

**World Meteorological Organization  
Ozone Secretariat  
41 Avenue Giuseppe Motta  
P.O. Box 2300  
Geneva 20, CH 1211 Switzerland**

**United Nations Environment Program  
United Nations Headquarters  
Ozone Secretariat  
P.O. Box 30552  
Nairobi, Kenya**

**United Kingdom Department of the Environment  
43 Marsham Street  
London, SW1P 3PY  
United Kingdom**

**U.S. Department of Commerce  
National Oceanic and Atmospheric Administration  
14th Street and Constitution Avenue, NW  
Hoover Building, Room 5128  
Washington, DC 20230  
USA**

**National Aeronautics and Space Administration  
Office of Space Science and Applications  
Earth Science and Applications Division  
Two Independence Square  
300 E Street, SW  
Washington, DC 20546  
USA**

WORLD METEOROLOGICAL ORGANIZATION  
GLOBAL OZONE RESEARCH AND MONITORING PROJECT—REPORT NO. 25

# **Scientific Assessment of Ozone Depletion: 1991**

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION  
UNITED KINGDOM DEPARTMENT OF THE ENVIRONMENT  
UNITED NATIONS ENVIRONMENT PROGRAM  
WORLD METEOROLOGICAL ORGANIZATION

# LIST OF INTERNATIONAL CONTRIBUTORS AND REVIEWERS

## Assessment Co-Chairs

Daniel L. Albritton and Robert T. Watson

## Chapter Coordinators

1: Paul Fraser	2: Richard S. Stolarski	3: Lamont R. Poole
4: William H. Brune	5: Ivar S. A. Isaksen	6: Susan Solomon
7: V. Ramaswamy	8: Michael J. Prather	9: Malcolm K. W. Ko
10: Charles H. Jackman	11: Richard L. McKenzie	

## Assessment Editors

Daniel L. Albritton • Robert T. Watson • Susan Solomon • Robert F. Hampson • Flo Ormond

## Authors, Contributors, and Reviewers

Daniel L. Albritton	US	V. Filyushkin	USSR
Fred N. Alyea	US	Vitali Fioletov	USSR
Roger Atkinson	US	Donald A. Fisher	US
John Austin	UK	John E. Frederick	US
T. Berntsen	Norway	Paul J. Fraser	Australia
Lane Bishop	US	A. Fried	US
Don Blake	US	J. A. Fuglestedt	Norway
M. Blumthaler	Austria	Sophie Godin	France
Rumen D. Bojkov	Switzerland	Keith Grant	US
Guy Brasseur	US	Robert F. Hampson	US
Christoph H. Brühl	Germany	Anne Hansson	Canada
William H. Brune	US	Neil Harris	UK
Bruce Callander	UK	Robert Harriss	US
Jack G. Calvert	US	Robert S. Harwood	UK
Daniel Cariolle	France	William Hill	US
Marie-Lise Chanin	France	Michio Hirota	Japan
William Chu	US	David J. Hofmann	US
Peter Connell	US	Abdel Moneim Ibrahim	Egypt
R. Anthony Cox	UK	Mohammad Ilyas	Malaysia
Paul J. Crutzen	Germany	Ivar Isaksen	Norway
Derek M. Cunnold	US	Charles H. Jackman	US
John DeLuisi	US	Evgeny A. Jadin	USSR
M. Ding	US	Colin Johnson	UK
Anne Douglass	US	Harols S. Johnston	US
Jae A. Edmonds	US	Rod L. Jones	UK
James W. Elkins	US	Igor L. Karol	USSR

