

SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 2002

*Pursuant to Article 6 of the Montreal Protocol
on Substances that Deplete the Ozone Layer*

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CONTENTS

SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 2002

PREFACE	ix
EXECUTIVE SUMMARY	xiii

CHAPTER 1: CONTROLLED SUBSTANCES AND OTHER SOURCE GASES

Lead Authors: S.A. Montzka and P.J. Fraser

Scientific Summary	1.1
1.1 Introduction	1.5
1.2 Halogenated Ozone-Depleting Gases in the Atmosphere	1.5
1.3 Halocarbon Sources Estimated from Industrial Production	1.19
1.4 Halocarbon Lifetimes, Ozone Depletion Potentials, and Global Warming Potentials	1.21
1.5 Methyl Bromide and Methyl Chloride	1.36
1.6 Atmospheric Halocarbon Observations Compared with Expectations	1.44
1.7 Other Trace Gases	1.51
1.8 Halogenated Source Gases in the Future	1.61
References	1.71

CHAPTER 2: VERY SHORT-LIVED HALOGEN AND SULFUR SUBSTANCES

Lead Authors: M.K.W. Ko and G. Poulet

Scientific Summary	2.1
2.1 Introduction	2.5
2.2 Dynamical and Chemical Characteristics of the Upper Troposphere (UT) and the Tropical Tropopause Layer (TTL)	2.7
2.3 Atmospheric Chemistry of Halogenated Very Short-Lived (VSL) Substances	2.15
2.4 Contribution of Halogenated VSL Substances to the Stratospheric Inorganic Halogen Budget	2.25
2.5 Estimates for the Potential Impact of Halogenated VSL Substances on Column Ozone	2.34
2.6 VSL Sulfur Species and Stratospheric Aerosols	2.39
References	2.44

CHAPTER 3: POLAR STRATOSPHERIC OZONE: PAST AND FUTURE

Lead Authors: P.A. Newman and J.A. Pyle

Scientific Summary	3.1
3.0 Introduction	3.5
3.1 Trends of Ozone and Temperature in the Polar Stratosphere	3.6
3.2 Basic Polar Stratospheric Processes	3.13
3.3 Quantification of Polar Ozone Loss: Observations and Models	3.41
3.4 Causes of Polar Stratospheric Temperature Trends	3.58
3.5 Chemical-Climate Modeling of the Past and Future Polar Stratosphere	3.66
References	3.81
Appendix 3A: Satellite Measurements in the Antarctic and Arctic	3.104

CONTENTS

CHAPTER 4: GLOBAL OZONE: PAST AND FUTURE

Lead Authors: M.P. Chipperfield and W.J. Randel

Scientific Summary	4.1
4.1 Introduction	4.5
4.2 Description of Past Changes in Ozone	4.6
4.3 Current Understanding of Past Changes in Stratospheric Aerosol, Water Vapor, and NO ₂	4.25
4.4 Current Understanding of Past Changes in Stratospheric Temperature	4.29
4.5 Chemical Influence on Past Changes in Ozone	4.37
4.6 Dynamical Influence on Past Changes in Ozone	4.52
4.7 Implications for Climate of Updated Stratospheric Ozone Changes	4.62
4.8 Future Changes in Ozone	4.63
4.9 Synthesis of Current Understanding of Past and Future Changes in Ozone	4.70
References	4.72
Appendix 4A: Description of Ozone Datasets	4.85
Appendix 4B: 2-D Model Scenarios	4.90

CHAPTER 5: SURFACE ULTRAVIOLET RADIATION: PAST AND FUTURE

Lead Authors: J.B. Kerr and G. Seckmeyer

Scientific Summary	5.1
5.1 Introduction	5.5
5.2 Current Understanding of Factors Affecting Surface UV Radiation	5.5
5.3 Available Resources for Studying Surface UV Radiation	5.11
5.4 UV Climatology, Temporal Changes, and Trends	5.20
5.5 Expectations of UV in the Future	5.25
References	5.31
Appendix 5A: Spectral Data Available from Databases	5.43
Appendix 5B: Internet Addresses for UV Sites	5.45

TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER

Lead Author: D.W. Fahey

Introduction	Q.1
I. Ozone in Our Atmosphere	Q.3
II. The Ozone Depletion Process	Q.8
III. Stratospheric Ozone Depletion	Q.21
IV. Controlling Ozone-Depleting Gases	Q.28
V. Implications of Ozone Depletion	Q.32
VI. Stratospheric Ozone in the Future	Q.36

APPENDICES

A LIST OF INTERNATIONAL AUTHORS, CONTRIBUTORS, AND REVIEWERS	A.1
B MAJOR ACRONYMS AND ABBREVIATIONS	B.1
C MAJOR CHEMICAL FORMULAE AND NOMENCLATURE FROM THIS ASSESSMENT	C.1

PREFACE

The present document will be part of the information upon which the Parties to the United Nations Montreal Protocol will base their future decisions regarding protection of the stratospheric ozone layer.

The Charge to the Assessment Panels

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.”

To meet this request, the Scientific Assessment Panel, the Environmental Effects Panel, and the Technology and Economic Assessment Panel have each prepared, about every 3-4 years, major assessment reports that updated the state of understanding in their purviews. These reports have been scheduled to be available to the Parties in advance of their meetings at which they will consider the need to amend or adjust the Protocol.

The Sequence of Scientific Assessments

The current 2002 report is the latest in a series of nine 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/or the United Nations Environment Programme (UNEP). This report is the fifth in the set of major assessments that have been prepared by the Scientific Assessment Panel directly as input to the Montreal Protocol process. The chronology of all the scientific assessments on the understanding of ozone depletion and their relation to the international policy process is summarized as follows:

<u>Year</u>	<u>Policy Process</u>	<u>Scientific Assessment</u>
1981		<i>The Stratosphere 1981: Theory and Measurements</i> . WMO No. 11.
1985	Vienna Convention	<i>Atmospheric Ozone 1985</i> . Three volumes. WMO No. 16.
1987	Montreal Protocol	
1988		<i>International Ozone Trends Panel Report 1988</i> . Two volumes. WMO No. 18.
1989		<i>Scientific Assessment of Stratospheric Ozone: 1989</i> . Two volumes. WMO No. 20.
1990	London Adjustments and Amendment	
1991		<i>Scientific Assessment of Ozone Depletion: 1991</i> . WMO No. 25.
1992		<i>Methyl Bromide: Its Atmospheric Science, Technology, and Economics (Montreal Protocol Assessment Supplement)</i> . UNEP (1992).
1992	Copenhagen Adjustments and Amendment	
1994		<i>Scientific Assessment of Ozone Depletion: 1994</i> . WMO No. 37.
1995	Vienna Adjustment	

PREFACE

<u>Year</u>	<u>Policy Process</u>	<u>Scientific Assessment</u>
1997	Montreal Adjustments and Amendment	
1998		<i>Scientific Assessment of Ozone Depletion: 1998.</i> WMO No. 44.
1999	Beijing Amendment	
2002		<i>Scientific Assessment of Ozone Depletion: 2002.</i> WMO No. 47.
2003	15 th Meeting of the Parties	

The Current Information Needs of the Parties

The genesis of *Scientific Assessment of Ozone Depletion: 2002* occurred at the 11th Meeting of the Parties to the Montreal Protocol in Beijing, China, at which the scope of the scientific needs of the Parties was defined in their Decision XI/17.5(a): “To request the Scientific Assessment Panel to include the following in the 2002 scientific assessment:

- (a) An evaluation of the observed trends in controlled substances and their consistency with reported production of ODS;
- (b) A quantification of the ozone-depleting impacts of new (e.g., short-lived) halogen-containing substances;
- (c) A characterization of methyl bromide sources and sinks and the likely quantitative implications of the results for the ozone layer;
- (d) A characterization of the known interrelations between ozone depletion and climate change including feedbacks between the two;
- (e) A description and interpretation of the observed changes in global and polar ozone and in ultraviolet radiation, as well as set future projections and scenarios for those variables, taking into account also the expected impacts of climate change...”.

The Assessment Process

The formal planning of the current assessment was started early in 2001. At the request of the Scientific Assessment Panel, the Parties suggested experts from their countries who could participate in the process, and those suggestions contributed about half of the participants who served as authors, contributors, and reviewers. Furthermore, an ad hoc international scientific steering group also suggested participants from the world scientific community. In addition, this steering group contributed to crafting the outline of the assessment report. As in previous assessments, the participants represented experts from the developed and developing world. The developing-world experts bring a special perspective to the process, and their involvement in the process contributes to capacity building.

The information of the 2002 assessment is contained in five chapters, with most containing past trends and future projections associated with ozone-layer topics:

- Chapter 1. Controlled Substances and Other Source Gases
- Chapter 2. Very Short-Lived Halogen and Sulfur Substances
- Chapter 3. Polar Stratospheric Ozone: Past and Future
- Chapter 4. Global Ozone: Past and Future
- Chapter 5. Surface Ultraviolet Radiation: Past and Future

The interactions between the ozone layer and the climate system are varied and appear appropriately as a special section in most of the chapters.

A special resource for the Panel’s work was the earlier report, *Aviation and the Global Atmosphere*. This 1999 assessment of the impacts of aviation on ozone depletion and climate change was a collaboration of the Intergovernmental Panel on Climate Change (IPCC) and the Scientific Assessment Panel of the Montreal Protocol. The assessment had been requested by the International Civil Aviation Organization (ICAO). Because this comprehensive study had been

recently done, the present 2002 assessment could cite the major relevant findings of the 1999 study and provide any updates of knowledge that had occurred.

The initial plans for the chapters of the 2002 Scientific Assessment Panel's report were examined at a meeting that occurred on 27-28 June 2001 in London, United Kingdom. The Lead Authors and Cochairs focused on the content of the draft chapters and establishing the needs for coordination among the chapters.

The first drafts of the chapters were examined at a meeting that occurred on 28-30 November 2001 in Fairfax, Virginia, United States, at which the Lead Authors, Cochairs, and a small group of international experts focused on the scientific content of the draft chapters.

The second drafts of the chapters were reviewed by 133 scientists worldwide in a mail peer review. Those comments were considered by the authors. At a Panel Review Meeting in Les Diablerets, Switzerland, held on 24-28 June 2002, the responses to these mail review comments were proposed by the authors and discussed by the 74 participants. Final changes to the chapters were decided upon at this meeting. The Executive Summary contained herein (and posted on the UNEP and WMO web sites on 23 August 2002) was prepared and completed by the attendees of the Les Diablerets meeting.

The 2002 State-of-Understanding Report

In addition to the scientific chapters and the Executive Summary, the assessment also focuses on a set of questions that are frequently asked about the ozone layer. Based upon the scientific understanding represented by the assessments, answers to these frequently asked questions were prepared, with different readerships in mind, e.g., students and the general public. These questions and answers are included in this report.

The final result of this two-year endeavor is the present assessment report. As the accompanying list indicates, the *Scientific Assessment of Ozone Depletion: 2002* is the product of 275 scientists from the developed and developing world who contributed to its preparation and review¹ (170 scientists prepared the report and 182 scientists participated in the peer review process).

¹ Participating were Albania, Argentina, Armenia, Australia, Austria, Belgium, Bolivia, Brazil, Canada, Chile, Colombia, Denmark, Egypt, Estonia, Finland, France, Germany, Greece, India, Iran, Italy, Japan, Kenya, Malaysia, New Zealand, Norway, Poland, Russia, South Africa, Sweden, Switzerland, Taiwan R.O.C., The Netherlands, The People's Republic of China, Togo, United Kingdom, United States of America, and Venezuela.

EXECUTIVE SUMMARY

The provisions of the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer include the requirement that the Parties to the Protocol base their future decisions on the current scientific, environmental, technical, and economic information that is assessed through panels drawn from the worldwide expert communities. To provide that input to the decision-making process, advances in understanding on these topics were assessed in 1989, 1991, 1994, and 1998. This information helped support discussions among the Parties that led to the subsequent Amendments and Adjustments of the 1987 Protocol. The 2002 Scientific Assessment summarized here is the fifth in that series.

RECENT MAJOR FINDINGS AND CURRENT SCIENTIFIC UNDERSTANDING

Since the *Scientific Assessment of Ozone Depletion: 1998*, numerous laboratory investigations, atmospheric observations, and theoretical and modeling studies have produced new key findings and have strengthened overall understanding of the ozone layer and its effect on ultraviolet (UV) radiation. These advances are highlighted in the following summary of the current understanding of the impact of human activities and natural phenomena on the ozone layer and the coupling of the ozone layer and the climate system.

Changes in Ozone-Depleting Compounds

- **In the troposphere (i.e., lower atmosphere), observations show that the total combined effective abundance of ozone-depleting compounds continues to decline slowly from the peak that occurred in 1992-1994. Total chlorine is declining, while bromine from industrial halons is still increasing, albeit at a slower rate than was occurring previously (and as reported in the 1998 Assessment).** Total tropospheric *chlorine* from the long- and short-lived chlorocarbons was about 5% lower in 2000 than that observed at its peak in 1992-1994, and the rate of change in 2000 was about –22 parts per trillion (ppt) per year (–0.6% per year). The once-dominant influence of methyl chloroform (CH_3CCl_3) on this total decline is diminishing because the atmospheric abundance of methyl chloroform is sharply decreasing. Total chlorine from the major chlorofluorocarbons (CFCs) is no longer increasing, in contrast to the slight increase that was occurring at the time of the 1998 Assessment. Specifically, in 2000, the atmospheric abundances of CFC-11 and CFC-113 continued to decrease, while the rate of increase of CFC-12 had slowed. Total tropospheric bromine from halons continued to increase at about 3% per year, which is about two-thirds of the rate for 1996 reported in the 1998 Assessment. The observed abundances of CFCs, hydrochlorofluorocarbons (HCFCs), and methyl chloroform in the lower atmosphere continue to be consistent with reported production and estimated emissions.
- **Analyses of air trapped in snow since the late 19th century have confirmed that non-industrial sources of the CFCs, halons, and major chlorocarbons were insignificant.** Since the previous Assessment, analyses of firn air (i.e., air trapped in snow above glaciers) have revealed the abundance of long-lived atmospheric species at the time the air became trapped. As a result, trends in the atmospheric abundance for many ozone-depleting substances have been traced over the past century, to well before significant industrial sources of the compounds existed. These records show that the mixing ratios of the CFCs, halons, carbon tetrachloride (CCl_4), methyl chloroform, and HCFCs in the oldest air sampled are negligible compared with the amounts measured in today's background atmosphere. Further, the deduced 20th century records for these compounds are broadly consistent with calculated histories based on records of industrial production. The data suggest that substantial natural sources exist for atmospheric methyl bromide (CH_3Br). They also show increases throughout the 20th century, but these increases do not allow unambiguous quantification of the industrial fraction of methyl bromide emissions in recent years. The estimate of this fraction, based on an assessment of understanding of the budget of this gas, remains at 10-40%, as given in the 1998 Assessment.

EXECUTIVE SUMMARY

- **The abundances of HCFCs in the lower atmosphere continue to increase.** HCFCs are among the gases used as transition substitutes for CFCs, halons, and chlorinated solvents. In the year 2000, HCFCs represented 6% of total chlorine abundance from anthropogenic gases in the lower atmosphere. The rate of increase in chlorine from HCFCs was constant at 10 parts per trillion per year from 1996 to 2000.
- **Observations in the stratosphere indicate that the total chlorine abundance is at or near a peak, while bromine abundances are probably still increasing.** The sum of hydrogen chloride (HCl) and chlorine nitrate (ClONO₂) is an effective surrogate for the abundance of stratospheric chlorine. An extended time series of ground-based measurements shows that the total stratospheric column amounts of these species, which have grown steadily for decades, have plateaued in recent years. Further, space-based measurements of HCl in the upper stratosphere indicate a broadly similar behavior. There are indications that bromine abundances in the stratosphere increased during the 1990s, but changes in stratospheric bromine are not as well characterized as those of stratospheric chlorine. These stratospheric changes are consistent with expectations based on the understanding of trace-gas trends in the troposphere, stratospheric chemistry, and atmospheric transport from the troposphere to the stratosphere.
- **Very short-lived organic chlorine-, bromine-, and iodine-containing source gases have the potential to deplete stratospheric ozone, but quantitative estimation of their potentials is more challenging than for longer-lived species like CFCs.** The very short-lived compounds reside in the atmosphere for a few months or less because they are rapidly decomposed chemically in the troposphere. Yet, a fraction of their emissions and the products from their tropospheric destruction can potentially reach the stratosphere. For example, observations suggest that non-anthropogenic bromoform (CHBr₃) produced largely in the oceans does make a non-negligible contribution to the total stratospheric bromine abundance. The magnitude of the ozone depletion by very short-lived compounds will depend critically on the location and season of their emissions and on the properties of their degradation products. The traditional use of a single number for their Ozone Depletion Potential (ODP), which is possible for longer-lived species, is therefore not directly applicable to the very short-lived species. Three-dimensional model simulations also suggest that very short-lived compounds emitted in the tropics would be more readily transported to the stratosphere than those emitted at higher latitudes, thus leading to greater ozone loss for tropical emissions. ODP values estimated by three-dimensional models are currently uncertain because of difficulties in modeling the complexities of transport processes and the lack of data on the products of the tropospheric degradation. A recent study on n-propyl bromide, one of the compounds proposed for possible future use, showed that for emissions that are uniform over the global land masses away from the poles, roughly 0.5% of the bromine emitted as n-propyl bromide reaches the stratosphere, resulting in an ODP of 0.04. Other ODP values reported in that study are up to 0.1 from tropical emission, and values up to 0.03 and 0.02 for emissions restricted to north of 20°N and 30°N, respectively. Therefore, the impact of very short-lived compounds can be significant if their emissions are large.

Changes in the Ozone Layer over the Poles and Globally

- **Springtime Antarctic ozone depletion due to halogens has been large throughout the last decade.** Since the early 1990s, the minimum total column (i.e., overhead) ozone amount has been ~100 Dobson units (DU). The monthly total column ozone amounts in September and October have continued to be about 40 to 50% below pre-ozone-hole values, with up to a local 70% decrease for periods of a week or so. During the last decade, the average ozone hole area in the spring has increased in size, but not as rapidly as during the 1980s. The area of the ozone hole varies from one year to another, and it is not yet possible to say whether the area of the ozone hole has maximized. In recent years, the ozone hole has also persisted into early summer, increasing its impact on ultraviolet radiation.
- **In some recent cold Arctic winters during the last decade, maximum total column ozone losses due to halogens have reached 30%.** Arctic winter/spring ozone loss is highly variable due to changes in stratospheric meteorological conditions from one winter to another, but it is now better understood because of numerous new observations and model comparisons. There is general agreement between analyses that quantify Arctic chemical ozone loss for the 1999/2000 winter/spring season. That well-studied year was distinguished by persistent low temperatures, an ozone loss reaching 70% near 20 km, and total column ozone losses greater than 80 Dobson units (~20-25%) by early spring. In contrast, during the warmer, more disturbed Arctic winter of 1998/1999, the

estimated chemical loss was very small. Three of the last four Arctic winters have been warm, with little ozone loss; six of the previous nine winters were cold, with larger ozone losses.

- **Ozone remains depleted in the midlatitudes of both hemispheres.** The global-average total column ozone amount for the period 1997-2001 was approximately 3% below the pre-1980 average values. Observed changes occur primarily in midlatitudes and in polar regions; no significant trends in total column ozone have been observed in the tropics (25°N-25°S). There are differences in ozone behavior between the two hemispheres. In particular, the average amounts of total column ozone over the period 1997-2001 were 3% and 6% below the pre-1980 values in the Northern Hemisphere midlatitudes (35°N-60°N) and the Southern Hemisphere midlatitudes (35°S-60°S), respectively. The seasonality of total column ozone changes (1997-2001 relative to pre-1980) is different in the Northern Hemisphere and Southern Hemisphere. Over Northern Hemisphere midlatitudes, the largest ozone decreases are observed during winter/spring (~4%), with summer/autumn decreases approximately half as large. Over Southern Hemisphere midlatitudes, long-term ozone decreases exhibit a similar magnitude (~6%) during all seasons.
- **Models including observed changes in halocarbons, source gases, and aerosols (i.e., airborne fine particles) capture the observed long-term ozone changes in northern and southern midlatitudes.** The two-dimensional assessment models also reproduce much of the interannual ozone variations in the midlatitudes of the Northern Hemisphere, but do less well in the Southern Hemisphere. For example, observations show different ozone behavior in the Northern and Southern Hemispheres following the major eruption of the Mt. Pinatubo volcano in the early 1990s, whereas models that include aerosol-enhanced, halocarbon-ozone chemistry suggest hemispherically symmetric ozone loss during the post-eruption period. Changes in dynamical processes help to explain some of the ozone variations in Northern Hemisphere midlatitudes. They have also contributed to winter/spring trends in the Northern Hemisphere. However, because chemical and dynamical processes are coupled, their contributions to ozone changes cannot be assessed in isolation.
- **Chemistry-climate models predict that springtime Antarctic ozone levels will be increasing by 2010 because of projected decreases of halogens in the stratosphere.** A return to pre-1980 total column ozone amounts in the Antarctic is expected by the middle of this century.
- **Arctic ozone depletion is highly variable and difficult to predict, but a future Arctic polar ozone hole similar to that of the Antarctic appears unlikely.** Low ozone, as seen in some recent years, can however be expected again, and the Arctic stratosphere will be most vulnerable to other perturbations (for example, if there were to be an increase in the abundance of stratospheric aerosols from volcanic eruptions) during the next decade or so. Sustained very low Arctic ozone column amounts similar to those seen in the Antarctic are not predicted by the current chemistry-climate models. Such extreme ozone depletion during the next decade or so, when halogen abundances should still be close to their maximum, would require conditions that are unprecedented in about 40 years of Northern Hemisphere meteorological observations and, therefore, are considered highly unlikely to occur in the future.
- **The global ozone layer recovery is expected to be linked mainly to decreasing chlorine and bromine loading, but other factors are likely to contribute.** The expected decrease in the amount of stratospheric chlorine and bromine over the next 50 years is predicted to lead to an increase in the global amount of total column ozone, although there are differences in the projected rate of this increase predicted by different models. Stratospheric cooling (due mainly to projected carbon dioxide (CO₂) increases) is predicted to enhance the future ozone increase in the upper stratosphere. However, a reliable assessment of this effect on total column ozone is limited by uncertainties in the lower stratospheric response to these changes. Changes in atmospheric transport are difficult to predict, and their impact on stratospheric ozone could be either positive or negative. Projected increases in methane (CH₄) and nitrous oxide (N₂O) are predicted to have small chemical effects on the rate of increase of global total column ozone in the next 50 years, but could become more significant later in the 21st century. Future changes in the ozone in the lower atmosphere are highly dependent upon the scenario adopted for future emissions of ozone precursors, but all scenarios adopted by the 2001 report of the Intergovernmental Panel on Climate Change (IPCC) lead to predicted increases in tropospheric ozone up to 2050.

EXECUTIVE SUMMARY

Changes in Ultraviolet Radiation

- **Changes in the duration and spatial extent of the ozone hole are more important for Antarctic surface ultraviolet (UV) radiation levels than the annual ozone minimum.** Enhanced values of UV radiation continue to be observed at high latitudes in the Southern Hemisphere under the Antarctic ozone hole. The highest biologically weighted UV doses under the ozone hole are typically not observed in October when maximum ozone depletion occurs, but in November and early December when solar elevations are higher and low ozone values are still prevailing.
- **Additional measurements continue to confirm that decreases in ozone column amounts lead to increases in UV radiation.** Calculations of UV irradiance based on relationships with total ozone and total irradiance (from pyranometers) suggest that UV irradiance has increased since the early 1980s by 6-14% at more than 10 sites distributed over mid- and high latitudes of both hemispheres. These results are consistent with spectral ultraviolet irradiance measurements and with estimates from satellite measurements. The complicated spatial and temporal distributions of the predominant variables that affect ultraviolet radiation at the surface (for example, clouds, airborne fine particles, snow cover, sea ice cover, and total ozone) continue to limit the ability to describe fully surface ultraviolet radiation on the global scale, whether through measurements or model-based approaches. As was noted in the previous Assessment, the spectral surface ultraviolet data records, which started in the early 1990s, are still too short and too variable to permit the calculation of statistically significant long-term (i.e., multidecadal) trends.

The Ozone Layer and Climate Change

- **The understanding of the impact of ozone depletion on climate change has been strengthened.** There has been a global and annual-mean cooling of the stratosphere over the past two decades, which can be largely attributed to the observed stratospheric ozone depletion and increases in well-mixed greenhouse gases and water vapor. As has been noted in past assessments, cooling of the lower stratosphere leads to cooling of the Earth's climate system. The vertical profile of ozone depletion in the lowermost stratosphere, which is an important factor in the magnitude of the radiative forcing, is now more accurately estimated from additional years of observations with reduced volcanic perturbations. Averaged ozone depletion has remained close to that of the late 1990s over much of the world, and therefore the recommended globally averaged radiative forcing of the climate system implied by this Assessment is the same as that recommended by the 2001 IPCC Assessment. The stratospheric radiative forcing due to ozone decreases since 1980 offsets about 20% of the positive forcing due to the increases in abundances of well-mixed greenhouse gases over that same time period.
- **Other atmospheric changes influence both the ozone layer and the climate system.** Observations have provided stronger evidence for a widespread increase in stratospheric water vapor, which plays a role both in cooling the lower stratosphere and in depleting ozone through chemical interactions, thereby contributing to climate processes. However, the water vapor trends are not fully defined, nor are their cause understood. Methane, nitrous oxide, and carbon dioxide are all important greenhouse gases, and all exert some influence on ozone depletion. Further, surface ultraviolet radiation may be directly affected, both positively and negatively, by the effects of climate change (for example, changing cloudiness), making prediction of long-term changes in surface radiation arising from all causes quite uncertain.
- **New research has begun to explore the coupling between climate change and the recovery of the ozone layer.** A number of models have been run to explore the feedback between climate and the ozone layer. As noted earlier, they have shown that past changes in ozone have contributed, together with well-mixed greenhouse gases, to a cooling of the stratosphere. Future changes in well-mixed greenhouse gases will affect the future evolution of ozone through chemical, radiative, and dynamic processes. In this highly coupled system, attribution is difficult; studies are ongoing. Stratospheric cooling (due mainly to projected carbon dioxide increases) is predicted to enhance future ozone amounts in the upper stratosphere. However, a reliable assessment of these effects on total column ozone is limited by uncertainties in lower stratospheric response to these changes.

ADDITIONAL SCIENTIFIC EVIDENCE AND RELATED INFORMATION

Halocarbon Abundances

- Trends of ozone-depleting substances in the atmosphere have been updated, and 20th century trends have been deduced from firn air. In 2000, tropospheric mixing ratios of CFC-11 and CFC-113 declined faster than in 1996, and mixing ratios of CFC-12 were still increasing, but more slowly. The rapid drop in global methyl chloroform emission has led to an exponential decay in its mixing ratio since 1998; mixing ratios of this gas in 2000 were less than one-half of the peak observed in 1992. The rate of decline observed for methyl chloroform during 2000 was about two-thirds of what it was in 1996.
- The total effect of all ozone-depleting halogens in the atmosphere, as estimated by calculating chlorine equivalents from atmospheric measurements of chlorine- and bromine-containing gases, continues to decrease. As of mid-2000, equivalent organic chlorine in the troposphere was nearly 5% below the peak value in 1992-1994. The recent decrease is slightly slower than in the mid-1990s, owing to the reduced influence of methyl chloroform on this decline.
- Substantial reductions in the emissions of ozone-depleting substances during the 1990s as inferred from atmospheric measurements are consistent with controls on production and consumption in the fully amended and adjusted Montreal Protocol. Consumption in developing countries is now a significant contributor to global emissions. The year 1999 was the first in which production and consumption of a class of ozone-depleting substances (the CFCs) was restricted in all Parties to the Montreal Protocol. Atmospheric measurements are consistent with emissions derived from reported production data for CFCs.
- The updated, best-estimate scenario for future halocarbon mixing ratios suggests that the atmospheric burden of halogens will return to the 1980 pre-Antarctic-ozone-hole levels around the middle of the 21st century, provided continued adherence to the fully amended and adjusted Montreal Protocol. Only small improvements would arise from further reduced production allowances in the future.
- Discrepancies reported in past assessments between atmospheric observations and expectations based on industry-reported production and emissions have narrowed substantially for HCFC-142b. This improvement stems from a better description of the functions relating emissions to usage in foam applications.

Halocarbon Lifetimes

- The global lifetime of carbon tetrachloride is estimated to be about 26 years, or about 25% shorter than in the previous (1998) Assessment. This shorter lifetime stems from identification of an ocean sink that is inferred from widespread observations of carbon tetrachloride undersaturation in surface waters of the ocean. Emissions inferred from atmospheric measurements and this lifetime are about 7 times greater than the limits to global production set for 2005.
- The lifetime of methyl chloroform has been revised from 4.8 years to 5.0 years based upon new observations. The implications of this change on estimates of atmospheric hydroxyl (OH) suggest lifetimes up to 5% longer for HCFCs, hydrofluorocarbons (HFCs), methane, and all other gases removed from the atmosphere by this important oxidant. These changes affect the Global Warming Potentials (GWPs) and Ozone Depletion Potentials (ODPs) calculated for these gases.

Methyl Bromide, Methyl Chloride, and Halons

- Atmospheric histories inferred from Southern Hemisphere air archives and Antarctic firn air suggest that, assuming similar changes have occurred in both hemispheres, the sum of organic bromine from methyl bromide (CH₃Br) and halons has more than doubled since the mid-1900s.

EXECUTIVE SUMMARY

- A substantial imbalance remains in estimates of source and sink magnitudes for both methyl bromide and methyl chloride (CH_3Cl); known sinks outweigh sources for both of these gases. New sources of methyl bromide from individual crops and ecosystems have been identified, and new sources of methyl chloride from tropical plants have been discovered. These findings have narrowed the budget imbalances for both of these gases.
- The best estimate for the global lifetime of methyl bromide remains at 0.7 (0.5-0.9) years. Additional studies directly related to estimating loss processes for methyl bromide have narrowed the uncertainties slightly, but do not suggest large revisions to this lifetime. The fraction of emissions derived from industrially produced methyl bromide is unchanged at 10-40% based upon the current understanding of source and sink magnitudes.

Very Short-Lived Ozone-Depleting Compounds

- Very short-lived natural and anthropogenic bromine and iodine source gases with surface concentrations of a few parts per trillion (ppt) could make a non-negligible contribution to the current inorganic bromine and iodine budgets, since the stratospheric concentrations of inorganic bromine and iodine are about 20 ppt and less than 1 ppt, respectively. The transport of inorganic bromine associated with very short-lived bromine source gases from the troposphere to the stratosphere may contribute to the stratospheric inorganic bromine budget.
- The most efficient route for transport of very short-lived substances and their degradation products from the surface to the stratosphere is in the tropics. In the tropics, the vertical transport times from the boundary layer to the upper troposphere are short, and air that enters the stratosphere through the tropical tropopause may remain in the stratosphere for a year or longer. A significant fraction of the emitted very short-lived substances can be expected to reach the tropical tropopause layer because current estimates indicate that air at the base of the layer is replaced by convection from the tropical boundary layer on a time scale of 10 to 30 days. A few percent of the air in the tropical tropopause layer is expected to enter the stratosphere through the tropical tropopause. Other transport pathways exist in the extratropics for the transfer of very short-lived substances and their degradation products to the extratropical lower stratosphere.
- The main uncertainties in estimating the impact of very short-lived source gases lie in the physical and dynamical processes transporting these substances into the stratosphere and in the chemistry of their degradation products. Given the complexity, three-dimensional numerical models are the preferred tools to evaluate the Ozone Depletion Potential for very short-lived source gases. Significant uncertainties exist in the treatment of dynamical and physical processes in such models.
- Two model studies simulated the atmospheric distribution of bromoform (CHBr_3), assuming a simplified ocean source that is uniform over space and time. The results indicate that the ocean source causes an average surface mixing of 1.5 ppt for bromoform and maintains about 1 ppt of bromine in the stratosphere. The simulation shows that one-half to three-fourths of the bromine from bromoform enters the stratosphere in the form of inorganic degradation products.
- The Ozone Depletion Potential was calculated from three separate model studies for n-propyl bromide (n-PB, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$). Reaction with hydroxyl (OH) removes n-PB, with local photochemical lifetimes in the tropical troposphere of about 10-20 days. Laboratory data, particularly on bromoacetone, indicate that n-propyl bromide degradation products have lifetimes shorter than a couple of days. Two of the three modeling studies provided values only for direct transport of n-PB to the stratosphere. The third study computed contributions from direct transport and the transport of degradation products to the stratosphere. In the latter study, values of the Ozone Depletion Potential are up to 0.1 for tropical emissions and 0.03 for emissions restricted to northern midlatitudes. In both cases, about two-thirds of the effect is from the transport of degradation products to the stratosphere.
- Laboratory data on iodine chemistry have led to downward revision of the efficiency of iodine for depleting ozone in the stratosphere. The revised estimated efficiency factor (~150-300) is still higher than that of bromine (~45).

Polar Ozone

ANTARCTIC

- Springtime Antarctic ozone depletion remains very large (with daily local total column values reaching 60-70% less than pre-ozone-hole conditions), with minimum values of about 100 DU (Dobson units) seen every year since the early 1990s. These observations reflect the almost complete ozone loss in the 12-20 km range and do not imply that ozone recovery has begun. Such low ozone is consistent with current understanding of stratospheric chemistry and dynamics.
- The area enclosed by the 220 DU contour (a measure of the severity of the ozone hole) shows an increase in recent years, so that it is not yet possible to say that the ozone hole has reached its maximum. Much of the change appears to be associated with processes at the edge of the polar vortex and is consistent with meteorological variability and the almost-constant halogen loading.
- Observations show that the Antarctic polar vortex and the associated ozone hole persist later than during the 1980s. Over the last decade, the vortex has generally broken up in late November to early December, in contrast to breakup in early November during the 1980s.
- Satellite and radiosonde observations show that the springtime Antarctic lower stratosphere has cooled. During the 1979-2000 period, the linear cooling trend exceeded 1.5 K/decade at 70°S. Modeling studies reaffirm that ozone loss is the major cause of the springtime cooling and the increased persistence of the Antarctic polar vortex. Well-mixed greenhouse gas increases contribute to the annually averaged cooling. Stratospheric water vapor increases may also be contributing.
- Coupled chemistry-climate model simulations, which include the combined effects of the changes in halogens and well-mixed greenhouse gases, broadly reproduce past trends in the total column ozone over the Antarctic. These models suggest that the minimum column ozone occurs prior to 2010 and that recovery to 1980 levels may be expected in the middle of the 21st century. The model response for the past and future changes is driven mainly by the changes in stratospheric halogen loading, with ozone recovery occurring after the peak of halogen loading.

ARCTIC

- The magnitude of halogen-induced loss of ozone for all Arctic winters during the last decade has now been studied with a variety of observationally based approaches. There is generally good agreement between different analyses that quantify the chemical loss. In the 1999/2000 winter, for which the most comprehensive studies were conducted, agreement was better than 20% in the Arctic stratosphere at about 20 km.
- The Arctic winter/spring total column ozone amounts continue to show a high interannual variability, reflecting the variable meteorology of the Northern Hemisphere stratosphere. Low column ozone amounts were present during the cold winter of 1999/2000. That year was distinguished by persistent low temperatures, a local loss reaching 70% at 20 km, and column losses greater than 80 DU (~20-25%). In the warmer, more-disturbed winters of 1998/1999 and 2000/2001, very small ozone loss was observed. Three of the last four Arctic winters have been warm, with little ozone loss; six of the previous nine winters were cold, with larger ozone losses.
- Significant chemical loss of ozone (~0.5 parts per million) in the lower stratosphere during January has been observed in several cold Arctic winters, contributing about 25% to the overall loss of ozone over the winter. The observations indicate that the loss occurred exclusively during periods when the air masses were exposed to sunlight. Nevertheless, these January ozone losses cannot be fully explained with the current understanding of the photochemistry.
- Coupled chemistry-climate models capture the typical interannual variability of Arctic ozone levels. Because Arctic temperatures are often near the threshold for polar stratospheric cloud (PSC) formation and hence the

EXECUTIVE SUMMARY

initiation of perturbed chemistry, there is a strong sensitivity to model temperature biases of only a few degrees Celsius. This places severe limits on the ability of the models to simulate past and predict future Arctic ozone behavior in winter.

- A number of coupled chemistry-climate models run for this Assessment suggest that minimum Arctic ozone would occur within the next two decades, the timing of which will depend on the meteorology. Low ozone, as seen in some recent years, can be expected again, and the Arctic stratosphere will be most vulnerable to other perturbations (e.g., aerosols from volcanic eruptions) during the next decade or so. Total column ozone amounts in the Arctic similar to the extreme lows seen in the Antarctic are not predicted by these models (in contrast to earlier simpler calculations considered in the 1998 Assessment). These extremely low values would require conditions that are unprecedented in about 40 years of Northern Hemisphere meteorological observations.
- Satellite and radiosonde observations show that the springtime Arctic lower stratosphere has cooled. However, because of large variability in the Arctic spring, the magnitude of the trend is uncertain there. A linear cooling trend (exceeding 1.5 K/decade) is observed during the 1979-2000 period at 70°N. Modeling studies now suggest that stratospheric ozone depletion has exerted an important influence on the springtime cooling of the Arctic lower stratosphere over the 1979-2000 period, but the degree of attribution is hindered by the large dynamical variability in that region.
- Observations of bromine monoxide (BrO) in the winter Arctic vortex by in situ and remote detection techniques are in broad agreement and are consistent with a total bromine budget of $\sim 20 \pm 4$ parts per trillion. Modeling studies of the latitudinal, seasonal, and diurnal variations in BrO column abundances agree well with observations from a number of ground sites, indicating that the processes that govern bromine partitioning and its budget in the polar regions are reasonably well understood.
- Bromine measurements now allow for more accurate assessment of the contribution of bromine to polar ozone loss. At present, the fractional contribution of bromine to total ozone loss ranges between 30 and 60%, depending on temperature and abundances of chlorine monoxide (ClO). Considering the observed leveling off of the strength of sources of chlorine, the role of bromine in polar ozone loss will continue to increase relative to that of chlorine until the current upward trends of the bromine source gases reverse.
- Removal of nitrogen compounds (denitrification) has been observed to occur in the Arctic lower stratosphere in several cold winters. Removal of up to 70% of the total reactive nitrogen was observed at some levels of the lower stratosphere in the winter of 1999/2000. Observations and modeling results show that denitrification in the 1999-2000 Arctic lower stratosphere increased ozone loss by as much as 30% at 20 km in spring.
- The understanding of what causes denitrification has been improved considerably by the discovery in 1999-2000 of large nitric-acid-containing particles (with diameters of 10 to 20 micrometers) in the Arctic polar lower stratosphere. Sedimentation of these particles can account for observed Arctic denitrification, although the mechanism of formation of these sedimenting particles is uncertain. Therefore, sedimentation of ice containing dissolved nitric acid, which has been the generally assumed mechanism in global stratospheric models, is not the dominant mechanism in the Arctic.
- The chemical composition of liquid and solid polar stratospheric cloud particles has been measured directly for the first time. Most of the measured compositions are in agreement with model calculations for liquid particles and nitric acid trihydrate, which have been used in stratospheric models for many years. These measurements improve confidence in the particle types used in microphysical models that are central to simulations of polar ozone loss.

Global Ozone

TOTAL COLUMN OZONE

- Global mean total column ozone for the period 1997-2001 was approximately 3% below the 1964-1980 average. Since systematic global observations began, the lowest annually averaged global total column ozone occurred in 1992-1993 (about 5% below the pre-1980 average). These changes are evident in each available global dataset.
- No significant trends in total column ozone have been observed in the tropics (25°N-25°S) for 1980-2000. A decadal variation of total column ozone (with peak-to-trough variations of ~3%) is observed in this region, approximately in phase with the 11-year solar cycle. Total column ozone trends become statistically significant in the latitude bands 25°-35° in each hemisphere.
- There are a number of differences in total column ozone behavior between the two hemispheres:
 - Averaged over the period 1997-2001, total column ozone in the Northern Hemisphere and Southern Hemisphere midlatitudes (35°-60°) were about 3% and 6%, respectively, below their pre-1980 average values.
 - The seasonality of total column ozone changes (1997-2001 relative to pre-1980) is different in the Northern Hemisphere and Southern Hemisphere extratropics. Over Northern Hemisphere midlatitudes, larger ozone decreases are observed during winter/spring (~4%), with summer/autumn decreases approximately half as large. Over Southern Hemisphere midlatitudes, long-term ozone decreases exhibit a similar magnitude (~6%) during all seasons.
 - Pronounced negative anomalies are observed in the Northern Hemisphere midlatitudes time series during 1992-1995 in the winter/spring seasons. Similar anomalies are not seen in the Southern Hemisphere midlatitudes.
 - There is a sharp drop in ozone at Southern Hemisphere midlatitudes during 1985-1986. A similar drop is not observed in the Northern Hemisphere.

VERTICAL OZONE DISTRIBUTION

- Ozone profile trends derived from the Stratospheric Aerosol and Gas Experiment (SAGE) satellite instrument show significant negative trends over latitudes 60°N to 60°S for altitudes ~35-50 km (with extremes near 40 km). Trend maxima of -7 to -8%/decade over the period 1979-2000 are observed in the 35°-60° latitude bands of both hemispheres, with no significant interhemispheric differences. These satellite results are in good agreement with independent Umkehr ozone measurements over the Northern Hemisphere midlatitudes.
- The updated SAGE data reveal significant negative trends extending throughout the tropics in the small amount of ozone above 30 km, a feature not observed in previous assessments based on shorter time records.
- The observed ozone depletion in the upper stratosphere is consistent with observed changes in anthropogenic chlorine. The vertical and latitudinal profiles of trends in the upper stratosphere are reproduced by photochemical models, but the magnitude of changes are sensitive to concurrent trends in temperature and methane (CH₄).
- Long-term ozonesonde measurements are primarily available for the Northern Hemisphere midlatitudes. Whereas ozone between 20 and 27 km decreased continuously during 1980-2000, ozone between 10 and 20 km decreased through the early 1990s and was relatively constant thereafter. This behavior is consistent with observed changes in Northern Hemisphere midlatitude column ozone.

EXECUTIVE SUMMARY

OZONE-RELATED CONSTITUENTS

- Stratospheric aerosol variability over the past 25 years has been dominated by the effects of episodic volcanic eruptions, with subsequent recovery. Following the large eruption of Mt. Pinatubo in 1991, relaxation to a nonvolcanic level continued to at least 1999. There is currently no evidence of a trend in the nonvolcanic aerosol loading.
- Stratospheric water vapor measurements at a single location (Boulder, Colorado, U.S., 40°N) for the period 1981-2000 show a statistically significant increase of approximately 1%/year over altitudes 15-28 km. For the shorter period 1991-2001, global satellite measurements covering latitudes 60°N-60°S show a similar trend of 0.6-0.8%/year for altitudes ~25-50 km, but no significant trend at lower altitudes. The increases in water vapor are substantially larger than can be explained by tropospheric methane trends. Characterization of stratospheric water vapor trends is limited by the lack of global long-term measurements.
- Stratospheric column nitrogen dioxide (NO₂) measurements from Lauder, New Zealand (45°S), for 1981-2000 and Jungfraujoch, Switzerland (46°N), for 1985-2001 show statistically significant positive trends of approximately 5%/decade. There are also transient decreases observed after the El Chichón and Mt. Pinatubo eruptions, which are broadly simulated by models that include heterogeneous chemistry on sulfate aerosols.

STRATOSPHERIC TEMPERATURE

- Observations indicate that, on an annual- and global-mean basis, the stratosphere has cooled over the last two decades. In the lower stratosphere, global and annual mean temperatures for the late 1990s are approximately 1 K lower than values in the late 1970s. Significant annual-mean cooling of the lower stratosphere over the past two decades is found over midlatitudes of both hemispheres (approximately 0.6 K/decade), but no significant trends are observed near the equator. The annual-mean temperature trends in the upper stratosphere are larger, with an approximately globally uniform cooling over 1979-1998 of about 2 K/decade near the stratopause (~50 km).
- Modeling studies indicate that changes in ozone, well-mixed greenhouse gases, and stratospheric water vapor can explain the major features of the observed global and annual-mean stratospheric cooling over the past two decades. Cooling due to ozone depletion dominates over the impact of well-mixed greenhouse gases in the lower stratosphere, while upper stratospheric temperature trends are due, roughly equally, to ozone and well-mixed greenhouse gas changes.

ATTRIBUTION OF PAST CHANGES IN OZONE

- The vertical, latitudinal, and seasonal characteristics of changes in midlatitude ozone are broadly consistent with the understanding that halogens are the primary cause, in line with similar conclusions from the 1998 Assessment.
- Assessment models forced by observed changes in halocarbons, source gases, and aerosols broadly reproduce the long-term changes observed in midlatitude total column ozone (35°N-60°N and 35°S-60°S) from 1980 to 2000, within the uncertainties of the observations and model range. However, the range of model results is large over Southern Hemisphere midlatitudes, which is at least partly due to their differing treatments of the Antarctic ozone hole. In addition, models suggest that the chemical signal of ozone loss following the major eruption of the Mt. Pinatubo volcano in the early 1990s should have been symmetric between the hemispheres, but observations show a large degree of interhemispheric asymmetry in midlatitudes.
- There is increased evidence that observed changes in atmospheric dynamics have had a significant influence on Northern Hemisphere midlatitude column ozone on decadal time scales. Natural variability, changes in greenhouse gases, and changes in column ozone itself are all likely to contribute to these dynamical changes. Furthermore, because chemical and dynamical processes are coupled, their contributions to ozone changes cannot be assessed in isolation.

FUTURE OZONE CHANGES

- The expected decrease in stratospheric chlorine loading over the next 50 years is predicted to lead to an increase in the global total column ozone, although there are differences in the rate of increase between different two-dimensional assessment models. Future ozone levels will also be influenced by other changes in atmospheric composition and by climate change. Because of year-to-year variability, it could take as long as a decade to demonstrate a leveling of total column ozone.
- Stratospheric cooling (due mainly to projected CO₂ increases) and the chemical influence of stratospheric methane increases are predicted to enhance future ozone increases in the upper stratosphere. However, a reliable assessment of these effects on total column ozone is limited by uncertainties in lower stratospheric response to these changes.
- Projected increases in methane (CH₄) and nitrous oxide (N₂O) (from the scenarios of the Intergovernmental Panel on Climate Change, 2001) are predicted to have small effects on the rate of increase of global column ozone in the next 50 years, when chlorine changes are the dominant effect. After that time, changes in CH₄ and N₂O become relatively more important.

Ultraviolet Radiation

- Annually averaged erythemal irradiance, as reconstructed from pyranometer (total irradiance), total ozone, and other meteorological measurements, increased by about 6-14% over the last 20 years at several mid- to high-latitude sites. Pyranometer and other meteorological data serve as proxies for parameters, other than ozone, that affect ultraviolet (UV) radiation. At some sites approximately half of the changes can be attributed to total ozone changes. These reconstructions are not UV measurements, and they contain several assumptions on the nature of radiative transfer. The reconstructions should not be considered to be representative on a global scale. It is believed that the increases of UV irradiance derived from the ground-based reconstructed data are clear indicators of the long-term changes that have occurred since the 1980s.
- There is clear evidence that the long-term UV changes are not driven by ozone alone, but also by changes in cloudiness, aerosols, and surface albedo. The relative importance of these factors depends on the local conditions. Results from studies using ground-based and aircraft instruments suggest that the influence of tropospheric aerosols on UV irradiance may be larger than previously thought and may affect large areas of the globe.
- UV increases associated with the ozone decline have been observed by spectral measurements at a number of sites in Europe, North and South America, Antarctica, and New Zealand. Episodes of elevated UV irradiance associated with low total column ozone amounts continue to occur in spring in mid-to-high latitudes.
- Satellite estimates of surface UV radiation from the Total Ozone Mapping Spectrometer (TOMS) dataset have been compared with ground-based measurements at several more sites since the previous Assessment. In general the estimates capture short-term and long-term variability. However, the estimates are systematically higher than ground-based measurements at many sites. The differences in monthly average erythemal UV irradiance range from about 0% at some clean sites to 40% at one site in the Northern Hemisphere. The fact that the agreement is better at the cleaner sites suggests that the differences are caused by aerosols and/or pollutants near the ground. New UV maps that include additional influencing parameters (e.g., cloud cover and albedo) derived from other satellite data, when taken together with TOMS or Global Ozone Monitoring Experiment (GOME) ozone data, yield better agreement with ground-based data.
- In the Antarctic, ozone depletion has been the dominant factor for increases in UV irradiance. The future evolution of UV radiation is therefore expected to follow the ozone recovery. However, because of changes in other influencing factors, such as changes in cloud cover, aerosols, or snow/ice cover, UV radiation may not return exactly to pre-ozone-hole values.

EXECUTIVE SUMMARY

- Elsewhere, including the Arctic, the impact on UV radiation of other influencing factors can be comparable to the impact of ozone depletion. The large uncertainties in future changes of these other factors prevent reliable predictions on the future evolution of UV irradiance. Furthermore, climate-change-induced trends in cloudiness and snow/ice cover are expected to be seasonally and geographically dependent, leading to differences in future UV irradiance in different parts of the world.
- A reanalysis of TOMS satellite data with respect to the influence of changes in cloudiness over Europe has confirmed that UV increases due to ozone depletion are partly masked by the increased cloudiness in some regions.

IMPLICATIONS FOR POLICY FORMULATION

The results from over three decades of research have provided a progressively better understanding of the interaction of humankind and the ozone layer. New policy-relevant insights into the roles of ozone-depleting gases have been conveyed to decisionmakers through the international state-of-understanding assessment process. The research findings in the *Scientific Assessment of Ozone Depletion: 2002* that are summarized above are direct current scientific input to governmental, industrial, and policy decisions associated with protection of the ozone layer.

- **The Montreal Protocol is working, and the ozone-layer depletion from the Protocol's controlled substances is expected to begin to ameliorate within the next decade or so.** The effectiveness of the Protocol is and will be shown by several indicators. Global observations show that the total combined effective abundances of anthropogenic chlorine-containing and bromine-containing ozone-depleting gases in the *lower atmosphere* (troposphere) peaked in the 1992-1994 time period and are continuing to decline. Furthermore, observations indicate that the *stratospheric* abundances of ozone-depleting gases are now at or near a peak. Thereafter, stratospheric ozone should increase, all other influences assumed constant, but ozone variability will make detection of the onset of the long-term recovery difficult. For example, based on assumed compliance with the amended and adjusted Protocol by all nations, the Antarctic ozone "hole," which was first discerned in the early 1980s, is predicted to disappear by the middle of this century—again with all other influences assumed constant.
- **The ozone layer will remain particularly vulnerable during the next decade or so, even with full compliance.** With the atmospheric abundances of ozone-depleting substances being near their highest, the human-influenced perturbations will be at or near their largest. Relative to the pre-ozone-hole abundances of 1980, the 1997-2001 losses in total column (i.e., overhead) ozone amounts are:
 - about 4% at northern midlatitudes in winter/spring;
 - about 2% at northern midlatitudes in summer/fall; and
 - about 6% at southern midlatitudes on a year-round basis.

Calculations yield that such changes in ozone correspond to increases in surface erythema radiation of at least 5, 2, and 7%, respectively, if other influences such as clouds remain constant. In Antarctica, the monthly total column ozone in September and October has continued to be about 40 to 55% below the pre-ozone-hole values, with up to a local 70% decrease for periods of a week or so. Arctic ozone is highly variable. Estimates of the cumulative winter/spring losses in the total column ozone amounts during the last 4 years range up to about 25%. Calculations of corresponding increases in surface erythema radiation are about 70 to 150% in the Antarctic springtime, with up to 300% increases for the short-lived local ozone decreases. In the Arctic winter/spring, the corresponding calculated increases are up to 40%. Furthermore, if there were to be an increase in the abundance of stratospheric particles from a major volcanic eruption like that of Mt. Pinatubo in 1991, then the peak losses in total column ozone and the increases in ultraviolet radiation could be larger. In the highly variable Arctic, larger depletion would be expected if an unusually and persistently cold Arctic stratospheric winter like that of the 1999/2000 winter/spring were to occur; conversely, smaller depletions are expected in particularly warm years.

- **Approaches to accelerating the recovery of the ozone layer are limited.** This Assessment has made hypothetical estimates of the *upper limits* of improvements that could be achieved if global anthropogenic *production* of ozone-depleting substances were to stop in 2003 or if global anthropogenic *emissions* of ozone-depleting substances were to stop in 2003. Specifically:

Production. Relative to the current control measures (Beijing, 1999) and recent production data, the equivalent effective stratospheric chlorine loading above the 1980 level, integrated from 2002 until the 1980 level is reattained (about 2050), could be decreased by the following amounts:

- 5%, if production of hydrochlorofluorocarbons (HCFCs) were to cease in 2003.
- 4%, if production of chlorofluorocarbons (CFCs) were to cease in 2003.
- 4%, if production of methyl bromide were to cease in 2003.
- 1%, if production of halons were to cease in 2003.
- 0.3%, if production of methyl chloroform were to cease in 2003.

These percentages would be about a factor of 2 smaller if the decreases were compared with the loading integrated from 1980, which is when significant ozone depletion was first detected. A hypothetical elimination of all anthropogenic production of *all* ozone-depleting substances would advance the return of stratospheric loading to the pre-1980 values by about 4 years.

Emissions. Similarly, the equivalent effective stratospheric chlorine loading above the 1980 level, integrated from 2002 until the 1980 level is reattained (about 2050), could be decreased by the following amounts:

- 11%, if emissions of halons were to cease in 2003.
- 9%, if emissions of chlorofluorocarbons (CFCs) were to cease in 2003.
- 9%, if emissions of hydrochlorofluorocarbons (HCFCs) were to cease in 2003.
- 4%, if emissions of methyl bromide were to cease in 2003.
- 3%, if emissions of carbon tetrachloride were to cease in 2003.
- 2%, if emissions of methyl chloroform were to cease in 2003.

Again, these percentages would be about a factor of 2 smaller if the decreases were compared with the loading integrated from 1980, which is when significant ozone depletion was first detected. A hypothetical elimination of all emissions derived from industrial production of *all* ozone depleting substances would advance the return of stratospheric loading to the pre-1980 values by about 10 years.

- **Failure to comply with the Montreal Protocol would delay or could even prevent recovery of the ozone layer.** For example, continued constant production of ozone-depleting substances at the 1999 amount would likely extend the recovery of the ozone layer well past the year 2100. The total atmospheric abundance of ozone-depleting gases will decline to pre-Antarctic-ozone-hole amounts only with adherence to the Montreal Protocol's full provisions on production of ozone-depleting substances.
- **Estimating the impacts of very short-lived ozone-depleting substances on depletion of the ozone layer requires new approaches, and, as requested by the Parties, this Assessment has described one such scientific approach.** The traditional concept of a *single-valued* Ozone Depletion Potential (ODP) is not directly applicable for these very short-lived ozone-depleting substances, because their impacts on the ozone layer will depend on the season and location of their emissions. These impacts would need to be assessed on a case-by-case basis, taking into account how much, when, and where they are emitted. Such estimates can provide insight into the stratospheric contribution of natural emissions of these very short-lived substances (for example, bromoform) and can provide scientific input into decisions associated with their industrial production/uses (for example, n-propyl bromide).
- **The issues of ozone depletion and climate change are interconnected.** The ozone-depletion phenomenon and the greenhouse-warming phenomenon share many common chemical and physical processes. For example, as the atmospheric abundances of the CFCs decline because of the Montreal Protocol's provisions, their greenhouse-warming contributions will decline. On the other hand, use of hydrofluorocarbons (HFCs) and HCFCs as substitutes for CFCs would cause the greenhouse-warming contributions of these new compounds to increase. Indeed,

EXECUTIVE SUMMARY

global observations of many HFCs and HCFCs, as well as of hydrogen fluoride, confirm that these contributions are currently increasing. As other examples, potential decisions associated with methane, nitrous oxide, and carbon dioxide stemming from their greenhouse roles will also have direct and indirect effects on stratospheric ozone. And, because ozone depletion acts to cool the climate system, recovery of the ozone layer over coming decades would tend to warm the climate system.

CHAPTER 1

Controlled Substances and Other Source Gases

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CHAPTER 1

CONTROLLED SUBSTANCES AND OTHER SOURCE GASES

Contents

SCIENTIFIC SUMMARY	1.1
1.1 INTRODUCTION	1.5
1.2 HALOGENATED OZONE-DEPLETING GASES IN THE ATMOSPHERE	1.5
1.2.1 Updated Atmospheric Observations of Ozone-Depleting Gases	1.5
1.2.1.1 Chlorofluorocarbons (CFCs)	1.5
1.2.1.2 Halons	1.9
1.2.1.3 Carbon Tetrachloride (CCl ₄)	1.9
1.2.1.4 Methyl Chloroform (CH ₃ CCl ₃)	1.11
1.2.1.5 Hydrochlorofluorocarbons (HCFCs)	1.11
1.2.1.6 Methyl Bromide (CH ₃ Br)	1.13
1.2.1.7 Methyl Chloride (CH ₃ Cl)	1.13
1.2.2 Twentieth Century Atmospheric Histories for Halocarbons from Firn Air	1.13
1.2.3 Total Atmospheric Chlorine	1.14
1.2.3.1 Total Organic Chlorine in the Troposphere	1.14
1.2.3.2 Total Inorganic Chlorine in the Stratosphere	1.15
1.2.3.3 Hydrogen Chloride (HCl) at 55 km Altitude in the Stratosphere	1.15
1.2.3.4 Stratospheric Chlorine Compared with Tropospheric Chlorine	1.15
1.2.4 Total Atmospheric Bromine	1.16
1.2.4.1 Total Organic Bromine in the Troposphere	1.16
1.2.4.2 Total Inorganic Bromine in the Stratosphere	1.17
1.2.4.3 Stratospheric Bromine Compared with Tropospheric Bromine	1.18
1.2.5 Effective Equivalent Chlorine and Effective Equivalent Stratospheric Chlorine	1.18
1.2.6 Fluorine in the Stratosphere	1.19
1.3 HALOCARBON SOURCES ESTIMATED FROM INDUSTRIAL PRODUCTION	1.19
1.3.1 CFCs and HCFCs	1.21
1.3.2 Halons	1.21
1.3.3 Carbon Tetrachloride (CCl ₄)	1.21
1.3.4 Methyl Chloroform (CH ₃ CCl ₃)	1.21
1.4 HALOCARBON LIFETIMES, OZONE DEPLETION POTENTIALS, AND GLOBAL WARMING POTENTIALS	1.21
1.4.1 Introduction	1.21
1.4.2 Lifetimes	1.22
1.4.3 Fractional Release Factors	1.27
1.4.4 Ozone Depletion Potential	1.28
1.4.5 Global Warming Potential	1.31
1.4.5.1 Radiative Forcing Updates	1.31
1.4.5.2 Direct Global Warming Potentials	1.34
1.4.5.3 Net Global Warming Potentials	1.34
1.4.6 Hydroxyl Radical Changes with Time	1.34
1.4.7 Other Sinks	1.36
1.5 METHYL BROMIDE AND METHYL CHLORIDE	1.36
1.5.1 Methyl Bromide (CH ₃ Br)	1.36
1.5.1.1 Anthropogenic and Anthropogenically Influenced Sources	1.37
1.5.1.2 Surface Interactions: Natural Sources and Sinks	1.38

1.5.1.3	Atmospheric Lifetime	1.39
1.5.1.4	A Twentieth Century, Southern Hemispheric Trend and Its Implications	1.39
1.5.1.5	Atmospheric Budget	1.40
1.5.2	Methyl Chloride (CH ₃ Cl)	1.40
1.5.2.1	Atmospheric Distribution and Trends	1.41
1.5.2.2	Sources of Atmospheric Methyl Chloride	1.41
1.5.2.3	Sinks of Atmospheric Methyl Chloride	1.43
1.5.2.4	Atmospheric Budget	1.43
1.6	ATMOSPHERIC HALOCARBON OBSERVATIONS COMPARED WITH EXPECTATIONS	1.44
1.6.1	Consistency Between Atmospheric Halocarbon Measurements and Known Sources and Sinks	1.44
1.6.1.1	CFCs	1.44
1.6.1.2	Methyl Chloroform	1.44
1.6.1.3	Carbon Tetrachloride	1.44
1.6.1.4	HCFCs	1.47
1.6.1.5	Halons	1.47
1.6.1.6	Regional Emissions	1.47
1.6.2	Are Atmospheric Measurements Consistent with Compliance with the Fully Amended Montreal Protocol?	1.47
1.7	OTHER TRACE GASES	1.51
1.7.1	Carbon Dioxide (CO ₂)	1.51
1.7.2	Methane (CH ₄)	1.53
1.7.3	Nitrous Oxide (N ₂ O)	1.55
1.7.4	Carbon Monoxide (CO)	1.56
1.7.4.1	Atmospheric Global Distribution and Trends	1.56
1.7.4.2	CO Sources and Sinks	1.56
1.7.4.3	Isotopic Data	1.56
1.7.5	Carbonyl Sulfide (COS)	1.57
1.7.6	Hydrofluorocarbons (HFCs)	1.57
1.7.6.1	HFC-134a	1.57
1.7.6.2	HFC-23	1.57
1.7.6.3	HFC-125, HFC-143a, and HFC-152a	1.59
1.7.7	Fluorocarbons (FCs), SF ₆ , and SF ₅ CF ₃	1.59
1.7.7.1	CF ₄ and C ₂ F ₆	1.59
1.7.7.2	C ₄ F ₈ and C ₃ F ₈	1.59
1.7.7.3	Sulfur Hexafluoride (SF ₆)	1.61
1.7.7.4	Trifluoromethylsulfurpentafluoride (SF ₅ CF ₃)	1.61
1.8	HALOGENATED SOURCE GASES IN THE FUTURE	1.61
1.8.1	Development of the Baseline Scenario Ab	1.61
1.8.2	Projecting Future Halocarbon Mixing Ratios	1.62
1.8.2.1	CFCs	1.62
1.8.2.2	Methyl Chloroform	1.62
1.8.2.3	Carbon Tetrachloride	1.62
1.8.2.4	Halons	1.67
1.8.2.5	HCFCs	1.68
1.8.2.6	Methyl Bromide and Methyl Chloride	1.68
1.8.2.7	Effective Equivalent Chlorine	1.68
1.8.3	Scenario Results: Calculated Mixing Ratios and EESC	1.68
1.8.4	Uncertainty in the Baseline Scenario	1.70
1.8.5	Potential Influence of Future Climate Change on Halogenated Source Gases	1.71
	REFERENCES	1.71

SCIENTIFIC SUMMARY

- As a result of the Montreal Protocol and its Amendments and Adjustments, organic chlorine in the global troposphere continues to decline slowly, and inorganic chlorine in the global stratosphere has stabilized.
 - (a) Total organic chlorine from long- and short-lived chlorocarbons continues to decline in the global troposphere. Total tropospheric chlorine in 2000 was about 5% lower than observed at its peak (3.7 ± 0.1 parts per billion (ppb)) in 1992-1994, and the rate of change in 2000 was about -22 parts per trillion per year (ppt yr^{-1}) ($-0.6\% \text{ yr}^{-1}$). The influence of methyl chloroform on this decline is diminishing. Total organic chlorine from chlorofluorocarbons (CFCs) is no longer increasing at Earth's surface.
 - (b) Total inorganic chlorine in the atmosphere, as estimated from hydrogen chloride and chlorine nitrate total column absorbance measurements, stopped increasing in 1997-1998 and has remained fairly constant since. Because most atmospheric hydrogen chloride and chlorine nitrate reside in the stratosphere, this result provides an estimate of chlorine changes in the stratosphere. These stratospheric changes are consistent with expectations based on our understanding of trace gas trends in the troposphere, stratospheric chemistry, and atmospheric mixing processes.
 - (c) Space-based measurements show that the global mean growth rate of hydrogen chloride at 55 km has been substantially less since 1997 than it was before that time. Although the measurements since 1997 also show short-term variations, the recent data do not show the steady increases observed in the early 1990s.
- Recent results from observations of tropospheric and stratosphere bromine show the following:
 - (a) As of 2000, total organic bromine from halons continued to increase in the troposphere at about $0.2 \text{ ppt Br yr}^{-1}$ ($\text{pmol mol}^{-1} \text{ yr}^{-1}$), and halons accounted for nearly 8 ppt of bromine. Global trend data for methyl bromide, a gas that is responsible for about half of the 20 ppt of total bromine in today's stratosphere, have not been updated since the previous Assessment. Atmospheric histories inferred from Southern Hemisphere air archives and Antarctic firn air suggest that, assuming similar changes in both hemispheres, total organic bromine from the sum of methyl bromide and halons has more than doubled since the mid-1900s.
 - (b) Measurements of inorganic bromine in the stratosphere indicate a rate of increase consistent with observed tropospheric trends of halons and methyl bromide, but mixing ratios that are 4-6 ppt higher. Additional stratospheric bromine stems from the transport of nonanthropogenic, very short-lived gases (such as bromoform and dibromomethane) and their degradation products to the stratosphere.
- Ozone-depleting halogens in the troposphere, as assessed by calculating chlorine equivalents from measurements of organic chlorine- and bromine-containing source gases, continue to decrease. As of mid-2000, equivalent organic chlorine in the troposphere was nearly 5% below the peak value in 1992-1994. The recent rate of decrease is slightly less than in the mid-1990s owing to the reduced influence of methyl chloroform on this decline.
- Trends of ozone-depleting substances in the atmosphere have been updated, and 20th century trends have been deduced from air trapped in snow above glaciers (firn air).
 - (a) In 2000, tropospheric mixing ratios of CFC-11 and -113 were decreasing faster than in 1996, and mixing ratios of CFC-12 were still increasing, but more slowly.
 - (b) Global methyl chloroform mixing ratios have been declining exponentially since 1998 because of the rapid drop in emissions to low levels; mixing ratios in 2000 were less than one-half of the peak observed in 1992. As a result, the rate of decline observed for methyl chloroform (and chlorine from methyl chloroform) during 2000 was about two-thirds of what it was in 1996.
 - (c) Newly reported measurements of air from firn allow inferences regarding 20th century histories of ozone-depleting substances in the atmosphere. These data confirm that nonanthropogenic sources of chlorofluorocarbons, halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons are insignificant. They are consistent, however, with there being substantial natural emissions of both methyl chloride and methyl bromide.

SOURCE GASES

- Atmospheric halocarbon measurements can provide some assessment of past global compliance with production restrictions in the Montreal Protocol, and these considerations provide the foundation for projecting halocarbon mixing ratios in future scenarios.
 - (a) The substantial reductions in emissions of ozone-depleting substances during the 1990s that are inferred from measured atmospheric trends are consistent with controls on production and consumption in the fully amended and adjusted Montreal Protocol. Consumption in developing countries is now a significant contributor to global emissions. The year 1999 is the first in which production and consumption of a class of ozone-depleting substances (the CFCs) were restricted in all Parties to the Montreal Protocol. Atmospheric measurements are consistent with emissions derived from reported global production data for CFCs.
 - (b) The updated, best-estimate scenario (Ab) for future halocarbon mixing ratios suggests that the atmospheric burden of halogens will return to the 1980, pre-Antarctic-ozone-hole levels around the middle of this century, provided continued adherence to the fully amended and adjusted Montreal Protocol. Only small improvements would arise from reduced production allowances in the future. Lack of compliance to the Protocol controls would delay or prevent recovery of stratospheric ozone.
- With respect to hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), the gases used as interim substitutes for CFCs, halons, and chlorinated solvents, this Assessment found the following:
 - (a) Organic chlorine from the HCFCs in the troposphere reached nearly 180 ppt in 2000 and represented 6% of total chlorine from anthropogenic gases. The rate of increase in organic chlorine from HCFCs remained constant at about 10 ppt yr⁻¹ from 1996 to 2000.
 - (b) Discrepancies reported in past Assessments between atmospheric observations and expectations based on industry-reported production and emissions have narrowed substantially for HCFC-142b. This improvement stems from a better description of the functions relating emissions to usage in foam applications.
 - (c) Mixing ratios of HFC-134a and -23 have continued to increase in recent years, and by 2000 each had approached about 15 ppt in the background atmosphere. Three additional HFCs (HFC-125, -124, and -152a) have been identified in the remote troposphere, but their abundance in 2000 was low (1-3 ppt).
- New lifetime recommendations are made in this Assessment:
 - (a) The global lifetime of carbon tetrachloride is estimated to be 26 years, or about 25% shorter than in the previous Assessment. This shorter lifetime stems from identification of an ocean sink that is inferred from widespread observations of carbon tetrachloride undersaturation in surface waters of the ocean. Emissions inferred from this shorter lifetime and measured trends in 1996 are about a factor of 2 larger than those estimated from industry production data for that year. This apparent discrepancy, however, is within the rather large uncertainties in both estimates. Emissions inferred from atmospheric measurements and a lifetime of 26 years are about 7 times greater than the limits to global production set for 2005.
 - (b) In this Assessment, the global lifetime of Halon-1211 is taken to be 16 years based upon the mid-range of modeling results. This lifetime estimate and estimates of emission magnitudes and atmospheric mixing ratios contain substantial uncertainties. Observational studies and emission histories have not reduced the uncertainties in the global lifetime of 9-25 years calculated in models.
 - (c) The lifetime of methyl chloroform has been revised from 4.8 to 5.0 years based upon new observations. The implications of this change on our estimates of atmospheric hydroxyl suggest slightly longer lifetimes for HCFCs, HFCs, methane, and all other gases removed from the atmosphere by this important oxidant.
- With respect to methyl bromide and methyl chloride, ozone-depleting gases with both natural and human-derived sources, this Assessment found the following:
 - (a) A substantial imbalance remains in estimates of source and sink magnitudes for both methyl bromide and methyl chloride; known sinks outweigh sources for both of these gases. New sources of methyl bromide from individual crops and ecosystems have been identified, and new sources of methyl chloride from tropical plants have been discovered. These findings have narrowed the budget imbalances for both of these gases. Additional studies continue to show that the ocean is a small (10-20 Gg yr⁻¹) net sink for atmospheric methyl bromide,

although this results from a balance of large production and loss terms. Our understanding of the saturation of methyl bromide in ocean waters has been refined, but the estimates of net flux between the ocean and atmosphere remain essentially unchanged.

- (b) Twentieth-century trends of methyl bromide and methyl chloride have been inferred for the Southern Hemisphere from analyses of firn air. Provided these gases are neither produced nor destroyed in the firn, these trends suggest 20th century increases in the Southern Hemisphere of about 3 ppt for methyl bromide and 50 ppt for methyl chloride.
 - (c) The best estimate for the global lifetime of methyl bromide remains at 0.7 (0.5-0.9) years. Additional studies directly related to estimating loss processes for methyl bromide have narrowed the uncertainties slightly, but they do not suggest large revisions to this lifetime. The fraction of emissions derived from industrially produced methyl bromide is unchanged at 10-40% based upon our current understanding of source and sink magnitudes.
- Approaches to further accelerating the date of the recovery of the ozone layer are limited. This Assessment has made hypothetical estimates of the upper limits of improvements that could be achieved if global anthropogenic *production* of ozone-depleting substances were to stop in 2003 or if global anthropogenic *emissions* of ozone-depleting substances were to stop in 2003. Specifically:

Production. Relative to the current control measures (Beijing, 1999) and trends in recent production data, the equivalent effective chlorine atmospheric loading above the 1980 level, integrated from 2002 until the 1980 level is reattained (about 2050), could be decreased by the following amounts:

- 5%, if production of hydrochlorofluorocarbons (HCFCs) were to cease in 2003.
- 4%, if production of chlorofluorocarbons (CFCs) were to cease in 2003.
- 4%, if production of methyl bromide were to cease in 2003.
- 1%, if production of halons were to cease in 2003.
- 0.3%, if production of methyl chloroform were to cease in 2003.

Emissions. Similarly, the equivalent effective chlorine atmospheric loading above the 1980 level, integrated from 2002 until the 1980 level is reattained (about 2050), could be decreased by the following amounts:

- 11%, if emissions of halons were to cease in 2003.
- 9%, if emissions of chlorofluorocarbons (CFCs) were to cease in 2003.
- 9%, if emissions of hydrochlorofluorocarbons (HCFCs) were to cease in 2003.
- 4%, if emissions of methyl bromide were to cease in 2003.
- 3%, if emissions of carbon tetrachloride were to cease in 2003.
- 2%, if emissions of methyl chloroform were to cease in 2003.

The decreases calculated for reduced production and emissions scenarios would be about a factor of 2 smaller if the decreases were compared with the loading integrated from 1980, which is when significant ozone depletion was first detected. Furthermore, the decreases calculated for the integrated equivalent effective chlorine atmospheric loading would be smaller if the cessation in production or emission occurred later than 2003.

The hypothetical elimination of all anthropogenic production of *all* ozone-depleting substances would advance the return of stratospheric loading to the pre-1980 values by about 4 years. The hypothetical elimination of all emissions derived from anthropogenic production of *all* ozone-depleting substances would advance the return of stratospheric loading to the pre-1980 values by about 10 years.

1.1 INTRODUCTION

This chapter provides an update on scientific progress since the previous *Scientific Assessment of Ozone Depletion* (WMO, 1999) regarding ozone-depleting substances (ODSs) in the atmosphere. This includes a discussion of the latest available data for observed trends in the troposphere and stratosphere, emissions, lifetimes, Ozone Depletion Potentials (ODPs), and Global Warming Potentials (GWPs). On the basis of this updated information, we relate observations of ODSs in the atmosphere to expectations, and discuss the evidence that the Montreal Protocol is effectively reducing ozone-depleting gases in the atmosphere.

Also explored in this chapter are the potential future mixing ratios of halocarbons based upon the current Montreal Protocol and recent trends in halocarbon production data. Scenarios are presented to investigate a range of possible future halocarbon mixing ratios. A number of hypothetical “cases” are also explored to demonstrate how production and emission of different ODSs will affect atmospheric halogen burdens in the future.

A discussion of non-ozone-depleting gases, such as carbon dioxide and methane, is also included here. Although they do not participate directly in ozone-destroying reactions, these gases influence stratospheric ozone indirectly by affecting the availability of inorganic chlorine and bromine, or by affecting stratospheric temperatures and thus the occurrence and persistence of polar stratospheric clouds, among other effects.

The discussions here focus on all significant ODSs with atmospheric lifetimes long enough that they are reasonably well mixed in the troposphere. This lifetime cutoff was taken to be 0.5 years. Classic methods for calculating ODPs for gases with lifetimes longer than 0.5 years are assumed to be valid. The details regarding budgets, sources, sinks, ODPs, etc., for gases with shorter lifetimes are discussed in Chapter 2.

1.2 HALOGENATED OZONE-DEPLETING GASES IN THE ATMOSPHERE

Atmospheric measurements of ozone-depleting substances provide a foundation for understanding changes in Earth’s protective ozone layer. Since the previous Assessment (WMO, 1999) additional measurements have refined our understanding of the amounts, distributions, and changes in ozone-depleting gases in the atmosphere. For example, measurements suggest that inorganic chlorine in the stratosphere has now stabilized. This plateau arises as a result of the slow but continued overall

decline in organic chlorine observed globally in the troposphere since 1992-1994. Also, new results from the analysis of firn air provide further evidence that most ozone-depleting gases are entirely of human origin. Details regarding these results and others are found here.

In this chapter and in subsequent ones, the terms concentration, mixing ratio, volume mixing ratio (assuming ideal gas behavior), abundance, amount, and loading refer to dry air mole fraction. These mole fractions are expressed, for example, as parts per trillion (ppt; pmol mol^{-1}). The term “ton” is used to represent a metric ton, which is 10^6 grams. Also, the term “Montreal Protocol” is used to indicate the fully amended and adjusted Montreal Protocol as of 2002 (Beijing Amendments), unless otherwise specified.

1.2.1 Updated Atmospheric Observations of Ozone-Depleting Gases

1.2.1.1 CHLOROFLUOROCARBONS (CFCs)

Updated ground-based measurements of chlorofluorocarbons (CFCs) show continued increases for global surface mixing ratios of CFC-12 (CCl_2F_2). Surface mixing ratios of CFC-113 ($\text{CCl}_2\text{FCClF}_2$) peaked around 1996 and have been decreasing slowly thereafter. The decrease noted for CFC-11 (CCl_3F) mixing ratios in 1996 has continued (Figure 1-1; Table 1-1; Montzka et al., 1999; Prinn et al., 2000). Observed rates of change in the lower atmosphere for all three of these CFCs were slightly smaller in 2000 than in 1996 (Table 1-1; Prinn and Zander et al., 1999). Although emissions of CFC-12 declined substantially during the 1990s, mixing ratios of CFC-12 continue to increase because emissions are still larger than the small losses associated with its long atmospheric lifetime (100 years).

Calibration differences between three global ground-based measurement networks—the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced GAGE (ALE/GAGE/AGAGE; denoted “AGAGE” in this chapter) network, the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL; denoted “CMDL” in this chapter) network, and the University of California at Irvine (UCI) network—are on the order of 1-2% for CFC-11 and -12, and are slightly smaller for CFC-113. The trends measured at Earth’s surface by these three networks are similar in recent years (Table 1-1).

Updated column abundance measurements of CFC-12 from the ground also show continued increases in the atmospheric burden of this gas (Figure 1-2; Zander et al., 2000). The mean rate of accumulation, however, has slowed

SOURCE GASES

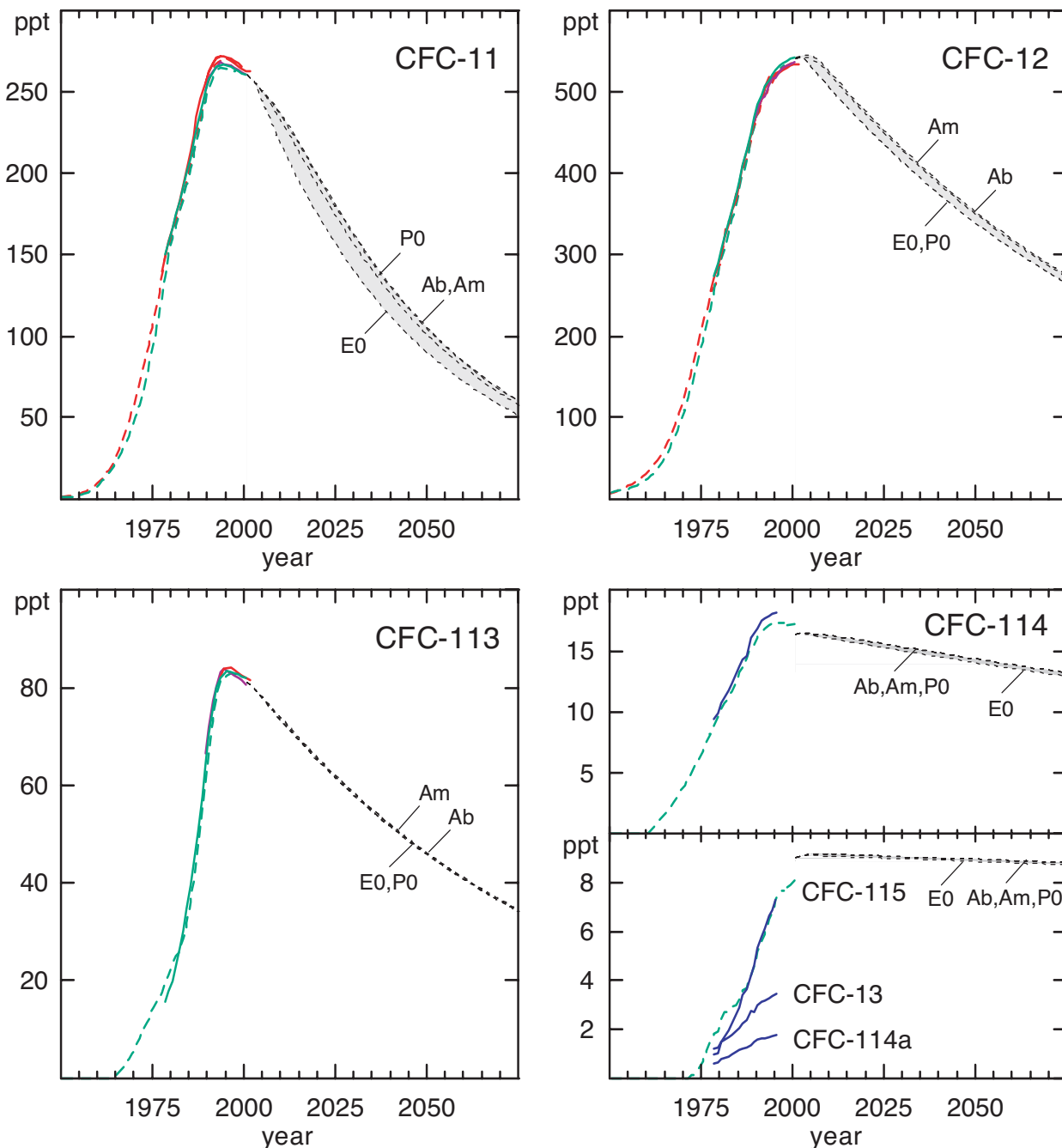


Figure 1-1. Past and potential future atmospheric mixing ratios of CFCs. Measurements of ambient air (solid lines) and histories inferred from measurements of firn air (long-dashed lines) define past burdens at Earth's surface. Potential future mixing ratios (short-dashed lines) have been calculated for different scenarios that are described in Section 1.8 (Ab, best guess; E0, zero emissions (not attainable, but defines a lower limit); Am, maximum allowed production; P0, zero production). Data sources for measurements of ambient air: AGAGE global monthly means (solid green lines: Prinn et al., 2000); CMDL global monthly means (solid red lines: Montzka et al., 1999); UCI global quarterly means (solid purple lines: D.R. Blake et al., 1996); and University of East Anglia (UEA) results from Cape Grim, Tasmania (for 41°S only) (solid blue lines: Oram, 1999). See the notes to Table 1-1 for more details regarding sampling frequencies and techniques. Antarctic histories have been derived from firn air extracted at the South Pole (red dashed lines: Butler et al., 1999) and Law Dome, Antarctica (green dashed lines: Sturrock et al., 2002). The shading shows the range of mixing ratios encompassed by the future scenarios.

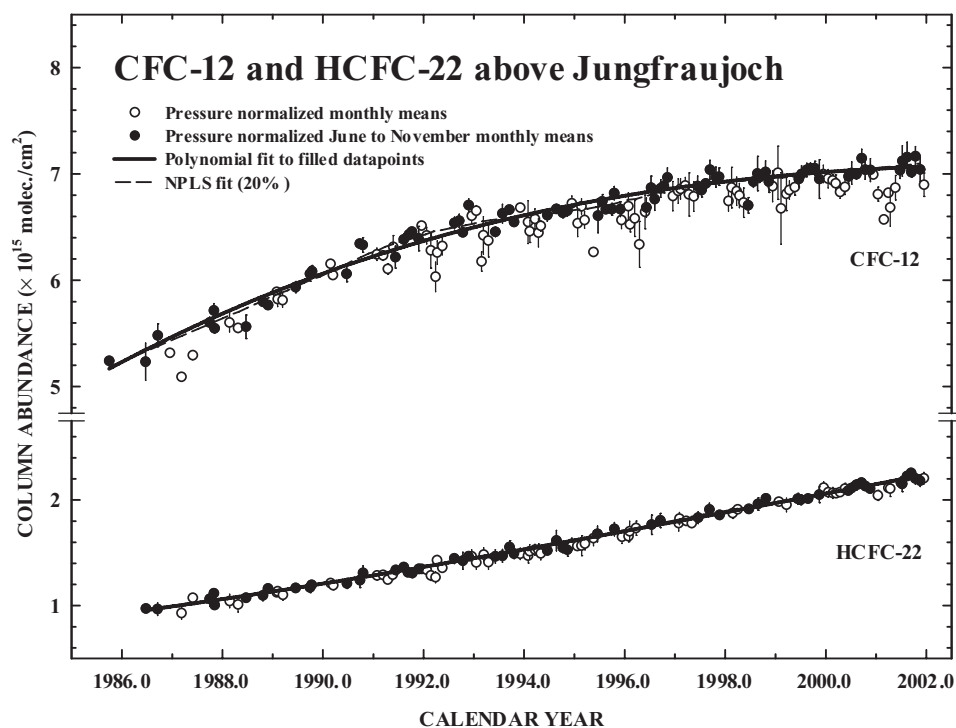


Figure 1-2. The time evolution of the monthly mean vertical column abundances of CFC-12 and HCFC-22 above the Jungfraujoch station, Switzerland, from 1985 to 2002 (update of Zander et al., 2000). Polynomial fits to the June to November columns are represented by the solid lines; nonparametric least-square fits (NPLS, dashed lines) are also shown but are noticeable only for CFC-12.

from $4.97 \times 10^{13} \text{ molec cm}^{-2} \text{ yr}^{-1}$ (or $+0.71\% \text{ yr}^{-1}$) in 1998 to $3.06 \times 10^{13} \text{ molec cm}^{-2} \text{ yr}^{-1}$ (or $+0.43\% \text{ yr}^{-1}$) in 2000.

Updated balloon-based measurements at northern midlatitudes also reveal continued increases for CFC-12 in the stratosphere, up to 21 km altitude. Growth rates between 1997 and 2001, however, are between 2 and 3 ppt yr^{-1} , which is less (significant at the 2σ level) than observed between 1978 and 1990, and also less (significant at the 1σ level) than observed between 1990 and 1997 (updated work from Engel et al., 1998).

Measured trends and atmospheric distributions continue to suggest that CFC emissions in 2000 were substantially smaller than in the late 1980s and early 1990s (Montzka et al., 1999; Prinn et al., 2000). The most recent trends and interhemispheric gradients suggest, however, that emissions are not yet insignificant. Persistent mixing ratio gradients (or lack thereof) across latitudes on hemispheric scales can provide some indication of emission locations, but they are generally not useful for delineating emission rates from any individual country despite assertions to the contrary in some studies (Libo et al., 2001).

A number of less abundant CFCs have been measured in the atmosphere. CFC-13 (CClF_3), CFC-114 ($\text{CClF}_2\text{CClF}_2$), and CFC-115 (CClF_2CF_3) have found use as specialist refrigerants (R-13, R-114, R-115), aerosol propellants (CFC-114, -115), and foam-blowing agents (CFC-114). Small amounts of CFC-13 are also emitted during aluminum production (Harnisch, 1997) and during the manufacture of CFC-12. CFC-114a (CCl_2FCF_3),

which is an isomer of CFC-114 ($\text{CClF}_2\text{CClF}_2$), has also been detected in the background atmosphere (Oram, 1999; Culbertson et al., 2000). The most likely origin of CFC-114a is as a byproduct of the CFC-114 production process (Chen et al., 1994).

Measurements of air samples collected at Cape Grim, Tasmania (41°S), show that the abundance of all four of these minor CFCs increased substantially between 1978 and the mid-1990s (Figure 1-1; Table 1-1; Oram, 1999). During the early 1990s, however, the growth rates began to decline and by 1995 had all fallen to below 0.4 ppt yr^{-1} . In late 1995, mixing ratios at Cape Grim were 3.5 ppt (CFC-13), 16.5 ppt (CFC-114), 1.8 ppt (CFC-114a), and 7.5 ppt (CFC-115) (Table 1-1).

More recent measurements from Cape Grim show mid-2000 mixing ratios of about 8 ppt and 16.7 ppt for CFC-115 and -114, respectively (Sturrock et al., 2001). CFC-115 was increasing at 0.1 ppt yr^{-1} , while CFC-114 had stopped growing altogether. Mangani et al. (2000) similarly reported negligible growth for CFC-114 in recent years from samples collected in Antarctica. For these gases, direct comparisons between reported results are difficult because they often do not overlap in time, and, in the case of CFC-114, the AGAGE and Mangani et al. (2000) measurements may include significant contributions from both $\text{C}_2\text{Cl}_2\text{F}_4$ isomers (CFC-114 and -114a).

Culbertson et al. (2000) measured CFC-13 and -114a in air samples collected at a rural, continental site in the United States in March-April 2000. The mean

SOURCE GASES

Table 1-1. Mixing ratios and growth rates of some important ozone-depleting substances.

Chemical Formula	Common or Industrial Name	Mixing Ratio (ppt)			Growth (1999-2000)		Laboratory, Method
		1996	1998	2000	(ppt yr ⁻¹)	(% yr ⁻¹)	
CFCs							
CCl ₂ F ₂	CFC-12	532.4	538.4	542.9	2.3	0.42	AGAGE, in situ ^a
		525.9	531.0	534.5	1.9	0.35	CMDL, in situ ^a
		523.2	529.3	534.0	1.8	0.34	CMDL, flasks ^a
		526.2	532.0	535.7	1.9	0.35	UCI, flasks ^a
CCl ₃ F	CFC-11	265.6	263.0	260.5	-1.1	-0.41	AGAGE, in situ ^a
		270.5	267.2	263.2	-2.0	-0.76	CMDL, in situ ^a
		269.5	265.9	262.6	-1.5	-0.56	CMDL, flasks ^a
		266.3	263.7	261.0	-1.0	-0.39	UCI, flasks ^a
CClF ₃	CFC-13	3.5					UEA, SH, flasks ^b
CCl ₂ FCClF ₂	CFC-113	83.2	82.9	82.0	-0.35	-0.43	AGAGE, in situ ^a
		84.2	83.0	82.1	-0.32	-0.39	CMDL, flasks ^b
		83.1	82.1	81.1	-0.49	-0.60	UCI, flasks ^a
CClF ₂ CClF ₂	CFC-114	16.5					UEA, SH, flasks ^b
CCl ₂ FCF ₃	CFC-114a	1.8					UEA, SH, flasks ^b
	CFC-114, -114a		17.1	17.2	-0.10	-0.58	AGAGE, in situ ^b
CClF ₂ CF ₃	CFC-115		7.8	8.1	0.16	0.20	AGAGE, in situ ^b
		7.5					UEA, SH, flasks ^b
Halons							
CBrClF ₂	Halon-1211		3.9	4.1	0.13	3.2	AGAGE, in situ ^b
		3.5	3.8	4.0	0.10	2.5	CMDL, flasks ^{a, b}
		3.4	3.6	3.9	0.12	3.2	UCI, flasks ^a
		3.8	4.2	4.4	0.13	2.9	UEA, SH, flasks ^b
CBrF ₃	Halon-1301		2.8	2.9	0.08	2.8	AGAGE, in situ ^b
		2.3	2.5	2.6	0.06	2.4	CMDL, flasks ^a
		2.0	2.2	2.3	0.05	2.2	UEA, SH, flasks ^b
CBrF ₂ CBrF ₂	Halon-2402	0.48					CMDL, flasks ^b
		0.42	0.42	0.43	0.001	0.2	UEA, SH, flasks ^b
CBr ₂ F ₂	Halon-1202	0.037	0.044				UEA, SH, flasks ^b
Chlorocarbons —see also Chapter 2							
CH ₃ Cl	Methyl chloride		538	536			AGAGE, SH, in situ ^b
		588					OGI, flasks ^c
CCl ₄	Carbon tetrachloride	100.5	98.2	96.1	-0.94	-0.97	AGAGE, in situ ^a
		103.2	101.9	99.6	-0.95	-0.95	CMDL, in situ ^a
		103.1	101.4	99.2	-1.03	-1.03	UCI, flasks ^a
CH ₃ CCl ₃	Methyl chloroform	90.3	64.6	45.4	-8.7	-17	AGAGE, in situ ^a
		96.9	68.9	46.4	-10.2	-20	CMDL, in situ ^a
		92.3	65.7	45.7	-9.1	-18	CMDL, flasks ^b
		93.6	71.7	47.6	-13.0	-24	UCI, flasks ^a
HCFCs							
CHClF ₂	HCFC-22	122.4	132.7	143.2	5.4	3.8	AGAGE, in situ ^a
		121.5	131.4	141.9	5.1	3.7	CMDL, flasks ^b
CH ₃ CCl ₂ F	HCFC-141b		9.5	13.0	1.8	15	AGAGE, in situ ^b
		5.4	9.1	12.7	1.7	15	CMDL, flasks ^b
		4.3					UT, flasks ^b

Table 1-1, continued.

Chemical Formula	Common or Industrial Name	Concentration (ppt)			Growth (1999-2000)		Laboratory, Method
		1996	1998	2000	(ppt yr ⁻¹)	(% yr ⁻¹)	
CH ₃ CClF ₂	HCFC-142b		10.4	12.5	1.1	9.4	AGAGE, in situ ^b
		7.7	9.6	11.7	1.0	8.9	CMDL, flasks ^b
		9.2					UT, flasks ^b
CHCl ₂ F	HCFC-21	0.29					UEA, SH, flasks ^b
CHCl ₂ CF ₃	HCFC-123	0.03					UEA, SH, flasks ^b
CHClFCF ₃	HCFC-124		0.89	1.34	0.35	30	AGAGE, in situ ^b
Bromocarbons —see also Chapter 2							
CH ₃ Br	Methyl bromide		9-10				Many ^d
			8.4	8.1			AGAGE, SH, in situ ^b

Global mixing ratios and growth rates at Earth's surface unless otherwise specified. AGAGE: 4-5 in situ electron capture detection (ECD) sampling sites, 2 in situ gas chromatography-mass spectrometry (GC-MS) sampling sites, 2 flask sampling sites; CMDL: 5 in situ sampling sites, 8-10 remote flask sampling sites; UEA: University of East Anglia, analysis of archive flasks and regularly sampled flasks filled at Cape Grim, Australia (41°S); UCI: quarterly sampling from a multitude of sites between 47°S and 71°N.; UT: University of Tokyo, 2 flask sampling sites; OGI: Oregon Graduate Institute, quarterly flask sampling at ~40 sites. NH, Northern Hemisphere; SH, Southern Hemisphere.

Data sources: AGAGE: Prinn et al. (2000); Sturrock et al. (2001); ftp://cdiac.esd.ornl.gov/pub/ale_gage_Agag. CMDL: Butler et al. (1999); Montzka et al. (1999, 2000); Hall et al. (2002); <http://www.cmdl.noaa.gov>. UEA: Fraser et al. (1999); Oram et al. (1995); Oram (1999). UCI: D.R. Blake et al. (1996); N.J. Blake et al. (2001). UT: Shirai and Makide (1998).

^a Measurements by gas chromatography with electron capture detection.

^b Measurements by gas chromatography with mass spectrometry detection.

^c Results from OGI for CH₃Cl have been scaled by 550/600; see Kurylo and Rodríguez et al. (1999).

^d See Section 1.5.

mixing ratio of CFC-13 was 3.6 ± 0.3 ppt, which is in reasonable agreement with the measurements of Oram (1999). Conversely, the mixing ratio of CFC-114a was 7.9 ± 0.8 ppt, which is substantially higher than that reported by Oram (1999).

1.2.1.2 HALONS

Although the phaseout was imposed on halon production in developed countries earlier than for all other halocarbons, mixing ratios of both Halon-1211 (CBrClF₂) and Halon-1301 (CBrF₃) continued to increase in the atmosphere in 2000 (Figure 1-3). Global surface mixing ratios of individual halons were less than 5 ppt in 2000 (Table 1-1). Since the previous Assessment (WMO, 1999) a new set of regular measurements has become available (Prinn et al., 2000; Sturrock et al., 2001). Among the laboratories studying long-term trends of halons in the atmosphere, calibration differences are about 10-15% (UCI < CMDL < AGAGE < University of East Anglia (UEA)) for Halon-1211 and about 25% (UEA < CMDL < AGAGE) for Halon-1301 (Butler et al., 1998; Fraser et al., 1999; Montzka et al., 1999).

For Halon-1211, all four laboratories report rates of increase in 2000 of about 3% yr⁻¹, or 0.1 to 0.13 ppt yr⁻¹ (Table 1-1). For Halon-1301, CMDL, UEA, and

AGAGE data suggest rates of increase of 0.05-0.08 ppt yr⁻¹ or 2-3% yr⁻¹ in 2000 (Table 1-1). For both these halons, these rates of increase are only slightly slower than observed during the first half of the 1990s.

Two less abundant halons have been further monitored in the atmosphere. Halon-2402 (CBrF₂CBrF₂) is present at between 0.4 and 0.5 ppt in the global atmosphere (Table 1-1; Butler et al., 1998; Fraser et al., 1999), and its rate of increase has slowed dramatically since the mid-1990s (Fraser et al., 1999; Figure 1-3). Halon-1202 (CBr₂F₂) has been measured in background air at mixing ratios of 0.04-0.05 ppt (Table 1-1; Figure 1-3; Engen et al., 1999; Fraser et al., 1999). During 1995-1996 the abundance of Halon-1202 was increasing at 17% yr⁻¹ (0.007 ppt yr⁻¹) in the Southern Hemisphere, although updated measurements by UEA suggest that this rate is much smaller now (Figure 1-3). Although this halon has been used by the military in a few minor applications, most is produced from over-bromination during the production of Halon-1211 (UNEP, 1998b).

