scale vertical structure essential to investigation of certain problems such as stratospheric-tropospheric mass exchange. An example of such exchange is presented by Kroening et al. (1968).
- By measuring both ozone and horizontal wind, the balloon and rocketsondes can provide first approximations to the ozone transports (e.g., Hering, 1966; Hutchings and Farkas, 1971). These are limited by the spatial extent of the observations, but at this time serve as the only source of long-term measurements.

Aircraft Measurements

Research aircraft have played a key role in furthering our understanding of the physical and chemical characteristics of the stratosphere. Although aircraft measurements are taken only over a limited altitude range, they provide detailed information on horizontal structure. High resolution data have provided important information on tropospheric-stratospheric exchange process as will be shown later in this chapter. Simultaneously measured meridional distributions of meteorological parameters and trace gases and substances near the tropopause have also yielded information on atmospheric constituent budgets and transport in the lower stratosphere. Table 5-2 summarizes the various well-known aircraft programs.

Satellite Characteristics

The nature of satellite coverage and observations strongly influences the types of problems for which these data can be effectively used. It is worth noting some of these features here.

- Satellites have the unique ability to obtain global measurements on a repeated basis with regular sampling in space and time. To date, most observations of the stratosphere have come from spacecraft in Sun-synchronous polar orbits such as those of the Nimbus and TIROS series. For these orbits the latitudinal sampling is controlled by instrument considerations, while the longitudinal spacing is determined by the distance the Earth rotates during one orbital period. Typically, these orbiters have periods of about 104-108 minutes, during which the rotation of the Earth (and therefore the separation between sub-satellite tracks) is 26° - 27° , with coverage of the whole globe once each 24 hours for both day-side and night-side portions of the orbit. At any latitude, all orbits view about the same local time. Thus, satellite coverage is very good for large-scale processes, and phenomena that do not change rapidly in times much less than a day.
- Since the same instrument is used at all locations, systematic errors will tend to be similar everywhere. Thus, although absolute values may be in error, differences, and thus spatial or temporal gradients, may be determined quite well. This is especially important for the calculation of geostrophic winds from temperatures, calculation of transports, and determination of seasonal and longer term trends.
- Satellite observations have an ability to reach regions of the atmosphere which are difficult to observe by conventional measurements. Satellites are the major data source for all altitudes over the oceans and in the Southern Hemisphere, and above 30 km altitude over Northern Hemisphere land areas.

Table 5-2
Aircraft Programs

Aircraft Programs	Agency	Aircraft Type	Measurements	References
Stratospheric-Tropospheric Exchange Project	NCAR	Sabreliner	Temperature and ozone in the vicinity of active tropopause	Shapiro, 1976, 1978
Global Atmospheric Sampling Program	NASA-Lewis	Commercial 747	Temperature, ozone, carbon monoxide, and CN along commercial air routes	Perkins et al, 1978 Falconer and Holdeman, 1976
Stratospheric Air Sampling Program	NASA-Ames	U-2	Temperature, ozone, nitric oxide and other stratospheric species over ITCZ and meridional and latitudinal surveys	Loewenstein et al, 1978 NASA TM 78577, 1979
Project Airstream	Department of Energy	WB-57	Whole air samples, chlorinated compounds particulates, radioactive debris, and tritium, latitudinal surveys from equator to 75°N three times per year	Department of Energy Reports of the Environment Measurement Laboratory, 1978, 1979
Project TROZ	Max Plank Institute for Aeronomy	Commercial 707	In situ ozone, meridional and seasonal variability	Fabian and Pruchniewicz, 1977
GAMETAG	NSF, Georgia Inst. of Tech.	NCAR-Electra	Hydroxyl, aerosols, ozone, nitrogen compounds, in troposphere	Davis, D.D. and others, 1978

- Finally, the use of satellite data in long-term trend detection requires that the data be routinely verified/calibrated against some standard. This is necessary to compensate for instrumental drift or change in the atmospheric state that are not included in the data processing. For the current satellite system, this is probably best accomplished by comparing the satellite data with the ground-based data discussed previously.

Satellite measurements, especially those from the Nimbus series, have greatly expanded the data on temperature and ozone in the stratosphere and lower mesosphere. Much of the temperature data has already been used for operational and research purposes. Other data, including the ozone data, are just beginning to be available and many more constituents will be measured in the future.

Satellite Measurements of Temperature

Satellite temperature sounders have been used since 1969 (table 5-3). Until 1975, all measurements were made looking downward, or nadir viewing. In this case, radiation received comes from a deep layer (Wark and Fleming, 1966). Measurements of radiation upwelling from a uniformly mixed constituent such as carbon dioxide, in the $15\mu\text{m}$ band allow one to obtain the mean black body temperature over the thickness of this layer, which is on the order of 12-20 km. The highest weighting functions for the early sounders such as SIRS and IRIS peaked at about 25 km. The later operational sounders, Infrared Temperature Profile Radiometer (ITPR) and Vertical Temperature Profile Radiometer (VTPR) were similar. Subsequently, the Selective Chopper Radiometer (SCR) launched on Nimbus-4 (1970) and Nimbus-5 (1972) had weighting functions peaking up to 45 km, and the Pressure Modulated Radiometer (PMR) launched in 1975 on Nimbus-6 allowed altitudes up to 80 km to be observed.

Present operational sounders on TIROS N have characteristics similar to the VTPR and the SCR. Recent results of studies utilizing a sample of 1200 simulated radiances from the three TIROS N sounding instruments and the regression techniques of Quiroz and Gelman (1972) shown in table 5-4, indicate the general level of precision that we might expect from this system. The temperature rms differences are on the order of 2°C up to about 10 mb, increase to about 4°C at 1 mb and become about 6°C at 0.4 mb.

The first atmospheric limb viewing instrument, the Limb Radiance Inversion Radiometer (LRIR) was also flown on Nimbus-6. By scanning across the limb, atmospheric emission is measured as a function of altitude, which allows vertical distribution of temperature (and trace constituents) to be determined. In addition, temperature weighting functions are only 4 km thick, from the tropopause to about 65 km (Gille and House, 1971). The narrow weighting functions and frequent samples (spaced 1.5 km apart vertically) allow higher vertical resolution and better depiction of atmospheric temperature structure than with downward viewing instruments. However, some horizontal resolution is lost since 50% of the energy (at 10 mb) received comes from a 300 km horizontal path. An additional disadvantage of the LIMS and LRIR is that the detector is actively cooled with an on-board cryogen which dissipates in orbit resulting in a 6-7 month lifetime. Table 5-5 presents the mean differences between a sample of rocket and LRIR retrievals, and the repeatability of the LRIR results. The Limb Infrared Monitor of the Stratosphere (LIMS) similar to LRIR, and the Stratospheric and Mesospheric Sounder (SAMS) also a limb viewing instrument, were flown on Nimbus-7.

Satellite Measurements of Ozone

Total Ozone

Satellite remote sensing methods for determining total ozone are basically divided into two techniques, that using backscattered UV sunlight (Dave and Mateer, 1967) and that using $9.6\mu\text{m}$ radiation emitted by the atmospheric ozone (Prabhakara et al., 1970). Both require the use of *a priori* statistical information on the

Table 5-3
Satellite Measurements - Temperature

EXPERIMENT			MISSION	Comments
Instrument Name	Accuracy	Altitude Range/Resolution		
IRIS	3K	0-25 km/10 km	Nimbus 3	Nadir looking only
SIRS	3K	0-25 km/10 km	Nimbus 3	Nadir looking only
IRIS	2-3K	0-25 km/10 km	Nimbus 4	Nadir looking only
SIRS	2-3K	0-25 km/10 km	Nimbus 4	Nadir looking with cross track scan
SCR	2-3K	0-60 km/10 km	Nimbus 4	Nadir looking only
VTPR	2-3K	0-25 km/10 km	NOAA-2	Cross track scanning
ITPR	2-3K	0-25 km/10 km	Nimbus 5	Cross track scanning
NEMS	2K	0-20 km/10 km	Nimbus 5	Nadir looking only
SCR	2-3K	0-50 km/10 km	Nimbus 5	Nadir looking only
HIRS	2K	0-40 km/10 km	Nimbus 6	Cross track scanning
SCAMS	2K	0-20 km/10 km	Nimbus 6	Cross track scanning
PMR	2-4K	40-85 km/10 km	Nimbus 6	Nadir looking only
LRIR	1K	15-65 km/2 km	Nimbus 6	Limb viewing
LIMS	1K	10-65 km/2 km	Nimbus 7	Limb viewing
SAMS	3K	10-120 km/10 km	Nimbus 7	Limb viewing
SSU HIRS-2 MSU	TOVS 2-3%	0-60 km/10 km	Tiros-N	Cross track scanning

Table 5-4
 RMS Temperature Error as a Function of Pressure
 Simulated from a Sample of 1200 Observations for a
 Nadir Temperature Sounder (Quiroz and Gelman, 1972)

Level (mb)	RMS Temperature Differences K (Retrieval vs. Actual)
100	2.6
70	1.8
50	2.1
30	2.4
10	2.1
5	2.8
2	3.3
1	4.2
0.4	5.7

Table 5-5
 Mean Difference Between LRIR and Rocketsonde Temperatures,
 and LRIR Repeatability. Mean Differences Based on 78
 Comparisons Within Three Hours. (From Bailey and Gille,
 1978, and Gille et al., 1979)

Pressure Level (mb)	Mean Difference (K) (LRIR minus Rocket)	Precision (K)
100	-1.1	1.0
50	0.2	0.5
30	-0.1	0.6
10	-0.7	0.6
5	-0.1	0.7
2	0.6	1.2
1	0.2	1.7
0.4	0.7	2.0
0.1	.3	2.0

ozone distribution. These techniques were evaluated with the backscatter UV spectrometer (BUV) and infrared interferometer spectrometer (IRIS) sensors flown on Nimbus satellites, and they were found to agree within ± 6 percent with simultaneous Dobson station data over a broad range of conditions (Mateer et al., 1971; Prabhakara, 1976; Fleig et al., 1978). This value includes station to station differences as well.

While satellite systems offer more extensive spatial coverage than the ground-based systems, it is important to recognize that certain caveats must be considered. The SBUV (Nimbus-7) and BUV (Nimbus-4) instruments are nadir viewing daylight sensors only, which means that for a typical polar orbit the data are about 27° in longitude apart. A single instrument provides limited longitudinal resolution. Also, as a daylight sensor it does not obtain retrievable information in the wintertime polar night. The Total Ozone Mapping System (TOMS) on Nimbus-7 has a side-scanning capability that resolves the longitudinal spatial sampling problem, but the winter polar limitation is still in effect.

For a $9.6\mu\text{m}$ instrument both day and night coverage is achieved, and when side-scanning capability is included, as in the NOAA HIRS-2 and the Air Force MFR instruments, the coverage is comparable to TOMS. The major difficulties with the infrared technique are that the total ozone retrievals must include a correction to the observed radiances for cloud contamination, and in the winter polar regions additional errors arise due to the lack of temperature contrast. The accuracies of satellite total ozone measurements are discussed in detail in Chapter 6.

Vertical Distribution of Ozone

Methods for remote sounding of the vertical distribution (Singer and Wentworth, 1957) using backscattered UV radiation have been discussed by Mateer (1972). The ozone profiles inferred from measurements of the UV Earth radiance are valid from above the ozone concentration maximum (about 30 km) to approximately 55 km, and have a vertical resolution of about 7 km. Instruments using the backscatter principle have been flown on satellites in several short-lived experiments (Iozenes et al., 1969; Rawcliffe and Elliot, 1966), while longer lived experiments were flown on OGO-4 (London et al., 1977) and on Nimbus-4 (Heath et al., 1973).

The longest lived experiment to date has been the BUV on Nimbus-4, which was launched in April 1970 and produced data until it was put in a standby mode in late 1977. The results, although of lower vertical resolution than direct rocket or balloon sounding data, agree, to about 10 percent, with simultaneous rocket measurements. The BUV was also flown on Atmospheric Explorer-E (AE-E), in a low inclination orbit (20°) in 1975 and initial results reported by Guenther et al. (1977). Results from preliminary analysis of Nimbus-4 BUV profiles have been reported by Deluisi et al. (1979). An improved version of the BUV called the SBUV was flown on Nimbus-7 and has an additional capability to measure the solar ultraviolet flux from $140\mu\text{m}$ to $340\mu\text{m}$. Additional comments concerning accuracies of ozone profile measurements appear in Chapter 6.

Gille et al. (1970), Russell and Drayson (1972), Gille et al. (1979), Bailey and Gille (1978) have discussed determination of the ozone profile from satellite measurements of limb emission in the $9.6\mu\text{m}$ band. The weighting functions are again of the order of 4 km wide, allowing high vertical resolution. Comparison of LRIR on Nimbus-6 with 4 rocket soundings indicates agreement to within 1 ppmv and precision of 0.3 ppmv from 30-60 km. (In percentage terms the agreement was within 5% from 30-60 km). Repeatability determined by a series of measurements within four degrees of latitude (where atmospheric variations are small) was better than 10% from 30 to 55 km. A similar instrument, LIMS, flew on Nimbus-7.

The Stratospheric Aerosol and Gas Experiment (SAGE) on Application Explorer Mission - B (AEM-B) was launched in early 1979. It is a four-channel grating spectrophotometer; three channels are for deducing the physical properties of stratospheric aerosols, the fourth for deducing vertical distributions of ozone concentration. SAGE is a solar occultation experiment; i.e., it obtains its basic data by the absorption of solar radiation viewed through the Earth's limb.

A summary of the history and status of satellite ozone measurements is given in Chapter 6 (see table 6-1).

DATA ORGANIZATION AND ANALYSIS OF STRATOSPHERIC FIELDS

Background

The optimal use of large sets of stratospheric measurements will result in a significant increase in the understanding of (1) the natural morphology of ozone, temperature, and other trace species, (2) the variations of these parameters over various time scales, and (3) the causes of these variations. Several analysis schemes are employed to utilize the various data bases available, ranging from relatively simple averaging of quantities, analyses using subjective or objective interpolation schemes, and finally, sophisticated statistical computations designed to handle large data sets or data with uneven spacing in time and/or space. The following sections summarize some of the more useful of these approaches.

Standard Atmospheres

Among the earliest attempts to assemble and organize upper atmospheric data from various sources into a coherent entity was the preparation of the United States Standard Atmosphere, 1962 and the subsequent supplements. This model utilized standard meteorological data for the troposphere, balloon data for the lower stratosphere, and the rocket data for the upper stratosphere, mesosphere, and thermosphere, all referred to a latitude of 45° North, average solar conditions, and averaged over a year. The U.S. Standard Atmosphere Supplements (1966) extended the altitude coverage to 1000 km based largely on Jacchia's empirical model (1965) and included systematic effects due to latitude, season, time of day, and solar activity. The U.S. Standard Atmosphere was updated in 1976 using new data for the region above 50 km and an analytic profile for the upper mesosphere and lower thermosphere rather than the earlier tabulation.

Empirical Models

Empirical models of the neutral thermosphere have been utilized for organizing large data bases in a form suitable for geophysical interpretation and comparison with other data (e.g., Jacchia, 1965; the OGO-6 and Mass Spectrometer and Incoherent Scatter (MSIS) models; Hedin et al., 1974, 1977). The application of this technique has recently been extended to include a few stratospheric parameters, primarily the temperature data derived from the Infrared Interferometer Spectrometer (IRIS) instrument carried on the Nimbus-4 satellite, from total ozone data obtained from the IRIS and BUUV instruments on Nimbus-4 and from ground measurements (see e.g. Reber et al., 1977; Keating et al., 1977).

The horizontal distribution of geophysical properties of the atmosphere (such as temperature, density, etc.) at a given height and time can be represented by a spherical harmonic expansion in terms of geographic latitude and longitude:

$$F(\theta, \lambda) = \sum_{\ell=0}^{\infty} \sum_{n=0}^{\infty} p_{\ell}^n(a_{\ell n} \cos n\lambda + b_{\ell n} \sin n\lambda) \quad (1)$$

where p_{ℓ}^n = Legendre's associated functions of latitude

θ = latitude (radians)

λ = longitude (radians)

This expansion can be further generalized by expanding the coefficients as a Fourier series in time to yield an analytic expression to represent periodic variations as well.

The expansion given above can represent variations of any complexity in the atmosphere (at a constant height). A standard product of the model generation is the set of coefficients for the various harmonics, orders, and cross terms of the expansions which provide quantitative assessments of variations such as the annual, semi-annual, latitudinal, longitudinal, etc. A simple example is the P_0^0 coefficient which is the global average of the parameter involved, such as of total ozone. Figure 5-6 (lower) shows the variation of global total ozone calculated in this manner on a monthly basis using the BUV data from Nimbus-4 and the Dobson ground data for the same time period. Integration of the spherical harmonics over the Northern and Southern Hemispheres individually provides the hemispherical variations shown in figure 5-6 (upper). For descriptive purposes, one can summarize all the systematic variations included in a large data set (such as obtained from satellites) in a relatively compact set of analytic expressions and the corresponding coefficients. Finally, the model can be expanded by including terms relating the systematic variations to other parameters, such as solar irradiance and magnetic activity.

Subjective Synoptic Analysis

The simplest and most straightforward analysis technique resulting in contoured hemispheric maps is that represented by the long-term, published subjective analyses from the Free University of Berlin (1958-1979). These analyses are for the 100-, 50-, 30-, and 10-mb height and temperature fields for daily Northern Hemisphere (12 GMT), extending from about 1958 to the present.

Objective Synoptic Analysis

Adjustment Technique

An analysis technique that has been in use for several years is the adjustment scheme suggested originally by Cressman (1959) and Yanai (1964). Basically, this method examines the data in the vicinity of an analysis grid-point and adds a "correction" factor to a first-guess value at that point. In practice, the influence of a data point is usually weighted so that those farthest from the grid-point are weighted least, with an upper limit designated on the distance from the grid-point. The first-guess field can be flexible and, in practice, has ranged from a zonal average data field to the analysis from the previous time period (persistence), to a forecast field via a numerical model using data from a previous time period as the initial condition.

The strength of this technique is that it can provide something more than a simple interpolation in large data-gap areas (if data were available previously), but it suffers in that it cannot consider the asynoptic nature of satellite data in a simple manner.

Within the NOAA, National Weather Service, the following stratospheric analyses, utilizing the above technique, are being prepared on a routine basis:

- 100-, 70-, and 50-mb maps of height, temperature, and wind, globally, at 00 GMT and 12 GMT available from late 1974 to the present.
- 70-, 50-, 30-, and 10-mb maps of height and temperature for the Northern Hemisphere at 12 GMT, available from 1964 to the present (Finger et al., 1965).
- 5-, 2-, and 0.4-mb maps of height and temperature for the Northern Hemisphere appropriate to the Wednesday of each week (Staff, Upper Air Branch, 1975, 1976); from 1964 to the present and with the 1-mb level added since July 1976.

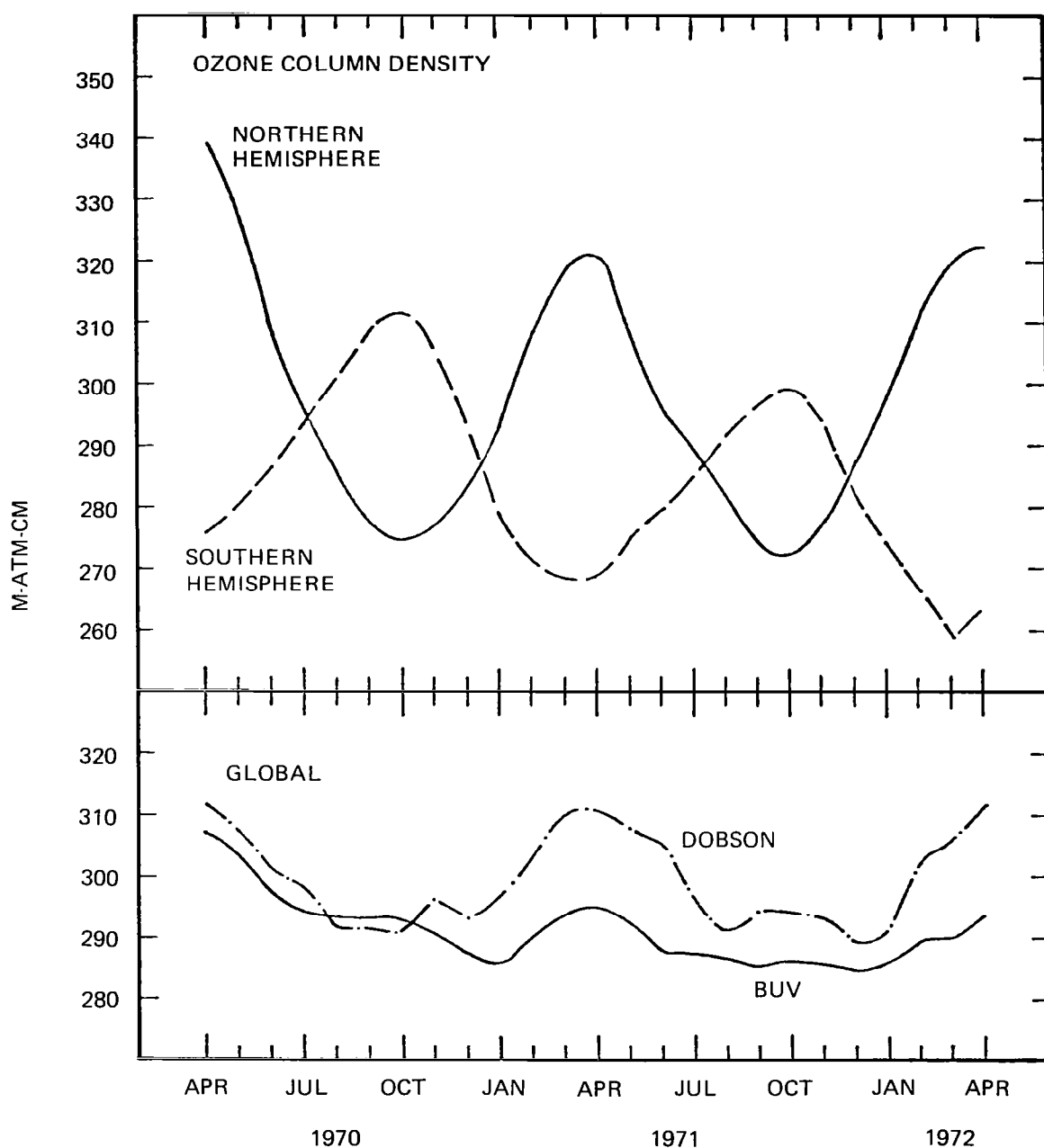


Figure 5-6. (Upper) The Northern and Southern total ozone variations determined by integrating the monthly averaged spherical harmonic expansion over the respective hemispheres. Note the different amplitudes between the hemispheres and that the April 1971 peak in the Northern Hemisphere is reflected directly as a peak in the global ozone variation.

(Lower) The global total ozone determined from the P_0^0 expansion coefficient on a monthly basis for the two-year period April 1970 to April 1972. (Reber, private communication, 1979)

More recently the National Weather Service has initiated a program of global daily (12 GMT) height and temperature analyses using satellite information at 100, 70, 50, 30, 10, 5, 2, 1 and 0.4 mb. After certification, all analyses will be available from the World Data Center, Asheville, North Carolina. An example of the 10-mb map is shown in the section entitled Sudden Warmings (figure 5-20).

Optimum Interpolation

Optimum interpolation is an analysis scheme based on statistical concepts (Gandin, 1963; Gandin and Kagan, 1974). Observed data are assigned weights so that the mean square error of interpolation to desired analysis points (usually points of a regular grid) is a minimum in a statistical sense. A reasonably intelligent "first guess" of each field is desirable; usually, a short period prediction, persistence, climatology, or some combination of these is used.

Optimum interpolation can be univariate or multivariate. In the former case, only observed data of the same kind as the field being analyzed are used. In the latter case, data which are related to the field being analyzed by gradient relationships (for example, wind data) to the geopotential height gradient *via* the geostrophic relationship are also used. The correlation statistics must be modified to include the gradient relationship.

The variable quality of observed data is allowed for in optimum interpolation. Poor quality data receive less weight, other factors being equal, in the analysis compared to data of good quality. The correlation of certain types of observational errors, which reduces the amount of independent information the observations contain, is also part of the analysis method.

Optimal Estimation

Satellite data are acquired continuously, regularly spaced in position and time. This regularity lends itself readily to optimal estimation techniques, using a Kalman filter. Rodgers (1977) described an approach in which, at a given latitude and time, a variable is represented by a mean and series of Fourier coefficients expressing the longitudinal variation. Information on the precision of these coefficients is contained in a covariance matrix which is also calculated.

At a given latitude, each new satellite overpass provides a new observation which may be used to update the previous estimate of the coefficients. This is done by combining the measurement, weighted inversely by its variance, with the weighted previous estimate. This results in a time series of estimates of the coefficients. The two may then be combined to yield a final optimal estimate of coefficients as a function of time. Perhaps the major result is that the coefficients can be used to produce optimal estimates of the instantaneous state of the atmosphere (synoptic maps), although the data are obtained asynchronously.

Rodgers (1977) applied this technique to Selective Chopper Radiometer (SCR) data. Kohri and Gille (1977) have studied the application of this approach to satellite data with realistic errors and data gaps. They found that the LRIR temperature, geopotential and ozone data allowed 6 longitudinal wavenumbers, although most of the variance is contained in the lowest wavenumbers. An ozone map using this technique on LRIR data every 4° of latitude is shown in figure 5-7.

From this analysis, the meridional cross sections are immediately obtained from the mean coefficients. The geopotential can be differentiated in the latitudinal direction to yield the zonal mean geostrophic wind, $\bar{U}$.

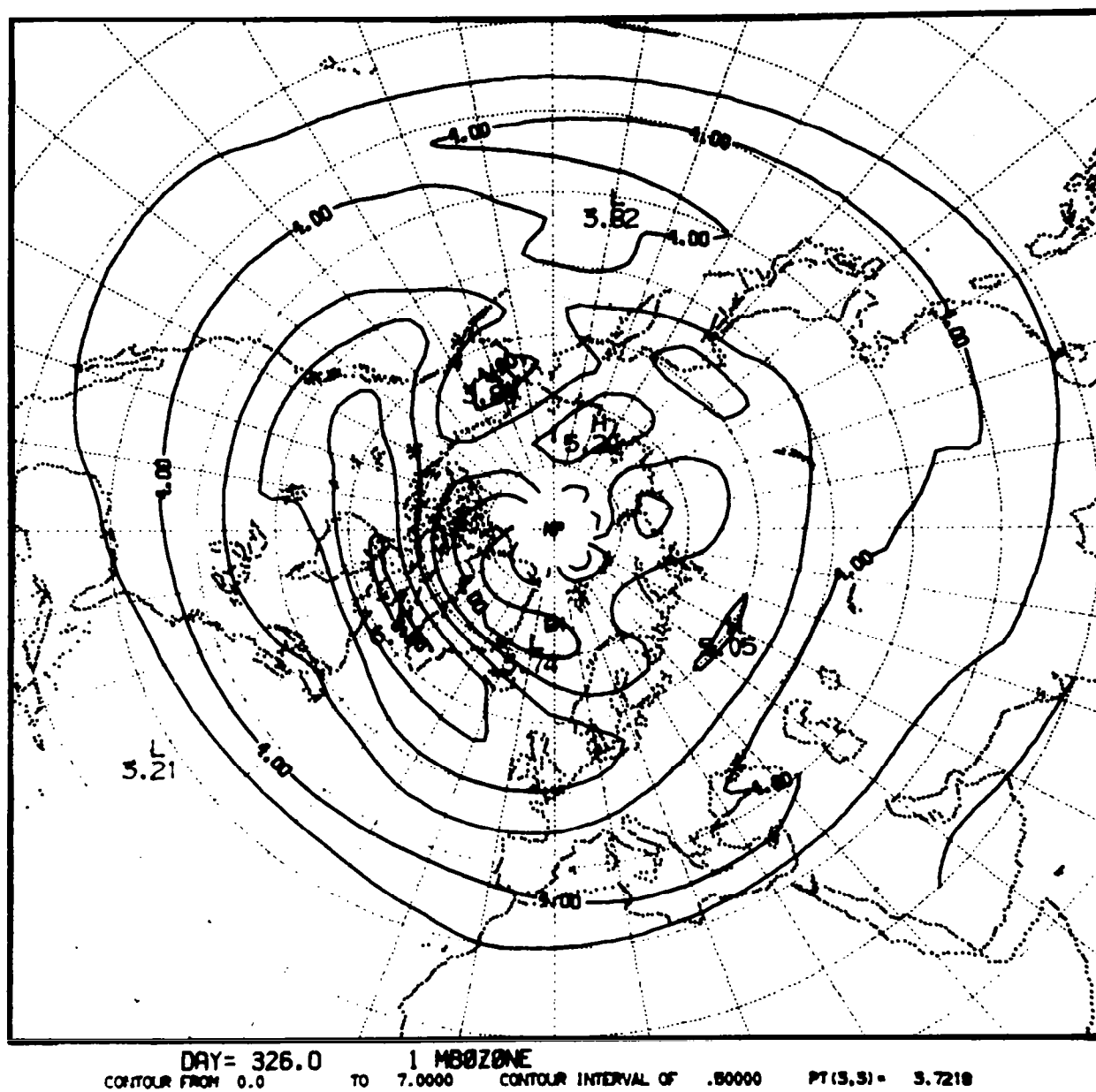


Figure 5-7. Northern Hemisphere analysis of ozone mixing ratio derived from LRIR on Nimbus-6 at 1 mb using optimal estimation technique. Contours are mixing ratio by volume at 0.5 ppmv intervals (Kohri and Gille, 1977).

Additionally, the meridional component of the geostrophic wave velocity, v' (sometimes termed eddy motion) can be obtained immediately from the coefficients of the geopotential, which facilitates calculation of meridional eddy transports. Zonal eddy components, v^* , may also be obtained by differentiating the geopotential coefficients in the latitudinal direction.

STRATOSPHERIC CIRCULATION

INTRODUCTION

The distribution of ozone within the stratosphere is strongly affected by stratospheric air motions transporting ozone and energy, which together with vertical motions influence the temperature distribution in the stratosphere. The temperature distribution is very important in the photochemistry of ozone. The motions, in turn, are strongly influenced by radiative sources and sinks of thermal energy, while ozone is the principal absorber of solar radiation in the stratosphere. The ozone distribution, the movement of air, and the radiative environment in the stratosphere, therefore, are all closely coupled.

In this section our current understanding of the circulation or motion field of the stratosphere and its interactions with the ozone distribution and the radiative processes in the stratosphere is presented. The first section introduces the nomenclature of the various types of motion which are observed in the stratosphere. The manner in which motions respond to radiative forcing and produce the usual patterns of temperature and wind, which is often called the general circulation, is discussed next. Several types of specific motion patterns are then discussed, including the quasi-biennial and semi-annual oscillations, sudden warmings and very short period motions. A separate section specifically details the present state of knowledge concerning how the ozone distribution is determined by both the influences of atmospheric motions and chemistry. A final section discusses the possible stratospheric response to solar variability.

TYPES OF MOTION

Atmospheric motions are described in terms of the zonal average and the deviations from that average. These deviations are referred to as eddy, or wave components. Waves which represent variations characterized by very large wavelengths (zonal wavenumbers 1-3) and by fairly long periods (several days or more) are known as planetary waves. Quasi-stationary planetary waves represent much of the variability observed in the extratropical stratosphere. Synoptic-scale waves are waves which have shorter horizontal wavelengths. Those synoptic-scale waves, which are important in the stratosphere, are essentially upward extensions of extratropical weather systems and are confined to the lower stratosphere. Several other long-period oscillations contribute to the variability of the equatorial stratosphere. These include the semi-annual, and quasi-biennial oscillations, as well as such equatorial waves as the Yanai and Kelvin waves. Finally, there is the prominent annual oscillation of the zonal mean itself. Short-period motions (i.e., those whose periods are on the order of 1 day or less) include the planetary-scale atmospheric tides, as well as much shorter scale waves. These short-period, small-scale waves are commonly divided into three groups: acoustic, inertial, and gravity waves. The first two of these groups, which are the result of compressibility or purely rotational effects, respectively, are generally unimportant in the stratosphere.

The characteristic periods and horizontal scales of the stratospheric waves, which are discussed in greater detail in this chapter, are summarized in table 5-6. The relative amplitudes of these waves as a function of height are plotted in figure 5-8. Synoptic-scale waves are vertically trapped and do not penetrate very high into the stratosphere. Quasi-stationary planetary waves are vertically trapped by the easterly zonal mean flow in summer, but can propagate vertically in the winter zonal mean westerlies, growing in amplitude with height as

Table 5-6

Stratospheric Wave Characteristics

Type of Wave	Period (days)	Zonal Wavenumber*
Planetary Waves	$\gtrsim 3$	1-3
Equatorial Waves		
Kelvin	12-20	1-2
Yanai	4-5	4-5
Synoptic-Scale Waves	$\gtrsim 3$	5-15
Atmospheric Tides	≤ 1	1-2
Gravity Waves	$\ll 1$	Wavelengths ~1-100 km

*Zonal wavenumber is the number of waves which could fit around a latitude circle.

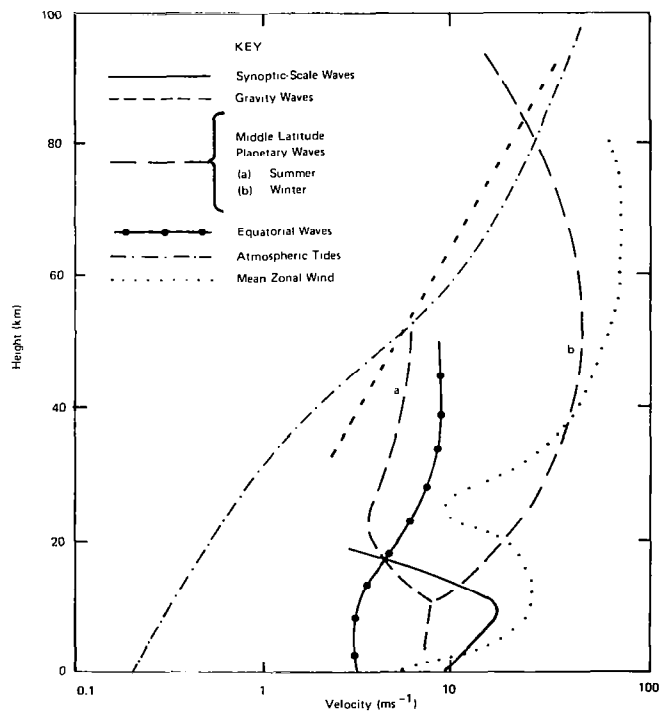


Figure 5-8. Vertical distribution of wind amplitudes (order of magnitude only) associated with various atmospheric wave components (from an original graph by T. Matsuno, private communication). For comparison, the mean zonal wind is shown for winter.

they do so. Equatorial waves which are important in the tropical stratosphere also propagate energy vertically, but they are subject to strong radiative damping at stratospheric heights. Gravity waves, and those atmospheric tidal components which can propagate vertically, are less affected by this radiative damping, so they continue to grow in amplitude as they propagate into the mesosphere. Before discussing the various waves in more detail, the mechanisms which maintain the background zonal flow itself will be considered in the next section.

GENERAL CIRCULATION OF THE STRATOSPHERE

Background

An understanding of the general circulation of the stratosphere implies an understanding of the physical processes by which the wind, temperature and other properties of the stratosphere are maintained. This understanding includes an appreciation of which atmospheric phenomena contribute most importantly to the maintenance of the mean state, seasonal fluctuations and interannual variability in the stratosphere. The traditional approach to these questions is through diagnosis of data and of numerical model output using the conservation laws known to govern the atmosphere: conservation of mass, momentum, heat, and energy. An integral part of most diagnostic studies of this type (see Lorenz, 1967 and 1969 for a review of the tropospheric general circulation) is the division of the meteorological fields being analyzed into a zonal mean part and the deviation from the zonal mean called the wave or eddy part of the flow field.

Mean Zonal Wind

The important features of the annual oscillation in the stratospheric and mesospheric zonal wind system are depicted in figure 5-9 from Murgatroyd (1969). The discussion which follows summarizes what is known observationally and theoretically about the annually-varying circumpolar jets which attain their maximum velocities in the 60 to 70 km region.

The traditional means of observing winds and temperatures in the region between about 30 km and 65 km has been the meteorological rocket network. Both the rocket data and winds derived geostrophically from satellite temperature data show that there are pronounced interhemispheric differences in the stratospheric jets in addition to the seasonal reversal that is evident in figure 5-9. They also show that the flow in summer is nearly independent of longitude, while in winter there are large-amplitude meanders in the circumpolar flow (i.e., planetary waves). It is important to note that the spatial resolution of the meteorological rocket network is not by itself sufficient to describe the annual variation of the distribution of zonal winds. Figure 5-9 indicates that the peak-to-peak range of the annual cycle of middle atmosphere zonal winds is about 140 m sec^{-1} .

This net annual cycle is driven mainly by differential radiative heating which has maximum amplitude at about 50 km. At this level, solar heating at the solstices is at maximum at the summer pole, decreasing toward the winter pole, where infrared radiative cooling predominates. Figure 5-10 is a cross section of net radiative heating rate constructed from a number of sources by Leovy (1964) which illustrates these features. The short-wave heating is principally due to absorption of solar radiation by ozone; thus, changes in the zonally averaged ozone concentration in the upper stratosphere will affect the zonal mean flow there. It is also important to note that throughout large portions of the stratosphere, there is normally a close balance between shortwave heating and infrared cooling, and that it is the much smaller residual sum of these which provides the *in situ* drive for the motions in these regions. As discussed later in this chapter, the uncertainties associated with radiative transfer calculations make accurate direct diagnosis of such small residuals difficult.

The response to such differential heating is a meridional overturning with rising motion in the high-latitude summer hemisphere and sinking motion in the high-latitude winter hemisphere. The action of Coriolis torque

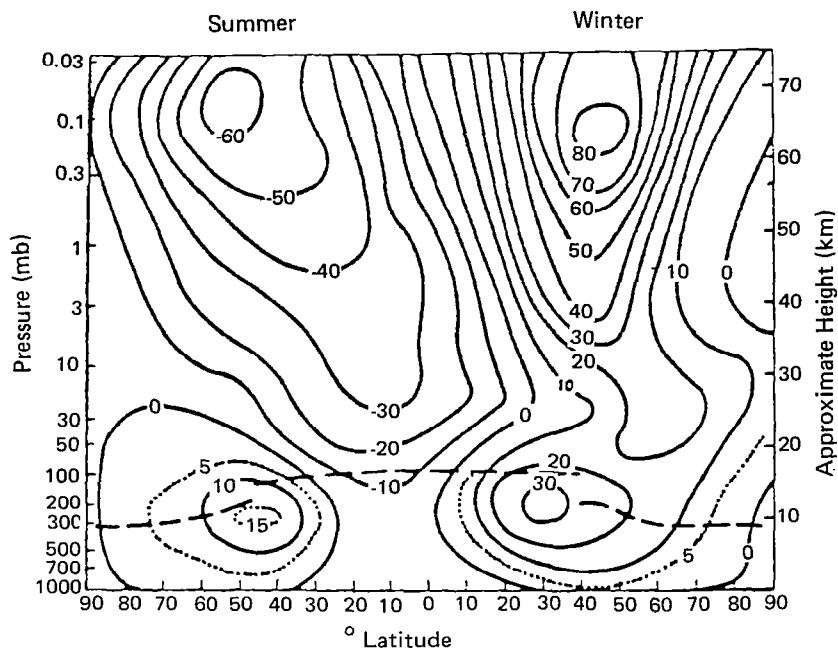


Figure 5-9. Schematic diagram showing zonal winds (m/sec) in the middle atmosphere at times of solstice (from Murgatroyd, 1969).

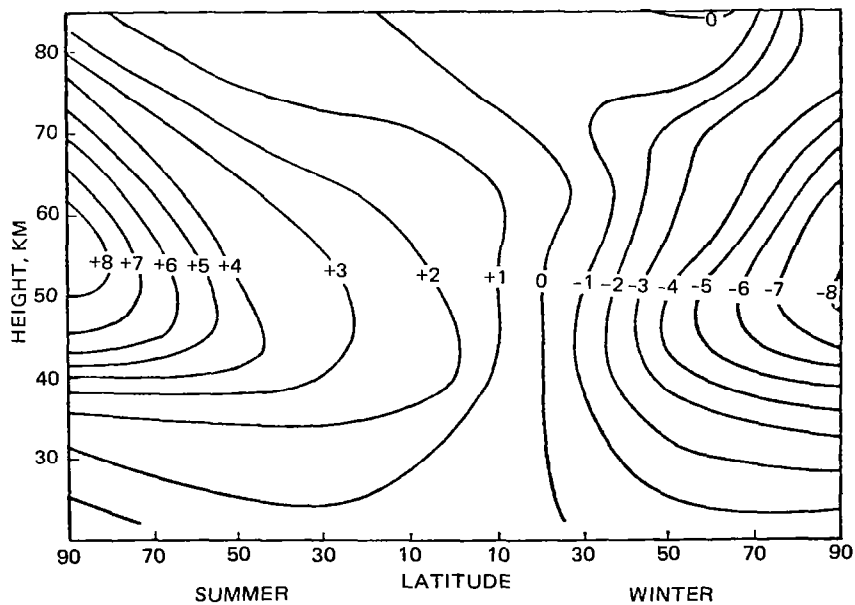


Figure 5-10. The zonal mean "external" heating $\bar{J}_e$ (K day^{-1}) for an atmosphere with standard horizontal mean radiative equilibrium temperature $T_0(z)$ (after Leovy, 1964).

(i.e., the Earth's rotation) on the upper branch of this global meridional cell produces the easterly (westward flowing) zonal wind jet in the summer hemisphere and the westerly (eastward flowing) zonal wind jet in the winter hemisphere. The return branch of this meridional cell is located at much lower levels, where the density is much higher and the flow is correspondingly weaker.

One of the earliest models of this middle atmosphere circulation was that of Murgatroyd and Singleton (1961), who calculated the meridional overturning by assuming that the differential heating pattern was balanced by the cooling and heating in the respective upward and downward branches of the overturning. Such a model is not useful for predicting the amplitude of the zonal wind jets, because it does not specify how the angular momentum put into the jets by Coriolis torque can be balanced. Such a model also ignores other mechanisms that can drive meridional overturning such as a horizontal flux of heat by the zonally-asymmetric (eddy) component of the motion field in the middle atmosphere.

The first model to incorporate most of the relevant processes in one form or another was that of Leovy (1964). His model predicts that meridional overturning and the zonal jets are a response to prescribed differential heating in the presence of parameterized horizontal fluxes of heat and momentum by eddies. Leovy presented results separately for the cases where the parameterization of these flux divergences took the form of a linear relaxation law (i.e., Newtonian cooling and Rayleigh friction) and where they took the form of conventional eddy diffusion. He was able to obtain summer and winter hemisphere jets of the observed amplitude and at the right levels by reasonable choices of the coefficients in his parameterizations. His model results also show a warm winter mesopause and cold summer mesopause which is in agreement with observation.

More recent models of the annual oscillation in the stratospheric zonal wind by Trenberth (1973a, b); Schoeberl and Strobel (1978a); and Holton and Wehrbein (1979) treat various processes more realistically than the Leovy (1964) model. These model studies indicate that we still need to understand in more detail the mechanics of the interaction between planetary waves, the zonal flow, and the nature of the mechanical dissipation before we can successfully simulate this interaction in numerical models of the annual oscillation.

In the upper stratosphere, the annual cycle of zonal mean wind and the associated temperature field is not smoothly varying, but often undergoes rapid irregular changes associated with large-scale wave activity in the winter hemisphere. These changes in zonal mean temperature, although apparently associated with planetary wave activity in the winter hemisphere (Madden, 1975), extend well into the summer hemisphere (Fritz and Soules, 1970; and Labitzke and Barnett, 1973). These intra-hemispheric oscillations emphasize the essentially global nature of the stratospheric general circulation, which becomes increasingly apparent at higher altitudes. Enhanced planetary wave (zonal wavenumber 1-3) activity often accompanies abrupt springtime transitions from winter to summer circulation patterns in both hemispheres. These transitions are similar in many respects to the major stratospheric mid-winter warmings which have been observed only in the Northern Hemisphere. Large amplitude planetary waves, which are coherent with planetary waves in the troposphere, are observed in the upper stratosphere and mesosphere in winter (Muench, 1965), but in the summer, wave activity is weak (Muench, 1968). However, in the lower stratosphere (below about 20 km), wave activity at both planetary and synoptic (zonal wavenumbers 4 to 15 or so) scales is present in all seasons, although it is greatest in winter.

Heat, Momentum and Energy Budgets

The extratropical lower stratosphere (30°- 90° latitude, 10-30 km) in the Northern Hemisphere has been comparatively well studied because relatively good coverage by rawinsonde observations has been available for some years. Extensive studies of the energy balance of this region have been performed for two complete years of data (Oort, 1964; Dopplack, 1971) and for a large number of shorter periods (Reed et al., 1963; Muench, 1965; and Julian and Labitzke, 1965, as well as others). The key finding of these studies was that the

lower stratosphere is driven very strongly from below by eddy energy fluxes. They also show that the eddies transport heat up the gradient of zonal mean temperature and that radiation tends to destroy the meridional gradients rather than produce them. Diagnosis of numerical general circulation models also indicates that the seasonal temperature variations in the lower stratosphere are controlled primarily by dynamical processes rather than by radiation (Manabe and Mahlman, 1976). An upward extension of the tropospheric meridional circulation feature known as the Ferrel cell is driven by eddy fluxes of heat and momentum in the lower polar stratosphere of both hemispheres (Vincent, 1968; Mahlman, 1969; Adler, 1975). The disturbances which are important in the lower stratosphere include planetary-scale eddies and vertical extensions of baroclinically unstable synoptic-scale eddies. These large scale eddies, together with the mean meridional circulation, dominate the transport in the lower stratosphere. Heat and momentum exchange by small-scale turbulence appears to be relatively unimportant (Lilly et al., 1974).

The extratropical *upper* stratosphere differs from the lower stratosphere in several respects. Because synoptic-scale eddies generated in the troposphere do not penetrate to these altitudes, the eddy activity is dominated by the planetary scale waves. In addition, the radiative forcing of the circulation becomes more important as one goes upward in the stratosphere. As noted earlier, radiative forcing is the principal drive for the zonal wind system in the upper stratosphere, and dynamical transports by eddies provide a mitigating influence rather than a determining influence. Between the lower stratosphere and the upper stratosphere, the relative importance of heat transport by eddies decreases, compared with heat transport by the mean meridional circulation. In the lower stratosphere, eddy heat transport is sufficient to drive a thermally indirect mean meridional circulation, whereas there is a gradual transition to a thermally direct, radiatively forced circulation as the stratopause is approached from below. The planetary wave energy originates in the troposphere primarily as a result of zonally asymmetric thermal and orographic forcing (Saltzman, 1968; Manabe and Terpstra, 1974). Furthermore, the propagation of these waves into the stratosphere is strongly dependent upon the zonal mean wind structure (Charney and Drazin, 1961; Dickinson, 1968a, 1968b; Matsuno, 1970; Simmons, 1974b; and Schoeberl and Geller, 1977). The zonal mean wind and planetary wave structures, therefore, are strongly interdependent.

The kinetic energy of the eddy component of the circulation is derived partially from local conversion from available potential energy in the stratosphere and partly from convergence of upward energy flux from below. Figure 5-11 shows energy box diagrams for three layers of the stratosphere during two months of Southern Hemisphere winter. Although these diagrams are based upon limited data, they demonstrate several general features of the energy cycle as a function of altitude in the stratosphere. Both the relative importance of the convergence of the upward flux of kinetic energy compared to conversion from potential energy and the absolute magnitude of the convergence per unit mass of the upward flux of energy increase with altitude in the upper portion of the stratosphere. The conversion of eddy available potential energy to eddy kinetic energy appears to be a manifestation of upward energy flux through the stratosphere rather than being associated with *in situ* baroclinic instability (McIntyre, 1972; and Hartmann, 1976). The eddy kinetic energy delivered to the stratosphere by upward flux from the troposphere is converted primarily into zonal mean kinetic energy through quasi-horizontal processes. Large transients in the amplitude of planetary waves can have a powerful effect on the zonal mean wind and temperature distributions as indicated by the stratospheric warming model of Matsuno (1971).

The relative importance of heat and momentum transport by small-scale turbulence in the upper stratosphere has not been precisely defined, but it may increase with altitude as a result of breaking of gravity waves (Hodges, 1967, 1969). An increase in turbulent momentum exchange may be especially important for the momentum balance of the upper stratosphere and mesosphere, where it appears that both planetary scale eddies and the mean meridional circulation transport momentum poleward. Observations suggesting the presence of high frequency synoptic-scale disturbances near the stratopause have been reported by Leovy and Ackerman (1973), but the importance of these phenomena for the general circulation of the stratosphere has not been determined.

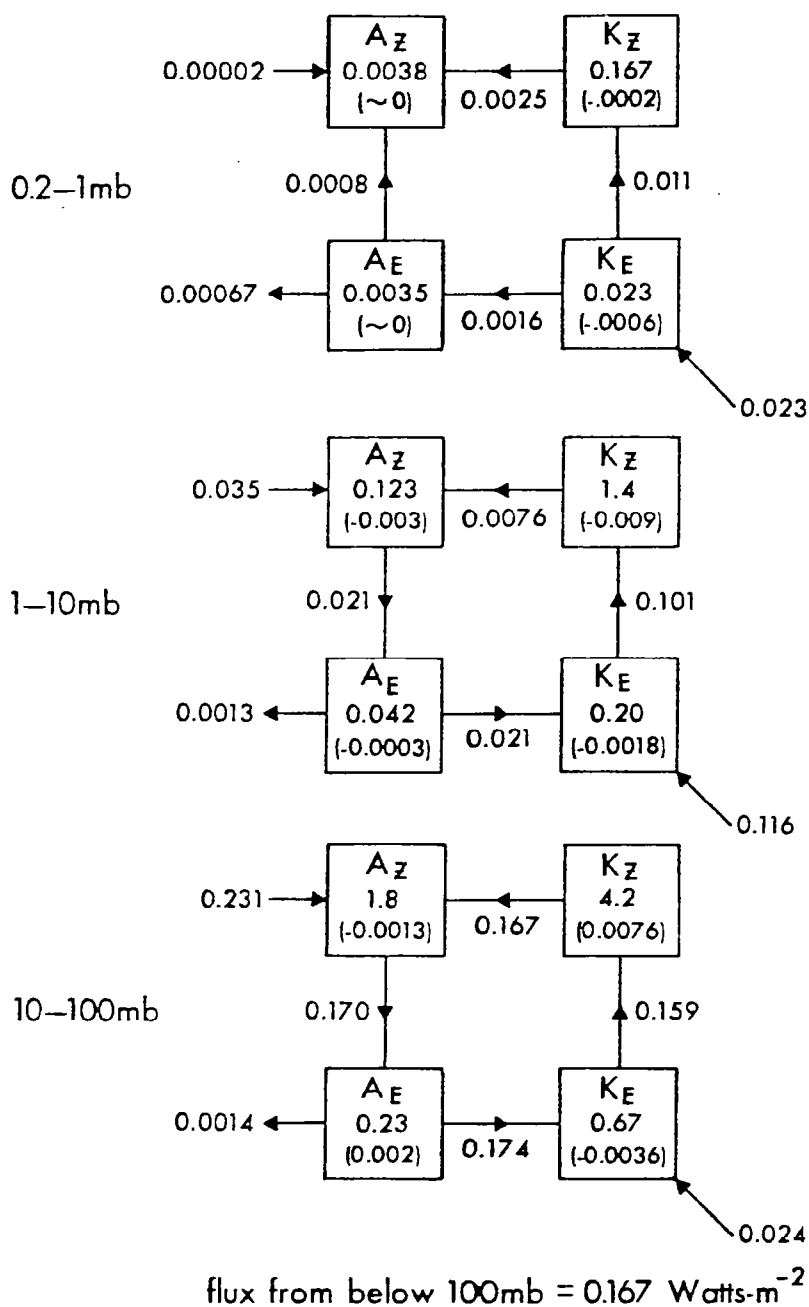


Figure 5-11. Energy box diagrams for three stratospheric layers for the period 1 July to 6 September, 1973, in the Southern Hemisphere (15° – 90° S) determined from analysis of satellite data. The larger numbers inside the boxes indicate the content of available (A_Z , A_E) and kinetic (K_Z , K_E) energies of the zonal mean and eddies and are in units of 10^5 Jm^{-2} . The arrows between boxes indicate the conversions between the four types of energy, the diagonal arrow indicates the convergence of the vertical flux of eddy kinetic energy into the layer, and the horizontal arrows to the left of the available potential energy boxes indicate the generation of energy by radiative processes. The units for the rates are W-m^{-2} (Hartmann, 1976).

In the upper stratosphere, interactions between radiation, photochemistry and dynamics become extremely important. Temperature and ozone photochemistry are closely coupled, since the radiation balance in the upper stratosphere is essentially between absorption of solar radiation by ozone and infrared cooling to space, and ozone, in turn, is inversely proportional to temperature because of the temperature dependence of some of the reactions controlling the photochemical production of ozone (Craig and Ohring, 1958; Lindzen and Goody, 1965; and Blake and Lindzen 1973). Both the zonal mean and the eddy component of the general circulation in the upper stratosphere are coupled to radiation and photochemistry, since the radiative heating drives the zonal mean circulation and damps upward propagating planetary waves. Radiative damping of upward propagating planetary waves has been the subject of several investigations (Dickinson, 1969; and Garcia and Geisler, 1974).

Contrast Between the Hemispheres

A description of the Southern Hemisphere stratosphere has been given by Labitzke and Van Loon (1972) and Knittel (1976). The circulations in the Northern and Southern Hemispheres are quite different, both in the troposphere and in the stratosphere, because of the differences in surface features in the two hemispheres. The surface temperature at the South Pole is much colder than the North Pole because of the high ice sheet covering the Antarctic Continent. These colder polar temperatures strongly influence the radiative environment of the polar stratosphere in the Southern Hemisphere compared to the Northern Hemisphere. In addition, the quasi-stationary planetary wave amplitudes in the Southern Hemisphere are smaller because the zonal asymmetries in orography and surface thermal contrast which force these waves are much smaller in the Southern Hemisphere than in the Northern. Approximately half of the total planetary wave energy in the Southern Hemisphere is contained in eastward traveling waves 2 and 3, which appear to be generated in the troposphere through the process of baroclinic instability rather than being primarily forced quasi-stationary waves as in the Northern Hemisphere (Phillpot, 1969; Leovy and Webster, 1976; and Hartmann, 1979). Although the Southern Hemisphere stratosphere has periods of substantial planetary wave activity, there are no observed occurrences of the major stratospheric warmings with concurrent wind reversals such as occur in the Northern Hemisphere. The reasons for this have not been isolated, but they seem likely to be related to the strong radiative influence of the cold Antarctic Continent which continuously acts to generate a strong poleward temperature gradient, and to the weaker planetary wave forcing due to greater zonal symmetry in the Southern Hemisphere.

Final Remarks

The preceding discussion indicates several deficiencies in our knowledge of the general circulation. The first is that there are inadequate observations of the annual oscillation of zonal winds in the stratosphere and of planetary wave motions in the upper stratosphere. Satellite-based observing techniques show great promise for providing the needed information in both of these areas. From the theoretical standpoint, it is evident that explicit modeling of the effect of planetary waves on the zonal wind system has not been successful. Furthermore, most models of the zonal wind system need considerable dissipation to reproduce the shape and magnitude of the zonal wind jets. The source of such dissipation in the atmosphere is not known, but may be due to motions on the space and time scales of internal gravity waves.

A major effort will be required to take temperature, ozone, and other trace gas data which are now, or soon will be, obtained from the current generation of research satellites and to convert them into useful data sets for diagnostic studies of the stratospheric general circulation. These data sets are invaluable in themselves and are also necessary for the verification and proper interpretation of numerical modeling studies of the upper atmosphere. A detailed month-by-month climatology of the global stratosphere comparable to the tropospheric studies published by Oort and Rasmussen (1971) and Newell et al. (1972) should be possible with data obtained from satellites in combination with conventional meteorological data. A few cross sections of zonal mean temperature from a single year of Selective Chopper Radiometer data have been published by

Barnett et al. (1972) and Barnett (1974), but a comprehensive study of several years of data including winds and eddy heat and momentum transport statistics has not been attempted. A proper matching between observational and numerical effort and refinement of both should be achieved in the near future. An important further refinement will be the proper integration of interactions between radiation, photochemistry, and dynamics into an overall understanding of the general circulation of the stratosphere. In addition, it is essential to obtain an adequate quantitative evaluation of the role of small scale motion, tides and turbulence in the general circulation of the upper stratosphere and mesosphere.

QUASI-BIENNIAL AND SEMI-ANNUAL OSCILLATION

Background

The annual oscillation was discussed in detail in the previous section on the Mean Zonal Wind. At mid- to high-latitudes, the annual oscillation accounts for most of the variance (that is, the deviation from the long-term mean) in the zonal wind. Closer examination of the wind data (mostly from balloons and rockets) reveals that the annual oscillation is not a simple seasonal reversal. There appear additional components which can be resolved into quasi-biennial and semi-annual oscillations which are not merely harmonics of the annual oscillation. With the availability of new data, especially from satellites, quasi-biennial and semi-annual oscillations have also been detected in the ozone and temperature variations.

The Quasi-Biennial Oscillation

Most of the variance, (i.e., deviation from some long-term mean) in zonal wind within 20° of the Equator and between about 18 and 30 km is contained in the *quasi-biennial oscillation*, whose period varies between about 2 and 2.5 years. The maximum of this zonal wind system is located directly over the Equator and descends with time. In the so-called *westerly phase* of the oscillation, the maximum winds are from the West. As this maximum slowly drifts downward, a descending easterly (that is, from the East) zonal wind appears in the upper part of the domain (35 km). The westerly jet begins to decay with time once it drifts down below about 25 km, and the easterly jet intensifies as it moves downward into the middle of the domain. When the easterly jet has replaced the original westerly jet, a half cycle has passed and the quasi-biennial oscillation is said to be in its *easterly phase*. Figure 5-12 from Coy (1979) shows a time-height cross section of zonal wind data from a single radiosonde station near the Equator. In this representation, the downward drift of the zonal wind is clearly seen. Also notable in this figure is the considerable variation in intensity from cycle to cycle.

Analysis of the day-to-day fluctuations in the observed wind in the tropical lower stratosphere was first undertaken by Yanai and Maruyama (1966) and Maruyama and Yanai (1967). It was soon established that the motions discovered by these authors were associated with a wave of 4 or 5 day period, zonal wavelength of about 10,000 km and phase propagation toward the West. This wave, known generally as the *Yanai wave* (or the mixed Rossby-gravity wave) is vertically propagating in the tropical lower stratosphere and is observed to have the largest amplitude there during the westerly phase of the quasi-biennial oscillation. Another type of wave, discovered by Wallace and Kousky (1968a), has a period of 10 to 20 days, zonal wavelength of 20,000 or 40,000 km and phase propagation toward the East. This wave is generally known as the *Kelvin wave*. It is vertically propagating in the tropical lower stratosphere and is observed to have largest amplitude there during the easterly phase of the quasi-biennial oscillation. Both the Yanai wave and the Kelvin wave are excited by processes in the troposphere.

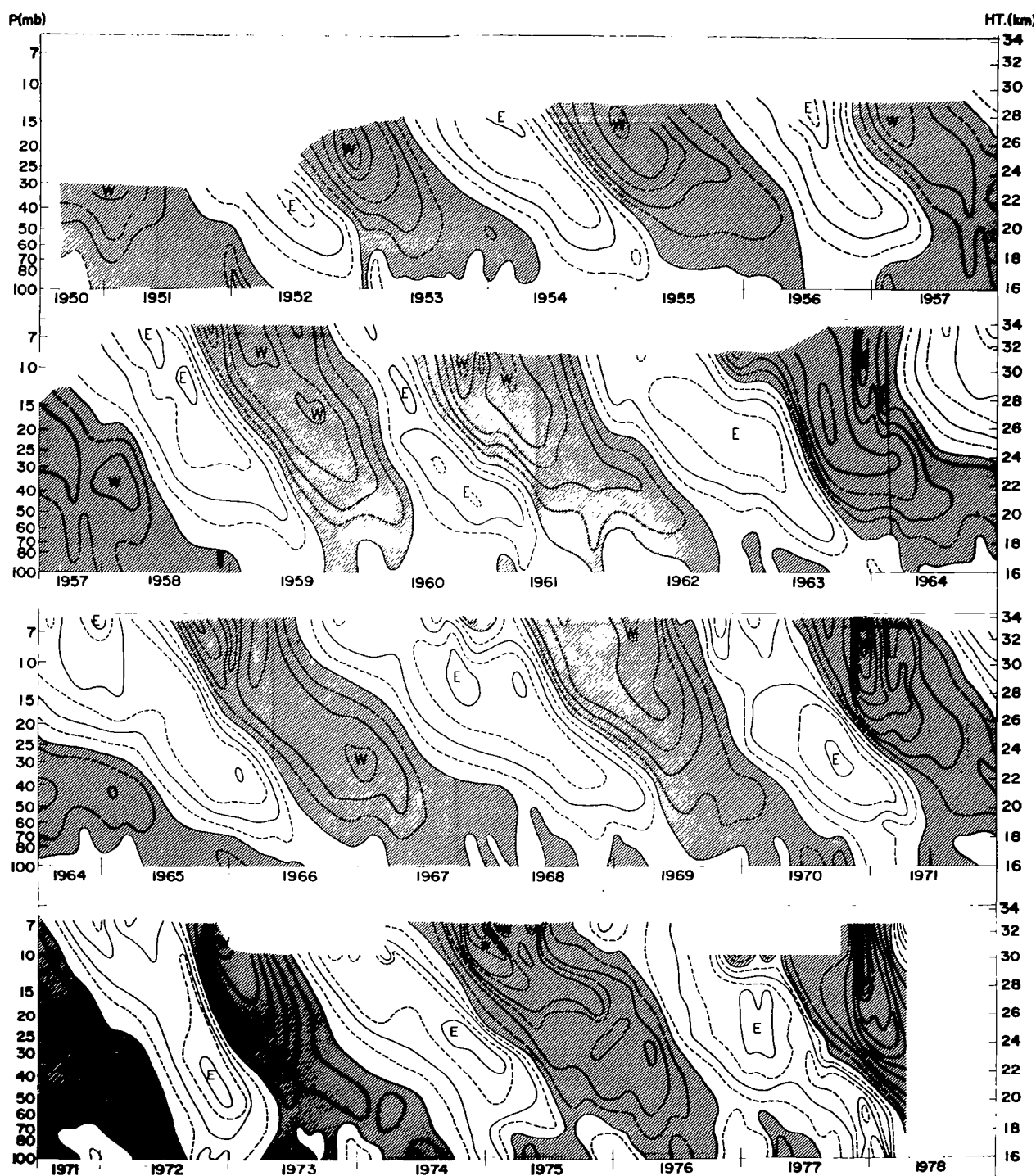


Figure 5-12. Time-height section of the zonal wind near 9° N with the 15-year average of the monthly means subtracted to remove annual and semi-annual cycles. Solid isotachs are placed at intervals of 10 ms⁻¹. Shaded areas indicate westerlies (Coy, 1979).

Wallace and Kousky (1968b) showed that there is an upward flux of westerly (i.e., positive) momentum associated with the observed Kelvin wave that is of sufficient magnitude to account for the westerly acceleration in the quasi-biennial oscillation. The vertical transport of momentum by the Yanai wave is a more complicated process, but it was shown by Lindzen (1970) that the net upward momentum flux by this wave is easterly (i.e., negative) and, hence, opposite to that of the Kelvin wave.

The theory which incorporates the vertical momentum fluxes carried by the Kelvin wave and the Yanai wave as the drive for the quasi-biennial oscillation was advanced by Lindzen and Holton (1968) and in somewhat revised form by Holton and Lindzen (1972). The mechanism works as follows: When the quasi-biennial oscillation is in its westerly phase, the frequency of the (eastward-propagating) Kelvin wave relative to the zonal flow decreases as the Kelvin wave penetrates into the westerly shear zone on the underside of the westerly jet. With the decrease of this so-called *intrinsic frequency*, the wave becomes more susceptible to damping by radiative cooling to space. By this process the Kelvin wave is essentially absorbed in the westerly shear zone of the quasi-biennial oscillation and, therefore, deposits westerly momentum there. The westerly jet thereby builds downward with time. Above this westerly jet, an easterly shear zone exists. As the (westward-propagating) Yanai wave penetrates this shear zone, its intrinsic frequency decreases and the wave becomes increasingly susceptible to radiative cooling to space. As the Yanai wave damps out, it deposits easterly momentum, which acts to bring downward an easterly shear zone and ushers in the easterly phase of the quasi-biennial oscillation.

The magnitude of the momentum flux carried by the Yanai and Kelvin waves observed in the lower stratosphere is about right to account for the observed amplitude and period of the quasi-biennial oscillation. Thus, there is little doubt that the above theory is essentially correct. Subsequent refinements of the theory have occurred in the light of deeper understanding of wave-zonal interactions from papers by Andrews and McIntyre (1976a) and Boyd (1976). These refinements are mainly concerned with questions of the horizontal structure of the quasi-biennial oscillation. Thus, Andrews and McIntyre (1976b) showed that the introduction of mechanical dissipation causes the Yanai wave to transport momentum horizontally away from the Equator. This resolves the problem that the Yanai wave is structured in such a way that its vertical momentum flux deposition should produce twin easterly jets either side of the Equator, rather than the observed single easterly jet centered on the Equator. Most recently, Holton (1979) has presented a numerical model which shows that in the presence of mechanical damping, both Kelvin and Yanai waves incident from below tend to produce a symmetric equatorial jet, even in the presence of cross-equatorial shears representative of those that could be generated by the annual cycle in the global zonal wind system.

There is also a quasi-biennial oscillation in ozone concentration. Figure 5-13 from Wilcox et al. (1977) shows the vertical distribution of amplitude and phase of the oscillation over eastern North America. The amplitude is largest in the lower polar stratosphere. The phase diagram shows that a low latitude maximum occurred around January of 1963, which was the time of maximum easterly winds in the quasi-biennial oscillation in tropical zonal winds. This evidence supports a theory of Dütsch and Ling (1973) in which an enhanced Hadley circulation during the easterly phase of the tropical quasi-biennial oscillation is hypothesized to lead to increased ozone advection into the region 20°-30° latitude and 20-25 km. Subsequent poleward transport by eddies in the altitude range leads to the Arctic maximum, which occurs about 8 months after the low latitude maximum as indicated in figure 5-13.

Semi-Annual Oscillation

In the tropical stratosphere, the annual cycle is weak and there is a region where most of the variance in the zonal wind is contained in a *semi-annual oscillation*. This region extends roughly 20° either side of the Equator and from 30 km to about 60 km. As described in the previous section, the quasi-biennial oscillation contains most of the variance below 30 km in this region of the tropics. Above about 60 km, little is known about the temporal variation of the zonal wind in the tropics.

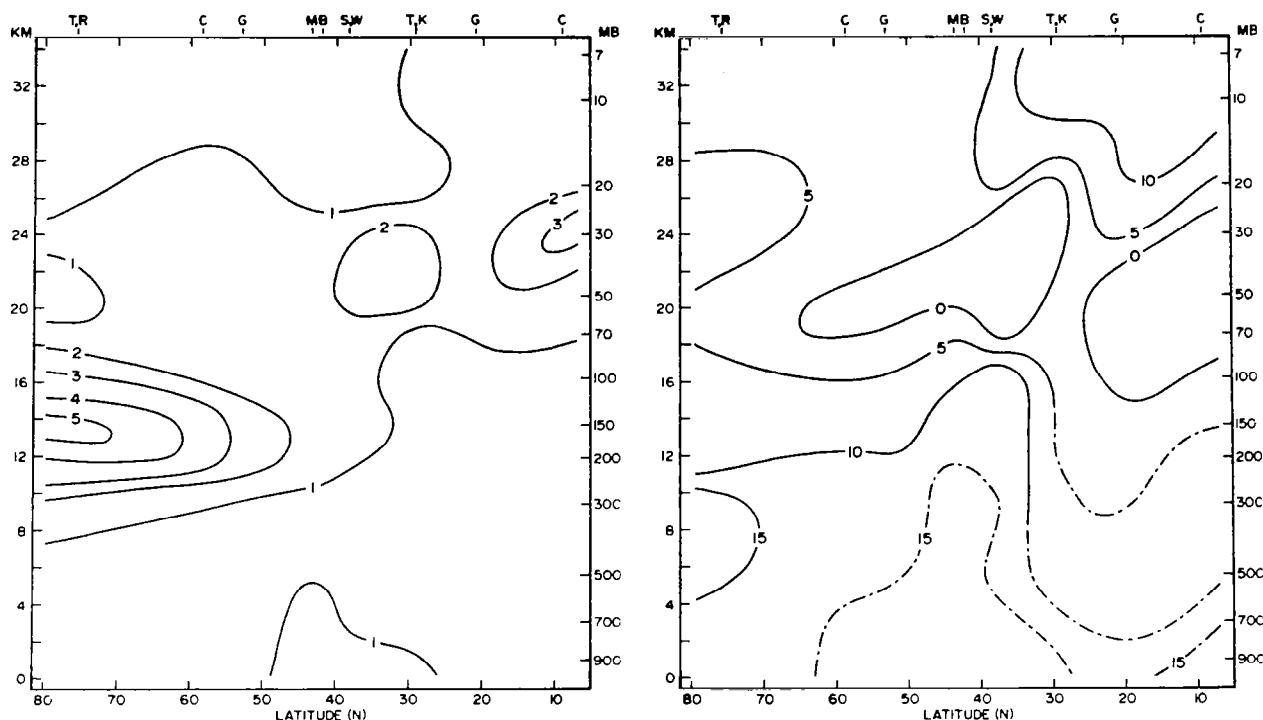


Figure 5-13. (Left) Amplitude of the quasi-biennial (29 month) oscillation in ozone concentration (10^{11} molecules cm^{-3}) near 80°W (Wilcox et al., 1977).
(Right) Phase of the quasi-biennial (29 month) oscillation in ozone concentration near 80°W . Isopleths are labeled with the number of months after 1 January 1963 that the first maximum occurs.

The semi-annual oscillation is beyond the rawinsonde ceiling and has to be observed with meteorological rockets. It was first described comprehensively by Reed (1965, 1966). It is reasonably well established that the oscillation has a peak-to-peak amplitude of about 60 m sec^{-1} and is centered on or very near the Equator. The westerly wind jet is situated at about 60 km and the easterly wind jet at about 50 km. A time-height cross section from a single rocket station on Kwajalein Island is shown in figure 5-14, which also shows the quasi-biennial oscillation. Although not obvious in this diagram, observational evidence by Reed (1966) indicates that the westerly phase of the semi-annual oscillation drifts downward with time while the easterly phase remains at the same altitude. This characteristic is relevant to the theory of the oscillation.

As explained by Wallace (1973), fundamental difficulties arise in ascribing a westerly zonal jet at the equator to any process other than convergence of vertical momentum flux by waves. Since Kelvin waves are the only known equatorial modes that carry westerly momentum upwards, it generally has been believed that the westerly acceleration of the semi-annual oscillation is the result of Kelvin wave absorption. This view is not without difficulties, however, since the Kelvin waves that are observed (in the lower stratosphere) are absorbed by the westerly phase of the quasi-biennial oscillation and would not be available during this lengthy period to drive the westerly phase of the semi-annual oscillation.

The first hard evidence for the needed Kelvin waves came from analysis of the rocket winds themselves by Hirota (1978), who isolated in these data an eastward propagating mode with a period of about 10 days and a

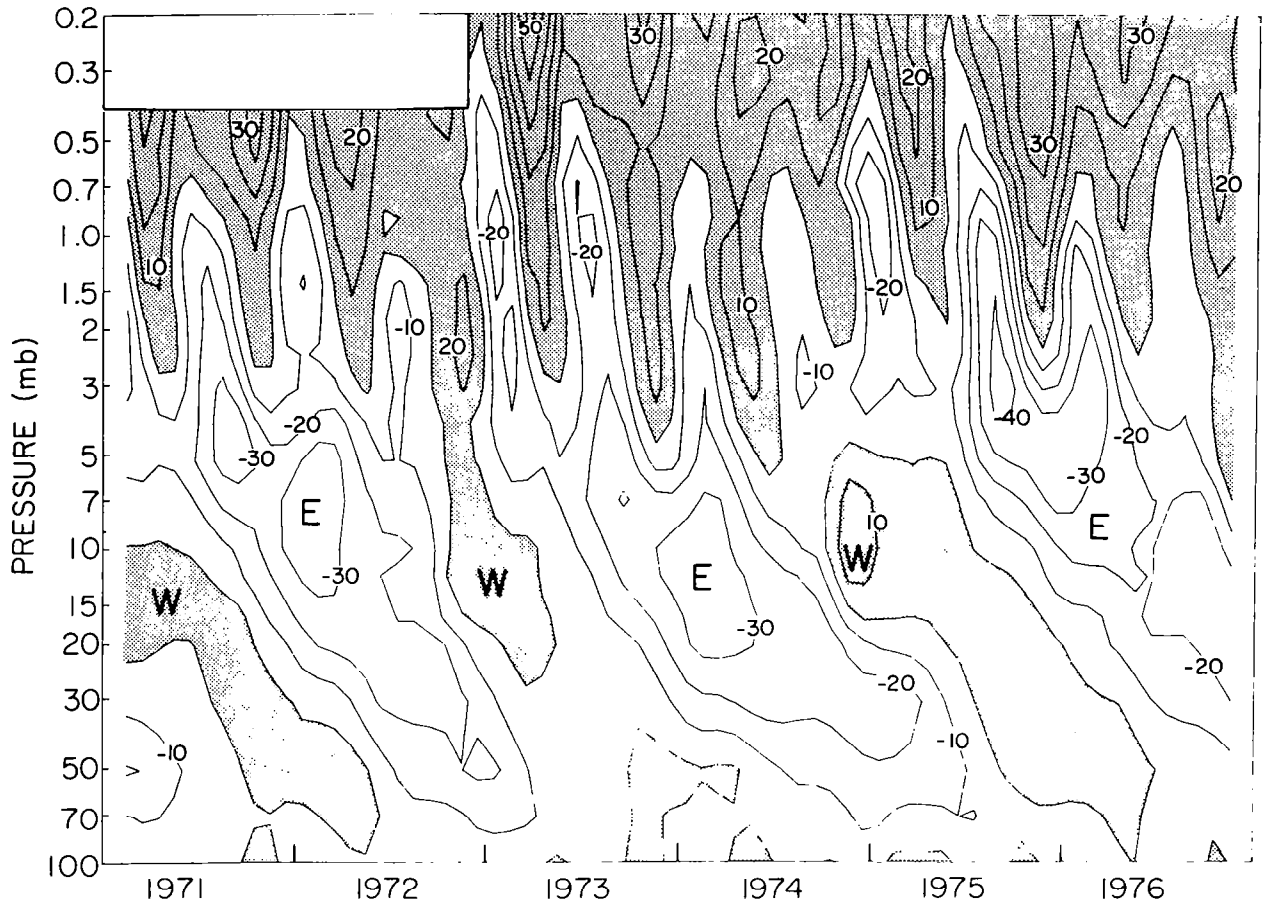


Figure 5-14. Time-height cross section showing observed zonal winds in the semi-annual oscillation (Coy, 1979).

vertical wavelength of 15 to 20 km. The observed period is somewhat less than the typical 15-day period for the Kelvin waves that are absorbed in the westerly phase of the quasi-biennial oscillation, hence these upper stratosphere waves must (for a given zonal wavelength) be moving somewhat more rapidly toward the east.

Dunkerton (1979) has presented a simple model of the semi-annual oscillation using radiative damping rates appropriate to the upper stratosphere and a Kelvin wave with features matching the wave observed by Hirota (1978). This model shows that the required westerly acceleration in the semi-annual oscillation can be provided if the upward momentum flux in the Kelvin wave is about one-third of the upward flux carried by the Kelvin waves involved in the quasi-biennial oscillation. It remains to be established by observation that Hirota's Kelvin wave carries this much momentum.

In the model of Dunkerton (1979), the easterly acceleration in the semi-annual oscillation is provided by a linear law of relaxation to a prescribed easterly jet. The actual source of easterly momentum has not yet been established. A traditional candidate has been a lateral transfer of momentum out of the tropics and into the winter hemisphere by upper stratosphere planetary waves. Such a hypothesis is consistent with the observation that the easterly regime of the semi-annual oscillation is fixed in altitude and does not propagate downward. The verification of the hypothesis is hampered by the lack of data suitable for deducing the latitudinal dependence of the horizontal momentum flux by planetary waves at these altitudes. A further uncertainty arises because of a present lack of knowledge in the area of how the relevant stationary planetary waves interact with the low latitude zonal flow.

Data assembled by Belmont et al. (1974) indicates that there is a secondary maximum in the semi-annual oscillation of zonal winds that is located near and above the stratopause in high northern latitudes. This is shown in figure 5-15, which is taken from that reference. The maximum westerly phase of the oscillation there occurs about a week after equinox, as determined from both rocketsonde (Belmont et al., 1974) and radio reflection data (Belmont and Nastrom, 1979). The stratospheric portion of the oscillation apparently arises from the non-sinusoidal variation in solar radiation heating in high latitudes (DeVore and Venkateswaran, 1977), although the mesospheric portion may be influenced by other effects.

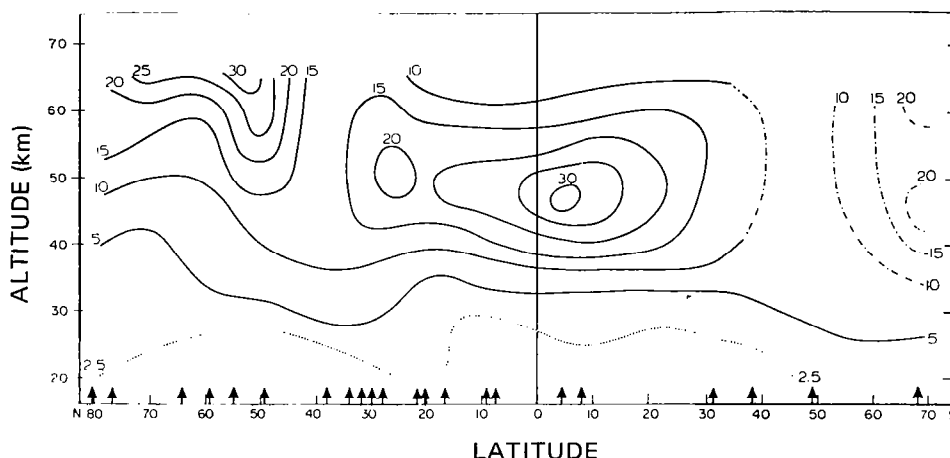


Figure 5-15. Amplitude (ms^{-1}) of the semi-annual wave. Arrows indicate location of rocket stations (Belmont et al., 1974).

Data from the Nimbus-4 backscattered ultraviolet experiment show a semi-annual oscillation in zonal mean total ozone content as shown in figure 5-16, taken from Hilsenrath et al. (1979a). As can be seen from this figure, some 40% of the variance from the annual mean in 1970 is contained in a semi-annual oscillation in equatorial latitudes. They show, however, that the semi-annual oscillation detected in the total ozone is a result of the annual oscillation in the two hemispheres whose phases are 6 months apart. In the following year, the semi-annual component is much reduced, possibly because of a quasi-biennial oscillation. In both years, the amplitude was large in high latitudes; however, the variance is near the noise level in the Northern Hemisphere but high in the Southern Hemisphere. The need to extrapolate data poleward of 67° latitude in winter makes this result somewhat uncertain.

SUDDEN WARMINGS

Background

Sudden warmings are strong increases of temperature in middle to high latitudes of the winter-spring hemisphere, associated with planetary zonal wave 1 and/or 2 disturbances in the stratospheric and tropospheric circulation. *Major* warming events commonly involve two or three warming and cooling episodes culminating in substantial net warming of the polar stratosphere, and a reversal of the mid-stratospheric mean zonal wind from westerly to easterly.

Aside from intrinsic interest in warmings as an extreme manifestation of dynamical processes in the stratosphere, they are important because of the associated changes in the circulation (which influence the

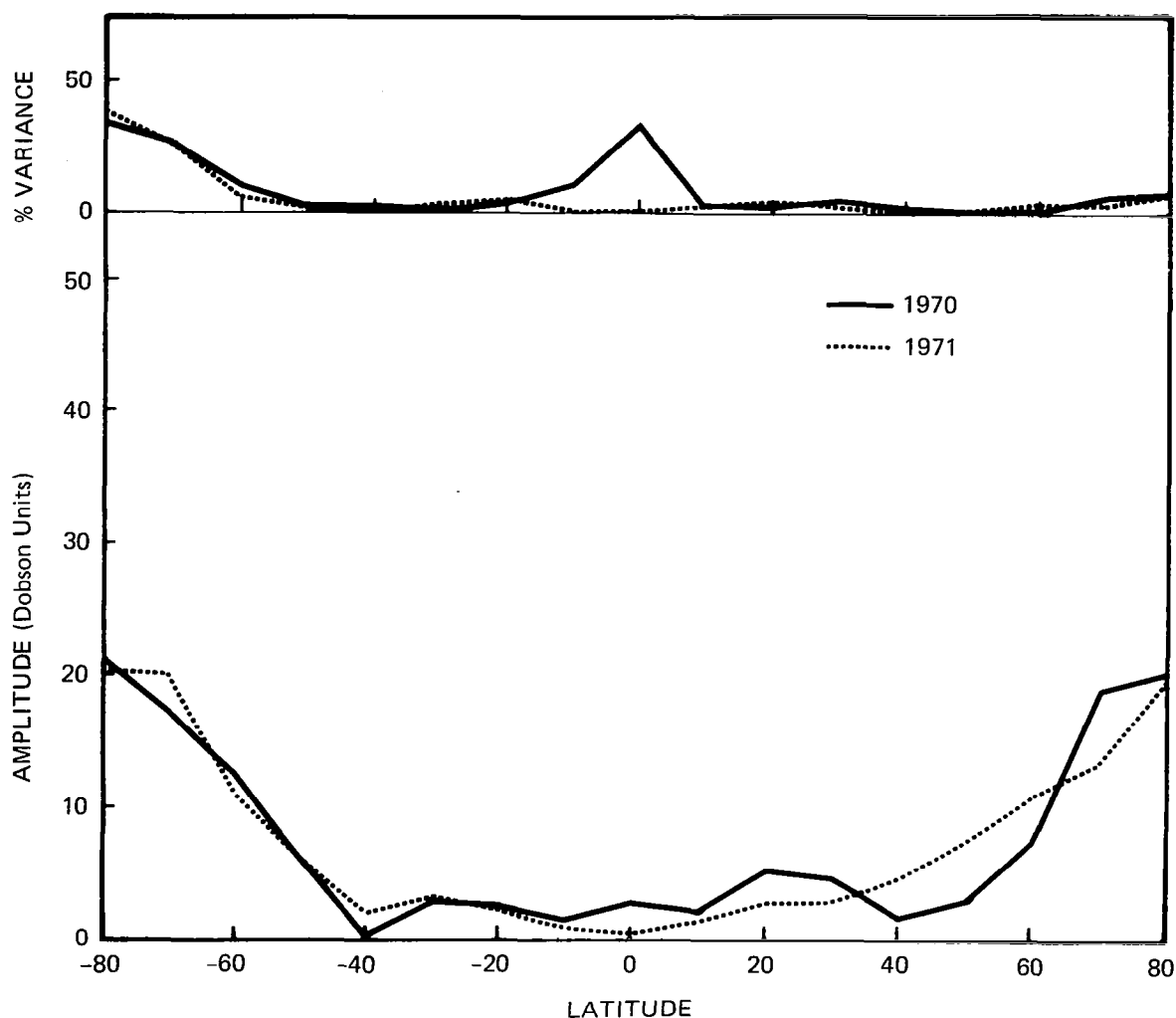


Figure 5-16. Below, amplitude of semi-annual wave and above, variance of second harmonic of total ozone from first and second year of BUW data (Hilsenrath et al., 1979a)

distribution of minor constituents) and because of the large temperature changes observed (which are important to the photochemistry of the upper stratosphere). The importance of temperature dependence in upper stratosphere chemistry has been stressed by various authors (e.g., Barnett et al., 1975, and Luther et al., 1977). Temperature increases by 30-80°C in one week, usually greatest near 40 km, have been observed. Observational evidence of ozone changes in warming events has been given by Zullig (1973); Ghazi et al. (1976), Miller et al. (1976), and others.

The knowledge of stratospheric warmings has been greatly expanded in the past decade by (1) a vastly improved observational framework, including satellite observations of both hemispheres, and (2) theoretical insights gained by dynamic modeling. Comprehensive descriptions have been given by Quiroz et al. (1975), Labitzke (1977), McInturff (1978), and Schoeberl (1978), among others while model simulations have been made by Matsuno (1971), Holton (1976), and others identified in the above descriptive papers. More recent simulations have been made by Haggard and Grose (1978), Schoeberl and Strobel (1979) and Lordi et al. (private communication). Recent comprehensive accounts of the observed planetary wave structure include, for the

stratosphere, Labitzke (1977) and for both the troposphere and stratosphere, Quiroz and Nagatani (1976), Labitzke (1978), and Quiroz (1979c). However, various important questions, some of which are discussed below, have not been resolved.

Frequency of Warmings and Circulation Reversals

As illustrated in figure 5-17, warmings of various degrees of significance are common. Several usually occur in any winter (this applies also to the Southern Hemisphere except that the season of greatest activity is delayed relative to the Northern Hemisphere). Warmings which affect the polar region over a deep stratospheric layer in such a way as to reverse the meridional gradient of mean stratospheric temperature (figure 5-17) are less frequent. Warmings accompanied by a circulation reversal (denoted by CR in figure 5-17) at 10 mb (30 km) are even less common: two wintertime cases in four years in this sample, and usually one case every spring. The Northern Hemisphere frequencies in this recent four-year sample are consistent with earlier data sets (e.g., Labitzke, 1977, for 1964/65 to 1976/77) and indicate a "major" *wintertime* event about once in two years. The traces in figure 5-17 further illustrate the great variability in warming activity from year to year. The downward penetration of zonal mean flow reversal is also variable. For example, in January, 1977 in connection with an exceptionally strong warming, the flow was reversed down to the lower troposphere (Quiroz, 1977; O'Neill and Taylor, 1979).

Significant warmings occur in the Southern Hemisphere as well, but mid-winter circulation reversals have not been observed (Quiroz, 1974). There are some systematic differences in the zonal circulation and long-wave activity of the two hemispheres, perhaps accounting for the observed delay in the occurrence of maximum total ozone in the Antarctic, relative to the Northern Hemisphere (Prabhakara et al., 1976).

Energy and Forcing from the Troposphere

Theoretical arguments indicate that upward flux of wave geopotential energy and the horizontal transports of heat and momentum are key factors in the development of stratospheric warmings. Figure 5-18 illustrates periods of strong geopotential flux through the base of the stratosphere (near 100 mb) and strong heat transports (peaking around January 25 and February 20 at 50 mb, 60°N) which were clearly important processes in the event of early 1979 (Quiroz, 1979c). In their analysis of the event of 1976-1977, O'Neill and Taylor (1979) indicated acceleration of the circulation reversal by the observed pattern of momentum transport. Further appraisal of these factors in a wide range of warming cases would serve to clarify the dominant processes.

Some features of stratospheric warmings have been simulated by introducing tropospheric forcing in zonal wavenumbers 1 or 2 which was held nearly constant for about 25 days in the work of Matsuno (1971) and Holton (1976). In the real atmosphere, the duration of sustained high wave amplitude is variable, and important contributions may be due to both zonal wavenumbers 1 and 2. Quiroz (private communication) has observed several discrete cases of large tropospheric wave amplitude, in each of several winters, with a wide range of "responses" in the stratosphere. Concurrent stratospheric flow conditions, the duration of tropospheric forcing (Geisler, 1974), and interaction between waves 1 and 2 may be among the most important factors influencing the response in the stratosphere. A need exists for isolating those tropospheric and stratospheric factors which, in combination, assure the occurrence of strong warming and circulation reversal.