Jack Kaye	US	F. Sherwood Rowland	US
James B. Kerr	Canada	Colin E. Roy	Australia
Leon F. Keyser	US	Nelson Antonio Sabogal	Colombia
Vyacheslav Khattatov	USSR	Eugenio Sanhueza	Venezuela
Jeffrey Kiehl	US	Toru Sasaki	Japan
Volker Kirchhoff	Brazil	H. Scheel	Germany
Dieter Kley	Germany	Mark R. Schoeberl	US
Malcolm K. W. Ko	US	M. D. Schwartzkopf	US
Charles E. Kolb	US	Wolfgang Seiller	Germany
Michael J. Kurylo	US	Keith Shine	UK
D. Lashof	US	Howard Sidebottom	Ireland
Yuan-Pern Lee	ROC	P. Simmonds	UK
Jane Leggett	US	Susan Solomon	US
Jos. Lelieveld	Germany	Johannes Staehelin	Switzerland
Conway B. Leovy	US	K. Stamnes	Germany
M.-T. Leu	US	Paul Steele	Australia
Pak Sum Low	Kenya	Richard S. Stolarski	US
Evgeny Lysenko	USSR	Frode Stordal	Norway
Sasha Madronich	US	Bhoganahalli Subbaraya	India
Yoshihiro Makide	Japan	A. Sutera	Italy
Andrew Matthews	New Zealand	L. W. Thomason	US
M. Patrick McCormick	US	Anne Thompson	US
Mack McFarland	US	Margaret A. Tolbert	US
Richard L. McKenzie	New Zealand	O. Brian Toon	US
Gèrard Mègie	France	Adrian F. Tuck	US
A. J. Miller	US	Richard Turco	US
Mario Molina	US	Guido Visconti	Italy
P. Muthusubramanian	India	Andreas Wahner	Germany
Paul Newman	US	Wei-Chyung Wang	US
Alan O'Neill	UK	David A. Warrilow	UK
Abraham Oort	US	Robert T. Watson	US
Michael Oppenheimer	US	Debra Weisenstein	US
D. C. Parashar	India	Ray F. Weiss	US
Stuart A. Penkett	UK	Tom Wigley	UK
M. C. Pitts	US	Steve Wofsy	US
Lamont R. Poole	US	Doug R. Worsnop	US
Michael J. Prather	US	Donald J. Wuebbles	US
Margarita Prendez	Chile	Ahmad Zand	Iran
Ronald G. Prinn	US	Rudi J. Zander	Belgium
John A. Pyle	UK	Joseph M. Zawodny	US
Lian Xiong Qiu	PRC	Christos Zerefos	Greece
V. Ramaswamy	US	Evgeny A. Zhadin*	USSR
Rei A. Rasmussen	US	Xiuji Zhou	PRC
A. R. Ravishankara	US	Ya-Hui Zhuang	Thailand
Henning Rodhe	Sweden	Sergei Zvenigorodsky	USSR
Jose M. Rodriguez	US		
Joan Rosenfield	US		

—  
•See Jadin

## Table of Contents

	<i>Page</i>
<b>Foreword</b> .....	ix
<b>Executive Summary</b> .....	xi
<b>Chapter 1 Source Gases: Concentrations, Emissions, and Trends</b>	
Scientific Summary .....	1.1
1.0 Introduction.....	1.3
1.2 CFCs and Carbon Tetrachloride: Global Distributions, Trends and Calibration .....	1.3
1.3 Methyl Chloroform and HCFC-22.....	1.11
1.4 Other Chlorinated Species.....	1.15
1.5 Halons and Other Brominated Species .....	1.15
1.6 Carbonyl Sulphide .....	1.16
1.7 Nitrous Oxide.....	1.16
1.8 Methane.....	1.19
1.9 Hydrogen.....	1.25
1.10 Carbon Monoxide .....	1.25
1.11 Non-Methane Hydrocarbons.....	1.30
1.12 Carbon Dioxide.....	1.31
<b>Chapter 2 Ozone and Temperature Trends</b>	
Scientific Summary .....	2.1
2.1 Introduction.....	2.3
2.2 Instruments.....	2.3
2.3 Observed Trends .....	2.4
2.4 Summary .....	2.31
<b>Chapter 3 Heterogeneous Processes: Laboratory, Field, and Modeling Studies</b>	
Scientific Summary .....	3.1
3.1 Introduction.....	3.3
3.2 Laboratory Measurements.....	3.3
3.3 Polar Stratospheric Cloud Characteristics and Climatology.....	3.6
3.4 Stratospheric Sulfate Aerosols .....	3.4
3.5 Evidence for Heterogeneous Processes in the Stratosphere.....	3.5

10

## **Chapter 4 Stratospheric Processes: Observations and Interpretation**

Scientific Summary .....	4.1
4.1 Introduction .....	4.3
4.2 Antarctic Ozone Depletion .....	4.3
4.3 The Perturbed Chemistry and Ozone Loss in the Arctic .....	4.6
4.4 Ozone Depletion at Middle Latitudes .....	4.9
4.5 Bromine Photochemistry .....	4.15
4.6 Effects of Volcanic Eruptions on Ozone .....	4.15

## **Chapter 5 Tropospheric Processes: Observations and Interpretation**

Scientific Summary .....	5.1
5.1 Introduction .....	5.3
5.2 Processes Controlling Tropospheric O <sub>3</sub> and OH .....	5.3
5.3 Complexities in O <sub>3</sub> and OH Predictions .....	5.5
5.4 Recent Developments in Processes Affecting O <sub>3</sub> and OH .....	5.5
5.5 Modeling Tropospheric Ozone Changes .....	5.8
5.6 Tropospheric Degradations of HFCs and HCFCs .....	5.15
Conclusions .....	5.21

## **Chapter 6 Ozone Depletion and Chlorine Loading Potentials**

Scientific Summary .....	6.1
6.1 Introduction .....	6.3
6.2 Model Calculations of CLPs and ODPs .....	6.4
6.3 Comparison of Modeled ODPs and Inferences from Observations .....	6.11
6.4 Time Dependent Effects .....	6.15