1.2.1.3 CARBON TETRACHLORIDE (CCl₄)

Global surface mixing ratios of carbon tetrachloride (CCl₄) have decreased since about 1990; mixing ratios in 2000 were between 95 and 100 ppt (Figure 1-4; Table

SOURCE GASES

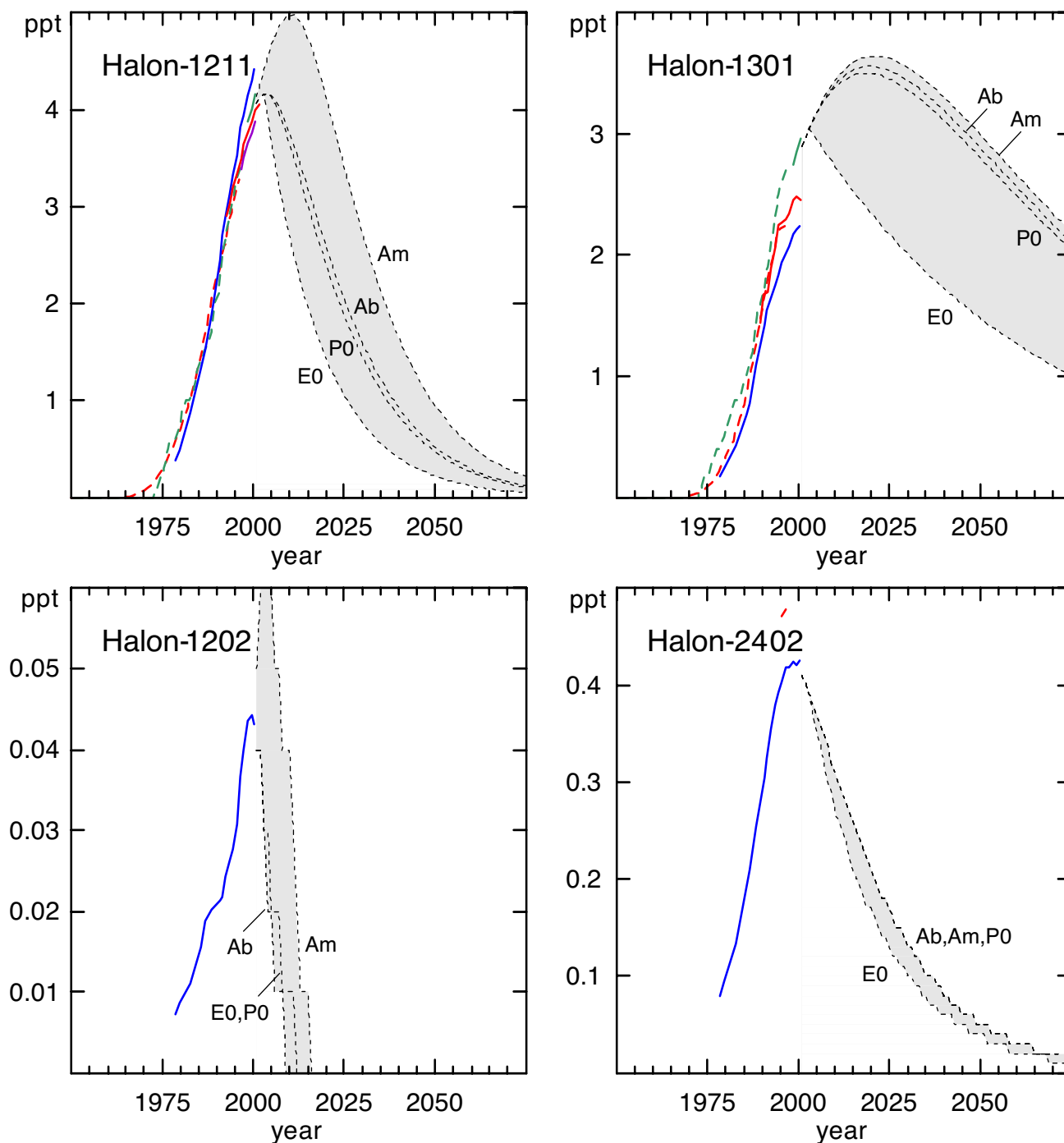


Figure 1-3. Past and potential future atmospheric mixing ratios of halons. Measurements of ambient air (solid lines) and histories inferred from measurements of firn air (long-dashed lines) define past burdens at Earth's surface. Potential future mixing ratios (short-dashed lines) have been calculated for different scenarios that are described in Section 1.8 and the caption to Figure 1-1. Data inferred from firn air are from the same sources as described in Figure 1-1. Data sources for measurements of ambient air: UEA from Cape Grim, Tasmania (for 41°S only) (solid blue lines: Fraser et al., 1999); AGAGE global mean data (solid green lines: Sturrock et al., 2001); UCI global quarterly means (solid purple lines: Blake et al., 2001); and CMDL global means (solid red lines: Butler et al., 1998; Montzka et al., 1999). The shading shows the range of mixing ratios encompassed by the future scenarios. See the notes to Table 1-1 for more details regarding sampling frequencies and techniques.

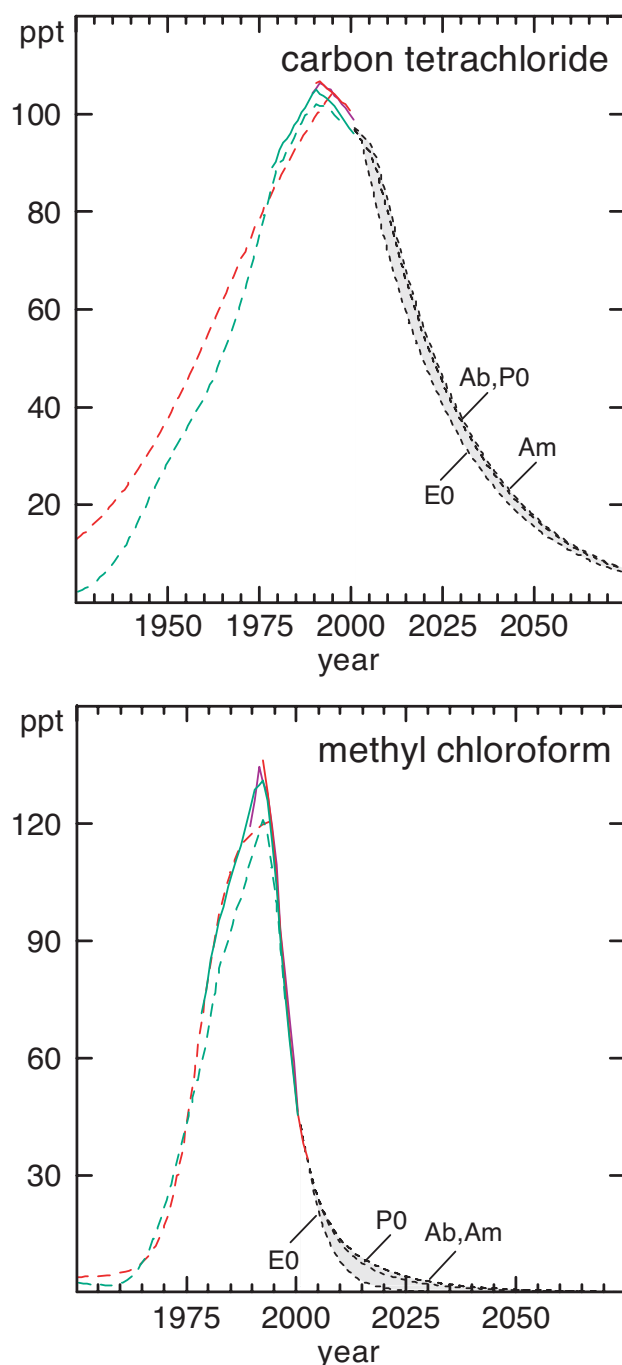


Figure 1-4. Past and potential future atmospheric mixing ratios of carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3). Measurements of ambient air (solid lines) and histories inferred from measurements of firn air (long-dashed lines) define past burdens at Earth's surface. Potential future mixing ratios (short-dashed lines) have been calculated for different scenarios that are described in Section 1.8 and the caption to Figure 1-1. Data sources and shading are the same as described in Figure 1-1.

1-1; Simmonds et al., 1998a; Montzka et al., 1999; Prinn et al., 2000). The observed rates of change have remained fairly constant since 1993 at about $-1\% \text{ yr}^{-1}$ or -1 ppt yr^{-1} . The interhemispheric difference has also been fairly constant at about 2% (North > South) since 1993 and suggests that significant emissions of carbon tetrachloride remain (see Section 1.6). Calibration differences between CMDL, UCI, and AGAGE are 3 to 4%.

1.2.1.4 METHYL CHLOROFORM (CH_3CCl_3)

The rapid decline in emissions of methyl chloroform (CH_3CCl_3) and its relatively short lifetime have together resulted in rapidly decreasing mixing ratios in recent years (Figure 1-4; Montzka et al., 2000; Prinn et al., 2001). The global mean surface mixing ratio in 2000 was approximately 46 ppt (Table 1-1), compared with the maximum of 130 ppt observed in 1992. Hemispheric differences were 2 to 3% in 2000, or much smaller than in earlier years.

Fairly constant exponential decay with a time constant of $(5.5 \text{ yr})^{-1}$ was observed for methyl chloroform during 1998-2000 (Montzka et al., 2000). This implies that the absolute rate of decline for methyl chloroform is becoming smaller: it peaked at -14 to -15 ppt yr^{-1} in 1995-1996, and was one-third less in 1999-2000, or about -10 ppt yr^{-1} (Table 1-1).

Scale differences between CMDL and AGAGE were stated as being $\sim 10\%$ in Prinn and Zander et al. (1999), and even larger among a broader range of laboratories. Since then scale revisions by AGAGE (Scripps Institution of Oceanography (SIO), SIO-93 to SIO-98; Prinn et al., 2000) and CMDL (Hall et al., 2002) suggest that the AGAGE-CMDL differences are now on the order of $<3\%$. There is a small time dependence to this difference. Similar mixing ratios are reported by UCI in 2000 (Table 1-1).

1.2.1.5 HYDROCHLOROFLUOROCARBONS (HCFCs)

Updated measurements of hydrochlorofluorocarbons (HCFCs) indicate that global mixing ratios of the three most abundant HCFCs continue to increase in the atmosphere, owing to sustained emissions (Figure 1-5). Updated measurements suggest global mixing ratios for HCFC-22 (CHClF_2) of 140-145 ppt in 2000 and a fairly constant growth rate of about 5 ppt yr^{-1} (Table 1-1; Figure 1-5; Simmonds et al., 1998b; Montzka et al., 1999). Sturrock et al. (2001) reported slightly faster increases from samples collected only at Cape Grim, Tasmania (6.3 ppt yr^{-1}). Hemispheric differences have been fairly constant in recent years at about 10% (North > South).

SOURCE GASES

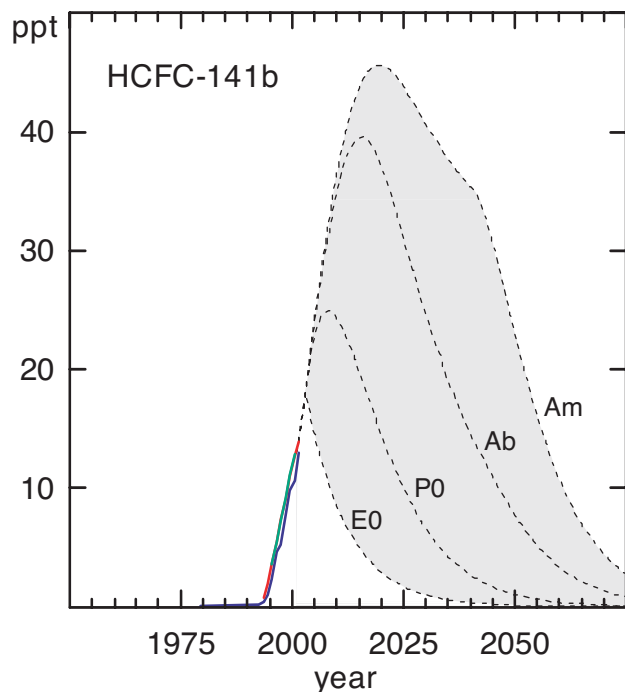
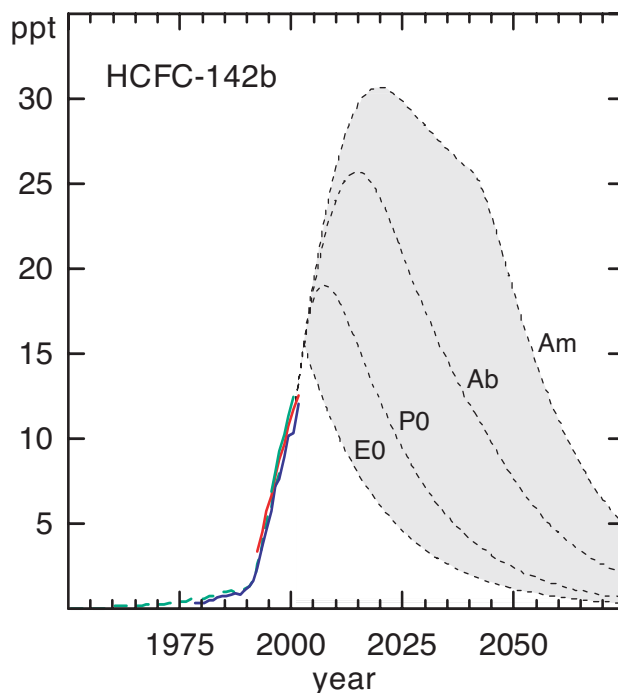
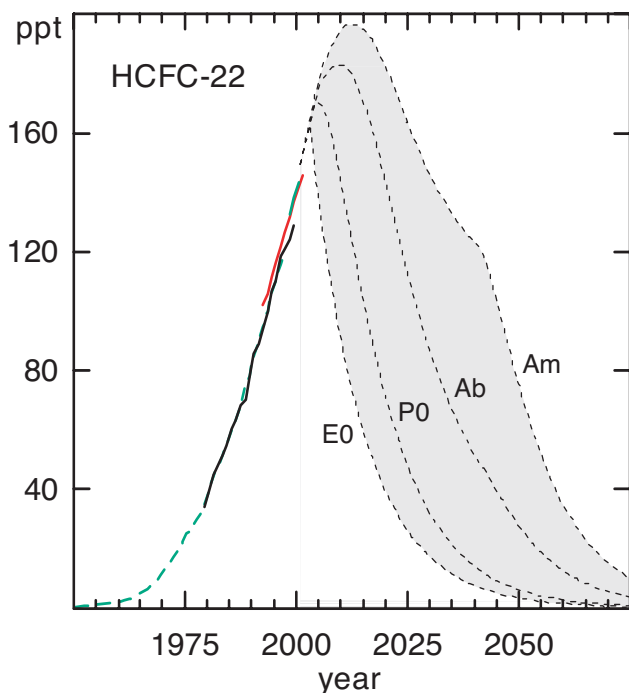


Figure 1-5. Past and potential future atmospheric mixing ratios of HCFCs. Measurements of ambient air (solid lines) and histories inferred from measurements of firn air (long-dashed lines) define past burdens at Earth's surface. Potential future mixing ratios (short-dashed lines) have been calculated for different scenarios that are described in Section 1.8 and the caption to Figure 1-1. Data sources: mixing ratios from Antarctic firn (long-dashed green line: Sturrock et al., 2002); AGAGE global means (solid green lines: Prinn et al., 2000; Sturrock et al., 2001); CMDL global means (solid red lines: Montzka et al., 1999); UEA from Cape Grim, Tasmania (for 41°S only) (solid blue lines: Oram et al., 1995); SIO from Cape Grim (41°S only) (solid black line: Miller et al., 1998). See the notes to Table 1-1 for more details regarding sampling frequencies and techniques. The shading shows the range of mixing ratios encompassed by the future scenarios.

Mean total column abundances of HCFC-22 measured above the Jungfraujoch station, Switzerland, in 1995 were 1.66×10^{15} molec cm^{-2} , increasing by 8.71×10^{13} molec $\text{cm}^{-2} \text{yr}^{-1}$ (or 5.2% yr^{-1}); for 2000, these figures were 2.11×10^{15} molec cm^{-2} , increasing by 8.93×10^{13} molec $\text{cm}^{-2} \text{yr}^{-1}$ (or 4.2% yr^{-1}), thus indicating that the absolute rate of atmospheric accumulation during those 5 years did not change substantially (Figure 1-2; an update of Zander et al., 2000).

Updated measurements show that the global mean surface mixing ratio of HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$) rose from about 5 ppt in mid-1996 to nearly 13 ppt in mid-2000 (Table 1-1; Figure 1-5; Montzka et al., 1994, 1999; Simmonds et al., 1998b; Prinn et al., 2000; Sturrock et al., 2001). The current growth rate is slightly less than 2 ppt yr^{-1} . Northern Hemispheric mean mixing ratios were approximately 3 ppt higher than Southern Hemispheric means in mid-2000.

Global mean surface mixing ratios of HCFC-142b (CH_3CClF_2) have risen from 7 to 8 ppt in mid-1996 to about 12 ppt in mid-2000, with a current growth rate of 1.0 ppt yr^{-1} (Table 1-1; Figure 1-5; Montzka et al., 1994; 1999; Simmonds et al., 1998b; Prinn et al., 2000; Sturrock et al., 2001). Northern Hemispheric means were 2 to 2.5 ppt higher than Southern Hemispheric means in mid-2000. Calibration differences are about 5% or less for HCFC-22, -141b, and -142b among laboratories reporting results recently (Table 1-1).

Since the previous Assessment, three other HCFCs have been reported in the background atmosphere: HCFC-123 (CHCl_2CF_3), HCFC-124 (CHClF_2), and HCFC-21 (CHCl_2F) (Table 1-1). From measurements at Cape Grim, Sturrock et al. (2001) reported late-1998 tropospheric mixing ratios of 0.53 ppt and 0.1 ppt for HCFC-124 and -123, respectively, the former having a growth rate of 0.06 ppt yr^{-1} (13%). Oram (1999) found similarly low levels of HCFC-123 at Cape Grim from archived samples collected between 1978 and 1993, but noted that the mixing ratio doubled between 1990 and 1993. Oram (1999) also reported measurements of HCFC-21 over the same period. Mixing ratios were typically in the range 0.2-0.4 ppt, with no significant trend.

1.2.1.6 METHYL BROMIDE (CH_3Br)

Our understanding of the concentration of methyl bromide (CH_3Br) in the atmosphere during the 1990s remains much the same as was given in the previous (1998) Assessment (WMO, 1999). No new global trends have been reported since those of Khalil et al. (1993). Recent data from research cruises encompassing a wide latitudinal span in both hemispheres (Yokouchi et al., 2000a; Li et al., 2001; Groszko and Moore, 1998; King et al., 2000), from aircraft missions (Schauffler et al., 1999), and from two midlatitude, ground-based sites (Miller, 1998) suggest that the mean global mixing ratio of atmospheric CH_3Br ranged from 9 to 10 ppt before reductions in industrial production began in the late 1990s, consistent with that reported in the 1998 Assessment. These new studies, along with that of Wingenter et al. (1998), suggest that the best estimate of the global, area-weighted, mean hemispheric ratio lies between 1.2 and 1.3 (North > South). This hemispheric ratio varies seasonally from 1.1 to 1.4, driven mainly by seasonality in Northern Hemispheric mixing ratios. Recent published comparisons between the National Center for Atmospheric Research (NCAR) and UCI show measurements agreeing within an average of 7% (Schauffler et al., 1999).

The vertical distributions and weak tropospheric gradient observed by N.J. Blake et al. (1996; 1997) are supported by measurements of Schauffler et al. (1999).

The tropospheric gradient in mixing ratio of 3-14% reported by Schauffler et al. (1999) is consistent with that reported in the 1998 Assessment, which noted a 0-15% vertical gradient in the tropospheric mixing ratio. Additionally Schauffler et al. (1999) noted that CH_3Br mixing ratios in the lower stratosphere (20 km) were reduced by 40% in the tropics and by 70% at Northern Hemispheric midlatitudes (July) relative to amounts observed in the troposphere.

1.2.1.7 METHYL CHLORIDE (CH_3Cl)

Khalil and Rasmussen (1999) recently published a detailed analysis of global measurements of methyl chloride (CH_3Cl) conducted over 16 years (1981-1997) at locations distributed throughout both hemispheres, during which methyl chloride reportedly decreased by about 4%. As noted in Chapter 2 of the 1998 Assessment (Kurylo and Rodríguez et al., 1999), Khalil and Rasmussen's global mean mixing ratio of 606 ppt is somewhat higher than the average of 550 ± 30 ppt obtained by other investigators. New results continue to suggest global means closer to 550 ppt than 600 ppt (Sturrock et al., 2001; Yokouchi et al., 2000b; Table 1-1). Khalil and Rasmussen (1999) reported a mean annual latitudinal distribution in the CH_3Cl mixing ratio in which the tropics were about 40 ppt higher than the poles, and they inferred that this had to be caused by a tropical terrestrial source. They also reported a seasonal cycle with an amplitude of about 10%, explicable mainly in terms of seasonal changes in hydroxyl radical (OH) abundance. In more recent work involving land-based and shipboard measurements extending from the Canadian Arctic through the Pacific and Indian Oceans to the Antarctic between 1996 and 1998, Yokouchi et al. (2000b) found CH_3Cl mixing ratios ranging from 500 ppt in the high Arctic and Antarctic to 570 ppt near the equator. Although this latitudinal distribution was measured only over a fraction of a year, it is similar to the annual mean distribution reported by Khalil and Rasmussen (1999).

1.2.2 Twentieth Century Atmospheric Histories for Halocarbons from Firn Air

Since the previous Assessment (WMO, 1999), 20th century atmospheric histories for halocarbons have been reconstructed from the analysis of air trapped in snow above glaciers, also known as firn air (Figures 1-1, 1-3, 1-4, and 1-5; Butler et al., 1999; Sturges et al., 2001a; Sturrock et al., 2002). Conclusions drawn from the firn-air results rely on the assumption that these halocarbons are neither produced nor destroyed in the firn. These firn-

SOURCE GASES

air data show that mixing ratios of CFCs, halons, and HCFCs in the oldest air sampled are generally less than 2% of the amounts measured today in the background atmosphere. Furthermore, and consistent with these halocarbons not being destroyed or produced in firm air over time, the 20th century atmospheric histories reconstructed from firm-air results and firm diffusion models are reasonably consistent with calculated histories based on records of industrial halocarbon production (Prinn et al., 2000). Somewhat higher amounts of carbon tetrachloride (5 ppt) and methyl chloroform (2-4 ppt) have been reported in the deepest and oldest samples, although these amounts were close to the detection limit of the instruments used in these analyses. These results suggest that nonindustrial sources of these halocarbons are insignificant.

Mixing ratios for methyl chloride and methyl bromide were only 10-30% lower than present day in firm air from Antarctica dating back to the early 1900s (Butler et al., 1999; Sturges et al., 2001a). The results are consistent with the presence of substantial nonindustrial emissions of these gases. Consistent results were observed for methyl bromide in firm samples at four different locations in Antarctica. These suggest that levels of methyl bromide in the Southern Hemisphere have increased by about 3 ppt since the early 20th century and about 2 ppt since the mid-20th century (see Section 1.5). Unfortunately, Northern Hemispheric firm-air profiles of methyl bromide show significant anomalies near the snow-ice transition, a feature not observed in the Antarctic profiles. For methyl chloride, firm data from both hemispheres suggest that the atmospheric burden over the last half of the 20th century

increased by about 10%. Additional details and discussion of these results appear in Section 1.5.

1.2.3 Total Atmospheric Chlorine

1.2.3.1 TOTAL ORGANIC CHLORINE IN THE TROPOSPHERE

Total organic chlorine (CCl_y) contained in long-lived chlorine-bearing source gases continues to decrease slowly in the lower atmosphere. In mid-2000, CCl_y was ~3.5 parts per billion (ppb) (Table 1-2), or about 5% lower than the peak observed in 1992-1994. The decrease still results primarily from the exponential decline observed for methyl chloroform (Table 1-2; Table 1-1; Figure 1-4). This situation is changing, however, because the absolute rate of decrease observed in 1999-2000 for methyl chloroform had diminished by one-third compared with 1995-1996 and will continue to lessen in the future (Montzka et al., 1999; see also Section 1.8).

By 2000 total chlorine from aggregated CFCs was no longer increasing (Table 1-2). Continued increases in chlorine from CFC-12 (3.6-4.6 ppt Cl yr^{-1}) in 2000 were similar in magnitude to declines in chlorine from the sum of CFC-11 and CFC-113 (Table 1-1).

The rate of increase in chlorine from HCFCs has been fairly constant since 1996 (Tables 1-1 and 1-2). HCFC-22 accounts for approximately 80% of chlorine from HCFCs in today's atmosphere and for about half of the annual increase in chlorine from all HCFCs (5 ppt Cl yr^{-1} out of about 10 ppt Cl yr^{-1}). Continued increases in

Table 1-2. Contributions of halocarbons to total organic chlorine (CCl_y) in the troposphere.

	Total CCl_y (ppt Cl)		Contribution to Total CCl_y (%)		Rate of Change in Total CCl_y (ppt Cl yr^{-1})	
	1996	2000	1996	2000	1996	2000
Aggregate CFCs	2161	2156	59	61	7.1	-0.6
CH_3Cl	550	550	15	16	0.0	0.0 ^a
CCl_4	407	384	11	11	-4.0	-3.8
Aggregate HCFCs	142	182	4	5	10.3	9.7
CH_3CCl_3	278	139	8	4	-40.8	-27.2
Short-lived gases ^b	100	100	3	3	0.0 ^a	0.0 ^a
Halon-1211	4	4	0	0	0.2	0.1
Total CCl_y	3642	3516			-27 (-0.8% yr^{-1})	-22 (-0.6% yr^{-1})

Bold-faced type is used to highlight the largest changes from 1996 to 2000. Some differences for 1996 from WMO (1999) arise because of small recent adjustments to absolute calibration scales and because the results presented here are an average of AGAGE and CMDL global means. Similar conclusions could be drawn with data from UCI (Table 1-1).

^a Presumed to be zero; not well documented.

^b Gases such as CH_2Cl_2 , CHCl_3 , and C_2Cl_4 .

HCFC-141b and -142b mixing ratios account for the additional annual chlorine increase.

The four minor CFCs accounted for about 50 ppt of Cl, or less than 1.5% of the total tropospheric chlorine burden in 2000 (CFC-13, -114, -114a, and -115). About 70% of this 50 ppt is from CFC-114. The current rate of growth for chlorine in these minor CFCs is small (<1 ppt Cl yr^{-1} ; Table 1-1).

1.2.3.2 TOTAL INORGANIC CHLORINE IN THE STRATOSPHERE

In a stratosphere unperturbed by polar stratospheric clouds or recent volcanism, more than 95% of inorganic chlorine (Cl_y) is accounted for by the two reservoirs hydrogen chloride (HCl) and chlorine nitrate (ClONO_2) (Zander et al., 1992, 1996). Furthermore, because tropospheric HCl and ClONO_2 mixing ratios are small, the sum of their vertical column abundances is a good surrogate of the Cl_y loading and its evolution in the stratosphere. Past reports of total column abundances of HCl and ClONO_2 , as well as their sum (Cl_y) derived from observations at Jungfraujoch (Switzerland, 46.5°N) through 1999, showed increases commensurate with trends in CCl_y at Earth's surface but delayed by 3-4 years owing to air transport rates between the troposphere and the stratosphere (Prinn and Zander et al., 1999; Mahieu et al., 2000).

An update of measurements from the Jungfraujoch now shows that the monthly mean total column abundances of HCl and ClONO_2 have stopped increasing (Figure 1-6). Updates of column abundance measurements of HCl at Kitt Peak (Arizona, U.S., 31.9°N) (Rinsland et al., 1991; Wallace et al., 1997) and of HCl and ClONO_2 at Lauder (New Zealand, 45°S) (Matthews et al., 1989; Reisinger et al., 1995) also show similar overall long-term trends. These results provide robust evidence that the loading of inorganic Cl_y in the unperturbed stratosphere has recently stabilized in response to the production regulations on ozone-depleting substances outlined in the Montreal Protocol. Within the uncertainty of these measurements, the trends in total column HCl and ClONO_2 are consistent with the trends for chlorinated organic trace gases measured at Earth's surface.

1.2.3.3 HYDROGEN CHLORIDE (HCl) AT 55 KM ALTITUDE IN THE STRATOSPHERE

An independent assessment of total Cl_y near the stratopause has been provided by measurements of HCl made since 1991 at 55 km altitude by the Halogen Occultation Experiment (HALOE) instrument aboard the Upper Atmosphere Research Satellite (UARS) (Russell et al., 1996; Prinn and Zander et al., 1999). At that altitude,

most Cl_y (~ 93 -95%, globally) is in the form of HCl. The broad changes in mean global HCl at 55 km measured by HALOE show a period of monotonically increasing HCl mixing ratios before 1997, and much slower mean changes thereafter (updates to Anderson et al., 2000; Figure 1-7). These long-term trends are consistent with expectations from ground-based measurements after considering lag times associated with transport of tropospheric air to the stratosphere and stratospheric mixing processes (Waugh et al., 2001; Hall and Plumb, 1994).

What remain unexplained in the HALOE HCl data are abrupt changes that occurred over shorter periods, such as those observed in early 1997 (Waugh et al., 2001; Engel et al., 2002) and in 2000 (Figure 1-7). These changes strongly suggest that additional atmospheric processes affect trends in HCl at 55 km (Randel et al., 1999; Considine et al., 1999). Several possible mechanisms likely to cause the early-1997, abrupt peaking of Cl_y at 55 km altitude were considered by Waugh et al. (2001) (such as changes in transport and chemistry partitioning), but none could explain a sharp decrease as early as 1997 in upper stratospheric Cl_y , given the measured tropospheric halocarbon trends and our understanding of atmospheric transport rates and mixing processes. HALOE measurements of methane, however, are anticorrelated with HCl since 1997. This suggests that transport may contribute to the variability observed in the HCl record, but transport effects alone do not resolve these tendencies (personal communication, J. Russell III, Hampton University, U.S., 2001).

1.2.3.4 STRATOSPHERIC CHLORINE COMPARED WITH TROPOSPHERIC CHLORINE

Evaluations of total chlorine (Cl_{tot}) in the stratosphere have been derived from measurements of CCl_y and Cl_y throughout the stratosphere with the Atmospheric Trace Molecule Spectroscopy (ATMOS) shuttle-based Fourier transform infrared (FTIR) spectrometer (Gunson et al., 1996). Average stratospheric Cl_{tot} was measured at 2.58 ± 0.10 ppb in 1985 (Zander et al., 1992) and 3.53 ± 0.10 ppb in 1994 (Zander et al., 1996). From measurements of a suite of chlorine-bearing source-, sink-, and reservoir species with a balloonborne FTIR spectrometer launched on 8 May and on 8 July 1997 from Fairbanks (Alaska, 64.8°N), Sen et al. (1999) derived a nearly constant value of Cl_{tot} , equal to 3.7 ± 0.2 ppb between 9 and 38 km altitude. Each of these studies confirmed that the bulk of inorganic stratospheric chlorine is well explained by the photodissociation of organic source gases measured in the troposphere after considering time lags associated with air transport and mixing processes.

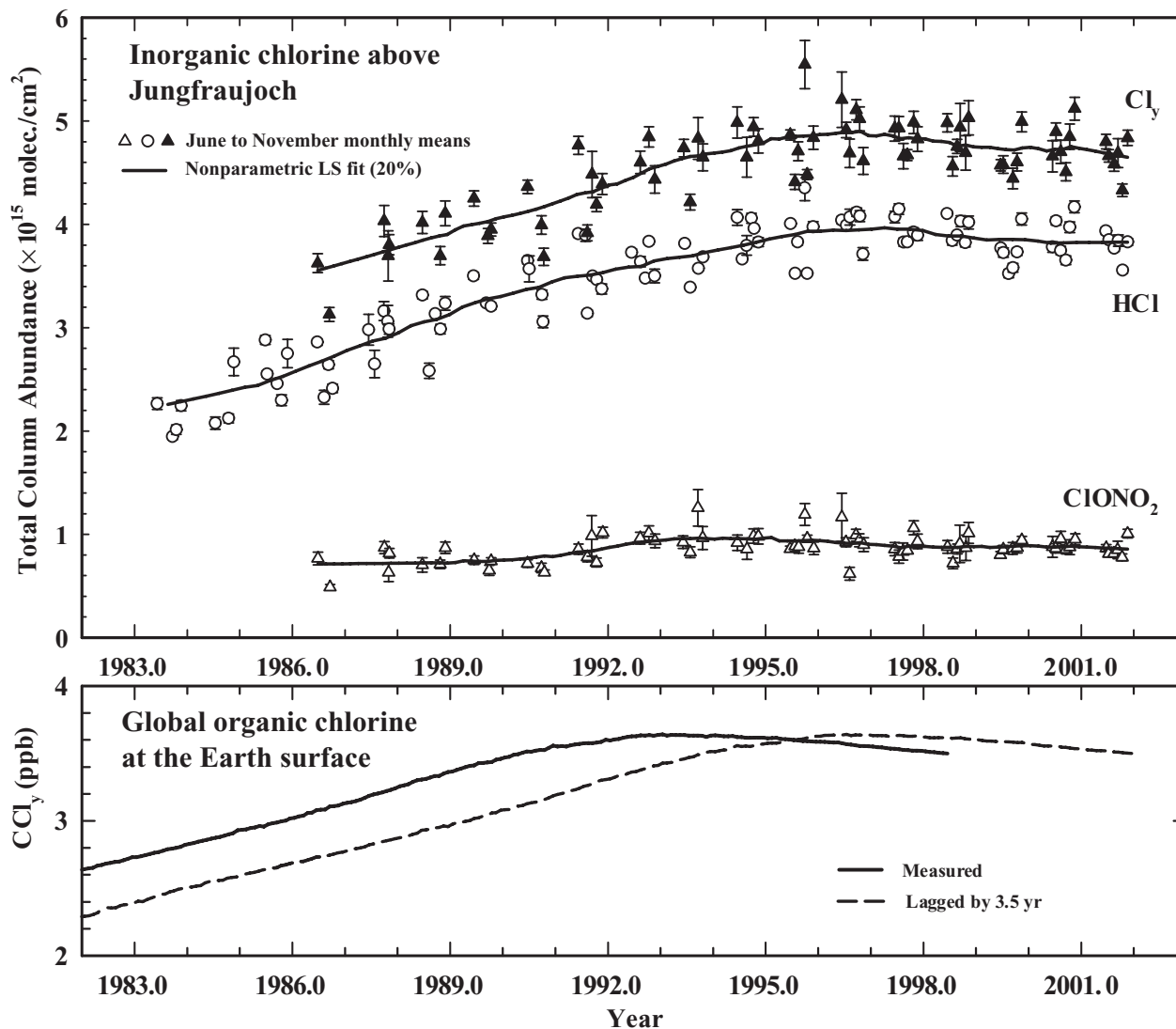


Figure 1-6. Upper frame: Time series of June to November (to avoid significant variability during winter and spring periods) monthly mean vertical column abundances of HCl (open circles) and ClONO_2 (open triangles) derived from solar observations at the Jungfraujoch between 1983 and 2001 (update from Mahieu et al., 2000). Inorganic chlorine (Cl_y , filled triangles) is obtained by summing the HCl and ClONO_2 column measurements. Lines represent nonparametric least-squares fits with 20% weighting. Lower frame: The temporal evolution of global organic chlorine loading (CCl_y) determined from in situ measurements at the ground (solid line: Prinn et al., 2000), and CCl_y lagged by 3.5 years (dashed line).

1.2.4 Total Atmospheric Bromine

1.2.4.1 TOTAL ORGANIC BROMINE IN THE TROPOSPHERE

Total organic bromine (CBr_y) in the troposphere results primarily from surface emissions of methyl bromide, halons, and short-lived bromocarbons. Recent trends in CBr_y are uncertain because global atmospheric trends in methyl bromide since 1992 are not yet well doc-

umented. Firn-air measurements suggest significant increases for this gas during 1900–1998, but they do not tightly constrain recent atmospheric trends. Changes in the growth rate of methyl bromide are perhaps likely during the 1990s because of the restrictions placed on industrial production in developed countries then (see the fully revised and amended Montreal Protocol).

Total organic bromine from halons has continued to increase since 1996 owing to continued anthropogenic production and use. The aggregate contribution of halons

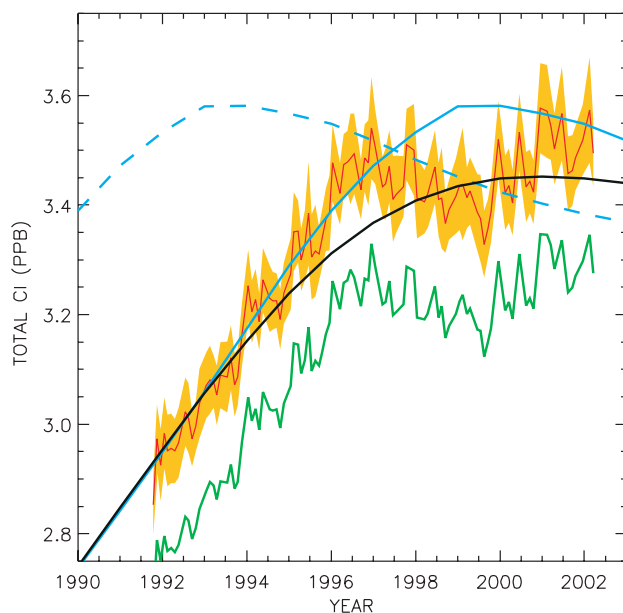


Figure 1-7. The time evolution of monthly mean HCl at altitudes of 54-56 km between 70°N and 70°S as measured by HALOE (green line: an update of Anderson et al., 2000). From this HCl record, total inorganic chlorine (Cl_y) mixing ratios at 55 km (red line) and their ± 1 standard deviations (orange shading) were derived using weighted contributions at 55 km altitude from all important source gases as determined from NCAR 2-D model calculations (Brasseur et al., 1990). Also shown are (i) CCl_y at Earth's surface based on the Ab scenario in Madronich and Velders et al. (1999) (dashed blue line), (ii) this surface result lagged by 6 years (solid blue line), and (iii) this lagged CCl_y convolved with a 3-yr-wide “age spectrum” (black line: an update of Waugh et al., 2001).

to CBr_y was 0.7 ppt in 1978, 6.7 ppt in 1996, and 7.7 ppt in 2000, and was increasing at $0.2 \text{ ppt Br yr}^{-1}$ in 2000 (Table 1-1; Figure 1-8).

Shorter-lived gases with predominantly natural sources, such as bromoform (CHBr_3) and dibromomethane (CH_2Br_2), also add to the bromine burden of the atmosphere. Atmospheric measurements indicate between 1 and 3 ppt of organic bromine is present near the tropopause in the form of these gases (Shauffler et al., 1998; Pfeilsticker et al., 2000). Although the precise amount of organic plus inorganic bromine delivered to the stratosphere by these short-lived gases is uncertain (see Chapter 2), we estimate that in 2000 methyl bromide accounted for about 50% of CBr_y , and the halons accounted for about 40% of CBr_y .

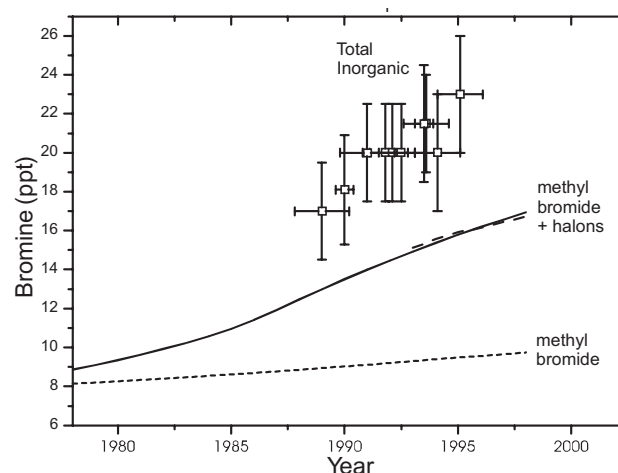


Figure 1-8. Past measured trends for bromine in the troposphere (lines) and stratosphere (points): global tropospheric bromine from methyl bromide as measured in ambient air and firn air (short dashed line: Khalil et al., 1993; Butler et al., 1999; Sturges et al., 2001a); global tropospheric bromine from the sum of methyl bromide plus halons as measured in ambient air, archived air, and firn air (solid line: Butler et al., 1999; Fraser et al., 1999; Sturges et al., 2001a), or as derived from firn-air and global flask samples (long-dashed line: Butler et al., 1998); and total inorganic bromine derived from stratospheric measurements of BrO and photochemical modeling that accounts for BrO/Br_y partitioning (open squares: Harder et al., 2000; Fitzenberger et al., 2000; Pfeilsticker et al., 2000). The years indicated on the abscissa are sampling times for tropospheric data. For stratospheric data, the date corresponds to when that air was last in the troposphere (i.e., sampling date minus mean time in stratosphere).

1.2.4.2 TOTAL INORGANIC BROMINE IN THE STRATOSPHERE

The burden and trend of inorganic bromine (Br_y) in the stratosphere can be estimated indirectly from measurements of organic source gases in the stratosphere (Shauffler et al., 1998; Wamsley et al., 1998) and from stratospheric bromine monoxide (BrO) measurements and calculated BrO/Br_y partitioning (Harder et al., 2000; Pfeilsticker et al., 2000; Sinnhuber et al., 2002). In stratospheric air in which most organic source gases had become oxidized, Br_y was estimated in early 1999 to be $18.4 (+1.8/-1.5)$ ppt from organic precursor measurements and 21.5 ± 3.0 ppt from coincident BrO measurements and photochemical modeling (Pfeilsticker et al.,

SOURCE GASES

2000; measurements were made at 25 km in air inferred to have a 5.6-yr mean age). Lower in the stratosphere, Br_y is a much smaller fraction of total bromine; these same investigators estimated Br_y to be 1.5 ppt in air just above the local Arctic tropopause (about 9.5 km).

1.2.4.3 STRATOSPHERIC BROMINE COMPARED WITH TROPOSPHERIC BROMINE

Spectrometric BrO measurements allow for estimates of total stratospheric Br_y . These measurements suggest an increase in Br_y over time and a stratospheric burden that is 4 to 6 ppt higher than indicated by the tropospheric burdens of halons and methyl bromide alone (Figure 1-8; an update of Pfeilsticker et al., 2000). Measurements of long- and short-lived gases at the tropopause and throughout the stratosphere suggest that an additional 1 to 3 ppt of bromine reaches the stratosphere in the form of organic short-lived gases, such as dibromomethane and bromoform (Schauffler et al., 1998; Wamsley et al., 1998; Pfeilsticker et al., 2000). This additional bromine does not appear to account for all the BrO measured, however. The remaining difference may suggest the presence of unmeasured, brominated organic gases reaching the stratosphere, or an influx of inorganic bromine into the stratosphere (see Chapter 2), or calibration errors either in the measurement of BrO or the organic source gases (Fitzenberger et al., 2000).

1.2.5 Effective Equivalent Chlorine and Effective Equivalent Stratospheric Chlorine

The net effect of changes in both atmospheric chlorine and bromine can be gauged roughly by computing effective equivalent chlorine (EECl) and effective equivalent stratospheric chlorine (EESC) from ground-based measurements of halocarbons (Prather and Watson, 1990; Daniel et al., 1995; Montzka et al., 1996a, 1999; WMO, 1999). EECl is calculated with ground-based halocarbon measurements, consideration of the enhanced efficiency of bromine to deplete stratospheric ozone (a factor of 45 used here; see discussion of α in Section 1.4.4), and consideration of the relative rates at which halocarbons decompose and release their halogen into the stratosphere. Ground-based measurement networks of the most abundant ODSs indicate that total ozone-depleting halogen measured in the troposphere peaked in 1992-1994 (Figure 1-9; Montzka et al., 1996a; Cunnold et al., 1997). Updated observations show that EECl in tropospheric air declined from 1995 through 2000 at a mean rate of about $1.2\% \text{ yr}^{-1}$, or $24 \text{ ppt EECl yr}^{-1}$. As of mid-2000, EECl was about 5% below the peak that was observed in 1992-1994.

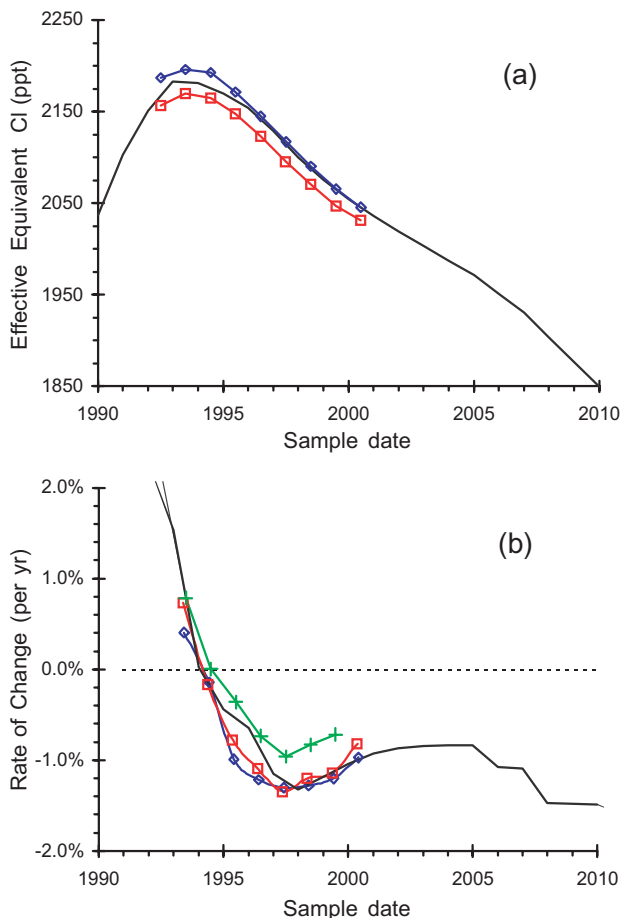


Figure 1-9. Burden and trends in aggregate tropospheric Cl plus Br from purely anthropogenic halocarbons expressed as effective equivalent chlorine. (a) Effective equivalent chlorine estimated from ground-based measurements of the major CFCs, methyl chloroform, carbon tetrachloride, Halon-1211, Halon-1301, and HCFCs (blue line with diamonds: Montzka et al., 1999; red line with squares: Prinn et al., 2000), and from the same gases as in scenario Ab (thin smooth line). The time scale on the x-axis refers to the date tropospheric air was sampled; to convert to effective equivalent stratospheric chlorine (EESC), add approximately 3 years to these dates. (b) The rate of change in effective equivalent chlorine as measured by [AGAGE + CMDL halon] measurements (red squares); CMDL measurements only (blue diamonds); [AGAGE + UEA halon] measurements (green plus symbols: halon data from Fraser et al., 1999); and in scenario Ab (thin solid line). Rates of change correspond to the 12-month difference over the previous 12 months. In both panels, total bromine was multiplied by 45, and the absolute fractional release assumed for CFC-11 was 0.8 (see Section 1.4.4).

Smaller declines and slower rates of decline are inferred when halon measurements by UEA at Cape Grim are considered (Figure 1-9; update of Fraser et al., 1999).

Although decreases observed for methyl chloroform are the primary reason for the turnover in EECI, the influence of methyl chloroform on EECI is diminishing. Furthermore, the increases still observed for CFC-12 and halons are slowing the decline of EECI (Fraser et al., 1999; Montzka et al., 1999). As a result of these influences, EECI decreased in 2000 at a rate that was only about two-thirds of the rate 3 to 4 years earlier (Figure 1-9). As the influence of methyl chloroform continues to lessen, a sustained decrease in EECI is assured only if trends for other halocarbons decrease further or become more negative (Montzka et al., 1999; see also Section 1.8).

Whereas EECI reflects the time evolution of equivalent effective halogen only in the troposphere, EESC provides an estimate of that burden in the stratosphere. EESC is derived by simply adding a 3-year time lag to EECI (see Section 1.8). Although EESC provides a useful measure to gauge the combined influence of tropospheric chlorine and bromine trends on stratospheric ozone-depleting halogen, it has important limitations. First, stratospheric halocarbon abundances lag tropospheric abundances by a few months to 6 years, depending upon location. Despite this range, a lag of 3 years is generally used in the calculation of EESC to approximate the mean transport time for air from the surface to the lower-mid stratosphere, which is where most ozone depletion has been observed. The 3 years is typical of the average age of air (time since air was in the troposphere; see Section 1.4.3) in these regions. Second, stratospheric halocarbon burdens are not determined by tropospheric burdens at a single time in the past. They instead represent a mean of tropospheric burdens from a range of earlier years (Hall and Plumb, 1994); this can result in errors with this simple technique especially when atmospheric mixing ratios are changing nonlinearly. Finally, Prather (1997) pointed out that the rate at which halogens are removed from the stratosphere has its own time scale in addition to the lag time associated with transport of halocarbons into the stratosphere. For short-lived halocarbons such as methyl bromide, whose tropospheric abundance could decrease rapidly relative to the rates at which air is transported into or out of the stratosphere, the decay of stratospheric inorganic halogen resulting from a rapid drop in tropospheric burden would be delayed and would not be well approximated by a single lag time. This effect is less important for most chlorinated ODSs because they have atmospheric lifetimes that are long relative to these transport rates.

Trends for EECI and EESC depend upon our understanding of the equivalency factor for bromine (α),

which varies over different latitudes and altitudes and is weighted by the distribution of stratospheric ozone (Daniel et al., 1999; see also Section 1.4.4). Although 45 represents a globally-weighted mean for α , higher estimates for this equivalency factor would suggest smaller decreases for EECI during years in which bromine continued to increase.

1.2.6 Fluorine in the Stratosphere

Measurements of hydrogen fluoride (HF) and carbonyl fluoride (COF_2), which are primarily concentrated in the stratosphere (Zander et al., 1992), provide an estimate of changes in the total fluorine burden of the atmosphere (Sen et al., 1996). Although fluorine does not catalytically destroy stratospheric ozone, trends in F_y^* (defined here as $F_y^* = [\text{HF}] + 2 \times [\text{COF}_2]$) have provided an independent measure of changes in the abundance of ozone-depleting substances (Gunson et al., 1994; Anderson et al., 2000).

Since the previous Assessment (WMO, 1999), long-term investigations of HF and COF_2 have continued, both from the ground and from space. Related Jungfraujoch results show a steady increase in column F_y^* until the mid-1990s, and a slower rate of increase afterward (Figure 1-10; updates to Mahieu et al., 2000 and Mélen et al., 1998). Two-dimensional (2-D) model calculations that include atmospheric histories for the most abundant, anthropogenic F-containing gases (CFC-12, CFC-11, CFC-113, HCFC-22, Halon-1211, and Halon-1301, which all are important ODSs) reproduce the measured trends in F_y^* above the Jungfraujoch station reasonably well (Figure 1-10; Chipperfield et al., 1997). This consistency provides further evidence that anthropogenic ODSs undergo photochemical degradation in the stratosphere and are responsible for the large increases in stratospheric chlorine and fluorine observed during the past 20 years or more. Similar conclusions have been drawn from analyses of the near-global mean HF measurements at 55 km from HALOE (Anderson et al., 2000) and from ATMOS measurements of individual F-containing gases between 1985 and 1994 over the altitude range of 8 to 60 km (Irion et al., 2002).

1.3 HALOCARBON SOURCES ESTIMATED FROM INDUSTRIAL PRODUCTION

The combination of halocarbon production data from both the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS, 2001) and the United Nations Environment Programme (UNEP, 2002) have allowed for the first time a rigorous estimate of total global production and consumption of ozone-depleting halocar-

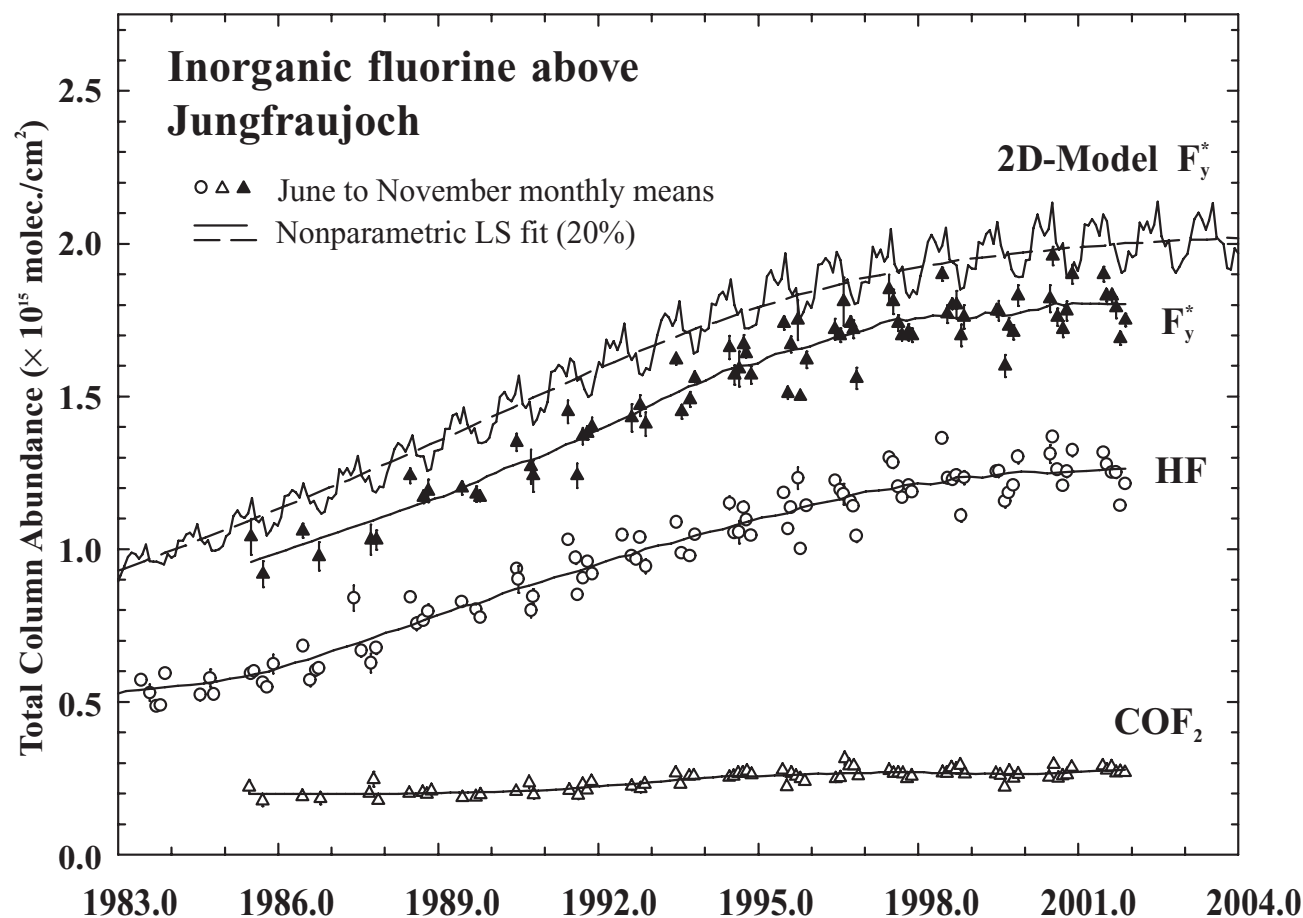


Figure 1-10. Time series of monthly mean vertical column abundances of HF (open circles: update from Mahieu et al., 2000); COF_2 (open triangles: update from Mélen et al., 1998); and their weighted sum, F_y^* (filled triangles; where $F_y^* = [\text{HF}] + 2 \times [\text{COF}_2]$) derived from observations at the Jungfraujoch (46.5°N) between 1983 and 2001. Only measurements from June to November are shown to avoid the significant variability observed during winter and spring. The thick lines through the individual datasets represent nonparametric least-squares fits with 20% weighting. Also shown is column F_y^* above the Jungfraujoch calculated with a two-dimensional model (Chipperfield et al., 1997). The model-calculated F_y^* minima occur in late summer/fall. The 10-12% high bias in the model calculations compared with the summer/fall observations is believed to arise in part from systematic uncertainties in the meridional transport of the 2-D model (see discussion in Chapter 4). Long-term column HF measurements above Kitt Peak indicate rates of change similar to those observed at the Jungfraujoch, but are not shown here (Rinsland et al., 2002b).

bons. Although the UNEP data provide more complete geographical coverage than AFEAS, they are not audited. The audited AFEAS data provide discrimination of production data by individual gases for all Parties other than China, India, and Korea. For this report, the aggregated additional production in these countries was subdivided into individual compounds as follows: HCFCs were treated as being produced in the same ratio as in the AFEAS data, and only CFC-11 and -12 contributed to the additional production of CFCs, consistent with there being little production of CFC-113 outside of the companies reporting to AFEAS (personal communication, M.R.

Harris, World Bank, 1999). In the case of methyl chloroform, global production data were derived from a similar combination of an industrial database (McCulloch and Midgley, 2001) and data in UNEP (2002). For the halons, global production data were derived from Fraser et al. (1999), updates to UNEP (1999), UNEP (2002), and also from reports to the Parties on the Multilateral Fund, for example, as described in Bingfeng et al. (2000).

None of these substances is emitted immediately after it is produced; emissions occur over a period during and after use that varies depending upon the application. In some cases, notably where the substance is used as a sol-

vent, emissions are prompt and can be well characterized in quantity and timing. Since the previous Assessment (WMO, 1999), emission functions that relate the quantities of fluorocarbons in use to the quantities released into the atmosphere have been intensively re-examined and, in some cases, revised (Ashford, 2000). In the case of HCFC-142b this has resulted in a significant change in the emission function and the calculated quantities emitted (AFEAS, 2001). It is also apparent that containment of most CFCs and HCFCs began to improve in the early 1990s. For example, emissions of CFC-11 from foam blowing showed a sharp reduction after about 1992 (McCulloch et al., 2001), and these changes are included in the revised release functions. Emissions from some refrigeration applications have been reduced in recent years (UNEP, 1998a; Calm, 1999), but these systems represent only a small fraction of total emissions from refrigeration. A single emission function for refrigeration has been used for more than 30 years (McCulloch et al., 2001, 2002).

Ongoing work by the Technology and Economic Assessment Panel (TEAP) has also allowed for independent estimates of halons, as discussed below.

1.3.1 CFCs and HCFCs

For substances used in refrigeration, there is an initial loss of between 5% (CFC-12) and 35% (HCFC-22), and complete emission within 10 years for the average system (Gamlen et al., 1986; Midgley and Fisher, 1993; McCulloch et al., 2002). This is consistent with the average linear loss rate of 11% yr⁻¹ described by Baker (1999). However, the actual distribution of emissions is approximately normal around 4.5 ± 2 years.

1.3.2 Halons

Halons are primarily used as fire extinguishing agents, although Halon-1301 also received minor use as a cold-temperature refrigerant. UNEP (1998b) suggests that production data as reported to the UNEP Ozone Secretariat is accurate. Two estimates of emissions for Halon-1211 and -1301 have been made using similar production data (Fraser et al., 1999; updated UNEP, 1999), but since very different emission functions were used, markedly different emission rates were obtained (see Section 1.6). Further, the extent of inadvertent halon emissions from some production facilities has yet to be characterized but may be substantial (UNEP, 1999).

1.3.3 Carbon Tetrachloride (CCl₄)

The principal identified use of carbon tetrachloride is as feedstock for the production of CFC-11 and -12, and

from this process releases to the atmosphere arise only from fugitive losses. Large discrepancies existed in UNEP consumption data for past years owing to confusion over reporting procedures, and although these have been addressed by TEAP (UNEP, 1998b), there may still be significant omissions and unrecorded sources (see Section 1.6). TEAP suggests emissions of 41(+50%, -25%) Gg from total production of 203 Gg in 1996 (UNEP, 1998b), but, as discussed in Section 1.6, this is only about half of the emissions necessary to account for observed burdens and trends in that year given the updated lifetime estimate of 26 years (see Section 1.4).

1.3.4 Methyl Chloroform (CH₃CCl₃)

Industrial production and release to the atmosphere of methyl chloroform declined dramatically in the 1990s (McCulloch and Midgley, 2001; UNEP, 2002). Global anthropogenic emissions in 1999-2000 were estimated at about 20 Gg yr⁻¹, or only 3% of the emissions estimated for 1989-1990, the peak emission years. Declines in emission closely follow declines in production because methyl chloroform was used predominantly in applications where releases occurred soon after sales.

Firn results (Butler et al., 1999; Sturrock et al., 2002) suggest mixing ratios in the early 1990s, before industrial production began, of less than 4 ppt and confirm that use by industry was the main source of atmospheric methyl chloroform.

Reports have suggested that small amounts of methyl chloroform are emitted from biomass burning. Upper limits quoted in an early study (Rudolph et al., 1995) have since been revised downward with additional laboratory work and suggest emissions may be on the order of 2-10 Gg yr⁻¹ from burning (Rudolph et al., 2000). Emissions of this magnitude would sustain global mixing ratios of 0.5-2 ppt, consistent with inferences from the analysis of firn air.

1.4 HALOCARBON LIFETIMES, OZONE DEPLETION POTENTIALS, AND GLOBAL WARMING POTENTIALS

1.4.1 Introduction

Halocarbon sinks chemically transform or physically remove halogen-containing source species from the atmosphere after release. Known atmospheric sinks for halocarbon source gases include photolysis, reaction with hydroxyl radical (OH) in both the troposphere and stratosphere, reaction with electronically excited atomic oxygen (O(¹D)) and atomic chlorine (Cl) chiefly in the strato-

SOURCE GASES

sphere, uptake in oceanic surface waters through chemical and biological degradation processes, biological degradation in soils, and possibly surface reactions on minerals. Not all halocarbon source gases become degraded by all of these sink processes. The quantitative determinations of trace gas sink strengths are of interest because the sinks control both the atmospheric lifetimes and the location of halogen release from source gases.

The important sink processes for atmospheric lifetime are those that have significant strength on a mass or molecule basis, that is, where loss frequency and atmospheric abundance are co-located. A simple definition of lifetime is the sum of the integrals over the entire atmosphere of the product of the first-order sink process frequencies (the local instantaneous lifetimes) and the normalized source gas mass or concentration distribution.

1.4.2 Lifetimes

For a given halocarbon, each relevant sink process contributes to the additive first-order total loss frequency, L , which is variable in space and time. A local halocarbon lifetime, τ_{local} , can be defined as the inverse of L evaluated at a point in space and time:

$$\tau_{\text{local}} = \frac{1}{L(x, y, z, t)} \quad (1-1)$$

For consideration of global effects of the halocarbon, L must be integrated globally, and the integral must be weighted by the distribution of the halocarbon on which the sink processes act. If we consider a normalized halocarbon distribution $n(x, y, z, t)$, a global instantaneous lifetime can be defined as

$$\tau_{\text{global}} = \frac{\int dV n(V, t) (=1)}{\int dV L(V, t) n(V, t)} \quad (1-2)$$

where V is an atmospheric volume element. This expression can be averaged over a year to determine the global, annually averaged lifetime. Because the total loss frequency L is the sum of the individual sink process frequencies, τ_{global} can also be expressed in terms of process lifetimes; for example,

$$\tau_{\text{global}} = \left[\frac{1}{\tau_{\text{OH}}} + \frac{1}{\tau_{\text{ocean}}} + \frac{1}{\tau_{\text{photolysis}}} + \frac{1}{\tau_{\text{other processes}}} \right]^{-1} \quad (1-3)$$

Note that in considering lifetime with respect to individual sink processes, which may be defined or analyzed over limited domains, the associated burden (the numerator in Equation (1-2)), however, must always be

global and include all communicating reservoirs. When the halocarbon distribution is time invariant, where emissions, sinks, and atmospheric transport are in long-term balance, the halocarbon burden $B(t)$ can be defined by

$$\frac{dB(t)}{dt} = E(t) - \frac{B(t)}{\tau_{\text{global}}} \quad (1-4)$$

and the lifetime τ_{global} becomes a scale factor relating the halocarbon emission rate $E(t)$ (or equivalently the sink rate) to the atmospheric burden. This steady-state lifetime is also formally equivalent to the scale factor relating the time-integrated atmospheric burden to a release of halocarbon at a single point in time (Prather, 1996). For source compounds that do not persist long enough to become well mixed in the troposphere (here assumed for gases with $\tau < 0.5$ years), distributions are strongly dependent on the pattern of emissions. Consequently, the concept of a single global lifetime, ODP, or GWP becomes inappropriate for such short-lived gases (see Chapter 2). In this chapter, only local lifetimes are reported for short-lived gases (Table 1-3), and these lifetimes are not derived from any actual steady-state global emission/distribution patterns. (GWPs for these gases are not reported in Table 1-6 because of these concerns.) Finally, a discussion of the ODP concept for short-lived gases is addressed in Chapter 2.

WMO (1999) and IPCC (2001) include detailed discussions of the various specific techniques for estimating steady-state and non-steady-state global lifetimes, to which the reader is referred. The techniques fall into four general categories: (1) lifetimes derived from model-calculated distributions and sink loss frequencies, (2) lifetimes inferred by inverse methods from direct observations of halocarbon abundance with high precision and accuracy over multiyear periods and requiring varying degrees of knowledge about actual emissions, (3) lifetimes determined relative to a reference species with an independently derived lifetime through observations of species correlations or knowledge of relative kinetic rate parameters, and (4) lifetimes determined from some combination of the above three techniques, where the total lifetime is determined as the combination of individual process lifetimes.

Important advancements have been made in our understanding of halocarbon lifetimes since WMO (1999). Those relate to improvements in understanding the lifetime of methyl chloroform and in choosing a globally representative temperature that allows better estimates of lifetimes of other gases destroyed by OH.

Recently reported analyses of methyl chloroform lifetime based on observations from global sampling net-

works over multiyear periods (Montzka et al., 2000; Prinn et al., 2000, 2001) suggest a slightly longer central value than previous World Meteorological Organization (WMO) and Intergovernmental Panel on Climate Change (IPCC) reports (Kurylo and Rodríguez et al., 1999; Prather and Ehhalt et al., 2001). Additionally, stratospheric in situ correlation measurements (Volk et al., 1997) derive a somewhat shorter stratospheric lifetime than was adopted in these Assessments. Because CH_3CCl_3 acts as the reference compound for the relative determination of lifetime with respect to tropospheric OH oxidation for the large suite of hydrogenated halocarbons, changes in CH_3CCl_3 lifetime need to be carefully considered. Equation (1-3) is employed to determine the value of τ_{OH} for CH_3CCl_3 (here derived to be 6.1 years, see below), where τ_{global} (= 5.0 years) is inferred from direct observations of CH_3CCl_3 and estimates of emissions; $\tau_{\text{photolysis}}$ (= 38–41 years) arises from loss in the stratosphere and is inferred from observed stratospheric correlations among CH_3CCl_3 , CFC-11, and the stratospheric age of the air mass observed; τ_{ocean} (= 94 years) is derived from a model of the oceanic loss process; and $\tau_{\text{other processes}}$ is taken to be zero.

The total atmospheric lifetime value adopted here of 5.0 years for methyl chloroform at steady state (i.e., unchanging distribution or balanced emission and loss) lies between the mean lifetimes inferred from observations for non-steady-state periods of 5.2 (+0.2/–0.3) years (Montzka et al., 2000) and 4.9 (+0.6/–0.5) years (Prinn et al., 2001) and below the observationally derived upper limit of 5.5 years (Montzka et al., 2000). Note that the difference between these observational lifetimes is not ascribed to simple uncertainties in calibration accuracy or measurement precision. The Prinn et al. (2001) value pertains to the average global OH during 1978–2000, whereas the Montzka et al. (2000) value refers specifically to 1998–1999, a time period for which Prinn et al. (2001) suggest that global OH fell below the long-term average, producing a longer instantaneous lifetime.

The oceanic sink lifetime of methyl chloroform has been reassessed recently based on a high-resolution model of ocean processes and surface mixing, and a value of 94 years was calculated (Yvon-Lewis and Butler, 2002), similar to the lifetime adopted in the previous Assessment (WMO, 1999). Given the above-mentioned revisions, the previously adopted process OH lifetime of 5.7 years would require an unrealistically long stratospheric-loss lifetime (much greater than 45 years), where recent reports indicate even shorter values (≤ 40 years). A longer lifetime of 6.1 years with respect to tropospheric hydroxyl radical reaction is consistent with stratospheric-loss lifetimes of 38 to 41 years. This range of stratospheric-loss lifetime lies between lower values inferred from tracer-tracer cor-

relations (Volk et al., 1997; Schauffler et al., 2002) and higher values calculated in multidimensional models (WMO, 1999). The general effect of this updated recommendation is to lengthen lifetimes of hydrogen-containing halocarbons and methane by about 7% relative to the two most recent Assessment reports, and to increase estimates for their ODP and GWP values by a similar amount.

Spivakovsky et al. (2000) have computed a global climatological distribution of tropospheric OH based on observed distributions of the OH-controlling quantities. Using this OH distribution and assuming a well-mixed distribution for the OH reaction partner, they show that selecting a temperature of 272 K to evaluate a tropospheric average OH rate constant produces a good fit over a wide range of activation energies in the Arrhenius rate constant expression. As in IPCC (2001), this value is adopted here in calculating lifetimes by reference to CH_3CCl_3 in Table 1-3. WMO (1999) used an earlier 277 K estimate for this value. The OH reaction rate constants used in generating the Table 1-3 lifetimes are the new recommendations of the NASA Panel for Data Evaluation (Sander et al., 2002).

The global lifetime for Halon-1211 (CBrClF_2) has been reassessed. This gas is destroyed exclusively by photolysis in both the troposphere and stratosphere, which makes it a somewhat special case among halogen source gases. Past lifetime recommendations that depend on cross section data and model calculations include 12–18 years (WMO, 1989), 18.5–20.1 years (WMO, 1991), 9.3–28.2 years (Kaye et al., 1994), and 20 years (WMO, 1995). The Halon-1211 lifetime has also been inferred from a comparison between observed atmospheric burdens and emission histories derived from halon production magnitudes. Uncertainty in both the atmospheric measurements and available release histories (Fraser et al., 1999; an update to UNEP, 1999) do not constrain these estimates to better than 11–30 years (see Section 1.6). Finally, the stratospheric component of the Halon-1211 lifetime has been inferred from correlating stratospheric observations of this halon to age of stratospheric air, nitrous oxide (N_2O), and CFC-11 (e.g., Volk et al., 1997). This stratospheric lifetime is difficult to combine appropriately with modeled estimates of tropospheric loss, although the available estimates suggest a global Halon-1211 lifetime of about 14 years. Because of the uncertainties surrounding observational-based lifetime estimates, the recommendation for the total steady-state lifetime of Halon-1211 is updated here to 16 years based primarily on reported model-calculated values known to include the tail of the Halon-1211 absorption between 300 and 400 nm (Burkholder et al., 1991; Fraser et al., 1999). Clearly additional laboratory, observational, and modeling studies will be needed to reduce the uncertainties in this lifetime.

SOURCE GASES

Table 1-3. Halogenated trace gas lifetimes.

Industrial Designation or Common Name	Chemical Formula	Lifetime (years)	Notes
Halogen-substituted methanes			
HFC-41	CH ₃ F	2.4	1
HFC-32	CH ₂ F ₂	4.9	1
HFC-23	CHF ₃	270	1
FC-14 (carbon tetrafluoride)	CF ₄	50 000	2
Methyl chloride	CH ₃ Cl	1.3	1, 3
Dichloromethane	CH ₂ Cl ₂	0.38	15, 16
Chloroform	CHCl ₃	0.41	15, 16
Carbon tetrachloride	CCl ₄	26	5
HCFC-31	CH ₂ ClF	1.3	4
HCFC-22	CHClF ₂	12.0	1, 6
HCFC-21	CHCl ₂ F	1.7	1, 6
CFC-13	CClF ₃	640	2
CFC-12	CCl ₂ F ₂	100	2, 7
CFC-11	CCl ₃ F	45	2, 7
Methyl bromide	CH ₃ Br	0.7	3
Dibromomethane	CH ₂ Br ₂	0.33	8, 15, 16
Bromoform	CHBr ₃	0.07	8, 15, 16
Bromodifluoromethane	CHBrF ₂	5.8	4
Bromochloromethane	CH ₂ BrCl	0.37	8, 15, 16
Bromodichloromethane	CHBrCl ₂	0.21	7, 15, 1
Dibromochloromethane	CHBr ₂ Cl	0.19	7, 15, 16
Halon-1301	CBrF ₃	65	2, 7
Halon-1211	CBrClF ₂	16	9
Halon-1202	CBr ₂ F ₂	2.9	17
Methyl iodide	CH ₃ I	0.02	7, 15, 16
Diiodomethane	CH ₂ I ₂	Minutes	7, 15, 16
Chloriodomethane	CH ₂ ClI	Hours	7, 15, 16
Trifluoroiodomethane	CF ₃ I	<0.005	2, 15
Halogen-substituted ethanes			
HFC-161	CH ₃ CH ₂ F	0.21	2, 15
HFC-152	CH ₂ FCH ₂ F	0.60	2, 15
HFC-152a	CH ₃ CHF ₂	1.4	1, 6
HFC-143	CH ₂ FCHF ₂	3.5	1
HFC-143a	CH ₃ CF ₃	52	1
HFC-134	CHF ₂ CHF ₂	9.6	1
HFC-134a	CH ₂ FCF ₃	14.0	1, 6
HFC-125	CHF ₂ CF ₃	29	1, 6
FC-116 (perfluoroethane)	CF ₃ CF ₃	10 000	2
chloroethane	CH ₃ CH ₂ Cl	0.11	15
1,1 dichloroethane	CH ₂ ClCH ₂ Cl	0.19	10, 15
Methyl chloroform	CH ₃ CCl ₃	5.0	9

Table 1-3, continued.

Industrial Designation or Common Name	Chemical Formula	Lifetime (years)	Notes
HCFC-142b	CH_3CClF_2	17.9	1, 6
HCFC-141b	$\text{CH}_3\text{CCl}_2\text{F}$	9.3	1, 6
HCFC-123	CHCl_2CF_3	1.3	6, 11
HCFC-124	$\text{CHClF}_2\text{CF}_3$	5.8	6, 11
CFC-113	$\text{CCl}_2\text{FCClF}_2$	85	2
CFC-113a	CCl_3CF_3	NA	NA
CFC-114	$\text{CClF}_2\text{CClF}_2$	300	2
CFC-115	CClF_2CF_3	1700	2
Halon-2402	$\text{CBrF}_2\text{CBrF}_2$	20	17
Halogen-substituted propanes			
HFC-281ea	$\text{CH}_3\text{CHFCH}_3$	0.06	15
HFC-263fb	$\text{CH}_3\text{CH}_2\text{CF}_3$	1.6	2
HFC-245ca	$\text{CH}_2\text{FCF}_2\text{CHF}_2$	6.2	1
HFC-245ea	$\text{CHF}_2\text{CHFCHF}_2$	4.0	2
HFC-245eb	$\text{CH}_2\text{FCHFCF}_3$	4.0	12
HFC-245fa	$\text{CHF}_2\text{CH}_2\text{CF}_3$	7.6	1
HFC-236cb	$\text{CH}_2\text{FCF}_2\text{CF}_3$	13.6	1
HFC-236ea	$\text{CHF}_2\text{CHFCF}_3$	10.7	1
HFC-236fa	$\text{CF}_3\text{CH}_2\text{CF}_3$	240	1
HFC-227ea	$\text{CF}_3\text{CHFCF}_3$	34.2	1
FC-218 (perfluoropropane)	$\text{CF}_3\text{CF}_2\text{CF}_3$	2600	2
n-propyl chloride	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	0.06	13, 15
HCFC-243cc	$\text{CH}_3\text{CF}_2\text{CFCl}_2$	26.4	4
HCFC-225ca	$\text{CHCl}_2\text{CF}_2\text{CF}_3$	1.9	11
HCFC-225cb	$\text{CHClF}_2\text{CF}_2\text{CClF}_2$	5.8	11
n-propyl bromide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	0.04	15, 16
n-propyl iodide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	0.003	7, 15, 16
isopropyl iodide	$\text{CH}_3\text{CHICH}_3$	0.002	7, 15
Halogen-substituted higher alkanes			
HFC-365mfc	$\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_3$	8.6	1
HFC-356mcf	$\text{CH}_2\text{FCH}_2\text{CF}_2\text{CF}_3$	1.2	1
HFC-356mff	$\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$	8.1	1
HFC-338pcc	$\text{CHF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$	12.3	1
FC-318 (perfluorocyclobutane)	$\text{c-C}_4\text{F}_8$	3200	1
FC-31-10 (perfluorobutane)	C_4F_{10}	2600	2
HFC-43-10mee	$\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$	15.9	1
HFC-458mfcf	$\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_3$	23.2	1
FC-41-12 (perfluoropentane)	C_5F_{12}	4100	2
HFC-55-10mcff	$\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_3$	7.7	2
FC-51-14 (perfluorohexane)	C_6F_{14}	3200	2

SOURCE GASES

Table 1-3, continued.

Industrial Designation or Common Name	Chemical Formula	Lifetime (years)	Notes
Fluorinated alcohols			
	CF ₃ CH ₂ OH	0.41	15
	CF ₃ CF ₂ CH ₂ OH	0.39	15
	(CF ₃) ₂ CHOH	2.0	4
Fluorinated ethers			
HFE-152a	CH ₃ OCHF ₂	1.6	1
HFE-143a	CH ₃ OCF ₃	4.3	1
HFE-134	CHF ₂ OCHF ₂	26	1
HFE-125	CHF ₂ OCF ₃	136	1
HFE-227ea	CF ₃ OCHFCF ₃	11	2
HFCE-235da2	CHF ₂ OCHClCF ₃	2.6	2
HFE-236ea2	CHF ₂ OCHFCF ₃	5.8	2
HFE-236fa	CF ₃ OCH ₂ CF ₃	3.7	2
HFE-245fa1	CHF ₂ CH ₂ OCF ₃	2.2	2
HFE-245fa2	CHF ₂ OCH ₂ CF ₃	4.9	1
HFE-245cb2	CH ₃ OCF ₂ CF ₃	5.1	4
HFE-254cb2	CH ₃ OCF ₂ CHF ₂	2.6	4
HFE-263fb2	CH ₃ OCH ₂ CF ₃	0.1	2
HFE-329mcc2	CF ₃ CF ₂ OCF ₂ CHF ₂	6.8	2
HFE-338mcf2	CF ₃ CF ₂ OCH ₂ CF ₃	4.3	2
HFE-347mcc3	CH ₃ OCF ₂ CF ₂ CF ₃	5.2	4
HFE-347mcf2	CF ₃ CF ₂ OCH ₂ CHF ₂	2.8	2
HFE-347pf3	CHF ₂ OCH ₂ CF ₂ CF ₃	5.9	4
HFE-347sy2	CF ₃ CF(OCH ₃)CF ₃	3.7	4
HFE-356mec3	CH ₃ OCF ₂ CHFCF ₃	0.94	2
HFE-356mff2	CF ₃ CH ₂ OCH ₂ CF ₃	0.4	15
HFE-356pcc3	CH ₃ OCF ₂ CF ₂ CHF ₂	0.93	2
HFE-356pcf3	CHF ₂ OCH ₂ CF ₂ CHF ₂	3.6	4
HFE-356pcf2	CHF ₂ CH ₂ OCF ₂ CHF ₂	2	2
HFE-365mcf3	CH ₃ OCH ₂ CF ₂ CF ₃	0.11	2, 15
HFE-374pc2 ^a	CH ₃ CH ₂ OCF ₂ CHF ₂	5	2
	CF ₃ CH(OCF ₃)CHF ₂	3.1	2
	(CF ₃) ₂ CFOCH ₃	3.4	2
HFE-7100	C ₄ F ₉ OCH ₃	5	2
HFE-7200	C ₄ F ₉ OC ₂ H ₅	0.77	2
H-Galden 1040x ^b	CHF ₂ OCF ₂ OCF ₂ CF ₂ OCHF ₂	6.3	2
HFE-236ca12	CHF ₂ OCF ₂ OCHF ₂	12.1	2
HFE-338pcc13	CHF ₂ OCF ₂ CF ₂ OCHF ₂	6.2	2
Other fluorinated species			
Trifluoromethylsulfurpentafluoride	SF ₅ CF ₃	800	18
Sulfur hexafluoride	SF ₆	3200	2

Table 1-3, continued.

Footnotes

For completeness, estimates for local lifetimes for some very short-lived ($\tau < 0.5$ years) species are included. As discussed in Chapter 2, the atmospheric lifetimes for these species (defined as the ratio of burden to emission; see Prather and Ehhalt et al., 2001) depend on the location and time of emission. Thus, these local lifetimes should not be used in estimation of semiempirical ODP, GWP, or EESC calculations for these gases.

Notes:

1. Global lifetime estimated from a process lifetime with respect to tropospheric OH calculated relative to 6.1 years for CH_3CCl_3 , assuming an average temperature of 272 K (Spivakovsky et al., 2000; Prather and Ehhalt et al., 2001); OH rate constants from Sander et al. (2002); and stratospheric loss lifetimes inferred from IPCC (2001).
2. Prather and Ehhalt et al. (2001) and Ramaswamy et al. (2001).
3. See Section 1.5 for further discussion related to methyl halide global lifetimes.
4. Lifetime calculated as in Note 1 except that no estimate of a stratospheric loss lifetime was available to include in the lifetime estimate listed. Hence this is an upper bound to the global lifetime estimate.
5. IPCC (2001) and including an oceanic loss term with 94-year lifetime observed in saturation data and ascribed to an unidentified process (Yvon-Lewis and Butler, 2002).
6. Including oceanic loss term from Yvon-Lewis and Butler (2002). The contribution of oceanic loss to the lifetime of HCFC-21, HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HFC-125, and HFC-152a is small; for HFC-134a and HCFC-142b it is negligibly small at the reported precision.
7. WMO (1999).
8. Lifetimes listed include local tropospheric photolysis lifetimes from Table 2-9 in Kurylo and Rodríguez et al. (1999). Consideration of only tropospheric OH loss results in local lifetimes of 0.34 years for CH_2Br_2 , 0.21 years for CHBr_3 , and 0.37 years for CH_2BrCl .
9. See Section 1.4 text for discussion.
10. OH rate constant from Qui et al. (1992).
11. Lifetime calculated as in Note 1, but with stratospheric loss from Naik et al. (2000).
12. Lifetime calculated as in Note 1, but with OH rate constant and stratospheric loss from Naik et al. (2000).
13. Markert and Nielsen (1992).
14. OH rate constant from DeMore and Bayes (1999).
15. The values estimated correspond to local lifetimes in the free troposphere. For species that react with OH, the process lifetime due to OH reaction is calculated using the rate constant at 275 K (for lifetimes greater than 10 days) or 300 K (for lifetimes less than 10 days) and OH concentration of $1 \times 10^6 \text{ molec cm}^{-3}$. These should not be used in estimating ODP, GWP, or EESC because the atmospheric burden for these short-lived gases ($\tau < 0.5$ years) depends on the location and time of emissions.
16. See Chapter 2.
17. From the 2-D model calculation in Fraser et al. (1999).
18. Takahashi et al. (2002).

^a Referred to as HFE-374pcf2 in past Assessments.

^b Also known as HFE-43-10pccc124.

Previous lifetime estimates of carbon tetrachloride were derived from observations and modeling of photolytic loss rates in the stratosphere (Volk et al., 1997; Prinn and Zander et al., 1999). Reports of widespread observations of undersaturation of carbon tetrachloride in the ocean (Huhn et al., 2001; Wallace et al., 1994) suggest an additional, significant loss for this gas (Yvon-Lewis and Butler, 2002). When combined with the other loss processes, a revised global lifetime of 26 (17-36) years is now calculated for this gas (Yvon-Lewis and Butler, 2002).

1.4.3 Fractional Release Factors

In considering the effect of halogen source gases on ozone, it is first necessary to determine the composition of tropospheric air entering the stratosphere, mostly through the tropical tropopause. For compounds with lifetimes measured in years, the amount of halogen entering the stratosphere for a specific level of emission is

inversely related to the lifetime at steady state. Once a halogen source gas is in the stratosphere, release of a halogen atom from the source gas through photolysis or chemical reaction is a function of stratospheric local lifetime or loss frequency and differs greatly from compound to compound. More complete release of the halogen atom catalyst in the stratosphere produces a greater extent of local photochemical loss of ozone, for a given source gas or in comparing source gases, all else being equal.

A point measurement of a given halogen source molecule in the stratosphere can be recast as a fractional release (FR), defined as

$$\text{FR} = \frac{\rho_{\text{entry}} - \rho_{\text{point}}}{\rho_{\text{entry}}} \quad (1-5)$$

where ρ is the source compound mixing ratio or mole frac-

SOURCE GASES

tion. Observations of halogen source compounds at high spatial resolution in the stratosphere, chiefly by in situ techniques, show a compact relationship when plotted as a scatter correlation of fractional release of compound x to that of compound y . Identifying compound y as CFC-11 produces the fractional release factor that is used in the semiempirical determination of ODPs. It is essentially a measure of the local release or availability of the inorganic halogen compounds that actually produce the ozone depletion, relative point by point to CFC-11. These relative fractional release factors are used in the calculation of ODP, EECl, and EESC.

Although the correlations are compact, they are typically not simply linear, because local loss frequencies differ from compound to compound. Conceptually, the fractional release factor could be globally integrated, weighted by the local ozone loss. In practice, Schauffler et al. (1999) suggest the use of a restricted range of the correlation representing mid-high latitudes, where the greatest loss of ozone occurs. Schauffler et al. (2002) report fractional release factors for three ranges of stratospheric age of air, G , determined from N_2O abundance observed during the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE), Stratospheric Tracers of Atmospheric Transport (STRAT), and Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) aircraft campaigns. High values of N_2O , near those in the troposphere, are associated with air that has recently entered the stratosphere, whereas low N_2O values are indicative of air that has cycled through the stratosphere by the mean circulation. The mean halocarbon fractional release values associated with ages of 2.0-4.5 years are appropriate for the midlatitude middle stratosphere. Earlier studies (Daniel et al., 1995) suggest a reference CFC-11 fractional release value of 0.8 for air that had passed through the mean circulation. Schauffler et al. (2002) relate this to older stratospheric air ($G = 4.5$ years). For 3.5-yr-old air, they indicate a CFC-11 fractional release of 0.55. Relative fractional release values derived from stratospheric observations of air of intermediate ages are given in Table 1-4. Because these are relative quantities, they are sensitive to nonlinearities in the slopes of correlation plots of release against age of air, but less sensitive to the absolute CFC-11 reference value.

Models and a semiempirical framework have been used to estimate fractional release factors for unmeasured or currently nonexistent atmospheric source gases (Solomon et al., 1992). Models predict ozone loss explicitly, however, so it is generally more straightforward to integrate the modeled ozone loss and calculated ODP directly as opposed to using a modeled release factor in

the semiempirical approach. The fractional release values for HCFC-141b and -142b used here and in past Assessments (Table 1-4) are based upon a semiempirical analysis of measured stratospheric profiles for methane and other gases (Solomon et al., 1992). A recent analysis of HCFC observations in the stratosphere, however, suggests the possibility for much smaller (by factors of 3 to 5) fractional release values and ODPs for HCFC-141b and -142b (Schauffler et al., 2002; Tables 1-4 and 1-5). Such low estimates are difficult to reconcile with the earlier estimates, given that only comparatively small refinements have been noted for reaction rate constants and other relevant model parameters since the original calculations were performed. Without additional research, changes to ODPs calculated for these HCFCs cannot be recommended at this time.

1.4.4 Ozone Depletion Potential

The Ozone Depletion Potential (ODP) is an integrative quantity, distinct for each halocarbon source species, that represents the extent of ozone depletion in the stratosphere expected from the halocarbon on a mass-for-mass basis relative to CFC-11. The formal definition of ODP is the ratio of integrated perturbations to total ozone, for a differential mass emission of a particular compound relative to an equal emission of CFC-11. An extensive discussion of the details of the ODP calculation is given in WMO (1995).

Solomon and coworkers (Solomon et al., 1992; WMO, 1995) introduced a semiempirical ODP formulation that takes advantage of the relative nature of the ODP definition to remove the requirement for explicit representations of ozone-controlling photochemistry in the context of chemistry-transport models. The quantities required are physical properties of the halocarbons, their lifetimes, a factor representing the distribution of inorganic halogen release in the stratosphere obtained from observation, and, in the case of bromine and iodine, an analysis of the catalytic efficiency of ozone destruction relative to chlorine, derived from knowledge of the kinetic parameters of the partitioning of the halogen radical families. For long-lived gases that are well mixed in the troposphere, the semiempirical ODP definition is

$$\text{ODP}(x) = (\text{fractional release factor}) \cdot \alpha \cdot \frac{\tau_x}{\tau_{\text{CFC-11}}} \cdot \frac{M_{\text{CFC-11}}}{M_x} \cdot \frac{n_x}{3} \quad (1-6)$$

where the fractional release factors are discussed in Section 1.4.3 above, α is the relative effectiveness of any halogen compared with chlorine for ozone destruction (taken to be

Table 1-4. Fractional release factors relative to CFC-11 (CCl₃F).

Compound	Relative Fractional Release Factor ^a	Schauffler et al. (2002) ^b	Notes
CFC-11	1		By definition
CFC-12	0.60	0.57 ± 0.05	1
CFC-113	0.75	0.65 ± 0.05	1
CFC-114		0.28 ± 0.02	
CFC-114a		0.63 ± 0.10	
CCl ₄	1.06	1.14 ± 0.06	1
HCFC-22	0.35	0.29 ± 0.02	1
CH ₃ CCl ₃	1.08	1.29 ± 0.16	1
HCFC-123	1.11		1
HCFC-124	0.52		1
HCFC-141b	0.72	0.23 ± 0.11	1
HCFC-142b	0.36	0.08 ± 0.04	1
HCFC-225ca	1.1		2
HCFC-225cb	0.5		2
CH ₃ Cl	0.80	0.85 ± 0.03	2, 3
CH ₃ Br	1.12		4
Halon-1301	0.62		4
Halon-2402	1.22		4
Halon-1211	1.18	1.24 ± 0.07	4

Notes for Relative Fractional Release Factors in column 2:

1. Daniel et al. (1995).
2. WMO (1999).
3. Solomon et al. (1992).
4. Schauffler et al. (1999).

^a These fractional release estimates are used after multiplication by 0.8 (to account for absolute fractional release of CFC-11) in the calculation of EESC (Table 1-17; Section 1.8). See Notes above for references.

^b Estimated for stratospheric air having a mean age of 2-4.5 years.

45 here for bromine; Daniel et al., 1999), τ_x is the global lifetime of the long-lived, well-mixed gas, M_x is the molecular weight, and n_x is the number of halogen atoms.

Daniel et al. (1999) have discussed, specifically for bromine, the definitions and determination of the effectiveness parameter, α , of a halogen radical family in catalyzing ozone destruction, relative to the chlorine radical family. Their suggested definition of α , to be most useful in the ODP definition given in Equation (1-6) above, is cast in terms of the column response of ozone perturbation to inorganic halogen change. Although appearing as a single, fixed, global quantity, it is actually an integrated result with sensitivity to both kinetic parameters for chlorine species and the other halogen of interest, and to atmospheric transport behavior. For this reason, there is no simple way to adjust α quantitatively to reflect new determinations, for example, of individual rate coefficients.

Because a single global value is required by the ODP definition, α represents the global correlation of local photochemical behaviors, for the catalyst of interest (e.g., bromine) and chlorine, with the distribution of ozone

loss. Relative effectiveness for localized regions may differ substantially. For example, Chipperfield and Pyle (1998) model a value of 60 for bromine in the Arctic vortex. The value of 45 used here represents a midlatitude result, which is intended to be more representative of the global mean relative to ozone depletion. An important point made by Danlin et al. (1996) and Chipperfield and Pyle (1998) is that the relative effectiveness, α , can be sensitive to the atmospheric state. Bromine is more effective relative to chlorine in the Arctic vortex for higher inorganic chlorine levels in the range of 2-4 ppb. Semiempirical ODP values calculated for the current atmosphere will be different from values calculated for a future atmosphere containing less chlorine and altered distributions of ozone loss.

Daniel et al. (1999) based their result on DeMore et al. (1997), which did not make a recommendation for products of the OH + chlorine monoxide (ClO) reaction, but discussed studies showing the predominant product channel is hydroperoxyl radical (HO₂) + Cl. Sander et al. (2000) do recommend a value for the product channel

SOURCE GASES

Table 1-5. Updated Ozone Depletion Potentials for long-lived halocarbons.

Halocarbon	Updated Model-Derived ^a	Updated Semiempirical ^b	Semiempirical Schaffler et al. (2002) ^c	WMO (1999) Model	WMO (1999) Semiempirical	Montreal Protocol
CFC-11		1				
CFC-12		1.0	0.96	0.82	0.9	1.0
CFC-113		1.0	0.90	0.90	0.9	0.8
CFC-114	0.94		1.00	0.85		1.0
CFC-115	0.44			0.40		0.6
Halon-1301		12		12	13	10.0
Halon-1211		6.0	6.0	5.1	5	3.0
Halon-2402		< 8.6				6.0
Halon-1202		1.3 ^d				
CCl ₄		0.73	0.78	1.20		1.1
CH ₃ CCl ₃		0.12	0.15	0.11	0.12	0.1
HCFC-22		0.05	0.041	0.034	0.05	0.055
HCFC-123		0.02		0.012	0.02	0.02
HCFC-124		0.02		0.026		0.022
HCFC-141b		0.12	0.037	0.086	0.1	0.11
HCFC-142b		0.07	0.014	0.043	0.066	0.065
HCFC-225ca		0.02		0.017	0.025	0.025
HCFC-225cb		0.03		0.017	0.03	0.033
CH ₃ Cl		0.02				
CH ₃ Br		0.38		0.37	0.37 ^e	0.6
Upper limits for selected hydrofluorocarbons						
HFC-134a				$< 1.5 \times 10^{-5}$		
HFC-23				$< 4 \times 10^{-4}$		
HFC-125				$< 3 \times 10^{-5}$		

^a Calculated from ODPs reported in Table 11-1 of WMO (1999) with lifetimes from Table 1-3 in this chapter.

^b Calculated with updated lifetimes (Table 1-3) and fractional release factors (column 2, Table 1-4) except in the case of Halon-1202.

^c Calculated with updated lifetimes (Table 1-3) and fractional release factors from Schaffler et al. (2002) (column 3, Table 1-4).

^d Derived from the semiempirical estimate in WMO (1991) by considering updated lifetimes for Halon-1202 and CFC-11 (Table 1-3) and an alpha of 45.

^e Value was erroneously reported in Table 11-1 of WMO (1999) as 0.57.

forming HCl, based on Lipson et al. (1999). Including this product channel can substantially diminish the modeled ClO abundance in the mid-stratosphere, by as much as a factor of 2. In reducing the fraction of inorganic chlorine present in the active ClO form, the new recommendation has the effect of moderating the chlorine-induced ozone change in that region, and consequently increasing the modeled efficiency of bromine relative to chlorine. Quantifying the change would require a comprehensive reanalysis, but because the region most affected contributes a relatively small portion of the column ozone change, the overall value for α should not change greatly, and the estimate of 45 from Daniel et al. (1999) remains the best available at the present time.

To separate their study of the effectiveness parameter, α , from the effects of halogen fractional release dis-

tributions for any source gas, Daniel et al. (1999) assumed a hypothetical bromine source species characterized by the CFC-11 fractional release pattern. They point out that sources with significantly shorter atmospheric lifetimes than CFC-11 would also be characterized by greater fractional release lower in the stratosphere, which would produce a larger effectiveness parameter value. The effect for iodine source species would be even more pronounced than for bromine sources. This interaction between the fractional release parameter and the effectiveness parameter introduces uncertainty into the ODP estimates and should be analyzed further for new source species of interest and in the light of projected changes in future stratospheric chlorine loading.

Table 1-5 includes both model and semiempirical ODP values. Semiempirical values are calculated using

updated lifetimes and two separate estimates of fractional release factors (listed in Table 1-4). The values for CFC-12 and CFC-113 are updated from the semiempirical ODPs in Table 11-1 of WMO (1999), which were based on the reference lifetimes of WMO (1995), not WMO (1999). The value of 0.38 for CH₃Br is based on a total lifetime of 0.7 years and is essentially unchanged from the semiempirical value given in Table 2-6 of the previous Assessment (Kurylo and Rodríguez et al., 1999) and the model-derived value reported in Table 11-1 of that Assessment (Madronich and Velders et al., 1999). (Note that the semiempirical value given in Table 11-1 of WMO (1999) was incorrectly recorded.) ODPs derived for HCFC-141b and -142b from the new observation-based fractional release factors are much lower than those derived from earlier model calculations (Schauffler et al., 2002; Solomon et al., 1992). Further work will be required to resolve these discrepancies.

1.4.5 Global Warming Potential

Global Warming Potentials (GWPs) are used to estimate the integrated climate forcing of various greenhouse gases compared with a reference gas, usually chosen to be carbon dioxide (CO₂). They provide a simple way to gauge how decisions affecting greenhouse gas emissions (e.g., in the Kyoto Protocol) may influence our future climate in a relative sense (see, e.g., Ramaswamy et al., 2001, and references therein). Furthermore they allow the effects of these potential actions to be roughly assessed in terms of a “carbon dioxide equivalent” emission. Radiative effects of CFC alternatives are also assessed with the use of GWPs.

Because of the recent publication of *Climate Change 2001: The Scientific Basis* (IPCC, 2001), we only report updates to that work here. We refer the reader to Chapter 6 of IPCC (2001) for a thorough discussion of radiative forcing and GWPs.

The GWP of a particular compound is defined as the ratio of the time-integrated radiative forcing from the instantaneous emission of 1 kg of some gas relative to that of 1 kg of a reference gas. Mathematically, the GWP is given by

$$\text{GWP}_x(\text{TH}) = \frac{\int_0^{\text{TH}} a_x \cdot [x(t)] dt}{\int_0^{\text{TH}} a_r \cdot [r(t)] dt} \quad (1-7)$$

where a_x is the radiative forcing of a unit mass of species x added to the current atmospheric composition, $x(t)$ is the atmospheric decay function of the pulse of species x , a_r

and $r(t)$ are the corresponding quantities for the reference gas, and TH is the time horizon over which the calculation is performed. The response function used in this chapter is the same as in Granier and Shine et al. (1999) and IPCC (2001). The formula for calculating $r(t)$ where CO₂ is the reference gas is also the same as in Granier and Shine et al. (1999) and Ramaswamy et al. (2001). We have adopted a present-day mixing ratio of atmospheric CO₂ of 370 ppm (μmol mol⁻¹; see Section 1.7.1), higher than that of both Granier and Shine et al. (1999) and Ramaswamy et al. (2001) (364 ppm), reflecting the continued increasing atmospheric abundance of this radiatively important gas. This increased CO₂ abundance, relative to Ramaswamy et al. (2001), leads to a decrease in the radiative forcing of a small addition of atmospheric CO₂, and a corresponding increase in all GWPs, of about 1.3%.

1.4.5.1 RADIATIVE FORCING UPDATES

Since Granier and Shine et al. (1999), three comprehensive modeling studies have been published that estimate the radiative forcing efficiency of many radiatively important gases. Two of these, Highwood and Shine (2000) and Jain et al. (2000), were considered in Ramaswamy et al. (2001), and the third, Sihra et al. (2001), was not published until after Ramaswamy et al. (2001). For the majority of gases appearing in Tables 1-6 and 1-7, the radiative forcing efficiencies calculated by Sihra et al. differ from the adopted Ramaswamy et al. (2001) values by less than 20%; for all but one of these gases, we retain the forcing efficiencies adopted for Ramaswamy et al. (2001). HCFC-21 is changed because of an error in its tabulated value in Granier and Shine et al. (1999) and Ramaswamy et al. (2001) (see notes to Table 1-6). Radiative efficiencies for six gases differed by more than 20% between the Sihra et al. (2001) work and Ramaswamy et al. (2001). Revisions to radiative forcing efficiencies for two of these gases (HCFC-123 and HCFC-225ca) are recommended and are discussed in the notes to Table 1-6. For the other four we retain the Ramaswamy et al. (2001) recommendation either because there was no other corroborative calculation to go along with the Sihra et al. (2001) result (i.e., for HFE-143a and H-Galden 1040x) or because the Sihra et al. values differed from those calculated in Jain et al. (2000) by more than 20% (i.e., for CH₃Br and CF₄). The significant differences between Sihra et al. (2001) and Jain et al. (2000) for these and some other gases (e.g., HCFC-225cb, HFC-134a, HFC-227ea, HFC-23, and HFC-32) suggest that further study and understanding is required before adopting new forcing efficiency values for these compounds.

SOURCE GASES

Table 1-6. Direct Global Warming Potentials (mass basis) for gases that have adequately characterized lifetimes.

