World Meteorological Organization
Global Ozone Research and Monitoring Project — Report No. 37

Scientific Assessment of Ozone Depletion: 1994

National Oceanic and Atmospheric Administration
National Aeronautics and Space Administration
United Nations Environment Programme
World Meteorological Organization

List of International Authors, Contributors, and Reviewers

Assessment Co-chairs

Daniel L. Albritton, Robert T. Watson, and Piet J. Aucamp

Chapter Lead Authors

1: Neil R.P. Harris
2: Eugenio Sanhueza
3: David W. Fahey
4: Roderic L. Jones
5: Andreas Volz-Thomas and Brian A. Ridley
6: Malcolm K.W. Ko
7: Frode Stordal
8: Keith P. Shine
9: Richard L. McKenzie
10: Stuart A. Penkett
11: Andreas Wahner and Marvin A. Geller
12: R.A. Cox
13: Susan Solomon and Donald J. Wuebbles

Coordinating Editor

Christine A. Ennis

Authors, Contributors, and Reviewers

Daniel L. Albritton	US
Marc Allaart	The Netherlands
Fred N. Alyea	US
Gerard Ancellet	France
Meinrat O. Andreae	Germany
James K. Angell	US
Frank Arnold	Germany
Roger Atkinson	US
Elliot Atlas	US
Piet J. Aucamp	South Africa
L. Avallone	US
Helmuth Bauer	Germany
Slimane Bekki	UK
Tibor Bérces	Hungary
T. Berntsen	Norway
Lane Bishop	US
Donald R. Blake	US
N.J. Blake	US
Mario Blumthaler	Austria
Greg E. Bodeker	South Africa
Rumen D. Bojkov	Switzerland
Charles R. Booth	US
Byron Boville	US
Kenneth P. Bowman	US
Geir Braathen	Norway
Guy P. Brasseur	US
Carl Brenninkmeijer	New Zealand
Christoph Brühl	Germany
William H. Brune	US
James H. Butler	US
Sergio Cabrera	Chile
Bruce A. Callander	UK
Daniel Cariolle	France
R. Cebula	US
William L. Chameides	US
S. Chandra	US
Marie-Lise Chanin	France
J. Christy	US
Ralph J. Cicerone	US
G.J.R. Coetzee	South Africa
Peter S. Connell	US
D. Considine	US
R.A. Cox	UK
Paul J. Crutzen	Germany

AUTHORS, CONTRIBUTORS, AND REVIEWERS

Derek N. Cunnold	US
John Daniel	US
Malgorzata Degórska	Poland
John J. DeLuisi	US
Dirk De Muer	Belgium
Frank Dentener	The Netherlands
Richard G. Derwent	UK
Terry Deshler	US
Susana B. Diaz	Argentina
Russell Dickerson	US
J. Dignon	US
Ed Dlugokencky	US
Anne R. Douglass	US
Tom Duafala	US
James E. Dye	US
Dieter H. Ehhalt	Germany
James W. Elkins	US
Christine Ennis	US
D. Etheridge	Australia
David W. Fahey	US
T. Duncan A. Fairlie	US
Donald A. Fisher	US
Jack Fishman	US
Eric L. Fleming	US
Frank Flocke	Germany
L. Flynn	US
P.M. de F. Forster	UK
James Franklin	Belgium
Paul J. Fraser	Australia
John E. Frederick	US
Lucien Froidevaux	US
J.S. Fuglestvedt	Norway
Reinhard Furrer	Germany
Ian E. Galbally	Australia
Brian G. Gardiner	UK
Marvin A. Geller	US
Hartwig Gernandt	Germany
James F. Gleason	US
S. Godin	France
Amram Golombek	Israel
Ulrich Görsdorf	Germany
Thomas E. Graedel	US
Claire Granier	US
William B. Grant	US
L. Gray	UK
William L. Grose	US
J. Gross	Germany
A. Grossman	US
Alexander Gruzdev	Russia
James E. Hansen	US
Neil R.P. Harris	UK
Shiro Hatakeyama	Japan
D.A. Hauglustaine	France
Sachiko Hayashida	Japan
G.D. Hayman	UK
Kjell Henriksen	Norway
Ernest Hilsenrath	US
David J. Hofmann	US
Stacey M. Hollandsworth	US
James R. Holton	US
Lon L. Hood	US
Øystein Hov	Norway
Carleton J. Howard	US
Robert D. Hudson	US
D. Hufford	US
Linda Hunt	US
Abdel M. Ibrahim	Egypt
Mohammad Ilyas	Malaysia
Ivar Isaksen	Norway
Tomoyuki Ito	Japan
Charles H. Jackman	US
Daniel J. Jacob	US
Colin E. Johnson	UK
Harold S. Johnston	US
Paul V. Johnston	New Zealand
Roderic L. Jones	UK
Torben S. Jørgensen	Denmark
M. Kanakidou	France
Igor L. Karol	Russia
Prasad Kasibhatla	US
Jack A. Kaye	US
Hennie Kelder	The Netherlands
James B. Kerr	Canada
M.A.K. Khalil	US
Vyacheslav Khattatov	Russia
J.T. Kiehl	US
S. Kinne	Germany
D. Kinnison	US
Volker Kirchhoff	Brazil
Malcolm K.W. Ko	US
Ulf Köhler	Germany
Walter D. Komhyr	US
Yutaka Kondo	Japan
Janusz W. Krzyścin	Poland

Antti Kulmala	Switzerland
Michael J. Kurylo	US
K. Labitzke	Germany
Murari Lal	India
K.S. Law	UK
G. LeBras	France
Yuan-Pern Lee	Taiwan
Frank Lefèvre	France
Jos Lelieveld	The Netherlands
Robert Lesclaux	France
J.S. Levine	US
Joel Levy	US
J. Ben Liley	New Zealand
Peter Liss	UK
David H. Lister	UK
Zenobia Lityńska	Poland
Shaw C. Liu	US
Jennifer A. Logan	US
Nicole Louisnard	France
Pak Sum Low	Kenya
Daniel Lubin	US
Sasha Madronich	US
Jerry Mahlman	US
Gloria L. Manney	US
Huiting Mao	US
W. Andrew Matthews	New Zealand
Konrad Mauersberger	Germany
Archie McCulloch	UK
Mack McFarland	US
M.E. McIntyre	UK
Richard L. McKenzie	New Zealand
Richard D. McPeters	US
Gérard Mégie	France
Paulette Middleton	US
A.J. Miller	US
Igor Mokhov	Russia
Mario Molina	US
G.K. Moortgat	Germany
Hideaki Nakane	Japan
Paul A. Newman	US
Paul C. Novelli	US
Samuel J. Oltmans	US
Alan O'Neill	UK
Michael Oppenheimer	US
S. Palermi	Italy
K. Patten	US
Juan Carlos Pelaez	Cuba
Stuart A. Penkett	UK
J. Penner	US
Thomas Peter	Germany
Leon F. Phillips	New Zealand
Ken Pickering	US
R.B. Pierce	US
S. Pinnock	UK
Michel Pirre	France
Giovanni Pitari	Italy
Walter G. Planet	US
R.A. Plumb	US
Jean-Pierre Pommereau	France
Lamont R. Poole	US
Michael J. Prather	US
Margarita Préndez	Chile
Ronald G. Prinn	US
Joseph M. Prospero	US
John A. Pyle	UK
Lian Xiong Qiu	China
Richard Ramaroson	France
V. Ramaswamy	US
William Randel	US
Philip J. Rasch	US
A.R. Ravishankara	US
William S. Reeburgh	US
C.E. Reeves	UK
J. Richardson	US
Brian A. Ridley	US
David Rind	US
Curtis P. Rinsland	US
Aidan E. Roche	US
Michael O. Rodgers	US
Henning Rodhe	Sweden
Jose M. Rodriguez	US
M. Roemer	The Netherlands
Franz Rohrer	Germany
Richard B. Rood	US
F. Sherwood Rowland	US
C.E. Roy	Australia
Jochen Rudolph	Germany
James M. Russell III	US
Nelson Sabogal	Kenya
Karen Sage	US
Ross Salawitch	US
Eugenio Sanhueza	Venezuela
K.M. Sarma	Kenya
T. Sasaki	Japan