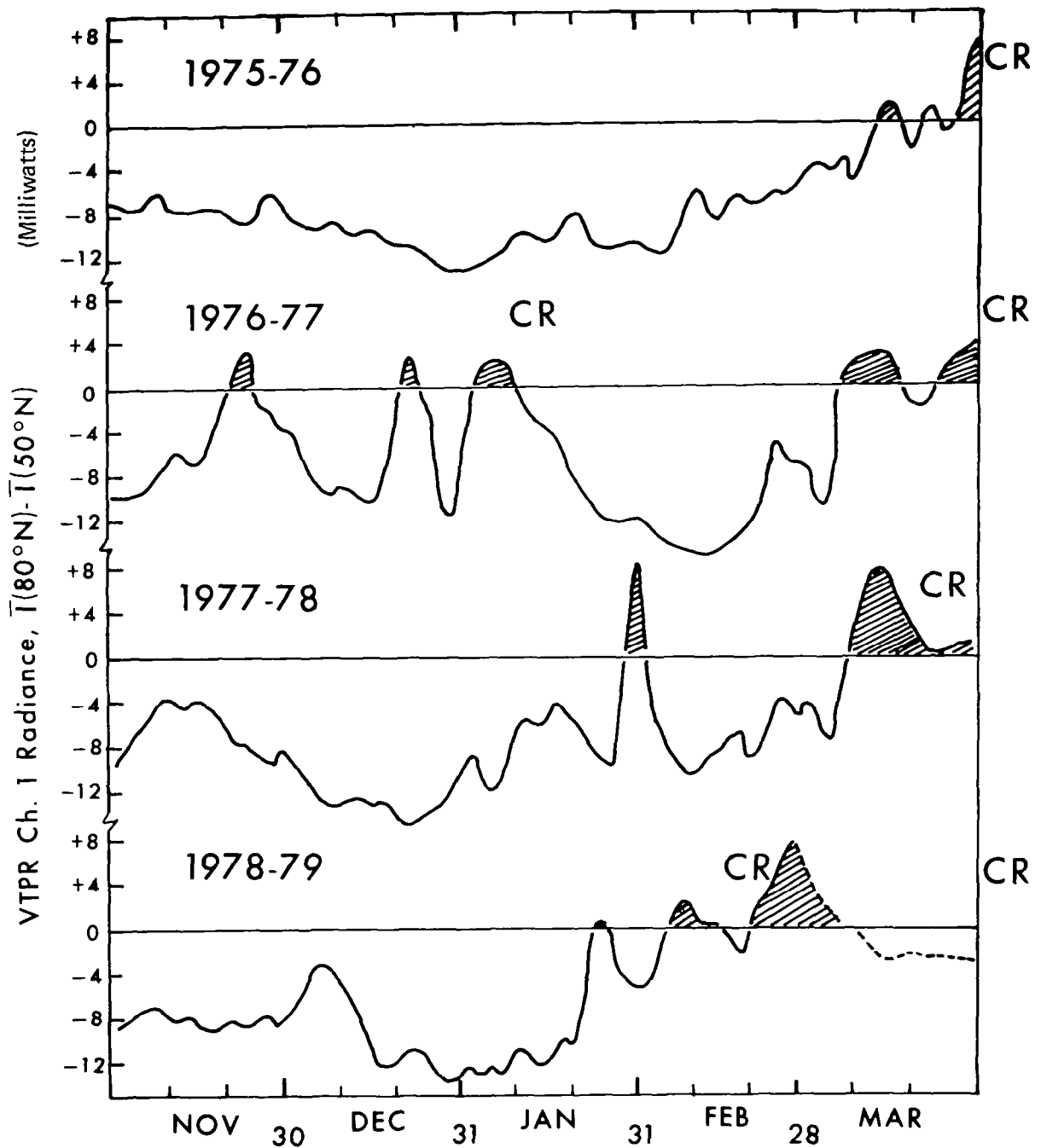


Figure 5-17. Traces of difference in mean zonal radiance at 80 and 50°N, showing several temperature gradient reversals. CR denotes circulation reversal at 10mb. Radiance for VTPR Ch. 1 is proportional to mean temperature of layer 100-2 mb (about 15-40 km). (adapted and expanded from Quiroz, 1978).

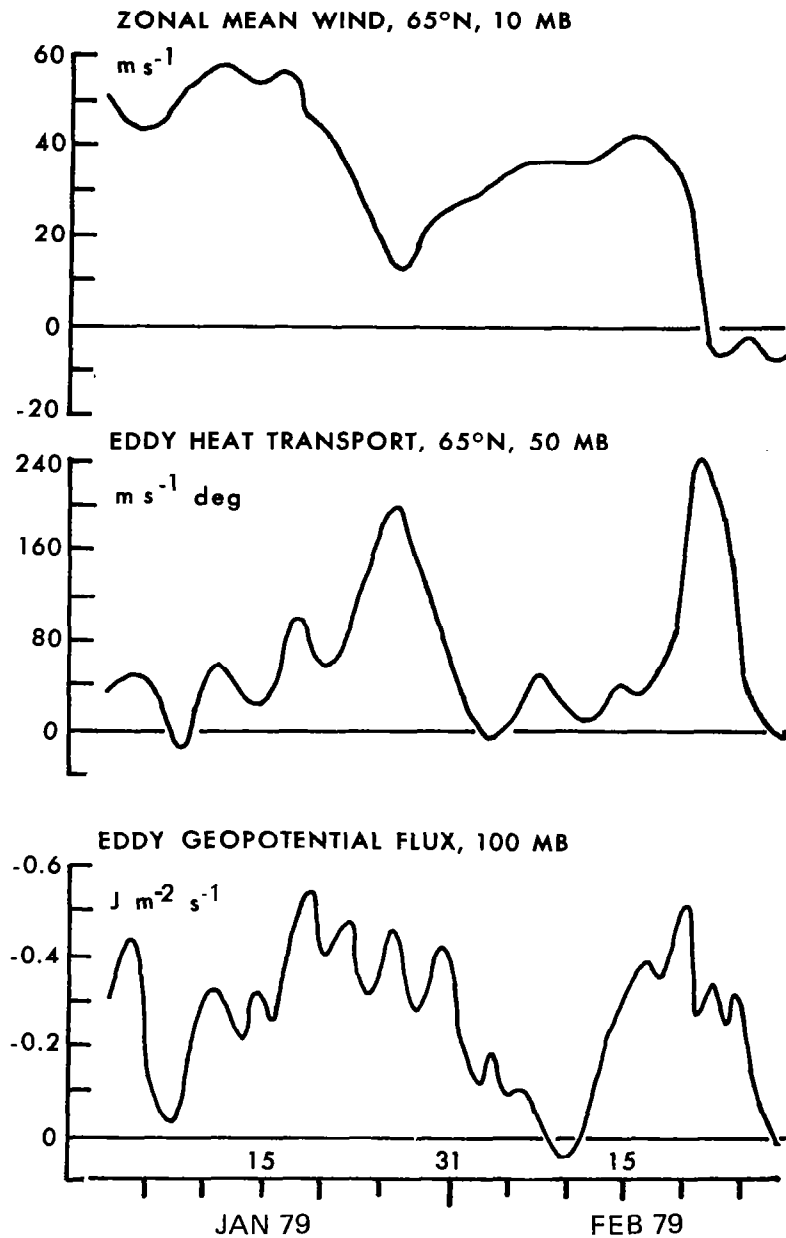


Figure 5-18. Zonal mean wind trace at 10 mb (showing wind flow reversal in late February) and associated traces of horizontal eddy heat transport at 50 mb and vertical eddy geopotential flux through 100 mb surface (integrated 20°N-Pole) (From Quiroz, 1979c).

Roles of Waves 1 and 2

Observational data for many winters typically show a numerical dominance in the amplitudes of the height and temperature of wave 1 over wave 2, in the stratosphere. Such data have led to the deduction (Labitzke, 1978) that “major” warmings are those exhibiting a large wave 1 height amplitude accompanied by a minimum in wave 2. However, wave 2 may have special importance, since (1) significant wave-wave interaction may occur in the troposphere in an early phase of a warming event, and (2) the reversal of the mean zonal circulation may actually be associated with strong amplification of tropospheric-stratospheric wave 2, as in late February, 1979 (Figures 5-18 and 5-19). In figure 5-18, note the attainment of zonal mean easterlies at 10 mb (65°N) in late February, keyed to a strong development of wave 2 (Figure 5-19), while wave 1 was declining in amplitude. The strong wave 1 development in late January, which accounted for a vast “Aleutian” anticyclone in the stratosphere (Figure 5-20), can be shown to be related to the superpositioning of the retrogressing wave 1 with the quasi-stationary wave 2, in the troposphere (Quiroz, 1979c). In view of such behavior, which was observed in the major warming event of December-January, 1976-1977 (Quiroz, 1977), it is important to elucidate the role of traveling and stationary components of these waves. In this connection, the recent theory of Tung and Lindzen (1979) is noteworthy.

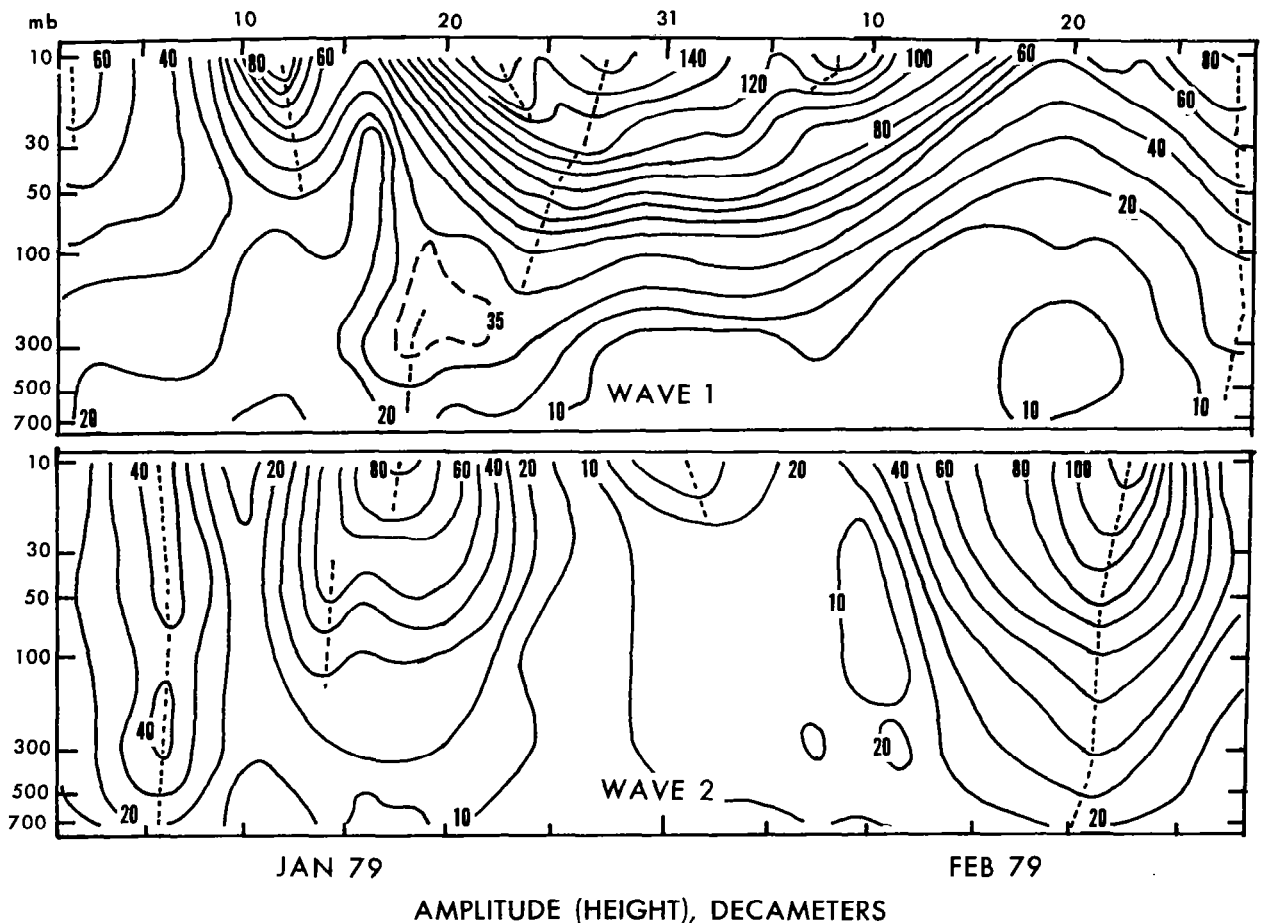


Figure 5-19. Isolines of height amplitude of zonal waves 1 and 2 at levels 700–10 mb (Quiroz, 1979c).

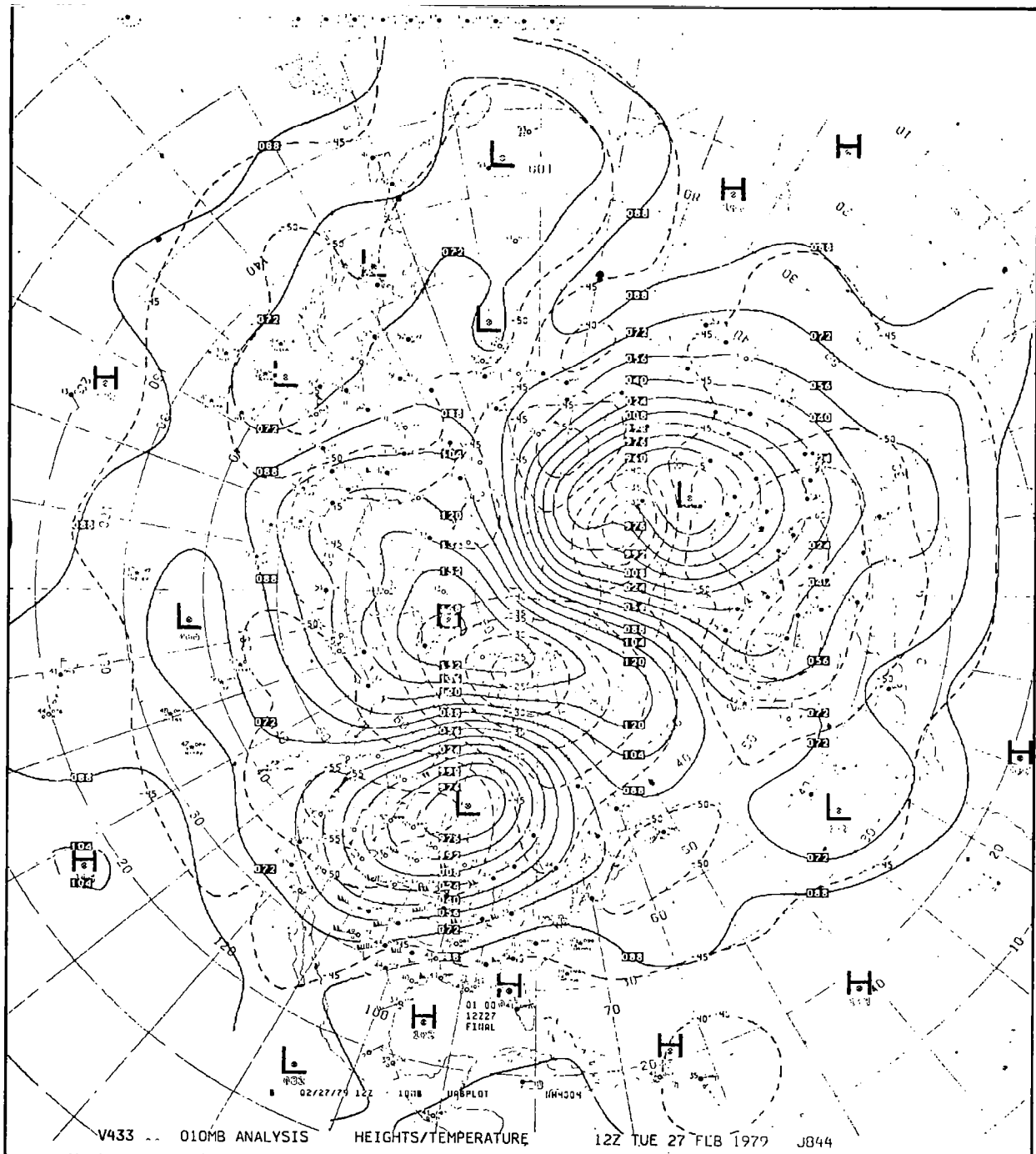


Figure 5-20. 10-mb map for 27 February 1979, showing split polar vortex and anticyclonic system extending over polar region, with warm centers near 100°W, 50°E and 75°N.

Low-Latitude Cooling

High-latitude warming is accompanied by low-latitude cooling, consistent with the concept of poleward heat flux, previously incorporated in the model simulation of Matsuno (1971). However, cooling can be discerned to prevail nearly simultaneously to polar latitudes of the opposite hemisphere. Further investigation of this structure and of the nature of low-amplitude cross-equatorial wave and zonal mean features may increase the understanding of the role of inter-hemispheric processes in stratospheric warmings.

Tropospheric Condition for Circulation Reversal

Finally, it should be emphasized that circulation reversals depend not only on the reversal of the meridional gradient of stratospheric temperature, but on the polar *tropospheric* condition as well. In contrast to the event of 1976-1977, the explosive dramatic warming in late January, 1978 (figure 5-17) did not involve a circulation reversal because a strong poleward pressure gradient was maintained in the troposphere during the short "life" of the stratospheric warming. This exemplifies the need for awareness of tropospheric conditions at all stages of a warming event.

Final Remarks

Stratospheric warmings are especially important because of the potential effects of the associated circulation patterns on the distribution of ozone and other constituents. A great deal is known about the warmings and some of the observed features have been reproduced, at least qualitatively in model simulations employing single-wave tropospheric forcing. To answer several important questions, research is needed to:

- Better define relationships between stratospheric temperature and height disturbances, on the one hand, and large planetary wave amplitudes in the troposphere, on the other, since strong tropospheric wave amplification is not a sufficient condition for strong stratospheric warming (in contrast to some model results).
- Improve knowledge of the relevant heat transport patterns in the troposphere and stratosphere, which may involve knowledge of the vertical structure of the responsible eddies and perhaps determination of the origin of amplifying waves.
- Define unambiguously the mode(s) of vertical propagation of a warming and determine the role of critical-level interaction.

SHORT-PERIOD MOTIONS

Background

The short-period motions in the stratosphere can be divided conveniently into two groups: (1) those whose typical time scales are comparable to a day, and (2) those whose time scales are short when compared to a day. The latter are usually of the order of one hour or less, and include internal gravity waves and the shorter period, intermittent fluctuations known as clear air turbulence (CAT). These various short-period motions are important in stratospheric studies for several reasons and are discussed in detail in the following sections.

- Short-period fluctuations of the meteorological fields complicate the analysis and interpretation of meteorological measurements taken with inadequate temporal or spatial resolution and coverage.
- Short-period, vertically propagating waves generated in, or transmitted by, the stratosphere may significantly affect the mesospheric circulation.

- Short-period motions such as CAT are important in the free exchange of air and chemical constituents across the tropopause.
- Fluxes of mass, momentum, and energy associated with short-period motions may be *locally* important in modulating longer period components of stratospheric circulation and photochemistry.

Atmospheric Tides

Atmospheric tides, characterized in the earlier section on Types of Motion, are planetary-scale, regular oscillations of wind, temperature, and pressure fields. The two most prominent tides are the thermally driven diurnal and semi-diurnal tides, whose periods are one, and one-half solar day, respectively. The classical theory of atmospheric tides, which has been thoroughly reviewed by Chapman and Lindzen (1970), is based upon the inviscid primitive equations, linearized about a motionless basic state, and generally has used highly idealized representations of the thermal forcing due to the ozone and water vapor absorptions of solar radiation. Yet, as shown in figure 5-21, this theory is remarkably successful in simulating the diurnal tidal winds observed in the stratosphere by rocketsondes. Similar agreement is obtained for the semi-diurnal winds, except that the phase reversal of the tide is observed near 50 km rather than at 25 km as predicted by the classical theory. Reed (1972) suggested that this discrepancy might be due to the theoretical neglect of the mean wind,

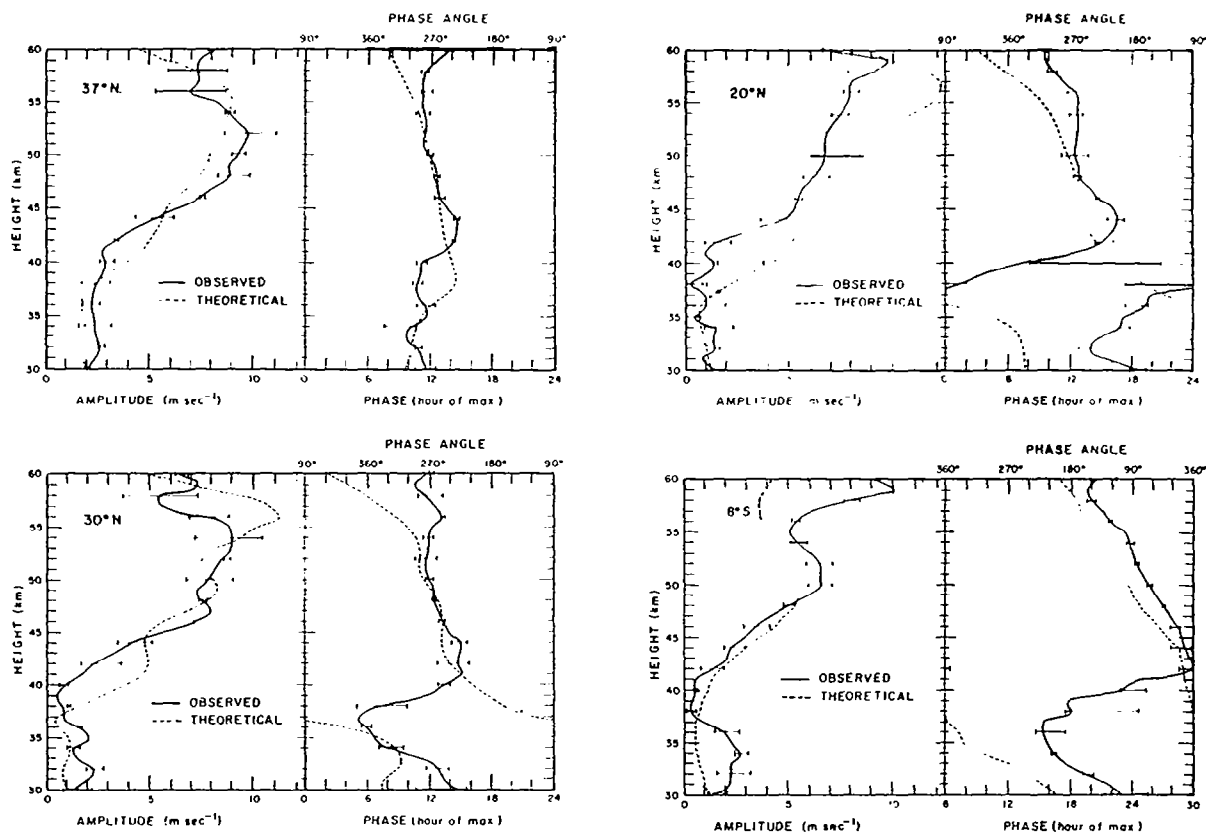


Figure 5-21. Comparison of Lindzen's theoretical predictions with the amplitude and phase (hour of maximum) of the diurnal variation of meridional wind observed between 30 and 60 km at different latitudes (Reed, Oard, and Sieminski, 1969).

but extension of the classical theory to include such winds and their geostrophically related temperature gradients does not entirely eliminate the problem (Lindzen and Hong, 1974; Walterscheid, 1978). More recently, Lindzen (1978) has suggested that an additional source of semi-diurnal forcing due to daily variations in tropical rainfall could raise the theoretical phase reversal height to 50 km, while simultaneously removing a rather persistent phase discrepancy of 44 minutes between the predicted and observed semi-diurnal surface pressure maxima.

The aforementioned atmospheric tides are functions of local time; that is, their zonal and temporal wavenumbers are identical, as would be expected for oscillations driven by the Sun's apparent motion overhead. However, not all tidal forcings have this simple form. Wallace and Patton (1970) showed that the diurnal surface heating was strongly modulated by land-sea differences. Using an idealized heating distribution, McKenzie (1968) demonstrated that topographically modified surface heating could produce diurnal atmospheric tides of different zonal wavenumbers, many of which would propagate vertically into the stratosphere. Although significant longitudinal differences have been observed in the diurnal tides below the stratopause, it is not clear whether these are due to topographic forcing, variations in the mean wind, or variations in the tropopause height. Large seasonal variations of the diurnal tides in the stratosphere also are observed, and these may be the result of seasonal changes in the background state (temperature and wind) or changes in the distributions of water vapor and of ozone (Wallace and Tadd, 1974; and Nastrom and Belmont, 1976).

Because tidal phase speeds are too large for critical level interactions to occur, atmospheric tides can interact with the mean zonal flow only during recent changes of the background state or in regions of strong heating or dissipation. Modifications of the stratospheric zonal mean wind by atmospheric tides are thought to be small compared to planetary wave effects. The ultimate fate — and thus effect — of those tidal components generated by longitudinal variations of topography and heating is presently unknown.

Gravity Waves; Turbulence

Gravity waves are generated in stably stratified layers by flow over topographic barriers or by other perturbations of the background flow. Their periods typically range from several minutes to an hour or more, and typical wavelengths are of the order of 100 km in the horizontal, and 1 km in the vertical. Like their atmospheric tidal counterparts, those gravity waves which can propagate vertically will grow in amplitude with height. Thus, although they are ubiquitous in the atmosphere, their largest amplitudes probably occur in the mesosphere just prior to their degeneration into turbulence or prior to their attenuation by nonlinear transfer of wave momentum and energy to other components of the circulation (Hines, 1970, and Hodges, 1969). The resulting vertical convergence of wave momentum flux, together with the atmospheric tides, may strongly influence the mean circulation of the mesopause region (Houghton, 1978). Models of the upper atmospheric zonal jets tend to require large dissipation to produce the observed decrease of the zonal wind above the stratopause (Leovy, 1964; Schoeberl and Strobel, 1978b; Holton and Wehrbein, 1979). Whether the dissipation required by these models is physically related to the dissipation generated by the turbulent breaking of upward propagating, short-period waves is not clear. The periods and horizontal wavelengths of gravity waves are such that, in many cases, gravity wave phase speeds, unlike those of atmospheric tides, can be less than stratospheric wind speeds. Where the phase velocity of the gravity wave equals the wind velocity, critical levels occur. Linear theory, with and without dissipation present, predicts that when an upward propagating gravity wave encounters a critical level, most of its wave momentum flux will be absorbed by the mean flow (Booker and Bretherton, 1967). More recent work (Fritts and Geller, 1976) indicates that the incident gravity wave can excite shear instabilities (Kelvin-Helmholtz waves) near the critical level of the wave. Since these instabilities will eventually dissipate into turbulence (Fritts, 1978), gravity wave critical levels may be an important source of stratospheric turbulence. In addition, nonlinear interactions, involving either the incident gravity wave or the subsequently amplifying Kelvin-Helmholtz billows, may generate neutral gravity waves capable of radiating momentum away from the critical level (Fritts, 1979). The wave momentum flux

associated with these radiating waves noticeably enhances the wave momentum flux (actually wave-action; see McIntyre and Andrews, 1978), which leaks to higher altitudes. It remains to be seen whether or not planetary-scale waves can also radiate part of their momentum during critical level interactions.

Kung (1967) estimated that the energy dissipation over the Northern Hemisphere at jet stream levels by subsynoptic-scale phenomena is comparable to the energy dissipation in the surface boundary layer. Much of this high-level dissipation may occur during episodes of CAT defined as any turbulence not directly associated with convective activity. The extent to which instabilities induced by gravity waves contribute to CAT is unknown since turbulence generated by shear instability of the background zonal jets near the tropopause is probably more common in the lower stratosphere (Bretherton, 1971).

To what extent CAT mixes the lower stratosphere is still uncertain, but the area and time-averaged effective vertical eddy diffusivity estimated from observations of the turbulent heat flux (Lilly et al., 1974; Heck, 1977; Cadet, 1977) appears to be an order of magnitude less than the vertical transport due to all scales of motion (Gudiksen et al., 1968). However, neglect of this dissipation could lead to overestimates of the strength of the jet stream near the tropopause. The turbulent-scale dissipation also appears to be an essential part of tropospheric-stratospheric exchange (Shapiro, 1978), as will be discussed later in the section entitled Mass Exchange Processes. As is the case for gravity waves, parameterization of the effects due to CAT have been hampered by the lack of detailed understanding of how large-amplitude waves in a stably stratified region degenerate into turbulence.

There is indirect evidence that motions may exist with vertical scales smaller than those usually associated with gravity waves, yet with a temporal coherence greater than that expected for turbulence. Observations of the vertical profiles of ozone (Evans et al., 1979) and other constituents such as $O(^3P)$, OH and ClO (Anderson, 1975, 1976, Anderson et al., 1977) show anomalous thin regions where the mass mixing ratio varies significantly within vertical distances of 1 to 2 km. The implication is that these quantities have been advected large distances in narrow layers; however, gravity waves with such small vertical scales will have time periods and amplitudes much too small to produce the required advection. Whether such motions actually exist is uncertain, since the available observational techniques do not have the vertical resolution and temporal consistency to directly measure the persistence of such motions. At this time, the question of the existence and nature of such motions remains unanswered.

Synoptic-Scale Instabilities

Partial reflection radiowave wind observations at high latitudes have shown large day-to-day variations in the amplitudes and phases of atmospheric tides, and of gravity waves at mesospheric heights. These same observations occasionally show a two-day oscillation in mesospheric winds which seems to be associated with an oscillation of similar period in stratospheric temperatures near 20 km at high latitude (Stening et al., 1978). Observations from many other sources suggest that transient motions have their largest amplitudes near both the stratopause and mesopause (Green, 1972). Furthermore, analysis of daily meteorological rocket data taken at Ft. Churchill (at 59°N) during December reveal large-amplitude, high-frequency disturbances above 45 km (Leovy and Ackerman, 1973). These latter observations, shown in figure 5-22, strongly suggest that at least some short-period transients are generated locally in the vicinity of the stratopause. These transients do not simply represent disturbances propagating from below. Studies by Simmons (1974a) and Pfister (1977) indicate that the zonal mean wind near the wintertime stratopause can become unstable, inducing amplifying waves whose characteristics are consistent with the analysis of Leovy and Ackerman (1973). Furthermore, zonally averaged geostrophic winds derived from satellite data show that the winter stratosphere is occasionally barotropically unstable (i.e., the zonal mean wind could transfer kinetic energy to an amplifying eddy) on individual days (Leovy and Webster, 1976).

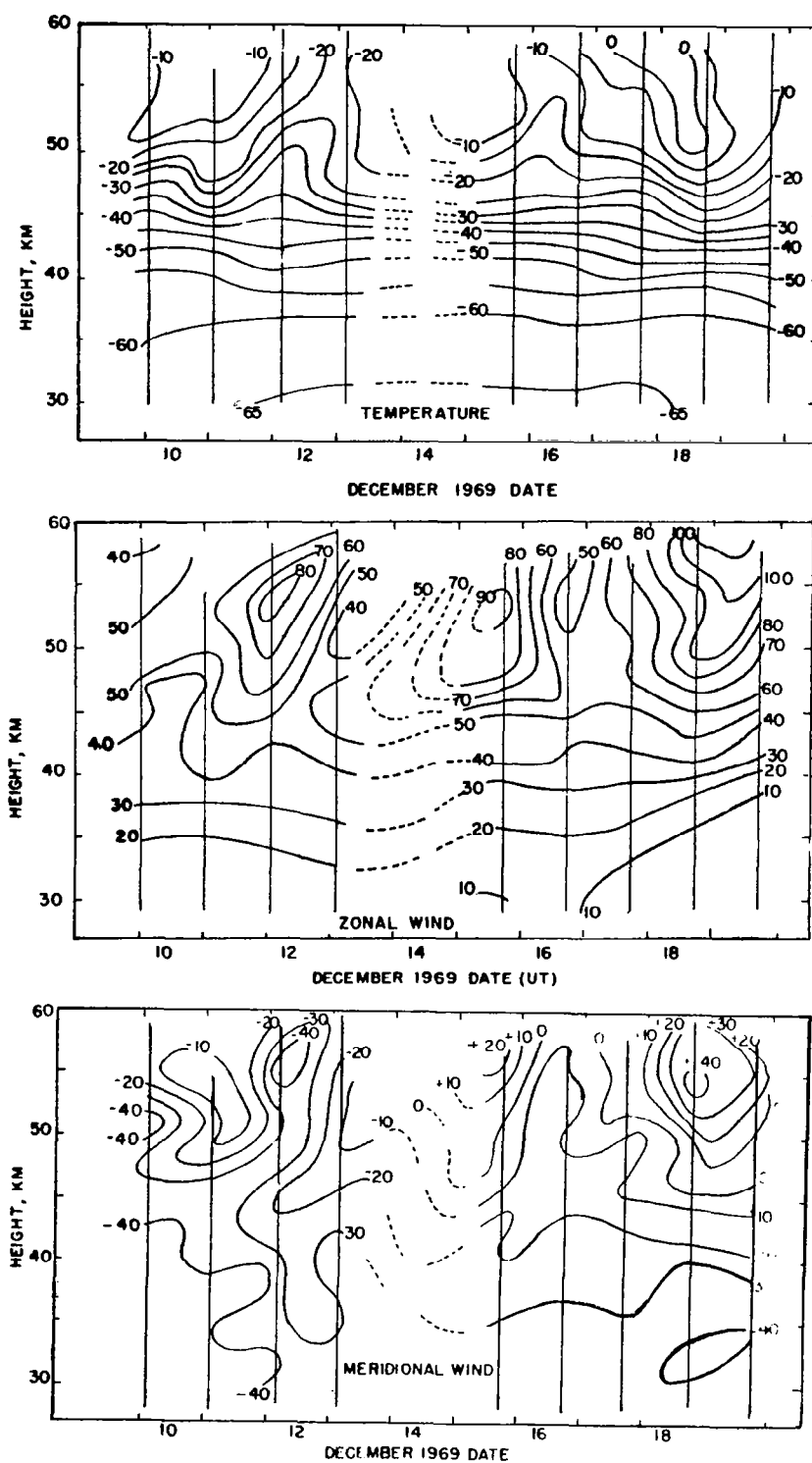


Figure 5-22. Time cross sections of temperature, zonal wind and meridional wind components over Ft. Churchill, December 1969 (Leovy and Ackerman, 1973).

To determine the prevalence and ultimate importance of unstable waves near the stratopause will require upper atmospheric observations with vertical resolution of less than a scale height, and with considerably greater temporal resolution than is presently available. For now, the eddy momentum and heat fluxes due to these waves appear to be of secondary importance to the stratospheric circulation, but are possibly of greater importance in the mesosphere (Dickinson, 1973a, and Simmons, 1977).

Instability mechanisms involving the zonal mean flow near the stratopause appear to excite only weak, shallow disturbances (Simmons, 1972). Although the eddy heat and momentum fluxes associated with these unstable waves could be important locally, the fluxes associated with vertically propagating planetary waves are far more important to the overall stratospheric circulation (Simmons, 1974b, and Matsuno, 1971).

OZONE CONTROL BY DYNAMICS AND CHEMISTRY

Background

The observed distribution of ozone has long intrigued atmospheric scientists because, although it is photochemically produced, its maximum total column abundances are found at high latitudes in the spring. This distribution implies that both photochemistry and atmospheric transport play important roles in determining the ozone distribution. The global network of Dobson stations has provided a substantial data base on this latitudinal distribution of columnar ozone and its seasonal variations (see figure 5-23 from Dütsch, 1971). Satellite observations provide additional evidence that the Dobson network captures the principal features of the zonal mean distribution of columnar ozone. In this section, the physical mechanisms believed to be responsible for the distribution of ozone are discussed. Emphasis is placed upon transport by atmospheric motions and its relationship with photochemical sources and sinks of ozone, rather than on the details of the photochemistry itself, which is treated elsewhere.

Physical Mechanisms

The ozone distribution in the atmosphere is affected by both photochemistry and dynamical influences. However, it is possible to divide the atmosphere into regions where photochemistry and dynamics, respectively, appear to be dominant. Figure 5-24 shows the photodissociation rate of molecular oxygen for solstitial conditions. Superimposed on figure 5-24 are dotted lines which indicate the approximate locations of the limits of the regions of dynamical and photochemical control. Between these two regions is a transition region where both dynamics and photochemistry are important in determining the ozone concentration. Division of the atmosphere into three separate regions is helpful, but somewhat artificial since, on one hand, dynamics can affect the distribution of photochemically active species in the upper stratosphere by altering the temperature there, while, on the other hand, photochemistry can affect the ozone concentration in the dynamically controlled region by alternating the ozone concentration near the upper boundary of the dynamically controlled region. Nevertheless, the division of the atmosphere into regions as shown in figure 5-24 is very useful in understanding the variations in ozone around latitude circles, which are associated with the presence of planetary waves. Figure 5-25 shows the phase of the zonal wavenumber 1 components of ozone, temperature and height at 60°N on November 1, 1975, observed by the Limb Radiance Inversion Radiometer (LRIR) (Gille et al., 1979). Around 10 mb, the ozone is in phase with the height and temperature, whereas at about 3 mb, there is a rapid variation in the phase of the ozone so that at 2 mb the ozone is about 180 degrees out of phase with the temperature, as would be expected from photochemical considerations alone. The mechanisms involved in this change of the phase of the ozone variation associated with planetary waves and its potential importance in enhancing ozone transport in the transition region have been discussed by Hartmann and Garcia (1979).

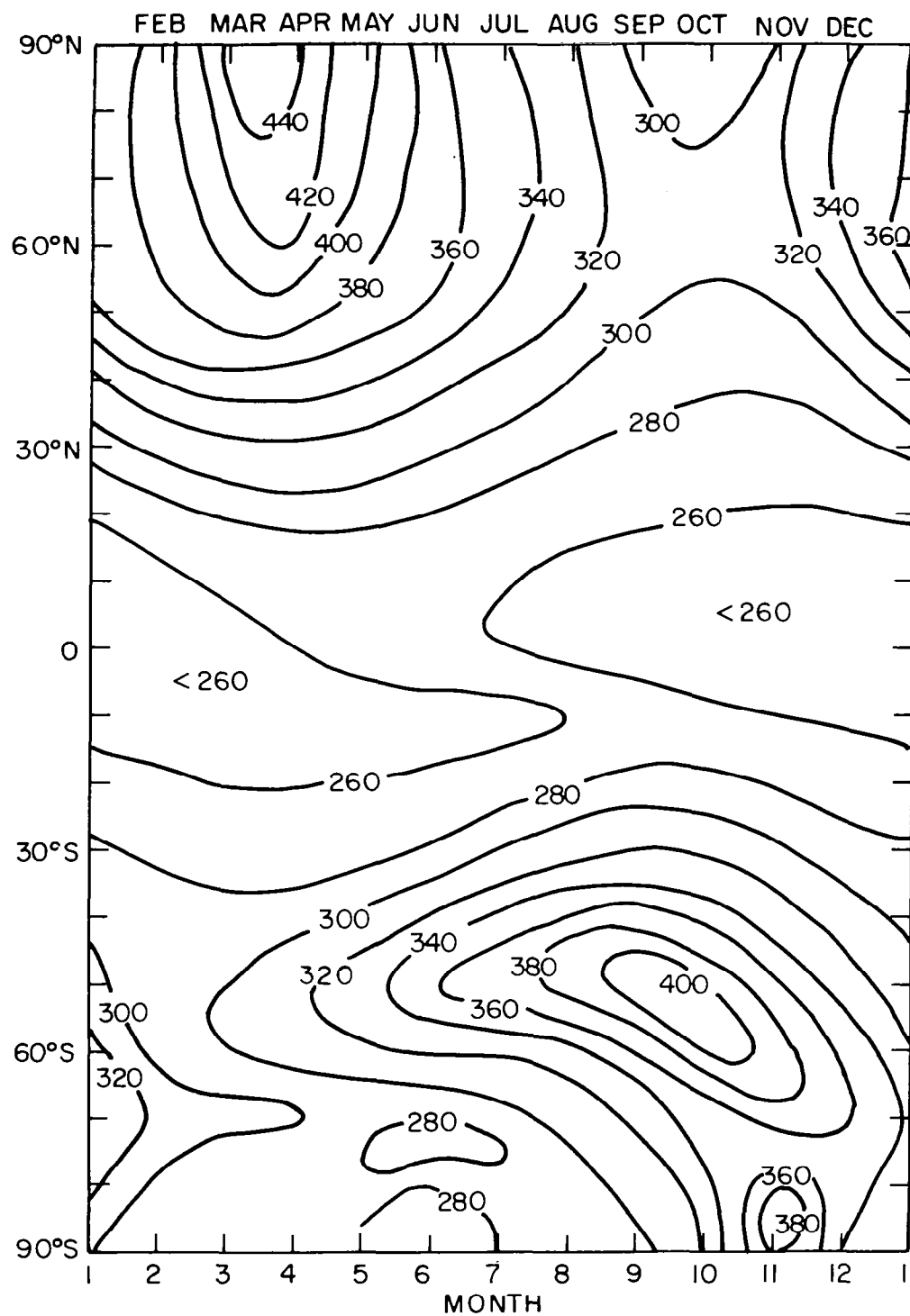


Figure 5-23. The observed behavior of columnar ozone (Dobson units) as a function of latitude and season (Dütsch, 1971).

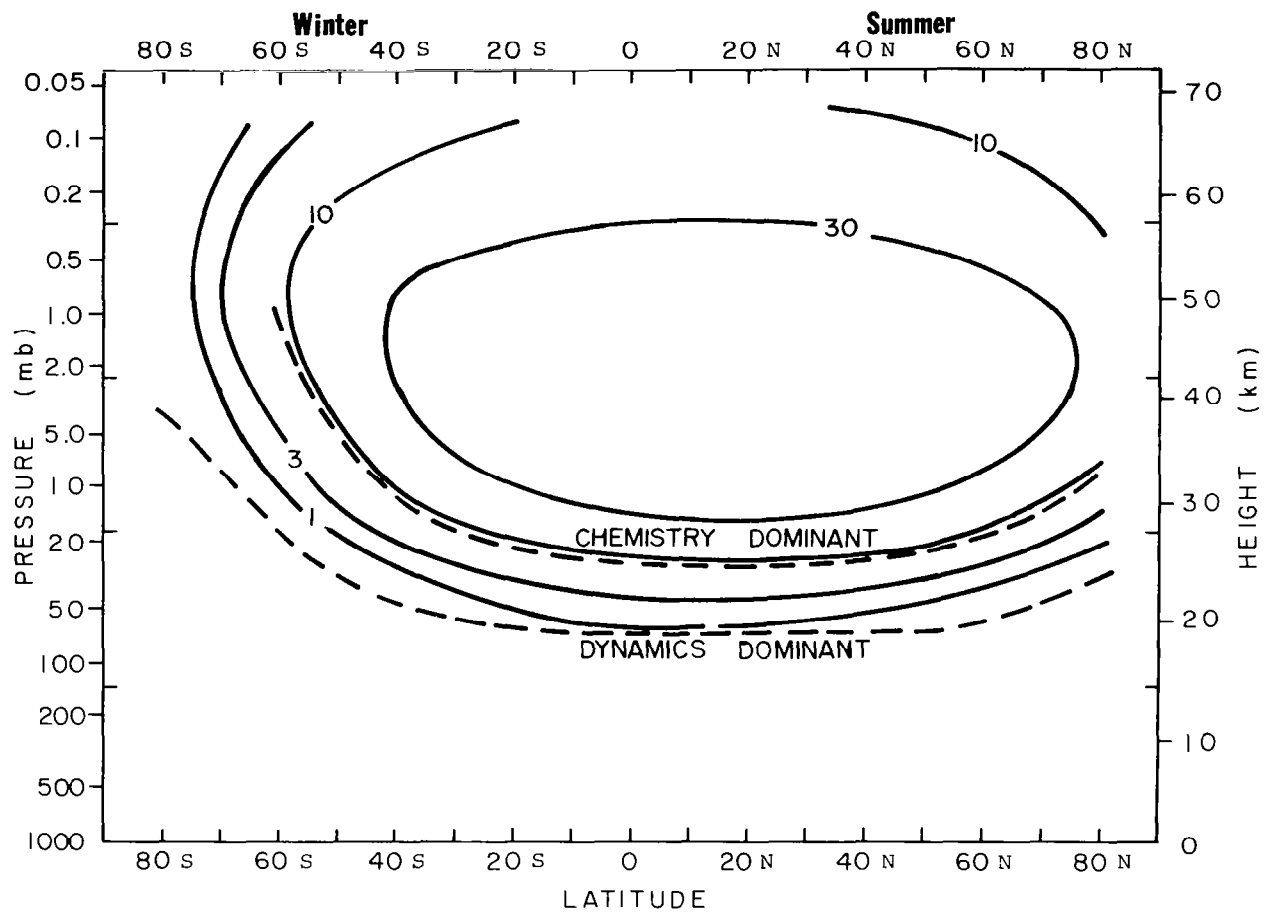


Figure 5-24. The calculated daily-averaged photodissociation rate for molecular oxygen during the solstitial seasons. Values have been weighted by the volume 10° latitude by 360° longitude by approximately 2.8 km ($\Delta Z = 0.40574$). The significance of the dashed lines is explained in the text (Cunnold et al., 1979).

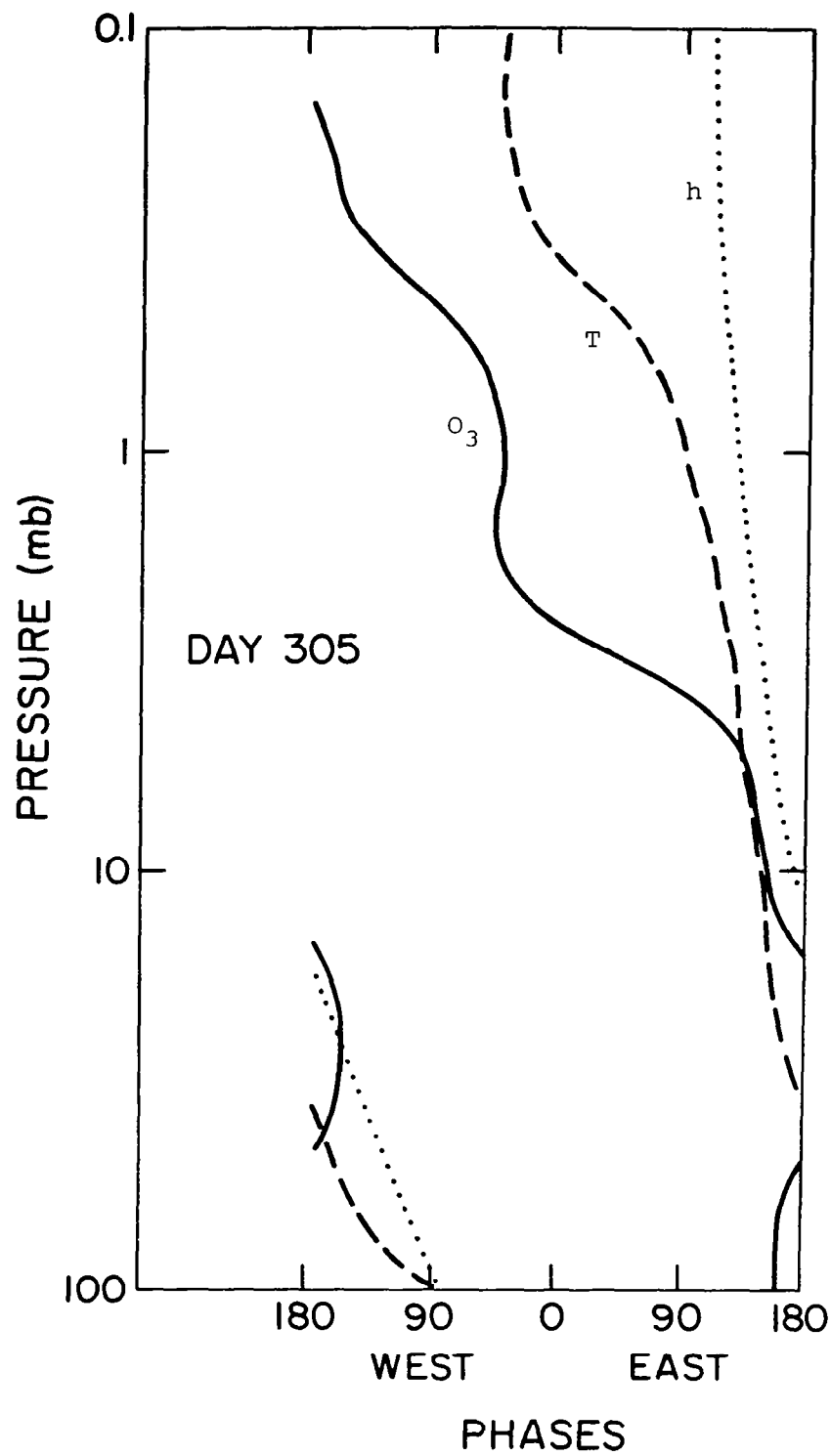


Figure 5-25. Phase of wave one in temperature, T , ozone mixing ratio, O_3 , and geopotential height, h , as a function of altitude on 1 November 1975 determined from analysis of LRIR data (Gille et al., 1979).

The types of motion which are principally responsible for the ozone transport in the stratosphere are the planetary waves, the mean meridional circulation and, in the lower stratosphere, the motions associated with the stratospheric extensions of synoptic scale disturbances in the troposphere. The nature of the horizontal transport of ozone in the lower stratosphere has been discussed by many researchers. For example, Martin and Brewer (1959) found significant correlations between vertical motions, temperature, and vorticity at 100 mb and total ozone. Newell (1961) has provided observational evidence for a strong positive correlation between meridional velocity, temperature in the lower stratosphere, and columnar ozone. His analyses also show that these horizontal fluxes of ozone may be quite transient. Hunt and Manabe (1968) analyzed the planetary wave structure of a tracer at 65 mb in their model calculations. The local concentration maxima seemed to be located to the east of the planetary wave troughs. Wallace (1978a) has described a mechanism to explain the counter-gradient fluxes of ozone in the winter lower stratosphere.

In the last few years, satellite observations of the global field of ozone have allowed more extensive studies of the transport of ozone in the stratosphere. One of the first studies, by Miller et al. (1977), used preliminary backscatter ultraviolet (BUV) ozone observations, together with conventional wind analyses, to calculate eddy transports. These are depicted, for 30 mb, in the upper part of figure 5-26. In addition, at 10 and 30 mb, meridional velocities were available from conventional analyses. They were used to obtain the mean meridional transports, which are shown (for 30 mb), in the lower part of figure 5-26. The near cancellation between the eddy and mean meridional transports in the lower stratosphere is clearly displayed. This near cancellation in the lower stratosphere is one of the severe problems in the experimental determination of net ozone transport.

Currently functioning satellite observing systems, discussed earlier in this chapter, will allow the simultaneous diagnoses of global fields of ozone and geostrophic winds, thus allowing a detailed climatology of the ozone transport to be attempted. Figure 5-27 shows a zonal cross section of the poleward ozone transport by eddies on November 1, 1975, determined from LRIR data (Gille et al., 1979). Although still in the early stages, analysis of satellite observations will soon greatly expand the knowledge of ozone transport.

Modeling of Transport and the Ozone Distribution

Three-dimensional models (or the General Circulation Models) provide the best analytical tool for describing transport processes. These models in most cases use the so-called primitive equations to calculate the various scales of transports directly. With the addition of chemistry and with a sufficiently high upper boundary, a reasonable estimate of the global distribution of ozone can be achieved. There are presently numerous 3-dimensional models which incorporate dynamics, chemistry, and radiation and varying degrees of feedback. A more complete discussion of the approaches and efforts for the various 1-, 2-, and 3-dimensional models was given in Chapter 2. For the purpose of this discussion the model of Cunnold et al. (1975) will be used to illustrate our ability to model and understand the processes which determine the global ozone distribution.

The model begins with a continuity equation where the local time rate of change of ozone is equal to the sum of the large scale flux convergence (by the 3-dimensional wind), the sub-scale transport effects (subgrid diffusion coefficients), and the physical and chemical sources and sinks. Figure 5-28 shows the simulation of the seasonal variation in total ozone as a function of latitude achieved in this Northern Hemisphere calculation as well as the observed Northern Hemisphere distribution of total ozone.

The photodissociation of molecular oxygen, which is responsible for the production of odd oxygen (which is 99% or more O_3 below approximately 45 km) is dependent on the ozone distribution, and has been calculated to yield the production rate given in figure 5-24. Figures 5-29, 5-30, and 5-31 depict the calculated contributions that horizontal advection by planetary waves, mean circulation, and chemistry, make to ozone change during the summer and winter seasons. These three contributions are approximately in balance at each "grid

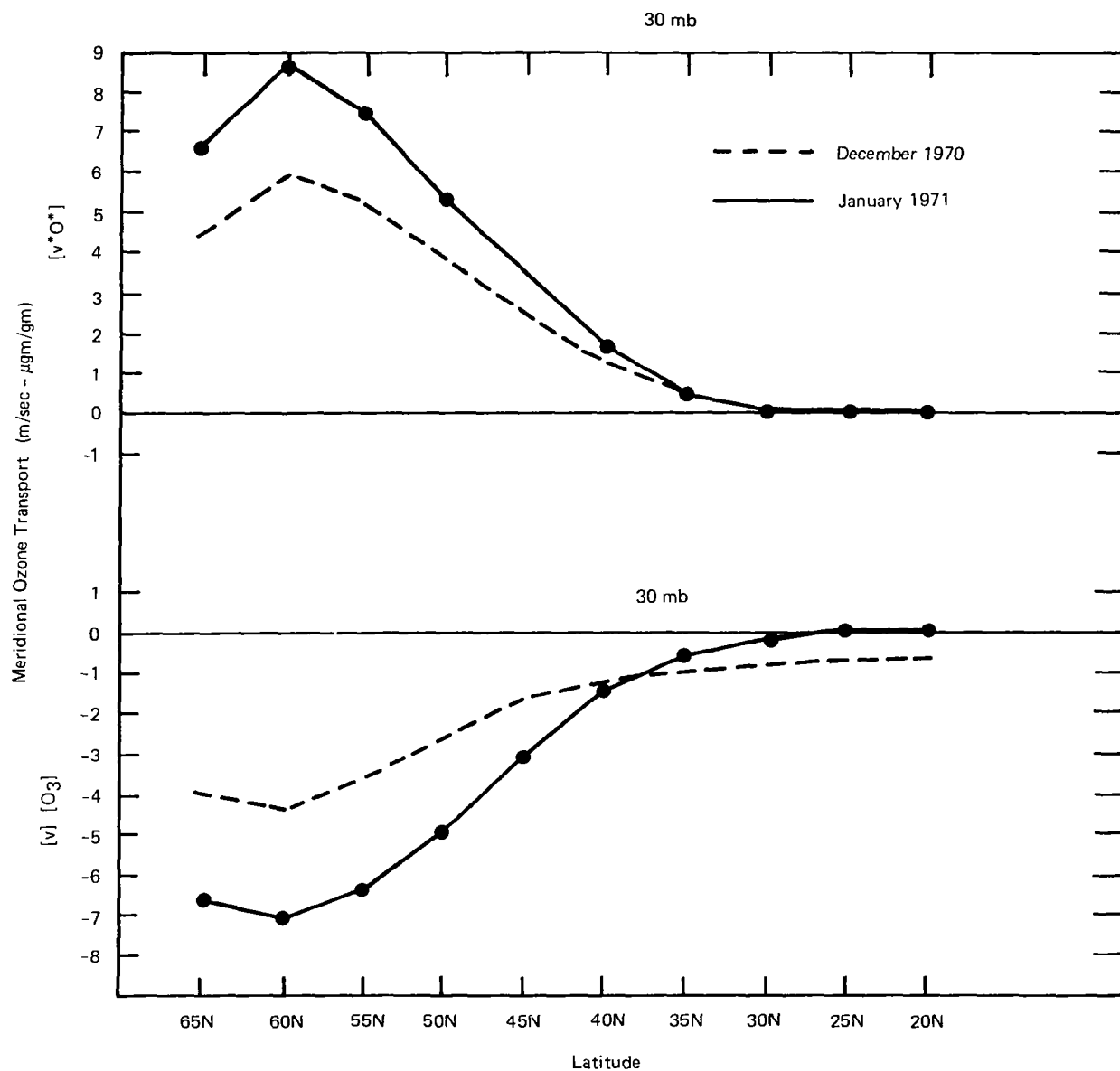


Figure 5-26. Meridional ozone transport by eddies (upper) and by the mean meridional winds (lower) derived from BUV ozone data and rawinsonde winds (Miller et al., 1977).

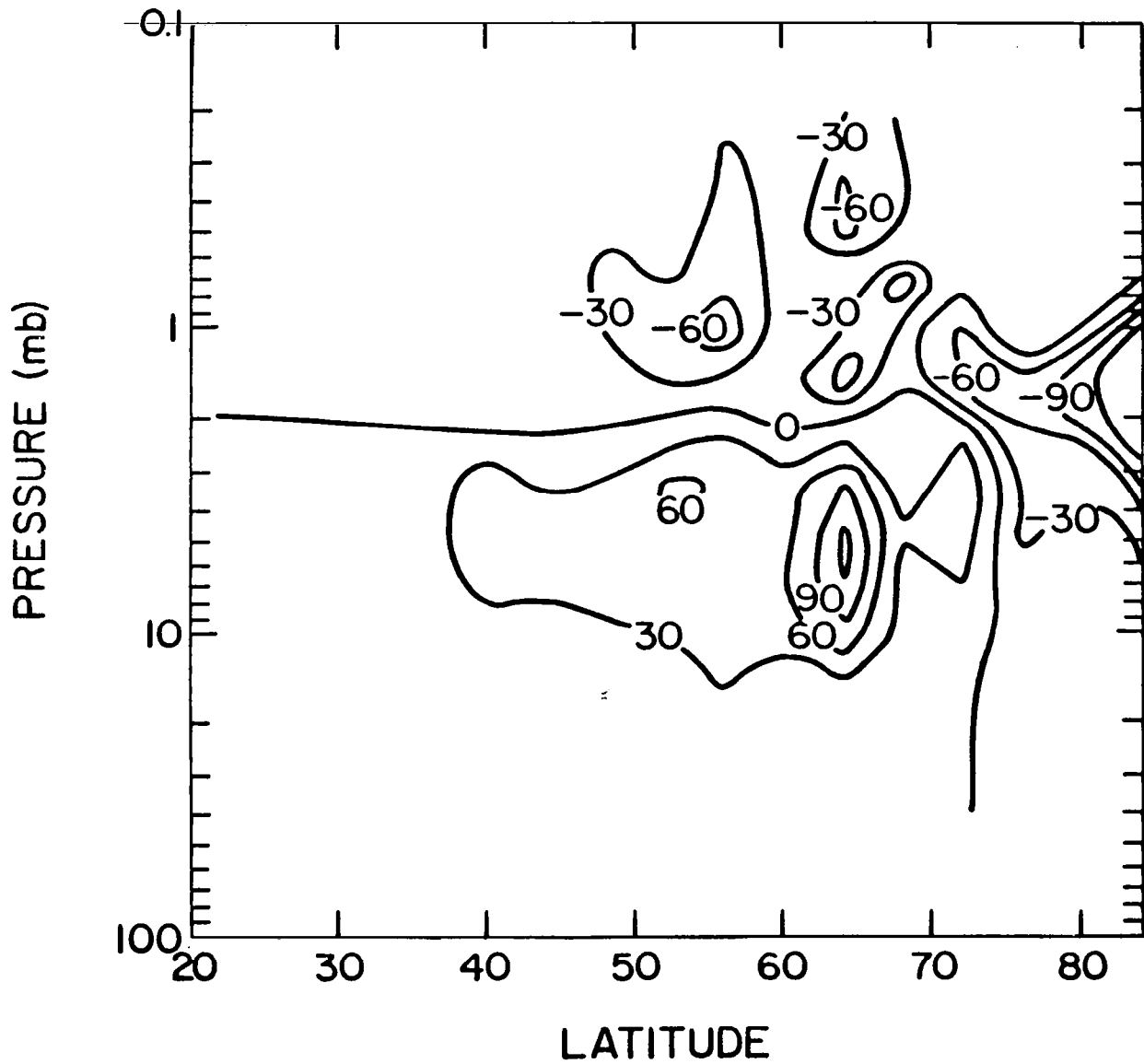


Figure 5-27. Cross section of zonally averaged $\overline{v'O_3}$, meridional transport of ozone by geostrophic eddy motions, for 1 November 1975. Units are ppmv m/sec. Eddy fluxes were derived from LRIR data (Gille et al., 1979).

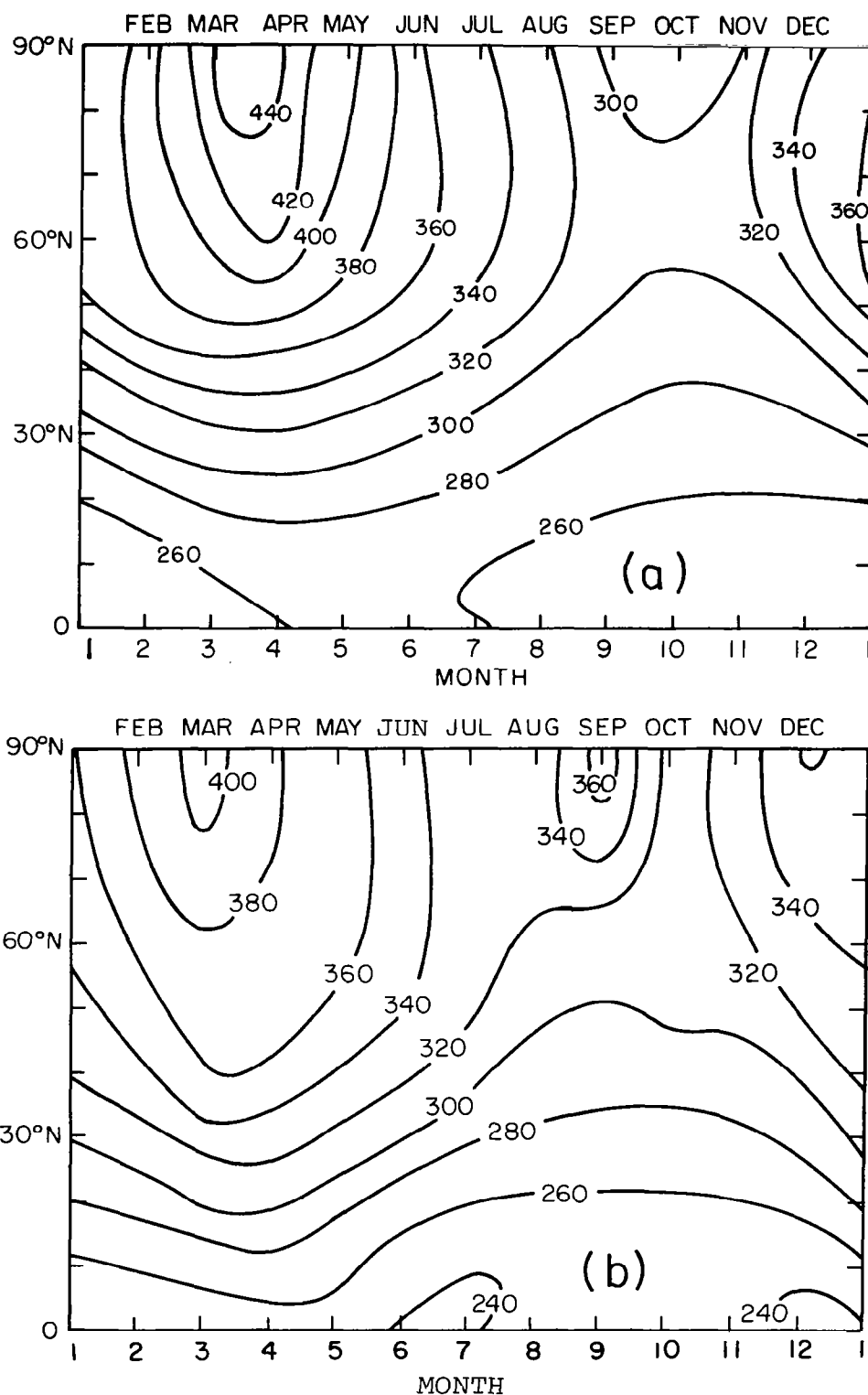


Figure 5-28. The columnar ozone variation (Dobson units) in the Northern Hemisphere. Model results from run 17 (b) are compared against observations (a) compiled by Dütsch (1971)..

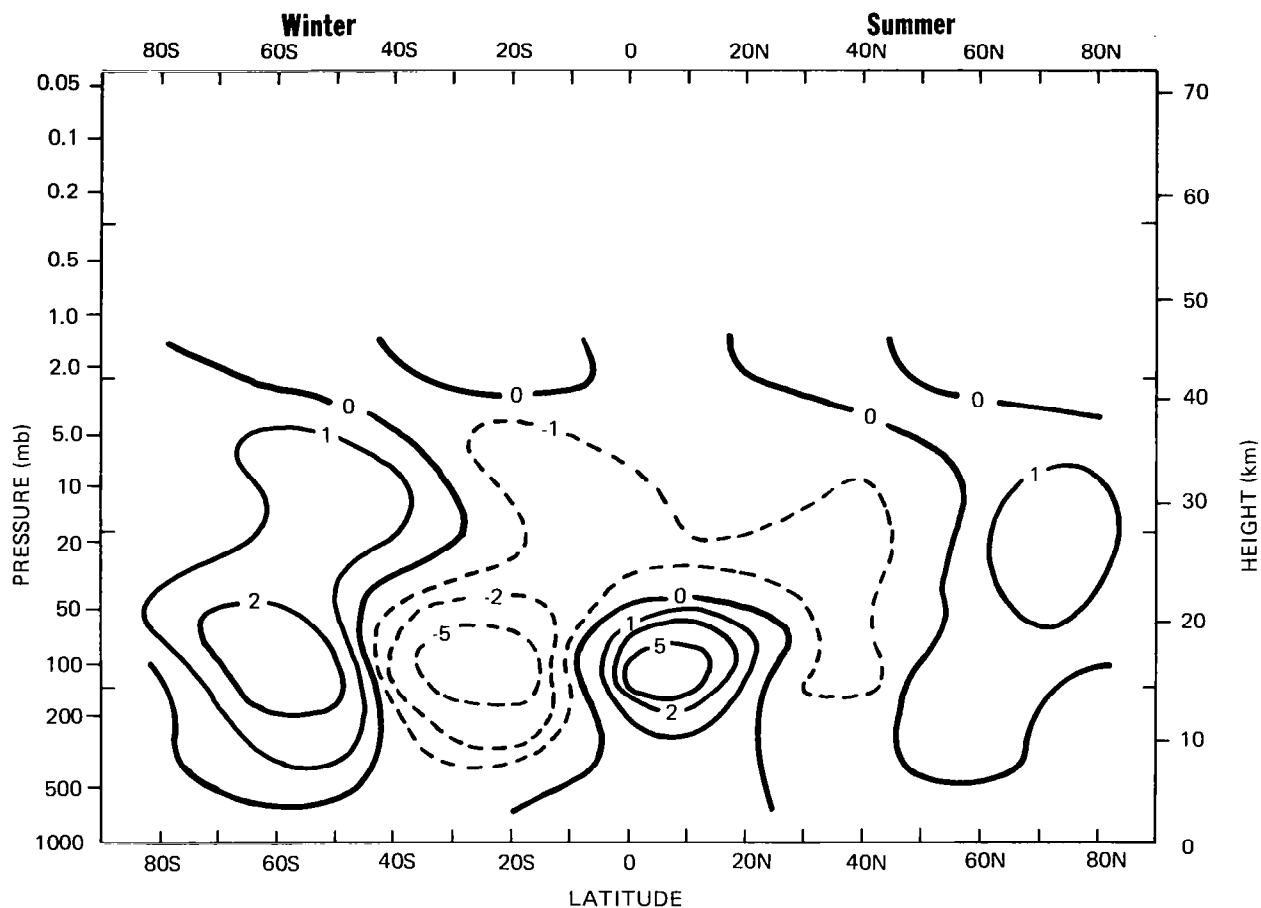


Figure 5-29. The calculated contribution to the ozone tendency resulting from horizontal advection by planetary waves. Values have been weighted by the volumes 10° latitude by 360° longitude by approximately 2.8 km ($\Delta Z = 0.40574$). (Cunnold et al., 1979.)

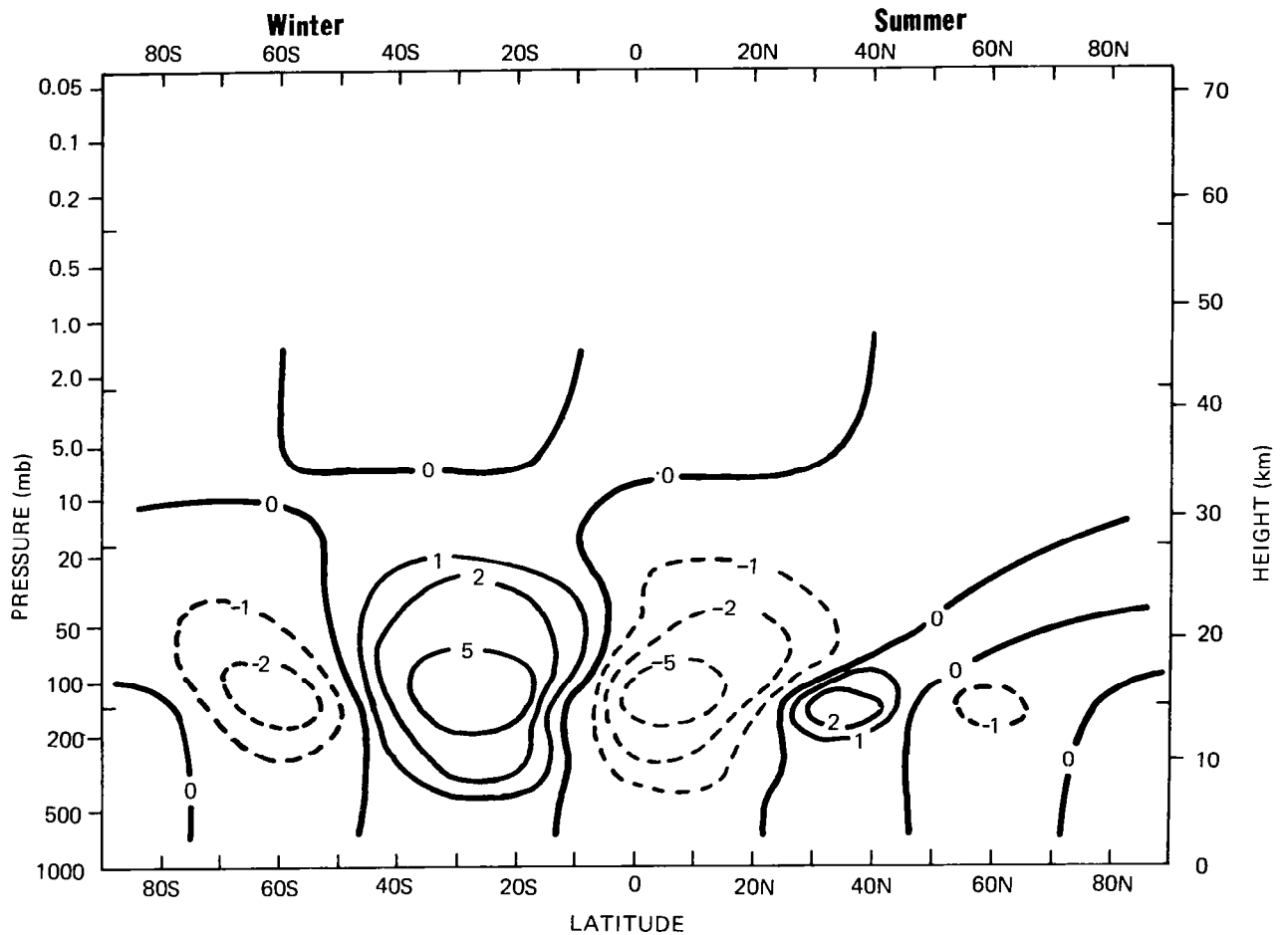


Figure 5-30. The calculated contribution to the ozone tendency resulting from horizontal and vertical transport by the mean circulation. Values have been weighted as in Figures 5-24 and 5-29. (Cunnold et al., 1979)

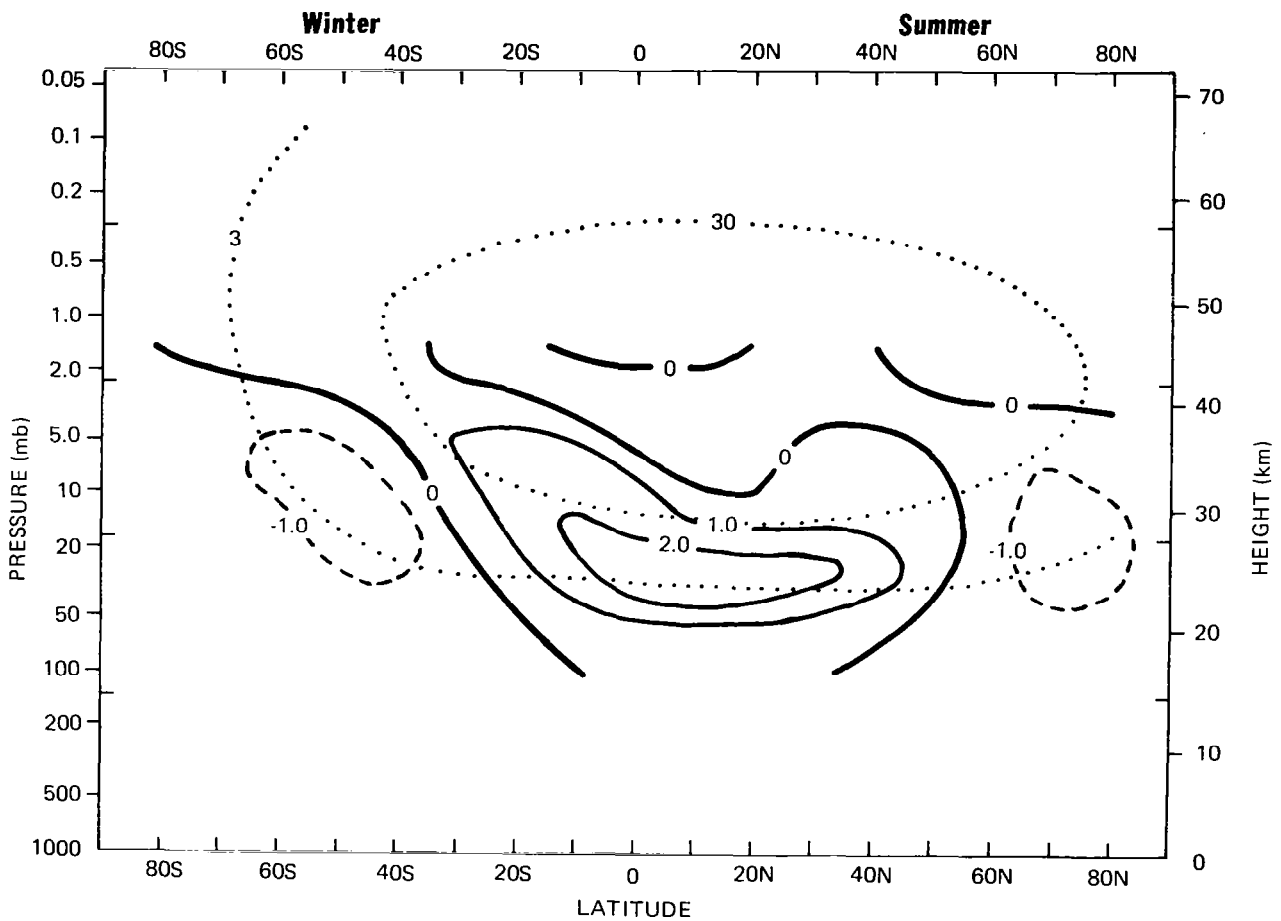


Figure 5-31. The calculated contribution to the ozone tendency resulting from chemistry. Values have been weighted as in Figures 5-24 and 5-29. The dotted lines show the chemical destruction rate of odd oxygen (Cunnold et al., 1979).

point", except in the lower stratosphere where vertical advection is responsible for downward transport of ozone. (This model utilized a diffusion coefficient of $10^2 \text{cm}^2/\text{sec}$ in the lower stratosphere). Figure 5-31 shows a net chemical production of ozone in the lower stratosphere between approximately 20 and 35 km altitude, centered in tropical regions of the summer hemisphere. At these heights, ozone is chemically destroyed at high latitudes, particularly in the winter hemisphere. Between approximately 25 km and 45 km in this model calculation, horizontal advection by eddies is primarily responsible for counterbalancing the net chemical production and loss of ozone as shown in figure 5-31, transporting ozone away from the source region in tropical latitudes and toward the weakly illuminated destruction region at high latitudes.

By comparing figures 5-29, 5-30 and 5-31, one can identify the dominant terms in the ozone continuity equation in each of the three zones identified in figure 5-24. In the dynamically controlled region (lower stratosphere), there is a near balance between zonal mean transport and horizontal eddy transport. At these levels, the transport of air parcels containing ozone is associated with a time scale which is much shorter than that for ozone changes within the parcel due to photochemistry. Thus, ozone acts as an almost inert tracer in the lower stratosphere. Its behavior should be similar to that of other essentially inert tracers (with a source in the stratosphere) and to isentropic potential vorticity. This relationship has been noted observationally by Hering (1966) for larger scale features over North America and by Danielsen (1968) and Danielsen et al. (1970) in their studies of tropopause folding events. Hartmann (1977) has used potential vorticity as a proxy to study tracer movements in the Southern Hemisphere stratosphere.

It has been demonstrated by Boyd (1976) and Andrews and McIntyre (1976a and b) and others that waves propagating into the stratosphere under idealistic conditions do not affect the zonal flow, and that, in fact, a wave induces a meridional circulation which just cancels its effect. It is only as a result of dissipative processes and wave transience that net transport in the lower stratosphere is produced. These conclusions also apply to an almost inert tracer (Mahlman et al, 1979). The cancellation between the contribution of eddies and mean circulation to ozone change seen in the lower stratosphere in figure 5-30 is not surprising and has been noted in previous three-dimensional model studies of ozone and in the observations cited earlier (Hunt and Manabe, 1968; and Mahlman, 1976).

The dissipative processes responsible for destroying ozone variations are chemistry (the production of tropospheric ozone from NO_2 as first suggested by Chameides and Walker (1973) is not included in this model), downscale transport of energy and ozone (represented by a vertical diffusion coefficient of $10^2 \text{cm}^2/\text{sec}$ in the lower stratosphere in this model) and surface destruction.

Because of the approximate balance between mean and eddy processes, conclusions concerning net ozone transport in the lower stratosphere and troposphere may require that dissipative processes be represented in a physically meaningful manner. For example, Mahlman et al. (1979), in their 3-dimensional model, produced a stronger-than-observed downward slope of mixing ratio surfaces at mid-latitudes. This was attributed to a neglect of chemistry in the lower stratosphere. However, numerical model studies of tracer transport should provide some insight into the trajectories of air parcels in the lower stratosphere and, to the extent to which wave transience is responsible for net transport, should also contribute to an understanding of the ozone budget. Mahlman et al. (1979) have found, for example, that wave transience is particularly important for transport at midlatitudes in winter. Mahlman and Moxim (1978) found in their tracer studies that the mean and eddy cancellation for tracer change in the lower stratosphere is particularly incomplete during the spring as planetary scale disturbances weaken, and is weak when the zonal mean flow in the stratosphere is weak. They attribute the latter effect to the absorption of planetary waves (and, hence alteration of the mean flow) at singular lines on which speed of the mean flow equals the phase speed of a planetary wave. It is also known from observations that large net transports of ozone occur during sudden warmings in the Northern Hemisphere. Much more study is needed on the ability of models to simulate wave transience, and on the effect of various representations of the dissipative processes on transport by wave motions.

The budget of ozone below 10 mb may be calculated by integrating the ozone continuity equation horizontally to obtain the budget of global mean ozone. The model then predicts a net production of ozone exists between 20 and 25 km, amounting to approximately 12 tons/sec. This chemically-produced ozone is transported vertically downward by the large scale eddies as shown by the model calculation in figure 5-32. Observations (e.g., Fabian and Pruchniewicz, 1977) indicate that, in fact, approximately 25 tons/sec are transported through the tropopause to be destroyed at the ground. Both observations (e.g., Danielson et al., 1970) and model calculations (e.g., Mahlman and Moxim, 1978, and Kida, 1977a and 1977b) indicate that much of this transfer occurs at midlatitudes in association with the jet stream, particularly in the spring. Stratospheric air may be injected into the troposphere (in a partially irreversible process) to the north of the jet stream by an induced direct circulation, and to the west of extra-tropical cyclones in the upper troposphere (Mahlman and Moxim, 1978). Additional evidence for these ideas is provided by the observed distribution of ozone in the upper troposphere (Fabian and Pruchniewicz, 1977) which exhibits a substantial maximum at mid-latitudes in the spring. This transfer is incompletely resolved in current stratospheric models (e.g., Mahlman and Moxim, 1978). A more extensive discussion of stratosphere-troposphere exchange is presented later in this chapter.

In the transition region where chemistry and dynamics are equally important, which is between the dotted lines in figure 5-24, there is a near balance between horizontal eddy transport and photochemical sources and sinks. This balance between eddy transport and zonal-mean photochemical disequilibrium in this model is consistent with conclusions derived from the mechanistic model of Hartmann and Garcia (1979). The probable importance of the transports produced in the transition region can be estimated by comparing the photochemical disequilibrium which they produce in middle latitudes (shown in figure 5-31) with the production of odd oxygen by O_2 dissociation shown in figure 5-24. Near the bottom of the transition region the chemical disequilibrium is of the same magnitude as the total of the oxygen production, so that a large deviation from the photochemical equilibrium concentration in the transition zone is possible. More work is required to evaluate how the details of the transition zone interaction affect the total ozone column of the atmosphere.

Calculated and observed meridional cross sections of ozone mixing ratios in the upper stratosphere can be compared in figure 5-33. It is seen in both cross sections that the ozone mixing ratio increases with latitude, up to approximately 60° latitude, in the winter hemisphere between 1 and 2 mb. Although the model predictions at latitudes higher than 60° in winter have yet to be verified, it can be surmised, from figures 5-24, 5-29, and 5-31, that this gradient appears to be defined by chemistry. However, there are limitations of this model (e.g., the cold pole temperatures) which suggest the need for further studies of the origins of this maximum. The analyses of satellite data by London et al. (1976a) show a tendency toward an increase of ozone with latitude at these levels in the winter hemisphere, but no marked peak is observed. Thus, at this time, the observed high latitude winter maximum at 1-2 mb is not completely understood; since NO_x , HO_x , O_x , and ClO_x all contribute to the ozone balance at this level, and species which sequester radicals (e.g., $ClNO_3$) are likely to have their maximum effect at high latitudes in winter. The complete explanation of this local maximum will probably have to await additional knowledge of the chemistry.

The budget of columnar ozone is evaluated by performing a vertical integration of the data in figures 5-29, 5-30, and 5-31. Figure 5-34 shows that columnar ozone is chemically produced at tropical latitudes of the winter hemisphere and at both tropical and midlatitudes of the summer hemisphere. It is chemically destroyed at high latitudes, with much of the destruction occurring in the winter hemisphere. Ozone is transported across the Equator from the summer to the winter hemisphere by the mean circulation and hence poleward by the midlatitude eddies. There is a small poleward transport by the midlatitude eddies in the summer hemisphere. At latitudes greater than 60° the decay of ozone from the spring maximum, which occurs over the course of the summer, appears to result from chemical and surface destruction of ozone (substantially offset by the transport of ozone from lower latitudes). At latitudes less than 40° the decay of ozone from the spring maximum may be produced by a transport of ozone into the winter hemisphere (Cunnold et al., private communication).

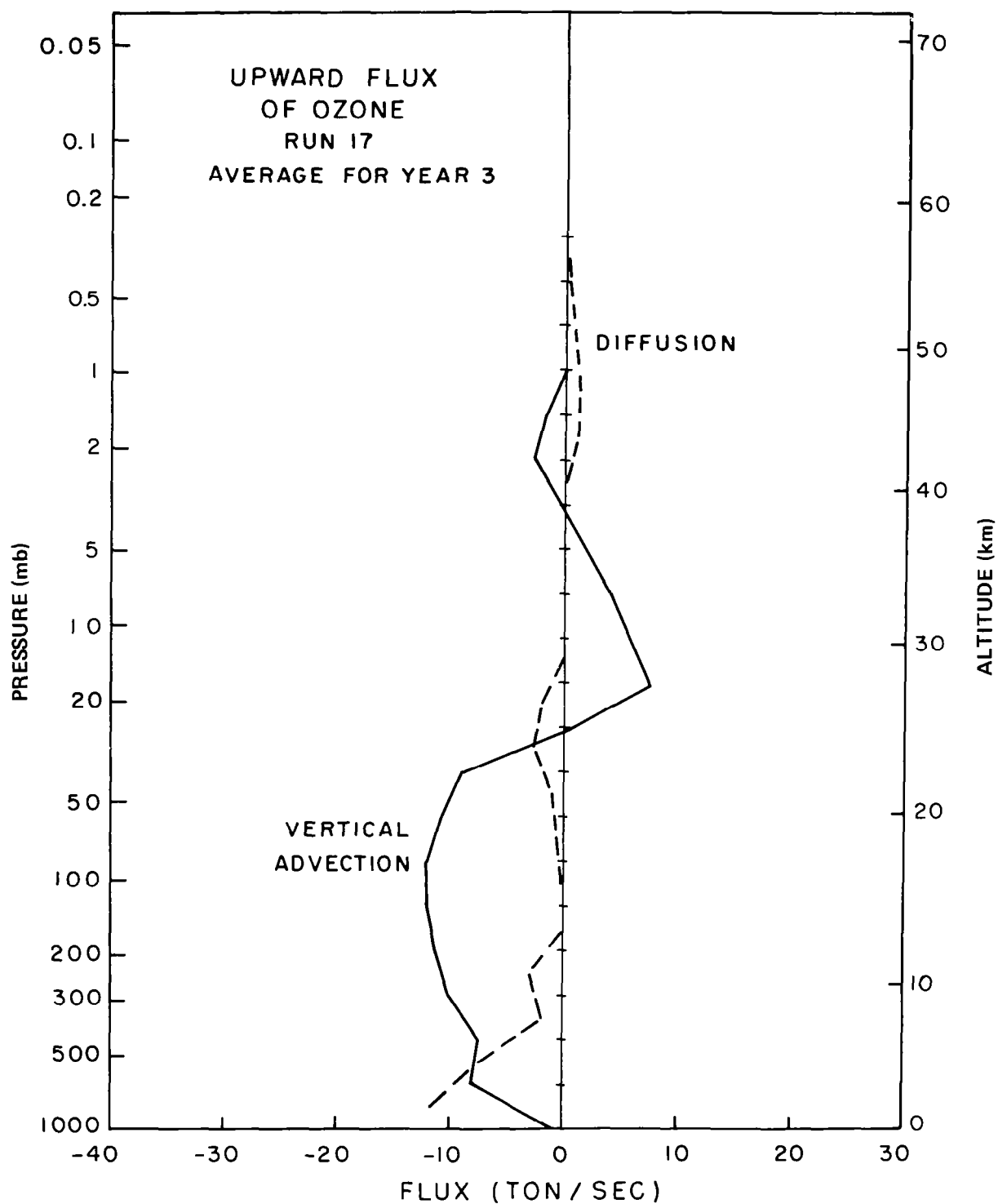


Figure 5-32. The calculated global-annual-mean vertical ozone fluxes resulting from planetary waves and diffusion (Cunnold et al., 1979).