## **Chapter 7 Radiative Forcing of Climate**

Scientific Summary .....	7.1
7.1 Introduction .....	7.3
7.2 Radiative Forcing .....	7.3
7.3 Global Warming Potential .....	7.4
7.4 Radiative Forcings Due to Non-Ozone Trace Gases (1979-1990) .....	7.9
7.5 Radiative Forcing Due to Ozone (1979-1990) .....	7.11
7.6 Radiative Forcing Due to Tropospheric Sulfate Aerosols .....	7.24
7.7 Radiative Forcing Due to Stratospheric Aerosols .....	7.26

## **Chapter 8 Future Chlorine-Bromine Loading and Ozone Depletion**

Scientific Summary .....	8.1
8.1 Introduction .....	8.5
8.2 Atmospheric Composition and Chemistry.....	8.5
8.3 The Currently Observed Atmosphere: 1980–1990 .....	8.14
8.4 Predicting the Future Atmosphere: 1990–2050.....	8.33
8.5 Options and Issues to 2100.....	8.46

## **Chapter 9 Predicted Aircraft Effects on Stratospheric Ozone**

Scientific Summary .....	9.1
9.1 Introduction.....	9.3
9.2 Impact of Aircraft Operation on Atmospheric Trace Gases .....	9.3
9.3 Model Studies of Ozone Response .....	9.5

## **Chapter 10 Predicted Rocket and Shuttle Effects on Stratospheric Ozone**

Scientific Summary .....	10.1
10.1 Introduction.....	10.3
10.2 The Exhaust Plume.....	10.3
10.3 Local and Regional Effects .....	10.5
10.4 Global Scale Effects.....	10.8
10.5 Effects of Particulates .....	10.10
10.6 Conclusions.....	10.10

## **Chapter 11 Ultraviolet Radiation Changes**

Scientific Summary .....	11.1
11.1 UV Measurements and Analyses .....	11.3
11.2 Changes in Ultraviolet Radiation Based on Measured and Computed Ozone Amounts....	11.11

## **Appendices**

A List Of International Contributors and Reviewers .....	A.1
B List of Figures .....	B.1
C List of Tables.....	C.1
D Major Acronyms and Abbreviations.....	D.1
E Chemical Formulae and Nomenclature .....	E.1

## FOREWORD

The Montreal Protocol on Substances that Deplete the Ozone Layer entered into force on 1 January 1989. Article 6 of the Protocol: Assessment and Review of Control Measures requires that

“Beginning in 1990, and at least every four years thereafter, the Parties shall assess the control measures provided for in Article 2 on the basis of available scientific, environmental, technical, and economic information. At least one year before each assessment, the Parties shall convene appropriate panels of experts qualified in the fields mentioned and determine the composition and terms of reference of any such panels. Within one year of being convened, the panels will report their conclusions, through the Secretariat, to the Parties.”

The second meeting of the Protocol Parties in London, U.K., in June 1990, asked the Secretariat to reconvene, provided for in Article 6, the assessment panels and outlined their terms of reference and timetables for completing assessments of available scientific, environmental, technology and economic information. In particular, the Parties requested that the Scientific assessment panel include an evaluation of the Ozone Depleting Potentials (ODPs) and Global Warming Potentials (GWPs) of substitutes; ODPs of “other halons” that might be produced in significant quantities; the impact on the ozone layer of revised control measures; and the impact on the ozone layer of engine emissions from high-altitude aircraft, rockets and space shuttles. The Parties also requested that the Technology and Economic panels assess the earliest technically feasible dates and the costs for reductions and total phaseout of 1,1,1-trichloroethane (methylchloroform); evaluation of the need for transitional substances in specific applications; quantity of controlled substances needed by developing countries and availability; and comparison of toxicity, flammability, energy efficiency and safety considerations of chemical substitutes and their availability.

At the third meeting of the Protocol Parties in Nairobi, Kenya, in June 1991, the merged Technology and Economic panel was requested to produce a list of full and complete trade names of substances including mixtures by November 1991; to evaluate the implications, possibilities, and difficulties, in particular for developing countries, of an earlier phaseout of controlled substances, for example by 1997; to identify the areas where transitional substances are required to facilitate the earliest possible phaseout of controlled substances and the quantities of transitional substances required; and to identify those transitional substances with the lowest ODPs required for those areas with, if possible, a feasible timetable for their elimination.

The reports of the assessment panels represent the judgement of several hundred experts of appropriate disciplines from developed and developing countries<sup>1</sup>. The reports of each of the three panels incorporated an extensive peer-review process in their original language (English). They will be published and distributed by UNEP in late 1991/early 1992. Copies will be made available to Parties to the Vienna Convention and Montreal Protocol; all other member states of the United Nations; and to interested organizations, institutions, and individuals worldwide.