AUTHORS, CONTRIBUTORS, AND REVIEWERS

Sue M. Schauffler	US
Hans Eckhart Scheel	Germany
Ulrich Schmidt	Germany
Rainer Schmitt	Germany
Ulrich Schumann	Germany
M.D. Schwarzkopf	US
Gunther Seckmeyer	Germany
Jonathan D. Shanklin	UK
Keith P. Shine	UK
H. Sidebottom	Ireland
P. Simmonds	UK
Paul C. Simon	Belgium
H. Singh	US
Paula Skřivánková	Czech Republic
Herman Smit	Germany
Susan Solomon	US
Johannes Staehelin	Switzerland
Knut Stamnes	US
L. Paul Steele	Australia
Leopoldo Stefanutti	Italy
Richard S. Stolarski	US
Frode Stordal	Norway
A. Strand	Norway
B.H. Subbaraya	India
N.-D. Sze	US
Anne M. Thompson	US
Xue X. Tie	US
Margaret A. Tolbert	US
Darin W. Toohey	US
Ralf Toumi	UK
Michael Trainer	US
Charles R. Trepte	US
Adrian Tuck	US
R. Van Dorland	The Netherlands
Karel Vanicek	Czech Republic
Geraint Vaughan	UK
G. Visconti	Italy
Andreas Volz-Thomas	Germany
Andreas Wahner	Germany
W.-C. Wang	US
D.I. Wardle	Canada
David A. Warrilow	UK
Joe W. Waters	US
Robert T. Watson	US
E.C. Weatherhead	US
Christopher R. Webster	US
D. Weisenstein	US
Ray F. Weiss	US
Paul Wennberg	US
Howard Wesoky	US
Thomas M.L. Wigley	US
Oliver Wild	UK
Paul H. Wine	US
Peter Winkler	Germany
Steven C. Wofsy	US
Donald J. Wuebbles	US
Vladimir Yushkov	Russia
Ahmed Zand	Iran
Rudi J. Zander	Belgium
Joseph M. Zawodny	US
Reinhard Zellner	Germany
Christos Zerefos	Greece
Xiu Ji Zhou	China

TABLE OF CONTENTS

SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 1994

PREFACE xi
EXECUTIVE SUMMARY xiii
COMMON QUESTIONS ABOUT OZONE xxv

PART 1. OBSERVED CHANGES IN OZONE AND SOURCE GASES

CHAPTER 1: OZONE MEASUREMENTS
Lead Author: Neil R.P. Harris
Scientific Summary 1.1
1.1 Introduction 1.5
1.2 Total Ozone 1.5
1.3 Ozone Profiles 1.23
1.4 Ozone and Aerosol since 1991 ..... 1.37
1.5 Antarctic Ozone Depletion 1.43
References 1.48

CHAPTER 2: SOURCE GASES: TRENDS AND BUDGETS
Lead Author: Eugenio Sanhueza
Scientific Summary 2.1
2.1 Introduction 2.3
2.2 Halocarbons 2.3
2.3 Stratospheric Inputs of Chlorine and Particulates from Rockets 2.15
2.4 Methane 2.16
2.5 Nitrous Oxide 2.20
2.6 Short-Lived Ozone Precursor Gases 2.22
2.7 Carbon Dioxide 2.26
References 2.27

PART 2. ATMOSPHERIC PROCESSES RESPONSIBLE FOR THE OBSERVED CHANGES IN OZONE

CHAPTER 3: POLAR OZONE
Lead Author: David W. Fahey
Scientific Summary 3.1
3.1 Introduction 3.3
3.2 Vortex Formation and Tracer Relations 3.5
3.3 Processing on Aerosol Surfaces 3.10
3.4 Destruction of Ozone 3.27
3.5 Vortex Isolation and Export to Midlatitudes 3.34
References 3.41

TABLE OF CONTENTS

CHAPTER 4: TROPICAL AND MIDLATITUDE OZONE
Lead Author: Roderic L. Jones
Scientific Summary 4.1
4.1 General Introduction 4.3
I. Chemical Processes Influencing Middle Latitude and Tropospheric Ozone 4.3
4.2 Introduction 4.3
4.3 Eruption of Mount Pinatubo 4.12
4.4 Photochemical Ozone Loss Processes at Midlatitudes 4.15
4.5 The Solar Cycle and Quasi-Biennial Oscillation (QBO) Effects on Total Ozone 4.16
II. Transport Processes Linking the Tropics, Middle, and High Latitudes 4.18
4.6 Introduction 4.18
4.7 Transport of Air from Polar Regions to Middle Latitudes 4.23
References 4.29

CHAPTER 5: TROPOSPHERIC OZONE
Lead Authors: Andreas Volz-Thomas and Brian A. Ridley
Scientific Summary 5.1
5.1 Introduction 5.3
5.2 Review of Factors that Influence Tropospheric Ozone Concentrations 5.3
5.3 Insights from Field Observations: Photochemistry and Transport 5.8
5.4 Feedback between Tropospheric Ozone and Long-Lived Greenhouse Gases 5.20
References 5.21

PART 3. MODEL SIMULATIONS OF GLOBAL OZONE

CHAPTER 6: MODEL SIMULATIONS OF STRATOSPHERIC OZONE
Lead Author: Malcolm K.W. Ko
Scientific Summary 6.1
6.1 Introduction 6.3
6.2 Components in a Model Simulation 6.4
6.3 Comparison of Model Results with Observation 6.12
6.4 Results from Scenario Calculations 6.25
6.5 Conclusions 6.33
References 6.33

CHAPTER 7: MODEL SIMULATIONS OF GLOBAL TROPOSPHERIC OZONE
Lead Author: Frode Stordal
Scientific Summary 7.1
7.1 Introduction 7.3
7.2 3-D Simulations of the Present-Day Atmosphere:
Evaluation with Observations 7.4
7.3 Current Tropospheric Ozone Modeling 7.6
7.4 Applications 7.13
7.5 Intercomparison of Tropospheric Chemistry/Transport Models 7.16
References 7.29

PART 4. CONSEQUENCES OF OZONE CHANGE

CHAPTER 8: RADIATIVE FORCING AND TEMPERATURE TRENDS
Lead Author: Keith P. Shine
Scientific Summary 8.1
8.1 Introduction 8.3
8.2 Radiative Forcing Due to Ozone Change 8.3
8.3 Observed Temperature Changes 8.12
8.4 Halocarbon Radiative Forcing 8.18
References 8.23