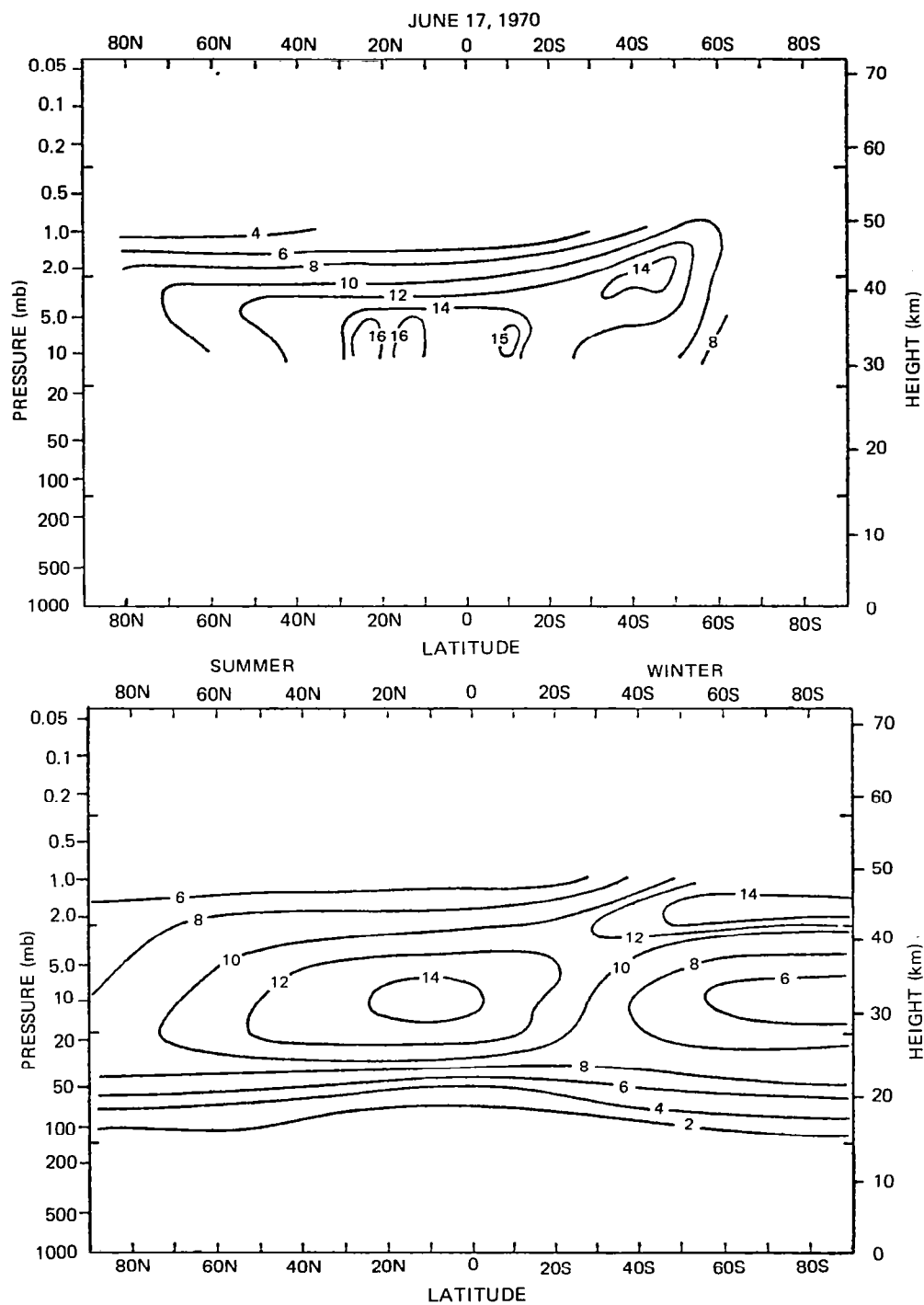


Figure 5-33. Calculated ozone mass mixing ratios ($\mu\text{gm/gm}$) (Cunnold et al., 1979) (lower figure) compared against BUJ observations by Krueger et al. (1973) (upper figure) for June 17, 1970 (supposedly typical of the summertime ozone distribution).

CONTRIBUTIONS TO HEIGHT INTEGRATED OZONE CHANGE

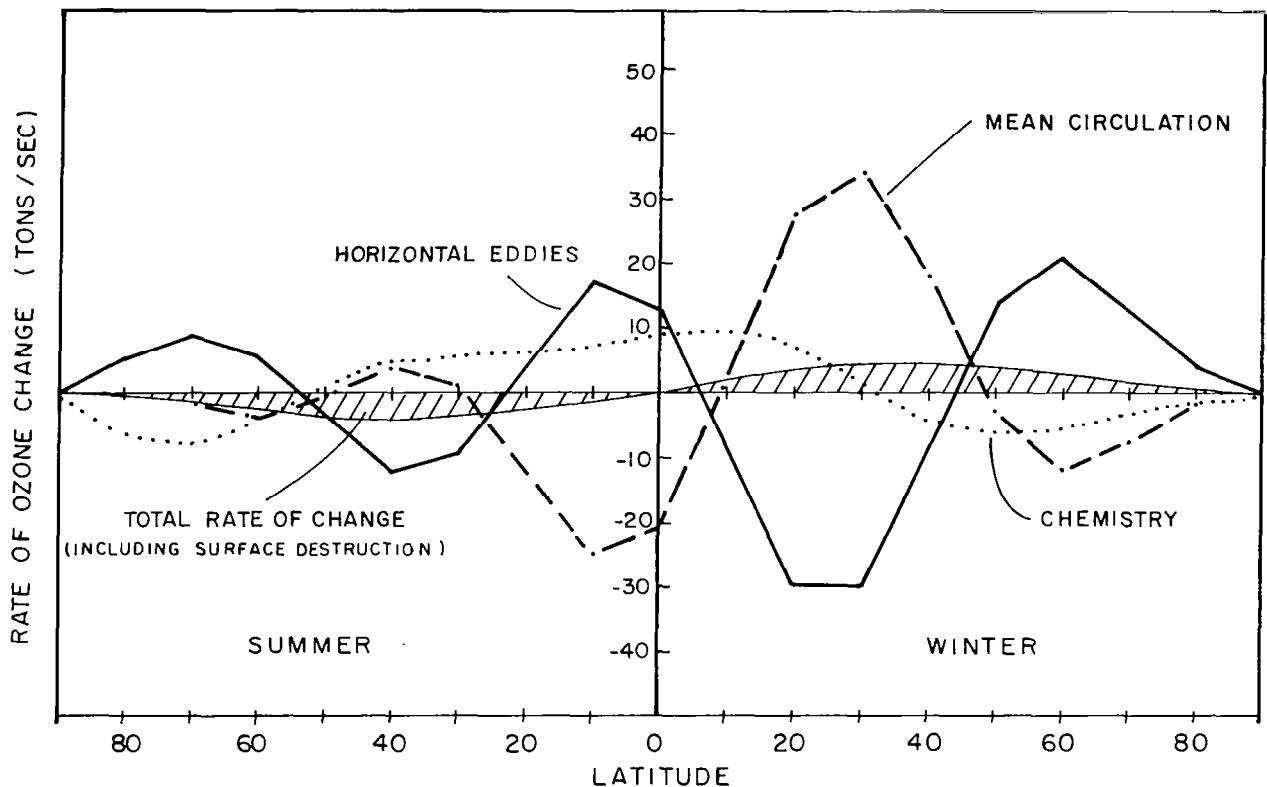


Figure 5-34. The calculated hemispheric budget of ozone in the 10° latitude intervals (integrated longitudinally) during the summer and winter (Cunnold et al., 1979).

Final Remarks

Thus, the zonal mean distribution of ozone below 1 mb and its seasonal variations are reasonably well defined in the Northern Hemisphere and some qualitative explanations requiring additional testing have been suggested for the principal features. It may be noted that for total ozone, Hilsenrath et al. (1979a) have found that 90% of the variance of the zonal mean total ozone is in the annual wave except in the tropics, and perhaps at high latitudes in the Southern Hemisphere. Differences between the ozone distributions in the Northern and Southern hemispheres are clearly indicated in figure 5-23 and are supported by the satellite data. The smaller annual columnar ozone maximum and the 1-month phase delay in the occurrence of this maximum at polar latitudes seem to be a well established feature of the Southern Hemisphere as shown by Hilsenrath et al. (1979a). These differences, compared with the Northern Hemisphere, are almost certainly related to the dynamical differences between the two hemispheres (see, for example, Newell et al., 1974). Wintertime flow is more zonal in the Southern Hemisphere, and the planetary wave amplitudes are generally weaker. However, more observations in the middle and upper stratosphere, which should be forthcoming from the satellites, will better define these interhemispheric differences in ozone.

SOLAR-STRATOSPHERIC RELATIONS

Background

Variations in extreme ultraviolet radiation from the Sun account for most of the observed variations in the structure of the thermosphere. Particle-induced radiations, in addition, can account for significant high latitude effects in the upper atmosphere. However, it has been difficult to demonstrate changes in tropospheric weather which might be directly related to variations in solar output. In the middle atmosphere, particularly in the stratosphere, it has been postulated that variations in the solar ultraviolet irradiance (in the spectral region absorbed by ozone) or in solar particle output may significantly and systematically perturb the stratosphere. Any relevant evidence of solar-related stratospheric variations is of considerable interest, not only for evaluating stratospheric trends of other origin, but also because of the possibility that variations in the zonal mean state of the stratosphere may influence weather and/or climatic processes in the troposphere (Bates, 1977). Several mechanisms possibly leading to solar-related stratospheric variations and some observations of such variations are considered in the following paragraphs.

Possible Mechanisms

The possible mechanisms leading to solar-related stratospheric variations include:

- Appreciable variation of UV flux at wavelengths affecting ozone. Heath and Thekackara (1977) infer a solar cycle dependent flux at wavelengths between 175 and 310 nm from a series of rocket and satellite experiments between 1966 and 1976. Callis and Nealy (1978) and Penner and Chang (1978) have made model calculations incorporating UV variations based on these observations, which indicate significant effects on stratospheric ozone and temperature. Their results and comparison with observations will be discussed below. On the other hand, there are some doubts about the reality of the UV variations inferred by Heath and Thekackara because of observational uncertainties. Solar UV variations are discussed in Chapter 7.
- Solar proton deposition in events associated with disturbed solar conditions, leading to an increased production of NO_x compounds in the stratosphere, affecting, in turn, the ozone budget (e.g., Crutzen et al., 1975).
- Relativistic electron precipitation events involving plasma interactions in the magnetosphere, where electrons precipitate to stratospheric depths (characteristic penetration depths have been given by Thorne, 1977).
- Modulation of cosmic rays by solar activity, leading to stratospheric modulation of NO_x , in turn affecting ozone (Ruderman and Chamberlain, 1975; and Chamberlain, 1977).

Evidence of Solar-Related Stratospheric Variations

Short-term effects include variations in ozone, temperature, and wind. A depletion of ozone during a solar proton polar cap absorption (pca) event was first observed in the mesosphere by Weeks et al. (1972). More recently, a 20 percent depletion above the 4-mb level (38 km) was observed during the pca event of August 1972 (figure 5-35, Heath et al., 1977), which was found to be consistent with the process described in the second mechanism above. Most remarkable was the persistence of this effect, the ozone depletion having been maintained long after the termination of the responsible source. The observed high-latitude depletion was attributed to production of odd nitrogen through proton bombardment. Rocket data evidence for ozone depletions during auroral X-ray events has been reported by Goldberg (1979). These data show a 25 percent reduction of ozone above 1 mb in figure 5-36 (Hilsenrath, private communication) following each of two night-time

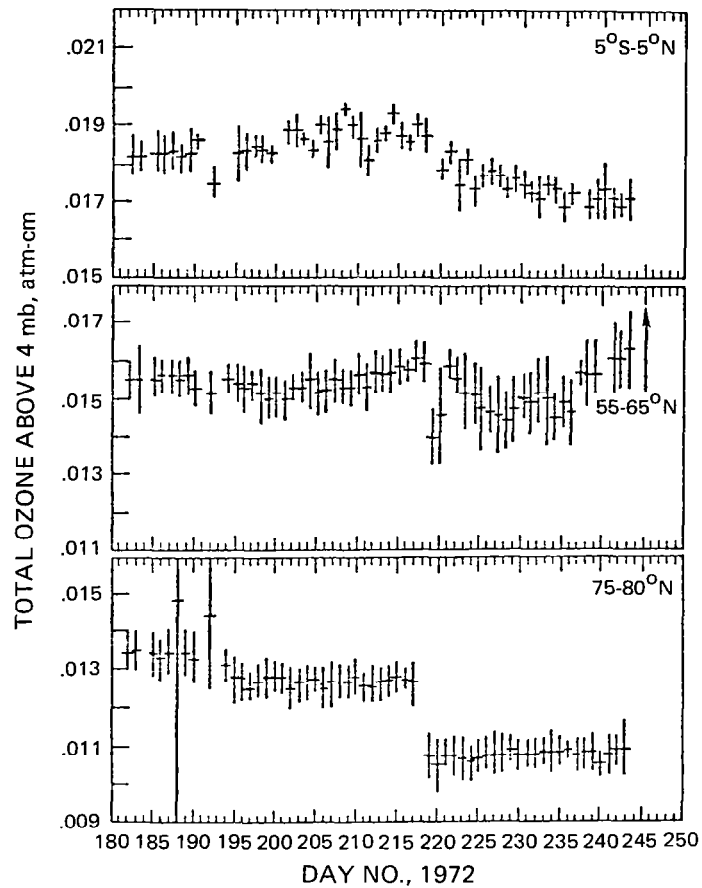


Figure 5-35. Daily zonally averaged total ozone (Nimbus-4 BUUV experiment) above 4 mb pressure level (about 38 km) for equatorial (top panel), middle (middle), and high (bottom) latitudes during July and August 1972.

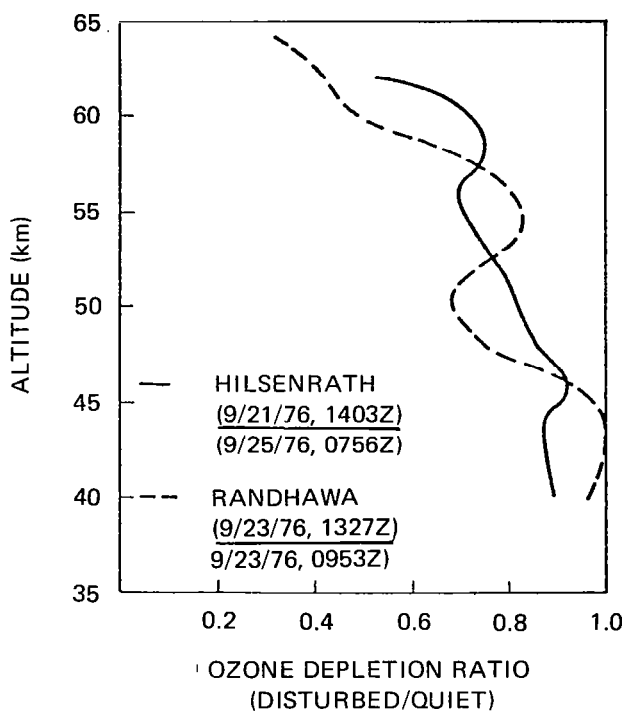
AUROROZONE I, POKER FLAT, ALASKA,
SEPTEMBER 1976

Figure 5-36. Ratio of nighttime vertical ozone distributions comparing post-auroral disturbance values to quiet time profiles preceding each event. The ratios were calculated from four independent rocket chemiluminescent detector soundings from Poker Flat, Alaska at the times shown. One comparison (Randhawa technique) was obtained on a single night. The second comparison (Hilsenrath technique) was obtained by comparison of quiet and post-disturbance values on separate nights (Hilsenrath, private communication).

X-ray auroral substorms. The ozone changes were observed again in two additional soundings performed during March, 1978, under similar conditions. However, Schoeberl and Strobel have shown that sizable as this effect is locally, its geophysical extent is too limited to affect global stratospheric dynamics directly.

In the mesosphere, there is evidence that temperature changes occur following geomagnetic storms (Ramakrishna and Seshamani, 1976). Finally, Reiter (1979) reports that troposphere-stratosphere exchanges are enhanced following solar flares. The importance of troposphere-stratosphere exchange in the chemical budget of the stratosphere is discussed in a later section.

Solar influences on the stratospheric circulation have been studied in terms of the solar rotation period (27 days). Ebel and Batz (1977) report statistically significant coherency values at both 27 and 13.5 day periods from cross-spectral analysis of the 10.7 cm solar radio flux and daily 10 mb height values. In the upper stratosphere, Nastrom and Belmont (1978) used a similar analysis technique to study the relationship between solar flux variations and zonal wind speed at 30-60 km. The amplitude of the zonal wind speed variations during winter (figure 5-37) shows two centers of maximum, near 50°N and 25°N above 50 km. The phases (times of maximum eastward speed) at these two centers differ by about 13.5 days (i.e., 180 degrees). These coherency studies indicate that there exists some connection between 10.7 cm flux and stratospheric circulation than if there were independent fluctuations in these parameters with the same period as Volland and Shaeffer (1979) claim.

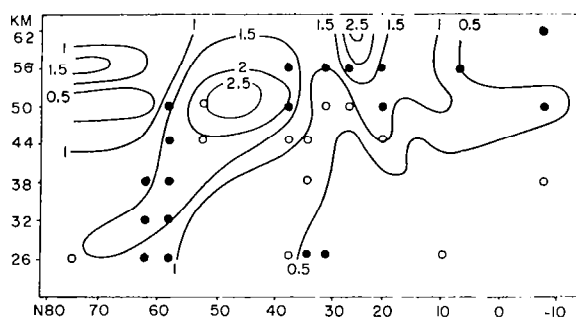


Figure 5-37. Amplitude (ms^{-1}) of the zonal wind variation during winter in the spectral band centered at 27.1 days. Amplitude is defined as the square root of the product of the spectral estimate in wind speed and the squared-coherency. Circles show locations of coherency values which exceed the 90% (open circles) or 95% (closed circles) confidence limit (Nastrom and Belmont 1978).

Stratospheric temperatures over a solar cycle have also been studied (e.g., Schwentek, 1971; Zlotnick and Rozwoda, 1976; and Angell and Korshover, 1978c). Most recently, Quiroz (1979a) has presented results (figure 5-38) which showed an overall temperature variation in the upper stratosphere of about 4K during solar cycle 20, with an overall coefficient of correlation near +0.9 between combined temperature data from seven rocketsonde stations (8°S - 64°N) and annual sunspot number. The variation appears fairly uniform among the stations, except at 50 km, where Poker Flat (64°N) and Ascension (8°S) show strong differences. The temperature range reported is within the model calculations mentioned in the first mechanism involving variations in UV radiation.

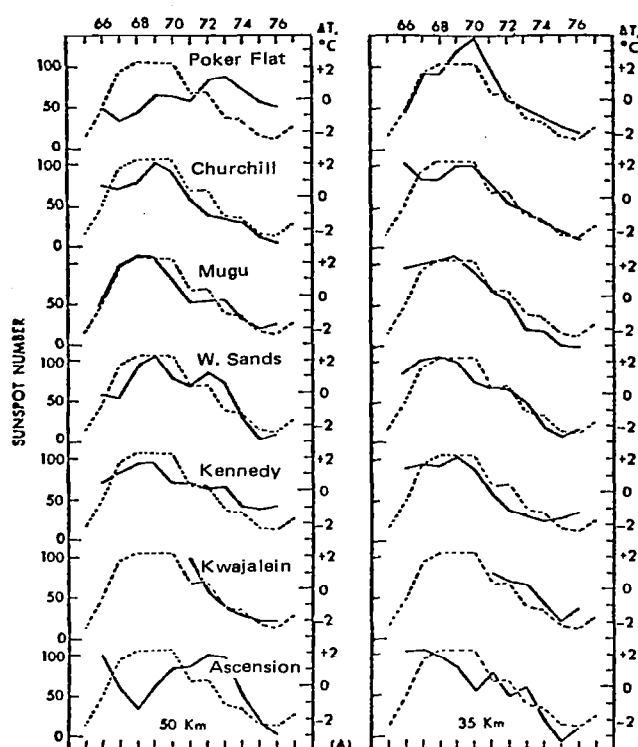


Figure 5-38. Mean summertime temperature departure from long-period average (3-year running averages) compared with sunspot number (dashed lines) (Quiroz, 1979a).

Long-term variation of stratospheric ozone over a solar cycle has been seen from statistical studies based on data from the global network of ground based Dobson stations (Angell and Korshover, 1973 and 1978d). The results are controversial, in part because of absolute and intercalibration errors among stations and gaps in data acquisition. The interpretation is confused by the fact that total ozone (Dobson) measurements are dominated by the maximum density of ozone found below about 25 km altitude. In this height regime, the residence time of atmospheric ozone is about two years, and its distribution and concentration are controlled by transport processes.

Penner and Chang (1978) using a one-dimensional model which includes major feedback mechanisms and chemical time delays showed that ozone changes would result from an eleven-year variation in the solar ultraviolet flux. Their calculated variation over a solar cycle is consistent with the analysis of total ozone data by Angell and Korshover (1978d). However, the agreement of their calculations above 30 km with Umkehr data was less satisfactory. The most recent calculations by Callis et al. (1979) using a time dependent radiative-convective-photochemical model also shows an ozone response to solar cycle variations in the ultraviolet. These calculations seem to produce ozone variations more consistent with the observations above 30 km. Both of these models produce temperature changes in the stratosphere consistent with the Quiroz (1979a) and Angell and Korshover (1978c) analyses of rocketsonde data. Both model calculations use solar ultraviolet variations as observed by Heath and Thekaekara (1977). The observations are still controversial, and there is an obvious need for regular and accurate observations of the solar ultraviolet flux. Further discussion of long-term ozone variations appear in Chapter 6.

Final Remarks

There are numerous studies which show that an atmospheric response is consistent with solar variability. However, in most cases the observations used to show solar cycle relationships are taken over one solar cycle. Pittcock's critical review of solar weather relationships (1978) points out several guidelines for interpreting solar related phenomena which are applicable to the stratosphere.

The evidence discussed for solar-related stratospheric variations is provocative, but not conclusive. Solar response at various time-scales does not appear implausible in the context of the mechanisms listed. However, it is evident that much work remains, including the development of an improved body of ultraviolet observations, in order to rigorously define solar relations in the middle atmosphere.

STRATOSPHERIC TROPOSPHERIC INTERACTIONS

INTRODUCTION

This section will consider the mass and chemical exchange, energy transfers, and electrical coupling between the stratosphere and the troposphere. The various meteorological processes responsible for the direct exchange of air and its associated chemical constituents across the tropopause are discussed. The dynamical coupling process that takes place through vertically propagating waves and the mean motions is then considered. The exchange of radiative energy across the tropopause is discussed. And finally, consideration is given to aspects of electrical coupling between the stratosphere and the troposphere.

MASS EXCHANGE PROCESSES

Background

The current research on stratospheric-tropospheric exchange processes is motivated, in part, by the awareness that the transport of anthropogenic and natural chemical constituents across the tropopause may bring about significant changes in the radiative and chemical budget of the Earth's atmosphere. These exchange processes are those arising from 1) mean meridional circulations, 2) seasonal variations in the height and potential temperature of the tropopause, 3) radiative cooling at the tropopause above jet stream and cumulonimbus cirrus clouds, 4) transverse mass circulation about subtropical and polar front jet stream systems, 5) vertical exchange during tropopause folding events within extratropical cyclones, 6) cumulonimbus clouds which penetrate the tropopause, 7) turbulent mixing processes in the vicinity of jet stream tropopause folding events, and 8) weak eddy diffusion across the vast quiescent expanses of the tropopause. This section discusses recent results which add to our understanding of tropospheric-stratospheric exchange by processes 1), 5), 6), and 7). The reader is referred to the review by Reiter (1975) for a comprehensive discussion of stratospheric-tropospheric exchange processes.

Definition of the Tropopause

The interface between the stratosphere and troposphere (the tropopause) was previously defined solely in terms of the discontinuity in the vertical lapse rate of temperature. This thermal definition of the tropopause has been replaced by Reed's (1955) concept of a "dynamical" tropopause based on potential vorticity. The dynamical tropopause is situated at the near-zero-order discontinuity in potential vorticity that separates the low values of that quantity in the troposphere from the values one to two orders of magnitude higher, which typify the stratosphere. Figures 5-39a and 5-39b present a cross section analysis from Shapiro (1974) in which the stratosphere is separated from the troposphere by the discontinuity in potential vorticity situated near the

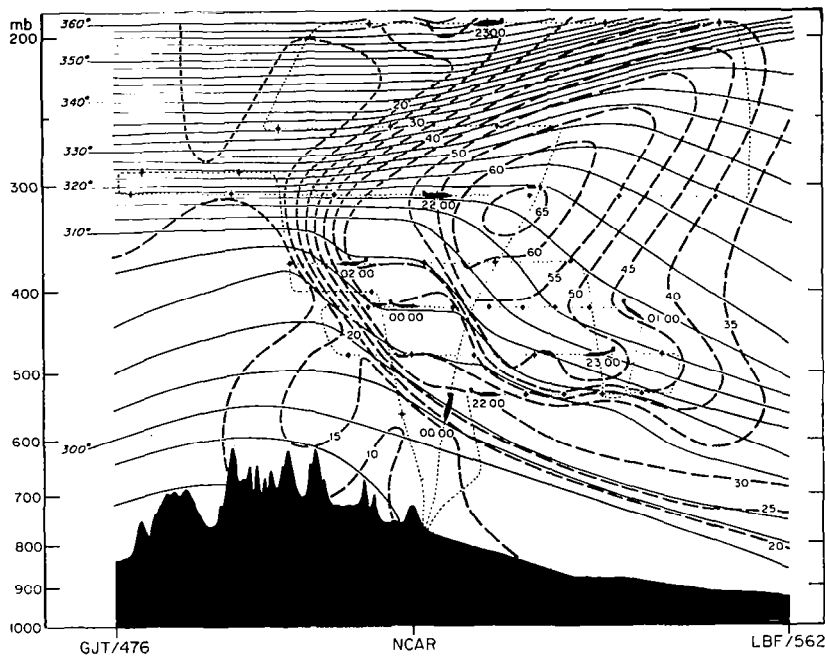


Figure 5-39a. Cross section of potential temperature and wind speed. Isentropes (K), solid lines; isotachs (m sec^{-1}), heavy dashed lines. Flight paths of the NCAR Buffalo and Sabreliner research aircraft, light dashed lines, with time (GMT) shown by the silhouetted aircraft and 10-minute intervals shown by time hacks. Positions of rawinsonde soundings indicated by station letters at bottom of figure (Shapiro, 1974).

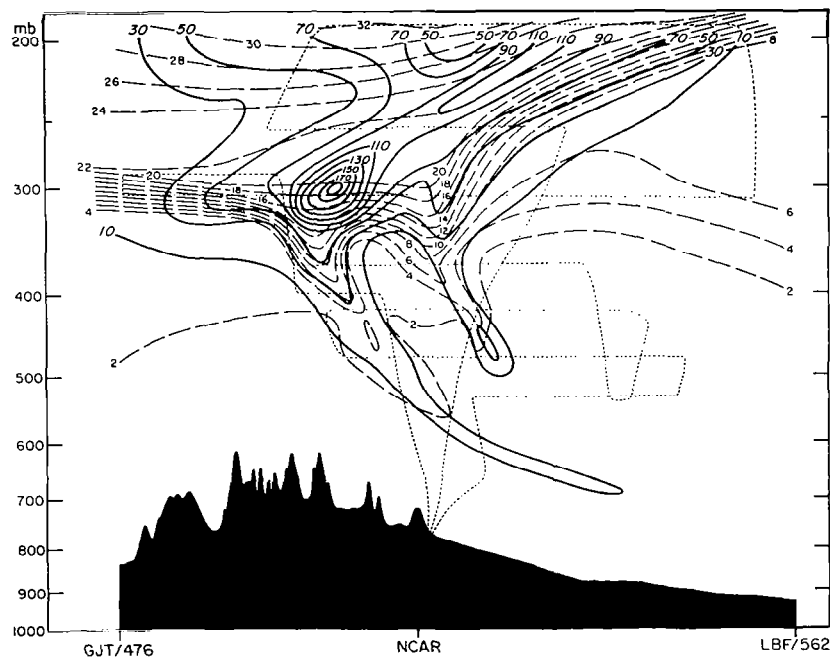


Figure 5-39b. Potential vorticity ($10^{-6} \text{ K mb}^{-1} \text{ sec}^{-1}$), solid lines; and ozone (0.01 ppm by volume), dashed lines; for flight cross section figure 5-39a (Shapiro, 1974).

$10 \times 10^{-6} \text{ K mb}^{-1} \text{ s}^{-1}$ isopleth of potential vorticity in figure 5-39b. In addition, figure 5-39b includes the ozone concentration distribution which takes the same configuration as potential vorticity in the vicinity of the dynamical tropopause.

Potential vorticity, P , is the vorticity (rotational tendency about a vertical axis) of an air parcel ($\zeta_\theta + f$), times its thermal stability, $-\partial\theta/\partial p$ as evaluated on surfaces of constant potential temperature, θ

$$P = -(\zeta_\theta + f) \partial\theta/\partial p$$

$$\zeta_\theta = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}$$

where u and v are the horizontal air velocity components in the west-east (x) and south-north (y) directions, respectively; and $f = 2\Omega\sin\phi$ is the vorticity associated with the Earth's rotation, Ω , as a function of latitude, ϕ . If one neglects as second order effects the contributions by diabatic and turbulent mixing processes, potential vorticity is nearly conserved along three-dimensional air parcel trajectories. It should be noted that because of the difference in stratospheric versus tropospheric potential vorticity, potential vorticity generation and destruction processes are essential to the exchange of air and chemical constituents between the stratosphere and troposphere.

Exchange by Lagrangian Mean Motions

The traditional diagnosis of mean mass exchange across the tropopause separates the motions into zonal mean meridional and eddy transport motions (Oort and Rasmussen, 1971). The resulting picture of the mean meridional circulation contains the thermally direct Hadley cell of the tropical and subtropical latitudes, the indirect Ferrel cell of middle latitudes, and the direct polar cell. The Eulerian concept of the general circulation, based upon point averages of the mean motions, which leads to the three cells mentioned above, is found to be difficult to reconcile with the chemical tracer circulation motions proposed by Brewer (1949) and Dobson (1951). In contrast to the Eulerian three-cell mean circulation, the Brewer-Dobson circulation, figure 5-40 (upper) contains a single direct Hadley cell, extending from Equator to pole, which defines the Lagrangian (parcel trajectory) mean motions. Implicit within the Lagrangian mean motions are the contribution by the eddy motions, which are predominant in middle latitudes. It should be noted, as discussed by Wallace (1978b), that the Stokes drift induced by the eddy motions in middle latitudes, when added to the Eulerian mean circulation, acts to counteract the effect of the indirect Ferrel cell of middle latitudes.

The resulting Lagrangian mean circulation, (the heavy arrows of figure 5-40, lower), is quite similar to the figure 5-40 (upper) Brewer-Dobson circulation. The individual contributions to the Lagrangian mean circulation schematically entered into figure 5-40 (lower) illustrates the complex processes which force the Lagrangian mean circulation.

A possible mechanism for the exchange of air between the troposphere and the stratosphere by the mean Lagrangian motion may be inferred from the circulation shown in figure 5-40. The ascending branch of the circulation in the equatorial tropics transports tropospheric air to the Dobson-Brewer "cold trap" for water vapor at the tropical tropopause, where the low water vapor saturation mixing ratio air and tropospheric trace constituents are incorporated into the tropical stratosphere. The northward moving motion of the circulation transports ozone from the upper-stratospheric tropical ozone production region toward the middle and high latitudes, where the descending branch of the circulation deposits the ozone into the ozone reservoir above the polar tropopause. Further sinking motions subsequently transport ozone-rich air into the extratropical troposphere.

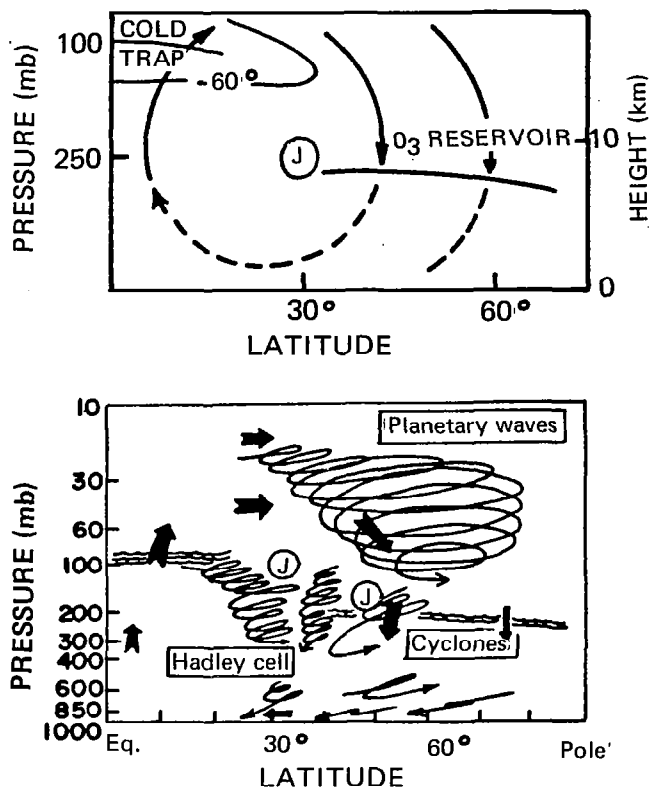


Figure 5-40. (Upper) The Brewer-Dobson model of the mean meridional circulation. Heavy lines denote the tropopause.

(Lower) Lagrangian mean meridional circulation, heavy arrows, from the numerical simulation of Kida (1977), showing contributions by the Hadley cell, extratropical cyclones; jet streams, J; planetary waves, and small-scale motions (thin lines).

Both figures are presented in Wallace (1978a).

Recent examples of Eulerian versus Lagrangian mean circulations are found in the numerical studies of Kida (1977) and Dunkerton (1978). These studies and the theoretical formulations of the Lagrangian motion concept by Andrews and McIntyre (1976a,b) suggest that it is useful to view the general circulation-scale exchange of air and trace constituents between the troposphere and the stratosphere in terms of the mean Lagrangian motions.

Exchange by Extratropical Cyclonic and Jet Stream Systems

The transport of potential vorticity, ozone, and radioactive particles from stratospheric to tropospheric levels through tropopause folding within the synoptic-scale (~ 4000 km) eddies of middle latitudes has been investigated by Reed (1955), Reed and Danielsen (1959), and Danielsen (1964), Staley (1960), and Shapiro (1974, 1976, 1978). It should be stressed that tropopause folding is not, in itself, evidence for stratospheric-tropospheric exchange. In the absence of diabatic and turbulent mixing processes, potential vorticity is conserved and tropopause folding is a reversible process, i.e., the stratospheric extrusion that occurs within the

subsiding northwesterly flow of extratropical cyclones is retracted back into the stratosphere in the ascending southwesterly flow in advance of the cyclonic disturbances. Measurements made from research aircraft by Kennedy and Shapiro (1975), and Shapiro (1976, 1978) quantitatively documented the magnitude of the potential vorticity altering turbulent fluxes of heat and momentum associated with CAT within tropopause folds. They also established the first-order importance of CAT in the free exchange of air and chemical constituents across the potential vorticity discontinuity of the tropopause.

Recent observations from Shapiro (1979) give evidence that tropopause folds are mixing regions for chemical constituents. This is illustrated in figures 5-41a, 5-41b, and 5-41c which present the meteorological, ozone, and condensation nuclei distributions, respectively, for a pronounced example of tropopause folding. Figures 5-41a and 5-41b reveal that the air within the fold contained both stratospheric levels of ozone and tropospheric concentrations of condensation nuclei. Figure 5-42 shows the turbulent fluxes of ozone and condensation nuclei for the upper and lower portion of this fold, which permitted the evaluation of the magnitude of vertical turbulent flux divergence as a mechanism for altering chemical concentrations within the fold. The calculations indicate a vertical flux divergence of ozone out of the fold, with a simultaneous flux convergence of tropospheric condensation nuclei into the fold. Cadle et al., (1979) presented evidence from aircraft measurements showing tropospheric concentrations of condensation nuclei within the stratosphere in the vicinity of an upper-level jet stream system. Therefore, the recent measurements from research aircraft suggest that small-scale turbulent mixing processes within tropopause folds act to entrain tropospheric chemical constituents into the stratosphere, while stratospheric ozone is simultaneously expelled into the troposphere.

Exchange by Convective Cloud Systems

The traveling synoptic disturbances of the InterTropical Convergence Zone (ITCZ) contain organized mesoscale convection systems within which are imbedded the "hot tower" cumulonimbus clouds first described by Riehl and Malkus (1958). The penetration of the tropical tropopause by these convection systems can lead to a vertical exchange between the stratosphere and troposphere. Houze et al. (1977) and Riehl (1977) present further evidence that less than 1% of the equatorial convective systems reach altitudes near the 16 km tropical tropopause. Thus, only a small percentage of the total tropical convection participates in the direct exchange process.

The role of deep tropical convection is to transport lower tropospheric constituents to the layer just below the tropical tropopause; from there the much weaker upward motion of the mean circulation performs the final cross-tropopause transport into the stratosphere. An example of tropopause-penetrating cumulonimbus clouds in extratropical latitudes is presented in Shenk (1974). The relative importance of tropical versus extratropical convective systems as exchange mechanisms is not clearly established at this time.

Discussion of Mass Exchange

A common factor among exchange mechanisms is the role of non-conserving potential vorticity processes as a requirement for stratospheric-tropospheric exchange. These potential vorticity altering processes range in space-time scale from the differential diabatic heating by the Sun, which forces the mean meridional circulation and provides the energy for the extratropical baroclinic waves with their associated tropopause folds, down to the diabatic heating within mesoconvective cloud systems and the turbulent mixing in the vicinity of jet stream-frontal zone tropopause folding systems. From the meteorological point of view, it is the contributions by mesoconvective and turbulent-scale motions to the total exchange process that are the most difficult to assess.

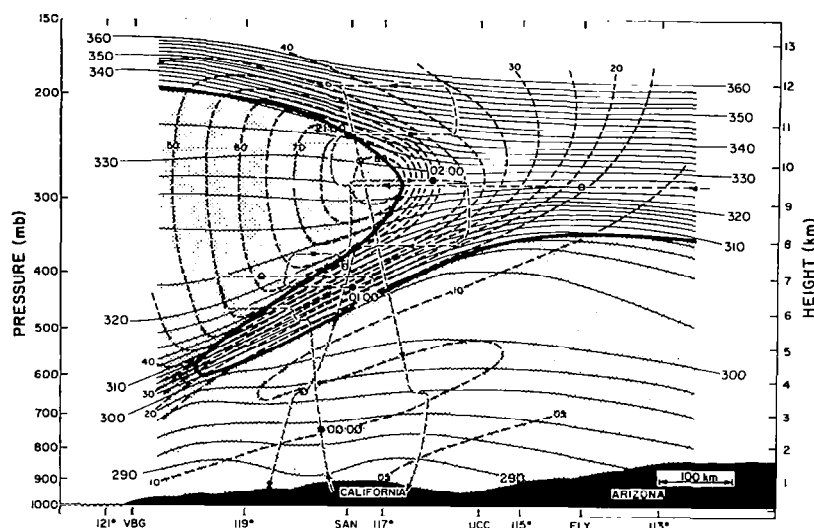


Figure 5-41a. Cross section through the 0000 GMT 13 March 1978 tropopause folding event. Potential temperature (K), thin solid lines; wind speed (meters/second), heavy dashed lines; Sabreliner flight track, thin dashed lines; the $10 \times 10^{-6} \text{K mb}^{-1} \text{s}^{-1}$ potential vorticity tropopause, heavy solid line (Shapiro, 1979).

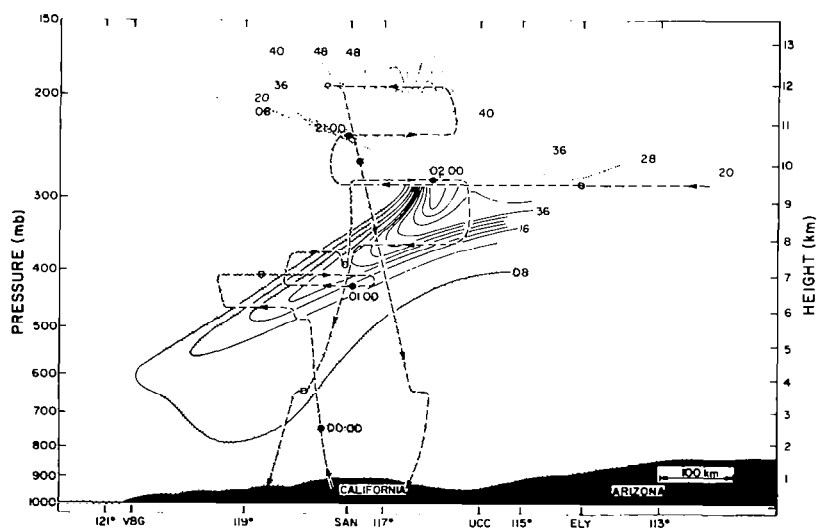


Figure 5-41b. Ozone concentration, 10^{-2} ppm (volume) for Figure 5-41a. Ozone analysis for upper flight track, dotted lines; lower flight track ozone, solid lines; the troposphere, stippled area (Shapiro, 1979).

Danielsen (1959), Danielsen and Mohnen (1976), Reiter (1972, 1975), and Mohnen and Reiter (1977) have presented number estimates for various individual components of the total exchange process. Nastrom (1977) documented the average ozone concentration and estimated the downward flux of ozone near the tropopause for the latitudinal belt 30N to 50N from an extensive ozone data set taken from the GASP program. However, these estimates are not repeated in this report, since it appears that the spatial and temporal contributions by exchange components smaller in scale than the mean and seasonal components have not been sufficiently observed to warrant quantitative evaluation.

In the absence of global measurements of the individual exchange components, estimates have been obtained of the total mass exchange and downward ozone flux across the tropopause by using global general circulation models to simulate the three-dimensional air motion trajectories and exchange processes. These models include parameterizations for sub grid-scale motions and physical processes which are not explicitly resolved by the grid resolution of the models. Results from such experiments are found in the tracer studies of Mahlman et al. (1979) and the dynamical-chemical atmospheric model of Cunnold et al. (1975). The total downward ozone flux estimates at the tropopause from the GFDL (Mahlman et al., 1979) and NCAR (Gidel and Shapiro, 1979) general circulation models have addressed the question of the asymmetry between the northern and southern hemispheric tropospheric concentrations described by Fishman and Crutzen (1978).

Final Remarks

The current understanding of the specific meteorological processes responsible for the exchange of air and chemical constituents between the stratosphere and troposphere has been discussed in this section. What is unclear, at present, is the magnitude and relative importance of the individual components that make up the total exchange across the tropopause. For example, it is essential to determine the amount of air that enters the stratosphere in equatorial regions through the mean and small-scale motions, as compared to the amount which enters via turbulent entrainment within middle and high-latitude tropopause folds, as well as return flow on the anticyclonic side of the jet. The impact of observed interhemispheric and latitudinal differences in anthropogenic sources of tropospheric chemical constituents upon the chemistry and energetics of the stratosphere is dependent in part upon the location of chemical source regions relative to the location of the major meteorological exchange processes. Furthermore, tropospheric chemical characteristics such as the observed larger amount of ozone in the Northern versus the Southern Hemisphere troposphere require the determination of the relative contributions by hemispheric asymmetry in *in situ* photochemical production (Fishman and Crutzen, 1978) and suggested hemispheric differences in the intensity of stratosphere to troposphere ozone transport (Gidel and Shapiro, 1979).

It remains for future coordinated research efforts to obtain simultaneous observations of the meteorological and chemical properties in the vicinity of the tropopause on scales ranging from the global to the mesoscale and turbulent scale, in order to arrive at quantitative evaluations for the individual exchange processes. Such efforts will require the use of satellite, conventional ground-based, and research aircraft measurements in conjunction with modeling efforts. Exchange processes coupled with our understanding of atmospheric chemical processes, would provide the basis for a new synthesis of the combined physical-chemical evolution of both the stratosphere and the troposphere.

DYNAMICAL COUPLING

Background

Whereas the previous discussion related to direct mass exchange, dynamical coupling deals with transports of physical quantities such as momentum and/or energy where no net mass exchange is necessarily involved. As in the discussion of mass exchange, both upward and downward interaction need to be considered.

Mechanisms

The role of tropospheric forcing of the stratospheric circulation is well appreciated. The mean meridional tropospheric motions that are forced by the differential heating of the Earth's surface are known to penetrate well into the lower stratosphere (Vincent, 1968). The extratropical planetary waves that exist as a consequence of surface airflow over continental topography and of the continent-ocean thermal differences are observed to penetrate upwards at least into the mesosphere (Green, 1972). Also, enhancements in the tropospheric planetary waves are crucial to present theories of stratospheric warmings (Matsuno, 1971, and Tung and Lindzen, 1979). The tropical waves that are believed to force the quasi-biennial oscillation in the lower tropical stratosphere (Holton and Lindzen, 1972), and to play a large role in forcing the semi-annual oscillation in the middle and upper tropical stratosphere (Hirota, 1978), are thought to be forced by tropical convective systems (Holton, 1972).

Recently, however, the concept that changes in the stratospheric circulation can significantly affect the troposphere has been examined more closely. Hines (1974) suggested one possible mechanism by which this might take place. The basis of this mechanism is that tropospherically forced planetary waves propagate their energy upward, where the stratospheric and mesospheric winds play a dominant role in determining the "refractive index" for these waves (see Charney, 1961; Matsuno, 1970; and Schoeberl and Geller, 1976) which then determines the transmission-reflection properties of the waves. Thus, changes in the middle atmosphere flow might lead to changes in tropospheric planetary wave amplitudes and phases. Some of the relevant dynamical model studies that relate to this mechanism are those of Bates (1977), Schoeberl and Strobel (1978a, b), and Mahlman et al. (1978). Both the approaches and the results of these latter studies differ with Bates (1977) which indicated that changes in the stratospheric mean zonal wind and/or temperature structure produced large changes in tropospheric planetary wave structure and the resulting heat flux. Bates' (1977) result was obtained analytically using a model which required a number of simplifying assumptions and resulted in a one-dimensional vertical structure equation. Schoeberl and Strobel (1978a,b) and Mahlman et al. (1978), using more complete dynamical formulations, did not find so marked tropospheric effects. Tung and Lindzen (1979) have indicated that in order for changes in the stratospheric mean flow to significantly affect tropospheric planetary waves, such changes must take place below the middle stratosphere where dissipative processes are relatively small. This conclusion is also supported by recent calculations of Geller and Alpert (private communication).

Ramanathan (1977) has suggested a combined dynamical-radiative stratospheric-tropospheric coupling process that may be important. He suggested that during a stratospheric warming, the warm high latitude stratosphere emits a sufficiently enhanced amount of infrared radiation so as to significantly decrease the pole-to-Equator temperature gradient in the troposphere, thus decreasing the tropospheric available potential energy. Observational studies indicate downward dynamical coupling from the stratosphere. Quiroz (1978) has shown that the circulation reversal that accompanied the 1976-77 stratospheric warming was observed to penetrate down to ground level.

In summary, the idea that tropospheric dynamics affect stratospheric dynamics has been around for at least twenty years, and is by now a well-accepted concept. A new concept that has emerged in the last five years is

that under some conditions, the coupling in the opposite direction can be significant. This subject is much more speculative, but with present and future theoretical work taken together with further joint analysis of stratospheric and tropospheric data, rapid progress in our understanding should be forthcoming.

RADIATIVE COUPLING

Background

The stratosphere and troposphere interact not only by exchange of mass and mechanical energy, but also by transfer of radiant energy across the tropopause. It is largely through this coupling that changes in the stratosphere may affect tropospheric climatology, while the upwelling radiative flux from the troposphere plays a very important role in the meteorology of the stratosphere.

The stratosphere receives shortwave radiation reflected from the surface, clouds and tropospheric aerosols, and long wave radiation emitted by all of these and by tropospheric CO_2 and H_2O . Variations in surface albedo and cloud amount may modify shortwave heating rates in the stratosphere, and introduce non-zonal forcing (Lindzen, 1965). In addition, reflected radiation from below also affects stratospheric photochemistry (Callis et al., 1975).

In the longwave (thermal infrared) region, ozone absorption at $9.6\mu\text{m}$ is of special interest since it allows efficient radiative communication from the cloud-tops or surface to the lower stratosphere. In fact, the same stratospheric airmass may be radiatively heated while passing over the warm tropical ocean, and cooled while going over a high, cold cloud. Changes in the surface temperature of $\sim 20^\circ$ between day and night, which is typical of desert regions, induce diurnal cooling rate fluctuations of $\sim 0.2^\circ/\text{day}$ in the lower stratosphere, which may provide a non-migrating tidal forcing (Fels, 1979, private communication). None of these effects have been studied in detail, nor has the role played by upwelling IR in maintaining the structure of the polar night stratosphere.

By contrast, the tropospheric effects of changes in the stratosphere, (as mediated by radiation), have received a great deal of attention in the past decade, due largely to fears that anthropogenic perturbations of the stratosphere will affect the troposphere. Although in principle these interactions are well described by the traditional methods of terrestrial radiative theory, in practice they proved rather delicate, demanding not only careful theoretical treatment, but also very accurate specification of atmospheric variables such as composition, thermal structure, cloud amounts, spectra, particle size distribution, and absorption. Often the required accuracy is beyond our present attainment.

The source of the delicacy lies in the complementary role played by short and longwave radiation. To an observer located in the troposphere, the stratosphere may be conveniently regarded as a highly nongrey screen, absorbing and scattering, on the one hand, portions of the incoming solar beam, and on the other, providing a source of downward infrared radiation. Generally these two effects have opposite signs, and assessment of the radiative effects of perturbations to the stratosphere is plagued by the difficulties common in such situations. These problems are illustrated by a consideration of the radiative effects of ozone, stratospheric aerosols and carbon dioxide, and of altered amounts of these constituents.

Radiative Properties of Ozone

Reducing O_3 allows more solar radiation to reach the tropopause, but cools the stratosphere, so less IR is emitted downward. The roles played by these two effects have been examined extensively by Ramanathan and co-workers (Ramanathan et al., 1976; Ramanathan, 1977; Ramanathan and Dickinson, 1979). They find that in a global mean sense there can be close cancellation between the two. In view of this, the methods for calculating O_3 radiative transfer may be important.

A sense of the variation by the use of different assumptions may be had by considering the change in downward solar flux across the tropopause due to a 30% uniform reduction in ozone between 12 and 40 km. Ramanathan et al. (1976) find an increase of 1.14 W/m^2 . The shortwave algorithm of Lacis and Hansen (1974) gives 1.07 W/m^2 and 1.00 W/m^2 , depending on cloud parameterization (Fels, 1978, private communication; Coakley, 1978). The compensating IR effect is calculated to be -1.5 W/m^2 so that the residual error due to uncertainty in the shortwave calculation is as much as 25%.

As emphasized by Ramanathan and Dickinson (1979), however, the delicacy of the global mean annual response may be illusory. They find that the IR effect is roughly uniform with latitude, while the solar effect is stronger at the Equator than at the poles on an annual average basis, so that there is likely to be a net cooling in high latitudes. They also found that changes in the shape of the O_3 profile may be more important than a uniform change in amount. In one case, a 60% reduction in O_3 to 40 km, with smaller variation above and below, (the columnar amount remaining constant) apparently leads to a net global increase in downward flux, with warming equatorward of 50° .

Changes in stratospheric temperature due to purely dynamical effects can also affect the energy input into the lower atmosphere. As mentioned previously, the $9.6\mu\text{m}$ O_3 band is especially important in this connection. A particularly interesting example, discussed earlier, in connection with stratospheric sudden warmings has been analyzed by Ramanathan (1977). He finds that the annual arctic surface energy budget has a non-trivial component (7-15%) due to the downward O_3 IR flux from the stratosphere, and that during a sudden warming this flux can increase by several W/m^2 leading to a rise in surface temperatures of a few degrees. This acts to decrease the available potential energy in the troposphere.

Radiative Properties of Aerosols

The lower stratosphere contains a complex mixture of particles (The *Junge Layer*), whose origin is not completely understood. During periods when there has been no large-scale volcanic activity for several years, the dominant constituents are sulfate compounds. The optical depth (at $0.5\mu\text{m}$) during such periods is probably $< .01$ (Toon and Pollack, 1976, Young and Elford, 1979). Immediately after large eruptions such as that of Agung in 1963, the stratospheric optical depth increased very substantially, values of 0.2 to 0.3 having been measured (Irvine and Peterson, 1970). In principle, such events present an excellent test of our understanding of radiative influences of the stratosphere on the troposphere, and of local thermal changes in the stratosphere. Unfortunately, the actual situation is complicated by the same type of cancellation between short and longwave effects discussed previously, and is beclouded further by our uncertainty about the scattering and absorption properties of the aerosols. *In situ* sampling (reviewed in Hansen et al., 1978), suggests that the initial pulse of ejectum from Agung contained a "large amount" of silicate dust, which settled out within a month, leaving a residue of sulfate particles. Since silicates both absorb and scatter in the visible and ultraviolet, while sulfates have low absorption, their radiative effects are quite different. This difference is less important in effect in the downward flux into the troposphere than in the *in situ* heating due to solar absorption.

Extensive calculations of the change in planetary albedo have been carried out by Herman et al. (1976), both for 75% H_2SO_4 particles, and more general aerosols with various values of single scattering albedo. In general, these cannot be used to calculate changes in the downward flux at the tropopause. As might be expected, the sulfate-type aerosol layer of an optical depth of about 0.03 increased the albedo at all latitudes and seasons, but most noticeably in the high latitude winter. These authors also emphasize that in general the change in planetary albedo due to aerosols depends on the albedo of the surface beneath, as well as the single scattering albedo.

The emission of downward IR by aerosols depends in an important way on their imaginary index of refraction in the IR, and on the size distribution of particles. The former is generally such that the single-scattering albedo is low, but the latter is highly variable and uncertain. The efficiency of the IR effect is extremely sensitive to the number of large ($>0.5\mu\text{m}$) particles; Pollack et al. (1976a) have shown, for example, that if the mode particle radius of a hypothetical basaltic silicate aerosol is taken as $0.25\mu\text{m}$, the aerosol acts to cool the surface. When the mode size is $0.5\mu\text{m}$, however, the greenhouse effect is sufficiently large to convert this to a heating.

In their discussion of the climatic effects of the Agung eruption Hansen et al. (1978) assumed that the long-lived H_2SO_4 component of the aerosols had an effective radius of $0.2\text{--}0.3\mu\text{m}$, so that the increase in downward flux of IR is only 25% of the decrease in the solar beam. Using a simplified radiative convective model with a $70\mu\text{m}$ ocean mixed layer, they find a decrease in tropical tropospheric temperature of $\sim 0.5^\circ$ one year after the eruption, a result which agrees with the observations of Newell and Weare (1976). There is an indirect reference in the literature to the work of Mason (1976), claiming that neither theory nor observation shows any tropospheric effect. Whether the manner in which the IR is treated accounts for the negative result is not known; certainly, however, the great sensitivity to the aerosol size distribution suggests that further observational work is necessary.

Radiative Properties of Carbon Dioxide

Although large temperature changes ($\sim -10^\circ$ at 50 km) are expected if the CO_2 burden of the atmosphere is doubled, the stratospheric effect is not likely to be important for the troposphere, for the fact that the stratosphere is essentially in radiative equilibrium largely determines the downward IR flux at its base. If, however, we wish to use observed temperatures and mixing ratios to calculate cooling rates to diagnose dynamical heating in the stratosphere, such uncertainties will be quite serious. The magnitude of the cooling rate error due to the uncertainties in spectral data is on the order of several tenths of a degree/day (Fels and Schwarzkopf, 1980), which is thought to be the size of dynamical heating in the lower and middle stratosphere.

The concentration of CO_2 is extremely uniform in space and time below 70 km, so that most of the uncertainty in the IR cooling rates arises from basic spectroscopic data. The data on which most calculations of CO_2 fluxes and cooling rates have been based are those of Drayson (1973), and the AFCRL compilation (McClatchy et al., 1973). Detailed comparisons carried out by Fels and Schwarzkopf (1980) show that spectrally integrated absorptions based on these two sources agree to within 2% at worst. This may be misleading, however, for the two data sets are not independent. Planet et al. (1978) have made tunable laser diode measurements of individual lines in the fundamental band, and find intensities as much as 7% less than those of Drayson. Of equal importance are the pressure broadened linewidths, which Planet et al. (1978) find to be $\sim 15\%$ greater than the values used by Drayson. Taking these numbers to be representative of all lines, it appears that for strong absorption which depends on the product of the strength and width, the discrepancy may be 4%, while in the weak region, as much as 7%.

Radiative Properties of Water Vapor

Although present in very small quantities ($10^{-5}\text{--}10^{-6}$ kg/kg), the strong IR features of water contribute on the order of $5\text{--}10\text{ W/m}^2$ to the downward IR flux at the tropopause, and less than $0.5^\circ/\text{day}$ to stratospheric cooling rates. These latter are comparable to those due to CO_2 in the lower stratosphere, but substantially smaller above 25 km. Possible changes in the tropical tropopause temperature could subsequently change the water vapor amount in the stratosphere and suggest that resulting IR flux changes could be on the order of several W/m^2 . Of equal significance is the fact that the amount of stratospheric water could be important in determining the size of the change in the downward IR flux when the temperature of the stratosphere changes due to other causes. The chief uncertainties in the radiative role of stratospheric water are due to poor knowledge of the water vapor mixing ratios.

Radiative Effects on Wave-Mean Flow Interactions

In this subsection on radiative exchanges, the discussion has emphasized the role played by radiation in energy transport. Radiative processes are also responsible for the excitation and damping of waves and other time-dependent disturbances. The past decade has seen a growing understanding of the important part played by wave-mean flow interactions in the stratospheric general circulation, and in tracer transport. Such phenomena as the quasi-biennial oscillation, and stratospheric warmings, and perhaps mean flow forcing by tides are obvious examples. These interactions, however, depend crucially on the relaxing of the so-called "non-acceleration" theorems (McIntyre, 1979). In simple terms these theorems say that waves will not permanently affect the mean state unless there are either transient or dissipative processes present. These include "critical level" interactions, wave breaking, viscous effects, and radiative damping or forcing. Of these, the easiest to handle theoretically are the radiative effects. The possibility that changes in radiative properties due to altered O_3 , CO_2 or aerosol levels might therefore affect the wave-mean flow interactions cannot be neglected and is currently under investigation.

Final Remarks

Considerable progress has been made in the last decade in understanding radiative processes in the stratosphere. It is likely that future research will concentrate on clarification of the local rather than global effects of changes in stratospheric composition, and on better measurement of the climatological and laboratory data.

ELECTRICAL COUPLING

Recent ideas regarding coupling between the upper and lower atmosphere involve perturbations of the global electrical circuit (e.g., Markson, 1978 and Roble and Hays, 1979). Such perturbations include modulations of the atmospheric electrical conductivity and electric fields. The stratosphere may participate in the electrical enhancement of thunderstorm activity, cloud growth, precipitation effects, etc. within the troposphere.

At this time, the proposed concepts are largely speculative, and more research is needed in this area. Electrical properties of the stratosphere, including fluctuations induced by the troposphere, are largely unknown; they are described by a limited number of rocket and balloon samplings of electrical conductivity and electric fields within this region. For a detailed account of this field, the reader is referred to *Middle Atmospheric Electrodynamics* (NASA, CP-2090) which is the proceedings of the recent workshop on the Role of the Electrodynamics of the Middle Atmosphere on Solar Terrestrial Coupling.

SUMMARY AND FUTURE NEEDS

This chapter has discussed the types of measurements that form the data base for studies of the meteorology of the stratosphere, together with discussion of some of the analytical techniques now used to analyze the spatial and temporal fields of stratospheric parameters from the input data. It was pointed out that different analysis strategies are used for synoptic (simultaneous) measurements, such as those with the worldwide radiosonde network, than for asynoptic (nonsimultaneous) satellite measurements. It is important to note that regardless of the analysis technique used, the original spacing of the observations will determine the scales of motion that are possible to study. In particular, since the transport of a physical quantity such as heat, momentum, or ozone mathematically takes the form of a covariance of a transport velocity and that quantity, it is crucial to have horizontal, vertical, and temporal resolutions that are sufficient to define the scales of variation that contain most of the variance about the mean. Also, of course, the variance in each measured variable that results from measurement inaccuracies should be small compared to that resulting from geophysical variability. With availability of larger amounts and more accurate data, more sophisticated data handling and analysis schemes will be required.

Our understanding of the stratospheric general circulation is improving, but further advances await analysis of existing data and acquisition and analysis of more extensive stratospheric data sets with better spatial and temporal resolution. Until recently, the existing picture of the stratospheric wind and temperature fields above the level where radiosonde measurements can be made (about 10 mb in pressure or 30 km in altitude) was based on sparse rocket measurements taken over many years. Satellite measurements are seen to be essential for continuous geographical and temporal coverage in the stratosphere, but they need to be complemented by measurements using other platforms such as aircraft, balloons, and rockets for investigations of small scale processes and for calibration of instruments on satellites.

Observationally, it is well known that in the middle latitude stratosphere there is a strong annual oscillation in the mean zonal winds, with strong westerlies existing in the winter, and strong easterlies existing in the summer. This annual march in the mean zonal flow is driven mainly by the differential heating of the ozonosphere. The observations also show that during the winter season, the stratospheric flow displays marked planetary scale waviness that is due to the upward extension of the tropospheric planetary waves driven as a consequence of the continent-ocean distribution while in the summer the flow is nearly circular. There have been recent advances in understanding how these planetary waves interact with the mean zonal flow in the stratosphere. However, to correctly model these interactions, it appears necessary to treat irreversible effects such as radiative processes and mechanical dissipative processes together with a proper description of transient processes.

One notable success in the interplay between theory and observation has been the explanation of the quasi-biennial oscillation in the equatorial lower stratospheric wind in terms of equatorial wave interactions with the mean zonal flow. However, this success was partially due to the existing observational capabilities being well-matched to the oscillation itself, as well as to the characteristics of the equatorial waves in terms of altitude, vertical resolution, and period. The fact that an explanation of the semi-annual oscillation has not yet been obtained is probably due, in large part, to the fact that the dynamical processes are not so well matched to existing observational capabilities. In the case of both the quasi-biennial oscillation and the semi-annual oscillations, it remains to be understood how the tropical oscillation is coupled to extratropical latitudes.

Our understanding of the interplay between the dynamical and chemical processes that determine the distribution of ozone has been hampered by the fact that existing observations are inadequate to provide a detailed budget of ozone. However, there does exist a general agreement between model results and ozone observations. Some improvement in this situation should be forthcoming with the analysis of data obtained from previous and existing satellites and from *in situ* measurements from aircraft, for example, but new observations will be required.

Part of the difficulty in studying the stratosphere observationally is that it is such an active region dynamically. For example, during every other winter, on the average, there occurs a major warming in which the temperature at high latitudes increases by tens of degrees Centigrade in only a few days, the sense of the zonal flow reverses (in the Northern Hemisphere), and ozone distributions are greatly altered. Also, each warming has a somewhat different character. Thus, one year's observations are not necessarily representative of any other year.

The cause of stratospheric warmings appears to be understood to the extent that they are known to be connected with enhancements in tropospheric energy flux transported upward by the planetary waves. However, this appears to be a necessary, but not a sufficient, condition for a warming to take place. Also, the cause of these planetary wave enhancements is not understood. It is not believed that short period motions such as tides or gravity waves play a major role in affecting the stratospheric mean flow directly through wave-mean flow interactions, as do planetary waves. However, there is evidence that gravity wave produced turbulence may play a major role in dissipating momentum. There is a newly developing radar technology which is being

applied to the remote sensing of winds and turbulence in the stratosphere. This should prove to be most valuable for investigations of stratospheric short period motions in the coming years. This technique will be least applicable to stratopause levels, however, due to minimum radar reflection at that level.

While synoptic scale instabilities (analogous to the highs and lows on a weather map) do not appear to be as important in influencing the global circulation as planetary scale motions in the stratosphere, there is some observational evidence for their existence. Further research is needed to determine if they give rise to locally important heat and momentum fluxes.

Much of the current concern about the stratosphere involves the effects of tropospheric sources of chemicals that are active photochemically in the stratosphere. To treat these problems rigorously, it is necessary to understand the manner in which tropospheric air enters the stratosphere. Several scales of motions appear to be responsible for this interchange of air, ranging from planetary scale circulations to turbulent exchange. Unfortunately, the relative importance of these scales is not known, and more observations are needed to establish this. Aircraft and radiosonde observations are particularly well suited to this problem due to their ability to provide resolution of structure in the vicinity of the tropopause.

Recent theoretical work has indicated the possible importance of dynamical and radiative coupling between the troposphere and stratosphere, in the sense that stratospheric changes may affect the troposphere. These are new results that need to be checked observationally. Even more speculative is the stratosphere's role in electrically coupling downward into the troposphere. There is evidence of solar related stratospheric variations. These have been studied statistically; however, the conclusions remain controversial. Mechanisms have been suggested, but there is need for more work both observationally and theoretically.

When the state of knowledge of meteorological processes in the stratosphere is examined, the first need identified is for an increased diagnosis effort on stratospheric processes, using data from different sources such as satellites, rockets, radar, lidar, balloons, and aircraft. The absence of such efforts leads to the use of model results that are not sufficiently validated against observations. Observational programs that are well matched to the problem being investigated in spatial resolution, temporal resolution, and duration need to be planned and executed. The data outputs from these programs need to be extensively analyzed and checked against proposed theoretical and numerical models.

CHAPTER 6

LONG PERIOD CHANGES IN STRATOSPHERIC PARAMETERS

INTRODUCTION

In the assessment of anthropogenic influences on stratospheric ozone, ideally one would like to have complete global ozone data sets extending over a time period such that any periodic and aperiodic variations in the natural atmosphere could be determined. Because the atmosphere is a complex, nonlinear system, it would also be necessary to have simultaneous measurements of a set of other parameters known to influence the ozone concentration (e.g., air temperature, N_2O , solar spectral irradiance, etc.). Finally, it would be convenient to have additional data sets of parameters which exist independently from ozone (e.g., potential vorticity), and subject to common atmospheric factors (e.g., transport), to verify that conclusions drawn from the ozone record are correct.

In reality, the ozone data sets are very short; one has to search for measurements that extend more than twenty years. The longest data sets of most trace constituents represent only local conditions and are thus subject to higher variability than found in global data sets. Furthermore, in some cases, it has been necessary to use surface or tropospheric measurements, rather than stratospheric data, to obtain information about trends. For those constituents that are long-lived, the results are assumed to apply to the lower stratosphere.

Observations made over the past 50 years of the total amount of ozone in a vertical column have established the average column abundance and the general pattern of latitudinal, longitudinal, seasonal, and meteorological variations. The average total amount of ozone is about 0.3 atm-cm at STP. The latitude variation and the seasonal variations at sub-polar latitudes are about $\pm 20\%$ of this average value. During a typical winter or spring month, day-to-day variations at mid-to-high latitudes could amount to $\pm 50\%$ and year-to-year variations of the annual average at individual stations could be as high as $\pm 10\%$.

Routine measurements of the vertical ozone distribution over the past 20 years have also indicated an ozone distribution pattern that varies with latitude, season, and meteorological conditions. Large latitudinal and seasonal variations, as high as $\pm 25\%$, are found at and below the level of maximum ozone. Also, day-to-day changes, sometimes larger than a factor of 2, are noted in the ozone concentrations below the level of ozone maximum. Variations above this level are relatively smaller. In addition, approximately 10% of the changes in the annual mean vertical distributions occur over periods of years, both locally and globally.

In this chapter an attempt is made to determine whether analysis of records can be used to find out what long period changes (if any) exist and to what extent (if any) they can be ascribed to human activity. The first problem is purely statistical; that is, to determine the "best" trend from a set of ozone observations. The second problem involves the interpretations of these trends.

A great deal of progress has been made in the recent past with the statistical problem; relatively small changes in the basic statistical characteristics of observed records can be detected. However, the interpretation of the statistical results is more difficult. Trends can occur for reasons independent of man's activity. First, there may be changes over long periods of natural origin. Since the records at most stations cover a period of only about 20 years, they are too short to permit understanding of the statistical properties of these variations. Second, there may exist trends in the observations because of changes in the instrument characteristics. Third, there can be apparent changes if the measurements are not representative of global conditions because the stations are geographically biased.

Trends due to the first two of these causes are generally unpredictable. With global sampling from satellites, the third problem in trend determination can be greatly reduced. Observed trends must exceed significantly

any reasonable trends produced by a combination of these effects before any part of the trend can be confidently ascribed to man-made changes in global ozone.

In this chapter, our knowledge of all these matters is summarized. The emphasis is on conventional total ozone records, which exist for a relatively long period, but for which the models predict only modest changes. Commentary is made on the vertical distributions of ozone in the upper stratosphere, where predicted changes are large, but where the records are relatively short. Also included are analyses of the evidence for long-term changes in atmospheric temperatures and in trace constituents important to the stratosphere.

AVAILABLE OBSERVATIONS FOR TREND ANALYSES

The techniques that are in common use for measurement of atmospheric ozone were reviewed in NASA RP-1010. In this report, primarily new developments since 1977 and the current data sources for trend analysis are discussed. Recent summaries of the satellite ozone measurement methods have been prepared by Krueger et al. (1979a) and Gille (1979) and an analysis of ozone variations from various data sets has been prepared by London and Angell (1979).

TOTAL OZONE

Ground Based Observations

At the present time, two ground-based instruments are used for measuring total ozone in the global network: the Dobson Spectrophotometer and the Soviet M-83 filter ozone photometer. The Dobson instrument is the World Meteorological Organization (WMO) designated standard instrument which is in use at about 75 stations, mostly in the Northern Hemisphere. The M-83 is used at about 35 stations, principally in the Soviet Union and Eastern Europe.

Observations with the Dobson instrument started in 1925, and with the M-83 in 1957. During the 1930s and 1940s, there were 3 to 5 Dobson stations at which total ozone observations were taken more or less routinely. These were in the Northern Hemisphere, and not all were in operation during the same period. The number of observing stations increased during the 1950s to 40 at the start of the International Geophysical Year 1957. Observations are normally made daily during daytime.

Satellite Observations

A chronology of satellite flights in which extensive ozone measurements have been made is given in table 6-1. Backscatter ultraviolet methods for total ozone measurements (Dave and Mateer, 1967) were first tested with the Nimbus-4 satellite backscatter ultraviolet (BUV) instrument, a nadir-viewing ultraviolet monochromator. The method uses measurements of the relative absorption of sunlight which has passed through the stratospheric ozone layer and is reflected from the lower atmosphere or the surface back to space. Because approximately seven years of global observations were acquired with the Nimbus-4 instrument, this data set is important for total ozone monitoring.

An improved version of the Nimbus-4 BUV, called the Solar-Backscatter Ultraviolet (SBUV) instrument, was launched on the Nimbus-7 satellite in October 1978. A second BUV-type instrument, the Total Ozone Mapping Spectrometer (TOMS), was also flown on Nimbus-7 to evaluate the backscatter ultraviolet technique for off-nadir soundings. This instrument is a monochromator, sensing the BUV total ozone wavelengths, but equipped with a cross-track optical scanner to measure the complete global ozone field (excluding polar night) with an average spatial resolution of 75 km. One of the objectives in development of the TOMS instrument

Table 6-1
Satellite Sensors for Ozone Data

Satellite and Instrument	Ozone Measurement	Data Record	Comments
OGO-4 BUV	Profile	Sep 67 - Jan 69	Solar spectral irradiance inferred from rocket ozonesonde for OGO-4 calibration. Ozone analysis not completed.
Nimbus-3 IRIS	Total	Apr - July 69	Short data set, analysis complete, poor quality data.
Nimbus-4 BUV	Profile & Total	Apr 70 - July 77	Solar spectral irradiance assumed invariant beyond 1970. Total O ₃ analysis completed. Profile analysis completed 1979. Validation with rockets and Dobson network.
Nimbus-4 IRIS	Total	Apr 70 - Jan 71	10 month's data, analysis complete.
Nimbus-6 LRIR	Profile	June 75 - Jan 76	Validation with rocket ozone profiles, day and night. Analysis not complete.
AE-5 BUV	Profile & Total	Nov 75 - May 77	Limited validation, preliminary analysis only, tropical latitudes.
Block 5 MFR series of 4 flights	Total (spatial scanning)	Mar 77 - July 77 July 77 - ---- July 78 - ---- June 79 - ----	O ₃ from regression against climatology. Validation with Dobson network. Ozone analysis not complete.
Nimbus-7 SBUV	Total & Profile (Nadir)	Nov 78 - ----	Validation by rockets, balloons and Dobson network. Analysis started.
Nimbus-7 TOMS	Total (spatial scanning)	Nov 78 - ----	Validation by Dobson network. Analysis started.
Nimbus-7 LIMS	Profile	Oct 78 - May 79	Validation by rockets and balloons. Analysis started.
TIROS-N HIRS	Total (spatial scanning)	Nov 78 - ----	Regression against Dobson stations. Analysis started.
Applications Explorer Mis- sion - SAGE	Profile	Jan 79 - ----	Solar occultation method, validation with rockets, limited daily coverage of the globe. Analysis started.

was to evaluate the sampling errors in global mean total ozone estimates from a nadir-viewing instrument. Both the SBUV and TOMS sensors have been collecting data since November 2, 1978.

The second method for remote sensing of total ozone uses atmospheric emissions from the $9.6\mu\text{m}$ band of ozone. The nadir-viewing Infrared Interferometer Spectrometer (IRIS) experiments on the Nimbus-3 and Nimbus-4 satellites produced data for the months of April through July 1969 and from April 1970 to early January 1971.

Since the time of the IRIS flights, several temperature sounding instruments have included a channel to sense the $9.6\mu\text{m}$ ozone band. Beginning in March 1977, the Multichannel Filter Radiometer (MFR) instrument on four of the Defense Meteorological Satellite Program series of satellites included such a channel. The most recent $9.6\mu\text{m}$ ozone sensor is part of the High Resolution Infrared Radiometer (HIRS) sensor on the Tiros-N Satellite, launched in November 1978.

VERTICAL DISTRIBUTION OF OZONE

Balloon-Borne Ozonesondes

The present network of *in situ* balloon observations of the vertical ozone distribution is based on two types of electrochemical instruments. The height ceiling for these ozonesondes is about 30 km as a result of the techniques used and the limitation of the carrier balloon. There are currently about 20 observing stations in the global network, with all but one in the Northern Hemisphere. Most stations use the Brewer-Mast type of instrument. Data for about half of these stations are available for slightly more than 10 years. Most stations take an average of only 2 to 4 observations per month. This limits the representativeness of the mean monthly ozone values for those stations.

Umkehr Observations

Zenith sky observations taken with a Dobson Spectrophotometer at several solar zenith angles during a morning or afternoon can be used to derive an ozone profile up to about 50 km. This technique (Craig, 1965) depends on Rayleigh scattering and ozone absorption in the stratosphere. As the solar zenith angle increases from 60 to 90 degrees, the center of the contribution function shifts from near the surface to about 45 km. The change in zenith sky radiance is then interpreted in terms of the gross features of an ozone profile.

At the present time, there are about 15 stations taking *routine* Umkehr observations, about half of which have records for slightly over 20 years. However, the observational frequency is highly irregular, and for most stations, considerable portions of the data record are completely missing. Only the Arosa and Tateno stations have published mean monthly values for at least 90% of their 20-year record, but long series of observations have also been made (but not yet processed) at several Australian stations.

Rocketsondes

Meteorological sounding rockets are the least expensive vehicles for direct measurements of the ozone distribution above balloon ozonesonde altitudes (approximately 30 km). Direct techniques can be based on absolute methods, generally measure with 1 to 2 km vertical resolution, and are normally accompanied by direct measurements of air temperature and winds.

Two techniques are available for rocket measurements of ozone from about 20 km to 60 km altitude. These are based on: (1) optical absorption of sunlight or moonlight in the Hartley and Huggins bands of ozone, and (2) chemiluminescence of dyes. To date, a total of 370 soundings, mostly optical type, have been reported.

The first rocket measurement was made in 1946 (Johnson et al., 1951) but routine measurements have been made only from 1976 to 1978. Data from all known launches are currently being assembled as part of the WMO-sponsored International Rocket Ozoneprobe Intercomparison, scheduled for October 1979.

Satellite Observations

The ultraviolet spectrum of the sunlit atmosphere contains information about the stratospheric ozone profile. The first satellite experiments to investigate this technique were flown in 1965, but the first global data set of significant duration for trend analysis was obtained from the backscatter ultraviolet experiment on the OGO-4 satellite in 1967. Table 6-1, presented earlier, lists the satellite ozone profile experiments. The most extensive data set (7 years) was obtained from the Nimbus-4 BUV which was launched in 1970. A similar instrument was launched on the AE-5 satellite in November 1975 to obtain tropical data. The Nimbus BUV ozone profile data set is now being extended with the SBUV on Nimbus-7.

A second major technique for measuring the ozone profile uses observations of the radiance of the Earth's limb in the $9.6\mu\text{m}$ band of ozone. The Limb Radiance Inversion Radiometer (LRIR) sensor on Nimbus-6 obtained global data from June 1975 to January 1976 using this method. Subsequent limb observations of the vertical distribution of ozone have been obtained on Nimbus-7 with the Limb Infrared Monitor of the Stratosphere (LIMS) sensor, an improved version of the LRIR experiment.

A third technique for profile soundings uses solar occultations as the satellite passes in or out of the Earth's shadow. Although the observations are not global, data will be available from the Stratospheric Aerosol and Gas Experiment (SAGE), launched in early 1979 aboard an Applications Explorer Mission (AEM) satellite.

MEASUREMENT ERRORS FOR TREND DETERMINATION

The reliability of a measurement may be expressed in terms of random errors (related to measurement precision) and systematic or bias errors (related to measurement accuracy). It is important to consider both of these errors in long-term (more than several years) *trend determinations* since the minimum length of record needed for determination of a significant trend depends upon the precision of individual measurements and their frequency, while variations with time of systematic measurement errors may be falsely interpreted as real changes in the parameter considered. The treatment of systematic errors is, furthermore, fundamentally linked to time scales. Systematic errors that vary during time periods considerably shorter than the period of record under consideration are generally treated as random errors. Thus, what appears to be a *trend* in a short observational record may be, instead, a short term *fluctuation* in a long record.

Procedures for combining measurement random errors are well defined by statistical theory (e.g., Ku, 1966). However, there is no generally accepted standard method for combining several systematic errors (Eisenhart, 1963). For a function of two variables $W = F(X, Y)$, where the systematic errors associated with X and Y are Δx and Δy , respectively, the bound $|\Delta w|$ for the systematic error in W is given by:

$$|\Delta w| = \left| \left(\frac{\partial F}{\partial X} \right) \Delta x + \left(\frac{\partial F}{\partial Y} \right) \Delta y \right| \quad (1)$$

assuming that Δx and Δy are small so that second and higher order terms in Δx and Δy are collectively negligible in the Taylor series expansion. Since the signs of Δx and Δy are not ordinarily known, an accepted procedure is to add the absolute values of the two terms together. (If the sign of either Δx or Δy is known, this information, of course, should not be ignored.) However, when the systematic errors are believed to be uncorrelated, an alternate approach is to take $|\Delta w|$ as the square root of the sum of the squares of

terms on the right hand side of (1) instead of adding together the absolute values of all terms. This procedure presupposes that some of the systematic errors may be positive and others negative, and that the two classes cancel to a certain extent.

TOTAL OZONE MEASUREMENT ERRORS

Dobson Spectrophotometer Total Ozone Measurement Errors

Estimates of Dobson spectrophotometer total ozone random and systematic measurement errors are summarized in table 6-2 where a distinction is made between systematic errors that do not affect ozone trend determinations and those that do.

Table 6-2
Dobson Ozone Spectrophotometer Measurement
Error Estimates

Type of Error	Estimated Value*
<u>Systematic Errors</u>	
1. Trend determinations not affected:	
(a) Absorption coefficient uncertainties	(0, +7)%
2. Trend determinations affected (change per decade):	
(a) O ₃ absorption coefficient affected by stratospheric temperature changes	± 0.5%
(b) Uncorrected instrument calibration drift	± 3%
(c) Solar spectrum changes	± 0.3%
(d) Aerosol changes	± 1%
(e) Tropospheric pollution changes with time	
— ozone	± 1%
— other absorbers (e.g., SO ₂)	± 2%
(f) Change in cloudiness	± 1%
<u>Random Standard Errors</u>	
3. AD direct sun observations	
— optimal	± 1.5%
— average	± 3%
4. Zenith sky observations	
— optimal	± 2.5%
— average	± 5%

* Using the usual convention $\pm 0.5\%$ means that the % error from this source lies between the limits -0.5 and +0.5, that is, in the interval (-0.5, +0.5)%.

A brief elaboration of the errors, in the order listed in the table, is given below:

- (1) Mounting experimental evidence from spectroscopic observations (DeLuisi, 1975; Basher, 1978), satellite observations (A. J. Miller, private communication, 1979), rocket ozonesonde measurements (Krueger, 1969) and balloon ozone soundings (Komhyr, 1979) suggests that Dobson spectrophotometer total ozone data may be systematically biased by up to +7% due to uncertainties in AD wavelength absorption coefficients used in data reduction, or by the presence of some anomalous absorber in the atmosphere. Although the existence of an anomalous atmospheric absorber might pose problems for ozone trend analyses if its abundance changes with time, the magnitude of the postulated error appears to be too large to be caused by unknown trace gas species. A systematic error in AD wavelength ozone absorption coefficients will not affect trend analysis results. Nevertheless, the problem of whether or not this error is real merits attention, particularly since Dobson total ozone observations provide *ground reference data* for satellite ozone measurements. A significant difference would imply either a calibration error in one of the systems or an incomplete model for the satellite retrievals.
- (2a) Fixed ozone absorption coefficients are used in reducing Dobson instrument observations. The absorption coefficients are temperature sensitive, and since stratospheric temperatures in the region of the ozone maximum may vary up to $\pm 5^\circ\text{C}$ during the course of several years (discussed under Long-Term Variations of Other Parameters), resulting maximum systematic errors in measured total ozone are estimated to be $\pm 0.5\%$ (Powell, 1971).
- (2b) The net effect of Dobson instrument calibration drifts (upward and downward), resulting from deterioration of optical and electronic components, mechanical shock, and contamination problems is estimated to be equivalent to a 0.3% per year drift in data from any 10 stations in the Dobson network.
- (2c) The occurrence of 15% changes in solar extra-terrestrial irradiance at 300.0 nm during the course of a sunspot cycle has been proposed (Heath and Thekaekara, 1977). If the irradiance change is assumed to be exponentially decreasing in the wavelength region 300.0 to 400.0 nm, calculations show that systematic ozone errors, assuming a constant extra-terrestrial solar irradiance when processing Dobson instrument data, do not exceed $\pm 0.3\%$ for observations on AD double pair wavelengths. The effects of changes in Fraunhofer structural features in the extra-terrestrial solar spectrum at the Dobson wavelengths during the course of a sunspot cycle or other longer period solar constant changes, if any, cannot be quantified at the present time, but presumably are small.
- (2d) Current estimates (see e.g., Shah, 1976; Thomas and Holland, 1977) of the effect of scattering and absorption by tropospheric and stratospheric aerosols on double-pair-wavelength type Dobson spectrophotometer measurements give total ozone errors of approximately 1% for highly polluted conditions. Considering the possibility of an increasing or decreasing aerosol pollution trend occurring at a station, this error translates into a systematic error of $\pm 1\%$, a result that is probably subject to upward revision by a factor of 2, pending additional research.
- (2e) Ozone is produced photochemically in polluted air near ground level. During times of extreme pollution and high solar insolation, a 10% ozone addition to the total ozone column may result. For a station located where local pollution is gradually increasing or decreasing during the course of several or more years, taking into account that highly polluted conditions do not occur on all days, the resulting contribution to total ozone systematic measurement error is estimated to $\pm 1\%$. A similar effect (Komhyr, 1979) involving other UV absorbers in polluted air (principally SO_2) translates into estimated systematic measurement errors of $\pm 2\%$.

- (2f) The estimated cloud-effect systematic ozone measurement errors of $\pm 1\%$ shown in table 6-2 stem from temporal cloud condition changes that may occur at a Dobson station. Biases arise from a relative increase or decrease in the frequency of observations made on clouds, or from changes in station observational procedures (e.g., observations on clouds may be avoided).
- (3) Measurement random standard errors associated with Dobson instrument total ozone amounts are also summarized in table 6-2. For an optimally maintained and operated instrument during a measurement program of several or more years duration, the random standard error of an individual AD-wavelength direct sun observation is estimated to be $\pm 1.5\%$. This estimate is based on consideration of random standard errors associated with periodic instrument calibrations, relatively short period fluctuations in the instrument calibration level, observer errors, aerosol effects stemming from varying haze conditions, and ozone absorption coefficient variations resulting from annual stratospheric temperature fluctuations. For an average observatory in the global total ozone station network, it is reasonable to assume a direct sun ozone measurement precision of $\pm 3\%$.
- (4) When direct sun total ozone data are compared with results of zenith sky observations, an agreement in results is obtained to within $\pm 2\%$ for about 70% of the pair measurements (Komhyr, 1961). Combining this result with the direct sun observational error data given above yields a measurement standard error of $+2.5\%$ for zenith sky observations at an optimally operated Dobson instrument observatory. For an average station in the global total ozone station network, it is likely that the measurement precision for zenith sky observations is $\pm 5\%$.

M-83 Ozone Total Ozone Measurement Errors

Total ozone observations with the M-83 filter ozonometer, developed by Gushchin in 1958 (Gushchin, 1974, 1977), are based on the measurement of solar irradiance ratios in three different broad spectral intervals in the Huggins ozone absorption band. In the past, performance evaluations of the instrument have been provided by Bojkov (1969) and Vanier and Wardle (1969). In comparisons with Nimbus-4 BUV total ozone values in 1970-1971, the rms difference with M-83 data was 18% vs. an rms difference with Dobson measurements of 5.3%. There has been improvement in the optics used in the M-83 instrument since 1971, mostly through the use of new light filters. As a result, errors associated with use of these instruments have been reduced.

A performance evaluation of an M-83 ozonometer during 1977-78 in Boulder, Colorado (Szwarc, 1978), indicated that within the air mass range 1.3 to 3.5, direct sun Dobson spectrophotometer and M-83 ozonometer ozone readings agreed to $\pm 3\%$, with the M-83 instrument data exhibiting an air mass dependence such that at an air mass approaching 1.0 measured ozone amounts were too low by about 5%. Observations on the clear zenith sky with the M-83 instrument gave similar results. However, ozone observations made on low, thick clouds using standard measurement and data processing techniques yielded total ozone amounts 20% to 30% too high. It is likely that these measurement errors can be substantially reduced by employing corrections empirically derived from quasi-simultaneous observations on direct sun and the cloudy zenith.

Satellite BUV Experiment Total Ozone Measurement Errors

The total ozone measurements from the Backscatter Ultraviolet (BUV) experiment are susceptible to some of the same errors that affect the ground based instruments like the Dobson spectrophotometer. However, there are other sources of errors that are unique to a satellite-based instrument which retrieves total ozone on a global basis under a very wide range of atmospheric conditions. (Dave, 1978; Fraser and Ahmad, 1978 and 1979; Bhartia et al., 1979; Klenk, 1979; Fleig et al., 1979). Table 6-3 lists the BUV and TOMS total ozone measurement errors, as they affect estimates of global ozone amounts.

Table 6-3
BUV and TOMS Total Ozone Measurement Error Estimates

Type of Error	Estimated Value
<u>Systematic Errors</u>	
(1) Trend determination not affected	
(a) Absorption coefficient uncertainties	laboratory measurement errors
(2) Trend determination affected (change per decade):	
(a) O ₃ abs. coeff. affected by strat. temp. changes	$\pm 0.5\%$
(b) Relative calibration errors between instruments	$< \pm 3\%$
(c) Solar spectrum changes	$\pm 0.3\%$ (Nimbus-4)
(d) Uncorrected calibration drifts	$\pm 1\%$ (Nimbus-4)
(e) Changes in stratospheric aerosol content	$<< 1\%$
<u>Random Errors</u>	
(3) (a) Noise and telemetry errors	$\pm 1\%$
(b) Cloud errors	$\pm 1\%$
(c) Profile errors	important only near terminator ($\pm 5\%$ for $> 80^\circ$ zenith angle)
(d) Surface reflectance errors	$< 1\%$
(e) Aerosols (tropospheric)	$\pm 0.5\%$

The following is a brief discussion of the errors in the order listed in the table.

- (1a) Ozone absorption coefficient uncertainties - Like any other ultraviolet instrument operating in the Hartley/Huggins band, the absolute accuracy of the total ozone measurement from the BUV is limited by the uncertainties in the measured ozone absorption coefficients. At present, an accurate ($\sim 1\%$), low temperature (-30 to -70°C), high resolution (~ 0.1 nm) absorption spectrum of ozone in the 300 - 400 nm range is not available. The effective absorption coefficients computed from the various reported measurements differ by as much as 25% for the primary BUV total ozone wavelength band centered

around 315.0 nm (Klenk, 1979a). Though an accurate measurement of the absolute amount of ozone is necessary for intercomparison of various instruments, use of a common set of absorption cross sections will not affect trend analysis results.