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency (W m ⁻² ppb ⁻¹)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Carbon dioxide	CO ₂	1.53×10^{-5} ^a	^b	1	1	1
Methane	CH ₄	3.7×10^{-4}	12.0 ^c	63 ^d	23 ^d	7 ^d
Nitrous oxide	N ₂ O	3.1×10^{-3}	114 ^c	278	300	158
Chlorofluorocarbons						
CFC-11	CCl ₃ F	0.25	45	6330	4680	1630
CFC-12	CCl ₂ F ₂	0.32	100	10340	10720	5230
CFC-13	CClF ₃	0.25	640	10160	14190	16520
CFC-113	CCl ₂ FCClF ₂	0.30	85	6150	6030	2700
CFC-114	CClF ₂ CClF ₂	0.31	300	7560	9880	8780
CFC-115	CClF ₂ CF ₃	0.18	1700	4990	7250	10040
Hydrochlorofluorocarbons						
HCFC-21	CHCl ₂ F	0.14 ^e	1.7	498	148	46
HCFC-22	CHClF ₂	0.20	12.0	4850	1780	552
HCFC-123	CHCl ₂ CF ₃	0.14 ^f	1.3	257	76	24
HCFC-124	CHClFCF ₃	0.22	5.8	1950	599	186
HCFC-141b	CH ₃ CCl ₂ F	0.14	9.3	2120	713	222
HCFC-142b	CH ₃ CClF ₂	0.20	17.9	5170	2270	709
HCFC-225ca	CHCl ₂ CF ₂ CF ₃	0.20 ^g	1.9	404	120	37
HCFC-225cb	CHClFCF ₂ CClF ₂	0.32	5.8	1910	586	182
Hydrofluorocarbons						
HFC-23	CHF ₃	0.16	270	9500	12240	10350
HFC-32	CH ₂ F ₂	0.09	4.9	1800	543	169
HFC-41	CH ₃ F	0.02	2.4	304	90	28
HFC-125	CHF ₂ CF ₃	0.23	29	5970	3450	1110
HFC-134	CHF ₂ CHF ₂	0.18	9.6	3200	1090	337
HFC-134a	CH ₂ FCF ₃	0.15	14.0	3370	1320	410
HFC-143	CH ₂ FCHF ₂	0.13	3.5	1160	347	108
HFC-143a	CH ₃ CF ₃	0.13	52	5540	4400	1600
HFC-152	CH ₂ FCH ₂ F	0.09	0.60	176	52	16
HFC-152a	CH ₃ CHF ₂	0.09	1.4	411	122	38
HFC-227ea	CF ₃ CH ₂ CF ₃	0.30	34.2	5760	3660	1200
HFC-236cb	CH ₂ FCF ₂ CF ₃	0.23	13.6	3420	1320	409
HFC-236ea	CHF ₂ CH ₂ CF ₃	0.30	10.7	3850	1350	420
HFC-236fa	CF ₃ CH ₂ CF ₃	0.28	240	7620	9650	7700
HFC-245ca	CH ₂ FCF ₂ CHF ₂	0.23	6.2	2200	682	212
HFC-245fa	CHF ₂ CH ₂ CF ₃	0.28	7.6	3180	1020	316
HFC-365mfc	CH ₃ CF ₂ CH ₂ CF ₃	0.21	8.6	2370	782	243
HFC-43-10mee	CF ₃ CH ₂ CH ₂ CF ₂ CF ₃	0.40	15.9	3890	1610	502
Chlorocarbons						
Methyl chloroform	CH ₃ CCl ₃	0.06	5.0	476	144	45
Carbon tetrachloride	CCl ₄	0.13	26	2540	1380	437
Methyl chloride	CH ₃ Cl	0.01	1.3	56	17	5
Bromocarbons						
Methyl bromide	CH ₃ Br	0.01	0.7	16	5	1

Table 1-6, continued.

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency (W m ⁻² ppb ⁻¹)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Bromodifluoromethane	CHBrF ₂	0.14	5.8	1290	397	123
Halon-1211	CBrClF ₂	0.30	16	4460	1860	578
Halon-1301	CBrF ₃	0.32	65	7970	7030	2780
Halon-2402	CBrF ₂ CBrF ₂	0.33 ^h	20	3460	1620	505
Fully fluorinated species						
Sulfur hexafluoride	SF ₆	0.52	3200	15290	22450	32780
Trifluoromethylsulfurpentafluoride	SF ₅ CF ₃	0.57	800	12370	17500	21500
FC-14	CF ₄	0.08	50000	3920	5820	9000
FC-116	C ₂ F ₆	0.26	10000	8110	12010	18280
FC-218	C ₃ F ₈	0.26	2600	5940	8690	12520
FC-31-10	C ₄ F ₁₀	0.33	2600	5950	8710	12550
FC-318	c-C ₄ F ₈	0.32	3200	6870	10090	14740
FC-41-12	C ₅ F ₁₂	0.41	4100	6120	9010	13330
FC-51-14	C ₆ F ₁₄	0.49	3200	6230	9140	13350
Halogenated alcohols and ethers						
	(CF ₃) ₂ CFOCH ₃	0.31	3.4	1130	338	105
	(CF ₃) ₂ CHOH	0.28	2.0	718	214	66
HFE-125	CHF ₂ OCF ₃	0.44	136	12970	14670	8530
HFE-134	CHF ₂ OCHF ₂	0.45	26	11470	6220	1970
HFE-143a	CH ₃ OCF ₃	0.27	4.3	2480	744	231
HFCE-235da2	CHF ₂ OCHClCF ₃	0.38	2.6	1150	343	107
HFE-245cb2	CH ₃ OCF ₂ CF ₃	0.32	5.1	2300	697	216
HFE-245fa2	CHF ₂ OCH ₂ CF ₃	0.31	4.9	2150	649	201
HFE-254cb2	CH ₃ OCF ₂ CHF ₂	0.28	2.6	1190	353	110
HFE-347mcc3	CH ₃ OCF ₂ CF ₂ CF ₃	0.34	5.2	1860	566	176
HFE-356pcf3	CHF ₂ OCH ₂ CF ₂ CHF ₂	0.39	3.6	1660	494	153
HFE-374pc2 ⁱ	CH ₃ CH ₂ OCF ₂ CHF ₂	0.25	5	1810	548	170
HFE-7100	C ₄ F ₉ OCH ₃	0.31	5	1310	397	123
HFE-7200	C ₄ F ₉ OC ₂ H ₅	0.30	0.77	189	56	17
H-Galden 1040x ^j	CHF ₂ OCF ₂ OC ₂ F ₄ OCHF ₂	1.37	6.3	5940	1840	572
HFE-236ca12	CHF ₂ OCF ₂ OCHF ₂	0.66	12.1	7560	2780	864
HFE-338pcc13	CHF ₂ OCF ₂ CF ₂ OCHF ₂	0.87	6.2	4770	1480	459

Lifetimes are from Table 1-3. GWPs for some gases that were tabulated in IPCC (2001) are not reported here because they have lifetimes less than 0.5 years (see notes to Table 1-3).

^a Assumes a global surface mean mixing ratio of 370 ppm.

^b CO₂ atmospheric response function is as described in WMO (1999) and Ramaswamy et al. (2001).

^c These lifetimes are adjustment times including feedbacks of emissions on lifetimes (see Ramaswamy et al., 2001).

^d The GWPs listed for methane include indirect effects of tropospheric ozone production and stratospheric water vapor production (Solomon and Wuebbles et al., 1995; Ramaswamy et al., 2001).

^e The Sihra et al., (2001) radiative efficiency for HCFC-21 of 0.14 W m⁻² ppb⁻¹ is adopted rather than the 0.17 W m⁻² ppb⁻¹ value in WMO (1999) and Ramaswamy et al. (2001). The value of 0.17 was incorrectly tabulated in WMO (1999) (see Sihra et al. (2001) for discussion of error).

^f The radiative efficiency from Sihra et al. (2001) and Jain et al. (2000) was adopted here because these studies were in good agreement and because the estimate adopted by Ramaswamy et al. (2001) originated from Fisher et al. (1990), in which a lower resolution calculation was performed.

^g The radiative efficiency from Sihra et al. (2001) and Jain et al. (2000) was adopted here because these studies were in good agreement and because the estimate adopted by Ramaswamy et al. (2001) was based upon an unpublished calculation made for WMO (1995).

^h Radiative efficiency from Sihra et al. (2001).

ⁱ Referred to as HFE-374pcf2 in past Assessments; however, the current name unambiguously defines the compound.

^j Also known as HFE-43-10pccc124.

SOURCE GASES

Table 1-7. Direct Global Warming Potentials (mass basis) relative to carbon dioxide for gases whose lifetimes are determined only by indirect means rather than by laboratory measurements, or for which uncertainty exists in our understanding of the important loss processes.

Industrial Designation or Common Name	Chemical Formula	Radiative Efficiency (W m ⁻² ppb ⁻¹)	Lifetime (years)	Global Warming Potential for Given Time Horizon		
				20 years	100 years	500 years
Nitrogen trifluoride	NF ₃	0.13	740	7780	10970	13240
Perfluorocyclopropane	c-C ₃ F ₆	0.42	>1000	>11950	>17070	>21920
HFE-227ea	CF ₃ CHFOCF ₃	0.40	11.0	4270	1520	471
HFE-236ea2	CHF ₂ OCHF ₂ CF ₃	0.44	5.8	3170	973	302
HFE-236fa	CF ₃ CH ₂ OCF ₃	0.34	3.7	1610	480	149
HFE-245fa1	CHF ₂ CH ₂ OCF ₃	0.30	2.2	948	282	88
HFE-329mcc2	CF ₃ CF ₂ OCF ₂ CHF ₂	0.49	6.8	2880	904	281
HFE-338mcf2	CF ₃ CF ₂ OCH ₂ CF ₃	0.43	4.3	1810	543	169
HFE-347mcf2	CF ₃ CF ₂ OCH ₂ CHF ₂	0.41	2.8	1240	368	114
HFE-356mec3	CH ₃ OCF ₂ CHFCF ₃	0.30	0.94	334	99	31
HFE-356pcc3	CH ₃ OCF ₂ CF ₂ CHF ₂	0.33	0.93	363	108	34
HFE-356pcf2	CHF ₂ CH ₂ OCF ₂ CHF ₂	0.37	2.0	876	260	81
	(CF ₃) ₂ CHOCHF ₂	0.41	3.1	1250	373	116
	-(CF ₂) ₄ CH(OH)-	0.30	0.85	239	71	22

All lifetimes were taken from Ramaswamy et al. (2001). The GWPs differ from those in Ramaswamy et al. (2001) because an additional significant figure was retained and because an updated CO₂ mixing ratio was assumed (370 ppm).

1.4.5.2 DIRECT GLOBAL WARMING POTENTIALS

The “direct” portion of a compound’s GWP represents the part that is due to the infrared absorptive and emissive properties that lead to a reduction in the net radiation exiting the troposphere. Here we have divided our compilation of direct GWPs into two tables. Table 1-6 includes compounds whose lifetimes are relatively well established, whereas Table 1-7 has compounds whose lifetimes are more uncertain, either because of a dearth of laboratory measurements or an incomplete understanding of the loss processes. Compounds characterized by lifetimes less than 0.5 years are not included in the tables because of the difficulties involved in making meaningful estimates of a global lifetime and a global radiative effect. In comparing Tables 1-6 and 1-7 with past direct GWP tables (e.g., Granier and Shine et al., 1999; Ramaswamy et al., 2001), note that there is now an additional significant figure tabulated for all GWP values greater than 10. This does not imply that there is any improvement in the accuracy of the GWP values, which is believed to be ±35%. The additional significant figure is included to facilitate tracking GWP changes in the future by reducing the impact of rounding.

1.4.5.3 NET GLOBAL WARMING POTENTIALS

As discussed in past Assessments, the impacts of many chlorocarbons and bromocarbons on climate are complicated by their destruction of stratospheric ozone. The destruction of ozone offsets part, and in some cases all, of the direct forcing for the period in the future when ozone destruction occurs. Table 1-8 includes estimates of these net GWPs for selected halocarbons. These values are updated from Daniel et al. (1995) for revised halocarbon lifetimes (Table 1-3), assumption of the relative effectiveness for ozone destruction of bromine compared with chlorine (assumed to be 45 here), future ozone loss scenario (using EESC from scenario Ab; see Section 1.8), and time of emission (assumed in year 2002 here).

The net GWP values here differ from those in Ramaswamy et al. (2001) primarily because of the different assumed time of emission of the radiatively active compound in conjunction with the time dependence of polar and global ozone depletion.

1.4.6 Hydroxyl Radical Changes with Time

Reaction with tropospheric hydroxyl radical (OH) is the chief sink for many of the halocarbons in the com-

Table 1-8. Net Global Warming Potentials of selected halocarbons (on an equal mass basis).

Species	Time Horizon = 2022 (20 years)			Time Horizon = 2102 (100 years)		
	Direct	Net		Direct	Net	
		Min	Max		Min	Max
CFC-11	6330	-938	4910	4680	-524	3660
CFC-12	10340	6660	9620	10720	7660	10120
CFC-113	6150	1770	5290	6030	2470	5330
HCFC-22	4850	4020	4690	1780	1420	1710
HCFC-123	257	-147	177	76	-44	53
HCFC-124	1950	1490	1860	599	450	570
HCFC-141b	2120	-34	1700	713	-109	552
HCFC-142b	5170	4260	4990	2270	1810	2180
CH ₃ CCl ₃	476	-2080	-26	144	-659	-13
CCl ₄	2540	-5460	972	1380	-3440	433
CH ₃ Br	16	-7650	-1490	5	-2270	-444
Halon-1211	4460	-67410	-9630	1860	-33360	-5050
Halon-1301	7970	-77490	-8780	7030	-59280	-5970

Net Global Warming Potentials are calculated from updated lifetimes and radiative data reported in this chapter, and include the indirect cooling effects that result from stratospheric ozone depletion as well as the direct radiative effects. The magnitude of the cooling is estimated using the future EESC of scenario Ab, a value for alpha of 45, and an emission pulse in the year 2002. The min/max ranges of the net GWPs reflect the uncertainty in the change in ozone radiative forcing from 1980 to 1990 of -0.153 to -0.03 W m^{-2} (Ramaswamy et al., 2001).

pendium of ODPs and GWPs discussed in this chapter. The halocarbon lifetimes, on which the ODPs and GWPs depend, are determined by the morphology of the steady-state halocarbon distributions, the kinetics of the OH reaction, and the OH distribution. The time horizon for halocarbon effects summarized by ODPs and GWPs is decades to centuries, and halocarbon lifetimes with respect to tropospheric losses can be decades. It is noteworthy that time invariance of the lifetimes is a typical assumption made to simplify the explanation of these concepts, which also effectively implies an unchanging OH distribution. Karlsdóttir and Isaksen (2000), however, present a multi-dimensional model result for the period 1980-1996 that produces an increase in mean global tropospheric OH levels of 7% over the period, driven largely by increases in low-latitude emissions of nitrogen oxides (NO_x) and carbon monoxide (CO).

The distribution of OH is controlled by local photochemistry comprising the interactions of ozone, water, solar ultraviolet radiation, CO, methane (CH_4), nitrogen oxides, and higher hydrocarbons. Wang and Jacob (1998) describe the relationship of OH abundance to a ratio of nitrogen oxide and hydrocarbon concentrations and ascribe the apparent constancy of OH over the historical industrial period to the conservation of this ratio even as emissions for both increased. The model and analysis of

Wang and Jacob (1998) suggests a 9% decline in weighted global OH from preindustrial time, but Prather and Ehhalt et al. (2001) note that no consensus exists on the magnitude of this change.

The importance of the OH distribution and its changes with time in the context of this chapter includes the effect of interannual variability on the methyl chloroform (CH_3CCl_3) reference OH lifetime. On longer time scales, changes in the OH distribution would change some halocarbon lifetimes, ODPs, and GWPs, increasing or decreasing their impacts relative to the current values. Future increases in direct and indirect greenhouse gases could produce these changes through direct participation in OH-controlling chemistry, indirectly through stratospheric ozone changes that could increase solar ultraviolet in the troposphere, and potentially through climate change effects on biogenic emissions, humidity, and clouds. Prinn et al. (2001) analyzed a 22-year record of global CH_3CCl_3 measurements and emission estimates and suggest that global OH over that period varied from about 5% above to 10% below the period average. This inferred variability in OH contributes to the uncertainty of the reference CH_3CCl_3 lifetime and other lifetimes based on it. These results through 1993 are essentially consistent with the conclusions of Krol et al. (1998, 2001), who used the same measurement and emission record but

SOURCE GASES

an independent calculation technique to infer an increase of $0.46\% \text{ yr}^{-1}$ over the shorter period of 1978-1993. Prinn et al. (2001) infer that OH values in the late 1990s are below those in the late 1970s to early 1980s, in agreement with the longer CH_3CCl_3 lifetime reported by Montzka et al. (2000) for 1998-1999 relative to the Prinn et al. (2001) value for the full-period average. Inferences regarding methyl chloroform lifetimes or trends in OH are quite sensitive to any errors in the absolute magnitude of estimated emissions. These errors could be significant and enhanced during the late 1990s because annual emissions were dropping precipitously then. Independent estimates of methyl chloroform emissions and their changes during the late 1990s would provide a useful independent assessment of these implied trends in global OH.

IPCC (Prather and Ehhalt et al., 2001), using scenarios generated by the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000) and on the basis of a comparison of results from 14 models, predicts that global OH could vary from a 20% decrease to a 6% increase by 2100. The range of these predicted changes is not materially greater than that already calculated by Prinn et al. (2001). On the other hand, a 9% decrease from preindustrial time to the present and a projected 20% decrease present to future would, in combination, give a substantial change from the preindustrial atmospheric state. The sense of the change is indicated to be most likely in the direction of longer halocarbon lifetimes with respect to oxidation by OH and enhanced atmospheric effects.

1.4.7 Other Sinks

Atmospheric in situ halocarbon sinks include photolysis and homogeneous gas-phase reactions with OH, Cl, and $\text{O}(\text{D})$. The dynamics of tropospheric mixing exposes tropospheric air to contact with the surface and allows for irreversible deposition as well. Organisms in surface ocean waters can both consume and produce halocarbons. Chemical degradation of dissolved halocarbons can also occur through hydrolysis. Physical dissolution into ocean waters occurs, but does not represent a significant sink for these halocarbons. These processes are highly variable in the ocean, depending on physical processes of the ocean mixed layer, temperature, productivity, surface saturation, and other variables. Determining a net global sink through observation is a difficult task. Yvon-Lewis and Butler (2002) have constructed a high-resolution model of the ocean surface layer, its interaction with the atmosphere, and physical, chemical, and biological ocean processes. They examined ocean uptake for a range of halocarbons, from knowledge of solubilities and chemical and biological

degradation rates. Although they do not find the ocean sink to be significant for HFCs and HCFCs compared with in situ atmospheric sinks, the reported 94-year oceanic loss lifetimes for CH_3CCl_3 and, coincidentally, for CCl_4 as well, must be included in determining the total lifetimes of these compounds.

Particular consideration of these surface sinks is pertinent for the halocarbons that serve as reference compounds, e.g., CFC-11 and CH_3CCl_3 , and for halocarbons with negligible atmospheric sinks. Kutsuna et al. (2000) have observed degradation of CH_3CCl_3 on the surface of aluminosilica clay mineral surfaces under laboratory conditions. They conclude that both on suspended particles under dust-storm conditions and on surface material in deserts, local sink rates may grow large enough to come within an order of magnitude of atmospheric sinks. Estimates of sink magnitudes on a global basis are not yet available, but would appear to be small.

1.5 METHYL BROMIDE AND METHYL CHLORIDE

Methyl bromide and methyl chloride differ from the other “long-lived” ozone-depleting gases because they have significant natural and anthropogenic sources. Recent research has focused on identifying and quantifying the natural sources and sinks of these two compounds. The calculated atmospheric budgets of both gases are largely out of balance, with identified sinks outweighing identified sources.

1.5.1 Methyl Bromide (CH_3Br)

Since the 1998 Scientific Assessment (WMO, 1999), many publications have appeared and have addressed the atmospheric history of methyl bromide (CH_3Br), its concentration and distribution in the atmosphere (see Section 1.2.1.6 of this chapter), its oceanic and terrestrial fluxes, and its mechanisms of production and degradation in nature. These studies have allowed for refinements in our understanding of atmospheric methyl bromide, but many of the significant uncertainties in 1998 remain. Although new sources have been identified, they do not balance current estimates of loss, which remain essentially unchanged from the previous Assessment (Table 1-9). Analyses of firm air provide for the first time an inferred, 20th century trend for atmospheric methyl bromide in the Southern Hemisphere. These results may provide additional constraints to our understanding of source and sink magnitudes. Interlaboratory differences for absolute calibration of atmospheric methyl bromide are approximately 10%.

Table 1-9. Summary of the estimated source and sink strengths of methyl bromide (CH₃Br).

Source or Sink Type	Source or Sink Best Estimate (Gg yr ⁻¹)	Source or Sink Full Range (Gg yr ⁻¹)
Sources		
Ocean ^a	63	23 to 119
Fumigation–soils ^b	26.5	16 to 48
Fumigation–durables ^b	6.6	4.8 to 8.4
Fumigation–perishables ^b	5.7	5.4 to 6.0
Fumigation–structures ^b	2	2 to 2
Gasoline	5	0 to 10
Biomass burning	20	10 to 40
Wetlands*	4.6	2.3 to 9.2
Salt marshes*	14	7 to 29
Shrublands*	1	0.5 to 2
Rapeseed*	6.6	4.8 to 8.4
Rice fields*	1.5	0.5 to 2.5
Fungus*	1.7	0.5 to 5.2
Peatlands*	0.9	0.1 to 3.3
<i>Subtotal (Sources)</i>	<i>159</i>	<i>77 to 293</i>
Sinks		
Ocean ^a	–77	–37 to –133
OH and hv	–80	–60 to –100
Soils ^c	–47	–32 to –154
Plants	(not quantified)	(not quantified)
<i>Subtotal (Sinks)</i>	<i>–204</i>	<i>–129 to –387</i>
<i>Total (Sources + Sinks) ^d</i>	<i>–45</i>	<i>–220 to +71</i>

See text for further explanation and references related to the values listed. Ranges listed for wetlands and shrublands were assumed here to be a factor of 2. Loss due to hydroxyl has been revised, considering the updated analysis of methyl chloroform (see Section 1.4). Table is adapted and augmented from Yvon-Lewis (2000).

* All asterisked items were estimated from measurements of net fluxes and may be influenced by sinks within them. Thus, they represent minimum gross fluxes.

^a The oceanic source has been adjusted to accommodate the slightly smaller undersaturations reported since the 1998 Assessment (WMO, 1999; see text). The source is calculated as source = net oceanic flux – sink, where net oceanic flux is –14 (–11 to –20) Gg yr⁻¹.

^b Fumigation estimates are taken directly from Kurylo and Rodríguez et al. (1999) and are based upon industrial production data for 1992.

^c Revised uptake to soils is included here as discussed in Varner et al. (1999a), Crill (2000), and Yvon-Lewis (2000).

^d The possible range for sources plus sinks here is not a straightforward calculation of highest and lowest values, because the oceanic net flux must hold to within the range of –11 to –20 Gg yr⁻¹. See p. 2.22 in Kurylo and Rodríguez et al. (1999) for a complete explanation. The total range given in this table is a range of extremes, requiring all sinks to be at their highest values while all sources are at their lowest possible values and vice versa. The likelihood of such occurrences is extremely low. Root mean square error on total sinks of –204 Gg yr⁻¹ is estimated from the indicated full ranges as –157 to –327 Gg yr⁻¹; root mean square error of –45 Gg yr⁻¹ on the sum of sources and sinks is estimated at –171 to +14 Gg yr⁻¹.

1.5.1.1 ANTHROPOGENIC AND ANTHROPOGENICALLY INFLUENCED SOURCES

The main anthropogenic sources of CH₃Br include fumigation of soils for planting and of agricultural products for import and export, biomass burning inasmuch as it is influenced by humans, and automobile emissions from burning of leaded gasoline (Table 1-9). Possible alterations of natural emissions associated with changes

in land-use patterns are not included here, nor are there data available to quantify them.

Methyl bromide use as a fumigant in non-Article 5(1) countries (developed countries as defined by the Montreal Protocol) was scheduled to have begun decreasing after 1998. The Montreal Protocol specifies that production of CH₃Br in developed countries be reduced from the 1991 levels by 25% in 1999 and by 50% in 2001. Data reported to the UNEP Ozone Secretariat

SOURCE GASES

(UNEP, 2002) are consistent with such a reduction and suggest further that global consumption in 1999 was ~11 Gg less than that in 1998.

Little has changed in our understanding of the degree to which the combustion of leaded fuel contributes to emissions of atmospheric CH_3Br . Currently about 86% of all gasoline sold in the world is unleaded, and this will likely rise to 89% by 2005 (personal communication, M.P. Walsh, international consultant, Arlington, Virginia, U.S., 2001). Automobile emissions today remain a small part of the global budget ($5 \pm 5 \text{ Gg yr}^{-1}$, or ~3% of the total emissive flux estimated from sinks), although they were substantially larger in the past (Thomas et al., 1997). Similarly, little new information on the emission of methyl bromide from biomass burning has emerged since 1998. The studies of N.J. Blake et al. (1996) and Mano and Andreae (1994) reported in the 1998 Assessment (WMO, 1999) remain our best estimates, supporting globally averaged emissions of 20 (10-40) Gg yr^{-1} .

1.5.1.2 SURFACE INTERACTIONS: NATURAL SOURCES AND SINKS

Ocean

New work continues to confirm that the ocean remains the largest identified source and second largest sink for atmospheric CH_3Br . This has allowed for refinements in our understanding of methyl bromide saturation, and there is some suggestion that methyl bromide in temperate waters is supersaturated in the spring and summer and undersaturated in the fall and winter (King et al., 2000), which is consistent with observations of seasonal cycles in the North Sea by Baker et al. (1999). This could explain some of the apparently anomalous supersaturations in the open ocean observed in previous investigations (e.g., Lobert et al., 1996; Groszko and Moore, 1998), although not all observed saturation anomalies fit such a pattern (e.g., King et al., 2000; Northeastern Atlantic data in Baker et al., 1999). Combining results from the various expeditions, and using a bimodal relationship to temperature similar to that suggested by Groszko and Moore (1998), King et al. (2000) determined that the overall effect of including these seasonal differences on a global scale lowered the estimated net flux slightly downward from -21 (-32 to -3) to -14 (-20 to -11) Gg yr^{-1} . These findings do not affect the estimate of lifetime relative to oceanic loss, but they do reduce the budget imbalance slightly (lifetime relative to oceanic loss is calculated directly from rates of hydrolysis and nucleophilic substitution in seawater and rates of air-sea exchange).

Two isotopic studies of CH_3Br consumption in the open ocean have been published, supporting the earlier

finding of significant biological removal of CH_3Br in seawater (Tokarczyk and Saltzman, 2001; Tokarczyk et al., 2001). The best estimate of the partial lifetime of atmospheric CH_3Br with respect to oceanic loss remains 1.9 (1.1-3.9) years (Yvon-Lewis and Butler, 1997), as reported in the 1998 Assessment (WMO, 1999).

Soils

Soil fluxes of CH_3Br are slightly better constrained than in 1998. The soil sink reported in the 1998 Assessment (WMO, 1999) was large, -42 Gg yr^{-1} , but also included large uncertainties (-214 to -10 Gg yr^{-1}). This wide range stems from two studies reporting substantially different means. Shorter et al. (1995) had estimated a global sink of $-42 \pm 32 \text{ Gg yr}^{-1}$, whereas Serca et al. (1998) arrived at $-143 \pm 70 \text{ Gg yr}^{-1}$. The difference between these two studies was in part due to the measurements for cultivated soils, but was also a function of the choice of procedure for extrapolating. The estimate for losses to agricultural soils is much larger in the Serca et al. (1998) study. Because of this, Serca et al. (1998) also suggested a mean flux of $-94 \pm 54 \text{ Gg yr}^{-1}$ by taking an arithmetic mean of the results from the two studies for agricultural soils. After making additional measurements at 40 globally distributed sites, Varner et al. (1999a) revised their estimate of agricultural losses upward, but only by a small amount. Based upon these new data and considerations of previously reported data, Crill (2000) revised the range for loss of atmospheric methyl bromide to soils, narrowing it to -154 to -32 Gg yr^{-1} . Adjusting the total soil loss for the new measurements of losses to cultivated soils, Yvon-Lewis (2000) suggested a mean flux of -47 Gg yr^{-1} , within the range reported by Crill (2000).

Recent reports have suggested that at least some soils can produce CH_3Br and even emit CH_3Br to the atmosphere. Keppler et al. (2000) identified an abiotic mechanism for the production of halogenated hydrocarbons in soil that yields high production rates. This mechanism involves iron, halide ion, and organic matter, and the reaction can be fast. How much of this production reaches the atmosphere, and whether such production is limited to peatlands or is ubiquitous, is presently unknown. The study of Rhew et al. (2001) showed that shrublands could be a net source or sink of CH_3Br and CH_3Cl . Because this study focused on net fluxes, it does not relate directly to estimates of lifetime.

Plants and Plant Ecosystems

In the 1998 Assessment (WMO, 1999), a potentially significant plant sink was reported but not quantified globally (Jeffers and Wolfe, 1997). Because of a lack

of additional studies related to this loss, calculating a partial lifetime of atmospheric methyl bromide from plants is not yet possible.

In the past 4 years, however, considerable attention has been given to the study of net fluxes from isolated, terrestrial ecosystems. Dimmer et al. (2001) measured CH_3Br net fluxes from Irish peatlands, Varner et al. (1999b) measured net fluxes from New Hampshire wetlands, and Rhew et al. (2000, 2001) studied the net fluxes of methyl bromide from salt marshes and shrublands. Extrapolating these measurements globally yields net flux estimates of 0.9 Gg yr^{-1} for peatlands, 4.6 Gg yr^{-1} for wetlands, and 14 Gg yr^{-1} for salt marshes. Shrublands were reported as having a net flux of $<1 \text{ Gg yr}^{-1}$. Lee-Taylor and Holland (2000), modeled published fungal production rates, deriving a global net flux of 1.7 Gg yr^{-1} . From studying cultivated crops, Gan et al. (1998) calculated a net flux of 6.6 Gg yr^{-1} for rapeseed, and Redeker et al. (2000) calculated a net flux of 1.5 Gg yr^{-1} for rice fields. What is important to note is that all these studies report measurements of net fluxes and, although useful in narrowing the gap between sources and sinks in the atmospheric budget of CH_3Br , they are not suited alone for determining gross fluxes or partial atmospheric lifetimes.

1.5.1.3 ATMOSPHERIC LIFETIME

Although new publications have confirmed biological losses in the ocean, refined the magnitude of losses to soils, and revised our understanding of global OH burdens (see Section 1.4.2), the best estimate of the methyl bromide global lifetime remains 0.7 years (0.5-0.9 year root mean square (rms) uncertainty; 0.4-1.1 year full range; Kurylo and Rodríguez et al. (1999)). A couple of things have the potential to change the calculated atmospheric lifetime of CH_3Br , however. First, the magnitude of the soil sink remains highly uncertain. Measurements have been made that help in reducing uncertainties, but the result also depends upon the method of extrapolation chosen. Furthermore, the determination that any additional sinks, such as plants, might be significant would reduce further the estimated lifetime for methyl bromide.

1.5.1.4 A TWENTIETH CENTURY, SOUTHERN HEMISPHERIC TREND AND ITS IMPLICATIONS

Since the previous Assessment (WMO, 1999), two papers have inferred atmospheric histories for methyl bromide from measurements of Antarctic firn air (Butler et al., 1999; Sturges et al., 2001a). These studies, based upon samples collected at a total of four locations in Antarctica, suggest that mixing ratios of methyl bromide in the Southern Hemisphere have increased by about 3 ppt since

1900 (Figure 1-11). The 2-ppt increase suggested for the latter half of the last century is roughly coincident with the onset of methyl bromide use as a fumigant in the early 1960s (Singh and Kanakidou, 1993), but other sources or sinks also may have changed over that time as well. The rate of increase of about $0.6\% \text{ yr}^{-1}$ from about 1970 to 1990 inferred from firn air agrees with the real-time measurements of Khalil et al. (1993) for the Southern Hemisphere during 1978-1993 and with the data obtained from archived flask air filled at Cape Grim, Tasmania, over this same period (Figure 1-11; Miller, 1998). The

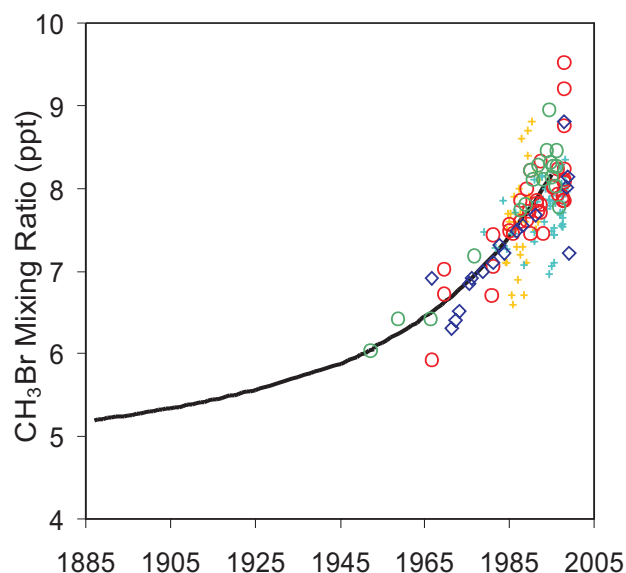


Figure 1-11. Southern Hemispheric history of methyl bromide suggested by Antarctic firn air measurements from four locations, and by archived air samples and flask samples collected at Cape Grim, Tasmania (41°S). The solid line is an atmospheric history derived from firn air measurements at South Pole, Antarctica, estimated with a vertical diffusion model that fits the history of the $\text{CH}_3\text{Br}/\text{CO}_2$ ratio to the observed CO_2 and CH_3Br firn air profiles (see Butler et al., 1999, for details). The green circles are firn data from Siple Dome, Antarctica, plotted against dates determined from CO_2 measurements and the ratio of CH_3Br and CO_2 diffusivities (Butler et al., 1999); the red circles are from firn air at Dronning Maud Land, Antarctica, and are plotted against dates adjusted from CFC-12 measurements and the ratio of CH_3Br and CFC-12 diffusivities (Sturges et al., 2001a); blue diamonds are similar data for Dome C, Antarctica (Sturges et al., 2001a); and yellow (Khalil et al., 1993) and light blue (Miller, 1998) plus symbols are from analyses of flask samples collected at Cape Grim.

SOURCE GASES

work of Butler et al. (1999), which reported results for firn air dating back to the end of the 19th century, indicated that atmospheric methyl bromide may have increased as much as 1 ppt in the first half of the 20th century, but the causes for this earlier apparent increase, and whether they continued into the latter half of the century, are unknown.

Atmospheric histories derived from the analysis of firn air, however, have significant uncertainties. Dating of firn air is imprecise (Schwander et al., 1988), and the atmospheric histories derived for methyl bromide presume that in situ production or degradation are insignificant during the long time that the firn air is exposed to the surrounding snow. Whereas all Antarctic sites sampled have yielded a similar atmospheric history for CH₃Br regardless of their differences in temperature, deposition rate, depth, and lock-in zone thickness (Figure 1-11), Arctic sites exhibited large elevations of methyl bromide and other gases near the bottoms of the profiles (not shown; Butler et al., 1999; Sturges et al., 2001a). Further, the profiles from the Northern Hemispheric sites differed dramatically from one another, as would be expected for site-specific disturbances. That this was not observed in the Antarctic increases confidence in the reported atmospheric history from these sites. The mechanism for increases of certain compounds, including methyl bromide, at the bottom of the Arctic profiles is not known.

An understanding of atmospheric changes for methyl bromide during the 20th century can provide some insight into the relative magnitude of present-day sources. Of particular interest is the magnitude of industrially derived emissions relative to the total annual flux of methyl bromide. This quantity can be estimated directly from our understanding of source and sink magnitudes: for emissions derived from fumigation of 41 Gg yr⁻¹, with an rms range of 30-62 Gg yr⁻¹, divided by the best estimates for sinks (204 Gg yr⁻¹ and rms range of 157-327; Table 1-9), the calculated contribution of industrially produced methyl bromide to a 10-ppt global atmospheric burden ranges from 10 to 40%. As suggested above, the atmospheric trend inferred from the Antarctic firn air provides a second approach for estimating this fraction. The results suggest that from 1950 to 1995, CH₃Br in the Southern Hemisphere increased by 2 to 2.5 ppt (Figure 1-11). If we assume that either Northern Hemispheric mixing ratios increased by the same proportion as in the Southern Hemisphere or that Northern Hemispheric mixing ratios in 1950 were the same as those in the Southern Hemisphere, then the firn results suggest that CH₃Br in the global atmosphere has increased 25-40% from 1950 to 1995, regardless of lifetime or other budget

considerations. Therefore, were this increase solely due to fumigation, 40% would represent an upper limit for the contribution from fumigation. However, it also appears from the firn data that CH₃Br in the Southern Hemisphere increased about 0.7 ppt during the first half of the century, perhaps because of changing land-use practices, increases in biomass burning, or the post-1925 onset of leaded-fuel combustion in automobiles. If this underlying trend had continued through the second half of the century, then the contribution of industrially produced methyl bromide would be 1.5-3 ppt, or 15-30% of the 1995 atmospheric burden. Given the assumptions above, then, the overall range of 15-40% for this fraction suggests emissions related to fumigation of 30-80 Gg yr⁻¹ in 1995. Although bromine emissions from combustion of leaded fuel have decreased dramatically since 1970, they were similar in 1950 to what they were in 1990 (Thomas et al., 1997) and do not strongly influence this conclusion.

1.5.1.5 ATMOSPHERIC BUDGET

The calculated budget for atmospheric methyl bromide remains out of balance, with estimated sinks still outweighing estimated sources (Table 1-9). However, the new findings on ecosystem net fluxes have narrowed the gap between calculated sources and sinks (Crill, 2000; Yvon-Lewis, 2000; Butler, 2000). The most complete summary is that of Yvon-Lewis (2000), from which Table 1-9 has been adapted and augmented. This budget is for the mid-1990s, before the scheduled reductions of methyl bromide production. Because measurements relating to plants usually involve estimates of net fluxes, any plant sink is incorporated implicitly into the source terms for those elements that are reported as such in the table. Quantifying the plant sink, while affecting the calculated lifetime, would not affect the budget balance.

1.5.2 Methyl Chloride (CH₃Cl)

Methyl chloride (CH₃Cl), the most abundant halocarbon in the atmosphere, is derived largely from natural sources. Until 1996 most of the input to the atmosphere was considered to originate from the oceans, but investigations in recent years have indicated that terrestrial sources, probably located in the tropics, dominate the atmospheric budget, and that these sources are more significant than hitherto appreciated. Moreover, the presumption that abiotic reactions constitute the only sinks for atmospheric CH₃Cl is being displaced by recognition that microbial degradation in soil may represent a measurable sink of atmospheric CH₃Cl. Although new findings have allowed constraints to be placed on some source

terms in the atmospheric budget, major uncertainties still exist regarding the magnitude of several sources and sinks. As is seen for methyl bromide, a shortfall is apparent between known sources and modeled sinks of methyl chloride.

1.5.2.1 ATMOSPHERIC DISTRIBUTION AND TRENDS

There is emerging evidence that CH_3Cl is elevated in air masses associated with land in the tropics (Khalil and Rasmussen, 1999; Yokouchi et al., 2000b; see also Section 1.2.1.7). CH_3Cl mixing ratios of up to 1400 ppt have been recorded in calm weather off the subtropical Okinawa and Hateruma Islands in southern Japan (Li et al., 1999; Yokouchi et al., 2000b) and up to 850 ppt at inland locations on various continents (Khalil and Rasmussen, 1999). Interestingly, the high CH_3Cl mixing ratios observed by the Japanese researchers were strongly correlated with elevated amounts of the plant-derived terpene, α -pinene, which has an atmospheric lifetime of only a few hours. This finding is consistent with high emissions of CH_3Cl from tropical coastlands. In subsequent work on the marine boundary layer in the Western Pacific and Southeastern Indian Ocean, Li et al. (2001) found that the CH_3Cl mixing ratio was enhanced (up to 950 ppt) in air masses derived from forested tropical islands.

An indication of long-term trends in atmospheric CH_3Cl has been obtained by analysis of air trapped in polar firn in Antarctica and Greenland (Figure 1-12; Butler et al., 1999). An increase of about 10% was inferred since the mid-1900s for both hemispheres, suggesting that the anthropogenic contribution, if reflected by the apparent 20th century increase, is comparatively small. Global measurements from 1981-1997 suggest an overall decrease of about 4% over this shorter period (Khalil and Rasmussen, 1999).

1.5.2.2 SOURCES OF ATMOSPHERIC METHYL CHLORIDE

The principal sources of atmospheric CH_3Cl identified to date are biomass burning and the oceans, although tropical plants may exceed all other sources (Yokouchi et al., 2002; Table 1-10). Except for the tropical plant source, the latest estimates of emissions do not differ substantially from those reported in the 1998 Assessment (WMO, 1999; Graedel and Keene, 1999). The net flux from the oceans was revised sharply downward in 1996 to 200-400 Gg yr^{-1} (Moore et al., 1996). This estimate represents the balance between emissions of CH_3Cl in tropical waters and uptake in the cold waters of latitudes above 50°. Khalil et al. (1999) analyzed data collected by several groups of

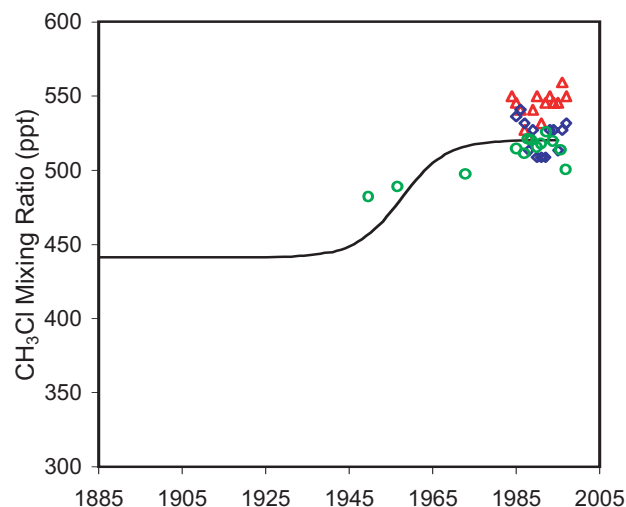


Figure 1-12. Southern Hemispheric history of methyl chloride suggested by Antarctic firn air measurements from two locations, and by atmospheric measurements from flask samples collected in Antarctica and at Cape Grim, Tasmania. The solid line is an atmospheric history derived from firn air measurements at South Pole, Antarctica, estimated with a vertical diffusion model that fits the history of the $\text{CH}_3\text{Cl}/\text{CO}_2$ ratio to the observed CO_2 and CH_3Cl firn air profiles (see Butler et al., 1999, for details). The open green circles are data from Siple Dome, Antarctica, plotted against dates derived from adjusted CO_2 measurements and diffusivities (Butler et al., 1999), and the open blue diamonds and red triangles are annual means of “real-time” measurements from flask samples collected in Antarctica and Cape Grim, respectively (Khalil and Rasmussen, 1999; these data have been lowered by 8.3% to account for a calibration difference).

investigators between 1983 and 1996 and confirmed the weaker oceanic source, calculating a net global flux of 600 Gg yr^{-1} (after adjusting for calibration). For biomass burning, Lobert et al. (1999) estimated emissions of CH_3Cl from nine different burning categories on a 1° latitude by 1° longitude grid. Fluxes were derived from biomass inventories based upon emission ratios relative to both CO and CO_2 and the chlorine content of the fuel feedstock. Calculated global emissions of 911 Gg yr^{-1} (range 655-1125 Gg yr^{-1}) from burning, most of which are believed confined to the tropics and subtropics, agree with the previous approximation of $1.0 \pm 0.5 \text{ Tg yr}^{-1}$ (Andreae et al., 1996; N.J. Blake et al., 1996; Rudolph et al., 1995).

Recently, Yokouchi et al. (2002) suggested that methyl chloride emissions from tropical plants might be

SOURCE GASES

Table 1-10. Estimated source and sink strengths for atmospheric methyl chloride (CH₃Cl).

Source or Sink Type	Source or Sink Best Estimate (Gg yr ⁻¹)	Source or Sink Full Range (Gg yr ⁻¹)
Sources		
Oceans	600 ^a	325 to 1300
Biomass burning	911 ^b	655 to 1125
Tropical plants	910 ^c	820 to 8200
Fungi	160 ^d	43 to 470
Salt marshes	170 ^e	65 to 440
Wetlands	40 ^{f, g}	6 to 270
Coal combustion	105 ^h	5 to 205
Incineration	45 ^h	15 to 75
Industrial	10 ^h	
Rice	5 ⁱ	
<i>Subtotal (Sources)</i>	<i>2956</i>	<i>1934 to 12,085</i>
Sinks		
Reaction with OH in troposphere	-3180 ^j	-2380 to -3970
Loss to stratosphere	-200 ^a	-100 to -300
Reaction with Cl in marine boundary layer	-370 ^{i, j}	-180 to -550
Microbial degradation in soil	-180 ^k	-100 to -1600
Loss to polar oceans	-75 ^{j, l, m}	-37 to -113
<i>Subtotal (Sinks)</i>	<i>-4005</i>	<i>-2797 to -6533</i>
Total (Sources + Sinks)	-1049	-4599 to +9288

The destructive flux from reaction with OH is calculated with revised OH (see Section 1.4).

^a Khalil et al. (1999), adjusted for calibration.

^b Lobert et al. (1999).

^c Yokouchi et al. (2002).

^d Watling and Harper (1998).

^e Rhew et al. (2000).

^f Varner et al. (1999a).

^g Dimmer et al. (2001).

^h McCulloch et al. (1999); Keene et al. (1999).

ⁱ Redeker et al. (2000).

^j Khalil and Rasmussen (1999), after calibration adjustment applied; see text.

^k Khalil and Rasmussen (2000), after calibration adjustment applied; see text.

^l Moore et al. (1996).

^m Unlike in Table 1-9, loss to polar oceans here is from field observations alone and is given as a net sink.

the largest known source. They determined that a specific group of ferns and trees in Southeast Asia alone produced 910 Gg yr⁻¹, about one-fourth of the annual flux as estimated by sinks. The uncertainty in this estimate is large, and this source certainly warrants additional investigation.

Release of CH₃Cl by wood-rotting fungi has been estimated by Watling and Harper (1998) at 160 Gg yr⁻¹ (Table 1-10), of which 75% is derived from tropical and subtropical forests. This assessment was based on the conservative assumption that only Cl⁻ from wood itself

was available for fungal uptake. If, however, Cl⁻ in leaf litter and soil is accessible to these fungi, emissions could be much greater. Dimmer et al. (2001) reported field measurements of CH₃Cl fluxes from forest floors. Although the sites (conifer plantations in Western Ireland) cannot be regarded as globally representative of temperate coniferous forest, an extrapolation of the observed emission fluxes led to an estimate of 85 Gg yr⁻¹ from such forests worldwide, suggesting that the order of magnitude of the overall flux from fungi in forest ecosystems is similar to that predicted by Watling and Harper (1998).

In addition to the methyl chloride source reported by Yokouchi et al. (2002), Rhew et al. (2000) found large net CH_3Cl fluxes from halophytic plant species in the middle and upper vegetation zones of Californian salt marshes. Assuming that the sites were representative of salt marshes globally, the authors postulated a global flux of 170 Gg yr^{-1} from this source (Table 1-10). Subsequent investigations on shrubland ecosystems in Southern California demonstrated significant emissions from some plant species at particular seasons (Rhew et al., 2001). However, such emissions were counterbalanced by soil uptake during other seasons, and therefore the biome was in fact a small net sink for CH_3Cl . Fluxes of CH_3Cl from peatland ecosystems have been monitored by investigators in Northeastern United States (Varner et al., 1999b) and Western Ireland (Dimmer et al., 2001), although in neither case was it clear whether emissions came from plants or the soil. On the basis of these measurements Varner et al. (1999b) postulated global emissions from wetlands of 48 Gg yr^{-1} , whereas Dimmer et al. (2001) estimated global emissions of 5 Gg yr^{-1} from peatlands and 35 Gg yr^{-1} from wetlands. These estimates must be treated with caution because data in each investigation were restricted to ecologically similar temperate sites and were collected over a short period. Emissions of CH_3Cl have also been noted from the soil of California rice paddies, which have been extrapolated to global emissions of 5 Gg yr^{-1} from this crop (Redeker et al., 2000).

A novel abiotic mechanism for formation of CH_3Cl in soils rich in organic matter in the presence of Fe^{3+} and high chloride concentrations has recently been proposed (Keppler et al., 2000). Such a process may yield significant fluxes in highly saline environments, but no field measurements have yet been conducted. Anthropogenic release of CH_3Cl during coal combustion, incineration, and industrial processes was quantified in the Reactive Chlorine Emissions Inventory (McCulloch et al., 1999). Emissions from these sources contribute in all about 160 Gg yr^{-1} , or less than 10% of total known sources (Table 1-10).

1.5.2.3 SINKS OF ATMOSPHERIC METHYL CHLORIDE

Reaction with OH radical is the dominant pathway for removal of CH_3Cl from the atmosphere. Khalil and Rasmussen (1999) estimated that the atmospheric lifetime of CH_3Cl with respect to OH attack varied from 0.8 years in the tropics to 12 years at the poles, with an average global lifetime of 1.4 years. This partial lifetime has been revised to 1.5 years in this Assessment based upon the considerations discussed in Section 1.4.2. Reaction with chlorine radicals in the marine boundary layer also could constitute another loss process, particularly in tropical lat-

itudes (Keene et al., 1996). Using a chlorine concentration of $5 \times 10^{-4} \text{ radicals cm}^{-3}$ in the marine boundary layer, Khalil and Rasmussen (1999) estimated this sink as up to 0.4 Tg yr^{-1} . This would represent a partial atmospheric lifetime of 13 years with respect to this loss alone.

Some evidence exists for a potentially substantial sink of atmospheric CH_3Cl involving microbially mediated uptake by soil (Khalil and Rasmussen, 2000). On the basis of measurements of CH_3Cl uptake by soils from Brazil and Greenland, these authors estimated a global uptake of 0.18 Tg yr^{-1} (0.2 Tg before adjusting for calibration discrepancies) by soils. This number is uncertain, and may be an underestimate; the ubiquitous occurrence in soil from pristine environments of microbial species capable of utilizing CH_3Cl as sole carbon and energy source implies a large and substantial soil sink for CH_3Cl (Harper, 2000; McAnulla et al., 2001). The loss of 0.2 Tg yr^{-1} (0.18 Tg yr^{-1} adjusted for calibration) translates to a partial atmospheric lifetime of 28 years.

Moore et al. (1996) noted undersaturations of CH_3Cl in the polar oceans, which Khalil and Rasmussen (1999) combined with other data to calculate a global, polar sink of 83 Gg yr^{-1} (75 Gg yr^{-1} adjusted for calibration). Uncertainties in the sink term given by Moore et al. (1996) suggest that this value could range from 37 to 113 Gg yr^{-1} . This small sink, if irreversible, amounts to an atmospheric lifetime of ~ 70 years.

Combining the lifetimes of 1.5, 13, 28, and 70 years for losses to reaction with OH, reaction with Cl, consumption in soils, and degradation in seawater, respectively, yields an atmospheric lifetime of 1.3 years for CH_3Cl (Table 1-3).

1.5.2.4 ATMOSPHERIC BUDGET

The imbalance between calculated emissions from known sources and the estimated global sink for atmospheric CH_3Cl is about 1.0 Tg yr^{-1} out of a total estimated flux of 4.0 Tg yr^{-1} (or 25%). All sources quantified to date are situated predominantly in the tropics, a location consistent with source deconvolution calculations. Using a global 3-D model of atmospheric CH_3Cl , Lee-Taylor et al. (2001) were able to reproduce the observations of Khalil and Rasmussen (1999) by adding a tropical terrestrial source of 2.5 Tg yr^{-1} and reducing emissions from Southeast Asia. Any major as-yet-unidentified source must necessarily show a similar global distribution to be consistent with observations. In this context observations of high CH_3Cl mixing ratios in air masses associated with forested tropical coastlines (Yokouchi et al., 2002) are highly significant and should provide a focus for future investigations on potential sources of atmospheric CH_3Cl .

SOURCE GASES

1.6 ATMOSPHERIC HALOCARBON OBSERVATIONS COMPARED WITH EXPECTATIONS

1.6.1 Consistency Between Atmospheric Halocarbon Measurements and Known Sources and Sinks

Consistency between atmospheric measurements and known sources and sinks for halocarbons are assessed here in two complementary ways: (1) atmospheric measurements are compared with mole fractions that are calculated from emissions derived from industrial production data (see Section 1.3), and (2) the industry-based annual emission estimates are compared with global emissions inferred from the atmospheric measurements. The measurements we consider here are global means estimated from multiple surface sampling sites (the AGAGE, CMDL, and UCI monitoring networks; D.R. Blake et al., 1996; Montzka et al., 1999; Prinn et al., 2000) and global means inferred from measurements at a single site (the Australian air archive, Langenfelds et al., 1996; Fraser et al., 1996). Calculations were performed with two-dimensional models (Cunnold et al., 1994, 1997; Fraser et al., 1999; Oram et al., 1995). Any unexpected differences between the calculated and observed mixing ratios or the calculated and the industry-based emission estimates may represent unaccounted for production and emissions, but these differences may also arise from systematic errors in measurement calibration or consistency, in halocarbon loss rates (lifetimes), or in modeling the atmosphere.

1.6.1.1 CFCs

Measured mixing ratios for CFC-11 and -12 are 5-10% higher than those calculated from emissions derived from production data throughout the entire period of measurement (Figure 1-13). For CFC-12 during the 1990s the discrepancy became small compared with the uncertainties in this analysis. For both these gases, mixing ratios reported by different laboratories agree quite well (Table 1-1), and this consistency argues against measurement error being the source of the discrepancies.

The differences noted for mixing ratios are also apparent in a comparison of emissions derived from measurements or industry production data before 1992 (Figure 1-14). The observations before that year suggest approximately 5-10% larger emissions of CFC-11 and -12 compared with those derived from industry production data. After 1992 the uncertainties in the analysis become large, and any discrepancies are well within this uncertainty. In the case of CFC-11, these differences also could be reconciled if its lifetime were somewhat longer than the cur-

rent best estimate of 45 years (see Section 1.4). For CFC-12, scaling the lifetime by some constant factor cannot remove these differences; in fact it seems most likely that the industry emissions estimates from 1993 to 1997 are slightly high. This is consistent with improved containment of CFCs in applications (UNEP, 1998a), although the extent to which practices to reduce ODSs emissions have been adopted is difficult to ascertain.

Past discussion regarding CFC-113 noted that observations substantially underestimated calculated global means (Fraser et al., 1996; Prinn and Zander et al., 1999; Figure 1-13). This situation stems from the presumption in these studies that significant amounts of CFC-113 were produced by companies not reporting to AFEAS. However, it is now apparent that the only significant source that is not counted by AFEAS is Russian production (Bingfeng et al., 2000). The actual Russian production is unknown, but capacity for CFC-113 amounted to some 12,000 tons yr^{-1} prior to the total shutdown that was accomplished there in 2000 (personal communication, E. Pedersen, World Bank, 2002). This represents a maximum of 5% of the 1989 reported production, with resulting emissions significantly less than the confidence limits on global emissions (Figure 1-14). The global emissions inferred from measurements are generally consistent with AFEAS data accounting for global production of this gas. There is a small divergence after 1995 for reasons not currently understood (Figure 1-14).

1.6.1.2 METHYL CHLOROFORM

For methyl chloroform artificially good agreement is shown in Figure 1-13, because industry release estimates are used here to derive the OH field and methyl chloroform lifetime (Prinn et al., 2001). An independently calculated OH field by Spivakovsky et al. (2000) results in a methyl chloroform lifetime within 10% of that inferred by Prinn et al. (2001), but a number of other models of the OH distribution give much larger differences (e.g., Hein et al., 1997; Hauglustaine et al., 1998). The small discrepancy between the measured and expected mixing ratios after 1996 has been interpreted as indicating lower OH values at that time (Prinn et al., 2001). On the basis of an uncertainty of approximately 3% (except during 1996-1999) for industry-based emissions of methyl chloroform, it has been concluded that the effective OH in a 12-box, 2-D model averaged from 1979 to 2000 has an uncertainty of $\pm 14\%$ (Prinn et al., 2001).

1.6.1.3 CARBON TETRACHLORIDE

With loss to the ocean now included (Yvon-Lewis and Butler, 2002), the lifetime of carbon tetrachloride is

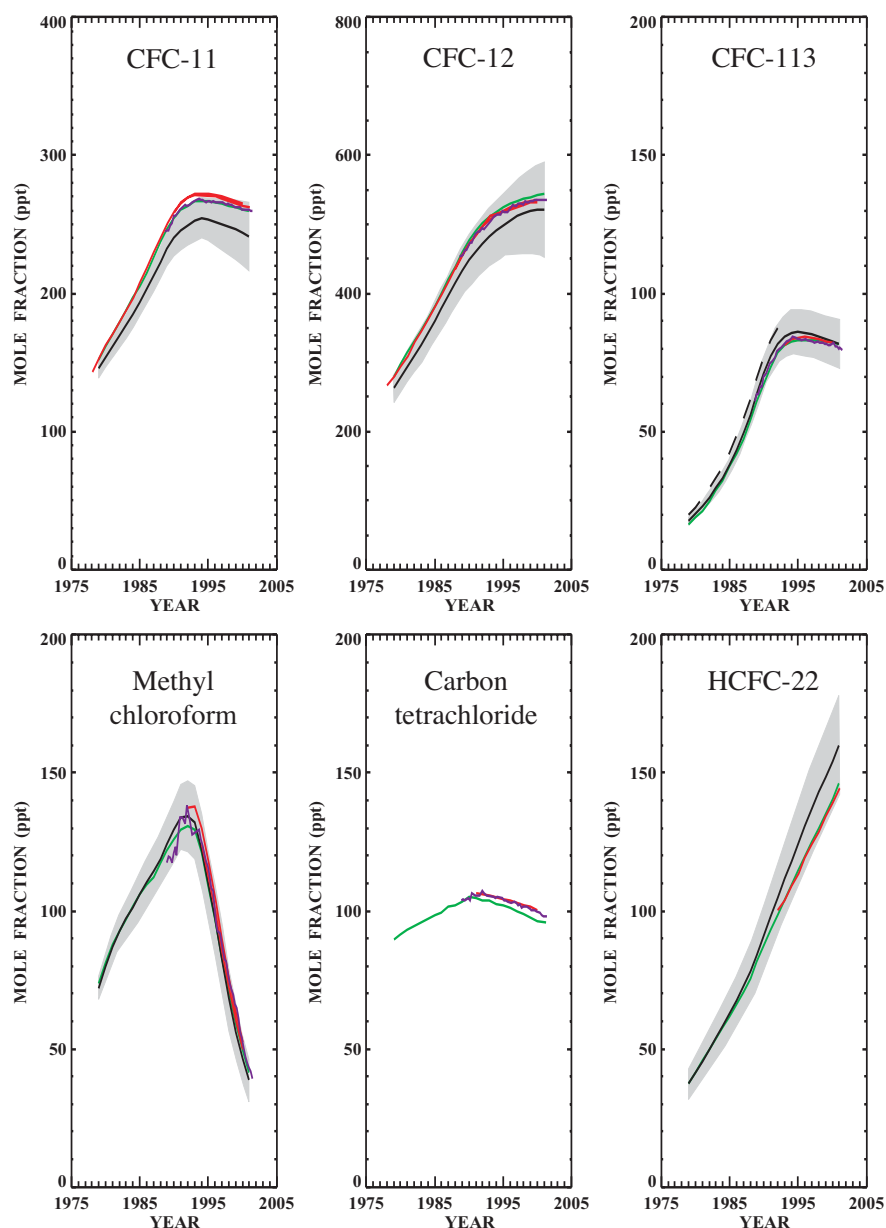


Figure 1-13. Measured and calculated global mean surface mixing ratios for major CFCs, methyl chloroform, carbon tetrachloride, and HCFC-22. Observations are from AGAGE in situ instruments (green lines: Prinn et al., 2000), from CMDL in situ instruments and flask measurements (red lines: Montzka et al., 1999), and from UCI flask measurements (purple lines: D.R. Blake et al., 1996, all gases except HCFC-22). For HCFC-22, the AGAGE global means before 1992 are derived from measurements of the Australian air archive (Miller et al., 1998) and a 12-box model calculation. Global surface mixing ratios were calculated with a 12-box model (Cunnold et al., 1997) using global emissions from a combination of AFEAS (2001) and UNEP (2002) data and lifetimes of 45 (29-76), 100 (77-185), 85 (54-143), 5.0 (4.5-5.6), and 12.0 (10.3-13.7) years for CFC-11, CFC-12, CFC-113, methyl chloroform, and HCFC-22, respectively (black lines). Uncertainties in calculated mixing ratios (shaded gray area) were derived from the lifetime ranges indicated, uncertainties in model parameters, and uncertainties in industry emissions estimates. No calculated mixing ratios are shown for carbon tetrachloride because an independent record for historic production and emission of this gas is lacking. For CFC-113 mixing ratios have also been calculated (black dashed line) based on global emission estimates by Fisher et al. (1994); corresponding calculations for the other gases are not shown because the results differ by less than 1% from the latest results.

SOURCE GASES

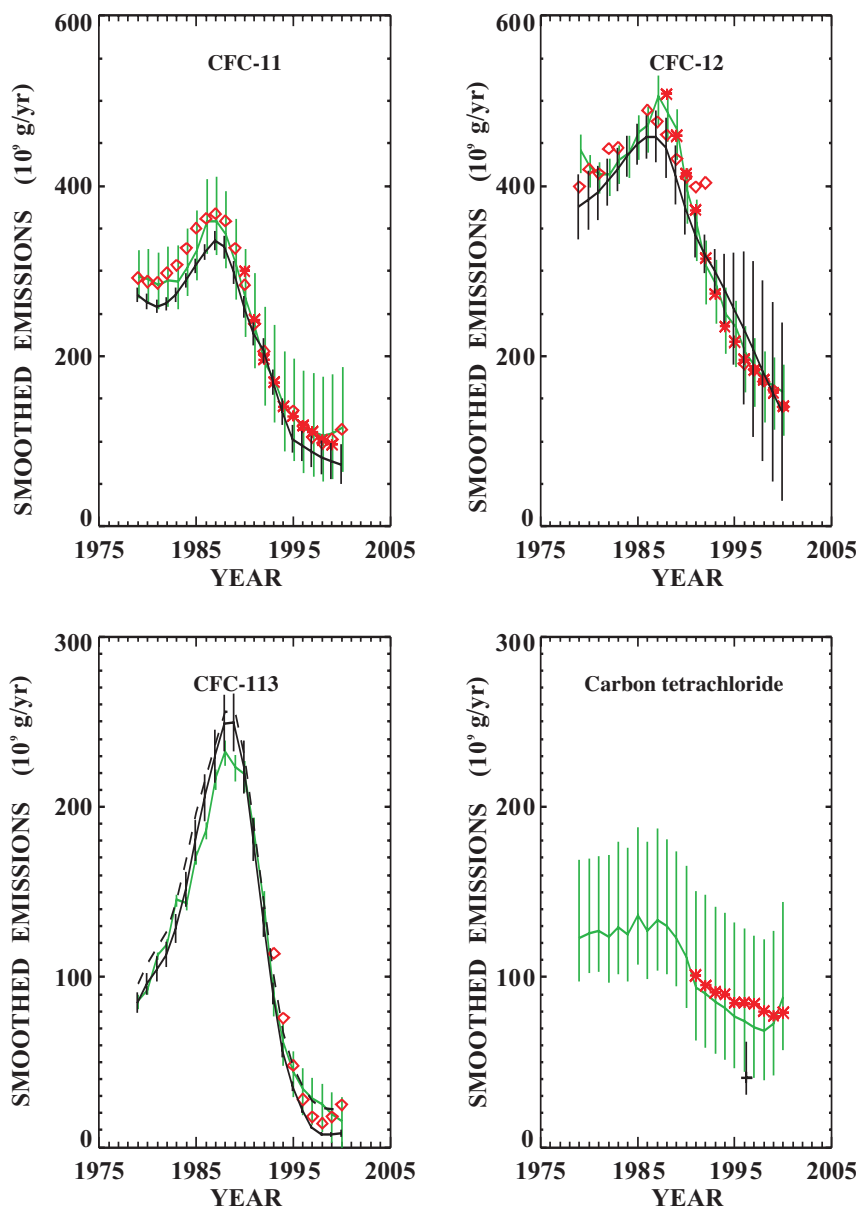


Figure 1-14. Estimates of annual emissions from industry (full black lines: based upon data from AFEAS (2001) and UNEP (2002); see Section 1.3) and inferred from measurements (green lines and red symbols) for CFC-11, CFC-12, CFC-113, and carbon tetrachloride. Uncertainties on industry emissions for CFC-11 are from McCulloch et al. (2001); for CCl_4 , see UNEP (1998b) and McCulloch et al. (2002). The black dashed line for CFC-113 indicates previous global emissions estimates that included an allotment from companies not reporting to AFEAS (Fisher et al., 1994). The only available global emission estimate for CCl_4 derived from industry data was made by UNEP (1998b) for 1996 and is indicated by a black symbol. Release estimates based on atmospheric measurements by AGAGE (green lines: Prinn et al., 2000) were made with a 12-box model (Cunnold et al., 1997) and lifetimes of 45 (29-76), 100 (77-185), 85 (54-143), and 26 (17-36) years for CFC-11, CFC-12, CFC-113, and carbon tetrachloride, respectively. The effect of these lifetime uncertainties, which were derived from an ensemble of model calculations reported in WMO (1999), and, for CCl_4 , uncertainty in the oceanic loss (Yvon-Lewis and Butler, 2002), is indicated by the green error bars. Emission estimates derived using the same AGAGE model applied to CMDL (Montzka et al., 1999) flask sample measurements (red diamonds) and CMDL in situ measurements (red asterisks) are also shown. All emission estimates derived from atmospheric measurements have been smoothed over 3-yr intervals to reduce the effects of measurement imprecision. Units of emission are 10^9 g yr^{-1} ($10^9 \text{ g} = 1 \text{ Gg}$).

estimated to be 26 (17-36) years, or about 25% shorter than in Prinn and Zander et al. (1999) (see Section 1.4.2). Emissions estimated for 1996 by TEAP (UNEP, 1998b) are below those inferred from measured trends and this lifetime (Figure 1-14), and suggest that either (1) releases of CCl_4 are higher than estimated, or (2) the current, best-estimate lifetime is too short (Figure 1-14). Calibration differences are too small to account for these large discrepancies (Table 1-1).

Uncertainties in lifetime estimates for CCl_4 are significant and account for much of the uncertainty range shown in Figure 1-14. Some insights into emissions of CCl_4 can be gleaned from a study of their relationship to CFC production, which was believed to account for the majority of carbon tetrachloride emissions (Simmonds et al., 1998a). The molar ratio, [total global CCl_4 emissions]/[total global production of CFC-11 and CFC-12], ranges between 0.12 and 0.16 during 1978-1993 when the global CCl_4 emissions are inferred from atmospheric measurements using a lifetime of 26 years (see Figure 1-15). Some fraction of global CCl_4 emissions, however, arises from processes not related to CFC production; TEAP (UNEP, 1998b) estimated that fraction at 30% in 1996. Such emissions, if included as a constant in other years, suggest fugitive emissions of CCl_4 arising from CFC production of $11 \pm 0.6\%$ during 1978-1993. After 1993 as global CFC production declines, however, this ratio increases dramatically (Figure 1-15). Such a change suggests either that fugitive releases of CCl_4 during CFC production have increased by a factor of between 1.5 and 2 in recent years, or that CCl_4 emissions not related to CFC production are much higher than previously realized.

1.6.1.4 HCFCs

In the past there have been large discrepancies between measured and calculated mixing ratios of HCFC-142b and, to a lesser extent, HCFC-141b (Montzka et al., 1994; Oram et al., 1995; Simmonds et al., 1998b). New industry-based emission estimates (see Section 1.3; AFEAS, 2001), however, result in much better agreement for HCFC-142b (Figures 1-16 and 1-17). For HCFC-142b and -141b, emissions inferred from measurements are still slightly larger than the industry estimates, whereas for HCFC-22 the industry releases appear to be on the high side, and a somewhat shorter lifetime (more OH) would result in a better fit. The incorporation of the time-dependent OH field derived by Prinn et al. (2001) worsens the differences between industry-derived emissions and those calculated from atmospheric observations of HCFC-22 (Figure 1-16). The effect of these potential OH changes on the other HCFC plots is negligible, and is not shown.

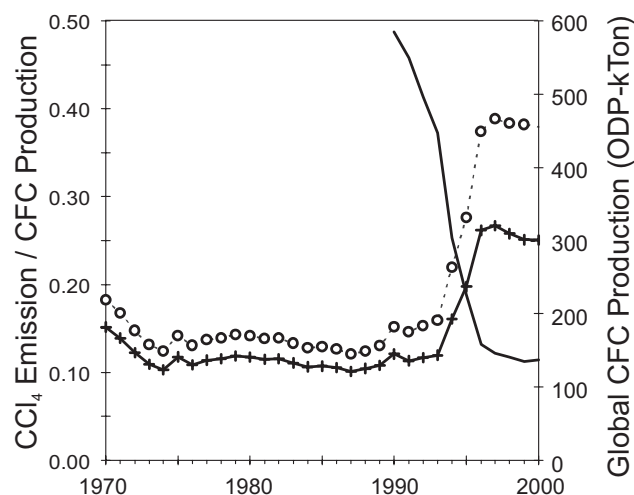


Figure 1-15. The molar ratio of global carbon tetrachloride emissions relative to aggregated CFC-11 and -12 global production (dashed line with open circles; left axis scale). In an attempt to better describe the fraction of CCl_4 emissions resulting from CFC production, this ratio is calculated alternatively by subtracting 22 Gg of CCl_4 emissions for all years (solid line with crosses; left axis scale) based upon UNEP (1998b) estimates that 30% of CCl_4 emissions in 1996 were unrelated to CFC production in 1996 (UNEP, 1998b). In this analysis global emissions for carbon tetrachloride were inferred from measurements (Prinn et al., 2000; Montzka et al., 1999) presuming a 26-yr global lifetime (Yvon-Lewis and Butler, 2002; Section 1.4.2). Also shown is the global aggregated CFC-11 and CFC-12 production in recent years (thin black line, right axis scale; UNEP, 2002).

1.6.1.5 HALONS

In the previous Assessment (WMO, 1999), substantial differences were noted between measured trends and mixing ratios of Halon-1211 and those derived from production data and release functions (Fraser et al., 1999; Butler et al., 1998). Since then TEAP (an update to UNEP, 1999) has made global estimates of emissions for both Halon-1211 and -1301 from independently derived functions that relate production to emission. For both halons, mixing ratios calculated from these two emissions histories are substantially different but provide a better picture of the uncertainties involved with this calculation than were possible previously (Figure 1-17). Fairly significant differences are also apparent in results from different laboratories for both halons: inter-laboratory differences range up to 15% for Halon-1211 and 30% for Halon-1301.

SOURCE GASES

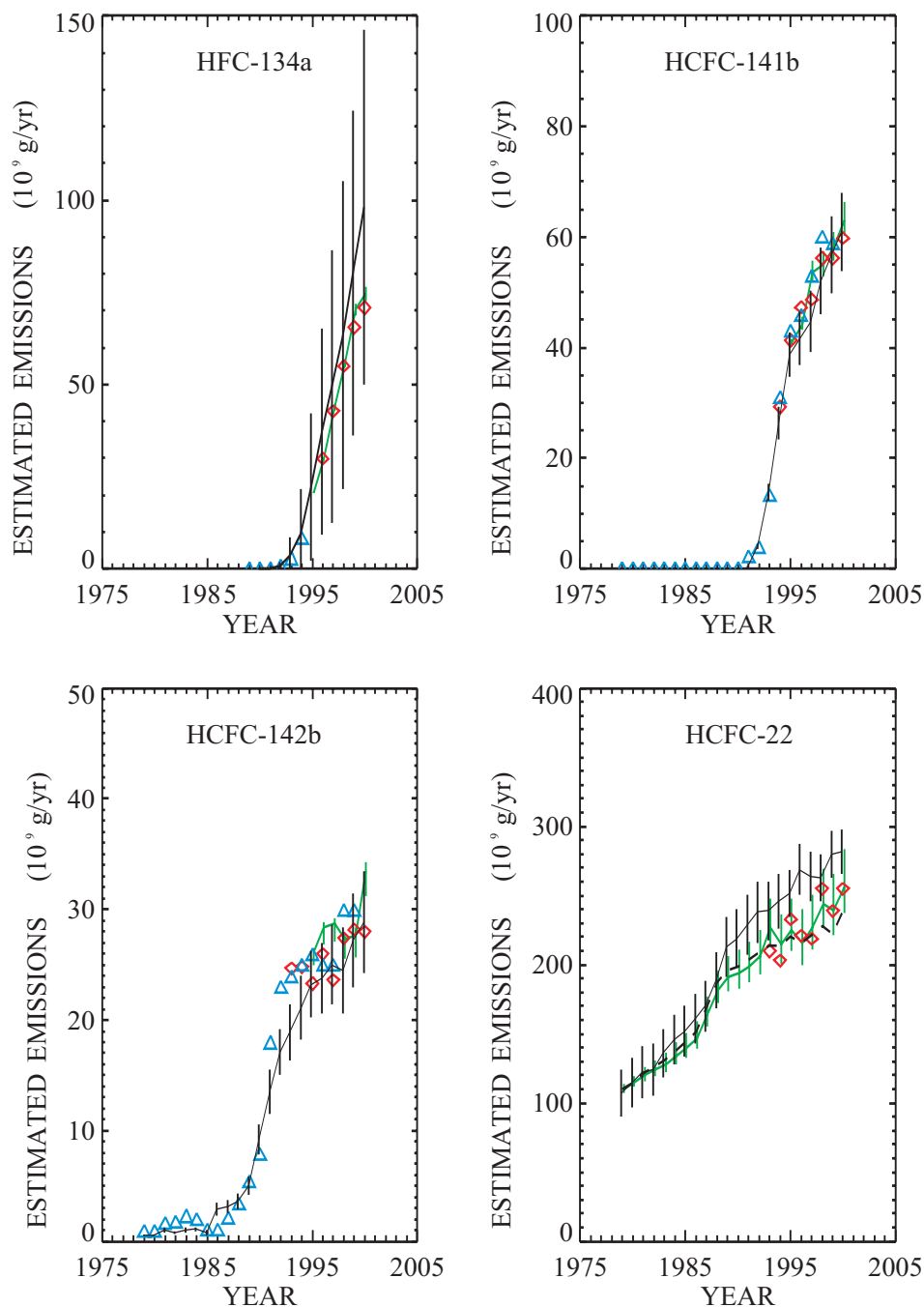


Figure 1-16. Estimates of emissions from industry (solid black lines) and inferred from measurements (green lines, red and blue symbols) for the most abundant HCFCs and HFC-134a. The green lines indicate global release estimates from measurements at one to three sites and the AGAGE model (Cunnold et al., 1997; Prinn et al., 2000; Miller et al., 1998) using global lifetimes of 14.0 years for HFC-134a, 9.3 years for HCFC-141b, 17.9 years for HCFC-142b, and 12.0 years for HCFC-22. The effect of an uncertainty of $\pm 14\%$ in the tropospheric lifetime of these compounds due to hydroxyl (see Prinn et al., 2001) is indicated by the green error bars. The red diamonds are annual release estimates obtained using the same AGAGE model applied to CMDL flask measurements (7-8 sites; Montzka et al., 1999). The blue triangles are estimates obtained from an independent set of measurements (at 41°S only) and a separate model (UEA: Oram et al., 1995, 1996). The black dashed line on the HCFC-22 panel indicates emissions inferred from AGAGE measurements with the time-dependent OH burden suggested by Prinn et al. (2001). Units of emission are 10^9 g yr^{-1} ($10^9 \text{ g} = 1 \text{ Gg}$).

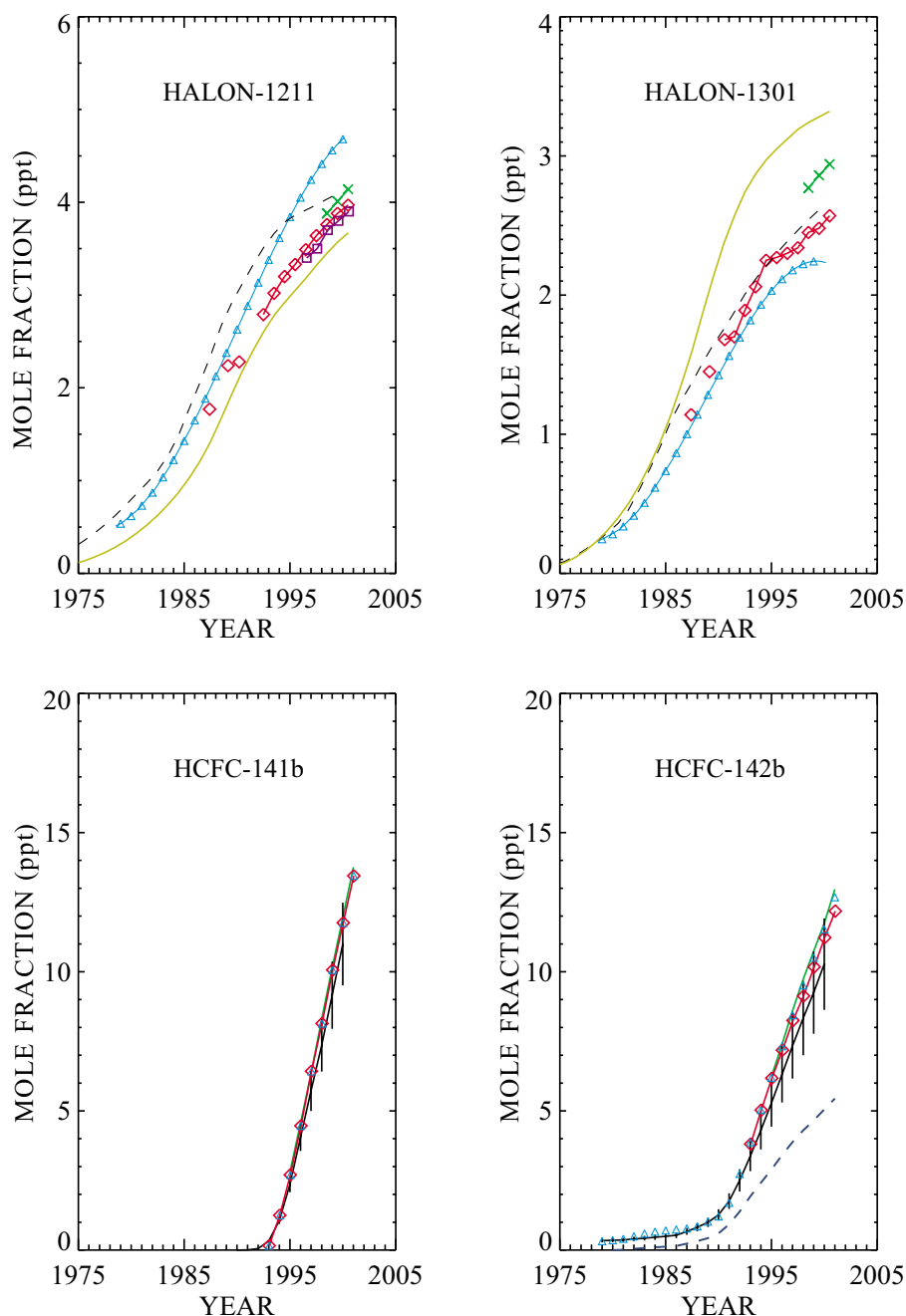


Figure 1-17. Observed and calculated global mean surface mixing ratios for selected halons and HCFCs over time. Observations are global means from CMDL flask measurements (open red diamonds: Butler et al., 1998; Montzka et al., 1999); global means from AGAGE in situ instruments (green crosses or solid green lines: Prinn et al., 2000; Sturrock et al., 2001); global means from UCI quarterly flask measurements (open purple squares: Blake et al., 2001, Halon-1211 only); and global means derived from an analysis of the Cape Grim Air Archive by UEA (blue triangles: Fraser et al., 1999; Oram et al., 1995). Mixing ratios were calculated with 2-D models and lifetimes of 17 years for Halon-1211 and 62 years for Halon-1301 (Fraser et al., 1999), 9.3 yrs for HCFC-141b, and 17.9 years for HCFC-142b. Mixing ratios calculated with emissions of halons derived from industry production data are from Fraser et al. (1999) (black dashed lines, halons only) and updated UNEP (1999) (gold line). Mixing ratios of HCFCs are calculated from a combination of AFEAS (2001) and UNEP (2002) emissions with updated release functions for HCFC-142b from foams (black lines; see Section 1.3), and, for comparison, with the older release function for HCFC-142b from foams (dashed blue line, HCFC-142b panel only).

SOURCE GASES

Within these rather large uncertainties there is broad consistency between calculated and observed mixing ratios for both halons.

1.6.1.6 REGIONAL EMISSIONS

Initially using a simple long-range transport model (Simmonds et al., 1996) and more recently a Lagrangian dispersion model (Ryall et al., 2000), the European emission source strengths required to support the AGAGE observations of pollution episodes at Mace Head, Ireland, have been determined (see Table 1-11). Simmonds et al. (1996) compared the pre-1995 estimates with industry-derived emission estimates for Europe. They showed agreement of the values within a factor of 2 and, in particular, roughly similar declines in the emissions from 1987 to 1994. These studies demonstrated the almost complete phaseout of European emissions of methyl chloroform and CFC-113. Although the releases of CFC-11 and -12 have dramatically declined, by more than a factor of 10, European emissions of these gases are still continuing at detectable and non-negligible levels. The contributions of source regions to Mace Head fall off rapidly to the east and south, with contributions falling by more than 3 orders of magnitude toward the eastern Mediterranean, which is a result of both fewer transport events to Mace Head and greater dilution during transport to Mace Head (Ryall et al., 2000).

1.6.2 Are Atmospheric Measurements Consistent with Compliance with the Fully Amended Montreal Protocol?

Atmospheric measurements can provide an indirect and independent assessment of production and consumption data reported to UNEP. This assessment can then be considered in light of the magnitude of known production reported to UNEP and limits to production and consumption outlined in the Montreal Protocol. Significant uncertainties in this approach arise from uncertainties in measurements and trace gas lifetimes, in model calculations of mixing ratios and emissions, and in the release functions that relate emissions to industry production data.

Global measurements can provide estimates of global emissions (Figures 1-14 and 1-16) and hence an indication of the accuracy of global production and consumption data, but this analysis addresses compliance only for ODSs that are restricted worldwide. Through 2001, limits to production and consumption of ODSs in both developed and developing countries applied only to CFCs. By 2005, global limits to production and consumption by Parties to the Protocol will apply also to halons, methyl chloroform, carbon tetrachloride, and methyl bromide.

Global production of ODSs declined dramatically during the 1990s because of limits set by the Protocol on production in developed (non-Article 5(1)) countries where most ODSs had occurred. In the data reported to UNEP, production in non-Article 5(1) countries was below the allowable limits throughout the 1990s (Figure 1-18).

As mentioned above, global limits apply only to CFC production and consumption at the present time; reported global production in 1999 was less than the allowed consumption during that year by about 20×10^3 ODP-tons. Measurements of all three major CFCs suggest 5-10% higher mixing ratios than expected based on reported global production in 1999 (Figure 1-13). These elevated mixing ratios do not necessarily imply additional unreported production of these gases in 1999; for CFC-11 and -12, the mismatch is present throughout the entire measurement period and unaccounted-for emissions in recent years cannot explain this discrepancy. In fact, observed and calculated mixing ratios for CFC-12 have been converging during the 1990s, indicating that emissions estimated by industry since 1995 may be overestimates by an average of about 30×10^3 ODP-tons yr^{-1} (or 30 Gg; Figure 1-14), consistent with improved containment in recent years (UNEP, 1998a). For CFC-113 good consistency is observed until the beginning of the 1990s. After that a small divergence becomes apparent. This mismatch could be reconciled with about 10×10^3 ODP-tons of additional CFC-113 emission in recent years. If the small discrepancies for CFCs noted here were all attributed to errors in reported production, the measured atmospheric trends would suggest slightly less aggregate CFC production in the late 1990s than reported to UNEP. CFC production reported to UNEP in 1999 was somewhat ($\sim 20 \times 10^3$ ODP-tons) below the Montreal Protocol limit for that year (UNEP, 2002); the atmospheric measurements are not inconsistent with this assertion.

For halons, production data reported to the UNEP Ozone Secretariat for 1995-1999 are similar to the global limit that will apply beginning in 2002. If the trends indicated by the data in 1998 and 1999 persist into the future, production would be quite below the limits allowed in 2002 (Figure 1-18). Assessing the accuracy of reported production with atmospheric measurements for halons (Figure 1-17) is difficult because of the rather large uncertainties in measurement calibration, in the relation between production and emission for halons, and in the atmospheric lifetime for Halon-1211. Within these rather large uncertainties the atmospheric observations are broadly consistent with known production reported to UNEP for both Halon-1211 and Halon-1301.

Table 1-11. European emission source strengths required to support the AGAGE observations of each halocarbon and greenhouse gas at Mace Head, Ireland, over the period 1987-2000 (emissions in thousand tons per year).

Year	CFC-11	CFC-12	CFC-113	CH ₃ CCl ₃	CCl ₄	CHCl ₃	CH ₄	N ₂ O
1987	215	153	68	207	27		47 900	2 200
1988	132	98	43	115	20		22 500	1 800
1989	94	87	63	159	26		22 700	1 300
1990	67	64	63	153	12		31 500	1 800
1991	52	59	44	108	14		35 200	2 700
1992	27	32	31	88	9		31 000	1 600
1993	20	22	21	75	6		23 600	1 600
1994	25	31	20	115	5		40 900	2 400
1995	9	15	5	31	3	20	24 800	1 400
1996	8	14	4	19	4	15	27 800	1 500
1997	9	13	2	8	3	19	27 300	1 700
1998	10	13	2	2	3	20	25 800	1 600
1999	9	11	1	0	2	19	32 000	1 600
2000	6	6	1	0	1	16	20 500	1 000

	HCFC-141b	HCFC-142b	HCFC-22	HFC-134a	HFC-152a
1995	8	6	23	3	0.4
1996	9	6	20	6	0.5
1997	13	9	34	11	0.7
1998	14	8			
1999	12	8	29	13	1
2000	9	4	20	10	0.7

A simple long-range transport model (Simmonds et al., 1996) was employed for the 1987-1994 period and a Lagrangian dispersion model (Ryall et al., 2000) thereafter.

For carbon tetrachloride, difficulties have arisen in reporting appropriate data to UNEP (UNEP, 1998b). In light of this, limits to production and consumption are compared with *emissions* derived from measurements rather than consumption or production data reported to the UNEP Ozone Secretariat (Figure 1-18). For most uses, emissions of CCl₄ closely follow sales, so this approach can yield some insight. Global limits on CCl₄ production apply only after 2005, so it is not meaningful to ask if atmospheric measurements suggest compliance until after that date. Inferred emissions in 1999, however, are about 7 times greater than the limits to global production set for 2005.

For methyl chloroform, global production reported in 1999 was substantially lower than the limit for non-Article 5(1) countries. In addition, production in 1999 was already comparable with the global production limit for 2002.

For HCFCs, limits to global production apply only after 2015. Global production is below the current consumption limit for non-Article 5(1) countries (Figure 1-18).

1.7 OTHER TRACE GASES

1.7.1 Carbon Dioxide (CO₂)

Changes in climate and meteorological conditions affect the ozone layer, because ozone depletion and climate change share common physical and chemical processes. Anthropogenic carbon dioxide (CO₂) is the major contributor to the increase in radiative forcing from trace gas changes since preindustrial times. For this reason, atmospheric CO₂, the global carbon cycle, and mankind's impacts on them through such activities as fossil fuel combustion and changes in land use are addressed in considerable detail in Chapter 3 of the IPCC *Climate Change 2001* report (Prentice et al., 2001). Similarly, the 2001 IPCC *Special Report on Emissions Scenarios*, or SRES (Nakićenović et al., 2000) presents a wide range of projected emissions of CO₂ and other radiatively important trace gases over the coming century. We present here only a very brief overview of the main points, and we refer the reader to those IPCC reports for detailed discussions and references.

SOURCE GASES

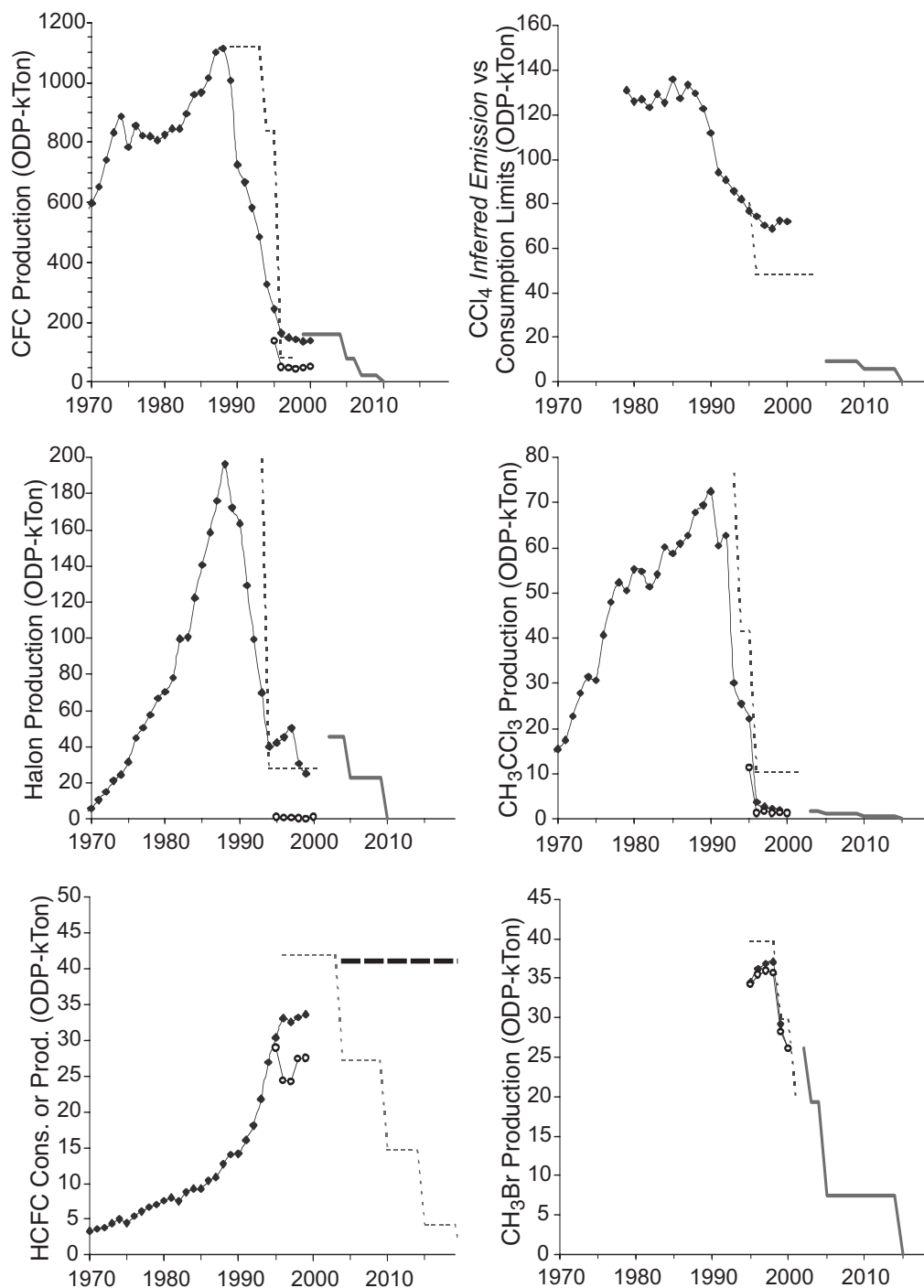


Figure 1-18. A comparison between reported global ODS production (filled solid diamonds with connecting lines: AFEAS, 2001; UNEP, 2002); ODS production reported in non-Article 5(1) countries (open circles with connecting lines: UNEP, 2002); and global ODS production limits (thick solid lines) as outlined in the fully revised and amended Montreal Protocol. Also shown are production or consumption limits for non-Article 5(1) countries in years before global limits apply (short-dashed lines). For CCl₄, global emissions inferred from measurements are shown instead of reported global production. For HCFCs, global limits to production and consumption apply only after 2015, so the non-Article 5(1) consumption limit (short-dashed lines) and production limit (thick long-dashed line) are shown instead. For some ODSs, global production in the late 1990s is higher than non-Article 5(1) limits because significant amounts were produced in countries operating under Article 5(1) during those years.

The atmospheric burden of CO₂ has increased by about 35% since 1750, to a mean abundance of ~370 parts per million (ppm) in 2000 (Table 1-12). Systematic measurements of atmospheric CO₂ since the late 1950s show a regular increase, with a mean growth rate at Earth's surface of ~1.5 ppm yr⁻¹ (0.4% yr⁻¹) over the past two decades (Figure 1-19; Tans et al., 2002). This increase is roughly half of that expected from the combustion of fossil fuels and cement production, the difference being due to CO₂ uptake by the oceans and by the terrestrial biosphere. There is considerable interannual variability in this rate of increase that is due to the effects of climate variability (e.g., El Niño events) on these uptake processes (Battle et al., 2000; Le Quere et al., 2002). This variability is also shown by measurements of total CO₂ column abundances above the Jungfraujoch (Zander et al., 2002).

CO₂ from fossil fuel burning will continue to be the dominant factor determining atmospheric CO₂ levels during the 21st century. Among the six emissions scenarios considered by the SRES (Nakićenović et al., 2000), the projected range of CO₂ abundances in 2100 was between 540 and 970 ppm, substantially higher than present-day amounts (Figure 1-19). Among the largest uncertainties in these projections are the effects of climate change on rates of deep ocean mixing, as well as on surface ocean and terrestrial biological productivity.

1.7.2 Methane (CH₄)

Atmospheric methane (CH₄) is a greenhouse gas whose radiative properties and atmospheric chemistry affect both climate and stratospheric ozone. Because methane is a sink for reactive chlorine and a source of H₂O vapor, it directly influences the availability of inorganic halogen for depleting stratospheric ozone. Furthermore, the atmospheric chemistry of methane affects hydroxyl radical (OH) abundance on global scales. This can alter degradation rates (lifetimes) of methane and ozone-depleting substances such as methyl chloroform and HCFCs. Finally, methane affects climate. Hansen and Sato (2001) estimate a change in radiative forcing for CH₄ in 2000 compared with preindustrial time, including direct and indirect effects, of $0.7 \pm 0.2 \text{ W m}^{-2}$, which is one-half the change in forcing due to CO₂ increases.

Although global concentrations of methane have varied in preindustrial times, amounts present in today's atmosphere are thought to be higher than at any time in the past 420,000 years. Whereas the globally averaged methane mole fraction in 2000 was estimated to be between 1752 ppb (updates of Dlugokencky et al., 2001) and 1784 ppb (AGAGE network, Tohoku University gravimetric scale; Cunnold et al., 2002) (Table 1-12),

measurements of CH₄ in air extracted from polar ice indicate that its abundance during the last 420,000 years of the preindustrial era varied between about 350 ppb during glacial times and about 700 ppb during interglacial periods (Petit et al., 1999). From ice-core measurements in Antarctica and Greenland, and Antarctic firn and archived air from southern midlatitudes, Etheridge et al. (1998) showed that the globally averaged methane mole fraction was relatively constant at 695 ppb from 1000 to 1800 A.D., and increased through the industrial era.

Systematic measurements of atmospheric CH₄ show that its global abundance at Earth's surface continues to increase (Figure 1-19); the average growth rate was $7.9 \pm 0.1 \text{ ppb yr}^{-1}$ from 1984 to 2000, and the rate of increase slowed from about 14 ppb yr^{-1} in the early 1980s to less than 5 ppb yr^{-1} in the late-1990s (except during 1998). The 1999-2000 global growth rate was less than 2 ppb yr^{-1} (Table 1-12). Significant interannual variability is superimposed on the long-term decrease in growth rate (Dlugokencky et al., 1998, 2001; Simpson et al., 2002; Cunnold et al., 2002). Monitoring of the vertical column abundance of CH₄ above the Jungfraujoch since the mid-1980s also confirms the continued slowing of the rate of CH₄ accumulation in the atmosphere, which was found equal to 0.72% in 1987-1988, 0.51% in 1991-1992, 0.32% in 1995-1996, and 0.14% in 1999-2000 (Zander et al., 2002).

The cause of the decrease in methane growth rate is not fully understood. Although the major sources of atmospheric methane are known, they are poorly quantified. Bottom-up assessments from individual sources of emission rates and their changes over time are not reliable enough to discern small changes in global emission rates. Changes in hydroxyl radical abundance also would affect methane growth rates, but much uncertainty remains regarding trends of this important atmospheric oxidant (see Section 1.4; Krol et al., 1998; Prinn et al., 2001). Dlugokencky et al. (1998) have suggested that the recent methane trends can be explained by an approach of the system to steady state, i.e., fairly constant emissions and lifetime in recent years. Resolution of these issues has important implications for projecting future concentrations.

IPCC (Prather and Ehhalt et al., 2001) calculated future CH₄ abundances from 2000 to 2100 based on CH₄ emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-19). By 2100, CH₄ mixing ratios range from about 1575 ppb (i.e., 10% below present-day mixing ratios; 1880 ppb in 2050) for IPCC scenario B1, which emphasized relatively small global population and resource-efficient technologies, to 3730 ppb (2560 ppb in 2050) for scenario E0 (not shown in Figure 1-19), which

SOURCE GASES

Table 1-12. Mixing ratios and growth rates for HFCs, FCs, sulfur hexafluoride, nitrous oxide, methane, carbon dioxide, and carbon monoxide.