CHAPTER 9: SURFACE ULTRAVIOLET RADIATION
Lead Author: Richard L. McKenzie
Scientific Summary 9.1
9.1 Introduction 9.3
9.2 Update on Trend Observations 9.3
9.3 Spectro-Radiometer Results 9.4
9.4 Implications of Recent Changes 9.12
9.5 Update on Predictions 9.14
9.6 Gaps in Knowledge 9.18
References 9.18

PART 5. SCIENTIFIC INFORMATION FOR FUTURE DECISIONS

CHAPTER 10: METHYL BROMIDE
Lead Author: Stuart A. Penkett
Scientific Summary 10.1
10.1 Introduction 10.3
10.2 Measurements, Including Interhemispheric Ratios 10.3
10.3 Sources of Methyl Bromide 10.7
10.4 Sink Mechanisms 10.11
10.5 The Role of the Oceans 10.13
10.6 Modeled Estimates of the Global Budget 10.15
10.7 Stratospheric Chemistry: Measurements and Models 10.18
10.8 The Ozone Depletion Potential of Methyl Bromide 10.20
10.9 Conclusions 10.23
References 10.23

CHAPTER 11: SUBSONIC AND SUPERSONIC AIRCRAFT EMISSIONS
Lead Authors: Andreas Wahner and Marvin A. Geller
Scientific Summary 11.1
11.1 Introduction 11.3
11.2 Aircraft Emissions 11.4
11.3 Plume Processes 11.10
11.4 NO_x/H_2O/Sulfur Impacts on Atmospheric Chemistry 11.13
11.5 Model Predictions of Aircraft Effects on Atmospheric Chemistry 11.15
11.6 Climate Effects 11.22
11.7 Uncertainties 11.25
Acronyms 11.27
References 11.28

TABLE OF CONTENTS

CHAPTER 12: ATMOSPHERIC DEGRADATION OF HALOCARBON SUBSTITUTES
Lead Author: R.A. Cox

Scientific Summary 12.1
12.1 Background 12.3
12.2 Atmospheric Lifetimes of HFCs and HCFCs 12.3
12.3 Atmospheric Lifetimes of Other CFC and Halon Substitutes 12.4
12.4 Atmospheric Degradation of Substitutes 12.5
12.5 Gas Phase Degradation Chemistry of Substitutes 12.6
12.6 Heterogeneous Removal of Halogenated Carbonyl Compounds 12.11
12.7 Release of Fluorine Atoms in the Stratosphere 12.11
12.8 CF_3O_x and $FC(O)O_x$ Radical Chemistry in the Stratosphere — Do These Radicals Destroy Ozone? 12.13
12.9 Model Calculations of the Atmospheric Behavior of HCFCs and HFCs 12.15
References 12.17

CHAPTER 13: OZONE DEPLETION POTENTIALS, GLOBAL WARMING POTENTIALS, AND FUTURE CHLORINE/BROMINE LOADING
Lead Authors: Susan Solomon and Donald J. Wuebbles

Scientific Summary 13.1
13.1 Introduction 13.3
13.2 Atmospheric Lifetimes and Response Times 13.4
13.3 Cl/Br Loading and Scenarios for CFC Substitutes 13.7
13.4 Ozone Depletion Potentials 13.12
13.5 Global Warming Potentials 13.20
References 13.32

APPENDICES
A List of International Authors, Contributors, and Reviewers A.1
B Major Acronyms and Abbreviations B.1
C Chemical Formulae and Nomenclature C.1

PREFACE

The present document is a scientific assessment that will be part of the information upon which the Parties to the Montreal Protocol will base their future decisions regarding protection of the stratospheric ozone layer.

Specifically, the Montreal Protocol on Substances That Deplete the Ozone Layer states (Article 6): "... the Parties shall assess the control measures ... on the basis of available scientific, environmental, technical, and economic information." To provide the mechanisms whereby these assessments are conducted, the Protocol further states: "... the Parties shall convene appropriate panels of experts" and "the panels will report their conclusions ... to the Parties."

Three assessment reports have been prepared during 1994 to be available to the Parties in advance of their meeting in 1995, at which they will consider the need to amend or adjust the Protocol. The two companion reports to the present scientific assessment focus on the environmental and health effects of ozone layer depletion and on the technology and economic implications of mitigation approaches.

The present report is the latest in a series of seven scientific assessments prepared by the world's leading experts in the atmospheric sciences and under the international auspices of the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP). The chronology of those scientific assessments and the relation to the international policy process are summarized as follows:

Year	Policy Process	Scientific Assessment
1981		*The Stratosphere 1981 Theory and Measurements.* WMO No. 11.
1985	Vienna Convention	*Atmospheric Ozone 1985.* 3 vol. WMO No. 16.
1987	Montreal Protocol	
1988		*International Ozone Trends Panel Report 1988.* 2 vol. WMO No. 18.
1989		*Scientific Assessment of Stratospheric Ozone:* 1989. 2 vol. WMO No. 20.
1990	London Amendment	
1991		*Scientific Assessment of Ozone Depletion: 1991.* WMO No. 25.
1992		*Methyl Bromide: Its Atmospheric Science, Technology, and Economics* (Assessment Supplement). UNEP (1992).
1992	Copenhagen Amendment	
1994		*Scientific Assessment of Ozone Depletion: 1994.* WMO No. 37 (This report.)
(1995)	Vienna Amendment (?)	

The genesis of *Scientific Assessment of Ozone Depletion: 1994* occurred at the 4th meeting of the Conference of the Parties to the Montreal Protocol in Copenhagen, Denmark, in November 1992, at which the scope of the scientific needs of the Parties was defined. The formal planning of the present report was a workshop that was held on 11 June 1993 in

Virginia Beach, Virginia, at which an international steering group crafted the outline and suggested scientists from the world community to serve as authors. The first drafts of the chapters were examined at a meeting that occurred on 2 - 4 March 1994 in Washington, D.C., at which the authors and a small number of international experts improved the coordination of the text of the chapters.

The second draft was sent out to 123 scientists worldwide for a mail peer review. These anonymous comments were considered by the authors. At a Panel Review Meeting in Les Diablerets, Switzerland, held on 18 - 21 July 1994, the responses to these mail review comments were proposed by the authors and discussed by the 80 participants. Final changes to the chapters were decided upon, and the Executive Summary was prepared by the participants.

The final result is this document. It is the product of 295 scientists from the developed and developing world[1] who contributed to its preparation and review (230 scientists prepared the report and 147 scientists participated in the peer review process).

What follows is a summary of their current understanding of the stratospheric ozone layer and its relation to humankind.

[1] Participating were Argentina, Australia, Austria, Belgium, Brazil, Canada, Chile, Cuba, Czech Republic, Denmark, Egypt, France, Germany, Greece, Hungary, India, Iran, Ireland, Israel, Italy, Japan, Kenya, Malaysia, New Zealand, Norway, Poland, Russia, South Africa, Sweden, Switzerland, Taiwan, The Netherlands, The People's Republic of China, United Kingdom, United States of America, and Venezuela.