- (2a) Fixed ozone absorption coefficients are assumed for BUUV data reduction.
- (2b) Pre-launch instrument calibration error - A 1% error in the relative radiometric calibration between the paired wavelengths causes approximately 1% error in the retrieved ozone (note that errors in the absolute calibration are not important). For a data set obtained from one satellite sensor (such as the Nimbus-4 BUUV) this error causes a systematic bias in the retrieved ozone, but does not impact the trend determination. However, in a program of long-term ozone monitoring using a series of such instruments, this error will cause an interexperiment bias which may affect the trend analysis. For the Nimbus-4 BUUV, the uncertainty caused by this error is estimated to be approximately 3%. In an operational program with improved pre-launch calibrations, this uncertainty can be significantly reduced.
- (2c) Solar spectrum changes - If in-flight solar calibrations are not available (such as with Nimbus-4), trend errors are comparable to Dobson network errors.
- (2d) Uncorrected instrument calibration drift - One of the most important sources of errors which affect the long-term trend determination is in the instrument calibration. In the case of the Nimbus-4 satellite BUUV, degradation of the diffuser plate for solar flux measurements caused a serious problem in maintaining long-term instrument calibration. Alternative schemes which assume constant surface reflectivity in selected geographic areas were developed to correct for drifts in instrument calibration but the accuracy of these schemes is limited to $\pm 1\%$. Several changes in the BUUV instrument design have been incorporated in the TOMS and SBUV sensors to minimize any degradation.
- (2e) Aerosol related uncertainties - From an extensive study of the effects of various types of aerosols on the BUUV ozone measurements (Dave, 1977), one can draw the following conclusions:
 - The most commonly occurring atmospheric aerosols (assumed to be non-absorbing) have very little effect ($< \pm 1\%$) on the retrieved ozone, even when present in large amounts.
 - For localized highly absorbing aerosol clouds that might occur over an active volcano, the ozone may be overestimated by as much as 5%. Given the rarity of such events, the error has negligible impact on global ozone studies.
- (3a) Instrument noise - An instrument noise of 1% in each channel causes an error of 1.7% in total ozone. The main source of the instrument noise in the case of the Nimbus-4 BUUV is the size of the word used in the transmission of the radiance data (digitization). The 1σ error in the retrieved total ozone as a result of this error is calculated to be approximately 1%. Digitization errors in the SBUV have been reduced to insignificant levels, so that measurement noise is the limiting factor.
- (3b) Cloud related uncertainties - When significant cloud cover is in the field-of-view, BUUV measures the ozone above the cloud top. Since most of the ozone in the atmosphere (approximately 94%) lies above the clouds, the error caused is not large. In the case of BUUV algorithm, the ozone below the cloud top is estimated using climatological information, and is added to the measured ozone. It is calculated that the 1σ error in total ozone, in the presence of clouds, is approximately 3%, caused by the variations in ozone amounts below the cloud. On a global basis, clouds are present in 5-10% of the soundings and thus are not a significant source of error ($< 0.3\%$).
- (3c) Profile shape related uncertainties - Unlike Dobson measurements, the BUUV total ozone estimation can depend on the vertical distribution of ozone in the atmosphere. This effect, however, becomes important only at solar zenith angles greater than 77° (Klenk, 1979b). As one approaches the terminator, the

dependence on profile rapidly increases, and no ozone is retrieved when the errors are estimated to be greater than 5%. The procedure effectively limits the retrieval to a maximum solar zenith angle of 82° to 85° depending on climatological profile errors.

- (3d) Surface reflectivity related uncertainties - The BUV algorithm assumes an isotropic spectrally-neutral reflecting surface at the base of the atmosphere. Effects of various highly anisotropically reflecting surfaces like sea or ice have been studied theoretically (Ahmad, 1977) and their effect on total ozone retrievals is found to be <0.5%. The wavelength dependence of reflectivity of various surfaces has been analyzed in BUV and TOMS data from 330 to 380 nm and found to result in less than 1% errors in total ozone.

Comparisons between simultaneous Nimbus BUV and Dobson total ozone data indicate that for 1272 direct sun coincidences in 1970, the BUV values average 3.4% less than Dobson values and the rms difference was 5.3%.

Infrared Sounding Total Ozone Measurement Errors

The basic principle in infrared remote sensing of ozone from the 9.6 μ m band is that the stratospheric ozone layer absorbs radiation from the surface and troposphere, and subsequently reemits to space at the temperature of the ozone layer. This absorption and reemission produce the spectral features in the 9.6 μ m spectral region which are then inverted, taking into account the radiation transfer physics. Obviously, the temperature profile information is intimately involved in this procedure. The ozone absorption in the 9.6 μ m band is relatively weak so that radiation from the surface and cloud tops also reaches the remote sensing platform. In view of this transparent nature of the band, the need for temperature profile information, and assumptions about the vertical ozone profile associated with all passive infrared sensing schemes, significant errors are inherent and appear in the total ozone estimates.

In addition, instrument calibration errors and random noise in the radiance measurements will introduce total ozone errors which depend on the particular instrument.

Prabhakara et al. (1976) have analyzed the data from the Nimbus-4 IRIS, and find that the time-dependent errors, reflecting a seasonally-dependent bias, as large as $\pm 10\%$ can result due to the various reasons explained above. An analysis of errors for individual instruments is not presently available. A comparison of MFR data with clear sky, near simultaneous ground-based observations from 32 Dobson stations for 20 days in the period May-July 1977 indicated that the MFR values were 2.3% lower than the Dobson with an rms difference of 6.6% (Lovill et al., 1978).

ERRORS IN OZONE PROFILE MEASUREMENT METHODS

Balloon Ozonesonde Observation Errors

Two types of balloon ozonesonde systems, with various modifications, currently in use in routine ozone vertical distribution monitoring programs are the Brewer-Mast ozonesonde (Brewer and Milford, 1960) and the ECC ozonesonde (Komhyr, 1969; Komhyr and Harris, 1971). The systematic and random measurement errors, associated with the use of these instrument types, are summarized in table 6-4.

Total ozone amounts derived from Brewer-Mast sonde data are about 25% lower than Dobson instrument results (Dütsch, 1974; Mateer, 1977). ECC ozonesondes use solution concentrations that are adjusted to yield total ozone amounts that agree on the average with Dobson total ozone data (Komhyr, 1979). After

normalization of the ozonesonde profiles to Dobson instrument total ozone, data from the two types of sondes assume the Dobson instrument systematic error referred to in an earlier section. Because of the normalization procedure used in correcting the ozonesonde data, however, systematic errors in ozonesonde values of $\pm 5\%$ may arise corresponding to postulated secular changes of $\pm 25\%$ in ozone amounts above 30 km (Pittock, 1977). In addition, height-dependent, systematic measurement errors occur for the sonde above 20 mb due to uncertainties associated with the pump efficiency factors used in processing the data.

Table 6-4
Brewer-Mast (BM) and Komhyr (ECC)* Balloon Ozonesonde Measurement Error Estimates

Type of Error	Estimated Value		
<u>Systematic Errors (Relative to Dobson Instrument Total Ozone Measurements)</u>			
(1) Trend determinations not affected:			
(a) Uncorrected data†	BM ECC	(0, -25)% (0, -2)%	
		20 mb	10 mb 5 mb
(b) Pump correction biases at pressure levels	BM ECC	± 1% (0, -1)%	± 4% (0, -4)% ± 7% (0, -7)%
(2) Trend determinations affected (changes per decade):			
(a) Secular changes in ozone above top of balloon sounding	BM ECC	± 5% ± 5%	
<u>Random Errors</u>			
(3) Errors include measurement errors inherent in instrument performance, Dobson spectrophotometer random measurement errors, and extrapolation (for total ozone) errors.			
(a) In troposphere		± 6%	
(b) Tropopause to 20 mb		± 4%	
(c) 20 mb to 5 mb		± 8%	

*Data apply to ECC sensors employing 1.5% KI solution.

†Published data are adjusted to Dobson total ozone.

Umkehr Observation Measurement Errors

The limited information available from the Umkehr method permits only the gross features of a vertical ozone profile (resolution, ~ 15 km) to be inferred from an inversion of the measurement (Mateer, 1965). In addition to this, random errors in any one particular Umkehr measurement will introduce errors in the inferred ozone profile. Nevertheless, it is expected that a large set of observations could substantially reduce the latter effects so that long-term trends in mid and upper stratospheric ozone might be reliably detected. Current estimations of the uncertainties in the Umkehr method are based upon the utilization of the Standard Evaluation System developed by Mateer and Dütsch (1964), which suffered because of a lack of sufficient *a priori* ozone statistics (e.g., ozonesonde and rocketsonde data) at that time. It is likely that the potential for the Umkehr method to detect trends can be improved by optimizing the inversion procedure.

The reliability of ozone vertical distribution data derived from Umkehr observations depends upon observer skill, instrument calibration errors (including uncertainties in ozone absorption coefficients), atmospheric effects, and shortcomings in measurement data inversion procedures. (Effects of variations in the solar UV spectrum are eliminated in the Umkehr measurement inversion procedure.)

Aerosol effects on Umkehr measurements have been investigated by DeLuisi (1969, 1979a) and DeLuisi et al. (1975). In general, the bias in ozone profiles due to aerosols is negative above 30 km, minimal near the major maximum between 20 and 30 km, and positive below 20 km. It was shown that the inferred ozone concentrations in the 32 to 45 km atmospheric layer were probably low by about 10% in the Northern Hemisphere at the time when stratospheric aerosols reached a peak optical depth following the eruption of Agung. In the case of tropospheric aerosols, the Umkehr error sensitivity is about one order of magnitude less (per optical depth) than the error sensitivity to stratospheric aerosols.

Because the ozone absorption coefficients for the Dobson wavelengths are moderately temperature-dependent, some error bias can be expected in the Umkehr ozone profiles. DeLuisi (1971) investigated temperature induced errors in Umkehr profiles for midlatitude summer and winter standard atmospheres. For an integrated total ozone amount of 0.344 atm-cm, he estimated that if summer-to-winter temperature changes are neglected in the reduction of Umkehr data, average errors of 2% to 3% in layers 2 to 8 and 5% in layer 9 appear in computed Umkehr ozone amounts. For trend estimates, in which the annual cycle is removed, these errors are assumed to be comparable to Dobson errors.

Shortcomings in the inversion procedure can be listed under two categories: those that are correctable to some extent, such as effects of surface reflectivity, temperature, aerosols, and approximations in radiative transfer calculations; and those due to the inherent non-uniqueness problem encountered in the inversion of most integral equations.

Some attempts to empirically evaluate the accuracy of Umkehr observations (Bojkov, 1966; Craig et al., 1967; Dütsch and Ling, 1969) have shown that the Standard Evaluation System retrievals give less ozone at the major maximum, but more ozone above and below the maximum, in comparison with ozone profiles measured concurrently with ozonesondes. In a study comparing Umkehr and ozonesonde observations at Arosa, Aspendale and Tallahassee, DeLuisi and Mateer (1971) obtained better agreement in Umkehr and ozonesonde data by using improved *a priori* statistics derived from 511 ozone soundings made in Boulder.

It is apparent from the foregoing discussion that systematic and random errors for Umkehr observations are difficult to assess. Table 6-5 gives provisional estimates for measurement errors. To obtain an estimate of the effect of random errors on deduced Umkehr profiles, DeLuisi (1979b) perturbed Umkehr measurement data with assumed measurement errors of 1% and 10%. Resulting root mean square deviations derived from the error-free and the perturbed data profiles are shown in figure 6-1. If an all-encompassing measurement error of $\pm 5\%$ is assumed for Umkehr observations, the measurement precision may be deduced, from figure 6-1, to be $\pm 25\%$ at 100 mb, $\pm 10\%$ at 50 mb, $\pm 5\%$ at 20 and 10 mb, and $\pm 6\%$ at 5 mb, with the errors gradually

increasing to $\pm 12\%$ at 1.5 mb. This implies, for example, that real changes in ozone at 20 and 10 mb, of magnitude somewhat greater than $\pm 5\%$ and of at least 10 km vertical extent may be detectable by the Umkehr technique.

Table 6-5
Umkehr Ozone Profile Measurement Error Estimates

Type of Error	Estimated Value
<u>Systematic Errors</u>	
(1) Trend determinations not affected	
(a) Absorption coefficient uncertainties	lab meas. errors
(2) Trend determinations affected	
(a) Stratospheric temp. changes @40 km	$\pm 0.5\%$
(b) Wavelength calibration errors	1% per 1% error in absorption coeff.
(c) Solar spectrum changes	None
(d) Ozone profile changes during 3-hour measurement time	constant bias if change is regular
(e) Changes in aerosol optical depth (τ), error @40 km	
(i) Stratospheric, Agung size event ($\tau = 0.02$)	(0, - 10)%
(ii) Tropospheric aerosols, $\tau = 0.2$	(0, - 4)%
<u>Random Errors</u>	
(3) Assuming an unbiased estimation and 5% random errors in Dobson measurement	
(a) 20 km (layer 3)	$\pm 15\%$
(b) 30 km (layer 6)	$\pm 7\%$
(c) 40 km (layer 8)	$\pm 9\%$

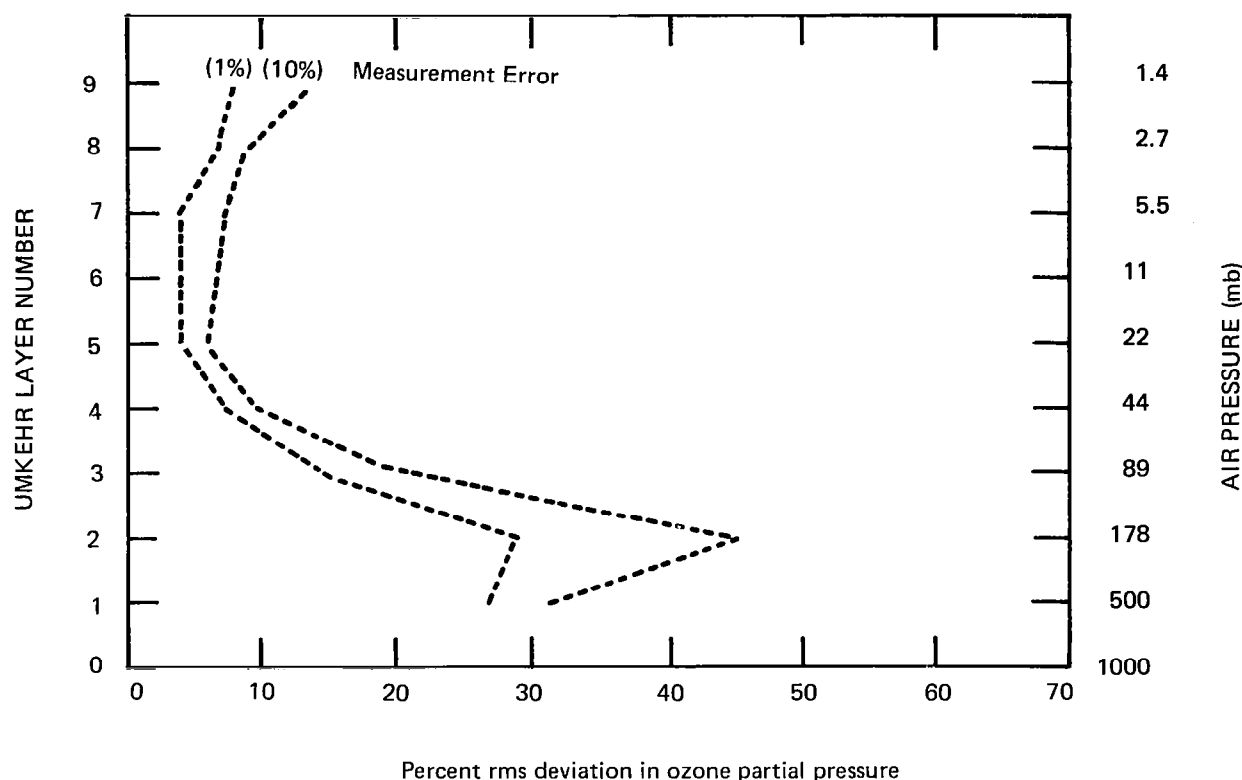


Figure 6-1. Umkehr ozone profile root mean square deviations resulting from perturbations of idealized, error-free Umkehr measurements with 1% and 10% measurement errors (DeLuisi, 1979b).

Rocket Ozonesonde Measurement Errors

U.S. Optical Ozonesonde

Optical ozonesondes are absolute sensors which measure the UV light absorption by ozone per unit height as the instrument ascends or descends through the atmosphere (Krueger et al., 1979b). Systematic errors are suppressed by measurement of the ratio of fluxes in wavelength pairs. Thus, internal sensitivity changes and external wavelength-independent influences are cancelled in the measurement, as in Dobson spectrophotometer measurements. However, unlike the Dobson technique, an absolute calibration is not required since the ozone density is computed from changes in ratio with altitude. The principal source of bias is due to errors in laboratory measurements of ozone absorption coefficients.

Random errors are of two types: (1) telemetry and photometer noise, and (2) effective absorption coefficient errors. The noise levels are equivalent to 1 to 4% random errors in ozone density for 2 km vertical resolution between 20 and 45 km, but can grow rapidly outside this altitude span. The largest source of error between individual instruments is due to instability of filter characteristics caused by aging and environmental conditions. These errors can be kept small through quality control of instruments and by minimizing the time

between calibration and flight. The extent of filter change varies with production batch, but all changes appear to be in the same direction. Nominal biases in ozone determination for a recent, worst-case, batch with 3 to 6 month intervals between calibration and flight are -2.5% , -7% , and -8% at 30, 40, and 50 km, respectively, at the 1σ level. These filter changes have affected approximately 10% of all the optical rocket soundings. The resulting errors, adjusted for fraction of instruments affected, are listed in table 6-6.

Table 6-6
Rocket Ozone-sonde Measurement Error Estimates

Type of Error	Estimated Value		
<u>Systematic Errors</u>	Altitude Level		
	30 km	40 km	50 km
(1) Trend determinations not affected:			
Optical (Krueger)	ozone absorption spectrum errors		
Chemiluminescent* (Hilsenrath)	$\pm 12\%$	$\pm 12\%$	$\pm 12\%$
(2) Trend determinations affected (change per decade):			
(a) Optical-ozone abs. coef. affected by stratospheric temperature changes.	$\pm 0.5\%$	$\pm 0.2\%$	$\pm 0.05\%$
<u>Random Errors</u>			
(3) Noise and calibration errors, not including radar errors			
Optical (Krueger)			
(a) Telemetry and sampling	$\pm 2.5\%$	$\pm 1.5\%$	(variable) ± 1 to 20%
(b) Filter calibrations, aging	(0,-0.3)%	(0,-0.7)%	(0,-0.8)%
(c) Filter calibrations, other components	$\pm 1\%$	$\pm 1\%$	$\pm 2\%$
Chemiluminescent (Hilsenrath)			
(a) Telemetry and sampling	$\pm 3\%$	$\pm 3\%$	$\pm 3\%$
(b) Calibration	$\pm \frac{1}{5}\%$	$\pm \frac{5}{8}\%$	$\pm \frac{1}{5}\%$

*Includes uncertainty in the ozone absorption coefficient at 254 nm.

Soundings with larger biases are eliminated from the data set by virtue of an internal consistency test applied in the data processing. Although a relatively small number of soundings are affected by this particular filter batch, all were launched in 1978 and 1979 and may result in a perturbation in a trend line. Additional calibration errors due to variations in other optical components are estimated to be $\pm 1\%$ at 30 and 40 km and $\pm 2\%$ at 50 km.

U.S. Chemiluminescent Ozonesonde

The chemiluminescent method is not absolute, and each instrument is calibrated by repeated exposure to known ozone concentrations at air pressures and flow rates expected in flight (Hilsenrath et al., 1979b).

Systematic errors in chemiluminescent ozonesondes arise from: (1) ozone absorption coefficient errors at 253.7 nm as used in the calibration standard, (2) nonlinearities in the chemiluminescence process, and (3) ozone losses in the instrument. These errors are estimated to be $\pm 12\%$.

Random errors in this sensor are due to sensor and telemetry noise and to flow modulation caused by parachute oscillations. These errors are about $\pm 3\%$ between 1 and 60 km. The standard error from the repeated calibrations is typically $\pm 8\%$.
20
5

BUV Ozone Profile Measurement Errors

The ozone profile measurements from the Nimbus type BUV instrument are susceptible to several different types of errors including both systematic and random errors; the latter including instrument errors and algorithmic errors. The algorithmic errors include first guess related errors, uncertainties due to limited altitude resolution, and profile uncertainties due to the use of wavelengths scattered in the troposphere.

Table 6-7 summarizes the profile measurement error estimates for the BUV instrument.

The following notes explain the error information contained in table 6-7.

- (1a) Ozone absorption coefficient uncertainties - The retrieval of ozone profiles from backscattered ultraviolet radiance requires an accurate knowledge of ozone absorption coefficients. A constant percentage error in all wavelengths will cause a scaling of the retrieved profile with only minor changes in the shape. Wavelength dependent errors in absorption coefficients are more serious. A 1% error in a single wavelength absorption coefficient will change the mixing ratio (or partial pressure) by approximately 1% in the layer in which that wavelength weighting function peaks. Since the peaks of weighting functions shift with solar zenith angle, such anomalous effects are indistinguishable from real changes in the profile with latitude.
- (1b) Instrument errors - A wavelength independent 1% error in instrument radiometric calibration will cause approximately 1.7% error in the mixing ratio for layers between 1 and 3 mb. The error will become progressively smaller as one goes down to 10-20 mb. Again, a wavelength dependent error is more serious as it distorts the retrieved profile.
- (2) The long-term radiometric stability of the BUV instrument is more crucial for profile determination than it is for total ozone determination. Moreover, any long-period changes in the solar flux in the 250 through 300 nm wavelength bands must be accurately monitored. For the Nimbus-4 BUV, the solar flux monitoring system failed shortly after launch. Approximately 5% changes in the short wavelength atmospheric radiances have been detected over a period of seven years. It cannot be established with any certainty whether these changes were due to (1) a shift in the instrument calibration; (2) a change in

the solar flux; or (3) changes in the upper level atmospheric ozone. Several design changes affecting calibration stability, implemented in the recently launched SBUV instrument, have worked, and it is believed that the long-term SBUV instrument calibration can be maintained to a few percent.

- (3a) Instrument noise - A 1% instrument noise in all channels will cause about 3% noise in layers between 1 and 3 mb. For lower layers, the effect will decrease to about 1.5% at 10 mb. For the Nimbus-4 BUV, the estimated 1σ noise is about 1%. For the Nimbus-7 SBUV, the noise is about 0.5%.

Table 6-7
BUV Ozone Profile Measurement Error Estimates

Type of Error	Estimated Value
<u>Systematic Errors</u>	
(1) Trend determinations not affected:	
(a) Absorption coefficient uncertainties	lab meas. errors
(b) Bias due to first guess errors	<0.5% (upper)* <1% (lower)*
(2) Trend determinations affected (change per decade):	
(a) O ₃ abs. coeff. affected by temperature changes	± 0.5%
(b) Relative calib. error between instruments	<3%
(c) Solar spectrum changes	<5%(Nimbus-4)
(d) Uncorrected calibration drifts	<10%(Nimbus-4)
<u>Random Errors</u>	
(3) (a) Noise and telemetry	± 2%
(b) Cloud and surface reflectivity errors	0 (upper) ± 1% (lower)
(c) Multiple scattering uncertainties	0 (upper) ± 3% (lower)
(d) First guess related errors	± 3% (upper) ± 6% (lower)

*Note: Upper profile levels extend from 35 to 50 km, lower levels are from 25 to 35 km.

(3b) Algorithmic Errors - Includes three types as follows:

- (i) First guess related - The BUV profile algorithm starts with a climatological profile as a first guess. Although the retrieved profiles are first guess dependent, the exact magnitude of this dependence and the error caused by it are difficult to quantify. From a simulation study based on realistic profiles, a reasonable estimate of 1σ error is $\pm 3\%$ in mixing ratio at each layer within the range of information (~ 1 to 10 mb). Outside the range at which the wavelength contribution functions peak, the retrieved profiles are constrained to the first guess and, as such, the errors there will increase to the natural variance of the ozone in those layers. However, it should be noted that for layers between 20 and 40 mb, the first guess variances are smaller than the natural variance because the first guess is selected using the total ozone as a predictor.
- (ii) Uncertainties due to limited altitude resolution - The half width of the weighting functions for the BUV profiling wavelengths is about 15 km. Therefore, the BUV can detect only the fluctuations in the profile that occur over comparable heights. When compared to high resolution measuring systems (e.g., rockets) the BUV will underestimate the natural variance in the layers.
- (iii) Profile errors arise due to the use of wavelengths at which tropospheric scattering is important since the longer wavelengths used with the BUV (295 nm) penetrate the stratospheric ozone layer. Use of these wavelengths in profile retrieval requires accounting for multiple scattering, surface reflectivity, and cloud and terrain height. The BUV profiling algorithm has been carefully designed to account for these effects. However, when it is determined that the uncertainty in the retrieved profile, using a particular wavelength, exceeds a maximum of $\pm 7\%$, that wavelength is not used in the profile determination. This restricts the retrievable information from BUV at low latitudes to levels between 1 and 7 mb. At higher latitudes, all wavelengths up to 305.8 nm are used to derive profiles which are valid from .7 to 20 mb.

OBSERVED TRENDS IN OZONE

TRENDS FROM GROUND BASED OBSERVATIONS

The ground based total ozone data set covers a longer time span than any other ozone data set and has been analyzed extensively for long-period variations. Ozone studies, based on combined data from stations, grouped by regions or the hemispheres, have been used for these analyses (Angell and Korshover 1976, 1978d; Komhyr et al., 1973; London and Kelly, 1974; Hill et al., 1977). These data have been smoothed in time and space to reduce the noise. By examining the observed variations, evidence was sought for the effects of solar activity, volcanic eruptions and atomic tests, and of linkage with other variables such as surface pressure, and recently, with CFM releases.

An example of such an analysis is given in figure 6-2 which shows the variation in total ozone between 1958 and 1977, for north and south temperate latitudes, the tropics, and the world. The north temperate average has been estimated from a 3, 3, 2, 1, 1 weighting of regional values for Europe, North America, Soviet Union, Japan, and India, respectively. The tropical average comes from about five stations scattered around the Equator. The south temperate average is derived from stations mostly in the Australia-New Zealand region. The world average results from a 1-3-4-3-1 weighting of north polar (not shown), north temperate, tropical, south temperate, and south polar (not shown) regions. The vertical bars extend two standard deviations from the mean.

As has been documented previously (NASA RP-1010) there was a notable increase in total ozone in the Northern Hemisphere during the 1960s, reaching a peak about 1970. This variation was not observed at south temperate latitudes. The estimated global variations shown in the bottom curve of figure 6-2 indicates an

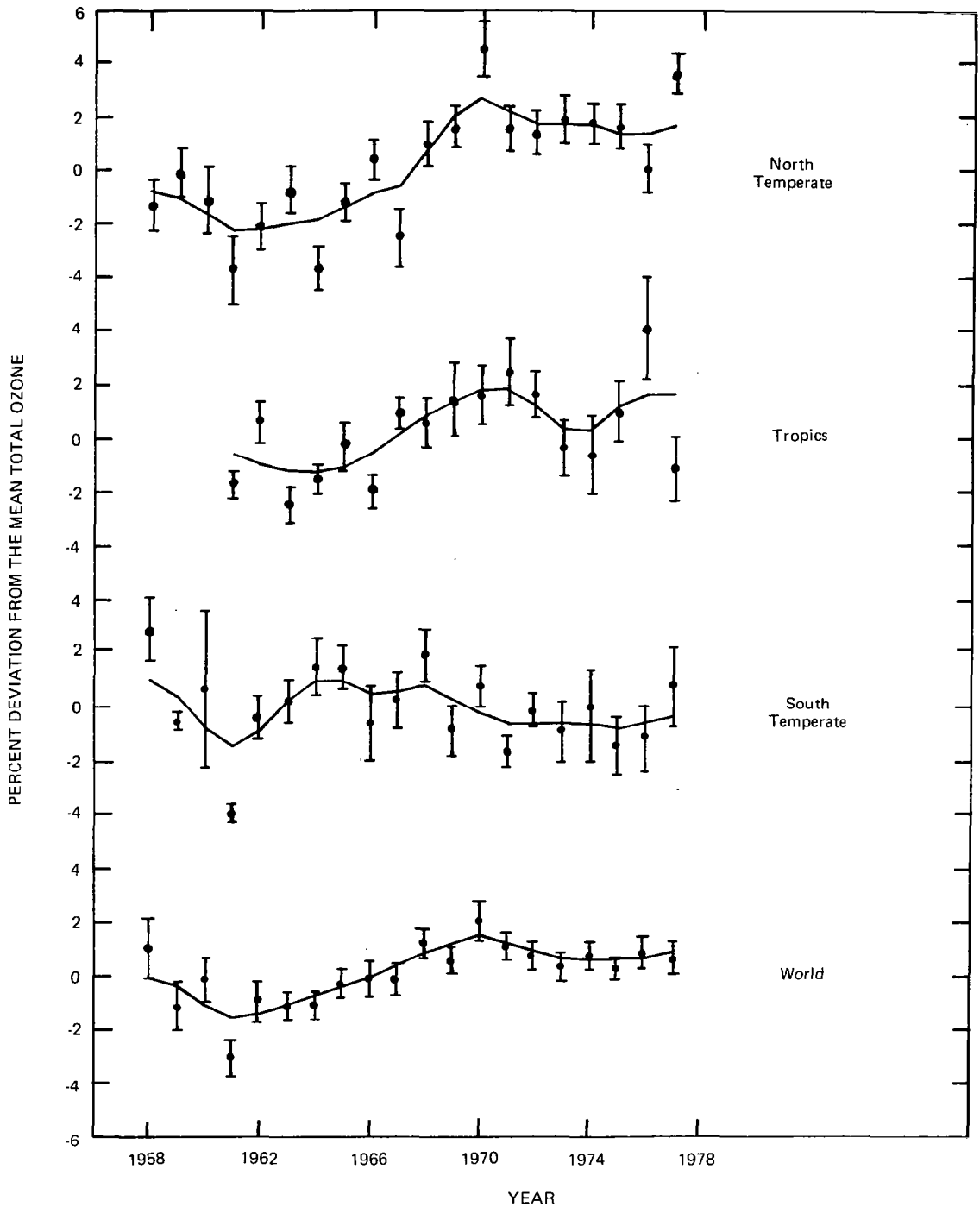


Figure 6-2. Time variation of the annual mean percentage deviation from the long-term regional average total ozone for north and south temperate zones and the tropics for the years from 1958 through 1977. A similar curve is shown at the bottom based on estimates of the global average total ozone amount. The vertical bars suggest a 95% confidence level.

increase of about 4% from 1961 to 1970 and a slight decrease from 1970 to 1977. The small changes shown for the Northern Hemisphere after 1970 seem to have resulted from the tendency for compensation between the tropics and midlatitude regions. The 1977 global average total ozone is approximately 1% above the long-term average.

TRENDS FROM SATELLITE OBSERVATIONS

Total ozone observations from the Nimbus-4 BUV instrument have been analyzed for changes during its seven years of operation. Global mean amounts were computed from area-weighted zonal mean values and an estimate of polar night values. Sufficient data were obtained to compute monthly global averages almost until the end of 1976. These observations are shown in figure 6-3. Beyond 1976, satellite operations became intermittent. Although both hemispheres are included, an annual cycle is still present due to hemispheric differences in their annual cycles. From this record, it is obvious that the seasonal variation (about 13 matm-cm) is dominated by the spring maximum of the annual wave in the Northern Hemisphere. However, over the seven-year data set a definite downward trend can be distinguished.

The analysis of ground-based data shown in figure 6-2 indicates that, during the time period of BUV observations on Nimbus-4, the Dobson-derived global ozone decreased by 0.8% between 1970 and 1973, remained constant for the next several years and then may have increased 0.2% by 1977. The BUV Nimbus-4 observations, after the removal of the annual wave, indicate a decrease of about 2.5% during the corresponding period from 1970 to 1973, and a gradual decrease thereafter of about 0.2% per year. Qualitatively, these data sets indicate a tendency for ozone decreases after 1970; however, the reasons for the differences in year-to-year fluctuations are not known at this time.

During the period between 1970 and 1978, there were four satellite instruments which operated long enough to permit computation of monthly mean global ozone amounts. The experiments which span this region are the IRIS and BUV, both flown on Nimbus-4, the Multifilter Radiometer (MFR) flown on a Block 5 satellite, and the SBUV on Nimbus-7. Tables 6-8a and 6-8b are comparisons for the monthly mean global amounts from the various experiments for the months of June and November. Unfortunately, the reported MFR data are not coincident with BUV data and a direct comparison is not possible.

The global ozone values shown for the IRIS experiment were listed in the study by Keating (1978). In June 1970, the global ozone value from IRIS was 4% higher than that derived from BUV observations. In November 1970, IRIS was about 6% higher. This is not inconsistent with the analysis of Prabhakara et al., (1976) which showed that the $9.7\mu\text{m}$ ozone retrievals have a seasonally-dependent bias.

Preliminary hemispheric and global ozone values obtained from the SBUV experiment for November 1978 are also shown in table 6-8b. It is interesting to note that the Northern Hemisphere ozone is virtually identical to the 1970 BUV value, but the Southern Hemisphere ozone has increased by about 12 matm-cm. This seems to provide additional evidence that there are significant interannual hemispheric differences in the ozone budget. In order to have the maximum sensitivity for the detection of global scale trends with the existing instrumentation, it is necessary both to monitor global ozone from space, and to maintain a high quality ground based network with the proper geographic distribution.

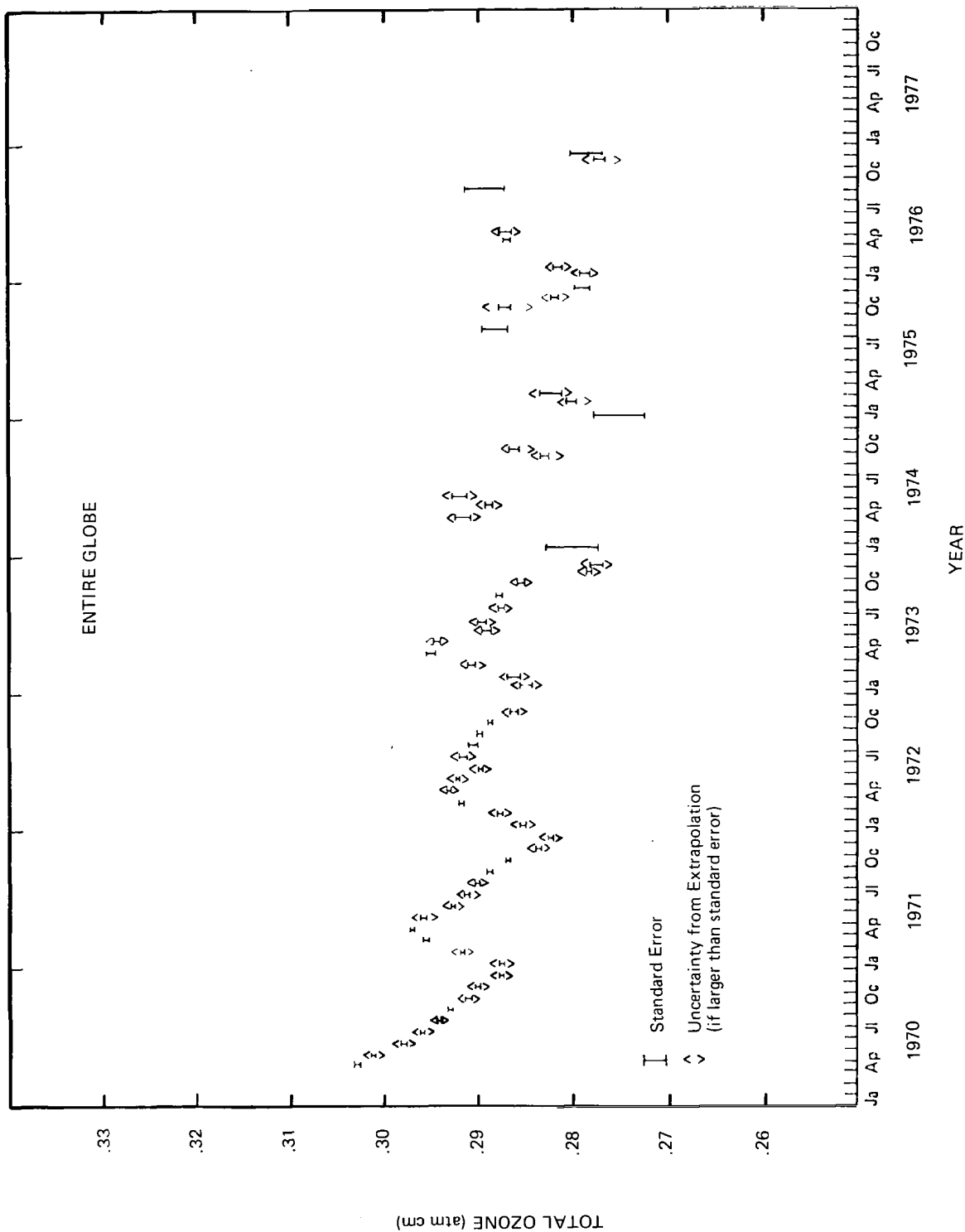


Figure 6-3. Time variation of global average total ozone amounts derived from Nimbus-4 BUV data from April 1970 through December 1976.

Table 6-8a
Hemispheric and Global Ozone for June

Hemisphere/ Global	(Year)								
	70	71	72	73	74	75	76	77	78
N. Hemisphere S. Hemisphere Global	Nimbus-4 BUUV								
	0.310	0.301	0.300	0.298	0.303	0.297	0.296		
	0.286	0.285	0.279	0.281	0.282	—	—		
	0.298	0.293	0.290	0.289	0.292	—	—		
Global	Nimbus-4 IRIS								
	0.311								

Table 6-8b
Hemispheric and Global Ozone for November

Hemisphere/ Global	(Year)								
	70	71	72	73	74	75	76	77	78
N. Hemisphere S. Hemisphere Global	Nimbus-4 BUUV and Nimbus-7 SBUV								
	0.275	0.271	0.271	0.271	—	0.274	0.267		0.276*
	0.305	0.296	0.301	0.286	0.296	0.289	0.286		0.316*
	0.290	0.284	0.286	0.278	—	0.283	0.277		0.296*
Global	Nimbus-4 IRIS								
	0.309								

*Nimbus-7 preliminary data

TRENDS FROM VERTICAL PROFILE DATA

Balloon Ozonesonde and Umkehr Observations

The primary effects of anthropogenic chlorine on ozone are expected to take place above 30 km, a region containing only 20% of the total ozone column. A comparison of long-term ozone changes has been made using balloon ozonesonde and Umkehr data (Angell and Korshover, 1979).

Umkehr networks exist in Europe (about 5 stations), India (about 3 stations), and Japan (3 stations). A north temperate average has been estimated from a 2-1-1 weighting of the respective regional values. For the Southern Hemisphere, data have been taken for many years at several stations in Australia, but the data are largely unprocessed.

For comparison with the Umkehr measurements in the 8 to 16, 16 to 24, 24 to 32 and 32 to 46 km layers, mean ozone values from balloon sondes have been determined for 8 to 16, 16 to 24 and 24 to 32 km layers. Mean ozone values also have been determined for the mid-troposphere, or the approximately 2 to 8 km layer. Ozonesonde networks exist in North America (5 stations), Europe (about 5 stations) and Japan (3 stations), and Australia. A north temperate average has been estimated from a 2-2-1 weighting of the respective regional Northern Hemisphere values.

Figure 6-4 shows the derived ozone variations in given height layers for north temperate latitudes. The vertical bars represent 95% confidence intervals. For ease of comparison, the vertical dashed line at the right shows the initial year of the ozonesonde record. The Umkehr data suggest an increase in ozone amount in all layers during the years between 1962 and 1970. In the 32 to 46 km layer of greatest sensitivity to anthropogenic effects, there appears to be a significant decrease in ozone between 1974 and 1975. This apparent decrease is believed to be mostly, if not entirely, an artifact due to biases introduced into the Umkehr technique by stratospheric aerosols from the volcano Fuego (Guatemala) eruption in the autumn of 1974 (DeLuisi et al., 1975) (Note the absence of an effect in the 24 to 32 km layer). In 1976 and 1977, the ozone amount in the 32 to 46 km layer increases again, presumably reflecting the decrease of the stratospheric aerosols. Because of the Fuego eruption, it is difficult to ascertain whether there has been any real decrease in ozone in the sensitive 32 to 46 km layer since 1970. If there has been a decrease, it has been very small. The ozone amount in this layer in 1977 was still almost 4% above the 18-year data set average. However, aerosols from the Agung eruption may have biased the average in the same way Fuego aerosols decreased the yearly values after 1974.

In the 24 to 32 km layer, both ozonesondes and Umkehr measurements suggest little ozone variation after 1969. The small extent of the vertical bars indicates the considerable consistency among station values in this height interval.

In the 16 to 24 km layer, the ozonesonde data suggest a 3 to 4% ozone decrease between 1969 and 1977 (superimposed on a strong quasi-biennial oscillation), while the Umkehr data indicate a smaller decrease, with even some evidence of a recent ozone increase.

In the 8 to 16 km layer, bracketing the tropopause, the discrepancy between ozonesonde and Umkehr trends becomes more obvious, although the greater spatial variability of ozone in this layer may contribute to the difference. The indicated 8% increase in mid-tropospheric ozone over the period of record is noted with interest, but is not discussed further here except to note that the increase has been large in industrialized Europe and Japan, and small in the rural areas of Canada (where most of the North American network stations are located). Ozonesonde data from Aspendale (38°S) show a decrease in the lower stratosphere and an increase above the 30 km level (Pittock 1974; Kulkarni, 1979).

To examine the consistency between total ozone trend and the trends aloft determined from ozonesondes and Umkehr measurements, figure 6-5 presents a comparison of the respective variations, where a 1-2-2-1 weighting has been applied to Umkehr values in 8 to 16, 16 to 24, 24 to 32 and 32 to 46 km layers (weighting proportional to relative ozone amount) to obtain an integrated ozone value, and a 1-2-2 weighting to ozonesonde values in the 8 to 16, 16 to 24 and 24 to 32 km layers to obtain an integrated ozone value. After 1970, the trends are similar, although the integrated ozonesonde values suggest a slightly greater ozone decrease, and the integrated Umkehr values a slightly smaller ozone decrease, than shown by the total ozone values. The greater increase of integrated Umkehr value than total ozone value, prior to 1970, presumably is due to artifacts in the Umkehr technique resulting from the Agung eruption in 1963.

Observed Ozone Variations from Rocket Data

Although rocket measurements of ozone have been made over a 30-year time span, most of the data have been collected at essentially random times of the day and year. For a trend estimate, it is necessary to know

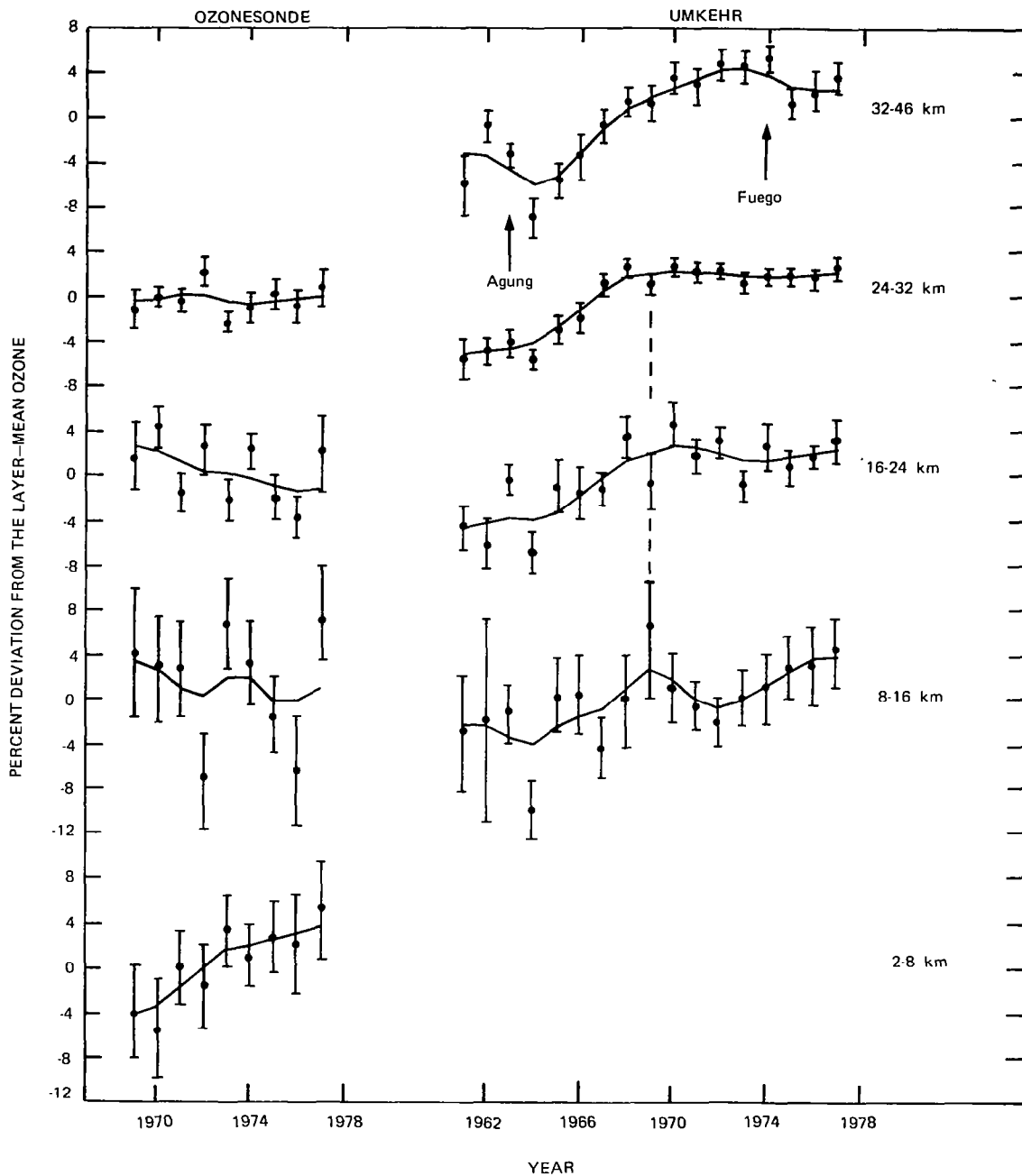


Figure 6-4. Time variation of the annual mean percentage deviation from long-term averages of ozone partial pressure for five altitude zones in the north temperate region. Data from balloon ozonesondes are shown at the left for the years 1969 through 1977. Umkehr results are given on the right for the years 1961 through 1977. The start of the ozonesonde record is indicated on the Umkehr record by the dashed vertical line. The occurrence of major volcanic eruptions (Agung and Fuego) is indicated on the highest Umkehr data set.

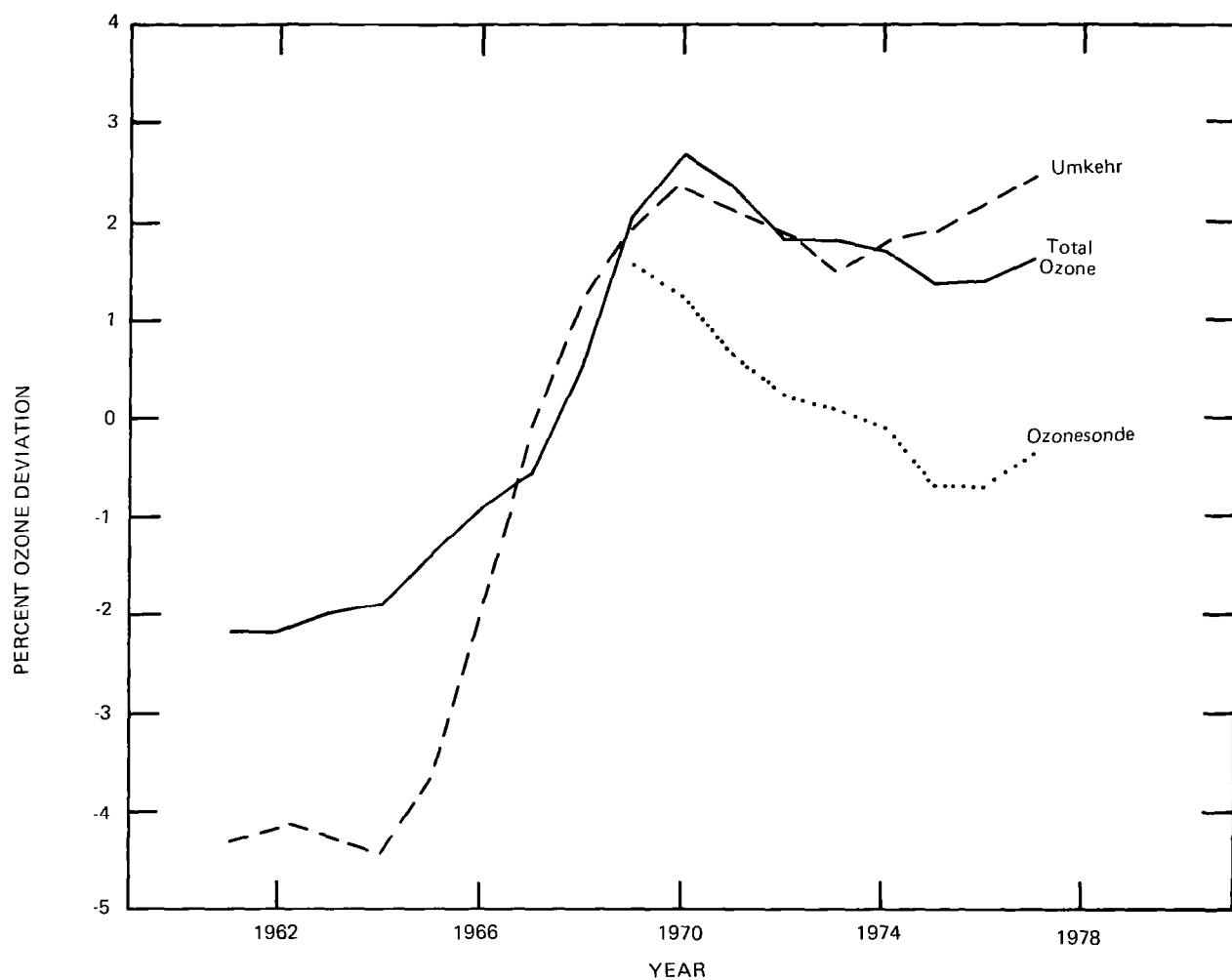


Figure 6-5. Comparison percentage deviations of total ozone computed from balloon ozonesonde and Umkehr average profiles with observed Dobson total ozone amounts for the north temperate region from 1961 to 1977.

whether non-random factors are present in the data set. An estimate of the global average vertical ozone distribution and its variability has been made from early data (Krueger, 1973). The mean distribution at northern midlatitudes was calculated for the 1976 U.S. Standard Atmosphere (Krueger and Minzner, 1976).

Diurnal ozone changes have been measured by Hilsenrath (1971) who finds a day-to-night increase above 47 km, but a decrease at lower altitudes at Wallops Island, Virginia. Krueger (private communication) has investigated local time effects on high altitude ozone and finds 10 to 15% increases from morning to afternoon near the mixing ratio maximum (35 km), and similar decreases near 50 km.

Watanabe and Tohmatsu (1976) find seasonal changes at all altitudes above 30 km, with winter ozone densities at 50 km at Kagoshima City, Japan being a factor of two greater than summer densities. Krueger and Wright (private communication), from a series of 35 monthly flights at local noon at Wallops Island, Virginia, find much smaller seasonal changes with winter mixing ratios at the 1 mb level exceeding summer values by 35%. The phase of the maximum was found to vary with altitude so that highest mixing ratios at 10 mb appear in summer. Fifty percent changes in the mesospheric ozone profile due to solar protons have been found in rocket observations by Weeks, Cuikay and Corbin (1972), and Hilsenrath recently found similar changes associated with a magnetic substorm (see Chapter 5 of this report).

These various effects are larger than the anthropogenic effects being sought in a trend analysis. To make use of the entire set of rocket measurements, one must have a determination of at least the seasonal and diurnal variations as a function of latitude. The Wallops Island data set is providing an initial estimate of seasonal changes at midlatitudes, and some information is becoming available for high latitudes (Fort Churchill, Manitoba) from a 20-month series of monthly flights.

The minimum change in ozone that can be detected from a random set of noontime flights can be estimated if the variability is known. Figure 6-6 illustrates the percentage variability in ozone mixing ratio and number density as a function of air pressure, for the Wallops Island data set. Of particular interest is a minimum variability ($\sim 10\%$) in the 3 to 5 mb region, near the level of maximum predicted CFM effects. This occurs just above the level where the mixing ratio variability becomes less than the density variability, as might be expected in the transition from dynamic to photochemical control of ozone.

Observed Ozone Profile Variations from Satellite Data

Stratospheric ozone data of global extent have been obtained from satellites since the late 1960s. These data have come from seven separate sensors, using three different techniques as listed earlier in table 6-1. Except for the Nimbus-4 BUV data set, each instrument acquired data over a time span that is very much less than a decade (a few months to one and one-half years). For the earlier flights, the data sets do not overlap in time, a factor needed to assess calibration differences. The data processing for recent flights is not yet completed. Thus, at the present time, an objective assessment of the trend over the last decade cannot be made by combining the satellite data sets. The Nimbus-4 BUV results, which extend for a seven-year period, have the potential for precise determination of variations in the global mean ozone concentrations near the 40 km level of maximum CFM depletions. Final BUV data production was completed in November, 1979. The interpretation of the observed variations in terms of trends is problematical due to the present uncertainty in long-term instrument stability as noted earlier in this chapter. It remains to be seen whether new techniques for determination of sensitivity changes can be devised. Based on early results, the Nimbus-7 SBUV appears to be quite stable since it was improved to avoid contamination effects, and contained internal devices to measure sensitivity changes.

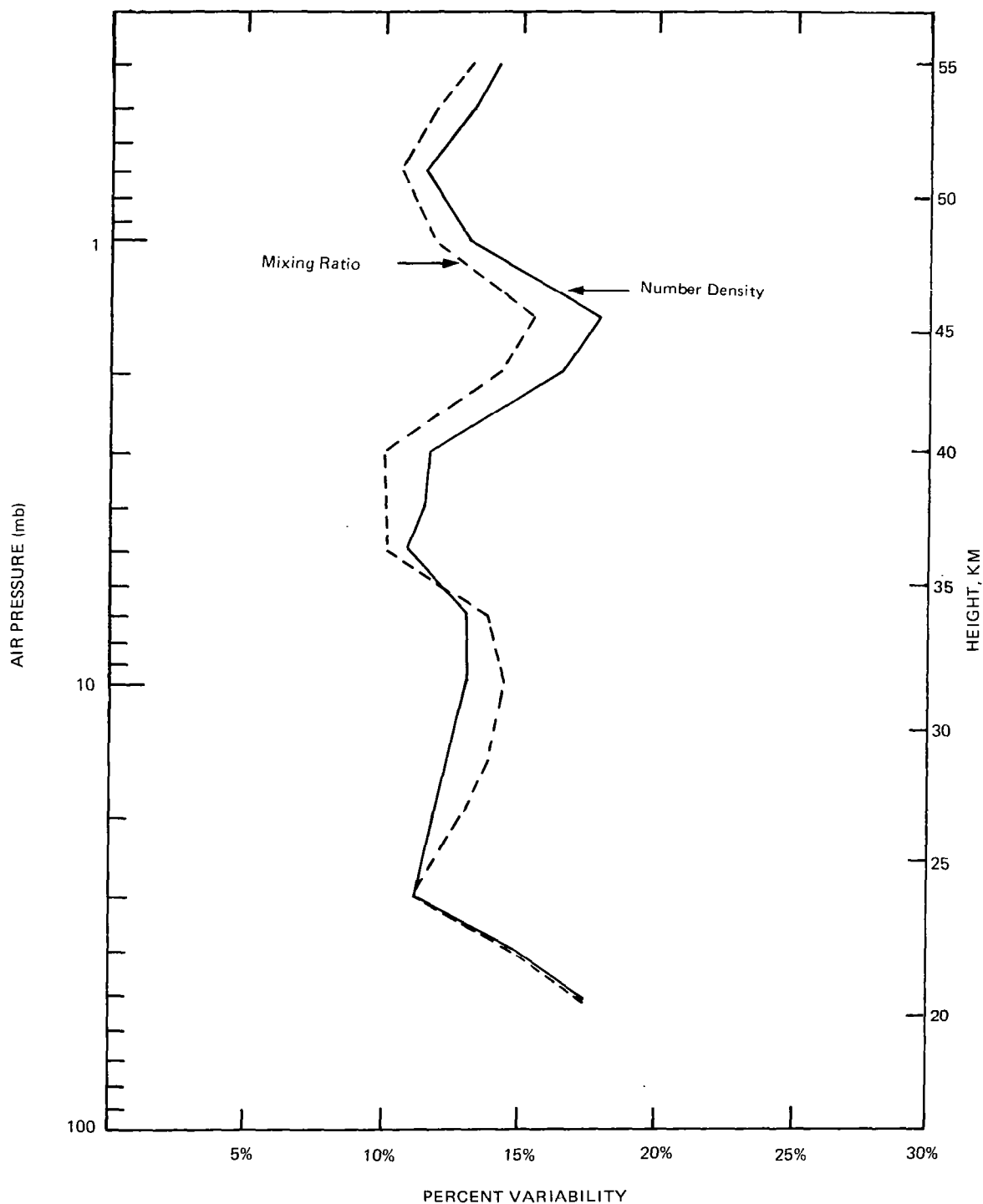


Figure 6-6. Observed percentage variability of ozone mixing ratio and ozone density versus air pressure in the stratosphere and lower mesosphere derived from optical rocket ozonesonde flights at Wallops Island, Va. The values represent one standard deviation. An approximate altitude scale is shown on the right (Krueger, private communication).

LONG-TERM VARIATIONS OF OTHER PARAMETERS

TEMPERATURE VARIATIONS

Long-term trends in the mean temperature of three stratospheric layers (10 to 30 mb, 30 to 50 mb, 50 to 100 mb) were recently estimated by Zerefos and Mantis (1977) from their analyses of radiosonde observations during the period from 1957 to 1972. Similar trends during this period were found in independent studies by Angell and Korshover (1978a; b) from analyses of radiosonde and Western Hemisphere rocketsonde (Angell and Korshover, 1978c) data taken during the period from 1964 to 1976. Results from the latter reference are shown in figure 6-7, in which seasonal data have been binomially smoothed after removal of the annual oscillation. A downward trend is clearly evident in the low latitude data, throughout the period in the lower stratosphere, and starting from solar maximum in the upper stratosphere. The trends are similar in the north polar regions for the middle and upper stratosphere, but upward in the lower stratosphere. Figure 6-8 shows the Angell and Korshover analysis, with error bars, of the 100 to 30 mb (16 to 24 km) layer in more detail, and with an extended period, from 1958 to 1977, separately for the equatorial (10S to 10N), north subtropical (10N to 30N), north temperate (30N to 60N) and north polar (60N to 90N) regions. The solid curves are again binomially smoothed values, and the ordinates for the north polar data are compressed by a factor of two. The years of the Agung (March 1963) and Fuego (September 1974) eruptions are marked by arrows below the north subtropics curve, which suggests that the downward trend may be due to a gradual settling of Agung dust.

Figure 6-9 shows the downward trend in the Northern Hemisphere monthly mean temperatures at 50, 100 and 200 mb for the period between 1964 and 1973, as analyzed by Oort (private communication, 1979) from the global rawinsonde network after removal of the seasonal variations.

The cause or causes of these observed temperature decreases are still unknown. Quiroz (1979a) has calculated high correlations between mean annual sunspot numbers and yearly temperature departures at 35 and 50 km, but warns that "it remains to be seen whether the relationships seen in solar cycle 20 hold in cycle 21." Quiroz (1979b) also points out that satellite data from 1969 on can perhaps be used to substantiate trends found from rocket measurements. In general, much care should be taken to insure continuity of calibrated measurements and their interpretation. Careful analysis of the wind field should be carried out to see whether temperature changes at the tropopause level have dynamical consequences predicted from circulation model sensitivity studies (e.g., Fels and Kaplan, 1975). Trends in the wind field are more difficult to see through the noise than are those of temperature, and most correlations found between motion fields in the stratosphere and troposphere can more easily be explained by tropospheric influence on the stratosphere than vice versa.

TRENDS IN TRACE SPECIES

This section discusses long-term measured variations for several trace species. Many other species, whose global abundances are suspected to have undergone long period changes (e.g., CO, H₂, OH, and stratospheric ClO_x), have not been included because few data that can be used to quantify trends are available. (It may be possible to estimate a trend for CO from available solar and planetary spectra). Table 6-9 summarizes the data discussed below in terms of percent changes.

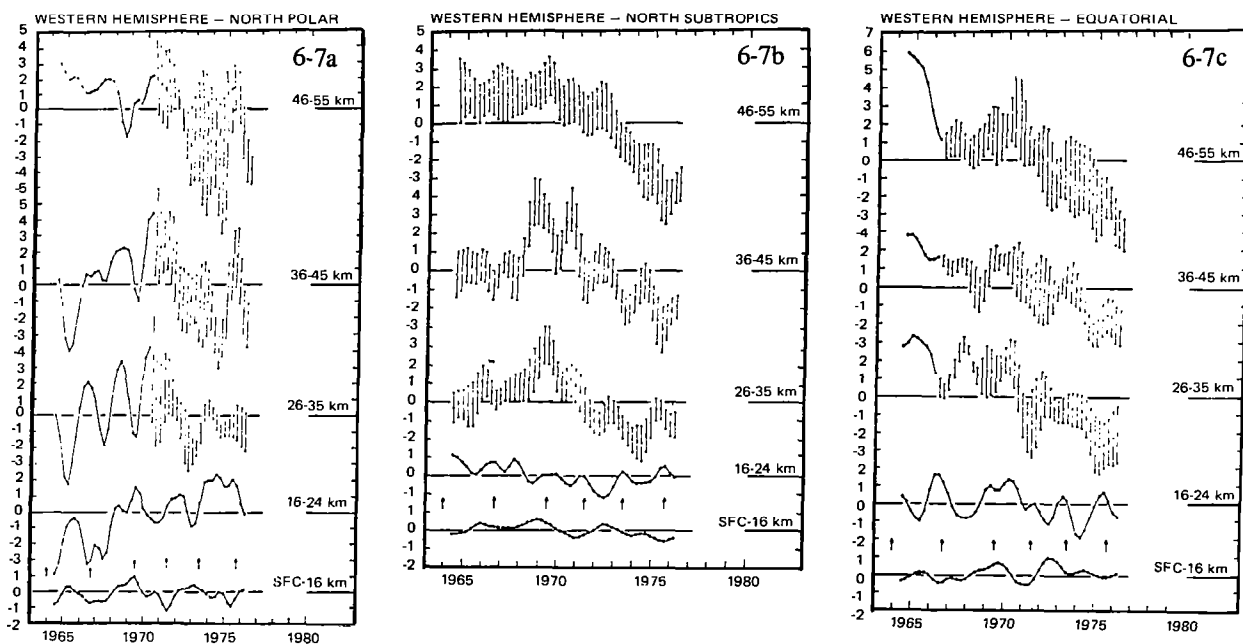


Figure 6-7a. Temperature variation ($^{\circ}\text{C}$) within given height layers (the top three based on rocketsonde data, the bottom two on radiosonde data) for north polar regions of the western hemisphere. When more than one station is available, the vertical bars on the rocketsonde data extend two standard deviations of the mean either side of the mean. The vertical arrows signify the time of quasi-biennial west wind maximum at 50 mb (20 km) on the tropics, and the tick marks are in summer of the given year.

Figure 6-7b. As in Figure 6-7a except for the north subtropics of the western hemisphere.

Figure 6-7c. As in Figure 6-7a except for the equatorial zone of the western hemisphere.

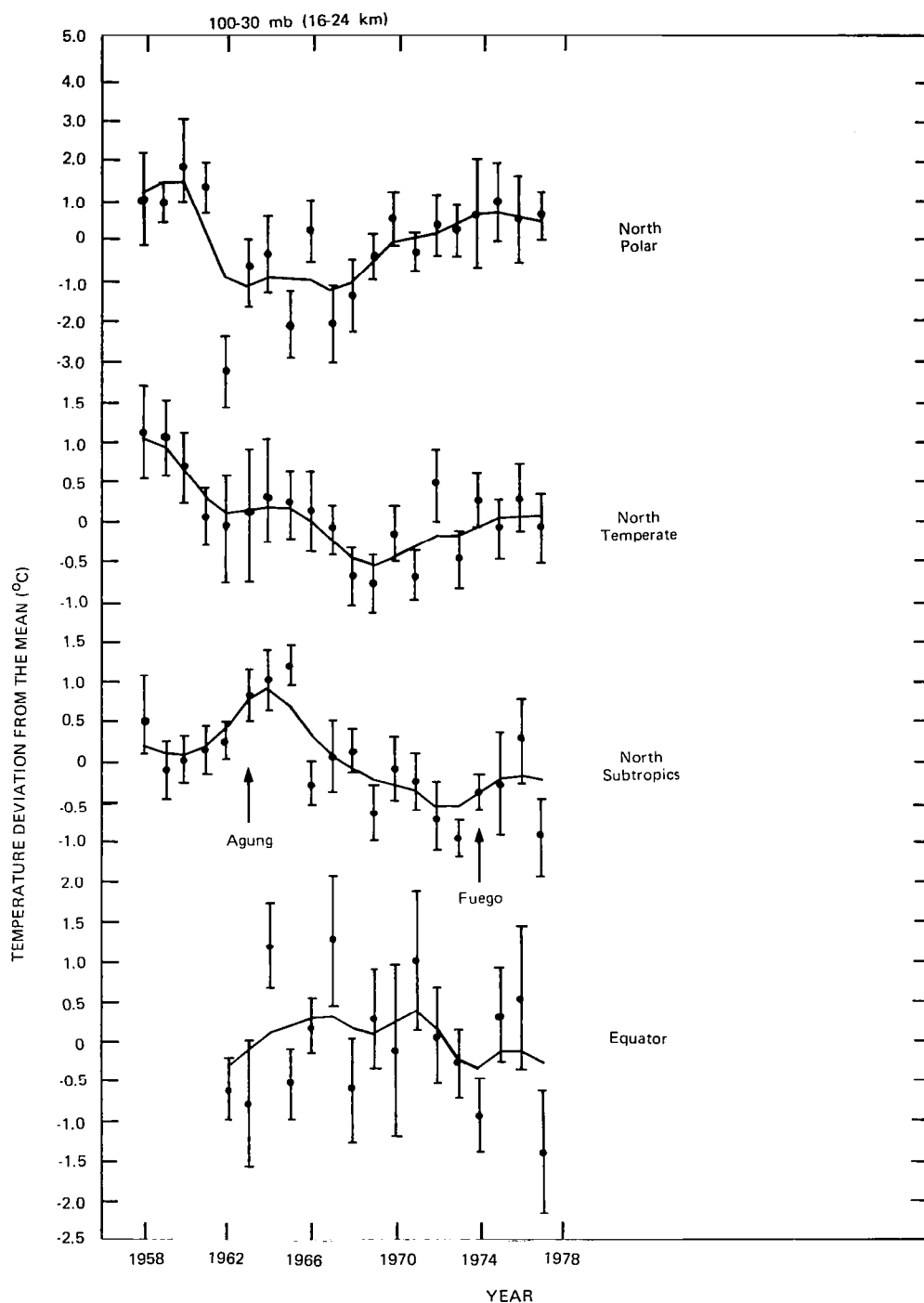


Figure 6-8. Time variation of the deviation from the long-term average air temperature for the north polar, temperate, and subtropical regions and tropics for the 100 to 30 mb (16 to 24 km) layer over the period from 1958 through 1977. Vertical bars indicate 95% confidence level. The times of major volcanic eruptions are indicated below the north subtropics curve.

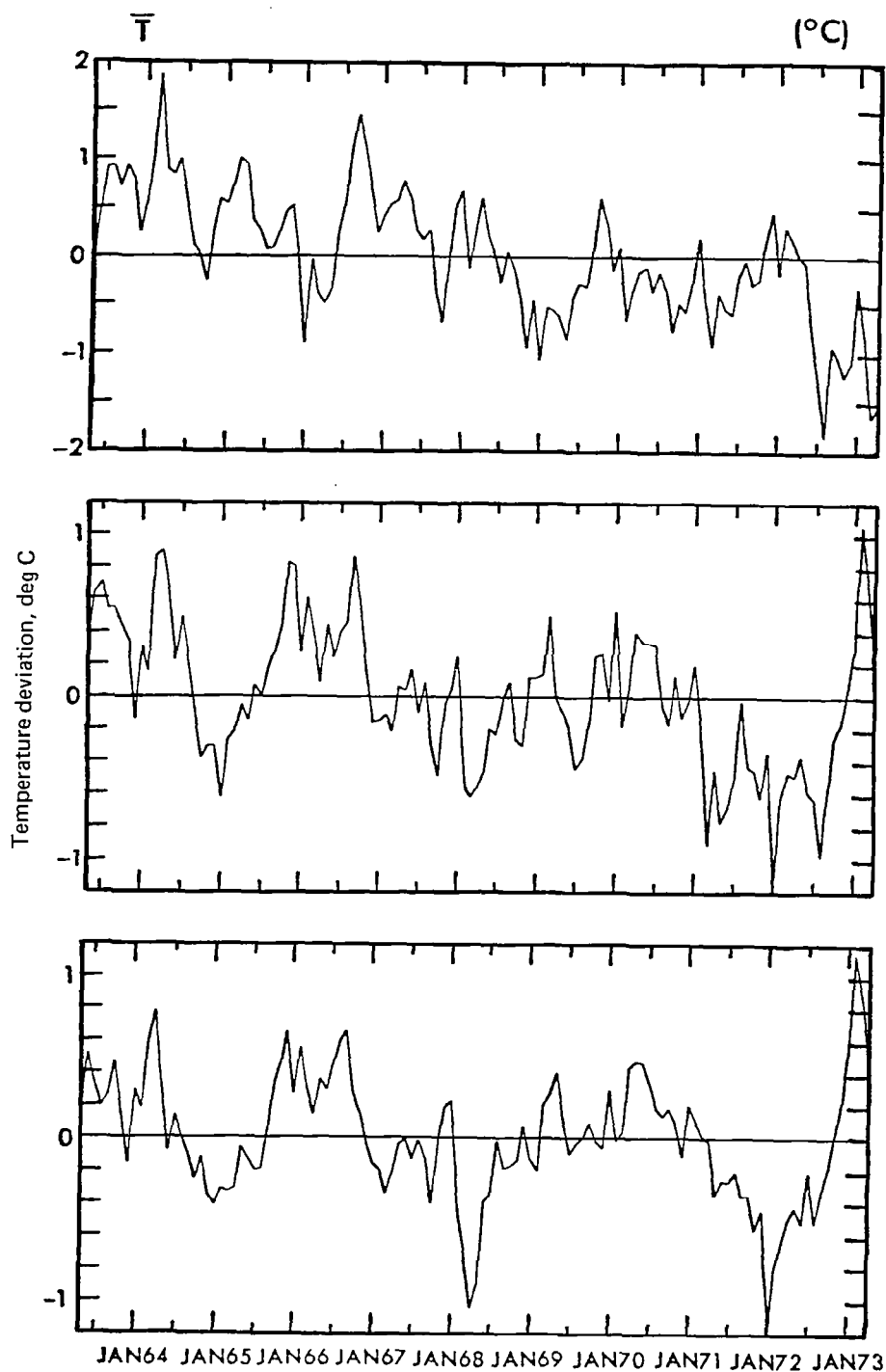


Figure 6-9. Northern Hemisphere mean monthly temperature deviation (in $^{\circ}\text{C}$) at 50 mb (top), 100 mb (middle) and 200 mb (bottom) for the 10-year period, May 1963 through April 1973. The 10-year average annual cycle has been removed.

Table 6-9
Percent Change Per Year for Various Trace Species

Species	NH [†]	SH [†]	Remarks	Reference
CF ₂ Cl ₂	11 ± 1	11 ± 1	Upper tropospheric data taken on balloon flights between 1976-1977	Goldan et al., 1979
	7.0 ± 0.4*		Weekly measurements taken at 4 stations from March 1977 to the end of 1978	Komhyr, 1979
	10		Spot measurements from 1975-1978	Singh et al., 1979
	8	8	Spot measurements from 1976-1978	Rasmussen, pvt. comm.
CFCl ₃	10 ± 2	15 ± 1.5	Upper tropospheric data taken on balloon flights between 1976-1977	Goldan et al., 1979
	8.5 ± 0.3*		Weekly measurements taken at 4 stations from March 1977 through 1978	Komhyr, 1979
	12		Spot measurements from 1975-1978	Singh et al., 1979
	9.1	8.0	Spot measurements from 1976-1978	Rasmussen, pvt. comm.
	13.2	14.6	Spot measurements from 1972-1975	Pack et al., 1977
CCl ₄	10.5	2.2	Spot measurements from 1972-1975 (Probably contamination problems in NH)	Pack et al., 1977
	2		Spot measurements from 1975-1978	Singh et al., 1979
	4		Spot measurements from 1977-1978	Penkett et al., 1979
	2	5	Spot measurements from 1976-1978	Rasmussen, pvt. comm.
CH ₃ CCl ₃	17		Spot measurements from 1975-1978	Singh et al., 1979
	5	5	Spot measurements from 1976-1978	Rasmussen, pvt. comm.
	15	17	Spot measurements from 1972-1976	Lovelock, 1977
N ₂ O	.2	0.2	(See text)	Weiss, pvt. comm.
	1 ± .5	1 ± 0.5	Upper troposphere data taken on balloon flights between 1976-1977	Goldan et al., 1979
CH ₄	0.3 ± 1		(Recalibrated) Spot measurements from 1970 and 1979	Heidt, 1979 Migeotte, 1949 Goldberg, 1951
CO ₂	0.4	0.4	Mauna Loa station measurements for 1958-1972	Keeling et. al., 1976b and 1976a.

* Indicated errors are one standard deviation, systematic errors have not been included.

† NH = Northern Hemisphere; SH = Southern Hemisphere

CF₂Cl₂ and CFCl₃

The concentration of tropospheric CF₂Cl₂, which was first measured in late 1973 (Lovelock, 1974), has been increasing. Recent trend estimates are given in table 6-9. The errors associated with these trend estimates have not always been quantified, but the rate of increase is consistent with the rate of increase of emissions (~20ppt/yr) from 1975 to 1977 (CMA, 1979). As an indication of the absolute errors in the measurements, the range of calibration errors among 16 laboratories has been found to be ±26% for CF₂Cl₂ (Rasmussen, 1978b). Consequently, trends computed from a combination of different data sets would be uncertain within these limits.

CFCl₃ has been measured in the troposphere since 1971 (Lovelock et al., 1973; Lovelock, 1974) and it is clear that the tropospheric concentration has been increasing. Recent estimates for the rate of growth are given in table 6-9. Most researchers are in general agreement with regard to the magnitude of recent increases, which seem consistent with the corresponding emissions data (about 13 ppt/yr for 1975 to 1977, CMA, 1979). The errors associated with the trend estimates of Goldan et al. (1979) and Komhyr (1979) are standard errors derived from a linear regression analysis. The true errors are larger for a variety of reasons. Calibration standards may drift over long periods of time and spatial variability (particularly large near emission sources) affects measurement results. In most cases, reliable estimates of these errors are not available, but they need to be quantified in order to validate model estimates of the fate of these species in the atmosphere. Absolute calibrations vary by ±18% (Rasmussen, 1978b).

In situ stratospheric measurements of CFCl₃ and CF₂Cl₂ date from 1973 (Heidt et al., 1975). The available measurements are fewer than in the troposphere and the natural variability larger, making accurate trend estimates much more difficult. A comparison of 1968 infrared data with data obtained in 1975 showed that both CFCl₃ and CF₂Cl₂ increased by more than a factor of 2 in the stratosphere, (Murcray et al., 1975b). However, the relative error in the August 1968 data limits the accuracy of the determination of the long-term trend. The 1968 data have a precision of only ±20%. The September 1975 results are reliable to ±5%.

CCl₄

Carbon tetrachloride was measured by Lovelock's group from 1972 to the end of 1975. The estimated trends from these early measurements, as well as more recent measurements, appear in table 6-9. These trend estimates are probably not statistically significant, due to the sparseness of data and general difficulty of measuring CCl₄ (a 9 laboratory intercomparison revealed differences of ±63%, Rasmussen, 1978b).

CH₃CCl₃

Fewer measurements for CH₃CCl₃ are available than for either CFCl₃, CF₂Cl₂ or CCl₄. The recent rate of increase of methyl chloroform has been estimated by various researchers in table 6-9. This species is more difficult to measure than the other halocarbons (in a 9 laboratory intercomparison, the range of errors was ±63% Rasmussen, 1978b). In addition, it is more difficult to maintain stable standards, and its spatial variability is larger. Thus, an accurate trend cannot be estimated at present.

N₂O

Weiss (private communication) reported preliminary results which suggest an increase of 0.5 ppb/yr between 1977 and 1979. These data were acquired at the NOAA Geophysical Monitoring for Climatic Change (GMCC) stations in the Pacific and Antarctica. Although the data base is not yet sufficient to accurately establish the trend, the rate of increase is consistent with the rise since 1961, inferred (Weiss et al., 1977) from stored samples of CO₂ and N₂O, which had been extracted from samples of Pacific air. Goldan et al. (1979)

observed an upward trend of N_2O in upper-tropospheric air samples which were obtained over Wyoming between 1977 and 1979. Their data are also too few to accurately determine the rate of increase, but their observations (3.2 ppb/yr) do not appear to be inconsistent with Weiss' measurements.

The existing background observations of N_2O represent a period too short to accurately determine a long-term trend, although three data sets suggest a slow increase. The quantification of any global change is one of the key problems in the N_2O budget, and the background studies are therefore extremely important.

CH_4

Methane observations exist from 1948 to the present. From 1948 to 1966, measurements were made of telluric absorption of solar infrared radiation (Migeotte, 1948; Goldberg, 1951; Fink et al., 1967). These data may be interpreted as showing a methane abundance of 1.5 to 1.6 ppmv, with error bounds which are hard to estimate. Equivalent width determinations are influenced by instrumental and subjective factors which make it difficult to quantitatively compare present-day and past measurements of methane infrared absorption.

Gas-chromatographic measurements of CH_4 commenced in 1968, indicating mixing ratios of 1.4 to 1.7 ppmv. Ehhalt and Heidt (unpublished work, 1979) maintained consistent calibration gases between 1970 and 1979. They report approximately 1.6 ppmv (corrected from earlier reports) for the atmospheric abundance of CH_4 in 1970, and about 1.65-1.70 ppmv in 1979.

Taken together, these data rule out a methane trend larger than $\pm 1\%$ per year, and they hint at a modest rate of increase ($\sim 0.3\%$ per year). Since CH_4 may be expected to exhibit small seasonal variations, and is known to vary geographically (Wilkniss et al., 1973; Ehhalt, 1978a), the spot measurements currently available are inappropriate for determination of whatever small trends may exist. The need for baseline measurements (with very careful verification of sampling and analysis procedures) is clear, although no such effort appears to be underway.

CO_2

One of the best documented of the anthropogenic changes to the global troposphere is the increase in concentration of carbon dioxide. For example, figure 6-10 shows the record of CO_2 data from Mauna Loa for the years 1958-1978. The station site was chosen to minimize contamination by regional and local sources (or sinks) of CO_2 , and the data were acquired using a highly stable infrared analyzer subject to periodic, precise calibrations (Keeling et al., 1976a, 1976b). This painstaking work produced accurate measurements of trends. The observations shown in figure 6-10 confirm that the atmospheric inventory is increasing presently at a rate of about 2×10^{14} molecules of carbon per year ($0.4\%/yr$). The rate of increase has itself been increasing, roughly doubling since the late 1950s.

Sulfur Compounds

Sulfur compounds have been measured in the stratosphere during the last two decades. Most of the stratospheric sulfur is present as impure sulfuric acid droplets formed largely from SO_2 injected from time to time by large volcanic eruptions. The sulfur from any given eruption remains in the stratosphere for a year or two. Maximum stratospheric sulfate concentrations have varied from about <0.01 to $3\mu\text{g}/\text{m}^3$, usually at a few kilometers above the tropopause; of course, near the erupting volcano, the sulfur concentrations have been very much higher. Long-term trends of the stratospheric sulfur content can be estimated based on the extent of volcanic activity at the present time. Details may be obtained in Cadle (1972); Cadle and Grams (1975); Cadle et al. (1976); Castleman et al. (1974); and Lamb (1970).

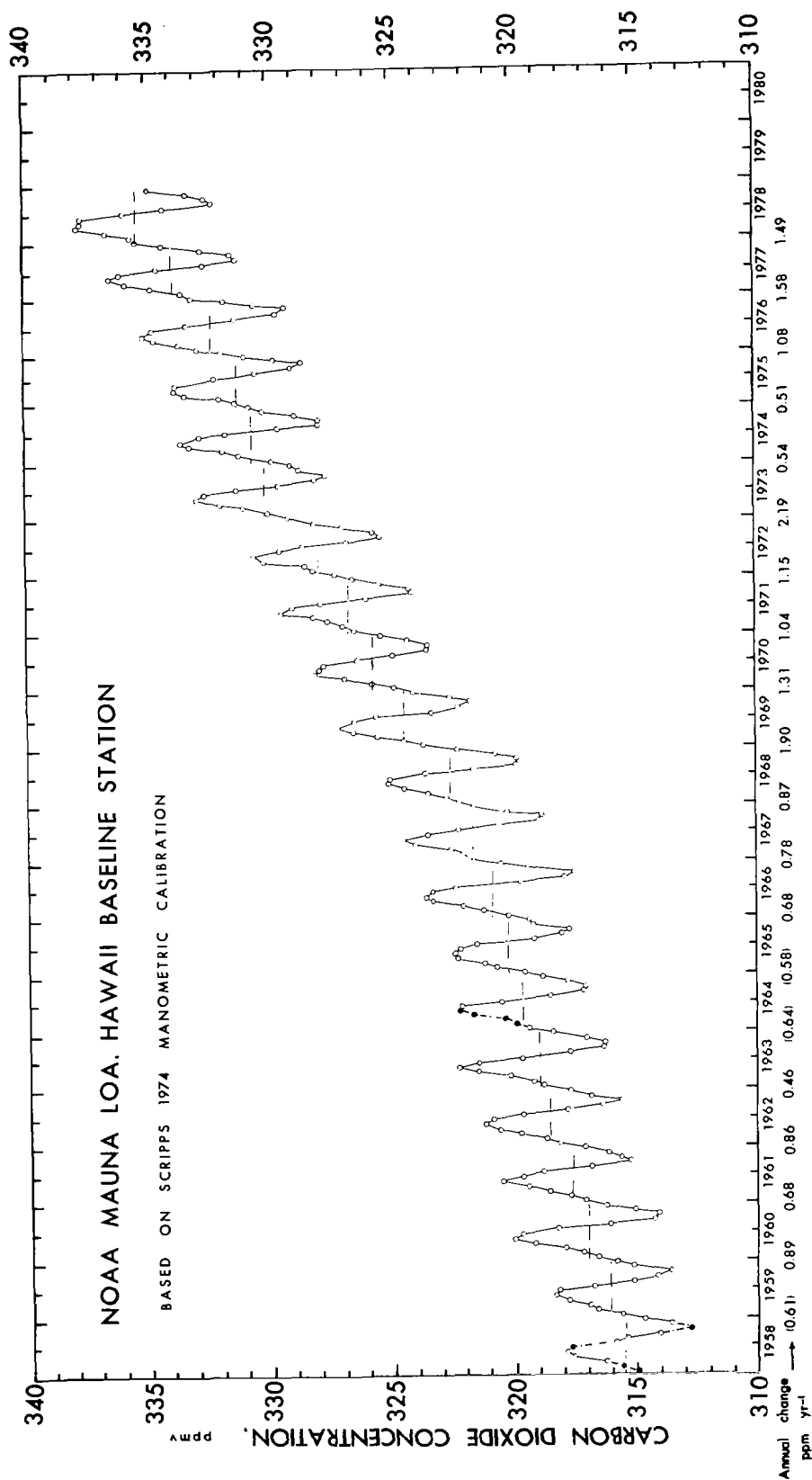


Figure 6-10. Mean monthly observed concentrations of atmospheric carbon dioxide at Mauna Loa, Hawaii (19°N, 3400 m). Data through 1976 is from Keeling (Scripps Institution of Oceanography); the remainder, calibrated against Keeling's data, is from NOAA. Solid dots are estimated values.

Discussion

The lack of good data for estimating trends in virtually all of the trace species discussed indicates a special need in this area. Several questions about the state of the atmosphere necessitate regular and careful long-term measurements of key trace chemicals. First, baseline studies are needed to provide a reference against which to assess changes in the atmospheric environment. Second, it should be clear that nature's own dynamics (e.g., biospheric fluctuations) should be observed and that several types of changes are possible: secular trends, cyclical behavior, and sudden or catastrophic shifts. The species that require monitoring are generally recognized. They are the long-lived molecules, such as CH_4 , N_2O , CF_2Cl_2 , CFCl_3 , CH_3CCl_3 and stratospheric H_2O , that decompose to yield stratospheric radicals and which are also important in the infrared energy budget.

Not so well recognized is the non-automatic character of long-term measurement programs. Absolute and reference calibration standards must be prepared, stored, cross-referenced and propagated. Sampling methods, instruments and locations must be well chosen and periodically reexamined. Instrumental drift must be guarded against and quantified, and data-reduction procedures must not be changed unduly. Finally, it must be recognized that continuity of personnel is needed. Thus, to succeed with this high priority item will require a proper mix of scientific talent, institutional or agency commitment, perserverance and innovative management.

WATER VAPOR TRENDS

Although a number of stratospheric water vapor measurements have been carried out since the middle 1940s, most have been made after 1972 using a variety of techniques. There exist only two long-term series, both using the frost point-hygrometer technique (Mastenbrook 1971, 1974a, 1974b; Murgatroyd et al., 1955; Cluley and Oliver, 1978), and a short series by Harries (1976) using the thermal emission spectroscopy technique. The systematic errors, considered reasonable, of the first technique are given as ± 8 to 10% and $\pm 20\%$ for the latter. New data on global distributions of water vapor are being collected by the Nimbus-7 SAMS and LIMS sensors.

The published measurements of Mastenbrook, made at Washington, D.C., cover the period 1964 to 1975. The British MRF aircraft measurements over Southern England cover the period 1954 and 1955 and 1972 to 1976. They were recently discontinued. Measurements were also made by Harries between 1970 and 1972 mostly over Southern England.

Thus, all measurements available for long-term analysis are made in midlatitudes (40° to 55°N). At the present time, nothing can be inferred about such trends in tropical, subtropical, and polar latitudes, nor of those occurring in the Southern Hemisphere. Whether the global water vapor concentration undergoes long-term variations is still unknown. Since the British measurements are made at or below 14 km, the following discussions are restricted to the lower stratosphere.

The observed mixing ratio as shown in figure 6-11 was lowest in 1954, 2.9 ppmv, and increased to 3.1 ppmv in 1955. The Washington measurements show an increase from 1969 to 1972/73, from 3.7 to 4.8 ppmv, and a steep decrease thereafter to 3.7 in 1975. The British measurement also shows a decrease from 5.4 ppmv in 1972 to 4.7 ppmv in 1976. Harries' measurements show an increase from 3.4 ppmv in 1970 to 4.1 ppmv in 1972.

These three independent data sets show changes larger than the measurement errors and the same general tendencies. Piecewise linear trends computed using regression analysis (Penndorf, 1978) are listed in table 6-10. Since the measurements so far indicate a nonlinear variation, linear trend computations may be

somewhat misleading. If the longer-term changes are periodic neither the amplitude nor the length of the period can be established at this time. Definitive conclusions are thwarted by the lack of long, corroborative data sets and the limited geographic coverage. The latter problem may be alleviated by the water vapor soundings from Nimbus-7, provided their results are validated.

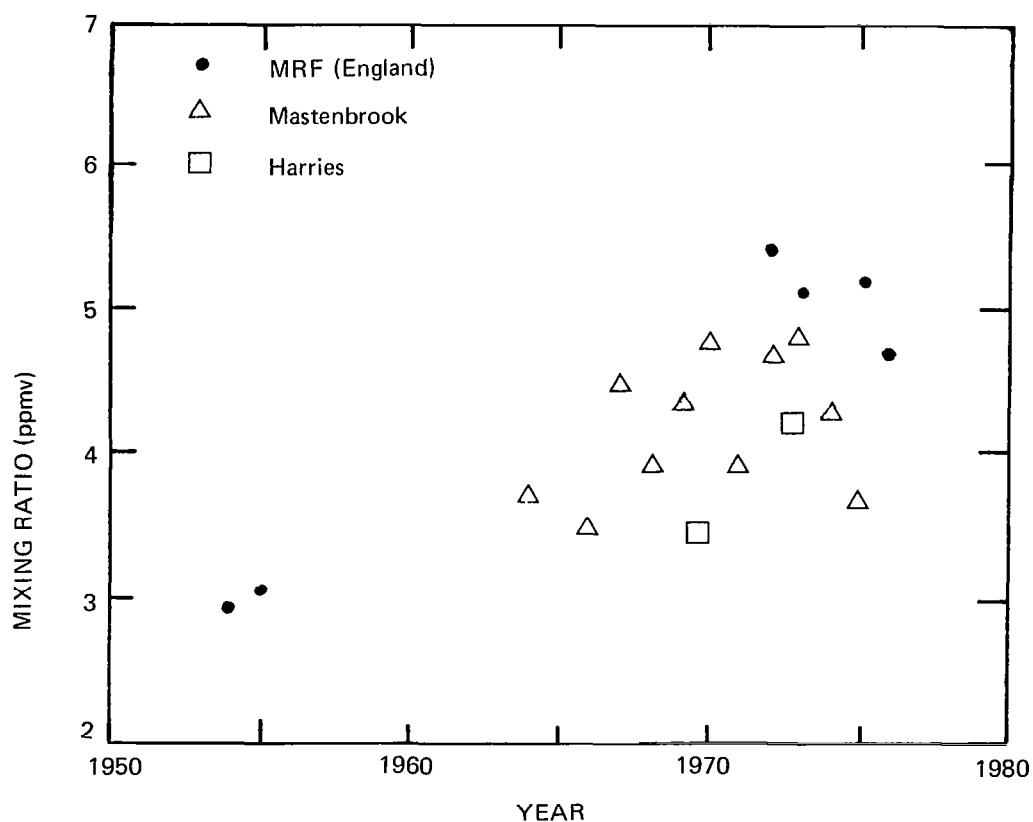


Figure 6-11. Long-term variations of annual mean water-vapor mixing ratios in the lower stratosphere in ppmv from 1954 to 1976. Notice difference between Washington, D. C. and England.