Species	Common or Industrial Name	Mixing Ratio			Growth (1999-2000)		Laboratory (No. of sites), Method
		1996	1998	2000	ppx yr ⁻¹	% yr ⁻¹	
HFCs (ppt)							
CHF ₃	HFC-23	11.7	13.5	15.5	0.9	5.8	UEA, SH (1), flask ^a
CHF ₂ CF ₃	HFC-125		0.92	1.4	0.3	22	AGAGE (2), in situ ^a
CH ₂ FCF ₃	HFC-134a		7.9	14.6	3.5	27	AGAGE (2), in situ ^a
		3.0	7.6	13.8	3.2	26	CMDL (8), flask ^a
CH ₃ CHF ₂	HFC-152a		1.3	1.7	0.2	12	AGAGE (2), in situ ^a
FCs (ppt)							
CF ₄	FC-14		76.0				MPAE, NH (1), flask ^a
CF ₃ CF ₃	FC-116	2.2					UEA, SH (1), flask ^a
c-C ₄ F ₈	FC-318	1.0					UEA, SH (1), flask ^a
SF ₆ (ppt)	Sulfur hexafluoride	3.5	3.9				UH, SH (1), flask ^b
		3.6					UEA, SH (1), flask ^a
		3.8	4.3	4.7	0.21	4.6	CMDL (7), flask ^b
			4.2	4.6	0.18	4.0	CMDL (5), in situ ^b
N ₂ O (ppb)	Nitrous oxide	312.7	314.1	316.0	1.0	0.32	AGAGE (4-5), in situ ^b
		312.0	313.8	315.7	0.85	0.27	CSIRO, SH (1), flask ^b
		312.2	313.2	315.2	1.0	0.32	CMDL (7), flask ^b
		312.7	314.3	317.2	1.1	0.35	CMDL (5), in situ ^b
CH ₄ (ppb)	Methane	1761.7	1774.7	1784.4	1.3	0.07	AGAGE (4-5), in situ ^c
		1681.3	1695.8	1707.6	1.7	0.10	CSIRO, SH (1), flask ^c
		1729.7	1743.2	1751.6	0.7	0.04	CMDL (42), flask ^c
		1751.2	1764.7	1771.1	2.1	0.12	UCI (~40), flask ^c
CO ₂ (ppm)	Carbon dioxide	361.6	365.4	368.6	1.1	0.31	CMDL (44), flask ^{d,*}
CO (ppb)	Carbon monoxide	112.1	144.5	112.2	-11.6	-9.9	AGAGE, NH (2-3), in situ ^c
		110.8	132.1	106.0	-13.5	-12.3	CMDL, NH (24), flask ^c
		52.3	56.4	51.0	-2.3	-4.4	AGAGE, SH (2), in situ ^c
		50.8	56.2	50.6	-2.2	-4.2	CSIRO, SH (1), flask ^c
		54.3	60.3	55.9	-1.8	-3.2	CMDL, SH (19), flask ^c

Global mixing ratios (dry air mole fractions) and growth rates are at Earth's surface unless otherwise specified as being from Northern Hemisphere (NH) or Southern Hemisphere (SH) sites only. Laboratories: Advanced Global Atmospheric Gases Experiment (AGAGE); Global Atmospheric Sampling Laboratory, Commonwealth Scientific and Industrial Research Organization (CSIRO), sampling at 41°S; Max-Planck-Institut für Aeronomie (MPAE), sampling at Lindau, Germany; Climate Monitoring and Diagnostics Laboratory (CMDL), National Oceanic and Atmospheric Administration (NOAA); University of East Anglia (UEA), sampling at 41°S; University of Heidelberg (UH), sampling at 41°S; University of California at Irvine (UCI), quarterly sampling at about 40 sites.

Data sources: AGAGE: Prinn et al. (2000); Cunnold et al. (2002); ftp://cdiac.esd.ornl.gov/pub/ale_gage_Agag. CMDL: Dlugokencky et al. (2001); Montzka et al. (1996b); Novelli et al. (1998); Tans et al. (2002); www.cmdl.noaa.gov. CSIRO: Langenfelds et al. (2002). MPAE: Harnisch et al. (1999). UEA: Oram et al. (1998); Oram (1999). UCI: Simpson et al. (2002). UH: Maiss and Brenninkmeijer (1998).

* Many other groups measure CO₂; only results from the most extensive network are included here (see Prentice et al., 2001).

^a Measurements by gas chromatography-mass spectrometric detection.

^b Measurements by gas chromatography-electron capture detection.

^c Measurements by gas chromatography-flame ionization detection.

^d Measurements by nondispersive infrared detection.

^e Measurements by gas chromatography-mercuric oxide reduction detection.

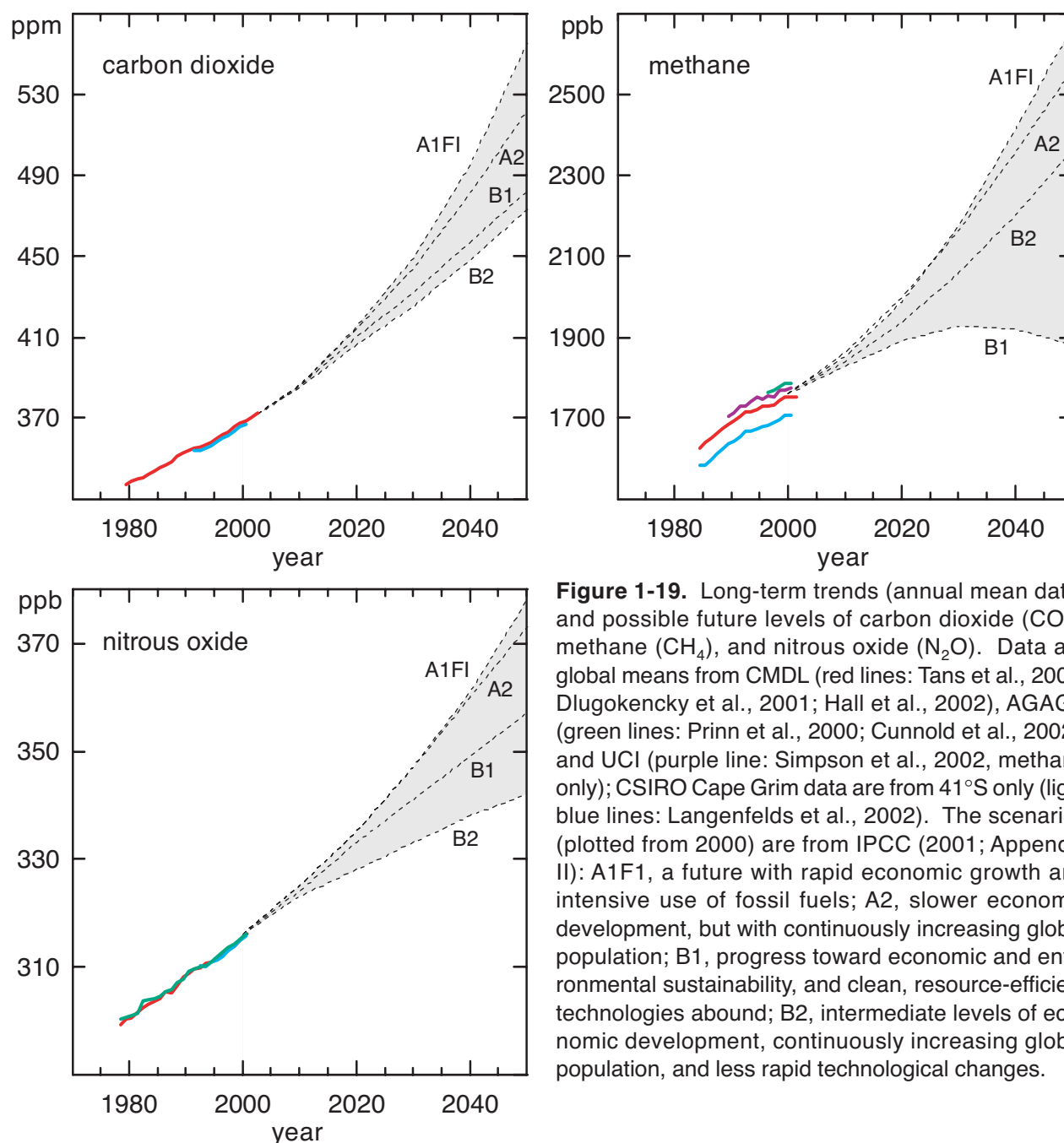


Figure 1-19. Long-term trends (annual mean data) and possible future levels of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Data are global means from CMDL (red lines: Tans et al., 2001; Dlugokencky et al., 2001; Hall et al., 2002), AGAGE (green lines: Prinn et al., 2000; Cunnold et al., 2002), and UCI (purple line: Simpson et al., 2002, methane only); CSIRO Cape Grim data are from 41°S only (light blue lines: Langenfelds et al., 2002). The scenarios (plotted from 2000) are from IPCC (2001; Appendix II): A1F1, a future with rapid economic growth and intensive use of fossil fuels; A2, slower economic development, but with continuously increasing global population; B1, progress toward economic and environmental sustainability, and clean, resource-efficient technologies abound; B2, intermediate levels of economic development, continuously increasing global population, and less rapid technological changes.

included rapid population growth through the century and regional solutions to environmental problems. Though the range of values is large, the scenarios provide a range of potential future atmospheric composition for given amounts of CH_4 emissions.

1.7.3 Nitrous Oxide (N_2O)

Nitrous oxide (N_2O) is the major source of ozone-depleting nitrogen oxides (NO_x) in the stratosphere. These

reaction products of N_2O photochemistry make a significant contribution to both anthropogenic and natural ozone depletion. New rate constants for some stratospheric reactions indicate an enhanced role for NO_x in ozone loss (Portmann et al., 1999). Consequently, it is possible that enhanced future N_2O emissions could noticeably delay stratospheric ozone recovery (Randeniya et al., 2002).

The atmospheric burden of N_2O has been increasing steadily for decades (Figure 1-19). NOAA/CMDL and AGAGE data show that the globally averaged

SOURCE GASES

mixing ratio in January 2001 was 315–317 ppb (Prinn et al., 2000; Hall et al., 2002). Its rate of increase has averaged ~ 0.75 ppb yr^{-1} , with some interannual variability since the late 1970s. Its lifetime is currently estimated at 120 (97–137) years, although its “perturbation” lifetime is 4–6% shorter (Prather, 1998).

Most updates in our understanding of the sources and sinks of atmospheric N_2O since the 1998 Assessment (WMO, 1999) were assessed in Chapter 4 of the Third Assessment Report (TAR) for the IPCC (Prather and Ehhlalt et al., 2001). A number of studies discussed in that report show a preindustrial tropospheric abundance of N_2O of ~ 270 ppb, suggesting an increase in the atmospheric burden of about 17% since then. Little has changed in our overall understanding of the atmospheric budget of this gas since the 1998 Assessment. Known sources of 15–18 Tg yr^{-1} , mainly from natural soils, agricultural activities, biomass burning, and the ocean, can be accounted for by known sinks and observed increases. However, the uncertainties in the source estimates are large. The suggested need for a large stratospheric or exotic source of N_2O to account for the isotopic composition of the troposphere has been found by a number of studies not to be necessary (Prather and Ehhlalt et al., 2001).

1.7.4 Carbon Monoxide (CO)

In the troposphere, carbon monoxide (CO) is closely linked to the cycles of ozone and methane, and plays an important role in the control of the OH radical concentration. Hydroxyl radical, in turn, controls the lifetime of many reduced compounds (e.g., CH_4 , HCFCs, HFCs, and CH_3CCl_3). Therefore, predicting future concentrations of these ozone-relevant and radiatively important gases depends partly on how well the CO budget and its potential for change is understood. CO could be assigned a GWP because of its effect on the lifetime of other greenhouse gases (e.g., Prather, 1996; Daniel and Solomon, 1998; Prather and Ehhlalt et al., 2001). In this regard, emitting 100 Tg of CO is equivalent to emitting 5 Tg of CH_4 (Wild and Prather, 2000; Derwent et al., 2001). Most budgets evaluated by Prather and Ehhlalt et al. (2001) estimate a current annual source of CO to the troposphere in the range of 2000 to 3000 Tg.

1.7.4.1 ATMOSPHERIC GLOBAL DISTRIBUTION AND TRENDS

Modern direct measurements indicate that trends in atmospheric CO were positive until the mid- to late-1980s at least in the Northern Hemisphere, but since then the mean trend has been negative (Zander et al., 2000; Khalil and Rasmussen, 1994; Mahieu et al., 1997; Novelli

et al., 1998), e.g., reaching a decrease of -0.6% yr^{-1} above the Jungfraujoch in 1999–2000 (Zander et al., 2002). CO exhibits both short- and long-term changes on regional and global scales and, after an overall increase over several decades, it appears that CO has declined in many parts of the world (Table 1–12; see also Kurylo and Rodríguez et al., 1999). Causes of these recent changes have not been identified with certainty, but decreases in tropical biomass burning (Yung et al., 1999), decreases in Northern Hemispheric urban emissions (Bradley et al., 1999), and increases in OH concentrations due to stratospheric ozone depletion (Krol et al., 1998; Law, 1999) may have played a role (although one study suggests *decreases* in OH in the 1990s (Prinn et al., 2000)). Short-term increases in CO column abundances and surface mixing ratios were observed during the strong El Niño of 1998, probably as a result of enhanced burning then (Wotawa et al., 2001; Rinsland et al., 2000). No long-term change has been detected in CO mixing ratios at Cape Point, South Africa, during 1978–1998 (Scheel et al., 1995).

1.7.4.2 CO SOURCES AND SINKS

CO has significant atmospheric photochemical sources from the oxidation of CH_4 and non-methane hydrocarbons, as well as emissions from fuel combustion and biomass burning. Considerable uncertainties exist in the CO budget. Recent evaluations of global sources and budget suggest that the principal sources are biomass burning, fossil fuel combustion, agricultural waste burning, biofuel combustion, and industrial processes. The global surface source is estimated at 1550 Tg yr^{-1} (Prather and Ehhlalt et al., 2001).

The most important sink of CO is reaction with OH. Uncertainties in OH distributions and the reaction rate constant of $\text{CO} + \text{OH}$ result in a large range of estimates for this sink. McCabe et al. (2001) have studied the kinetics of $\text{CO} + \text{OH}$ for atmospheric conditions in the laboratory, decreasing the uncertainty in the rate coefficient significantly. Atmospheric CO is consumed by soils; recent studies (Potter et al., 1996; Sanhueza et al., 1998; King, 2000) suggest global consumption by soils of 100–300 Tg yr^{-1} , lower than the 190–580 Tg yr^{-1} proposed by Conrad and Seiler (1985), which has been widely used in previous Assessment budgets.

1.7.4.3 ISOTOPIC DATA

Isotopic studies of atmospheric CO (Brenninkmeijer et al., 1999) provide an absolute technique by which atmospheric mixing ratios of CO are determined (Brenninkmeijer et al., 2001). Confirmation that CO undergoes mass-independent fractionation (Röckmann et

al., 2001) indicates that previous ^{13}C data may need a small, but significant, correction (Röckmann and Brenninkmeijer, 1998). Additional work is needed in defining fractionation of some CO production processes, notably, CH_4 and non- CH_4 hydrocarbon oxidation, and its combustion sources.

1.7.5 Carbonyl Sulfide (COS)

Carbonyl sulfide (COS) is the most abundant sulfur-containing trace gas in the atmosphere. Because it has a lifetime that is long relative to atmospheric mixing times (>1 year), much of the COS emitted or produced in the troposphere reaches the stratosphere. Some fraction of stratospheric COS becomes photolyzed and contributes sulfur to the stratospheric aerosol layer. This aerosol provides surfaces that enhance the concentration of ozone-depleting radicals; it also plays an important role in the radiative balance of the atmosphere. Earlier work had suggested that COS might be the main source of nonvolcanic sulfate to the stratosphere (Crutzen, 1976). More recent work, however, based on revised reaction rates, cross sections, and photolytic quantum yields, has suggested that COS may account for a smaller fraction of the sulfate present in the stratospheric Junge layer than previously thought (Chin and Davis, 1995; Kjellstrom, 1998; see also Chapter 2).

A combination of results from total column abundances (Rinsland et al., 2002a; Mahieu et al., 1997; Griffith et al., 1998), periodic surface measurements (Bandy et al., 1992; Thornton et al., 1996), and an analysis of firn air in both hemispheres (Sturges et al., 2001b) suggests that the atmospheric burden of COS was fairly constant from the mid-1900s to the early 1990s. In the 1990s updated results suggest a slight decrease (about $1\% \text{ yr}^{-1}$ or smaller) (Mahieu et al., 1997; Sturges et al., 2001b); Rinsland et al. (2002a) have inferred a mean tropospheric decrease from 1978 to 2002 at 32°N equal to $0.25 \pm 0.04\% \text{ yr}^{-1}$. Firn air results suggest that the recent decreases may have been more pronounced in the Northern Hemisphere than in the Southern Hemisphere (Sturges et al., 2001b); they also point to the possibility of lower COS mixing ratios in the oldest air sampled in Antarctica. Results from an Antarctic ice core suggest that preindustrial mixing ratios of COS were 25% lower than observed in the modern atmosphere (Aydin et al., 2002).

Although numerous sources and sinks of COS have been identified, much uncertainty remains regarding the magnitude of these fluxes. Until recently, best estimates of total sources outweighed sinks for COS by $\sim 30\%$, despite evidence to suggest fairly constant mixing ratios over time in the atmosphere. More recent work by Kuhn et al. (1999), Kesselmeier et al. (1999), and Simmons et

al. (1999) confirmed the earlier work of Castro and Galloway (1991) and suggests a much enhanced role for soils in the removal of COS from the atmosphere. With this new understanding of soil losses and some revision in the net influence of open and coastal oceans, Watts (2000) suggested that the magnitude of known sinks is similar to known sources despite the large uncertainties. The magnitude of sinks or sources and a mean atmospheric concentration of about 500 ppt imply a COS global lifetime of about 4 years (Chin and Davis, 1995; Watts, 2000).

1.7.6 Hydrofluorocarbons (HFCs)

The most abundant hydrofluorocarbons (HFCs) in the present-day atmosphere are HFC-23 (CHF_3) and HFC-134a (CH_2FCF_3). Since the previous Assessment, the tropospheric abundance of each has continued to increase. In addition, three more HFCs have been identified in the background atmosphere: HFC-125 (CHF_2CF_3), HFC-143a (CH_3CF_3), and HFC-152a (CH_3CHF_2). Their atmospheric mixing ratios are relatively low but are increasing at significant rates.

1.7.6.1 HFC-134a

HFC-134a (CH_2FCF_3) is used extensively as a refrigerant and air-conditioning agent, and to a lesser degree as a foam-blowing agent. Updated measurements show that the global mean surface mixing ratio of HFC-134a had risen to just under 15 ppt by mid-2000 (Table 1-12; Figure 1-20; Simmonds et al., 1998b; Montzka et al., 1999; Prinn et al., 2000; Sturrock et al., 2001). The current growth rate of about 3.0 ppt yr^{-1} has approximately doubled since 1996. Calibration differences between CMDL and AGAGE are less than 5%.

IPCC (Prather and Ehhalt et al., 2001) calculated future HFC-134a abundances from 2000 to 2100 based on HFC-134a emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-20). By 2100, HCFC-134a mixing ratios range from about 380 ppt (290 ppt in 2050) in IPCC scenario B1 to 960 ppt (535 ppt in 2050) in IPCC scenario A1.

1.7.6.2 HFC-23

Although HFC-23 (CHF_3) has found minor uses in refrigeration, plasma etching, and as a fire extinguishant, its major atmospheric source is as a byproduct from the manufacture of HCFC-22 (Oram et al., 1998). In addition, Engen et al. (1998) reported elevated levels of HFC-23 when sampling the emissions from an aluminum production plant.

SOURCE GASES

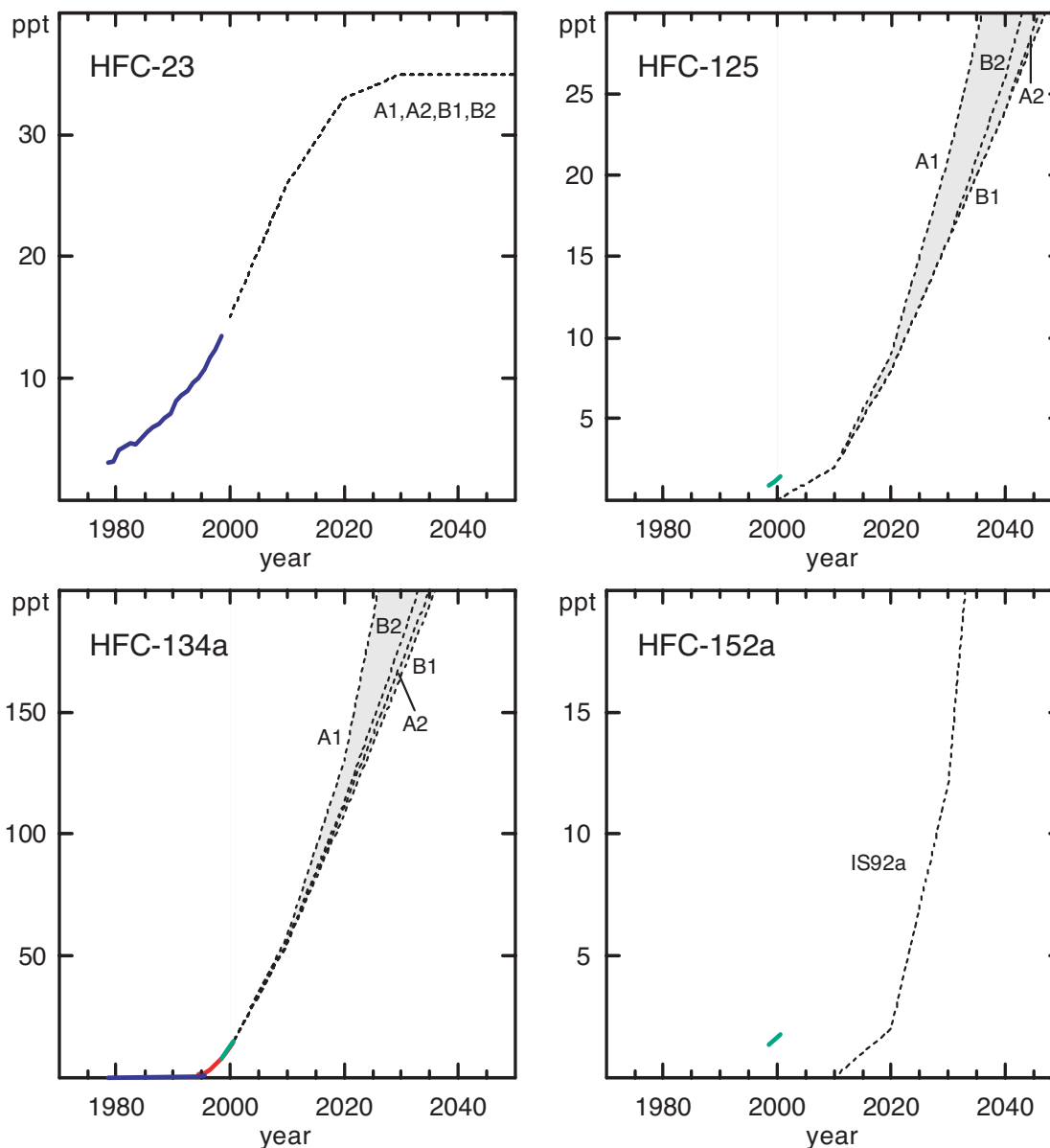


Figure 1-20. Long-term trends (annual mean data) and possible future levels of HFCs. Data are global means from CMDL (red line: Montzka et al., 1996b, HFC-134a only), and AGAGE (green lines: Prinn et al., 2000; Sturrock et al., 2001). Cape Grim results are for 41°S only (blue lines: Oram et al., 1996; 1998). The scenarios (plotted after 2000) are from IPCC (2001; Appendix II).

The only available time series of tropospheric HFC-23 measurements are those of Oram et al. (1998). The mixing ratio of HFC-23 at Cape Grim has risen from 2 ppt in 1978 to 15.5 ppt in 2000 (Table 1-12; Figure 1-20). Despite the emission reductions that have occurred in developed countries as a result of improved HCFC-22 process control and capture of the HFC-23 byproduct, the growth rate of HFC-23 at Cape Grim has increased in recent years from 0.55 ppt yr⁻¹ in 1995 to 0.9 ppt yr⁻¹ (6% yr⁻¹) in late 1999. This may have resulted from increased

HCFC-22 production in developing countries recently (McFarland and van Gerwen, 2000).

The presence of HFC-23 in the atmosphere has been confirmed by Engen et al. (1998) and Culbertson et al. (2000). In the latter study, a mean mixing ratio of 18 ± 2 ppt was measured in air samples collected at a rural, continental site in the United States in March-April 2000.

IPCC (Prather and Ehhalt et al., 2001) calculated future HFC-23 abundances from 2000 to 2100 based on HFC-23 emission rates in the six illustrative scenarios in

the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-20). By 2100, HCFC-23 mixing ratios are about 32-34 ppt (35 ppt in 2050) in all IPCC scenarios.

1.7.6.3 HFC-125, HFC-143a, AND HFC-152a

The major use of HFCs -125 (CHF_2CF_3) and -143a (CH_3CF_3) is as refrigerants, whereas HFC-152a (CH_3CHF_2) is used primarily as a foam-blowing agent and aerosol propellant. The current tropospheric background abundance of these HFCs is relatively low, in the range of 1-3 ppt (Table 1-12; Prinn et al., 2000; Culbertson et al., 2000; Sturrock et al., 2001). Southern Hemispheric growth rates in mid-2000, based on measurements at Cape Grim, were about 0.2 ppt yr⁻¹ and 0.1 ppt yr⁻¹ for HFC-125 and HFC-152a, respectively (Sturrock et al., 2001).

IPCC (Prather and Ehhalt et al., 2001) calculated future HFC-125, -143a, and -152a abundances from 2000 to 2100 based on respective emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-20; HFC-143a not shown). By 2100, mixing ratios are about 60-140 ppt for HFC-125 (30-60 ppt in 2050), 90-200 ppt for HFC-143a (40-70 ppt in 2050), and 80 ppt for HFC-152a, (55 ppt in 2050) for all these IPCC scenarios.

1.7.7 Fluorocarbons (FCs), SF₆, and SF₅CF₃

Due to a combination of long atmospheric lifetimes (>1000 years) and strong infrared absorption cross sections, fluorocarbons (FCs) are among the most potent greenhouse gases known, having GWPs about 4 orders of magnitude higher than that of CO₂ (see Table 1-6). These gases are useful tracers of atmospheric transport in both the troposphere and the stratosphere. The only important sinks for FCs and sulfur hexafluoride (SF₆) are photolysis or ion reactions in the mesosphere.

1.7.7.1 CF₄ AND C₂F₆

The most abundant FCs in the present-day atmosphere are CF₄ (FC-14) and C₂F₆ (FC-116). Approximately 50% of the current atmospheric burden of CF₄ (~80 ppt) was present in preindustrial times, implying a natural, probably geochemical, source (Harnisch et al., 1996a; Harnisch and Eisenhauer, 1998). The predominant source of both compounds in recent times is believed to be the aluminum industry. Other minor sources include the semiconductor industry and from the production of CCIF₂CF₃ (CFC-115), where C₂F₆ can be formed as a byproduct due to overfluorination.

The current background atmospheric mixing ratio of CF₄ is about 80 ppt (Table 1-12; Harnisch et al., 1999;

Culbertson et al., 2000). The measurements of Harnisch et al. (1999) show that the growth rate of CF₄ has slowed in recent years from 1.07 ± 0.14 ppt yr⁻¹ over the period 1978-1990 to 0.72 ± 0.11 ppt yr⁻¹ between 1992 and 1998 (Figure 1-21). These growth rates correspond to global emission rates of $(16.3 \pm 2.0) \times 10^6$ kg yr⁻¹ and $(11.0 \pm 1.7) \times 10^6$ kg yr⁻¹ and, allowing for estimated emissions of CF₄ from the semiconductor industry, imply a reduction of CF₄ emissions from aluminum production of about 40%. This observation concurs with an aluminum industry estimate of a 30% decrease in FC emissions between 1990 and 1993 (Marks, 2000).

The current background atmospheric concentration of C₂F₆ is about 3 ppt (Harnisch et al., 1996b; Oram, 1999; Culbertson et al., 2000). Analysis of the Cape Grim air archive shows that the mixing ratio of C₂F₆ in the Southern Hemisphere has increased from 0.7 ppt in 1978 to 2.2 ppt in late 1995 (Figure 1-21; Oram, 1999). The growth rate over this period was approximately constant at 0.08 ppt yr⁻¹, which contrasts strongly with the behavior of CF₄ whose growth rate has declined since the early 1990s. Assuming emissions of C₂F₆ from aluminum production have fallen along with those of CF₄, an additional, increasing source of C₂F₆ is required to maintain a constant emission rate.

IPCC (Prather and Ehhalt et al., 2001) calculated future CF₄ and C₂F₆ abundances from 2000 to 2100 based on respective emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-21). Mixing ratios projected for 2100 in the range of IPCC scenarios are 210-400 ppt for CF₄ (135-185 ppt in 2050) and 10-25 ppt for C₂F₆ (7-10 ppt in 2050).

1.7.7.2 c-C₄F₈ AND C₃F₈

Since the previous Assessment (WMO, 1999), two other FCs have been detected in the background atmosphere, perfluorocyclobutane (c-C₄F₈; FC-318) and perfluoropropane (C₃F₈; FC-218). The origin of c-C₄F₈ is uncertain, although it is used in small amounts by the semiconductor industry (cleaning and plasma etching), and in very small amounts in some refrigeration blends (Harnisch, 2000). C₃F₈ is used for plasma etching and a small amount ($\sim 0.1 \times 10^6$ kg yr⁻¹) is emitted during aluminum production (Harnisch, 1997, 2000).

The abundance of c-C₄F₈ at Cape Grim increased from 0.6 ppt in 1978 to about 1 ppt by late 1995 (Table 1-12; Figure 1-21; Oram, 1999). The 1995 growth rate of 0.012 ppt yr⁻¹ was about 80% lower than the maximum of 0.057 ppt yr⁻¹ measured over the period 1983-1989. In this way, its behavior is similar to that of CF₄, whose growth rate has slowed in response to reduced emissions

SOURCE GASES

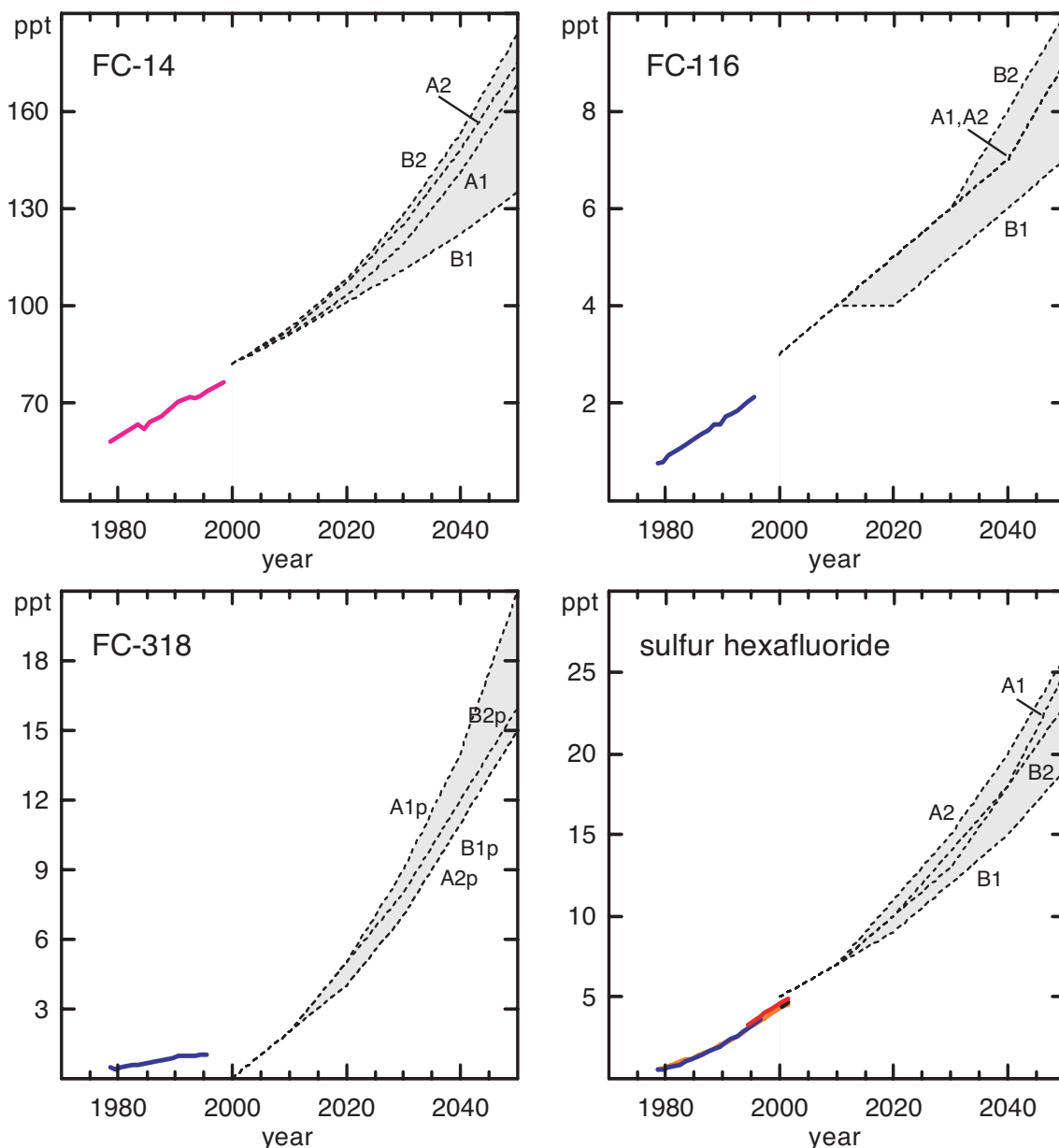


Figure 1-21. Long-term trends (annual mean data) and possible future levels of fluorocarbons and sulfur hexafluoride. Data are from the Northern Hemisphere (pink line: MPAE, Harnisch et al., 1999, FC-14 only), means from Cape Grim, Tasmania (blue lines: UEA, Oram, 1999; black line: SIO, Vollmer and Weiss, 2002, SF₆ only; orange line: UH, Maiss and Brenninkmeijer, 1998, SF₆ only), and global surface means (red line: CMDL, Hall et al., 2002, SF₆ only). The scenarios (plotted from 2000) are from IPCC (2001; Appendix II).

from the aluminum industry. However, $c\text{-C}_4\text{F}_8$ has not been reported in studies of the composition of emissions from aluminum plants, so the cause of the observed decrease in growth rate remains unclear. Measurements of $c\text{-C}_4\text{F}_8$ have also been reported in stratospheric air. Sturges et al. (2000a) reported a Northern Hemispheric, upper tropospheric mixing ratio of about 1.0 ppt for 1994,

and Travnicek (1998) reported a 1997 mixing ratio of 0.7 ppt and calculated an annual global emissions rate of about $0.7 \times 10^6 \text{ kg yr}^{-1}$ over the period 1978-1997.

In recent years the first atmospheric measurements of C_3F_8 have also been reported. From a stratospheric profile collected in 1997, Sturges et al. (2000a) estimated an upper tropospheric mixing ratio of approximately 0.3

ppt. The full profile between 11 and 32 km implies a long atmospheric lifetime for this gas and recent tropospheric increases. In addition, Culbertson et al. (2000) measured a similar mean C_3F_8 mixing ratio of 0.26 ± 0.03 ppt in samples collected at a rural, continental U.S. site in March-April 2000.

1.7.7.3 SULFUR HEXAFLUORIDE (SF_6)

Sulfur hexafluoride (SF_6) is used mostly as an insulating fluid in step-down transformers and as a cover gas in magnesium production. Atmospheric SF_6 continues to rise (Table 1-12, Figure 1-21), with current (2000) global surface means estimated at 4.7 ppt (Hall et al., 2002) and global growth rates of 4-5% yr^{-1} . Vertical column abundances of SF_6 monitored above the Jungfraujoch increased by an average of 3.49×10^{12} molec cm^{-2} yr^{-1} from 1987 to 2001, which corresponds to 12.9% yr^{-1} during 1987-1988 and 5.1% yr^{-1} during 1999-2000 (Zander et al., 2002). IPCC (Prather and Ehhalt et al., 2001) calculated future SF_6 abundances from 2000 to 2100 based on respective emission rates in the six illustrative scenarios in the IPCC *Special Report on Emissions Scenarios* (Nakićenović et al., 2000; Figure 1-21). By 2100 mixing ratios are estimated to be about 55-65 ppt (20-25 ppt in 2050) in all these scenarios.

1.7.7.4 TRIFLUOROMETHYLSULFURPENTAFLUORIDE (SF_5CF_3)

Another long-lived greenhouse gas has recently been found in the atmosphere (Sturges et al., 2000b). Trifluoromethylsulfurpentafluoride (SF_5CF_3) has an atmospheric lifetime of about 800 years (Table 1-3; Takahashi et al., 2002) and, on a per-molecule basis, has the largest radiative forcing of any gas found in the atmosphere to date. Measurements of SF_5CF_3 in air trapped in polar snow (firn) show its abundance has risen from near zero in the 1960s to about 0.12 ppt in 1999, and is currently growing at 0.008 ppt yr^{-1} . The only known source of SF_5CF_3 is as a byproduct of the manufacture of certain fluorinated chemicals (Santoro, 2000).

1.8 HALOGENATED SOURCE GASES IN THE FUTURE

Scenarios were developed to describe the range of future mixing ratios of ODSs given our current understanding of sources, sinks, banks or reservoirs of unemitted material and emission rates from these, and potential future production. The baseline scenario Ab was designed as a best estimate of future trace gas mixing ratios based upon current trends in production and con-

sumption, and limits to these as defined by the fully amended and adjusted Montreal Protocol. Scenario Am was an attempt to define atmospheric mixing ratios in a world where future production and consumption rates were at the maximum allowed by the fully amended and adjusted Montreal Protocol. It must be kept in mind that for some gases, notably the HCFCs, this concept is ill defined because upper limits to global production apply only after 2016. The Pc scenario was constructed to show how continued constant production of ODSs at 1999 rates into the future, in clear violation of the Montreal Protocol, would affect future EESC. Hypothetical scenarios were also developed in which emissions of all ODSs (E0) or a selected class of ODSs ceased in 2003. These hypothetical cases were constructed to show how future emissions of different compound classes affect future EESC and to define a lower limit to future EESC. Additional, potentially achievable cases were also constructed to show the effects of zero production from 2003 onward for groups of ODSs and all ODSs together (P0). More details regarding the assumptions made in developing these scenarios and cases are included in Tables 1-13 and 1-14.

1.8.1 Development of the Baseline Scenario Ab

To create the baseline scenario Ab, a set of emissions was derived for each halocarbon for 1950-2000 so that mixing ratios calculated in a simple box model would match as closely as possible the observed mixing ratios (Tables 1-15 and 1-16; Figure 1-22). Where possible, emissions were based on historical industry production data and emission functions as described in Section 1.3 (e.g., McCulloch and Midgley, 2001; McCulloch et al., 2001; AFEAS, 2001; UNEP, 2002). Some discrepancies exist, however, between measured and calculated mixing ratios (see Section 1.6), and in order to provide a history without discontinuities, scale factors were sometimes applied to these emissions to better match the observed atmospheric mole fractions (Tables 1-15 and 1-16).

Future emissions were derived for 2000-2100 based upon (1) current trends in halocarbon production and emission, (2) the size of unemitted reserves (adjusted to reflect scale factors applied to past emissions), (3) relationships between production and emission as a function of application, and between reserves and emission, and (4) considering future production restrictions outlined in the latest Amendments (Beijing) of the Montreal Protocol. The Beijing Amendments (1999) to the Montreal Protocol included limits on the production of HCFCs in both developed (freeze in 2004) and developing (freeze in 2016) countries, stricter limits on the production of ODSs by

SOURCE GASES

developed countries for use in developing countries, as well as a global phaseout of a new species, bromochloromethane (CH_2BrCl), in 2002.

For methyl chloride and methyl bromide, scenarios were developed for past years based upon available firm air and real-time measurements (Khalil et al., 1993; Khalil and Rasmussen, 1999; Butler et al., 1999; Sturges et al., 2001a). Mixing ratios were set for the late 1990s at 9.5 ppt CH_3Br and 550 ppt for CH_3Cl based upon discussions in Kurylo and Rodríguez et al. (1999). Future mixing ratios in scenarios were calculated assuming that restrictions on production resulted in emission reductions in the same year (Table 1-13). Future emissions of CH_3Cl were kept constant to sustain a mixing ratio of 550 ppt for all scenarios.

1.8.2 Projecting Future Halocarbon Mixing Ratios

Future mixing ratios of a trace gas depend upon future emission rates and the rate at which the gas is removed from the atmosphere. Atmospheric removal rates are determined by the chemical and physical characteristics of a trace gas, and cannot be purposefully altered by humans. In the absence of emissions, future mixing ratios can be calculated on the basis of trace gas lifetimes. Because lifetimes of ODSs range from less than 1 year to more than 100 years, however, the expected rate of decline in the absence of emissions varies substantially for different halocarbons.

Emissions of most ODSs, however, are not yet insignificant. Substantial amounts of some ODSs exist in current applications and will be released to the atmosphere in future years. Furthermore, production of some halocarbons continues under the allowances prescribed by the Montreal Protocol. Predicting future mixing ratios of ODSs requires a good understanding of emission rates of ODSs from present-day applications, the size of produced but unemitted reserves (banks), the magnitude of future production, and halocarbon atmospheric lifetimes. Managing or controlling future mixing ratios is possible only through controlling current rates of emission and future production.

In what follows, some salient points regarding future halocarbon mixing ratios and the development of scenarios are discussed.

1.8.2.1 CFCs

Reserves of unemitted but produced CFCs vary substantially for different individual CFCs because they were used in different applications. CFC-11 was used extensively in foams from which only a small portion of the CFC becomes released each year. As a result a very

large reservoir of CFC-11 exists in foams today, and future emissions will depend mostly upon the rate at which CFC-11 escapes from foams together with the amount of future production. Emission models suggest that the reservoir of unemitted CFC-12 and -113 is substantially smaller, owing to use in applications where release is more rapid (AFEAS, 2001). For these two gases, future emissions will be more closely tied to the magnitude of future production. Differences in the calculated future scenarios reflect the size of reserves for each gas relative to the potential magnitude of future production (Figure 1-1).

1.8.2.2 METHYL CHLOROFORM

Reserves of produced but unemitted methyl chloroform (CH_3CCl_3) are thought to be small owing to past use predominantly as a solvent and cleaning agent. Accordingly, future emissions should be closely tied to future production. Known production in recent years has been about 20 Gg yr^{-1} (McCulloch and Midgley, 2001), or quite small compared with earlier years, and should decrease as the allowances for production and consumption in developing countries diminish through 2015. The exponential decline in mixing ratios in recent years will continue as long as methyl chloroform emissions remain small relative to its atmospheric burden. Future production within limits allowed by the Protocol could slow this decline (Figure 1-4). Furthermore, if some nonindustrial emissions exist and persist in the future, perhaps as a result of biomass burning (Rudolph et al., 2000), the exponential rate of decay would slow until some non-zero steady-state mixing ratio was reached. Current estimates of non-industrial emission magnitudes suggest that this steady-state mixing ratio would be <2 ppt (see Section 1.3).

1.8.2.3 CARBON TETRACHLORIDE

Significant mismatches between observed and calculated mixing ratios of carbon tetrachloride (CCl_4) suggest potential difficulty in reliably estimating future amounts of this important ODS (see Section 1.6). Improvements in this area will come only after certain questions are addressed. These questions include the following: (1) How much carbon tetrachloride is emitted from processes not related to the production of CFCs, and how have these releases changed over time? (2) Are fugitive releases of CCl_4 on the order of 11% from production of CFCs in the years 1978-1993 reasonable? (3) Did those fugitive releases more than double to become about 25% in 1995-1999 as the bulk of CFC production shifted to countries operating under Article 5(1) of the Montreal Protocol (Figure 1-15; Article 5(1) refers to developing countries as defined by the Montreal Protocol)?

Table 1-13. Description of scenarios for future ODS emissions.

Scenario	Description
Ab: Baseline (best-guess scenario following the Beijing Amendments, 1999) = Reference	Developed countries (non-Article 5(1)): Future production of CFCs was continued at the current level of capacity for "essential uses" and export to Article 5(1) countries. The bank of unemitted reserves in 2000 was estimated to be 656 Gg for CFC-11 and 60 Gg for CFC-12. Future production of CCl_4 was governed by the quantities required for CFC manufacture; global emissions of CCl_4 were estimated as a fraction (40%) of global CFC production (see Figure 1-15). Future production of methyl chloroform was zero. Emission of halons in future years was estimated as a percentage of unemitted global reserves: 98 Gg for Halon-1211 and 62 Gg for Halon-1301 in 2000. Production of HCFCs was continued with the same trends as now; after 2003 production is assumed to decline according to consumption limits required by the Protocol. Controls on global production of CH_3Br were presumed to result in a global emission decrease of 30 Gg yr^{-1} (out of 212 Gg yr^{-1}) in the future as governed by the phase-out schedule of the Protocol; 75% of this emission was phased out according to the schedule for production decreases in non-Article 5(1) countries, and 25% was phased out according to this schedule in Article 5(1) countries. Emissions from quarantine pre-shipment applications were held constant into the future at 12 Gg yr^{-1}; emissions from biomass burning and gasoline combustion were also held constant in all scenarios. Developing countries (Article 5(1)): Production of CFCs and methyl chloroform was allowed to continue at the current (frozen) level, with phase down dates mandated in the Montreal Protocol, and there was no production allotted in Countries with Economies in Transition (the de facto situation). Emissions of carbon tetrachloride were estimated at almost 40% of CFC-11 and -12 produced. Emissions of halons were estimated as a percentage of unemitted global reserves. The size of this unemitted stock of Halon-1211 in 2000 was enhanced slightly to account for potential additional production in Article 5(1) countries. For Halon-1301 production in A5(1) countries was taken from Fraser et al. (1999). Production and consumption of HCFCs was kept constant at current levels until phase down is required (after 2015). For a discussion of future production and emission of CCl_4 and CH_3Br, see the discussion for non-Article 5(1) countries.
Am: Maximum production	Production of CFCs, halons, and HCFCs is projected forward at the maximum allowed under the Protocol. CFCs: The maximum global production allotment for CFCs is, according to UNEP (2002), 160 ODP-ktons yr^{-1} through 2004, decreasing to zero in 2010. This is 17.5% above the 1999 production in the Ab scenario. For the maximum scenario, the Ab production of CFC-11, -12, and -113 was therefore multiplied by 1.175 for the years 2000-2004 (a scale factor of 1.0 was applied to CFC production during 2005-2009). The emissions of carbon tetrachloride were consequently also multiplied by the same factor, since they are linked in the calculation to the production of CFC-11 and -12. The UNEP production limit for CCl_4 was not applied. Halons: For Halon-1211 a global bank of 114 Gg in 2000 was used, instead of 98 Gg as in Ab. For the combined halons, a total global production was applied of 45 ODP-ktons through 2004, and 22.5 ODP-ktons split among the years 2005-2009. This production was divided over Halon-1211 and -1301 according to their production split in 1999 in the Ab scenario. HCFCs: Future production and consumption of HCFCs was estimated by keeping production in non-Article 5(1) countries constant at the 1999 level of 27 ODP-ktons yr^{-1} and by increasing production in Article 5(1) countries by 3% yr^{-1} starting in 1999 at 9.4 ODP-ktons yr^{-1}. The Protocol limits for production and consumption were applied for later years. The production of HCFCs in future years was split among HCFC-22, -141b, and -142b, as it was in 1999 (AFEAS, 2001). Production of methyl chloroform and methyl bromide are all at their practical maxima and so are the same as in the Ab scenario.
Pc: Continued production	Continued production of all ODSs at a constant level reported by UNEP (2002) for the year 1999 was assumed. This additional production would be in excess of the limits set by the amended Montreal Protocol. Global production magnitudes reported by UNEP (ODP-Gg yr^{-1}) for 1999 and used in this scenario were: 147.2 for CFCs, 25.2 for halons, 1.78 for methyl chloroform, and 36.2 for HCFCs. Carbon tetrachloride production was kept constant in the future at 67.7 Gg yr^{-1} based upon production of CFC-11 and -12 in 1999. Methyl bromide emission was held constant at the 1999 level. For the CFCs (CFC-11, -12, and -113), halons (1211 and 1301), and HCFCs (HCFC-22, -141b, and -142b), the 1999 production of the individual species was calculated from the aggregated ODP-weighted UNEP total using the ratio in the Ab scenario for 1999.

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Table 1-14. Description of cases for future ODS production and emissions.

Case	Description
E0: Zero emission (hypothetical scenario)	Anthropogenic emissions of all ODSs set to zero from 2003 onward, i.e., banks destroyed and production stopped. In practice, this is an unachievable scenario. This case is used to show the natural removal rates of ODS from the atmosphere and describes a lower limit for ODS mixing ratios in the future atmosphere.
Emission contribution of CFCs to Ab	No emission of CFCs (including from existing equipment) from 2003 onward. Other species as in scenario Ab.
Emission contribution of CCl ₄ to Ab	No emission of carbon tetrachloride (including from existing equipment) from 2003 onward. Other species as in scenario Ab. Since the emissions of CCl ₄ are fugitive and in the calculations related to the production of CFC-11 and -12, this is the same as a zero production case.
Emission contribution of CH ₃ CCl ₃ to Ab	No emission of methyl chloroform (including from existing equipment) from 2003 onward. Other species as in scenario Ab.
Emission contribution of halons to Ab	No emission of halons (including from existing equipment) from 2003 onward. Other species as in scenario Ab.
Emission contribution of HCFCs to Ab	No emission of HCFCs (including from existing equipment) from 2003 onward. Other species as in scenario Ab.
Emission contribution of CH ₃ Br to Ab	No anthropogenic emission of methyl bromide (including from existing equipment) from 2003 onward. Total reduction of 42 Gg (30 for controllable uses and 12 for Quarantine and Pre-Shipment (QPS) uses). Other species as in scenario Ab. The emissions of CH ₃ Br are from dispersive uses, so there is no substantial bank. As a result, this case is identical to a zero methyl bromide production case. Nonindustrial emissions of 160-170 Gg yr ⁻¹ were presumed and were kept constant in the future.
P0: Zero production	Production of all ODSs set to zero from 2003 onward. Emissions continue based upon size of unemitted reserves (based on the cases described below).
Production contribution of CFCs to Ab	No production of CFCs from 2003 onward. Emission of CFC-12 equals its production after 2002 (bank is depleting rapidly), so for CFC-12 this equals zero emissions. Production of CFC-114 and -115 already zero in Ab. Non-CFCs as in scenario Ab.
Production contribution of CH ₃ CCl ₃ to Ab	No production of methyl chloroform from 2003 onward. Other species as in scenario Ab.
Production contribution of halons to Ab	No production of halons from 2003 onward. Global production of Halon-1211 and -1301 in 1999 is, according to Fraser et al. (1999), 29.0 ODP-ktons and according to UNEP (2002), 25.2 ODP-ktons in 1999. This case was derived by estimating emissions from the halon production predicted in Fraser et al. (1999) for 2003-2009 (zero after 2009) and subtracting these emissions from those calculated in the Ab scenario. Halon-1202 emissions were presumed to be zero, since they arise as a byproduct of Halon-1211 production. Halon-2402 production was limited to Russia. The amount produced decreased rapidly from 2.45 ktons in 1990 to 0.152 ktons in 1999 (UNEP, 1999). The 1996 number is only a small fraction of the emission. Halon-2402 production is therefore assumed zero in this case (from 2003 onward) (same as in Ab, in agreement with Madronich and Velders et al. (1999) and Fraser et al. (1999)).
Production contribution of HCFCs to Ab	No production of HCFCs from 2003 onward. Other gases as in scenario Ab.
Production contribution of CH ₃ Br to Ab	No production of CH ₃ Br from 2003 onward. Because emissions are presumed to be prompt after production, this case is identical to the case of zero CH ₃ Br emissions.

Table 1-15. Source of production, emission, and observation data used in creating scenarios.

	Details Related to Creating Mean Set of Global Observations ^a			Details Related to Calculating Expected Mixing Ratios and Past Mixing Ratios in Scenarios from a Simple Box Model Calculation ^b			
	Mean AGAGE/CMDL Ratio (s.d.)	Period of Overlap	Source of Mean Observations after Scaling ^c	Lifetime Used In Box Model (years)	Production Data Source	Emission Function Revised?	Emission Scale Factor ^d
CFC-12	1.008 (0.002)	1991-1999	AGAGE	100	AFEAS, UNEP	No	1.045 (1980) 0.8 (1993-94)
CFC-11	0.980 (0.002)	1990-1999	AGAGE	45	AFEAS, UNEP	Yes, foam ^e	1.068
CFC-113	0.993 (0.005)	1994-1999	AGAGE	85	AFEAS only	No	0.98
CCl ₄	0.973 (0.006)	1993-1999	AGAGE	26	^f	^f	^f
CH ₃ CCl ₃	0.975 (0.008)	1993-1999	AGAGE	4.8	^g	No	Variable (0.9 to 1.25)
HCFC-22	0.993 (0.007)	1998-2000	CMDL	11.8	AFEAS, UNEP	No	1.0
HCFC-141b	1.011 (0.006)	1998-2000	CMDL	9.2	AFEAS, UNEP	No	1.0
HCFC-142b	1.049 (0.008)	1998-2000	CMDL	18.5	AFEAS, UNEP	Yes, foam ^h	1.0
Halon-1211	1.068 (0.006)	1998-2000	CMDL	16	ⁱ	No	1.18 (1992)
Halon-1301	1.139 (0.004)	1998-2000	CMDL	65	^j	No	Variable
CH ₃ Br	NA	NA	^k	0.7	NA	NA	NA
CH ₃ Cl	NA	NA	^l	1.3	NA	NA	NA

NA, Not available.

^a Mean halocarbon measurements were derived from the longest available global data record after adjusting this data record by the factor $[1 \pm (1-x)/2]$, where x is the mean AGAGE/CMDL ratio indicated. Scenarios were created to match these measurements for past years. AGAGE data are reported on the SIO-98 scale (Prinn et al., 2000); CMDL data are reported on scales as described in Hall et al. (2002).

^b Calculated mixing ratios also appear in Scenarios and provide the basis for calculating future emissions and mixing ratios. Citations referred to are AFEAS (2001) and UNEP (2002) unless otherwise specified.

^c Data record from the group indicated was scaled by half the AGAGE vs. CMDL ratio.

^d To create a set of emissions consistent with global observations (Section 1.8 only), emissions derived from industrial production were scaled by this factor up to the point at which measurements become available.

^e McCulloch et al. (2001).

^f CCl₄ emission estimated in the future from CFC-11 and -12 production (see text).

^g McCulloch and Midgley (2001).

^h Emission functions for foams adjusted as described in Ashford (2000) and McCulloch et al. (2001).

ⁱ Updated UNEP (1999).

^j Fraser et al. (1999).

^k Southern Hemispheric firm data were scaled by a constant of 1.16 to approximate global mixing ratios (see Section 1.5).

^l Southern Hemispheric firm data were scaled by a constant of 1.06 to approximate global mixing ratios (see Section 1.5).

SOURCE GASES

Table 1-16. Calculated global surface mixing ratios (ppt) in the Ab baseline scenario. Dates are for the beginning of the year indicated.

Year	CFC-12		CFC-114		CCl ₄		HCFC-22		HCFC-142b		Halon-1202		Halon-2402		CH ₃ Cl	
	CFC-11		CFC-113		CFC-115		CH ₃ CCl ₃		HCFC-141b		Halon-1211		Halon-1301		CH ₃ Br	
1990	256.3	474.1	68.0	15.4	5.1	105.7	124.7	82.0	0.0	1.2	2.27	0.03	1.66	0.31	9.0	550.5
1991	262.6	488.0	74.0	15.7	5.6	105.8	128.8	88.1	0.0	1.7	2.54	0.03	1.85	0.34	9.0	550.6
1992	267.4	500.2	78.3	15.9	6.0	105.5	129.1	94.4	0.0	2.4	2.79	0.03	1.98	0.36	9.1	550.6
1993	271.2	511.5	81.4	16.0	6.5	105.1	127.8	100.8	0.2	3.3	2.94	0.03	2.07	0.38	9.2	550.6
1994	271.2	518.7	82.9	16.1	7.0	104.5	118.8	106.8	0.9	4.2	3.10	0.04	2.17	0.40	9.3	550.7
1995	270.6	524.8	83.2	16.2	7.5	103.7	107.8	112.8	2.1	5.2	3.25	0.04	2.33	0.42	9.4	550.7
1996	269.5	530.0	83.2	16.2	7.9	102.7	97.0	118.6	3.8	6.3	3.40	0.04	2.46	0.43	9.5	550.7
1997	268.2	534.2	82.7	16.3	8.3	101.6	82.9	125.0	5.5	7.4	3.55	0.05	2.55	0.43	9.5	550.7
1998	266.6	537.4	82.6	16.3	8.6	100.5	69.3	130.5	7.1	8.5	3.69	0.05	2.64	0.43	9.5	550.7
1999	264.7	539.5	82.3	16.3	8.8	99.2	58.6	136.1	9.0	9.4	3.83	0.05	2.73	0.42	9.5	550.7
2000	262.6	540.5	81.7	16.4	9.0	97.9	49.9	141.6	10.8	10.5	3.97	0.05	2.82	0.41	9.3	550.7
2001	260.5	541.2	81.1	16.4	9.1	96.7	42.6	149.3	13.0	12.2	4.07	0.04	2.90	0.41	9.3	550.7
2002	258.2	541.9	80.4	16.4	9.1	95.5	36.6	156.4	15.4	13.9	4.13	0.04	2.97	0.40	9.1	550.7
2003	255.8	542.7	79.6	16.4	9.1	94.4	31.6	162.9	18.1	15.5	4.16	0.03	3.04	0.39	9.0	550.7
2004	253.3	541.9	78.8	16.4	9.2	93.3	27.5	168.9	20.9	17.1	4.16	0.03	3.11	0.38	8.9	550.7
2005	250.7	541.1	78.0	16.4	9.2	92.3	24.0	174.4	23.8	18.7	4.14	0.02	3.17	0.37	8.8	550.7
2006	248.0	538.5	77.2	16.4	9.2	90.3	21.2	178.2	26.5	20.1	4.09	0.02	3.23	0.36	8.5	550.7
2007	245.2	536.0	76.3	16.4	9.2	88.5	18.8	180.6	28.9	21.3	4.03	0.02	3.28	0.35	8.5	550.7
2008	242.4	531.4	75.5	16.3	9.2	85.6	16.7	182.0	31.1	22.3	3.95	0.01	3.32	0.34	8.4	550.7
2009	239.3	526.9	74.7	16.3	9.2	82.8	15.0	182.7	33.0	23.2	3.86	0.01	3.37	0.32	8.4	550.7
2010	236.1	522.5	73.9	16.3	9.2	80.1	13.6	182.8	34.8	24.0	3.76	0.01	3.40	0.31	8.4	550.7
2011	232.7	517.3	73.0	16.2	9.2	77.1	12.3	182.5	36.5	24.7	3.66	0.01	3.44	0.30	8.4	550.7
2012	229.2	512.2	72.2	16.2	9.2	74.2	11.2	180.8	37.7	25.2	3.54	0.00	3.46	0.29	8.4	550.7
2013	225.6	507.1	71.3	16.2	9.2	71.4	10.3	178.2	38.5	25.5	3.43	0.00	3.49	0.28	8.4	550.7
2014	221.9	502.0	70.5	16.1	9.2	68.7	9.5	174.8	39.1	25.6	3.31	0.00	3.51	0.27	8.4	550.7
2015	218.2	497.0	69.7	16.1	9.2	66.1	8.7	171.0	39.4	25.7	3.19	0.00	3.52	0.26	8.4	550.7
2016	214.3	492.1	68.9	16.0	9.1	63.6	8.0	167.0	39.6	25.7	3.07	0.00	3.54	0.25	8.2	550.7
2017	210.5	487.2	68.1	16.0	9.1	61.2	7.4	162.0	39.3	25.5	2.95	0.00	3.55	0.24	8.2	550.7
2018	206.6	482.3	67.3	15.9	9.1	58.9	6.9	156.2	38.8	25.1	2.83	0.00	3.55	0.23	8.2	550.7
2019	202.7	477.5	66.5	15.9	9.1	56.7	6.3	150.1	38.0	24.7	2.71	0.00	3.56	0.22	8.2	550.7
2020	198.9	472.8	65.7	15.8	9.1	54.6	5.9	143.9	37.1	24.1	2.59	0.00	3.56	0.21	8.2	550.7
2021	195.0	468.1	64.9	15.8	9.1	52.5	5.4	137.6	36.1	23.6	2.48	0.00	3.55	0.20	8.2	550.7
2022	191.2	463.4	64.2	15.7	9.1	50.5	5.0	131.2	34.9	22.9	2.37	0.00	3.55	0.19	8.2	550.7
2023	187.4	458.8	63.4	15.7	9.1	48.6	4.7	124.8	33.7	22.3	2.26	0.00	3.54	0.18	8.2	550.7
2024	183.6	454.2	62.7	15.6	9.1	46.8	4.3	118.6	32.4	21.6	2.16	0.00	3.53	0.18	8.2	550.7
2025	179.9	449.7	62.0	15.6	9.1	45.0	4.0	112.6	31.0	20.9	2.05	0.00	3.52	0.17	8.2	550.7
2030	162.0	427.8	58.4	15.3	9.1	37.1	2.8	86.8	24.7	17.6	1.59	0.00	3.44	0.13	8.2	550.7
2035	145.5	406.9	55.1	15.1	9.0	30.6	1.9	66.9	19.1	14.6	1.22	0.00	3.33	0.10	8.2	550.7
2040	130.5	387.1	51.9	14.8	9.0	25.3	1.3	51.6	14.6	12.0	0.93	0.00	3.19	0.08	8.2	550.7
2045	116.9	368.2	49.0	14.6	9.0	20.9	0.9	39.3	11.0	9.8	0.70	0.00	3.04	0.06	8.2	550.7
2050	104.7	350.2	46.2	14.4	9.0	17.2	0.6	27.6	7.7	7.6	0.52	0.00	2.88	0.05	8.2	550.7
2055	93.8	333.2	43.5	14.1	8.9	14.2	0.5	18.7	5.2	5.8	0.39	0.00	2.72	0.04	8.2	550.7
2060	83.9	316.9	41.0	13.9	8.9	11.7	0.3	12.5	3.4	4.4	0.29	0.00	2.56	0.03	8.2	550.7
2065	75.1	301.5	38.7	13.7	8.9	9.7	0.2	8.3	2.1	3.4	0.21	0.00	2.41	0.02	8.2	550.7
2070	67.2	286.8	36.5	13.4	8.9	8.0	0.2	5.5	1.3	2.6	0.16	0.00	2.25	0.02	8.2	550.7
2075	60.2	272.8	34.4	13.2	8.8	6.6	0.1	3.6	0.8	1.9	0.12	0.00	2.11	0.01	8.2	550.7
2080	53.8	259.5	32.4	13.0	8.8	5.4	0.1	2.4	0.5	1.5	0.09	0.00	1.97	0.01	8.2	550.7
2085	48.2	246.8	30.6	12.8	8.8	4.5	0.1	1.6	0.3	1.1	0.06	0.00	1.83	0.01	8.2	550.7
2090	43.1	234.8	28.8	12.6	8.8	3.7	0.0	1.0	0.2	0.8	0.05	0.00	1.71	0.01	8.2	550.7
2095	38.6	223.3	27.2	12.4	8.7	3.1	0.0	0.7	0.1	0.6	0.03	0.00	1.59	0.01	8.2	550.7
2100	34.5	212.4	25.6	12.2	8.7	2.5	0.0	0.5	0.1	0.5	0.03	0.00	1.48	0.00	8.2	550.7

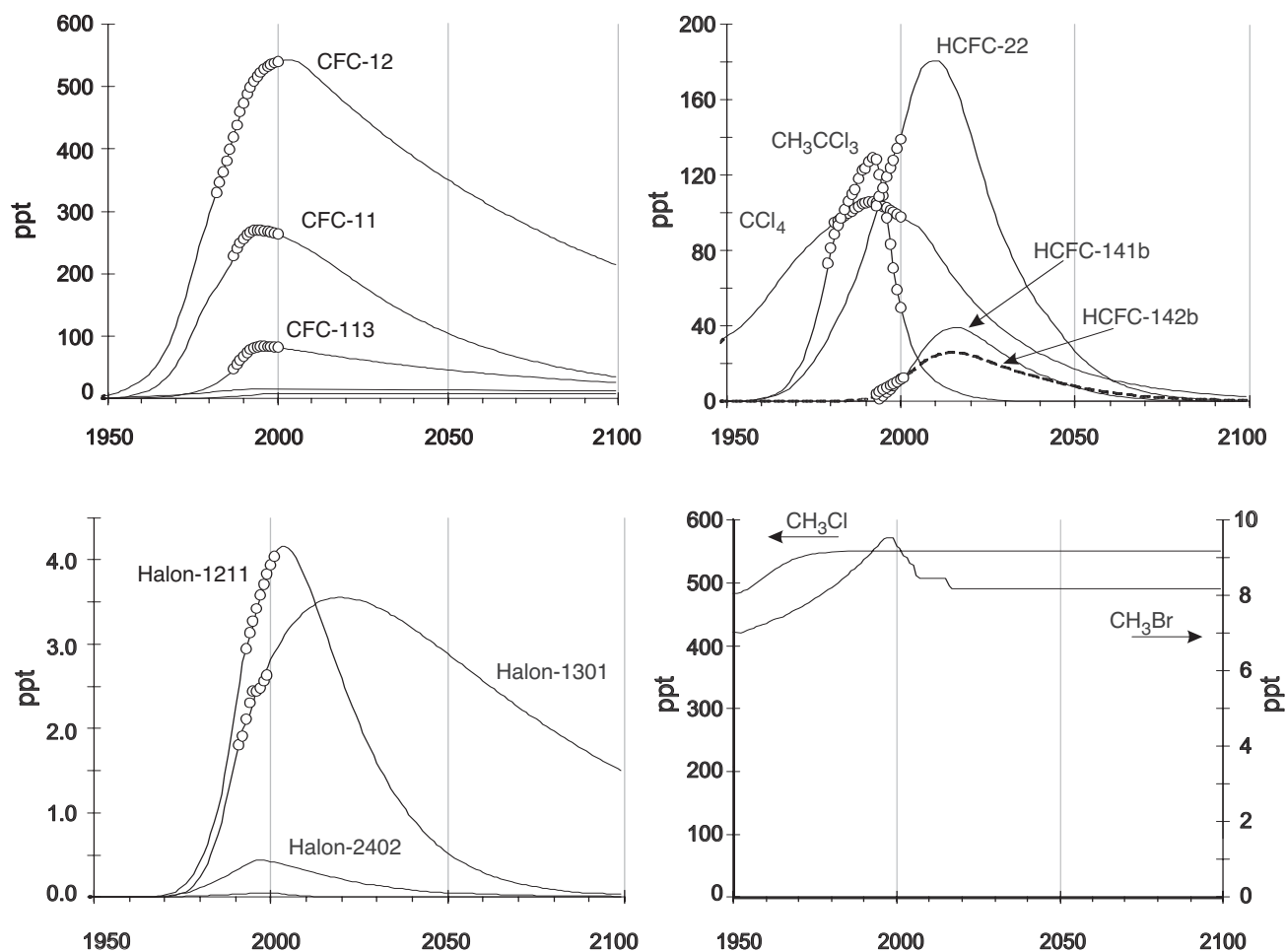


Figure 1-22. Global atmospheric surface mixing ratios (ppt) in the baseline scenario Ab (lines) and the mean AGAGE-CMDL observations (circles; see Table 1-15 for origin; Prinn et al., 2000; Montzka et al., 1999).

In the Ab and Am scenarios, future emissions of CCl₄ were estimated from CFC production and a molar ratio [total CCl₄ emission]/[global CFC production] of 0.38 as estimated for recent years (see Figure 1-15). These projections (Figure 1-4) will be reasonable for carbon tetrachloride only if *all* significant emissions of this gas become diminished in the future along the time frame projected for reductions in CFC production.

1.8.2.4 HALONS

A large fraction of present-day halon emissions arise from use of a banked halon, defined here as material that is contained in inventories and installed equipment. As a result, future mixing ratios are tied to the rate of emissions from these halon banks in addition to the magnitude of future production (Figure 1-3). Although progress has been made in reducing production for future uses (UNEP, 1997), halon banks are large relative to current emission

rates (Butler et al., 1999; Fraser et al., 1999; UNEP, 1999, and updates). In the Ab scenario, mixing ratios of Halon-1301 continue to increase until about 2020 primarily because of emission from reserves. Scenario results for Halon-1211 also suggest that emissions from reserves are important, but the magnitude and date of peak mixing ratios are strongly influenced by future production rates as well (Figure 1-3).

Additional uncertainty in future halon mixing ratios arises because the size of these reserves is not well defined; this added uncertainty is not explicitly included in the calculated scenarios but is considered elsewhere (see Section 1.8.4). For Halon-1211, estimates of reserves derived from production data and functions relating releases to production vary from 65 to 136 Gg in 2000 (Fraser et al., 1999; UNEP, 1999, updated). Reserves calculated with emissions derived from atmospheric measurements (Butler et al., 1998, 1999) and an atmospheric lifetime of 16 years are about 100 Gg in 2000; those

SOURCE GASES

derived from independent measurements at Cape Grim by UEA (Fraser et al., 1999) are substantially smaller. For reference, current increases observed for Halon-1211 of 0.1 ppt yr^{-1} would require emissions of about 10 Gg yr^{-1} to sustain (for a 16-yr lifetime). For Halon-1301, estimates of reserves range from 45 Gg (UNEP, 1999, updated) to 65 Gg (Fraser et al., 1999) and, for reference, measurements suggest annual emissions of about 3 Gg yr^{-1} (for a 65-yr lifetime).

1.8.2.5 HCFCs

Uncertainty in future mixing ratios of HCFCs stems primarily from projecting how these gases will fulfill the needs of developing nations. Consumption is currently frozen in non-Article 5(1) countries, and soon reductions in consumption will be mandated there as well (see Figure 1-18). Production in non-Article 5(1) countries, however, is capped only after 2004; this production could provide a substantial allotment of HCFC for use in Article 5(1) countries, depending upon demand. In addition, production in Article 5(1) countries is not restricted until after 2015, although the extent to which these countries would invest substantial capital in the manufacture and use of such time-limited materials remains a major uncertainty. Production (as ODP-tons) in developing countries averaged 10% of production in non-Article 5(1) countries in the late 1990s (UNEP, 2002).

In the Ab scenario, future global HCFC *production* was presumed to decrease according to the *consumption* limits outlined for non-Article 5(1) countries and a small, constant allotment was included for production in countries operating under Article 5(1) of the Protocol. This scenario would underestimate future production, emissions, and consequent mixing ratios of HCFCs if demand for these gases in developing countries increased substantially in future years. In the Am scenario, production and consumption of HCFCs was increased as described in Table 1-13. This enhanced demand leads to higher HCFC mixing ratios in the future (Figure 1-5); this enhanced HCFC production accounts for about one-third of the 14.5% higher integrated EESC calculated for scenario Am compared with scenario Ab (Table 1-17).

1.8.2.6 METHYL BROMIDE AND METHYL CHLORIDE

Atmospheric releases resulting from industrial production represent only a fraction of total releases of these gases to today's atmosphere (see Section 1.5). Uncertainty in the magnitude of this fraction limits our ability to accurately describe how methyl bromide mixing ratios will respond to production limits in the revised and amended Montreal Protocol (Section 1.5.1.4). Scenarios

for methyl bromide were developed by prescribing future emission decreases of about 30 Gg , or 15% of the total annual flux, according to the schedule of production restrictions in the current Protocol (Table 1-13; see also Section 1.5). Anthropogenic emissions from quarantine and preshipment applications (12 Gg yr^{-1}) and from non-fumigation activity (biomass burning and automobile emissions) were kept constant in the future in all scenarios. No limits apply to methyl chloride production or consumption; total emissions of this gas were held constant in the future in all scenarios.

Both methyl bromide and methyl chloride are unique among ozone-depleting halocarbons because a substantial fraction of their sources and sinks arises from biological processes. These processes may be affected significantly by changes in future climate. Because our understanding of these process is limited, we cannot predict if such changes would act to enhance or diminish mixing ratios of these gases in the future atmosphere (see also Section 1.8.5).

1.8.2.7 EFFECTIVE EQUIVALENT CHLORINE

As the influence of methyl chloroform on effective equivalent chlorine (EECl) has lessened, the decline observed for EECl has slowed (see Section 1.2; Figure 1-9). This is because mixing ratios of CFC-12, halons, and the HCFCs continued to increase in 2000. Future trace gas trends in scenario Ab (the best-guess scenario) result in continued declines in EECl in the near future; the mean rate of change for EECl during 2000-2010 in this scenario is $-0.9\% \text{ yr}^{-1}$ (Figure 1-9). In scenario Ab, EECl continues to decline because projected mixing ratios for CFC-12 and total bromine peak and subsequently begin decreasing during 2000-2005, and because enhanced declines in other CFCs are projected for that period as well (Figure 1-22). In scenario Am, EECl decreases at $-0.7\% \text{ yr}^{-1}$, slightly slower than in the Ab scenario.

1.8.3 Scenario Results: Calculated Mixing Ratios and EESC

The concept of effective equivalent stratospheric chlorine (EESC) has been used in the past to gauge the net effect of tropospheric halocarbon trends on the loading of ozone-depleting halogen in the stratosphere (Prather and Watson, 1990; Solomon and Wuebbles et al., 1995; Madronich and Velders et al., 1999; Daniel et al., 1995). As such, EESC provides a rough estimate of the time scale for ozone recovery in an otherwise unchanging atmosphere. The concept of EESC has limitations, however, particularly because of stratospheric mixing processes and other effects (Prather, 1997; see also discussion in Section

Table 1-17. Comparison of scenarios and cases: the year when EESC drops below the 1980 level, and integrated EESC differences (relative to baseline scenario Ab).^a

Scenarios and Cases	Year (x) when EESC is expected to drop below 1980 value ^a	Percent difference in $\int_{1980}^x \text{EESC } dt$ above the 1980 level relative to scenario Ab ^a	Percent difference in $\int_{2002}^x \text{EESC } dt$ above the 1980 level relative to scenario Ab ^a
Scenarios			
Ab: Beijing Amendments (1999)	2043.9	0.0	0.0
Am: Maximum allowed production	2048.0	8.3	14.5
Pc: Continued production	Not reached	>115 ^b	>202 ^b
Cases^c			
P0: Zero production of all anthropogenic ODSs	2039.9	-8.1	-14.1
Contribution CFC production to Ab	2042.8	-2.2	-3.8
Contribution CH ₃ CCl ₃ production to Ab	2043.9	-0.2	-0.3
Contribution Halon production to Ab	2043.6	-0.6	-1.1
Contribution HCFC production to Ab	2042.6	-3.1	-5.4
Contribution anthropogenic CH ₃ Br production to Ab	2042.9	-2.3	-4.0
E0: Zero emission of all anthropogenic ODSs	2033.8	-19.3	-33.8
Contribution CFC emissions to Ab	2041.1	-5.4	-9.4
Contribution CCl ₄ emissions to Ab	2043.5	-1.5	-2.7
Contribution CH ₃ CCl ₃ emissions to Ab	2043.7	-0.9	-1.6
Contribution Halon emissions to Ab	2040.7	-6.1	-10.8
Contribution HCFC emissions to Ab	2042.3	-4.9	-8.6
Contribution anthropogenic CH ₃ Br emissions to Ab	2042.9	-2.3	-4.0

^a The dates and percent differences in integrated EESC were calculated with the fractional release values in column 2 of Table 1-4.

^b The integrated percent differences indicated for Scenario Pc represent lower limits because the integration was run only through 2100 and EESC in this scenario does not reach the 1980 level by 2100 (see Figure 1-23).

^c Contributions of ozone-depleting substances to future EESC were calculated in the hypothetical "Cases" by setting production or emission to zero in 2003 and subsequent years for the indicated chemical or group of chemicals.

1.2.5). Furthermore, the chemical and dynamical state of the atmosphere has not been constant, and changes in aerosols, trace gas mixing ratios, and stratospheric temperatures are also expected to influence ozone chemistry and the efficiency of halogens to deplete stratospheric ozone in the future. Whereas different scenarios are gauged in this chapter in terms of integrated EESC and the date when EESC returns to the value estimated for 1980, discussions relating to future ozone concentrations in light of the broad range of additional atmospheric changes that are possible can be found in Chapters 3 and 4.

EESC was calculated as described in past Assessments for the updated scenarios. These calculations were performed with a slightly reduced efficiency for bromine relative to chlorine, on a per-atom basis, for the destruction of ozone compared to WMO (1999) ($\alpha = 45$; see Section 1.4.4). Furthermore, an absolute fractional

release of 0.8 for CFC-11 was included in this calculation to provide consistency with past reports, although the data of Schauffler et al. (2002) suggest that a more appropriate estimate may be 0.55. This absolute degradation amount does not affect calculations of ODP or relative changes in EESC presented in this chapter, but it is important when considering the influence short-lived gases have on the burden of ozone-depleting halogen, particularly in the lower stratosphere (see Chapter 2).

Despite the limitations of EESC, different scenarios and cases are compared with respect to the year (x) EESC returns to the value estimated for 1980, and by the percentage differences in time-integrated EESC from 2002 or 1980 through the year (x) (Table 1-17; Solomon and Wuebbles et al., 1995; Madronich and Velders et al., 1999). Because of the revised value for alpha, and because time-varying past histories for CH₃Br and CH₃Cl are now

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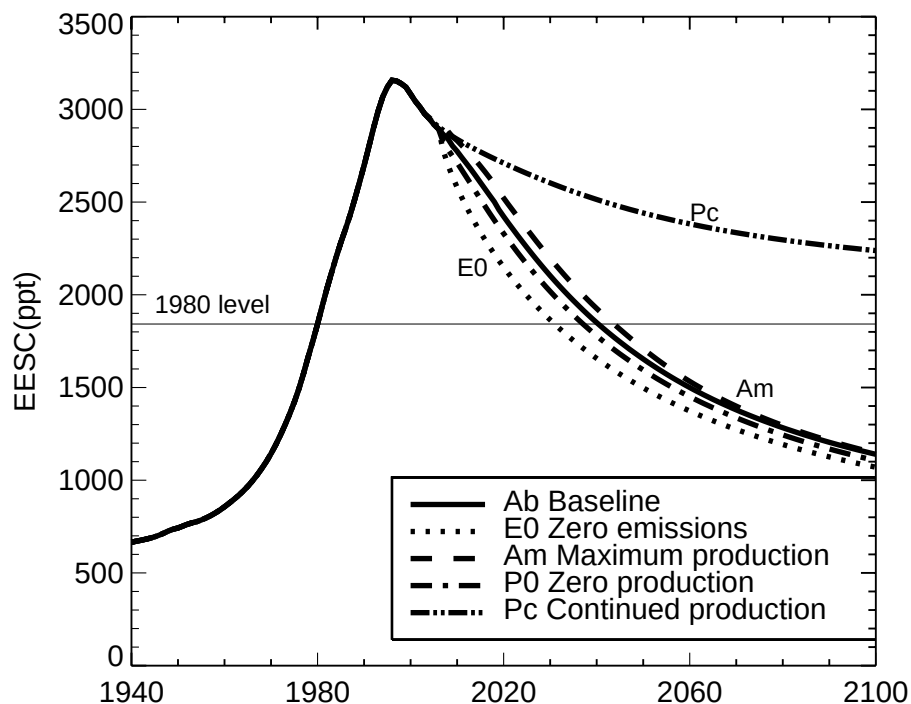


Figure 1-23. Estimates of future EESC based on the baseline scenario (Ab, solid line), the maximum scenario (Am, long-dashed line), and the hypothetical cases of zero emissions in 2003 and thereafter (E0) and zero production in 2003 and thereafter (P0) of all anthropogenic ODSs. Also shown are results from the scenario with continued ODS production in the future at 1999 rates (Pc), production that is substantially larger than allowed in the fully revised and amended Montreal Protocol. Additional description of these scenarios is found in Tables 1-13 and 1-14.

considered (Section 1.8.1), the EESC value in 1980 is calculated here to be 1.784 ppb, somewhat lower than in Madronich and Velders et al. (1999).

Future EESC and time-integrated EESC were calculated from halocarbon mixing ratios in selected scenarios (Table 1-17). For the baseline scenario (Ab), the calculated EESC reaches the 1980 level again in about 2044. This is a few years earlier than estimated in Madronich and Velders et al. (1999), 4 years longer than if production of all ODSs were to cease in 2003, and 10 years longer than if emission of all ODSs were negligible after 2003. In the maximum-emissions scenario (Am), EESC drops to the 1980 level in about 2048.

The cases provide a gauge of maximum potential reductions in EESC that would be achievable from further restrictions to future production or future production *and* emission of ODSs. Implementation of any new control measures, however, must include a consideration of costs and feasibility in addition to any atmospheric benefits, but those considerations are not discussed here. From the zero-production cases presented in Table 1-17, the influence of future ODS production allowances is apparent. Allowances for continued production of HCFCs, methyl bromide, and CFCs have the largest influence on integrated EESC in the future. The zero-emission cases quantify the contribution of future emissions plus future production to future EESC (relative to the Ab scenario) and suggest that ODS emissions from reserves of unemitted material will affect EESC as much as or more than the current future

ODS production allowances. The exception is methyl bromide, where reserves are presumed to be negligible; its influence on future EESC is primarily dependent upon the magnitude of future production.

To show the effect of noncompliance with the Montreal Protocol, the Pc scenario was constructed. This scenario demonstrates that with continued, constant production of ODSs, even at the reduced amounts reported for 1999, EESC remains well above the 1980 level through 2100 (Figure 1-23). In the Pc scenario, the integrated EESC through 2100 is about 3 times as high as in the baseline scenario (Table 1-17). The results from this scenario demonstrate clearly that atmospheric halogen will decline to pre-Antarctic-ozon-hole conditions only with adherence to future limits on production of ozone-depleting substances.

1.8.4 Uncertainty in the Baseline Scenario

The Ab scenario is constructed as a best guess for future ODSs emissions and mixing ratios. There are several sources of uncertainties in these quantities.

First, uncertainty in the Ab scenario arises because of our inability to predict future global HCFC production. Limits apply to production or consumption of HCFCs in countries operating under Article A5(1) of the Protocol only after 2016 based upon amounts produced or consumed in 2015.

Second, emissions of carbon tetrachloride not related to industrial CFC production are poorly character-

ized. Accordingly, it is difficult to know accurately how emissions not related to CFC production will change in the future.

Third, there are uncertainties in the release rates of ODSs to the atmosphere. In these scenarios, future annual emissions are calculated as a fraction of the unemitted reserves (or “bank”). This release fraction is based on an analysis of the quantities present in, and emitted from, the banks over the past decade (1990-1999). These release fractions are held constant from 2000 onward. Destruction of reserves or changes in the use patterns of ODSs would change the estimated release fraction and thereby the emissions and shape of the effective equivalent stratospheric chlorine (EESC) curve in the future, but less so for the integrated EESC values. For integrated EESC, when the emissions occur is less important; if the ODS reaches the stratosphere before the EESC value falls below the 1980 value (approximately 2040), it contributes to the integrated value.

Fourth, the size of reserves of produced but unemitted ODSs is uncertain. In creating scenario Ab, historical emissions were adjusted so that the calculated mixing ratios were consistent with measurements. These adjustments depend on the lifetimes and release rates to the atmosphere of ODSs, and they affect our estimates of present-day banks of unemitted ODSs. This is especially true for Halon-1211, considering the large uncertainty in reserves and in its global lifetime. To understand the influence these uncertainties have on the calculation of future EESC, selected sensitivity tests were performed and compared with the results of the Ab scenario. If the lifetime of Halon-1211 were 11 years, EESC would drop to the 1980 amount (integrated from 2002 onward) 2.0 years earlier, and the integrated EESC would be 7.9% smaller than compared with the Ab scenario in which a 16-yr lifetime for Halon-1211 is presumed. An additional future production for this halon totaling 22.9 Gg over the years 2000 to 2009 (from Fraser et al., 1999) and a 35-Gg larger bank in 2000 yields an increase in integrated EESC of 3.5% (integrated from 2002) and a delay in recovery of only 0.5 years. Smaller Halon-1211 reserves in 2000 of 65 Gg (Fraser et al., 1999; instead of 98 Gg in Ab) result in integrated EESC being -3.4% compared with the Ab scenario.

Fifth, a simple box model is used for the calculation of mixing ratios in scenarios, as has been done in past ozone Assessments. Advantages of the simple model are that it maintains consistency with past reports and is more easily interpreted than the 2-D and 3-D interactive models. Simple box models have many limitations that affect the accuracy of atmospheric mixing ratios calculated from emissions. For example, the exponential decay time constant of a trace gas in the absence of emissions is the same

as the trace gas lifetime in a one-box model. In the real atmosphere, however, this time constant can be different from the steady-state trace gas lifetime (Prather, 1996). Although such effects are thought to be small for long-lived ODSs, they are predicted to be substantial for some short-lived gases such as methyl bromide (Prather, 1997).

Sixth, accurate predictions of future halocarbon mixing ratios rely on an understanding of loss rates in the future (see Section 1.8.5). The composition of the atmosphere is changing, and this may alter the chemical or dynamical processes that regulate lifetimes of ODSs (Krol et al., 1998; Prinn et al., 2001; Butchart and Scaife, 2001).

1.8.5 Potential Influence of Future Climate Change on Halogenated Source Gases

About 80% of the equivalent chlorine in today's atmosphere arises from direct anthropogenic release of ODSs. Climate change could influence future atmospheric amounts of these gases by affecting the rates at which these gases are removed from the atmosphere (Prinn et al., 2001; Butchart and Scaife, 2001). For CFCs, halons, and CCl_4 , rates of atmospheric removal are governed by the flux of high-energy light in the stratosphere and the rate at which air is mixed through the stratosphere. If changes in climate were to affect rates of air transport through the stratosphere, trace gas lifetimes would be altered. The lack of predictive understanding of such changes does not allow a reliable estimate of whether lifetimes would become longer or shorter in the future in an atmosphere with elevated greenhouse gas abundances. For methyl chloroform, HCFCs, methyl halides, and other chemically reduced gases, climate change could influence loss rate through changes in mean global concentrations of the hydroxyl radical. This oxidant plays a key role in determining the lifetime of these important ozone-depleting substances. Amounts of this short-lived, but powerful atmospheric oxidant depend directly on humidity, sunlight, temperature, and the abundance of many different trace gases likely to be affected by climate change and human behavior in the future.

The remaining 20% of ODSs in today's atmosphere arises from CH_3Cl , CH_3Br , and short-lived brominated gases (see Section 1.2.4 and Chapter 2). These gases are unique among ODSs because the predominant sources are believed to be nonindustrial, and climate change could affect the magnitude of sources for these gases. As a result there is less direct control over mixing ratios of these gases in the atmosphere. Our current understanding is limited for predicting even the net change in sources and sinks one might expect in the future for these methyl halides as

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a result of climate change or wide-scale land-use change. The influence of temperature on air-sea concentration differences have been identified recently (Groszko and Moore, 1998; King et al., 2000), but the relevance of this information to trace gas fluxes in and out of the future ocean has yet to be demonstrated.

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CHAPTER 2

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CHAPTER 2

VERY SHORT-LIVED HALOGEN AND SULFUR SUBSTANCES

Contents

SCIENTIFIC SUMMARY	2.1
2.1 INTRODUCTION	2.5
2.2 DYNAMICAL AND CHEMICAL CHARACTERISTICS OF THE UPPER TROPOSPHERE (UT) AND THE TROPICAL TROPOPAUSE LAYER (TTL)	2.7
2.2.1 Moist Convection and the Tropical Tropopause Layer	2.8
2.2.2 Stratosphere-Troposphere Exchange	2.12
2.2.2.1 Exchange Across the Tropical Tropopause	2.12
2.2.2.2 Exchange Across the Extratropical Tropopause	2.12
2.2.3 Chemistry in the UT and TTL	2.13
2.2.4 Chemical Tracer Observations for Model Evaluation	2.14
2.3 ATMOSPHERIC CHEMISTRY OF HALOGENATED VERY SHORT-LIVED (VSL) SUBSTANCES ...	2.15
2.3.1 Removal of the Halogen Source Gases	2.16
2.3.2 Production and Removal of Degradation Products	2.18
2.3.2.1 Degradation Mechanisms for Source Gases	2.18
2.3.2.2 Intermediate Products	2.19
2.3.2.3 Inorganic Bromine and Iodine Species	2.20
2.3.3 Degradation Mechanism for n-Propyl Bromide (n-PB)	2.22
2.3.4 Stratospheric Iodine Chemistry	2.24
2.4 CONTRIBUTION OF HALOGENATED VSL SUBSTANCES TO THE STRATOSPHERIC INORGANIC HALOGEN BUDGET	2.25
2.4.1 Observed Concentrations and Sources of Organic Chlorine, Bromine, and Iodine Compounds ...	2.26
2.4.1.1 Chlorine Compounds	2.26
2.4.1.2 Bromine Compounds	2.29
2.4.1.3 Iodine Compounds	2.29
2.4.2 Estimates of Contributions from VSL Halogen Source Gases	2.30
2.4.3 Modeling Studies	2.32
2.4.4 Information Needed for Future Evaluation	2.33
2.5 ESTIMATES FOR THE POTENTIAL IMPACT OF HALOGENATED VSL SUBSTANCES ON COLUMN OZONE	2.34
2.5.1 Review of Methodolgy for Calculating ODPs for Long-Lived Source Gases	2.35
2.5.2 Modified Approach for Estimating ODP for Halogenated VSL Substances	2.36
2.5.3 Existing Modeling Studies on ODP for n-PB	2.37
2.5.4 Information Required for Evaluating Ozone Impact from VSL Source Gases	2.38
2.6 VSL SULFUR SPECIES AND STRATOSPHERIC AEROSOLS	2.39
2.6.1 Introduction	2.39
2.6.2 Chemistry of the VSL Sulfur Species	2.40
2.6.3 Sources for the Stratospheric Sulfate Layer	2.42
2.6.3.1 Direct Input from Explosive Volcanic Eruptions	2.42
2.6.3.2 VSL Precursors Emitted in the Troposphere	2.42
2.6.4 How Can We Predict Future Changes in the Stratospheric Sulfate Layer?	2.43
REFERENCES	2.44

SCIENTIFIC SUMMARY

Definition of Very Short-Lived Substances

Very short-lived (VSL) substances are substances that have chemical lifetimes comparable with tropospheric transport time scales, with the result that the steady-state mixing ratio of the substance in the troposphere depends on where and when (time of the year) it is released. In practice, this happens for species with atmospheric lifetimes of a few months or less.

Ozone Depletion Potential (ODP) for Halogen Source Gases

- The Ozone Depletion Potential (ODP) of a halogen source gas X ($\text{ODP}(X, \bar{x}_e, t_e)$) is defined as the time-integrated effect on stratospheric ozone caused by emission of X at location $\bar{x}_e$ and time t_e relative to the time-integrated effect on stratospheric ozone from the same mass emission of CFC-11 (CCl_3F) at the same location and time.
- In the general case, $\text{ODP}(X, \bar{x}_e, t_e)$ consists of two terms: $\text{ODP}_{\text{SGI}}(X, \bar{x}_e, t_e)$ and $\text{ODP}_{\text{PGI}}(X, \bar{x}_e, t_e)$. $\text{ODP}_{\text{SGI}}(X, \bar{x}_e, t_e)$ (source gas injection (SGI) term) and $\text{ODP}_{\text{PGI}}(X, \bar{x}_e, t_e)$ (product gas injection (PGI) term) represent the effects caused by inorganic halogen atoms that are transported to the stratosphere in the form of the source gas and in the form of degradation products, respectively.
- For long-lived source gases, the value for $\text{ODP}_{\text{SGI}}(X, \bar{x}_e, t_e)$ is independent of $\bar{x}_e$ and t_e , and $\text{ODP}_{\text{PGI}}(X, \bar{x}_e, t_e)$ is negligible in comparison to $\text{ODP}_{\text{SGI}}(X, \bar{x}_e, t_e)$. Thus, a single value of ODP can be obtained based on the atmospheric lifetime of the source gas independent of location and time of emission. These are the traditional single-value ODPs reported in the literature.
- For VSL source gases, the $\text{ODP}_{\text{SGI}}(X, \bar{x}_e, t_e)$ value depends on the location and time of emission. The $\text{ODP}_{\text{PGI}}(X, \bar{x}_e, t_e)$ value depends also on the properties of the degradation products.
- If degradation of the VSL source gases gives rise to significant inorganic halogen concentration in the upper troposphere (UT), this may lead to ozone depletion in that region. The question then arises if this depletion should be added to the ODP value, which traditionally refers only to depletion in the stratosphere. It also points to the need to evaluate the role of halogen chemistry in the UT.

Transport from the Boundary Layer to the Stratosphere

- The most efficient route for irreversible transport of VSL source gases and their degradation products from the surface to the stratosphere is in the tropics, because the vertical transport times from the surface to the upper troposphere are short, and air that enters the stratosphere through the tropical tropopause remains there for more than a year.
- In the tropics, the transition from tropospheric to stratospheric air takes place in a “tropical tropopause layer” (TTL) between the secondary tropical tropopause (STT, 11-13 km) and the thermal tropical tropopause (TTT, 16-17 km). Transport of VSL source gases and degradation products from the surface to the UT and the lower part of the TTL is primarily through convection. From the TTL, a small fraction of the air enters the stratosphere via slow ascent through the tropical tropopause or via isentropic transport into the extratropical lower stratosphere.
- Current estimates indicate that air at the base of the TTL is replaced by convection from the tropical boundary layer on a time scale of 10-30 days. Thus, a significant fraction of the emitted VSL source gases can be expected to reach the TTL in regions of deep convection.
- In the extratropics, exchange across the tropopause maintains a “transition layer” of 1-2 km with chemical characteristics intermediate between those of the UT and LS (lower stratosphere). Frontal lifting can transport air on time scales of a few days to the UT or even occasionally into the LS. Through such mechanisms, VSL source gases are expected to enter the transition layer.

VERY SHORT-LIVED SUBSTANCES

Chemistry for VSL Halogens

- Inorganic chlorine, bromine, and iodine have the potential to destroy stratospheric ozone. For the same concentration in the stratosphere, iodine is most efficient in removing ozone, followed by bromine and chlorine. Laboratory data on iodine stratospheric chemistry have led to downward revision of the iodine efficiency in depleting ozone in the stratosphere. The estimated efficiency factor relative to chlorine (~150-300) is still higher than that of bromine (~45).
- The main uncertainties in estimating the impact of VSL halogen source gases on stratospheric ozone lie in the physical and dynamical processes transporting halogen into the stratosphere and the behavior of their intermediate degradation products; uncertainties in the gas-phase chemistry of the source gases are minor.
- The products expected from many of the bromine and iodine VSL source gases considered in this chapter are all rapidly converted to inorganic halogen. The inorganic halogen multiphase chemistry for bromine and iodine is not very well known. Heterogeneous processes that recycle reservoir species to reactive inorganic bromine and iodine may significantly increase the efficiency of halogen injection (via the PGI pathway) into the stratosphere.
- The odd-hydrogen (HO_x) chemistry in the upper troposphere is very critical both for the destruction/production of ozone and for the delivery of VSL source gases to the stratosphere. The understanding of this chemistry requires a better knowledge of the sources and processes for the oxygenated organics (carbonyl compounds, peroxides, etc.) and for the nitrogen oxides (NO_x) and total reactive nitrogen (NO_y) species.

VSL Halogen Source Gases in the Present-Day Atmosphere

- The observed concentrations of VSL halogen source gases are typically a few parts per trillion (ppt) for bromine and iodine VSL source gases, and up to 20 ppt for VSL chlorine source gases. The majority of these gases are of natural origin.
- Two model studies simulated the atmospheric distribution of bromoform (CHBr_3) assuming a simplified uniform (space and time) ocean source. The calculated atmospheric distributions indicate that an average surface mixing ratio of 1.5 ppt at the surface could maintain about 1 ppt of inorganic bromine in the stratosphere. The simulation shows that one-half to three-fourths of the bromine enters the stratosphere in the form of inorganic products. These results can be used as a guideline for estimating contributions from other source gases that have local photochemical lifetimes of about 10 days, no long-lived intermediate degradation product, and relatively uniform sources over the globe.
- Very short-lived bromine and iodine source gases with surface concentrations of a few ppt could have large effects on the current inorganic bromine and odd-iodine budget because the stratospheric concentrations of inorganic bromine and iodine are about 20 ppt and less than 1 ppt, respectively. The transfer of inorganic bromine from the UT may account for the current discrepancy in the stratospheric inorganic bromine budget (as discussed in this chapter and in Chapters 3 and 4).

Modeling Studies to Determine Values for the ODP of n-Propyl Bromide

- n-propyl bromide (n-PB; $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$) is removed by reaction with OH, with local photochemical lifetimes in the tropical troposphere of about 10-20 days. Laboratory data indicate that its degradation products, and particularly bromoacetone, have lifetimes shorter than a day.
- Given the complexity of atmospheric processes, three-dimensional numerical models are the preferred tool to evaluate the ODP for VSL source gases. Results for n-PB from three separate model studies that computed $\text{ODP}(\text{n-PB}, \bar{x}_e, t_e)$ were assessed. These results can be used as a guideline for other gases with similar local photochemical lifetimes (~10 days) and degradation schemes.

- Two of the three studies provided values only for $ODP_{SGI}(n\text{-PB}, \bar{x}_e, t_e)$. In the third study, which computed contributions from $ODP_{PGI}(n\text{-PB}, \bar{x}_e, t_e)$, the values of $ODP(n\text{-PB}, \bar{x}_e, t_e)$ are 0.04 for uniform emission over land. In this case, 0.5% of the bromine emitted as n-PB reaches the stratosphere, with about two-thirds entering in the form of degradation products. The model simulations also give 0.1 for tropical emission and 0.02-0.03 for emissions restricted to Northern midlatitudes.

VSL Sulfur Species and Stratospheric Sulfate

- A sulfur (S) source of 0.06-0.15 Tg (S) yr⁻¹ is needed to maintain the observed burden of the background stratospheric sulfate layer during periods with low volcanic activity. Current model estimates indicate that degradation of carbonyl sulfide (OCS) in the stratosphere can account for 20-50% of the needed source, with the balance from transport of sulfur VSL gases (dimethyl sulfide (DMS; CH₃SCH₃), hydrogen sulfide (H₂S), sulfur dioxide (SO₂)) and sulfate formed in the troposphere.
- Our current best estimates for the surface sources of sulfur are 10-30 Tg (S) yr⁻¹ for DMS, 1-2 Tg (S) yr⁻¹ for OCS, 0.5-1.5 Tg (S) yr⁻¹ for CS₂, 6-9 Tg (S) yr⁻¹ for H₂S, and 67-100 Tg (S) yr⁻¹ for SO₂. Emission from aircraft engines provides a source of 0.06 Tg (S) yr⁻¹ in the upper troposphere and lower stratosphere.
- Model simulations show that a few tenths of one percent of the SO₂ emitted at the ground reaches the stratosphere. This is consistent with estimates for VSL halogen source gases. For DMS, multiphase oxidation may occur and reduce its possible transfer to the UT.
- Previous climate calculations assumed that the change in stratospheric sulfate loading is proportional to changes in total SO₂ emission. Changes in the spatial distribution of the emission can have a large effect. Depending on how much of the sulfur gas is converted to small sulfate particles in the UT, the change in surface area per unit mass of sulfur transferred to the stratosphere could differ.