EXECUTIVE SUMMARY

Recent Major Scientific Findings and Observations

The laboratory investigations, atmospheric observations, and theoretical and modeling studies of the past few years have provided a deeper understanding of the human-influenced and natural chemical changes in the atmosphere and their relation to the Earth's stratospheric ozone layer and radiative balance of the climate system. Since the last international scientific assessment of the state of understanding, there have been several key ozone-related findings, observations, and conclusions:

- **The atmospheric growth rates of several major ozone-depleting substances have slowed, demonstrating the expected impact of the Montreal Protocol and its Amendments and Adjustments.** The abundances of the chlorofluorocarbons (CFCs), carbon tetrachloride, methyl chloroform, and halons in the atmosphere have been monitored at global ground-based sites since about 1978. Over much of that period, the annual growth rates of these gases have been positive. However, the data of recent years clearly show that the growth rates of CFC-11, CFC-12, halon-1301, and halon-1211 are slowing down. In particular, total tropospheric organic chlorine increased by only about 60 ppt/year (1.6%) in 1992, compared to 110 ppt/year (2.9%) in 1989. Furthermore, tropospheric bromine in halons increased by only about 0.25 ppt/year in 1992, compared to about 0.85 ppt/year in 1989. The abundance of carbon tetrachloride is actually decreasing. The observed trends in total tropospheric organic chlorine are consistent with reported production data, suggesting less emission than the maximum allowed under the Montreal Protocol and its Amendments and Adjustments. Peak total chlorine/bromine loading in the troposphere is expected to occur in 1994, but the stratospheric peak will lag by about 3 - 5 years. Since the stratospheric abundances of chlorine and bromine are expected to continue to grow for a few more years, increasing global ozone losses are predicted (other things being equal) for the remainder of the decade, with gradual recovery in the 21st century.

- **The atmospheric abundances of several of the CFC substitutes are increasing, as anticipated.** With phase-out dates for the CFCs and other ozone-depleting substances now fixed by international agreements, several hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are being manufactured and used as substitutes. The atmospheric growth of some of these compounds (*e.g.*, HCFC-22) has been observed for several years, and the growth rates of others (*e.g.*, HCFC-142b and HCFC-141b) are now being monitored. Tropospheric chlorine in HCFCs increased by 5 ppt/year in 1989 and about 10 ppt/year in 1992.

- **Record low global ozone levels were measured over the past two years.** Anomalous ozone decreases were observed in the midlatitudes of both hemispheres in 1992 and 1993. The Northern Hemispheric decreases were larger than those in the Southern Hemisphere. Globally, ozone values were 1 - 2% lower than would be expected from an extrapolation of the trend prior to 1991, allowing for solar-cycle and quasi-biennial-oscillation (QBO) effects. The 1994 global ozone levels are returning to values closer to those expected from the longer-term downward trend.

EXECUTIVE SUMMARY

- **The stratosphere was perturbed by a major volcanic eruption.** The eruption of Mt. Pinatubo in 1991 led to a large increase in sulfate aerosol in the lower stratosphere throughout the globe. Reactions on sulfate aerosols resulted in significant, but temporary, changes in the chemical partitioning that accelerated the photochemical ozone loss associated with reactive hydrogen (HO_x), chlorine, and bromine compounds in the lower stratosphere in midlatitudes and polar regions. Absorption of terrestrial and solar radiation by the Mt. Pinatubo aerosol resulted in a transitory rise of 1°C (globally averaged) in the lower-stratospheric temperature and also affected the distribution of ozone through circulation changes. The observed 1994 recovery of global ozone is qualitatively consistent with observed gradual reductions of the abundances of these volcanic particles in the stratosphere.

- **Downward trends in total-column ozone continue to be observed over much of the globe, but their magnitudes are underestimated by numerical models.** Decreases in ozone abundances of about 4 - 5% per decade at midlatitudes in the Northern and Southern Hemispheres continue to be observed by both ground-based and satellite-borne monitoring instruments. At midlatitudes, the losses continue to be much larger during winter/spring than during summer/fall in both hemispheres, and the depletion increases with latitude, particularly in the Southern Hemisphere. Little or no downward trends are observed in the tropics (20°N - 20°S). While the current two-dimensional stratospheric models simulate the observed trends quite well during some seasons and latitudes, they underestimate the trends by factors of up to three in winter/spring at mid- and high latitudes. Several known atmospheric processes that involve chlorine and bromine and that affect ozone in the lower stratosphere are difficult to model and have not been adequately incorporated into these models.

- **Observations have demonstrated that halogen chemistry plays a larger role in the chemical destruction of ozone in the midlatitude lower stratosphere than expected from gas phase chemistry.** Direct *in situ* measurements of radical species in the lower stratosphere, coupled with model calculations, have quantitatively shown that the *in situ* photochemical loss of ozone due to (largely natural) reactive nitrogen (NO_x) compounds is smaller than that predicted from gas phase chemistry, while that due to (largely natural) HO_x compounds and (largely anthropogenic) chlorine and bromine compounds is larger than that predicted from gas phase chemistry. This confirms the key role of chemical reactions on sulfate aerosols in controlling the chemical balance of the lower stratosphere. These and other recent scientific findings strengthen the conclusion of the previous assessment that the weight of scientific evidence suggests that the observed middle- and high-latitude ozone losses are largely due to anthropogenic chlorine and bromine compounds.

- **The conclusion that anthropogenic chlorine and bromine compounds, coupled with surface chemistry on natural polar stratospheric particles, are the cause of polar ozone depletion has been further strengthened.** Laboratory studies have provided a greatly improved understanding of how the chemistry on the surfaces of ice, nitrate, and sulfate particles can increase the abundance of ozone-depleting forms of chlorine in the polar stratospheres. Furthermore, satellite and *in situ* observations of the abundances of reactive nitrogen and chlorine compounds have improved the explanation of the different ozone-altering properties of the Antarctic and Arctic.

- **The Antarctic ozone "holes" of 1992 and 1993 were the most severe on record.** The Antarctic ozone "hole" has continued to occur seasonally every year since its advent in the late-1970s, with the occurrences over the last several years being particularly pronounced. Satellite, balloon-borne, and ground-based monitoring instruments revealed that the Antarctic ozone "holes" of 1992 and 1993 were the biggest (areal extent) and deepest (minimum amounts of ozone overhead), with ozone being locally depleted by more than 99% between about 14 - 19 km in October, 1992 and 1993. It is likely that these larger-than-usual ozone depletions could be attributed, at least in part, to sulfate aerosols from Mt. Pinatubo increasing the effectiveness of chlorine- and bromine-catalyzed ozone destruction. A substantial Antarctic ozone "hole" is expected to occur each austral spring for many more decades because stratospheric chlorine and bromine abundances will approach the pre-Antarctic-ozone-"hole" levels (late-1970s) very slowly during the next century.

- **Ozone losses have been detected in the Arctic winter stratosphere, and their links to halogen chemistry have been established.** Studies in the Arctic lower stratosphere have been expanded to include more widespread observations of ozone and key reactive species. In the late-winter/early-spring period, additional chemical losses of ozone up to 15 - 20% at some altitudes are deduced from these observations, particularly in the winters of 1991/2 and 1992/3. Model calculations constrained by the observations are also consistent with these losses, increasing the confidence in the role of chlorine and bromine in ozone destruction. The interannual variability in the photochemical and dynamical conditions of the Arctic polar vortex continues to limit the ability to predict ozone changes in future years.