<sup>1</sup> Australia, Austria, Bahamas, Belgium, Benin, Brazil, Canada, Chile, China, Columbia, Czechoslovakia, Denmark, Ecuador, Egypt, France, Germany, Greece, India, Indonesia, Iran, Ireland, Italy, Japan, Jordan, Kenya, Liechtenstein, Malaysia, Mexico, Netherlands, New Zealand, Nigeria, Norway, Papua New Guinea, Saudi Arabia, Singapore, South Africa, South Korea, Sweden, Switzerland, Thailand, Trinidad and Tobago, Tunisia, Uganda, USSR, United Kingdom, United States of America, Venezuela, and Yugoslavia.



The panel reports were chaired as follows:

- The Report of the Ozone Scientific Assessment Panel, chaired by Dr. Robert Watson and Dr. Daniel Albritton (United States of America). One hundred forty-three scientists from 28 countries contributed to the preparation and review of this report (129 scientists from 27 countries prepared the report, and 79 scientists from 25 countries participated in the peer review process).
- The Report of the Environmental Effects Assessment Panel, chaired by Dr. Jan van der Leun (Netherlands) and Dr. Manfred Tevini (Germany). Fifty-eight scientists from 22 countries participated in the preparation and peer review of the report (22 scientists from nine countries prepared the report, and 36 scientists from 18 countries peer reviewed the report).
- The Report of the Technology and Economic Assessment Panel, chaired by Dr. Stephen Andersen (United States of America) and Mr. Steve Lee-Bapty (United Kingdom). Two hundred forty experts from 38 countries prepared the report. Hundreds of expert advisors and peer reviewers from additional countries participated in the peer review process. The Technology and Economic review panel report is a summary of six detailed Technical and Economic Options reports prepared by international subcommittees of sector specific experts. The six technical reports are: (i) Refrigeration, Air Conditioning and Heat Pumps, chaired by Dr. L. Kuijpers (The Netherlands), Dr. H. Haukas (Norway), Mr. P. Vodianitskaia (Brazil) and Mr. J. Kanyua (Kenya); (ii) Rigid and Flexible Foams, chaired by Ms. J. Lupinacci (US) and Mr. P. Vieira (Brazil); (iii) Solvents, Coatings, and Adhesives, chaired by Dr. S. Andersen (US) and Mr. J. Corona (Mexico); (iv) Aerosols, Sterilants and Miscellaneous Uses of CFCs, chaired by Ms. A. Hinwood (Australia) and Mr. J. Pons Pons (Venezuela); (v) Halon Fire Extinguishing Agents, chaired by Mr. G. Taylor (Canada) and Major T. Morehouse (US); and (vi) Economics, chaired by Dr. R. Van Slooten (UK) and Mrs. M. Holmes-Hanek (Bahamas).

## EXECUTIVE SUMMARY OF THE SCIENTIFIC ASSESSMENT OF OZONE DEPLETION

### RECENT MAJOR SCIENTIFIC FINDINGS

Over the past few years, there have been highly significant advances in the understanding of the impact of human activities on the Earth's stratospheric ozone layer and the influence of changes in chemical composition on the radiative balance of the climate system. Specifically, since the last international scientific review (1989), there have been five major advances:

- **Global Ozone Decreases:** Ground-based and satellite observations continue to show decreases of total column ozone in winter in the Northern Hemisphere. For the first time, there is evidence of significant decreases in *spring and summer* in both the Northern and Southern Hemispheres at middle and high latitudes, as well as in the southern winter. No trends in ozone have been observed in the tropics. These downward trends were larger during the 1980s than in the 1970s. The observed ozone decreases have occurred predominantly in the *lower* stratosphere.
- **Polar Ozone:** Strong Antarctic ozone holes have continued to occur and, in 4 of the past 5 years, have been deep and extensive in area. This contrasts to the situation in the mid-1980s, where the depth and area of the ozone hole exhibited a quasi-biennial modulation. Large increases in surface ultraviolet radiation have been observed in Antarctica during periods of low ozone. While no extensive ozone losses have occurred in the Arctic comparable to those observed in the Antarctic, localized Arctic ozone losses have been observed in winter concurrent with observations of elevated levels of reactive chlorine.
- **Ozone and Industrial Halocarbons:** Recent laboratory research and reinterpretation of field measurements have strengthened the evidence that the Antarctic ozone hole is primarily due to chlorine- and bromine-containing chemicals. In addition, the weight of evidence suggests that the observed middle- and high-latitude ozone losses are largely due to chlorine and bromine. Therefore, as the atmospheric abundances of chlorine and bromine increase in the future, significant additional losses of ozone are expected at middle latitudes and in the Arctic.
- **Ozone and Climate Relations:** For the first time, the observed global lower-stratospheric ozone depletions have been used to calculate the changes in the radiative balance of the atmosphere. The results indicate that, over the last decade, the observed ozone depletions would have tended to cool the lower stratosphere at middle and high latitudes. Temperature data suggest that some cooling indeed has taken place there. The observed lower-stratospheric ozone changes and calculated temperature changes would have caused a decrease in the radiative forcing of the surface-troposphere system in the middle to high latitudes that is larger in magnitude than that predicted for the chlorofluorocarbon (CFC) increases over the last decade. In addition, the ozone depletion may indeed have offset a significant fraction of the radiative forcing due to increases of all greenhouse gases over the past decade.
- **Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs):** A new semi-empirical, observation-based method of calculating ODPs has better quantified the role of polar processes in this index. In addition, the direct GWPs for tropospheric, well-mixed, radiatively-active species have been recalculated. However, because of the incomplete understanding of tropospheric chemical processes, the indirect GWP of methane has not, at present, been quantified reliably. Furthermore, the concept of a GWP may prove inapplicable for the very short-lived, inhomogeneously mixed gases, such as the nitrogen oxides. Hence, many of the indirect GWPs reported in 1990 by the Intergovernmental Panel on Climate Change (IPCC) are likely to be incorrect.