Model Evaluations

- In order to evaluate the contribution of VSL source gases to halogen and sulfur loading, global 3-D model simulations are required. Simulating aerosol microphysics in the troposphere with very short time constants in global-scale models presents a large challenge. Significant uncertainties exist in the treatment of dynamical and physical loss processes in such models.
- Further evaluation of model performance against observations is necessary, particularly relating to rapid transport processes and treatments of cloud scavenging. Various tracers can be used to test specific components: radon-222 and short-lived hydrocarbons for continental convection; methyl iodide, dimethylsulfide, and ozone for marine convection; lead and beryllium isotopes, and soluble gases for precipitation scavenging; and ozone for stratosphere-troposphere exchange.

2.1 INTRODUCTION

An important component of previous Assessments (e.g., WMO, 1999, 1995) is the discussion of the observed concentrations, budgets, trends, and atmospheric lifetimes of source gases that affect stratospheric ozone. These gases are mostly emitted at the surface. The source gas and its degradation products are transported to the stratosphere, where they could affect the ozone abundance. Examples of these include nitrogen species from nitrous oxide (N_2O); chlorine, bromine, and iodine species from organic halogen-containing chemicals; and methane (CH_4) reacting to produce water vapor in the stratosphere. Sulfur species found in the troposphere (e.g., carbonyl sulfide (OCS), carbon disulfide (CS_2), hydrogen sulfide (H_2S), dimethyl sulfide (DMS , CH_3SCH_3), sulfur dioxide (SO_2)) provide the source of sulfur to maintain the stratospheric sulfate layer. The sulfate aerosol particles provide sites for heterogeneous reactions that control the partitioning of the nitrogen and halogen radicals. One aim of the Assessments is to establish the tools that enable one to predict how changes in emissions of the various source gases would affect ozone. In the case of the halogen species, it is done in terms of the equivalent chlorine concentration estimated from emissions and lifetimes. A similar connection could be made for the sulfur source gases if one could predict how the stratospheric sulfate may change in response to changes in emissions. In this chapter, we restrict the discussion to halocarbons and the sulfur gases. Other species with similar lifetimes are affected by many of the same processes discussed in this chapter. One example is oxides of nitrogen released at the ground (from combustion and biomass burning) and produced in the free troposphere (by lightning or aircraft engines). They are not included in this chapter.

The purpose of this chapter is to discuss how very short-lived (VSL, defined later in this section) substances released at the surface or produced in situ in the troposphere could affect ozone in the stratosphere. Because the subject is relatively new, this chapter will deviate from the standard approach of providing a detailed review and assessment of the information in the published literature. The current state of our understanding does not provide concrete evaluations to assess the merit of the approaches and make recommendations for specific values, e.g., of Ozone Depletion Potentials (ODPs). Instead, the chapter focuses on outlining viable approaches with emphasis on how observations may be used in future evaluations. If certain simplifying assumptions are made, order-of-magnitude estimates for some of the parameters can be provided so that policymakers can start to consider how best to approach the problem. The emphasis of the chapter is on the issues needed to be resolved and the observations needed for evaluation.

In the discussion, it is often convenient to distinguish among the different forms in which the halogen atoms and sulfur atoms are transported to the stratosphere. Halogen atoms bound in the source gases and the intermediate degradation products are referred to here as organic halogen. The final products are referred to as inorganic halogen; these include, in the case of chlorine, the reservoir species (hydrogen chloride (HCl), chlorine nitrate (ClONO_2), hypochlorous acid (HOCl)) and the radical species (atomic chlorine (Cl), chlorine monoxide (ClO)). For sulfur, an analogous approach would identify OCS , CS_2 , H_2S , and DMS as source gases, and SO_2 and various forms of sulfate (SO_4) in gaseous, liquid, or solid form as the final product. As seen in Section 2.6, this turns out not to be desirable, because SO_2 and SO_4 are also released at the surface. We will refer to a sulfur species as sulfate or sulfate precursor in the discussion.

A major goal in the study of halogen source gases has been to track the life cycle of a source gas so that one can evaluate how its emission may affect the inorganic halogen budget in the present-day stratosphere. This is accomplished by combining the amount of the source gas emitted at the surface with the percentage of the emitted halogen atoms that is delivered to the stratosphere. It is important to provide values for the latter because it allows one to define the relative ODP of an individual source gas. Traditional methods for evaluating the contribution of organic halogen source gases with lifetimes of 1 year or longer have been reviewed and assessed in previous Assessments (e.g., WMO, 1995, 1999). However, such methods cannot be applied to VSL species. To understand why, we examine the processes that deliver the final products to the stratosphere. For ease of discussion, we will present the arguments in the context of the halogen species. It should be noted that many of the ideas are equally applicable to the sulfur species.

Figure 2-1 illustrates that there are two pathways for delivering the final products to the stratosphere. For the source gas injection (SGI) pathway, the source gas is transported to the stratosphere and then reacts to release the halogen atoms. For a given emission location and time, its efficiency depends mostly on the properties of the source gas (essentially its removal rate by chemical or physical processes in the troposphere as compared with the transport rate from the ground to the stratosphere). The product gas injection (PGI) pathway involves transport to the stratosphere of intermediate or final products produced in the troposphere. Its efficiency depends also on the properties of the degradation products.

To put things in perspective, we provide some rough numerical estimates for the two pathways for long-lived source gases that have uniform mixing ratios in the

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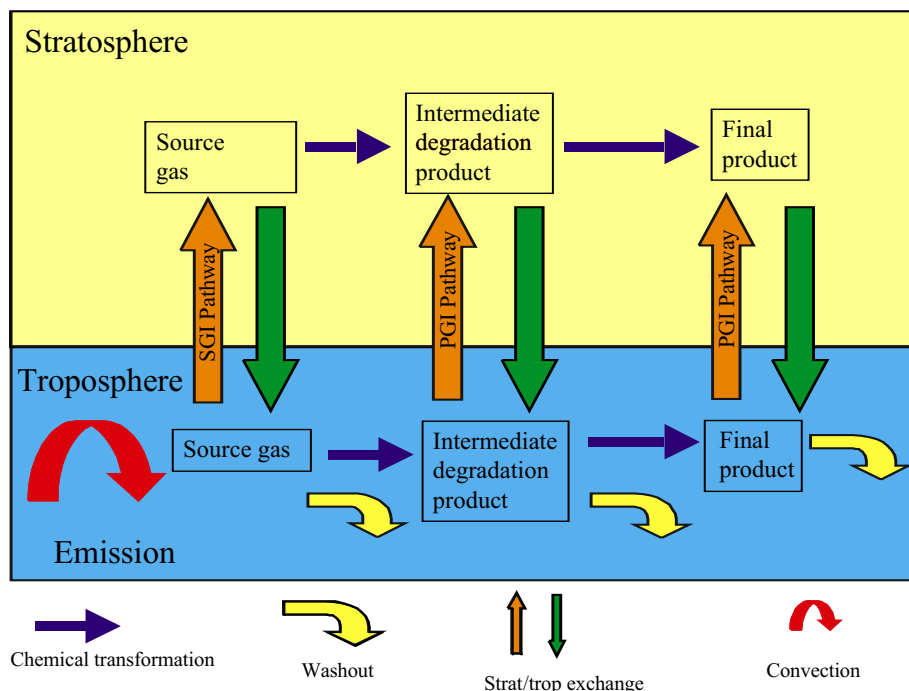


Figure 2-1. Schematic diagram showing the two pathways through which a source gas released at the surface delivers its degradation products to the stratosphere. The orange arrows and green arrows represent transport into and out of the stratosphere, respectively. The two pathways are labeled SGI for source gas injection and PGI for product gas injection.

troposphere. Long-lived source gases that are inert in the troposphere (most chlorofluorocarbons) are recycled between the troposphere and stratosphere until they are all removed via photochemical reactions in the stratosphere. Thus, 100% of the final product is delivered to the stratosphere via the SGI pathway. For long-lived source gases that are removed efficiently in the troposphere (most hydrogenated chlorofluorocarbons), at least 90% of the mass burden is found in the troposphere at steady state. If we assume that the local lifetimes in the troposphere and stratosphere are similar, this would imply that 90% of the final product is released in the troposphere. Thus, only 10% is delivered to the stratosphere via the SGI pathway. If one assumes that less than 1% of the degradation products (in the form of intermediate degradation products or inorganic halogen) released in the troposphere is transported to the stratosphere, then the supply from the PGI pathway (0.009 of emission) is a factor of 10 smaller than from the SGI pathway (0.1 of emission). This is why the contribution from the PGI pathway is usually ignored in considering the long-lived source gases.

We now explain the criteria for classifying a substance as VSL, as distinct from those discussed in Chapter 1 of this report. The established method for estimating inorganic halogen loading from the SGI pathway depends on the observed fact that the mixing ratio of the long-lived source gas is essentially uniform in the troposphere. [Note that the key issue is the difference in mixing ratio between

the boundary layer (BL) and the upper troposphere (UT). A small interhemispheric difference (~20%) in the BL will not affect the accuracy.] In these cases, the fraction of the emitted halogen atoms entering the stratosphere is independent of the location and time of emission. The inorganic halogen loading in the stratosphere can be estimated from the steady-state burden of the source gas, which is related to its atmospheric lifetime. Details of the transport processes in the troposphere play no role. As the local lifetime of the source gas gets shorter, its mixing ratio will no longer be uniform in the troposphere. The method used for long-lived species is no longer accurate when the mixing ratio in the UT is less than half of the mixing ratio in the BL. A survey of chemicals in the atmosphere indicates that this occurs when the local lifetime (inverse of the local removal rate) is 0.5 years or shorter. This will serve as the criteria for identifying VSL species.

The fraction of the emitted halogen atoms that are transported to the stratosphere via the PGI pathway depends on the properties of the intermediate and final products as well. Consider first the situation where the intermediate products are so short lived that, for practical purposes, the inorganic halogen species can be treated as being produced by the initial reaction experienced by the source gas. Many of the inorganic halogen species are water soluble or will react in solution to form water-soluble products. They are removed efficiently in the lower troposphere, with a local residence time of about 10 days.

In order for the PGI pathway to provide an effective source to the stratosphere, the products should be produced at least as fast as the washout rate (Ko et al., 1997). Thus, the PGI pathway will be important if the local photochemical lifetime of the source gas is of the order of 10 days or shorter.

The properties of the intermediate products could change the estimate in a significant way. If the intermediate products are long lived in the troposphere (i.e., with a photochemical lifetime longer than the source gas or the washout lifetime of the inorganic halogen), they could serve as a vehicle for transporting halogen atoms to the stratosphere and deliver much more of the degradation products via the PGI pathway. An example of an intermediate product having lifetime longer than the source gas is phosgene (COCl_2) formed from degradation of trichloroethene (C_2HCl_3). At the same time, if the local photochemical lifetimes of the intermediate products in the stratosphere are longer than their residence times in the stratosphere, they may be removed from the stratosphere before they release their halogen atoms. This will effectively decrease the efficiency of the SGI pathway (see Kindler et al., 1995).

Many of the same issues apply to the VSL sulfate precursor gases and how their fates in the troposphere would affect the stratospheric aerosol layer. In addition to the release of source gases at the surface, there is a direct way of injecting sulfur species into the stratosphere through explosive volcanic eruptions. In this chapter, we will briefly review the effects of volcanoes, building on work from the previous Assessment (Godin and Poole et al., 1999). The major emphasis here is on the role of the VSL precursor gases.

The structure of this chapter is as follows. Section 2.2 discusses the transport mechanisms in the troposphere and cross-tropopause exchange, and the chemical environment in the upper troposphere. Section 2.3 describes the removal mechanisms of the VSL halogen source gases and their degradation products. It also includes a brief discussion of the ozone removal efficiency of iodine in the stratosphere. Section 2.4 discusses how VSL halogen source gases may contribute to the inorganic halogen budget in the current stratosphere. The observations for these source gases are reviewed, with emphasis on our understanding of the budgets. Section 2.5 focuses on the issue of evaluating the inorganic halogen loading estimates and ozone depletion estimates of VSL halogen source gases. In addition to natural species, the discussion includes industrial species and the information that is needed on emission inventories to estimate their impact. Finally, Section 2.6 discusses the effects of sulfur-containing VSL gases and how they affect future trends in the stratospheric sulfate layer.

2.2 DYNAMICAL AND CHEMICAL CHARACTERISTICS OF THE UPPER TROPOSPHERE (UT) AND THE TROPICAL TROPOPAUSE LAYER (TTL)

The critical parameters for understanding the processes that control fluxes of key trace gases from the troposphere to the stratosphere are the mixing ratios of the trace gases in the upper troposphere (UT) and in the tropical tropopause layer (TTL) and the transport rates across the tropopause. We employ the following definitions in this chapter: the UT is the region from about 8-12 km, which is capped by the tropopause in the extratropics, and which overlaps with the lowest part (~1 km) of the TTL in the tropics. The TTL is bounded above by the thermal tropical tropopause (TTT; defined here as the cold point of the sounding) at about 16-17 km, and bounded below by a secondary tropical tropopause (STT) at 11-13 km. The STT is related to large-scale circulation in that it corresponds to the maximum Hadley-cell outflow (Highwood and Hoskins, 1998). At these levels, convection is no longer able to maintain a moist adiabatic temperature lapse rate, owing to the rapid decreases with height of the cumulus mass flux, and IR radiative cooling. Within the TTL there is a gradual transition from tropospheric to stratospheric dynamical and chemical characteristics. However, the rapid decrease with height of the convective outflow, and the rapid transition from clear-sky radiative cooling to radiative heating, combine to make the transition at the TTT fairly sharp (see, e.g., Folkins et al., 1999; Hartmann et al., 2001; Jensen et al., 2001; Thuburn and Craig, 2000). The TTL is a relatively new concept, and its nature and regional variations are still under investigation. The concentrations of trace gases in the UT and TTL are controlled by transport, physical and chemical removal processes in the troposphere and lower stratosphere, and the location and timing of emissions.

We consider two broad classes of transport mechanisms, illustrated in Figure 2-2. The first is deep moist convection, which transports air rapidly from the boundary layer to the UT, with a fraction detraining well into the TTL and some directly into the stratosphere. The second is large-scale stratosphere-troposphere exchange (STE), which transports air from the TTL upward into the stratospheric overworld, and laterally into the extratropical lower stratosphere. In addition, this section includes a discussion of extratropical STE, the chemical environment in the UT and TTL, and a survey of the database of observations that are needed to critically evaluate the results of models.

The numerical simulation of very short-lived substances is difficult because of the wide range of scales on

Chemical and Transport Processes Affecting VSLS

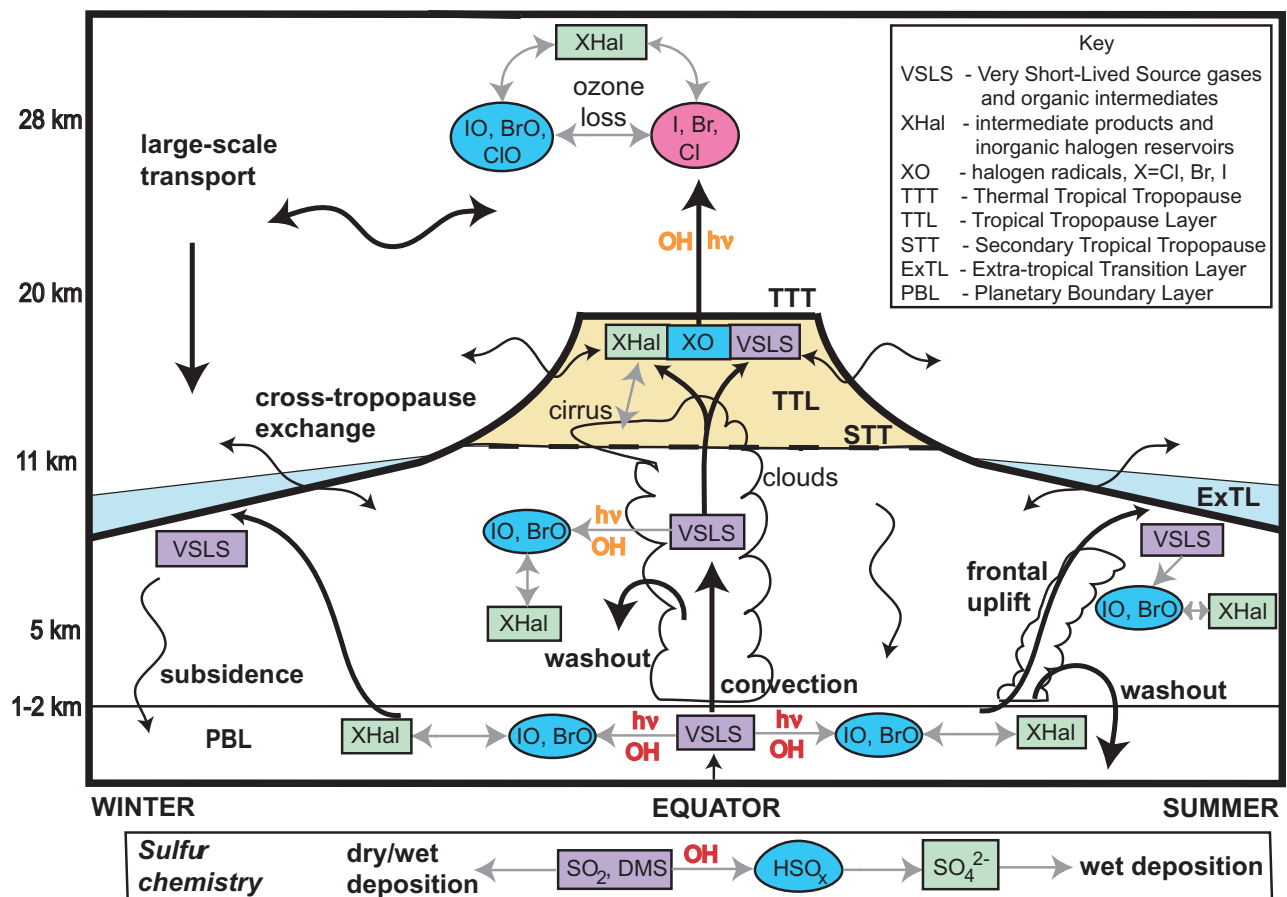


Figure 2-2. Chemical and dynamical processes affecting VSL substances in the troposphere and stratosphere. Figure courtesy of K.S. Law, R.A. Cox, and P.H. Haynes, Cambridge University, U.K.

which relevant processes occur, ranging from microphysical (uptake of gases in cloud droplets) to synoptic and global (advection). Global models are hindered by their coarse spatial and temporal resolutions (which are typically at best of the order of 100 km in the horizontal, 0.5 km in the vertical in the free troposphere and 0.1 km in the BL, and 10 minutes in time). This results in the need for “parameterizations” of important subgrid-scale processes. Regional models are able to resolve small-scale processes better, but their limited spatial domain requires the specification of boundary conditions, which makes it difficult to extrapolate to global-scale estimates. In one comparison of simulated results from global tropospheric chemistry transport models with ozone (O_3) data from the Measurement of Ozone and Water Vapor by Airbus In-service Aircraft (MOZAIC) program, it was found that the models generally smeared out observed gradients, that they performed less well in regions where meteorological analyses, used as input, are expected to be

less reliable, and that higher resolution seemed more important than an extensive hydrocarbon chemistry scheme for the quality of the simulated upper tropospheric O_3 (Law et al., 2000).

2.2.1 Moist Convection and the Tropical Tropopause Layer

Moist convection is characterized by rapid updrafts (driven by latent heat release from condensing water) with sustained velocities of up to several meters per second over regions of the order of a kilometer in diameter. The updrafts are balanced by downdrafts (largely driven by evaporating precipitation) with a similar spatial extent, and by large-scale subsidence over a much larger area where clear-sky radiative cooling occurs. In the UT (particularly the tropics), where moist convective adjustment holds, trace gases are strongly influenced by rapid upward transport within convective clouds and slow descent out-

side convectively active regions, and nearly all air parcels have had recent contact with the tropical boundary layer. Convective clouds are often associated with the formation of precipitation (rain, snow, and graupel) and anvil cirrus clouds. This leads to efficient scavenging of soluble gases by precipitation where convection is active.

Convective events are highly stochastic. An individual cloud can transport air parcels (thermals) from the BL to the UT in less than an hour. However, the actual concentration of the source gases and degradation products in the UT and TTL depends on how quickly they are evacuated from the BL, how often thermals reach and penetrate the UT and the TTL, and how much old air from the midtroposphere (which has much smaller concentrations of the source gas) is entrained into the convective cores.

An estimate for the mean evacuation time for the BL in the tropics can be obtained using relatively well-defined values for the Hadley cell circulation and the clear-sky radiative cooling. The observed annual mean mass flux from the boundary layer in the Hadley circulation between 15°N and 15°S is about $10^{11} \text{ kg s}^{-1}$ (Hartmann, 1994). This, however, is the net mass flux arising from the difference between the upward flux in convection and the clear-sky subsidence. The clear-sky radiative cooling rate in the tropical lower troposphere is $\sim 1.6 \text{ K day}^{-1}$ (e.g., Hartmann et al., 2001). Because convective disturbances cover less than 10% of the tropics, the above cooling rate implies a downward mass flux between 15°N and 15°S of about $2.0 \times 10^{11} \text{ kg s}^{-1}$ (assuming descent along a dry adiabat). Thus the upward flux from the boundary layer in convection must be about $3.0 \times 10^{11} \text{ kg s}^{-1}$. Assuming that the BL has a 100-hPa depth, then the mass between 15°N and 15°S is about $1.3 \times 10^{17} \text{ kg}$. The upward flux from the BL then implies an evacuation time of about 5 days if one assumes that the material is taken from the whole BL rather than just from the top of the BL. On the basis of a 3-D general circulation model simulation, Prather and Jacob (1997) estimated a mean evacuation rate of the 130-hPa-deep BL in the tropics of $18\% \text{ day}^{-1}$ (see the GISS results in Figure 2-3), which implies an e-folding removal time of 5.5 days, consistent with the above estimate. This estimate is at the low end of the 5-10 day estimate made in Kley et al. (1996) based on data from a different general circulation model, and is slightly longer than the estimate of 4 days made by Cotton et al. (1995). The actual evacuation rate will vary regionally, depending on the strength and frequency of convective events.

The GISS model results in Figure 2-3 show that the magnitude of the mass flux across the STT ($1.4 \text{ g m}^{-2} \text{ s}^{-1}$) is about half that of the mass flux out the BL ($2.8 \text{ g m}^{-2} \text{ s}^{-1}$). As indicated above, the latter mass flux implies a

replacement time for the BL of about 5 days. Since the TTL and BL have similar depths of about 100 hPa, the average replacement time for the whole TTL by air crossing the STT should be of the order of 10 days. However, the replacement time is not uniform with altitude. Much of the detrainment in the UT and TTL occurs near the STT, and within the TTL the mass flux decreases rapidly with height, but the precise height dependence has not yet been reliably determined. The local replacement time (defined as the replacement time of a layer of air by detrainment from convective clouds) can be estimated by assuming that the upward mass flux from convection is balanced by the clear-sky subsidence. Folkins et al. (2002) used this method to obtain replacement times of 5 days near the STT, and 100 days at 16 km. An alternative estimate can be obtained by using measured profiles of CO and O₃ (Dessler, 2002), yielding 10-30 days for the lower TTL and 50-90 days for the upper TTL. It is difficult to quantify the uncertainty in these estimates at present, but it is likely that global models with different contemporary convection parameterizations could produce numbers that differ by at least a factor of 2.

The replacement time can be used to estimate how much additional chemical transformation has occurred for the VSL species in air parcels since they have left the BL. The actual concentration of the species will depend also on the entrainment of old air as the convective column ascends the free troposphere. If the BL air has been diluted by 50% during the ascent, the replacement time for the TTL by BL air will be a factor of 2 larger than the estimates cited above. Cloud-resolving model simulations (Lu et al., 2000) indicate that only a very small amount of tracers that are produced in situ in the middle troposphere are entrained into the updrafts, but instead are forced aside and downward due to rising thermals. The wealth of literature on studies using cloud-resolving models (e.g., Lu et al., 2000; Redelsperger et al., 2000; Bechtold et al., 2000) reveals the immense complexity of transport in cumulus clouds and the difficulties of representing this in large-scale models.

The general transport characteristics of convection have also been studied using idealized tracers in a 3-D global chemistry-transport model, with a fixed uniform mixing ratio at the surface and a specified local decay rate (Crutzen and Lawrence, 2000). It was found that an insoluble gas with a lifetime of 30 days was 40-50% as abundant in the tropical UT as at the surface, whereas with a lifetime of 10 days the tropical UT abundance was 25-30% of the surface mixing ratio (see Figure 2-4). Lower values were computed in the UT outside the tropics: 25-35% and 10-15% for the 30- and 10-day lifetime tracers, respectively. As discussed above, these estimates depend

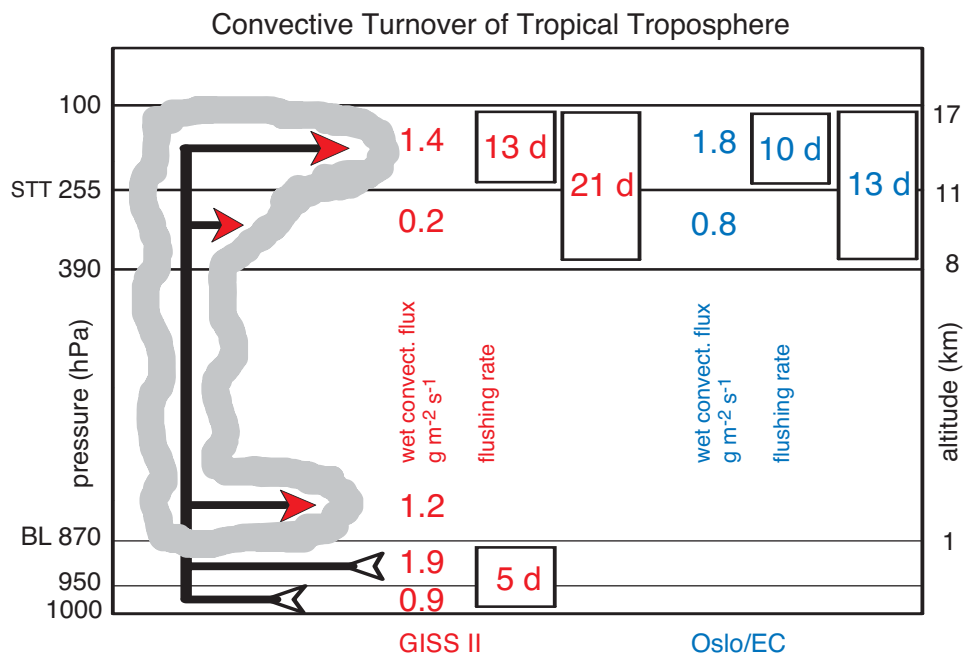


Figure 2-3. Convective turnover rates in the tropical troposphere. The results are from two models, GISS II (Goddard Institute for Space Studies), using winds generated by a general circulation model, and the Oslo CTM, driven by European Centre for Medium-Range Weather Forecasts (ECMWF) winds; based on Prather and Jacob (1997). The gray shaded outline provides a schematic representation of the structure of the convective cloud. The arrows represent entrainment fluxes (lower two arrows) and detrainment fluxes (top three arrows). The average convective mass fluxes (in $\text{g m}^{-2} \text{s}^{-1}$) and the implied turnover time constant (inverse of turnover rate; in days) of the reservoirs are given for each model (in red for the GISS II model and in blue for the Oslo model). The column mass densities in each reservoir are: $1.3 \times 10^6 \text{ g m}^{-2}$ for the boundary layer between 870 and 1000 hPa; $1.4 \times 10^6 \text{ g m}^{-2}$ for the upper troposphere located between 390 and 255 hPa; and $1.6 \times 10^6 \text{ g m}^{-2}$ for the tropical tropopause layer located between 255 and 100 hPa. The values from the GISS II model are calculated for the region between 12°S and 12°N for May-August conditions, whereas those for the Oslo model are for 22°S - 22°N for January-December 1997. Figure courtesy of M. Prather, University of California-Irvine, U.S.

strongly on the respective model formulations, and thus could differ significantly from the results obtained with other models. Such modeling studies, unfortunately, are rarely repeated once the first ones have been published.

The situation is even more complex for soluble gases because of the variable relationship between updraft mass flux and the amount of precipitation. Crutzen and Lawrence (2000) also examined this issue using idealized soluble tracers. Compared with the calculated concentration of an insoluble gas, they found that about 15%, 50%, and 85% of gases with Henry's Law solubility constants of 10^3 , 10^4 , and 10^5 M atm^{-1} , respectively, were scavenged by precipitation before they reached the UT (see Figure 2-5). This result was nearly independent of season, geographical location, and the decay rate applied to the tracers, but was strongly dependent on the assumptions made about whether tracers were rejected from, retained

in, or additionally scavenged by ice, snow, and graupel. Similar studies using cloud-resolving models (Barth et al., 2001; Yin et al., 2001) have also indicated that it is important to consider kinetic limitations to trace gas uptake in precipitation, because assuming Henry's Law equilibrium, as is generally done for the long time steps of global models, will lead to an overestimate of the amount of gases that can be taken up into precipitation, and thus to the scavenging loss of highly soluble gases. A promising approach for future studies is the use of observations of peroxides with various solubilities together with insoluble tracers like CO to test parameterizations of convective scavenging (e.g., Mari et al., 2000). At present it is difficult to apply these results to inorganic halogenated species because of a lack of observations, combined with the fact that they are also produced in situ in the UT and can have highly variable mixing ratios at the ground.

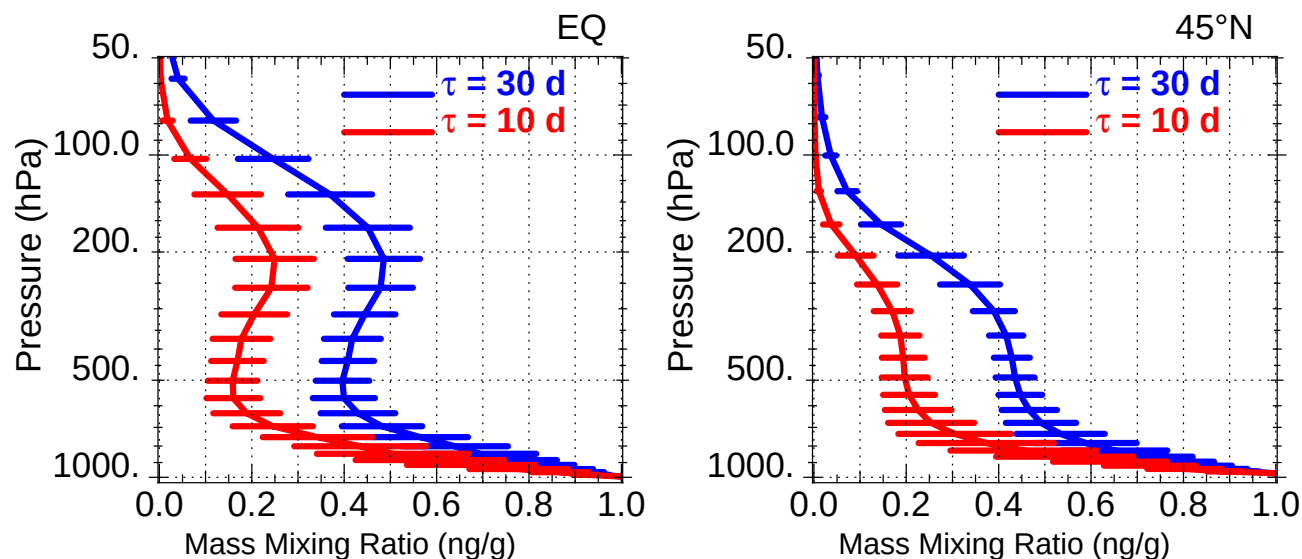


Figure 2-4. Zonal mean vertical profiles of surface tracers at the equator and 45°N, plus the standard deviation around the respective latitude bands (horizontal bars), for insoluble tracers with decay lifetimes (τ) of 30 and 10 days; computed with the Model of Atmospheric Transport and Chemistry–Max-Planck-Institute for Chemistry (MATCH-MPIC) for July 1993. Based on Crutzen and Lawrence (2000).

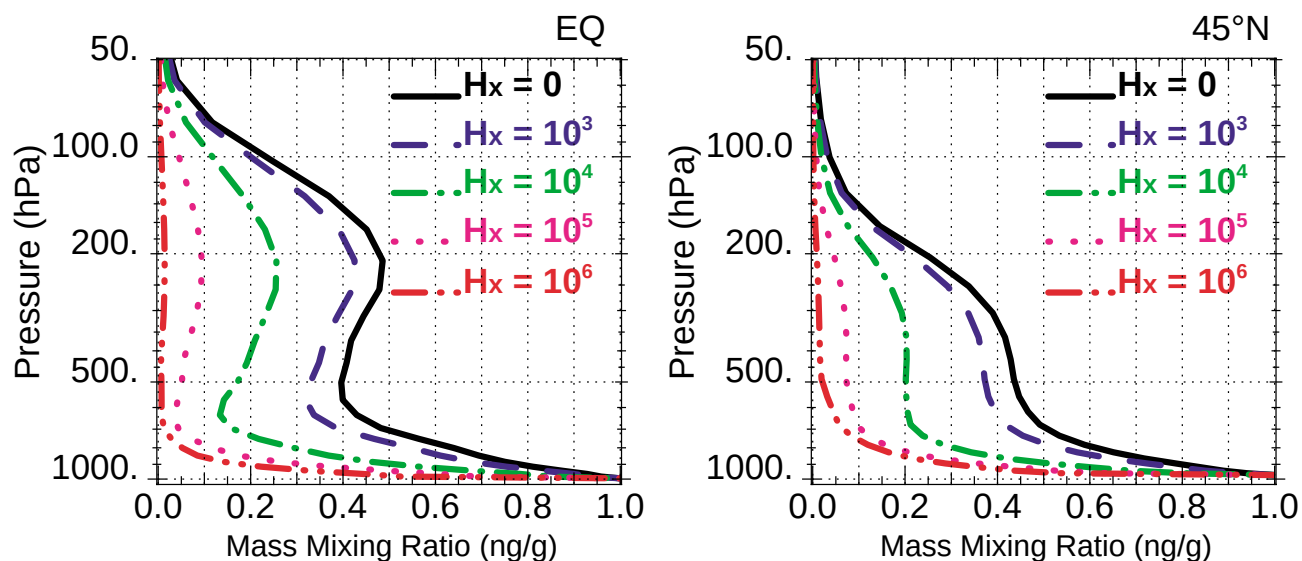


Figure 2-5. Zonal mean vertical profiles of surface tracers at the equator and 45°N for tracers with decay lifetimes of 30 days and Henry's Law solubilities varying from $H_x = 0$ to $H_x = 10^6 \text{ M atm}^{-1}$ (insoluble to highly soluble); computed with MATCH-MPIC for July, 1993. Based on Crutzen and Lawrence (2000).

Although this section has focused on the role of deep convection, it is important to note that other processes can also contribute significantly to the transport of air parcels from the BL into the mid- and upper troposphere, especially in the extratropics. In particular, recent attention has been given to forced uplift associated with synoptic-scale frontal systems, which may be the pri-

mary mode of vertical transport in many regions of the extratropics (Stohl, 2001; Zahn, 2001; Kowol-Santen et al., 2001). Because frontal lifting is also associated with clouds and precipitation, similar uncertainties for the scavenging of soluble gases as discussed above will apply. The issue of frontal lifting is likely to see considerable progress prior to the next Assessment. Other processes,

VERY SHORT-LIVED SUBSTANCES

such as variations in the BL height in association with non-zero large-scale vertical velocities, as well as topographical effects, can also contribute to the evacuation of the BL.

2.2.2 Stratosphere-Troposphere Exchange

Most air arriving in the lower stratosphere passes through the tropical tropopause (e.g., Holton et al., 1995), although net transport of chemical constituents across the subtropical and extratropical tropopauses is also known to take place. Because the net large-scale motion is upward in the tropical lower stratosphere and downward in the extratropical lower stratosphere, air entering the lower stratosphere via the tropical tropopause is believed to have a larger residence time (>1 year) in the stratosphere. The precise mechanisms of the cross-tropopause transport and their consequences for short-lived substances are still controversial. Furthermore, it is also important to know the form of halogenated gases in the UT, because soluble gases are subject to removal from the UT by precipitation (as discussed in the previous section), as well as by slower sedimentation of cirrus ice (Lawrence and Crutzen, 1998), both of which can occur at rates that can compete with the residence time of gases in the TTL. In this section, we discuss how one may obtain estimates of the flux across the tropopause by examining the mixing ratios of the species near the tropopause and the mass flux across the tropopause.

2.2.2.1 EXCHANGE ACROSS THE TROPICAL TROPOPAUSE

The transition from air having compositions typical of the troposphere to air typical of the stratosphere does not occur abruptly across the tropical tropopause (TT). Above the level where the clear-sky mass flux is mostly upward, air parcels are rising slowly into the stratosphere, driven by the Brewer-Dobson circulation (speed of order $30\text{--}50\text{ m day}^{-1}$). However, some deep convection penetrates deep into the TTL, and a small fraction of the air leaving the boundary layer (about 0.1%, based on Gettelman et al., 2002) is directly lofted across the TT. Thus, a small fraction of the air encountered directly above and below the TT may have a distinct “BL character.” At the same time, convective overshooting and breaking waves can mix material back downward (Fujiwara et al., 1998; Sherwood and Dessler, 2001), and therefore not all the air in the TTL is transported irreversibly into the stratosphere. Notably, the radiative properties of the TTL are sensitive to the stratospheric O_3 distribution (Thuburn and Craig, 2000), which is in turn sensitive to the transport of constituents through the TTL.

It is also likely that some of the air in the TTL has a stratospheric origin, entering via lateral mixing from the extratropical stratosphere (Figure 2-2). A 20-yr climatology of intrusions from the extratropics into the tropics (Vaugh and Polvani, 2000) showed that Rossby wave-breaking events can result in transport of tongues of extratropical air deep into the tropics, and a more detailed look at four Rossby wave-breaking events (Scott et al., 2001) was used to “infer a potentially significant contribution to the global stratosphere-troposphere exchange from the wave-breaking processes.” Studies of mixing in the other direction also help give an indication of the time scales for two-way mixing, which can be comparable with convective time scales. For example, Dethof et al. (2000) reported a contour advection study using European Centre for Medium-Range Weather Forecasts (ECMWF) water vapor fields, in which they found that the isentropic transport of water vapor into the extratropical lower stratosphere is similar in magnitude to upward transport in tropical regions. Furthermore, the work of Strahan et al. (1998) also showed evidence of such isentropic transport based on the seasonal cycle of carbon dioxide simulated in a global chemical transport model.

Finally, according to Rosenlof and Holton (1993), the annual flux across the 100-hPa surface (i.e., TT) in the 15°N and 15°S latitude range is $8.5 \times 10^9\text{ kg s}^{-1}$. Because this is only $\sim 3\%$ of the flux of air out of the tropical BL computed above (Section 2.2.1), the vast majority of the air parcels in deep convection are circulated back down into the free troposphere to eventually re-enter the BL, or are transported isentropically into the extratropical lower stratosphere. A quantification of these fractions is not yet possible.

2.2.2.2 EXCHANGE ACROSS THE EXTRATROPICAL TROPOPAUSE

Exchange of air across the extratropical tropopause is accomplished by processes on a large range of temporal and spatial scales. Although the net (downward) mass exchange rates are controlled by global-scale processes as part of the Brewer-Dobson circulation (Holton et al., 1995), two-way exchange occurs on synoptic and sub-synoptic scales and may have important consequences for chemical species. Synoptic-scale frontal systems and to a lesser extent midlatitude deep convection frequently bring constituents from the boundary layer to the upper troposphere, leading to strong chemical contrasts across the tropopause. These processes may also transport trace constituents, including VSL substances, their degradation products and inorganic halogen into the lowermost stratosphere.

Previous analysis of observed and modeled carbon dioxide (CO_2) levels (Bolin and Bischof, 1970; Strahan et

al., 1998) suggested that there is not a large degree of communication between the UT and lower stratosphere (LS) in midlatitudes because of a clear separation in the seasonal cycle in these different regions. It was postulated that this is due to the bulk of air in the lower extratropical stratosphere originating either through the tropical stratosphere or possibly via lateral transport from the TTL. Analysis of CO₂ data from the Earth Resources (ER-2) high-altitude research aircraft (Hintsa et al., 1998) at 40°N also indicated that most of the air in the lower stratosphere must have entered laterally from the subtropics or tropics. However, there was also evidence that air entered the lower stratosphere directly from the midlatitude upper troposphere in conjunction with mixing processes near the tropopause.

Several more recent observational studies support the existence of a transition layer between the extratropical upper troposphere and lower stratosphere (see Figure 2-2). The layer exhibits chemical characteristics that are intermediate between these two regions. For example, ozone and carbon monoxide (CO) data collected as part of the Stratosphere-Troposphere Experiments by Aircraft Measurements (STREAM) program show the existence of a transition layer that varies in thickness between winter and summer (Hoor et al., 2001), being deeper in summer. A study of total reactive nitrogen (NO_y) and nitrous oxide (N₂O) relationships also showed that more exchange appears to occur in the summer months. This results in a deeper summertime transition layer with higher excess NO_y concentrations (i.e., in excess of what can be expected from photochemical destruction of N₂O) which may have been transported into the transition layer by deep convection (Fischer et al., 2000). Another study showed that frontal uplifting can be important for transporting trace gases (sulfur hexafluoride (SF₆), deuterated water vapor (HDO)) from the subtropics in the troposphere into the Arctic lower stratosphere during winter (Zahn, 2001).

These findings are consistent with seasonal variations in exchange predicted by model studies based on wind fields from large-scale meteorological datasets (Chen, 1995; Haynes and Shuckburgh, 2000). In effect, exchange at middle and high latitudes associated with synoptic eddies and frontal systems produces a transition layer in winter and summer that corresponds to potential temperatures between 310K and 330K. In winter at lower latitudes and higher levels the subtropical jet acts as an effective barrier to transport across the tropopause. Trajectory analyses point to frontal uplifting being a more effective exchange mechanism in the fall (Seo and Bowman, 2001) as well as the winter (Stohl, 2001). In summer the subtropical jet is a less effective barrier, and additional exchange results in a layer extending up to ~360 K. Deep convection at midlatitudes may also be important, but its effects are not yet well quantified.

In principle, the transition layer is a region in which concentrations of VSL substances and their degradation products may be relatively high and in which substantial in situ ozone depletion may take place. Clearly, further clarification of the mechanisms controlling the characteristics of the transition layer, the origin of air in this layer, and its seasonal evolution are needed. Also, time scales on which air parcels remain in this region, e.g., before returning to the troposphere, are unknown. All these factors have implications for the lifetimes and impact of VSL substances and their degradation products in this region.

2.2.3 Chemistry in the UT and TTL

Modeling the transport of VSL substances into the stratosphere requires an accounting of photochemical losses in the troposphere, particularly in the upper troposphere and tropical tropopause layer, where the VSL substances may reside for some time before ascent to the stratosphere. This section focuses mainly on the UT. Currently very few chemical observations of species other than ozone are available in the TTL, which is of critical importance for delivery of VSL substances to the stratosphere. Because the TTL is dry, sources other than water vapor are likely to dominate the supply of odd-hydrogen (HO_x) radicals there.

Loss by photolysis in the UT can be calculated with confidence if absorption cross section and quantum yield data are available, because observed ultraviolet (UV) actinic fluxes in the UT are typically within 15% of values computed from clear-sky radiative transfer models (Shetter et al., 2002). Loss by reaction with hydroxyl radical (OH) and possibly other radicals is more difficult to constrain. Work over the past 5 years has profoundly changed our understanding of HO_x (OH + HO₂) chemistry in the UT (Jaeglé et al., 2001). Aircraft measurements of HO_x radicals (Wennberg et al., 1998; Brune et al., 1998, 1999; Tan et al., 2002) and supporting photochemical models have shown that photolysis of acetone and of convected peroxides and aldehydes provides a large source of HO_x to the UT, comparable with or exceeding the source from oxidation of water vapor (Chatfield and Crutzen, 1984; Jaeglé et al., 1997, 1998a, 2000; Prather and Jacob, 1997; McKeen et al., 1997; Crawford et al., 1999; Müller and Brasseur, 1999; Collins et al., 1999; Wang et al., 2000; Ravetta et al., 2001). Current photochemical models constrained with aircraft observations reproduce observed HO_x concentrations in the UT to within the instrument accuracy (±40%), and account for 60-70% of the observed variance (Jaeglé et al., 2001). Large unresolved biases remain at sunrise and sunset, in cirrus clouds, and under high-NO_x conditions (Brune et al., 1999; Faloona et al., 2000; Jaeglé et al., 2000). The

VERY SHORT-LIVED SUBSTANCES

40% uncertainty in HO_x translates into errors in the computed concentrations of some VSL species in the UT and TTL.

Our ability to represent UT radical chemistry in global models remains weak, despite the constraints offered by HO_x and NO_x measurements from aircraft. Limitations are not so much in our understanding of the fast HO_x photochemistry as they are in defining the factors that control the concentrations of HO_x precursors and NO_x . Recognized uncertainties in models include (1) the sources of UT NO_x from lightning and from vertical transport of surface emissions, the chemical cycling between NO_x and nitric acid (HNO_3), and possible complications involving peroxyxynitric acid (HNO_4) chemistry (Lawrence et al., 1995; Folkins et al., 1998; Jaeglé et al., 1998b; Keim et al., 1999; Liu et al., 1999; Folkins and Chatfield, 2000; Schultz et al., 2000; Staudt et al., 2002); (2) the sources and chemistry of oxygenated species (peroxides; acetone and other carbonyls) and their deep convective transport to the UT (Zuo and Deng, 1999; Jaeglé et al., 2000; Jacob et al., 2002); and (3) low-temperature rate constants for critical reactions such as methylperoxy radical (CH_3O_2) plus hydroperoxyl radical (HO_2) (Tyndall et al., 2001; Ravetta et al., 2001). The possible role of halogen radicals themselves in influencing HO_x chemistry, and in turn the fate of other halogens, is another unresolved issue (Borrmann et al., 1996; Crawford et al., 1996; Davis et al., 1996; Solomon et al., 1997). These issues are particularly relevant in the presence of convective clouds, and studies with cloud-resolving models (e.g., Wang and Prinn, 2000) are providing additional insights.

2.2.4 Chemical Tracer Observations for Model Evaluation

Observations of chemical tracers offer valuable diagnostic information for testing atmospheric transport of VSL substances in global models. Of particular interest is the simulation of vertical transport from the BL to the UT and across the tropopause. An ideal chemical tracer for testing vertical transport in models should have the following properties: (1) well-defined boundary conditions (concentrations or fluxes) in the BL or in the LS; (2) well-defined production and loss rates within the atmospheric column; (3) an atmospheric lifetime such that the transport processes of interest translate into measurable concentration gradients; and (4) extensive observations for model evaluation statistics. No single tracer fully meets all these conditions, but several are sufficiently close to be helpful.

Table 2-1 summarizes the utility of various chemical tracers for global model evaluation of the key transport processes related to simulations of VSL substances. Current models can reproduce the vertical distributions of radon-222 (^{222}Rn), nonmethane hydrocarbons, and CO without evident bias, providing some confidence in the simulation of convective transport from the BL to the UT at least in a global-mean sense (Jacob et al., 1997). Simulations of ozone and ^7Be indicate that models often overestimate the downward transport of air from the LS to the UT (Bey et al., 2001; Liu et al., 2001). Aircraft observations of soluble gases in convective outflows suggest that the scavenging of these gases during deep convection from the BL to the UT can be successfully described on the basis of Henry's Law solubility and knowledge of gas retention upon cloud freezing (Mari et al., 2000). However, global models generally overestimate HNO_3 in the UT (Thakur et al., 1999), possibly because of insufficient scavenging, including neglect of cirrus precipitation (Lawrence and Crutzen, 1998). Overall, the suite of tracers in Table 2-1 provides important information for testing transport and scavenging processes of key relevance to VSL substances, and it is essential that any chemical transport model used to simulate VSL substances be first validated with an appropriate ensemble of these tracers.

Ozone is a particularly valuable tracer of vertical transport in the UT/LS region, but it has so far been underutilized for this purpose. It is the only gas sampled regularly enough in the UT (by both ozonesondes and aircraft) to provide data representative of actual monthly means (Logan, 1999; Thompson and Witte, 1999; Emmons et al., 2000; Lawrence, 2001). Ozone has a lifetime against chemical loss of months to years in the UT/LS; hence its vertical concentration gradient is primarily determined by transport and chemical production (Folkins et al., 1999). Vertical profiles of ozone across the tropopause region and correlations with water vapor provide an important test for evaluating the nature of the tropopause and cross-tropopause mass flux in global models (Law et al., 2000). Of particular relevance for VSL substances, ozonesonde profiles in the tropics can be used to diagnose vertical transport in the TTL and ascent into the stratosphere (Folkins et al., 1999). One difficulty with the use of ozone as a tracer of vertical transport is that its long lifetime in the UT allows for horizontal propagation of signals associated with vertical transport, and varying chemical production along these horizontal transport trajectories may have a major effect on concentrations (Pickering et al., 1992; Lawrence et al., 1999; Martin et al., 2002).

Table 2-1. Chemical tracers useful for evaluating simulations of vertical transport in the troposphere, scavenging in the troposphere, and stratosphere/troposphere exchange (STE) processes in global models.

Tracer	Application	Source	Sink ^a	Selected References	Pros and Cons
²²² Rn	Vertical transport over continents	Soils	Radioactive decay (lifetime 5.5 days)	Jacob et al. (1997); Dentener et al. (1999)	Pros: well-defined sink, relatively uniform continental source Cons: poor definition of source variability, sparse observations
Nonmethane hydrocarbons, CO	Vertical transport over continents	Anthropogenic and biogenic emissions	Reaction with OH	Blake et al. (1997); Bey et al. (2001)	Pros: extensive aircraft data, correlations between species provide additional constraints Con: poor source definition
CH ₃ I	Vertical transport over oceans	Oceans	Photolysis (lifetime ~5 days in tropics)	Blake et al. (1996); Bell et al. (2002)	Pro: extensive aircraft data Con: poor source definition
²¹⁰ Pb	Vertical transport, aerosol scavenging	Decay of ²²² Rn	Wet deposition	Preiss et al. (1996); Rasch et al. (2000)	Pros: extensive surface data, good source definition Con: sparse aircraft data
⁷ Be	STE, subsidence	Cosmic rays	Radioactive decay (lifetime 77 days), wet deposition	Dibb et al. (1997); Liu et al. (2001)	Pros: extensive surface data, good source definition Con: sparse aircraft data
¹⁰ Be	STE (together with ⁷ Be)	Cosmic rays	Wet deposition (lifetime against radioactive decay ~10 ⁶ years)	Dibb et al. (1994); Koch and Rind (1998)	Pro: well-defined STE tracer Con: very sparse data
¹⁴ CO	STE, OH	Cosmic rays	Reaction with OH (lifetime 1-3 months)	Jöckel et al. (1998); Jöckel et al. (2002)	Pro: well-defined source distribution Cons: uncertain total source strength, sparse aircraft data
O ₃	Deep convection, STE	Photochemistry, transport from stratosphere	Photochemistry, deposition	Folkens et al. (1999); Logan (1999)	Pros: extensive sonde and aircraft data, correlation with water vapor provides additional constraints Con: complicated chemistry
Soluble gases: ^b CH ₃ OOH, HCHO, H ₂ O ₂ , HNO ₃	Scavenging in deep convection	Boundary layer chemistry	Scavenging, chemistry	Mari et al. (2000); Crutzen and Lawrence (2000)	Pros: extensive aircraft observations Cons: difficulty of separating convective transport and scavenging processes

^a All lifetimes are given as “e-folding” lifetimes, which are the inverse of the first-order removal rate.

^b CH₃OOH, methyl hydroperoxide; HCHO, formaldehyde; H₂O₂, hydrogen peroxide; HNO₃, nitric acid.

2.3 ATMOSPHERIC CHEMISTRY OF HALOGENATED VERY SHORT-LIVED (VSL) SUBSTANCES

This section presents an assessment of the state of knowledge of the kinetics and mechanisms of the chemical processes that determine the local lifetimes and distributions of the VSL organic halogen source gases and their degradation products in the atmosphere. The compounds to be considered are summarized in Table 2-2. They were selected because they have been either observed in the atmosphere or proposed for applications

that may lead to release. Fully fluorinated VSL substances are not covered in this Assessment, because the F-containing radicals produced in their degradation do not deplete ozone.

Section 2.3.1 deals with the kinetic data and reaction mechanisms for the organic source gases, which determine the efficiency of the SGI (source gas injection) pathway, as defined in Section 2.1. The efficiency of the PGI (product gas injection) pathway depends on the kinetic data and reaction mechanisms of the degradation products and the inorganic halogen species. These are discussed in Section 2.3.2. Some of the species were

VERY SHORT-LIVED SUBSTANCES

Table 2-2. VSL organic halogen source gases assessed in this report.

Source Gas	Formula
Bromochloromethane ^a	CH ₂ BrCl
Dibromomethane (methylene bromide) ^a	CH ₂ Br ₂
Dibromochloromethane ^a	CHBr ₂ Cl
Bromodichloromethane ^a	CHBrCl ₂
Tribromomethane (bromoform) ^a	CHBr ₃
1-bromopropane (n-propyl bromide or n-PB)	n-C ₃ H ₇ Br; CH ₃ CH ₂ CH ₂ Br
Iodomethane ^a	CH ₃ I
Trifluoroiodomethane ^a	CF ₃ I
Iodoethane (ethyl iodide) ^a	C ₂ H ₅ I; CH ₃ CH ₂ I
1-iodopropane (n-propyl iodide) ^a	n-C ₃ H ₇ I; CH ₃ CH ₂ CH ₂ I
2-iodopropane (isopropyl iodide) ^a	i-C ₃ H ₇ I; CH ₃ CHICH ₃
Chloriodomethane ^a	CH ₂ ClI
Bromiodomethane	CH ₂ BrI
Diiodomethane ^a	CH ₂ I ₂
Dichloromethane (methylene chloride) ^a	CH ₂ Cl ₂
Trichloromethane (chloroform) ^a	CHCl ₃
Trichloroethene (trichloroethylene) ^a	C ₂ HCl ₃ ; CHClCCl ₂
Tetrachloroethene (perchloroethylene) ^a	C ₂ Cl ₄ ; CCl ₂ CCl ₂
1,2-dichloroethane	C ₂ H ₄ Cl ₂ ; CH ₂ ClCH ₂ Cl

^a Assessed in the 1999 Assessment (Kurylo and Rodríguez et al., 1999), which dealt only with the atmospheric observations of these species and their interpretation. The laboratory chemical data were not assessed in detail.

assessed in the most recent Assessment report (Kurylo and Rodríguez et al., 1999), and the current Assessment provides an update and extends that work to include the inorganic halogen chemistry in the UT/LS region. The degradation mechanism for n-propyl bromide is discussed in Section 2.3.3. Section 2.3.4 provides the state of knowledge of iodine chemistry in the stratosphere, which is used for the evaluation of the ozone removal efficiency of iodine.

2.3.1 Removal of the Halogen Source Gases

The atmospheric removal of the VSL halogen source gases under consideration is primarily initiated via reaction with the OH radical and/or by UV photodissociation. Removal via reactions with Cl atoms and nitrate radicals (NO₃) is expected to be of only minor importance. Table 2-3 summarizes the kinetic and photochemical parameters for the VSL halogen source gases. For larger molecules such as n-propyl bromide (n-PB, CH₃CH₂CH₂Br), the reaction rate constant with OH depends on the site of the OH reaction (see also Section 2.3.3).

Table 2-4 summarizes estimated values of the local lifetimes for some VSL halocarbons. For the chlorine- and bromine containing compounds, reaction with OH is the dominant loss process, apart from tribromomethane (CHBr₃) and dibromochloromethane (CHBr₂Cl), where photolysis contributes at least a comparable amount. For alkyl iodides (such as CH₃I, C₂H₅I, n-C₃H₇I, i-C₃H₇I, CH₂ClI, CH₂BrI, and CH₂I₂), photolysis is always the dominant loss process leading to prompt release of iodine atoms:



Local lifetimes for these iodides can be estimated from their absorption cross sections (Rattigan et al., 1997; Roehl et al., 1997; Mössinger et al., 1998): 4-12 days for CH₃I, 2-8 days for C₂H₅I, 1-3 days for i-C₃H₇I, 0.5-1.5 days for n-C₃H₇I, hours for CH₂ClI and CH₂BrI, and minutes for CH₂I₂. The ranges reflect variations with latitude, altitude, and seasons. Reaction with OH may also be a significant loss process for n-C₃H₇I and i-C₃H₇I, but I atoms are still believed to be released promptly (Cotter et al., 2001).

Table 2-3. Kinetic and photochemical parameters for the degradation reactions of halogenated VSL source gases.

Species	OH Rate Constant, k ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)	$k_{300\text{K}}$ ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)	Photolysis Rate Constant, J^a (s^{-1})	Comments and References ^b
CH ₂ BrCl	$2.0 \times 10^{-12} \exp(-870/T)$	1.1×10^{-13}	7.7×10^{-10}	Sander et al. (2002)
CH ₂ Br ₂	$2.0 \times 10^{-12} \exp(-840/T)$	1.2×10^{-13}	$<1 \times 10^{-8}$	Sander et al. (2002); Kurylo and Rodríguez et al. (1999)
CHBr ₂ Cl		5.7×10^{-14}	7.2×10^{-8}	Chiorboli et al. (1993); Kurylo and Rodríguez et al. (1999)
CHBrCl ₂		1.2×10^{-13}	5.2×10^{-8}	Bilde et al. (1998); Kurylo and Rodríguez et al. (1999)
CHBr ₃	$1.35 \times 10^{-12} \exp(-600/T)$	1.8×10^{-13}	1×10^{-6}	Sander et al. (2002); Kurylo and Rodríguez et al. (1999)
n-C ₃ H ₇ Br	$3.1 \times 10^{-12} \exp(-330/T)$ $6.6 \times 10^{-18} T^2 \exp(154/T)$ $k_\alpha = 1.44 \times 10^{-12} \exp(-450/T)$ $k_\beta = 2.5 \times 10^{-18} T^2 \exp(265/T)$ $k_\gamma = 2.9 \times 10^{-12} \exp(-957/T)$	1.0×10^{-12} 9.9×10^{-13} $k_\alpha/k = 0.32$ $k_\beta/k = 0.56$ $k_\gamma/k = 0.12$	$<1 \times 10^{-8}$	First rate constant value from Sander et al. (2002), second value and third set of values from Gilles et al. (2002) (see Figure 2-8 for explanation of α , β , and γ); J values from Herndon et al. (2001) and Kozlov et al. (2002)
i-C ₃ H ₇ Br	$1.75 \times 10^{-12} \exp(-260/T)$ $3.6 \times 10^{-12} \exp(-390/T)$	7.4×10^{-13} 9.7×10^{-13}		Sander et al. (2002), Teton et al. (1996); no data
CH ₃ I	$2.9 \times 10^{-12} \exp(-1100/T)$	7.2×10^{-14}	3×10^{-6}	Sander et al. (2002); Roehl et al. (1997)
CF ₃ I	$2.8 \times 10^{-11} \exp(-2100/T)$	2.4×10^{-14}	8×10^{-6}	Sander et al. (2002), Gilles et al. (2000); Rattigan et al. (1997), Roehl et al. (1997), Solomon et al. (1994b)
C ₂ H ₅ I		3×10^{-13} 7.7×10^{-13}	5×10^{-6}	Estimation based on correlation between Cl and OH abstraction rate coefficients from Cotter et al. (2001); Roehl et al. (1997)
n-C ₃ H ₇ I		1.47×10^{-12}	2×10^{-5}	Carl et al. (1998); Roehl et al. (1997)
i-C ₃ H ₇ I		1.22×10^{-12}	8×10^{-6}	Carl et al. (1998); Roehl et al. (1997)
CH ₂ ClI			1×10^{-4}	No kinetic data; Rattigan et al. (1997), Roehl et al. (1997)
CH ₂ BrI			3×10^{-4}	No kinetic data; Mössinger et al. (1998)
CH ₂ I ₂			4×10^{-3}	No kinetic data; Mössinger et al. (1998), Roehl et al. (1997)
CH ₂ Cl ₂	$1.9 \times 10^{-12} \exp(-870/T)$	1.0×10^{-13}		Sander et al. (2002); no data
CHCl ₃	$2.2 \times 10^{-12} \exp(-920/T)$	1.0×10^{-13}		Sander et al. (2002); no data
C ₂ HCl ₃	$5.0 \times 10^{-13} \exp(445/T)$	2.2×10^{-12}		Atkinson et al. (2001); no data
C ₂ Cl ₄	$9.4 \times 10^{-12} \exp(-1200/T)$	1.7×10^{-13}		Atkinson et al. (2001); no data
CH ₂ ClCH ₂ Cl	$1.05 \times 10^{-11} \exp(-1142/T)$	2.3×10^{-13}		Qiu et al. (1992); no data

^a The values for the photolysis rate constants are globally and seasonally averaged estimates for 5-km altitude based on cross sections and quantum yields measured in several laboratories (because different models were used, the values should be considered approximate).

^b References cited for photolysis follow semicolon. Rate constants, cross sections, and quantum yields that have been evaluated in International Union of Pure and Applied Chemistry (IUPAC) (Atkinson et al., 2001) and NASA Jet Propulsion Laboratory (NASA-JPL) (Sander et al., 2002) are indicated by the corresponding citations.

VERY SHORT-LIVED SUBSTANCES

Deposition of the source gases into the ocean would constitute a permanent removal if there are efficient chemical and/or biological pathways to transform the species in the water. Estimates for the ocean removal lifetime show that ocean removal has a negligible effect on the local photochemical lifetime of the VSL halogen source gases (Yvon-Lewis and Butler, 2002).

2.3.2 Production and Removal of Degradation Products

2.3.2.1 DEGRADATION MECHANISMS FOR SOURCE GASES

As stated, the atmospheric degradation of the source gas is primarily initiated via reaction with OH and/or by UV photodissociation. The radicals produced following the initiation reaction are rapidly converted into more stable products. Halogen atoms may be released in the initiation reaction or during the subsequent sequence of reactions occurring in the degradation mechanism.

The degradation mechanism for the halogen-containing compounds parallels that previously reported for the hydrochlorofluorocarbons (HCFCs) (Cox et al., 1995). However, many of the reactions and reaction intermediates in the degradation have not been studied or observed in the laboratory. In those cases, formulation of the elementary steps in the degradation mechanisms has been based on analogy with known mechanisms. Both OH reaction and UV photolysis loss processes will lead to the rapid formation of alkylperoxy radicals. The degradation of the halocarbons leads to the formation of carbonyl halides, peroxyhalides, hydroxyhalomethanes, and haloperoxy acids. The yield of a specific degradation product will depend to some extent on the atmospheric conditions (temperature and pressure) as well as the atmospheric concentrations of nitric oxide (NO), nitrogen dioxide (NO₂), HO₂, and organic peroxy radicals (RO₂).

A general degradation mechanism for the halo-methanes is shown in Figure 2-6, and a summary of the degradation products derived from the various source gases is given in Table 2-5. Upon photolysis, the singly iodinated compounds (alkyl iodides) and the dihalo-iodo compounds (CH₂CH₂I, CH₂BrI, and CH₂I₂) eliminate an I atom with unit quantum yield. Photolysis therefore does not lead to the formation of iodine-containing organic degradation products, with the exception of CH₂I₂, which could form HIC(O) as a minor product. Photolysis also removes trifluoroiodomethane (CF₃I) rapidly from the atmosphere, with CF₃ and I as photolysis products. The atmospheric degradation of the CF₃ radical does not lead to significant ozone destruction, as discussed in Cox et al.

Table 2-4. Local photochemical lifetimes (in days) for halogenated VSL substances. The local lifetimes are estimated using the reaction rate constant with OH and estimated photolysis rates as indicated in the table.

Compound	τ_{OH}^a	τ_J^b	τ_{local}^c
CH ₂ BrCl	150	15000	150
CH ₂ Br ₂	120	5000	120
CHBr ₂ Cl	120 ^d	161	69
CHBrCl ₂	120 ^e	222	78
CHBr ₃	100	36	26
n-C ₃ H ₇ Br (n-PB)	13 ^f	>1200 ^f	13
i-C ₃ H ₇ Br	17 ^f	^g	17
CH ₃ I	220 ^f	7 ^h (4-12) ⁱ	7
C ₂ H ₅ I	15-39 ^{e, f}	5 ^h (2-8) ⁱ	4
n-C ₃ H ₇ I	7.9 ^{e, f}	0.6 ^h (0.5-1.5) ⁱ	0.5
i-C ₃ H ₇ I	9.5 ^{e, f}	1.4 ^h (1-3) ⁱ	1.2
CH ₂ CH ₂ I	^g	0.1	0.1
CH ₂ BrI	^g	0.04	0.04
CH ₂ I ₂	^g	0.003	0.003
CH ₂ Cl ₂	140	>15000	140
CHCl ₃	150	>15000	150
C ₂ HCl ₃	4.6 ^f	>15000	4.6
C ₂ Cl ₄	100 ^f	1.2 × 10 ⁵ ^f	99
C ₂ H ₄ Cl ₂	70 ^f		70

^a Calculated for T = 275 K with reaction rate constants from *JPL 00-3* (Sander et al., 2000) and [OH] = 1 × 10⁶ molec cm⁻³ unless specified otherwise. Values are rounded to 2 significant figures.

^b Globally and seasonally averaged photolysis constant (*J*) value estimated for 5 km, unless specified otherwise.

^c From $(\tau_{local})^{-1} = (\tau_{OH})^{-1} + (\tau_J)^{-1}$, unless specified otherwise; the oceanic lifetime is not included (see text).

^d Estimated *T* dependence of reaction rate (Kurylo and Rodríguez et al., 1999).

^e Calculated for 300 K.

^f Calculated using OH rate constant from Table 2-3.

^g No data.

^h Surface value.

ⁱ Range for different altitudes and latitudes.

(1995). The photolysis of multiple-substituted halo-methanes (CH₂BrCl, CH₂Br₂, CHBr₂Cl, CHBr₃) will lead to the direct elimination of a halogen atom and the formation of a formyl halide.

H-abstraction by OH is the primary loss process for several of the less photo-labile compounds (CH₂BrCl, CH₂Br₂, and CH₃CH₂CH₂Br (n-PB)) and is of secondary importance for the iodoalkanes (C₂H₅I, CH₃CHICH₃, and CH₃CH₂CH₂I). For CH₂BrCl and CH₂Br₂, upon reaction with OH, it is likely that carbonyls such as HC(O)Br, C(O)BrCl, and C(O)Br₂ will be produced and these may

be potential carriers of bromine to the stratosphere. For the nonmethane compounds such as $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (n-PB), reaction at the different carbon sites will lead to the formation of different degradation products. The scheme of the degradation mechanism for n-PB is detailed in Section 2.3.3.

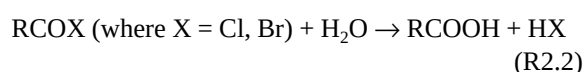
2.3.2.2 INTERMEDIATE PRODUCTS

The kinetics for the reactions involving the intermediate products are much less well understood than for the reactions of the source gases. In most cases, this does not matter because the initiation reaction is the rate-determining step for the release of inorganic halogen atoms. When there is a competition among alternative pathways such as RO_2 (where R is an alkyl or substituted alkyl group) reactions or alkoxy radical (RO) reactions, the lack of kinetic knowledge limits the ability to accurately predict the extent to which stable products are formed.

The first generation of stable products following initiation of gas-phase degradation consists generally of

carbonyl or peroxide species. Depending on the mechanism of degradation, halogen substitution may be retained at the α or β position. Table 2-6 summarizes the data that are known for the reactions of stable halogenated species generated in the first steps of degradation of VSL substances. Much less is known about the site-specific kinetics of these reactions. Generally, the presence of a halogen atom leads to an overall reduction in the rate coefficients compared with the hydrogenated species.

Halogenated carbonyls are slightly soluble in water. Once in solution, they undergo hydrolysis, which then represents the driving force for their multiphase removal from a given air mass. This chemical reaction may be written as



The uptake coefficient, γ_{het} , which is a convolution of all steps involved in the multiphase processing, is expected

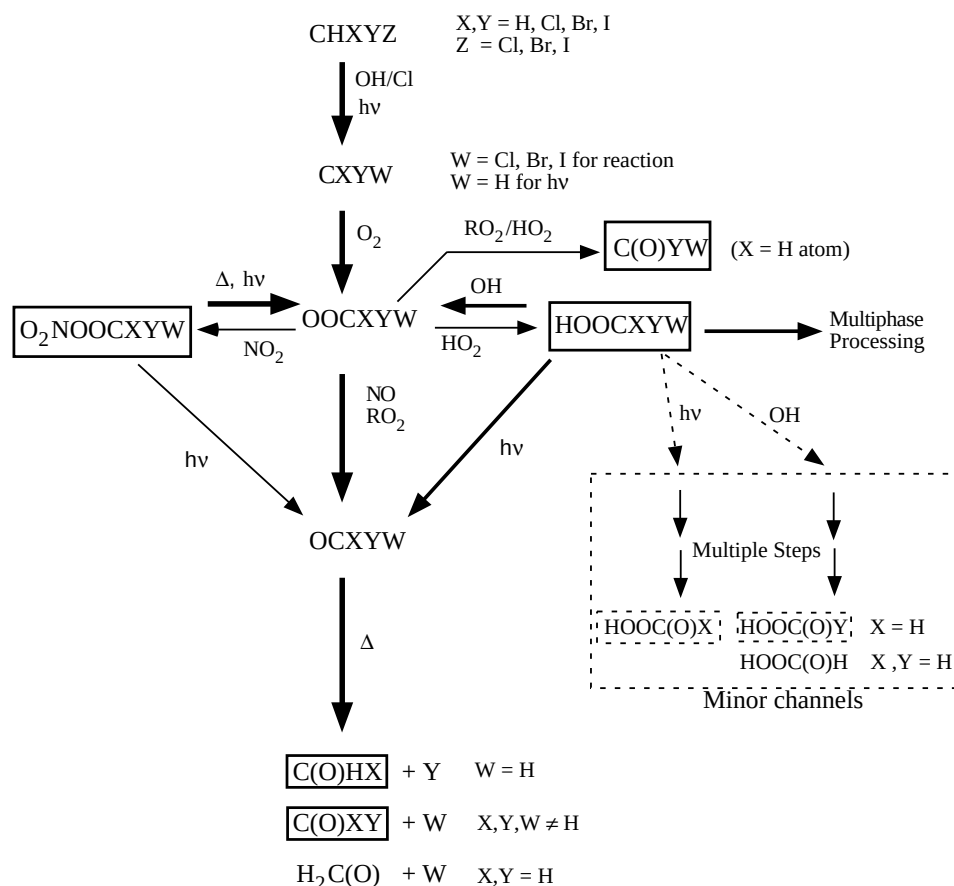


Figure 2-6. Halomethane degradation mechanism. Stable intermediate products containing halogens are enclosed in solid boxes. Minor pathways and products are indicated by dashed arrows and boxes.

VERY SHORT-LIVED SUBSTANCES

Table 2-5. Summary of the degradation products from halogenated VSL substances.

Source Gas	Major Degradation Products	Minor Degradation Products
CH ₂ BrCl	HCIC(O), inorganic bromine	HClBrC(OOH)
CH ₂ Br ₂	HBrC(O), inorganic bromine	HBr ₂ C(OOH)
CHBr ₂ Cl	HCIC(O), ClBrC(O), inorganic bromine	HBr ₂ C(OOH), ClBr ₂ C(OOH)
CHBrCl ₂	HCIC(O), Cl ₂ C(O), inorganic bromine	Cl ₂ BrC(OOH), HCl ₂ C(OOH)
CHBr ₃	HBrC(O), Br ₂ C(O)	Br ₃ C(OOH), HBr ₂ C(OOH)
n-C ₃ H ₇ Br (n-PB)	CH ₃ C(O)CH ₂ Br, inorganic bromine, CH ₂ BrCH ₂ C(O)H	Hydroperoxy compounds, peroxy carbonyl nitrates, peroxy nitrates
CH ₃ I	Inorganic iodine	—
CF ₃ I	Inorganic iodine	—
C ₂ H ₅ I	Inorganic iodine	CH ₂ IC(O)H
n-C ₃ H ₇ I	Inorganic iodine	CH ₃ C(O)CH ₂ I, CH ₂ ICH ₂ C(O)H
i-C ₃ H ₇ I	Inorganic iodine	CH ₃ CHIC(O)H
CH ₂ ClI	Inorganic chlorine and iodine	H ₂ CIC(OOH)
CH ₂ BrI	Inorganic bromine and iodine	H ₂ BrC(OOH)
CH ₂ I ₂	Inorganic iodine	HIC(O), H ₂ IC(OOH)
CH ₂ Cl ₂	HCIC(O)	HCl ₂ C(OOH)
CHCl ₃	Cl ₂ C(O)	HCl ₂ C(OOH)
C ₂ HCl ₃	Cl ₂ C(O), HCIC(O)	HCIC(OH)C(O)Cl, HCIC(OH)C(OOH)Cl ₂ , Cl ₂ C(OH)C(O)H, HCIC(OOH)C(OH)Cl ₂
C ₂ Cl ₄	Cl ₂ C(O), ClC(O)OH	Cl ₂ C(OH)CCl ₂ (OOH)
CH ₂ ClCH ₂ Cl	HCIC(O), inorganic chlorine	CH ₂ ClCHCl(OOH)

to be small for all compounds. Current estimates give an upper limit of 10^{-3} (de Bruyn et al., 1995; George et al., 1994), which indicates that cloud removal may play a role if gas-phase reactions are slow. It must also be emphasized that, for the compounds with very low reactivity, cloud evaporation may re-inject these compounds into the air, possibly at a different altitude, before multiphase processing can occur.

2.3.2.3 INORGANIC BROMINE AND IODINE SPECIES

Br and I atoms released in the troposphere through the degradation of the source gases and their degradation products undergo a series of reactions in which they are

interconverted among the oxides (XO) and inorganic reservoirs: HX (hydrogen halides), XONO₂ (halogen nitrates), and HOX (hypohalous acids), where here X = Br or I. The partitioning reactions for the inorganic reservoirs are common to bromine and iodine, and are illustrated in Figure 2-7. Bromine does not form higher oxides but iodine monoxide (IO) can react with bromine monoxide (BrO) or IO at a rate competitive with HO₂ to form iodine dioxide (OIO) (Cox et al., 1999; Rowley et al., 2001). The chemical reactions of OIO are not well known. Photodissociation to the ground state of atomic oxygen (O(³P)) + IO is not favored thermodynamically in its main visible absorption band (Misra and Marshall, 1998) and is slow (Ingham et al., 2000). This photolysis

Table 2-6. Kinetic and photochemical parameters for the gas-phase reactions of the degradation products of halogenated VSL substances.

Species	Radical ^a	k (cm ³ molec ⁻¹ s ⁻¹)	k_{300} (cm ³ molec ⁻¹ s ⁻¹)	Photolysis Rate Constant, J ^b (s ⁻¹)	Comments and References ^c
Cl ₂ C(O)	OH		$<5.0 \times 10^{-15}$	2×10^{-9}	Atkinson et al. (1997); Cox et al. (1995)
Br ₂ C(O)					No kinetic or photochemical data
BrClC(O)					No kinetic or photochemical data
HCIC(O)	OH		$<5.0 \times 10^{-13}$	1×10^{-8}	Atkinson et al. (1997) (limited experimental data); Cox et al. (1995)
HCIC(O)	Cl	$1.2 \times 10^{-11} \exp(-820/T)$	7.9×10^{-13}		Atkinson et al. (1997)
HBrC(O)				3×10^{-6}	No kinetic data; estimate
CH ₃ C(O)CH ₂ Br				1×10^{-4}	No kinetic data; Burkholder et al. (2002)
CH ₂ ClC(O)H	OH		3.1×10^{-12}		Atkinson et al. (1997)
CCl ₃ C(O)Cl					No kinetic or photochemical data
HOI				1.2×10^{-2}	No kinetic data; Bauer et al. (1998)
HOBr	OH		$<5 \times 10^{-13}$	3×10^{-3}	Kukui et al. (1996), upper limit; Ingham et al. (1998)
HOBr	Cl		8×10^{-11}		Kukui et al. (1996), products are BrCl and OH
CH ₂ ClOOH	Cl ^d		5.9×10^{-13}		Wallington et al. (1996), no kinetic data for OH reactions and photolysis
CCl ₂ BrOOH					No kinetic or photochemical data
BrONO ₂				$\sim 1 \times 10^{-3}$	Burkholder et al. (1995)
IONO ₂				4×10^{-2}	Mössinger et al. (2002)
OIO				$<10^{-2}$ (O(³ P) channel) 0.3-2.2 (I + O ₂ channel)	No kinetic data; Ingham et al. (2000) (upper limit for O(³ P) channel), Ashworth et al. (2002) (products are I + O ₂)

^a Cl atom reactions included if $k_{\text{Cl}} > 50 \times k_{\text{OH}}$ or no OH kinetic data available.

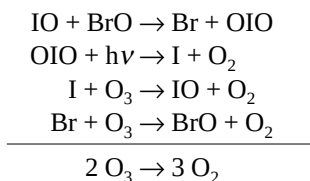
^b Atmospheric photolysis rate constants are globally and seasonally averaged estimates for 5-km altitude (because different models were used, the values should be considered approximate).

^c References cited for photolysis follow semicolon.

^d Strongly deactivating compared with reaction of Cl + CH₃OOH ($k_{300} = 5.9 \times 10^{-11}$ cm³ molec⁻¹ s⁻¹) (Atkinson et al., 1997).

VERY SHORT-LIVED SUBSTANCES

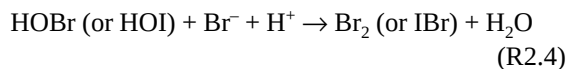
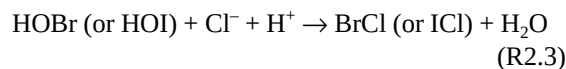
pathway would lead to a null cycle for ozone. However, photolysis to $I + O_2$ may occur (Ashworth et al., 2002), leading to an ozone loss cycle:



Thus OIO is a potentially significant atmospheric iodine species, and indeed has been detected in the marine boundary layer (Allan et al., 2001). Further oxidation of OIO, either by gas-phase or multiphase processes, to IO_3^- is a likely sink for tropospheric iodine, leading to the iodate observed in precipitation (Truesdale and Jones, 1996).

The relative importance of the halogen nitrates and HOX reservoirs depends on the local NO_2 and HO_2 concentrations, and on the presence of an aqueous phase where halogen nitrates may be hydrolyzed to form HOX. The inorganic reservoirs are removed from the troposphere by incorporation into aerosols, cloud droplets, and ice particles (cirrus clouds in the UT). However, the incorporation of the reservoirs into aerosols may not lead to permanent loss. Laboratory studies (Abbatt and Waschewsky, 1994;

Fickert et al., 1999; Holmes et al., 2001; Mössinger and Cox, 2001) show that HOX and $XONO_2$ species react very efficiently with Cl^- and Br^- on aerosols and ice particles, releasing the corresponding halogen or inter-halogen molecules, which all photodissociate to atomic halogens:



Reactions (R2.3) and (R2.4) are very efficient in acidic solutions or on HCl or hydrogen bromide (HBr)-doped surfaces. These reactions (and similar reactions involving $XONO_2$) have been the focus of many studies, especially in connection with their role in stratospheric halogen activation. They also play a role in tropospheric chemistry, particularly in the marine environment where sea salt aerosols contain Cl^- and Br^- ions. Additional reactive halogen is produced autocatalytically, leading for example to the so-called “bromine explosion” observed in the Arctic (e.g., Barrie and Platt, 1997). To be efficient, these reactions require cold conditions (such as frozen aerosols in the Arctic troposphere) and sustained levels of particles (such as ice or sulfuric acid aerosols in the stratosphere) that may be observed, for instance, under volcanic influence. Table 2-7 lists the required parameters for an assessment of the fate of some of the HOX and $XONO_2$ species.

Reactions similar to (R2.3) and (R2.4) efficiently recycle iodine and bromine into radical forms, thereby effectively increasing the lifetime of tropospheric halogens. This explains the relatively high abundance of IO in the marine boundary layer. There are also recent direct observations that show that BrO may be present in the upper troposphere at a concentration of 0.4-2 parts per trillion (ppt), which is much higher than predicted on the basis of known photochemical sources and heterogeneous removal rates (Fitzenberger et al., 2000). Such observations indicate that the recycling processes may be important, leading to a significant increase of the efficiency of the product gas injection (PGI) pathway in supplying inorganic halogen species to the stratosphere.

2.3.3 Degradation Mechanism for n-Propyl Bromide (n-PB)

The compound 1-bromopropane (or n-propyl bromide (n-PB), $CH_3CH_2CH_2Br$) has been suggested for use in a variety of applications that would lead to its release into the troposphere. A reliable estimate of the amount of inorganic bromine that will be delivered to the strato-

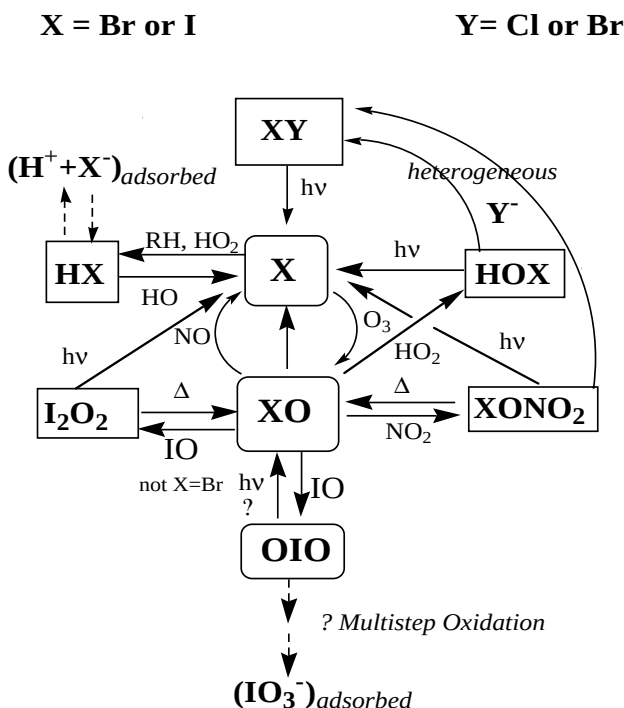


Figure 2-7. Inorganic halogen tropospheric chemistry.

Table 2-7. Data for the multiphase chemistry of some inorganic degradation products. The column for γ_{het} gives the reaction probability per collision with the surfaces.

Molecule	Henry's Law Constant (M atm ⁻¹)	Reaction	γ_{het}	Temperature (K)	References
HOBr (hypo-bromous acid)	>1900	Water	>0.01	274	Blatchley et al. (1992)
		NaCl	6.5×10^{-3}	300	Atkinson et al. (2001)
		NaBr	0.18	300	Atkinson et al. (2001)
		HCl-doped ice	4×10^{-3} to 0.3	180-222	Chu and Chu (1999)
		Sulfuric acid	>0.01	238	Waschewsky and Abbatt (1999)
BrONO ₂ (bromine nitrate)	$>7.1 \times 10^4$	Water	0.06	>273	Aguzzi and Rossi (1999)
		NaCl	0.3	—	Aguzzi and Rossi (1999)
		NaBr	0.3	—	Aguzzi and Rossi (1999)
		HCl-doped ice	>0.2	200	Atkinson et al. (2001)
		Sulfuric acid	>0.2	294	Atkinson et al. (2001)
HOI (hypoiodous acid)	>45	Water	—	—	Thompson and Zafiriou (1983)
		NaCl	1.6×10^{-2}	278-298	Atkinson et al. (2001)
		NaBr	3.4×10^{-2}	278-298	Mössinger and Cox (2001)
		HCl-doped ice	5×10^{-2}	200	Holmes et al. (2001)
		Sulfuric acid	1.5×10^{-2} to 7×10^{-2}	195-252	Holmes et al. (2001)
IONO ₂ (iodine nitrate)	—	Water	—	—	—
		NaCl	>0.1	253	Holmes et al. (2001)
		NaBr	>0.1	253	Holmes et al. (2001)
		HCl-doped ice	>0.05	243	Holmes et al. (2001)
		Sulfuric acid	>0.3	253	Holmes et al. (2001)

sphere from release of n-PB requires better knowledge of its degradation mechanism and a guess as to the possible future quantities produced and emitted.

The degradation mechanism for n-PB is outlined in Figure 2-8. Recent laboratory measurements have determined the site-specific OH rate coefficients over the temperature range 230 to 360 K (Gilles et al., 2002). The kinetic data are reported in Table 2-3. The reaction rate constants reported by Gilles et al. (2002) and that recommended in Sander et al. (2002) give estimated local lifetimes of 13 days (Table 2-4).

Bromoacetone ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{Br}$) was observed as a major degradation product following the OH reaction at the $-\text{CH}_2-$ site of the n-PB molecule (β channel in Figure 2-8). Burkholder et al. (2002) have recently shown that $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{Br}$ will rapidly photolyze in the atmosphere ($\sim$ hours). The photolysis products were not determined, but the possible bromine-containing products are expected to liberate bromine within days. The reaction of OH at the $-\text{CH}_2\text{Br}$ group in $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (α channel) will lead

to the rapid elimination of Br and the formation of $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{H}$. The reaction of OH at the CH_3- group in $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (γ channel) will predominantly lead to the formation of bromoaldehydes, $(\text{O})\text{CHCH}_2\text{CH}_2\text{Br}$ and $(\text{O})\text{CHCH}_2\text{Br}$. These compounds are expected to degrade in the atmosphere ($\sim$ days) through reaction with OH and UV photolysis. Minor reactions of the reaction intermediates can lead to the formation of peroxy nitrates (containing the OONO_2 group), peroxy carbonyl nitrates (PAN-type compounds, resulting from the further oxidation of the bromoaldehydes), and alkyl hydroperoxides (containing the OOH group). The peroxy nitrates will thermally decompose rapidly under all tropospheric conditions. The alkyl hydroperoxides will be removed via a combination of OH reaction, UV photolysis, and multiphase processing. The rates for these processes are not known but are expected to lead to atmospheric lifetimes on the order of days. The only possible degradation products of n-PB with atmospheric lifetimes longer than the parent compound are the peroxy carbonyl nitrates, but

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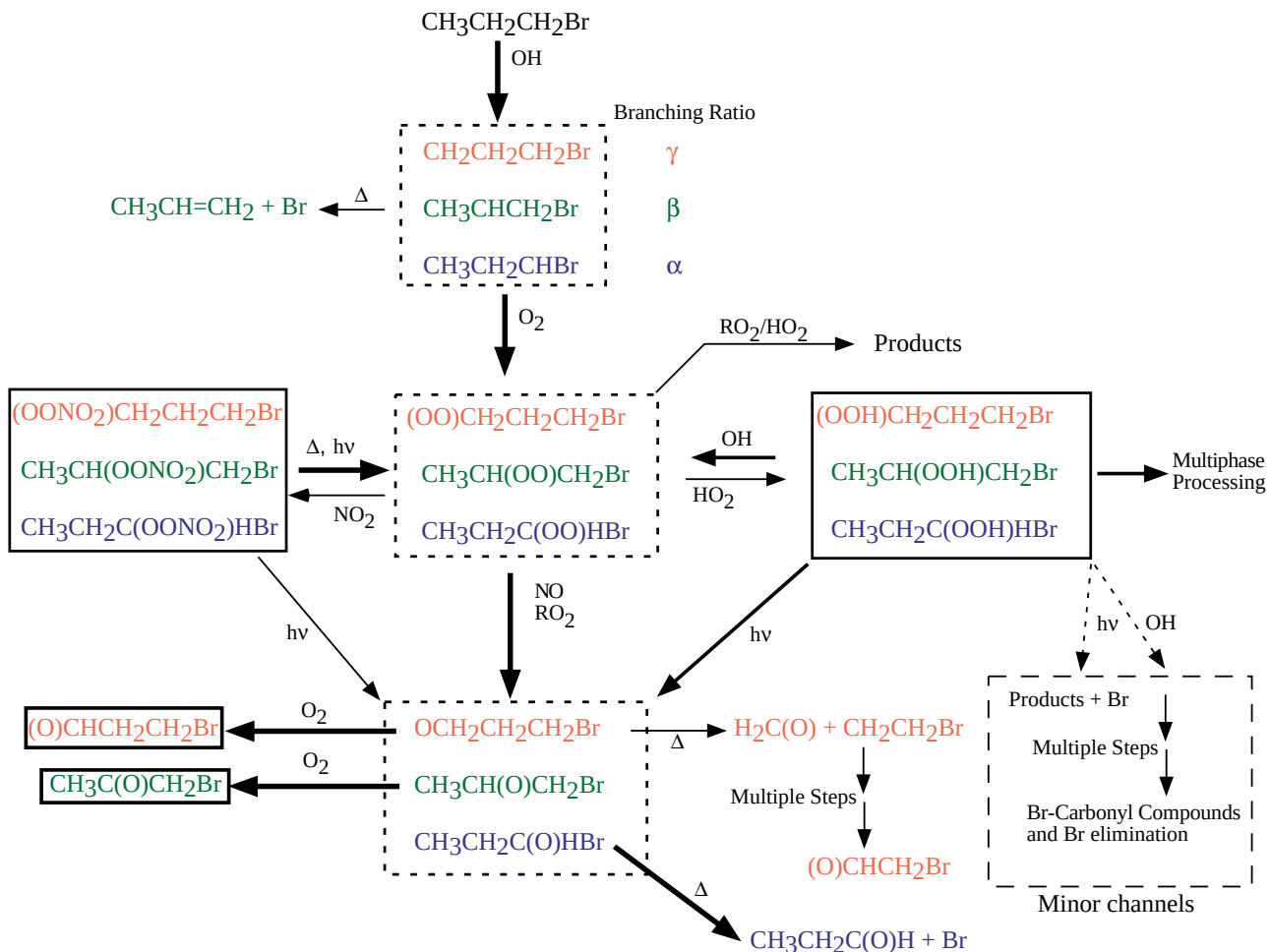


Figure 2-8. Degradation mechanism of n-propyl bromide (CH₃CH₂CH₂Br). The major channel (β , in green) leads to the formation of bromoacetone (CH₃C(O)CH₂Br) (see text for details). Dashed and solid boxes as for Figure 2-6.

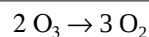
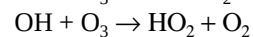
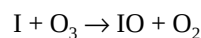
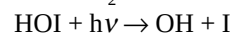
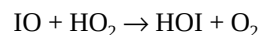
only if they are formed, if they contain Br, and if they are rapidly transported into the low-temperature environment of the upper troposphere. In conclusion, it is very likely that the product gas injection pathway for n-PB is from transport of inorganic halogen rather than intermediate products.

2.3.4 Stratospheric Iodine Chemistry

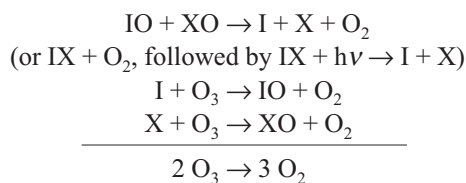
Although the chemistry of chlorine and bromine in the stratosphere is reasonably well known, this is not the case for iodine. Chameides and Davis (1980) were the first to describe the atmospheric photochemistry of iodine in the marine boundary layer, where the iodine is produced from the oceanic source of volatile alkyl iodides. If alkyl iodides or their degradation products could enter the stratosphere, the I atom would be rapidly converted to IO through reaction with O₃. Recycling of IO to I through

reactions with ClO, BrO, and HO₂ would constitute catalytic O₃ removal cycles.

Solomon et al. (1994a) provided the first estimate for the ozone removal efficiency of iodine in the stratosphere. In their study, inorganic iodine was partitioned among I, IO, hydrogen iodide (HI), hypoiodous acid (HOI), and iodine nitrate (IONO₂), with 90% of the iodine in the form of I and IO. The ozone removal cycles were identified as

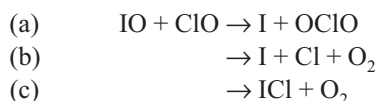


and



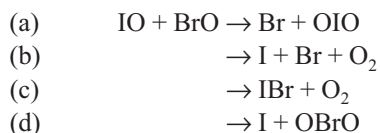
where here X is Br or Cl. At the time the study was done, rate data were not available for the reactions of IO with BrO and ClO. Solomon et al. (1994a) assumed a rate of $1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for both rate coefficients and estimated that the ozone removal efficiency for iodine is about 1000 times that of chlorine. It was suggested that the coupling of a low natural abundance of iodine species with increasing bromine and chlorine levels has contributed to the trend in ozone loss in the lowermost stratosphere.

Laboratory work in the past 5 years has significantly improved the knowledge of the relevant kinetic data. For the IO + ClO reaction, the rate coefficient has been found to be much lower than estimated by Solomon et al. (1994a), by a factor between 8 at 298 K and 5 at temperatures of the lower stratosphere (Bedjanian et al., 1997; Turnipseed et al., 1997). Furthermore, three product channels have been identified:



Channel (a), which leads to a null cycle for ozone depletion, is the major channel: $k_a/(k_a+k_b+k_c) = 0.55$. The channels that lead to ozone loss, (b) and (c), account for a significant fraction of the reaction: $(k_b+k_c)/(k_a+k_b+k_c) = 0.45$ at 298 K (Bedjanian et al., 1997; Turnipseed et al., 1997).

Several studies reported rate coefficients for the IO + BrO reaction ranging from 7×10^{-11} to $10 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Gilles et al., 1997; Laszlo et al., 1997; Bedjanian et al., 1998; Rowley et al., 2001). The possible channels for this reaction are:



The branching ratio for channel (a) here has been measured to be >0.65 (Bedjanian et al., 1998) while channels (b) and (c) account for less than 0.35 of the reaction at 298 K (Gilles et al., 1997; Bedjanian et al., 1998). The OIO molecule formed in channel (a) has been unambiguously

detected in this reaction (Cox et al., 1999). As discussed in Section 2.3.2.3, photolysis of OIO would efficiently produce I + O₂, and channel (a) could lead to an ozone loss cycle. However, uncertainties in OIO chemistry do not allow any firm conclusions regarding the ozone depletion efficiency of iodine in the stratosphere. The new data obtained for the IO + IO reaction are not discussed here, because this reaction, which also produces OIO, is not relevant to stratospheric iodine chemistry, but could be important in the marine boundary layer.

Laboratory investigations of the temperature dependence of the IO + HO₂ reaction (Maguin et al., 1992; Canosa-Mas et al., 1999; Cronkhite et al., 1999; Knight and Crowley, 2001) lead to a somewhat higher rate coefficient (up to a factor 3 at stratospheric temperatures) than that used in the calculations of Solomon et al. (1994a). This, associated with the reduced effect of the reactions of IO with both ClO and BrO, will increase the relative importance of the HO₂ cycle in the ozone loss due to iodine. Finally, in all reactions of IO with other radicals, the existence of a termolecular channel (similar to the ClO dimer-forming channel for ClO + ClO) was not observed.

The laboratory data in Sander et al. (2000) have been used for a recent re-evaluation of the ozone removal efficiency of iodine relative to chlorine; a value of 150–300 is used in this chapter (see Section 2.5) based on estimates provided by Bedjanian et al. (1998) and simulations using the Atmospheric and Environmental Research, Inc., model (see Ko et al., 1998). However, these estimates, which are lower than the value of 1000 initially suggested by Solomon et al. (1994a), are still very uncertain because of the lack of knowledge about OIO chemistry, and also about the heterogeneous reactions that could be very important for iodine, since all the inorganic reservoirs are reactive toward stratospheric particles (both ice and sulfuric acid (H₂SO₄) surfaces). Many data are still missing for these heterogeneous processes, such as those needed to estimate the hydrolysis rate of IONO₂. When such data are available, a multidimensional atmospheric model should be used to perform a more rigorous calculation of the ozone removal efficiency of iodine.

2.4 CONTRIBUTION OF HALOGENATED VSL SUBSTANCES TO THE STRATOSPHERIC INORGANIC HALOGEN BUDGET

There are two independent ways to obtain the total local concentration of inorganic halogen species in the present-day stratosphere. The first method (inorganic method) is to add up the measured concentrations of each inorganic species (HCl, ClONO₂, HOCl, ClO, Cl₂O₂, etc., in the case of chlorine). A variant of this method uses

VERY SHORT-LIVED SUBSTANCES

measured concentrations of a subset of the inorganic halogen species (e.g., BrO) and derives the other concentrations using a photochemical model. The second method (the organic method) is to add the contributions from each source gas by taking the difference between the measured concentration of the source gas and its expected concentration in an air parcel based on when it first entered the stratosphere (see, e.g., Prather and Watson, 1990; Woodbridge et al., 1995; Wamsley et al., 1998). Contributions from transport of very short-lived (VSL) source gases, degradation products, and inorganic halogen species from the troposphere are usually ignored in the organic method. Agreement between the two methods provides some reassurance, but not irrefutable, that our understanding of the present-day halogen budget may be correct. For example, Woodbridge et al. (1995) carried out a study of the inorganic chlorine budget and concluded that inorganic chlorine (Cl_y) concentrations derived using the two methods are in reasonable agreement. However, the work of Wamsley et al. (1998) showed that derived inorganic bromine (Br_y) using the organic method is 30% smaller than the expected Br_y from the measured BrO, but that these differences are barely within calculated uncertainties. Recent analyses by Pfeilsticker et al. (2000) of a different dataset concluded that the two methods give values that agree within the estimated uncertainties (approximately ± 3 ppt) (see Chapters 3 and 4).

The measured concentrations of VSL source gases such as CH_3I and CHBr_3 are sufficiently high near the tropical tropopause that they could make a non-negligible contribution (see Table 2-8; review by Kurylo and Rodríguez et al., 1999; Sturges et al., 2000). This section summarizes the observations of the VSL halogen source gases and provides an estimate of their contribution to the present-day halogen budget in the stratosphere. Recent modeling studies are also reviewed and provide some estimates of the amount of Br_y entering the stratosphere from particular substances (CHBr_3 , n-PB) and their degradation products.

2.4.1 Observed Concentrations and Sources of Organic Chlorine, Bromine, and Iodine Compounds

The atmospheric distribution and sources of organic chlorine, bromine, and iodine compounds were reviewed in Kurylo and Rodríguez et al. (1999). Recent measured concentrations of the species in the tropical troposphere from Transport and Chemical Evolution over the Pacific (TRACE-P) and Pacific Exploratory Mission in the Tropical Pacific (PEM-Tropics) A and B are summarized in Table 2-8 and compared with values given in

the previous Assessment (Kurylo and Rodríguez et al., 1999). Burdens estimated using the numerator in the right-hand side of Equation (2.3) in Section 2.4.2 are given in Table 2-9. The estimated local lifetimes from Table 2-4 were used to calculate the sources for each species. These values were compared with previous estimates found in the literature. More recently, measurements taken from bottle samples collected on commercial aircraft as part of the European Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) project (<http://www.caribic-atmospheric.com/>) have also been analyzed for concentrations of halogen-containing source gases. These will prove useful in future studies. Reported measurements of degradation products or inorganic species in the troposphere are scarce, but include OIO (Allan et al., 2001), BrO (Fitzenberger et al., 2000), and phosgene (Kindler et al., 1995).