- **The link between a decrease in stratospheric ozone and an increase in surface ultraviolet (UV) radiation has been further strengthened.** Measurements of UV radiation at the surface under clear-sky conditions show that low overhead ozone yields high UV radiation and in the amount predicted by radiative-transfer theory. Large increases of surface UV are observed in Antarctica and the southern part of South America during the period of the seasonal ozone "hole." Furthermore, elevated surface UV levels at mid-to-high latitudes were observed in the Northern Hemisphere in 1992 and 1993, corresponding to the low ozone levels of those years. However, the lack of a decadal (or longer) record of accurate monitoring of surface UV levels and the variation introduced by clouds and other factors have precluded the unequivocal identification of a long-term trend in surface UV radiation.

- **Methyl bromide continues to be viewed as a significant ozone-depleting compound.** Increased attention has been focused upon the ozone-depleting role of methyl bromide. Three potentially major anthropogenic sources of atmospheric methyl bromide have been identified (soil fumigation, biomass burning, and the exhaust of automobiles using leaded gasoline), in addition to the natural oceanic source. Recent laboratory studies have confirmed the fast rate for the $BrO + HO_2$ reaction and established a negligible reaction pathway producing HBr, both of which imply greater ozone losses due to emissions of compounds containing bromine. While the magnitude of the atmospheric photochemical removal is well understood, there are significant uncertainties in quantifying the oceanic sink for atmospheric methyl bromide. The best estimate for the overall lifetime of atmospheric methyl bromide is 1.3 years, with a range of 0.8 - 1.7 years. The Ozone Depletion Potential (ODP) for methyl bromide is calculated to be about 0.6 (relative to an ODP of 1 for CFC-11).

- **Stratospheric ozone losses cause a global-mean negative radiative forcing.** In the 1991 scientific assessment, it was pointed out that the global ozone losses that were occurring in the lower stratosphere caused this region to cool and result in less radiation reaching the surface-troposphere system. Recent model studies have strengthened this picture. A long-term global-mean cooling of the lower stratosphere of between 0.25 and 0.4°C/decade has been observed over the last three decades. Calculations indicate that, on a global mean, the ozone losses between 1980 and 1990 offset about 20% of the radiative forcing due to the well-mixed greenhouse-gas increases during that period (*i.e.*, carbon dioxide, methane, nitrous oxide, and halocarbons).

- **Tropospheric ozone, which is a greenhouse gas, appears to have increased in many regions of the Northern Hemisphere.** Observations show that tropospheric ozone, which is formed by chemical reactions involving pollutants, has increased above many locations in the Northern Hemisphere over the last 30 years. However, in the 1980s, the trends were variable, being small or nonexistent. In the Southern Hemisphere, there are insufficient data to draw strong inferences. At the South Pole, a decrease has been observed since the mid-1980s. Model simulations and limited observations suggest that tropospheric ozone has increased in the Northern Hemisphere since pre-industrial times. Such changes would augment the radiative forcing from all other greenhouse gases by about 20% over the same time period.

- **The atmospheric residence times of the important ozone-depleting gases, CFC-11 and methyl chloroform, and the greenhouse gas, methane, are now better known.** A reconciliation of observed concentrations with known emissions using an atmospheric model has led to a best-estimate lifetime of 50 years for CFC-11 and 5.4 years for methyl chloroform, with uncertainties of about 10%. These lifetimes provide an accurate standard for gases destroyed only in the stratosphere (such as CFCs and nitrous oxide) and for those also reacting with tropospheric hydroxyl radical, OH (such as HCFCs and HFCs), respectively. Recent model simulations of methane perturbations and a theoretical analysis of the tropospheric chemical system that couples methane, carbon monoxide, and OH have demonstrated that methane perturbations decay with a lengthened time scale in a range of about 12 - 17 years, as compared with the 10-year lifetime derived from the total abundance and losses. This longer response time and other indirect effects increase the estimate of the effectiveness of emissions of methane as a greenhouse gas by a factor of about two compared to the direct-effect-only values given in the 1991 assessment.

Supporting Scientific Evidence and Related Issues

Ozone Changes in the Tropics and Midlatitudes and Their Interpretation

- Analysis of global total-column ozone data through early 1994 shows substantial decreases of ozone in all seasons at midlatitudes (30° - 60°) of both hemispheres. For example, in the middle latitudes of the Northern Hemisphere, downward trends of about 6% per decade over 1979 - 1994 were observed in winter and spring and about 3% per decade were observed in summer and fall. In the Southern Hemisphere, the seasonal difference was somewhat less, but the midlatitude trends averaged a similar 4% to 5% per decade. There are no statistically significant trends in the tropics (20°S - 20°N). Trends through 1994 are about 1% per decade more negative in the Northern Hemisphere (2% per decade in the midlatitude winter/spring in the Northern Hemisphere) compared to those calculated without using data after May 1991. At Northern midlatitudes, the downward trend in ozone between 1981 - 1991 was about 2% per decade greater compared to that of the period 1970 - 1980.

- Satellite and ozonesonde data show that much of the downward trend in ozone occurs below 25 km (*i.e.*, in the lower stratosphere). For the region 20 - 25 km, there is good agreement between the trends from the Stratospheric Aerosol and Gas Experiment (SAGE I/II) satellite instrument data and those from ozonesondes, with an observed annual-average decrease of 7 ± 4% per decade from 1979 to 1991 at 30° - 50°N latitude. Below 20 km, SAGE yields negative trends as large as 20 ± 8% per decade at 16 - 17 km, while the average of available midlatitude ozonesonde data shows smaller negative trends of 7 ± 3% per decade. Integration of the ozonesonde data yields total-ozone trends consistent with total-ozone measurements. In the 1980s, upper-stratospheric (35 - 45 km) ozone trends determined by the data from SAGE I/II, Solar Backscatter Ultraviolet satellite spectrometer (SBUV), and the Umkehr method agree well at midlatitudes, but less so in the tropics. Ozone declined 5 - 10% per decade at 35 - 45 km between 30°- 50°N and slightly more at southern midlatitudes. In the tropics at 45 km, SAGE I/II and SBUV yield downward trends of 10 and 5% per decade, respectively.

- Simultaneous *in situ* measurements of a suite of reactive chemical species have directly confirmed modeling studies implying that the chemical destruction of ozone in the midlatitude lower stratosphere is more strongly influenced by HO_x and halogen chemistry than NO_x chemistry. The seasonal cycle of ClO in the lower stratosphere at midlatitudes in both hemispheres supports a role for *in situ* heterogeneous perturbations (*i.e.*, on sulfate aerosols), but does not appear consistent with the timing of vortex processing or dilution. These studies provide key support for the view that sulfate aerosol chemistry plays an important role in determining midlatitude chemical ozone destruction rates.

- The model-calculated ozone depletions in the upper stratosphere for 1980 - 1990 are in broad agreement with the measurements. Although these model-calculated ozone depletions did not consider radiative feedbacks and temperature trends, including these effects is not likely to reduce the predicted ozone changes by more than 20%.

- Models including the chemistry involving sulfate aerosols and polar stratospheric clouds (PSCs) better simulate the observed total ozone depletions of the past decade than models that include only gas phase reactions. However, they still underestimate the ozone loss by factors ranging from 1.3 to 3.0.