## SUPPORTING EVIDENCE AND RELATED ISSUES

### Global Ozone

- Independent observations from the ground-based Dobson and M83/M124 instruments and the Total Ozone Mapping Spectrometer (TOMS) satellite instrument all show, for the first time, that there are significant decreases in total-column ozone, after accounting for known natural variability, in winter and now in spring and summer in both the Northern and Southern Hemispheres at middle and high latitudes, but not in the tropics. The following table illustrates some of these points.

**Total Ozone Trends (percent per decade with 95 percent confidence limits)**

Season	TOMS: 1979-91			Ground-based: 26°N-64°N	
	45°S	Equator	45°N	1979-1991	1970-1991
Dec-Mar	-5.2 ± 1.5	+0.3 ± 4.5	-5.6 ± 3.5	-4.7 ± 0.9	-2.7 ± 0.7
May-Aug	-6.2 ± 3.0	+0.1 ± 5.2	-2.9 ± 2.1	-3.3 ± 1.2	-1.3 ± 0.4
Sep-Nov	-4.4 ± 3.2	+0.3 ± 5.0	-1.7 ± 1.9	-1.2 ± 1.6	-1.2 ± 0.6

- There is strong *combined* observational evidence from balloonsondes, ground-based Umkehr, and the Stratospheric Aerosol and Gas Experiment (SAGE) satellite instruments that, over the past decade, annual average ozone has decreased in the middle- and high-latitude stratosphere below 25 km (about 10 percent near 20 km).
- Ozone losses in the upper stratosphere have been observed by ground-based Umkehr and SAGE satellite instruments. Changes in the shape of the vertical distribution of ozone near 40 km are qualitatively consistent with theoretical predictions but are smaller in magnitude.
- Measurements indicate that ozone levels in the troposphere up to 10 km above the few existing balloonsonde stations at northern middle latitudes have increased by about 10 percent per decade over the past two decades. However, the data base for ozone trends in the upper troposphere, where it is an effective greenhouse gas, is sparse and inadequate for quantifying its contribution to the global radiative balance. It should be noted that the response of ozone in the upper troposphere is particularly sensitive to oxides of nitrogen injected by aircraft.
- The temperature record indicates that a small cooling (about 0.3°C per decade, globally averaged) has occurred in the lower stratosphere over the last two decades, which is in the sense of that expected from the observed ozone change.
- Increases continue in the atmospheric abundances of source gases that affect ozone and the radiative balance. Although methane has continued to increase in the atmosphere, the rate of increase has slowed, for reasons that are not understood. Methyl bromide is the major contributor to stratospheric bromine (15 parts per trillion by volume or pptv). The sources of methyl bromide are not well characterized; however, significant anthropogenic emissions have been suggested.
- Recent laboratory studies have identified key heterogeneous reactions and have allowed a more quantitative assessment of the role of global stratospheric sulfate aerosols in leading to enhanced abundances of reactive chlorine species.
- Limited observations suggest that the abundance of chlorine monoxide (ClO) in the lower stratosphere at northern middle latitudes is greater than that predicted by models containing only currently known gas phase chemistry, and the observed seasonal and latitudinal dependences are inconsistent with those pre-

dicted. Some new studies that incorporate currently known heterogeneous processes provide an improved simulation for some observed gases, such as ClO and nitric acid.