Table 6-10
Long-Term Trends in Water Vapor Mixing Ratios in the
Lower Stratosphere ($\approx 14 - 15$ km, after Penndorf, 1978)

Source of Data	Period	Trend (ppmv/decade)	Remarks
Mastenbrook	1964-73	$+ 1.2 \pm 0.8$	Based on annual mean values
Mastenbrook	1972-75	$- 3.5 \pm 0.9$	
MRF, England	1954-55	$+ 1.9$	*Based on raw data; seasonal variation is taken out
MRF, England	1972-76	$- 1.9 \pm 0.7$	

*Trend from 2 years of data only.

TREND DETECTABILITY - TOTAL OZONE

FORMULATION OF THE PROBLEM

To evaluate our ability to detect anthropogenic trends, specifically CFM-induced trends, we consider in this section the global amount of total ozone as deduced from the available observations. In the next section the analysis problem for upper stratospheric ozone is discussed. Strictly speaking any quantification of this ability must be related to the method and the data sets used in estimating a trend, and to the nature of modelers' predicted trends. That is, detectability thresholds are influenced by the statistical methodology, the quality of the data used, including their spatial and temporal distributions, and the uncertainty in the predicted trend.

Consider the situation where a long meandering time series is contained in a meteorological data set. Without having any hypothesized trend, one can readily find 10-year periods in which there appears to be a trend relative to the preceding record, and statistical tests would probably prove the trend to be *statistically* significant. One could then formulate hypotheses regarding the cause, but trend detectability has little meaning in such a context.

On the other hand, a significant trend may begin at some time, T , and go undetected for many years because there were no reasons to suspect a change at time T . Thus, the threshold for detecting a trend beginning at a specified time T , is quite different from that if no time were specified. In this discussion, trend detection thresholds will be based on our capability to detect a specified trend.

When attempting to detect a trend due to one specified cause—such as a CFM-induced trend—the envelope of uncertainty related to an estimated trend in the data must be viewed relative to the envelope of uncertainty about the predicted trend. If these envelopes diverge, then eventually a time will come when the data begin to refute the predicted trends. Both of these uncertainty envelopes must be used in any assessment of the plausibility of predicted trends.

At the present time, global ozone determinations are derived from an ensemble of instruments, where spatial distribution is not optimized, and whose calibration and quality of data varies over time and from location to location.

The data base under examination for trends thus contains several types of errors which can affect the accuracy of a trend estimate. Let x represent an ozone variable, either total column ozone or the ozone concentration at some level. Now let Δx be the estimated change in ozone over a 10-year period based on the best statistical methods applied to a data set extending back approximately 20 years prior to that period. This estimated change is related to the true change in global ozone over that period, Δx_{true} , as follows:

$$\Delta x_{\text{meas}} = \Delta x_{\text{true}} + \Delta x_{\text{stat}} + \Delta x_{\text{spat}} + \Delta x_{\text{inst}}$$

The term Δx_{stat} is a statistical error resulting from random noise and systematic very short-term time dependencies in the data base, neither of which are removed by the statistical (averaging) process. The term Δx_{spat} is a spatial error which results from the fact that a trend in the integrated global ozone is being estimated by measurements made at discrete locations*. A large amount of spatial variability exists in the ozone. Some of this is related to large-scale waves in the mean pressure field whose time variation is relatively slow. A 10-year period may not be long enough for this effect to average out at a discrete set of locations. The third error, Δx_{inst} , results from any trends in the ensemble of instrument calibrations and/or measurement accuracy which would appear as a trend in the ozone data, e.g., an instrument drift.

Fixed biases, such as errors in standardized absorption coefficients, do not affect trend estimates. Any random error whose mean over a sufficiently long data record is essentially zero is presumably included as a part of the statistical error. Thus, Δx_{spat} and Δx_{inst} are related to measurement errors which themselves may show trends over 10 years. These trends, appearing in Δx_{meas} , would either be mistaken for an ozone trend or would cancel an ozone trend depending on their direction.

A measure of our ability to detect any real change in global ozone, whether man-made or natural, over 10 years is given by the mean square error:

$$E [\Delta x_{\text{meas}} - \Delta x_{\text{true}}]^2 = \sigma_{\text{stat}}^2 + \sigma_{\text{spat}}^2 + \sigma_{\text{inst}}^2$$

where $E[]$ indicates an expected value.

The charge is to determine our ability to detect a CFM-induced trend. To do this, one must distinguish among different components of a true change. The true change may be a result of several causes; i.e.,

$$\Delta x_{\text{true}} = \Delta x_{\text{nat}} + \Delta x_{\text{CFM}} + \Delta x_{\text{other}}$$

where Δx_{nat} is made up of low-frequency natural variations in global ozone due to meteorological and possibly extra-terrestrial causes, and $\Delta x_{\text{CFM}} + \Delta x_{\text{other}}$ includes CFM related changes and all other man-made effects. A measure of our error in isolating a CFM-related trend would be:

$$\Delta x_{\text{meas}} - \Delta x_{\text{CFM}} = \Delta x_{\text{nat}} + \Delta x_{\text{other}} + \Delta x_{\text{stat}} + \Delta x_{\text{spat}} + \Delta x_{\text{inst}}$$

whose variance is given by:

$$E [\Delta x_{\text{meas}} - \Delta x_{\text{CFM}}]^2 = \sigma_{\text{nat}}^2 + \sigma_{\text{other}}^2 + \sigma_{\text{stat}}^2 + \sigma_{\text{spat}}^2 + \sigma_{\text{inst}}^2$$

The variances associated with the statistical methodology (σ_{stat}^2), the spatial sampling (σ_{spat}^2) and the instrument (σ_{inst}^2) can all be reduced by improvements in the measurement accuracy, the sampling density and statistical methods. In fact, it is at least theoretically possible to reduce these errors to such an extent that they are insignificant compared to $\sigma_{\text{nat}}^2 + \sigma_{\text{other}}^2$. The σ_{nat}^2 variance can be reduced somewhat

*An analogous error arises from the bias involving discrete temporal observations.

with longer data records that allow some of the systematic low-frequency natural variations to be accounted for in the statistical models. For example, possible systematic solar cycle effects may be removed from σ_{nat}^2 by having a sufficient number of cycles in the data. However, very long-period meteorological effects would still remain.

A NASA-sponsored Symposium on Ozone Trend Detectability (NASA, 1977) was held to examine the various error sources and to assess their impact on the methods used to estimate ozone trends. At that time, the nature of errors was discussed but a quantitative estimate of their magnitudes was not made. Since then, each of the sources of error has been at least partially reviewed, and estimates of their relative magnitudes have been made. A discussion of each variance component is contained in the following section. *It should be emphasized that the values given for the individual standard errors in estimating the threshold for trend detection are, for the most part, quite soft.* The continuation of satellite and ground-based observations, along with additional research on observed ozone variability, will certainly reduce the uncertainty of these values.

STATISTICAL ESTIMATION ERRORS

In this section methods are described that have been applied to the total ozone data discussed earlier to detect slow changes in the global mean which might be expected if CFMs do, in fact, destroy ozone. Because M-83 observations are subject to relatively large errors, and satellite data over extended periods of time have not been readily available, these methods have been applied to the network of Dobson data.

If the monthly ozone measurements at a station have some known patterns of variation, they can be filtered out. For example, seasonal effects can be removed by subtracting monthly constants or taking twelve month differences. A linear trend beginning at some specified time could be similarly removed if its slope were known. If the slope were not known, one could be estimated to remove the trend most effectively. For example, a simple least squares fit could be used if the monthly values were uncorrelated and of equal variance. This is not so here. Adjacent observations are correlated and generally have different variances. Thus, to remove the seasonal effects and to estimate trends, one must at the same time determine the correlation and variance structure.

If, in fact, all the trends have been removed, then residuals will resemble data generated by a stationary random process. These are the data analogs of colored noise, and they may be specified either by their spectral or autocorrelational structure. To get finite parameter models, it is natural to fit autoregressive moving average (ARMA) models. If trends are regarded as signals, we are trying to detect signals in a noise environment. It is clear that the trends sought are low-frequency signals, which may be confused with low-frequency noise in the short data series available.

Hill and Sheldon (1975) began by fitting an ARMA model to the longest available (monthly) series, that measured at Arosa from 1932 to 1970, and examined its fit to subsequent data through 1974 to see if there were any signs of lack of fit. The series was seasonally filtered. Pagano and Parzen (1975) fitted autoregressive models to the data before 1970 from 35 stations, and then looked for lack of fit with recent data.

Hill et al. (1977) rephrased the CFM detection problem as follows: (1) find a number of globally representative stations with long and essentially independent records, (2) assume that the CFM effect was trivial before 1970 (now known to be incorrect), so that earlier records should show only seasonal variations and later records should also have a linear trend, (3) fit an ARMA model to twelve-month differences of the data from each of the stations to 1970, (4) use these models to make the most efficient slope estimates from the data in the 70s for each station, and (5) average the station slope estimates and compare their average slope with its estimated variance. They used the nine stations at Edmonton, Arosa, Tateno, Mauna Loa, Huan-cayo, Kodaikanal, MacQuarie Island, Buenos Aires, and Aspendale.

No statistically significant trend was found in the data from any station, individually, nor in the 9-station average. Their estimated change in ozone for the 6 years, 1970 thru 1975, averaged over 9 stations, was $-.47$ matm-cm, which is $-.15\%$ of the global average of 307 matm-cm. Individual station trends ranged from $+9.7$ matm-cm ($+3\%$ per 6 years) at MacQuarie Island to -13.3 matm-cm (-4% per 6 years) at Kodaikanal.

G. Watson made similar analyses using seasonally filtered data and different fitting procedures that allowed all the data to be used in steps 3 and 4 above. Watson's technique (National Academy of Sciences, 1979) produced a standard error of the trend which was approximately 50% lower than that of Hill et al. (1977). Assuming that parametric time series models are fitted to 9 stations and their individual trends averaged to provide *global* trends, the best estimate of σ_{stat} ranges from .4 to .8% per decade, the larger value being that of Hill, et al. A value of .6% will be used in the computation of thresholds, although uncertainties in this value clearly exist due to the methodology.

INSTRUMENT ERRORS

A discussion of error sources which are associated with the Dobson instrument has been given earlier. Of these sources, those affecting a trend estimate (i.e., possible trending errors) are listed in table 6-11 (Komhyr, personal communication). To combine these error ranges into an estimate of the total instrument error,

Table 6-11
Dobson Measurement Errors which Affect the Observed
Change Over 10 Years at a Single Station

Source of Error	Range (Percent)	Distribution About Zero	Standard Deviation (Percent)
Trends in stratospheric temperature affecting absorption coefficients	± 0.5	uniform	0.3
Pollution trends including aerosols, tropospheric ozone, and other gases, which are correlated at a particular station	± 4	Normal = sum of three uniform variates	2.0
Cloudiness changes	± 1	uniform	0.6
Calibration drifts	± 1	prob ($\pm 3\%$) = 0.1 prob ($\bar{0}$) = 0.9	0.9
Solar spectral variation	± 0.3	uniform	0.2
Combined single station rms error = 2.30			
rms error for 9-station average: *Assuming independence			.77
Assuming correlated solar effect			.79
Value used			$\sigma_{\text{inst}} = 0.8$

*Solar effect assumed same at all stations, other errors independent.

assumptions regarding the distribution of errors within this range were made. Errors were assumed not normally distributed, an assumption which gives added weight (probability) to errors near 0, but instead were assumed to have a uniform distribution within the given ranges. The one exception to this was the error due to a calibration drift, in which case it was estimated that for 90% of the stations this error is negligible, whereas for 10% a drift of $\pm 3\%$ is present. The sum of uniformly distributed errors still tends toward a normal or Gaussian distribution whose mean is, in this case, zero, and whose variance is the sum of the variances, assuming independence. The standard error resulting from instrument-related sources when estimating the trend at a single station is computed as 2.30%. Assuming that a global trend is estimated by averaging the 10-year trends at 9 stations, then its standard error is one-third ($\sqrt{1/9}$) that at a single station. Thus, the value of σ_{inst} is estimated to be 0.77%. This may be somewhat underestimated since the errors at all stations are not totally uncorrelated. If one takes the extra-terrestrial effect to be perfectly correlated at all 9 stations and all other errors to be uncorrelated, then the standard error associated with Dobson observations at the 9 stations is $\sigma_{\text{inst}} = 0.79\%$. A value of 0.8% will be used in the calculations for trend detectability thresholds.

SPATIAL SAMPLING ERRORS

Long-wave pressure patterns (troughs and ridges) often persist in their spatial distributions for several years, possibly changing gradually, or they can change abruptly. Ozone concentrations are correlated (negatively) to these pressures. Thus, a sudden or gradual change in the pressure distribution could result in an ozone trend at the monitoring stations even when there is no change in the ozone integrated over the globe. In addition, long-term variation in observing conditions, such as would be associated with climatic variations of cloudiness, could incorrectly affect *observed* trends. Both spatial and temporal observational biases would be minimized with use of a long-period satellite total ozone monitoring system.

In a study on the use of Dobson station observations near 50°N latitude to provide an estimate of the average total ozone over the entire 50° latitude zone (Miller et al., 1979), it was suggested that an error of as much as $\pm 4\%$ could occur in the 10-year trend estimate.

Extrapolating this to the entire Dobson network, these errors would be reduced somewhat due to the decreased amplitude of long-wave patterns at lower latitudes. The standard deviation associated with these spatial sampling errors in a 10-year global difference is estimated to be between 1 and 2%. This should be added to an error associated with lack of data over the polar regions, an error which may, in fact, be random but will not be averaged out over short time intervals. This error is estimated to be approximately 0.3%. Assuming the first error is 1.5%, the rms spatial sampling error is therefore $\sigma_{\text{spat}} = 1.53\% \sim 1.5\%$.

LONG-TERM NATURAL TRENDS

The Dobson data do not extend over a sufficiently long period to remove long-term natural trends. On the basis of such low-frequency behavior in other geophysical and meteorological records, it is estimated that such natural trends may cause errors between 1 and 3% over a 10-year period. A value of 2% will be used for σ_{nat} . This estimate can be reduced slightly if solar cycle influences are present in this low frequency behavior.

OTHER ANTHROPOGENIC TRENDS

Chemical modelers estimate that standard errors of approximately 1% should be included to cover other anthropogenic trends, not related to CFM release, which might result from other chemicals introduced into the stratosphere. The standard errors estimated are given in table 6-12. Due to the unaccounted changes in the concentration of tropospheric and stratospheric chemical species, there are likely to be systematic trends in the ozone data of $\pm 2\%$ (2σ) in a 10-year period. Past trends and the expected future changes in CO_2 , N_2O ,

CH_3CCl_3 , CO, H_2O and others all lead to estimated changes in the ozone concentration. It is difficult to estimate the exact amount of possible systematic bias introduced into the ozone data. However, current understanding of atmospheric chemistry and the sensitivity of ozone to individual changes in the concentration of these chemical species would indicate the above estimate to be reasonable and conservative.

Table 6-12
Standard Errors in Estimating Global Changes in Ozone

Symbol	Cause	Value (Percent)	Comment
σ_{stat}	Statistical methodology, random errors and unmodeled short-term time dependencies	0.6	Based on time series analysis of 9 Dobson stations
σ_{inst}	Possible trending errors in Dobson instruments	0.8	Assuming 9-station average with correlated error due to solar effects
σ_{spat}	Spatial sampling	1.5	Extrapolated from bias seen at 50°N latitude
σ_{nat}	Natural long-term variation in global ozone	2.0	Estimated to range between 1 and 3 percent
σ_{other}	Other possible anthropogenic changes	1.0	Best guess of modelers

ESTIMATING THRESHOLDS OF TREND DETECTABILITY

There are three thresholds that can be identified. A threshold for detecting a real change in total ozone after allowing for statistical, instrumental and spatial errors is suggested by $E[(\Delta x_{\text{meas}} - \Delta x_{\text{true}})^2]$. Substituting $\sigma_{\text{stat}} = 0.6$, $\sigma_{\text{inst}} = 0.8$ and $\sigma_{\text{spat}} = 1.5$ into the equation above, one has

$$E[(\Delta x_{\text{meas}} - \Delta x_{\text{true}})^2] = 3.25 = (1.8)^2$$

The standard error is 1.8%, and 2 standard errors representing a 95% confidence interval is $\pm 3.6\%$. Thus, if an observed global change in ozone over 10 years exceeds 3.6%, it may be judged as a true change and not attributable to statistical errors, possible instrument errors or spatial biases. It would be anomalous in the sense that it is not consistent with the behavior of the ozone data prior to that 10-year period.

The question of whether a change is CFM-related or otherwise anthropogenic will require an even higher threshold. Allowing for a possible low-frequency natural change, one has

$$E[(\Delta x_{\text{meas}} - \Delta x_{\text{anthr}})^2] = \sigma_{\text{nat}}^2 + (1.8)^2 = 7.24 = (2.69)^2$$

where $\Delta x_{\text{anthr}} = \Delta x_{\text{CFM}} + \Delta x_{\text{other}}$. The standard error is 2.69%, and the threshold for detectability becomes 5.4%. An observed trend exceeding this threshold may be suspected as anthropogenic in that it is no longer within the range of natural low-frequency variations.

To further conclude that an observed anthropogenic trend is CFM-related, one must account for an estimated 1% standard error due to other chemical species affecting the ozone. This increases the standard error to 2.87% and the threshold to 5.74%. It appears that an observed 10-year global trend must exceed approximately 6%, or 18 matm-cm, before it can be surmised that the CFMs are implicated. The 3 thresholds just discussed are summarized in table 6-13.

Table 6-13
Thresholds for Detecting Changes in Ozone Using Best
Statistical Methods and Dobson Network Data

Threshold*	Purpose
Percent change globally in 10 years	
±1.2	For detecting any net change or trend in Dobson data sets after allowing for uncertainty due to statistical error (i.e., noise in data) and methodology.
±3.6	For detecting a true change in global average total ozone after allowing for uncertainty due to statistical error, instrument drifts and spatial sampling biases.
±5.4	For detecting an anthropogenic effect after making additional allowance for possible low-frequency natural variations.
±5.7	For detecting a CFM effect after allowing for errors above plus possible variations due to other anthropogenic changes.

*95% confidence (2σ) level

Conclusions associated with these thresholds, viewed without the uncertainty limits associated with CFM-related depletion predictions, are applicable only to situations where measured trends exceed the thresholds. If Δx_{meas} is below the highest threshold, in the case of $\pm 6\%$, no conclusions can be drawn as to whether or

not predictions are valid. This conclusion would have to be reached on the basis of both uncertainty envelopes—those of the estimate Δx_{meas} and of the predictions. As long as Δx_{meas} is within both envelopes, the CFM-related depletion is still a viable hypothesis.

Δx_{meas} and its threshold can be used to test hypothesized values for ozone depletion due to CFMs. For example, if a hypothesized depletion is $D\%$ (say 10%) over a decade, it can be rejected if D does not fall within $\Delta x_{\text{meas}} \pm \text{threshold}$. In this way, certain hypothesized upper limits of depletion may be ruled out by the empirical trend analysis.

Table 6-14 gives a corresponding set of potential thresholds if one assumes that data from a satellite ozone monitoring system are available. The errors resulting from the spatially poor distribution of Dobson stations should be reduced by a factor of five (from 1.5 to 0.3). It is also assumed that the Dobson records are carefully corrected for errors such as instrument drifts and calibration changes. Errors due to other anthropogenic trends are assumed to be reduced from 1.0 to .7%. The resulting thresholds are 1.6%, 4.3% and 4.5%. The σ_{nat}^2 was not changed because the length of data records was assumed to be the same. The latter two assume that no progress can be made in understanding and reducing natural trend biases. However, it should be pointed out that the inclusion and analysis of other meteorological data sets may aid in quantifying and reducing the long-term natural trend biases.

Table 6-14
Potential Thresholds for a Projected
Satellite Global Ozone Monitoring Program
Integrated with Calibrated Dobson Network

Potential Threshold*	Purpose
± 1.6	For detecting a real change after accounting for statistical error (0.6), instrument error (0.4) and spatial error (0.3). Improvements in spatial biases through use of satellite data and correlated pressure measurements.
± 4.3	For detecting an anthropogenic change after accounting for natural variation (2.0).
± 4.5	For detecting a CFM effect after accounting for other chemical effects (0.7). Some improvement in this error can be achieved by measurements of other species in stratosphere.

*95% confidence (2σ) level

TREND DETECTION - VERTICAL DISTRIBUTION

The numerical models of ozone depletion due to CFMs and other anthropogenic influences predict generally larger and more rapid fractional depletions, by a factor of 3, in the upper stratosphere around the 40 km level than in total ozone. It is, therefore, arguable that monitoring ozone concentrations at these heights in the atmosphere may lead to earlier and more reliable detection of statistically significant effects which may be due to these influences.

At 40 km altitude, appreciable trends in ozone concentration due to non-anthropogenic causes may be expected due to two main sources. Trends in temperature at this level will affect the ozone concentration through the photochemistry and could amount to $\sigma_T = 2\%$ per decade if the temperature variation and its effect on ozone are unknown. Possible variations in the solar spectrum might lead to an additional trend in ozone of about $\sigma_S = \pm 1\%$ per decade. Trends in the strength of the atmospheric transport, on the other hand, will not lead to appreciable trends in ozone concentration at these levels because the ozone is close to photochemical steady-state (except in the winter polar regions which have a small area relative to the sunlit atmosphere).

At 30 km altitude, where data are available from the existing balloon-borne ozonesonde network, the possible trend in ozone which would be induced by a natural trend in temperature is of the order of $\pm 0.5\%$. The trend due to a changing solar spectrum at 30 km will also be smaller than at 40 km and is put at $\pm 0.5\%$. However, the predicted fluorocarbon effect on ozone is also reduced to one half of that at 40 km.

These and other uncertainties in the estimation of decadal trends in ozone at 30 km altitude by balloon-borne ozonesondes and at 40 km altitude by rocketsondes, the Umkehr method and satellite methods, respectively, are summarized in table 6-15.

Balloon-borne ozone sensors at a few locations in Western Europe since 1966, the U.S. for a few years, at four stations in Canada, one in Australia since 1965, and more recently in India and Japan, and one station in Antarctica give some data up to altitudes of about 30 km. Of these, only the European and Canadian networks and the Australian station have records long enough to establish a useful data base at this time. These records were obtained with Brewer-Mast ozonesondes, with data adjusted to agree with nearby Dobson instrument total ozone values and subject to the errors discussed earlier.

While statistically significant trends were reported in ozone concentrations at 30 km and above at Aspendale in Australia (Pittock, 1974, 1977a), such trends by themselves can in no way be considered representative of hemispheric or global averages at these levels. If a sufficiently detailed global analysis of the temperature and/or pressure-height or wind fields existed at these heights over the data period, such trends could be interpreted in a climatological context so as to be possibly indicative of a more general picture. Available meteorological data may be somewhat inadequate for such a purpose, although less so over Europe and North America.

Similar problems of lack of geographical representativeness occur with the rocketsonde and Umkehr methods. Estimates for the uncertainties in decadal trend determinations by each method is given as σ_G in table 6-15.

At lower altitudes, the Umkehr method suffers from another problem of non-representativeness when used for ozone monitoring. This is due to the fact that Umkehr measurements cannot be made under thick or highly variable cloud conditions. Since ozone content in the lower stratosphere is generally positively correlated with cloudiness this leads to a systematic bias towards low ozone content in these layers. According to

Table 6-15
Standard Error Estimates, σ , of the Estimated Decadal Trend in Ozone
Concentration at the Indicated Heights for the Existing
Balloon- and Rocket-Borne Ozone-sonde Data Sets, the
Existing Umkehr Network Data, and the Projected
Satellite Global Ozone Monitoring Program

Standard Error in Trend, 1% (per decade)	Balloon Ozone- sonde at 30 km	Rocket Ozone- sonde at 40 km	Umkehr method at 40 km	Satellite at 40 km
σ_T	0.5	2	2	2
σ_S	0.5	NA	1	1
σ_G	5	5	5	0.5
σ_{stat}	3	7.5 @1km resolution	5 @ 15 km resolution	0.1 @ 15 km resolution
σ_A	0.1	0.1	2	0.2
σ_E	1	NA	NA	NA
σ_C	1	NA	1	1
σ_{rms}	6.0	9.2	7.8	2.5

σ_T is the standard error estimate due to non-anthropogenic trends in temperature effects on measurements

σ_S is that due to effects on data of possible variations in the solar spectrum

σ_G is that due to lack of geographical representativeness

σ_{stat} is that due to random errors in individual measurements and short time-scale variations (the "white-noise" problem)

σ_A is that due to a trend in aerosol content

σ_E is that due to extrapolation to the top of the atmosphere in balloon soundings

σ_C is that due to drift in absolute calibration

σ_{rms} is the overall uncertainty estimate

NA indicates "not applicable"

Pittock (1970), this effect causes underestimates of average ozone content at one midlatitude station (Aspendale, 38°S) around 10 to 15 km altitude of 20% or more. This can vary from year-to-year and could seriously affect trend estimates at these levels.

At the 40 km level, the ozone is close to photochemical steady-state. The geographical bias in the observing network enters here because of the geographical variations of temperature at this level, which will affect the photochemical equilibrium concentrations. In the satellite case the only representativeness problem concerns the absence of observations in the polar night. This may contribute $\pm 0.5\%$ to the uncertainty in the trend over a decade.

The white noise problem arises from random errors in individual measurements and short time-scale variations. This problem is reduced in cumulative effect on the trend estimates by more frequent observations, and the best current estimate of its magnitude for each method is given by σ_{stat} in table 6-15. These estimates are based on an assumed frequency of five balloon soundings per month, one rocket sounding per month, and 15 Umkehr measurements per month. The σ_{stat} values have been reduced on the basis of an assumed five independent pieces of information per time interval from the existing balloon-sonde network, only one from the existing rocket-sounding program, and five from the Umkehr observation network. This term would be significantly reduced by an increase in the number of stations and frequency of observations. A small increase in the rocketsonde network to four or five stations would render the rocketsonde network competitive with the existing Umkehr network, particularly as it has better vertical resolution. In the case of satellite observations, time series of global mean data suggest that σ_{stat} will be much smaller, of the order of 0.2% per decade.

A trend in the aerosol content in the stratosphere may cause a minor error in the Umkehr method decadal trend estimates, σ_A , of $\pm 2\%$, but in the event of a major volcanic eruption this effect would be larger unless allowance were made for the aerosols in estimating the ozone trend.

In the case of the balloon-borne ozonesondes, an uncertainty, σ_E of about $\pm 1\%$ in the decadal trend may be caused by the need to extrapolate from the maximum height reached by the sounding to the top of the atmosphere. Unknown trends above the maximum balloon height could cause false contributions to the estimated trend below via the procedure which corrects the data to agree with the total ozone amount measured by the Dobson spectrophotometer.

Finally, there is a problem of calibration drift σ_C . The balloon and the Umkehr methods each rely on the calibration of the Dobson spectrophotometer network, which was discussed in the previous section. This is subject to a possible decadal drift of about $\pm 1\%$. In the case of the projected satellite monitoring system there is, as part of *The National Plan for Ozone Monitoring and Early Detection of Stratospheric Change*, a requirement for a ground-based calibration/verification program using rocket and balloon-borne ozonesondes to achieve a yearly 2σ precision of $\pm 5\%$. This goal implies an error due to drift in an estimated trend of about $\pm 1\%$ per decade.

Summing up the various contributions to the overall uncertainty, σ_{rms} , in decadal trend estimates, using the root mean square method, it is found that the projected monitoring system should yield trend estimates good within one standard error of about $\pm 2.5\%$ per decade, or a 95% confidence limit of $\pm 5\%$. This would only be achieved, however, if the satellite calibration stability were ascertained by careful and repeated rocket ozonesonde validation flights.

The existing balloonsonde network should achieve a standard error of the global decadal trend estimate of about $\pm 5\%$ at the 30 km level. At the 40 km level, where anthropogenic-induced trends may be larger, both the rocketsonde and Umkehr network presently may achieve an accuracy of about ± 8 or 9% in the decadal trend. In both cases more observations at more stations could significantly lower these uncertainties.

The present estimated uncertainties are based on general knowledge of the methods and available data, but not on an exhaustive data analysis. They are given as general guides to problems and capabilities and subject to possible revision in the light of further analysis.

The nomenclature used in this section is not completely identical to that used in the previous section. For purposes of comparison, a combination of σ_A and σ_E and σ_C is equivalent to σ_{inst} , σ_G corresponds to σ_{spat} , and a combination of σ_T and σ_S is equivalent to σ_{nat} , and σ_{other} has not been estimated, but modeling of other possible anthropogenic effects suggests it would be larger at 30 or 40 km altitude than in the case of the total ozone column.

The final figures, σ_{rms} , in the table 6-15, thus correspond to 1σ threshold limits equivalent to the third limit in table 6-13 and the second limit in table 6-14. Thus, the potential threshold at the 95% confidence level (2σ) for the projected global ozone monitoring program to detect a real 10-year trend in ozone concentration at 40 km, is about 5.0% per decade. Given that the expected anthropogenic trend at the 40 km level is three times larger than that in the total ozone column amount (see e.g., Chapter 7), this is perhaps the most hopeful approach to early detection of anthropogenic effects. Increased investments in expanded networks of balloon- or rocket-borne ozonesondes or in Umkehr observations are also attractive possibilities.

SUMMARY

The prime purpose of this chapter was to arrive at some estimate of a threshold, or likely value, of our ability to detect a projected chlorofluoromethane (CFM) induced decrease of total ozone and the ozone concentration in the middle and upper stratosphere. In this chapter we have discussed: what is known of the ozone variations; how certain we are of this information; what can be done to improve the data bank through future observations; and what can be done to effect a reduction of the uncertainty of the information. The problem of ozone trend detectability was discussed earlier in the section on Measurement and Analysis of Ozone Variation in NASA RP-1010. This chapter differs from the past report in that it:

- Includes estimates of various observation errors
- Discusses observed trends in other atmospheric parameters known to influence the long period changes in ozone (e.g., other trace species, stratospheric temperature, etc.)
- Makes use of additional observed data (particularly satellite data) in analysis of past changes
- Provides estimates of the thresholds of trend detectability of observed total ozone and ozone concentration in the stratosphere.

Estimates of variations of the global amount of total ozone during the past 20 years, derived almost exclusively from the ground based observations provided by the Dobson network, show changes of the order of a few percent, the most significant of which was the unexplained increase of about 4 percent in global total ozone (largely Northern Hemisphere) during the 10-year period 1961 to 1970. Data derived from satellite observations (BUV) indicate a decrease of total ozone in the period 1970-72 (~ 2.5 percent) but no strong variation for the years 1972-77. Although there is some uncertainty in these estimated variations, it is important to note that, in general, the pattern of total ozone changes derived from satellite and ground based data for common periods of observations are quite consistent and both data sets indicate that Northern Hemisphere variations dominate the global pattern.

Observations of stratospheric ozone concentrations are still too sparse to allow for definitive statements concerning past long-term trends of global stratospheric ozone.

Evaluation of long period past ozone trends and those projected for the future is complicated by uncertainties of the time changes, both anthropogenic and natural, of the other parameters such as trace gases, stratospheric temperature and winds, etc., which influence the ozone amount through both photochemical and dynamic interactions. It appears that there has been a downward trend of global mean temperature in the Northern Hemisphere lower stratosphere of about 2°C for the period 1964-73 with probably little change since then. The cause of this temperature trend is not known although it is suggested that long period temperature variations in the middle and upper stratosphere may be associated with the 11-year solar cycle. Most of the trace gases of interest, including water vapor, seem to be increasing at a rate of about 2 to 10 percent per year. However, except for a few gases such as CO₂ there is a lack of representative, long-term, and well-calibrated measurements for necessary quantitative estimates of global trends of the species discussed in this chapter.

The difficulty in distinguishing between the measured and true value of ozone variations results from uncertainties due to statistical variability, instrumental error, and bias in the time or space distribution of the observations. In addition, it is necessary to separate CFM produced ozone changes from those changes resulting from *natural* or other anthropological influences. For convenience, the problem of ozone trend detection was treated as a change over a 10-year interval 1980 to 1990. On the basis of our evaluation of the standard errors of the individual items that contribute to uncertainty in the ozone changes, we have estimated that the threshold for detecting changes in global total ozone using the ground based network is ± 6 percent for 10 years at the 95 percent (2σ) confidence level. If satellite observations are used to complement the ground-based Dobson measurements and if improvements are made in the observational systems, this threshold value could be reduced to ± 4.5 percent per 10 years. The threshold for detection of a CFM produced ozone trend in mid-stratosphere is about ± 5 to 10 percent per 10 years if *natural* and other anthropogenic influences are important.

We emphasize that many of the numbers used in arriving at estimates given in this chapter, particularly those involving low frequency natural variations, are very soft. These latter, of course, involve the general problem of climate predictability and the influences of long period climatic changes on ozone variations. More firm estimates of the threshold values could be developed with a carefully planned program of *continuous* ozone observations made with intercalibrated satellite and ground-based systems. In addition, the thresholds could be lowered by reduction of the uncertainty in long-term meteorological effects and reduction of the ground-based Dobson network errors.

RECOMMENDATIONS

- Since the threshold of detecting an anthropogenic trend in ozone cannot be precisely quantified at this time, the emphasis should be put on reducing the two major uncertainties in the present values, which are geographical sampling bias and long-term natural-trend bias. Comparisons between satellite and ground-based station data and the use of detailed total ozone field from the Total Ozone Mapping Spectrometer observations are potentially important for correcting sampling bias that may exist in the present Dobson network. Analysis of long-term meteorological data sets in conjunction with ozone data will also contribute to reducing uncertainties due to long-term natural ozone trends.
- Rapid initiation of an integrated ozone monitoring plan is strongly recommended. The monitoring system should consist of satellite total ozone and profile sounders, operated in conjunction with a well calibrated set of Dobson stations, and with regular and frequent launches of rocket and balloon ozonesondes, such as is recommended in the Federal Ozone Monitoring Plan.
- Continued efforts are recommended toward improvement and extension of international Dobson ozone spectrophotometer network, which still represents the most extensive ground-based source of total ozone data.

- Conventional sounding programs (balloons, rockets, Umkehr) should be continued and expanded for independent analyses of long-term variations in stratospheric ozone, in addition to validation of satellite derived ozone profiles.
- Increased theoretical and observational research efforts to understand the physical association between global transport processes and ozone changes are recommended.
- Early detection of anthropogenic trends in ozone would be more likely using data pertaining to the 35 to 45 km altitude region. Increased frequency and spatial coverage by rocket- and balloon-borne ozonesondes and by Umkehr observations, as well as satellite monitoring systems, would greatly enhance the capability for early detection.
- Accumulating evidence from ozone observations with different instruments suggests that Dobson spectrophotometer AD wavelength effective ozone absorption coefficients may be erroneous. Because Dobson instrument observations represent a long-term data set and provide *ground truth* for satellite ozone measurements, a concerted effort is recommended to establish the absolute error in the ozone absorption coefficients, particularly at the Dobson wavelengths.
- Further studies are needed to reduce errors associated with long-term Dobson instrument calibration drifts, the dependence of ozone absorption coefficients on changing stratospheric temperatures, the effects of stratospheric and tropospheric aerosols on measurement, and interferences caused by UV absorbers in polluted tropospheric air such as sulfur dioxide and photochemically-produced ozone.
- Little is known about the variability of long-lived atmospheric species such as CH_4 , N_2O , CF_2Cl_2 , CFCl_3 , CH_3CCl_3 , and stratospheric H_2O which decompose in the stratosphere to yield radicals which directly impact on ozone. Long-term observational programs, with improved calibration techniques should be implemented. The existing series of stratospheric water vapor soundings should be continued.
- All efforts should be made to process and validate existing ozone profile data sets.
- Recently detected trends of stratospheric temperature require further investigation, including careful analysis of satellite data at levels normally sounded only by rockets. The analysis should be extended to earlier periods, if possible, and care should be taken to insure calibration and continuity of future measurements and their interpretation.

CHAPTER 7

MODEL PREDICTIONS

INTRODUCTION

In previous chapters, the present status of stratospheric science has been discussed in some detail. The three basic elements of stratospheric science—laboratory measurements, atmospheric observations, and theoretical studies are intimately interconnected, since results from each element serve to refine and validate results from the other elements. A major focus of the continuing development of the field is on achieving the ability to predict, with reasonable confidence, the effect on ozone of particular anthropogenic sources of pollution.

This chapter discusses the current status of such model predictions. Simply stated, a prediction is an attempt to answer the question: Compared with the present state of the stratosphere, what changes will occur as a result of a change in one or more chemical species? To answer this question, changes in the amount and distribution of stratospheric ozone are considered almost exclusively. Modifications of the aerosol layer and of the temperature distribution are only briefly discussed, as are the implications for possible climate changes.

In NASA RP-1010, (Hudson, 1977) the primary emphasis was on the effects on ozone of anthropogenic sources of CFCl_3 and CF_2Cl_2 . In addition to CFCl_3 and CF_2Cl_2 , the present study includes other forms of pollution identified as being potentially capable of producing significant ozone changes. Predictions are made of effects of ground level releases of CH_3CCl_3 and of chemicals produced by aircraft, rockets, and atmospheric nuclear explosions. Changes in N_2O , H_2O , CO and CO_2 are also considered.

A number of 1-D photochemistry models exist, and many of these were used to provide results for this chapter. Each of the models is referred to in the text by the name of the institution where the model is used. The investigators who participated in the workshop and provided the results from the model are identified in table 7-1, which also cites references that discuss the particular model. However, it must be remembered that a research group may have more than one model, and that models have evolved considerably over the past five years. Thus, the models used in this study may differ in some respects from those discussed in these references. Each research group, except GSFC, used only one model to obtain the results presented in this chapter; two models are used by GSFC because one of the models (denoted GSFC-UNC) is substantially less sophisticated than the others. This model is used in uncertainty studies (as described later in the chapter), and thus it is important to document how well the GSFC-UNC model compares with the others. The different models were compared and found to produce generally consistent results in that any substantial differences were traced to model input data and boundary conditions. Further comparisons are contained later in this chapter and in Chapter 4.

There are certain limitations inherent in 1-D photochemistry models, as discussed in Chapter 2, but 1-D models still provide the best current predictive capability. This is because: (1) they can include all known chemistry and chemical-radiative feedback, (2) they have been shown to be reasonably consistent with most observations of the current atmosphere, (3) many of the current 1-D models have been extensively intercompared for consistency, and (4) some reasonable method of uncertainty analysis can be applied to their predictions. Where appropriate, selected two-dimensional (2-D) model predictions are also used, especially their diagnostic capability for assessing the latitude dependence of effects.

Table 7-1
Institutions and Workshop Participants Associated with Models Used to Provide
Predictions in this Report

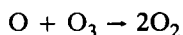
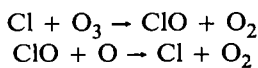
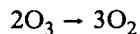
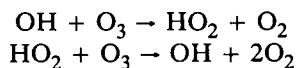
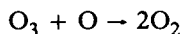
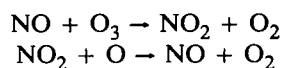
	Institute	Participants	References
LLL	Lawrence Livermore Laboratory	Chang, J., and Duewer, W. Penner, J., and Wuebbles, D.	Chang et al. (1974, 1979) Penner & Chang (1979)
DuPont	E. I. DuPont de Nemours	Jesson, P., and Miller, C.	Miller et al. (1978, 1979)
LaRC	NASA/Langley Research Center	Callis, L.	Natarajan et al. (1979), Callis et al. (1979)
RDA	Research and Development Associates (RDA) and NASA Ames Research Center	Turco, R., and Whitten, R.	Turco & Whitten (1975, 1977, 1978)
Harvard	The Center for Earth and Planetary Physics Harvard University	Logan, J.	Wofsy et al. (1975) Logan et al. (1978) Wofsy (1978)
CalTech	California Institute of Technology	Yung, Y.	Yung et al. (1979)
NOAA	NOAA/Environmental Research Laboratory, Boulder, CO	Liu, S.	Liu et al. (1976)
GSFC	NASA/Goddard Space Flight Center	Herman, J.	Herman (1979)
GSFC-UNC	NASA/Goddard Space Flight Center	Butler, D., and Stolarski, R.	Rundel et al. (1978) Stolarski et al. (1978)
AER	Atmospheric Environmental Research	Sze, D.	Sze and Wu (1976)

CURRENT UNDERSTANDING OF STRATOSPHERIC CHEMISTRY

The use of photochemical models for the prediction of perturbations of the stratospheric ozone layer depends on an understanding of the physical and chemical processes that control the behavior of the stratosphere. This understanding has evolved from the original pure oxygen chemistry proposed by Chapman (1930) to the current concept of an interacting radiative-chemical-dynamical system. Because the perturbations discussed herein are generally chemical in nature, the most important criterion in the selection of a perturbation model is its accurate representation of the chemistry of the stratosphere. This has led to intense work on the development of 1-D parameterized transport models. In this type of model, simplifications of dynamical processes have been made in order to focus on understanding the complexities of the chemistry.

In the stratosphere, odd-oxygen is formed mainly through the photolysis of O_2 in the upper stratosphere and is destroyed by reaction with itself and various catalysts. The reaction, $O + O_3 \rightarrow 2O_2$, accounts for a relatively minor fraction of odd-oxygen loss in the stratosphere. The major loss processes for odd-oxygen involve the catalytic effects of various free radical species.

The major recognized catalytic loss mechanisms for odd-oxygen involve NO_x ($NO + NO_2$), HO_x ($OH + HO_2 + H$) and ClO_x ($Cl + ClO$) in such reaction sequences as:



In addition to the examples given above, there are many other reaction sequences, some of comparable importance.

RECENT DEVELOPMENTS

Since NASA RP-1010, new measurements of various reaction rate constants have led to an increased awareness of the importance of interactions among the various catalytic species. The rate constant recommendations made by DeMore et al. (1979) are used throughout this chapter. They are slightly different from those in Chapter 1, and differ from the recommendations in NASA RP-1010 for many reactions. Most of the differences from NASA RP-1010 are either modest in magnitude, or involve reactions that have little influence on model predictions.

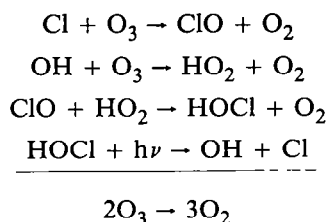
DeMore et al. (1979) recommend significant increases in the rates of the reactions: $HO_2 + O_3 \rightarrow OH + 2O_2$ and $HO_2 + NO \rightarrow OH + NO_2$. The rate for the second reaction was given in NASA RP-1010 as $8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ independent of temperature. This represented a large increase over previous evaluations of this rate coefficient and was based on the measurements of Howard and Evenson (1977). DeMore et al (1979) and Chapter 1 of this report recommend a temperature-dependent rate constant based on the measurements

of Zahniser and Howard (private communication, 1979) and Howard (1979) which gives an even larger value at stratospheric temperatures. These revisions in recommended rate constants shift the balance within the HO_x species toward OH and away from HO_2 . Larger OH concentrations have opposite effects on the efficiencies of the chlorine and nitrogen catalysis of ozone loss. Since OH removes chlorine from the inactive HCl reservoir through the reaction $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$ returning it to the active Cl form, one effect of an OH increase is to increase the calculated efficiency of ozone destruction by chlorine. The effect on the odd-nitrogen catalysis of ozone loss is the opposite because the reaction $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ ties up NO_x in the inactive HNO_3 reservoir. Thus, the effect of these rate changes is to increase the sensitivity of stratospheric photochemical models to chlorine additions, while decreasing the sensitivity to NO_x perturbations.

Other important revisions include the photolysis rate of NO by Frederick and Hudson (1979a), $\text{NO} + h\nu \rightarrow \text{N}(^4\text{S}) + \text{O}$, and the reactions of N atoms with NO , O_2 and O_3 . The net result of these changes is the slower destruction of odd nitrogen (the sum of N, NO, NO_2 , $2\text{xN}_2\text{O}_5$, ClONO_2 and HNO_3) in the upper stratosphere and lower mesosphere, leading to larger predicted concentrations of odd nitrogen than previously obtained. Computations with the older rates yielded a peak odd nitrogen of approximately 18 to 20 ppbv, while the newer rates increase this amount to 23 to 25 ppbv. The possibility that the ionospheric odd-nitrogen sources could provide a significant contribution to the stratospheric budget is also increased. As stated in Chapter 4, these higher values are in greater disagreement with the measurements of the individual odd-nitrogen species.

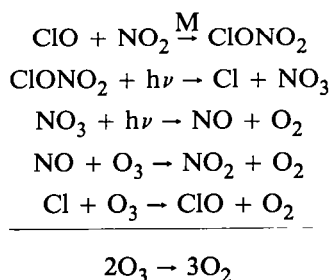
In addition to changes in long-recognized photochemistry, recent developments have occurred which introduce essentially new chemistry into the models. Among these are the formation reactions of HOCl and HO_2NO_2 : $\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$ and $\text{HO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{HO}_2\text{NO}_2$. Both reactions have been measured to be quite rapid. Subsequent chemistry is poorly known, but these species strengthen the couplings between HO_x and ClX and HO_x and NO_x .

Although the coupling between HO_x and ClX ties up some ClX in a relatively inactive form, ClX catalysis may actually be increased because of the reaction sequence:



This provides an odd-oxygen destruction sequence which is effective in the lower stratosphere where oxygen-atom concentrations are low.

Earlier model calculations (e.g. as described in Hudson, 1977) generally assumed that the products of ClONO_2 photolysis were $\text{ClO} + \text{NO}_2$, simply returning to the formation reactants with no net effect on ozone. Current results given in Chapter 1 indicate that the products are $\text{Cl} + \text{NO}_3$. Some of the NO_3 formed will photolyze to NO and O_2 giving a net ozone destruction via the following reaction sequence:



If the products of peroxyntic acid (HO_2NO_2) photolysis are $\text{OH} + \text{NO}_3$, analogous ozone destruction processes will exist.

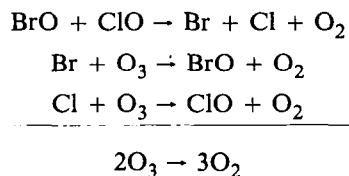
A reaction between OH and ClO has recently been measured by Leu and Lin (1979). Two sets of products are possible:



Branch (a) accounts for most of the products observed by Leu and Lin (1979) and has relatively little effect on model calculations, but branch (b) is potentially a major route for the conversion of ClO_x into the relatively stable species HCl , and will be important if even a few percent of the overall reaction goes through this branch. It is also possible that the rate of reaction (b) is pressure dependent.

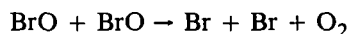
In addition to newly recognized reactions of ClO_x , HO_x , and NO_x , attention has been directed to the potential role of bromine in stratospheric chemistry. In the past, bromine has received little attention because it has a much smaller ambient concentration than chlorine; about 10 pptv BrX compared to 2 ppbv ClX (Lazrus et al., 1975, 1976). However, recent calculations by various workshop participants have shown that at mixing ratios of approximately 10 to 100 pptv, bromine species can influence stratospheric composition. Thus, bromine could become a serious environmental problem if substantial increases in its anthropogenic emissions occur. (Wofsy et al., 1975; Bauer, 1978).

Bromine has the potential for enhancing the destruction of ozone by chlorine through the coupling reaction of BrO with ClO . The Br and Cl atoms formed in this reaction quickly react with ozone to complete a catalytic cycle:



With 20 pptv of bromine in the stratosphere, the depletion of ozone by CFMs is estimated to be enhanced by 5 to 20% (See e.g. Yung et al., 1979; and results presented later in this chapter). Thus, for low bromine levels, the chlorine-bromine synergism with respect to ozone depletion is of moderate importance.

Unlike chlorine, there are no known efficient reservoirs for Br and BrO because HBr and BrONO_2 are rapidly destroyed by sunlight. Accordingly, on a molecule-for-molecule basis, bromine should destroy ozone more effectively than chlorine. If bromine levels were high (more than 100 pptv), bromine consumption of ozone would increase more rapidly than the bromine concentration itself because of the fast reaction,



Thus, as bromine concentrations increase, the importance of bromine catalysis of odd-oxygen loss quickly increases relative to that of other catalytic cycles. In fact, because of the reaction $\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$, bromine and chlorine should together be more efficient in destroying ozone.

The net result of the changes and additions to the chemical description of the stratosphere is an increased perception of the interconnection of the catalytic cycles. Although many of these reactions have been known and used in the models for some time, their importance has recently increased as has the perception of their role in synergistic and interference effects. The stratospheric photochemistry system is now viewed as one in which the ozone production-and-loss processes involve a number of species in an interconnected manner so that a perturbation in any one of these affects all of the others.

In addition to changes in the perception of stratospheric chemistry, other features of 1-D models have evolved. Many models now include details of methane oxidation, and an attempt to incorporate consistent calculations of water vapor. Those models having their lower boundary at ground level have attempted to improve the representation of the troposphere and have included flux boundary-conditions. Most model calculations now take multiple scattering into account, and employ more sophisticated treatment of diurnal averaging. The potential importance of temperature feedback effects is widely appreciated, although most model calculations do not include such temperature feedback. The current treatment of radiative cooling in 1-D photochemical models is probably too crude to be satisfactory below 30 km (Dickinson, 1973b).

A number of 2-D photochemical models are under development, and some results are now available from Whitten et al. (1979), Vupputuri (1976), Crutzen (1975a), Brasseur (1978), Harwood and Pyle (1975), Widhopf (1975), and Hidalgo (1978). These models permit the examination of latitudinal differences in photolysis rates, and offer some improvement in the parameterization of transport. Although such models do not offer much hope for computing the effects of chemical changes on transport processes, they do provide an improvement over 1-D models in their ability to treat latitudinal and seasonal effects.

MODELING OF THE PRESENT STRATOSPHERE

The modeling groups listed in table 7-1 were requested to perform a standard set of calculations, using the recommended set of rate constants and photolysis cross sections described in DeMore et al. (1979). However, most models include some chemical reactions for which no recommendation was given, and some used the photolysis rate for NO given by Cieslik and Nicolet (1973) while others used that suggested recently by Frederick and Hudson (1979a). Thus, the photochemical reaction rates used in the different models are similar but not identical. Since no other attempt was made to standardize the models, they differ somewhat in the choice of solar-flux values, boundary conditions, standard atmosphere (30°N, or midlatitude mean), vertical diffusion coefficients, and actual type of calculation performed (steady-state or time-dependent treatment of the diurnal variation of insolation). On the other hand, most models employed similar values for many of these parameters, and this is reflected in the agreement between the different model results. Although the vertical diffusion coefficients may differ, they are all tuned to the same measured concentration of CH₄, N₂O, CF₂Cl₂ and CFCl₃. The models all used global average, equinoctial, or 30°N (midlatitude) conditions.

TRACE SPECIES

A comparison of the model results was made for both the ambient atmosphere and for several specific perturbations. The results for the ambient atmosphere are shown in the figures in Chapter 4, which also present the measurements of atmospheric constituents. Rather than presenting individual calculations, the range of model results is represented by a band. In most cases, the agreement among the calculated profiles is satisfactory (within a factor of 1.5) and the larger discrepancies can be attributed to specific differences in photochemical input.

Calculated profiles for the HO_x species agree remarkably well with each other, primarily because the models used identical rate constants for the HO_x partitioning reactions (HO₂ + NO and HO₂ + O₃) and HO_x formation and destruction reactions and similar H₂O and CH₄ profiles. For the NO_x species, the width of the band of computed profiles arises in large part from use of different NO photolysis rates. The range of ClX profiles comes partly from the different total ClX used (1.9 to 2.3 ppb), but also reflects the use of two formation rates for chlorine nitrate given in Chapter 1. This alters the partitioning among the members of the ClX family. The agreement between the different model calculations is as good as could be expected considering that the models are not identical.

The comparison of model results with observations (discussed in detail in Chapter 4) is summarized here to focus on implications of some specific problem areas for perturbation calculations. There is a general agreement between the computed ClO concentrations and the average of the recent measurements by Anderson (1979) and Menzies (1979). However, the measured ClO concentrations in the summers of 1977 and 1978 were much higher than the model calculations, and also present theories cannot explain the gradient in the ClO profile below approximately 35 km. The sum of $\text{NO} + \text{NO}_2 + \text{HNO}_3$ in the models is larger than that derived by summing concurrent measurements of the individual species. Part of this latter discrepancy could be removed if the vertical diffusion coefficients in the 1-D model were tuned to fit the N_2O , CF_2Cl_2 and CFCl_3 measurements, rather than a compromise between fitting these and the CH_4 profile. However, with the present photochemical models, it is not possible to fit the N_2O , CF_2Cl_2 , CFCl_3 and CH_4 profiles with a unique set of vertical diffusion coefficients, unless a method can be found to reduce calculated OH in the lower stratosphere (where no data for OH exist). Discrepancies between the calculated and measured HNO_3/NO_2 ratio would also be reduced by lower calculated OH in the lower stratosphere. (See e.g. McConnell and Evans, 1978).

Disagreements such as these between measurements of atmospheric constituents and model calculations contribute significantly to the uncertainty in perturbation calculations. For example, smaller OH concentrations in the lower stratosphere would have large impacts on the results of NO_x or ClX perturbation calculations, but in opposite directions. This topic is explored further in the section on uncertainties in model predictions.

PREDICTED OZONE ABUNDANCE

Stratospheric models which employ recommended reaction rate coefficients (Chapter 1) predict high-altitude (about 50 km) ozone abundances smaller than measurements of upper stratospheric ozone as noted by Butler (1978) and Poppoff et al. (1978). This disagreement arose when the predicted upper stratospheric abundance of OH was increased to levels which are in approximate agreement with measurements by Anderson (1976); larger concentrations of OH increase the loss rate of ozone due to reactions of HO_x species. The cause of the discrepancy between measurement and prediction of high-altitude ozone may be caused, in part, by heavier weighting of winter ozone data in the empirical model of Krueger and Minzner (1976). The relevance to ozone perturbations is not clear because only a negligible part of the total ozone change occurs at these altitudes.

In the lower stratosphere, 1-D model predictions of ozone abundance disagree with each other by as much as 30% as a result of differing globally averaged vertical transport rates (eddy diffusivities). After the introduction of the new value of the rate coefficient for the reaction $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$, but before the measurement of the new rate coefficient for $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$, lower stratospheric ozone was overestimated by all photochemical models. However, when the rate coefficient for the latter reaction was increased to its current value (see Chapter 1), the problem of excessive low-altitude ozone largely disappeared (see e.g. Whitten et al., 1978).

PERTURBATIONS

The model calculations of stratospheric perturbations taken one at a time are the subject of this section. Possible interactions among simultaneous perturbations will be considered in the next section. The perturbations considered are ground release of halocarbons, N_2O and CO_2 , changes in tropospheric OH, high-altitude aircraft operations, rocket exhausts, atmospheric nuclear explosions, and natural events and variations.

GROUND-LEVEL HALOCARBON RELEASES

Chlorofluoromethane Effects

Most studies of atmospheric halocarbon perturbations have been concerned with the effects on ozone of fluorocarbons 11 and 12. The historical release rates, current inventories, and atmospheric budgets of these

fluorocarbons (and other halogen compounds) are reviewed in Chapter 3. Calculations of ozone reductions caused by FC-11 and FC-12 made for this assessment are presented in table 7-2. The results indicate an ozone-depletion efficiency of about 3% of the ozone column per ppbv of ClX, added and roughly a 15 to 18% eventual ozone decrease for continuous FC-11 and FC-12 release at 1975 rates (with more or less the present set of reaction rates).

Table 7-2

Steady-State Perturbations for 1975 Emission Rates of Fluorocarbons 11 and 12*

Modeling Group	ΔClX ppbv	$-\Delta \text{O}_3$ (col) (%)	$-\Delta \text{O}_3$ (40 km) (%)	$-\Delta \text{O}_3$ (20 km) (%)	$-\Delta \text{O}_3$ (col)
					ΔClX (%/ppbv)
LLL	5.5	15	38	17	2.7
DuPont	6.2	18.3	46.1	16.5	3.0
LaRC	6.7	16.2	43	14.8	2.4
RDA	5.5	16	42	17	2.9
Harvard	6.6	18	41	19	2.7
Cal Tech	6.9	18	50	19	3.1
NOAA	5.8	18	39	17	3.1
GSFC	7.0	18	39	18	2.6
GSFC-UNC	6.9	15.4	55	9	2.2
AER	5.8	16.7	52	14	2.9
*Fluorocarbon 11 at 9.4×10^6 and Fluorocarbon 12 at 13.0×10^6 molecules $\text{cm}^{-2} \text{sec}^{-1}$					

Figure 7-1 shows the predicted ozone reductions as a function of altitude for the steady-state case outlined above using the DuPont model. The large percentage ozone reduction near 40 km is a well-known feature of photochemical model predictions. However, the large absolute ozone reductions below 30 km are a relatively new feature due largely to the increased reaction rates used for $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ and $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2$, and to the inclusion of HOCl chemistry in models. Although the largest relative changes in ozone continue to be at about 40 km (as in previous predictions), the bulk of the absolute ozone decrease is now calculated to occur below 30 km.

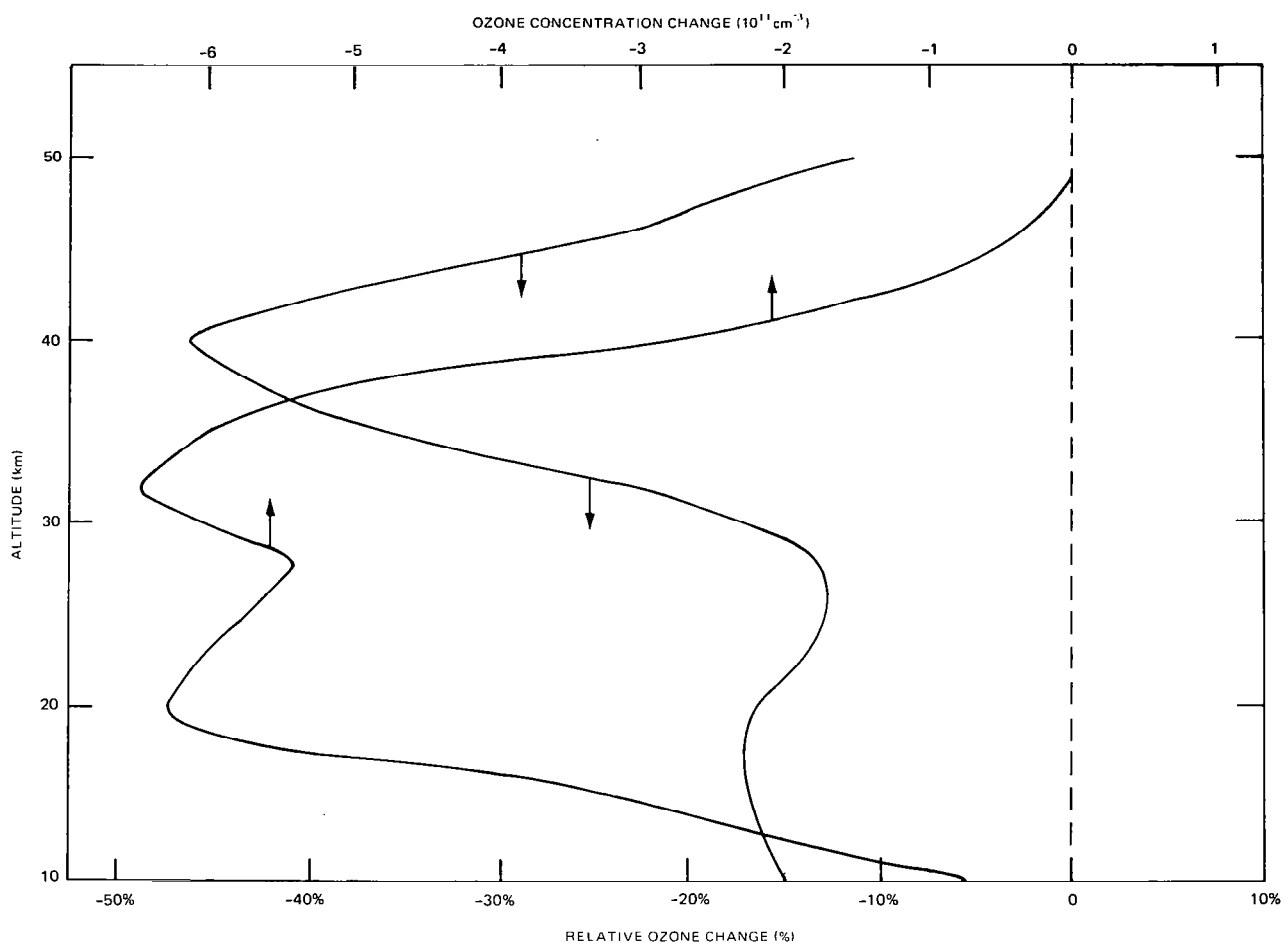


Figure 7-1. Predicted ozone reductions as a function of altitude.

Three scenarios of potential fluorocarbon ozone reductions as calculated with the RDA model are shown in figure 7-2. For this model, the eventual buildup of CIX caused by continuous fluorocarbon release at 1975 rates is about 6 ppbv, and the corresponding ozone column reduction is about 18%. Although the United States fluorocarbon production rates have begun to decline in recent years, CFM production in the rest of the world has remained approximately constant. Even if production were to cease immediately, the fluorocarbons already in the atmosphere would be expected to continue to affect ozone for many decades as shown by curve 1 of figure 7-2. Also, it takes approximately 5 to 10 years following cessation of CFM production for ozone recovery to begin, even without accounting for the protracted leakage of fluorocarbons from sealed refrigeration units; the slow recovery is attributable to a delay in transit of fluorocarbons from the troposphere to the middle stratosphere.

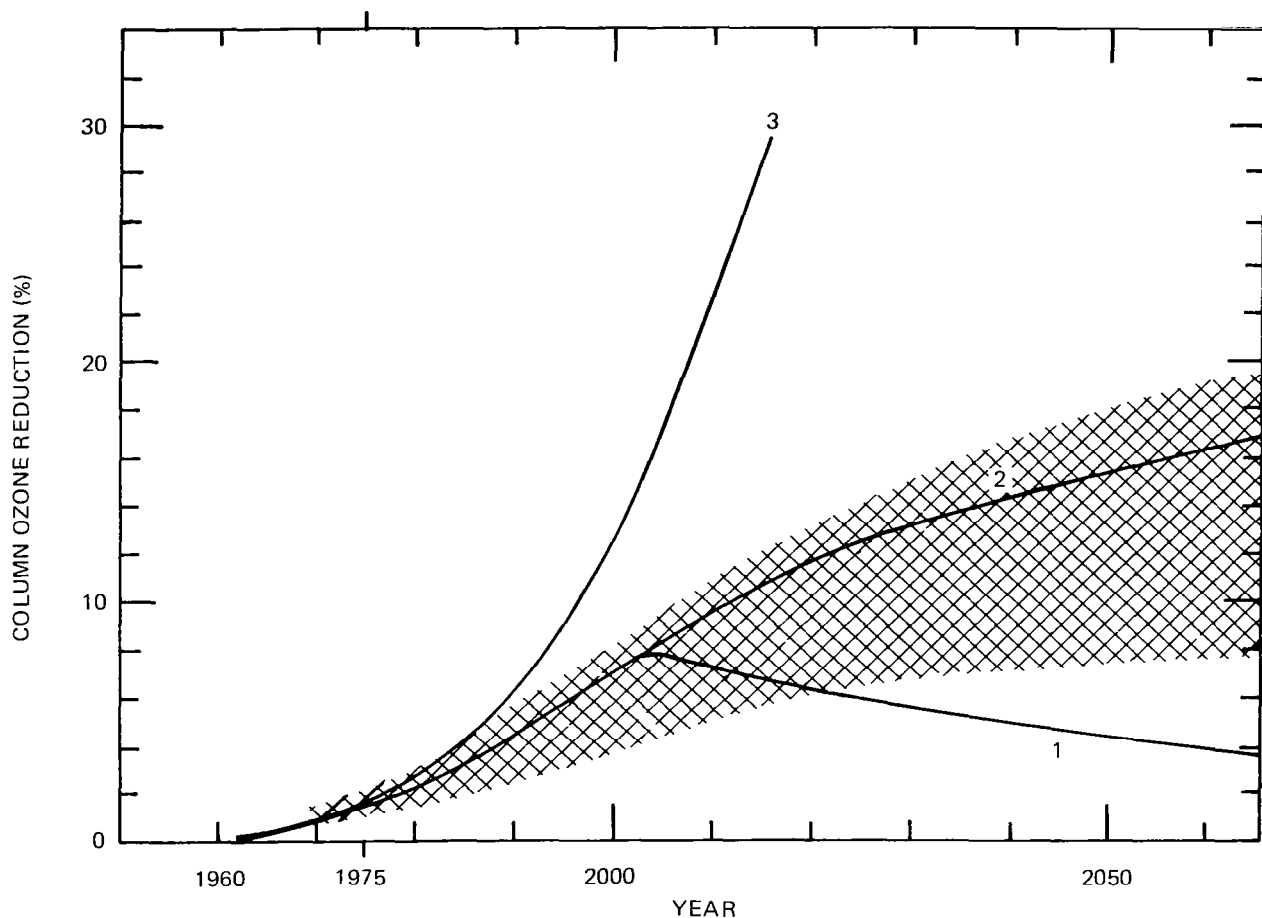


Figure 7-2. Typical model predictions of time-dependent ozone depletions for three fluorocarbon production (release) scenarios beyond 1975. They are (1) constant FC-11 and FC-12 release at 1975 rates until the year 2,000, with no subsequent release; (2) constant release at 1975 rates indefinitely; and (3) release starting at the 1975 rates and growing by 5% per year for several decades. The tropospheric lifetimes of fluorocarbons 11 and 12 are assumed to be greater than 100 years. The fluorocarbon ozone reduction in 1975 is taken to be 1.5%. For curve 2, the cross-hatched area reflects the widest range of model predictions available for this assessment.

If fluorocarbons have natural sinks other than stratospheric photodecomposition, the ozone depletion curves in figure 7-2 would be reduced in magnitude and the response times would be shortened. The shortening would roughly follow to the relationship.

$$\tau^{-1} \sim \tau_p^{-1} + \tau_T^{-1}$$

where τ is the overall fluorocarbon lifetime in the atmosphere, τ_p is the average lifetime due to stratospheric photolysis (approximately 60 years for FC-11 and approximately 100 years for FC-12 in current models), and τ_T is the lifetime due to other (tropospheric) processes. With a constant fluorocarbon emission rate, the eventual steady-state fluorocarbon concentration and concomitant ozone reduction vary roughly in proportion to τ . Thus, a tropospheric FC-12 loss process with a 100-year time constant could reduce the eventual impact of FC-12 on ozone by one-half. The short-term time dependent behavior would not be significantly affected, however.

One natural fluorocarbon sink is the adsorption and subsequent photolysis on sand surfaces. This has been the subject of recent analysis by Rebbert and Ausloos (1978), Gab, et al. (1978) and others. Accurate estimates of the lifetimes attributable to this sink are not yet available. Thus, uncertainties remain in the atmospheric lifetimes of CFMs, and this has a direct bearing on the uncertainties in the corresponding stratospheric perturbation scenarios.

Two-dimensional model calculations of fluorocarbon-ozone perturbations show that the largest ozone decreases occur at high latitudes in winter; the increase in the computed ozone column depletion from the Equator to the pole is a factor of 1.5 in the winter hemisphere and 1.2 in the summer hemisphere (Borucki et al., 1979). Two-dimensional model calculations of global ozone reductions are generally consistent with the one-dimensional model results.

Other Chlorine Perturbations

Changes in the column content of ozone due to the continued release of chlorine from other chlorocarbon compounds can be estimated from a knowledge of a few simple parameters. The ozone reduction efficiency of table 7-2 relates the column ozone change to the increase in the ClX mixing ratio in the upper stratosphere. The ClX increase can be estimated from a knowledge of the release rate and the atmospheric residence time of the chlorocarbon, and is given by

$$\Delta \text{ClX} = \frac{\phi \cdot \tau \cdot \gamma}{H \cdot M} \times 10^9 \text{ (ppbv)}$$

where ϕ is the release rate of the chlorocarbon in molecules $\text{cm}^{-2}\text{sec}^{-1}$ (assumed constant in time), τ is the atmospheric residence time in seconds, γ is the number of chlorine atoms released from the chlorocarbon, H is the atmospheric scale height ($\sim 8 \times 10^5 \text{ cm}$), and M is the total atmospheric concentration at the ground ($2.5 \times 10^{19} \text{ molecules cm}^{-3}$). Then the change in the ozone column abundance $N(\text{O}_3)$ is given by

$$\Delta N(\text{O}_3) = E \cdot \Delta \text{ClX}$$

where E is the efficiency (3% per part per billion of ΔClX according to table 7-2).

As an example, this analysis can be applied to methyl chloroform. Assume a release rate for CH_3CCl_3 at the ground of $5 \times 10^7 \text{ molecules cm}^{-2}\text{sec}^{-1}$. (This is a globally averaged value equivalent to about 1.7×10^6 metric tons of CH_3CCl_3 released each year worldwide, or about three times current production rates.) The tropospheric lifetime of CH_3CCl_3 is determined by its reaction with OH. Adopting a six-year lifetime*, an emission rate of $5 \times 10^7 \text{ molecules cm}^{-2}\text{sec}^{-1}$ leads to a steady-state CH_3CCl_3 concentration of about 450 pptv. Because each methyl chloroform molecule has three chlorine atoms, each of which may be released upon decomposition, and the efficiency for ozone reduction is close to 3% per ppbv of ClX, a corresponding steady-state ozone decrease of about 4% is estimated. This value is consistent with detailed model calculations made for this assessment.

Ozone reductions caused by other chlorocarbons may be estimated on a similar basis, using individual budget information tabulated in Chapter 5.

*Estimates of the CH_3CCl_3 lifetime are quite uncertain, reflecting, in part, uncertainties in tropospheric OH. Other researchers have estimated CH_3CCl_3 lifetimes in the range of 6 to 12 years. The impact of CH_3CCl_3 on ozone will vary roughly in proportion to its lifetime. Recent measurements of the reaction between OH and CH_3CCl_3 by Kurylo (private communication, 1979, see Chapter 1) suggest that a minimum six-year residence time is likely.

Bromine And Fluorine Perturbations

Table 7-3 compares model predictions of ozone reductions corresponding to 20 pptv of bromine in the stratosphere. Current stratospheric bromine levels are thought to be 10 to 20 pptv (Lazrus et al. 1976; Wofsy et al. 1975; Yung et al. 1979). Large increases in atmospheric bromine have not been forecast, but the synergistic interaction with chlorine is considered later in this chapter.

Known fluorine chemistry suggests a negligible impact on ozone if fluorine is released in moderate quantities (i.e., up to at least a few ppbv) into the stratosphere (Stolarski and Rundel, 1975; Watson et al. 1977).

Table 7-3

Column Ozone Change Due to N_2O , BrX and Combined Perturbations

The first column is the change in the column content of ozone when the N_2O flux at the lower boundary is doubled. The second column is the ozone column changed when the N_2O flux is doubled and CFMs are added at the rate defined in table 7-2 carried out to steady-state. Columns 3 and 4 are the ozone column content changes due to addition of 20 pptv of CH_3Br at the lower boundary and the combination of CH_3Br and CFMs again carried to steady-state.

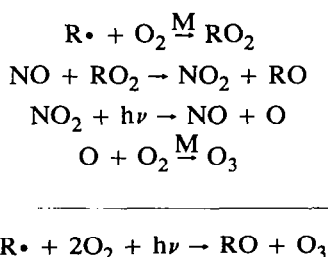
	$2\times\phi N_2O$ $\Delta N(O_3)$ (%)	$2\times\phi N_2O$ + CFM $\Delta N(O_3)$ (%)	20 pptv BrX $\Delta N(O_3)$ (%)	20 pptv BrX + CFM $\Delta N(O_3)$ (%)
ILL	-2.1	-15, -11*		—
DuPont	+1.3	- 9.1	-1.1	-19.3
LaRC	-1.9	-11		—
RDA	+0.2	—	-2.0	—
Harvard	+3.6	- 8.8	-1.0	-19.5
Cal Tech	+3.3	-10	-2.4	—
NOAA	-1.2	-10	-1.0	-19
GSFC	+1.5	-11	-0.8	-16.2
GSFC-UNC		- 8.3		

*-15% when slow $ClONO_2$ formation rate is used, -11% when fast formation rate is used (see Chapter 1 or DeMore et al., 1979).

NITROGEN CYCLE CHANGES AND NITROUS OXIDE (N₂O)

Nitrous oxide, which is the major source of stratospheric NO_x, is a by-product of the biospheric nitrogen cycle. Possible changes in the atmospheric N₂O content as a result of increased nitrogen fertilizer usage or other disturbances in the global nitrogen cycle have been discussed by many authors (see Chapter 3 and references therein). In order to compare model sensitivity to N₂O changes, a test case was run by each group in which the flux of N₂O into the atmosphere from the ground was doubled compared to the normal value used in the model. Table 7-3 shows the results of these runs. The most notable points about these results are that not all models show the same sign for the ozone change, principally because of different NO photolysis rates, and that the magnitude of the ozone change is significantly smaller than had been previously predicted (see Johnston, 1977 and references therein).

The primary reason for the change is the increased value of the reaction rate constant for NO + HO₂ → NO₂ + OH. NO_x in the stratosphere still catalytically destroys ozone but two other effects are now more pronounced. One is the creation of ozone through smog reactions (so called because they are virtually identical to reactions which cause photochemical smog in urban air). The sequence of reactions is as follows:



where R• could be a hydrogen atom or an organic radical. The rate of this process in the stratosphere is limited by the second reaction, and thus, increased values of its rate constant have led to enhanced levels of ozone production. The other effect is the enhanced interference of NO_x in the normal HO_x catalytic destruction of ozone. This is especially pronounced in the lower stratosphere where HO_x reactions with ozone are the dominant loss mechanism. The resulting decrease in this destruction by added NO_x appears as an effective production rate. The net effect is that in the lower stratosphere such production exceeds destruction for added NO_x while in the upper stratosphere the opposite still prevails. The net effect on column ozone is a balance of these two responses to added NO_x. The changes in rates have also increased the predicted concentration of OH and this, in turn, leads to enhanced conversion of NO_x to HNO₃ and to a lower proportion of the atmospheric odd nitrogen being in the more chemically active NO_x form.

EFFECTS OF CHANGES IN CO₂

Associated with the anticipated rise in fossil fuel consumption is a concomitant increase in atmospheric CO₂. Such an increase has already occurred with a 5% increase between 1958 and 1974 (Eriksson, 1978). Large increases in CO₂ (i.e., factor of 2) are expected to have the following effects on the stratosphere:

- Increased temperatures in the lower stratosphere (1 to 2 K) and reduced temperatures in the upper stratosphere (10 to 20 K).
- Increased temperatures at the tropical tropopause (2 to 3 K) which may affect stratospheric water vapor.
- Slightly increased intensity of tropospheric hydrological cycle which may alter scavenging rates of soluble gases.
- Increase of zonal mean eddy kinetic energy in the stratosphere.

The most significant of these effects is believed to be the rather large decrease in upper stratospheric temperatures. These changes can lead to significant O_3 increases above 35 km through temperature sensitive photochemistry. Increasing levels of CO_2 and CFMs have opposing effects on O_3 , but both reduce upper stratospheric temperatures. This complicates the attribution of any observed O_3 and temperature trends to a particular cause. These thermal structure changes due to CO_2 and CFM increases may alter the phase and amplitude of long planetary-waves, leading to changes in the dynamic climatology of the stratosphere and possibly tropospheric effects. It is important that these potential interactions receive further study.

PERTURBATIONS INDUCED BY CHANGES IN TROPOSPHERIC OH

The concentrations of many important species in the stratosphere are in large part determined by processes which occur in the troposphere, in particular reactions with the OH radical. Reaction with OH is the major tropospheric sink for important trace gases such as CO, CH_4 , H_2 , CH_3Cl , CH_3Br , CH_3CCl_3 , and NO_2 . CO and NO_x play an important role in regulating the concentration of tropospheric OH, and Wofsy (1976) has suggested that a hemispheric asymmetry in OH exists as a result of the asymmetry in the CO distribution noted by Seiler (1974). Sze (1977) and Chameides et al. (1977a) discussed the possibility that continued CO emissions might lead to a decrease in OH and therefore to an increase in the global concentrations of CH_4 and CH_3Cl , which could indirectly affect stratospheric ozone.

Several important developments in tropospheric photochemistry have occurred recently, and at present, there are many inconsistencies in tropospheric models and estimates of the budgets for CO, NO_x and O_3 . Ambient OH concentrations are uncertain by at least a factor of 5. Moreover, inhomogeneities in background trace-gas concentrations make it difficult to analyze tropospheric photochemistry with a global 1-D model. For these reasons, a quantitative assessment has not been made of trends in either tropospheric or stratospheric ozone that might result from future surface emissions of CO and NO_x . Quantitative analysis of halocarbon perturbations (e.g., CH_3CCl_3) to stratospheric ozone is also hindered by a lack of knowledge of ambient OH concentrations as a function of latitude, altitude, season and location.

HIGH-ALTITUDE AIRCRAFT OPERATIONS

Table 7-4 summarizes the current model results for point source injections of nitrogen oxides at two different altitudes, 17 and 20 km. In each case the ozone-column change is positive for the injection rate of 1×10^8 molecules $cm^{-2}sec^{-1}$. Also shown is the local change in the ozone concentration at 20 and 40 km illustrating the tendency of the competing mechanisms to give ozone decreases in the upper stratosphere and compensating increases in the lower stratosphere. Because the upper and lower stratospheric changes of ozone do not depend on the injected NO_x flux in exactly the same way and because the change in the ozone column is small compared to the local positive and negative changes, the response of the ozone column is a nonlinear function of the magnitude of the NO_x injection rate as shown in figure 7-3 from Turco et al. (1978). These results suggest that, for large enough NO_x injections, ozone reduction would occur. To place these results in the context of proposed SST operations the so-called upper bound CIAP fleet corresponds to about 2×10^8 molecules $NO_x cm^{-2} sec^{-1}$ when globally averaged. The amount of NO_x injection required to reverse the sign of the ozone column change is many times the upper bound CIAP fleet.

The above considerations have been for NO_x injections only. High altitude aircraft will also inject H_2O in potentially significant amounts leading to increases in HO_x concentrations (Turco et al., 1978). Figure 7-3 indicates the effect of inclusion of H_2O injection with the NO_x injection at 20 km as calculated in the RDA model. In addition, figure 7-4 presents a typical altitude profile of ozone concentration change illustrating that a large ozone increase at low altitudes offsets a smaller decrease at high altitudes. SST calculations made with a 2-D model by Whitten et al. (1977) indicate that the ozone reductions at the Equator are about 1/3 less than at 70°N latitude.

Table 7-4

Steady-State Ozone Perturbation for an NO_x Injection Rate of 1×10^8 NO Molecules/ $\text{cm}^2\text{-sec}^*$

Modeling Group	Injection at 17-18 km			Injection at 20 km		
	ΔO_3 (col) (%)	ΔO_3 (40 km) (%)	ΔO_3 (20 km) (%)	ΔO_3 (col) (%)	ΔO_3 (40 km) (%)	ΔO_3 (20 km) (%)
LLL	+1.4	-1.9	+5.0	+1.3	---	---
DuPont	+2.6	-1.2	+5.1	+2.9	-1.9	+ 7.7
LaRC	+1.4	-1.2	+3.2	+1.1	-2.4	+ 4.1
RDA	+2.6	-1.5	+6.0	+2.4	-2.0	+ 6.3
Harvard	+3.4	-1.1	+6.9	+4.6	-2.3	+11.
Cal Tech	+2.2	-1.4	+5.1	---	---	---
NOAA	+1.3	-1.0	+2.0	+1.2	-2.3	+ 3.0
GSFC- UNC	+1.5	-1.1	+4.4	+2.2	---	---

*Or about 1.1×10^9 kg NO_2 /yr over the globe.

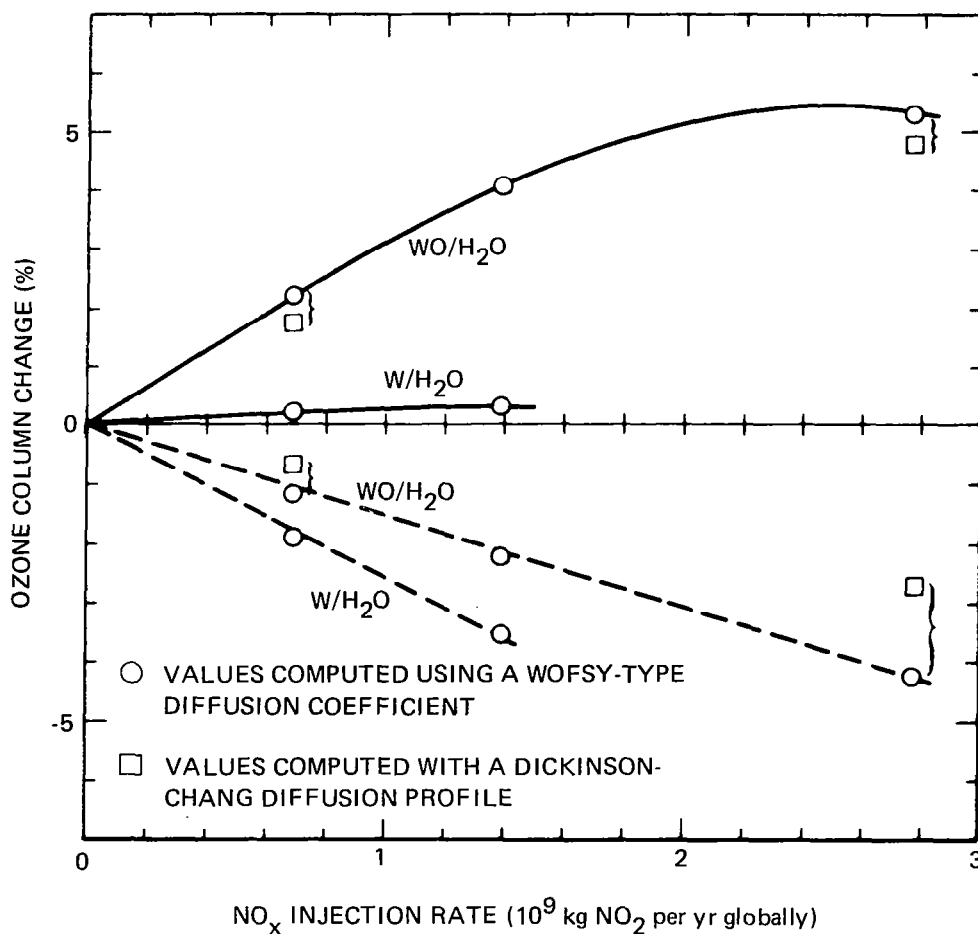


Figure 7-3. Steady-state perturbations of the vertical ozone column above 10 km (solid line) and 30 km (dashed line) as a function of the rate of a steady NO_x injection at 20 km. Results are shown both with W/ H_2O and without (WO/ H_2O) simultaneous water vapor release (Turco et al., 1978).

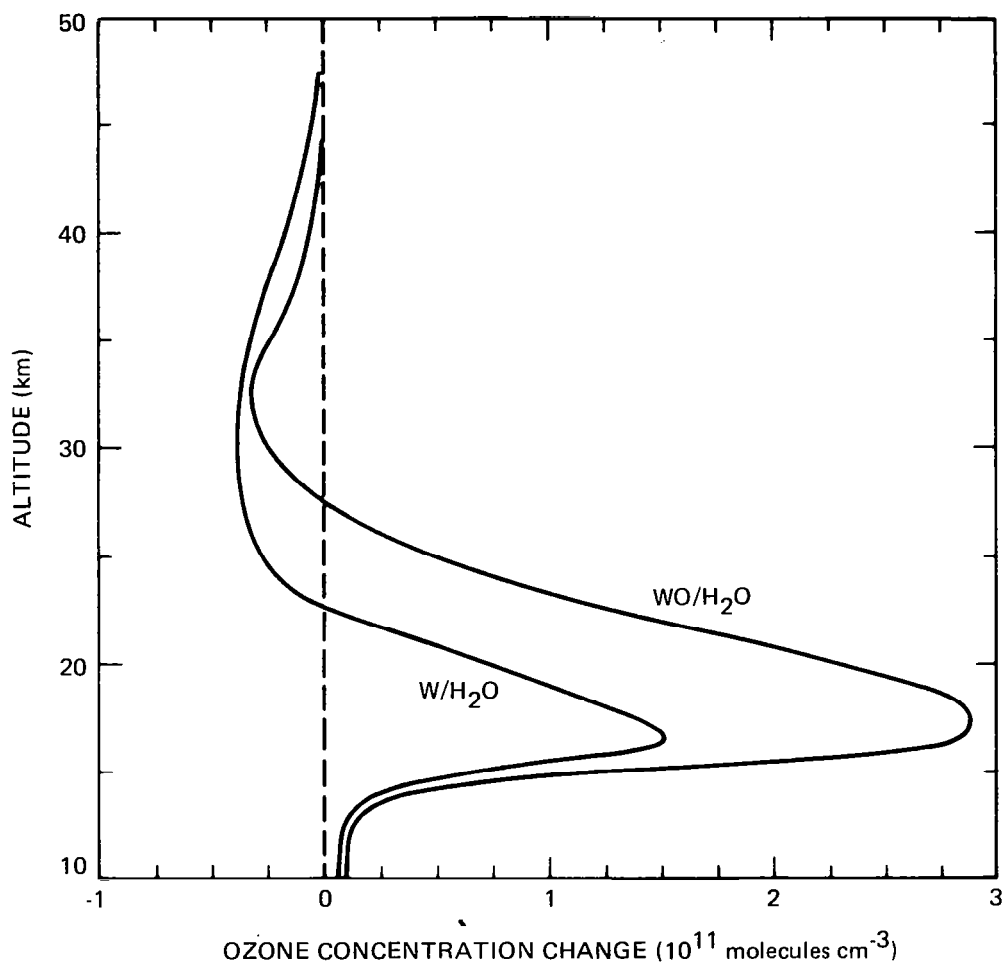


Figure 7-4. Calculated steady-state stratospheric ozone concentration changes due to an NO_x injection of 7×10^8 kg NO_2 per year (globally averaged) both with and without water vapor emission (from Turco et al., 1978). The LLL model indicates a lower sensitivity to H_2O in the lower stratosphere (Duewer, Private communication).

Engine emissions of high-altitude aircraft also include soot and sulfur dioxide which have the potential to affect the stratospheric aerosol layer. Recent calculations by Turco et al. (1979b) indicate that a fleet of several hundred SSTs would perturb the aerosol layer by less than 20% leading to probably insignificant climatic alterations. See also Oliver et al. (1977) and Pollack et al. (1976b).

ROCKET EXHAUSTS AND BY-PRODUCTS

Space shuttle launch and re-entry operations generate NO_x . However, Potter (1978) reports that the amounts are too small to produce a noticeable change in ozone. Greatly increased rocket activity associated with the construction of a satellite power system (SPS) could lead to increased rates of NO_x generation. Launch generated NO_x is predicted by R. P. Turco (private communication) to have less than a 0.01% effect on global ozone, (for ~ 400 launches/yr) but the related re-entry problem has not yet been carefully analyzed.

The solid-fueled boosters to be used on space shuttle launch vehicles release HCl into the stratosphere as an exhaust constituent. Current 1-D model calculations indicate that 60 space shuttle launches per year could reduce the ozone layer by 0.2 to 0.3% worldwide. Calculations made with a 2-D model by R. C. Whitten (private communication), which assumed launches at 30°N , indicate that: (1) the corridor effect is minimal with improved chemistry and transport parameterizations; (2) the largest ozone reduction occurs at high northern latitudes for all seasons; and (3) the increase in column ozone reduction in going from the Equator to 70°N is approximately a factor of 2.

Space shuttle is predicted to inject $8 \cdot 10^7$ kg/yr of water vapor into the stratosphere while the proposed Heavy Lift Launch Vehicle would inject $2 \cdot 10^9$ kg/yr for 300 launches per year. These injections may be compared with the natural stratospheric injection rate due to Hadley cell upwelling in the tropics of the order of 10^{12} kg/yr. (Ellsaesser and Kley, private communication). Thus, the direct rocket injections are not expected to have much effect.

The solid-fueled boosters on the space shuttle also inject aluminum oxide particles into the stratosphere (Potter, 1978). Calculations by Turco et al. (1979b) suggest that these particles would have only a small effect on stratospheric aerosols, and probably a negligible effect on global climate. (See also Hofmann et al., (1975) and Pollack et al., 1976b)

ATMOSPHERIC NUCLEAR EXPLOSIONS

There are two contexts in which this source of stratospheric perturbation is considered: previous atmospheric tests and a potential nuclear war. The former are particularly important to study because ozone data records exist for comparison to the models. The primary effect in both cases is augmentation of the rate of stratospheric odd-nitrogen production.