- Some unresolved discrepancies between observations and models exist for the partitioning of inorganic chlorine species, which could impact model predictions of ozone trends. These occur for the ClO/HCl ratio in the upper stratosphere and the fraction of HCl to total inorganic chlorine in the lower stratosphere.

- The transport of ozone-depleted air from polar regions has the potential to influence ozone concentrations at middle latitudes. While there are uncertainties about the importance of this process relative to *in situ* chemistry for midlatitude ozone loss, both directly involve ozone destruction by chlorine- and bromine-catalyzed reactions.

- Radiosonde and satellite data continue to show a long-term cooling trend in globally annual-average lower-stratospheric temperatures of about 0.3 - 0.4°C per decade over the last three decades. Models suggest that ozone depletion is the major contributor to this trend.

- Anomalously large downward ozone trends have been observed in midlatitudes of both hemispheres in 1992 and 1993 (*i.e.*, the first two years after the eruption of Mt. Pinatubo), with Northern-Hemispheric decreases larger than those of the Southern Hemisphere. Global-average total-ozone levels in early 1993 were about 1% to 2% below that expected from the long-term trend and the particular phase of the solar and QBO cycles, while peak decreases of about 6 - 8% from expected ozone levels were seen over 45 - 60°N. In the first half of 1994, ozone levels returned to values closer to those expected from the long-term trend.

- The sulfur gases injected by Mt. Pinatubo led to large enhancements in stratospheric sulfate aerosol surface areas (by a maximum factor of about 30 - 40 at northern midlatitudes within a year after the eruption), which have subsequently declined.

- Anomalously low ozone was measured at altitudes below 25 km at a Northern-Hemispheric midlatitude station in 1992 and 1993 and was correlated with observed enhancements in sulfate-aerosol surface areas, pointing towards a causal link.

- Observations indicate that the eruption of Mt. Pinatubo did not significantly increase the HCl content of the stratosphere.

- The recent large ozone changes at midlatitudes are highly likely to have been due, at least in part, to the greatly increased sulfate aerosol in the lower stratosphere following Mt. Pinatubo. Observations and laboratory studies have demonstrated the importance of heterogeneous hydrolysis of N_2O_5 on sulfate aerosols in the atmosphere. Evidence suggests that $ClONO_2$ hydrolysis also occurs on sulfate aerosols under cold conditions. Both processes perturb the chemistry in such a way as to increase ozone loss through coupling with the anthropogenic chlorine and bromine loading of the stratosphere.

EXECUTIVE SUMMARY

- Global mean lower stratospheric temperatures showed a marked transitory rise of about 1°C following the eruption of Mt. Pinatubo in 1991, consistent with model calculations. The warming is likely due to absorption of radiation by the aerosols.

Polar Ozone Depletion

- In 1992 and 1993, the biggest-ever (areal extent) and deepest-ever (minimum ozone below 100 Dobson units) ozone "holes" were observed in the Antarctic. These extreme ozone depletions may have been due to the chemical perturbations caused by sulfate aerosols from Mt. Pinatubo, acting in addition to the well-recognized chlorine and bromine reactions on polar stratospheric clouds.

- Recent results of observational and modeling studies reaffirm the role of anthropogenic halocarbon species in Antarctic ozone depletion. Satellite observations show a strong spatial and temporal correlation of ClO abundances with ozone depletion in the Antarctic vortex. In the Arctic winter, a much smaller ozone loss has been observed. These losses are both consistent with photochemical model calculations constrained with observations from *in situ* and satellite instruments.

- Extensive new measurements of HCl, ClO, and $ClONO_2$ from satellites and *in situ* techniques have confirmed the picture of the chemical processes responsible for chlorine activation in polar regions and the recovery from those processes, strengthening current understanding of the seasonal cycle of ozone depletion in both polar regions.

- New laboratory and field studies strengthen the confidence that reactions on sulfate aerosols can activate chlorine under cold conditions, particularly those in the polar regions. Under volcanically perturbed conditions when aerosols are enhanced, these processes also likely contribute to ozone losses at the edges of PSC formation regions (both vertical and horizontal) just outside of the southern vortex and in the Arctic.

- Satellite measurements have confirmed that the Arctic vortex is much less denitrified than the Antarctic, which is likely to be an important factor in determining the interhemispheric differences in polar ozone loss.

- Interannual variability in the photochemical and dynamical conditions of the vortices limits reliable predictions of future ozone changes in the polar regions, particularly in the Arctic.

Coupling Between Polar Regions and Midlatitudes

- Recent satellite observations of long-lived tracers and modeling studies confirm that, above 16 km, air near the center of the polar vortex is substantially isolated from lower latitudes, especially in the Antarctic.

- Erosion of the vortex by planetary-wave activity transports air from the vortex-edge region to lower latitudes. Nearly all observational and modeling studies are consistent with a time scale of 3 - 4 months to replace a substantial fraction of Antarctic vortex air. The importance of this transport to *in situ* chemical effects for midlatitude ozone loss remains poorly known.

- Air is readily transported between polar regions and midlatitudes below 16 km. The influence of this transport on midlatitude ozone loss has not been quantified.

Tropospheric Ozone

- There is observational evidence that tropospheric ozone (about 10% of the total-column ozone) has increased in the Northern Hemisphere (north of 20°N) over the past three decades. The upward trends are highly regional. They are smaller in the 1980s than in the 1970s and may be slightly negative at some locations. European measurements at surface sites also indicate a doubling in the lower-tropospheric ozone concentrations since earlier this century. At the South Pole, a decrease has been observed since the mid-1980s. Elsewhere in the Southern Hemisphere, there are insufficient data to draw strong inferences.

- There is strong evidence that ozone levels in the boundary layer over the populated regions of the Northern Hemisphere are enhanced by more than 50% due to photochemical production from anthropogenic precursors, and that export of ozone from North America is a significant source for the North Atlantic region during summer. It has also been shown that biomass burning is a significant source of ozone (and carbon monoxide) in the tropics during the dry season.

- An increase in UV-B radiation (*e.g.*, from stratospheric ozone loss) is expected to decrease tropospheric ozone in the background atmosphere, but, in some cases, it will increase production of ozone in the more polluted regions.

- Model calculations predict that a 20% increase in methane concentrations would result in tropospheric ozone increases ranging from 0.5 to 2.5 ppb in the tropics and the northern midlatitude summer, and an increase in the methane residence time to about 14 years (a range of 12 - 17 years). Although there is a high degree of consistency in the global transport of short-lived tracers within three-dimensional chemical-transport models, and a general agreement in the computation of photochemical rates affecting tropospheric ozone, many processes controlling tropospheric ozone are not adequately represented or tested in the models, hence limiting the accuracy of these results.

Trends in Source Gases Relating to Ozone Changes

- CFCs, carbon tetrachloride, methyl chloroform, and the halons are major anthropogenic source gases for stratospheric chlorine and bromine, and hence stratospheric ozone destruction. Observations from several monitoring networks worldwide have demonstrated slowdowns in growth rates of these species that are consistent (except for carbon tetrachloride) with expectations based upon recent decreases in emissions. In addition, observations from several sites have revealed accelerating growth rates of the CFC substitutes, HCFC-22, HCFC-141b, and HCFC-142b, as expected from their increasing use.