- Present models containing only gas phase processes cannot simulate the observed seasonal ozone depletions at middle and high latitudes. However, models incorporating currently known heterogeneous processes on sulfate aerosols predict substantially greater ozone depletion (*e.g.*, a factor of 2 to 3 at middle latitudes) from chlorine and bromine compounds compared to models containing only gas phase processes. Indeed, the heterogeneous models simulate most of the observed trend of column ozone in middle latitudes in summer but only about half of that in winter.
- There is not a full accounting of the observed downward trends in global ozone. Plausible mechanisms include (i) local heterogeneous chemistry on stratospheric sulfate aerosols (as evidenced by, for example, elevated levels of ClO and the presence of sulfate aerosols at the altitudes of the observed ozone depletion) and (ii) the transport of both ozone-depleted and chemically perturbed polar air to middle latitudes (as evidenced by high levels of reactive chlorine and low levels of reactive nitrogen, which are characteristic of chemically perturbed polar air). Although other possible mechanisms cannot be ruled out, those involving chlorine and bromine appear to be largely responsible for the ozone loss and are the only ones for which direct evidence exists.
- Since the middle latitude ozone losses are apparently due in large part to chlorine and bromine, greater ozone losses are expected as long as the atmospheric levels of these compounds continue to increase. With the increases in the levels of chlorine and bromine that are estimated for the year 2000, the additional ozone losses during the 1990s are expected to be comparable to those already observed for the 1980s.
- There are numerous ways in which further increases in stratospheric halogen abundances can be reduced. The following table illustrates the effects of reducing the emissions of several types of halocarbons. Four aspects are shown: (i) the change in peak chlorine loading, (ii) the times at which chlorine abundances have decreased back to 2 parts per billion by volume (ppbv) (the abundance in the late 1970s, which is when the Antarctic ozone hole started and when the accelerated trends in total-column ozone losses in the Northern Hemisphere began), (iii) the times at which chlorine abundances have decreased back to 3 ppbv (the abundance in the middle to late 1980s), and (iv) a measure of the cumulative ozone loss for the time period that the chlorine levels are above 3 ppbv. All of the values in the table are relative to the reference scenario (AA).
- Stratospheric bromine is 30 to 120 times more efficient than stratospheric chlorine in destroying ozone on a per atom basis. Therefore, 1 pptv of stratospheric bromine is equivalent to 0.03–0.12 ppbv of stratospheric chlorine.

### Scenarios for Reducing Chlorine Emissions

Scenario	Peak Cl (ppbv)	Years at 3 ppbv	Years at 2 ppbv	Integral (Cl>3 ppbv)
AA	4.1	2027	2060	22.7
AA3	-0.18	-10 yrs	-7	-7.6
D	-0.03	0	0	-1.3
D3	-0.10	0	0	-2.9
E	0.00	-7	-3	-2.0*
E3	-0.03*	-10	-3	-4.4*
F20	+0.01	0	0	+0.8
F40	+0.02	+1	0	+1.5
G20	+0.01	+5	+2	+4.2
AA3 + D3	-0.21	-11	-7	-10.4

\*These values should be reduced by a factor of about 2 to 3 when evaluating ozone loss rather than chlorine loading.

#### Definitions of scenarios:

**AA: Montreal Protocol (10-year lag of 10 percent of CFCs plus CCl<sub>4</sub>; no lag for CH<sub>3</sub>CCl<sub>3</sub> and halons). HCFC-22 increases at 3 percent per year from 1991 to 2020, ramps to 0 by 2040. No substitution of CFCs with HCFCs.**

#### Nonsubstitution scenarios:

- AA3: 3-year acceleration of CFCs and CCl<sub>4</sub> schedules.
- D: 3-year acceleration of CH<sub>3</sub>CCl<sub>3</sub> schedule.
- D3: CH<sub>3</sub>CCl<sub>3</sub> on the accelerated CFC phase-out schedule.
- E: HCFC-22 ramp to zero between 2000 and 2020.
- E3: HCFC-22 on the accelerated CFC phase-out schedule.

#### Substitution scenarios:

HCFC substitutions: begin in 1995, no growth to 2000, 3 percent per year to 2020, ramp to zero by 2030. HCFC-A has a 2-year lifetime, one chlorine, and an ODP of 0.013; HCFC-B has a 20-year lifetime, one chlorine, and an ODP of 0.13.

- F20: 20 percent initial substitution, HCFC-A.
- F40: 40 percent initial substitution, HCFC-A.
- G20: 20 percent initial substitution, HCFC-B.

#### Polar Ozone

- The Antarctic ozone hole in 1991 was as deep and as extensive in area as those of 1987, 1989, and 1990. The low value of total-column ozone measured by TOMS in early October in 1991 was 110 Dobson units, which is a decrease of about 60 percent compared to the ozone levels prior to the late 1970s. The previously noted quasi-biennial modulation of the severity of the ozone hole did not occur during the past 3 years. This apparent lack of variability in recent years may imply that halogen chemistry is becoming dominant over dynamically induced fluctuations on Antarctic ozone depletion.
- Recent laboratory studies of heterogeneous processes, reevaluated field measurements, and modeling studies have strengthened the confidence that the cause of the Antarctic ozone hole is primarily chlorine and bromine emissions.

- High concentrations of ClO have been observed in winter in the Arctic stratosphere between 16 and 20 km. These observations have been incorporated into diagnostic models that have calculated localized ozone depletions of about 10 percent at these altitudes over a period of about a month, which are consistent with concurrent ozone measurements.