Nuclear Tests

During 1961 and 1962, the US and USSR detonated some 340 megatons (MT) of explosives in the atmosphere, producing some 2 to 4×10^{34} NO molecules in the stratosphere (primarily from the Soviet tests in Novaya Zemlya at 75°N). Since the ambient stratospheric loading of NO_y ($= \text{NO} + \text{NO}_2 + \text{HNO}_3$) is of order 4 to 15×10^{34} molecules, a significant effect was anticipated by Foley and Ruderman (1973) but not observed by Angell and Korshover (1973) (See also Bauer and Gilmore, 1975).

The question is: Why was no effect observed? There are a number of factors, all of which appear to have worked together:

- The biggest effects on ozone would undoubtedly have been observed at high latitudes in late fall and winter following the Soviet test series in the Fall of 1962. Observations of ozone are very difficult at these times and latitudes because of the low solar zenith angle, the high frequency of clouds, and the particular limitations of the M-83 photometer compared to the Dobson (note that in 1961 and 1962, there were no satellite observations).
- Most of the NO injections caused by the large explosions occurred between 20 to 30 km. As the understanding of stratospheric photochemistry developed, it became recognized that NO_x injections below approximately 20 km will increase ozone, while only injections at higher altitudes reduce ozone by the catalytic cycles. The absolute magnitude of expected changes has also decreased, and the latest 1-D calculations of W. Duewer et al. (private communication, June 1979) give a maximum ozone reduction of 2% if it is assumed that the 58 MT bomb cloud rose to 33 km (*Foley-Ruderman cloud rise*). But if it is assumed that this cloud only rose to 19 km (*Seitz' estimate*), the net ozone change was a maximum *increase* of 1%. By contrast, using earlier (1974) chemistry, an 8 to 10% ozone reduction was computed for either estimate of cloud rise.
- A 1-D global/annual average model, such as the calculations of Duewer et al. (1977), overestimates the effects of the actual (late fall-high latitude) injections because the initial insolation needed for photochemical reactions to take place was very weak, and the strong winter circulation then took much of the injected NO_x out of the stratosphere before it was able to affect the ozone through catalytic cycles. As reported by Quiroz (private communication 1979), there was a particularly strong inversion in the stratospheric circulation in January 1963 which swept the injected NO_x due to the 180 MT Soviet test series of 1962 out of the atmosphere even faster than during an average winter.

Potential Nuclear War

During a large-scale nuclear exchange, approximately 10,000 megatons (TNT equivalent) of nuclear explosives might be detonated in the atmosphere. Depending on the yield of the explosions, average column ozone depletions of 30 to 60% for the first year (over the Northern Hemisphere) have been predicted by Duewer et al. (1978). These results are consistent with earlier calculations by MacCracken and Chang (1975), and Whitten et al. (1975).

NATURAL EVENTS AND VARIATIONS

A variety of natural phenomena can also affect the stratosphere. Among these are impulsive phenomena, solar-proton events and volcanic eruptions and more gradual variations such as solar UV output and interplanetary magnetic field modulation of galactic cosmic rays.

Solar-Proton Events

Solar-proton events (SPE) involve high-energy protons which can penetrate into the atmosphere to 35 km and below, producing ionization, NO_x molecules, and OH radicals (Frederick, 1976). The series of flares of 4 to 8 August 1972 gave rise to approximately 3×10^{33} NO molecules and 4.5×10^{33} OH radicals, which may be compared with the ambient stratospheric loading of 4 to 15×10^{34} molecules of NO_y (= NO + NO₂ + HNO₃) and 1.5 to 3×10^{33} molecules of HO_x (= OH + HO₂) according to Bauer (1978) (Note that the HO_x lifetime is only about one hour.)

The only large SPE on which there are adequate observational data is that of August 1972. Crutzen et al. (1975a) predicted an ozone reduction at high geomagnetic latitudes and high altitudes (approximately 45 km) which has been observed by Heath et al. (1977). However, the lower altitude behavior (less than 30 km) where most ozone resides has not been adequately investigated; this domain is particularly significant because it is here that details of the chemistry and dynamics and their interaction are important in explaining the observed phenomena.

SPEs appear to take place primarily during the decrease in solar activity following a solar maximum. From other large events of 1956, 1959, and 1960, a large variability is reported; see e.g. Bauer (1978).

There are other ionizing events that might be expected to produce NO_x and HO_x (such as aurorae, X-ray flares, relativistic electron precipitation events, and galactic cosmic ray deposition), but they either produce their effects in the mesosphere far above the ozone layer, or have such a weak intensity (galactic cosmic rays) that no evidence of an effect on ozone has been observed.

Volcanic Eruptions

Volcanic eruptions inject large amounts of various materials into the atmosphere. (Table 7-5 lists two estimates of stratospheric injections caused by the 1963 eruptions of Mt. Agung, Bali at Latitude 8.5° , Longitude 115.5°E). From volcanic eruptions, water, sulfur compounds (mainly SO_2) and hydrochloric acid would probably be injected sometimes above the local tropopause and would be expected to produce a significant and long-lasting reduction of OH in the upper troposphere and lower stratosphere according to Cadle and Friend (private communication), with significant effects on stratospheric ozone. A preliminary and partial calculation of the effects of HCl alone has been made by Stolarski and Butler (1978), but no realistic simulation has yet been made.

A large explosive volcanic eruption may inject a large amount of water into the stratosphere: two current estimates of the stratospheric water injection due to the 1963 eruption of Mt. Agung indicate (2×10^{10} – 10^{11}) kg injected into the stratosphere (16–23 km)—see Bauer (1979)—which could be locally significant.

Significant explosive volcanic eruptions occur every few years, as noted by Bauer (1978), but the 1963 Agung eruption has been the largest in the past 25 years. However, the eruption of Krakatoa in 1883 sent some 3 to 10 times more material into the atmosphere than that of Agung, while the eruption of Tambora in 1816 was some 3 to 10 times that of Krakatoa. It is possible that these events represent statistical 100-year and 250-year volcanic eruptions.

Solar UV Variability

The solar ultraviolet irradiance determines the overall level of stratospheric ozone, principally by the photodissociation processes that lead to the original formation of ozone, and also by the local heating resulting from the absorption of solar UV and the changes in temperature, photochemistry, and dynamics resulting from this heating.

There are indications that solar UV irradiance shows some time variation: EUV ($\lambda < 100$ nm) increases significantly from solar flares, variation with the 27-day solar rotation period, and according to Vidal-Madjar (1977), the intensity at Lyman α (121.6 nm) varies by a factor of 2 between solar maximum/high activity and solar minimum/low activity. There is also an effective 6.6% variation in the solar constant associated with the variation in Sun-Earth distance between summer and winter.

Table 7-5

Two Estimates of the Stratospheric Source Function of the 1963 Agung Eruption Cloud

Source	Mass, kg	
	Estimate of Cadle et al. (1977) based primarily on atmospheric data	Estimate of S. Self (private communication, May 1978) based primarily on volcanological data ^a
Fine ash ^b	1.0×10^{10}	9.0×10^9
Total gas	—	2.9×10^{10}
Water vapor ^c	1.2×10^{11}	2.2×10^{10}
Total S as H_2SO_4 ^d	1.8×10^{10}	2.1×10^9
HCl ^e	1.2×10^9	7.3×10^8

^a Based on 17 March and 16 May eruptions.

^b Cadle et al. (1977) do not specify the particle size; Self refers to particles $< 2 \mu\text{m}$ diameter.

^c The mean stratospheric water vapor loading is 2×10^{12} kg.

^d 6.1×10^9 kg H_2SO_4 (the geometric mean of the Cadle and Self estimates) contain 3.3×10^{34} S atoms so that presumably 4 to 8×10^{34} OH radicals are consumed in the formation of sulfuric acid.

^e 9.4×10^8 kg HCl (the geometric mean of the Cadle and Self estimates) contain 1.5×10^{34} molecules. This impulsive injection corresponds roughly to the same number of Cl atoms as did the *annual emission rate* in 1973; and it is considered that this steady-state emission will eventually produce a 2 to 20% steady-state reduction in total ozone (cf., National Academy of Sciences, 1976, p. 8). Also see Stolarski and Butler (1978).

Note: 1) For modeling the stratospheric injection due to the 1963 Agung eruption in its effect on stratospheric photochemistry, the Cadle and Self estimates for HCl, H_2O and SO_2 injections provide respectively upper and lower bound estimates.

2) These estimates do not incorporate the results of the recent atmospheric samplings of Cadle et al. (1979), Lepel et al. (1978), and Stith et al. (1978).

However, for longer wavelengths and longer time periods, the character and magnitude of any variation becomes quite uncertain. Heath and Thekaekara (1977) have reviewed measurements of solar UV in the 180 to 350 nm wavelength range over the period from 1964 to 1975, and infer a 20 to 50% variation over the 200 to 300 nm wavelength range, which they correlate with the 11-year sunspot cycle. The problem has been reviewed by numerous others, such as White (1977), Delaboudiniere et al. (1978), Nicolet (1979), and Simon (1978), who neither accept nor refute the conclusion of Heath and Thekaekara (1977) but seem to indicate that their results represent an upper bound on the magnitude of the effect. In fact, it is difficult (if not impossible) to infer a solar cycle trend over a total period of 11 years. Thus, Nicolet (1979) points out that the variation in calibration procedures over the 1964 to 1975 time period is large so that the precision of the individual measurements is on the order of 25%, with an unknown accuracy.

Calculations of ozone depletion over an 11-year sunspot cycle have been made by Callis and Nealy (1978) and Penner and Chang (1978), who find that the extreme model of Heath and Thekaekara (1977) leads to an increase in total ozone of 8 to 10% going from solar minimum to solar maximum. This would be a very large effect, dominating all others over the 1957 to 1975 time frame for which there exist global ozone measurements. However, it must be noted that the best current estimates of total ozone over this period made by Angell and Korshover (1973, 1976, 1978d) provide no unambiguous evidence that total ozone varies with solar cycle.

COUPLED PERTURBATIONS

Most previous assessments of possible changes in stratospheric ozone have focused on the effects of a single perturbation, such as NO_x emissions by high flying aircraft, use of chlorofluorocarbons, and the possibility of an increase in global N_2O . In the real atmosphere many changes are occurring and will continue to occur at the same time. Thus studies of simultaneous perturbations and their interactions will prove to be necessary to understanding of atmospheric changes. Several published studies, (Logan et al. 1978; and Liu et al. 1976) have addressed the question of simultaneous perturbations and show that they interact in a nonlinear fashion, as expected given the coupling reactions in the $\text{ClX} - \text{HO}_x - \text{NO}_x$ photochemistry.

An example of such coupling is that the effect on the ozone column of an increase in stratospheric chlorine depends on the background N_2O . At higher concentrations of N_2O , more chlorine will be present in the form of chlorine nitrate. This, together with the reaction $\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$ suppresses the concentration of ClO and therefore reduces the efficiency of the chlorine catalytic cycle for ozone destruction.

The net effect of NO_x injections into the lower stratosphere on ozone column-density is a balance between NO_x catalyzed ozone destruction NO_x interference in other catalytic cycles, and NO_x enhanced ozone-producing smog reactions. If water vapor is injected together with the NO_x , it will modify all of these effects, as well as contributing directly to HO_x induced destruction of ozone.

A newly appreciated synergistic effect is the interaction of BrX with ClX radicals. The key reaction is $\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$ by which the presence of BrX radicals permits a recycling of ClO to Cl without atomic oxygen and provides an avenue for ClX catalyzed ozone destruction at night.

A number of modeling groups have made studies of combined perturbations. In particular, the groups who contributed to this report performed calculations with doubled N_2O flux together with a steady-state CFM release at 1975 production rates, and a 20 pptv addition of BrX together with the same CFM perturbation. The results for column O_3 change are given in table 7-3. In the $\text{N}_2\text{O} + \text{CFM}$ case, the effects (with one exception) are less than those for CFM alone, regardless of whether the model used predicts an ozone increase or decrease due to N_2O doubling. In no case is the resulting effect a simple addition of the separate ozone changes for the two perturbations. In the case of BrX combined with CFM, a simple addition of the effects dominates for the small amounts of BrX considered.

Obviously, the possibilities for combined perturbations of stratospheric ozone are many. In assessing an individual source of pollution, all of the other changes taking place in the real atmosphere can be ignored. However, to predict the actual fate of global ozone, it is necessary to include all of the expected changes in both the natural and anthropogenic inputs to the atmosphere, and this produces considerable additional sources of uncertainty.

UNCERTAINTIES

There are two types of uncertainties present in predictions of stratospheric response to perturbations: uncertainties in model input parameters and uncertainties inherent in the model representing the atmosphere.

UNCERTAINTIES IN MODEL INPUT PARAMETERS

To date, two techniques have been developed and applied to the quantification of uncertainties in predictions of stratospheric ozone depletion. The first of these is the sensitivity technique as described in NAS (1976) and in Hudson (1977). The second technique is the Monte-Carlo approach which is described by Stolarski et al. (1978). Both of these methods have been applied extensively to the question of chlorofluoromethane effects on the stratospheric ozone, but neither has been used to study the other possible pollutants. The most recent results for the CFM problem were performed by Butler (private communication 1979). The input set used was essentially the same as that recommended by Hudson (1977) except for more current values for the rates of the reactions $\text{HO}_2 + \text{O}_3$, $\text{NO} + \text{HO}_2$, $\text{OH} + \text{O}_3$, for the photolysis rate of N_2O ; and for the quantum yield of $\text{O}(^1\text{D})$ in O_3 photolysis. Considering changes in the input data set currently in use, the qualitative features of the results are emphasized.

Table 7-6 below gives results of CFM-induced ozone depletion for the Monte-Carlo technique using two different distribution functions for input parameters. In the Log-Normal case, the random numbers used to vary input parameters followed a Gaussian distribution of unit width, while in the Square case, the random numbers were uniformly distributed between plus and minus one. In both cases, the random factors were applied to the log of the input parameter and the size of the factor was proportional to the uncertainty in the individual parameter. The centerline ozone depletion was 19.75% for steady-state CFM release at 1975 rates.

Table 7-6
Monte Carlo Uncertainty Factors

Computed uncertainty factors on change of the column content of ozone for a steady-state CFM addition. The computed centerline value should be multiplied by the appropriate factor to obtain the $\pm 1\sigma$ and $\pm 2\sigma$ values. Log normal and square refer to two different input probability distributions as explained in the text.

	-2σ	-1σ	$+1\sigma$	$+2\sigma$
Log Normal	.38	.66	1.23	1.51
Square	.61	.79	1.15	1.33

This implies a 2σ range of the prediction of 7.5% to 29.8% for uncertainties in reaction rates and photolysis parameters. The square input distribution eliminates all cases where any parameter is more than 1σ away from its accepted value and clearly narrows the range of uncertainty.

In these results, the output was found to be best fit by a linear normal distribution, but the mean of the distribution was always below the center-line result. This indicates a small saturation on the high side which may be due to physical feedbacks, or to the intrinsic lack of linearity in a percentage depletion. The extent to which uncertainty factors are constant (given different sized CFM perturbations) was tested. At a smaller perturbation, the uncertainties increased.

Another result of the Monte-Carlo study dealt with the elimination of nonphysical cases from the uncertainty distributions. In this exercise, a given case was eliminated if certain well-measured quantities, (such as ozone or nitrous oxide) differed from the center-line result by more than a given factor. About one-third of the cases were eliminated by this test, and although they were distributed more broadly than all the cases taken together, the remaining distribution did not give significantly smaller uncertainties.

Studies were made to examine the uncertainty due to reaction rates only. The results did not differ significantly from those for rates and photolysis parameters together. This indicates that photolysis parameters contribute little to the uncertainty of CFM effects on ozone, and the sensitivity results confirm this.

Table 7-7 shows the sensitivities and uncertainties calculated with the same model used in the Monte-Carlo studies.

In principle, the uncertainties arising from the eddy-profile determination are also quantifiable. Several groups have studied the same models with different eddy coefficients (see figure 7-5). Wuebbles (private communication, 1979) compared the studies with the Chang (1974) profile, the Hunten (1975a) profile, and the NAS (1976) profile and found maximum change in the 1978 level of ozone depletion from CFM of roughly a factor of 1.25. This involves both changes in the ultimate steady-state value of ozone depletion and in the time history of CFM injection into the stratosphere. Miller (private communication, 1979) indicates that comparing the DuPont standard profile with the Chang-Dickinson (NAS 1976) profile gives a factor of 1.08 difference in the steady-state result. Stolarski (private communication, 1979) has studied the effects of a simple scaling of $K(z)$ values and found a sensitivity of 0.35 when the lower-boundary conditions were constant fluxes. When the lower boundaries were fixed mixing ratios, the sensitivity was almost nonexistent. Although these results are not subject to systematic quantitative comparison, they do indicate that eddy coefficients can be a significant source of uncertainty for CFM induced ozone depletion.

Very little quantitative work has been done on uncertainties in perturbations other than CFMs. This means that very little quantitative data are known, but some qualitative comments can be made. All CIX perturbations can be expected to be sensitive to the same reaction rates and photolysis parameters as the CFM case, and thus, their uncertainty should be similar. Continuous sources such as SSTs and rockets are much more sensitive to transport parameters than are perturbations arising from ground-level changes in long-lived species such as N_2O , CFM, CO_2 , etc. This is because of the direct competition between transport to the tropospheric removal region and photochemical activity in the stratosphere, and is compounded by the differences in photochemistry in both the lower and upper stratosphere.

UNCERTAINTIES DUE TO MODEL CONSTRUCTION

In general, uncertainties in atmospheric models fall into two major categories: (1) uncertainties due to physical approximations and (2) uncertainties due to omitted chemistry. The first category includes such known factors as latitudinal effects, radiative transfer approximations and feedback mechanisms. These will become more quantifiable as the state-of-the-art improves, but at present, cannot be determined with accuracy. The second category is basically unquantifiable. As understanding of the chemistry of the atmosphere advances, important omissions in the chemical scheme may be discovered and incorporated, but it is impossible to assess, at any given time, the effect such omissions have on perturbations. Theorists generally strive to include all of the important chemical reactions and species in their models and to provide estimates on that basis. However, they also speculate on the possible missing chemistry, and ask the kineticists to supply the necessary experimental data to assess the importance of such chemistry.

Table 7-7
Sensitivities and Uncertainties of Ozone Depletion Due to CFM at 1975 Rates*

Input	$f_{2\sigma}$	S-	U-	S+	U+	Sc	Uc
$N_2O + O(^1D) \rightarrow NO + NO$	1.58	-0.338	-0.179	-0.488	-0.225	-0.429	-0.198
$O + O_2 + M \rightarrow O_3 + M$	1.38	-0.142	-0.046	-0.147	-0.047	-0.145	-0.047
$NO + HO_2 \rightarrow NO_2 + OH$	5.01 (-) 3.47 (+) 4.17 (c)	0.166	0.268	0.175	0.218	0.180	0.257
$O + O_3 \rightarrow O_2 + O_2$	1.58	-0.059	-0.027	-0.087	-0.040	-0.072	-0.033
$H_2O + O(^1D) \rightarrow OH + OH$	1.58	0.132	0.061	0.104	0.048	0.119	0.055
$OH + HO_2 \rightarrow H_2O + O_2$	3.16	-0.126	-0.145	-0.252	-0.290	-0.180	-0.207
$OH + O \rightarrow H + O_2$	2.00			-0.019	-0.013	-0.014	-
$OH + O_3 \rightarrow HO_2 + O_2$	2.00	-0.279	-0.193	-0.372	-0.257	-0.323	-0.223
$HO_2 + O_3 \rightarrow OH + O_2 + O_2$	1.58 (-) 3.98 (+) 7.94 (c)	0.056	0.155	0.085	0.118	0.080	0.166
$O(^1D) + M \rightarrow O + M$	1.38	0.275	0.075	0.275	0.095	0.295	0.075
$NO + O_3 \rightarrow NO_2 + O_2$	1.45	-0.170	-0.070	-0.186	-0.068	-0.170	-0.070
$NO_2 + O \rightarrow NO + O_2$	1.15	-0.175	-0.027	-0.206	-0.028	-0.200	-0.027
$NO_2 + OH + M \rightarrow HNO_3 + M$	1.58	0.264	0.122	0.228	0.105	0.247	0.114
$HNO_3 + OH \rightarrow NO_3 + H_2O$	1.26	-0.013		-0.030	-	-0.020	-
$CH_4 + OH \rightarrow CH_3 + H_2O$	1.58	0.092	0.043	0.093	0.043	0.093	0.043
$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	1.58	0.023	0.011	0.017		0.020	-
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	100.00				0.013	-	-
$N + NO \rightarrow N_2 + O$	1.58	0.032	0.015	0.039	0.018	0.036	0.017
$N + O_2 \rightarrow NO + O$	1.58	-0.035	-0.016	-0.031	-0.014	-0.033	-0.015
$H_2CO + OH \rightarrow HCO + H_2O$	2.51	-0.058	-0.054	-0.061	-0.056	-0.061	-0.056
$Cl + HO_2 \rightarrow HCl + O_2$	3.98	-0.022	-0.031	-0.091	-0.126	-0.047	-0.065
$Cl + O_3 \rightarrow ClO + O_2$	1.32	0.184	0.051	0.156	0.043	0.170	0.047
$ClO + O \rightarrow Cl + O_2$	1.58	0.477	0.220	0.405	0.186	0.442	0.204
$Cl + CH_4 \rightarrow HCl + CH_3$	2.29 (-) 1.32 (+) 1.74 (c)	-0.101	-0.084	-0.117	-0.032	-0.110	-0.061
$HCl + OH \rightarrow H_2 + Cl$	1.26	0.288	0.066	0.233	0.054	0.259	0.060
$ClO + NO \rightarrow NO_2 + Cl$	2.00	-0.105	-0.073	-0.119	-0.082	-0.112	-0.078
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	2.00	-0.021	-0.015	-0.031	-0.022	-0.026	-0.018
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	1.23 (-) 2.00 (+) 1.62 (c)		-0.041	-0.193	-0.133	-0.168	-0.081
$HNO_3 + O \rightarrow OH + NO_2$	(-) 100. (+) 2. (c) 14.1		-0.014	-0.019	-0.013	-	-0.018

*All quantities with absolute values less than 0.010 have been suppressed.

Table 7-7 (Continued)

Input	$f_{2\sigma}$	S-	U-	S+	U+	Sc	Uc
N ₂ O Flux (lower b.c.)	1.26	-0.437	-0.101	-0.513	-0.118	-0.472	-0.107
CH ₄ Flux (lower b.c.)	1.45	-0.127	-0.047	-0.150	-0.055	-0.137	-0.051
H ₂ O MR (lower b.c.)	1.45	0.087	0.032	0.089	0.033	0.087	0.033
Odd N Velocity (lower b.c.)	2.51	0.029	0.027	0.011	0.010	0.018	0.016
Odd Cl Velocity (lower b.c.)	2.00	-0.048	-0.033	-0.024	-0.016	-0.034	-0.024
CH ₃ Cl Flux (lower b.c.)	2.00	-0.012		-0.028	-0.019	-0.019	-0.013
Odd N Velocity (Upper b.c.)	2.00	0.014	-	0.015	0.010	0.016	0.011
Odd O _x Velocity (lower b.c.)	2.00	0.013		0.014		0.014	-
O(¹ D) quantum yield	1.11	-0.296	-0.030	-0.294	-0.030	-0.297	-0.030
O(¹ D) relative yield 300-305 nm	1.10	-0.034			-	-0.026	-
O(¹ D) relative yield 305-310 nm	1.69	-0.028	-0.015	-0.038	-0.020	-0.033	-0.018
$\lambda > 3200 \text{ \AA}$	1.10	0.393	0.036	0.394	0.036	0.393	0.036
1900-2000 $\text{\AA}$	1.45	0.087	0.032	0.109	0.040	0.098	0.036
2000-2050 $\text{\AA}$	1.45	0.048	0.018	0.060	0.022	0.053	0.020
2100-2150 $\text{\AA}$	1.45	-0.056	-0.021	-0.062	-0.023	-0.059	-0.022
2150-2200 $\text{\AA}$	1.45	-0.020		-0.025		-0.022	-
2600-2700 $\text{\AA}$	1.10	-0.016		-0.013	-	-0.013	-
2700-2800 $\text{\AA}$	1.10	-0.020		-0.022		-0.019	-
2800-2900 $\text{\AA}$	1.10	-0.038	-	-0.039	-	-0.037	-
2900-2950 $\text{\AA}$	1.10	-0.035	-	-0.036	-	-0.038	-
2950-3000 $\text{\AA}$	1.10	-0.033		-0.033	-	-0.034	-
3000-3050 $\text{\AA}$	1.10	-0.046		-0.045		-0.047	-
3050-3100 $\text{\AA}$	1.10	-0.046	-	-0.045	-	-0.045	-
$\sigma(\text{O}_3)$	1.20	0.276	0.051	0.257	0.047	0.266	0.049
$\sigma(\text{O}_2) \lambda > 2000 \text{ \AA}$	1.32	0.443	0.122	0.390	0.108	0.418	0.115
$\sigma(\text{O}_2) \text{SRB} (\lambda < 2000 \text{ \AA})$	1.74	0.054	0.030	-0.105	-0.058	-0.055	-0.030
$\sigma(\text{HNO}_3)$	1.20	-0.176	-0.036	-0.206	-0.038	-0.200	-0.037
$\sigma(\text{H}_2\text{CO} - \text{CO})$	1.45	0.069	0.025	0.071	0.026	0.070	0.026
$\sigma(\text{ClONO}_2)$	1.32	0.188	0.052	0.164	0.045	0.176	0.049
$\sigma(\text{H}_2\text{O}_2)$	1.74	0.035	0.020	0.026	0.014	0.031	0.017
$\sigma(\text{N}_2\text{O})$	1.32	0.373	0.103	0.340	0.094	0.355	0.098
$\sigma(\text{CFCl}_3)$	1.10	-0.051		-0.050	-	-0.052	-
$\sigma(\text{CF}_2\text{Cl}_2)$	1.15	-0.024		-0.024		-0.024	-
$\sigma(\text{NO}_2)$	1.45	0.125	0.046	0.140	0.052	0.133	0.049
$\sigma(\text{NO})$	2.29	0.031	0.025	0.042	0.035	0.037	0.031

*All quantities with absolute values less than 0.010 have been suppressed.

Note: The first column labeled $f_{2\sigma}$ is the estimated factor by which the input parameter should be multiplied and divided to give the 95% confidence limits. The remaining six columns are the model computed sensitivities and uncertainties determined in the following way: model runs at the central value, $\pm 1\sigma$, and $\pm 2\sigma$ are made. Column 6 is the central sensitivity obtained from the difference of the $+1\sigma$ and -1σ runs. Column 7 is the corresponding uncertainty, i.e. the sensitivity times $\ln f_{2\sigma}$. Columns 2 and 3 are the low side sensitivities and uncertainties obtained from the -2σ and central model runs while columns 4 and 5 are the corresponding high side values.

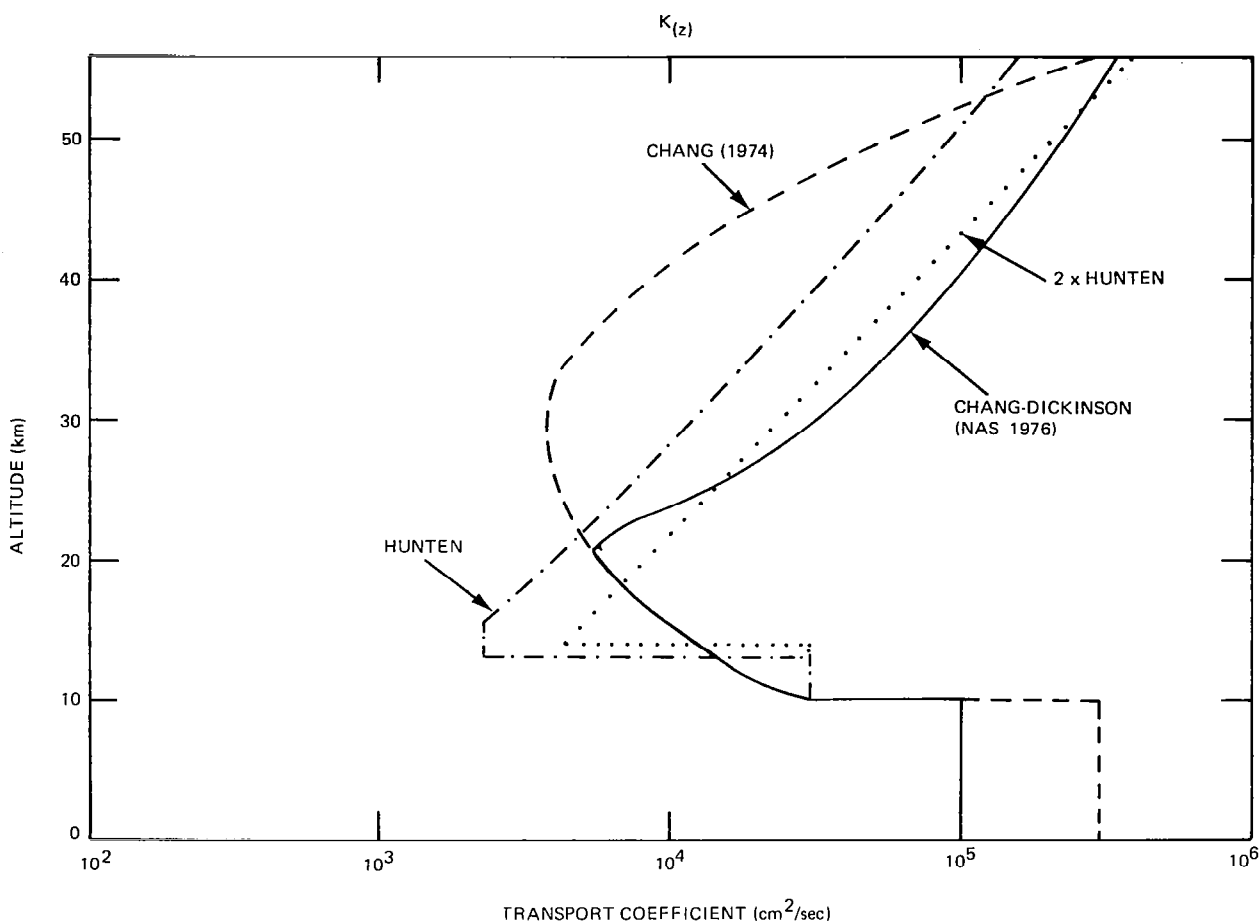


Figure 7-5. Profiles of eddy transport coefficients.

Uncertainties Due to Diurnal, Latitudinal, and Seasonal Variations

Over the past few years, it has been found that replacing 24-hour-average approximations with detailed diurnal variations has had a major impact on the magnitude of the estimated perturbation in stratospheric ozone from CFMs. In a similar manner, the coupling effects due to variations in atmospheric dynamics and photochemistry with latitude and season may also influence calculated perturbations.

At present, the only practical techniques for assessing latitudinal and seasonal effects are 2-D models with parameterized transport. These models can include sufficient chemistry to make the assessment meaningful, and yet, do not require excessive amounts of computation time. Despite objections concerning the atmospheric dynamics of parameterized transport 2-D models (see Chapter 2), such models should perform an inherently better job of describing the chemical behavior of the atmosphere than 1-D parameterized transport models.

In general, the accuracy of parameterized transport models for large perturbation predictions is limited by the magnitude of dynamic feedback mechanisms. The models also suffer from the problems associated with specification of an accurate transport parameterization (because of the present inadequate data base), and from the question of whether an eddy-transport parameterization can ever really describe transport of long-lived species in a suitable manner. Nevertheless, recent developments in the theory of Lagrangian transport of

mass in the atmosphere by Dunkerton (1978) and Andrews and McIntyre (1978a) lend credence to the concept that a 2-D parameterized transport treatment of the dynamics in a primarily photochemical model may be capable of permitting a realistic description. This is especially true if allowance is made for an asymmetric eddy-diffusion tensor in the model. As has been noted by Danielsen and Louis (1977), asymmetries in the eddy-diffusion tensor are equivalent to modifications in the mean meridional stream function for mass transport. Thus, suitable choices in the asymmetric portion of the eddy-diffusion tensor provide the possibility of obtaining a Lagrangian-mean meridional flow field different from the ordinary Eulerian flow field used as the basis for many current 2-D models. Although there may be difficulties with 2-D models at high altitudes where the chemical behavior of the atmosphere is determined to a large extent by photochemistry, the objections to the use of parameterized transport are not nearly as convincing.

If a 2-D parameterized transport model reasonably describes the observed latitudinal and seasonal behavior of certain key long-lived trace species in the lower stratosphere and troposphere (such as N_2O , ozone, and CFMs), then it is possible that it also provides a good description of the behavior of most other chemical species as well. There are several reasons for this. First, in terms of the chemical behavior of the atmosphere, if the model calculates the transport of long-lived species correctly then the photochemistry dictates inter-conversion between short-lived species within long-lived families. Secondly, the generally upward-moving long-lived species such as CFMs, N_2O , and CH_4 may all undergo a similar general scheme of transport and chemistry in the lower stratosphere (characterized by upwelling in the tropics to provide maximum mixing ratios) and in the middle tropical stratosphere (characterized by major photochemical destruction). The behavior of the general downward-moving species such as ozone (below 30 km), odd nitrogen and ClX in the lower stratosphere are virtually the inverse of the calculation for the long-lived species.

Given the potential of 2-D parameterized transport models to provide an improved description of the behavior of chemical species in the atmosphere the uncertainties due to latitudinal and seasonal averaging procedures of 1-D models may be assessed by comparison with 2-D model results. Such a comparison has been carried out by Whitten et al. (1977) using the NASA Ames 2-D model as a basis. In this comparison the predicted global mean perturbations in stratospheric ozone in a CFM scenario are roughly in agreement for the 1-D and 2-D models, assuming similar vertical transport. Furthermore, there are indications that the trace species concentrations calculated in the 1-D model are quite similar to the 2-D model results at approximately 30° latitude (seasonally averaged). Therefore, for this particular type of perturbation, the tentative conclusion is that the uncertainties due to latitudinal and seasonal effects are small. Results from the Ames 2-D model for certain other perturbations such as SSTs and solid-fueled rockets produce conclusions similar to those for CFMs, although so-called corridor effect related to the pattern of injections (i.e., at midlatitudes in the Northern Hemisphere) must be considered.

Uncertainties Due to Missing Chemistry

Uncertainties due to missing chemistry in 1-D models are very difficult to assess, even in the case of proposed but unmeasured reactions. Significant discrepancies between model predictions and actual experimental measurements in the atmosphere may be an indication of chemistry omitted from models. Such discrepancies should receive careful attention, since if omitted chemistry is the cause, it could have a profound influence on the magnitude of certain perturbation predictions.

The comparison of model-computed ambient concentration with measurements suggests several systematic differences between model and observation. A number of speculative mechanisms have been proposed by McConnell and Evans (1978), and Prasad and Burton (1979) to correct these differences. However, the identification of the actual sources of differences between model and observation is difficult. Thus there is a suggestion that present models omit (or poorly represent) some significant chemical or physical processes or that the data coverage is somehow inadequate and that substantial changes in computed sensitivities may occur.

Uncertainties Due to Treatment of Radiative Transfer

The transport of solar radiation through the atmosphere is a key factor in determining the rate of photodissociation of atmospheric species. One-dimensional atmospheric models employ a number of simplifying approximations in the calculation of radiative transfer, which lead to uncertainties with respect to both species concentration profiles and perturbation estimates.

The present state-of-the-art 1-D model treatment of radiative transfer includes absorption of radiation by O_2 and O_3 , multiple scattering by atmospheric molecules, and reflection of radiation by the ground. Individual atmospheric 1-D models handle the calculation with varying degrees of sophistication. For example, in the case of multiple scattering, it is often common to use phase functions other than the Rayleigh-phase function (e.g., isotropic or double stream). This type of approximation has been shown by Miller et al. (1978) to be accurate for certain solar zenith angles, but remains to be tested at zenith angles greater than 60° .

Most state-of-the-art 1-D models neglect curvature effects in the treatment of radiation transfer and assume a flat parallel atmosphere. This approach is valid for solar zenith angles less than 75° , but it can also lead to inaccuracies in the calculated diurnal variations in short-lived species near sunrise and sunset. In the case of perturbation calculations, the inaccuracies introduced by the neglect of curvature are believed to be quite small. Although simple corrections for curvature effects exist in the pure absorption situation, the inclusion of multiple scattering in the calculation leads to a complicated 2-D problem.

The majority of 1-D models neglect scattering by aerosol particles and clouds in the radiation transfer calculations, and instead lump these effects into an increased albedo at ground level. Some testing of the implications of this approximation on photolysis rates has been carried out by Callis (1977), but additional work must be performed to determine the impact on perturbations.

The albedo at the surface of the Earth is known to be a function of latitude and season, but such effects are not included in 1-D models because of global averaging. There is a need for the latitudinal and seasonal variation of albedo to be included in 2-D models to provide an assessment of this uncertainty. Sensitivity studies of the type described above should also be carried out to examine the sensitivity of various perturbations to the adopted ground-level value of the albedo. Although the reflection of radiation at the Earth's surface is known to be nondiffuse, 1-D models commonly assume diffuse reflection for simplicity. Further studies should focus on the implications of the diffuse-reflection approximation on the uncertainties of 1-D model predictions.

For some processes (e.g., NO and H_2O photolysis), the penetration of light through the Schumann-Runge absorption bands of O_2 is of great importance. A number of somewhat different treatments by Hudson and Mahle (1972), Nicolet and Vergison (1971), Ackerman and Biaume (1970a), Fang, et al. (1974), Turco (1975) are in current use. All such approximations are sensitive to the shape and width of the O_2 absorption lines. These parameters are uncertain enough to have a substantial effect on processes such as NO photolysis, as noted by Frederick and Hudson (1979a).

Feedbacks

There are a number of atmospheric processes that can serve as positive or negative feedbacks on stratospheric ozone perturbation. Many of these have been hypothesized but few are included in most 1-D models. The most prominent is temperature feedback. It is well known that ozone absorption of ultraviolet sunlight is the principal heat source in the middle atmosphere. As ozone is perturbed, the temperature structure responds and feedback through temperature-dependent rate coefficients and atmospheric pressure to mitigate or enhance the ozone change. This effect has been calculated by several groups such as Chandra et al. (1978) using Newtonian cooling approximations which are questionable below 30 km. The feedback effect was not

found to be substantial, and most groups have continued omitting this from their calculations. There is also a further feedback such that a change in temperature structure implies a change in transport. To use this in a 1-D model, a temperature-dependent eddy coefficient would have to be devised, and there is no basis for doing so.

A combined temperature and dynamics feedback that has received considerable mention is the tropical tropopause cold trap. The concept is that the water-vapor content of the lower stratosphere is substantially controlled by the temperature of the tropical tropopause and limited to the saturation mixing ratio at this temperature. Thus, if the temperature is changed at this point in the atmosphere, the water-vapor abundance can change throughout the stratosphere. Dobson et al. (1946) and Brewer (1949) originated this idea which was more recently discussed by Liu et al. (1976) and Chapter 3 of this report. At present, the basis for quantifying this feedback and including it in routine model calculations does not exist, and thus, despite its long history, it too must remain a source of uncertainty.

A further source of feedback is potential changes in the troposphere and biosphere that might result if ozone-column density in the stratosphere changes substantially. Chemical changes resulting from altered UV flux may be expressed in modified OH concentrations which would, in turn, change the tropospheric lifetimes of compounds such as CH_3Cl and CH_3CCl_3 . Living organisms and the ecosystems in which they are imbedded may respond directly to UV change, or indirectly to climatic or chemical changes, and alter the biogenic sources of N_2O , CH_4 , or CH_3Cl , which form key minor constituents of the stratosphere. Most stratospheric 1-D models now include the troposphere and attempt to account for the direct chemical feedbacks of the troposphere. However, as indicated earlier, the 1-D approximation is not as physically appropriate in the troposphere as in the stratosphere, and tropospheric chemistry appears both more complex and less well understood than stratospheric chemistry. As yet, there is no quantitative basis for assessing climatic or biospheric response. Thus, tropospheric feedbacks are a considerable source of unquantified uncertainty.

There may be direct climatic feedbacks which are as yet undetermined. In addition to the changes in transport and UV heating already alluded to, there are potential changes in radiative balance arising from changes in ground albedo, modified abundances of IR active gases, and changes in aerosol content of the atmosphere. An assessment of these feedbacks must await general improvements in the understanding of the atmosphere.

CONCLUSION

The uncertainties associated with estimating the long-term impact of several perturbing influences to the stratospheric ozone layer continue to be large. However, prospects appear good for improving the situation in the near future.

The easily quantifiable uncertainties related to existing model parameter inputs such as reaction rates, cross sections, boundary conditions, etc., can be reduced significantly in the near future through the availability of new kinetic and atmospheric data. On the other hand, the reduction of uncertainties due to model construction is not as close because of the time delay required to bring about advances in modeling capabilities. Although 1-D models continue to be a powerful tool for approximating trace species behavior on a globally averaged basis and for making assessments of perturbations, the need still exists for additional development in the area of 2-D modeling.

Because of presently unquantifiable uncertainties (such as omitted processes) models must be used as diagnostic tools to compare theoretical predictions with measurements. When discrepancies are discovered a search must be made for the possible role of missing chemistry, omitted physical processes, or inappropriate numerical approximations.

REFERENCES

- Ackerman, M., Stratospheric water vapor from high resolution infrared spectra, *Planet. Space Sci.*, **22**, 1265-1267, 1974.
- Ackerman, M., and F. Biaume, Structure of the Schumann-Runge bands from the 0-0 to the 13-0 band, *Aeronom. Acta.*, **68**, 1-20, 1970a.
- Ackerman, M., and F. Biaume, Structure of the Schumann-Runge bands from the 0-0 to the 13-0 band, *J. Mol. Spectr.*, **35**, 73, 1970b.
- Ackerman, M., and C. Muller, Stratospheric methane and nitrogen dioxide from infrared spectra, *Pure Appl. Sci.*, 106-108, 1325-1335, 1973.
- Ackerman, M., J. C. Fontanella, D. Frimout, A. Girard, N. Louisnard, and C. Muller, Simultaneous measurements of NO and NO₂ in the stratosphere, *Planet. Space Sci.*, **23**, 651-660, 1975.
- Ackerman, M., D. Frimout, A. Girard, M. Gottignier, and C. Muller, Stratospheric HCl from infrared spectra, *Geophys. Res. Lett.*, **3**, 81-83, 1976.
- Adams, N. G., and D. Smith, The selected ion flow tube (SIFT); a technique for studying ion-neutral reactions, *Int. J. Mass Spectrom. Ion Phys.*, **21**, 349-359, 1976.
- Adler, R. F., Mean meridional circulation in the Southern Hemisphere stratosphere based on satellite information, *J. Atmos. Sci.*, **32**, 893-898, 1975.
- A. D. Little, Inc., Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons, Prepared for the Environmental Protection Agency, publication number EPA-450/3-75-073, 1975.
- Ahmad, Z., The applicability of the BUUV algorithm for estimating the total ozone in the presence of a sea surface, Systems & Applied Sciences Corporation, Report 1977.
- Aikin, A. C., and K. Maeda, Ozone changes due to solar flare X-rays, Am. Met. Soc. Conf. on Meteorology of the Upper Atmosphere, Boston, Mass. 1978.
- Aikin, A. C., and E. J. Maier, A balloon-borne photoionization mass spectrometer for measurement of stratospheric gases, To be published *Rev. Sci. Instr.*, **49**, 1034-1040, 1978.
- Air Weather Service, Accuracies of radiosonde data, Tech. Rep. 105-133, National Oceanic and Atmospheric Administration, 1955.
- Albritton, D. L., Ion-neutral reaction-rate constants measured in flow reactors through 1977, *Atom. Data Nucl. Tables*, **22**, 1-101, 1978.
- Allen, M. A., and Y. L. Yung, Vertical transport in the mesosphere as deduced from CO: Implications for stratospheric NO_x budget, *Geophys. Res. Lett.*, 1979.
- Amimoto, S. T., A. P. Force, and J. R. Wiesenfeld, Ozone photochemistry: Production and deactivation of O(¹D₂) following photolysis at 248 nm, *Chem. Phys. Lett.*, **60**, 40-43, 1978.
- Amimoto, S. T., A. P. Force, and J. R. Wiesenfeld, Results presented at the National Meeting, American Chemical Society, Honolulu, April 1979.

- Anderson, J. G., Rocket-borne ultraviolet spectrometer measurement of OH resonance fluorescence with diffusive transport model for mesospheric photochemistry, *J. Geophys. Res.*, **76**, 4634-4652, 1971.
- Anderson, J. G., Rocket measurement of OH in the mesosphere, *J. Geophys. Res.*, **76**, 7820-7824, 1971a.
- Anderson, J. G., The absolute concentration of $O(^3P)$ in the Earth's stratosphere, *Geophys. Res. Lett.*, **2**, 231-238, 1975.
- Anderson, J. G., The absolute concentration of OH ($X^2\Pi$) in the Earth's stratosphere, *Geophys. Res. Lett.*, **3**, 165-168, 1976.
- Anderson, J. G., Report to NASA HQ, November 1978.
- Anderson, J. G., J. J. Margitan, and D. H. Stedman, Atomic chlorine and the chlorine monoxide radical in the stratosphere: Three in situ observations, *Science*, **198**, 501-503, 1977.
- Anderson, J. G., H. J. Grassl, R. E. Shetter, and J. J. Margitan, Stratospheric free chlorine measured by balloon borne in situ resonance fluorescence, manuscript dated February 1979.
- Andrews, D. G., and M. E. McIntyre, Planetary waves in horizontal and vertical shear: The generalized Eliassen-Palm relation and the mean zonal acceleration, *J. Atmos. Sci.*, **33**, 2031-2048, 1976a.
- Andrews, D. G., and M. E. McIntyre, Planetary waves in horizontal and vertical shear: Asymptotic theory for equatorial waves in weak shear, *J. Atmos. Sci.*, **33**, 2049-2053, 1976b.
- Andrews, D. G., and M. E. McIntyre, An exact theory of nonlinear waves in a Lagrangian-mean flow, *J. Fluid Mech.*, **89**, 609-646, 1978a.
- Andrews, D. G., and M. E. McIntyre, On wave-action and its relatives, *J. Fluid Mech.*, **89**, 647-664, 1978b.
- Angell, J. K., and J. Korshover, Quasi-biennial and long-term fluctuations in total ozone, *Mon. Weather Rev.*, **101**, 426-443, 1973.
- Angell, J. K., and J. Korshover, Global analysis of recent total ozone fluctuations, *Mon. Weather Rev.*, **104**, 63-75, 1976.
- Angell, J. K., and J. Korshover, Global temperature variation, surface-100 mb: An Update into 1977, *Mon. Weather Rev.*, **106**, 755-770, 1978a.
- Angell, J. K., and J. Korshover, Estimate of global temperature variations in the 100-30 mb layer between 1958 and 1977, *Mon. Weather Rev.*, **106**, 1422-1432, 1978b.
- Angell, J. K., and J. Korshover, Recent rocketsonde-derived temperature variations in the Western Hemisphere, *J. Atmos. Sci.*, **35**, 1758-1764, 1978c.
- Angell, J. K., and J. Korshover, Global ozone variations: An update into 1976, *Mon. Weather Rev.*, **106**, 725-737, 1978d.
- Angell, J. K., and J. Korshover, Comparison of ozone variations derived from ozonesondes and Umkehr measurements for the period 1969-76, *Mon. Weather Rev.*, **107**, 601-607, 1979.

- Arguello, G., and M. J. Molina, Ultraviolet absorption spectrum of CH_3OOH vapor, submitted to *Geophys. Res. Lett.*, 1979.
- Arijs, E., J. Ingels, and D. Nevejans, Mass spectrometric measurements of the positive ion composition of the stratosphere, *Nature*, **271**, 642-644, 1978.
- Arnold, F., and D. Krankowsky, A new concept for the D-region ion chemistry as inferred from a mass spectrometer measurement, *COSPAR Symp. Sol. Terr. Phys.*, 17 June-1 July, Sao Paulo, Brazil, 1974.
- Arnold, F., and D. Krankowsky, Ion composition and electron and ion loss processes in the earth's atmosphere, in *Dynamical and Chemical Coupling of the Neutral and Ionized Atmosphere*; edited by B. Grandal and J. A. Holtet, 93-127, D. Riedel Publ., 1977.
- Arnold, F., and G. Henschen, First mass analysis of stratospheric negative ions, *Nature*, **275**, 521-522, 1978.
- Arnold F., and W. Joos, Rapid growth of atmospheric cluster ions at the cold mesopause, *Geophys. Res. Lett.*, **6**, 763-766, 1979.
- Arnold, F., J. Kissel, D. Krankowsky, H. Wieder, and J. Zahringer, Negative ions in the lower ionosphere: A mass-spectrometric measurement, *J. Atmos. Terr. Phys.*, **33**, 1169-1175, 1971.
- Arnold, F., D. Krankowsky, and K. H. Marien, First mass spectrometric measurements of positive ions in the stratosphere, *Nature*, **267**, 30-32, 1977.
- Arnold, F., H. Bohringer, and G. Henschen, Composition measurements of stratospheric positive ions, *Geophys. Res. Lett.*, **5**, 653-656, 1978.
- Arvesen, J. C., R. N. Griffin, Jr., and B. D. Pearson, Jr., Determination of extraterrestrial solar spectral irradiance from a research aircraft, *Appl. Opt.*, **8**, 2215-2232, 1969.
- Artzner, G., The solar H-Lyman-alpha line: Wavelength and profile measurement, *Astron. Astrophys.*, **70**, L11-L14, 1978.
- Atkinson, R., and J. N. Pitts, Jr., Kinetics of the reactions of the OH radical with HCHO, and CH_3CHO over the temperature range 299-426 K, *J. Chem. Phys.*, **68**, 3851-3854, 1978.
- Ausloos, P., R. E. Rebbert, and L. Glasgow, Photodecomposition of chloromethanes adsorbed on silica surfaces, *J. of Res. of National Bureau of Standards*, **82**, 1-8, 1977 (See also Rebbert, R. E., and P. Ausloos, Decomposition of N_2O over particulate matter, *Geophys. Res. Lett.*, **5**, 761-764, 1978.)
- Baer, F., and F. Alyea, Effects of spectral truncation and general circulation and long-range prediction, *J. Atmos. Sci.*, **28**, 457-480, 1971.
- Bailey, D. K., Some quantitative aspects of electron precipitation in and near the auroral zone, *Rev. Geophys.*, **6**, 289-364, 1968 (See also Correction, *Rev. Geophys.*, **7**, 666, 1969).
- Bailey, D. K., R. R. Brown, and M. H. Rees, Simultaneous forward-scatter, riometer, and bremsstrahlung observations of a daytime electron precipitation event in the auroral zone, *J. Atmos. Terr. Phys.*, **32**, 149-169, 1970.

- Bailey, P. L., and J. C. Gille, An approximate method for non-linear inversion of limb radiance observations, *Developments in Atmospheric Science*, **9**, *Remote Sensing of the Atmosphere*, Fymat and Zuev, editors, Elsevier Pub., 1978.
- Baker-Blocker, A., T. M. Donahue, and K. H. Mancy, Methane flux from wetlands areas, *Tellus*, **29**, 245-250, 1977.
- Barker, J. R., S. W. Benson, and D. M. Golden, The decomposition of dimethyl peroxide and the rate constant for $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2 + \text{HO}_2$, *Int. J. Chem. Kinet.*, **9**, 31-53, 1977.
- Barnett, J. J., The mean meridional temperature behavior of the stratosphere derived from measurements by the selective chopper radiometer on Nimbus-4, *Quart. J. Roy. Meteorol. Soc.*, **100**, 505-530, 1974.
- Barnett, J. J., M. J. Cross, R. S. Harwood, J. T. Houghton, C. G. Morgan, G. E. Peckham, C. D. Rodgers, S. D. Smith, and E. J. Williamson, The first year of the selective chopper radiometer on Nimbus-4, *Quart. J. Roy. Meteorol. Soc.*, **98**, 17-37, 1972.
- Barnett, J. J., J. T. Houghton, and J. A. Pyle, The temperature dependence of the ozone concentration near the stratopause, *Quart. J. Roy. Meteorol. Soc.*, **101**, 245-257, 1975.
- Basher, R. E., Intercomparison of prototype New Zealand filter instrument and Dobson spectrophotometer, NASA Technical Paper 1227, 1978.
- Bates, J. R., Dynamics of stationary ultra-long waves in middle latitudes, *Quart. J. Roy. Meteorol. Soc.*, **103**, 397-430, 1977.
- Batt, L., Comments following paper by D. Golden in Chemical Kinetic Data Needs for Modelling the Lower Troposphere, *NBS Special Publ.* **557**, 62-64, 1979.
- Bauer, E., A catalog of perturbing influences on stratospheric ozone, 1955-1975, *Federal Aviation Administration Report FAA-EQ-78-20*, 1978.
- Bauer, E., A catalog of perturbing influences on stratospheric ozone, 1955-1975, *J. Geophys. Res.*, in press, 1979.
- Bauer, E., and F. R. Gilmore, Effect of atmospheric nuclear explosions on total ozone, *Rev. Geophys. Space Phys.*, **13**, 451-458, 1975.
- Belmont, A. D., and G. D. Nastrom, Long-period waves in mesospheric winds at Saskatoon, *J. Geomag. Geoelec.*, **31**, in press, 1979.
- Belmont, A. D., D. G. Dartt, and G. D. Nastrom, Periodic variations in stratospheric zonal wind from 20 to 65 km, at 80°N to 70°S, *Quart. J. Roy. Meteorol. Soc.*, **100**, 203-211, 1974.
- Berg, W. W., and J. W. Winchester, Organic and inorganic gaseous chlorine concentrations in relation to the particle size distribution of chlorine in the marine aerosol, *J. Geophys. Res.*, **82**, 5945-5953, 1977.
- Bergeman, T. H., and S. C. Wofsy, The fine structure of O_2 ($\text{B}^3\Sigma_u^-$), *Chem. Phys. Lett.*, **15**, 104-107, 1972.
- Berger, M. J., and S. M. Seltzer, Bremsstrahlung in the atmosphere, *J. Atmos. Terr. Phys.*, **34**, 85-108, 1972.

- Berger, M. J., S. M. Seltzer, and K. Maeda, Some new results on electron transport in the atmosphere, *J. Atmos. Terr. Phys.*, **36**, 591-617, 1974.
- Bhartia, P. K., V. G. Kaveeshwar, and A. J. Fleig, Error analysis of the BUV technique of measuring total ozone, in preparation, 1979.
- Bigg, E. K., A. Ono, and W. J. Thomson, Aerosols at altitudes between 20 and 37 km, *Tellus*, **22**, 550-563, 1970.
- Blake, D., and R. S. Lindzen, Effect of photochemical models on calculated equilibria and cooling rates in the stratosphere, *Mon. Weather Rev.*, **101**, 783-802, 1973.
- Blamont, J., J.-P. Pommerehne, and G. Souchon, Observations crépusculaires du NO₂ stratosphérique, *C. R. Acad. Sci. Paris*, **281**, Série B, 247-252, 1975.
- Bolin, B., Changes of land biota and their importance for the carbon cycle, *Science*, **196**, 613-615, 1977.
- Bojkov, R. D., Differences in vertical ozone distribution deduced from Umkehr and ozonesonde data at Goose Bay, *J. Appl. Meteorol.*, **5**, 872-877, 1966.
- Bojkov, R. D., Differences in Dobson spectrophotometer and filter ozonometer measurements of total ozone, *J. Appl. Meteorol.*, **8**, 362-368, 1969.
- Booker, J. R., and F. P. Bretherton, The critical layer for internal gravity waves in a shear flow, *J. Fluid Mech.*, **27**, 513-539, 1967.
- Borucki, W. J., R. C. Whitten, H. T. Woodward, L. A. Capone, C. A. Riegel, and S. Gaines, Stratospheric ozone decrease due to chlorofluoromethane photolysis: predictions of latitude dependence, in press, *J. Atmos. Sci.*, 1979.
- Borucki, W. J., R. C. Whitten, L. A. Capone, C. A. Riegel, Two-dimensional model predictions of the sensitivity of CFM-induced ozone depletions, (abstract) *Eos Trans. AGU*, **60**, 269, 1979.
- Boyd, J. P., The noninteraction of waves with the zonally averaged flow on a spherical earth and the interrelationships of eddy fluxes of energy, heat, and momentum, *J. Atmos. Sci.*, **33**, 2285-2291, 1976.
- Brasseur, G., Un modele bidimensionnel du comportement de l'ozone dans la stratosphere, *Planet. Space Sci.*, **26**, 139-159, 1978.
- Brasseur G., and M. Nicolet, Chemospheric processes of nitric oxide in the mesosphere and stratosphere, *Planet. Space Sci.*, **21**, 939-961, 1973.
- Bremner, J. M., and A. M. Blackmer, Nitrous oxide: Emission from soils during nitrification of fertilizer nitrogen, *Science*, **199**, 295-296, 1978.
- Bretherton, F. P., GARP and clear air turbulence, *Bull. Amer. Meteorol. Soc.*, **52**, 17-21, 1971.
- Brewer, A. W., Evidence for a world circulation provided by the measurements of helium and water vapour distribution in the stratosphere, *Quart. J. Roy. Meteorol. Soc.*, **75**, 351-363, 1949.
- Brewer, A. W., and J. R. Milford, The Oxford-Kew ozonesonde, *Proc. Roy. Soc. London*, **256A**, 470-495, 1960.

- Brewer, A. W., C. T. McElroy, and J. B. Kerr, Spectrophotometric nitrogen dioxide measurements, *Proceedings of the Third CIAP Conference*, U.S. Dept. of Transportation, DOT-TSC-OST-74-15, 257-263, 1974.
- Brewer, A. W., and K. P. B. Thompson, A radiometer-sonde for observing stratospheric emission due to water vapor in its rotational band, *Quart. J. Roy. Meteorol. Soc.*, **98**, 187-192, 1972.
- Brix, P., and G. Herzberg, Fine structure of the Schumann-Runge bands near the convergence limit and the dissociation energy of the oxygen molecule, *Can. J. Phys.*, **32**, 110-135, 1954.
- Broadfoot, A. L., The solar spectrum 2100-3200 Å, *Astrophys. J.*, **173**, 681-689, 1972.
- Brockman, P. L., C. H. Bair, and F. Allario, High resolution spectral measurement of the HNO₃ 11.3 μm band using tunable lasers, *Appl. Opt.* **17**, 91-100, 1978.
- Broecker, W., and T.-H. Peng, Gas exchange rates between air and sea, *Tellus*, **26**, 21-28, 1974.
- Broecker, W. S., T. Takahashi, H. J. Simpson, and T.-H. Peng, Fate of fossil fuel carbon dioxide and the global carbon budget. *Science*, **206**, 409-418, 1979.
- Brown, L., R. Hunt, and A. Pine, Wavelengths, line strengths and assignments in the Doppler limited spectrum of formaldehyde from 2700 to 2000 cm⁻¹, *J. Molec. Spect.*, **75**, 406-428, 1979.
- Brueckner, G. E., J.-D. F. Bartoe, O. K. Moe, and M. E. VanHoosier, Absolute solar ultraviolet intensities and their variations with solar activity. I. The wavelength region 1750-2100 Å, *Astrophys. J.*, **209**, 935-944, 1976.
- Bruner, E. C., Jr., and R. W. Parker, Hydrogen geocorona and solar Lyman-alpha line 1. Rocket measurement of the solar line profile, *J. Geophys. Res.*, **74**, 107-113, 1969.
- Bruner, E. C., Jr. and W. A. Rense, Rocket observations of profiles of solar ultraviolet emission lines, *Astrophys. J.*, **157**, 417-424, 1969.
- Buijs, H. L., G. L. Vail, and G. Tremblay, Simultaneous measurement of the volume mixing ratio of HCl and HF in the stratosphere, Report submitted to Manufacturing Chemists Association, July 15, 1977, also *Geophys. Res. Lett.* to be published.
- Burke, R., Remarks made at the NATO Advanced Study Institute held in La Baule, France, September 4 to 16, 1978.
- Burkhardt, E. G., C. A. Lambert, and C. K. N. Patel, Stratospheric nitric oxide: Measurements during day-time and sunset, *Science*, **188**, 1111-1113, 1975.
- Burnett, C. R., and E. B. Burnett, Spectroscopic measurements of the vertical abundance of hydroxyl (OH) in the earth's atmosphere, (abstract) *Eos Trans. AGU*, **60**, 336, 1979.
- Burrows, J. P., G. W. Harris, and B. A. Thrush, Rates of reaction of HO₂ with HO and O studied by laser magnetic resonance, *Nature*, **267**, 233-234, 1978.

- Burrows, J. P., D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, Laboratory studies of the reactions of hydroperoxy radicals (HO_2) having stratospheric importance, WMO Symposium on the Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere, Toronto, WMO Publ. 511, World Meteorological Organization, Geneva, pp. 25-28 1978.
- Bush, Y. A., A. L. Schmeltekopf, F. C. Fehsenfeld, D. L. Albritton, J. R. McAfee, P. D. Goldan, and E. E. Ferguson, Stratospheric measurements of methane at several latitudes, *Geophys. Res. Lett.*, **5**, 1027-1029, 1978.
- Busoletti, E., and J. P. Baluteau, Determination of $\text{H}_2\text{O}/\text{O}_2$ stratospheric mixing ratio from high resolution spectra in the far infrared, *Infrared Phys.*, **14**, 293-302, 1974.
- Butler, D. M., The uncertainty in ozone calculations by a stratospheric photochemistry model, *Geophys. Res. Lett.*, **5**, 769-772, 1978.
- Butler, D. M., R. S. Stolarski, and W. L. Chameides, Effect of ground level emissions of carbon monoxide and nitrogen oxides on tropospheric and stratospheric ozone, submitted to *J. Geophys. Res.*, 1979.
- Cadet, D., Energy dissipation within intermittent clear air turbulence patches, *J. Atmos. Sci.*, **34**, 137-142, 1977.
- Cadle, R. D., Composition of the stratospheric sulfate layer, (abstract) *Eos Trans. AGU*, **53**, 812-820, 1972.
- Cadle, R. D., and P. Crutzen, Volcanic emissions of halides and sulfur compounds to the troposphere and stratosphere, *J. Geophys. Res.*, **80**, 1650-1652, 1975.
- Cadle, R. D., and G. W. Grams, Stratospheric aerosol particles and their optical properties, *Rev. Geophys. Space Phys.*, **13**, 475-501, 1975.
- Cadle, R. D., A. L. Lazrus, W. H. Pollock, and J. P. Shedlovsky, The chemical composition of aerosol particles in the tropical stratosphere, *Proc. Symp. Tropical Meteorol.*, **KIV**, 1, 1970.
- Cadle, R. D., P. Crutzen, and D. Ehhalt, Heterogeneous chemical reactions in the stratosphere, *J. Geophys. Res.*, **80**, 3381-3385, 1975.
- Cadle, R. D., C. S. Kiang, and J. F. Louis, The global scale dispersion of the eruption clouds from major volcanic eruptions, *J. Geophys. Res.*, **81**, 3125-3132, 1976.
- Cadle, R. D., F. G. Fernald, and C. L. Frush, Combined use of lidar and numerical diffusion models to estimate the quantity and dispersion of volcanic eruption clouds in the stratosphere: Vulcan Fuego, 1974, and Augustine, 1976. *J. Geophys. Res.*, **82**, 1783-1786, 1977.
- Cadle, R. D., B. J. Huebert, A. L. Lazrus, and W. I. Rose, Jr., Implications of studies of Guatemalan volcanoes with regard to stratospheric trace constituents (abstract), *Eos Trans. AGU*, **59**, 1223, 1978.
- Cadle, R. D., A. L. Lazrus, B. J. Huebert, L. E. Heidt, W. I. Rose, Jr., D. C. Woods, R. L. Chuan, R. E. Stoiber, D. B. Smith, and R. A. Fielinski, Atmospheric implications of studies of Central American volcanic eruption clouds, submitted to *J. Geophys. Res.*, 1979.
- Cadle, R. D., M. A. Shapiro, and G. Langer, Concentrations of condensation nuclei in the vicinity of jet-stream maxima, *Arch. Meteorol. Geoph. Bioklim.*, **Ser. A**, **28**, 1-10, 1979.

- Callis, L. B., Scattering, photochemistry, and the spectral albedo between 200 and 725 nanometers, *Proc. Symposium on Radiation in the Atmosphere*, H. J. Bolle ed., Science Press, Princeton, NJ, 1977.
- Callis, L. B., and J. E. Nealy, Solar UV variability and its effect on stratospheric thermal structure and trace constituents, *Geophys. Res. Lett.*, **5**, 249-252, 1978.
- Callis, L. B., V. Ramanathan, R. Boughner, and B. Barkstrom, The stratosphere: scattering effects, a coupled 1-D model, and thermal balance effects, *Proceedings of the Fourth CIAP Conference, Rep. DOT-TSC-OST-75-38*, pp 224-233, U. S. Department of Transportation, Washington, D. C., 1975.
- Callis, L. B., M. Natarajan, J. E. Nealy, Ozone and temperature trends associated with the 11-year solar cycle, *Science*, **204**, 1303-1306, 1979.
- Campbell, I. M., D. F. McLaughlin, and B. J. Handy, Rate constants for the reactions of hydroxyl radicals with alcohol vapors at 292 K, *Chem. Phys. Lett.*, **38**, 362-364, 1976.
- Carver, J. H., H. P. Gies, T. I. Hobbs, B. R. Lewis, and D. G. McCoy, Temperature dependence of the molecular oxygen photoabsorption cross section near H Lyman alpha line, *J. Geophys. Res.*, **82**, 1955-1960, 1977.
- Castleman, A. W., Jr., Aerosol chemistry, *The Physics and Chemistry of Upper Atmosphere*, B. M. McCormac, editor, D. Reidel Publishing Co., Dordrecht-Holland, 143-157, 1973.
- Castleman, A. W., Jr., Nucleation processes and aerosol chemistry, *Space Sci. Rev.*, **15**, 547-589, 1974.
- Castleman, A. W., Jr., Nucleation and molecular clustering about ions, *Advances in Colloid and Interface Science*, **10**, A. Zettlemoyer, editor, Elsevier Scientific Publishing Co., Amsterdam, 73, 1979a.
- Castleman, A. W., Jr. *Kinetics of Ion-Molecule Reactions*, **40**, 295, Pierre Ausloos, editor, Plenum Publishing Co., 1979b.
- Castleman, A. W., Jr., H. R. Munkelwitz, and B. Manowitz, Isotopic studies of the sulfur component of the stratospheric sulfur layer, *Tellus*, **26**, 222-234, 1974.
- Castleman, A. W., Jr., and I. N. Tang, Kinetics of the association reaction of SO₂ with the hydroxyl radical, *J. Photochem.*, **6**, 349-354, 1976/77.
- Castleman, A. W., Jr., R. E. Davis, H. R. Munkelwitz, I. N. Tang, and W. P. Wood, Kinetics of association reactions pertaining to H₂SO₄ aerosol formation, *Int. J. Chem. Kinetics, Symp. No. 1*, 629-640, 1975a.
- Castleman, A. W., Jr., R. E. Davis, I. N. Tang, J. A. Bell, Heterogeneous process and the chemistry of aerosol formation in the upper atmosphere, *Proceedings of the Fourth CIAP Conference, Rep. DOT-TSC-OST-75-38*, pp. 470-477, U. S. Department of Transportation, Washington, D. C., 1975.
- Cavanaugh, L. A., C. F. Schadt, and E. Robinson, Atmospheric hydrocarbon and carbon monoxide measurements at Point Barrow, Alaska, *Environ. Sci. Technol.*, **3**, 251-257, 1969.
- Cess, R. D., Climate change: An appraisal of atmospheric feedback mechanisms employing zonal climatology, *J. Atmos. Sci.*, **33**, 1831-1843, 1976.
- Cess, R. D., Biosphere: Albedo feedback and climate modeling, *J. Atmos. Sci.*, **35**, 1765-1768, 1978.

- Chaloner, C. P., J. R. Drummond, J. T. Houghton, R. F. Jarnot, H. K. Roscoe, Stratospheric measurement of H_2O and the diurnal change of NO and NO_2 , *Nature*, **258**, 696-697, 1975.
- Chaloner, C. P., J. R. Drummond, J. T. Houghton, R. F. Jarnot, and H. K. Roscoe, Infrared measurements of stratospheric composition, I. The balloon instrument and water vapor measurements, *Proc. Roy. Soc., London*, **A 364**, 145-159, 1978.
- Chamberlain, J. W., A mechanism for inducing climatic variations through the stratosphere: Screening of cosmic rays by solar and terrestrial magnetic fields, *J. Atmos. Sci.*, **34**, 737-743, 1977.
- Chameides, W. L., The photochemical role of tropospheric nitrogen oxides, *Geophys. Res. Lett.*, **5**, 17-20, 1978.
- Chameides, W. L., Effect of variable energy input on nitrogen fixation in instantaneous linear discharges, *Nature*, **277**, 123-125, 1979.
- Chameides, W. L., and R. J. Cicerone, Effects of non-methane hydrocarbons in the atmosphere, *J. Geophys. Res.*, **83**, 947-952, 1978.
- Chameides, W., and J. Walker, A photochemical theory of tropospheric ozone, *J. Geophys. Res.*, **78**, 8751-8760, 1973.
- Chameides, W. L., S. C. Liu, and R. J. Cicerone, Possible variations in atmospheric methane, *J. Geophys. Res.*, **82**, 1795-1798, 1977a.
- Chameides, W. L., D. H. Stedman, R. R. Dickerson, D. W. Rusch, and R. J. Cicerone, NO_x production in lightning, *J. Atmos. Sci.*, **34**, 143-149, 1977b.
- Chan, L. Y., J. A. Kadlecsek, V. A. Mohnen, and J. DelSanto, Ion molecule interactions of atmospheric importance, *Interim Report to N.S.F.*, ASRC Publ. No. 681, State Univ. of New York at Albany, 1978.
- Chandra, S., D. M. Butler, and R. S. Stolarski, Effect of temperature coupling on ozone depletion prediction, *Geophys. Res. Lett.*, **5**, 199-202, 1978.
- Chandrasekhar, S., Stochastic problems in physics and astronomy, *Rev. Mod. Phys.*, **15**, 1-89, 1943.
- Chang, J. S., Simulations, perturbations, and interpretations, *Proceedings of the Third CIAP Conference*, Rep. DOT-TSC-OST-74-15, 330-341, U. S. Department of Transportation, Washington, D. C., 1974.
- Chang, J. S., and J. R. Barker, Reaction rate and products for the reaction $\text{O}(^3\text{P}) + \text{H}_2\text{CO}$, *J. Phys. Chem.*, submitted for publication, 1979.
- Chang, J. S., and F. Kaufman, Kinetics of the reactions of hydroxyl radicals with some halocarbons: CHFC_2 , CHF_2Cl , CH_3CCl_3 , C_2HCl_3 , and C_2Cl_4 , *J. Chem. Phys.*, **66**, 4989-4994, 1977.
- Chang, J. S., and F. Kaufman, Upper bound and probable value of the rate constant of the reaction $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$, *J. Phys. Chem.*, **82**, 1683-1686, 1978.
- Chang, J. S., A. C. Hindmarsh, and N. K. Madsen, Simulation of chemical kinetics transport in the stratosphere in *Stiff Differential Systems*, edited by R. A. Willoughby, Plenum Publ. Corp., New York, 51 pp, 1974.

- Chang, J. S., D. J. Wuebbles, and D. D. Davis, A theoretical model of global tropospheric OH distribution, *UCRL-78392 Rev. 1*, 1977.
- Chang, J. S., W. H. Duewer, and D. J. Wuebbles, The atmospheric nuclear tests of the 1950's and 1960's: A possible test of ozone depletion theories, *J. Geophys. Res.*, **84**, 1755-1765, 1979.
- Chang, J. S., A. C. Baldwin, and D. M. Golden, An explanation of the preferential formation of less stable isomers in three-body reactions: $\text{Cl} + \text{NO}_2 + \text{M}$; $\text{ClO} + \text{NO}_2 + \text{M}$., *J. Chem. Phys.*, **71**, 2021-2024, 1979.
- Chapman, S., On ozone and atomic oxygen in the upper atmosphere, *Phil. Mag.*, **10**, 369-383, 1930.
- Chapman, S., and R. S. Lindzen, *Atmospheric Tides*, Gordon and Breach, New York, 200 pp, 1970.
- Chapman, C. J., and R. P. Wayne, The reaction of atomic oxygen and hydrogen with nitric acid, *Int. J. Chem. Kinet.*, **6**, 617-630, 1974.
- Charney, J. G., and P. G. Drazin, Propagation of planetary-scale disturbances from the lower into the upper atmosphere, *J. Geophys. Res.*, **66**, 83-109, 1961.
- Chupp, E. L., D. J. Forrest, R. R. Higbie, A. N. Suri, C. Tsai, and P. P. Dunphy, Solar gamma ray lines observed during the solar activity of August 2 to August 11, 1972, *Nature*, **241**, 333-335, 1973.
- CIAP 1974, *The Effects of Stratospheric Pollution by Aircraft*, A. J. Grobecker, S. C. Coroniti, and R. H. Cannon, Jr., Department of Transportation, DOT-TST-75-50, 1974.
- Cicerone, R., Atmospheric carbon tetrafluoride: A nearly inert gas, *Science*, **206**, 59-61, 1979.
- Cicerone, R. J., D. H. Stedman, R. S. Stolarski, Estimate of the 1974 stratospheric concentration of gaseous chlorine compound (ClX), *Geophys. Res. Lett.*, **2**, 219-222, 1975.
- Cicerone, R. J., J. D. Shetter, D. H. Stedman, T. J. Kelly, and S. C. Liu, Atmospheric N_2O : Measurements to determine its sources, sinks and variations, *J. Geophys. Res.*, **83**, 3042-3050, 1978.
- Cieslik, S., Détermination expérimentale des forces d'oscillateur des principales bandes des systèmes β , γ , δ et ϵ de la molécule NO, *Bull. Cl. Sci. Acad. Roy. Belg.*, **63**, 884-901, 1977.
- Cieslik, S., Sections efficaces d'absorption intégrées des raies des bandes δ et ϵ de la molécule NO, *Bull. Cl. Sci. Acad. Roy. Belg.*, **64**, 265, 1978.
- Cieslik, S., and M. Nicolet, The aeronomic dissociation of nitric oxide, *Planet. Space Sci.*, **21**, 925-938, 1973.
- Clark, J. H. E., a quasigeostrophic model of the winter stratospheric circulation, *Mon. Weather Rev.*, **98**, 443-461, 1970.
- Clemesha, B. R., and D. M. Simonich, Stratospheric dust measurements, 1970-1977, *J. Geophys. Res.*, **83**, 2403-2408, 1978.
- Cluley, A. P., and M. J. Oliver, Aircraft measurements of humidity in the low stratosphere over southern England, *Quart. J. Roy. Meteorol. Soc.*, **104**, 511-526, 1978.

- Clyne, M. A. A., and P. Holt, Reaction kinetics involving ground $X^2\Pi$ and excited $A^2\Sigma^+$ hydroxyl radicals, Part I, *J. Chem. Soc., Faraday Trans. II.*, **75**, 569-581, 1979.
- CMA, World Production and Release of Chlorofluorocarbons 11 and 12 through 1978, Chemical Manufacturers Association, Fluorocarbons Technical Panel, August 6, 1979.
- Coakley, J. A., Jr., Radiative-convective calculations of surface temperature changes caused by changes in stratospheric ozone, *Proceedings of the AMS Third Conference on Atmospheric Radiation*, 289-292, June 28-30, 1978.
- Coakley, J. A., Jr., A study of climate sensitivity using a simple energy balance model, *J. Atmos. Sci.*, **36**, 260-269, 1979.
- Cohen, Y., Consumption of dissolved nitrous oxide in an anoxic basin, Saanich Inlet, B. C., *Nature*, **272**, 235-237, 1978.
- Cohen, Y., and L. I. Gordon, Nitrous oxide in the oxygen minimum of the Eastern Tropical North Pacific, *Deep Sea Res.*, **25**, 509-524, 1978.
- Cohen, Y., and L. I. Gordon, Nitrous oxide production in the ocean, *J. Geophys. Res.*, **84**, 347-353, 1979.
- Cole, R. K., and E. T. Pierce, Electrification in the earth's atmosphere for altitudes between 0 and 100 kilometers, *J. Geophys. Res.*, **70**, 2735-2749, 1965.
- Cox, R. A., Kinetics of HO_2 radical reactions of atmospheric interest, WMO Symposium on the Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere, Toronto, WMO Publ. 511, World Meteorological Organization, Geneva, 17-24, 1978.
- Cox, R. A., and G. Tyndall, Rate constants for reactions of CH_3O_2 in the gas phase, *Chem. Phys. Lett.*, **65**, 357-360, 1979.
- Cox, R. A., and K. Patrick, Kinetics of the reaction of $HO_2 + NO_2(+M) \rightarrow HO_2NO_2$ using molecular modulation spectrometry, *Int. J. Chem. Kinet.*, **11**, 635-648, 1979.
- Cox, S. K., Observations of cloud infrared effective emissivity, *J. Atmos. Sci.*, **33**, 287-289, 1971.
- Coy, L., An unusually large westerly amplitude of the quasi-biennial oscillation, *J. Atmos. Sci.*, **36**, 174-176, 1979.
- Craig, R. A., *The Upper Atmosphere: Meteorology and Physics*, Academic Press, New York, 1965.
- Craig, R. A., and C. Ohring, The temperature dependence of ozone radiational heating rates in the vicinity of the mesopeak, *J. Meteorol.*, **15**, 59-62, 1958.
- Craig, R. A., J. J. DeLuise, and I. Steutzer, Comparison of chemiluminescent and Umkehr observations of ozone, *J. Geophys. Res.*, **72**, 1667-1671, 1967.
- Cravens, T. E., J. C. Gerard, A. I. Stewart, and D. W. Rusch, Latitudinal gradient of nitric oxide in the thermosphere, *J. Geophys. Res.*, in press, 1979.
- Crescentini, G., and F. Bruner, Evidence for the presence of the Freon 21 in the atmosphere, *Nature*, **279**, 311-312, 1979.

- Cressman, G. P., An operational objective analysis system, *Mon. Weather Rev.*, **87**, 367-374, 1959.
- Cronn, D. R., American Chemical Society Fall Meeting, Miami Beach, 1978.
- Cronn, D., and E. Robinson, Tropospheric and stratospheric vertical profiles of ethane and acetylene, *Geophys. Res. Lett.*, **6**, 641-644, 1979.
- Cronn, D. R., R. A. Rasmussen, and E. Robinson, Measurements of tropospheric halocarbons by gas chromatography-mass spectrometry, *Phase II Report*, Wash. St. Univ., Pullman, WA, 79 pp, 1977.
- Crutzen, P. J., A two-dimensional photochemical model of the atmosphere below 55 km: Estimates of natural and man-caused ozone perturbations due to NO_x , *Proceedings of the Fourth CIAP Conference, Rep. DOT-TSC-OST-75-38*, pp. 264-279, U. S. Department of Transportation, Washington, D. C. 1975.
- Crutzen, P. J., The possible importance of CSO for the sulfate layer of the stratosphere, *Geophys. Res. Lett.*, **3**, 73-76, 1976.
- Crutzen, P. J., I. S. A. Isaksen, and G. C. Reid, Solar proton events: Stratospheric sources of nitric oxide, *Science*, **189**, 457-458, 1975.
- Crutzen, P. J., and J. Fishman, Average concentrations of OH in the northern hemisphere troposphere and the budgets of CH_4 , CO, and H_2 , *Geophys. Res. Lett.*, **4**, 321-324, 1977.
- Cunnold, D., F. Alyea, N. Phillip, and R. Prinn, A three-dimensional dynamical-chemical model of atmospheric ozone, *J. Atmos. Sci.*, **32**, 170-194, 1975.
- Cunnold, D., F. N. Alyea, and R. G. Prinn, A methodology for determining the atmospheric lifetime of fluorocarbons, *J. Geophys. Res.*, **83**, 5493-5500, 1978.
- Cunnold, D. M., F. N. Alyea, and R. G. Prinn, Preliminary calculations concerning the maintenance of the zonal mean ozone distribution in the Northern Hemisphere, *Pure Appl. Geophys.*, in press, 1979.
- Daley, R., C. Girard, J. Henderson, and I. Simmonds, Short term forecasting with a multi-level spectral primitive equation model; Part 1 - Model formulation, *Atmosphere*, **14**, 98-134, 1976.
- Dalgarno, A., Atmospheric reactions with energetic particles, *Space Res.*, **7**, 849-861, 1967.
- Danielsen, E. F., A determination of the mass transported from the stratosphere to the troposphere over North America during a thirty-six hour interval, *Mitt. Deut. Wetterdienstes*, **20**, 10-11, 1959.
- Danielsen, E. F., Report on Project Springfield, *Rep. DASA-1517*, Def. Atomic Supp. Agency, Washington, D.C., 1964.
- Danielsen, E. F., Stratospheric-tropospheric exchange based on radioactivity, ozone and potential vorticity, *J. Atmos. Sci.*, **25**, 502-518, 1968.
- Danielsen, E. F., and R. Bleck, Tropospheric and stratospheric ducting of stationary mountain lee waves, *J. Atmos. Sci.*, **27**, 758-772, 1970.
- Danielsen, E. F., and J. F. Louis, Transport in the stratosphere studies in geophysics—The Upper Atmosphere and Magnetosphere, National Research Council, National Academy of Sciences, 141, 1977.

- Danielsen, E. F., and V. A. Mohnen, Project DUSTORM report: Ozone measurements and meteorological analysis of tropopause folding, *ASRC-SUNY-PUB-394*, State Univ. of New York at Albany, 1976.
- Danielsen, E., R. Bleck, J. Shedlozsky, A. Westburg, P. Hagenson, and W. Pollack, Observed distribution of radioactivity, ozone, and potential vorticity associated with tropopause folding, *J. Geophys. Res.*, **75**, 2353-2361, 1970.
- Dave, J. V., Effects of aerosols on the estimation of total ozone in an atmospheric column from the measurements of its ultraviolet radiance, *J. Atmos. Sci.*, **35**, 899-911, 1978.
- Dave, J. V., and C. L. Mateer, A preliminary study of the possibility of estimating total atmospheric ozone from satellite measurements, *J. Atmos. Sci.*, **24**, 414-427, 1967.
- Davenport, J. E., H. I. Schiff, K. H. Welge, quoted in Cvetanovic, R. V., Excited state chemistry in the stratosphere, *Can. J. Chem.*, **52**, 1452-1464, 1974.
- Davidson, J. A., H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltekopf, and C. J. Howard, Temperature dependence of $O(^1D)$ rate constants for reactions with N_2O , H_2 , CH_4 , HCl , and NH_3 , *J. Chem. Phys.*, **67**, 5021-5025, 1977a.
- Davidson, J. A., F. C. Fehsenfeld, and C. J. Howard, The heats of formation of NO_3 , and NO_3 association complexes with HNO_3 and HBr , *Int. J. Chem. Kinet.*, **9**, 17-29, 1977b.
- Davidson, J. A., H. I. Schiff, T. J. Brown, and C. J. Howard, Temperature dependence of the rate constants for reactions of $O(^1D)$ atoms with a number of halocarbons, *J. Chem. Phys.*, **69**, 4277-4279, 1978.
- Davidson, J. A., C. J. Howard, H. I. Schiff, and F. C. Fehsenfeld, Measurements of the branching ratios for the reaction of $O(^1D)$ with N_2O , *J. Chem. Phys.*, **70**, 1697-1704, 1979.
- Davies, M. J. E., NO_3 as a possible stratospheric constituent, Masters thesis, University of Toronto, 1974.
- Davis, D. D., R. B. Klemm, and M. Pilling, A flash photolysis-resonance fluorescence kinetics study of ground-state sulfur atoms. I. Absolute rate parameters for reaction of $S(^1P)$ with $O_2(^1\Sigma)$, *Int. J. Chem. Kinetics*, **4**, 367-382, 1972.
- Davis, D. D., and others, AGU Fall Meeting, Session on GAMETAG (abstracts), *Eos Trans. AGU*, **59**, 1079-1082, 1978.
- Davis, D. D., W. Heaps, and T. McGee, Direct measurements of natural tropospheric levels of OH via an airborne tunable dye laser, *Geophys. Res. Lett.*, **3**, 331-333, 1976.
- Davis, D. D., A. R. Ravishankara, and S. Fischer, SO_2 oxidation via the hydroxyl radical: Atmospheric fate of HSO_x radicals, *Geophys. Res. Lett.*, **6**, 113-116, 1979.
- Delaboudiniere, J. P., R. F. Donnelly, H. E. Hinteregger, G. Schmidtke, and P. C. Simon, Intercomparison/compilation of relevant solar flux data related to aeronomy, *COSPAR Technique Manual No. 7*, 1978.
- DeLuisi, J. J., A study of the effect of haze upon Umkehr measurements, *Quart. J. Roy. Meteorol. Soc.*, **95**, 181-187, 1969.

- DeLuisi, J. J., Effect of the temperature dependence of ozone absorption on vertical ozone distributions deduced from Umkehr observations, *J. Geophys. Res.*, **76**, 2131-2137, 1971.
- DeLuisi, J. J., Measurements of the extraterrestrial solar radiant flux from 2981 to 4000 Å and its transmission through the earth's atmosphere as it is affected by dust and ozone, *J. Geophys. Res.*, **80**, 345-354, 1975.
- DeLuisi, J. J., Shortened version of the Umkehr method for observing the vertical distribution of ozone, *Appl. Opt.*, **18**, 3190-3197, 1979.
- DeLuisi, J. J., Umkehr vertical ozone profile errors caused by the presence of stratospheric aerosols, *J. Geophys. Res.*, **84**, 1766-1770, 1979a.
- DeLuisi, J. J., and C. L. Mateer, On the application of the optimum statistical inversion technique to the evaluation of Umkehr observations, *J. Appl. Meteorol.* **10**, 328-334, 1971.
- DeLuisi, J. J., B. M. Herman, R. S. Browning, and R. K. Sato, Theoretically determined multiple-scattering effects of dust on Umkehr observations, *Quart. J. Roy. Meteorol. Soc.*, **101**, 325-331, 1975.
- DeLuisi, J., C. Mateer, and D. Heath, Comparison of seasonal variations of upper stratospheric ozone concentrations revealed by Umkehr and Nimbus-4 BUV observations, *J. Geophys. Res.*, **84**, 3728-3732, 1979.
- Demerjian, K. L., J. A. Kerr, and J. G. Calvert, The mechanism of photochemical smog formation, *Adv. Environ. Sci. and Tech.*, **4**, 1-262, 1974.
- DeMore, W. B., Rate constant ratio for the reactions of OH with O₃, and CO, *Int. J. Chem. Kinet. Symp.* No. 1, 273-279, 1975.
- DeMore, W. B., Reaction of HO₂ with O₃ and the effect of water vapor on HO₂ kinetics, *J. Phys. Chem.*, **83**, 1113-1118, 1979.
- DeMore, W. B., and E. Tschuikow-Roux, Temperature dependence of the reactions of OH and HO₂ with O₃, *J. Phys. Chem.*, **78**, 1447-1451, 1974.
- DeMore, W. B., L. J. Stief, F. Kaufman, D. M. Golden, R. F. Hampson, M. J. Kurylo, J. J. Margitan, M. J. Molina, and R. T. Watson, Chemical kinetic and photochemical data for use in stratospheric modeling, *JPL Publication 79-27*, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 1979.
- DeVore, J., and S. V. Venkateswaran, Mesospheric response to modifications in ozone photochemistry, Collection of Extended Summaries at Joint Assembly, Seattle, WA, CMUA Sessions IAGA/IAMAP, paper no. 15, November, 1977.
- Dickinson, R. E., On the exact and approximate linear theory of vertically propagating planetary Rossby waves forced at a spherical lower boundary, *Mon. Weather Rev.*, **96**, 405-415, 1968a.
- Dickinson, R. E., Planetary Rossby waves propagating vertically through weak westerly wind wave guides, *J. Atmos. Sci.*, **25**, 984-1002, 1968b.
- Dickinson, R. E., Vertical propagation of planetary Rossby waves through an atmosphere with Newtonian cooling, *J. Geophys. Res.*, **74**, 929-938, 1969.