2.4.1.1 CHLORINE COMPOUNDS

Current measurements indicate that the mixing ratio of inorganic chlorine is about 3 parts per billion (ppb) in the upper stratosphere (based on measurement of HCl) and about 1.5 ppb in the lower stratosphere (based on the organic method). The VSL chlorine compounds have free-tropospheric concentrations in the range 1-50 parts per trillion (ppt). Many of them have an anthropogenic component in their sources. Methylene chloride (dichloromethane, CH_2Cl_2), trichloroethylene (trichloroethene, C_2HCl_3), and perchloroethylene (tetrachloroethene, C_2Cl_4) are mainly used as industrial solvents, and 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) is used as a lead scavenger in leaded gasoline. Concentrations of these gases in some urban areas reach ppb levels but their concentrations in the free troposphere are in the 1-30 ppt range (Blake et al., 1999a, 2001). Khalil et al. (1999) and references therein also suggested that natural emissions of chloroform (CHCl_3), predominantly from oceans, are important sources. This VSL also appears to have other small sources such as pulp and paper processing and water treatment. Biomass burning is thought to be a very minor source for CHCl_3 . Many of the VSL chlorine source gases exhibit significant seasonal and latitudinal variations in their concentrations (Wang et al., 1995; Yokouchi et al., 1996; Blake et al., 1999a). This could be due to variations in the emissions and variations in OH, because reaction with OH is the major removal process. Phosgene (COCl_2) is not emitted directly to the atmosphere but is a breakdown product of methyl chloroform and some of the gases listed above (Kindler et al., 1995). Its atmospheric concentration is in the 10-60 ppt range and its lifetime

Table 2-8. Estimated values for f_{BL}^X (median tropical surface (<1 km) mixing ratios) and f_{UT}^X (median mixing ratios in the tropical upper troposphere (8-12 km)). The data for TRACE-P were collected over the Western Pacific and the South China Sea, 23.5°N to 8°N. The data for PEM-Tropics A and B were from over the remote Pacific, 15°N to 15°S.

Species	Estimated Tropospheric Mixing Ratio ^a (pptv)	Estimated 10-km Tropical Mixing Ratio ^a (pptv)	f_{BL}^X and Range ^b from: TRACE-P ^c (331) ^d PEM-Tropics B ^c (572) ^d PEM-Tropics A ^c (337) ^d (pptv)	f_{UT}^X and Range ^b from: TRACE-P ^c (280) ^d PEM-Tropics B ^c (433) ^d PEM-Tropics A ^c (241) ^d (pptv)	Estimated $\frac{f_{UT}^X}{f_{BL}^X}$ from: TRACE-P PEM-Tropics B PEM-Tropics A
C ₂ HCl ₃	NH, 1-5; SH, 0.01-0.1	0-0.1	1 (0.3-2.0) N/A N/A	0.2 (0.02-0.28) N/A N/A	0.2 N/A N/A
CH ₃ I	0.1-2.0	0.05-0.2	0.6 (0.5-0.8) 0.42 (0.3-0.5) 0.445 (0.4-0.6)	0.03 (0.02-0.08) 0.09 (0.06-0.12) 0.061 (0.04-0.09)	0.05 0.2 0.15
CHBr ₃	0.6-3.0	0.4-0.6	1.1 (0.9-1.5) 1.82 (1.0-2.3) 1.83 (1.4-2.2)	0.3 (0.2-0.5) 0.54 (0.4-0.7) 0.42 (0.3-0.5)	0.3 0.3 0.2
CH ₂ ClCH ₂ Cl	NH, 20-40; SH, 5-7	14.9 ± 1.1	8.8 (5.7-14.5) 1.53 (0.8-1.7) N/A	2.9 (2.2-3.3) 0.92 (0.7-1.3) N/A	0.3 0.6 N/A
CHBr ₂ Cl	0.1-0.5	0.04-0.11	0.07 (0.06-0.08) 0.20 (0.14-0.26) 0.175 (0.14-0.21)	0.04 (0.03-0.05) 0.10 (0.08-0.12) 0.08 (0.06-0.11)	0.6 0.5 0.5
CHBrCl ₂	0.12-0.6	0.04-0.11	0.19 (0.17-0.22) 0.21 (0.14-0.26) 0.17 (0.15-0.20)	0.14 (0.12-0.15) 0.13 (0.11-0.14) 0.08 (0.05-0.11)	0.7 0.6 0.5
C ₂ Cl ₄	NH, 5-15; SH, 0.7-1.5	1-3	6.5 (4.5-10.3) 2.34 (1.5-2.9) 1.3 (1.2-1.16)	2.1 (1.7-2.5) 1.38 (1.2-1.7) 1.4 (1.2-1.6)	0.3 0.6 1.1
CH ₂ Br ₂	0.8-3.4	0.6-0.9	1.15 (1.0-1.2) 1.33 (1.1-1.5) 1.07 (0.93-1.18)	0.9 (0.7-1.0) 0.92 (0.85-1.0) 0.81 (0.77-0.85)	0.8 0.7 0.8
CH ₂ Cl ₂			34 (27-39) 13.9 (9-16) 11.4 (10.9-13) ^e	17 (16-19) 10.1 (9-12) 13.1 (12.4-14) ^e	0.5 0.7 1.1
CHCl ₃	NH, 10-15; SH, 5-7	3.1 ± 0.7	11.4 (9.0-13.3) 6.6 (5.2-7.1) 6.0 (5.7-6.4)	6.9 (6.3-7.5) 5.1 (4.8-5.6) 5.8 (5.6-6.1)	0.6 0.8 1.0

In columns 4-6, for each species, the first value is for data from TRACE-P; the second, from PEM-Tropics B; and the third, from PEM-Tropics A. N/A denotes data not available.

^a From Kurylo and Rodríguez et al. (1999).

^b Range is 25th-75th quartile.

^c The results for PEM-Tropics A and B can be found in Blake et al. (1999a,b, 2001, 2002). For a description of the campaigns and data availability, go to http://www-gte.larc.nasa.gov/gte_fld.htm.

^d Number of samples.

^e Data from a subset of cans (BL, n = 89; UT, n = 41) analyzed by E. Atlas, NCAR, U.S.

VERY SHORT-LIVED SUBSTANCES

Table 2-9. Estimated local lifetimes, burdens, removal rates, and sources for some halogenated VSL compounds.

Compound	τ_{local} (days)	Estimated Burden (Gg)	Estimated Removal Rate (Gg yr ⁻¹)	Estimated Source from Inventory or Estimate of Biogeochemical Cycle (Gg yr ⁻¹)
CH ₂ BrCl	150 ^a	1.2 (Br) ^{*1}	2.9 (Br) ^c	
CH ₂ Br ₂	120 ^a	18-22 (Br) ^b	55-67 (Br) ^c	
	120 ^a	19 (Br) ^{*1}	58 (Br) ^c	
CHBrCl ₂	78 ^a	1.3-1.5 (Br) ^b	6.1-7.0 (Br) ^c	
	78 ^a	1.2 (Br) ^{*1}	5.5 (Br) ^c	
CHBr ₂ Cl	69 ^a	0.8-2.2 (Br) ^b	4.2-12 (Br) ^c	
	69 ^a	2.3 (Br) ^{*1}	12 (Br) ^c	
CHBr ₃	26 ^a	11-18 (Br) ^b	150-250 (Br) ^c	
	26 ^a	14 (Br) ^{*1}	200 (Br) ^c 285 ^{*2, d}	209 (47-370) (Br) ^{*3}
CH ₃ I	5 ^e	1.7-2.2 ^b (I)	120-160 (I) ^c	90-450 (I) ^{*4}
	6 ^f	4.8 (I) ^f	214 (I) ^f	
C ₂ H ₅ I	4 ^a	0.5 (I)	46 (I) ^c	
CH ₂ Cl ₂	140 ^a	83-250 (Cl) ^b	220-650 (Cl) ^c	583 (or 487 (Cl)) ^{*5} (industrial)
	140 ^a	250 (Cl) ^{*6}	650 (Cl) ^c	160 (Cl) ocean ^{*6}
	180 ^{*6, e}	250 (Cl) ^{*6}	500 (Cl) ^{*6, d}	49 (Cl) biomass burning ^{*6}
CHCl ₃	150 ^a	66-130 (Cl) ^b	160-320 ^c	564 (Cl) ^{*6}
	150 ^a	210 (Cl) ^{*7}	511 ^c	
	183 ^{*7, e}	210 (Cl) ^{*7}	470 (350-600) ^{*7, e} 412(Cl) ^{*6, d}	
C ₂ Cl ₄	99 ^a	17-85 (Cl) ^b	63-310 (Cl) ^c	366 (or 313 (Cl)) ^{*5} (industrial)
	99 ^a	160 (Cl) ^{*6}	590 (Cl) ^c	16 (Cl) ocean ^{*6}
	133 ^{*6, e}	160 (Cl) ^{*6}	440 (Cl) ^{*6, e}	2 (Cl) fossil fuel ^{*6}
C ₂ HCl ₃	4.6 ^a	3.1 (Cl) ^b	260 (Cl) ^c	241 (or 195 (Cl)) ^{*5} (industrial)
	4.6 ^a	5.30 (Cl) ^{*6}	440 (Cl) ^c	20 (Cl) ocean ^{*6}
	5.5 ^{*6, e}	5.30 (Cl) ^{*6}	350 (Cl) ^{*6, e}	3 (Cl) fossil fuel ^{*6}
COCl ₂	70 ^g	250 (Cl) ^{*1}	1000 ^c	
CH ₂ ClCH ₂ Cl	70 ^a	5-26 (Cl) ^b	26-130 (Cl) ^c	700 ^{*8}

References: ^{*1} Kurylo and Rodríguez et al. (1999); ^{*2} Dvortsov et al. (1999); ^{*3} Carpenter and Liss (2000); ^{*4} Singh et al. (1983), Liss and Slater (1974), Moore and Groszko (1999); ^{*5} McCulloch et al. (1999); ^{*6} Keene et al. (1999); ^{*7} Khalil et al. (1999); ^{*8} Khalil (1998).

^a From Table 2-4.

^b Burden estimated using Equation (2.3) with the median BL mixing ratios from Table 2-8 and estimated scale height given in Table 2-10. The range reflects the three different median mixing ratios from TRACE-P, PEM-Tropics A, and PEM-Tropics B.

^c From estimated lifetime and estimated burden, i.e., (column 3)/(column 2). The range reflects range in estimated burden.

^d From 2-D model.

^e From 12-box model as calculated in reference 3.

^f From 3-D model simulation from Bell et al. (2001).

^g Wet-removal lifetime.

from wet deposition is about 2 months. Textor et al. (2002) revisited the issue of volcanic injection of chlorine to the stratosphere. However, reliable numerical estimates are not yet available.

2.4.1.2 BROMINE COMPOUNDS

Based on measured concentrations of BrO in the lower stratosphere, the concentration of Br_y is estimated to be about 20 ppt. The observed concentrations of VSL bromocarbons in the BL are in the 0.02-5 ppt range. Most have higher concentrations in the marine BL in regions with high ocean productivity. This indicates a possible marine source, although the exact mechanism for production is not well understood in most cases. Dibromomethane (CH₂Br₂; methylene bromide) is reasonably well mixed throughout the troposphere, compared with other bromocarbons, in part because of its widespread marine emissions and also because its lifetime is about 4 months (Table 2-4). Blake et al. (2002) reported mixing ratios of 0.8-1.2 ppt to altitudes of 12 km in tropical regions, and Schauffler et al. (1999) observed concentrations of 0.3-0.7 ppt at altitudes of 15-19 km in the tropics. The lower values from Schauffler et al. (1999) are consistent with the fact that Stratospheric Tracers of Atmospheric Transport (STRAT) data were obtained in the regions and seasons when convection was less prevalent. Bromoform (CHBr₃) is mainly emitted from marine source(s), but it has recently been reported that it may also have a minor source from industrial processes (Blake et al., 2002). Photolysis dominates its removal (Table 2-4). Blake et al. (2002) reported average marine boundary layer (MBL) mixing ratios of 0.7-1.9 ppt from their Pacific airborne samples collected between 35°N and 50°S. Higher marine boundary layer concentrations were observed in equatorial regions. Average mixing ratios for the 8-12 km region for all latitudes were 0.4-0.6 ppt, with the highest concentrations observed again in the equatorial latitudes. Halomethanes CH₂BrCl, CHBrCl₂, and CHBr₂Cl are thought to be produced by similar mechanisms and therefore have similar source distributions (Carpenter et al., 1999). CH₂BrCl has the longest average lifetime (Table 2-4) of the three gases and thus the highest overall concentrations. Schauffler et al. (1999) reported CH₂BrCl mixing ratios of 0.15-0.25 ppt at 10 km in the tropics, decreasing to about 0.01 ppt at 20 km. CHBrCl₂ concentrations were 0.1-0.15 ppt at 10 km and dropped to below 0.03 ppt at 15 km. Tropical concentrations of CHBr₂Cl were 0.05-0.2 ppt at 10 km and decreased to below 0.02 ppt above 15 km. These observations are consistent with photolysis being a significant removal process for CHBr₂Cl and CHBrCl₂ (see Section 2.3).

2.4.1.3 IODINE COMPOUNDS

Iodocarbons are mainly emitted from marine sources, and their generally very short lifetimes are reflected in their concentrations, typically 0.01-1 ppt. Methyl iodide (CH₃I) is the most prevalent iodocarbon in the atmosphere. CH₃I concentrations in the MBL are higher at low latitudes and midlatitudes, and show clear seasonal variations at midlatitudes with the highest concentrations in summer (Blake et al., 1999a; Yokouchi et al., 2001). Continental CH₃I concentration measurements are scarce. Bell et al. (2002) simulated the distribution of CH₃I in the troposphere using a 3-D model and an ocean source parameterized in terms of ocean productivity. The model calculated a mean atmospheric lifetime (defined as atmospheric burden divided by photochemical loss) of CH₃I against photolysis of about 6 days. The ratio of upper tropospheric (8-12 km) to lower tropospheric (0-2 km) concentrations in the tropical marine environment ranges from 0.11 in subsiding regions to 0.40 in upwelling regions (Bell et al., 2002). In the upper troposphere and lower stratosphere, CH₃I has been observed at concentrations of 0.0-0.2 ppt (Blake et al., 1999a; Sturges et al., 2001). Bell et al. (2002) calculated a net sea-to-air flux of 210 Gg yr⁻¹, which falls within the range of previous estimates (100-500 Gg yr⁻¹). Photochemical production of CH₃I in the seawater is consistent with the recent MBL observations (Yokouchi et al., 2001). Biomass burning (<10 Gg yr⁻¹; Andreae et al., 1996), rice fields (90 Gg yr⁻¹; Redeker et al., 2000; Muramatsu and Yoshida, 1995), wetlands (7.3 Gg yr⁻¹), and peatlands (1.4 Gg yr⁻¹; Dimmer et al., 2001) are the main continental sources. However, higher emissions from biomass burning of 20 Gg yr⁻¹ have also been reported (Muramatsu and Yoshida, 1995).

Carpenter et al. (2000) reported the automated measurements of biogenic alkyl halides at Mace Head, Ireland, including the detection of CH₂BrI and the first non-Arctic measurements of CH₂I₂ and CH₂ClI. The atmospheric mixing ratios of CH₂I₂ (<0.02-0.36 ppt), CH₂ClI (<0.02-0.21 ppt), CH₂BrI (<0.02-0.32 ppt), C₂H₅I (<0.02-0.21 ppt), and CH₃I (0.12-1.47 ppt) were used to calculate iodine atom emissions. The largest contribution of iodine atoms to the marine boundary layer was from CH₂I₂ (lifetime on the order of a few minutes). Annual global atmospheric input of 0.04 Gg yr⁻¹ by macroalgae was estimated by Giese et al. (1999). Thus, polyhalogenated iodine compounds released from macroalgae make a very small contribution to the global iodine budget (only 0.01-0.05% of total CH₃I emission), but are likely a significantly source of iodine to coastal atmospheres (Bassford et al., 1999; Baker et al., 2000).

VERY SHORT-LIVED SUBSTANCES

Current estimates of total inorganic iodine concentrations in the stratosphere are based on column measurements of IO (Wennberg et al., 1997; Pundt et al., 1998; Wittrock et al., 2000). The estimated range is from less than 0.05 ppt to 0.7 ppt.

2.4.2 Estimates of Contributions from VSL Halogen Source Gases

In this section, we describe a simple method for estimating the percentage of halogen atoms (emitted as organic source gases at the surface) that are transported to the stratosphere via the two pathways identified in Figure 2-1. Numerical estimates can be obtained using observed concentrations of the source gases and their degradation products, or using model output. The paucity of observations limits this analysis to providing an order-of-magnitude estimate. The exercise also helps to identify useful diagnostics for comparing model results. For simplicity, we assume that the intermediate products are sufficiently short lived that their contributions to the PGI pathway are small.

Consider a source gas X that contains $n_X^{h_X}$ halogen atoms and is emitted at $\mathcal{E}$ moles (h_X) yr^{-1} , where h_X is inorganic halogen species (Cl, Br, or I) found in compound X . The fractions of the emissions that enter the stratosphere via the SGI pathway ($\mathcal{J}_{\text{SGI}}^X$) and the PGI pathway ($\mathcal{J}_{\text{PGI}}^X$) are given by

$$\begin{aligned}\mathcal{J}_{\text{SGI}}^X &= \frac{n_X^{h_X} \times f_{\text{TT}}^X \times |wM_{\text{TT}}| \times A}{\mathcal{E}} \\ \mathcal{J}_{\text{PGI}}^X &= \frac{f_{\text{TT}}^{h_X} \times |wM_{\text{TT}}| \times A}{\mathcal{E}} = \frac{f_{\text{TT}}^{h_X}}{n_X^{h_X} \times f_{\text{TT}}^X} \times \mathcal{J}_{\text{SGI}}^X\end{aligned}\quad (2.1)$$

where f_{TT}^X and $f_{\text{TT}}^{h_X}$ are the mixing ratios for X and h_X near the tropical tropopause, w is the large-scale upward velocity across the tropopause, M_{TT} is the air density at the tropical tropopause in moles per unit volume, and A is the area of the Earth. To get a numerical value for $|wM_{\text{TT}}|$, we note that

$$|wM_{\text{TT}}| = \frac{M_{\text{surf}} \times \int_0^{Z_T} e^{-\frac{z}{H_0}} dz}{\tau_{\text{res-trop}}^{\text{air}}}\quad (2.2)$$

where $\tau_{\text{res-trop}}^{\text{air}}$ is the replacement time for tropospheric air against transport out of the troposphere, z is altitude, H_0 is the atmospheric scale height of air, M_{surf} is the air density (in moles per unit volume) at the surface, and Z_T is the altitude of the tropopause. Rosenlof and Holton (1993) provided an estimate of the mass flux across 100 mb that can be used to give a value of 17 years for $\tau_{\text{res-trop}}^{\text{air}}$.

The emission $\mathcal{E}$ is equal to the removal rate of X in the stratosphere and troposphere. We derive an expression for the removal rate assuming that the removal in the stratosphere can be ignored and that the local lifetime is uniform in the troposphere:

$$\begin{aligned}\mathcal{E} &= n_X^{h_X} \times \iiint \frac{M(\vec{x}) \times f^X(\vec{x})}{\tau_{\text{local}}^X(\vec{x})} dV \\ &\approx \frac{n_X^{h_X} \times M_{\text{surf}} \times f_{\text{BL}}^X \times A \times \int_0^{Z_T} e^{-\frac{z}{H_0}} \times f_{\text{norm}}^X(z) dz}{\tau_{\text{local}}^X}\end{aligned}\quad (2.3)$$

where $M(\vec{x})$, $f^X(\vec{x})$, and $\tau_{\text{local}}^X(\vec{x})$ are the air density, mixing ratio, and local lifetime of X as a function of $\vec{x}$. The local photochemical lifetime of X is taken from Table 2-4 and assumed to be approximately uniform in the troposphere, f_{BL}^X is the mixing ratio of X in the boundary layer, and $f_{\text{norm}}^X(z)$ is the normalized altitude profile of $f^X(\vec{x})$ and has the value 1 in the 1-km-thick BL and falls off with the assumed scale height H_f^X given in Table 2-10. Note that although $f_{\text{norm}}^X(z)$ is used to estimate the burden of the source gas, f_{TT}^X is expected to be larger than

$$f_{\text{BL}}^X \times \exp\left[-(Z_T - 1)/H_f^X\right]$$

because convection will carry additional source gas to the TTL. Model results in Figure 2-4 clearly show that the mixing ratio between 500 and 200 hPa do not follow a simple exponential decrease with height. The contribution to the burden from the extra source gas carried by convection to the TTL is ignored in this estimate. Combining Equations (2.1), (2.2), and (2.3) gives

$$\mathcal{J}_{\text{SGI}}^X = \frac{f_{\text{TT}}^X}{f_{\text{BL}}^X} \times \frac{\tau_{\text{local}}^X}{\tau_{\text{res-trop}}^{\text{air}}} \times K(H_0, H_f^X)\quad (2.4)$$

where $K(H_0, H_f^X)$ is a simple quadrature in terms of the scale heights (see footnote b in Table 2-10).

Table 2-8 gives the observed median surface concentrations and the median concentrations at 10 km in the tropics for several VSL source gases from the TRACE-P and PEM-Tropics A and B campaigns. In lieu of values for f_{TT}^X , it is assumed that X is well mixed in the TTL and $f_{\text{TTL}}^X \sim f_{\text{UT}}^X$. Using the $f_{\text{UT}}^X / f_{\text{BL}}^X$ values in Equation (2.4) gives estimated values of $\mathcal{J}_{\text{SGI}}^X$ (see Table 2-10) ranging from 0.03% to 3% for source gases with local lifetimes of 5 days to 150 days. The values derived for the VSL source gases with 100-day lifetimes are comparable with previous

Table 2-10. Values used to estimate the fraction of halogen atoms transported to the stratosphere via the SGI pathway ($\mathcal{F}_{SGI}^X$) (see Section 2.4.2).

Species	Local Lifetime ^a (days)	Estimated H_f^X (km)	$K(H_0, H_f^X)$ ^b	Estimated $\frac{f_{UT}^X}{f_{BL}^X}$: ^c TRACE-P PEM-Tropics B PEM-Tropics A	$\mathcal{F}_{SGI}^X$ Calculated Using Eq. (2.4): TRACE-P PEM-Tropics B PEM-Tropics A	Model Estimate of $\mathcal{F}_{SGI}^X$
C ₂ HCl ₃	4.6	1	4.8	0.2 N/A N/A	0.0008 N/A N/A	
CH ₃ I	7	1	4.8	0.05 0.2 0.15	0.00026 0.0011 0.000803	
CHBr ₃	26	2	3.3	0.3 0.3 0.2	0.0042 0.0042 0.0028	
CH ₂ ClCH ₂ Cl	70	5	2.0	0.3 0.6 N/A	0.0065 0.013 N/A	
CHBr ₂ Cl	69	5	2.0	0.6 0.5 0.5	0.013 0.011 0.011	
CHBrCl ₂	78	10	1.5	0.7 0.6 0.5	0.013 0.011 0.0093	
C ₂ Cl ₄	99	10	1.5	0.3 0.6 1.1	0.0071 0.014 0.032	0.01 ^{*1}
CH ₂ Br ₂	120	15	1.3	0.8 0.7 0.8	0.020 0.018 0.020	
CH ₂ Cl ₂	140	15	1.3	0.5 0.7 1.1	0.015 0.021 0.033	0.014 ^{*2} , 0.02 ^{*3}
CHCl ₃	150	15	1.3	0.6 0.8 1.0	0.019 0.025 0.031	0.004 ^{*4} , 0.02 ^{*1}

In columns 5 and 6, for each species, the first value is for data from TRACE-P; the second, from PEM-Tropics B; and the third, from PEM-Tropics A. References: ^{*1} Kindler et al. (1995); ^{*2} Keene et al. (1999); ^{*3} Graedel and Keene (1995); ^{*4} Khalil (1998), results are from 12-box model.

^a From Table 2-4.

$$K(H_0, H_f^X) = \int_0^{Z_T} e^{-\frac{z}{H_0}} dz \bigg/ \int_0^{Z_T} e^{-\frac{z}{H_0}} \times f_{\text{normal}}^X(z) dz \text{ where } f_{\text{normal}}^X(z) = 1 \text{ for } z \leq 1 \text{ km; } f_{\text{normal}}^X(z) = e^{-\frac{z-1}{H_f^X}} \text{ for } z \geq 1 \text{ km.}$$

The integral is calculated assuming that areas in the tropics and extratropics are equal and Z_T is 15 km and 10 km for the tropics and the extratropics, respectively. See Section 2.4.2 for definitions of other terms.

^c From Table 2-8.

VERY SHORT-LIVED SUBSTANCES

results derived using a 12-box numerical model (see reference cited in Table 2-10).

For $\mathcal{J}_{\text{PGI}}^X$, we use the following estimate:

$$\mathcal{J}_{\text{PGI}}^X = \frac{f_{\text{TT}}^{h_X}}{n_X^{h_X} \times f_{\text{TT}}^X} \times \mathcal{J}_{\text{SGI}}^X \approx \frac{\tau_{\text{PG-X}}}{\tau_{\text{local}}^X} \times \mathcal{J}_{\text{SGI}}^X \quad (2.5)$$

where $\tau_{\text{PG-X}}$ is the local residence time (against chemical degradation, transport, and washout) for the product gas from the degradation of X . If there is no long-lived intermediate product for species X , $\tau_{\text{PG-X}}$ will correspond to the washout lifetime of the inorganic halogen species. Using a nominal value of 10 days would indicate that $\mathcal{J}_{\text{PGI}}^X$ is comparable with $\mathcal{J}_{\text{SGI}}^X$ for source gases having local lifetimes of about 10 days, and a tenth of $\mathcal{J}_{\text{SGI}}^X$ for source gases having lifetimes of order 100 days. If there is a long-lived intermediate ($\tau_{\text{PG-X}}$ longer than half a year), the value for $\mathcal{J}_{\text{PGI}}^X$ could approach $(1 - \mathcal{J}_{\text{SGI}}^X)$.

It is important to recognize the assumptions that were used to obtain these estimates. In the procedure, we assumed that the flux through the tropopause is governed by the large-scale circulation with uniform f_{TT}^X and $f_{\text{TT}}^{h_X}$ along the tropopause and that the concentrations of X or h_X are uniform within the TTL so that observations collected in the upper troposphere can be used. In addition, we did not include transport along isentropic surfaces in the subtropics or sub-synoptic-scale stratosphere-troposphere exchange events that occur in the extratropics. In estimating the chemical removal rate of the source gas, it is assumed that the local photochemical lifetime is uniform in the troposphere. A similar assumption is made for the washout rate of the inorganic halogen. However, these two parameters are likely to vary strongly with latitude and season and to be very dependent on the location of emissions.

To relate the concentration of inorganic halogen in the stratosphere ($f_{\text{Strat}}^{h_X}$) to the concentration of the source gas at the surface (f_{BL}^X), one can proceed as follows. For simplicity, it is assumed that the source gas contains one halogen atom. Take the case in which the concentration of the source gas is 1 ppt in a 1-km layer above the surface and the lifetime of the gas is 10 days. The emission needed to balance the removal in the BL is estimated to be 8×10^8 moles yr^{-1} . If one assumes that 0.1 to 1% of the flux emitted in the troposphere enters the stratosphere as odd halogen, the flux is 0.8×10^6 to 8×10^6 moles yr^{-1} . Taking a stratospheric residence time of 2 years (see, e.g., Holton, 1990) would mean that the average mixing ratio for inorganic halogen in the stratosphere is about 0.1 to 1

ppt. The typical concentrations for VSL halogen source gases are of order several ppt for bromine and iodine source gases, and up to 50 ppt for chlorine source gases. The current inorganic chlorine concentration in the stratosphere is about 3 ppb. It is thus unlikely that VSL chlorine source gases will make a significant contribution to the chlorine budget in the middle and upper stratosphere. However, they may still make a contribution close to the tropopause. In the case of bromine (with inorganic bromine concentration at 20 ppt and iodine at <1 ppt), it is likely that the effects from VSL halogen source gases will be important throughout the stratosphere.

2.4.3 Modeling Studies

We now review some of the modeling work on the contribution of VSL source gases to the stratospheric inorganic halogen budget. There have been two recent model studies on bromoform (CHBr_3). In both studies it was assumed that the degradation products immediately released their Br atoms. Dvortsov et al. (1999) used a global two-dimensional (2-D) model with parameterized convection and washout prescribed as a function of altitude, resulting in washout time constants ranging from about 9 days at the ground to 17 days just below the tropopause. Emissions were assumed to be uniform over the ocean and were adjusted to give a surface concentration of 1.5-2 ppt CHBr_3 . In their model simulation, sufficient bromine atoms (in its organic and inorganic form) were transported to the stratosphere to maintain ~ 1 ppt Br_y . Note that 75% of the flux came through the tropical tropopause as Br_y . Nielsen and Douglass (2001) ran an offline 3-D model using assimilated winds to simulate CHBr_3 and Br_y . Their washout time constant was fixed at ~ 6 days throughout the troposphere. Surface fluxes and mixing ratios were treated in a manner similar to that of Dvortsov et al. (1999). Figure 2-9 shows their average modeled tropical CHBr_3 profile again compared with PEM-Tropics data, plus measurements in the tropical tropopause layer (TTL) from the STRAT campaign. Nielsen and Douglass (2001) also calculated that ~ 1 ppt Br_y is derived from CHBr_3 in the lower stratosphere, with 50% of this amount transported as inorganic bromine.

Although both model studies agree well with data up to about 10 km, both studies overestimate CHBr_3 in the TTL compared with the STRAT data. Because the models maintain too much CHBr_3 in the TTL, Nielsen and Douglass (2001) estimate that CHBr_3 contributes to maintaining, at most, 15% of the Br_y in the stratosphere. The relative effect of this contribution is likely to be greatest in the layer immediately above the tropopause, where Br_y from CHBr_3 would increase total Br_y by $\sim 45\%$. These

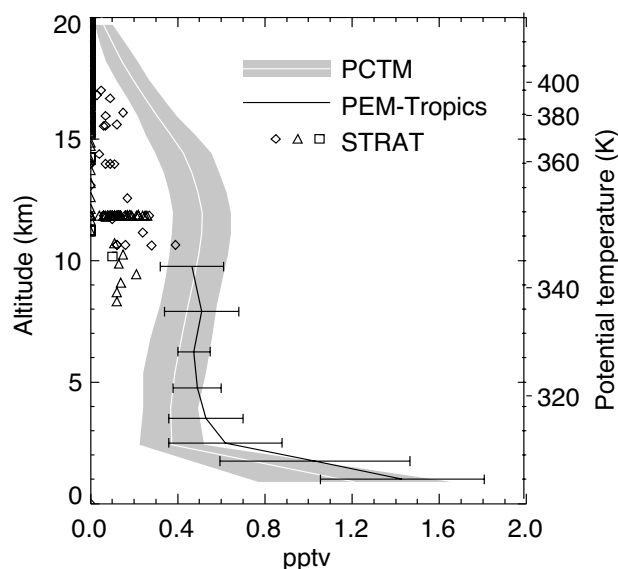


Figure 2-9. Results from 3-D model simulations (PCTM, parameterized chemistry and transport model) of tropical CHBr_3 and comparison with PEM-Tropics and STRAT data within 30° of the equator. The different symbols denote data taken at different times (diamonds for data taken in January and February, triangles for July and August, and squares for December). The model overestimates the transport of CHBr_3 to the tropical upper troposphere (see Nielsen and Douglass, 2001). Figure courtesy of A. Douglass, NASA GSFC, U.S.

modeling studies, together with the observationally based studies of Wamsley et al. (1998) and Pfeilsticker et al. (2000), suggest the importance of including shorter lived species in the stratospheric bromine budget.

Several recent studies provide estimates for the impact of 1-bromopropane (n-PB) on stratospheric bromine levels (Olsen et al., 2000; Bridgeman et al., 2000; Wuebbles et al. 2001) (see Section 2.5.3). They all noted that the idea of a single lifetime is flawed for VSL species and that mixing ratios of n-PB reaching the tropical upper troposphere depend strongly on the latitude and season of the emissions. The Wuebbles et al. (2001) study used a global 3-D model with a parameterized chemistry scheme to investigate transport of n-PB and its degradation products across the tropical tropopause. They found that tropical emissions were twice as likely to enter the stratosphere as high-latitude emissions, in qualitative agreement with the other two studies. Wuebbles et al. (2001) showed that up to 0.5% of the Br emitted as n-PB at the surface entered the stratosphere, with only one-third of Br in the form of n-PB (the SGI pathway). The remainder was mostly in the form of inorganic bromine (the PGI

pathway). However, these values are likely to change as more reliable information on the degradation of n-PB becomes available.

All the modeling studies emphasize that the lack of knowledge about the fate of the degradation products limits our ability to quantify their contribution to halogen loading in the stratosphere. Up to now, little attention has been paid to evaluation of model simulations of the processes and time scales necessary to understand the transport and chemistry of VSL substances. For example, cross-tropopause transport rates are very important for determining the effects of Br_y on O_3 loss in the lowermost stratosphere, yet neither observations nor models are able to fully agree on the degree of communication between the troposphere and stratosphere (see Section 2.2.2.2). Furthermore, few models had their transport evaluated in this region against observations. Examples of such studies include the analyses by Strahan et al. (1998) and Douglass et al. (1999). These studies evaluated the tropopause behavior of different models participating in the Global Modeling Initiative by comparisons with the known phase lag between UT and LS CO_2 . Clearly more studies of this type are required.

2.4.4 Information Needed for Future Evaluation

In summary, it can be concluded that the effects of VSL halogen source gases on halogen loading in the stratosphere are likely to be limited to bromine and iodine budgets in the present-day atmosphere. It is unlikely that VSL chlorine compounds will make a significant contribution to the chlorine budget.

It is clear that more observations of VSL substances, their degradation products, and inorganic halogen species are required in the troposphere and the stratosphere if we are to reduce the uncertainties surrounding our estimates of the contribution of these compounds to the present halogen loading in the stratosphere. In particular, measurements are needed in the TTL and the lowermost stratosphere. This could be particularly challenging if the sequestration of halogen ions in aerosol particles turns out to be important (Murphy and Thomson, 2000). It is encouraging that several independent models simulate similar amounts ($\sim 0.5\%$) of Br_y input into the stratosphere from n-PB, although this cannot be easily verified using available observations. The observed $f_{\text{UT}}^X / f_{\text{BL}}^X$ ratios as defined in Table 2-8 for specific source gases could provide useful constraints although one must also have a good knowledge of the distribution of surface source strengths. Improved estimates will be brought about by improvements in modeling capabilities

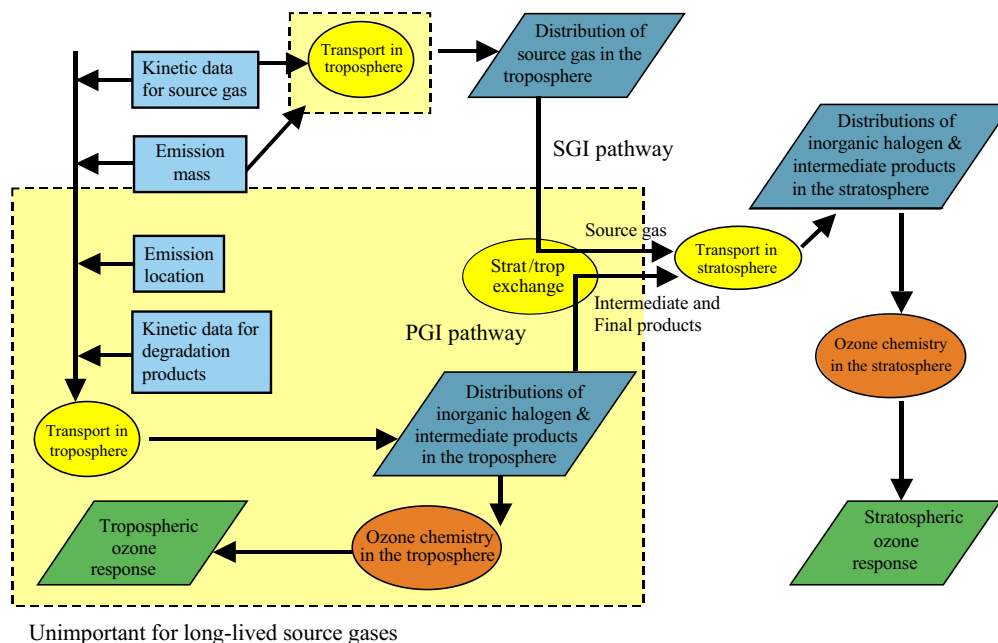


Figure 2-10. Schematic showing information needed to assess the ozone depletion estimate of halogen source gases. Items in rectangles are species specific. Items in ovals are common to all species. Items in parallelograms are model predictions. Several processes are highlighted in two yellow-colored boxes with heavy dashed outlines. The simulation of these processes in numerical models has not been fully evaluated.

and parameterization of processes like convection and washout. Cross-tropopause transport in the tropics, through the TTL region, also requires thorough evaluation in global models including tests of tropical ascent rates and exchange with the extratropics. These studies need to be coupled to better understanding of degradation products, their local lifetimes and solubilities (also see Section 2.3).

2.5 ESTIMATES FOR THE POTENTIAL IMPACT OF HALOGENATED VSL SUBSTANCES ON COLUMN OZONE

An operational definition for the Ozone Depletion Potential (ODP) of a species X is given by

$$\text{ODP}(X, \vec{x}_e, t_e) = \frac{\Delta \text{O}_3(X, E)}{\Delta \text{O}_3(\text{CFC-11}, E)} \quad (2.6)$$

where $\Delta\text{O}_3(X, E)$ is the steady-state percent change in stratospheric ozone burden due to emission of X at the rate of $E \text{ g yr}^{-1}$ at a specific location ($\vec{x}_e$) and time (t_e) of the year. The ODP value is defined relative to the ozone-depleting efficiency of CFC-11 (CCl_3F). An equivalent definition for ODP is the cumulative ozone depletion for the same mass pulse emission (same location and time of

year) of X versus that of CFC-11 (Prather, 1996, 1997, 2002). This latter definition leads naturally to using the ODP values in equivalent effective stratospheric chlorine (EESC) calculations (Daniel et al., 1995; Madronich and Velders et al., 1999).

Figure 2-10 shows the information needed and the procedure for calculating the change in column ozone from emission of a halogen source gas at the Earth's surface. The procedure for calculating ODP was originally developed for halocarbons (Wuebbles, 1981, 1983) with lifetimes sufficiently long (more than 1 year) that their mixing ratios are uniform in the troposphere and the increase in inorganic halogen in the troposphere is expected to be small. For those gases, the processes in the yellow boxes in Figure 2-10 are unimportant, and thus the ODP value is independent of location and time of emission. The methods (either using results from numerical models or using measured quantities in semiempirical approaches) for calculating ODP values for long-lived source gases have been reviewed in previous reports, and they are judged to give reliable results. However, many of the processes in the yellow boxes and how well they are simulated in models have not been evaluated. Thus, assessing the reliability of the ODP values for very short-lived (VSL) halogen source gases emitted at the Earth's surface requires further evaluations.

Several recent efforts to address these issues include a workshop on VSL compounds in March 1999 sponsored by the U.S. Environmental Protection Agency (EPA) and the National Aeronautics and Space Administration (NASA) (Wuebbles and Ko, 1999); the findings of a special United Nations Environment Programme (UNEP) report (UNEP, 2000); and several recent publications (Bridgeman et al., 2000; Olsen et al., 2000; Wuebbles et al., 2001). We review the methods used to compute ODP for long-lived source gases in Section 2.5.1, and in Section 2.5.2 we contrast them with the new method needed for the VSL source gases. Some of the results for ODP based on numerical models are reviewed in Section 2.5.3. A brief discussion on performing the chlorine loading calculation is presented in Section 2.5.4.

2.5.1 Review of Methodology for Calculating ODPs for Long-Lived Source Gases

Because the ODP value of a long-lived source gas is independent of the location and time of emission, we will suppress the $\bar{x}_e$ and t_e notations in this section. Solomon et al. (1992) provided an expression for computing a semiempirical value for the ODP ($ODP_{s-e}(X)$) of a long-lived source gas. This is useful for relating ODP values to measured quantities that could be used to evaluate the model-calculated results. We will follow a similar procedure here and express $\Delta O_3(X, E)$ as a product of two factors:

$$\Delta O_3(X, E) = HL_X(E) \times \delta_X \quad (2.7)$$

where $HL_X(E)$ is the steady-state stratospheric inorganic halogen loading (chlorine, bromine, or iodine mixing ratio in mole fraction) associated with emission of X at E g yr⁻¹ and δ_X is the ozone-removal efficiency per unit inorganic halogen loading from X . Note that the definitions for $HL_X(E)$ and δ_X are related in that there is more than one way to quantify the halogen loading. One could either use the average mixing ratio of the inorganic halogen in the stratosphere ($HL_X^{Avg}(E)$) or the mixing ratio at the stratopause ($HL_X^{Strp}(E)$), where Strp means stratopause). Depending on which definition one chooses, δ_X will take different values. Using this notation,

$$\begin{aligned} ODP_{s-e}(X) &= \frac{HL_X(E)}{HL_{CFC-11}(E)} \times \frac{\delta_X}{\delta_{CFC-11}} \\ &= CLP(X) \times \zeta_X \end{aligned} \quad (2.8)$$

where $CLP(X)$ is the chlorine loading potential and ζ_X is the ratio of the ozone-removal efficiency factors. For long-lived source gases where the contribution from the PGI pathway to the inorganic halogen loading in the stratosphere is small compared with that from the SGI pathway, the steady-state mixing ratio of h_X at the stratopause (that results from a constant emission of X) is approximately equal to the mixing ratio of X in the troposphere (see Prather and Watson, 1990). Now

$$HL_X^{Strp}(E) = \frac{1}{M} \times \frac{E \times \tau_X}{\mu_X} \times n_X^{h_X} \quad (2.9)$$

where μ_X is the gram molecular weight, τ_X is the atmospheric lifetime of X , $n_X^{h_X}$ is the number of halogen atoms in X , and M is the number of moles of air in the atmosphere. Thus, for long-lived species like those treated in Chapter 1,

$$\begin{aligned} CLP^{Strp}(X) &= \frac{HL_X^{Strp}(E)}{HL_{CFC-11}^{Strp}(E)} \\ &= \frac{\mu_{CFC-11}}{\mu_X} \times \frac{\tau_X}{\tau_{CFC-11}} \times \frac{n_X^{h_X}}{n_{CFC-11}^{Cl}} \end{aligned} \quad (2.10)$$

The efficiency factor ζ_X^{Strp} has two components: $\zeta_X^{Strp} = \zeta^S \times \zeta_X^D$. The values for the first component (ζ^S , S for speciation) depend on whether the halogen is chlorine, bromine, or iodine. The other factor (ζ_X^D , D for distribution) has to do with the distribution of the inorganic halogen in the stratosphere. Equation (2.8) corresponds to the same definition used in Chapter 1, with ζ^S identified with the α factor, and ζ_X^D is the fractional release factor. When a numerical model is used to calculate $ODP(X)$ via Equation (2.6), one can identify the value for $\zeta^S \times \zeta_X^D$ with the $ODP(X)/CLP^{Strp}(X)$ ratio. From this perspective, the value for $\zeta^S \times \zeta_X^D$ corresponds to a spatial and seasonal average weighted by the ozone response in the lower stratosphere. Thus, it is not possible to pick values for ζ^S and ζ_X^D at a specific location and time to represent the $ODP(X)/CLP^{Strp}(X)$ ratio. A way to proceed is to pick a conventional value for ζ^S and define ζ_X^D as $ODP(X)/CLP^{Strp}(X)$ divided by ζ^S . The value for ζ^{Cl} is 1 by definition. Based on the $ODP(X)/CLP^{Strp}(X)$ ratios for chlorine species (see Table 1-5), the value for ζ_X^D ranges from 0.35 for HCFC-22 ($CHClF_2$) to 1.08 for methyl chloroform (CH_3CCl_3). Model simulations by Ko et al. (1998) gave a value of 58 for $\zeta^{Br} \times \zeta_{CH_3Br}^D$ for CH_3Br . The con-

VERY SHORT-LIVED SUBSTANCES

vention is to take ζ^{Br} to be 45, implying that $\zeta_{\text{CH}_3\text{Br}}^D$ has the value of 1.3. The kinetic data are less complete for iodine. Solomon et al. (1994a) provided an estimate of 100-2000 for ζ^{I} based on estimated reaction rate constants. Bedjanian et al. (1998) gave 150 using updated rate data. A more recent study using JPL-2000 rates (Sander et al., 2000) from the Atmospheric and Environmental Research, Inc. (AER) model (Ko et al., 1998) gave a value of 300 for $\zeta^{\text{I}} \times \zeta_{\text{CH}_3\text{I}}^D$ for CH_3I . This could be interpreted as 150 for ζ^{I} and 2 for $\zeta_{\text{CH}_3\text{I}}^D$. However, considering the missing data on some of the reservoir species (see Section 2.3.4), we will use a range of 150-300 for ζ^{I} . A useful guideline for ζ_X^D is that ζ_X^D is greater or smaller than 1 depending on whether the local lifetime of X in the lower stratosphere is shorter or longer than the local lifetime of CFC-11 (~2 years). From the values of fractional release measured for CFC-11 in the lower stratosphere, ζ_X^D should generally not be much larger than 2. Thus, the estimate for long-lived source gases is

$$\text{ODP}_{s-e}^{\text{long-lived}}(X) = \frac{\mu_{\text{CFC-11}}}{\mu_X} \times \frac{\tau_X}{\tau_{\text{CFC-11}}} \times \frac{n_X^{h_X}}{3} \times \left(\begin{array}{c} \zeta^{\text{Cl}} = 1 \\ \zeta^{\text{Br}} = 45 \\ \zeta^{\text{I}} \approx 150 \rightarrow 300 \end{array} \right) \times \zeta_X^D \quad (2.11)$$

2.5.2 Modified Approach for Estimating ODP for Halogenated VSL Substances

The inorganic halogen loading from a VSL source gas is maintained by the transport of halogen atoms affected by the SGI and PGI pathways. Solomon et al. (1994b) suggested a method to estimate the contribution from the SGI pathway based on the observed concentration of the VSL source gas near the tropopause. We will restrict the discussion in this subsection to emissions at the Earth's surface. Thus, $\vec{x}_e$ can be represented by θ_e and ϕ_e , corresponding to the latitude and longitude of the emission location. It should be noted that certain applications (e.g., inerting fuel tanks in aircraft) involve release of the chemical in the atmosphere above the surface. In those cases, the ODP value will also depend on the altitude at which the VSL substance is released. In this section, using the notation from Section 2.4 (Equation (2.1)) and $\mathcal{L} = E \times n_X^{h_X} / \mu_X$, we obtain

$$\begin{aligned} \text{HL}_X^{\text{Avg}}(E(\theta_e, \phi_e, t_e)) &= \text{HL}_{X\text{-SGI}}^{\text{Avg}}(E(\theta_e, \phi_e, t_e)) \\ &\quad + \text{HL}_{X\text{-PGI}}^{\text{Avg}}(E(\theta_e, \phi_e, t_e)) \\ &= \frac{E(\theta_e, \phi_e, t_e) \times n_X^{h_X}}{\mathcal{M}_{\text{Strat}} \times \mu_X} \times \tau_{\text{res-strat}}^{h_X} \\ &\quad \times (\mathcal{J}_{\text{SGI}}^X(\theta_e, \phi_e, t_e) + \mathcal{J}_{\text{PGI}}^X(\theta_e, \phi_e, t_e)) \end{aligned} \quad (2.12)$$

where $\mathcal{M}_{\text{Strat}}$ is the number of moles of air in the stratosphere, and E , $\mathcal{J}_{\text{SGI}}^X$, and $\mathcal{J}_{\text{PGI}}^X$ are functions of θ_e , ϕ_e , and t_e . The residence time for the inorganic halogen in the stratosphere is designated by $\tau_{\text{res-strat}}^{h_X}$. Strictly speaking, $\tau_{\text{res-strat}}^{h_X}$ could also be a function of θ_e , ϕ_e , and t_e because material that enters the tropical lower stratosphere has residence times different from material that enters the extra-tropical lower stratosphere. We do not consider this for now.

The expression for $\text{HL}_{\text{CFC-11}}^{\text{Avg}}(E)$ is much simpler:

$$\text{HL}_{\text{CFC-11}}^{\text{Avg}}(E) = \frac{1}{\mathcal{M}_{\text{Strat}}} \times \frac{E \times 3}{\mu_{\text{CFC-11}}} \times \tau_{\text{res-strat}}^{h_{\text{CFC-11}}} \quad (2.13)$$

where we used the facts that for CFC-11, $\mathcal{J}_{\text{SGI}}^X = 1$, $\mathcal{J}_{\text{PGI}}^X = 0$, and it contains three chlorine atoms. We left off the explicit θ_e , ϕ_e , and t_e dependence because the loading for CFC-11 will only depend on the averaged annual tropospheric emission independent of location.

Using Equations (2.12) and (2.13) in Equation (2.8), we obtain

$$\begin{aligned} \text{ODP}_{s-e}^{\text{VSL}}(X, \theta_e, \phi_e, t_e) &= \text{ODP}_{s-e\text{-SGI}}^{\text{VSL}}(X, \theta_e, \phi_e, t_e) \\ &\quad + \text{ODP}_{s-e\text{-PGI}}^{\text{VSL}}(X, \theta_e, \phi_e, t_e) \\ &= \frac{\mu_{\text{CFC-11}}}{\mu_X} \times \frac{n_X^{h_X}}{3} \times \frac{\tau_{\text{res-strat}}^{h_X}}{\tau_{\text{res-strat}}^{h_{\text{CFC-11}}}} \\ &\quad \times \left\{ (\zeta_{X\text{-SGI}}^{\text{Avg}} \times \mathcal{J}_{\text{SGI}}^X(\theta_e, \phi_e, t_e)) \right. \\ &\quad \left. + (\zeta_{X\text{-PGI}}^{\text{Avg}} \times \mathcal{J}_{\text{PGI}}^X(\theta_e, \phi_e, t_e)) \right\} \end{aligned} \quad (2.14)$$

Similar to the discussion in Section 2.5.1, we use the expression

$$\zeta_{X\text{-SGI/PGI}}^{\text{Avg}} = \zeta^S \times \tilde{\zeta}_{X\text{-SGI/PGI}}^D(\theta_e, \phi_e, t_e)$$

where $\tilde{\zeta}_{X\text{-SGI/PGI}}^D$ is the distribution factor for h_X maintained by either the SGI or PGI pathway. Thus, for VSL com-

pounds, the concept of a single ODP generally provided to policymakers for long-lived species needs to be replaced with a table of ODP values, essentially a matrix of ODP values depending on the location and season of emissions.

To obtain an order-of-magnitude estimate for the ODP values, we assume $\mathcal{J}_{\text{SGI}}^X + \mathcal{J}_{\text{PGI}}^X$ has values between 0.001 and 0.01 for a VSL source gas with no long-lived intermediate products. We will also assume that the product $\left(\tau_{\text{res-strat}}^{h_X} / \tau_{\text{res-strat}}^{h_{\text{CFC-11}}}\right) \times \tilde{\zeta}_{X\text{-SGI/PGI}}^D$ is of order 1. This is reasonable because a species with smaller fractional release in the lower stratosphere will have a larger $\tau_{\text{res-strat}}^{h_X}$. These values give

$$\text{ODP}_{s,e}^{\text{VSL}*} \approx (0.001 \rightarrow 0.01) \times \frac{\mu_{\text{CFC-11}}}{\mu_X} \times \frac{n_X^{h_X}}{3} \times \begin{pmatrix} \zeta^{\text{Cl}} = 1 \\ \zeta^{\text{Br}} = 45 \\ \zeta^{\text{I}} \approx 150 \rightarrow 300 \end{pmatrix} \quad (2.15)$$

where the notation VSL^* serves as a reminder that the estimate is valid only for VSL source gases with no long-lived intermediate products.

The ODP estimate given by Equation (2.15) represents ozone depletion in the stratosphere. If degradation of the source gas leads to sufficiently high local concentrations of inorganic halogen species in the free troposphere, there can be a decrease in ozone in the free troposphere on a regional scale. Observed depletion of ozone in the boundary layer of the polar region following polar sunrises has been attributed to inorganic bromine (see, e.g., Barrie and Platt, 1997). In polluted regions, the VSL halocarbons can also act as a volatile organic compound (VOC) to produce ozone. The expected tropospheric ozone response will depend on the NO_x , HO_x , and hydrocarbon distributions in the region. Thus, the expected response will again depend on the location and time of emission. This raises an interesting issue as to whether and how one should include such effects in the ODP estimates.

2.5.3 Existing Modeling Studies on ODP for n-PB

If one is confident that a numerical model can correctly predict the halogen loading and ozone depletion in the stratosphere, one can then use the model results in Equation (2.6) to compute an ODP. Two-dimensional models of the stratosphere have been the accepted tools for calculating the ozone response in the stratosphere. Most of them lack parameterizations for convection and

do not represent realistically washout processes in deriving the transport of the VSL source gases and their degradation products to the stratosphere. Three-dimensional chemical transport models (CTMs) are more suited for studies of tropospheric processes but generally do not have complete representations of the stratosphere and its processes. In both cases, the model results must be interpreted with care because there has been no study that comprehensively evaluates how well models simulate the processes in the troposphere.

Many of the lessons learned come from studies of n-propyl bromide. Earlier studies (Nelson et al., 1997; Wuebbles et al., 1998, 1999) based on analyses assuming emissions evenly distributed across the globe had derived an atmospheric lifetime for n-PB due to its reaction with OH of 11-14 days. The single-valued ODPs for n-PB using the traditional approach in Wuebbles et al. (1998, 1999) have been supplanted by the following analyses using the new approach.

Olsen et al. (2000) applied the low-resolution (8° latitude $\times$ 10° longitude $\times$ 9 layers) three-dimensional University of California at Irvine (UCI) tropospheric chemical transport model to determine the amount of VSL substances reaching the stratosphere via the SGI pathway for a range of atmospheric lifetimes, and for various seasons and latitudes of emission. The model-calculated inorganic halogen loadings from n-PB sustained by the SGI pathway were used as a scaling parameter to obtain ODP values for different emission scenarios based on the relation between ODP and loading computed from a 2-D model (Wuebbles et al., 1999). The estimated ODP values from Olsen et al. (2000) range from 0.0002 (for summer emissions at 56° to 64°N) to as large as 0.06 for tropical emissions (as shown in Table 2-11).

Bridgeman et al. (2000) used the TOMCAT three-dimensional global chemical-transport model ($5.6^\circ \times 5.6^\circ \times 31$ levels) to evaluate the atmospheric lifetime and amount of n-PB reaching the stratosphere as a function of location and season of emission. They then used an empirical approach to the calculation of ODPs, based on the derived lifetime and the fraction of n-PB emissions reaching the stratosphere. For n-PB, they derived ODPs that vary from 0.0033 for emissions from Europe to 0.0109 for emissions from Indonesia. The study assumed that any bromine atoms released in the troposphere would be removed by rainout with 100% efficiency before reaching the stratosphere. Thus, the contribution from the PGI pathway was ignored. They did suggest that such transport of degradation products could significantly increase the amount of bromine reaching the stratosphere.

Wuebbles et al. (2001) used the Model of Ozone and Related Chemical Tracers, version 2 (MOZART2)

VERY SHORT-LIVED SUBSTANCES

Table 2-11. Summary of existing studies that have determined a range of ODP values for the case of n-propyl bromide (n-PB), updated from the evaluation in UNEP (2000).

Study	Range of ODP Values ^a	Effects of Halogen Loading from the PGI Pathway
Bridgeman et al. (2000)	0.0033-0.0109	No
Olsen et al. (2000)	0.0002-0.06	No
Wuebbles et al. (2001)	0.016-0.105	Yes

^a Range for the different set of calculations performed in each study. The extreme range of values in Olsen et al. (2000) was due to calculating separate results for individual seasons.

three-dimensional chemical-transport model ($5^{\circ} \times 5^{\circ} \times 34$ levels) in combination with their two-dimensional model to compute ODPs for n-PB. An effort was made to quantify the effects of degradation products. With then-available information, bromoacetone was considered to be the intermediate degradation product with the largest concentration, having a local lifetime of about 1 day. The three-dimensional model was used with simplified chemistry having bromoacetone as the only intermediate degradation product. For n-PB emitted uniformly over global land masses north of 60°S and south of 70°N , their three-dimensional model calculations suggest that about 0.44% of the emitted bromine enters the stratosphere. About 33% of the bromine reaching the stratosphere results from the direct transport of n-PB to the stratosphere and about 19% due to the transport of bromoacetone to the stratosphere. The rest (48%) is from transport of inorganic bromine. Calculated ODP values for other emission scenarios are given in Table 2-12.

Recent data (Burkholder et al., 2002) suggest that the lifetime of bromoacetone is of the order of hours rather than days. Thus, the contribution from bromoacetone may be considerably smaller in evaluating the ODPs for n-PB. As an estimate of the effects of the newly evaluated much shorter atmospheric lifetime, Table 2-12 uses the model results in the Wuebbles et al. (2001) paper to estimate the resulting ODPs if no bromoacetone had reached the stratosphere. The resulting ODP values are reduced, but only slightly. However, the estimate did not account for the likely increase in the amount of inorganic bromine that would reach the stratosphere if the bromoacetone lifetime was reduced to a few hours, and the different distribution in inorganic bromine in the two cases.

Table 2-12. Estimated ODP for n-PB as a function of location of emissions based on Wuebbles et al. (2001).

Emission Scenario	Derived ODP Range	Modified ODP Range (Reduced Bromoacetone)
Global	0.033-0.040	0.027-0.038
North America	0.018-0.019	0.015-0.017
United States	0.016-0.019	0.013-0.018
North America + Europe + Asia	0.021-0.028	0.017-0.026
Indonesia + Southeast Asia	0.087-0.105	0.071-0.100

Estimates are based on combined results from analyses with the University of Illinois at Urbana-Champaign (UIUC) two-dimensional model and the MOZART2 three-dimensional model. Emissions were evenly distributed over the land masses based on their representation in the three-dimensional model. The range represents different assumptions on the degradation chemistry. In the simulation, bromoacetone is the major intermediate degradation product that is transported to the stratosphere. The last column gives the estimated ODPs assuming that bromoacetone does not reach the stratosphere.

In summary, the existing studies for n-PB have shown that the ODP for a VSL source gas does vary with location and season of the emissions, by more than a factor of 5 for this particular gas, with the largest values for tropical emission. However, there remain significant uncertainties in the existing studies. Better treatments of tropospheric convection processes and wet scavenging processes could be particularly important to reducing the uncertainties for ODPs.

2.5.4 Information Required for Evaluating Ozone Impact from VSL Source Gases

As discussed above, unlike for the longer lived compounds, the ODP for the VSL source gases cannot be viewed as an intrinsic property of the substance that is equally applicable worldwide. The location and timing of the emissions are important to determine a meaningful set of ODP values for VSL halogen source gases. Figure 2-10 shows the different steps needed in estimating the ozone depletion effects of long-lived species and VSL halogen source gases. Future studies of ODPs for VSL substances require careful consideration of the following parameters:

- Determination that the vapor pressure of the substance, at atmospheric temperatures at the point of emission, is sufficient to generate a significant gas-phase concentration in the atmosphere.
- Determination of the atmospheric reactivity of the VSL substance (with OH, through photolysis, etc.) and its water solubility.
- Evaluation of the degradation products, their water solubility, and their chemical behavior in the troposphere.
- Determination of the potential uses of the VSL substance, where the VSL substance will be used and likely emitted, and the likely seasonal variations in the emissions (see, e.g., data compiled for n-PB by the UNEP Technology and Economic Assessment Policy (TEAP) task force (UNEP, 2001)).

Given the complexity of the processes in the troposphere, it is unlikely that they could be treated in 2-D models. Three-dimensional models of the global troposphere and stratosphere are necessary to determine accurately the resulting set of ODPs for a newly considered VSL substance.

As discussed in Section 2.5.1, the ODP represents the cumulated effects from the same mass pulse emission relative to CFC-11. The time evolutions of the effects are distinctly different for long-lived species and VSL source gases. For long-lived species, the full effect is realized after a few years' delay and then decreases exponentially according to the atmospheric lifetime of the source gas. For CFC-11, this means that the cumulative effect is spread over about 100 years. For VSL source gases, the effect lasts about 5 years. Thus, the short-term (5 years after emission) effects from a VSL source gas can be 20 times larger than indicated by its ODP value. For fully analyzing the potential effects on ozone, it is important to consider the projected amount of future use and resulting emissions of the VSL substances and evaluate the time-dependent effects (e.g., Wuebbles and Calm, 1997; Calm et al., 1999). One approach often used for evaluating future emissions is the concept of equivalent chlorine loading, or more appropriately for determining stratospheric ozone loss, its variation, equivalent effective stratospheric chlorine (EESC) (e.g., Solomon and Wuebbles et al., 1995; Daniel et al., 1995; Madronich and Velders et al., 1999; Calm et al., 1999). As demonstrated in Chapter 1, EESC can be very useful for evaluating the effects on ozone from long-lived halocarbons. However, given that the halogen loading from VSL source gases as given by Equation (2.13) is very different from Equation (2.8), one cannot use the normal EESC formulation for VSL source gases. A modified procedure is needed for such calculations.

2.6 VSL SULFUR SPECIES AND STRATOSPHERIC AEROSOLS

2.6.1 Introduction

Stratospheric aerosol consists mainly of super-cooled hydrated H_2SO_4 particles with a sulfuric acid mass fraction in the range of 50-80%. At very low temperatures in the wintertime polar stratosphere, nitric acid can be taken up on sulfuric acid particles to form a ternary solution $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$. Stratospheric aerosols can stay liquid to very low temperatures. Other aerosol components can also be present (Carslaw et al., 1997; Murphy et al., 1998; Murphy and Thomson, 2000). The presence of soot in the lower stratosphere has been observed and documented (Pueschel et al., 1992, 1997; Strawa et al., 1999), although measurements remain scarce. Smoke from boreal forest fires has also been observed in some occasions in the lower stratosphere (Fromm et al., 2000).

The particles form a persistent aerosol layer, the stratospheric sulfate aerosol (SSA) layer or Junge layer, which extends from the tropopause up to ~25 km altitude. This layer shows strong variability at annual or longer time scales due to the dominant influence of explosive volcanic eruptions that inject sulfur compounds into the stratosphere (see, e.g., Godin and Poole et al., 1999). For example, satellite observations from the Stratospheric Aerosol and Gas Experiment (SAGE) II show that it took 6 years for the stratospheric aerosol concentrations to return to their pre-Pinatubo-eruption levels of 1991 (Kent et al., 1995, 1998; Thomason et al., 1997a,b) after a 100-fold increase in mass loading. It is generally believed that the observed sulfate loading after the year 2000 is representative of the background sulfate aerosol unaffected by large explosive volcanic eruptions.

Changes in stratospheric aerosols will affect stratospheric ozone in at least two ways. First, heterogeneous reactions occurring on the aerosol surface affect the partitioning of chemical species between reservoirs and free radicals. This is primarily due to the heterogeneous conversion of active NO_x to NO_y reservoirs, which significantly alters the partitioning of HO_x and halogen species. Thus, an increase in the aerosol surface area tends to convert more of the halogen reservoirs to radicals and hence affects the catalytic cycles leading to ozone depletion. Second, changes in aerosol loading change the radiative balance, and therefore the temperature, in the lower stratosphere. This in turn changes the transport circulation, resulting in a redistribution of ozone. Effects from both mechanisms were evident after the Mt. Pinatubo eruption (see, e.g., Pitari and Mancini, 2002).

VERY SHORT-LIVED SUBSTANCES

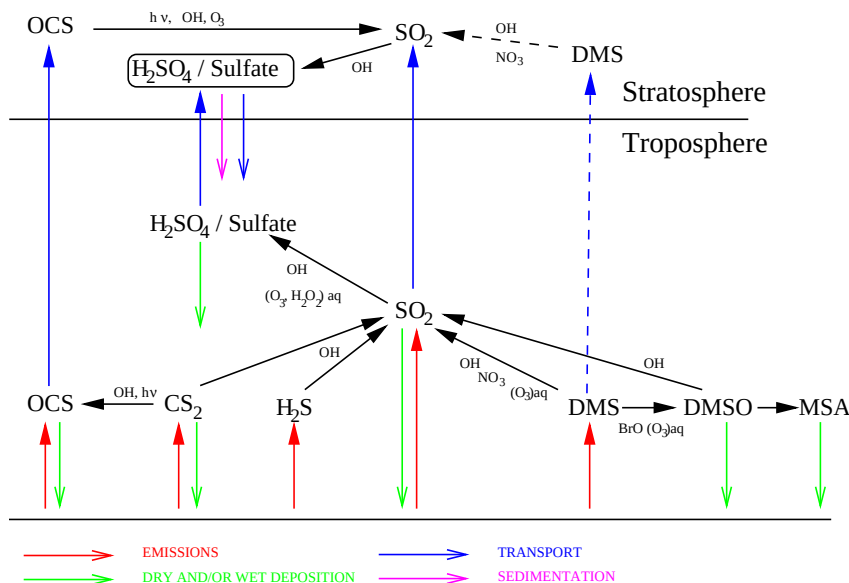


Figure 2-11. Schematic diagram of the tropospheric and stratospheric sulfur cycles. The contributions from oxidation of DMS in the stratosphere have not been quantified. Those processes are indicated by dashed arrows. Production of SO₂ from OCS in the troposphere and direct emission of H₂SO₄ are not shown because their effects on the budget in the troposphere are small compared with the other processes.

The purpose of this section is to examine the processes that determine how injection of sulfur from large explosive volcanic eruptions and release of VSL precursor gases in the troposphere might affect the SSA. Stratospheric aerosol is maintained by the supply of sulfur (in gas and liquid forms) to the stratosphere that is balanced with removal by transport out of the stratosphere. The residence time for aerosols in the stratosphere is of the order of 1 year. It is not possible to define a single residence time for aerosols, because it changes with the size distribution of the aerosol particles and it also depends on where the aerosol particles are formed in the stratosphere. The supply to the stratosphere could be in the form of sulfate (Brock et al., 1995) or gas-phase sulfate precursors. Figure 2-11 summarizes the processes that control the gas-phase sulfate precursor gases. Sulfate precursors released from the Earth's surface include sulfur dioxide (SO₂), hydrogen sulfide (H₂S), and organic gases such as dimethyl sulfide (DMS, CH₃SCH₃), carbonyl sulfide (OCS), and carbon disulfide (CS₂). DMS, H₂S, and SO₂ can be oxidized in the lower troposphere via gas-and/or aqueous-phase processes with a lifetime of a few days or less, forming sulfate aerosol as the main final product. Thus they behave like the VSL halogen source gases discussed earlier in this chapter. The present emission rates have been estimated as 10-30 Tg (S) yr⁻¹ for DMS, 1-2 Tg (S) yr⁻¹ for OCS, 0.5-1.5 Tg (S) yr⁻¹ for CS₂, 6-9 Tg (S) yr⁻¹ for H₂S, and 67-100 Tg (S) yr⁻¹ for SO₂ (see recent review in Watts, 2000; Penner et al., 2001). The dominant natural source of sulfur is DMS, of which

about 80-95% is emitted from the oceans. The source for SO₂ consists mostly of anthropogenic sources from fossil fuel use (~70 Tg (S) yr⁻¹), with volcanic outgassing (including small eruptions) and biomass burning contributing 8-20 Tg (S) yr⁻¹ (Graf et al., 1997; Andres and Kasgnoc, 1998) and 2.5 Tg (S) yr⁻¹ (Hao et al., 1990), respectively. Note that portions of the latter sources are deposited directly into the free troposphere and can reach the stratosphere more efficiently. The amount of sulfur emitted by aviation in the upper troposphere and lower stratosphere was estimated to be 0.06 Tg (S) yr⁻¹ in 1992 (see Fahey and Schumann et al., 1999). The Mt. Pinatubo eruption is estimated to have injected 20 Tg (S) directly into the lower stratosphere.

2.6.2 Chemistry of the VSL Sulfur Species

Here we discuss briefly the chemistry of each of the VSL sulfur species and some of the current uncertainties. Oxidation of H₂S in the troposphere is well understood. It reacts with OH and produces mainly SO₂. Oxidation of CS₂ occurs by reaction with OH and possibly by a mechanism involving direct photoabsorption by CS₂, both mechanisms occurring at comparable rates (Jones et al., 1983). Both routes form OCS and SO₂ as the main stable products. DMS reacts in the gas phase with OH during the day and with NO₃ at night. Figure 2-12 shows the DMS degradation mechanism. SO₂ is the major oxidation product, with dimethyl sulfoxide (DMSO, CH₃S(O)CH₃) and methanesulfonic acid (MSA,

VERY SHORT-LIVED SUBSTANCES

than transport of the same mass of sulfur in gaseous form, which will preferentially condense on existing sulfate particles. The mechanisms and conditions necessary for new particle formation are still not well understood (de Reus et al., 2000).

2.6.3 Sources for the Stratospheric Sulfate Layer

2.6.3.1 DIRECT INPUT FROM EXPLOSIVE VOLCANIC ERUPTIONS

Direct injections of volcanic sulfur into the stratosphere are sporadic and unpredictable. Explosive volcanic eruptions reach the stratosphere in general at least once every 2 years (Simkin, 1993). Typically, sulfur gases, mainly SO₂ and H₂S, contribute 2 to 35% (in volume) to the volcanic gas emissions. OCS and CS₂ contribute only a small fraction (10⁻⁴ to 10⁻²% in volume).

Most models simulate the aerosol evolution after a volcanic eruption assuming that all the sulfur is injected in the form of SO₂. This will not lead to a large error for the sulfur species because H₂S oxidizes to SO₂ within 2 days in the troposphere and within 10 days in the stratosphere. The Mt. Pinatubo eruption is estimated to have deposited 20 Tg (S) in the stratosphere. After the Mt. Pinatubo eruption, 98% of the observed stratospheric aerosol was volatile (Deshler et al., 1992; Sheridan et al., 1992), indicating that homogeneous nucleation is the most important process for stratospheric aerosol formation in the disturbed atmosphere. Within the volcanic layers, Deshler et al. (1992) found an increase of 1-2 orders of magnitude in the concentration of condensation nuclei. Model calculations that successfully reproduced Mt. Pinatubo sulfate aerosol (Timmreck and Graf, 2000; Weisenstein et al., 1997) were based on homogeneous nucleation.

Observations (Russell et al., 1996) and model studies (Zhao et al., 1995; Timmreck and Graf, 2000) show that it takes about 3 months to build up the sulfate peak. The volcanically enhanced stratospheric aerosol layer can be observed for several years after major eruptions. The aerosol optical depth at 550 nm first peaked to >0.2 three months after Mt. Pinatubo, and then reduced within 6 years to the background value of 0.003. This represents an e-folding time of approximately 17 months (McCormick and Veiga, 1992; Ansmann et al., 1997). The relatively faster removal of large compared with small particles from the stratosphere leads to a more rapid decrease in aerosol mass than in aerosol surface (Ansmann et al., 1997; Godin and Poole et al., 1999).

The presence of the volcanic aerosol would change the transport circulation in the lower stratosphere (see, e.g., Kinne et al., 1992; Schoeberl et al., 1993). Most of the model studies do not take this into account. Questions have also been raised whether a sufficiently large volcanic injection could also affect the HO_x cycle in the stratosphere. From simple consideration of stoichiometry, it can be assumed that one molecule of H₂O is produced per H₂S oxidized. For SO₂, it is assumed that no net gain or loss of HO_x results from SO₂ oxidation (Read et al., 1993; McKeen et al., 1984). Finally, approximately three molecules of H₂O are needed to oxidize SO₂ and condense sulfuric acid to sulfate aerosols (Bekki, 1995). Two-dimensional model simulations (Bekki et al., 1996) showed that a hypothetical injection of 6000 Tg SO₂ could dehydrate the stratosphere. Given that most large eruptions inject about several tens of teragrams of sulfur, this effect is probably not important under most conditions.

2.6.3.2 VSL PRECURSORS EMITTED IN THE TROPOSPHERE

It has been long recognized that oxidation of OCS in the stratosphere is an important source of stratospheric background sulfate aerosol (Crutzen, 1976). Carbonyl sulfide is emitted at the Earth's surface by natural and anthropogenic sources, and is also formed by the oxidation of CS₂ (Chin and Davis, 1993, and the references therein; Watts, 2000). Chin and Davis (1995) used available OCS atmospheric observations and improved laboratory reaction-rate data to show that oxidation of OCS produces 0.03 Tg (S) yr⁻¹ in the stratosphere. This corresponds to 5% of the OCS emission from the surface and is only 20-50% of the recently revised estimates of the sulfur flux (0.06-0.15 Tg (S) yr⁻¹) needed to maintain the background stratospheric sulfate layer (Chin and Davis, 1995). Later model studies seem to support these conclusions and attribute the other major source to SO₂ supplied from the troposphere. For example, Weisenstein et al. (1997) found in their 2-D model, which includes a microphysical treatment of the particles, that OCS oxidation could account for 0.049 Tg (S) yr⁻¹ of sulfate production in the stratosphere, and that convective transport of SO₂ in the tropical troposphere could provide 50% of the background sulfate aerosol. Kjellström (1998) estimated that the sulfate production from OCS was 3 to 12 times smaller than the stratospheric background source of sulfate aerosols, and that the transport of SO₂ from the troposphere was the major supplier for the background sulfate aerosol. A very recent global 3-D model study (Pitari et al., 2002) estimated that OCS photochemical oxidation could account for about 43% of the total background strat-

ospheric sulfate aerosol, whereas the upward transport of tropospheric sulfate and SO₂ contribute 30% and 27%, respectively. There are important uncertainties in such model results because of uncertainties in the model description of how transport processes control the amount of VSL substances such as SO₂ and sulfate delivered to the stratosphere (see Section 2.2).

Of particular interest is how changes in anthropogenic SO₂ emissions would affect the sulfate loading in the stratosphere. Chin et al. (2001) and Pitari et al. (2002) performed simulations to compute the sulfate loading from anthropogenic SO₂ emission. Using the most recent estimate of emission of 69 Tg (S) yr⁻¹ from the Intergovernmental Panel on Climate Change *Special Report on Emissions Scenarios* (IPCC-SRES) (Nakićenović et al., 2000), they calculated burdens of 0.7-0.8 Tg (S) sulfate in the troposphere and 0.07-0.09 Tg (S) sulfate in the stratosphere. A residence time for sulfate in the stratosphere of 1-2 years would imply that about 0.05-0.15% of the SO₂ surface emission enters the stratosphere. No study has been done for SO₂ emissions from volcanic degassing and biomass burning. It is important to remember that because of different emission locations, the effect will not necessarily scale with the emission strengths. Kjellström et al. (1999) estimated that aircraft emissions contribute less than 1% of the total sulfate mass in regions of high air traffic.

2.6.4 How Can We Predict Future Changes in the Stratospheric Sulfate Layer?

If anthropogenic SO₂ emissions can account for more than half of the stratospheric background sulfate aerosol, future changes in anthropogenic SO₂ emission could have an important impact on stratospheric sulfate aerosol loading. One can ask whether the past secular trend in anthropogenic SO₂ emission has caused an

increase in the loading of stratospheric aerosol. This question cannot be easily answered from the limited existing set of observations. Analysis of time series related to the stratospheric aerosol layer does not show any evidence of a trend in the nonvolcanic aerosol loading between the late 1970s, the late 1980s, and the late 1990s to the present (see Chapter 4). The average global anthropogenic SO₂ emission strength has probably been fairly constant between 1980 and 1990, the increases in some regions being compensated by decreases in other regions (Boucher and Pham, 2002). However, changes in the geographical distribution of anthropogenic SO₂ emissions may also modify the fraction of surface SO₂ emissions that contribute to the stratospheric sulfate aerosol layer. Finally, since the contribution of tropospheric volcanic emissions to the total atmospheric sulfate burden is nearly equal to that from anthropogenic sources (Graf et al., 1997), the climatological stratospheric aerosol levels are also determined by outgassing associated with volcanic activity that is highly variable in space and time and unpredictable.

Future changes in the stratospheric sulfate layer have been estimated by performing model simulations using the IPCC projected emission scenarios for years 2030 and 2100 (Nakićenović et al., 2000). Table 2-13 summarizes the model results of Chin et al. (2001). The first simulation, SC1, is taken from the IPCC SRES (scenario A2) to represent the anthropogenic emissions in year 2000. Simulations 2 and 3 (SC2 and SC3) are based on the SRES preliminary emission scenario A2p, which projects a regionally inhomogeneous economic development for years 2030 and 2100, respectively. Simulation 4 (SC4) is from another SRES preliminary emission scenario (B1p) for year 2100, which assumes a convergent world with a rapid introduction of new and more efficient technologies. It can be deduced from the values in Table 2-13 that every 1 Tg (S) yr⁻¹ increase in anthropogenic SO₂

Table 2-13. Estimated sulfur emission rates in years 2000, 2030, and 2100 and the model-calculated corresponding tropospheric and stratospheric sulfate burdens. The cited values for the simulated burdens are from Chin et al. (2001).

Emission Rates and Stratospheric Sulfate Burdens	SC1 2000	SC2 2030	SC3 2100	SC4 2100
Anthropogenic emission, SO ₂ (T (S) yr ⁻¹)	69.0	111.9	60.4	28.7
Oceanic emission, DMS (Tg (S) yr ⁻¹)	16.1	16.1	16.1	16.1
Volcanic emission, SO ₂ (Tg (S) yr ⁻¹)	4.8	4.8	4.8	4.8
Tropospheric burden (Tg (S))	0.656	1.124	0.647	0.372
Stratospheric burden (Tg (S))	0.069	0.143	0.068	0.044

Volcanic emissions are for the continuously erupting volcanoes only and are from Andres and Kasgnoc (1998). Anthropogenic emissions are from four scenarios in the IPCC SRES (Nakićenović et al., 2000).

VERY SHORT-LIVED SUBSTANCES

emission could roughly result in 9 Gg (S) of sulfate burden increase in the troposphere and 1 Gg (S) in the stratosphere. Using the emission rates of SC2, Pitari et al. (2002) have estimated that the stratospheric non-OCS sulfate burden will be 0.14 Tg (S) in 2030, a value similar to that in Table 2-13.

Using a coarse-grid model with simple chemistry, Pitari et al. (2002) showed the increase in surface emission of SO₂ between year 2000 (SC1) and 2030 (SC2) will result in an increase in aerosol surface area of up to 0.5 μm² cm⁻³ in the Northern Hemisphere, at altitudes between 100 and 200 hPa. The increase in the stratospheric surface area would cause a slowdown of the stratospheric ozone recovery rate expected from the reduction in the CFCs.

Overall it can be concluded that representation of the processes controlling the SSA budget in models is very much simplified and the calculations of impacts of future changes in nonvolcanic sulfur emissions are therefore very uncertain. More studies are needed to understand the relative contributions of surface emission of VSL sulfur substances to the present and future stratospheric sulfate aerosol burden. In addition to the general problems of transport of VSL species in the troposphere (discussed in Section 2.2), areas of uncertainty are the role of aerosol nucleation in the upper troposphere; the mechanism of gas-phase DMS oxidation; the heterogeneous reactions of VSL sulfur substances on aerosol surfaces; the induced changes in the radiation balance and circulation in the lower stratosphere; and the magnitude of future emissions. The attempts by several modeling groups (e.g., Pitari and Mancini, 2002; Timmreck, 2001; Pitari et al., 2002) represent promising starts. However, such models must be extended to include a more complete treatment of the processes in the troposphere and be thoroughly evaluated with measurements (see, e.g., Lohmann et al., 2001).

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VERY SHORT-LIVED SUBSTANCES

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CHAPTER 3

Polar Stratospheric Ozone: Past and Future

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CHAPTER 3

POLAR STRATOSPHERIC OZONE: PAST AND FUTURE

Contents

SCIENTIFIC SUMMARY	3.1
3.0 INTRODUCTION	3.5
3.1 TRENDS OF OZONE AND TEMPERATURE IN THE POLAR STRATOSPHERE	3.6
3.1.1 Polar Ozone Trends	3.6
3.1.2 Polar Temperature Trends	3.10
3.2 BASIC POLAR STRATOSPHERIC PROCESSES	3.13
3.2.1 Transport and Dynamics	3.13
3.2.1.1 The Polar Vortex: Mean Structure	3.13
3.2.1.2 Polar Vortex: Causes of Interannual Variability and Its Implications	3.13
3.2.1.3 Polar Transport and Mixing	3.19
3.2.2 Polar Stratospheric Clouds	3.21
3.2.2.1 Observations of PSC Physical Properties and Their Interpretation	3.21
3.2.2.2 Particle Composition	3.24
3.2.2.3 Denitrification	3.25
3.2.2.4 Dehydration	3.28
3.2.3 Polar Ozone Chemistry	3.28
3.2.3.1 Chlorine	3.29
3.2.3.2 Bromine	3.33
3.2.4 The Polar Summer Lower Stratosphere	3.37
3.2.4.1 Summertime NO _x Chemistry	3.38
3.2.4.2 Summertime HO _x Chemistry	3.39
3.2.4.3 Summertime Cl _y Chemistry	3.40
3.3 QUANTIFICATION OF POLAR OZONE LOSS: OBSERVATIONS AND MODELS	3.41
3.3.1 Approaches to Quantify Chemically Induced Ozone Loss in the Arctic	3.42
3.3.1.1 Approaches That Use Explicit Transport Calculations	3.42
3.3.1.2 Approaches That Use the Relation of Ozone to an Inert Tracer	3.43
3.3.2 Arctic Ozone Loss During the Last Decade	3.45
3.3.2.1 Ozone Loss Rates Near the Maximum of the Ozone Concentration	3.45
3.3.2.2 Vertical Profiles of Ozone Loss	3.45
3.3.2.3 Effect of Ozone Loss on the Total Ozone Column	3.48
3.3.2.4 Chemical Ozone Loss in the Arctic Winter 1999/2000	3.50
3.3.3 Consistency Between the Different Observational Techniques	3.50
3.3.4 The Effect of Denitrification on Ozone Loss	3.51
3.3.5 Model Studies of Arctic Ozone Loss	3.54
3.3.5.1 Chemical Transport Models	3.54
3.3.5.2 Specific Model Studies	3.55
3.3.6 Quantifying Antarctic Ozone Loss	3.57
3.3.7 Model Studies of Antarctic Ozone Loss	3.57
3.3.8 Conclusion	3.58
3.4 CAUSES OF POLAR STRATOSPHERIC TEMPERATURE TRENDS	3.58
3.4.1 Introduction	3.58
3.4.2 Modeling Techniques	3.58

3.4.2.1	Fixed Dynamical Heating (FHD) Models	3.59
3.4.2.2	General Circulation Models (GCMs)	3.59
3.4.3	Causes of Polar Stratospheric Temperature Trends	3.59
3.4.3.1	Polar Ozone	3.59
3.4.3.2	Well-Mixed Greenhouse Gases (WMGHGs)	3.63
3.4.3.3	Combined Changes in WMGHGs and Stratospheric Ozone	3.63
3.4.3.4	Stratospheric Water Vapor	3.64
3.4.3.5	Solar Changes	3.64
3.4.3.6	Volcanoes	3.64
3.4.4	Timing of the Springtime Cooling Trend	3.65
3.4.5	Summary and Conclusions	3.65
3.5	CHEMICAL-CLIMATE MODELING OF THE PAST AND FUTURE POLAR STRATOSPHERE	3.66
3.5.1	Introduction	3.66
3.5.2	The Uncertainties in Chemistry-Climate Models	3.68
3.5.2.1	Temperature Biases	3.68
3.5.2.2	The Simulation of Polar Stratospheric Clouds	3.69
3.5.2.3	The Position of the Upper Boundary of the GCM	3.72
3.5.2.4	Predictions of Planetary Waves	3.73
3.5.2.5	Stratospheric Water Vapor Changes	3.75
3.5.3	Model Assessments	3.75
3.5.3.1	The 1960-2000 Time Frame: Ozone Depletion	3.77
3.5.3.2	The 2000-2020 Time Frame: Start of Ozone Recovery	3.77
3.5.3.3	The 2020-2060 Time Frame: Complete Ozone Recovery	3.79
3.5.3.4	Attribution of Model Ozone Changes	3.80
3.5.4	Summary	3.80
	REFERENCES	3.81
	APPENDIX 3A: SATELLITE MEASUREMENTS IN THE ANTARCTIC AND ARCTIC	3.104

SCIENTIFIC SUMMARY*

- **Springtime Antarctic ozone depletion remains very large.** Severe depletion, leading to minimum values around 100 (Dobson units (DU)), has been seen every year since the early 1990s. The main processes are well understood.
- **Some estimates of the severity of the Antarctic ozone hole, e.g., the area enclosed by the 220-DU contour, show an increase at some times in recent years, and therefore it is not yet possible to say that the ozone hole has reached its maximum.** Much of the change appears to be associated with processes at the edge of the polar vortex and is consistent with meteorological variability and the almost constant halogen loading. The observations do not show evidence of ozone recovery; this is expected due to the slow decrease of stratospheric chlorine and bromine to pre-ozone-hole levels (see Chapter 1).
- **Meteorological observations show that the Antarctic polar vortex is persisting later than was observed during the 1970s.** Over the last decade, the vortex has broken up in the early-December period in contrast to a breakup in late-November during the 1970 to 1980 period.
- **There was very large local ozone depletion in the Arctic vortex in 1999/2000, reaching 70% by early April in a narrow region around 20 km.** Integrated column losses were greater than 80 DU. The winter of 1999/2000 was characterized by persistent low temperatures and a strong vortex. In contrast, in the warmer more disturbed polar vortex of 1998/1999, the estimated loss was very small. These observations are consistent with our expectation that Arctic ozone losses are largest in cold stratospheric winters.
- **The Arctic winter/spring ozone column continues to be variable, reflecting the variable meteorology of the Northern Hemisphere (NH) stratosphere.** Lower column ozone was present during the cold winter of 1999/2000 than in the warmer, more disturbed winters of 1998/1999 and 2000/2001, reflecting the variability in the dynamical and chemical processes that control the ozone layer in the NH stratosphere. It is not possible to isolate the importance of these factors just from observations; model studies are needed to do this. The Arctic Oscillation can be used as an index to describe variability, but not causality.
- **The magnitude of chemical loss of ozone for all Arctic winters during the last decade has now been studied with a variety of observationally based approaches.** There is generally good agreement between different analyses for quantifying losses: for the 1999/2000 winter, agreement was better than 20% in the Arctic stratosphere around 20 km.
- **Satellite and radiosonde observations show that the springtime Arctic and Antarctic lower stratospheres have cooled.** However, because of large variability in the Arctic spring, the magnitude of the trend is uncertain there. During the 1979 to 2000 period the linear temperature trend exceeds -1.5 K/decade at 70°N and 70°S .
- **Modeling studies now demonstrate that the stratospheric ozone depletion has exerted an important influence on the springtime cooling of the Arctic lower stratosphere over the 1980 to 2000 period, but the degree of attribution is hindered by the large dynamical variability in this region.** In Antarctica modeling studies reaffirm that ozone loss is the major cause of the springtime cooling and the increased persistence of the Antarctic polar vortex. Well-mixed greenhouse gases and stratospheric water vapor increases also contribute to the annually averaged cooling.
- **A laboratory study of the rate of formation of ClOOCl (the chlorine monoxide dimer), the initial step for the most important polar ozone loss cycle, suggests it is up to 25% faster (depending on temperature) than previous estimates based on data extrapolations to low polar temperatures.** This leads to faster calculated rates of chemical ozone loss.

* Editor's note added in press: The preparation and review of this Assessment report were completed by August 2002. The observations of the unusual Antarctic ozone hole of 2002 occurred thereafter and hence are not included here. Such subsequent observations will, of course, be included in future reports and assessments.

POLAR OZONE

- **In situ observations of the rate of decay of chlorine monoxide (ClO) at sunset are consistent with the new laboratory rate for $\text{ClO} + \text{ClO} + \text{M}$ and recommended cross sections for ClOOCl .** This suggests that errors in model representation of the partitioning of ClO and its dimer cannot account for discrepancies between modeled and measured Arctic ozone losses observed in January.
- **Modeling studies of the latitudinal, seasonal, and diurnal variations in bromine monoxide (BrO) column abundances agree well with observations from a number of ground sites, indicating that the processes that govern bromine partitioning in the polar regions are reasonably well understood.**
- **Observations of BrO in the winter Arctic vortex by in situ and remote detection techniques are in broad agreement and consistent with a total bromine budget of $\sim 20 \pm 4$ parts per trillion.** This result now allows for more accurate assessment of the contribution of bromine to polar ozone loss. At present, the fractional contribution of bromine to total ozone loss ranges between 30% and 60%, depending on temperature and abundances of ClO. Considering the observed leveling off of abundances of sources of chlorine (reported in Chapter 1), the role of bromine in polar ozone loss will continue to increase relative to that of chlorine until the current upward trends of the bromine source gases reverse.
- **New laboratory and field studies have led to refinements in the recommendations for the rate constants of several key reactions that couple the photochemistry of odd hydrogen (HO_x) and nitrogen oxides (NO_x) (species that are largely controlled by natural processes) and to the discovery of a new process (near-infrared photolysis of peroxyxynitric acid (HNO_4)).** Together with new observations of HO_x , NO_x , and ozone in late spring and summer, these studies have demonstrated that our understanding of the photochemistry of HO_x and NO_x in the lower summertime stratosphere is fundamentally sound.
- **Removal of nitrogen compounds (denitrification) has been observed to occur in the Arctic lower stratosphere in several cold winters.** Denitrification of up to 70% of the total reactive nitrogen was observed at some levels of the lower stratosphere in winter 1999/2000. Observations and modeling results show that denitrification in the 1999/2000 Arctic lower stratosphere increased ozone loss by as much as 30% at 20 km in spring.
- **Our understanding of what causes denitrification has improved considerably by the discovery of large nitric-acid-containing particles in the Arctic polar lower stratosphere during the winter of 1999/2000.** Sedimentation of these particles can account for observed Arctic denitrification, although the mechanism of formation of these sedimenting particles remains uncertain. Sedimentation of ice containing dissolved nitric acid, which has been the preferred mechanism in stratospheric models, was not the dominant mechanism in the Arctic in 1999/2000. These observations show that denitrification can occur at higher temperatures than previously thought.
- **Synoptic and mesoscale motions (baroclinic and gravity waves) can lead directly to, and enhance, polar stratospheric cloud (PSC) formation in both hemispheres.** For the first time, operational meteorological analyses have been demonstrated to contain credible information about the gravity-wave field in high latitudes.
- **Model calculations suggest that the magnitude and vertical extent of denitrification could increase considerably in a future colder Arctic stratosphere, leading to increased ozone loss over a broader altitude range in the lower stratosphere.** The denitrification mechanism is not well represented in current global models, which is one of the limiting factors in the ability of the models to reproduce the large ozone losses observed in cold Arctic winters and to reliably predict future ozone losses in the Arctic.
- **The chemical composition of liquid and solid PSC particles has been measured directly for the first time.** Measured compositions are in agreement with model calculations for liquid particles and nitric acid trihydrate, which have been used in stratospheric models for many years. These measurements give confidence in the micro-physical models that are central to simulations of polar ozone loss.

- **Significant chemical loss of ozone (~0.5 parts per million by volume) in the lower stratosphere during January has been observed in several cold Arctic winters.** The observations indicate that the loss occurred exclusively during periods when the air masses are exposed to sunlight. These January ozone losses cannot be fully explained with our current understanding of the photochemistry. For some cold Arctic winters the ozone loss during January contributes about 25% to the overall loss of ozone over the winter.
- **Coupled chemistry-climate simulations broadly reproduce past trends in total ozone over the Antarctic.** The coupled chemistry-climate models have studied the future evolution of minimum Antarctic ozone. These models suggest that the minimum column ozone may have already occurred or should occur within the next decade, and that recovery to 1980 levels may be expected in the 2045 to 2055 period. The model response is driven mainly by the changes in stratospheric halogen loading, with a small delay in ozone recovery due to cooling of the lower stratosphere.
- **The area of the Antarctic ozone hole depends on processes near the edge of the polar vortex.** Area estimates amongst the coupled chemistry-climate models are uncertain because vortex-edge temperatures are near the threshold for PSC formation and these temperatures are difficult to predict.
- **Coupled chemistry-climate models now capture the typical interannual variability of Arctic ozone levels.** However, temperatures are often near the threshold for PSC formation and, hence, the initiation of perturbed chemistry. This places severe constraints on model predictions of past and future ozone behavior. A number of coupled chemistry-climate models run for this Assessment suggest that minimum Arctic ozone would occur within the next two decades, depending on the meteorology. Very low Arctic ozone columns, similar to those seen in the Antarctic, are not predicted by these models (in contrast to earlier simpler calculations considered in the previous Assessment). Such low levels in the Arctic would require weak dynamical forcing that is unprecedented in NH observations.

3.0 INTRODUCTION*

This chapter provides an update on our understanding of recent changes in polar ozone and of the polar vortex, and considers possible future developments. It builds on earlier Assessments, concentrating mainly, but not exclusively, on work reported since the previous United Nations Environment Programme/World Meteorological Organization (UNEP/WMO) assessment report (WMO, 1999).

The previous Assessment reported that the Antarctic ozone hole continued unabated, with essentially near-complete destruction of ozone in late winter/spring in the lower stratosphere, and that the factors controlling the depletion (meteorological preconditioning, halogen activation, ozone depletion in sunlight) were well understood. In the Arctic, substantial ozone losses were reported in several winters during the 1990s, depending on the meteorological conditions. The Assessment highlighted the vulnerability of the Arctic to large ozone losses in a cold winter while chlorine abundances remain high during the next decade or so. Less chemical loss was to be expected in the Arctic in winters with a warm, disturbed vortex. Difficulties with the precise quantification of Arctic ozone loss were indicated. The previous Assessment highlighted specific uncertainty issues surrounding the understanding of the different types of polar stratospheric clouds (PSCs), and the process of denitrification, which can limit our ability to model present and future polar ozone loss.

The coupling between atmospheric chemistry and climate has been recognized increasingly in recent assessments. In WMO (1999) a late-winter/springtime cooling in the Arctic polar lower stratospheric temperatures of ~3 to 4 K/decade was noted (although with the large dynamical variability in that region the statistical significance of the trend was not high), and the role of ozone, water vapor, and the well-mixed greenhouse gases was explored. Three-dimensional (3-D) coupled chemistry-climate models were used for the first time to look at the possible recovery of the ozone layer; these models all indicated a delay in recovery beyond the time of the peak in stratospheric halogen abundance.

Since the previous Assessment there has been considerable progress in basic research that we report below. Satellite datasets on ozone and temperature have been further extended. In addition, scientific impetus has been provided by several major field campaigns to study the

Arctic stratosphere. Results are reported here from the National Aeronautics and Space Administration (NASA) Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) campaign, aimed at understanding the summer polar stratosphere; the European Union (EU) Third European Stratospheric Experiment on Ozone (THESEO), a polar and middle-latitude campaign; and the joint NASA/EU Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE)-THESEO 2000. These campaigns produced new data to address some of the uncertainties remaining after the previous Assessment.

Section 3.1 updates polar ozone measurements in both Antarctica and the Arctic, concentrating on the winter and spring seasons when the largest ozone depletion is observed. The total ozone columns are considered, and updated information on various possible indicators of ozone recovery, suggested in the previous Assessment, is presented briefly. The updated polar temperature trends are also presented here.

Section 3.2 reviews our understanding of the relevant physical and chemical processes controlling the polar vortex and its composition. The Arctic field campaigns have provided new data on a disturbed winter with considerable exchange between polar and middle latitudes (1998/1999) and on the cold polar winter of 1999/2000, which led to large local ozone depletion. Many new complementary constituent measurements provide an important constraint on chemical loss processes. Important new measurements of particles were also made in the winter polar stratosphere, leading to advances in our understanding of particle composition and denitrification. Improved understanding of the dynamics in and around the polar vortex has also been developed.

Section 3.3 looks in detail at our quantitative understanding of polar ozone loss. In earlier assessments it was recorded that models often fail to quantify correctly the observed ozone loss. A variety of methods to derive ozone loss from measurements are reviewed in this section. Estimated losses in recent Arctic and Antarctic winters are considered and compared with each other and with model estimates.

In the previous Assessment (WMO, 1999), it was recognized that the future development of the ozone layer does not depend just on changes in stratospheric halogen loading but also, very importantly, on a number of other factors connecting chemistry and climate. These factors are discussed in Section 3.4. Temperature changes are

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POLAR OZONE

particularly important, since polar heterogeneous chemistry is strongly temperature dependent, and furthermore, temperature changes are related to the strength of the polar vortex, descent within the vortex, and mixing with lower latitudes. The attribution of the trends in polar stratospheric temperatures (presented in Section 3.1.2) is discussed, and the roles of changes in well-mixed greenhouse gases, ozone, water vapor, and aerosol particles are reviewed. Future stratospheric temperature changes are discussed.

Finally, in Section 3.5, possible future states of the polar stratosphere are explored in sensitivity calculations using coupled chemistry-climate models. Results from these models were reported for the first time in an assessment in WMO 1999, and the models are still being developed. An extensive review of the present uncertainties in chemistry-climate models is presented here, followed by some examples of sensitivity calculations to consider the polar stratosphere during the next 50 years.

3.1 TRENDS OF OZONE AND TEMPERATURE IN THE POLAR STRATOSPHERE

3.1.1 Polar Ozone Trends

Ozone is primarily produced in the midlatitudes and tropics by photodissociation of oxygen by hard ultraviolet (UV) radiation (below 242 nm) and is transported toward the poles by the Brewer-Dobson circulation. The result is an annual cycle in ozone, shown by the climatological values in Figure 3-1. Because of the stronger Brewer-Dobson circulation in the Northern Hemisphere (NH), the Arctic is both warmer and has larger column ozone amounts than the Antarctic. In the NH, there is usually a maximum in the column in late winter/early spring. At the South Pole, there is less annual variation (larger annual variations are expected at the vortex edge). In recent years, the annual cycle has been modified by polar ozone depletion, most obviously in the Southern Hemisphere (SH).

Figure 3-1 also shows recent year-round ozone measurements from the Arctic Ny Ålesund station (78.9°N, 11.9°E) and the South Pole station, updating polar observations since the previous Assessment. The Antarctic observations in the last few years continue to show the extremely low spring ozone values that have characterized the ozone hole during the 1990s. The low Antarctic values begin with the chemical ozone losses during August and September and end upon the breakup of the vortex in November or December. During the Arctic summer, ozone is destroyed photochemically, especially at these high latitudes during continuous sunlight condi-

tions (Brühl et al., 1998), and the climatological seasonal minimum is reached in autumn.