- Methane levels in the atmosphere affect tropospheric and stratospheric ozone levels. Global methane increased by 7% over about the past decade. However, the 1980s were characterized by slower growth rates, dropping from approximately 20 ppb per year in 1980 to about 10 ppb per year by the end of the decade. Methane growth rates slowed dramatically in 1991 and 1992, but the very recent data suggest that they have started to increase in late 1993. The cause(s) of this behavior are not known, but it is probably due to changes in methane sources rather than sinks.

- Despite the increased methane levels, the total amount of carbon monoxide in today's atmosphere is less than it was a decade ago. Recent analyses of global carbon monoxide data show that tropospheric levels grew from the early 1980s to about 1987 and have declined from the late 1980s to the present. The cause(s) of this behavior have not been identified.

Consequences of Ozone Changes

- The only general circulation model (GCM) simulation to investigate the climatic impacts of observed ozone depletions between 1970 and 1990 supports earlier suggestions that these depletions reduced the model-predicted warming due to well-mixed greenhouse gases by about 20%. This is consistent with radiative forcing calculations.

- Model simulations suggest that increases in tropospheric ozone since pre-industrial times may have made significant contributions to the greenhouse forcing of the Earth's climate system, enhancing the current total forcing by about 20% compared to that arising from the changes in the well-mixed greenhouses gases over that period.

- Large increases in ultraviolet (UV) radiation have been observed in association with the ozone hole at high southern latitudes. The measured UV enhancements agree well with model calculations.

- Clear-sky UV measurements at midlatitude locations in the Southern Hemisphere are significantly larger than at a corresponding site in the Northern Hemisphere, in agreement with expected differences due to ozone column and Sun-Earth separation.

- Local increases in UV-B were measured in 1992/93 at mid- and high latitudes in the Northern Hemisphere. The spectral signatures of the enhancements clearly implicate the anomalously low ozone observed in those years, rather than variability of cloud cover or tropospheric pollution. Such correlations add confidence to the ability to link ozone changes to UV-B changes over relatively long time scales.

- Increases in clear-sky UV over the period 1979 to 1993 due to observed ozone changes are calculated to be greatest at short wavelengths and at high latitudes. Poleward of 45°, the increases are greatest in the Southern Hemisphere.

- Uncertainties in calibration, influence of tropospheric pollution, and difficulties of interpreting data from broadband instruments continue to preclude the unequivocal identification of long-term UV trends. However, data from two relatively unpolluted sites do appear to show UV increases consistent with observed ozone trends. Given the uncertainties of these studies, it now appears that quantification of the natural (*i.e.*, pre-ozone-reduction) UV baseline has been irrevocably lost at mid- and high latitudes.

- Scattering of UV radiation by stratospheric aerosols from the Mt. Pinatubo eruption did not alter total surface-UV levels appreciably.

Related Phenomena and Issues

Methyl Bromide

- Three potentially major anthropogenic sources of methyl bromide have been identified: (i) soil fumigation: 20 to 60 ktons per year, where new measurements reaffirm that about 50% (ranging from 20 - 90%) of the methyl bromide used as a soil fumigant is released into the atmosphere; (ii) biomass burning: 10 to 50 ktons per year; and (iii) the exhaust of automobiles using leaded gasoline: 0.5 to 1.5 ktons per year or 9 to 22 ktons per year (the two studies report emission factors that differ by a factor of more than 10). In addition, the one known major natural source of methyl bromide is oceanic, with emissions of 60 to 160 ktons per year.

- Recent measurements have confirmed that there is more methyl bromide in the Northern Hemisphere than in the Southern Hemisphere, with an interhemispheric ratio of 1.3.

- There are two known sinks for atmospheric methyl bromide: (i) atmospheric, with a lifetime of 2.0 years (1.5 to 2.5 years); and (ii) oceanic, with an estimated lifetime of 3.7 years (1.5 to 10 years). The overall best estimate for the lifetime of atmospheric methyl bromide is 1.3 years, with a range of 0.8 to 1.7 years. An overall lifetime of less than 0.6 years is thought to be highly unlikely because of constraints imposed by the observed interhemispheric ratio and total known emissions.

- The chemistry of bromine-induced stratospheric ozone destruction is now better understood. Laboratory measurements have confirmed the fast rate for the BrO + HO_2 reaction and have established a negligible reaction pathway producing HBr, both of which imply greater ozone losses due to emissions of compounds containing bromine. Stratospheric measurements show that the abundance of HBr is less than 1 ppt.

- Bromine is estimated to be about 50 times more efficient than chlorine in destroying stratospheric ozone on a per-atom basis. The ODP for methyl bromide is calculated to be about 0.6, based on an overall lifetime of 1.3 years. An uncertainty analysis suggests that the ODP is unlikely to be less than 0.3.

Aircraft

- Subsonics: Estimates indicate that present subsonic aircraft operations may be significantly increasing trace species (primarily NO_x, sulfur dioxide, and soot) at upper-tropospheric altitudes in the North-Atlantic flight corridor. Models indicate that the NO_x emissions from the current subsonic fleet produce upper-tropospheric ozone increases as much as several percent, maximizing at northern midlatitudes. Since the results of these rather complex models depend critically on NO_x chemistry and since the tropospheric NO_x budget is uncertain, little confidence should be put in these quantitative model results at the present time.

- Supersonics: Atmospheric effects of supersonic aircraft depend on the number of aircraft, the altitude of operation, the exhaust emissions, and the background chlorine and aerosol loadings. Projected fleets of supersonic transports would lead to significant changes in trace-species concentrations, especially in the North-Atlantic flight corridor. Two-dimensional model calculations of the impact of a projected fleet (500 aircraft, each emitting 15 grams of NO_x per kilogram of fuel burned at Mach 2.4) in a stratosphere with a chlorine loading of 3.7 ppb, imply additional (*i.e.*, beyond those from halocarbon losses) annual-average ozone column decreases of 0.3 - 1.8% for the Northern Hemisphere. There are, however, important uncertainties in these model results, especially in the stratosphere below 25 km. The same models fail to reproduce the observed ozone trends in the stratosphere below 25 km between 1980 and 1990. Thus, these models may not be properly including mechanisms that are important in this crucial altitude range.

- Climate Effects: Reliable quantitative estimates of the effects of aviation emissions on climate are not yet available. Some initial estimates indicate that the climate effects of ozone changes resulting from subsonic aircraft emissions may be comparable to those resulting from their CO_2 emissions.

Ozone Depletion Potentials (ODPs)

- If a substance containing chlorine or bromine decomposes in the stratosphere, it will destroy some ozone. HCFCs have short tropospheric lifetimes, which tends to reduce their impact on stratospheric ozone as compared to CFCs and halons. However, there are substantial differences in ODPs among various substitutes. The steady-state ODPs of substitute compounds considered in the present assessment range from about 0.01 - 0.1.

- Tropospheric degradation products of CFC substitutes will not lead to significant ozone loss in the stratosphere. Those products will not accumulate in the atmosphere and will not significantly influence the ODPs and Global Warming Potentials (GWPs) of the substitutes.

- Trifluoroacetic acid, formed in the atmospheric degradation of HFC-134a, HCFC-123, and HCFC-124, will enter into the aqueous environment, where biological, rather than physico-chemical, removal processes may be effective.

- It is known that atomic fluorine (F) itself is not an efficient catalyst for ozone loss, and it is concluded that the F-containing fragments from the substitutes (such as CF_3O_x) also have negligible impact on ozone. Therefore, ODPs of HFCs containing the CF_3 group (such as HFC-134a, HFC-23, and HFC-125) are likely to be much less than 0.001.