### Ozone-Climate Relations

- The ozone losses observed in the lower stratosphere over the last decade are predicted to have increased the visible and ultraviolet incoming solar radiation reaching the surface-troposphere system and decreased the downward infrared radiation reaching the surface-troposphere system. For models that allow for the temperature of the stratosphere to adjust to the loss of ozone, the net effect is a decrease in radiative forcing. For middle and high latitudes throughout the year, the magnitude of this decrease may be larger than the predicted increases in the radiative forcing due to the increased abundances of CFCs over the last decade. Indeed, this ozone-induced decrease in radiative forcing could be offsetting a significant fraction of the increased forcing attributed to the increases in the abundances of all greenhouse gases over the same period. Changes in the global annual average radiative forcing due to the observed ozone depletion are predicted to be comparable in magnitude, but opposite in sign, to those attributed to the CFCs over the last decade.
- Current tropospheric models exhibit large differences in their predictions of changes in ozone, the hydroxyl radical, and other chemically active gases due to emissions of methane, nonmethane hydrocarbons, carbon monoxide, and nitrogen oxides. This arises from uncertainties in the knowledge of background chemical composition and an inadequate understanding of chemical reactions and dynamical processes. Hence, these deficiencies limit the accuracy of predicted changes in the abundance and distribution of tropospheric ozone, which is a greenhouse gas, and in the lifetimes of a number of other greenhouse gases, including the HCFCs and HFCs, which depend upon the abundance of the hydroxyl radical.

### Ozone Depletion and Global Warming Potentials (ODPs and GWPs)

- Steady-state and time-dependent ODPs have been recalculated with improved models that have incorporated more accurate reaction rate coefficients and absorption cross sections and known heterogeneous processes on sulfate aerosols. The numerical values are generally similar to those in previous assessments.
- A new semi-empirical, observation-based method of calculating ODPs has been developed. The resulting values are generally larger (up to a factor of two as compared to some model-based estimates) for species with long stratospheric lifetimes (*e.g.*, HCFC-22 and HCFC-142b) and slightly smaller for species with short stratospheric lifetimes (*e.g.*, carbon tetrachloride and methyl chloroform). Since this approach utilizes more atmospheric observations and fewer model calculations in characterizing polar ozone losses, it is considered to be better than standard model ODPs, at least in the polar regions.
- The direct GWPs (with five different time horizons: 20, 50, 100, 200, and 500 years) for tropospheric, well-mixed, radiatively active species have been recalculated using updated lifetimes for methane, nitrous oxide, and the halocarbons and following the same methodology of IPCC (1990). With the exception of methane, new GWP results indicate only modest changes from the IPCC values, but uncertainties still exist in these calculations due to limitations in knowledge of the carbon cycle.
- Because of incomplete understanding of tropospheric chemical processes, the indirect GWP of methane has not been quantified reliably at the time of this report, although improvements and quantifications of uncertainties in the near future are highly likely. The signs of the net changes in radiative forcing from known indirect effects have been established for some of the trace gases: methane, carbon monoxide, and non-methane hydrocarbons, which are all positive. The sign of the changes in radiative forcing due to the nitro-

gen oxides cannot currently be established. Furthermore, the basic concept of a GWP may indeed prove to be inapplicable for the very short-lived, inhomogeneously mixed gases, such as the nitrogen oxides and the nonmethane hydrocarbons. Hence, the IPCC (1990) indirect GWPs are not only uncertain, but many are also likely to be incorrect (*e.g.*, for the nitrogen oxides).