In the Arctic, the March-to-April ozone maximum is occasionally reduced below the climatology in some years (e.g., in 1997, the cyan triangles in Figure 3-1) because of severe chemical ozone loss and reductions in ozone transport (Andersen and Knudsen, 2002). In these low-ozone years, the column ozone rapidly increases with the breakup of the vortex (e.g., early April 1997). Of the most recent winters, 1999/2000 also has somewhat lower ozone columns than the climatology, as discussed later. Extremely low Ny Ålesund column ozone values at the beginning of 1996 (Figure 3-1, dark red triangles) can partially be explained by the early onset of the ozone depletion that year (see Section 3.3.2). The lowest 1996 values occur in an “ozone mini-hole” event (Weber et al., 2002) (see Section 3.2.1.2). A complicating factor in the upper panel in Figure 3-1 is that occasionally Ny Ålesund is outside the vortex, as is evident from the large variations on a broad range of spatial and temporal scales.

Extremely high Ny Ålesund column ozone values in December 1998 (Figure 3-1, gray diamonds) and February 2001 (red circles) were caused by sudden warmings and the associated ozone transport. The warmings in those years also resulted in high temperatures, thereby preventing the formation of polar stratospheric clouds.

The largest ozone depletion occurs in the polar vortices during springtime. Figure 3-2 shows the springtime ozone values in the Arctic and Antarctic (63° to 90°) since 1970 (updated from Newman et al., 1997). The Arctic column ozone averages were extremely low during the mid-1990s, but have been relatively high in four of the last five winters. As noted in the previous paragraph and as is apparent in Figure 3-1, these higher ozone values are associated with stratospheric sudden warmings. The downward secular ozone trend apparent through 1997 and its reversal over the last few years can be associated with a long-term variation of stratospheric warmings.

Figure 3-2 also shows that the Antarctic ozone hole continued to display the low values over the last 4 years that were apparent during the early and mid-1990s. The notably higher value in October 2000 resulted from greater dynamical activity, as is also apparent in Figure 3-1.

The polar column ozone averages of Figure 3-2 in the 63° to 90° region generally coincide with the polar vortices. However, in the NH the vortex is usually smaller and the 63° to 90° region may contain air outside the vortex. The absolute minimum in the NH occurred in 1997, when the vortex was cold, very large, and pole-centered. However, the column chemical ozone loss in the vortex was probably larger in 1995, 1996, and 2000 (see Section 3.3.2.3). However, Andersen and Knudsen

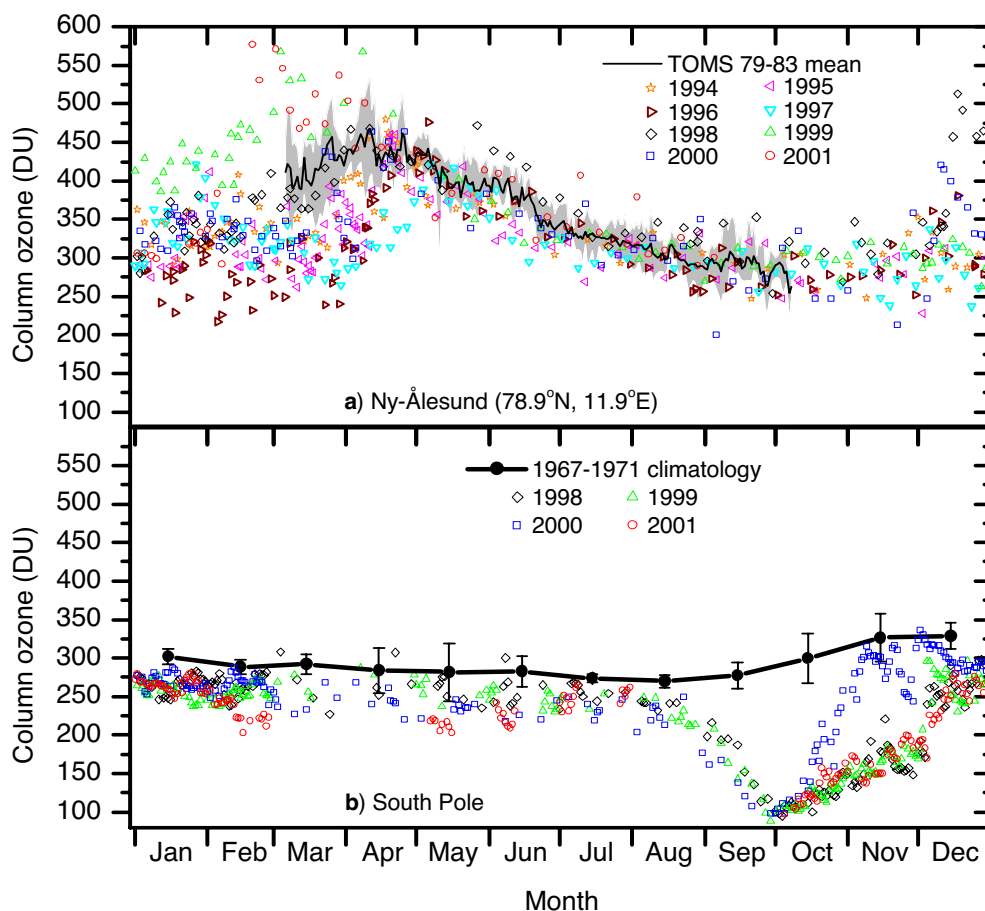


Figure 3-1. The column ozone determined from (a) ozonesondes launched from Ny Ålesund and (b) ozonesonde and Dobson measurements at South Pole, as a function of day of year. Symbols give individual measurements. The solid line in panel (a) is the daily TOMS mean column ozone for the Ny Ålesund station from 1979 to 1983, with the shading indicating the range. The solid line in (b) is a climatology for the South Pole from 1967 to 1971 (with 1σ error bars indicated). Courtesy Peter von der Gathen (Alfred Wegener Institute) and Samuel Oltmans (NOAA-CMDL).

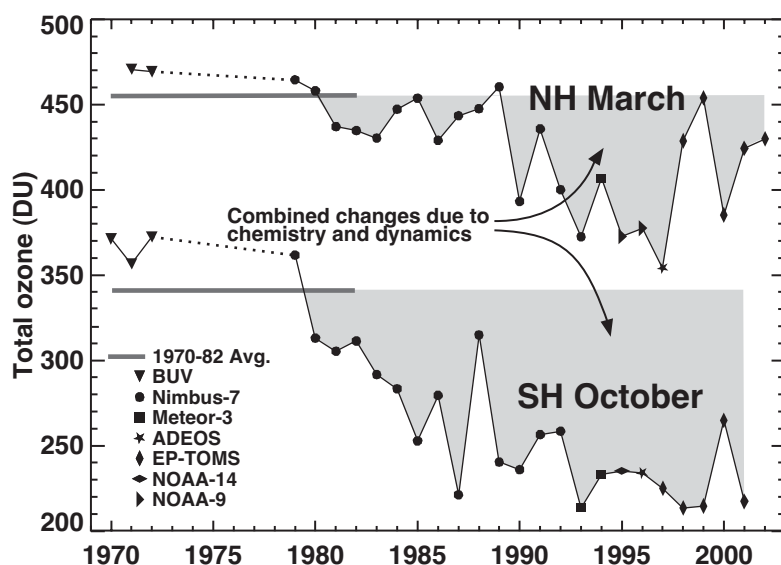


Figure 3-2. Average total ozone poleward of 63° latitude in March in the Northern Hemisphere (NH) and October in the Southern Hemisphere (SH). Symbols indicate the satellite data that have been used in the different years. The horizontal gray lines represent the average total ozone for the years prior to 1983 for the NH and SH. The lighter gray shading shows the combined differences resulting from chemical losses and dynamical processes. Updated from Newman et al. (1997).

POLAR OZONE

(2002) have argued that about 75% of the 63° to 90°N depletion from 1992 to 2000 relative to the 1979-to-1982 average is due to ozone depletion inside the vortex, so the plot does give a good indication of the Arctic vortex depletion.

Large total column ozone trends have been seen in both the Arctic and Antarctic polar vortices during the spring (Figure 3-3). To obtain these trends with better correlation with the polar vortices, a potential vorticity coordinate (equivalent latitude) remapping technique was applied to a trend analysis of homogenized satellite data from the Total Ozone Mapping Spectrometer (TOMS) and the Global Ozone Monitoring Experiment (GOME) (Bodeker et al., 2001; see also Appendix 3A for satellite data descriptions). In this coordinate the centers of the vortices are at 90° and the edges at about 60° to 75° (as shown by the x points in Figure 3-3). After a regression model including trends and variability (seasonal cycle, quasi-biennial oscillation (QBO), solar cycle, volcanic effects, and El Niño-Southern Oscillation (ENSO)) was applied to the data from 1978 to 1998, statistically significant linear trends were obtained.

The largest Arctic negative trend ($1.04 \pm 0.39\% \text{ yr}^{-1}$) is observed in March, whereas the largest Antarctic negative trend ($2.51 \pm 0.62\% \text{ yr}^{-1}$) is observed in October (updated from Bodeker et al. (2001) to include the additional years 1999 and 2000). In the Arctic vortex the 1978 to 1998 trend was largely due to severe vortex depletions in the 1990s (Section 3.3.2). The addition of the warmer winter of 1998/1999, when no significant ozone depletion in the vortex occurred, reduced the downward trends. In the Antarctic vortex trends have weakened due to saturation of the ozone losses. Hence, the trends, with 1999 and 2000 data included, have slightly smaller negative trends than previous estimates in the Antarctic spring column ozone. In the Arctic, Figure 3-3 shows steep gradients in the trends across the edge of the vortex. It also reveals statistically significant negative ozone trends in May, June, and July just inside the Antarctic vortex, which were not found in previous trend analyses, but confirms earlier findings (Roscoe et al., 1997; Lee et al., 2001) (see Section 3.3.7).

Because the ozone loss mainly occurs in the 12- to 20-km layer, the partial column ozone from 12 to 20 km

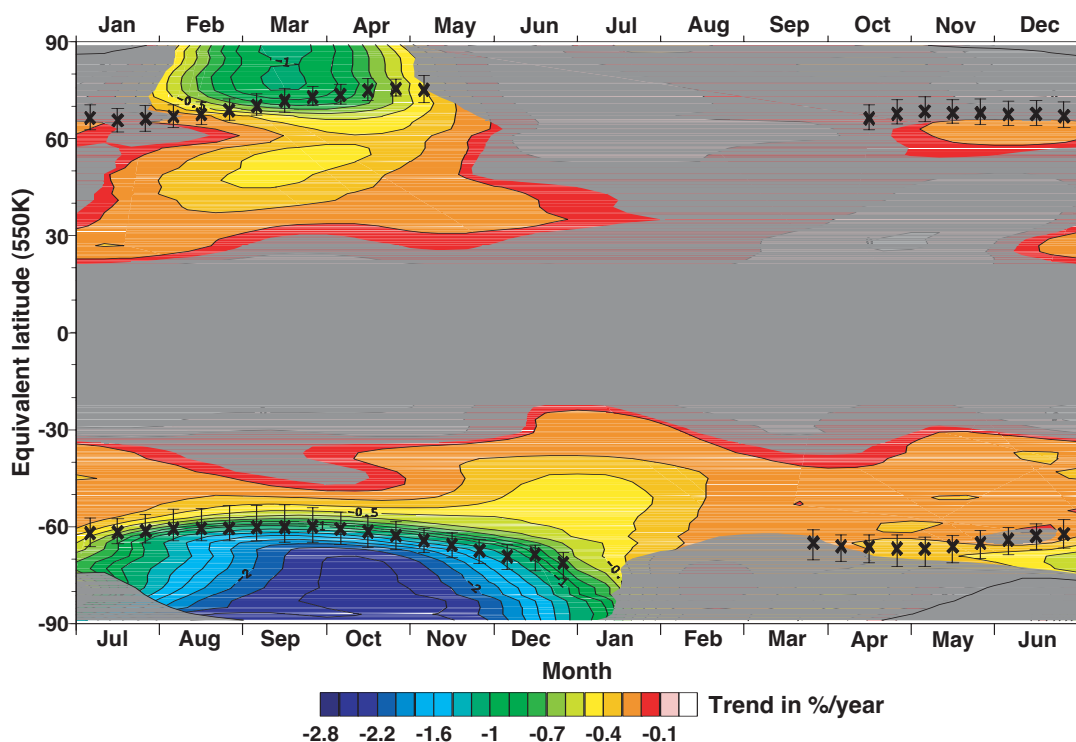


Figure 3-3. Total column ozone trends as a function of equivalent latitude and season using corrected TOMS and GOME data from November 1978 to December 2000. Gray shaded regions indicate where trends are statistically insignificant (at 95% confidence). The crosses show the mean position of the vortex (remnant) edge(s) over the time period when the position could be determined, and the “error bars” on each cross show the mean width of the vortex boundary (Nash et al., 1996). The equivalent latitude is calculated on the 550-K isentropic surface (Bodeker et al., 2001).

provides a good representation of the long-term decrease of the stratospheric ozone in Antarctica and could be used as an indicator of ozone recovery (see WMO, 1999). Figure 3-4 gives monthly averaged partial column ozone in September, October, and November (SON) based on ozonesonde observations at Syowa (1968 to 2001). The partial column ozone has decreased considerably from the early 1970s (~80% in September, ~85% in October, ~80% in November). The October partial column has not shown appreciable change since 1992. On the other hand, the September and November partial columns continued to show small reductions during the 1990s. The averaged partial column ozone over the 3 months (September to November) has also shown decreases during the 1990s, with relatively smaller interannual variability. Because Syowa is located near the vortex edge region, these September and November ozone reductions during the 1990s may be related to cooling near the vortex collar.

Spatially averaged characteristics of the Antarctic ozone hole from 1979 to 2001 based on the total column ozone observed by satellites (TOMS series for 1979-2001, and Television Infrared Observation Satellite (TIROS) Operational Vertical Sounder (TOVS) for 1995) are shown in Figure 3-5. These parameters include the maximum area, the minimum total column ozone, the ozone mass deficiency, and the date of the ozone hole's disappearance. The maximum area of the ozone hole increased rapidly during the 1980s and gradually during the 1990s, with year-to-year variations, and reached a maximum in 2000. The minimum total ozone, which usually appears in late September or in early October, has been approximately 100 Dobson units (DU) since 1993 (Figure 3-5) after the considerable decrease during the 1980s and the early 1990s. The ozone mass deficiency in the ozone hole (O_3 MD) is defined as the ozone mass deficiency from 300 DU in the sunlit area poleward of 60°S averaged for 105 days (1 September to 15 December). O_3 MD varied in concert with the Antarctic ozone hole area and was at the highest level ever in 2000. The date of the disappearance of the Antarctic ozone hole (disappearance of the total ozone values below 220 DU) has generally been occurring later in the season. As a whole, observations show that the Antarctic ozone hole has been slightly larger in the last few years in comparison with the mid-1990s. These observational results could be explained by ozone decreases near the vortex edge (e.g., Bodeker et al., 2001, 2002; Lee et al., 2001). Although the size of the Antarctic polar vortex has not increased, it has been stronger, as shown in Figure 3-6. There has been a tendency toward a cooling of the vortex due to ozone depletion, and the polar vortex has been more persistent, with some interannual variability (the temperature trends and persistence of the Antarctic polar vortex are discussed in

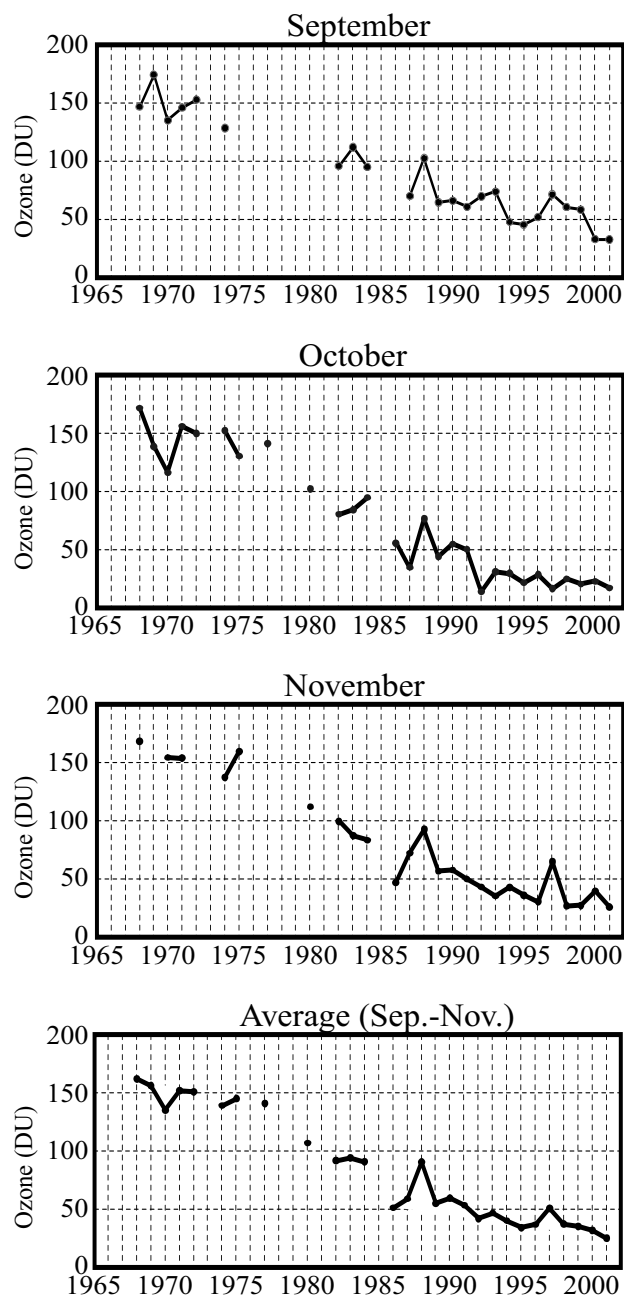


Figure 3-4. Partial column ozone in the 12- to 20-km layer in September, October, and November, and the average for September-November, over Syowa in Antarctica from 1968 to 2001. Update of Figure 4-27 of WMO (1999) by Japan Meteorological Agency.

the next section, Section 3.1.2). These conditions could result in more extensive polar stratospheric clouds (PSCs) in the sunlit vortex edge, and larger chemical depletion of ozone. This expands the area of the hole, and delays its disappearance into the late-spring period.

POLAR OZONE

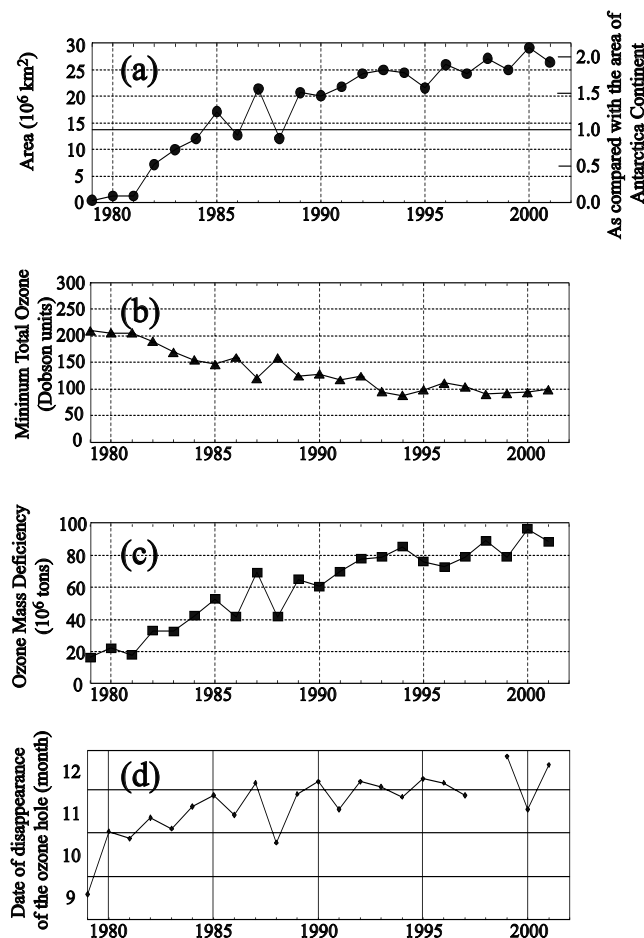


Figure 3-5. Evolution of the Antarctic ozone hole (defined by total ozone values below 220 DU) based on satellite data for the period 1 September to 1 December of each year. Panel (a) shows the maximum area covered by ozone hole values (left axis in millions km²; right axis gives size relative to Antarctic area), (b) the minimum total column ozone measured each year, (c) the maximum ozone mass deficiency from 300 DU during the period 1 September to 15 December (in Mt), and (d) the date of disappearance of the ozone hole values (Uchino et al., 1999; data updated to 2001).

The ozone hole has expanded in area somewhat since the early 1990s. The top panel of Figure 3-5 displays the maximum area of the ozone hole observed in the 1979 to 2001 period. There appears to be a steady increase of ozone hole size since the early 1990s. However, maximum values are sensitive to the timing of individual dynamical events in the early-September period (e.g., the 30 million km² single-day value in 2000). Figure 3-7 dis-

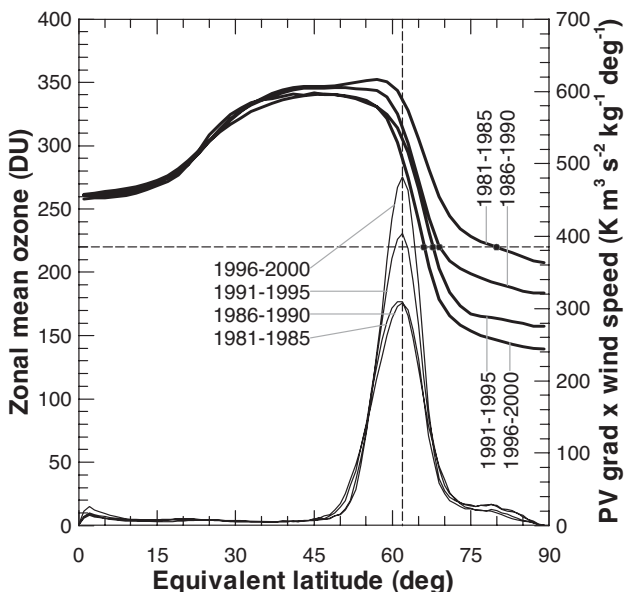


Figure 3-6. October SH average zonal mean total column ozone (top four thick solid lines plotted against the left ordinate) and October average vortex strength (gradient of potential vorticity (PV) multiplied by zonal wind speed; thin solid lines plotted against the right ordinate) for each of the four analysis periods (Bodeker et al., 2002).

plays the average size of the ozone hole (determined by the area enclosed by the 220-DU total ozone contour) over this same period, as determined from TOMS observations (see Appendix 3A for TOMS data description). Again, larger sizes are observed in the 1998 to 2001 period as compared with the 1992 to 1997 period. These size estimates are generally consistent with predictions that the ozone hole would have slight growth over the 1992 to 1995 period and maximum sizes occurring in the period after 1996 (Schoeberl et al., 1996).

3.1.2 Polar Temperature Trends

Substantial observational temperature data on the polar stratosphere are available from ~1979, including radiosonde and satellite measurements, and analyses of various types (Ramaswamy et al., 2001). Figure 3-8 illustrates the time series of temperatures at 70°N (March) and 70°S (November) from National Centers for Environmental Protection (NCEP) reanalyses and Climate Prediction Center (CPC) analyses (for descriptions, see WMO, 1999, Chapter 5). There are large interannual variations manifest in both hemispheres that generally complicate the determination of statistically significant trends.

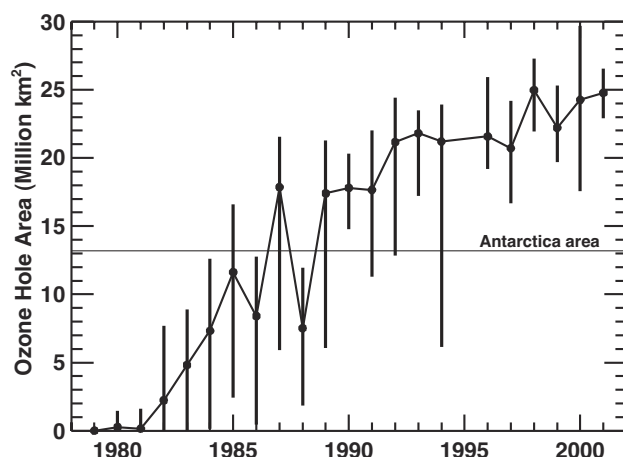


Figure 3-7. Area of the Antarctic ozone hole (defined by total ozone values below 220 DU) based on TOMS satellite data. The points show the average of the daily areas (in millions km²) between 7 September and 13 October. The vertical lines show the range of values over this same period.

The Microwave Sounding Unit channel-4 (MSU-4) data and the Stratospheric Sounding Unit (SSU) derived temperature trends (1979 to 1998) for 70°N and 70°S are shown in Figure 3-9 (see also Figures 3-39 and 3-40). These are an update to the 1979 to 1994 trends presented in Ramaswamy et al. (2001). The 70° latitude is chosen for comparison, because this is the highest latitude for which SSU trend data are available. Both MSU-4 (black line) and SSU-15X (gray line) signals originate from a range in altitude in the stratosphere and do not correspond to one particular height. The SSU peak signal corresponds to a pressure of roughly 50 hPa and shows a statistically significant (at the 2 σ level) cooling of nearly 3 K/decade at 70°N in March, April, and May (MAM) and 70°S in September, October, and November (SON), and approximately 1.2 K/decade for the annual average temperature change at both poles. The instrument also shows cooling significant at the 1 σ level for most other seasons. The MSU-4 data (peak signal from approximately 100 hPa) also shows a significant cooling during the spring in both hemispheres (−1.8 K/decade at 70°N and −1.1 K/decade at 70°S) and at both poles. These MSU-4 trends are roughly half the magnitude of the SSU trend. The observed satellite trends for this period indicate cooling in all seasons at both 70°N and 70°S.

It should be noted that the magnitude and statistical significance of the trends in both regions are dependent on the end-year considered. This is more crucial for the Arctic, especially during winter/spring when

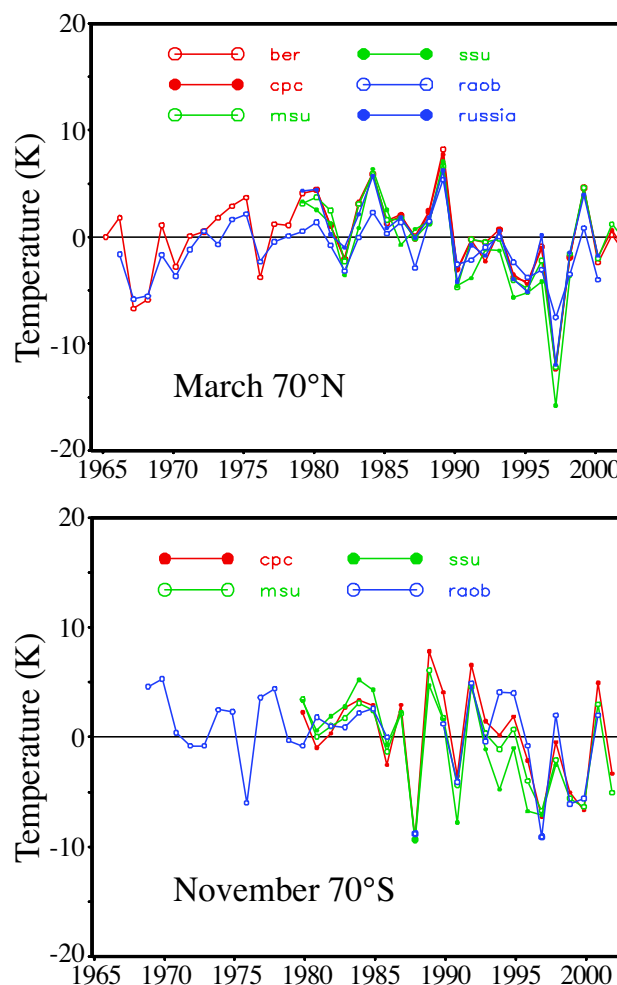


Figure 3-8. Zonal mean temperature deviation from the long-term mean in the lower stratosphere during March at 70°N (top) and November at 70°S (bottom). The red filled circles are 50-hPa NCEP/CPC objective analysis data; the open red circles are from the 50-hPa Freie Universität Berlin analyses; the open green circles are the MSU channel-4 satellite data (approximately a layer mean between 12 and 22 km); the filled green circles are the SSU channel-15X data (approximately a layer mean between 12 and 28 km); the open blue circles are the UK Meteorological Office adjusted and gridded radiosonde (RAOB) data at 50 hPa, and the filled blue circles are 50-hPa Russian radiosonde data from high northern latitudes. For each dataset, the deviation was determined with respect to the monthly mean of the time series (see Ramaswamy et al. (2001) for further details on the datasets). Figure assembled in cooperation with the Stratospheric Processes and Their Role in Climate (SPARC) Stratospheric Temperature Trends Assessment project.

POLAR OZONE

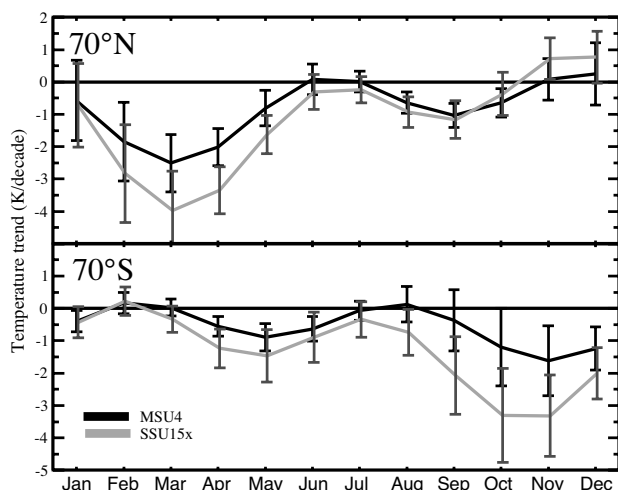


Figure 3-9. Stratospheric temperature trends for the period 1979 to 1998 at 70°N (top panel) and 70°S (bottom) for MSU-4 (black line) and SSU-15X (gray line) for each month of the year. The error bars represent the 95% confidence limits of the trend estimates. Figure provided by W.J. Randel (NCAR).

the time series reveals large interannual variations in temperatures (see Figure 3-8; also Labitzke and Van Loon, 1995). The trend sensitivity can be appreciated by comparing the latest (1979 to 1998) MSU trend at 70°N (March, as shown in Figure 3-9) with the corresponding MSU trends shown in WMO (1995, Figure 8.11 for the period 1979 to 1991).

Comparison of the satellite 1979 to 2000 annual-mean trends with those obtained for the 1979 to 1994 period (WMO, 1999) shows that there is now a statistically significant cooling at the 95% confidence level in the mid-to-high southern latitudes (Ramaswamy et al., 2002a). The northern midlatitudes continue to exhibit a statistically significant cooling trend (see WMO, 1999) while the higher latitudes (Arctic region) now have a cooling trend significant at the 90% confidence level. As in the satellite data, the 1979 to 2000 sonde trends yield an annually averaged cooling trend in the northern polar region. The sonde trend is somewhat smaller than the satellite trend (see Figure 3-39), although this may be partially due to the time period for the trend analysis being longer in the sonde data (note that 3 of the last 4 years have been relatively warmer; see Figure 3-8). The CPC analysis at 50 hPa also shows a cooling at both poles, consistent with the satellite data and sonde data.

Because ozone is radiatively active in both the infrared and the ultraviolet, large chemically driven polar ozone losses can potentially alter the dynamics of the strat-

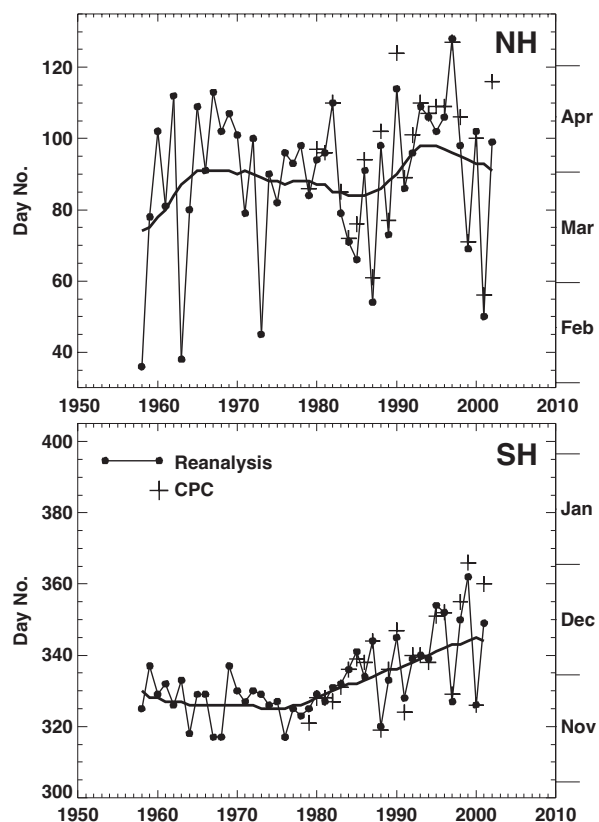


Figure 3-10. The vortex breakup date from 1958 to 2002 on the 500-K surface in the Northern (top) and Southern (bottom) Hemispheres using the method described in Nash et al. (1996; see also Waugh et al., 1999). The thin lines with filled dots are the dates calculated from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis data. The thick lines are these same data time-filtered to remove the year-to-year fluctuations. The crosses are the breakup dates calculated from the NCEP/Climate Prediction Center analyses for the period 1979 to 2002.

osphere by cooling the polar stratosphere (Kiehl et al., 1988; see also WMO, 1990). Randel and Wu (1999a) have shown such an Antarctic cooling using radiosonde and conventional meteorological analyses, and Compagnucci et al. (2001) using MSU retrievals. This cooling strengthens the meridional temperature gradient, thereby strengthening the Antarctic polar vortex. Waugh et al. (1999) and Zhou et al. (2000) have additionally shown that the Antarctic vortex has strengthened over the last two decades, with breakup dates occurring later in the spring, consistent with the polar cooling forced by the ozone loss. Figure 3-10 displays these stratospheric polar

vortex breakup dates in the NH (top) and SH (bottom), as determined using a wind average along the edge of the polar vortex (see Nash et al., 1996). The SH breakup date shows variations of 1 to 2 weeks, with a trend from late November in the 1980s to mid-December over the last few years. The NH breakup dates also show considerable variation, but without a linear trend. As discussed in Waugh et al. (1999), the variations in dynamics (i.e., eddy wave driving) do not explain the longer term trends of the breakup in the SH. Hence, the observed late breakups in the SH (and possibly the NH) are presumably related to radiative changes from ozone losses.

3.2 BASIC POLAR STRATOSPHERIC PROCESSES

3.2.1 Transport and Dynamics

This section discusses the structure and dynamics of the polar stratosphere, including trace gas transport. Section 3.2.1.1 gives a brief overview of the mean vortex structure, providing a context for the later assessment. Section 3.2.1.2 assesses recent studies of the dynamics and structure, including variability and trends. An important point is the apparent delay in polar vortex breakdown in springtime of the Southern (and possibly Northern) Hemispheres; extending the cold winter season is a critical factor in increasing the likelihood of chemical ozone loss, but even in the absence of chemical processes, the continued isolation of the polar region into the springtime leads to a “dynamical” ozone deficit. Section 3.2.1.3 examines transport processes, including the mean meridional circulation and issues of transport inside, outside, and across the boundary of the polar vortex; these play a crucial role in fixing the distributions of ozone and other trace gases, which impacts both the physical processes (such as radiative heating) and chemical ozone loss.

3.2.1.1 THE POLAR VORTEX: MEAN STRUCTURE

The winter stratospheric circulation is dominated by the polar night jet, which is at the edge of the polar vortex. Understanding the polar vortex dynamics is central to our ability to understand recent ozone change and to predict future ozone.

The polar vortex structure is well understood: absence of solar heating in winter leads to low temperatures, which are offset by the adiabatic warming caused by the descending branch of the Brewer-Dobson circulation. This circulation is caused by the damping of planetary and gravity waves in the middle atmosphere (e.g., Fels, 1985). An illustration of the polar vortex (Figure 3-

11) shows the polar night jet (peaking near 60°N at about 45 km) and the strong descent (shown by the meridional stream function). Descent in the polar region leads to (diabatic) downward transport, carrying ozone and other trace gases from the mesosphere to the lower stratosphere during winter (e.g., Rosenfield and Schoeberl, 2001).

The asymmetry of the polar vortices in the two hemispheres is a consequence of the different topographic features: the weaker wave activity propagating from the SH troposphere provides less forcing and therefore a weaker Brewer-Dobson circulation than in the NH (e.g., Randel and Newman, 1998). The Antarctic vortex is more symmetric, stronger, and colder than the Arctic, as illustrated by the 50-hPa geopotential height distributions in middle winter (Figure 3-12). Even in the absence of chemical ozone destruction, these dynamical differences lead to substantially more ozone in the Arctic than in the Antarctic vortex, especially in springtime.

The main impacts of these dynamical differences on Arctic (compared with Antarctic) ozone arise from the stronger diabatic descent, which transports trace species downward more rapidly, the weaker isolation of the Arctic, and the decreased likelihood of PSC formation. Since PSCs form at temperatures near 195 K at 50 hPa (see Section 3.2.2), they can form every winter in the Antarctic vortex core, but only on colder-than-average days in the Arctic (e.g., Pawson et al., 1995; Pawson and Naujokat, 1999).

While these basic mechanisms that determine the vortex structure and tracer transport in polar regions are now well understood, there are important aspects for which the complexity is only partially described. Recent results pertaining to these uncertainties are assessed in the next section (3.2.1.2).

3.2.1.2 POLAR VORTEX: CAUSES OF INTERANNUAL VARIABILITY AND ITS IMPLICATIONS

Differences between the hemispheres, caused by the stronger wave driving in the NH, are also evident in the year-to-year variations. Figure 3-9 shows what appear to be robust temperature trends in the springtime, but interpretation of such trends is complex, because of the large interannual variability of high-latitude temperature (Figure 3-8), which varies with time of year and is different in the two hemispheres (Figure 3-13; e.g., Scaife et al., 2000b). Southern Hemispheric variability peaks in late winter and spring (e.g., Kuroda and Kodera, 1998), whereas variability in the NH is large throughout the season (e.g., Labitzke, 1982). The variability of the stratosphere (defined in terms of departures from the long-term mean) is characterized by a “see-saw” of temperature and mass

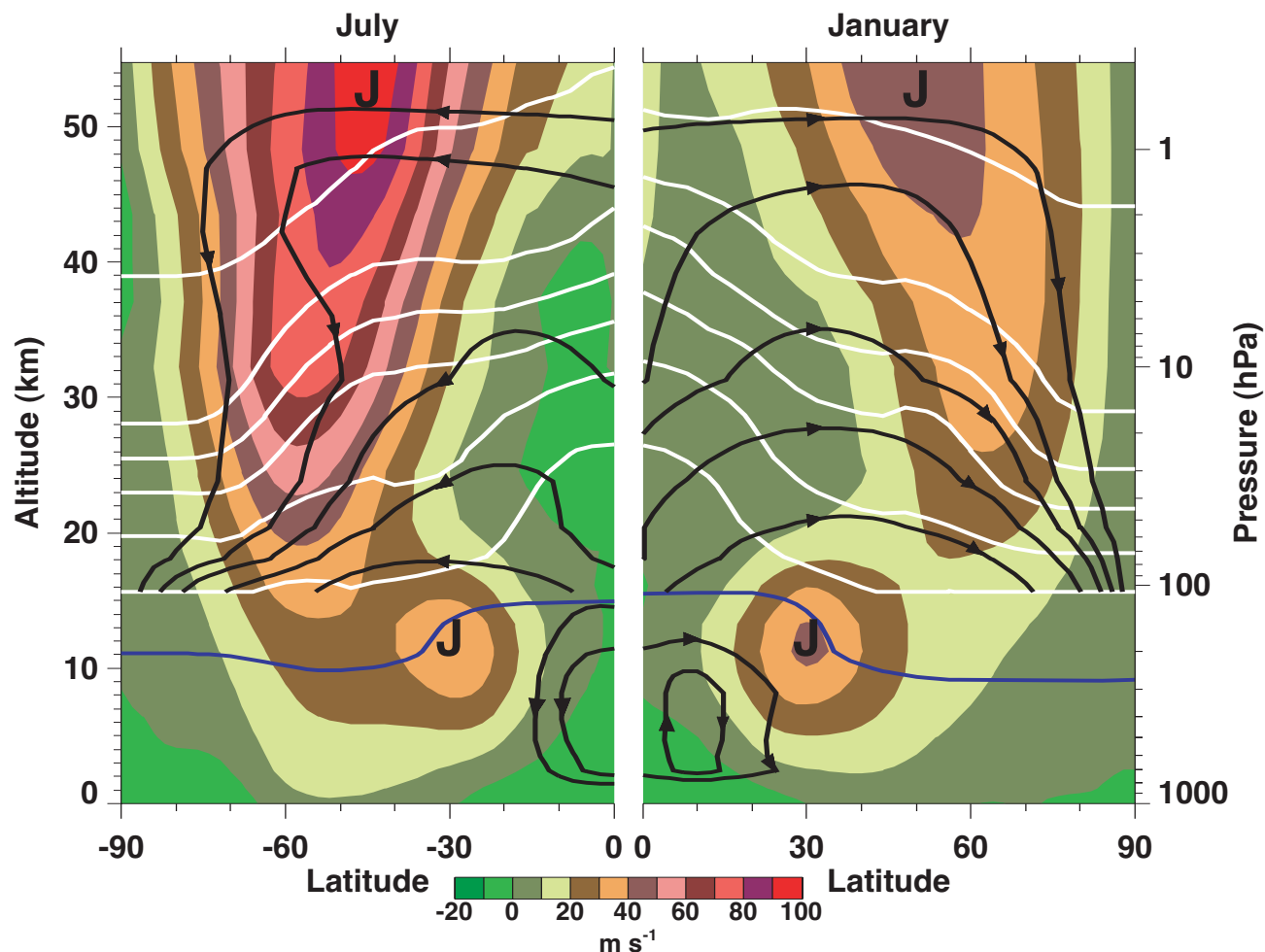
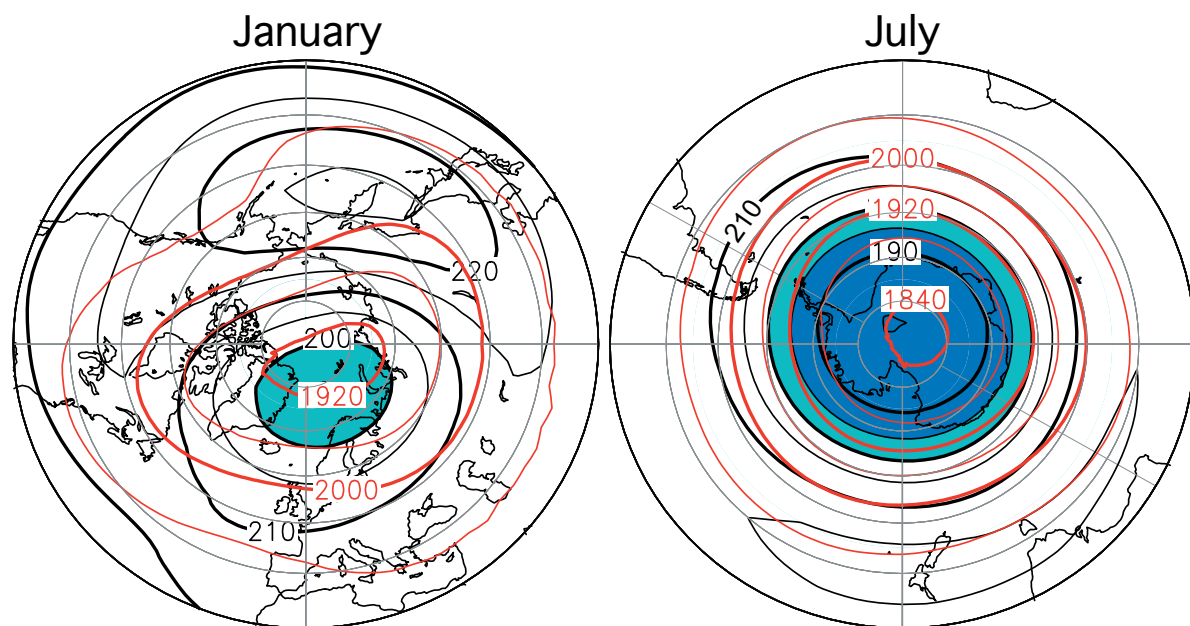


Figure 3-11. Zonal-mean sections of zonal velocity (shaded), the mean meridional streamfunction (black lines), and an atmospheric trace gas (white contours) for midwinter (July in the Southern Hemisphere and January in the Northern Hemisphere). The data were obtained from multiannual climatologies. The figure illustrates the stronger polar night jet in the Southern Hemisphere, the stronger subtropical jet in the northern winter, along with consistent differences in the strength and structure of the mean meridional circulation and trace gas distributions.

between the polar region and midlatitudes (e.g., Labitzke, 1982; Kodera et al., 1996): anomalously weak wave forcing leads to a strong polar vortex and a weak Brewer-Dobson circulation, with a cold polar region and warmer midlatitudes (the converse is true for strong wave forcing). Newman et al. (2001) demonstrated the quantitative linkage between the upward-propagating wave activity through the tropopause region and the strength of the polar vortex.

The occurrence of a strong, cold polar vortex leads to anomalously low ozone in the polar region, because the transport of ozone-rich air is weak and because the potential for PSC processing, a precursor to chemical ozone loss, is enhanced. This means that in years with weak tro-

pospheric wave forcing, a stronger polar vortex will result in less ozone in the polar region. Chipperfield (1999) reported results from a 6-year simulation using the SLIMCAT chemical transport model (CTM), driven by the United Kingdom Meteorological Office (UKMO) analyses of the meteorology. The horizontal winds and temperatures are taken from the UKMO analyses, and the vertical motion is diagnosed using a radiation scheme. The model simulates the interannual variations in chlorine activation during northern winters and reproduces the repeatable pattern of activation observed during southern winters. Chipperfield and Jones (1999) utilized the same model to evaluate the relative contributions of photochemical and dynamical processes to interannual



Geopotential Height (gpm) and Temperature (K) at 50 hPa

Figure 3-12. Polar stereographic projections for January in the Northern Hemisphere and July in the Southern Hemisphere. The geopotential height (red contours; geopotential decimeters (gpm)) and temperature (black contours; K) for 50 hPa are shown. Light-blue shading indicates regions colder than 200 K, while dark-blue shading shows regions colder than 195 K. Data are 19-year means from the United Kingdom Meteorological Office-processed TOVS data (Scaife et al., 2000b).

variability in northern high-latitude ozone, and showed that dynamical variations dominate interannual variability. Hadjinicolaou et al. (2002) find similar results using a long run of the same transport model, driven by European Centre for Medium-Range Weather Forecasts (ECMWF) analyses but using a simplified chemical scheme.

In the NH, the anomalies in polar vortex strength are a part of what is now known as the Arctic Oscillation (AO) (Thompson and Wallace, 1998). The AO and its Southern Hemispheric counterpart are also referred to as the annular modes. The annular structure of the AO in the stratosphere can be traced to the surface, with a strong link to the North Atlantic Oscillation (NAO) in the NH (Thompson and Wallace, 1998). Whereas there is some debate about the role of the stratosphere in forcing anomalies in the tropospheric component of the AO (e.g., Perlwitz and Graf, 2001; Ambaum et al., 2001), that is beyond the scope of this Assessment of stratospheric ozone. This discussion focuses on the stratospheric component of the AO.

A high (low) AO index corresponds to a strong (weak) vortex and low (high) polar ozone column values (Thompson and Wallace, 2000; Hartmann et al., 2000). Thompson et al. (2000) estimated that approximately 40% of recent apparent polar ozone loss in March could be

explained by the tendency of the AO to remain positive in the springtime, which describes a strong, cold, and isolated polar vortex. However, on the basis of the observations alone, it cannot be determined whether the signal in ozone is caused by the AO anomaly, or whether the AO anomaly is a consequence of ozone depletion, or whether both are coherently forced by some other factor.

There is strong evidence that the AO signal originates near the subtropical stratopause and propagates poleward and downward through the mechanism of wave forcing (e.g., Baldwin and Dunkerton, 1999, 2001; Kuroda and Kadera, 1999; Kadera et al., 2000; Christiansen, 2001). Kadera and Kuroda (2000) show how the interannual variability of wave forcing can cause such anomalies to take different phases in different years.

Isolating causes of variability and the factors that drive trends is not straightforward. Apart from the link between the AO strength and the upward propagation of planetary waves, other mechanisms have been related to the polar vortex. Model simulations reveal that a substantial year-to-year variability in the stratospheric vortex (and, hence, the AO) can exist in the absence of variations in boundary conditions or other forcing mechanisms (e.g., Yoden et al., 1999; Hamilton et al., 1999). This variability, forced by internal dynamics of the atmosphere, means that

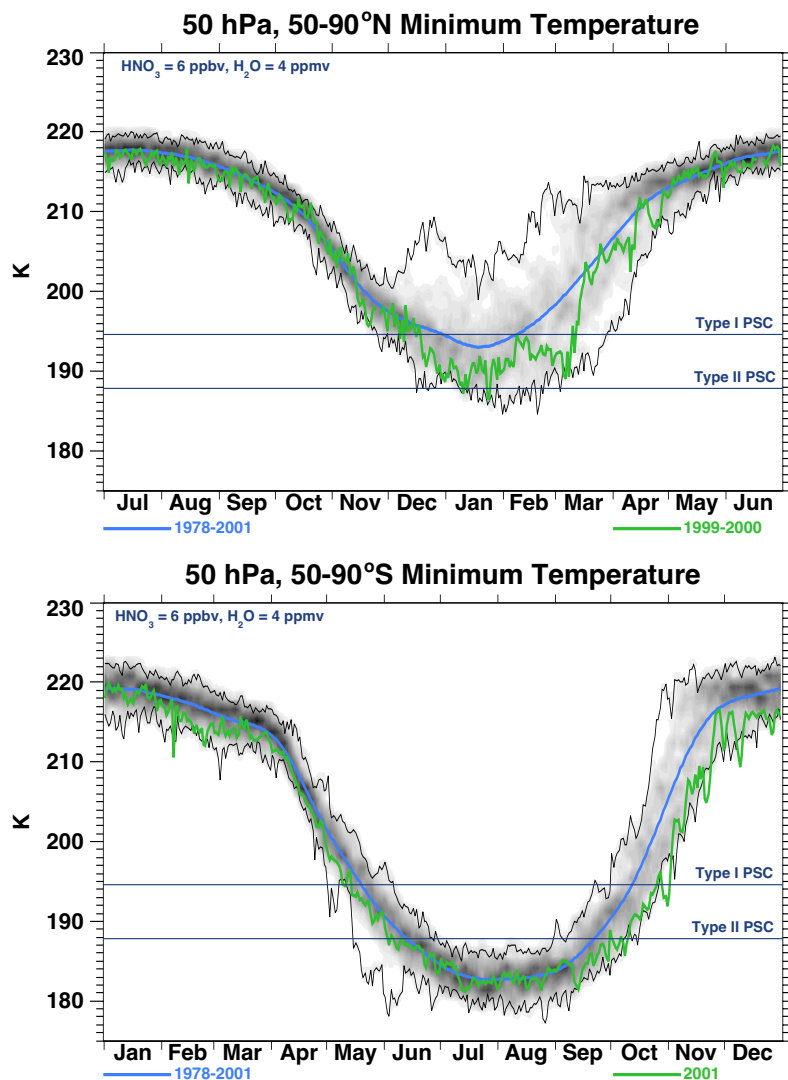


Figure 3-13. Time series showing binned distributions of 50-hPa minimum polar temperatures for 50°-90°N (top) and 50°-90°S (bottom). The blue line shows the 1978-2001 mean, and the thin black lines show the maximum-minimum values. Shading shows the density of observations, with heavy shading indicating a high probability and light shading indicating a low probability. Data are binned into intervals of 5 days by 2 K, and therefore the maximum number of observations in any bin is 95 (for 19 years of data). The green line shows the values for 1999-2000 (top panel) and 2001 (bottom panel). The seasonal cycles are offset by 6 months so that the seasonal progression in each hemisphere is contrasted. Thresholds for PSC formation are indicated by the horizontal lines. Data were processed as in Scaife et al. (2000b).

many factors often invoked as causes of interannual variability in the real atmosphere may or may not be significant. Despite this, there is some evidence of coupling between the polar vortex and other atmospheric variations; the main relationships that have been studied are the QBO of tropical winds, the 11-year variability of solar radiation, the phase of the ENSO, and major volcanic eruptions. Although polar vortex composites grouped according to these mechanisms show apparent signals, several factors complicate their interpretation and robustness. The most severe complications are that the observational record covers only about four decades and that some of the forcing factors vary in unison. For instance, following Labitzke and van Loon (1997) and grouping northern midwinter polar vortex structure according to the solar cycle (high or low) and the phase of the QBO (East or West) leads to 12 winters in the low/West category, with a strong polar vortex; however, 5 of these 12

winters coincide with ENSO cold events or volcanic eruptions, which have the same anomalies (see Figure 3-14). Determining robust relationships from observations on the basis of these overlapping factors and the internal variability is thus impossible.

Models have been used to address these questions. The SKYHI general circulation model (GCM) with an artificially forced QBO reproduces observed QBO-related interannual variability in the Arctic vortex (stronger when the tropical winds are westerly, weaker when easterly) and variations in wintertime stationary wave patterns (Hamilton, 1998). Shindell et al. (1999b) found that the QBO significantly modulated the strength and propagation of planetary-wave energy in the troposphere in the Goddard Institute for Space Studies (GISS) model, leading to higher (3- to 5-K) zonal-mean temperatures at high southern latitudes for late winter and early spring during the QBO easterly phase. Niwano and Takahashi

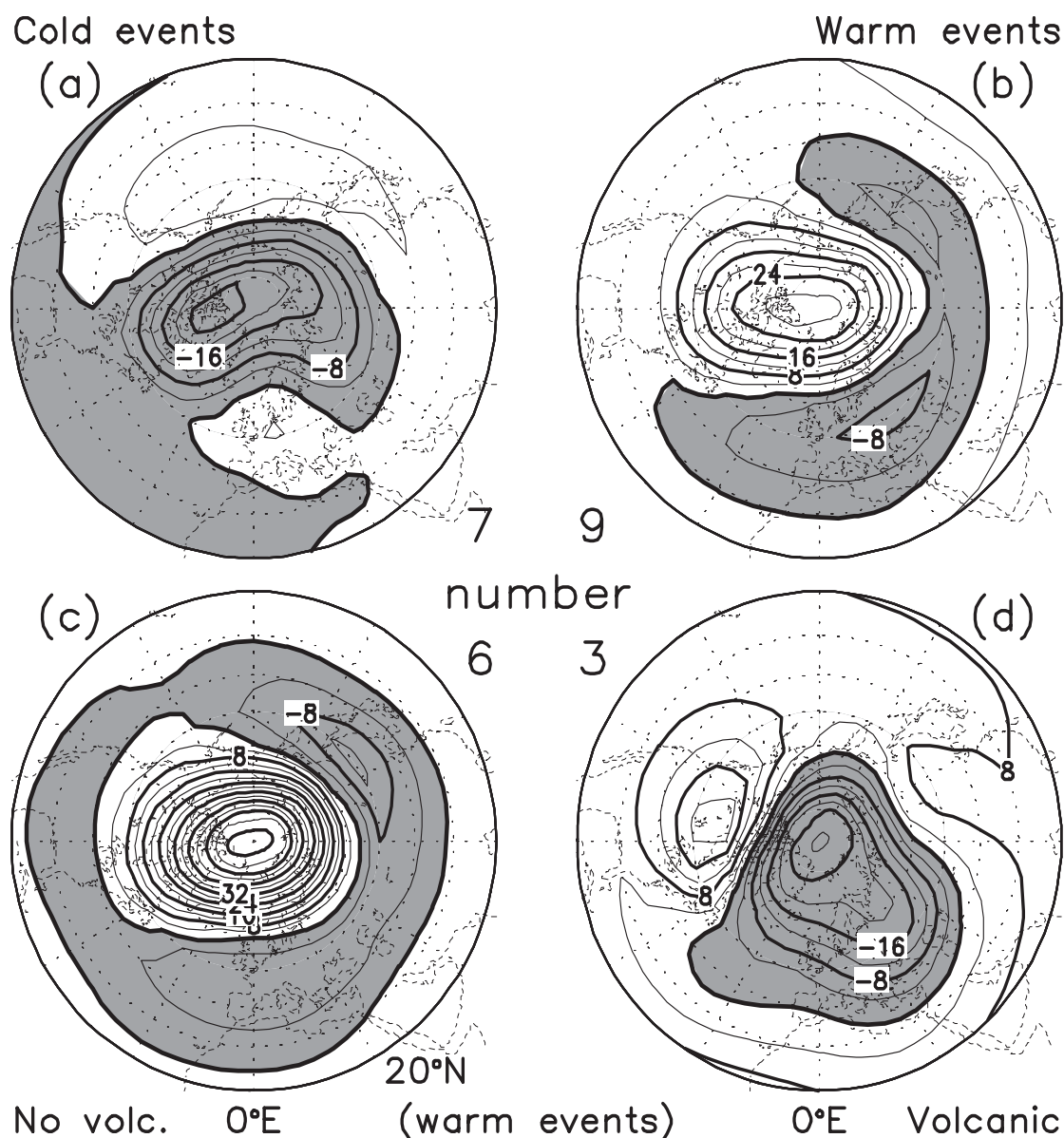


Figure 3-14. The anomalies in January/February 30-hPa geopotential height revealed by composite anomaly plots for ENSO and volcanic events, 1958-1997, as determined from Freie Universität Berlin analyses. The two top panels are (a) the composite anomaly of the seven winters with ENSO cold events, and (b) that for the nine warm events. The anomalies are in gpm and are relative to the mean of the years with no ENSO events. The lower two panels show the warm-event anomalies of panel (b), but further split into (c) the 6 years with no volcanic events and (d) the 3 years with them. These results were updated from van Loon and Labitzke (1987) and Labitzke and van Loon (1989).

(1998) studied the influence of the QBO on the NH winter circulation; their model reproduced the relationship between the polar vortex strength and the QBO phase and a related NAO pattern in the troposphere. These and earlier studies have worked on the premise that the lower stratospheric winds impact planetary wave propagation, whereas more recent work (Gray et al., 2001) has shown

that the polar vortex anomalies are more strongly related to winds near the tropical stratopause (which are indirectly affected by the QBO).

There are two important factors in isolating the impacts of solar forcing on the circulation and climate. First, stratospheric ozone changes modulate the response of the temperature to the changes in solar irradiance

(Haigh, 1994). However, studies of solar impacts on ozone, mostly using two-dimensional (2-D) models, have been plagued by an inability to reproduce the solar-ozone relationship detected in observations (e.g., Brasseur, 1993; Hood and Zhou, 1999). Second, inclusion of the correct spectral dependence of solar irradiance variations in the atmospheric heating rate calculations is essential to capture the correct vertical structure of heating rates (Haigh, 1999; Shindell et al., 1999a; Larkin et al., 2000). However, even incorporating these feedbacks, climate model studies generally remain inconclusive about the role of solar-induced perturbations in the variability of the Arctic polar vortex.

Volcanic aerosol loading can possibly impact polar ozone by perturbing stratospheric chemistry and transport. Chemical perturbations from heterogeneous reactions on aerosols are discussed in Section 3.2.2. Increased volcanic aerosol loading of the tropical lower stratosphere leads to a warmer tropical lower stratosphere some months after a volcanic eruption (e.g., Robock, 2000), which is discussed in more detail in Chapter 4. The polar response to this tropical warming has a northern polar vortex remaining anomalously cool in the winter following the eruption (e.g., Kodera, 1994), as shown in Figure 3-14. Figure 3-14 shows that the three volcanic eruptions affected winters with ENSO warm events and that they “reverse” the ENSO anomalies, leading to anomalously strong, cold polar vortices (van Loon and Labitzke, 1987; Labitzke and van Loon, 1989), thereby increasing the likelihood of negative polar ozone anomalies. Based on only three events (and because of the factors discussed above), these results must be interpreted with caution. This relationship has also been isolated in models (Kirchner et al., 1999; Ramachandran et al., 2000).

Although temperatures low enough for PSC formation occur on the large scales (e.g., Pawson and Naujokat, 1997, 1999), the likelihood of their occurrence is enhanced by the temperature perturbations induced by medium-scale waves (e.g., Grewe and Dameris, 1997; Sato et al., 2000; Teitelbaum et al., 2001), as well as by inertial gravity waves (e.g., Dörnbrack et al., 2001, 2002). The temperature perturbations induced by these waves can cause sufficient additional cooling for PSCs to form in locations where the large-scale flow would not support them. This is particularly important on the vortex edge, where the processed air can be irreversibly transported into the middle latitudes (in the presence of breaking waves) and where the air masses are more likely to be illuminated, enhancing the potential for ozone depletion.

Ozone mini-holes occur because of synoptic-scale, reversible advection (e.g., McKenna et al., 1989; Newman et al., 1988) related to upper tropospheric anticyclonic

structures. The high tropopause, coupled with ascending motion, leads to extremely low total ozone values with lifetimes of up to several days. Steinbrecht et al. (1998) show that correlations in tropopause height correlate with ozone concentration changes in the region up to 23 km, illustrating the depth of the disturbances. However, the low ozone values themselves are short-lived features that are unrelated to chemical loss. The dynamical forcing that causes ozone mini-holes also causes adiabatic cooling, which can lead to synoptic-scale temperature perturbations of sufficient magnitude to allow PSC formation (e.g., McKenna et al., 1989; Grewe and Dameris, 1997). The importance of baroclinic disturbances in producing PSC formation near the polar vortex edge has been discussed by Hood et al. (2001) and Teitelbaum et al. (2001). Orsolini and Limpasuvan (2001) showed how these disturbances are linked to the storm tracks, which vary in unison with the AO. There is thus a flow-dependent nature to the likelihood of synoptic-scale PSC formation and to the likelihood that PSCs contribute to ozone loss on the vortex edge region.

Just as baroclinic waves help PSC formation on the synoptic scales, mesoscale disturbances from gravity waves are also important. Volkert and Intes (1992) demonstrated PSC formation in wave crests over Scandinavia in their model of topographically forced gravity waves. The importance of gravity-wave PSCs was also demonstrated by Deshler et al. (1994) and Meilinger et al. (1995). High-resolution radiosonde data have recently provided much-needed information on stratospheric gravity-wave morphologies in and around the Antarctic (Pfenniger et al., 1999; Zink and Vincent, 2001) and Arctic (Whiteway and Duck, 1999; Yoshiki and Sato, 2000). Although the microphysical effects of a background spectrum of gravity waves are smaller than first thought (Bacmeister et al., 1999), it is now accepted that mesoscale temperature decreases due to large-amplitude gravity waves, particularly mountain waves, can lead to temperatures low enough for PSC formation (Carslaw et al., 1998b, 1999; Schulz et al., 2001), and lead to structure inside larger scale PSCs (Toon et al., 2000). PSCs are discussed in Section 3.2.2 of this chapter.

Important advances have been made in our ability to model lower stratospheric gravity waves and, especially, to resolve such waves in global meteorological analyses. Dörnbrack et al. (2001) demonstrated that the high-resolution ECMWF operational meteorological analyses capture gravity-wave structures over Scandinavia. This represents an important advance for applying the analyses to our understanding of the gravity-wave morphology and its importance for PSC formation. An additional advance of some importance was made by

Dörnbrack et al. (2002), who detected inertia-gravity waves over Scandinavia in the ECMWF analyses and in situ data, noting their role for PSC formation. The isolation of gravity waves in such operational analyses points to their potential utility in mountain wave forecasting and analysis, meaning that the off-line models that have been used for such studies could eventually become unnecessary.

Another important role played by gravity waves (from all sources) is that they transport momentum into the middle atmosphere; as these waves break, they deposit momentum to the mean flow, constituting an important driving mechanism for the Brewer-Dobson circulation. The importance of these waves for driving the flow and reducing biases in global models is discussed in more detail in Section 3.5.2.1.

3.2.1.3 POLAR TRANSPORT AND MIXING

This section discusses in detail the physical processes that lead to the redistribution of trace gases in the polar regions. Trace gas distributions are determined by the balance between the slow, mean-meridional circulation and the more rapid, quasi-isentropic mixing (e.g., Holton, 1986); the following discussion examines these components of transport in and around the polar vortex and the exchange across the vortex edge.

Manney et al. (2002) examine impacts of using different meteorological analyses, which affect the amount of exchange between middle latitudes and the vortex. Despite the uncertainties, the consensus is that the vortex remains quite isolated in wintertime. Vertical transport leads to descent of tracers in and around the vortices, while mixing redistributes ozone and trace gases on isentropic levels; there is some exchange across the vortex edge, associated with large-scale mixing events.

Descent in the Polar Vortex

Descent inside the polar vortex builds up (or maintains) lower stratospheric ozone over the winter, making it an important process to understand. The descending branch of the Brewer-Dobson circulation is driven by wave forcing of the flow (see Section 3.2.1.1). Descent rates can be determined in several manners: (1) “directly” from the vertical velocities produced in routine meteorological analysis systems, such as the UKMO (Swinbank and O’Neill, 1994) and the Data Assimilation Office (DAO) (Rood et al., 1997), (2) based on the cross-isentropic transport determined by diabatic heating rates, and (3) using measurements of long-lived trace gases with well-understood vertical gradients. The various estimates are in reasonably good agreement, showing stronger

descent in the upper stratosphere than in the lower stratosphere and unmixed descent from the upper to the lower stratosphere. The strongest unmixed descent occurs in the Antarctic vortex. Descent in the Arctic vortex is more variable; it occurs on the vortex edge when the temperature is higher there (e.g., Manney et al., 1999).

Schoeberl et al. (1995) used Halogen Occultation Experiment (HALOE) methane (CH_4) data to estimate the descent rate as 1.8 km/month inside the Antarctic vortex in February to October 1992 (see Appendix 3A for HALOE data description). Descent rates over Antarctica were deduced from the Improved Stratospheric and Mesospheric Sounder (ISAMS) carbon monoxide (CO) data for April to July 1992 by Allen et al. (2000) and from the Polar Ozone and Aerosol Measurement (POAM) III H_2O data by Nedoluha et al. (2000). Abrams et al. (1996) demonstrated strong descent in the upper stratosphere (3.2 km/month at 40 km) with weak descent in the lower stratosphere (0.8 km/month at 20 km) based upon the Atmospheric Trace Molecule Spectroscopy (ATMOS) data from November 1994. Kawamoto and Shiotani (2000) also used HALOE data and UKMO meteorological analyses to investigate the interannual variability of the descent rate, using the February–October (winter) averages in 1992 to 1997 HALOE CH_4 data (see Appendix 3A for POAM and HALOE data descriptions). They found that the descent varies between 1.2 and 1.8 km/month using the 0.6 parts per million by volume (ppmv) CH_4 contour inside the polar vortex and is consistent with the wave driving determined from the UKMO analyses. To summarize, the various estimates of polar descent rates give reasonably consistent results, given that they are presented for different levels, seasons, and years.

The Vortex Core

The degree of mixing within the vortex core has come under scrutiny because of assumptions about representing the bulk behavior of the vortex with irregular temporal and spatial sampling. If the core is well mixed, then measurements anywhere within the vortex will suffice to characterize its behavior. If the core is not well mixed, then more frequent sampling at separated locations is necessary to do this. Schoeberl et al. (1990) assumed that the vortex was relatively well mixed in assessing ozone loss using Earth Resources-2 (ER-2) data from the Airborne Arctic Stratospheric Expedition (AASE)-I mission during the Arctic winter of 1988/1989. Richard et al. (2001) used ER-2 data from the SOLVE-THESEO 2000 campaign to show that tracer-tracer relationships inside the vortex during the Arctic winter of 1999/2000 are distinct and compact, suggesting a rapid mixing in the Arctic vortex. Whereas current evidence suggests that the Arctic vortex

is relatively well mixed in the absence of intrusions of air from the vortex edge, Lee et al. (2001) present evidence that the Antarctic vortex is separated into two regions: a strongly mixed vortex core and a weakly mixed ring of air extending to the vortex boundary.

Transport Across the Vortex Edge and Mixing

The balance of mass and trace gases in and around the polar vortex is determined by the downward transport and exchange across the vortex edge. Any vertical gradient in the vortex-averaged mass flux will be compensated for by flow across the vortex edge. The discussion below will separate the transport across the vortex edge in winter from transport occurring as the polar vortex breaks down.

Planetary-wave breaking can be responsible for vortex shrinking as well as sharpening of the vortex edge (e.g., Thuburn and Lagneau, 1999). A number of studies have shown considerable variability in the width of the Antarctic vortex edge when it is perturbed (Teitelbaum et al., 1999; Perez et al., 2000), which results in nonlinear irreversible transport and mixing of vortex air into mid-latitudes (Teitelbaum et al., 1999). Lidar observations at Dumont d'Urville (66.4°S, 140°W) allow sampling at and around the moving vortex edge (Godin et al., 2001); observations of Mt. Pinatubo aerosols, made during October and November 1992, show the sharpness of the vortex edge and low mixing between the inner vortex and the outside air above 400 K.

The first obstacle to determining the cross-vortex flow is to unambiguously define the vortex edge. Chen (1994) defined it as the potential vorticity (PV) contour that has the smallest lengthening rate; he found a vertical dependence to the transport across the edge, with more transport out of the vortex at potential temperatures lower than 400 K than at higher levels. Tuck et al. (1995) reached similar conclusions using ER-2 data, showing also that the vortex edge region can be quite wide. This viewpoint of the polar vortex as a reasonably well isolated entity is now generally accepted, but the amount of "leakage" from the vortex (as a function of altitude) is not yet well understood. Different proposed definitions of the vortex edge include the wind maximum and the strongest gradients in PV (e.g., Bowman, 1996; Nash et al., 1996). The uncertainty in defining the vortex edge remains, so there is no unambiguous estimate of the vertical structure of cross-vortex transport. Mechanisms for the transport are at least qualitatively understood and are discussed here.

Recent results continue to sustain our understanding of the vortex edge impermeability (Chen, 1994) and of the polar vortex as a quasi-isolated containment

vessel. Norton and Chipperfield (1995) and Jones and MacKenzie (1995) had argued that ozone-depleted air from the polar vortices makes only a small contribution to middle-latitude ozone loss. High-resolution, single-level models with weak dissipation (e.g., Juckes and McIntyre, 1987; Mo et al., 1998; Thuburn and Lagneau, 1999; Sobel and Plumb, 1999) have further confirmed that the export of air from the polar vortex is constrained. Vincent and Tranchant (1999) also found little mixing across the vortex edge at 520 K in the Antarctic. Li et al. (2002) used a CTM driven by analyzed winds to show that less air is indeed exported from the Antarctic polar vortex to middle latitudes than descends into the troposphere.

Laminae and filaments could be an important mechanism in the mixing of air across the quasi-impermeable vortex edge. Such structures are common in winter and spring. As pointed out in the previous Assessment (WMO, 1999) the filaments/laminae, i.e., material sheets that tilt outward with increasing height (Schoeberl and Newman, 1995; Newman and Schoeberl, 1995) with initial horizontal scales of a few thousand kilometers, can lead to irreversible mixing on the time scale of 20 to 25 days over which they decay. Laminae have been detected in a variety of data types, including in situ aircraft observations (Newman et al., 1996); sondes and lidar (Bird et al., 1997; Orsolini et al., 1997; Teitelbaum et al., 2000); and satellites (Manney et al., 1998, 2000). They have been successfully modeled (e.g., Orsolini et al., 1997). Waugh and Dritschel (1999) analyzed the relationship between Rossby wave breaking and vortex structure. These studies show that filamentation can lead to vortex air being peeled off and eventually mixed irreversibly into the surf zone, although some air may rejoin the polar vortex. Furthermore Manney et al. (1998, 2001) have also shown that lamination processes within the polar vortex did not result from exchange across the vortex edge but rather from transport variations within the vortex.

Hence, there is a need to assess the behavior of laminae and the magnitude of their contribution to the total exchange between the vortex and midlatitudes. Appenzeller and Holton (1997) attempted to diagnose the production of tracer laminae using satellite data and meteorological analyses, as a first step in determining their contribution to transport. Nevertheless, there arose some limitations regarding the use of such a diagnostic (Kettleborough and Holton, 1999), because (1) it does not include small vertical scales that are relevant in defining tracer lamination, and (2) there can be reversible contributions. In other words, the proposed diagnostic could overestimate the transport and mixing.

A principal challenge to modeling polar ozone in the NH and the effects of polar processes on middle lati-

tudes is to ensure that the models produce the appropriate balance among the many processes that contribute directly or indirectly to the polar lower stratospheric ozone tendency. Both transport and photochemical processes contribute. The year-to-year variability in meteorological fields is significant, and the northern vortex may be cold and strong, as in the 1996/1997 and 1999/2000 winters, or warmer and more disturbed, as in the 1997/1998 winter (Sinnhuber et al., 2000; Guirlet et al., 2000). Simulations have focused on replicating observations for ozone and other trace gases, and quantifying model sensitivity to various processes (Chipperfield and Pyle, 1998). Such studies point out the importance of developing a better understanding of the physical processes (e.g., those leading to denitrification), so that model parameterizations respond appropriately to changes in temperature, water vapor, or nitric acid (HNO_3) that may result from climate change.

Millard et al. (2002) utilized diagnostics developed by Lee et al. (2001) to quantify the importance of polar processes to ozone change at middle latitudes. Both the chemical processes that contribute to polar ozone loss and the transport processes that impact mixing between high latitudes and middle latitudes vary depending on the meteorology of a particular year. CTMs have been utilized to address questions concerning specific winters. For example, Lefèvre et al. (1998) utilized a CTM forced by winds from ECMWF to show that both transport and photochemical processes contributed to the record-low ozone observed by TOMS during northern spring 1997 (Figure 3-2). Like the studies of Guirlet et al. (2000), their results are broadly consistent with observations. However, as shown by Douglass et al. (2001), the model results separating photochemical and transport contributions are sensitive to the vertical velocity and to the ozone vertical gradient.

The breakdown of the polar vortex, whether by a major midwinter warming or in the final warming, allows vortex air to be mixed relatively easily with air from middle latitudes. Atkinson and Plumb (1997) showed that as the Antarctic vortex breaks down, a substantial amount of ozone-depleted air is transported to middle latitudes. Once there, it can effectively mix with the ambient air masses. Effective diffusivity has been used as a diagnostic for mixing by Allen and Nakamura (2001), who show increases in mixing lengths as the polar vortices break up.

3.2.2 Polar Stratospheric Clouds

PSCs play two important roles in polar ozone chemistry. First, the particles support chemical reactions leading to active chlorine formation, which can catalyti-

cally destroy ozone. Second, nitric acid (HNO_3) removal from the gas phase can increase ozone loss by perturbing the reactive chlorine and nitrogen chemical cycles in late winter and early spring.

PSCs are divided into two main categories. Type I PSC particles contain nitric acid, either in the form of liquid ternary solutions with water and sulfuric acid or as solid hydrates of nitric acid. Type II PSCs are made of ice particles. Knowledge of PSC particle sizes, number concentrations, composition, phase, and evolution is central to efforts to develop prognostic models of how PSCs affect the chemistry of the polar stratosphere. In situ observations of PSCs from balloons or aircraft are often used to obtain detailed information on cloud particle size distribution and composition. Remote sensing platforms, such as lidar and satellites, provide complementary information on phase and large-scale time evolution of PSCs, respectively. We now briefly review recent advances in our understanding of PSC properties and their effect on denitrification and dehydration.

3.2.2.1 OBSERVATIONS OF PSC PHYSICAL PROPERTIES AND THEIR INTERPRETATION

In Situ

The previous Assessment (WMO, 1999) described considerable improvements in our understanding of liquid PSCs but highlighted the outstanding uncertainties in the properties of solid particles. Solid nitric-acid-containing PSC particles are important because, in contrast to the submicron liquid aerosol, they may be present with sufficiently low number concentrations ($<10^{-2} \text{ cm}^{-3}$) to allow a few particles to grow to large sizes, leading to sedimentation and denitrification. Our understanding of the range of solid-particle number concentrations and sizes that can form in the polar stratosphere has improved since the previous Assessment as a result of new in situ observations.

Observations in the Arctic stratosphere at altitudes from 16 to 20 km in January to March 2000 detected a population of large nitric acid particles with very low number concentrations (Fahey et al., 2001; Northway et al., 2002a); see Figure 3-15. Large particles, with sizes and number concentrations similar to those observed by Fahey et al. (2001), were detected by the Multiangle Aerosol Spectrometer Probe (MASP) (Carslaw et al., 2002). These measurements (Fahey et al., 2001; Northway et al., 2002a) are very important because they provide conclusive evidence that such large particles are composed principally of nitric acid (probably present as nitric acid hydrates).

Observations of large nitric acid particles raise several questions. The most obvious question is how these particles compare with previous observations in the Arctic and Antarctic. Balloonborne instruments such as the optical particle counter (OPC) (e.g., Deshler et al., 1991, 1994; Deshler and Oltmans, 1998; see also WMO, 1999, and references therein), which has flown in many previous Arctic winters, are capable of detecting particles up to 20 μm in diameter with number concentrations greater than about $6 \times 10^{-3} \text{ cm}^{-3}$. However, this is higher than the average particle concentrations ($\sim 10^{-4} \text{ cm}^{-3}$) measured by Fahey et al. (2001). It is interesting to note that in earlier Antarctic measurements, the OPC instrument, which operated at a different inlet flow rate, detected large PSC particles with number concentrations as low as 10^{-4} cm^{-3} (Table 3-1). The forward scattering spectrometer probe (FSSP) instrument, which measured PSC size distributions during the 1989/1990 Arctic winter (Dye et al., 1992), detected PSCs with total number concentrations of about 10^{-3} cm^{-3} . Some particles were observed up to 13-

μm diameter with concentrations of $\sim \text{few} \times 10^{-4} \text{ cm}^{-3} \mu\text{m}^{-1}$, similar to those observed by Fahey et al. (2001). These large particles were attributed to ice (Wofsy et al., 1990), although some of them could certainly have been nitric acid trihydrate (NAT). Thus populations of very few ($\sim 10^{-4} \text{ cm}^{-3}$) large PSC particles have been observed previously, but it is only through recent measurements (Fahey et al., 2001) that we have learned that such large particles are indeed enriched in nitric acid.

The second question is whether these large particles present at very low number concentrations can denitrify the stratosphere. Simple calculations presented by Fahey et al. (2001) demonstrate that large nitric acid particles can grow to their optimal observed sizes in about 5 to 8 days, implying that they must have nucleated several kilometers above the aircraft flight altitude. Instantaneous downward flux calculations of nitric acid contained in such large particles indicate that the large particles were capable of causing significant denitrification (Fahey et al., 2001; Northway et al., 2002b). Three-dimensional model simulations of particle growth further show that the observed PSC sizes are consistent with growing NAT and/or nitric acid dihydrate (NAD) particles (Carslaw et al., 2002). However, it is important to note that PSCs with size distributions differing from those measured in winter 1999/2000 have been observed in previous winters in both hemispheres (see Table 3-1). Model simulations by Jensen et al. (2002) show that previously observed PSC particle size distributions (Dye et al., 1992; Hofmann and Deshler,

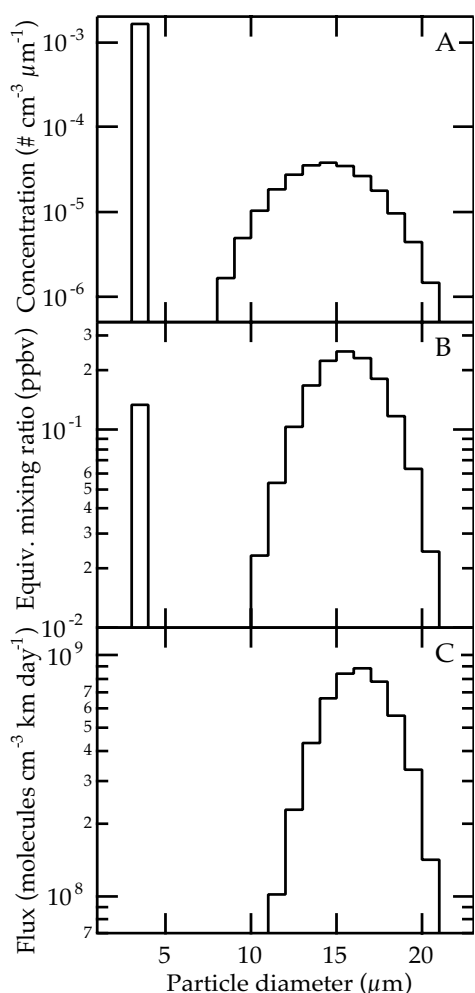


Figure 3-15. Results from the statistical simulation of total reactive nitrogen (NO_y) values observed by the ER-2 NO_y instrument on 20 January 2000 (Fahey et al., 2001). Panels show (A) the adjusted best-fit size distribution and number concentration, (B) the equivalent gas-phase mixing ratio of HNO_3 derived from the distribution, and (C) the derived flux of HNO_3 at 60 hPa ($\sim 19.5 \text{ km}$). The size distribution is given by the Gaussian functions in the caption of Figure 3 of Fahey et al. (2001) adjusted to account for size-dependent sampling efficiency. The adjustments, which are in addition to a basic particle enhancement factor of 12.8, range from +30% to -10% over the size range and are calculated with a fluid dynamical model of the particle separator. The concentration integral of the large (small) mode is $2.3 \times 10^{-4} \text{ cm}^{-3}$ ($2 \times 10^{-3} \text{ cm}^{-3}$) with an estimated uncertainty of $\pm 30\%$. The lower limit of the vertical axis in (A) corresponds to the detection of a single particle over the 800-s observation period. The total gas-phase HNO_3 of the large (small) mode is 1.5 ppbv (0.2 ppbv). The HNO_3 flux of the combined distribution is $5 \times 10^9 \text{ molecules cm}^{-3} \text{ km day}^{-1}$ or $2.2 \text{ ppbv km day}^{-1}$ at 60 hPa. Adapted from Fahey et al. (2001).

Table 3-1. Observations of solid PSC number density and particle size.

Number Density (cm ⁻³)	Average Diameter (μm)	Atmospheric References	Location
10 ⁻¹ -1	1-2	Voigt et al. (2000a, b)	Arctic
10 ⁻³ -10 ⁻²	1-4	Dye et al. (1992) ^a	Arctic
10 ⁻⁴ -10 ⁻²	4-10	Hofmann and Deshler (1991) ^a	Antarctic
10 ⁻⁵ -10 ⁻³	10-20	Fahey et al. (2001) ^b ; Northway et al. (2002a) ^b	Arctic

^a Note that these measurements are mode diameters of a lognormal distribution. Some particles, most likely containing nitric acid, were observed up to 13 μm in diameter (Wofsy et al., 1990).

^b These observations on the average show PSC number densities of about 2×10^{-4} cm⁻³ with a mode diameter centered near 14 μm, assuming a nitric acid trihydrate (NAT) composition.

1991), with number concentrations in the range of 10⁻² to 10⁻³ cm⁻³, are also capable of efficiently denitrifying the polar stratosphere.

A third question is how these large nitric acid particles form in the polar stratosphere. Both homogeneous (Tabazadeh et al., 2001) and heterogeneous (Tolbert and Toon, 2001; Drdla et al., 2002) freezing mechanisms have been suggested to account for the formation of large nitric acid particles. For such nucleation mechanisms to operate, the cooling caused by synoptic-scale uplift of air masses (Teitelbaum et al., 2001; Spang et al., 2001; Hendricks et al., 2001; Saitoh et al., 2002) can provide favorable conditions for solid PSCs to form. Laboratory observations show that concentrated aqueous nitric acid aerosols can homogeneously crystallize into hydrates of nitric acid (Disselkamp et al., 1996; Bertram and Sloan, 1998a, b; Prenni et al., 1998; Salcedo et al., 2001). The stratospheric particle system has also been studied using thin films, where gas-phase nitric acid and H₂O are absorbed by cold aqueous sulfuric acid solutions (Iraci et al., 1994, 1995, 1998). The results of these thin-film experiments show that HNO₃ uptake in sulfuric acid can cause freezing of nitric acid hydrates in solution. Tabazadeh et al. (2001) have recently extrapolated the laboratory homogeneous freezing rates of Salcedo et al. (2001) and obtained nucleation rates sufficient to produce large nitric acid particles in a microphysical model. Note that the nucleation rates extrapolated from Salcedo et al. (2001) are much higher than upper limits derived from earlier bulk freezing experiments with 1-milliliter samples, which used stratospheric temperatures and liquid-phase compositions (Koop et al., 1995, 1997). Modeling studies (Drdla et al., 2002) further show that heteroge-

neous freezing can also produce large particles if only a very small fraction (<0.1%) of stratospheric aerosol particles contained an effective freezing nucleus, although it is not clear what the freezing nucleus should be (Biermann et al., 1996). In addition to direct homogeneous and heterogeneous freezing mechanisms, the large particles may also form by a gradual sedimentation from the base of “mother clouds” containing much higher number concentrations of small solid particles (Füglister et al., 2002; Dhaniyala et al., 2002), such as those generated by lee wave clouds (Carslaw et al., 1998a).

The freezing mechanisms described above are all capable of producing low number concentrations of sedimenting nitric acid particles. However, model simulations do strongly suggest that the large nitric acid particles, observed during the winter of 1999/2000, were unlikely to have nucleated in synoptic-scale ice clouds, which were not sufficiently prevalent in the days preceding the observations (Carslaw et al., 2002; Drdla et al., 2002). Further analysis of satellite data in the Antarctic also seems to suggest that large nitric acid particles formed in the winter of 1992 independent of synoptic-scale ice clouds (Tabazadeh et al., 2000). Formation of denitrifying particles when polar temperatures are above the ice frost point will allow denitrification to occur at higher temperatures than previously assumed in 3-D chemical models (see Section 3.2.2.3).

A final question is whether these large particles observed in situ can also be detected by lidar. Aircraft lidar observations in January to March 2000 detected regions of enhanced aerosol backscatter in regions where large nitric acid particles were detected (Flentje et al., 2000). However, Flentje et al. (2000) inferred an approx-

POLAR OZONE

imate size for the particles based on the sedimentation speed of the particle layer, rather than directly from the lidar signal. Their derived particle sizes are in reasonable agreement with in situ observations (Fahey et al., 2001).

Overall, the assessment of both the Arctic and Antarctic studies, on observed and inferred PSC particle sizes, indicates that large nitric acid particles cannot initially nucleate on synoptic-scale ice clouds. However, the formation mechanism of large nitric acid particles still remains uncertain. Thus, more laboratory and field studies are needed to better test which of the above mechanisms is most likely to dominate the rate of large nitric acid particle production in the polar stratosphere.

Remote

Lidar observations are useful for constraining PSC particle sizes. Depolarization measurements by lidar can also provide strong evidence for the presence of solid PSC particles. As indicated above, only large solid PSC particles can cause denitrification, and lidar observations provide valuable information on the horizontal and vertical extents of solid PSC particle distributions in the stratosphere.

Lidar studies provide new estimates of the occurrence of solid PSC particles, which is an important parameter for constraining microphysical models. Toon et al. (2000) have reanalyzed lidar observations from all DC-8 flights during the 1989/1990 Arctic winter and find that large solid PSC particles are more common in the Arctic stratosphere than the smaller liquid PSC particles (Type Ib). Three years of lidar observations from Ny Ålesund (79°N) (Biele et al., 2001) have shown that at least 50% of PSCs contained solid particles, with some of these clouds being of Type Ib, normally attributed to pure liquid clouds. Several studies have also derived new estimates of solid particle number concentrations. Gobbi et al. (1998) have analyzed many Antarctic lidar vertical profiles and estimate that solid PSC particles constituted less than 1% of the available condensation nuclei (therefore, typically less than 0.1 particles cm⁻³). Toon et al. (2000) derived similar values for the 1989/1990 winter Arctic stratosphere. Biele et al. (2001) and Tsias et al. (1999) estimate that many depolarizing clouds must typically contain fewer than about 0.005-0.01 cm⁻³ solid particles and that such particles can rarely grow to their equilibrium sizes. In summary, all the lidar studies discussed here suggest that large solid particles that can cause denitrification are widely distributed in both hemispheres.

Some clouds observed by lidar are consistent with high number densities of small solid nitric acid particles (typically >1 cm⁻³ and <2 µm in diameter) (Tsias et al., 1999; Toon et al., 2000; Hu et al., 2002). These clouds are frequently associated with the outflow from mountain

waves (e.g., Hu et al., 2002). Efficient NAT nucleation on numerous small ice particles formed in wave clouds could be an important mechanism for generating such a dense population of small solid PSC particles (Carslaw et al., 1998a, 1999; Wirth et al., 1999; Larsen et al., 2002). Some studies suggest that small solid PSC particles generated by wave clouds may also play a central role in producing large nitric acid particles that lead to denitrification (see the previous section on in situ observations).

Satellite instruments are also capable of observing PSC particles. Stratospheric Aerosol Measurement (SAM) II (McCormick et al., 1981), Cryogenic Limb Array Etalon Spectrometer (CLAES) (Mergenthaler et al., 1997), Polar Ozone and Aerosol Measurement (POAM) (Steele et al., 1999; Fromm et al., 1997, 1999; Bevilacqua et al., 2002), and Improved Limb Atmospheric Sounder (ILAS) (Kondo et al., 2000; Irie et al., 2001) instruments have taken many aerosol extinction vertical profiles of PSCs in the Arctic and Antarctic stratosphere over the last two decades (see Appendix 3A for satellite data descriptions). Several recent studies have paired up aerosol extinction measurements with water and nitric acid gas-phase measurements onboard the same (Tabazadeh et al., 2000; Stone et al., 2001; Nedoluha et al., 2000; Dessler et al., 1999) or different satellites (Santee et al., 2002) to determine the scale and magnitude of denitrification and dehydration in both polar regions (see Sections 3.2.2.3 and 3.2.2.4).

3.2.2.2 PARTICLE COMPOSITION

Inferred Particle Compositions

PSCs that exist at temperatures greater than the ice frost point have long been accepted to be composed of nitric acid and water, either in the form of a nitric acid hydrate or as supercooled solution droplets of nitric acid, sulfuric acid, and water (supercooled ternary solution, STS). Numerous attempts have been made to infer the composition of nitric-acid-containing PSCs by comparing particle volumes (either measured directly or derived from satellite extinction) and/or gas-phase nitric acid concentrations with equilibrium model calculations assuming various particle compositions (WMO, 1999; Hopfner et al., 1998; Steele et al., 1999; Santee et al., 2002; Saitoh et al., 2002; Strawa et al., 2002). These studies have provided strong support for the existence of STS droplets, but confirmation of the presence of different nitric acid hydrates has been more difficult to establish (WMO, 1999). This difficulty may be due to the fact that nitric acid hydrate particles, which can be considerably larger than STS droplets, are often not in thermodynamic equilibrium (e.g., Tsias et al., 1999; Biele et al., 2001).

Direct Determinations of Particle Composition

New in situ observations using an aerosol mass spectrometer have measured PSC particle composition (Schreiner et al., 1999, 2002; Voigt et al., 2000a, b; Larsen et al., 2000, 2002). The mole ratio of nitric acid to water observed using an aerosol mass spectrometer in a mountain-induced gravity wave cloud over Scandinavia (Voigt et al., 2000b) shows close agreement with an STS droplet composition predicted by a model. The same aerosol mass spectrometer flown in January 2000 detected NAT particles, identified by a H_2O to HNO_3 mole ratio of 3:1 and confirmed to be solid particles from co-located backscatter measurements (Voigt et al., 2000a; Larsen et al., 2000); see Figure 3-16. These direct observations of particle composition in PSCs are important because they confirm that the thermodynamic models used to predict liquid aerosol compositions (e.g., Carslaw et al., 1997a) are reliable, and that NAT, long predicted to exist in the stratosphere (Hanson and Mauersberger, 1988), actually does exist there.

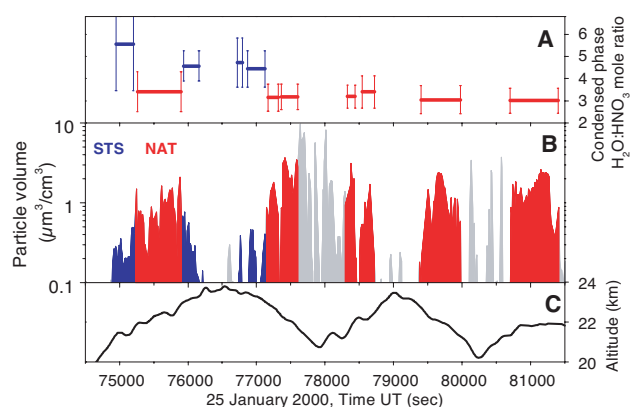


Figure 3-16. In situ observations of PSCs using an aerosol mass spectrometer, showing particles with a $\text{HNO}_3/\text{H}_2\text{O}$ ratio consistent with supercooled $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ droplets. Panel A displays the measured molar ratios, panel B shows particle volume, and panel C shows the balloon altitude. The red color indicates the presence of nitric acid trihydrates (NAT), blue indicates supercooled ternary solution (STS) particles, and gray represents particles with insufficient information to derive molar ratios. Adapted from Voigt et al. (2000a).

3.2.2.3 DENITRIFICATION

Observations of Denitrification

In situ Arctic observations from the ER-2 aircraft in January to March 2000 detected the most severe and extensive denitrification observed in the Arctic stratosphere (Popp et al., 2001); see Figure 3-17. Average removal of as much as 60% of total reactive nitrogen (NO_y) was observed throughout the core of the vortex near 20 km (Figure 3-17). Waibel et al. (1999) have also analyzed balloonborne observations of denitrification in 1995. These observations reveal an approximate 50% reduction in NO_y at 20 km. Using tracer measurements to eliminate deficits due to mixing (see Section 3.3.1.2), Waibel et al. (1999) concluded that at least 82% of the observed NO_y loss at 20 km was due to denitrification. Sugita et al. (1998) and Hints et al. (1998) have also observed similar levels of Arctic denitrification near 20 km, in 1995 and 1996 winters, respectively. Together, these observations show that some Arctic air parcels were

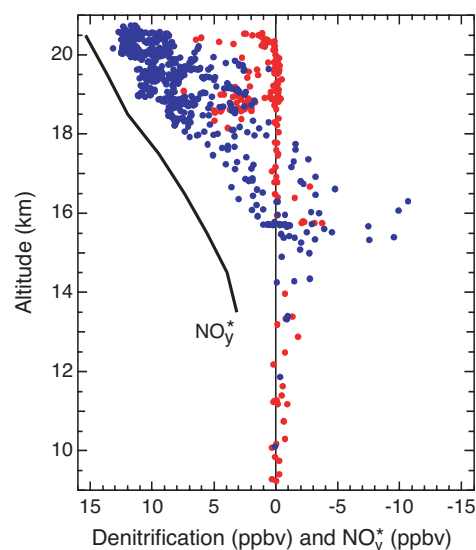


Figure 3-17. Vertical profiles of redistributed NO_y in the 1999-2000 Arctic vortex. Positive values of denitrification represent NO_y removal. Blue and red symbols represent measurements made at greater than 70°N and less than 70°N equivalent latitude, respectively. The solid black line representing NO_y^* (the maximum available NO_y at a given altitude) was determined from altitude-bin-averaged N_2O values for measurements made throughout the winter at equivalent latitudes greater than 70°N . Maximum ER-2 flight altitudes of 20 to 12 km represent a potential temperature of approximately 460 to 475 K. Adapted from Popp et al. (2001).

POLAR OZONE

severely denitrified (>50%) near 20 km in several cold winters.

Figure 3-18 shows the time evolution of HNO_3 in both hemispheres for a number of winters on three potential temperature surfaces, based on Microwave Limb Sounder (MLS) observations (see Appendix 3A for MLS data description). Large irreversible depletions (>80%) in HNO_3 vapor amounts occur only in the SH (Santee et al., 1999), but much smaller irreversible depletions (~20%) have also been observed in cold Arctic air parcels (Dessler et al., 1999; Santee et al., 2000, 2002). However, large permanent depletions in HNO_3 concentrations (>40%) have been observed in cold Arctic winters by satellite instruments with finer vertical resolution than MLS (~6-km vertical resolution), such as the ILAS instrument, which has a 1- to 2-km vertical resolution (Kondo et al., 2000; Irie et al., 2002; see also Appendix 3A for satellite data descriptions). Thus, extensive denitrification does occur in both hemispheres based on both in situ and remote sensing observations. However, severe denitrification in the Arctic must be narrow in depth because if the denitrified layers were deeper than 6 km, then MLS would have been able to detect this irreversible loss in gas-phase nitric acid (Tabazadeh et al., 2001). Individual nitric acid vertical profiles from the ILAS instrument (Kondo et al., 2000; Irie et al., 2002) during the winter of 1996/1997 further show that the vertical range of denitrification in the Arctic is typically ~2 to 3 km deep (from about 18 to 21 km), with immediate nitrification occurring below this altitude range.

Tabazadeh et al. (2000) have shown that denitrification over a broad altitude range (>10 km in depth) occurs rapidly in the Antarctic when the duration of an average PSC event is about 2 weeks (defined to be the time spent by an isentropic air parcel below 195 K at 450-K potential temperature). Tabazadeh et al. (2000) suggest that deep extensive denitrification currently occurs only in the Antarctic because average Arctic PSC events last nearly half as long as those in the Antarctic. Antarctic denitrification rapidly occurs during the mid- to late-June time period (see Figure 3-18). The short persistence of PSC events in the NH limits the extent of severe denitrification to only a few kilometers, as observed in many past cold Arctic winters (Popp et al., 2001; Sugita et al., 1998; Hints et al., 1998; Kondo et al., 2000; Irie et al., 2001, 2002). In Section 3.3.4, the effect of denitrification depth on ozone loss is assessed for both hemispheres.

Model Simulations of Denitrification

Improvements in our understanding of PSC particle sizes and number concentrations (Section 3.2.2.1)

now allow for more sophisticated treatments of denitrification in models. Current 3-D chemical transport models include highly simplified representations of denitrification that are now recognized to be incorrect. These models assume that nitric acid is carried downward on sedimenting ice particles wherever temperatures are lower than the ice frost point (Chipperfield et al., 1993; Considine et al., 2000). Removal of nitric acid on sedimenting ice particles is clearly not operating in the Arctic because models, using this assumption, have been unable to produce any denitrification by this mechanism (Chipperfield and Pyle, 1998; Davies et al., 2002).

Drdla et al. (2002) have used a coupled microphysical-chemistry trajectory model to show that synoptic-scale ice clouds could not have caused the massive denitrification observed during the 1999/2000 winter. They concluded that the large nitric acid particles that caused denitrification were not nucleated on ice particles.