- New laboratory measurements and associated modeling studies have confirmed that perfluorocarbons and sulfur hexafluoride are long-lived in the atmosphere and act as greenhouse gases.

- The ODPs for several new compounds, such as HCFC-225ca, HCFC-225cb, and CF_3I, have been evaluated using both semi-empirical and modeling approaches, and are found to be 0.03 or less.

Global Warming Potentials (GWPs)

- Both the direct and indirect components of the GWP of methane have been estimated using model calculations. Methane's influence on the hydroxyl radical and the resulting effect on the methane response time lead to substantially longer response times for decay of emissions than OH removal alone, thereby increasing the GWP. In addition, indirect effects including production of tropospheric ozone and stratospheric water vapor were considered and are estimated to range from about 15 to 45% of the total GWP (direct plus indirect) for methane.

- GWPs, including indirect effects of ozone depletion, have been estimated for a variety of halocarbons, clarifying the relative radiative roles of ozone-depleting compounds (*i.e.*, CFCs and halons). The net GWPs of halocarbons depend strongly upon the effectiveness of each compound for ozone destruction; the halons are highly likely to have negative net GWPs, while those of the CFCs are likely to be positive over both 20- and 100-year time horizons.

Implications for Policy Formulation

The research findings of the past few years that are summarized above have several major implications as scientific input to governmental, industrial, and other policy decisions regarding human-influenced substances that lead to depletion of the stratospheric ozone layer and to changes of the radiative forcing of the climate system:

- **The Montreal Protocol and its Amendments and Adjustments are reducing the impact of anthropogenic halocarbons on the ozone layer and should eventually eliminate this ozone depletion.** Based on assumed compliance with the amended Montreal Protocol *(Copenhagen, 1992)* by all nations, the stratospheric chlorine abundances will continue to grow from their current levels (3.6 ppb) to a peak of about 3.8 ppb around the turn of the century. The future total bromine loading will depend upon choices made regarding future human production and emissions of methyl bromide. After around the turn of the century, the levels of stratospheric chlorine and bromine will begin a decrease that will continue into the 21st and 22nd centuries. The rate of decline is dictated by the long residence times of the CFCs, carbon tetrachloride, and halons. Global ozone losses and the Antarctic ozone "hole" were first discernible in the late 1970s and are predicted to recover in about the year 2045, other things being equal. The recovery of the ozone layer would have been impossible without the Amendments and Adjustments to the original Protocol *(Montreal, 1987)*.

- **Peak global ozone losses are expected to occur during the next several years.** The ozone layer will be most affected by human-influenced perturbations and susceptible to natural variations in the period around the year 1998, since the peak stratospheric chlorine and bromine abundances are expected to occur then. Based on extrapolation of current trends, observations suggest that the maximum ozone loss, relative to the late 1960s, will likely be:

  (i) about 12 - 13% at Northern midlatitudes in winter/spring (*i.e.*, about 2.5% above current levels);
  (ii) about 6 - 7% at Northern midlatitudes in summer/fall (*i.e.*, about 1.5% above current levels); and
  (iii) about 11% (with less certainty) at Southern midlatitudes on a year-round basis (*i.e.*, about 2.5% above current levels).

  Such changes would be accompanied by 15%, 8%, and 13% increases, respectively, in surface erythemal radiation, if other influences such as clouds remain constant. Moreover, if there were to be a major volcanic eruption like that of Mt. Pinatubo, or if an extremely cold and persistent Arctic winter were to occur, then the ozone losses and UV increases could be larger in individual years.

- **Approaches to lowering stratospheric chlorine and bromine abundances are limited.** Further controls on ozone-depleting substances would not be expected to significantly change the timing or the magnitude of the peak stratospheric halocarbon abundances and hence peak ozone loss. However, there are four approaches that would steepen the initial fall from the peak halocarbon levels in the early decades of the next century:

  (i) If emissions of methyl bromide from agricultural, structural, and industrial activities were to be eliminated in the year 2001, then the integrated effective future chlorine loading above the 1980 level (which is related to the cumulative future loss of ozone) is predicted to be 13% less over the next 50 years relative to full compliance to the Amendments and Adjustments to the Protocol.
  (ii) If emissions of HCFCs were to be totally eliminated by the year 2004, then the integrated effective future chlorine loading above the 1980 level is predicted to be 5% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.
  (iii) If halons presently contained in existing equipment were never released to the atmosphere, then the integrated effective future chlorine loading above the 1980 level is predicted to be 10% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.
  (iv) If CFCs presently contained in existing equipment were never released to the atmosphere, then the integrated effective future chlorine loading above the 1980 level is predicted to be 3% less over the next 50 years relative to full compliance with the Amendments and Adjustments to the Protocol.

- **Failure to adhere to the international agreements will delay recovery of the ozone layer.** If there were to be additional production of CFCs at 20% of 1992 levels for each year through 2002 and ramped to zero by 2005 (beyond that allowed for countries operating under Article 5 of the Montreal Protocol), then the integrated effective future chlorine loading above the 1980 level is predicted to be 9% more over the next 50 years relative to full compliance to the Amendments and Adjustments to the Protocol.

- **Many of the substitutes for the CFCs and halons are also notable greenhouse gases.** Several CFC and halon substitutes are not addressed under the Montreal Protocol (because they do not deplete ozone), but, because they are greenhouse gases, fall under the purview of the Framework Convention on Climate Change. There is a wide range of values for the Global Warming Potentials (GWPs) of the HFCs (150 - 10000), with about half of them having values comparable to the ozone-depleting compounds they replace. The perfluorinated compounds, some of which are being considered as substitutes, have very large GWPs (*e.g.*, 5000 - 10000). These are examples of compounds whose current atmospheric abundances are relatively small, but are increasing or could increase in the future.

- **Consideration of the ozone change will be one necessary ingredient in understanding climate change.** The extent of our ability to attribute any climate change to specific causes will likely prove to be important scientific input to decisions regarding predicted human-induced influences on the climate system. Changes in ozone since pre-industrial times as a result of human activity are believed to have been a significant influence on radiative forcing; this human influence is expected to continue into the foreseeable future.

PART 1

Observed Changes in Ozone and Source Gases

Chapter 1
Ozone Measurements

Chapter 2
Source Gases:
Trends and Budgets

PART 2

Atmospheric Processes Responsible for the Observed Changes in Ozone

Chapter 3
Polar Ozone

Chapter 4
Tropical and Midlatitude Ozone

Chapter 5
Tropospheric Ozone

PART 3

Model Simulations of Global Ozone

Chapter 6
Model Simulations of Stratospheric Ozone

Chapter 7
Model Simulations of Global Tropospheric Ozone

PART 4

CONSEQUENCES OF OZONE CHANGE

Chapter 8
Radiative Forcing and Temperature Trends

Chapter 9
Surface Ultraviolet Radiation

PART 5

Scientific Information for Future Decisions

Chapter 10
Methyl Bromide

Chapter 11
Subsonic and Supersonic Aircraft Emissions

Chapter 12
Atmospheric Degradation of Halocarbon Substitutes

Chapter 13
Ozone Depletion Potentials, Global Warming Potentials, and Future Chlorine/Bromine Loading