### Related Issues

- **Ultraviolet Radiation:** Significant increases in ultraviolet radiation have been observed over Antarctica in conjunction with periods of intense ozone depletion. Under clear-sky conditions, these increases are consistent with theoretical predictions. Furthermore, a erythemal radiative amplification factor of  $1.25 \pm 0.20$  has been deduced from simultaneous measurements of column ozone and surface ultraviolet radiation at a clean air site, which is in agreement with a model-calculated value of 1.1. Therefore, for the first time, the response of ground-level ultraviolet radiation to changes in column ozone has been observed and quantified.
- **Supersonic Aircraft:** A previous, independent assessment of the impact of a projected fleet of supersonic aircraft on stratospheric ozone has reported the prediction that the ozone loss increases with the amount of nitrogen oxides emitted. These models used gas phase chemistry and assessed ozone loss for the case of 500 aircraft flying at Mach 2.4 between 17 and 20 km with an annual fuel use of  $7 \times 10^{10}$  kg/yr. The annual average loss of column ozone at middle latitudes in the Northern Hemisphere is predicted to be 2 to 6 percent. For a comparable fleet operated at Mach 3.2 between 21 and 24 km, the comparable column ozone loss is 7 to 12 percent. However, recent evidence has shown that reactions on sulfate aerosols can change the partitioning of nitrogen oxides. Two model studies incorporating this heterogeneous chemistry have recently reexamined the Mach 2.4 case and found substantially less ozone change ( $-0.5$  to  $+0.5$  percent). These implications are being examined as part of a separate assessment.
- **Shuttles and Rockets:** The increase in the abundance of stratospheric chlorine from one projection of U.S. annual launches of nine Space Shuttles and six Titan rockets is calculated to be less than 0.25 percent of the annual stratospheric chlorine source from halocarbons in the present-day atmosphere (with maximum increases of 0.01 ppbv in the middle and upper stratosphere in the northern middle and high latitudes). The TOMS ozone record shows no detectable changes in column ozone immediately following each of several launches of the Space Shuttles.
- **Volcanoes, Ozone Loss, and Climate Perturbations:** Major volcanic eruptions, such as Mt. Pinatubo, substantially increase the stratospheric abundance of sulfate aerosols for a few years. Since laboratory and field data show that heterogeneous processes can lead to increased levels of reactive chlorine in the stratosphere, such injections have the potential to increase ozone losses temporarily. Furthermore, the increased levels of stratospheric sulfate aerosols are predicted to warm the lower stratosphere by about  $4^{\circ}\text{C}$  (which has been observed) and cool the Earth's surface by a much smaller amount.
- **Tropospheric Sulfate Aerosols and Climate:** Fossil fuel emissions over the past century have increased the tropospheric sulfate aerosol concentrations. Their contribution to the direct radiative forcing of the clear-sky Northern Hemisphere is opposite to that due to the greenhouse gases and is estimated to be a substantial fraction of the trace gas forcing.

### IMPLICATIONS FOR POLICY FORMULATIONS

The findings and conclusions of the research of the past few years have several major implications as input to policy decisions regarding human-influenced substances that lead to stratospheric ozone depletions and to changes in the radiative forcing of the climate system:

- **Continued Global Ozone Losses:** Even if the control measures of the amended Montreal Protocol (London, 1990) were to be implemented by all nations, the current abundance of stratospheric chlorine (3.3 to 3.5 ppbv) is estimated to increase during the next several years, reaching a peak of about 4.1 ppbv around the turn of the century. With these increases, the additional middle latitude ozone losses during the 1990s are expected to be comparable to those observed during the 1980s, and there is the possibility of incurring widespread losses in the Arctic. *Reducing these expected and possible ozone losses requires further limitations on the emissions of chlorine- and bromine-containing compounds.*
- **Approaches to Lowering Global Risks:** Lowering the peak and hastening the subsequent decline of chlorine and bromine levels can be accomplished in a variety of ways, including an accelerated phase-out of controlled substances and limitations on currently uncontrolled halocarbons. A significant reduction in peak chlorine loading (a few tenths of a ppbv) can be achieved with accelerated phase-out schedules of CFCs, carbon tetrachloride, and methyl chloroform. Even stringent controls on HCFC-22 would not significantly reduce peak chlorine loading (at most 0.03 ppbv, especially when ODP weighted), but do hasten the decline of chlorine. A 3-year acceleration of the phase-out schedule for the halons would reduce peak bromine loading by about 1 pptv. If the anthropogenic sources of methyl bromide are significant and their emissions can be reduced, then each 10 percent reduction in methyl bromide would rapidly result in a decrease in stratospheric bromine of 1.5 pptv, which is equivalent to a reduction in stratospheric chlorine of 0.045 to 0.18 ppbv. *This gain is comparable to that of a 3-year acceleration of the scheduled phase-out of the CFCs.*
- **Elimination of the Antarctic Ozone Hole:** The phase-out schedule of the amended Montreal Protocol, if fully complied by all nations and if there are no continued uses of HCFCs, affords the opportunity to return to stratospheric chlorine abundances of 2 ppbv sometime between the middle and the end of the next century. This is the level at which the Antarctic ozone hole appeared in the late 1970s and hence is about the level that is thought to be necessary (other conditions assumed constant, including bromine loading) to eliminate the ozone hole. *Such levels could never have been reached under the provisions of the original Protocol (Montreal, 1987).*
- **Uncertain Greenhouse Role of CFCs:** The weight of evidence suggests that a large part of the observed lower stratospheric decrease in ozone is the result of CFC emissions. Furthermore, the radiative impact of this ozone decrease may have largely offset the predicted direct radiative perturbations, at middle to high latitudes, due to the CFC increases over the last decade. *Hence, even the sign of the overall radiative effect of CFC increases on the climate system over the last decade is uncertain.*
- **Utility of GWPs:** The direct GWPs are a useful indicator of the relative radiative effects of long-lived, well-mixed, radiatively active trace species. However, GWPs may be inapplicable for comparing the direct radiative effects of a long-lived, well-mixed gas to the indirect effects of a short-lived gas (for example, carbon dioxide to the nitrogen oxides). *For the latter need, the application of new tools, such as three-dimensional, fully coupled chemistry-climate models may be required.*