- Dickinson, R. E., Baroclinic instability of an unbounded zonal shear flow in a compressible atmosphere, *J. Atmos. Sci.*, **30**, 1520-1527, 1973a.
- Dickinson, R. E., Method of parameterization for infrared cooling between altitudes of 30 and 70 kilometers, *J. Geophys. Res.*, **78**, 4451-4457, 1973b.
- Ditchburn, R. W., and P. A. Young, The absorption of molecular oxygen between 1850 and 2500 Å, *J. Atmos. Terr. Phys.*, **24**, 127-139, 1962.
- Dobson, G. M. B., Recent work on the stratosphere, *Quart. J. Roy. Meteorol. Soc.*, **77**, 488-494, 1951.
- Dobson, G. M. B., A. W. Brewer, and B. Cwilog, Meteorology of the lower stratosphere, *Proc. Roy. Soc. London Ser. A.*, **185**, 144-175, 1946.
- Donahue, T. M., The problem of atomic hydrogen, *Ann. Geophys.*, **22**, 175-188, 1966.
- Donovan, R. J., L. J. Kirsch, and D. Husain, Rate of the reaction of $S(3p^4\ ^1D_2)$ with OCS, *Nature*, **222**, 1164-1165, 1969.
- Dopplack, T. G., The energetics of the lower stratosphere including radiative effects, *Quart. J. Roy. Meteorol. Soc.*, **97**, 209-237, 1971.
- Dotan, I., J. A. Davidson, G. E. Streit, D. L. Albritton, and F. C. Fehsenfeld, A study of the reaction $O_3^- + CO_2 \leftrightarrow CO_3^- + O_2$ and its implications on the thermochemistry of CO_3 and O_3 and their negative ions, *J. Chem. Phys.*, **67**, 2874-2879, 1977.
- Drayson, S. R., A listing of wave numbers and intensities of carbon dioxide absorption lines between 12 and 20 μm , Rept. 036350-4-T, Univ. of Michigan, Ann Arbor, Michigan, 1973.
- Drummond, J. R., and R. F. Jarnot, Infrared measurements of stratospheric composition II. Simultaneous NO and NO₂ measurements, *Proc. Roy. Soc. London, Ser. A*, **364**, 237-254, 1978.
- Drummond, J. R., J. M. Rosen, and D. J. Hofmann, Balloon-borne chemiluminescent measurement of NO to 45 km, *Nature*, **265**, 319-320, 1977.
- Dubin, M., Ozoneosphere trough from tropospheric storms, Presented at the Spring meeting of the American Geophysical Union, 1975.
- Duewer, W. H., D. J. Wuebbles, and J. S. Chang, Effects of NO photolysis on NO_y, mixing ratios, *Nature*, **265**, 523-525, 1977.
- Duewer, W. H., D. J. Wuebbles, and J. S. Chang, The effects of a massive pulse injection of NO_x into the stratosphere, Proceedings of the WMO Symposium on the Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere, *WMO publication*, **511**, 207-212, 1978.
- Dunkerton, T., On the mean meridional mass motions of the stratosphere and mesosphere, *J. Atmos. Sci.*, **35**, 2325-2333, 1978.
- Dunkerton, T., On the role of the Kelvin wave in the westerly phase of the semiannual zonal wind oscillation, *J. Atmos. Sci.*, **36**, 32-41, 1979.

- Dütsch, H., Photochemistry of atmospheric ozone, *Advances in Geophysics*, **15**, Academic Press, 219-322, 1971.
- Dütsch, H. U., Regular ozone soundings at the aerological station of the Swiss Meteorological Office at Payerne, Switzerland 1968-1972, Laboratory for Atmospheric Physics, ETH, Zurich, Switzerland, Lapeth—10 September 1974.
- Dütsch, H. U., and Ch. Ling, Critical comparison of the determination of ozone distribution by the Umkehr method and electrochemical sonde, *Ann. Geophys.*, **25**, 211-214, 1969.
- Dütsch, H. U. and C. C. Ling, Six years of regular ozone soundings over Switzerland, *Pure Appl. Geophys.*, **106**, 1151-1168, 1973.
- Ebel, A., and W. Batz, Response of stratospheric circulation at 10 mb to solar activity oscillations resulting from the sun's rotation, *Tellus*, **29**, 41-47, 1977.
- Ehhalt, D. H., The atmospheric cycle of methane, *Tellus*, **26**, 58-70, 1974.
- Ehhalt, D. H., In situ measurements of stratospheric trace constituents, *Rev. Geophys. Space Phys.*, **16**, 217-224, 1978a.
- Ehhalt, D. H., The CH₄ concentration over the ocean and its possible variation with latitude, *Tellus*, **30**, 169-176, 1978b.
- Ehhalt, D. H., and L. E. Heidt, The concentration of molecular H₂ and CH₄ in the stratosphere, *Pure Appl. Geophys.*, **106-108**, 1352-1360, 1973.
- Ehhalt, D. H., N. Roper, and H. E. Moore, Vertical profiles of nitrous oxide in the troposphere, *J. Geophys. Res.*, **80**, 1653-1655, 1975.
- Ehhalt, D. H., U. Schmidt, and L. E. Heidt, Vertical profiles of molecular hydrogen in the troposphere and stratosphere, *J. Geophys. Res.*, **82**, 5907-5911, 1977.
- Ehhalt, D. H., U. Schmidt, A. Volz, A. Khedim, P. J. Johnsen, P. Fabian, R. Borchers, K. H. Weiler, W. Seiler, F. Muller, and X. Oeser, The vertical distribution of H₂, CH₄, CO, N₂O, CFC1₃, and CF₂Cl₂ in the troposphere and stratosphere at midlatitudes, preprint, 1978.
- Eisenhart, C., Realistic evaluation of the precision and accuracy of instrument calibration systems, *J. Res. NBS*, **67C**, 161-187, 1963.
- Elkins, J. W., Aquatic sources and sinks for nitrous oxide, Thesis, Harvard University, 1979.
- Elkins, J. W., S. C. Wofsy, M. B. McElroy, C. E. Kolb, and W. A. Kaplan, Aquatic sources and sinks for nitrous oxide, *Nature*, **275**, 602-606, 1978.
- Ellsaesser, M.W., Water budget of the stratosphere, in *Proceedings of the Third CIAP Conference, Rep. DOT-TSC-OST-74-15*, 273-283, U.S. Department of Transportation, Washington, D.C., 1974.
- Environmental Measurement Laboratory Quarterly Reports, Dept. of Energy *EML-344*, 1978, *EML-349*, January 1979.
- EOS, *Abstracts of Special Session on GAMETAG*, **59**, 1081-1082, 1978.

- Eriksson, E., The yearly circulation of chloride and sulfur in nature, Part III, *Tellus*, **12**, 63-109, 1960.
- Eriksson, E., The atmospheric carbon dioxide problem, *Tellus*, **30**, 350-357, 1978.
- Evans, R. D., *The Atomic Nucleus*, McGraw-Hill Publ. Co., New York, 1955.
- Evans, W. F. J., E. J. Llewellyn, and A. V. James, Balloon observations of the temporal variation of the infrared atmospheric oxygen bands in the airglow, *Planet. Space Sci.*, **17**, 933-947, 1969.
- Evans, W. F. J., and E. J. Llewellyn, Molecular oxygen emissions in the airglow, *Annales de Geophysique*, **26**, 167-178, 1970.
- Evans, W. F. J., J. B. Kerr, D. I. Wardle, J. C. McConnell, B. A. Ridley, and H. I. Schiff, Intercomparison of NO, NO₂, and HNO₃ measurements with photochemical theory, *Atmosphere*, **14**, 189-198, 1976.
- Evans, W. F. J., J. B. Kerr, C. T. McElroy, R. S. O'Brien, B. A. Ridley, and D. I. Wardle, The odd nitrogen mixing ratio in the stratosphere, *Geophys. Res. Lett.*, **4**, 235-238, 1977.
- Evans, W. F. J., H. Fast, J. B. Kerr, C. T. McElroy, R. S. O'Brien, D. I. Wardle, J. C. McConnell, and B. A. Ridley, Stratospheric constituent measurements from project stratoprobe, WMO Symposium on the Geophysical Aspects and Consequences of Change in the Composition of the Stratosphere, Toronto WMO Publ. 511, World Meteorological Organization, Geneva, 55-60, 1978.
- Evans, W. F. J., I. A. Asbridge, Observations of a notch in the stratospheric ozone layer, *J. Geophys. Res.*, **84**, 2519-2524, 1979.
- Eyre, J. R., and H. K. Roscoe, Radiometric measurement of stratospheric HCl, *Nature*, **266**, 243-244, 1977.
- Fabian, P., and P. Pruchniewicz, Meridional distribution of ozone in the troposphere and its seasonal variations, *J. Geophys. Res.*, **82**, 2063-2073, May 1977.
- Fabian, P., R. Borchers, K. H. Weiler, U. Schmidt, A. Volz, D. H. Ehhalt, W. Seiler, and H. Oeser, Simultaneously measured vertical profiles of H₂, CH₄, CO, N₂O, F-11, F-12, NO and O₃ in the midlatitude stratosphere and troposphere, *J. Geophys. Res.*, **84**, 3149-3154, 1979a.
- Fabian, P., J. A. Pyle, and R. J. Wells, The August 1972 solar proton event and the atmospheric ozone layer, *Nature*, **277**, 458, 1979b.
- Fairchild, C. E., E. J. Stone, and G. M. Lawrence, Photofragment spectroscopy of ozone in the UV region 270-310 nm and at 600 nm and at 600 nm, *J. Chem. Phys.*, **69**, 3632-3638, 1978.
- Falconer, P. B., and J. D. Holdeman, Measurements of atmospheric ozone made from a GASP-equipped 747 airlines: Mid-March, 1975, *Geophys. Res. Lett.*, **3**, 101-104, 1976.
- Fang, T. M., S. C. Wofsy, and A. Dalgarno, Opacity distribution functions and absorption in Schumann-Runge bands of molecular oxygen, *Planet. Space Sci.*, **22**, 413-425, 1974.
- Farlow, N. H., K. G. Snetsinger, H. Y. Lem, D. M. Hayes, and B. M. Tooper, Nitrogen-sulfur compounds in stratospheric aerosols, *J. Geophys. Res.*, **83**, 6207-6212, 1978.
- Farlow, N. H., G. V. Ferry, H. Y. Lem, and D. M. Hayes, Latitudinal variations of stratospheric aerosols, *J. Geophys. Res.*, **84**, 733-743, 1979.

- Farmer, C. B., Infrared measurements of stratospheric composition, *Can. J. Chem.*, **52**, 1544-1559, 1974.
- Farmer, C. B., and O. F. Raper, The HF:HC1 ratio in the 14 to 38 km region of the stratosphere, *Geophys. Res. Lett.*, **11**, 527-530, 1977.
- Farmer, C. B., O. F. Raper, C. Muller, B. D. Robbins, and R. A. Toth, Simultaneous spectroscopic measurements of stratospheric species: O₃, CH₄, CO, CO₂, N₂O, H₂O and HC1 at north midlatitudes, submitted to *J. Geophys. Res.*, 1979.
- Fehsenfeld, F. C., and D. L. Albritton, Comment on halocarbon decomposition by natural ionization, *Geophys. Res. Lett.*, **4**, 61-63, 1977.
- Fehsenfeld, F. C., and D. L. Albritton, to be submitted to *J. Geophys. Res.*, 1979.
- Fehsenfeld, F. C., and E. E. Ferguson, Laboratory studies of negative ion reactions with atmospheric trace constituents, *J. Chem. Phys.*, **61**, 3181-3193, 1974.
- Fehsenfeld, F. C., C. J. Howard, and A. L. Schmeltekopf, Gas phase chemistry of HNO₃, *J. Chem. Phys.*, **63**, 2835-2841, 1975.
- Fehsenfeld, F. C., P. J. Crutzen, A. L. Schmeltekopf, C. J. Howard, D. L. Albritton, E. E. Ferguson, J. A. Davidson, and H. I. Schiff, Ion chemistry of chlorine compounds in the troposphere and stratosphere, *J. Geophys. Res.*, **81**, 4454-4460, 1976a.
- Fehsenfeld, F. C., E. E. Ferguson, G. E. Streit, and D. L. Albritton, Stratospheric ion chemistry and the 11-year variation in polar ozone, *Science*, **194**, 544-545, 1976b.
- Fehsenfeld, F. C., I. Dotan, D. L. Albritton, C. J. Howard, and E. E. Ferguson, Stratospheric positive ion chemistry of formaldehyde and methanol, *J. Geophys. Res.*, **83**, 1333-1336, 1978.
- Fels, S. B., and L. D. Kaplan, A test of the role of long-wave radiative transfer in a general circulation model, *J. Atmos. Sci.*, **32**, 779-789, 1975.
- Fels, S. B., and M. D. Schwarzkopf, The simplified exchange approximation: A new method for radiative transfer calculations, *J. Atmos. Sci.*, **32**, 1475-1488, 1975.
- Fels, S., and M. D. Schwarzkopf, An efficient, accurate algorithm for calculating CO₂ 15 μ m cooling rates, to be submitted to *J. Geophys. Res.*, 1980.
- Ferguson, E. E., Rate constants of thermal energy binary ion-molecule reactions of aeronomic interest, *Atom. Data Nucl. Data Tables*, **12**, 159-178, 1973.
- Ferguson, E. E., Sodium hydroxide ions in the stratosphere, *Geophys. Res. Lett.*, **5**, 1035-1038, 1978.
- Ferguson, E. E., Ion-molecule reactions in the atmosphere, *Kinetics of Ion-Molecule Reactions*, 377-403, Plenum, 1979a.
- Ferguson, E. E., Ion chemistry of the middle atmosphere, in *Middle Atmosphere Electrodynamics*, NASA CP-2090, ed. N. C. Maynard, 71-88, 1979b.
- Ferguson, E. E., and W. F. Libby, Mechanism for the fixation of nitrogen by lightning, *Nature*, **229**, 37, 1971.

- Ferguson, E. E., F. C. Fehsenfeld, and D. L. Albritton, Ion chemistry of the earth's atmosphere, in *Gas-Phase Ion Chemistry*, 45-82, 1979.
- Finger, F. G., H. M. Woolf, and C. E. Anderson, A method for objective analysis of stratospheric constant-pressure charts, *Mon. Weather Rev.*, **93**, 619-638, 1965.
- Finger, F. G., M. E. Gelman, F. J. Schmidlin, R. Leviton, and B. W. Kennedy, Compatibility of meteorological rocketsonde data as indicated by international comparison tests, *J. Atmos. Sci.*, **32**, 1705-1714, 1975.
- Fink, W., D. H. Rank, and T. A. Wiggins, Abundance of CH_4 in the earth's atmosphere, *J. Opt. Soc. Amer.*, **54**, 472-474, 1967.
- Finlayson-Pitts, B. J., and T. E. Kleindienst, The reaction of hydrogen atoms with ozone: Evidence for a second reaction path producing HO_2 and $\text{O}(^3\text{P})$, *J. Chem. Phys.*, **70**, 4804-4806, 1979.
- Fishman, J., and P. J. Crutzen, The origin of ozone in the troposphere, *Nature*, **274**, 855-858, 1978.
- Fleig, A. J., R. S. Fraser, B. W. Guenther, D. F. Heath, E. Hilsenrath, L. U. Novak, V. G. Kaveeshwar, R. D. McPeters, C. L. Mateer, and A. J. Miller, Global ozone determination from Nimbus-4 BUV spacecraft data, *Developments in Atmospheric Science*, **9**, *Remote Sensing of the Atmosphere*, Edit. Fymat and Zuev, Elsevier, 97-106, 1978.
- Fleig, A. J., V. G. Kaveeshwar, P. K. Bhartia, K. D. Lee, Dobson BUV comparison, in preparation, 1979.
- Fletcher, I. S., and D. Husain, The collisional quenching of electronically excited oxygen atoms, $\text{O}(^1\text{D}_2)$, by the gases NH_3 , H_2O_2 , C_2H_6 , C_3H_8 and $\text{C}(\text{CH}_3)_4$, using time-resolved attenuation of atomic resonance radiation, *Can. J. Chem.*, **54**, 1765-1770, 1976a.
- Fletcher, I. S., and D. Husain, Absolute reaction rates of oxygen ($^1\text{D}_2$) with halogenated paraffins by atomic absorption spectroscopy in the vacuum ultraviolet, *J. Phys. Chem.*, **80**, 1837-1840, 1976b.
- Fletcher, I. S., and D. Husain, The collisional quenching of $\text{O}(^1\text{D})$ by COCl_2 , COFCl , and COF_2 using atomic absorption spectroscopy in the vacuum ultraviolet, *J. Photochem.*, **8**, 355-361, 1978.
- Foley, H. M., and M. A. Ruderman, Stratospheric NO production from past nuclear explosions, *J. Geophys. Res.*, **78**, 4441-4450, 1973.
- Fontanella, J. C., A. Girard, L. Gramont, and N. Louisnard, Vertical distribution of NO, NO_2 , and HNO_3 as derived from stratospheric absorption infrared spectra, *Appl. Opt.*, **14**, 825-839, 1975.
- Fraser, R. S., and Z. Ahmad, The effect of surface anisotropy on the accuracy of total ozone estimates from satellite observations, *Third Conference on Atmospheric Radiation of the American Meteorological Society*, Davis, California, June 28-30, 1978.
- Fraser, R. S., and Z. Ahmad, The effect of surface reflection and clouds on the estimation of total ozone from satellite measurements, *Fourth National Aeronautics and Space Administration Weather and Climate Program Science Review*, NASA Conference Publication 2076, Goddard Space Flight Center, January 24-25, 1979.
- Fraser, P. J., and G. I. Pearman, Atmospheric halocarbons in the Southern Hemisphere, *Atmos. Environ.*, **12**, 839-844, 1978.

- Frederick, J. E., Solar corpuscular emission and neutral chemistry in the earth's middle atmosphere, *J. Geophys. Res.*, **81**, 3179-3186, 1976.
- Frederick, J. E., and R. D. Hudson, Predissociation of nitric oxide in the mesosphere and stratosphere, *J. Atmos. Sci.*, **36**, 737-745, 1979a.
- Frederick, J. E., and R. D. Hudson, Predissociation linewidths and oscillator strengths for the (2-0) to (13-0) Schumann-Runge bands of O₂, *J. Molec. Spec.*, **74**, 247-258, 1979b.
- Frederick, J. E., and D. W. Rusch, On the chemistry of metastable atomic nitrogen in the F-Region deduced from simultaneous satellite measurements of the 5200 Å airglow and atmospheric composition, *J. Geophys. Res.*, **82**, 3509-3517, 1977.
- Free University of Berlin, Meteorologische Abhandlungen Institute Fur Meteorologic Zentraleinrichtun 2, der Freien Universit Berlin, 1958-1979.
- Freney, J. R., O. T. Denmead, and J. R. Simpson, Nitrous oxide emission from soils at low moisture contents, *Soil Biol. Biochem.*, **11**, 167-173, 1979.
- Friedlander, S. K., and C. S. Wang, *J. Colloid and Interface Sci.*, **22**, 126, 1966.
- Friedman, H., The Sun's ionizing radiations, Chap. 4 in *Physics of the Upper Atmosphere*, ed. J. A. Ratcliffe, Academic Press, New York, 133-218, 1960.
- Friend, J. P., Properties of the stratospheric aerosol, *Tellus*, **18**, 465-473, 1966.
- Friend, J. P., The global sulfur cycle, in *Chemistry of the Lower Atmosphere*, S. I. Rasool ed., New York: Plenum Press, 177-201, 1973.
- Friend, J. P., and R. Vosta, Nucleation by free radicals from the photo-oxidation of sulfur dioxide in air, *J. Phys. Chem.*, submitted, 1978.
- Friend, J. P., R. Leifer, and M. Trichon, On the formation of stratospheric aerosols, *J. Atmos. Sci.*, **30**, 465-479, 1973.
- Fritts, D. C., The nonlinear gravity wave-critical level interaction, *J. Atmos. Sci.*, **35**, 397-413, 1978.
- Fritts, D. C., The excitation of radiating waves and Kelvin-Helmholtz instabilities by the gravity wave-critical level interaction, *J. Atmos. Sci.*, **36**, 12-23, 1979.
- Fritts, D. C., and M. A. Geller, Various stabilization of gravity wave critical level flows, *J. Atmos. Sci.*, **33**, 2276-2284, 1976.
- Fritz, S., and S. D. Soules, Large-scale temperature changes in the stratosphere observed from Nimbus-3, *J. Atmos. Sci.*, **27**, 1091-1097, 1970.
- Gab, S., J. Schmitzer, H. W. Thormm, and F. Korte, Mineralization of chlorofluorocarbons in the sunlight of the troposphere, *Angew. Chem. Int. Ed. Engl.*, **17**, 366-367, 1978.
- Gage, K. S., and B. B. Balsley, Doppler radar probing of the clear atmosphere, *Bull. Amer. Meteorol. Soc.*, **59**, 1074-1093, 1978.

- Galbally, I. E., Man-made carbon tetrachloride in the atmosphere, *Science*, **193**, 573-576, 1976.
- Gandin, L. S., Objective analysis of meteorological fields. In Russian, Gidrometeorologicheskoe Izdatel'stvo (GIMIZ), Leningrad (English translation, Israel Program for Scientific Translation, Jerusalem, 1965, 242 pp), 1963.
- Gandin, L. S., and R. L. Kagan, Construction of a system for objective analysis of heterogeneous data based on the method of optimum interpolation and optimum agreement, *Meteorologiya i Gidrologiya*, **5**, 1-11. (English translation, Joint Publication Research Service, Arlington, Virginia.), 1974.
- Garcia, R. R., and J. E. Geisler, Vertical structure of stationary planetary waves in the presence of altitude-dependent zonal winds and dissipation, *J. Geophys. Res.*, **79**, 5613-5623, 1974.
- Geisler, J. E., A numerical model of the sudden stratospheric warming mechanism, *J. Geophys. Res.*, **79**, 4989-4999, 1974.
- Gelbard, F., and J. H. Seinfeld, The general dynamic equation for aerosols: Theory and application to aerosol formation and growth, *J. Colloid and Interface Science*, 1979.
- Ghazi, A., A. Ebel, and D. F. Heath, A study of satellite observations of ozone and stratospheric temperatures during 1970-1971, *J. Geophys. Res.*, **81**, 5365-5373, 1976.
- Gidel, L. T., and M. A. Shapiro, General circulation model estimates of the net vertical flux of ozone in the lower stratosphere and the implications for the tropospheric ozone budget, submitted *J. Geophys. Res.*, 1979.
- Gille, J. C., Middle atmospheric processes revealed by satellite observations, *J. Atmos. Terr. Phys.*, **41**, 707-722, 1979.
- Gille, J. C., F. B. House, R. A. Craig, and J. R. Thomas, Nimbus limb radiance inversion experiment, *Honeywell Aerospace Div. Technical Report 6SD-47, Volume 1*, 1970.
- Gille, J. C., and F. B. House, On the inversion of limb radiance measurements: Temperature and thickness, *J. Atmos. Sci.*, **28**, 1427-1442, 1971.
- Gille, J. C., P. L. Bailey, and J. M. Russell, III, Temperature and composition measurements from the LRIR and LIMS experiments on Nimbus-6 and -7, *Proc. of the Roy. Meteorol. Soc., Lon.*, in press, 1979.
- Gillespie, H. M., J. Garraway, and R. J. Donovan, Reaction of $O(^1D)$ with halomethanes, *J. Photochem.*, **7**, 29-40, 1977.
- Girard, A., J.-C. Fontanella, R. Giraudet, and N. Louisnard, Simultaneous measurements of nitrogen dioxide and nitric acid in the lower stratosphere, *J. de Chimie Physique*, **74**, 809-813, 1977.
- Girard, A., J. C. Fontanella, and L. Gramont, Detection de l'oxyde azotique dans la stratosphere, *C. R. Acad. Sci., Paris* **276**, Serie B, 845-846, 1973.
- Girard, A., J. Besson, R. Giraudet, and L. Gramont, Correlated seasonal and climate variations of trace constituents in the stratosphere, *Pure Appl. Geophys.*, **117**, 381-394, 1978/79.

- Glasgow, L. C., J. P. Jesson, R. B. Ward, Urban-nonurban relationships of halocarbons, *Atmos. Environ.*, **12**, 962, 1978.
- Gold, T., Terrestrial sources of carbon and earthquake outgassing, *J. Petr. Geol.*, **1**, 3-19, 1979.
- Goldan, P. D., Y. A. Bush, F. C. Fehsenfeld, D. L. Albritton, P. J. Crutzen, A. W. Schmeltekopf, and E. E. Ferguson, Tropospheric N₂O mixing ratio measurements, *J. Geophys. Res.*, **83**, 935-939, 1978.
- Goldan, P. D., W. C. Kuster, D. L. Albritton, and A. L. Schmeltekopf, Stratospheric CFC1₃, CF₂Cl₂, and N₂O height-profile measurements at several latitudes, submitted to *J. Geophys. Res.*, 1979.
- Goldberg, L., The abundance and vertical distribution of CH₄ in the earth's atmosphere, *Astrophys. J.*, **113**, 567-581, 1951.
- Goldberg, R. A., An experimental search for causal mechanisms in sun/weather climatic relationships, in *Solar Terrestrial Influences on Weather and Climate*, ed. by B. M. McCormac and T. Seliga, Reidel, 161-173, 1979.
- Goldberg, R. A., and A. C. Aiken, Studies of positive-ion composition in the equatorial D-region ionosphere, *J. Geophys. Res.*, **76**, 8352-8364, 1971.
- Goldberg, R. A., and G. Witt, Ion Composition in a Noctilucent Cloud, Goddard Space Flight Center, Greenbelt, Maryland, July 1977.
- Goldman, A., D. G. Murcray, F. H. Murcray, W. J. Williams, J. N. Brooks, and C. M. Bradford, Vertical distribution of CO in the atmosphere, *J. Geophys. Res.*, **78**, 5273-5283, 1973.
- Goldman, A., F. G. Fernald, W. J. Williams, and D. G. Murcray, Vertical distribution of NO₂ in the stratosphere as determined from balloon measurements of solar spectra in the 4500Å region, *Geophys. Res. Lett.*, **5**, 257-260, 1978.
- Goody, R. M., *Atmospheric Radiation, I Theoretical Basis*, Oxford University Press, 436 pp, 1964.
- Goody, R. M., Time variations in a tropospheric N₂O in Eastern Massachusetts, *Planet. Spa. Sci.*, **17**, 1319-1320, 1969.
- Gough, M. P., and H. L. Collin, Energetic electron precipitation as a source of ionization in the nighttime D-region over the midlatitude rocket range, South Uist, *J. Atmos. Terr. Phys.*, **35**, 835-850, 1973.
- Graedel, T. E., The homogeneous chemistry of atmospheric sulfur, *Rev. Geophys. Space Phys.*, **15**, 421-428, 1977.
- Graedel, T. E., The oxidation of atmospheric sulfur compounds, in *The Question of Atmospheric Sulfates*, Air Pollution Control Assoc., 1978.
- Graedel, T. E., Reduced sulfur emission from the open oceans, *Geophys. Res. Lett.*, **6**, 329-332, 1979.
- Graedel, T. E., The kinetic photochemistry of the marine atmosphere, *J. Geophys. Res.*, **84**, 273-286, 1979a.
- Graham, R. A., and H. S. Johnston, The photochemistry of NO₃ and the kinetics of the N₂O₅-O₃ system, *J. Phys. Chem.*, **82**, 254-268, 1978.

- Graham, R. A., E. C. Tuazon, A. M. Winer, J. N. Pitts, Jr., L. T. Molina, L. Beaman, and M. J. Molina, High resolution infrared absorptivities for gaseous chlorine nitrate, *Geophys. Res. Lett.*, **4**, 3-6, 1977.
- Graham, R. A., A. M. Winer, and J. N. Pitts, Jr., Pressure and temperature dependence of the unimolecular decomposition of HO_2NO_2 , *J. Chem. Phys.*, **68**, 4505-4510, 1978a.
- Graham, R. A., A. M. Winer, and J. N. Pitts, Ultraviolet and infrared absorption cross sections of gas phase HO_2NO_2 , *Geophys. Res. Lett.*, **11**, 909-911, 1978b.
- Granot, L., R. O. Hallberg, and H. Rodhe, Nitrogen, phosphorus and sulphur-global cycles, *Ecological Bulletins*, **22**, B. H. Svensson and R. Soderlund, Eds., 89-134, 1976.
- Green, A. E. S., T. Sawada, B. C. Edgar, and M. A. Uman, Production of carbon monoxide by charged particle deposition, *J. Geophys. Res.*, **78**, 5284-5291, 1973.
- Green, J. S. A., Large-scale motion in the upper stratosphere and mesosphere: An evaluation of data and theories, *Phil Trans. Roy. Soc. London*, **A271**, 577-583, 1972.
- Grenda, R. N., and H. W. Goldstein, Non-urban measurements of methane and ethane under varying atmospheric conditions, *J. Geophys. Res.*, **82**, 5923-5927, 1977.
- Griffing, G. W., Ozone and oxides of nitrogen production during thunderstorms, *J. Geophys. Res.*, **82**, 943-950, 1977.
- Gringel, W., K. H. Kaselau, and R. Muhleisen, Recombination rates of small ions and their attachment to aerosol particles, *Pure Appl. Geophys.*, **116**, 1101-1112, 1978.
- Gruner, P., and H. Kleinert, Die Dammerungerscheinungen, in *Problemen der Kosmischen Physik*, **10**, 1-113, Henre Grand, Hamburg, 1977.
- Gudiksen, P. H., A. W. Fairhall, and R. T. Reed, Roles of mean meridional circulation and eddy diffusion in the transport of trace substance in the lower stratosphere, *J. Geophys. Res.*, **73**, 4461-4473, 1968.
- Guenther, B., R. Dasgubta, and D. Heath, Twilight ozone measurements by solar occultation, *Geophys. Res. Lett.*, **4**, 434-436, 1977.
- Gushchin, G. P., Comparison of ozonometric instruments, actinometry, atmospheric optics, ozonometry, Trudy, GGO No. 279, Israel program for Scientific Translations, Jerusalem, 1974.
- Gushchin, G. P., On the technique for measuring of atmospheric ozone at the world network of stations, *Proc. Joint Symp. on Atmos. Ozone*, Dresden, August 9-17, 1976, Vol. I, 135, Berlin, 1977.
- Hack, W., A. W. Preuss, and H. Gg. Wagner, Messung der Geschwindigkeit der Reaction von OH- und HO_2 -Radikalen mit Hilfe der Laser-Magnetischen Resonanz, *Ber. Bunsenges., Phys. Chem.*, **82**, 1167-1171, 1978.
- Haggard, K. V., and W. L. Grose, Analysis of the energetics of a sudden stratospheric warming simulated with a three-dimensional spectral circulation model, paper presented at Amer. Meteorol. Soc. Conference on Meteorology of Upper Atmos., Boston, Oct. 24-27, 1978.
- Hahn, J., and C. Junge, Atmospheric nitrous oxide: A critical review, *Z. Naturforsch.*, **32a**, 190-214, 1977.

- Hansen, J. E., W. C. Wang, and A. A. Lacis, Mount Agung eruption provides test of a global climatic perturbation, *Science*, **199**, 1065-1068, 1978.
- Hamill, P., C. S. Kiang, and R. D. Cadle, The nucleation of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solution aerosol particles in the stratosphere, *J. Atmos. Sci.*, **34**, 150-162, 1977a.
- Hamill, P., O. B. Toon, and C. S. Kiang, Microphysical processes affecting stratospheric aerosol particles, *J. Atmos. Sci.*, **34**, 1104-1119, 1977b (and references contained therein).
- Hamilton, E. J., Jr., and R. R. Lii, The dependence on H_2O and on NH_3 of the kinetics of the self reaction of HO_2 in the gas phase formation of $\text{HO}_2 \cdot \text{H}_2\text{O}$ and $\text{HO}_2 \cdot \text{NH}_3$ complexes, *Int. J. Chem. Kinet.*, **9**, 875-885, 1977.
- Harries, J. E., Measurements of stratospheric water vapor using far-infrared techniques, *J. Atmos. Sci.*, **30**, 1691-1698, 1973.
- Harries, J. E., The distribution of water vapor in the stratosphere, *Rev. Geophys. Space Phys.*, **14**, 565-575, 1976.
- Harries, J. E., Ratio of HNO_3 to NO_2 concentrations in the daytime stratosphere, *Nature*, **274**, 235-236, 1978.
- Harries, J. E., N. R. Swann, and D. G. Moss, H_2O , O_3 , N_2O , and HNO_3 in the arctic stratosphere, *Nature* **250**, 475-476, 1974.
- Harries, J. E., D. G. Moss, N. R. Swann, G. F. Neill, and P. Gildwarg, Simultaneous measurements of H_2O , NO_2 , and HNO_3 in the daytime stratosphere from 15 to 35 km, *Nature*, **259**, 300-302, 1976.
- Harries, J. E., N. R. Swann, and M. J. Bangham, to be submitted to *Appl. Opt.*, 1979.
- Harris, G. W., and J. N. Pitts, Jr., Rate constant for the reaction of OH radicals with hydrogen peroxide at 298K, *J. Chem. Phys.*, **70**, 2581-2582, 1979.
- Harrison, A. W., Midsummer stratospheric NO_2 at latitude 45°S , *Can. J. Phys.*, **57**, 1110-1117, 1979.
- Hartmann, D. L., The dynamical climatology of the stratosphere in the Southern Hemisphere during late winter 1973, *J. Atmos. Sci.*, **33**, 1789-1802, 1976.
- Hartmann, D. L., On potential vorticity and transport in the stratosphere, *J. Atmos. Sci.*, **34**, 968-977, 1977.
- Hartmann, D. L., A note concerning the effect of varying extinction on radiative-photochemical relaxation, *J. Atmos. Sci.*, **35**, 1125-1130, 1978.
- Hartmann, D. L., Baroclinic instability of planetary waves on a sphere, *J. Atmos. Sci.*, **36**, in press, 1979.
- Hartmann, D., and R. Garcia, A mechanistic model of ozone transport by planetary waves in the stratosphere, *J. Atmos. Sci.*, **36**, 350-364, 1979.
- Harwood, R. S., and J. A. Pyle, A two-dimensional mean circulation model for the atmosphere below 80 km, *Quart. J. Roy. Meteorol. Soc.*, **101**, 723-747, 1975.

- Harwood, R. S., and J. A. Pyle, Studies of the ozone budget using a zonal mean circulation model and linearized photochemistry, *Quart. J. Roy. Meteorol. Soc.*, **103**, 319-343, 1977.
- Hasson, V., and R. W. Nicholls, Absolute spectral absorption measurements on molecular oxygen from 2640-1920 Å: II. Continuum measurements 2430-1920 Å, *J. Phys. B. Atomic Molec. Phys.*, **4**, 1789-1797, 1971.
- Hayashi, Y., Spectral analysis of tropical disturbances appearing in a GFDL general circulation model, *J. Atmos. Sci.*, **31**, 180-218, 1974.
- Heath, D. F., and M. P. Thekaekara, The solar spectrum between 1200 and 3000 Å, *In the Solar Output and its Variation*, Oran R. White, Editor, Colorado Associated University Press, Boulder, Colorado, 193-212, 1977.
- Heath, D. F., L. L. Mateer, and A. J. Krueger, The Nimbus-4 BUUV atmospheric ozone experiment; two years operation, *Pure Appl. Geophys.*, **106-108**, 1238-1253, 1973.
- Heath, D. F., A. J. Krueger, and P. J. Crutzen, Solar proton event: Influence on stratospheric ozone, *Science*, **197**, 886-889, 1977.
- Heck, W., A comparison of estimated and directly measured turbulent heat fluxes in the lower stratosphere, *Mon. Weather Rev.*, **105**, 1337-1340, 1977.
- Hedin, A. E., H. G. Mayr, C. A. Reber, N. W. Spencer, and G. R. Carignan, Empirical model of global thermospheric temperature and composition based on data from the OGO 6 quadrupole mass spectrometer, *J. Geophys. Res.*, **79**, 215-225, 1974.
- Hedin, A. E., C. A. Reber, G. P. Newton, N. W. Spencer, H. C. Brinton, and H. G. Mayr, A global thermospheric model based on mass spectrometer and incoherent scatter data: MSIS 2, Composition, *J. Geophys. Res.*, **82**, 2148-2156, 1977.
- Heicklen, J., *Colloid Formation and Growth: A Chemical Kinetics Approach*, Academic Press, NY, 1976.
- Heidner, R. F., III, and D. Husain, Electronically excited oxygen atoms, $O(^1D_2)$. A time-resolved study of the collisional quenching by the gases H_2 , D_2 , NO , N_2O , CH_4 and C_3O_2 using atomic absorption spectroscopy in the vacuum ultraviolet, *Int. J. Chem. Kinet.*, **5**, 819-831, 1973.
- Heidner, R. F., III, D. Husain, and J. R. Weisenfeld, Kinetic investigation of electronically excited oxygen atoms, $O(^1D_2)$ by time-resolved attenuation of atomic resonance radiation in the vacuum ultraviolet, *J. Chem. Soc. Faraday Trans. II*, **69**, 927-938, 1973.
- Heidt, L. E., and J. P. Krasnec, Tropospheric distributions of CO , CH_4 , CO_2 , and N_2O in the Northern and Southern Hemispheres (abstract), *Eos Trans. AGU*, **59**, 1077, 1978.
- Heidt, L. E., R. Lueb, W. Pollock, and D. H. Ehhalt, Stratospheric profiles of CCl_3F and CCl_2F_2 , *Geophys. Res. Lett.*, **2**, 445-447, 1975.
- Heidt, L. E., W. H. Pollock, and R. A. Lueb, Stratospheric measurements of CF_2Cl_2 , $CFCI_3$ and N_2O , *Proceedings, Joint Sym. Atmospheric Ozone*, Dresden, GDR., 1976.

- Heidt, L. E., W. Pollock, R. Lueb, and D. Ehhalt, Vertical profiles of stratospheric water vapor, in *Upper Atmosphere Programs, No. 79-3*, Office of Environment and Energy, Federal Aviation Administration, Washington, D.C., 1979.
- Hering, W., Ozone and atmospheric transport processes, *Tellus*, **18**, 329-336, 1966.
- Herman, J. R., The response of stratospheric constituents to a solar eclipse, sunrise, and sunset, *J. Geophys. Res.*, **84**, 3701-3710, 1979.
- Herman, B. M., S. R. Browning, and R. Rabinoff, The change in earth-atmosphere albedo and radiational equilibrium temperatures due to stratospheric pollution, *J. Appl. Meteorol.*, **15** 1057-1067, 1976.
- Heroux, L., and R. A. Swirbalus, Full-disk solar fluxes between 1230 and 1940 A, *J. Geophys. Res.*, **81**, 436, 1976.
- Herron, J. T., and R. D. Penzhorn, Mass spectrometric study of the reactions of the atomic oxygen with ethylene and formaldehyde, *J. Phys. Chem.*, **73**, 191-196, 1969.
- Hidalgo, H., Status of representative two-dimensional models of the stratosphere and troposphere as of mid-1978, *Federal Aviation Administration Report FAA-AEE-78-23*, 1978.
- Hidalgo, H., and P. J. Crutzen, The tropospheric and stratospheric composition perturbed by NO_x emissions of high altitude aircraft, *J. Geophys. Res.*, **82**, 5833-5866, 1977.
- Hidy, G. M., and J. R. Brock, editors, *The Dynamics of Aerocolloidal Systems*, **1**, Pergamon, NY, 1971.
- Hill, R. D., A survey of lightning energy estimates, *Rev. Geophys. Space Phys.*, **17**, 155-164, 1979.
- Hill, W. J., and P. N. Sheldon, Statistical modeling of total ozone measurements with an example using data from Arosa, Switzerland, *Geophys. Res. Lett.*, **2**, 541-544, 1975.
- Hill, W. J., P. N. Sheldon, J. J. Tiede, Analyzing worldwide total ozone for trends, *Geophys. Res. Lett.*, **4**, 21-24, 1977.
- Hilsenrath, E., Ozone measurements in the mesosphere and stratosphere during two significant geophysical events, *J. Atmos. Sci.*, **28**, 295-297, 1971.
- Hilsenrath, E., B. Guenther, and P. Dunn, Water vapor in the lower stratosphere measured from aircraft flight, *J. Geophys. Res.*, **82**, 5453-5458, 1977.
- Hilsenrath, E., J. A. Krueger, R. A. Goldberg, J. S. Randhawa, R. O. Olsen, J. D. Mitchell, and J. R. Barcus, Measured effects of auroral X-ray absorption in the lower mesosphere on ozone and electrical conductivity, Am. Met. Soc. Conf. on Meteorol. of the Upper Atmosphere, Boston, Mass, 1978.
- Hilsenrath, E., D. F. Heath, and B. M. Schlesinger, Seasonal and interannual variations in total ozone revealed by the Nimbus-4 backscattered ultraviolet experiment, *J. Geophys. Res.*, **84**, in press, 1979a.
- Hilsenrath, E., R. L. Coley, P. T. Kirschner, and B. Gammill, A rocket ozonesonde for geophysical research and satellite intercomparisons *NASA TM 79712*, NASA Goddard Space Flight Center, Greenbelt, Maryland, 1979b.

- Hines, C. O., Eddy diffusion coefficients due to instabilities in internal gravity waves, *J. Geophys. Res.*, **75**, 3937-3939, 1970.
- Hines, C. O., A possible mechanism for the production of sun-weather correlations, *J. Atmos. Sci.*, **31**, 589-591, 1974.
- Hirota, I., Equatorial waves in the upper stratosphere and mesosphere in relation to the semi-annual oscillation of the zonal wind, *J. Atmos. Sci.*, **35**, 714-722, 1978.
- Hitchcock, D. R., Atmospheric sulfates from biological sources, *J. Air Pollut. Contr. Assoc.*, **26**, 210-215, 1976.
- Hitchcock, D. R., A. R. Bandy, T. E. Graedel, B. B. Hicks, R. B. Husar, and W. T. Patrick, Report of the Sulfur Panel, in *Proc. NSF Workshop on Atmospheric Chemistry*, in preparation, 1979.
- Hodges, R. R., Generation of turbulence in the upper atmosphere by internal gravity waves, *J. Geophys. Res.*, **72**, 3455-3458, 1967.
- Hodges, R. R., Eddy diffusion coefficients due to instabilities in internal gravity waves, *J. Geophys. Res.*, **74**, 4086-4090, 1969.
- Hofmann, D. J., D. E. Carroll, and J. M. Rosen, Estimate of the contribution of the Space Shuttle effluent to the natural stratospheric aerosol, *Geophys. Res. Lett.*, **2**, 113-116, 1975.
- Holland, P. M., and A. W. Castleman, Jr., Gas phase complexes: Considerations of the stability of clusters in the sulfur trioxide-water system, *Chem. Phys. Lett.*, **56**, 511-514, 1978.
- Hollinden, G. A., M. J. Kurylo, and R. B. Timmons, Electron spin resonance study of the kinetics of the reaction of $O(^3P)$ atoms with H_2S , *J. Chem. Phys.*, **74**, 988-991, 1970.
- Holton, J. R., Waves in the equatorial stratosphere generated by tropospheric heat sources, *J. Atmos. Sci.*, **29**, 368-375, 1972.
- Holton, J. R., A semi-spectral numerical model for wave-mean flow interactions in the stratosphere: Applications to sudden stratospheric warmings, *J. Atmos. Sci.*, **33**, 1639-1649, 1976.
- Holton, J. R., and R. S. Lindzen, An updated theory for the quasi-biennial cycle of the tropical stratosphere, *J. Atmos. Sci.*, **29**, 1076-1080, 1972.
- Holton, J., and Wehrbein, A numerical model of the zonal mean circulation of the middle atmosphere, *Pure Appl. Geophys.*, in press, 1979.
- Horowitz, A., F. Su, and J. G. Calvert, Unusual H_2 - forming chain reaction in the 3130A photolysis of formaldehyde-oxygen mixtures at 25°C, *Int. J. Chem. Kinet.*, **10**, 1099-1117, 1978.
- Horvath, J. J., and C. J. Mason, Nitric oxide mixing ratios near the stratopause measured by a rocket-borne chemiluminescent detector, *Geophys. Res. Lett.*, **5**, 1023-1026, 1978.
- Houghton, J. T., The stratosphere and mesosphere, *Quart. J. Roy. Meteorol. Soc.*, **104**, 1-29, 1978.
- Houze, R. A., Jr., and Chee-Pong Cheng, Radar characteristics of tropical convection observed during GATE: mean properties and trends over the summer season, *Mon. Weather Rev.*, **105**, 964-980, 1977.

- Howard, C. J., Temperature dependence of the reaction $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$, *J. Chem. Phys.*, **71**, 2352-2359, 1979.
- Howard, C. J., and K. M. Evenson, Rate constants for the reactions of OH with ethane and some halogen substituted ethanes at 296K, *J. Chem. Phys.*, **64**, 4303-4306, 1976.
- Howard, C. J., and K. M. Evenson, Kinetics of the reaction of HO_2 with NO, *Geophys. Res. Lett.*, **4**, 437-440, 1977.
- Hoxit, T. R., and R. M. Henry, Diurnal and annual temperature variations in the 30-60 km region as indicated by statistical analysis of rocketsonde data, Paper presented at the Int. Conf. on Aerospace and Aeronautical Meteorology, Washington, D.C., 1972.
- Hudson, R. D., editor, *Chlorofluoromethanes and the Stratosphere*, NASA Reference Publication 1010, 266 pp, 1977.
- Hudson, R. D., and S. H. Mahle, Photodissociation rates of molecular oxygen in the mesosphere and lower thermosphere, *J. Geophys. Res.*, **77**, 2902-2914, 1972.
- Hudson, R. D., V. L. Carter, and E. L. Breig, Predissociation in the Schumann-Runge band system, of O_2 : Laboratory measurements and atmospheric effects, *J. Geophys. Res.*, **74**, 4079-4086, 1969.
- Huertas, M. L., Ph. D. Thesis, University Paul Sabatier de Toulouse, order No. 493, 1972.
- Hunt, B. G., Experiments with a stratospheric general circulation model, Part IV, Inclusion of the hydrologic cycle, *Mon. Weather Rev.*, **104**, 333-350, 1976.
- Hunt, B. G., Atmospheric vascillations in a general circulation model I: The large scale energy cycle, *J. Atmos. Sci.*, **35**, 1133-1143, 1978a.
- Hunt, B. G., Atmospheric vascillations in a general circulation model II: Tropospheric-stratospheric coupling and stratospheric variability, *J. Atmos. Sci.*, **35**, 2052-2067, 1978b.
- Hunt, B. G., and S. Manabe, Experiments with a stratospheric general circulation model I: Radiative and dynamic aspects, *Mon. Weather Rev.*, **96**, 477-502, 1968.
- Hunt, B. G., and S. Manabe, Experiments with a stratospheric general circulation model II: Large scale diffusion of tracers in the stratosphere, *Mon. Weather Rev.*, **96**, 503-539, 1969.
- Hunten, D. M., Vertical transport in atmospheres, in *Atmospheres of Earth and the Planets*, ed. B. M. McCormac, Dordrecht, Holland, 59-72, 1975.
- Hunten, D. M., Estimates of stratospheric pollution by an analytic model, *Proc. Nat. Acad. Sci., USA* **72**, 4711-4715, 1975a.
- Huntingdon, A. T., The collection and analysis of volcanic gases from Mount Etna, *Phil. Trans. Roy. Soc. London, Ser. A.*, **274**, 119-128, 1973.
- Hutchings, J. W., and E. Farkas, The vertical distribution of atmospheric ozone over Christchurch, New Zealand, *Quart. J. Roy. Meteorol. Soc.*, **97**, 249-254, 1971.

- Hyson, P., Stratospheric water vapor measurements over Australia, 1973-1976, *Quart. J. Roy. Meteorol. Soc.*, **104**, 225-227, 1978.
- Imhof, W. L., J. B. Reagan, and E. E. Gaines, Observations of enhanced precipitation of relativistic electrons at the trapping boundary: Its role in ionospheric chemistry and ozone depletion, (abstract) *Eos Trans. Am. Geophys. Union*, **58**, 464, 1977.
- Inman, R. E., R. B. Ingersoll, and E. A. Levy, Soil: A natural sink for carbon monoxide, *Science*, **172**, 1229-1231, 1971.
- Inn, E. C. Y., B. J. Tyson, and J. C. Arvesen, Atmospheric halocarbon experiment, in NASA Technical Memorandum X-73630, *Interhemispheric Survey of Minor Upper Atmospheric Constituents during October-November 1976*, Compiled by D. G. Gauntner and L. C. Haughney, Lewis Research Center, Cleveland, Ohio, 44135, 79-93, March, 1977.
- Inn, E. C. Y., J. F. Vedder, B. J. Tyson, and D. O'Hara, COS in the stratosphere, *Geophys. Res. Lett.*, **6**, 191-193, 1979.
- Izenberg, J. A., J. A. Krasuipollskiy, A. P. Kuznetsov, and A. I. Ledebinskii, An investigation of planetary ozone distribution from satellite measurements of ultraviolet spectra, *Atmos. Ocean. Phys.*, **5**, 219-223, 1969.
- Irvine, W. V., and F. W. Peterson, Observations of atmospheric extinction from 0.315 to 1.06 microns, *J. Atmos. Sci.*, **27**, 62-69, 1970.
- Jacchia, L. G., Static diffusion models on the upper atmosphere with empirical temperature profiles, *Smithsonian Contrib. Astrophys.*, **8**, 215-257, 1965.
- Jackman, C. H., H. S. Porter, and J. E. Frederick, Upper limits on the production rate of NO per ion pair, *Nature*, **280**, 170, 1979.
- Jaeschke, W., R. Schmitt, and H. W. Georgii, Preliminary results of stratospheric SO₂ measurements, *Geophys. Res. Lett.*, **3**, 517-519, 1976.
- Jaffe, R. L., and S. R. Langhoff, Theoretical study of the photodissociation of HOCl, *J. Chem. Phys.*, **68**, 1638-1648, 1978.
- Jarnot, R. F., Radiometric measurements of atmospheric minor constituents, D. Phil. Thesis, Oxford University, 1976.
- Johnsen, R., C. M. Huana, and M. Biondi, The formation and breakup of NO⁺·N₂ clusters in N₂ at low temperatures, *J. Chem. Phys.*, **63**, 3374-3378, 1975.
- Johnson, R. G., and W. L. Imhof, Direct satellite observations on bremsstrahlung radiation as a technique to investigate its role in meteorological processes, in *Possible Relationships Between Solar Activity and Meteorological Phenomena*, NASA SP-366, 89, 1975.
- Johnson, F. S., J. D. Purcell, and R. Tousey, Measurements of the vertical distribution of atmospheric ozone from rockets, *J. Geophys. Res.*, **56**, 583-594, 1951.
- Johnson, F. S., J. D. Purcell, R. Tousey, and K. Watanabe, Direct measurements of the vertical distribution of atmospheric ozone to 70 km altitude, *J. Geophys. Res.*, **57**, 157-177, 1952.

- Johnston, H. S., Analysis of the independent variables in the perturbation of stratospheric ozone by nitrogen fertilizers, *J. Geophys. Res.*, **82**, 1767-1772, 1977.
- Johnston, H. S., and S. Solomon, Thunderstorms as possible micrometeorological sink for stratospheric water, *J. Geophys. Res.*, **84**, 3155-3158, 1979.
- Johnston, H. S., D. Kattenhorn, and G. Whitten, Use of excess carbon 14 data to calibrate models of stratospheric ozone depletion by supersonic transports, *J. Geophys. Res.*, **81**, 368-380, 1976.
- Jourdain, J. L., G. Le Bras, G. Poulet, J. Combourieu, P. Rigaud, and B. Leroy, UV absorption spectrum of ClO ($A^2\pi - X^2\pi$) up to the (1,0) band, *Chem. Phys. Lett.*, **57**, 109-112, 1978.
- JPL 79-27, *Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling*, Evaluation Number 2, NASA Panel for Data Evaluation, W. DeMore Chairman, Jet Propulsion Laboratory, 124 pp, 1979.
- Julian, P. K., and K. Labitzke, A study of atmospheric energetics during the January and February 1963 stratospheric warming, *J. Atmos. Sci.*, **22**, 597-610, 1965.
- Junge, C. E., Residence time and variability of tropospheric trace gases, *Tellus*, **26**, 477-488, 1974.
- Junge, C. E., and J. E. Manson, Stratospheric aerosol studies, *J. Geophys. Res.*, **66**, 2163-2182, 1961.
- Junge, C. E., C. W. Chagnon, and J. E. Manson, Stratospheric aerosols, *J. Meteorol.*, **18**, 81-108, 1961.
- Kadlecek, J., V. A. Mohnen, and J. DelSanto, Atmospheric ion molecule interactions involving chlorofluorocarbons, ASRC-SUNY Publ. No. 414, State University of New York at Albany, 1977.
- Kajimoto, O., and R. J. Cvetanovic, Absolute quantum yield of $O(^1D_2)$ in the photolysis of ozone in the Hartley Band, *Int. J. Chem. Kinet.*, **11**, 605-612, 1979.
- Kaplan, W. A., J. W. Elkins, C. E. Kolb, M. B. McElroy, S. C. Wofsy, and A. P. Duran, Nitrous oxide in freshwater systems: An estimate for the yield of atmospheric N_2O from disposal of human waste, *Pure Appl. Geophys.*, **116**, 423-438, 1978.
- Kasahara, A., and T. Sasamori, Simulation experiments with a 12-layer stratospheric global circulation model II: Momentum balance and energetics in the stratosphere, *J. Atmos. Sci.*, **31**, 408-421, 1974.
- Kasahara, A., T. Sasamori, and W. M. Washington, Simulation experiments with a 12-layer stratospheric global circulation model I: Dynamical effect of earth's orography and thermal influence of continentality, *J. Atmos. Sci.*, **30**, 1229-1251, 1973.
- Kaufman, F., and B. Reimann, paper presented at 13th Informal Conference on Photochemistry, Clearwater Beach, Florida, January 1978.
- Keating, G. M., Relations between monthly variations of global ozone and solar activity, *Nature*, **274**, 873-874, 1978.
- Keating, G. M., E. J. Prior, C. P. Prabhakara, L. R. Lake, and J. Y. Nicholson, Spherical harmonic representation of global ozone from Nimbus-4 IRIS measurements (abstract), *Eos Trans. AGU*, **59**, 1201, 1977.

- Kebarle, P., Ion thermochemistry and solvation from gas phase ion equilibria, *Ann. Rev. Phys. Chem.*, **28**, 445-476, 1977.
- Keefe, D., P. J. Noland, and T. A. Rich, *Proc. Royal Irish Academy*, **60A**, 6, 1959.
- Keeling, C. D., Industrial production of carbon dioxide from fossil fuels and limestone, *Tellus*, **25**, 174-198, 1973.
- Keeling, C. D., and R. B. Bacastow, Impact of industrial gases on climate, in *Energy and Climate*, 72-95, National Academy of Sciences, Washington, D.C., 1978.
- Keeling, C. D., R. B. Bacastow, A. E. Bainbridge, C. A. Ekdahl, Jr., P. R. Guenther, L. S. Waterman, and J. F-S. Chin, Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii, *Tellus*, **28**, 538-551, 1976a.
- Keeling, C. D., J. A. Adams, Jr., C. A. Ekdahl, Jr., and P. R. Guenther, Atmospheric carbon dioxide variations at the south pole, *Tellus*, **28**, 552-564, 1976b.
- Kellogg, W. W., R. D. Cadle, E. R. Allen, A. L. Lazrus, and E. A. Martell, The sulfur cycle, *Science*, **175**, 587-596, 1972.
- Kennedy, J. S., Energy generation through radiative processes in the lower stratosphere, MIT Report 11, AT(30-1), 2241, 1 December 1964.
- Kennedy, P. J., and M. A. Shapiro, The energy budget of a clear air turbulence zone as observed by aircraft, *Mon. Weather Rev.*, **103**, 650-654, 1975.
- Kent, G. S., M. C. W. Sandford, and W. Keenliside, Laser radar observations of dust from comet Bennett, *J. Atmos. Terr. Phys.*, **33**, 1257-1262, 1971.
- Kerr, J. B., and C. T. McElroy, Measurement of stratospheric nitrogen dioxide from the AES stratospheric balloon program, *Atmosphere*, **14**, 166-171, 1976.
- Kiang, C. S., D. Stauffer, V. A. Mohnen, J. Bricard, and D. Vigla, Heteromolecular nucleation theory applied to gas-to-particle conversion, *Atmos. Environ.*, **7**, 1279-1283, 1973.
- Kiang, C. S., R. D. Cadle, and G. K. Yue, $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-H}_2\text{O}$ Ternary aerosol formation mechanism in the stratosphere, *Geophys. Res. Lett.*, **2**, 41-44, 1975.
- Kida, H., A numerical investigation of the stratospheric general circulation and stratospheric tropospheric mass exchange. I. Long term integration of a simplified general circulation model, *J. Meteorol. Soc. Japan*, **55**, 52-70, 1977a.
- Kida, H., A numerical investigation of the stratospheric general circulation and stratospheric tropospheric mass exchange. II. Lagrangian motion of the atmosphere, *J. Meteorol. Soc., Japan*, **55**, 71-88, 1977b.
- Klemm, R. B., Absolute rate parameters for the reactions of formaldehyde with O-atoms and H-atoms over the temperature range 250-500K, *J. Chem. Phys.*, **71**, 1987-1993, 1979.
- Klemm, R. B., S. Glicker, and L. J. Stief, Relative quantum yield for the production of O-atom and S-atom from the photodissociation of OCS in vacuum-UV, *Chem. Phys. Lett.*, **33**, 512-517, 1975.

- Klenk, K. F., Absorption coefficients of ozone for the backscatter ultraviolet experiments, submitted to *Appl. Opt.*, 1979a.
- Klenk, K. F., Errors due to profile shape in the derivation of total columnar ozone from nadir measurements of the solar backscattered radiation, Systems and Applied Sciences Corporation, Riverdale, Maryland, 1979b.
- Kley, D., G. M. Lawrence, and E. J. Stone, The yield of $N(^2D)$ atoms in the dissociative recombination of NO^+ , *J. Chem. Phys.*, **66**, 4157-4165, 1977.
- Kley, D., E. J. Stone, W. R. Henderson, J. W. Drummond, W. J. Harrop, A. L. Schmeltekopf, and T. L. Thompson, *in situ* measurements of the mixing ratio of water vapor in the stratosphere, *J. Atmos. Sci.*, in press, 1979.
- Knauth, H. D., H. Alberti, and H. Clausen, The equilibrium constant of the gas reaction $Cl_2O + H_2O \rightarrow 2HOCl$ and the UV spectrum of $HOCl$, *J. Phys. Chem.*, **83**, 1604-1612, 1979.
- Knittel, J., Ein Beitrag zur Klimatologie der Stratosphäre der Südhalbkugel, *Meteorol. Abh., Series A*, **2**, 1976.
- Kochanski, A., Cross sections of the mean zonal flow and temperature along $80^\circ W$, *J. Meteorol.*, **12**, 95-106, 1955.
- Kockarts, G., Penetration of solar radiation in the Schumann-Runge bands of molecular oxygen, in *Mesospheric Models and Related Experiments*, Ed. G. Fiocco, Reidel Publ. Co., Dordrecht-Holland, 160-176, 1971.
- Kockarts, G., Absorption and photodissociation in the Schumann-Runge bands of molecular oxygen in the terrestrial atmosphere, *Planet. Space Sci.*, **24**, 589-604, 1976.
- Kohri, W. J., J. C. Gille, and P. L. Bailey, Mapping of LRIR data by sequential estimation of Fourier coefficients, Collection of Extended Summaries at Joint Assembly, Seattle, WA, CUMA Sessions IAGA/IAMAP, Paper No. 12, November 1977.
- Komhyr, W. D., Measurements of atmospheric ozone at Moosonee, Canada, July 1, 1957 to July 31, 1960, *Canadian Met. Memoirs*, No. 6, Met. Branch, Dept. Transport., 1961.
- Komhyr, W. D., Electrochemical concentration cells for gas analysis, *Ann. Geophys.*, **25**, 203-210, 1969.
- Komhyr, W. D., Errors in Dobson spectrophotometer total ozone measurements due to use of inexact AD-wavelength effective ozone absorption coefficients and interference by SO_2 , submitted to *Geophys. Res. Lett.*, 1979.
- Komhyr, W. D., and T. B. Harris, Development of an ECC ozonesonde, NOAA Tech. Report ERL 300-APCL 18, 1971.
- Komhyr, W. D., R. D. Grass, and G. Slocum, Total ozone increases over North America during the 1960s, *Pure Appl. Geophys.*, **106-108**, 981-999, 1973.
- Komhyr, W. D., E. G. Dutton, G. M. Thompson, Fluorocarbon-11 and-12 tropospheric residence times, growth rates, abundances, and inter-hemispheric mixing parameters, determined from 1977 and 1978 measurements at NOAA, GMCC baseline stations, submitted to *Geophys. Res. Lett.*, 1979.

- Koyama, T., Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen, *J. Geophys. Res.*, **68**, 3971-3973, 1963.
- Kritz, M. A., Formation mechanisms of the stratospheric aerosols, Ph.D. dissertation, Yale University, University Microfilms, Ann Arbor, Michigan, 1975.
- Kroening, J. L., J. M. Rosen, and H. T. Mantis, On the transport of material across the tropopause, *J. Geophys. Res.*, **73**, 5463-5465, 1968.
- Krueger, A. J., Atmospheric absorption anomalies in the ultraviolet near an altitude of 50 km, *Science*, **166**, 998-1000, 1969.
- Krueger, A. J., The mean ozone distribution from several series of rocket soundings to 52 km at latitudes from 58°S to 64°N, *Pure Appl. Geophys.*, **106-108**, 1272-1280, 1973.
- Krueger, A. J., and R. A. Minzner, A mid-latitude model for the 1976 U.S. Standard Atmosphere, *J. Geophys. Res.*, **81**, 4477-4481, 1976.
- Krueger, A. J., and D. Wright, Some results from rocket ozone (RocoZ) soundings at Wallops Island, VA (abstract), *Eos Trans. AGU*, **60**, 268, 1979.
- Krueger, A. J., B. Guenther, A. J. Fleig, D. F. Heath, E. Hilsenrath, R. McPeters, and C. Prabhakara, Satellite ozone measurements, *Phil Trans. Proc. Roy. Soc., Lon. Ser. A.*, in press, 1979a.
- Krueger, A. J., P. Simeth, B. Ellefson, W. R. McBride, M. E. Hills, C. A. Flanagan, B. Gamill, S. Park, Design of an optical ozonesonde for the Super Loki-Dart rocket, NASA Reference Publication, in preparation, 1979b.
- Krumins, M. W., and W. C. Lyons, Corrections for the upper stratosphere temperatures using a thin film loop mount, *NOLTR 72-152*, Naval Ordnance Laboratory, 1972.
- Ku, H. H., Notes on the use of propagation of error formulas, *J. Res. NBS*, **70C**, 331-341, 1966.
- Kuhn, P. M., Zonal profiles of atmospheric water vapor, NOAA Tech. Rept. ERL 319-APCL 33, U.S. Dept. of Commerce, Boulder, Colorado, 11 pp, 1975.
- Kuhn, P. M., and L. P. Stearns, Radiometer observation of water vapor injection by thunderstorms, *J. Atmos. Sci.*, **30**, 507-509, 1973.
- Kuhn, P. M., L.P. Stearns, and N. S. Lojko, Latitudinal profiles of stratospheric water vapor, *Geophys. Res. Lett.*, **2**, 227-230, 1975.
- Kulkarni, R. N., Measurements of NO₂ using the Dobson spectrometer, *J. Atmos. Sci.*, **32**, 1641-1643, 1975.
- Kulkarni, R. N., Nitrogen dioxide and ozone measurement over Australia, *Quart. J. Roy. Meteorol. Soc.*, **102**, 461-464, 1976.
- Kulkarni, R. N., Ozone studies in the Southern Hemisphere and their usefulness for understanding the stratospheric circulation, *Pure Appl. Geophys.*, in press, 1979.
- Kung, E. C., Diurnal and long-term variations of the kinetic energy generation and dissipation for a five year period, *Mon. Weather Rev.*, **95**, 593-606, 1967.

- Kurylo, M. J., Flash photolysis resonance fluorescence investigation of the reactions of OH radicals with OCS and CS₂, *Chem. Phys. Lett.*, **58**, 238-242, 1978.
- Kurylo, M. J., and A. H. Laufer, New mechanistic information on OH reactions with carbonyl and tricarbonyl compounds, *J. Chem. Phys.*, **70**, 2032-2033, 1979.
- Kurzeja, R. J. The diurnal variation of minor constituents in the stratosphere and its effect on ozone concentrations, *J. Atmos. Sci.*, **32**, 899-909, 1975.
- Labitzke, K., Interannual variability of the winter stratosphere in the Northern Hemisphere, *Mon. Weather Rev.*, **105**, 762-770, 1977.
- Labitzke, K., On the different behavior of the zonal harmonic height waves 1 and 2 during the winters 1970/71 and 1971/72, *Mon. Weather Rev.*, **106**, 1704-1713, 1978.
- Labitzke, K., and J. J. Barnett, Global time and space changes of satellite radiances received from the stratosphere and lower mesosphere, *J. Geophys. Res.*, **78**, 483-496, 1973.
- Labitzke, K., and H. Van Loon, The stratosphere in the Southern Hemisphere, *Meteorol. Monogr.*, **13**, 113-138, 1972.
- Lacis, A. A., and J. E. Hansen, A parameterization for the absorption of solar radiation in the earth's atmosphere, *J. Atmos. Sci.*, **31**, 118-133, 1974.
- Lacis, A. A., W. C. Wang, and J. E. Hansen, Correlated, K-distribution method for radiative transfer in climate models: Application to effect of cirrus clouds on climate, *Fourth NASA Weather and Climate Science Review*, NASA CP 2076, ed. E. Kreins, 309-314, 1979.
- Lamb, H. H., Volcanic dust in the atmosphere: With a chronology and assessment of its meteorological significance. *Phil. Trans. Roy. Soc. London, Ser. A.*, **266**, 425-533, 1970.
- Lamontagne, R. A., J. Swinnerton, and V. J. Linnenbom, C1-C4 hydrocarbons in the north and south Pacific, *Tellus*, **26**, 71-77, 1974.
- Lanzerotti, L. J., Measures of energetic particles from the Sun, in *The Solar Output and Its Variation*, ed. by O. R. White, 383-403, Colorado Associated University Press, Boulder, Colorado, 1977.
- Lanzerotti, L. J., and C. G. MacLennan, Relative importance of solar electrons, protons, and alphas in the November 1969 PCA event, in *Proc. COSPAR Symp. Solar Particle Event of November 1969*, AFCRL-72-0474, 85, 1972.
- Larsen, T. R., and G. R. Thomas, Energy spectra measured during a relativistic electron precipitation event on 2 February 1969, *J. Atmos. Terr. Phys.*, **36**, 1613, 1974.
- Larsen, T. R., J. B. Reagan, W. L. Imhof, L. E. Montbriand, and J. S. Belrose, A coordinated study of energetic electron precipitation and D-region electron concentrations over Ottawa during disturbed conditions, *J. Geophys. Res.*, **81**, 2200-2212, 1976.
- Lazrus, A. L., and B. W. Gandrud, Stratospheric sulfate aerosol, *J. Geophys. Res.*, **79**, 3424-3431, 1974a.
- Lazrus, A. L., and B. W. Gandrud, Distribution of stratospheric nitric acid vapor, *J. Atmos. Sci.*, **31**, 1102-1108, 1974b.

- Lazrus, A. L., B. Gandrud, and R. D. Cadle, Chemical composition of air filtration samples of the stratospheric sulfate layer, *J. Geophys. Res.*, **76**, 8083-8088, 1971.
- Lazrus, A. L., B. W. Gandrud, R. N. Woodard, and W. A. Sedlacek, Stratospheric halogen measurements, *Geophys. Res. Lett.*, **2**, 437-439, 1975.
- Lazrus, A. L., B. W. Gandrud, R. N. Woodard, and W. A. Sedlacek, Direct measurements of stratospheric chlorine and bromine, *J. Geophys. Res.*, **81**, 1067-1070, 1976.
- Lazrus, A. L., B. W. Gandrud, J. Greenberg, J. Bonelli, E. Mroz, and W. A. Sedlacek, Midlatitude seasonal measurements of stratospheric acidic chlorine vapor, *Geophys. Res. Lett.*, **4**, 587-589, 1977.
- Lazrus, A. L., R. D. Cadle, B. W. Gandrud, J. P. Greenberg, B. J. Huebert, and W. I. Rose, Jr., *J. Geophys. Res.*, submitted, 1979.
- Lee, L. C., and T. G. Slanger, Observations on $O(^1D \rightarrow ^3P)$ and $O_2(b\ ^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-)$ following O_2 photodissociation, *J. Chem. Phys.*, **69**, 4053-4060, 1978.
- Lee, L. C., and T. G. Slanger, Atmospheric OH production - The $O(^1D) + H_2O$ reaction rate, *Geophys. Res. Lett.*, **6**, 165-166, 1979.
- Lemaire, P., J. Charra, A. Jouchoux, A. Vidal-Madjar, G. E. Artzner, J. C. Vial, R. M. Bonnet, and A. Skumanich, Calibrated full disk solar HI Lyman- α and Lyman- β profiles, *Astrophys. J.*, **223**, L55-L58, 1978.
- Leovy, C. B., Simple models of thermally driven mesospheric circulations, *J. Atmos. Sci.*, **21**, 327-341, 1964.
- Leovy, C. B., and T. Ackerman, Evidence for high-frequency synoptic disturbances near the stratopause, *J. Atmos. Sci.*, **30**, 940-942, 1973.
- Leovy, C. B., and P. J. Webster, Stratospheric long waves: Comparison of thermal structure in the Northern and Southern hemispheres, *J. Atmos. Sci.*, **33**, 1624-1638, 1976.
- Lepel, E. A., K. M. Stefansson, and W. H. Zoller, The enrichment of volatile elements in the atmosphere by volcanic activity: Augustine volcano 1976, *J. Geophys. Res.*, **83**, 6213-6220, 1978.
- Leu, M. T., Rate constant for the reaction $HO_2 + NO \rightarrow OH + NO_2$, *J. Chem. Phys.*, **70**, 1662-1666, 1979.
- Leu, M. T., and C. L. Lin, Rate constants for the reactions of OH with ClO, Cl₂, and Cl₂O at 298K, *Geophys. Res. Lett.*, **6**, 425-428, 1979.
- Levine, J. S., R. E. Hughes, W. L. Chameides, and W. E. Howell, N₂O and CO production by electric discharges: Atmospheric implications, *Geophys. Res. Lett.*, **6**, 557-559, 1979.
- Levy, H., Normal atmosphere: Large radical and formaldehyde concentrations predicted, *Science*, **173**, 141-143, 1971.
- Levy, H., Photochemistry of the lower troposphere, *Planet. Space Sci.*, **20**, 919-935, 1972.
- Levy, H., II, J. D. Mahlman, and W. J. Moxim, A preliminary report on the numerical simulation of the three-dimensional structure and variability of atmospheric N₂O, *Geophys. Res. Lett.*, **6**, 155-158, 1979.

- Lewis, B. R., J. H. Carver, T. I. Hobbs, D. G. McCoy, and H. P. F. Gies, Experimentally determined oscillator strengths and linewidths for the Schumann-Runge band system of molecular oxygen I. The (6-0) - (14-0) bands, *J. Quant. Spectrosc. Radiat. Transfer*, **20**, 191-203, 1978.
- Lilly, D. R., D. E. Waco, and S. I. Adelfang, Stratospheric mixing estimated from high-altitude turbulence measurements, *J. Appl. Meteorol.*, **13**, 488-493, 1974.
- Lin, C. L., and W. B. DeMore, Reactions of $O(^1D)$ with methane and ethane, *J. Phys. Chem.*, **77**, 863-869, 1973.
- Lindauer, G. C., and A. W. Castleman, Jr., Initial size distribution of aerosols, *Nucl. Sci. Engr.*, **43**, 212-217, 1971.
- Lindzen, R. S., The radiative-photochemical response of the mesosphere to fluctuations in radiation, *J. Atmos. Sci.*, **22**, 469-478, 1965.
- Lindzen, R. S., Vertical momentum transport by large scale disturbances in the equatorial lower stratosphere, *J. Meteorol. Soc. Japan.*, **38**, 81-83, 1970.
- Lindzen, R. S., Effect of daily variations of cumulo-nimbus activity on the atmospheric semi-diurnal tide, *Mon. Weather Rev.*, **106**, 526-533, 1978.
- Lindzen, R. S., and R. M. Goody, Radiative and photochemical processes in mesospheric dynamics: I. Models for radiative and photochemical processes, *J. Atmos. Sci.*, **22**, 341-348, 1965.
- Lindzen, R. S., and J. R. Holton, A theory of the quasi-biennial oscillation, *J. Atmos. Sci.*, **35**, 1095-1107, 1968.
- Lindzen, R. S., and S-S. Hong, Effects of mean winds and horizontal temperature gradients on solar and lunar semi-diurnal tides in the atmosphere, *J. Atmos. Sci.*, **31**, 1431-1440, 1974.
- Liss, P. S., and P. G. Slater, Flux of gases across the air-sea interface. *Nature*, **247**, 181-184, 1974.
- Liu, S. C., T. M. Donahue, R. J. Cicerone, and W. L. Chameides, Effect of water vapor on the destruction of ozone in the stratosphere perturbed by Cl_x or NO_x pollutants, *J. Geophys. Res.*, **81**, 3111-3118, 1976.
- Liu, S. C., and G. C. Reid, Sodium and other minor constituents of meteoric origin in the atmosphere, *Geophys. Res. Lett.*, **6**, 283-286, 1979.
- Loewenstein, M. and H. F. Savage, Latitudinal measurements of NO and O_3 in the lower stratosphere from 5° to 82° north, *Geophys. Res. Lett.*, **2**, 448-450, 1975.
- Loewenstein, M., W. L. Starr, and D. G. Murcray, Stratospheric NO and HNO_3 observations in the Northern Hemisphere for three seasons, *Geophys. Res. Lett.*, **5**, 531-535, 1978.
- Loewenstein, M., W. J. Borucki, H. F. Savage, J. G. Borucki, and R. C. Whitten, Geographical variations of NO and O_3 in the lower stratosphere, *J. Geophys. Res.*, **83**, 1874-1882, 1978.
- Logan, J. A., M. Prather, S. Wofsy, and M. B. McElroy, Atmospheric chemistry: Response to human influence, *Phil. Trans. Roy Soc. London, Ser. A*, **290**, , 187-234, 1978.

- London, J., and J. K. Angell, The observed distribution of ozone and its variations, Vol. I, Ozone and perturbation, *Man and Stratospheric Ozone*, CRC Press, to be published, 1979.
- London, J., and J. Kelley, Global trends in total atmospheric ozone, *Science*, **184**, 987-989, 1974.
- London, J., J. E. Frederick, and G. P. Anderson, Satellite observations of the global distribution of stratospheric ozone, *J. Geophys. Res.*, **82**, 2543-2556, 1976a.
- London, J., R. D. Bojkov, S. Oltmans, and J. I. Kelley, Atlas of the global distribution of total ozone July 1957-June 1967, *NCAR Technical Note*, NCAR/TN/113+STR, 1976b.
- Lorenz, E. N., The nature and theory of the general circulation of the atmosphere, WMO publication, TP 115, 1967.
- Lorenz, E. N., The nature of the global circulation: A present view, in the *Global Circulation of the Atmosphere*, G. A. Corby, Ed., *London Roy. Meteorol. Soc.*, 3-41, 1969.
- Louis, J. F., J. London, and E. F. Danielsen, The interaction of radiation and the meridional circulation of the stratosphere, *Proceedings of the IAMAP/IAPSO Combined First Special Assemblies*, Melbourne, Australia, Vol. II, 1205-1214, 1974.
- Lovelock, J. E., Atmospheric halocarbons and stratospheric ozone, *Nature*, **252**, 202-294, 1974.
- Lovelock, J., Atmospheric halocarbons, their tropospheric sources and sinks, (abstract), *Eos Trans. AGU*, **57**, 670, 1976.
- Lovelock, J. E., Methyl chloroform in the troposphere as an indicator of OH radical abundance, *Nature*, **267**, 32, 1977.
- Lovelock, J. E., R. J. Maggs, and R. A. Rasmussen, Atmospheric dimethyl sulfide and the natural sulphur cycle, *Nature*, **237**, 452-453, 1972.
- Lovelock, J. E., R. J. Maggs, and R. J. Wade, Halogenated hydrocarbons in and over the Atlantic, *Nature*, **241**, 194-196, 1973.
- Lovill, J. E., T. J. Sullivan, R. L. Weichel, J. S. Ellis, J. G. Huebel, J. A. Korver, P. P. Weidhaas, and F. A. Phelps, Total ozone retrieval from satellite multichannel filter radiometer measurements, *UCRL-52473*, Lawrence Livermore Laboratory, Univ. of Calif., 1978.
- Luther, F. M., and R. J. Gelinas, Effect of molecular multiple scattering and surface albedo on atmospheric photodissociation rates, *J. Geophys. Res.*, **81**, 1125-2232, 1976.
- Luther, F., D. Wuebbles, and J. Chang, Temperature feedback in a stratospheric model, *J. Geophys. Res.*, **82**, 4935-4942, 1977.
- MacCracken, M. C., and J. S. Chang, eds., A preliminary study of the potential chemical and climatic effects of atmospheric nuclear explosions, Lawrence Livermore Laboratory Report UCRL-51653, April, 1975.
- Mack, G. P. R., and B. Thrush, Reaction of oxygen atoms with carbonyl compounds, *J. C. S. Faraday I*, **69**, 208-215, 1973.

- Madden, R. A., Oscillations in the winter stratosphere: Part 2. The role of horizontal eddy heat transport and the interaction of transient and stationary planetary-scale waves, *Mon. Weather Rev.*, **103**, 717-729, 1975.
- Maeda, K., and A. C. Aikin, Variations of polar mesospheric oxygen and ozone during auroral events, *Planet. Space Sci.*, **16**, 371-384, 1968.
- Maeda, K., and D. F. Heath, Asymmetries in ozone depressions between the polar stratosphere following a solar proton event, NASA Technical Memorandum 79696, November 1978.
- Mahlman, J. D., Some fundamental limitations of simplified-transport model, *Proceedings of the Fourth CIAP Conference, Rep. DOT-TSC-OST-75-38*, pp. 132-146, U. S. Department of Transportation, Washington, D. C., 1975.
- Mahlman, J. D., Preliminary results from a three dimensional general circulation/tracer model, *Proceedings of the Second CIAP Conference*, A. J. Broderick, Ed., DOT-TSC-OST-73-4, 321-337, 1976.
- Mahlman, J. D., Heat balance and mean meridional circulation in the polar stratosphere during the sudden warming of January 1958, *Mon. Weather Rev.*, **97**, 534-540, 1979.
- Mahlman, J. D., and W. J. Moxim, Tracer simulation using a global general circulation model: Results from a midlatitude instantaneous source experiment, *J. Atmos. Sci.*, **35**, 1370-1374, 1978.
- Mahlman, J. D., R. W. Sinclair, and M. D. Schwarzkopf, Simulated response of the atmospheric circulation to a large ozone reduction, WMO Symposium on the Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere, Toronto, WMP Publ. 511, World Meteorological Organization, Geneva, 219-221, 1978.
- Mahlman, J. D., H. Levy II, and W. J. Moxim, three dimensional tracer structure and behavior as simulated in two ozone processor experiments, *J. Atmos. Sci.*, in press, 1979.
- Maier, E. J., A. C. Aikin, and J. E. Ainsworth, Stratospheric nitric oxide and ozone measurements using photoionization mass spectrometry and UV absorption, *Geophys. Res. Lett.*, **5**, 37-40, 1978.
- Malinconico, L. L., Jr., Fluctuations in SO₂ emissions during recent eruptions of Etna, *Nature*, **278**, 43-45, 1979.
- Manabe, S., and B. G. Hunt, Experiments with a stratospheric general circulation model: I. Radiative and dynamic effects, *Mon. Weather Rev.*, **96**, 477-539, 1968.
- Manabe, S., and J. D. Mahlman, Simulation of seasonal and interhemispheric variations in the stratospheric circulation, *J. Atmos. Sci.*, **33**, 2185-2217, 1976.
- Manabe, S., and R. F. Strickler, Thermal equilibrium of the atmosphere with a convective adjustment, *J. Atmos. Sci.*, **21**, 361-385, 1964.
- Manabe, S., and T. B. Terpstra, The effects of mountains on the general circulation of the atmosphere as identified by numerical experiments, *J. Atmos. Sci.*, **31**, 3-42, 1974.
- Manabe, S., and R. T. Wetherald, Thermal equilibrium of the atmosphere with a given distribution of relative humidity, *J. Atmos. Sci.*, **24**, 241-259, 1967.

- Manabe, S., and R. T. Wetherald, The effects of doubling the CO₂ concentration of the climate of a general circulation model, *J. Atmos. Sci.*, **32**, 3-15, 1975.
- Mankin, W. G., and M. T. Coffey, Airborne Fourier Transform Spectroscopy, Topical Meeting on Atmospheric Spectroscopy, August 30 - September 1, 1978, Keystone, Colorado, 1978.
- Manson, J. E., C. E. Junge, and C. W. Chagnon, The possible role of gas reactions in the formation of the stratospheric aerosol layer, in *Chemical Reactions in the Lower and Upper Atmosphere*, edited by R. D. Cadle, 139-154, Interscience, New York, 1961.
- Manufacturing Chemists Association, World production and release of chlorofluorocarbons 11 and 12 through 1977, E. I. DuPont de Nemours and Company, Wilmington, Delaware, July 17, 1978a.
- Manufacturing Chemists Association, 1977 World Production and Sales of FC-22, June 26, 1978b.
- Margitan, J. J., and J. G. Anderson, Kinetics of the reaction HO₂ + NO → OH + NO₂ paper presented at the 13th Informal Conference on Photochemistry, Clearwater Beach, Florida, January 1978.
- Margolis, J. S., R. T. Menzies, and E. D. Hinkley, Bandstrength Determination of the fundamental vibration-rotation spectrum of ClO, *Appl. Opt.*, **17**, 1680-1682, 1978.
- Markson, R., Solar modulation of atmospheric electrification and possible implications for the Sun-weather relationship, *Nature*, **273**, 103-109, 1978.
- Maroulis, P. J., A. L. Torres, and A. R. Bandy, Atmospheric concentrations of carbonyl sulfide in the southwestern and eastern United States, *Geophys. Res. Lett.*, **4**, 510-512, 1977.
- Martin, D. W., and A. W. Brewer, A synoptic study of day-to-day changes of ozone over the British Isles, *Quart. J. Roy. Meteorol. Soc.*, **85**, 393-403, 1959.
- Martin, L. R., A. G. Wren, and M. Wun, Chlorine atom and ClO wall reactions products, final report prepared for the National Science Foundation, The Ivan A. Getting Laboratories, The Aerospace Corp., El Segundo, Calif., 1978.
- Maruyama, T., and M. Yanai, Evidence of large scale disturbances in the equatorial lower stratosphere, *J. Meteorol. Soc. Japan*, **45**, 196-199, 1967.
- Marx, W., F. Bahe, and V. Schurath, The NO yield of O(¹D) + N₂O as function of kinetic energy, *Ber. Bunsenges Phys. Chem.*, **83**, 225-230, 1979.
- Mason, B. J., The Physics of Clouds, Chapter 1, *Oxford Press*, London, 2nd Ed., 1961.
- Mason, B. J., Man's influence not yet felt by climate, News story by John Gribben, *Nature*, **264**, 608, 1976.
- Mason, C. J., and J. J. Horvath, The direct measurement of nitric oxide concentration in the upper atmosphere by a rocket-borne chemiluminescent detector, *Geophys. Res. Lett.*, **3**, 391-394, 1976.
- Mastenbrook, H. J., Water vapor distribution in the stratosphere and high troposphere, *J. Atmos. Sci.*, **25**, 299-311, 1968.
- Mastenbrook, H. J., The variability of water vapor in the stratosphere, *J. Atmos. Sci.*, **28**, 1495-1501, 1971.

- Mastenbrook, H. J., Water vapor measurements in the lower stratosphere, *Can. J. Chem.*, **52**, 1527-1531, 1974a.
- Mastenbrook, H. J., Stratospheric water vapor distribution and variability, Proc. Intern. Conf. on Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations, Melbourne, IAMAP **1**, 233, 1974b.
- Mateer, C. L., On the information content of Umkehr observations, *J. Atmos. Sci.*, **22**, 370-381, 1965.
- Mateer, C. L., A review of some aspects of inferring the ozone profile by inversion of ultraviolet radiance measurements, *Mathematics of Profile Inversion*, edited by L. Colin NASA TMX-62-150, 2-24, 1972.
- Mateer, C. L., Method of evaluation of Canadian ozonesonde data, Internal Report No. ATRB-8907, Canadian Atmospheric Environment Service, October 1977.
- Mateer, C. L., and H. U. Dütsch, Uniform evaluation of Umkehr observations from world ozone network, 1 and 2, *Res. Report*, NCAR, Boulder, Colorado, 1964.
- Mateer, C. L., D. F. Heath, and A. J. Krueger, Estimation of total ozone from satellite measurements of backscattered ultraviolet earth radiances, *J. Atmos. Sci.*, **28**, 1307-1311, 1971.
- Matsuno, T., Vertical propagation of stationary planetary waves in the winter northern hemisphere, *J. Atmos. Sci.*, **27**, 871-883, 1970.
- Matsuno, T., A dynamical model of the stratospheric sudden warming, *J. Atmos. Sci.*, **28**, 1479-1494, 1971.
- Matsuno, T., Lagrangian motion of air parcels in the stratosphere in the presence of planetary waves, submitted to *Pure Appl. Geophys.*, 1979.
- Matsuno, T., and K. Nakamura, The Eulerian and Lagrangian mean meridional circulations in the stratosphere at the time of a sudden warming, *J. Atmos. Sci.*, **36**, 640-654, 1979.
- Matthias, A. D., A. M. Blackmer, and J. M. Bremner, Diurnal variability of the concentration of nitrous oxide in surface air, *Geophys. Res. Lett.*, **6**, 441-443, 1979.
- Mauersberger, K., and R. Finstad, Stratospheric constituent measurements with a mass spectrometer-beam system (abstract), *Eos Trans. AGU*, **59**, 1148, 1978.
- McCarthy, R. L., F. A. Bower, and J. P. Jesson, The fluorocarbon-ozone theory I: production and release. World production and release of CCl_3F and CCl_2F_2 (Fluorocarbons 11 and 12) through 1975, *Atmos. Environ.*, **11**, 491-497, 1977.
- McClatchey, R. A., W. S. Benedict, S. A. Clough, D. E. Burch, R. F. Calfee, K. Fox, L. S. Tothman, and J. S. Garing, AFCRL Atmospheric Absorption Line Parameter Compilation, Environmental Research Paper No. 434, *AFCRL TR-73-0096*, 78 pp., 1973.
- McConnell, J. C., M. B. McElroy, and S. C. Wofsy, Natural sources of atmospheric CO, *Nature*, **233**, 187-188, 1971.
- McConnell, J. C., and H. I. Schiff, Methyl chloroform: Impact on stratospheric ozone, *Science*, **199**, 1974-1977, 1978.

- McConnell, J. C., and W. F. J. Evans, Implications of low stratospheric hydroxyl concentrations for CFM and SST scenario calculations of ozone depletion, (abstract), *Eos Trans., AGU*, **59**, 1078, 1978.
- McElroy, M. B., S. C. Wofsy, and Y. L. Yung, The nitrogen cycle: Perturbations due to man and their impact on atmospheric N_2O and O_3 , *Phil. Trans. Roy. Soc., Lon., Ser. B*, **277**, 159-181, 1977.
- McFarland, M., D. Kley, J. W. Drummond, A. L. Schmeltekopf, and R. H. Winkler, Nitric oxide measurements in the equatorial Pacific region, *Geophys. Res. Lett.*, **6**, 605-608, 1979.
- McGhan, M., A. W. Shaw, and L. R. Megill, Measurement of NO profiles in the stratosphere using a dropsonde, submitted to *Geophys. Res. Lett.*, 1979.
- McInturff, R. M., ed., Stratospheric Warmings: Synoptic, Dynamic, and General Circulation Aspects, *NASA Reference Publication 1017*, 166 pp., 1978.
- McInturff, R. M., and F. G. Finger, The compatibility of radiosonde data at stratospheric levels over the northern hemisphere, *ESSA Technical Memorandum WBTM DATAC*, **2**, 61 pp., 1968.
- McIntyre, M. E., Baroclinic instability of an idealized model of the polar night jet, *Quart. J. Roy. Meteorol. Soc.*, **98**, 165-174, 1972.
- McIntyre, M. E., Towards a Lagrangian mean description of stratospheric circulations and chemical transports, submitted to *Phil Trans. Roy. Soc. London (Series A)*, 1979.
- McIntyre, M. E., and D. G. Andrews, Generalized Eliassen - Palm and Charney - Drazon theorems for waves on axisymmetric mean flows in compressible atmospheres, *J. Atmos. Sci.*, **35**, 175-185, 1978.
- McKenney, D. J., and D. L. Wade, Rates of evolution from N-fertilized soil, *Geophys. Res. Lett.*, **5**, 777-779, 1978.
- McKenzie, D. J., The diurnal atmospheric tide with Newtonian cooling and longitudinally dependent drives, Ph.D. thesis, University of Washington, 139 pp., 1968.
- McKinnon, D., and H. W. Morewood, Water vapor distribution in the lower stratosphere over North and South America, *J. Atmos. Sci.*, **27**, 483-493, 1970.
- McMurry, P. N., On the relationship between aerosol dynamics and the rate of gas-to-particle conversion, Ph.D. thesis, Calif. Inst. of Technology, 1977.
- Meakin, P., P. S. Gumerman, L. C. Glasgow, and J. P. Jesson, The fluorocarbon-ozone theory - III. Fluorocarbon mixing and photolysis. The effects of eddy diffusion and tropospheric lifetime on CCl_3F and CCl_2F_2 tropospheric mixing ratios, *Atmos. Environ.*, **12**, 1271-1285, 1978.
- Megill, L. R., J. C. Haslett, and H. I. Schiff, Rocket observations of $O_2(^1\Delta_g)$ *Can. J. Phys.*, **47**, 2351-2354, 1969.
- Meira, L. G., Jr., Rocket measurements of upper atmospheric nitric oxide and their consequences to the lower ionosphere, *J. Geophys. Res.*, **76**, 202-212, 1971.
- Menzies, R. T., Remote measurement of ClO in the stratosphere, *Geophys. Res. Lett.*, **6**, 151-154, 1979.

- Michael, J. V., D. A. Whytock, J. H. Lee, W. A. Payne, L. J. Stief, Absolute rate constant for the reaction of atomic chlorine with hydrogen peroxide over the temperature range 265-400K, *J. Chem. Phys.*, **67**, 3533-3536, 1977.
- Migeotte, M. V., Methane in the earth's atmosphere, *Astrophys. J.*, **107**, 400-403, 1948.
- Mihelcic, D., D. H. Ehhalt, G. F. Kulesa, J. Klomfass, M. Trainer, U. Schmidt, and H. Rohrs, Measurement of free radicals in the atmosphere by matrix isolation and electron paramagnetic resonance, *Pure Appl. Geophys.*, **116**, 530-536, 1978.
- Miller, A. J., and F. J. Schmidlin, Rocketsonde repeatability and stratospheric variability, *J. Appl. Meteorol.*, **10**, 320-327, 1971.
- Miller, A. J., H. M. Woolf, and F. G. Finger, Small-scale wind and temperature structure as evidenced by meteorological rocket systems, *J. Appl. Meteorol.*, **7**, 390-399, 1968.
- Miller, A. J., R. M. Nagatani, K. B. Labitzke, E. Klinker, K. Rose, and D. F. Heath, Stratospheric ozone transport during the mid-winter warming of December 1970-January 1971, *Proc. Joint Symp. Atmos. Ozone., Dresden, German Dem. Rep.*, 135-148, 1977.
- Miller, A. J., R. M. Nagatani, J. D. Laver, and B. Korty, Utilization of 100 mb mid-latitude height fields as an indicator of sampling effects on total ozone variations, *Mon. Weather Rev.*, **107**, 782-787, 1979.
- Miller, C., P. Meakin, R. G. E. Franks, and J. P. Jesson, The fluorocarbon-ozone theory V. One-dimensional modeling of the atmosphere: the base case, *Atmos. Environ.*, **12**, 2481-2500, 1978.
- Miller, C., D. L. Filkin, and J. P. Jesson, The fluorocarbon-ozone theory, VI. Atmospheric modeling: Calculation of the diurnal steady state, *Atmos. Environ.*, **13**, 381-394, 1979.
- Mintz, Y., and M. Schlesinger, Ozone production and transport with the UCLA general-circulation model, *Proceedings of the Fourth CIAP Conference*, T. M. Hard and A. J. Broderick, eds., U.S. Department of Transportation, DOT-TSC-OST-75-38, 201-222, 1975.
- Mohnen, V. A. Discussion of the formation of major positive and negative ions up to the 50 km level, *Pure Appl. Geophys.*, **84**, 141-151, 1971.
- Mohnen, V. A., Can ions contribute to stratospheric aerosol formation?, *Proceedings of the Fourth CIAP Conference, Rep. DOT-TSC-OST-75-38*, pp. 478-479, U. S. Department of Transportation, Washington, D. C., 1975.
- Mohnen, V. A., and C. S. Kiang, Ion-molecule interactions of atmospheric importance, *ASRC-SUNY Publ. No. 681*, 1978.
- Mohnen, V. A., and E. R. Reiter, The issue of stratospheric ozone intrusion, *International Conference on Oxidants, 1976 - Analysis of Evidence and Viewpoints, Part III*, EPA-600/3-77-115, U.S. Environ. Prot. Agency, 1977.
- Molina, M. J., and F. S. Rowland, Predicted present stratospheric abundances of chlorine species from photodissociation of carbon tetrachloride, *Geophys. Res. Lett.*, **1**, 309-312, 1974.
- Molina, L. T., and M. J. Molina, Ultraviolet spectrum of HOCl, *J. Phys. Chem.*, **82**, 2410-2414, 1978.

- Molina, L. T., T. Ishiwata, and M. J. Molina, Quantum yield for production of OH in the photolysis of HOCl at 310 nm, submitted to *J. Chem. Phys.*, 1979a.
- Molina, L. T., L. Beaman, J. Cook, and M. J. Molina, Ultraviolet absorption spectrum of HClO₄ vapor, submitted to *J. Photochem.*, 1979b.
- Moortgat, G. K., and C. E. Junge, The role of the SO₂ oxidation for the background stratospheric sulfate layer in the light of new reaction rate data, *Pure Appl. Geophys.*, **115**, 759-774, 1977.
- Moortgat, G. K., and P. Warneck, CO₂ and H₂ quantum yields in the photodecomposition of formaldehyde in air, *J. Chem. Phys.*, **70**, 3639-3651, 1979.
- Morita, Y., M. Kanada, and H. Ishikawa, The vertical profiles of the small ion density and the electric conductivity in the atmosphere in 19 kilometers, *J. Geophys. Res.*, **76**, 3431-3436, 1971.
- Morris, E. D., and H. Niki, Mass spectrometric study of the reaction of hydroxyl radical with formaldehyde, *J. Chem. Phys.*, **55**, 1991-1992, 1971.
- Moseley, J. T., P. C. Cosby, and J. R. Peterson, Photodissociation spectroscopy of CO₃, *J. Chem. Phys.*, **65**, 2512-2517, 1976.
- Mroz, E. J., A. L. Lazrus, and J. C. Bonnell, Direct measurements of stratospheric fluoride, *Geophys. Res. Lett.*, **4**, 149-150, 1977.
- Muench, H. S., On the dynamics of the winter stratosphere circulation, *J. Atmos. Sci.*, **22**, 349-360, 1965.
- Muench, H. S., Large-scale disturbances in the summertime stratosphere, *J. Atmos. Sci.*, **25**, 1108-1115, 1968.
- Muramatsu, H., Dissociation rates of oxygen and ozone molecules in the stratosphere and the mesosphere, *Papers in Meteorol. Geophys.*, **26**, 219-264, 1975.
- Murcray, D. G., Fluorocarbon research program, Manufacturing Chemists Association, *Rev. 10*, Washington, D.C., p. 32, October 31, 1978.
- Murcray, D. G., A. Goldman, A. Csoeke-Poeckh, F. H. Murcray, W. J. Williams, and R. N. Stocker, Nitric acid distribution in the stratosphere, *J. Geophys. Res.*, **78**, 7033-7038, 1974.
- Murcray, D. G., A. Goldman, W. J. Williams, F. H. Murcray, J. N. Brooks, J. Van Allen, R. N. Stocker, J. J. Kusters, D. B. Barker, and D. E. Snider, Recent results of stratospheric trace - gas measurements from balloon-borne spectrometers, *Proceedings of the Third CIAP Conference DOT-TSC-OST-74-15*, 184-192, U.S. Dept. of Transportation, Washington, D.C., 1974.
- Murcray, D. G., A. Goldman, W. J. Williams, F. H. Murcray, J. N. Brooks, R. N. Stocker, and D. E. Snyder, Stratospheric mixing ratio profiles of several trace gases as determined from balloon-borne infrared spectrometers, *Proceedings of the International Conference on Structure Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations, Vol. I*, 292-303, IUGG, Paris, 1975.
- Murcray, D. G., D. B. Barker, J. N. Brooks, A. Goldman, and W. J. Williams, Seasonal and latitudinal variation of the stratospheric concentrations of HNO₃, *Geophys. Res. Lett.*, **2**, 223-224, 1975a.

- Murcray, D. G., F. S. Bonono, J. N. Brooks, A. Goldman, F. H. Murcray, and W. J. Williams, Detection of fluorocarbons in the stratosphere, *Geophys. Res. Lett.*, **2**, 109-112, 1975b.
- Murcray, D. G., A. Goldman, W. J. Williams, F. H. Murcray, F. S. Bonono, G. M. Bradford, G. R. Cole, P. L. Hanst, and M. J. Molina, Upper limit for stratospheric ClONO_2 from balloon-borne infrared measurements, *Geophys. Res. Lett.*, **4**, 227-230, 1977.
- Murcray, D. G., W. J. Williams, D. B. Barker, A. Goldman, C. Bradford, and G. Cook, Measurements of constituents of interest in the chemistry of the ozone layer using IR techniques, Proceedings of the WMO Symposium on the Geophysical Aspects and Consequences of Change in the Composition of the Stratosphere, *WMO No. 511*, pp 61-68, Toronto, June 1978.
- Murcray, D. G., F. J. Murcray, and F. H. Murcray, submitted to *Geophys. Res. Lett.*, 1979.
- Murgatroyd, R. J., *WMO Tech. Note, No. 68*, 1965.
- Murgatroyd, R. J., The structure and dynamics of the stratosphere, in *The Global Circulation of the Atmosphere*, G. A. Corby, Ed., London, *Roy. Meteorol. Soc.*, 194-202, 1969.
- Murgatroyd, R. J., and R. M. Goody, Sources and sinks of energy from 30 to 90 km, *Quart. J. Roy. Meteorol. Soc.*, **84**, 225-234, 1958.
- Murgatroyd, R. J., P. Goldsmith, and W. E. H. Mollings, Some recent measurements of humidity from aircraft up to heights of about 50,000 ft. over Southern England, *Quart. J. Roy. Meteorol. Soc.*, **81**, 533-537, 1955.
- Narcisi, R. S., A. D. Bailey, L. Della Lucca, C. Sherman, and D. M. Thomas, Mass spectrometric measurements of negative ions in the D- and lower E-regions, *J. Atmos. Terr. Phys.*, **33**, 1147-1159, 1971.
- Narcisi, R. S., A. D. Bailey, L. E. Wlodyka, and C. R. Philbrick, Ion composition measurements in the lower ionosphere during the November 1966 and March 1970 solar eclipses, *J. Atmos. Terr. Phys.*, **34**, 647-658, 1972.
- National Academy of Sciences, Halocarbons: Effects on Stratospheric Ozone, National Academy of Sciences, Washington, D. C., 1976.
- National Academy of Sciences, Stratospheric Ozone Depletion by Halocarbons: Chemistry and Transport, National Academy of Sciences, Washington, D. C., 1979.
- NASA RP-1010, Chlorofluoromethanes and the Stratosphere, ed. R. D. Hudson, 266 pp, 1977.
- NASA, Proceedings of NASA-sponsored Symposium on Ozone Trend Detectability, edited by J. W. Campbell, July 28-29, 1977, Boulder, CO, unpublished manuscript, 1977.
- NASA CP-2090, Middle Atmosphere Electrodynamics, Report of the Workshop on the role of Electrodynamics of the Middle Atmosphere on Solar-Terrestrial Coupling, N. C. Maynard, ed., 261 pp, 1979.
- NASA TM-78577, 1977 Intertropical Convergence Zone Experiment, ed. by I. G. Popoff, W. A. Page, and A. P. Margozi, 488 pp, 1979.

- Nastrom, G. D., Vertical and horizontal fluxes of ozone at the tropopause from the first year of GASP data, *J. Appl. Meteorol.*, **16**, 740-744, 1977.
- Nastrom, G. D., and A. D. Belmont, Diurnal stratospheric tide in meridional wind, 20 to 60 km, by season, *J. Atmos. Sci.*, **33**, 321-337, 1976.
- Nastrom, G. D., and A. D. Belmont, Preliminary results on 27-day solar rotation variation in stratospheric zonal winds, *Geophys. Res. Lett.*, **5**, 665-668, 1978.
- Natarajan, M., L. B. Callis, and J. E. Nealy, Solar UV variability: Effects on stratospheric ozone, trace constituents, and thermal structure submitted to *J. Geophys. Res.*, 1979.
- Naughton, J. J., V. Lewis, D. Thomas, J. B. Finlayson, Fume compositions found at various stages of activity at Kilauea volcano, Hawaii, *J. Geophys. Res.*, **80**, 3963-3966, 1975.
- Naylor, J. A., Error evaluation of a meteorological rocket temperature sounding system, *NASA Contractor Report CR-141415*, September 1976.
- Neely, W. B., and J. H. Plonka, Estimation of time-averaged hydroxyl radical concentration in the troposphere, *Environ. Sci. Technol.* **12**, 317-321, 1978.
- Newell, R. E., and B. C. Weare, Factors governing tropospheric mean temperature, *Science*, **194**, 1413-1414, 1976.
- Newell, R., The transport of trace substances in the general circulation of the stratosphere, *Pure Appl. Geophys.*, **49**, 131-158, 1961.
- Newell, R. E., J. W. Kidson, D. G. Vincent, and C. J. Boer, *The General Circulation of the Tropical Atmosphere and Interactions with Extra-Tropical Latitudes*, Cambridge, MIT Press, 258 pp., 1972.
- Newell, R. E., G. J. Boer, and J. W. Kidson, Proc. CACGP Symposium on Trace Gases, Mainz, W. Germany, 1973.
- Newell, R. E., J. W. Kidson, D. G. Vincent, and G. J. Boer, *The General Circulation of the Tropical Atmosphere and Interactions with Extra-Tropical Latitudes*, Vol. II, MIT Press, Cambridge, MA, 1974.
- Newson, R. L., An experiment with a tropospheric and stratospheric three-dimensional general circulation model, *Proceedings of the Third CIAP Conference*, A. J. Broderick and T. M. Hards, eds., U.S. Department of Transportation, DOT-TSC-OST-74-15, 461-474, 1974.
- Nguyen, B. C., A. Gaudry, B. Bonsang, and G. Lambert, Reevaluation of the role of dimethyl sulphide in the sulphur budget, *Nature*, **275**, 637-639, 1978.
- Nicolet, M., Aeronomic reactions of hydrogen and ozone, in *Mesospheric Models and Related Experiments*, G. Fiocco, ed., Springer-Verlag, 1-51, 1971.
- Nicolet, M., On production of nitric oxide by cosmic rays in the mesosphere and stratosphere, *Planet. Space Sci.*, **23**, 637-649, 1975a.
- Nicolet, M., Stratospheric ozone: An introduction to its study, *Rev. Geophys. Space Phys.*, **13**, 593-636, 1975b.

- Nicolet, M., Solar UV radiation and its absorption in the mesosphere and stratosphere, *Pure Appl. Geophys.*, **118**, in press, 1979.
- Nicolet, M., and A. Vergison, L'oxyde azoteux dans la stratosphere, *Aeronom. Acta.*, **90**, 1-26, 1971.
- Nicolet, M., and S. Cieslik, The atmospheric problem of the nitric oxide dissociation, *Planet. Space Sci.* (to be published) 1979.
- Nicolet, M., and W. Peetermans, Atmospheric absorption in the O₂ Schumann-Runge band spectral range and O₂ total photodissociation rates in the stratosphere and mesosphere, *Planet. Space Sci.* (to be published) 1979.
- Niki, H., E. E. Daby, and B. Weinstock, Data reported in Twelfth Symposium (International) on combustion, p. 277, The Combustion Institute, 1969.
- Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, Fourier transform IR spectroscopic observation of chlorine nitrite, ClONO, formed via $\text{Cl} + \text{NO}_2 (+\text{M}) \rightarrow \text{ClONO} (+\text{M})$, *Chem. Phys. Lett.*, **59**, 78-79, 1978a.
- Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, Relative rate constants for the reaction of hydroxyl radical with aldehydes, *J. Phys. Chem.*, **82**, 132-134, 1978b.
- Nolan, P. J., The recombination law for weak ionization, *Proc. Roy. Irish Acad.*, **49A**, 67-90, 1943.
- Nordlie, B. E., The composition of the magmatic gas of Kilauea and its behavior in the near surface environment, *Amer. J. Sci.*, **271**, 417-463, 1971.
- Noxon, J. F., Day Airglow, *Space Science Rev.*, **8**, 92-134, 1968.
- Noxon, J. F., Nitrogen dioxide in the stratosphere and troposphere measured by ground-based absorption spectroscopy, *Science*, **189**, 547-549, 1975.
- Noxon, J. F., Atmospheric nitrogen fixation by lightning, *Geophys. Res. Lett.*, **3**, 463-465, 1976.
- Noxon, J. F., Stratospheric NO₂ in the Antarctic Winter, *Geophys. Res. Lett.*, **5**, 1021-1022, 1978.
- Noxon, J. F., Stratospheric NO₂, 2, Global behavior, *J. Geophys. Res.*, **84**, 5067-5076, 1979.
- Noxon, J. F., R. B. Norton, and W. R. Henderson, Observation of atmospheric NO₃, *Geophys. Res. Lett.*, **5**, 675-678, 1978.
- Noxon, J. F., E. C. Whipple, Jr., and R. S. Hyde, Stratospheric NO₂, Observational method and behavior at mid-latitude, *J. Geophys. Res.*, **84**, 5047-5065, 1979.
- O'Brien, R. S., and W. F. J. Evans, Unpublished water vapor profile data reported in *Upper Atmospheric Programs*, No. 79-3, Office of Environment and Energy, Federal Aviation Administration, Washington, D. C., 1979.
- Ogawa, M., Absorption cross sections of O₂ and CO₂ continua in the Schumann and far-UV regions, *J. Chem. Phys.*, **54**, 2550-2556, 1971.

- Oliver, R. C., E. Bauer, H. Hidalgo, K. A. Gardner, and W. Wasylkiwskyj, Aircraft emissions: potential effects on ozone and climate: a review and progress report, Federal Aviation Administration Report, *FA-EQ-77-3*, 1977.
- Olszyna, K., R. D. Cadle, and R. G. DePena, Stratospheric heterogeneous decomposition of ozone, *J. Geophys. Res.*, **84**, 1771-1775, 1979.
- O'Neill, A., and B. F. Taylor, A study of the major stratospheric warming of 1976/77, *Quart. J. Roy. Meteorol. Soc.*, **105**, 71-92, 1979.
- Oort, A. H., On the energetics of mean and eddy circulation in the lower stratosphere, *Tellus*, **16**, 309-327, 1964.
- Oort, A. H., and E. M. Rasmusson, Atmospheric circulation systems, NOAA Professional Paper, **5**, U.S. Government Printing Office, 1971.
- Pack, D. H., J. E. Lovelock, G. Cotton, and C. Curthoys, Halocarbon behavior from a long time series, *Atmos. Environ.*, **11**, 329-344, 1977.
- Pagano, M., and E. Parzen, Time series modeling of total ozone measurements, *Technical Report 35*, Stat. Sci., SUNY at Buffalo, 1975.
- Paltridge, G. W., Experimental measurements of the small-ion density and electrical conductivity of the stratosphere, *J. Geophys. Res.*, **70**, 2751-2761, 1965.
- Paltridge, G. W., Stratospheric small-ion density measurements from a high-altitude jet aircraft, *J. Geophys. Res.*, **71**, 1945-1952, 1966.
- Park, C., and G. P. Menees, Odd nitrogen production by meteoroids, *J. Geophys. Res.*, **83**, 4029-4035, 1978.
- Park, J. H., The equivalent mean absorption cross sections for the O₂ Schumann-Runge bands: Application to the H₂O and NO photodissociation rates, *J. Atmos. Sci.*, **31**, 1893-1897, 1974.
- Parry, H. D., Ozone depletion by chlorofluoromethanes? Yet another look, *J. Appl. Meteorol.*, **16**, 1137-1148, 1977.
- Patel, C. K. N., E. G. Burkhardt, and C. A. Lambert, Spectroscopic measurements of stratospheric nitric oxide and water vapor, *Science*, **184**, 1173-1176, 1974.
- Paulikas, G. A., Precipitation of particles at low and middle-latitudes, *Rev. Geophys. Space Phys.*, **13**, 709-734, 1975.
- Penkett, S. A., K. A. Brice, R. G. Derwent, and A. E. J. Eggleton, Measurement of CCl₃F and CCl₄ at Harwell over the period January 1975-November 1977, *Atmos. Environ.*, **13**, 1011-1019, 1979.
- Penndorf, R., Analysis of ozone and water vapor field measurement data, Report No. FAA-EE-78-29, NTIS, Springfield, VA, 1978.
- Penner, J. E., and J. S. Chang, Possible variations in atmospheric ozone related to the 11-year solar cycle, *Geophys. Res. Lett.*, **5**, 817-820, 1978.

- Penner, J. E., and J. S. Chang, The relation between atmospheric trace species variabilities and solar UV variability submitted to *J. Geophys. Res.*, 1979.
- Perkins, P. J., J. D. Holdeman, and B. J. Gauntner, Aircraft cabin ozone measurements on B747-100 and B747-3P aircraft, *NASA TM 79060*, 41 pp., 1978.
- Perner, D., D. H. Ehhalt, H. W. Patz, U. Platt, E. P. Roth, and A. Volz, OH-radicals in the lower troposphere, *Geophys. Res. Lett.*, **3**, 466-468, 1976.
- Peyton, T. O., R. V. Steele, and W. R. Mabey, Carbon disulfide, carbonyl sulfide. Literature Review and Environmental Assessment. Environmental Protection Agency Report No. *EPA-600/9-78-009*, Washington, D. C., 1976.
- Pfister, L., Possible barotropic instability in the upper stratosphere, Ph.D. thesis, University of Washington, 236 pp., 1977.
- Philen, D., W. Heaps, and D. D. Davis, Boundary layer and free tropospheric OH measurements at tropical and subtropical latitudes in the Northern and Southern Hemisphere (abstract), *Eos. Trans. AGU*, **59**, 1079, 1978.
- Phillpot, H. R., Antarctic stratospheric warming reviewed in the light of 1967 observations, *Quart. J. Roy. Meteorol. Soc.*, **95**, 329-348, 1969.
- Pierotti, D., and R. A. Rasmussen, Combustion as a source of nitrous oxide in the atmosphere, *J. Geophys. Res.*, **3**, 265-267, 1976.
- Pierotti, D., and R. A. Rasmussen, The atmospheric distribution of nitrous oxide, *J. Geophys. Res.*, **82**, 5823-5832, 1977a.
- Pierotti, D., and R. A. Rasmussen, Atmospheric measurement of nitrous oxide and the halocarbons, Interim report to NASA, Washington State University, 51 pp., 1977b.
- Pierotti, D., and R. A. Rasmussen, Nitrous oxide measurements in the Eastern Tropical Pacific Ocean, *Tellus*, **31**, in press 1979.
- Pierotti, D., L. E. Rasmussen, and R. A. Rasmussen, the Sahara as a possible sink for trace gases, *Geophys. Res. Lett.*, **5**, 1001-1004, 1978.
- Pirkle, R. J., H. N. Volltrauer, W. Felder, and A. Fontijn, Measurements on $O(^1D)/N_2O$ and HNO_2/O_3 kinetics, *Report No. FAA-AEQ-77-10*, prepared for High Altitude Pollution Programs, U.S. Department of Transportation, Washington, D. C., June, 1977.
- Pittock, A. B., On the representativeness of mean ozone distributions, *Quart. J. Roy. Meteorol. Soc.*, **96**, 32-39, 1970.
- Pittock, A. B., Trends in the vertical distribution of ozone over Australia, *Nature*, **249**, 641-643, 1974.
- Pittock, A. B., Climatology of the vertical distribution of ozone over Aspendale, (38S, 145E), *Quart. J. Roy. Meteorol. Soc.*, **103**, 575-584, 1977.
- Pittock, A. B., A critical look at long-term sun-weather relationships, *Rev. Geophys. Space Phys.*, **16**, 400-420, 1978.

- Planet, W. G., G. L. Tettemer, and J. S. Knoll, Temperature dependence of intensities and widths of N_2 - broadened lines in the $15\ \mu m$ CO_2 band from tunable laser measurements, *J. Quant. Spectrosc. Radiative Transfer.*, **20**, 547-556, 1978.
- Plumb, R. A., Eddy fluxes of conserved quantities by small amplitude waves, *J. Atmos. Sci.*, **36**, 1699-1704, 1979.
- Plumb, I. C., K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, Kinetics of the reaction of CH_3O_2 with NO, *Chem. Phys. Lett.*, **63**, pp. 255-258, 1979.
- Pollack, J. B., O. B. Toon, C. Sagan, Volcanic explosions and climatic change: A theoretical assessment, *J. Geophys. Res.*, **81**, 1071-1083, 1976a.
- Pollack, J. B., O. B. Toon, A. Summers, W. Van Camp, and B. Baldwin, Estimates of the climatic impact of aerosols produced by space shuttles, SST's and other highflying aircraft, *J. Appl. Meteorol.*, **15**, 247-258, 1976b.
- Pollack, J. B., O. B. Toon, A. Summers, B. Baldwin, C. Sagan, and W. Van Camp, Stratospheric aerosols and climatic change, *Nature*, **263**, 551-555, 1976c.
- Pomerantz, M. A., and S. P. Duggal, The Sun and cosmic rays, *Rev. Geophys. Space Phys.*, **12**, 343-361, 1974.
- Poppoff, I. G., R. C. Whitten, R. P. Turco, and L. A. Capone, An assessment of the effect of supersonic aircraft operations on the stratospheric ozone content, *NASA Reference Publication 1026*, 1978.
- Porter, H. S., C. H. Jackman, and A. E. S. Green, Efficiencies for production of atomic nitrogen and oxygen by relativistic proton impact in air, *J. Chem. Phys.*, **65**, 154-167, 1976.
- Potemra, T. A., Precipitating energetic electrons in the mid-latitude lower ionosphere, in *Physics and Chemistry of Upper Atmosphere*, ed., by B. M. McCormac, p. 67, D. Reidel, Dordrecht, Netherlands, 1973.
- Potemra, T. A., Ionizing radiation affecting the lower ionosphere, in *ELF-VLF Radio Wave Propagation*, ed. by J. A. Holtet, p. 21, D. Reidel, Dordrecht, Netherlands, 1974.
- Potemra, T. A., and A. J. Zmuda, Precipitating energetic electrons as an ionization source in the mid-latitude nighttime D region, *J. Geophys. Res.*, **75**, 7161-7167, 1970.
- Potter, A. E., Environmental effects of the space shuttle, *J. Environ. Sci.*, **21**, 15-21, 1978.
- Powell, D. B. B., The absorption coefficients of ozone for the Dobson spectrophotometer: A direct determination of their ratios and temperature dependence, *Quart. J. Roy. Meteorol. Soc.*, **97**, 83-86, 1971.
- Prabhakara, C., and E. B. Rodgers, Studies of the lower stratospheric thermal structure and total ozone from Nimbus 4 IRIS, NASA Tech. Note D-8134, Goddard Space Flight Center, Greenbelt, MD, 1976.
- Prabhakara, C., B. J. Conrath, R. A. Hanel, and E. J. Williamson, Remote sensing of atmospheric ozone using the $9.6\ \mu m$ band, *J. Atmos. Sci.*, **27**, 689-697, 1970.

- Prabhakara, C., E. B. Rodgers, B. J. Conrath, R. A. Hanel, and V. G. Kunde, The Nimbus-4 infrared spectroscopy experiment 3: Observations of the lower stratospheric thermal structure and total ozone, *J. Geophys. Res.*, **81**, 6391-6399, 1976.
- Prasad, S. S., and P. G. Burton, Possible existence and role of excited ozone precursors in the stratosphere, *Planet. Space Sci.*, **21**, 411-418, 1979.
- Pratt, R., and P. Falconer, Circumpolar measurements of ozone, particles and carbon monoxide from the 50th anniversary of a Pan American airliner, *J. Geophys. Res.*, in press, 1979.
- Prinz, D. K., The spatial distribution of Lyman α on the sun, *Astrophys. J.*, **187**, 369-375, 1974.
- Quiroz, R. S., The determination of the amplitude and altitude of stratospheric warmings from satellite-measured radiance changes, *J. Appl. Meteorol.*, **10**, 555-574, 1970.
- Quiroz, R. S., Stratospheric warmings in the Southern Hemisphere deduced from satellite radiation data, 1969-73, *Proc. Intern. Conf. Structure, Composition, and General Circulation of the Upper and Lower Atmospheres*, Vol. 2, 525-539, 1974.
- Quiroz, R. S., The tropospheric-stratospheric polar vortex breakdown of January 1977, *Geophys. Res. Lett.*, **4**, 151-154, 1977.
- Quiroz, R. S., Precursors of stratospheric warmings and constraints on their development, Paper presented at *Amer. Meteorol. Soc., Conf. on Meteorol. of Upper Atmos.*, Boston, October 24-27, 1978.
- Quiroz, R. S., Stratospheric temperatures during solar cycle 20, *J. Geophys. Res.*, **84**, 2415-2450, 1979a.
- Quiroz, R. S., The contribution of satellite remote-sounding data in stratospheric research, in *Remote Sounding of the Atmosphere from Space*, H. J. Bolle, ed., Oxford, Pergamon Press, 69-82, 1979b.
- Quiroz, R. S., Tropospheric-stratospheric interaction in the major warming event of January-February 1979, *Geophys. Res. Lett.*, **6**, 645-648, 1979c.
- Quiroz, R. S., and M. E. Gelman, Direct determination of thickness of stratospheric layers from single-channel satellite radiance measurements, *Mon. Weather Rev.*, **100**, 788-795, 1972.
- Quiroz, R. S., and R. M. Nagatani, A study of tropospheric-stratospheric interaction based on combined satellite and rawinsonde data, *Proc. Symp. on Meteorol., Obs. from Space*, Philadelphia, June 8-10, 368-373, 1976.
- Quiroz, R. S., A. J. Miller, and R. M. Nagatani, A comparison of observed and simulated features of sudden stratospheric warmings, *J. Atmos. Sci.*, **32**, 1723-1736, 1975.
- Ramakrishna, S., and R. Seshamani, Day night dependence of geomagnetic activity effects on mesospheric temperature, *J. Geophys. Res.*, **81**, 6173-6176, 1976.
- Ramanathan, V., Radiative transfer within the earth's troposphere and stratosphere: A simplified radiative convective model, *J. Atmos. Sci.*, **33**, 1330-1346, 1976.
- Ramanathan, V., Troposphere-stratosphere feedback mechanism: Stratospheric warming and its effects on the polar energy budgets and the tropospheric circulation, *J. Atmos. Sci.*, **34**, 439-447, 1977.

- Ramanathan, V., and R. E. Dickinson, The role of stratospheric ozone in zonal and seasonal radiative energy balance of the earth-troposphere system, *J. Atmos. Sci.*, **36**, 1084-1104, 1979.
- Ramanathan, V., and W. L. Grose, A numerical simulation of seasonal stratospheric climate: Part 1. Zonal temperatures and winds, *J. Atmos. Sci.*, **35**, 600-614, 1978.
- Ramanathan, V., L. B. Callis, and R. E. Boughner, Sensitivity of surface temperature and atmospheric temperature to perturbations in the stratospheric concentration of ozone and nitrogen dioxide, *J. Atmos. Sci.*, **33**, 1092-1112, 1976.
- Rao-Vupputuri, R. K., Numerical experiments on the steady state meridional structure and ozone distribution in the stratosphere, *Mon. Weather Rev.*, **101**, 510-527, 1973.
- Raper, O. F., C. B. Farmer, R. A. Toth, and B. D. Robbins, The vertical distribution of HCl in the stratosphere, *Geophys. Res. Lett.*, **4**, 531-534, 1977.
- Rasmussen, R. A., American Chemical Society Meeting, Miami Beach, 1978a.
- Rasmussen, R. A., Interlaboratory comparison of fluorocarbon measurements, *Atmos. Environ.*, **12**, 2505-2508, 1978b.
- Rasmussen, R. A., and J. Krasnec, GASP latitude survey flight, WSU preliminary results, in NASA Technical Memorandum X-73630, *Interhemispheric Survey of Minor Upper Atmospheric Constituents during October-November 1976*, compiled by D. G. Gauntner and L. C. Haughney, Lewis Research Center, Cleveland, Ohio 44135, 95-105, March 1977.
- Rasmussen, R. A., and E. Robinson, Atmospheric hydrocarbon concentrations in global background air samples, *Report No. 77-13-48*, Wash. St. Univ., Pullman, WA, 13 pp., 1977.
- Rawcliffe, R. D., and D. D. Elliot, Latitude distribution of ozone at high altitudes deduced from a satellite measurement of the earth's radiances at 2840Å, *J. Geophys. Res.*, **71**, 5077-5089, 1966.
- Reagan, J. B., Ionization processes, in *Dynamical and Chemical Coupling Between the Neutral and Ionized Atmosphere*, edited by B. Grandal and J. A. Holtet, p. 145, D. Reidel, Dordrecht, Netherlands, 1977.
- Reagan, J. A., R. W. Nightingale, R. E. Meyerott, R. C. Gunton, R. G. Johnson, J. E. Evans, and W. L. Imhof, Effects of the August 1972 solar particle events on stratospheric ozone, *Tech. Report LMSC-D630455*, Lockheed Palo Alto Res. Lab., Palo Alto, Calif., 1978.
- Reber, C. A., F. Huang, and D. F. Heath, A global empirical model of stratospheric ozone (abstract), *Eos Trans. AGU*, **58**, 6, 462, 1977.
- Rebbert, R. E., and P. J. Ausloos, Decomposition of nitrous oxide and chlorofluoromethanes absorbed on particulate matter, WMO Symposium on the Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere, Toronto, WMO Publ. 511, World Meteorological Organization, Geneva, pp. 31-35, 1978.
- Rebbert, R. E., and P. Ausloos, Decomposition of N₂ over particulate matter, *Geophys. Res. Lett.*, **5**, 761-764, 1978.

- Redfield, A. C., B. H. Ketchum, and F. A. Richards in *The Sea*, **2**, 20-77 Wiley - Interscience, New York, 1963.
- Reed, R. J., A study of a characteristic type of upper-level frontogenesis, *J. Meteorol.*, **12**, 226-237, 1955.
- Reed, R. J., The quasi-biennial oscillation of the atmosphere between 30 and 50 km over Ascension Island, *J. Atmos. Sci.*, **22**, 331-333, 1965.
- Reed, R. J., Zonal wind behavior in the equatorial stratosphere and lower mesosphere, *J. Geophys. Res.*, **71**, 4223-4233, 1966.
- Reed, R. J., Further analysis of semidiurnal tidal motions between 30 and 60 kilometers, *Mon. Weather Rev.*, **100**, 579-582, 1972.
- Reed, R. J., and E. F. Danielsen, Fronts in the vicinity of the tropopause, *Arch. Meteorol. Geophys. Bioklim*, **A-11**, 1-11, 1959.
- Reed, R. J., and K. E. German, A contribution to the problem of stratospheric diffusion by large scale mixing, *Mon. Weather Rev.*, **93**, 313-321, 1965.
- Reed, R. J., J. Wolfe, and H. Nishimoto, A spectral analysis of the energetics of the stratospheric sudden warming of early 1957, *J. Atmos. Sci.*, **20**, 256-275, 1963.
- Reed, R. J., M. J. Oard, and M. Sieminski, A comparison of observed and theoretical diurnal tidal motions between 30 and 60 km, *Mon. Weather Rev.*, **97**, 456-459, 1969.
- Reid, G. C., The production of water-cluster positive ions in the quiet daytime D-region, *Planet. Space Sci.*, **25**, 275-292, 1977.
- Reid, G. C., The middle atmosphere, in *Middle Atmosphere Electrodynamics*, ed. by N. C. Maynard, NASA CP-2090, pp. 27-42, 1979.
- Reid, G. C., and J. R. McAfee, and P. J. Crutzen, Effects of intense stratospheric ionisation events, *Nature*, **275**, 489-492, 1978.
- Reimann, B., and F. Kaufman, Rate constant of the reaction $\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$, *J. Chem. Phys.*, **69**, 2925-2928, 1978.
- Reiter, E. R., Atmospheric Transport Processes, Part 3: Hydrodynamic Traces, *AEC Critical Review Series*, U.S. Atomic Energy Commission, 212 pp., 1972.
- Reiter, E. R., Stratospheric-tropospheric exchange processes, *Rev. Geophys. Space Phys.*, **13**, 459-474, 1975.
- Reiter, R., Influences of solar activity on the electric potential between the ionosphere and the Earth, *Solar Terrestrial Influences on Weather and Climate*, Columbus, Ohio, ed., by B. M. McCormac and T. Seliga, Reidel, 243-251, 1979.
- Reiter, R., and M. Reiter, Relations between the contents of nitrate and nitrite ions in precipitations and simultaneous atmospheric electric processes. *Recent Advances in Atmospheric Electricity*, L. G. Smith Ed., Pergamon Press 175-194, 1958.

- Research Triangle Institute, Investigations of ozone and ozone precursor concentrations at nonurban locations in the eastern United States, U.S. Environmental Protection Agency, *Publ. No. EPA-4503-74-034*, 1974.
- Ridley, B. A., H. I. Schiff, A. W. Shaw, L. R. Megill, L. Bates, L. C. Howlett, H. LeVaux and T. E. Ashenfelter, Measurements in situ of nitric oxide in the stratosphere between 17.4 km and 22.9 km, *Nature*, **245**, 310-314, 1973.
- Ridley, B. A., and L. C. Howlett, An instrument for nitric oxide measurements in the stratosphere, *Rev. Sci. Instr.*, **45**, 742-746, 1974.
- Ridley, B. A., H. I. Schiff, A. W. Shaw, L. Bates, L. C. Howlett, H. LeVaux, L. R. Megill, and T. E. Ashenfelter, Measurements of nitric oxide in the stratosphere between 17.4 and 22.9 km, *Planet. Space Sci.*, **22**, 19-24, 1974.
- Ridley, B. A., H. I. Schiff, A. Shaw, and J. R. Megill, In situ measurements of stratospheric nitric oxide using a balloon-borne chemiluminescent instrument, *J. Geophys. Res.*, **80**, 1925-1929, 1975.
- Ridley, B. A., J. T. Bruin, H. I. Schiff, and J. C. McConnell, Altitude profile and sunset decay measurements of stratospheric nitric oxide, *Atmosphere*, **14**, 180-188, 1976.
- Ridley, B. A., M. McFarland, J. T. Bruin, H. I. Schiff, and J. C. McConnell, Sunrise measurements of stratospheric nitric oxide, *Can. J. Phys.*, **55**, 212-221, 1977.
- Riehl, H., Vertical distribution of energy transfer and radar echo tops in the equatorial trough zone, *Mon. Weather Rev.*, **105**, 230-231, 1977.
- Riehl H., and J. S. Malkus, On the heat balance in the equatorial trough zone, *Geophysica.*, **6**, 503-538, 1958.
- Riekert, H., Untersuchungen zur Beweglichkeit der Kleinionen in der freien atmosphere, Dissertation, Universitat Tübingen, 1971.
- Robbins, D. E., and J. Carnes, Variations in the upper atmospheric ozone profile, WMO Symposium on the Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere, Toronto, Publ. 511, World Meteorological Organization, Geneva, pp. 131-137, 1978.
- Roberts, W. O., and R. H. Olson, Geomagnetic storms and wintertime 300-mb trough development in the North Pacific-North America area, *J. Atmos. Sci.*, **30**, 135-140, 1973a.
- Roberts, W. O., and R. H. Olson, New evidence for effects of variable solar corpuscular emission on the weather, *Rev. Geophys. Space Phys.*, **11**, 731-740, 1973b.
- Robinson, G. D., Water vapor in the lower stratosphere (abstract), *Eos Trans. AGU*, **59**, 1085, 1978.
- Robinson, E., and R. C. Robbins, Sources, abundance and fate of gaseous atmospheric pollutants, Stanford Research Institute Final Report Project Pr 6755, Menlo Park, CA., 1968.
- Roble, R. G., and P. B. Hays, Electrical coupling between the upper and lower atmosphere, *Solar Terrestrial Influences on Weather and Climate*, ed. B. M. McCormac and T. Seliga, Reidel, 233-241, 1979.

- Rodgers, C. D., Statistical principles of inversion theory, *Inversion Methods in Atmospheric Remote Soundings*, ed., by A. Deepak, Academic Press, 117-138, 1977.
- Rogers, J. W., A. T. Stair, Jr., T. C. Degges, C. L. Wyatt, and D. J. Baker, Rocketborne measurement of mesospheric H₂O in the auroral zone, *Geophys. Res. Lett.*, **4**, 366-368, 1977.
- Rodhe, H. Budgets and turnover times of atmospheric sulfur compounds, *Atmos. Environ.*, **12**, 671-680, 1978.
- Rogowski, R. S., C. H. Bair, W. R. Wade, J. M. Hoell, and G. E. Copeland, Infrared vibration-rotation spectra of the ClO radical using tunable diode laser spectroscopy, *Appl. Opt.*, **17**, 1301-1302, 1978.
- Rosen, J. M., Stratospheric dust and its relationship to the meteoric influx, *Space Sci. Rev.*, **9**, 58-89, 1969.
- Rosen, J. M., The boiling point of stratospheric aerosols, *J. Appl. Meteorol.*, **10**, 1044-1046, 1971.
- Rosen, J. M., D. J. Hofmann, and S. P. Singh, A steady-state stratospheric aerosol model, *J. Atmos. Sci.*, **35**, 1304-1313, 1978.
- Rosenberg, T. J., and L. J. Lanzerotti, Direct energy inputs to the middle atmosphere, in *Middle Atmosphere Electrodynamics*, ed. by N. C. Maynard, NASA CP-2090, 43-70, June, 1979.
- Rosenberg, T. J., L. J. Lanzerotti, D. K. Bailey, and J. D. Pierson, Energy spectra in relativistic electron precipitation events, *J. Atmos. Terr. Phys.* **34**, 1977-1990, 1972.
- Rossler, F., The aerosol layer in the stratosphere, *Space Research*, North Holland Publ. Co., Amsterdam, Vol. VIII, 633-636, 1968.
- Rothman, L. S., Update of the AFGL atmospheric absorption line parameters compilation, *Appl. Opt.*, **17**, 3517-3518, 1978.
- Rothman, L. S., S. A. Clough, R. A. McClatchey, L. G. Young, D. E. Snider, and A. Goldman, AFGL trace gas compilation, *Appl. Opt.*, **17**, 507, 1978.
- Rottman, G. R., Disc values of the solar ultraviolet flux, 1150 to 1900 Å, (abstract) *Eos Trans. AGU*, **56**, 1157, 1974.
- Rotty, R., Present and future production of CO₂ from fossil fuels - A global appraisal, paper presented at ERDA Workshop on Significant Environmental Concerns, Miami, FL, March 7-11, 1977.
- Rowland, F. S., J. E. Spencer, and M. J. Molina, Stratospheric formation and photolysis of chlorine nitrate, *J. Phys. Chem.* **80**, 2711-2713, 1976.
- Rundel, R. D., D. M. Butler, and R. S. Stolarski, Uncertainty propagation in a stratospheric model 1. Development of a concise stratospheric model, *J. Geophys. Res.*, **83**, 3063-3073, 1978.
- Ruderman, M. A., and J. W. Chamberlain, Origin of the sunspot modulation of ozone: Its implications for stratospheric NO injection, *Planet. Space Sci.*, **23**, 247-268, 1975.
- Russell, J. M., III, and R. S. Drayer, The inference of atmospheric ozone using satellite horizon measurements in the 1042 cm⁻¹ band, *J. Atmos. Sci.*, **29**, 376-390, 1972.

- Safary, E., J. Romand, and B. Vodar, Ultraviolet absorption spectrum of gaseous hydrogen fluoride, *J. Chem. Phys.*, **19**, 379-380, 1951.
- Sagawa, E., and T. Itoh, Mass spectrometric observation of SO₂ in the stratosphere, *Geophys. Res. Lett.*, **4**, 29-32, 1977.
- Saltzman, B., Surface boundary effects on the general circulation and macro-climate: A review of the theory of the quasi-stationary perturbations in the atmosphere, in Causes of Climatic Change, *Meteor. Monogr.*, **8**, No. 30, 159 pp., 1968.
- Samain, D., and P. C. Simon, Solar flux determination in the spectral range 150 - 210 nm, *Solar Phys.*, **49**, 33-41, 1976.
- Sams, R. L., and W. B. Olson, High resolution infrared spectrum of the ν_2 band of HOC1, *J. Molec. Spect.*, submitted 1979.
- Sandalls, F. J., and S. A. Penkett, Measurements of carbonyl sulphide and carbon disulphide in the atmosphere, *Atmos. Environ.*, **11**, 197-199, 1977.
- Sannigrahi, A. B., S. D., Peyerimhoff, and R. J. Buenker, Non-empirical SCF and CI study of the SOH radical, *Chem. Phys.*, **20**, 381-389, 1977.
- Sarachik, E. S., Tropical sea surface temperature: An interactive one-dimensional atmosphere-ocean model, submitted to *J. Atmos. Sci.*, 1979.
- Schlesinger, M. E., and Y. Mintz, Numerical simulation of ozone production, transport and distribution with a global atmospheric general circulation model, submitted to *J. Atmos. Sci.*, **36**, 1325-1361, 1979.
- Schmeltekopf, A. L., D. L. Albritton, P. J. Crutzen, P. D. Goldan, W. J. Harrop, W. R. Henderson, J. R. McAfee, M. McFarland, H. I. Schiff, and T. L. Thompson, Stratospheric nitrous oxide altitude profiles at various latitudes, *J. Atmos. Sci.*, **34**, 729-736, 1977a.
- Schmeltekopf, A. L., E. E. Ferguson, P. D. Goldan, and J. R. McAfee, Stratospheric measurements of N₂O, F-11, and F-12, (abstract) *Eos Trans. AGU*, **58**, 464, 1977b.
- Schmidt, U., Molecular hydrogen in the atmosphere, *Tellus*, **26**, 78-90, 1974.
- Schoeberl, M. R., Stratospheric warmings: Observations and theory, *Rev. Geophys. Space Phys.*, **16**, 521-538, 1978.
- Schoeberl, M. R., and M. A. Geller, The structure of stationary planetary waves in winter in relation to the polar night jet intensity, *Geophys. Res. Lett.*, **3**, 117-180, 1976.
- Schoeberl, M. R., and M. A. Geller, A calculation of the structure of stationary planetary waves in winter, *J. Atmos. Sci.*, **34**, 1235-1255, 1977.
- Schoeberl, M. R., and D. F. Strobel, The zonally averaged circulation of the middle atmosphere, *J. Atmos. Sci.*, **35**, 577-591, 1978a.
- Schoeberl, M. R., and D. F. Strobel, The response of the zonally averaged circulation to stratospheric ozone reductions, *J. Atmos. Sci.*, **35**, 1751-1757, 1978b.

- Schoeberl, M. R., and D. F. Strobel, Numerical simulation of sudden stratospheric warmings, Naval Res. Lab. Memorandum Report-4013, 71 pp., June, 1979.
- Schofield, K., Evaluated chemical kinetic rate constants for various gas phase reactions, *J. Phys. Chem. Ref. Data*, **2**, 25-84, 1973.
- Schwentek, H., The sunspot cycle 1958/70 in ionospheric absorption and stratospheric temperature, *J. Atmos. Terr. Phys.*, **33**, 1839-1853, 1971.
- Searcy, J. Q., and J. B. Fenn, Clustering of water on hydrated protons in a supersonic free jet expansion, *J. Chem. Phys.*, **61**, 5282-5288, 1974.
- Seiler, W., The cycle of atmospheric CO, *Tellus*, **26**, 117-135, 1974.
- Seward, F. D., The geographical distribution of ~ 100 keV electrons above the earth's atmosphere, *Rep. UCRL-51456*, Univ. of Calif., Lawrence Livermore Lab., Livermore, Oct. 1973.
- Shah, G. M., The effect of aerosols attenuation on determination of atmospheric ozone from measurements with a Dobson spectrophotometer, *J. Atmos. Sci.*, **33**, 2462-2464, 1976.
- Shapiro, M. A., A multiple-structured frontal zone jet stream system as revealed by meteorologically instrumented aircraft, *Mon. Weather Rev.*, **102**, 244-253, 1974.
- Shapiro, M. A., The role of turbulent heat flux in the generation vorticity in the vicinity of upper-level jet stream systems, *Mon. Weather Rev.*, **102**, 892-906, 1976.
- Shapiro, M. A., Further evidence of the mesoscale and turbulent structure of upper-level jet stream-frontal zone systems, *Mon. Weather Rev.*, **106**, 1101-1111, 1978.
- Shapiro, M. A., The exchange of chemical constituents between the stratosphere and troposphere through turbulent mixing processes within tropopause folds, Submitted to *J. Atmos. Sci.*, 1978.
- Shardanand and A. D. Prasad Rao, Collision-induced absorption of O₂ in the Herzberg continuum, *J. Quant. Spectrosc. Radiat. Transfer*, **17**, 433, 1977.
- Shenk, W. E., Cloud top height variability of strong convective cells, *J. Appl. Meteorol.*, **13**, 917-922, 1974.
- Shepherd, E. S., The gases in rocks and some related problems, *Amer. Jour. Sci.*, **35A**, 311-351, 1938.
- Shimazaki, T., T. Ogawa, and B. C. Farrell, Simplified methods for calculating photodissociation rates of various molecules in the Schumann-Runge band systems in the upper atmosphere, *NASA Tech. Note TN D-8399*, March 1977.
- Simon, P. C., Balloon measurements of solar fluxes between 1960 Å and 2300 Å, *Proceedings of the Third CIAP Conference, Rep. DOT-TSC-OST-74-15*, pp. 137-142, U. S. Department of Transportation, Washington, D. C., 1974.
- Simon, P. C., Nouvelles mesures de l'ultraviolet solaire dans la stratosphere *Bulletin Acad. Roy. Belgique, Cl. Sc.*, **61**, 399-409, 1975.
- Simon, P. C., Irradiation solar flux measurements between 120 and 400 nm. Current position and future needs, *Planet. Space Sci.*, **26**, 355-365, 1978.

- Simmons, A. J., Baroclinic instability and planetary waves in the polar stratosphere, Ph.D. thesis, University of Cambridge, 1972.
- Simmons, A. J., Baroclinic instability at the winter stratopause, *Quart. J. Roy. Meteorol. Soc.*, **100**, 531-540, 1974a.
- Simmons, A. J., Planetary scale disturbances in the polar winter stratosphere, *Quart. J. Roy. Meteorol. Soc.*, **100**, 76-108, 1974b.
- Simmons, A. J., Baroclinic instability in the summer mesosphere, *Quart. J. Roy. Meteorol. Soc.*, **103**, 211-214, 1977.
- Singer, S. F., and R. C. Wentworth, A method for the determination of the vertical ozone distribution from a satellite, *J. Geophys. Res.*, **62**, 299-308, 1957.
- Singh, H. B., American Chemical Society Fall Meeting, Miami Beach, 1978.
- Singh, H. B., D. P. Fowler, and T. O. Peyton, *Science*, **192**, 1231-1235, 1976.
- Singh, H. B., L. J. Salas, H. Shigeishi, and A. H. Smith, Atmospheric Fates of Halogenated Compounds: Second Year (Phase I) Summary Report, *EPA Grant R-80380202*, SRI Project 4487, Stanford Research Institute, Menlo Park, California, 1977.
- Singh, H. B., L. J. Salas, J. Shigeishi, and E. Scribner, Global Distribution of Selected Halocarbons, Hydrocarbons, SF₆, N₂O, Phase II Interim Report, EPA-600/3-78400, SRI International, Menlo Park, California, 72 pp., 1978.
- Singh, H. B., L. Salas, and H. Shigeishi, The distribution of nitrous oxide (N₂O) in the global atmosphere and the Pacific Ocean, *Tellus*, **31**, 313-320, 1979b.
- Singh, H. B., L. J. Salas, H. Shigeishi, and E. Scribner, Atmospheric halocarbons, hydrocarbons, and sulfur hexafluoride: Global distributions, sources, and sinks, *Science*, **203**, 899-903, 1979a.
- Singleton, C. L., R. S. Irwin, W. S. Nip, and R. J. Cvetanovic, Kinetics and mechanism of the reaction of oxygen atoms with hydrogen sulfide *J. Phys. Chem.*, **83**, 2195-2200, 1979.
- Slagle, I. R., F. Balocchi, and D. Gutman, Study of the reactions of oxygen atoms with hydrogen sulfide, methanethiol, and methyl sulfide, *J. Phys. Chem.*, **82**, 1333-1336, 1978.
- Smagorinsky, J., S. Manabe, and J. L. Holloway, Jr., Numerical results from a nine-level general circulation model of the atmosphere, *Mon. Weather Rev.*, **93**, 727-768, 1965.
- Smardzewski, R. R., and M. C. Lin, Matrix reactions of oxygen atoms with H₂S molecules, *J. Chem. Phys.*, **66**, 3197-3204, 1977.
- Smith, D., M. J. Church, and T. M. Miller, Mutual neutralization of simple and clustered positive and negative, *J. Chem. Phys.*, **68**, 1224-1229, 1978.
- Smith, E. V. P., and D. M. Gottlieb, Solar flux and its variations, *Space Science Revs.*, **16**, 771-802, 1974.

- Smith, R. D., Rate constant and activation energy for the gaseous reaction between hydroxyl and formaldehyde, *Int. J. Chem. Kinetics.*, **10**, 519-528, 1978.
- Smith, W. L., and H. M. Woolf, The use of eigenvectors of statistical covariance matrices for interpreting satellite sounding radiometer observations, *J. Atmos. Sci.*, **33**, 1127-1140, 1976.
- Sparks, R. S., L. Carson, K. Shobatake, M. L. Kowalczyk, and Y. T. Lee, Dynamics of photodissociation of O_3 , paper presented at the 7th International Symposium on Molecular Beams, Riva Del Garda, Italy, May 28-June 1, 1979.
- Spjeldvik, W. N., and R. M. Thorne, The cause of storm after effects in the middle latitude D region, *J. Atmos. Terr. Phys.*, **37**, 777-795, 1975.
- Staff, Upper Air Branch, Synoptic analyses, 5-, 2-, and 0.4-mb surfaces for January 1972 through June 1973, *NASA SP-3091*, Washington, D. C., 205 pp., 1975.
- Staff, Upper Air Branch, Synoptic analyses, 5-, 2-, and 0.4-mb surfaces for July 1973 through June 1974, *NASA SP-3102*, NASA, Washington, D. C., 140 pp., 1976.
- Staley, D. O., Evaluation of potential vorticity changes near the tropopause and the related vertical motions, vertical advection of vorticity and the transfer of radioactive debris from stratosphere to troposphere, *J. Meteorol.*, **17**, 591-620, 1960.
- Stanford, J. L., Possible sink for stratospheric water vapor at the winter antarctic pole, *J. Atmos. Sci.*, **30**, 1431-1436, 1973.
- Stanford, J. L., Stratospheric water vapor upper limits inferred from upper air observations, *Bull. Amer. Meteorol. Soc.*, **55**, 194-212, 1974.
- Stening, R. J., C. E. Meek, A. H. Manson, and D. G. Stephenson, Winds and wave motions to 110 km at mid-latitudes, VI. Tidal, gravity and planetary waves, 1976, *J. Atmos. Sci.*, **35**, 2194-2204, 1978.
- Stief, L. J., D. F. Nava, W. A. Payne, and J. V. Michael, Rate constant for the reaction of hydroxyl radical with formaldehyde over the temperature range 228-362K, to be submitted to *J. Chem. Phys.*, 1979.
- Stith, J. L., P. V. Hobbs, and L. F. Radke, Airborne particle and gas measurements in the emissions from six volcanoes, *J. Geophys. Res.*, **83**, 4009-4018, 1978.
- Stoiber, R. E., D. C. Leggett, T. F. Jenkins, R. P. Murrmann, and W. I. Rose, Jr., Organic compounds in volcanic gas from Santiaguito Volcano, Guatemala, *Geol. Soc. Amer. Bull.*, **82**, 2299-1302, 1971.
- Stolarski, R. S., and R. D. Rundel, Fluorine photochemistry in the stratosphere, *Geophys. Res. Lett.*, **2**, 443-444, 1975.
- Stolarski, R. S., and D. M. Butler, Possible effects of volcanic eruption on stratospheric minor constituent chemistry. *Pure Appl. Geophys.* **117**, 486-497, 1978.
- Stolarski, R. S., D. M. Butler, and R. D. Rundel, Uncertainty propagation in a stratospheric model: II. Monte Carlo analysis of imprecisions due to reaction rates, *J. Geophys. Res.*, **83**, 3074-3078, 1978.

- Streit, G. E., C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, Temperature dependence of $O(^1D)$ rate constants for reactions with O_2 , N_2 , CO_2 , O_3 and H_2O , *J. Chem. Phys.*, **65**, 4761-4764, 1976.
- Strobel, D. F., Odd nitrogen in the mesosphere, *J. Geophys. Res.*, **76**, 8384-8393, 1971.
- Strobel, D. F., Nitric oxide in the D region, *J. Geophys. Res.*, **77**, 1337-1339, 1972.
- Strobel, D. F., Parameterization of the atmospheric heating rate from 15 to 120 km due to O_2 and O_3 absorption of solar radiation, *J. Geophys. Res.*, **83**, 6225-6230, 1978.
- Strobel, D. F., Parameterization of the thermal relaxation rate in the stratosphere, *J. Geophys. Res.*, **84**, 2469-2470, 1979.
- Stuvier, M., Atmospheric carbon dioxide and carbon reservoir changes, *Science*, **199**, 253-258, 1978.
- Swider, W., and T. J. Keneshea, Decrease of ozone and atomic oxygen in the lower mesosphere during a PCA event, *Planet. Space Sci.*, **21**, 1969-1973, 1973.
- Swider, W., T. J. Keneshea, and C. I. Foley, An SPE-disturbed D-region model, *Planet. Space Sci.*, **26**, 883-892, 1978.
- Sze, N. D., Anthropogenic CO emissions: Implications for the atmospheric CO-OH-CH₄ cycle, *Science*, **195**, 673-675, 1977.
- Sze, N. D., Stratospheric fluorine: A comparison between theory and measurements, *Geophys. Res. Lett.*, **5**, 781-783, 1978.
- Sze, N. D., and M. K. W. Ko, Is CS₂ a precursor for atmospheric COS?, *Nature*, **278**, 731-732, 1979a.
- Sze, N. D., and M. K. W. Ko, CS₂ and COS in the stratospheric sulfur budget, *Nature*, **280**, 308-310, 1979b.
- Sze, N. D., and H. Rice, Nitrogen cycle factors contributing to N₂ production from fertilizer, *Geophys. Res. Lett.*, **3**, 343-340, 1976.
- Sze, N. D., and W. F. Wu, Measurements of fluorocarbons 11 and 12 and model validation: An assessment, *Atmos. Environ.*, **10**, 1117-1125, 1976.
- Szwarc, V. S., An evaluation of the U.S.S.R. M-83 ozonometer, NOAA-AIR Resources Laboratories', unpublished manuscript, 1978.
- Thiemans, M. W., and S. E. Schwartz, The fate of HS radical under atmospheric conditions, Paper presented at 13th Informal Conference on Photochemistry, Clearwater, FL, 1978.
- Thomas, A., and F. G. Finger, Technical Attachment 74-8, National Meteorological Center Newsletter 74-6, 1974.
- Thomas, G. E., and D. E. Anderson, Jr., Global atomic hydrogen density derived from OGO-6 Lyman- α measurements, *Planet. Space Sci.*, **24**, 303-312, 1976.
- Thomas, R. W. L., and A. C. Holland, Ozone estimates derived from Dobson direct sun measurements: Effect of atmospheric temperature variations and scattering, *Appl. Opt.*, **16**, 613-618, 1977.

- Thorne, R. M., Energetic radiation belt electron precipitation: A natural depletion mechanism for stratospheric ozone, *Science*, **195**, 287-289, 1977.
- Thorne, R. M., and T. R. Larsen, An investigation of relativistic electron precipitation events and their association with magnetospheric substorm activity, *J. Geophys. Res.* **81**, 5501-5506, 1976.
- Thrane, E. V., On the diurnal and seasonal variations of the D and E regions above Kjeller, in *Magnetosphere-Ionosphere Interactions*, ed., by K. Folkestad, p. 29, Universitetsforlaget, Oslo, Norway, 1972.
- Tohmatsu, T., The hydrogen and helium ultraviolet glow, its origins and aeronomical significance, *Space Res.*, **10**, 608-622, 1970.
- Toon, O. B., and J. B. Pollack, Physical properties of the stratospheric aerosols, *J. Geophys. Res.*, **78**, 7051, 1973.
- Toon, O. B., and J. B. Pollack, A global average model of atmospheric aerosols for radiative transfer calculations, *J. Appl. Meteorol.*, **15**, 225-246, 1976.
- Torr, D. G., and M. R. Torr, Review of rate coefficients of ionic reactions determined from measurements made by the Atmospheric Explorer satellite, *Rev. Geophys. Space Phys.*, **16**, 327-340, 1978.
- Torres, A. L., P. J. Maroulis, A. B. Goldberg, and A. R. Bandy, Measurements of tropospheric OCS on the 1978 GAMETAG flights (abstract), *Eos Trans. AGU*, **56**, 1082, 1978.
- Toth, R. A., C. B. Farmer, R. A. Schindler, O. F. Raper, and P. W. Schaper, Detection of nitric oxide in the lower atmosphere, *Nature Phys. Sci.*, **244**, 7-8, 1973.
- Tousey, R., The extreme ultraviolet spectrum of the sun, *Space Sci. Rev.*, **2**, 3-69, 1963.
- Trenberth, K. E., Global model of the general circulation of the atmosphere below 75 km with an annual heating cycle, *Mon. Weather Rev.*, **101**, 287-305, 1973a.
- Trenberth, K. E., Dynamical coupling of the stratosphere with the troposphere and sudden stratospheric warmings, *Mon. Weather Rev.*, **101**, 306-322, 1973b.
- Tsay, C. Y., Analysis of large scale wave disturbances in the tropics simulated by an NCAR global circulation model, *J. Atmos. Sci.*, **31**, 330-339, 1974.
- Tung, K. K., and R. S. Lindzen, A theory of stationary long waves. Part I. A simple theory of blocking, Harvard Univ., Center for Earth and Planet. Phys. Report, 1977.
- Tung, K. K., and R. S. Lindzen, A theory of stationary long waves. Part I. A simple theory of blocking, *Mon. Weather Rev.*, **107**, 714-734, 1979.
- Turco, R. P., Photodissociation rates in the atmosphere below 100 km, *Geophys. Surveys*, **2**, 153-192, 1975.
- Turco, R. P., and R. C. Whitten, Chlorofluoromethanes in the stratosphere and some possible consequences to ozone, *Atmos. Environ.*, **9**, 1045-1061, 1975.
- Turco, R. P., and R. C. Whitten, The NASA-Ames Research Center one-and two-dimensional stratospheric models 1: the one-dimensional model, *NASA Technical Paper 1002*, 1977.

- Turco, R. P., and R. C. Whitten, A note on the diurnal averaging of aeronomical models, *J. Atmos. Terr. Phys.*, **40**, 13-20, 1978.
- Turco, R. P., R. C. Whitten, I. G. Poppoff, and L. A. Capone, SST's, nitrogen fertilizer and stratospheric ozone, *Nature*, **276**, 805-807, 1978.
- Turco, R. P., P. Hamill, O. B. Toon, R. C. Whitten, and C. S. Kiang, A one-dimensional model describing aerosol formation and evolution in the stratosphere. I. Physical processes and numerical analogs, *J. Atmos. Sci.*, **36**, 699-717, 1979a.
- Turco, R. P., O. B. Toon, J. B. Pollack, R. C. Whitten, I. G. Poppoff, and P. Hamill, Stratospheric aerosol modification by supersonic transport and space shuttle operation with climate implications, *J. Appl. Meteorol.*, in press, 1979b.
- Turco, R. P., R. C. Whitten, O. B. Toon, J. P. Pollack, and P. Hamill, Carbonyl sulfide, stratospheric aerosols and terrestrial climate, submitted to *Nature*, 1979c.
- Turman, B. N., Analysis of lightning data from the DMSP satellite, *J. Geophys. Res.*, **83**, 5019-5024, 1978.
- Turner, D. L., and D. C. Conway, Stability of the $\text{NO}^+ \cdot \text{N}_2$ ion cluster, *J. Chem. Phys.*, **65**, 3944-3947, 1976.
- Turner, R. E., A study of the influence of eddies on a zonal mean circulation model, submitted to *J. Atmos. Sci.*, 1979.
- Tyson, B. J., J. F. Vedder, J. C. Arveson, and R. B. Brewer, Stratospheric measurements of CF_2Cl_2 and N_2O , *Geophys. Res. Lett.*, **5**, 369-372, 1978a.
- Tyson, B. J., J. C. Arveson, and D. O'Hara, Interhemispheric gradients of CF_2Cl_2 , CFC1_3 , CCl_4 , and N_2O , *Geophys. Res. Lett.*, **5**, 535-538, 1978b.
- Vanier, J., and D. I. Wardle, The effects of spectral resolution on total ozone measurements, *Quart. J. Roy. Meteorol. Soc.*, **95**, 395-399, 1969.
- Vedder, J. F., B. J. Tyson, R. B. Brewer, C. A. Boitnott, and E. C. Y. Inn, Lower stratosphere measurements of variation with latitude of CF_2Cl , CFC1_3 , CCl_4 , and N_2O , *Geophys. Res. Lett.*, **5**, 33-36, 1978.
- Velinov, P., On ionization in the ionospheric D region by galactic and solar cosmic rays, *J. Atmos. Terr. Phys.*, **30**, 1891-1905, 1968.
- Vidal-Madjar, A., Evolution of the solar Lyman alpha flux during four consecutive years, *Solar Phys.*, **40**, 69-86, 1975.
- Vidal-Madjar, A., The solar spectrum at Lyman alpha 1216Å, in *The Solar Output and Its Variations*, ed., by O. R. White, Associated University Press, Boulder, p. 213-236, 1977.
- Viggiano, A. A., R. A. Perry, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, The role of H_2SO_4 in stratospheric negative-ion chemistry, *J. Geophys. Res.*, 1979.
- Vincent, D. G., Mean meridional circulation in the Northern Hemisphere lower stratosphere during 1964 and 1965, *Quart. J. Roy. Meteorol. Soc.*, **94**, 333-349, 1968.

- Volland, H., Can sunspots influence our weather?, *Nature*, **269**, 400-401, 1977.
- Volland, H., and J. Shaeffer, Cause and effect in some types of sun-weather relationships, *Geophys. Res. Lett.*, **6**, 17-20, 1979.
- Vupputuri, R. K. R., The steady state structure of the natural stratosphere and ozone distribution in a 2-D model incorporating radiation and O-H-N photochemistry and the effects of stratospheric pollutants, *Atmosphere*, **14**, 214-236, 1976.
- Vupputuri, R. K. R., The structure of the natural stratosphere and the impact of chlorofluoromethanes on the ozone layer investigated in a 2-D time dependent model, *Pure Appl. Geophys.*, in press, 1978.
- Wallace, J. M. General circulation of the tropical lower stratosphere, *Rev. Geophys. Space Phys.*, **11**, 191-222, 1973.
- Wallace, J. M., Trajectory slopes, countergradient heat fluxes and mixing by lower stratospheric waves, *J. Atmos. Sci.*, **35**, 554-558, 1978a.
- Wallace, J. M., A Lagrangian view. *Advanced Study Program Summer Lecture Notes*, NCAR, Boulder, Colorado, 25-39, 1978b.
- Wallace, L., and D. M. Hunten, Dayglow of the oxygen A band, *J. Geophys. Res.*, **73**, 4813-4834, 1968.
- Wallace, J. M., and V. E. Kousky, Observational evidence of Kelvin waves in the tropical stratosphere, *J. Atmos. Sci.*, **25**, 900-907, 1968a.
- Wallace, J. M., and V. E. Kousky, On the relation between Kelvin waves and the quasi-biennial oscillation, *J. Meteorol. Soc. Japan*, **46**, 496-502, 1968b.
- Wallace, J. M., and D. B. Patton, Diurnal temperature variations: Surface to 30 kilometers, *Mon. Weather Rev.*, **98**, 548-552, 1970.
- Wallace, J. M., and R. F. Tadd, Some further results concerning the vertical structure of atmospheric tidal motions within the lowest 30 kilometers, *Mon. Weather Rev.*, **102**, 795-803, 1974.
- Walshaw, C. D., and C. D. Rodgers, The effect of the Curtis-Godson approximation on the accuracy of radiative heating rate calculations, *Quart. J. Roy. Meteorol. Soc.*, **89**, 122-130, 1963.
- Walterscheid, R. L., The influence of mean zonal motion on the solar semi-diurnal atmospheric tide: A spectral study, Ph.D. thesis, University of California, Los Angeles, 1978.
- Wang, C. C., L. I. Davis, Jr., C. H. Wu, S. Japan, H. Niki, and B. Weinstock, Hydroxyl radical concentrations measured in ambient air, *Science*, **189**, 797-800, 1975.
- Wang, W. C., Y. L. Yung, A. A. Lacis, T. Mo, and J. E. Hansen, Greenhouse effects due to man-made perturbations of trace gases, *Science*, **194**, 685-690, 1976.
- Wark, D. Q., and M. E. Fleming, Indirect measurements of atmospheric temperature profiles from satellites: 1. Introduction, *Mon. Weather Rev.* **94**, 351-362, 1966.

- Warneck, P., Cosmic radiation as a source of odd nitrogen in the stratosphere, *J. Geophys. Res.*, **77**, 6589-6591, 1972.
- Washida, N., and K. D. Bayes, The reaction of methyl radicals with atomic and molecular oxygen, *Int. J. Chem. Kinet.*, **8**, 777-794, 1976.
- Watanabe, T., and T. Tohmatsu, An observational evidence for the seasonal variation of ozone concentration in the upper stratosphere and the mesosphere, *Rept. Ionos. and Space Res. Japan*, **30**, 47-50, 1976.
- Waters, J. W., J. J. Gustincic, R. K. Kakar, A. R. Kerr, H. K. Roscoe, and P. N. Swanson, *Report NASA TMX-73630*, NTIS, Springfield, VA, 1977.
- Waters, J. W., J. J. Gustincic, R. K. Kakar, H. K. Roscoe, P. N. Swanson, T. G. Phillips, T. DeGraauw, and A. R. Kerr, Aircraft search for millimeter wavelength emission by stratospheric ClO, *J. Geophys. Res.*, in press, 1979.
- Watson, R. T., P. E. Smokler, and W. B. DeMore, Assessment of an F₂ or N₂O₄ atmospheric injection from an aborted space shuttle mission, *J. P. L. Publication #77-81*, 1977.
- Watson, R. T., G. Machado, B. C. Conaway, S. Wagner, and D. D. Davis, A temperature dependent kinetics study of the reaction of OH with CH₂ClF, CHCl₂F, CHClF₂, CH₃CCl₃, CH₃CF₂Cl, and CF₂ClCFC1₂, *J. Phys. Chem.*, **81**, 256-262, 1977.
- Wayne, R. P., D. N. Mitchell, R. P. Harrison, and P. J. Allen, Spectroscopy and kinetics of the NO₃ radical, paper presented at the 13th Informal Conference on Photochemistry, Clearwater Beach, Florida, January 4-7, 1978.
- Webb, W. L., Scale of stratospheric detail structure, *Space Research V*, Amsterdam, North Holland Publishing Co., 997-1007, 1965.
- Webber, W. R., The production of free electrons in the ionosphere D layer by solar and galactic cosmic rays and the resultant absorption of radio waves, *J. Geophys. Res.*, **67**, 5091-5106, 1962.
- Weeks, L. H., Lyman-alpha emission from the sun near solar minimum, *Astrophys. J.*, **147**, 1203-1205, 1967.
- Weeks, L. H., R. S. Cuikay, and J. R. Corbin, Ozone measurements in the mesosphere during the solar proton event of 2 November 1969, *J. Atmos. Sci.*, **29**, 1138-1142, 1972.
- Weickmann, H., C. Van Valin, and J. M. Anderson, Review of natural sources and sinks of stratospheric water vapor, CIAP Monograph 3, *The Stratosphere Perturbed by Propulsion Effluents*, pp. 7-4 to 7-12, DOT-TST-75-33, NTIS, Springfield, VA, 1975.
- Weiss, R. F., Unpublished data, 1979.
- Weiss, R. F., and H. Craig, Production of atmospheric nitrous oxide by combustion, *Geophys Res. Lett.*, **3**, 751-753, 1976.
- Weiss, R. F., W. Dowd, and H. Craig, Nitrous oxide: Atmospheric concentrations 1964-76, industrial sources, and air-sea exchange, International Conference on Problems Related to the Stratosphere, Sept. 15-17, 1976, Logan, Utah, *JPL Publ. 77-12*, p. 59, 1977.

- Wells, J. S., R. L. Sams, and W. J. Lafferty, The high resolution infrared spectrum of the ν_1 band of HOC1, *J. Molec. Spec.*, **77**, 349-364, 1979.
- Went, F. W., Organic matter in the atmosphere and its possible relation to petroleum formation, *Proc. Nat'l. Acad. Sci.*, **46**, 212-221, 1960.
- White, D. E., and G. A. Waring, Volcanic emanations, Geological Survey Professional Paper 440-K, in *Data of Geochemistry*, Sixth Edition, M. Fleischer, Technical Editor, pp. K-1 to K-9, 1963.
- White, J. N., and W. C. Gardiner, Jr., Thermochemical properties of the HSO radical, *Chem. Phys. Lett.*, **58**, 470-472, 1978.
- White, O. R.: Editor, *The Solar Output and Its Variation*, Colorado Associated University Press, Boulder, 1977.
- Whitten, R. C., W. J. Borucki, and R. P. Turco, Possible ozone depletions following nuclear explosions, *Nature*, **257**, 38-39, 1975.
- Whitten, R. C., W. J. Borucki, V. R. Watson, T. Shimazaki, H. T. Woodward, C. A. Riegel, L. A. Capone, and T. Becker, The NASA-Ames Research Center one - and two-dimensional stratospheric models II. The two-dimensional model, *NASA TP-1003*, 1977.
- Whitten, R. C., W. J. Borucki, L. A. Capone, and R. P. Turco, The effect of the reaction $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$ on stratospheric ozone, *Nature*, **275**, 523-524, 1978.
- Whytock, D. A., R. B. Timmons, J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, Absolute rate of the reaction of $\text{O}(^3\text{P})$ with hydrogen sulfide over the temperature range 263 to 495K, *J. Chem. Phys.*, **65**, 2052-2055, 1976.
- Widhopf, G. F., A two-dimensional photochemical model of the stratosphere including initial results of inert tracer studies, Proceedings of the Fourth CIAP Conference *Rep. DOT-TSC-OST-75-38*, 316-331, U.S. Dept. of Transportation, Washington, D. C., 1975.
- Wilcox, R. W., G. D. Nastrom, and A. D. Belmont, Periodic variations of total ozone and of its vertical distribution, *J. Appl. Meteorol.*, **16**, 290-298, 1977.
- Wilkniss, P. E., R. A. Lamontagne, R. E. Larson, J. W. Swinnerton, C. R. Dickson, and T. Thompson, Atmospheric trace gases in the Southern Hemisphere, *Nature*, **245**, 45-47, 1973.
- Williams, W. J., J. J. Kostus, A. Goldman, and D. G. Murcay, Measurements of the stratospheric mixing ratio of HCl using an infrared absorption technique, *Geophys. Res. Lett.*, **3**, 383-385, 1976.
- Willis, D. M., The energetics of Sun-weather relationships: Magnetospheric processes, *J. Atmos. Terr. Phys.*, **38**, 685-698, 1976.
- Wofsy, S. C., Interactions of CH_4 and CO in the earth's atmosphere, *Ann. Rev. Earth and Planet. Sci.*, **4**, 441-469, 1976.
- Wofsy, S. C., Temporal and latitudinal variations of stratospheric trace gases: A critical comparison between theory and experiment, *J. Geophys. Res.*, **83**, 364-378, 1978.

- Wofsy, S. C., and M. B. McElroy, On vertical mixing in the stratosphere and lower mesosphere, *J. Geophys. Res.*, **78**, 2619-2624, 1973.
- Wofsy, S. C., J. C. McConnell, and M. B. McElroy, Atmospheric CH₄, CO, and CO₂, *J. Geophys. Res.*, **77**, 4477-4493, 1972.
- Wofsy, S. C., M. B. McElroy, and Y. L. Yung, The chemistry of atmospheric bromine, *Geophys. Res. Lett.*, **2**, 215-218, 1975.
- Wofsy, S. C., M. B. McElroy, and N. D. Sze, Freon consumption: Implications for atmospheric ozone, *Science*, **187**, 535-537, 1975.
- Wood, W. P., and J. Heicklen, The photooxidation of carbon disulfide, *J. Phys. Chem.*, **75**, 854-860, 1971.
- Woodwell, G. M., A. H. Whittaker, W. A. Reimers, G. E. Likens, C. C. Delwiche, D. B. Botkin, The biota and the world carbon budget, *Science*, **199**, 141-146, 1978.
- Wu, M.-F., Observations and analysis of trace constituents in the stratosphere, Annual report, Contract DOT-05-20217, Env. Res. Tech., Lexington, Mass., 1973.
- Yanai, M., An experimental objective analysis in the tropics, Technical Paper Number 62, Department of Atmospheric Science, Colorado State University, 21 pp., 1964.
- Yanai, M., and T. Maruyama, Stratospheric wave disturbance propagating over the equatorial Pacific, *J. Meteorol. Soc. Japan*, **44**, 291-294, 1966.
- Yoshinari, T., Nitrous oxide in the sea, *Mar. Chem.*, **9**, 189-202, 1976.
- Young, C. E., D. Edelson, and W. E. Falconer, Water cluster ions: Rates of formation and decomposition of hydrates of the hydronium ion, *J. Chem. Phys.*, **53**, 4295-4302, 1970.
- Young, S. A., and W. G. Elford, Stratospheric aerosol optical thickness measurement at 35 °S, *Nature*, **278**, 540-541, 1979.
- Yung, Y. L., P. J. Pinto, R. T. Watson, and S. P. Sander, Atmospheric bromine and ozone perturbations in the lower stratosphere, *J. Atmos. Sci.*, in press, 1979.
- Zafiriou, O. C., Reaction of methyl halides with seawater and marine aerosols, *J. Marine Res.*, **33**, 75-81, 1975.
- Zander, R., G. Roland, and L. Delbouille, Confirming the presence of hydrofluoric acid in the upper stratosphere, *Geophys. Res. Lett.*, **4**, 117-120, 1977.
- Zbinden, P. A., M. A. Hidalgo, P. Eberhardt, and J. Geiss, Mass spectrometer measurements of the positive ion composition in the D and E regions of the ionosphere, *Planet. Space Sci.*, **23**, 1621-1642, 1975.
- Zerefos, C. S., and H. T. Mantis, Climatic fluctuations in the Northern Hemisphere stratosphere, *Arch. Met. Geoph. Biokl., series B*, **25**, 33-39, 1977.
- Zettlemoyer, A. C., ed., *Nucleation*, Dekker, N.Y., 1969.

- Zettlemoyer, A. C., ed., *Nucleation Phenomena*, Elsevier Scientific Publishing Co., Amsterdam, 1977.
- Zikmunda, J., and V. A. Mohnen, Ion annihilation by aerosol particles from ground level to 60 km height, *Meteorol. Rundschau*, **25**, 10-14, 1972.
- Zimmerman, P. R., R. B. Chatfield, J. Fishman, P. M. Crutzen, and P. L. Hanst, Estimates on the production of CO and H₂ from the oxidation of hydrocarbon emissions from vegetation, *Geophys. Res. Lett.*, **5**, 679-682, 1978.
- Zipf, E. C., and M. Dubin, Laboratory studies of the formation of NO_x compounds and ozone by lightning, (abstract) *Eos Trans. AGU*, **57**, 965, 1976a.
- Zipf, E. C., and M. Dubin, Laboratory studies on the synthesis of N₂O and NO₂ and on the destruction of CF₂Cl₂ by lightning, (abstract) *Eos Trans. AGU*, **57**, 156, 1976b.
- Zlotnik, B., and W. Rozwoda, The influence of solar activity on the temperature of the stratosphere, *Artificial Satellites*, **2**, 55, 1976.
- Zmuda, A. J., and T. A. Potemra, Bombardment of the polar cap ionosphere by solar cosmic rays, *Revs. Geophys. Space Phys.*, **10**, 981-991, 1972.
- Zullig, W., Relation between the intensity of the stratospheric polar vortex and the accumulation of ozone in the winter hemisphere, *Pure Appl. Geophys.*, **106-108**, 1544-1552, 1973.

APPENDIX
STRATOSPHERE WORKSHOP
PARTICIPANTS AND CONTRIBUTORS

Chairman — Robert D. Hudson
Co-Chairman — Edith I. Reed
Vice Chairman — Rex McGill

LABORATORY MEASUREMENTS

W. DeMore — Chairman
Jet Propulsion Laboratory

L. Stief — Co-Chairman
Goddard Space Flight Center

R. Watson — Halogen Chemistry
Jet Propulsion Laboratory

R. Hampson, Jr. — NO_x and $\text{O}(^1\text{D})$ Chemistry
National Bureau of Standards

M. Kurylo — NO_x and $\text{O}(^1\text{D})$ Chemistry, Sulfur
National Bureau of Standards

J. Margitan — HO_x Chemistry
University of Michigan

L. Stief — Methane Oxidation Chemistry
Goddard Space Flight Center

D. Golden — Three-Body Reactions
SRI International

A. Castleman, Jr. — Heterogeneous Reactions
University of Colorado

F. Fehsenfeld — Ionic Reactions
Environmental Research Laboratory

D. Albritton — Ionic Reactions
Environmental Research Laboratory

M. Molina — Photolysis, UV Spectra
University of California at Irvine

R. Menzies — Infrared Spectra
Jet Propulsion Laboratory

C. Howard
Environmental Research Laboratory

J. Michael
Goddard Space Flight Center

MODELS

D. Strobel — Chairman
Naval Research Laboratory

J. Frederick — Co-Chairman
Goddard Space Flight Center

Y. Yung — Photochemical Models
California Institute of Technology

J. Hansen — 1-D Radiative-Convective
Goddard Institute of Space Studies

D. Andrews — 2-D Lagrangian Dynamics
Massachusetts Institute of Technology

M. Schoeberl — 2-D and 3-D, Dynamics
Naval Research Laboratory

J. Mahlman — 3-D General Circulation
Geophysical Fluid Dynamics Laboratory

W. Grose
Langley Research Center

R. Prinn
Massachusetts Institute of Technology

W. Wang
Goddard Institute of Space Studies

BUDGETS

R. Cicerone — Chairman
Scripps Institute of Oceanography

R. Cadle — Sulfur Budget
National Center for Atmospheric Research

R. Stewart — Co-Chairman
Goddard Space Flight Center

H. Singh — Natural Halogen Budget
SRI International

S. Liu — Sources and Sinks of NO_x
Environmental Research Laboratory

J. Jesson — Anthropogenic Halogen Budget
E.I. DuPont de Nemours & Company

S. Wofsy — N_2O Budget
Harvard University

J. Harries — Water Vapor
National Physical Laboratory

W. Broecker — CO_2 Budget
Lamont Geophysical Observatory

D. Kley — Water Vapor
Environmental Research Laboratory

W. Chameides — Hydrocarbon and Hydrogen
University of Florida

E. Inn
Ames Research Center

H. Ellsaesser — H_2O Budget in Stratosphere
Lawrence Livermore Laboratory

A. Schmeltekopf
Environmental Research Laboratory

T. Graedel — Sulfur Budget
Bell Laboratories

RADICALS, RESERVOIRS, AND IONS

J. Anderson — Chairman
Harvard University

J. McConnell — NO , NO_2 , HNO_3 , etc.
York University

W. Heaps — Co-Chairman
Goddard Space Flight Center

J. Noxon — HO_x
Environmental Research Laboratory

J. Anderson — Chlorine
Harvard University

D. Ehhalt — CO , Methane Oxidation Fragments
Institut für Chemie der KFA

J. Waters — Cl , ClO
Jet Propulsion Laboratory

M. Nicolet — UV Flux and J-Values
Brussels University

D. Murcray — ClONO_2 , HOCl
University of Denver

V. Mohnen — Ion Composition
State University of New York at Albany

N. Sze — HCl , HBr , HF , Sulfur
Atmospheric & Environmental Research, Inc.

A. Aikin — Energetic Particles, X-Rays, etc.
Goddard Space Flight Center

W. Evans
Atmospheric Environment Service

D. Wuebbles
Lawrence Livermore Laboratory

C. Farmer
California Institute of Technology

METEOROLOGY OF THE STRATOSPHERE

M. Geller — Chairman
University of Miami

R. Quiroz — Stratospheric Warmings
National Meteorological Center

E. Hilsenrath — *Co chairman*
Goddard Space Flight Center

R. Goldberg — Solar Disturbance Effects
Goddard Space Flight Center

J. Gille — Satellite Data
National Center for Atmospheric Research

R. Zurek — Short Period Motions
Jet Propulsion Laboratory

A. Miller — Non-Satellite Data
National Meteorological Center

M. Shapiro — Troposphere/Stratosphere Exchange
National Center for Atmospheric Research

C. Reber — Empirical Models
Goddard Space Flight Center

S. Fels — Radiative Interactions
Geophysical Fluid Dynamics Laboratory

D. Hartmann — General Circulation
University of Washington

G. Nastrom
Control Data Corporation

D. Cunnold — Ozone Distribution
Georgia Institute of Technology

D. Rind
Goddard Institute for Space Studies

J. Geisler — Stratospheric Oscillations
University of Miami

LONG PERIOD CHANGES IN STRATOSPHERIC PARAMETERS

J. London — Chairman
University of Colorado

R. Penndorf — Water Vapor

A. Krueger — Co-Chairman
Goddard Space Flight Center

J. Penner — Other Species
Lawrence Livermore Laboratory

J. London — Conventional Ozone Data
University of Colorado

W. Komhyr — Reliability of Ozone Data
Air Resources Laboratory

D. Heath — Satellite Ozone Data
Goddard Space Flight Center

A. Oort — Temperature and Circulation
Geophysical Fluid Dynamics Laboratory

J. Campbell — Time Series Analyses of Ozone
Langley Research Center

J. Angell
Air Resources Laboratory

W. Hill
Allied Chemical Corporation

L. Kaplan
Goddard Space Flight Center

H. Panofsky
Pennsylvania State University

A. Pittock
University of Arizona

G. Reinsel
University of Wisconsin

G. Watson
Princeton University

MODEL PREDICTIONS

R. Stolarski — Chairman
Goddard Space Flight Center

D. Butler — Co-Chairman
Goddard Space Flight Center

R. Turco — Halocarbons
R&D Associates

W. Duewer — Nitrogen Oxides
Lawrence Livermore Laboratory

R. Rundel — Large Rockets
Johnson Space Center

L. Callis — Carbon Dioxide
Langley Research Center

E. Bauer — Natural Events
Institute for Defense Analysis

J. Logan — Ground Level Perturbations
Harvard University

R. Whitten — Latitudinal Effects
Ames Research Center

D. Butler — Uncertainties
Goddard Space Flight Center

J. Chang
Lawrence Livermore Laboratory

J. Herman
Goddard Space Flight Center

S. Liu
Environmental Research Laboratory

C. Miller
E.I. DuPont de Nemours & Company

EDITORIAL COMMITTEE

R. Hudson — Chairman

E. Reed

R. Megill

L. Steif

J. Frederick

R. Stewart

Ex Officio — R. Seals, NASA Headquarters

W. Heaps

E. Hilsenrath

A. Krueger

D. Butler

R. Stolarski

1. Report No. NASA RP-1049	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle The Stratosphere: Present and Future		5. Report Date December 1979	
		6. Performing Organization Code GSFC Code 963	
7. Author(s) Edited by Robert D. Hudson and Edith I. Reed		8. Performing Organization Report No.	
9. Performing Organization Name and Address Goddard Space Flight Center Greenbelt, Maryland 20771		10. Work Unit No.	
		11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Reference Publication	
		14. Sponsoring Agency Code	
15. Supplementary Notes			
16. Abstract This document reports the conclusions of a Workshop held by the National Aeronautics and Space Administration in June, 1979, to assess those aspects of our current knowledge that pertain to the modification of the stratosphere by anthropogenic activities which lead to the release of halocarbons, nitrous and nitric oxide, carbon dioxide, etc. Naturally occurring perturbations such as related to solar or volcanic activity are likewise considered. The basis of model description is given in terms of the laboratory data for rates and cross sections and the types of models suitable for various purposes. Observed distributions of various trace species are considered in terms of their sources and removal mechanisms and are compared to values from models. Stratospheric meteorology is discussed in terms of the effects of dynamics on the distribution of species. Model predictions of ozone depletion are given for various scenarios; the accuracy to which such changes in ozone content may be detected in available observational data is discussed.			
17. Key Words (Selected by Author(s)) Stratosphere Ozone Chlorofluoromethanes Model results		18. Distribution Statement Unclassified - Unlimited STAR 47 Meteorology and Climatology	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 432	22. Price*

*For sale by the National Technical Information Service, Springfield, Virginia 22151.