Jensen et al. (2002) have used a one-dimensional version of the Community Aerosol and Radiation Model for Atmospheres (CARMA) microphysics cloud model to show that solid nitric acid number densities in the range of 10^{-2} to 10^{-3} cm^{-3} are the most efficient in causing rapid denitrification. The CARMA cloud model has also been used to show (see Figure 4 in Tabazadeh et al., 2001) that the vertical range over which denitrification occurs is normally quite deep in the Antarctic (>10 km) but limited in the Arctic, in general agreement with many observations of denitrification in both hemispheres (i.e., Santee et al., 1999; Popp et al., 2001; Sugita et al., 1998; Hints et al., 1998; Kondo et al., 2000; Irie et al., 2001, 2002). The Arctic denitrified layers are shallow in depth mainly because the stratosphere, even in cold winters, is too warm below about 17 km for nitric acid hydrate particles to exist.

Waibel et al. (1999) simulated denitrification by assuming that ice acted as the nucleus for NAT formation. Most of the denitrification calculated in the model was caused primarily by sedimentation of NAT particles, with a fixed number concentration of $5 \times 10^{-3} \text{ cm}^{-3}$, released upon ice evaporation. In these 3-D model simulations, in which a simplified treatment of horizontal transport was used, NAT particles were assumed to be in equilibrium with gas-phase nitric acid.

Davies et al. (2002) have included a parameterization in a 3-D CTM of NAT particle sedimentation assuming sizes and number concentrations representative of those observed by Fahey et al. (2001). NAT particles were assumed to be in equilibrium with gas-phase nitric acid in these simulations. The calculated denitrification magnitude was similar to that observed in winter 1999/2000. In contrast, the modeled denitrification was significantly less than observed when NAT was allowed

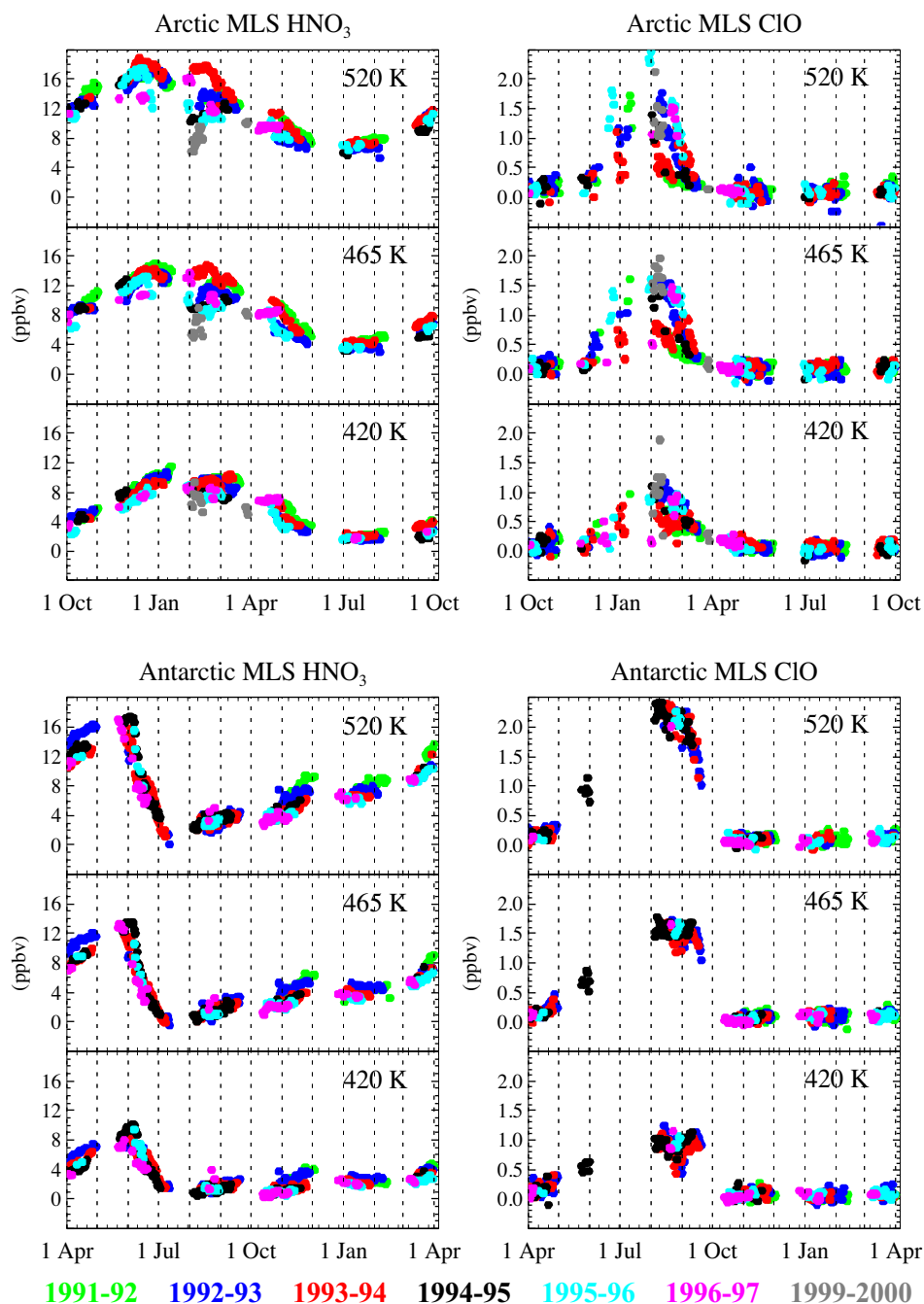


Figure 3-18. Time series of Upper Atmosphere Research Satellite (UARS) MLS HNO_3 (left, ppbv) and ClO (right, ppbv) at 520 K (~ 21 km), 465 K (~ 19 km), and 420 K (~ 17 km) for both the Northern (top) and Southern (bottom) Hemispheres. Values shown are averages of data points with solar zenith angle $< 88^\circ$ (daylight) in the 70° - 80° equivalent latitude bin. These values represent the best estimates of the abundances at these particular potential temperature surfaces based on the MLS measurements; it should be borne in mind, however, that correlations between these levels may have been introduced either during the retrieval process (since the retrieval pressure grid is finer than the width of the averaging kernels) or through interpolation of the retrieved data onto potential temperature surfaces, and thus the true number of completely independent pieces of information is likely to be less than the number of surfaces shown here. For the daily averages in this equivalent latitude bin the precision is roughly 0.15 ppbv for HNO_3 and 0.05 ppbv for ClO . Different years are represented by different colors as indicated in the legend. The x-axis tick mark increment is 10 days; dotted vertical lines demark calendar months. The 1991 to 1997 and 2000 data are adapted from Santee et al. (1999) and (2000), respectively.

POLAR OZONE

to nucleate only on ice particles. This result is consistent with previous simulations (Carslaw et al., 2002; Drdla et al., 2002) showing that the observed large nitric acid particles could not have nucleated on synoptic-scale ice clouds during the winter of 1999/2000.

Mann et al. (2002) have developed a 3-D model of denitrification that takes into account the time dependence of both growth and sedimentation of large NAT particles. In these simulations, NAT particle growth times are on the order of several days, and therefore the magnitude of denitrification strongly depends on individual particle growth cycles. In fact, the extent of modeled denitrification is strongly amplified when areas of low temperature are stable and concentric with the vortex, allowing for individual particles to persist for a longer time and to grow to larger sizes. Thus the area of low temperatures by itself is perhaps not the best indicator for predicting the severity of denitrification in the Arctic.

In summary, new model calculations show that the long-accepted mechanism of nitric acid removal on sedimenting ice particles cannot account for observed levels of denitrification. Denitrification is most likely caused by sedimentation of large nitric acid particles. Various models are able to reproduce, in broad terms, the observed levels of denitrification by assuming sedimentation of large nitric acid particles. In addition, recent model calculations show that Arctic denitrified layers are normally shallow in depth because the stratosphere is too warm below about 17 km to allow for large particles to carry much nitric acid beyond this altitude. Establishing the formation mechanism of the large nitric acid particles will be important for the development of realistic models of denitrification. The sensitivity of ozone loss to denitrification is discussed in Section 3.3.4.

3.2.2.4 DEHYDRATION

Figure 3-19 shows the time evolution of water vapor in the SH during 1998 (Nedoluha et al., 2000). Severe dehydration is observed over a 10-km altitude range. Similar results are also obtained from analysis of MLS water vapor data during the Antarctic winter of 1992 (Stone et al., 2001; see also Appendix 3A for MLS data description). In the Arctic, removal of ~1 ppm of water vapor over a 1- to 2-km altitude range has been observed by the ILAS instrument (Pan et al., 2002). The lack of extensive and deep dehydration in the Arctic is also supported by in situ observations (Vömel et al., 1997; Hintsa et al., 1998; Herman et al., 2002). Overall, the Arctic climate, even in cold years, is too warm to allow for formation of widespread persistent ice clouds that lead to dehydration. The sensitivity of ozone loss to dehydration is discussed in Section 3.3.4.

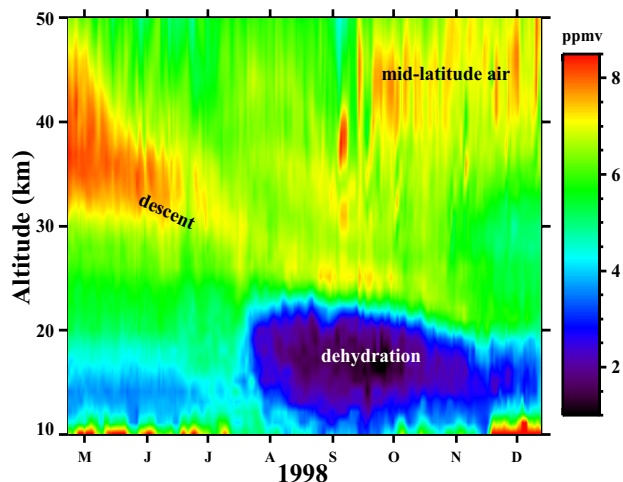
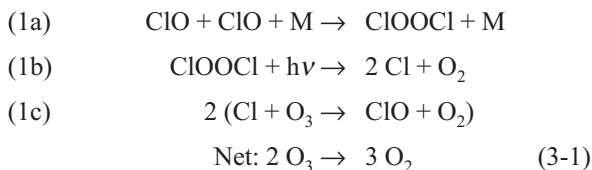


Figure 3-19. The water vapor mixing ratio as measured by POAM in the Southern Hemisphere from 27 April 1998 to 12 December 1998. Profiles are obtained from daily averages of the measurements from POAM, which generally provides 14 measurements per day. Measurements from both inside and outside of the vortex are included. The POAM measurement latitude biannually cycles from 88°S at the equinoxes (March 21 and September 21) to 62°S at the solstices (June 21 and December 21). Adapted from Nedoluha et al. (2000).

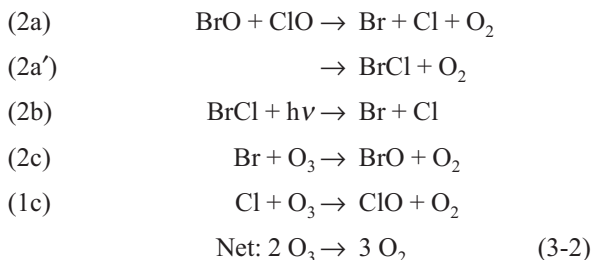
3.2.3 Polar Ozone Chemistry

The chemical loss of polar ozone during winter and spring occurs primarily by two gas-phase catalytic cycles that involve halogen oxide radicals:

Cycle 1



Cycle 2



Abundances of chlorine monoxide (ClO) in the polar vortex are greatly elevated by reactions of inactive chlorine reservoir species on various types of polar stratospheric clouds (PSCs) that form when temperatures drop below about 195 K (see Section 3.2.2). Abundances of bromine monoxide (BrO) determine the removal rate by Cycle 2, which contributes about 50% to the total chemical loss rate of polar ozone (Chipperfield and Pyle, 1998). In contrast to ClO, the abundance of BrO is not strongly affected by reactions involving PSCs because less than half of the available inorganic bromine budget is sequestered in reservoirs such as bromine nitrate (BrNO₃) and hydrogen bromide (HBr) prior to processing.

Since the previous Assessment, new studies have addressed the rates of ozone destruction by Cycles 1 and 2 in an effort to reconcile apparent discrepancies between measured and modeled chemical loss rates of Arctic ozone (see Section 3.3). The chlorine and bromine cycles are discussed separately below in Sections 3.2.3.1 and 3.2.3.2. Model calculations reveal that, at present and for the foreseeable future, winter polar ozone loss will be dominated by reactions involving ClO and BrO (e.g., Chipperfield and Pyle, 1998; Shindell et al., 1998b).

3.2.3.1 CHLORINE

A number of modeling studies have had difficulty accounting for observed chemical loss rates of Arctic ozone, particularly during midwinter when insolation is weakest (see Section 3.3). As a consequence, attention has focused on reducing uncertainties in key rate parameters, in particular those for formation and photolysis of the chlorine oxide dimer (ClOOC1), i.e., parameters k_{1a} (first-order reaction-rate constant) and J_{1b} (photolysis rate). These reactions determine the rate of ozone loss by Cycle 1, such that uncertainties in these kinetic parameters couple directly into the uncertainties in modeled ozone loss rates. Results of these studies are summarized in the section below on chlorine photochemistry.

The loss of polar ozone via Cycles 1 and 2 is determined by the temporal evolution of ClO. Numerous studies have examined the seasonal variations of inorganic chlorine partitioning, including production of high abundances of reactive chlorine (ClO_x, defined as [ClO] + 2 [ClOOC1]) by PSCs (“activation”); maintenance of high abundances of ClO_x throughout the winter; and deactivation of ClO_x back to hydrogen chloride (HCl) and chlorine nitrate (ClONO₂) (“recovery”). These results are summarized in the section below on chlorine seasonal evolution.

Simultaneous measurements of most of the major inorganic and organic chlorine species provide the ability to examine the overall chlorine budget for the Arctic and

Antarctic stratospheres during periods of rapid ozone loss. These investigations can assess the possible role of species not considered in standard models, such as higher oxides of chlorine. The results of these studies are summarized below (the section on the chlorine budget).

Chlorine Photochemistry

Our understanding of the key kinetic parameters governing ozone loss by Cycle 1 (k_{1a} and J_{1b}) has improved through new laboratory studies and atmospheric observations. Bloss et al. (2001) found k_{1a} to be up to 25% larger than the value recommended in the Jet Propulsion Laboratory (JPL) *Publication 00-3* compendium (Sander et al., 2000; hereafter referred to as *JPL 00-3* in this chapter) at temperatures below 210 K. The impact of this increase on calculated ozone loss rates depends on the manner in which the models treat ClO. In the case of models constrained by observed abundances of ClO, the rate of ozone loss due to Cycle 1 is roughly proportional to the increase in k_{1a} . For models that allow ClO and ClOOC1 to repartition within the constraint of constant active chlorine, the total loss rate is largely independent of this change in k_{1a} , because ClO abundances respond in the opposite sense to the change in the rate constant (Figure 3-20). Thus, the maximum effect of an increase in k_{1a} based on the results of Bloss et al. (2001) is to increase total ozone loss rates by no more than 25% under cold polar conditions. Such an increase is insufficient to resolve fully the factor-of-2 discrepancies between modeled and measured Arctic ozone loss rates during January found in several recent studies (e.g., Woyke et al., 1999; Becker et al., 2000).

The recommended absorption cross section for ClOOC1 has not changed since the previous Assessment. However, there have been several important laboratory and theoretical studies (Moore et al., 1999; Kaledin and Morokuma, 2000; Toniolo et al., 2000) of the product yields from photolysis of ClOOC1 at wavelengths longer than 300 nm, the spectral region that contributes most to the overall photolysis rate of ClOOC1. These new results reduce a significant uncertainty in our knowledge of ozone loss rates. Only the production of chlorine atoms and chloroperoxy radical (ClOO), leading to $2\text{Cl} + \text{O}_2$ upon the rapid thermal decomposition of ClOO at polar temperatures, results in catalytic loss of ozone; production of ClO + ClO from ClOOC1 photolysis leads to a null cycle that has no effect on ozone. Moore et al. (1999) recently reported that two chlorine atoms and molecular oxygen (O₂) are the primary products of photolysis of ClOOC1 at 248 nm and at 308 nm. The ClOO product rapidly decomposes to atomic chlorine (Cl) and O₂ due to excess vibrational energy. This conclusion is further supported by

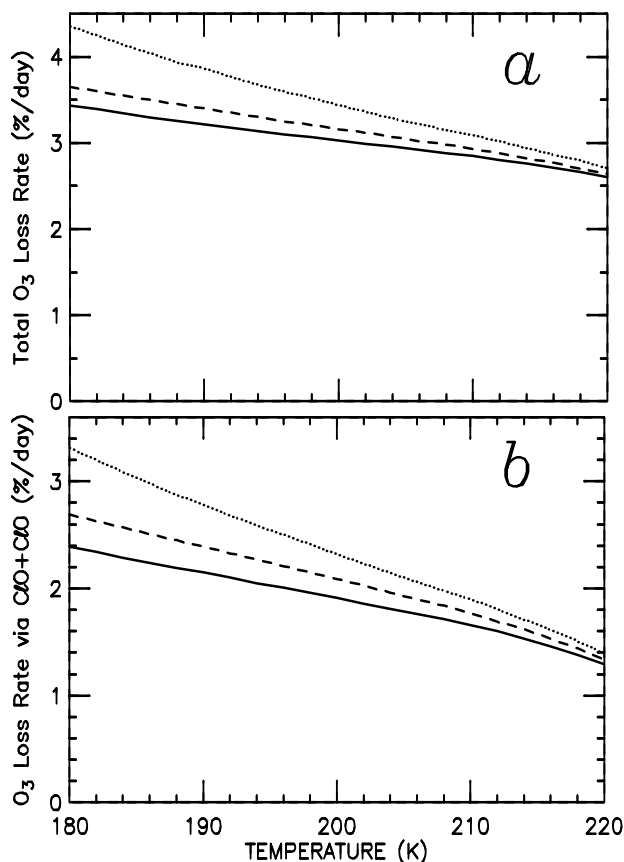


Figure 3-20. (a) Calculations of 24-hour average total chemical ozone loss rate for an air mass at 70°S, 50 hPa, as a function of temperature for mid-September conditions (e.g., ClO + 2·ClOOCl = 2 ppb; BrO + BrCl = 10 ppt; O₃ = 2 ppm; declination = 5°S) assuming the following: case 1, JPL 00-3 (Sander et al., 2000) kinetics (solid line); case 2, the Bloss et al. (2001) value for k_{1a} and the noontime concentration of ClO fixed at the same value used in case 1 (dotted line); and case 3, the Bloss et al. value for k_{1a} and the noontime concentration of ClO + 2·ClOOCl fixed at the same value used in case 1 (dashed line). (b) Same as (a), except chemical loss rates due to just the ClO + ClO cycle are shown. Case 2 approximates the effect of the Bloss et al. value for k_{1a} on a model calculation constrained by measured ClO. Case 3 approximates the effect of Bloss et al. k_{1a} within a free-running CTM or GCM, where ClO and ClOOCl are allowed to equilibrate. Adapted from Bloss et al. (2001).

electronic structure calculations (Kaledin and Morokuma, 2000; Toniolo et al., 2000). These studies reduce the uncertainties of the product yield of ClOOCl photolysis

at key wavelengths for chemical loss of polar ozone relative to earlier laboratory investigations.

Several new sets of atmospheric observations provide quantitative tests of our understanding of k_{1a} and J_{1b} . Recent balloonborne in situ observations of the rate of decay of ClO immediately after sunset in the Arctic vortex (Vömel et al., 2001) are explained better by the larger value for k_{1a} at temperatures near 190 K than by the value recommended by JPL 00-3 (Figure 3-21). An analysis of data obtained during five winters (1996 to 2000) (Solomon et al., 2002) found good agreement between measurements of column ClO and model calculations employing the value of J_{1b} / k_{1a} from JPL 00-3, in contrast to an earlier report, using only data for 1996, that indicated the ratio J_{1b} / k_{1a} might be 50% too low (Solomon et al., 2000). A similar conclusion had been reached in a study of earlier ground-based ClO observations over Antarctica (Shindell and de Zafra, 1995).

The chemical loss rate of ozone, particularly during early winter, is also sensitive to the dependence of J_{1b} on solar zenith angle (SZA). Avallone and Toohey (2001) concluded, based on an examination of in situ observations of ClO obtained at SZAs between 79° and 90°, that the photolysis rate of ClOOCl varied with SZA in a manner generally consistent with recommended absorption cross sections for ClOOCl. An analysis of the data they presented using the larger Bloss et al. (2001) value for k_{1a} yields values for J_{1b} that agree well with photolysis rates using JPL 00-3 cross sections. The significantly smaller value for J_{1b} based on absorption cross sections of Huder and DeMore (1995) appears to be inconsistent with these results and those of Shindell and de Zafra (1995), Raffalski et al. (1998), Stachnik et al. (1999), and Solomon et al. (2002). Furthermore, there is no evidence from any of these studies that supports the notion that ClOOCl may photolyze at an appreciable rate in optically thin spectral regions (i.e., >420 nm). Such a process could enhance ozone loss rates at high SZAs and account for some of the discrepancy between measured and modeled ozone loss rates in midwinter (Rex et al., 2002b; see also Section 3.3).

Chlorine Seasonal Evolution

Another element critical in accounting for ozone loss is the temporal evolution of the ozone-destroying halogen radicals. Mixing ratios of ClO remain elevated (~1 to 2 parts per billion by volume (ppbv)) from May/June until September (Figure 3-18) for all years over Antarctica for which observations are available (WMO, 1995; WMO, 1999; Santee et al., 2000; Wagner et al., 2001, 2002; Solomon et al., 2002), in the region where temperatures between 14 and 24 km remain very low

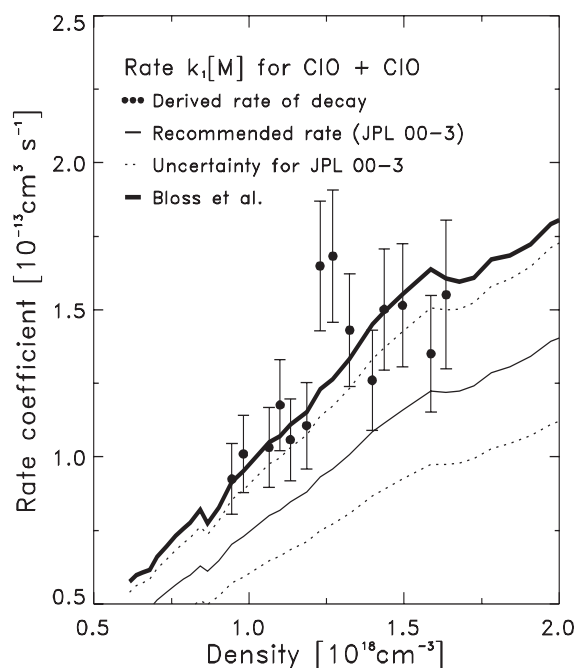


Figure 3-21. Derived rate of decay of ClO (points with 1σ error bars) from atmospheric observations of ClO obtained in the Arctic vortex during SOLVE-THESEO 2000 compared with the product of $M \cdot k_{1a}$ from the JPL 00-3 (Sander et al., 2000) recommendation (thin solid line) and from the laboratory study of Bloss et al. (2001) (thick solid line). Uncertainties for the JPL 00-3 rate are given by the dashed lines. Uncertainties for the laboratory measurement of Bloss et al. (2001) are not shown for clarity, but they are approximately the same size as the error bars for the results based on the ClO observations. Adapted from Vömel et al. (2001).

(below PSC thresholds) for several months (Figure 3-13, bottom). In addition, the southern polar vortex remains intact well into the spring season. Under these conditions, the total amount of ozone destroyed over Antarctica is nearly complete for an 8- to 10-km-thick altitude layer, a condition that is relatively insensitive to the chemical loss rate at contemporary abundances of inorganic chlorine (WMO, 1999).

Three-dimensional CTMs are able to simulate the seasonal evolution of ClO in the Antarctic polar vortex remarkably well (Ricaud et al., 1998; Solomon et al., 2000, 2002). Figure 3-22 compares ground-based column measurements of ClO above Scott Base, Antarctica (77.8°S), with calculations from the SLIMCAT model. Comparisons for the ClO mixing ratio at 480 K are also shown. During mid- to late winter, the rise of ClO is determined primarily by increasing solar illumination at

midday. The good agreement between theory and observations of column ClO during this time period suggests that the altitude range over which chlorine is activated is well reproduced by the model. During early spring, the short-term fluctuations in ClO are related to movement of the vortex over Scott Base, and the longer-term decline in ClO is the result of recovery into the reservoirs HCl (the primary sink for ClO_x in the denitrified Antarctic vortex)

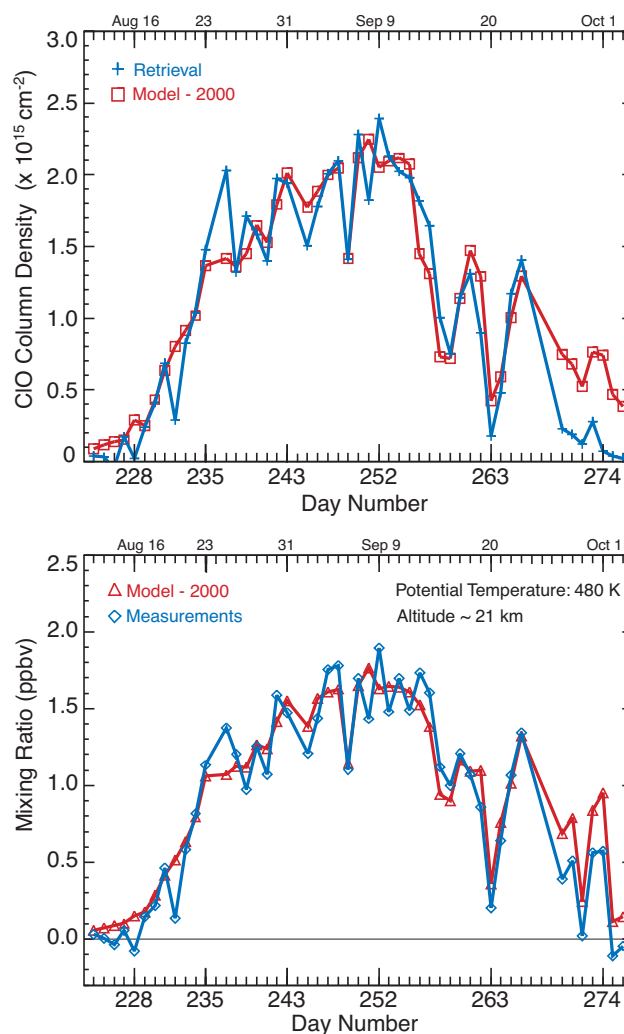


Figure 3-22. Top panel: Retrieved ClO column density (day-night difference) for 11 August through 4 October 2000 over Scott Base, Antarctica (78°S) (blue line), and the same quantity calculated using the SLIMCAT model assuming JPL 97-4 (DeMore et al., 1997) kinetics (red line). Bottom panel: Same as top panel, except for ClO mixing ratio (day-night difference) at 480 K. Adapted from Solomon et al. (2002).

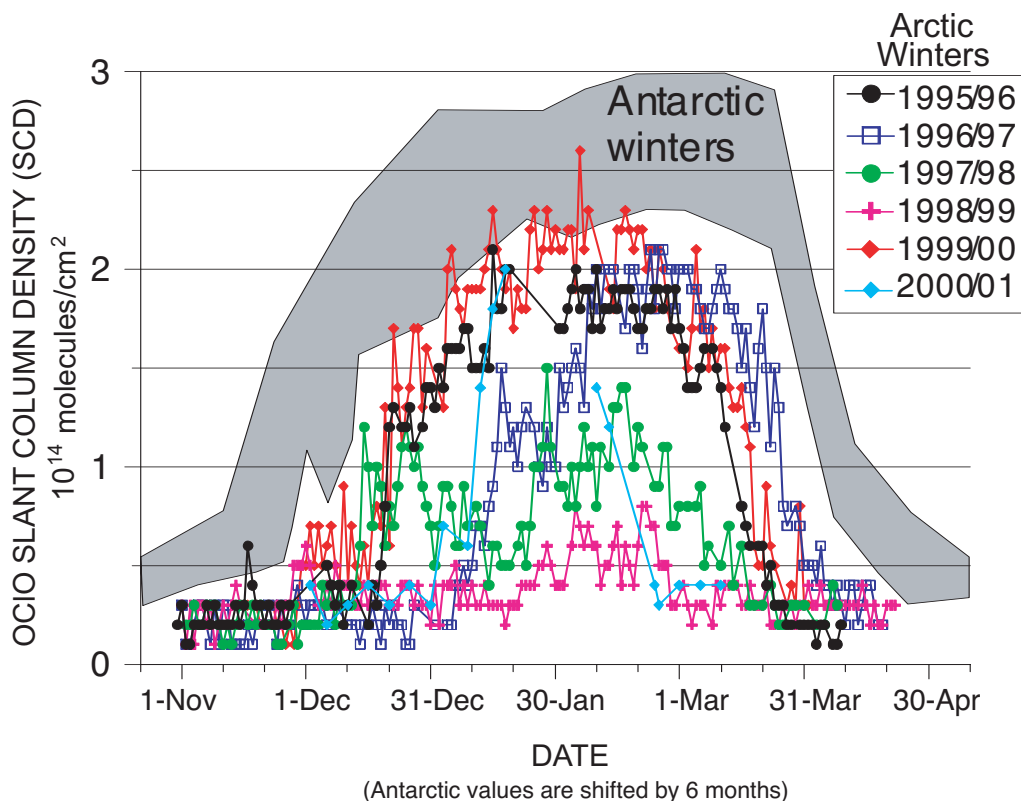


Figure 3-23. Daily maximum slant column density (SCD) of OCIO, at SZA of 90°, measured by GOME for a number of Arctic and Antarctic winters. Data for individual Arctic winters are shown, as indicated, whereas the range of data for Antarctic winters is shown by the shaded region. The time associated with the Antarctic measurements has been shifted by 6 months to facilitate comparison with Arctic observations at comparable seasons. The air mass factor (ratio of SCD to vertical column density) depends on the height profile of OCIO, which is not known a priori. Consequently, the SCD is the preferred choice for comparison of Arctic and Antarctic data. Adapted from Wagner et al. (2001, 2002).

and ClNO_3 (Solomon et al., 2002). As a result of widespread suppression of gas-phase HNO_3 in SLIMCAT, high abundances of ClO are sustained throughout the early spring season (September) until ozone is nearly completely removed. In October, HCl is observed to reappear much faster than ClNO_3 in the core of the vortex due to the shift in partitioning of Cl/ClO and nitric oxide/nitrogen dioxide (NO/NO_2) to favor Cl and NO driven by exceedingly low ozone, while ClO recovers mainly to ClNO_3 in the edge region of the Antarctic vortex (e.g., Douglass et al., 1995; Ricaud et al., 1998). Because most models simulate these features reasonably well, they are able to account for Antarctic ozone loss in a quantitative manner.

The situation for the Arctic winter is quite different, because chemical ozone loss depends more critically upon the details of chlorine activation and deactivation, and the timing of the breakup of the northern polar vortex. During cold Arctic winters, high levels of ClO are observed throughout the polar vortex (Raffalski et al., 1998;

Stachnik et al., 1999; Klein et al., 2000; Santee et al., 2000). Considerably more year-to-year variability is seen in Arctic measurements of ClO compared with Antarctic data, and peak values of Arctic ClO for cold winters are somewhat lower than observed in the Antarctic (Figure 3-18). Recent GOME measurements of chlorine dioxide (OCIO) (Figure 3-23), which indicate much greater year-to-year variability in active chlorine for the Arctic as well as considerably higher levels of active chlorine for the Antarctic (Wagner et al., 2001, 2002), provide a picture consistent with the MLS observations of ClO. The GOME observations of Antarctic OCIO are also consistent with earlier ground-based observations of OCIO (Miller et al., 1999; see also Appendix 3A for satellite data descriptions).

The MLS and GOME measurements show that elevated levels of ClO_x in the Arctic, even for cold years, decline rapidly in early spring, in contrast to the Antarctic, where high ClO_x persists well into spring (Figures 3-18 and 3-23). Consequently, the total quantity of ozone destroyed

in the Arctic vortex depends strongly on the rate of chlorine deactivation, which in turn is related to the extent of denitrification (e.g., Rex et al., 1997; Waibel et al., 1999; Tabazadeh et al., 2000) and the efficiency of chlorine reactivation (e.g., Solomon, 1999; Hanisco et al., 2002; Drdla and Schoeberl, 2002). Abundances of ClO_x over the Arctic decrease rapidly when temperatures increase above ~ 200 K, because of photochemical release of NO_x from nitric acid that remains in excess of reactive chlorine throughout the winter. During this recovery period, observations have shown that ClNO_3 is the primary inorganic chlorine species, representing $>80\%$ of the available chlorine (Chapter 3 of WMO, 1995). It has long been assumed that chlorine can be readily reactivated on PSCs during this recovery period (provided temperature drops below ~ 195 to 200 K), leading to significant additional ozone loss. However, a recent study based on analyses of in situ observations of hydroxyl radical (OH) and hydroperoxyl radical (HO_2) (Hanisco et al., 2002) concludes that key heterogeneous reactions that reactivate chlorine proceed more slowly than currently recommended rates. The consequences of this finding have yet to be explored in photochemical model studies of Arctic ozone loss.

Most important, however, 3-D chemistry and transport models (Ricaud et al., 1998; Massie et al., 2000; van den Broek et al., 2000) as well as trajectory simulations (Woyke et al., 1999; Danilin et al., 2000) are able to simulate well the high levels of ClO observed in the Arctic, indicating that chlorine activation schemes used in photochemical models are relatively accurate in describing large-scale features of chlorine activation. Recent model simulations also suggest that the rate and extent of halogen activation in the polar vortex are not as sensitive to PSC composition as previously thought (Carslaw et al., 1997b; Becker et al., 1998; Woyke et al., 1999; Danilin et al., 2000). This lack of sensitivity arises because most heterogeneous halogen activation rates are much faster at low temperatures than deactivation rates of ClO_x for air parcels outside of PSCs (e.g., Solomon, 1999).

Although models simulate the seasonal evolution of ClO in the Arctic reasonably well for cold winters, they have some difficulty for warm winters, where minimum temperatures are close to the threshold for formation of PSCs (e.g., Klein et al., 2000). For the winter of 1998/1999, ground-based observations of ClO from Ny Ålesund, Spitzbergen (78.9°N), revealed little or no enhancements above background levels, whereas the SLIMCAT model predicted ClO mixing ratios as high as 1.0 ppbv. This discrepancy has been attributed to a small cold bias (~ 1 K) in the UKMO temperatures input to the SLIMCAT model (Klein et al., 2000; Knudsen et al., 2002), although it is also possible that the PSC nucleation scheme in SLIMCAT is

unrealistic at temperatures near NAT thresholds. In either case, such a problem highlights the extraordinary sensitivity of Arctic ClO to temperatures and microphysics schemes for winters where the minimum temperatures are very close to the threshold for formation of PSCs.

Chlorine Budget

Ideally, an assessment of the chlorine budget should be based on simultaneous measurements of the primary inorganic (e.g., HCl , ClNO_3 , ClO , ClOOCl) and organic (e.g., chlorofluorocarbons and other chlorine-containing halocarbons) chlorine species. A significant number of studies, all of which lack observations of ClOOCl , have indicated good agreement between the inorganic and organic chlorine budget for the lower polar stratosphere (e.g., von Clarmann et al., 1995; Engel et al., 1997; Mickley et al., 1997; Ricaud et al., 1998; Michelsen et al., 1999; Pierson et al., 1999). For example, balloon-borne microwave and whole-air sampler measurements of $[\text{HCl}] + [\text{ClO}] + 2[\text{ClOOCl}^*]$ versus N_2O for air in the core of the Arctic vortex on 27 January 1995 (Stachnik et al., 1999), made under conditions of highly elevated ClO , agree well with estimates of inorganic chlorine based on the measured decomposition of organic halocarbons. The above-mentioned studies relied on calculated concentrations of ClOOCl , termed ClOOCl^* , assuming a steady-state relation with measured ClO . Their validity is supported by the good agreement between laboratory rates for k_{1a} and J_{1b} (needed to calculate ClOOCl^*) and values inferred for these kinetic parameters from the time rate of change of ClO in the atmosphere (Avallone and Toohey, 2001; Vömel et al., 2001).

Also, these findings are consistent with reasonably good agreement (differences of about $\pm 15\%$) between the disappearance of organic chlorine (CCl_y) species and the appearance of inorganic chlorine (Cl_y) species observed for the summer polar stratosphere (Section 3.2.4.3), a region of the atmosphere for which the contribution to Cl_y is dominated by HCl and ClNO_3 .

3.2.3.2 BROMINE

Cycle 2 ($\text{BrO} + \text{ClO}$; see beginning of Section 3.2.3) makes important contributions to polar ozone loss. As shown below in the section on bromine monoxide abundances, there is now reasonably good agreement between measurements of BrO obtained by various techniques. This is a significant advance in our understanding because important differences had been noted in the previous Assessment (WMO, 1999). This convergence of measurements allows for fairly accurate assessment of the contribution of bromine to chemical loss of polar ozone.

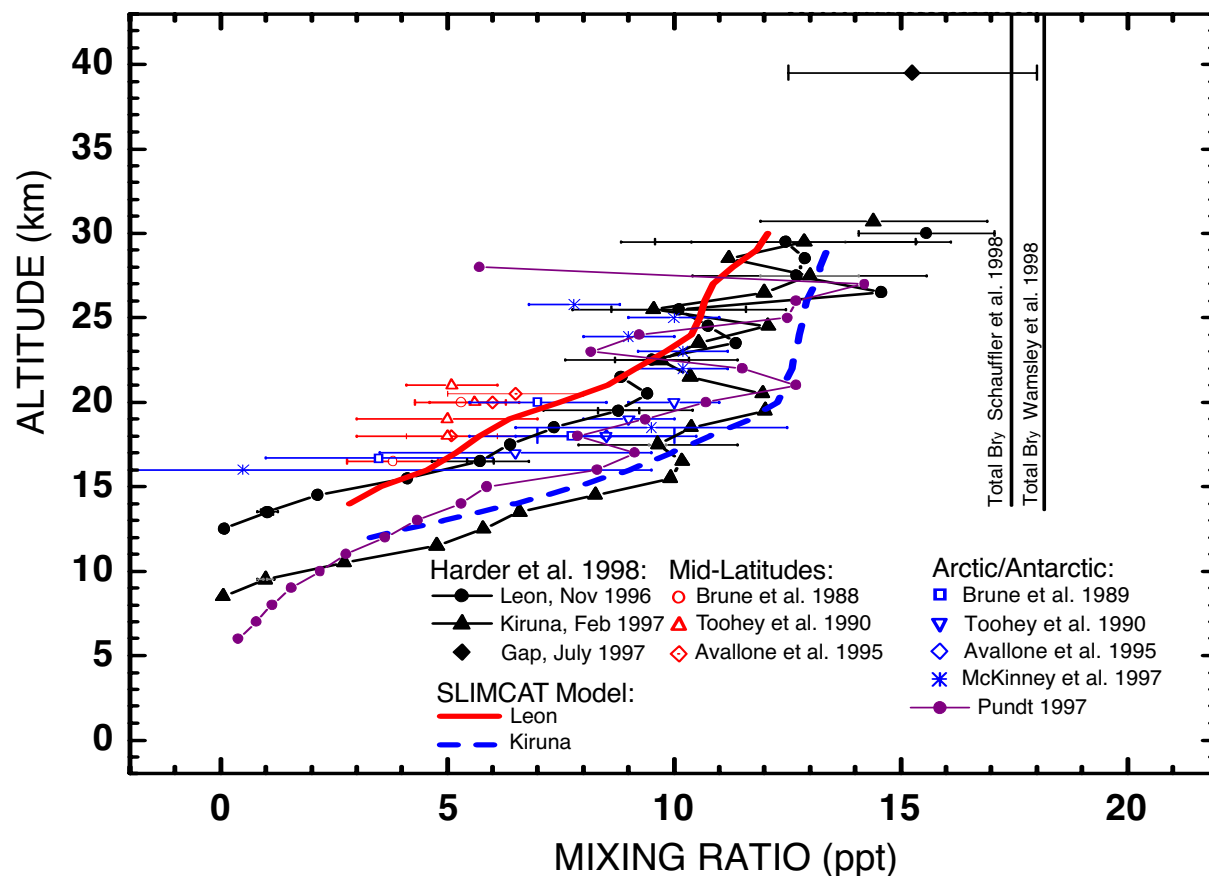


Figure 3-24. Measurements of profiles of BrO obtained at midlatitudes, in the Arctic and the Antarctic, by the in situ resonance fluorescence technique (red and blue open symbols and blue * symbol) and by the remote Differential Optical Absorption Spectroscopy (DOAS) technique (closed symbols). Also shown are two estimates of total inorganic bromine (total Br_y) loading at the top of the atmosphere based on measured abundances of brominated source gases (thin vertical lines). Calculations of profiles for BrO from the SLIMCAT model, appropriate for conditions of the DOAS observations of BrO from León, Spain (42.6°N), and Kiruna, Sweden (67.9°N), are shown by the red solid and blue dashed lines. See Harder et al. (1998) for the full citation of the references given on the figure. Adapted from Harder et al. (1998).

Profiles of inorganic bromine (Br_y) based on measurements of BrO have recently been compared with estimates based on the observed falloff (with increasing height) of the organic source species. These comparisons, discussed in the section on bromine trends and budget, show a slight offset that may result from either direct influx of ~3 parts per trillion by volume (pptv) of inorganic bromine across the tropical tropopause or some organic species not accounted for. Finally, profile measurements of BrO discussed also in the bromine budget section have been used to determine trends in total bromine loading that can be compared with trends based on the organic bromine (CBr_y) content of the lower atmosphere.

Bromine Monoxide (BrO) Abundances

Harder et al. (1998) compared in situ BrO measurements from the ER-2 aircraft and a balloon flight with profiles of BrO obtained by the Differential Optical Absorption Spectroscopy (DOAS) technique (Figure 3-24). There is a systematic difference in these two sets of observations, where DOAS measurements are somewhat larger than in situ, although this is within the combined uncertainties of the measurements. Consequently, the estimates of the inorganic bromine budget based on these sets of measurements have ranged from ~16 pptv (in situ) to ~20 pptv (DOAS) (Avallone et al., 1995; Pfeilsticker et

al., 2000). It is important to note that, because these sets of observations were obtained 5 years apart, more than half of this difference can be explained by trends in the bromine source gases, as discussed in the next section.

Sinnhuber et al. (2002) compared ground-based zenith sky measurements obtained at 11 sites with simulations from the SLIMCAT model in an effort to examine the detailed processes that govern the partitioning of BrO. Comparisons for three sites are shown in Figure 3-25. The simulated abundances of BrO generally agree to within ~10% of the observations over a wide range of seasons, latitudes, and solar zenith angles. The results are consistent with a total stratospheric bromine loading (sum of organic and inorganic) of 20 ± 4 pptv, in agreement with the values deduced from previous remote measurements of BrO.

The SLIMCAT model tends to overestimate BrO column abundances at high latitudes, typically when ClO abundances are elevated (Figure 3-25). Conversely, Friess et al. (1999) find a discrepancy in the opposite sense between BrO slant column measurements made at Kiruna, Sweden (67.9°N), in winter and SLIMCAT model calculations that use *JPL 97-4* kinetics (DeMore et al., 1997; hereafter referred to as *JPL 97-4* in this chapter) and a bromine loading of 20 pptv (the model underestimates midday measured BrO columns by 20 to 40%). Sinnhuber et al. (2002) note that the discrepancy highlighted in their study can be reduced by increasing the rate constant for reaction 3-2a' to the upper limit of the uncertainty of the *JPL 00-3* recommendation. Friess et al. (1999), however, report that the discrepancy they found is evidence for several pptv of BrO in the free troposphere. The Friess et al. (1999) interpretation is consistent with interpretations based on other remote observations of BrO (e.g., Harder et al., 1998; Fitzenberger et al., 2000).

The discrepancies outlined above have a relatively minor impact on ozone loss rates calculated directly from Cycle 2 or on observed abundances of ClO and BrO in the polar vortices. However, they do raise questions about the completeness of our understanding of coupled bromine/chlorine chemistry. Similar questions have been raised based on aircraft observations of BrO at 20 km (in situ) and 12 km (remote) within the perturbed polar vortex. Specifically, Avallone and Toohey (2001) report that mixing ratios of BrO did not drop to near-zero as expected with increasing SZA after sunset, when reservoir species like bromine nitrate (BrNO₃), bromine chloride (BrCl), and hypobromous acid (HOBr) are expected to sequester nearly all available reactive bromine. Similarly, Wahner and Schiller (1992) previously reported non-zero BrO column abundances above 12 km in darkness that were difficult to explain. Avallone and Toohey (2001) suggest

that thermal decomposition of a weakly bound molecule, such as BrOOCl (bromochloroperoxide), may be able to maintain a few pptv of BrO following sunset, but note that such a process would have little impact on ozone loss rates because of the rapid decline of ClO at sunset. The existence of adducts of bromine and chlorine oxides has been postulated in theoretical studies (Gleghorn, 1997; Bridgeman and Rothery, 1999; Gomez and Pacios, 1999; Papayannis et al., 2001) and has been observed in an argon matrix (Johnsson et al., 1995).

The previous Assessment noted the spectroscopic detection of bromine dioxide (OBrO) in the midlatitude stratosphere, with implied mixing ratios as high as 20 pptv (Renard et al., 1997). As such, OBrO would be the dominant nighttime reservoir for inorganic bromine in the midlatitude stratosphere. The same group has since reported the presence of smaller amounts of OBrO in the nighttime, polar stratosphere (Renard et al., 1998). However, abundances of even a few hundredths of a part per trillion (ppt) of OBrO in the nighttime stratosphere are contrary to our present understanding of bromine photochemistry (Chipperfield et al., 1998). Erle et al. (2000) recently reported measurements of upper limits for OBrO that are appreciably smaller than values observed by Renard et al. (1997, 1998), indicating that one of the sets of observations is in error or that abundances of OBrO are highly variable. The explanations for non-zero BrO mixing ratios in darkness and possible detection of OBrO remain a mystery.

Bromine Trends and Budget

During the Arctic winter of 1998/1999, vertical profiles of all known major organic bromine species were measured between 9 and 28 km (Pfeilsticker et al., 2000) (Figure 3-26). The expected profile for inorganic bromine that was inferred from the source gases agrees well (i.e., differences are within the measurement uncertainties) with a second profile that was estimated from spectroscopic observations of BrO and a photochemical model estimate of the BrO/Br_y ratio (see Figure 3-26) (Pfeilsticker et al., 2000). This result indicates that the budget of bromine and its photochemistry in the lower stratosphere are reasonably well understood. For early 1999, the mixing ratio of total bromine estimated at 25 km in air of 5.6-year mean age was 18.4 (+1.8, -1.5) pptv based on organic precursor measurements, and 21.5 ± 3.0 pptv from BrO measurements. This slight offset allows for the possibility of a bromine influx of 3.1 (-2.9, +3.5) pptv from the troposphere to the stratosphere (Pfeilsticker et al., 2000).

Attempts to quantify temporal trends in inorganic bromine in the stratosphere traditionally have been ham-

POLAR OZONE

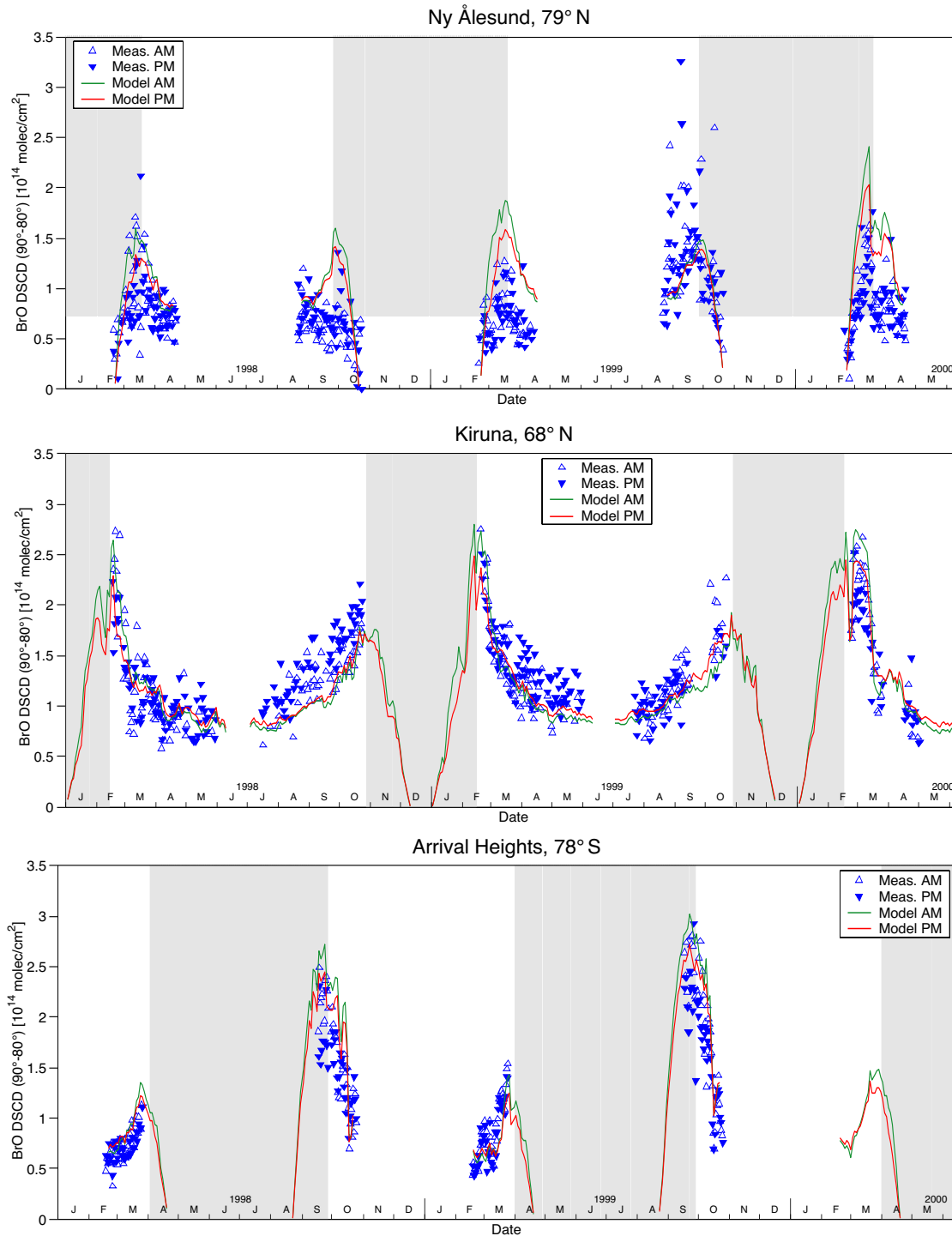


Figure 3-25. Comparison of measured and modeled differential slant column densities (DSCD) of BrO over Ny Ålesund, Spitzbergen (78.9°N), Kiruna, Sweden (67.9°N), and Arrival Heights, Antarctica (78°S). The differential slant columns were calculated from observations and model results obtained between solar zenith angles of 90° and 80° for the morning (AM) and evening (PM). However, when a solar zenith angle of 80° was not reached at high latitude (shaded regions), local noon values were used as a reference instead. Calculated values of BrO are from the SLIMCAT model. Adapted from Sinnhuber et al. (2002).

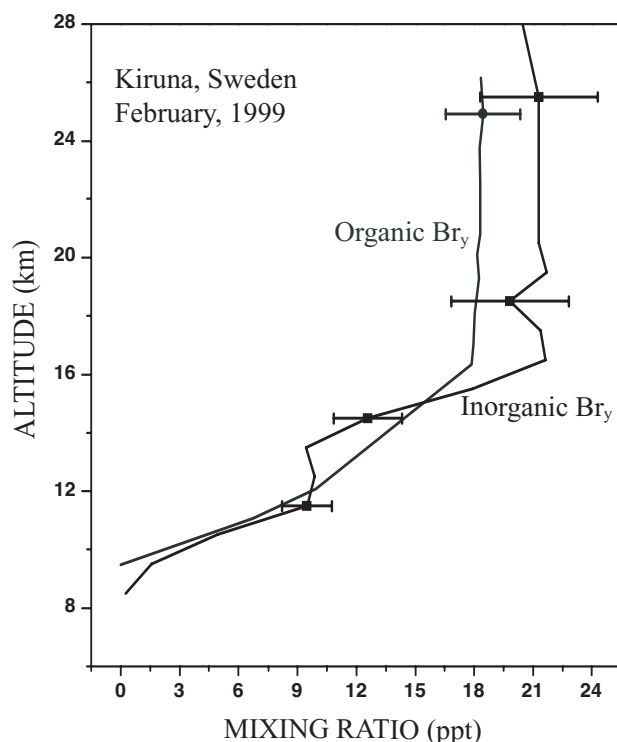


Figure 3-26. Vertical profile of total inorganic bromine (labeled Inorganic Br_y) based on the observed falloff of brominated source gases (labeled Organic Br_y) and based on measured BrO and a model calculation of the BrO/Br_y ratio. Measurements were obtained in the Arctic vortex, above Kiruna, Sweden (67.9°N), during the winter of 1998/1999. Adapted from Pfeilsticker et al. (2000).

pered by the lack of long-term observations and the relatively small quantities (~10 pptv or less) of the bromine species. However, a recent analysis of stratospheric measurements of BrO may shed some light on this issue, which is important in the context of polar ozone loss because the source of bromine to the stratosphere is expected to have increased by nearly 30% over the past decade (Wamsley et al., 1998).

Pfeilsticker et al. (2000) have taken the approach of estimating the abundance of total inorganic bromine (Br_y) based on measurements of BrO and model calculations of the BrO/Br_y ratio (Figure 1-8 in Chapter 1 of this Assessment; see also Figure 2.12 of EC (2001)). They rely on separate measurements of carbon dioxide (CO₂) or sulfur hexafluoride (SF₆) and model simulations to determine the age of air versus altitude. Their analysis of stratospheric data obtained between 1996 and 2000, reported in EC (2001), is consistent with a rate of increase of total bromine of about 0.7 pptv/year, broadly consis-

tent with the increase in tropospheric organic bromine over this time period (Figure 1-8).

This result suggests that the contribution of bromine to ozone loss in the polar regions has increased faster than that of chlorine because of abundances of bromine that continue to increase at a time when those of chlorine are leveling off (see Chapter 1). Model studies indicate that catalytic cycles involving BrO account for as much as 60% (depending on abundances of ClO and temperatures) of the total chemical loss of ozone in the Arctic for cold winters (Chipperfield and Pyle, 1998). The contribution of BrO reactions to the total loss of Antarctic ozone is somewhat less than for the Arctic because of lower temperatures and widespread denitrification in the SH vortex. Considering the observed leveling off of chlorine source gases, the relative role of bromine in polar ozone loss will continue to increase until the upward trend of bromine source gases reverses. However, since ozone loss by the BrO cycle also depends on ClO, future major declines in Cl_y are expected to lead to reductions in chemical loss of polar ozone essentially independent of changes to Br_y (Chipperfield and Pyle, 1998).

3.2.4 The Polar Summer Lower Stratosphere

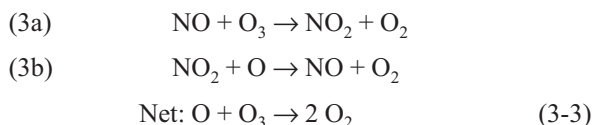
In both hemispheres, the annual cycle of total ozone has a strong decrease from the spring maximum to a minimum by mid-fall (e.g., Dobson, 1966; Dütsch, 1974; Bowman and Krueger, 1985; see also Figure 3-1). Column abundance of ozone declines by ~35% at high northern latitudes during summer (Toon et al., 1999; Lloyd et al., 1999). The rate of chemical ozone destruction in late spring/early summer is as large as in the winter polar stratosphere. This large decline, and the fact that the summer circulation is weak and quite zonally symmetric, makes the summer period a good test of understanding. Models typically have been unable to capture the full magnitude of the decline. To address this issue, the POLARIS experiment was flown from Fairbanks, Alaska, with three deployments during the early spring, summer, and early fall of 1997. This mission examined the seasonal ozone decrease using a complete payload of instruments aboard the NASA ER-2 high-altitude aircraft (Newman et al., 1999).

The summer lower stratosphere is mixed by waves that penetrate in the presence of the weak summer westerlies (Wagner and Bowman, 2000). Orsolini (2001), however, has shown that remnants of polar vortex air can retain their identity until well into the summer in the lower stratosphere. Rosenlof (1999) has studied the annual cycle of ozone transport in high northern latitudes. She found

POLAR OZONE

that the seasonal cycle in transport was an important contributor to the seasonal march of ozone at high latitudes during middle to late summer, with the eddy contribution to ozone reduction more than offsetting the ozone increase by advection at this time. In early summer, transport is weak and in situ photochemical destruction dominates the ozone tendency. In contrast, Pierce et al. (1999) using a Lagrangian model with HALOE data found that the transport term was important (see Appendix 3A for HALOE data descriptions).

In situ measurements of nitrogen oxides (NO_x), odd hydrogen (HO_x), and ClO_x radical species (Fahey et al., 2000) and long-lived tracers of stratospheric transport (Toon et al., 1999) confirm the summertime loss of ozone is due primarily to the gas-phase catalytic cycle:



Fahey et al. (2000) calculated the ozone chemical tendency based on measurements of radicals from the major families and found that chemical processes dominate overall tendency in the midsummer. Although this ozone loss process is generally understood (Brühl et al., 1998), ozone abundances calculated using two- or three-dimensional models tend to exceed observations for high-latitude summer (e.g., Chipperfield, 1999). This discrepancy has been attributed to inadequacies in model transport (e.g., Fahey and Ravishankara, 1999).

New measurements of NO_x , HO_x , and ClO_x species in the summer polar stratosphere have provided quantitative tests of our understanding of processes that regulate the abundance of radicals in each family. Measurements in the summer polar stratosphere are particularly useful because heterogeneous reactions, normally the dominant loss process for NO_x , proceed at slower rates than gas-phase loss reactions because of uninterrupted periods of solar illumination that restrict the buildup of dinitrogen pentoxide (N_2O_5) (e.g., Gao et al., 1999; Osterman et al., 1999). In the sections that follow, we briefly assess recent advances in our understanding of stratospheric photochemistry based on these observations.

3.2.4.1 SUMMERTIME NO_x CHEMISTRY

Observations of NO , NO_2 , HNO_3 , and NO_y obtained in the summer polar stratosphere revealed higher levels of NO_x (relative to total NO_y) and NO_2 (relative to HNO_3) than could be accounted for by constrained photochemical box models using the *JPL 97-4* (DeMore et al.,

1997) set of recommended kinetic parameters (Gao et al., 1999; Jucks et al., 1999; Osterman et al., 1999; Cohen et al., 2000; Perkins et al., 2001) (Figure 3-27). During polar summer, production and loss of NO_x are regulated primarily by the $\text{OH} + \text{NO}_2$ and $\text{OH} + \text{HNO}_3$ reactions for a broad range of altitudes (e.g., Osterman et al., 1999). New laboratory data for $\text{OH} + \text{NO}_2$ (Dransfield et al., 1999; Brown et al., 1999a) and $\text{OH} + \text{HNO}_3$ (Brown et al., 1999b) led to a re-evaluation of the rate constant for both of these reactions in the *JPL 00-3* compendium (Sander et al., 2000). Use of the *JPL 00-3* kinetic parameters significantly improves the agreement between measured and modeled ratios of NO_x/NO_y and NO_2/HNO_3 (Gao et al., 1999; Jucks et al., 1999; Osterman et al., 1999; Cohen et al., 2000; Perkins et al., 2001; Salawitch et al., 2002b) (Figure 3-27).

It has also been proposed that the reaction of $\text{OH} + \text{NO}_2$ produces HOONO (pernitrous acid) in addition to HNO_3 (nitric acid) (McGrath and Rowland, 1994; Mathieu and Green, 2000; Golden and Smith, 2000, and references therein). Recent spectroscopic observations indicate a yield for HOONO of about 5% at 253 K and 26 hPa (Nizkorodov and Wennberg, 2002). The formation of the HOONO isomer is also supported by several recent kinetic studies (Donahue et al., 2001; Hippler et al., 2002). Implications of HOONO production have yet to be fully explored, but box model calculations of Golden and Smith (2000) indicate this process leads to small increases in calculated NO_x and small decreases in calculated ozone, for the high-latitude summer stratosphere.

Simultaneous measurements of ozone, NO , NO_2 , ClO , and HO_2 during polar summer provide a stringent test of our understanding of the rapid photochemistry linking NO to NO_2 (Del Negro et al., 1999). Photolysis rates for NO_2 (J_{NO_2}) inferred from the chemical measurements are in excellent agreement with values calculated with radiative models and those measured with a spectroradiometer (Del Negro et al., 1999). Recently, this comparison has been extended to larger SZAs of 80° to 93° (Gao et al., 2001a). Values of J_{NO_2} derived from the in situ chemical measurements agree well (differences $<11\%$) with results from a multiple-scattering actinic flux model. The linearity of the correlation between these two computations of J_{NO_2} over the SZA range 80° to 93° demonstrates that the model scattering calculation is accurate for twilight conditions (Gao et al., 2001a).

Loss of ozone by NO_x chemistry in the summer polar regions may become more important in the future because of rising levels of NO_2 (Liley et al., 2000; McLinden et al., 2001). Nitrous oxide (N_2O), the source gas for NO_x and NO_y , is rising at about 3% per decade (e.g., McLinden et al., 2001). Interestingly, concentra-

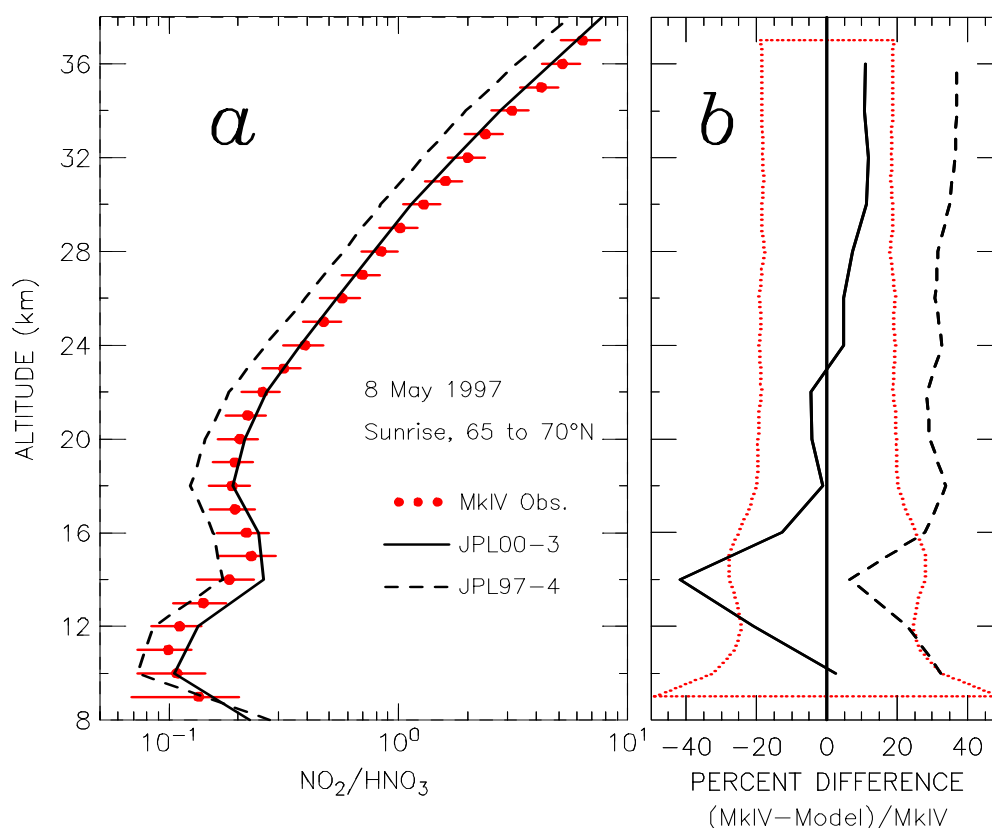


Figure 3-27. (a) MkIV observations (red points with error bars) of the NO_2/HNO_3 ratio at sunrise obtained during a balloon flight in the Arctic stratosphere on 8 May 1997. Constrained photochemical steady-state model calculations of the ratio, for the solar zenith angle of the observations, are shown for kinetic parameters from the JPL 00-3 (Sander et al., 2000) evaluation (solid line) and from the JPL 97-4 (DeMore et al., 1997) evaluation (dashed line). Error bars on the observations represent 1σ precision, based on considerations such as residuals in the spectral fitting, combined in quadrature with spectroscopic uncertainties. (b) Percentage difference between measured NO_2/HNO_3 and values from the two model calculations. The red dotted lines denote the 1σ measurement uncertainty. After Osterman et al. (1999) and Salawitch et al. (2002b).

tions of NO_2 at SH midlatitudes have been observed to be increasing at a faster rate of 5% per decade (Liley et al., 2000). This increase has been interpreted as being due to rising N_2O as well as declining levels of ozone, which alter the NO/NO_2 partitioning and the diurnal variation of NO_x (McLinden et al., 2001); see also Chapter 4.

3.2.4.2 SUMMERTIME HO_x CHEMISTRY

Measurements of OH and hydroperoxyl radical (HO_2) in the high-latitude stratosphere during late spring provide an important test of our understanding of HO_x sources throughout the day because abundances of these species are nearly in photochemical steady state under the slowly varying SZA conditions up to 93° (Wennberg et al., 1999). Observed abundances of OH and HO_2 in the lower stratosphere significantly exceed those from stan-

dard model calculations for $\text{SZA} > 80^\circ$ (Wennberg et al., 1999; Salawitch et al., 2002b) (Figure 3-28).

An important change in the JPL 00-3 kinetics evaluation, relative to the JPL 97-4 evaluation, is that the recommended reaction probability for BrNO_3 hydrolysis dropped from 0.8 to about 0.2 for conditions of the high-latitude, springtime lower stratosphere. Consequently, a model using JPL 00-3 kinetics (Figure 3-28) does not predict the observed “morning rise” of HO_2 ; the calculated nighttime buildup of HOBr , which releases HO_x at sunrise, is limited because of this rate change (Salawitch et al., 2002b). The OH and HO_2 measurements suggest the presence of a photolytic source of HO_x that operates more efficiently than known HO_x sources during twilight and that operates at an essentially constant rate for $80^\circ < \text{SZA} < 93^\circ$ (e.g., this photolytic process must occur

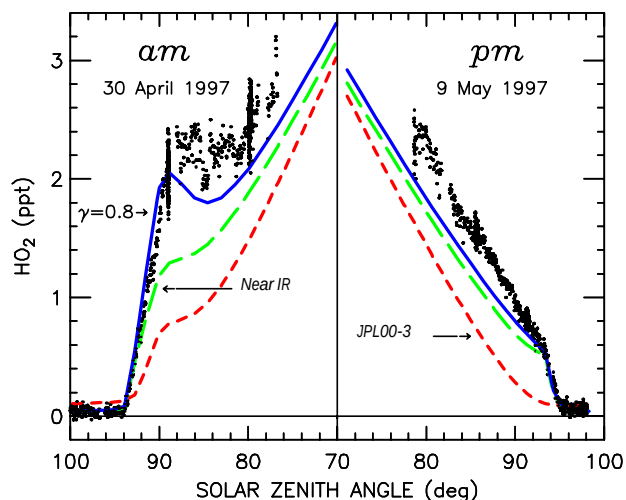


Figure 3-28. Observations of HO_2 obtained on the morning of 30 April 1997 and the afternoon of 9 May 1997 near 64°N in the lower stratosphere (Wennberg et al., 1999) compared with constrained photochemical model simulations using three sets of kinetic parameters: (1) JPL 00-3 (Sander et al., 2000) (red dashed lines); (2) allowing for near-IR photolysis of HO_2NO_2 based on cross sections and quantum yields from Roehl et al. (2001) (green dashed lines); and (3) allowing for near-IR photolysis of HO_2NO_2 and for a reaction probability of 0.8 for BrNO_3 hydrolysis (blue solid lines). After Salawitch et al. (2002b).

longward of 650 nm, which remains optically thin even for SZAs near 93°) (Wennberg et al., 1999).

Including a photolytic pathway for photolysis of HO_2NO_2 (peroxynitric acid) via excitation of purely vibration modes longward of 760 nm (the near IR) based on recent laboratory measurements of cross sections and quantum yields (Roehl et al., 2001), a process first suggested by Donaldson et al. (1997), leads to significant improvements in measured and modeled HO_x near twilight due to the rapid photolysis of HO_2NO_2 (Wennberg et al., 1999; Salawitch et al., 2002b) (Figure 3-28). The near-IR photolysis of HO_2NO_2 reduces calculated levels of this species, resolving a large discrepancy between standard model calculations and observations of HO_2NO_2 at high latitudes (Salawitch et al., 2002b). The lower calculated abundance of HO_2NO_2 also reduces the efficiency of the $\text{OH} + \text{HO}_2\text{NO}_2$ sink of HO_x , resulting in rather large (e.g., 20 to 60%) increases in 24 hour averaged HO_x for the high-latitude spring lower stratosphere and upper troposphere compared with models that neglect this process (Salawitch et al., 2002b). Nonetheless, the observed “morning rise” of HO_2 is still underestimated by a model

including near-IR photolysis of HO_2NO_2 . This discrepancy might be due to the actual rate of BrNO_3 hydrolysis proceeding at a faster rate than the JPL 00-3 recommendation, the presence of other twilight photolytic sources of HO_2 besides HOBr and HO_2NO_2 , less than 100% efficiency for production of H_2O from the $\text{OH} + \text{HO}_2\text{NO}_2$ reaction, or a systematic error in the measurements of OH and HO_2 (Wennberg et al., 1999; Salawitch et al., 2002b).

Balloonborne observations of OH , HO_2 , H_2O , and ozone obtained over Fairbanks, Alaska, also suggest important gaps in our understanding of several HO_x reactions (Jucks et al., 1998). Discrepancies between measured and modeled abundances of OH and HO_2 are reduced with a $\sim 25\%$ downward adjustment of the ratio of the rate constants for atomic oxygen ($\text{O} + \text{HO}_2$) and $\text{O} + \text{OH}$ and either a 25% reduction to the rate constant for $\text{OH} + \text{HO}_2$ (the primary HO_x sink) or a 25% increase in the HO_x production rate (Jucks et al., 1998). These modifications are within the uncertainties of the laboratory measurements and are consistent with the results of HO_x model/measurement studies discussed in the previous Assessment. The new insight provided by the simultaneous observations of OH and HO_2 is that the required modifications to the rate constants appear not to appreciably affect odd oxygen production rates in the upper stratosphere (Jucks et al., 1998).

3.2.4.3 SUMMERTIME Cl_y CHEMISTRY

The first in situ observations of ClONO_2 were obtained in the high-latitude stratosphere during the summer of 1997 (Stimpfle et al., 1999). These observations are in good agreement with values of ClONO_2 determined using a photochemical steady-state relation constrained by simultaneous observations of $[\text{ClO}]$ and $[\text{NO}_2]$ (the ratio of measured to modeled ClONO_2 is 1.15 ± 0.36). These results, together with a study that used balloonborne remote measurements (Sen et al., 1999), confirm the photochemical mechanism by which abundances of NO_x regulate the abundance of ClO in regions of the stratosphere that are NO_x -limited (i.e., mixing ratio of $\text{NO}_x >$ mixing ratio of ClO_x).

Simultaneous observations of ClONO_2 and HCl from a balloon (Sen et al., 1999) and the ER-2 aircraft (Voss et al., 2001) test our understanding of the kinetic processes that regulate the partitioning within the inorganic chlorine (Cl_y) family. Model calculations using JPL 00-3 recommendations agree extremely well with the balloonborne remote observations of both ClONO_2 and HCl (Figure 3-29), whereas the aircraft in situ measurements of the ratio $[\text{ClONO}_2]/[\text{HCl}]$ are ~ 55 to 60% lower than values based on a steady-state calculation (Voss et al., 2001). This dis-

crepancy has not been resolved and is the subject of ongoing investigations.

Simultaneous observations of the major inorganic and organic chlorine species in the summer polar stratosphere provide a test of the chlorine budget. The observed increase in the inorganic chlorine content (e.g., $\text{HCl} + \text{ClNO}_3 + \text{HOCl} + \text{ClO}$) of stratospheric air with decreasing N_2O , from both the ER-2 and MkIV, agrees well (differences less than $\sim 10\%$) with estimates of inorganic chlorine based on the observed disappearance of organic source molecules (Sen et al., 1999; Bonne et al., 2000) (Figure 3-29). However, the ER-2-based estimate of inorganic chlorine is $\sim 15\%$ less than the MkIV estimate for mixing ratios of N_2O below about 175 ppbv. This offset is probably due to differences in the measurements of ClNO_3 noted in the previous paragraph. These results extend the conclusions of the previous Assessment regarding the good quantitative link between abundances of inorganic chlorine species and their halogen sources to a new region of the atmosphere (i.e., polar summer) and to a new class of observations (i.e., in situ). These findings are particularly relevant for the discussion of the chlorine budget for the winter polar stratosphere (Section 3.2.3.1).

3.3 QUANTIFICATION OF POLAR OZONE LOSS: OBSERVATIONS AND MODELS

Quantification of the degree of chemical ozone loss in the polar stratosphere is hampered by the pronounced dynamically induced variability of the ozone layer in these regions in winter/spring. Precise quantification of the chemically induced contribution to observed changes in the ozone abundance are particularly difficult in the Arctic stratosphere, where the degree of ozone loss is smaller and the dynamic activity is more pronounced than in the Antarctic. Over the last decade a number of approaches have been developed to overcome these difficulties. Major challenges have been to (1) assess how reliable the results of these approaches are and, hence, how precise current estimates of the degree of Arctic ozone losses are, and (2) determine whether the degrees of ozone losses calculated by up-to-date chemical models agree with the observational results within the combined uncertainties of the models and the observations. The latter question is crucial to assess our current ability to make projections of future polar ozone losses in a potentially colder stratosphere.

Severe Arctic ozone loss has been reported for some recent cold Arctic winters. No significant loss was found during warmer winters. The large Arctic ozone losses result from increased levels of radical halogen

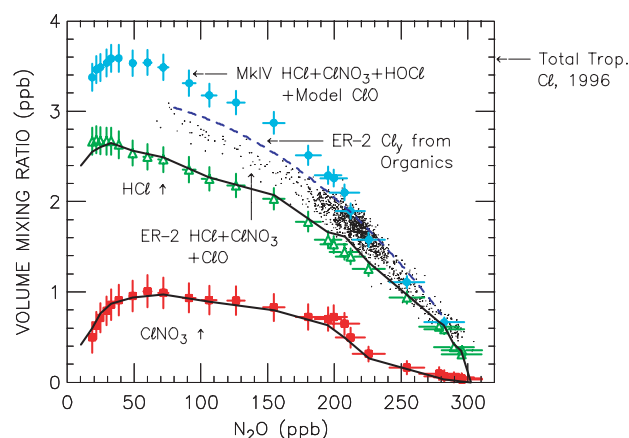


Figure 3-29. Measurements of chlorine species from balloon and in situ instruments during POLARIS. MkIV balloonborne measurements of the volume mixing ratio of HCl (green open triangles) and ClNO_3 (red solid squares) versus N_2O observed over Fairbanks, Alaska (64.8°N), on 8 May 1997 are shown, along with calculated values of HCl and ClNO_3 (solid black lines) found using a constrained photochemical model (Sen et al., 1999, updated for JPL 00-3 (Sander et al., 2000) kinetics). The dashed blue line shows an estimate of Cl_y based on ER-2 measurements of the organic source molecules during POLARIS (Sen et al., 1999). The sum $\text{HCl} + \text{ClNO}_3 + \text{HOCl}$ measured by MkIV plus calculated ClO (aqua solid dots) is also shown; calculated ClO makes a negligible contribution to this sum except for the highest altitudes (e.g., $\text{N}_2\text{O} < 50$ ppb) because the MkIV observations are obtained at twilight. Error bars for the MkIV measurements represent 1σ precision. ER-2 measurements of the sum $\text{HCl} + \text{ClNO}_3 + \text{ClO}$ are shown by the black dots (Bonne et al., 2000). Because the ER-2 observations are obtained at altitudes below ~ 20 km, species such as HOCl , Cl , etc., are estimated to make a negligible (e.g., < 20 ppt) contribution to the sum and are therefore neglected. Finally, the arrow in the right margin denotes the total chlorine content, 3.59 ppb, of the entire suite of tropospheric organic compounds for 1996 (WMO, 1999, Table 1-2).

species that result from heterogeneous chemical processing on the surface of polar stratospheric clouds (WMO, 1999; cf. also Sections 3.2 and 3.3.2 of this Assessment). Currently about 80 to 85% of the stratospheric chlorine is provided by the decomposition of anthropogenic organic chlorinated species (Zander et al.,

POLAR OZONE

1992, 1996; Gunson et al., 1994; Russell et al., 1996; Sen et al., 1999). Because the relevant ozone destruction cycles are linear to quadratic in the concentration of active chlorine, by far the largest fraction of the ozone losses discussed in this section is of anthropogenic origin. However, no quantitative study exists to precisely quantify the small degree of ozone loss that would be expected in a cold Arctic winter for natural levels of halogens in the stratosphere.

3.3.1 Approaches to Quantify Chemically Induced Ozone Loss in the Arctic

Two principal techniques are currently used to quantify chemically induced ozone losses in the Arctic:

- (1) Studies that take into account the effect of transport explicitly by using transport calculations based on meteorological analyses.
- (2) Studies that allow for transport effects implicitly by using the relation between ozone and a long-lived chemical tracer.

In the following, approaches that have been used in a consistent way for several winters are briefly assessed.

3.3.1.1 APPROACHES THAT USE EXPLICIT TRANSPORT CALCULATIONS

Bulk Advection

In this section, approaches are assessed that use explicit transport calculations to advect bulk quantities like vortex averages or gridded ozone fields and compare these with later measurements of ozone, a concept first published by Manney et al. (1994).

The “vortex average” technique involves analysis of the temporal evolution of the mean profile of ozone within the polar vortex on surfaces of potential temperature. Ozone measurements by ozonesondes (e.g., Knudsen et al., 1998; Rex et al., 1998; Lucic et al., 1999; Tzvetkova et al., 2002) or a remote sensing instrument, e.g., the POAM II satellite instrument (Bevilacqua et al., 1997) have been analyzed with this approach. The boundary of the polar vortex is usually defined by isolines of potential vorticity. Potential temperature and potential vorticity are conserved quantities in the polar stratosphere over time scales of a couple of weeks, so this coordinate system largely eliminates variability due to rapid and reversible dynamics. The slow irreversible descent of air across surfaces of potential temperature is usually accounted for by a diabatic correction calculated from descent rates using a radiative transfer model that is based on temperatures from a meteorological assimilation

system. In the absence of mixing across the vortex edge, changes in ozone can be attributed to chemical loss. The largest uncertainties connected with this approach are (1) possible mixing across the vortex edge, which may impact the average ozone abundance inside the polar vortex, (2) any time-varying bias in the sampling of the vortex, which may lead to changes in the derived vortex average, since ozone is not uniform within the vortex, and (3) uncertainties in the calculated diabatic corrections. Knudsen et al. (1998) used an approach based on domain-filling trajectory calculations to estimate the effect of mixing across the vortex edge for the Arctic winter of 1996/1997. For that winter, at the altitude of the maximum loss, they found an insignificant impact of mixing on the ozone loss derived from the vortex average technique.

In the “transport model” approach, a 3-D CTM is initialized with ozone observations during the early winter period. The model advects ozone passively, i.e., without chemical conversion, throughout the winter, using analyzed winds and, depending on the vertical transport scheme in the model, also temperatures. Ozone measurements throughout the winter are compared with the passively advected ozone. Evolving deficits between observed ozone and the model passive ozone indicate chemical loss. This approach has been used with the Reactive Processes Ruling the Ozone Budget in the Stratosphere (REPROBUS) model using data from the POAM satellite instruments and from the ground-based network of Système d’Analyse par Observation Zénithale (SAOZ) instruments (e.g., Lefèvre et al., 1998; Goutail et al., 1999; Deniel et al., 2000). Hansen et al. (1997), Guirlet et al. (2000), and Sinnhuber et al. (2000) have used this approach with the SLIMCAT model, using ozone lidar data, SAOZ data, and ozonesonde data, respectively. This approach relies on the assumption that the model transport scheme realistically represents the transport of air over a time period of several months. But when the derived ozone loss is averaged over the polar vortex, as is the case in many studies, the approach only depends on a correct representation of average transport properties like, e.g., vortex-averaged vertical subsidence and average rates of exchange of air across the vortex edge. Possible systematic errors in these average properties are the largest source of uncertainty in the transport model approach. Another source of concern is the initialization of the model ozone with data from a different type of instrument (usually measurements of the HALOE or MLS satellite instruments; see Appendix 3A for satellite data descriptions) than is used for the ozone observations later on. Systematic discrepancies between the different instruments make altitude-dependent correction factors necessary; these are often on the order of 5%, which is a substantial

fraction of the ozone changes observed over the course of warmer Arctic winters. The method is sensitive to the vertical variation of the correction, because early-winter measurements from one instrument at higher altitude are compared with late-winter measurements from another instrument at lower altitude.

Manney et al. (e.g., 1995a, b, 1996a, b, 1997) used a similar approach based on “trajectory ensemble” calculations to analyze ozone data of the MLS on the UARS satellite (see Appendix 3A for MLS data description). Trajectory calculations are started at all points on the gridded MLS data and are run forward in time for a few weeks. Succeeding MLS measurements are interpolated to the locations of the trajectories. The differences in ozone are attributed to chemistry. The results are stated as vortex-averaged ozone loss or are analyzed versus equivalent latitude, PV, etc. During the UARS north-looking yaw cycle, continuous time series of ozone loss can be derived, whereas only accumulated losses are stated across the south-looking yaw cycles, when measurements in the Arctic are not available. Schoeberl et al. (2002) advected ozone, using trajectory ensemble calculations initialized from early-winter ozone observations, over the course of the winter and then compared this early winter ozone with late-winter ozone observations. Again the advected and the observed ozone fields are averaged over the polar vortex before they are compared, thus reducing the sensitivity of the approach to transport features of individual air masses. The trajectory ensemble approach uses 3-D trajectory calculations that are several months long for the advection. Using trajectories instead of a grid-point advection scheme eliminates any potential bias due to numerical diffusion of the advection scheme. The largest uncertainty of the trajectory ensemble method comes from possible systematic biases in the long-term trajectory calculations, e.g., due to possible uncertainties in the vertical transport, which is based on calculated diabatic descent rates.

Lagrangian Ozone Measurements (Match)

“Match” is a Lagrangian technique to determine the rate of chemical ozone loss. In active Match campaigns, ozonesonde launches from a large network of about 35 ground stations are coordinated in real time to probe individual air masses twice over an interval of a few days (so-called “match events,” e.g., von der Gathen et al., 1995; Rex et al., 1997, 1998, 1999b, 2002a). The coordination is based on calculations of air parcel trajectories that allow for diabatic descent. Several hundreds to more than a thousand ozonesondes are launched in a Match campaign. The initial launch subsequently results in several

match events with later sondes at different altitudes. The coordination results in hundreds to thousands of match events per winter. Chemical ozone loss rates are derived from a statistical analysis of subsets of match events from a certain time period (typically 14 days long) and altitude region (typically 20 K broad) by calculating linear regressions of the difference in ozone between both measurements and the sunlit time that the air mass encountered. The overall ozone loss during the winter is calculated by accumulating the measured loss rates. Sasano et al. (2000) and Terao et al. (2002) have used a similar approach to analyze the ozone measurements from the ILAS satellite instrument (see Appendix 3A for ILAS data descriptions).

The largest uncertainties in this method are possible systematic errors in the trajectory calculations, including the calculated diabatic subsidence rates. Individual Match events depend on a correct representation of the motion of individual air masses by the trajectories. Therefore, the length of the trajectory calculations used in Match is limited to 10 days, and the majority of the Match events rely on ~5–7 days trajectories. But ozone loss rates are calculated in a statistical process from subsets of several tens of Match events, so that the derived average ozone loss rates are only sensitive to systematic trajectory errors, e.g., possible systematic biases in the calculated diabatic descent rates. A statistical analysis of the data shows that observed ozone losses occur exclusively during sunlit periods along the trajectories. This suggests that any systematic biases in the trajectory calculations, if present, are so small that they do not significantly affect the derived ozone loss rates (e.g., Rex et al., 1998, 1999b, 2002b).

3.3.1.2 APPROACHES THAT USE THE RELATION OF OZONE TO AN INERT TRACER

In midwinter, ozone abundances inside the polar vortex show a relatively compact relation to abundances of many long-lived tracer species such as nitrous oxide (N_2O) or methane (CH_4). In the absence of mixing, any reduction of ozone versus an inert tracer indicates chemical loss of ozone. This approach was first used by Proffitt et al. (1990). More recently, early-winter and late-winter measurements of ozone, N_2O , CH_4 , and HF by the HALOE satellite instrument have been used to identify chemical loss of ozone during various winters (e.g., Müller et al., 1996, 1997; see also Appendix 3A for satellite data descriptions). The evolution of the ozone-versus- N_2O relation through the winter of 1999/2000 was studied using data from in situ instruments onboard two balloon-borne platforms and the NASA ER-2 high-altitude aircraft (Salawitch et al., 2002a; Richard et al., 2001).

Two fundamental issues affect the validity of the tracer relation approach. First, the existence of a compact universal relation between ozone and inert tracers has been questioned, and, second, the impact of mixing on results from studies of the ozone-versus-tracer relation has been discussed. Here we assess the current status of the discussion on these two points.

During polar summer the chemical lifetime of ozone in the middle and upper stratosphere is comparable with or shorter than transport time scales, so the ozone-tracer relationship in the Arctic stratosphere in fall is not expected to be compact and universal (Plumb and Ko, 1992). But in fall, the lifetime of ozone in the middle and lower stratosphere gets sufficiently long, and it can be expected that mixing within the early polar vortex leads to compacting of the ozone-tracer relations inside the vortex. These slowly evolving, more-compact relations inside the vortex are quite different from the extra-vortex relations, with less ozone inside at a given tracer level than outside. The degree of compactness and the definition of this inner vortex “early-winter relation” is critical for the validity of the tracer relation approach. Richard et al. (2001) and Salawitch et al. (2002a) used initial ozone-versus- N_2O reference relations measured well inside the polar vortex in midwinter (December/early-January). They showed that these relations were sufficiently compact and representative of initial conditions inside the polar vortex, an essential condition for the validity of the approach. But observations of the ozone-versus-methane relation measured well inside the Arctic vortex in midwinter for 1999/2000 were significantly lower (ozone differences of ~ 1.5 ppmv for values of $\text{CH}_4 = 0.5$ ppmv) than the suite of initial HALOE-based reference relations (Müller et al., 1999, and references therein) measured in the vortex edge region in October for earlier Arctic winters (Salawitch et al., 2002a). The validity of these early-winter HALOE reference relations is currently the subject of numerous ongoing investigations (see Appendix 3A for satellite data descriptions). Generally results from the tracer relation approach are more reliable when the initial reference relation is measured late (i.e., December/early-January) and deep inside the vortex.

The second issue brought up regarding the validity of tracer relation studies is related to mixing. These considerations apply also for studies that assess the degree of denitrification based on changes in the otherwise very compact relation between NO_y and N_2O . If the relation between two tracers is curved, as is the case for these species, the results of the tracer relation approach can be compromised by mixing between air masses that are widely separated in tracer space (e.g., Waugh et al., 1997; Michelsen et al., 1998; Rex et al., 1999a; Plumb et al.,

2000; Ray et al., 2002). Isentropic mixing across the edge of the polar vortex or mixing of air masses inside the vortex that underwent different descent during the winter are examples for such long-range mixing in tracer space. Furthermore, the ozone/tracer relations inside the vortex are different from the relations outside the polar vortex. After substantial ozone loss, these differences can be very pronounced (several ppmv). Hence, any mixing across the vortex edge directly impacts the ozone/tracer relation inside the vortex and could represent a potential source of uncertainty for the tracer relation approach.

One can attempt to distinguish mixing and chemical ozone loss (or denitrification) by using simultaneous measurements of two long-lived tracers (e.g., CH_4 and N_2O) to estimate the impact of mixing (Rex et al., 1999a). However, this method is dependent on the assumption that there had been a single mixing event after the bulk of the descent and is not applicable if there is intermittent mixing at descent (Plumb et al., 2000). A more general approach is the use of a linear combination of several long-lived tracers to form an artificial tracer that has a compact and linear relationship with ozone (or NO_y) (Esler and Waugh, 2002). Because of its linearity, this artificial relation is unaffected by mixing within the vortex, so deviations from this relationship can be more directly attributed to chemical ozone loss (denitrification). But mixing across the edge of the vortex edge is still a source of uncertainty, because the outside vortex relations are often different from the inside relations (for ozone versus N_2O this is always the case; for NO_y versus N_2O this is the case after denitrification inside of the vortex). These attempts to correct for the impact of mixing in tracer relation studies were mainly focused on studies that used the relation of NO_y versus N_2O to assess denitrification.

Salawitch et al. (2002a) noted that considerations that are valid for the NO_y -versus- N_2O relation (e.g., the relation χ_2 versus χ_1 in Plumb et al. (2000) resembles NO_y versus N_2O) should not be applied to the interpretation of the ozone-versus- N_2O relation in the vortex, because ozone mixing ratios, unlike NO_y , do not approach zero at the top of the vortex because of the influence of photochemistry at 40 km. Hence, the curvature of the ozone-versus- N_2O relation for low N_2O (i.e., N_2O between 10 and 40 ppbv) is much less pronounced than that of NO_y versus N_2O , and mixing cannot lead to the observed changes in the ozone tracer relations that have been observed e.g., by HALOE. More quantitatively, simultaneous measurements of multiple long-lived tracers have been used to argue that the impact of mixing on estimates of chemical ozone loss by the tracer relation approach for the Arctic winter of 1999/2000 was negligible. Based on

the temporal evolution of CO_2 , CFC-11 (CCl_3F), N_2O , and ozone within the vortex, studies of Richard et al. (2001) and Salawitch et al. (2002a) demonstrated that the vast majority of the observed changes in the $\text{O}_3/\text{N}_2\text{O}$ relations were due to chemistry and could not have been caused by dynamics. The isolation of the Arctic vortex for that winter was also noted by a multivariate analysis of the time evolution of nearly a dozen tracers with varying lifetimes (Ray et al., 2002). Rex et al. (2002a) showed that during January to March 2000, any mixing across the vortex edge would have led to an underestimation of the ozone loss by tracer relation studies, and therefore the results of tracer relation studies that rely on initial relations from early January can be regarded as conservative estimates of the loss. These results from the Arctic winter of 1999/2000 support the validity of the tracer relation approach, provided the reference relation is defined in midwinter, but it is currently not clear whether these results can be applied to other, more dynamically active winters (e.g., Salawitch et al., 2002a).

3.3.2 Arctic Ozone Loss During the Last Decade

Since the previous Assessment (WMO, 1999), a number of approaches to quantify the degree of chemical ozone loss in the Arctic have been used in a consistent way for several winters during the 1990s. Because of these long-term efforts, the extent and the variability of Arctic ozone losses are now well characterized for the last 10 years. Several techniques have revealed a large interannual variability of chemical ozone losses in the Arctic.

3.3.2.1 OZONE LOSS RATES NEAR THE MAXIMUM OF THE OZONE CONCENTRATION

The Match approach was used consistently over the last decade to study the evolution of chemical ozone loss at about 475 K potential temperature (~ 19 km altitude). At polar latitudes this level is close to the maximum concentration of ozone in the ozone layer. Figure 3-30 shows the measured ozone loss rates for the winters 1991/1992 to 2000/2001 (compilation of Match results based on Rex et al. (1997, 1998, 1999b, 2002a) and Schulz et al. (2000, 2001)). Little or no significant ozone loss was observed in 1997/1998 and 1998/1999. The accumulated ozone loss during the winter was particularly large in 1995/1996 and 1999/2000, when relatively large loss rates were sustained for extended periods of time. The chemical ozone loss rate in the Arctic stratosphere is clearly controlled by temperature. Blue shaded areas in Figure 3-30 indicate the geographical areas (A_{PSC}) where

temperatures have been below T_{PSC} (the NAT equilibrium temperature based on 5-ppmv water vapor and an average HNO_3 profile based on measurements; T_{PSC} is a convenient threshold that roughly indicates the onset of rapid heterogeneous chemistry in the stratosphere, independent of the actual composition of the PSCs). All periods of rapid chemical ozone loss in Figure 3-30 are associated with preceding large values of A_{PSC} . No significant chemical loss of ozone was observed in warm winters, when T_{PSC} was not reached or only barely reached.

3.3.2.2 VERTICAL PROFILES OF OZONE LOSS

The determination of vertical profiles of ozone loss requires quantification of ozone losses over a broad altitude range. Ozone loss observations are typically most reliable at levels around 475 K. Below 400 K or above 550 K the uncertainty of observational studies is typically significantly larger. The problems at lower levels are that (1) a strong vertical gradient in the average ozone mixing ratio profile largely amplifies the uncertainty introduced by diabatic descent, and (2) larger dynamical activity via synoptic-scale waves makes explicit transport calculations less reliable and leads to larger degrees of mixing, which is problematic for all approaches. Above 550 K, average poleward motion and influx into the polar vortex, followed by mixing, is the main problem. The strong diabatic descent at higher altitudes causes additional uncertainty only in winters when the vertical gradient in the average ozone mixing ratio profile is significant at these levels, which is not always the case (e.g., compare 1998/1999 with 1997/1998 in Figure 3-31).

Figure 3-31 shows ozone losses derived from the vortex average approach in the vertical region between $\Theta = 360$ and 570 K (update from Rex et al. (2002a) for various winters). Results at the lowest and highest levels shown are less reliable. It is based on several hundred ozonesonde measurements per winter inside the vortex from a network of about 35 sounding stations. The vortex-averaged ozone profiles have been plotted against the “spring-equivalent potential temperature” ($e\Theta$), which is the potential temperature that a given air mass reached at the end of March due to diabatic subsidence. Through use of $e\Theta$, which is a conserved quantity, diabatic effects are accounted for. In the absence of mixing across the vortex edge, any change in the vortex-averaged ozone versus $e\Theta$ profile indicates chemical loss of ozone. In Figure 3-31, the large interannual variability of the ozone loss stands out. During the winter of 1998/1999, no significant loss of ozone was found at any part of the profile. In contrast, the loss of ozone in 1999/2000 exceeded 70% in a ~ 1 -km-thick region centered around 460 K. This local

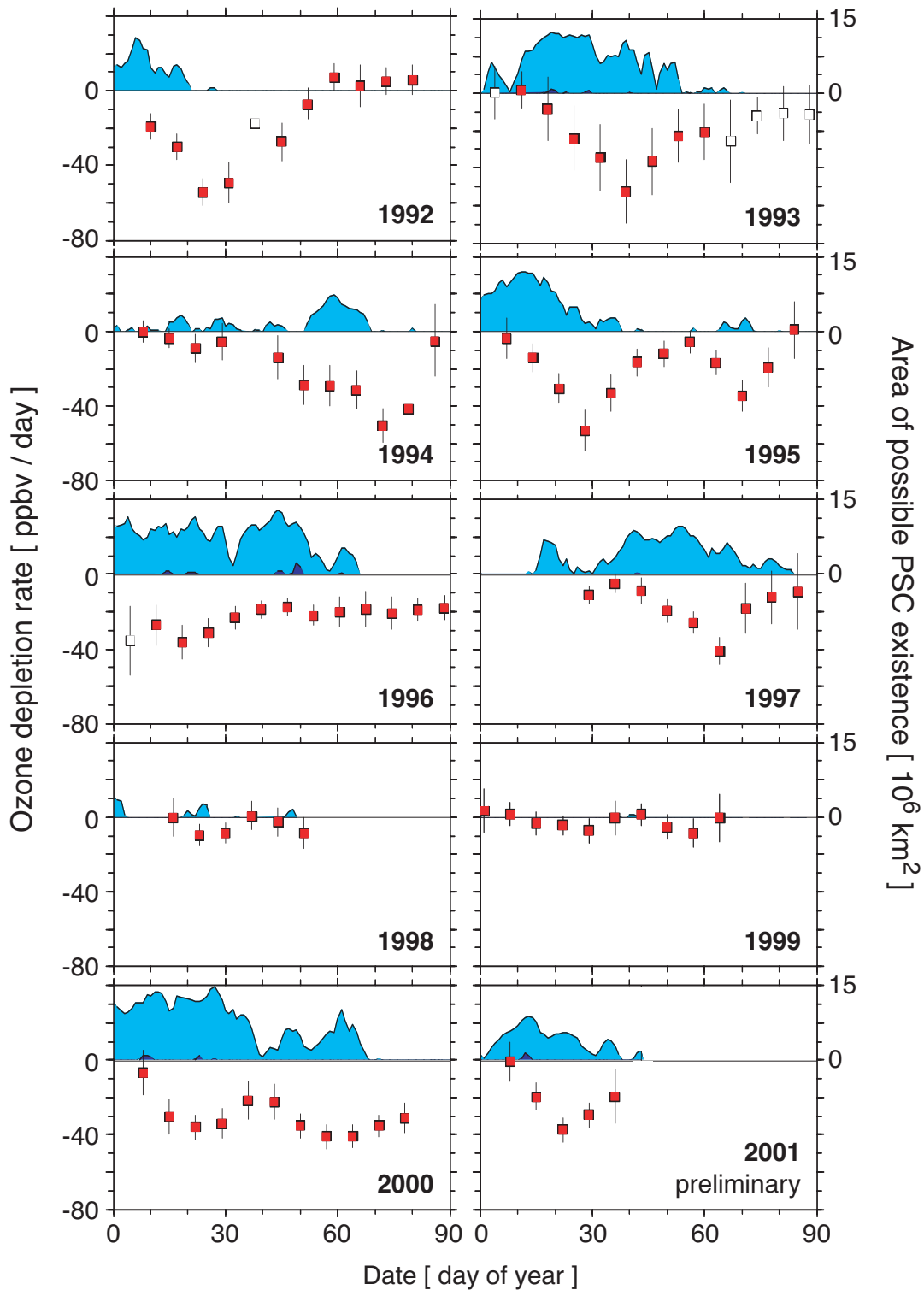


Figure 3-30. Ozone loss rates from Match at 475 K for various winters (squares) and A_{PSC} at 475 K (blue shaded areas). Red squares indicate 10 matches or more; white squares indicate fewer than 10 matches. Error bars are the 1σ errors of the fit of ozone differences (matches) as a function of sunlit time in the time period considered.

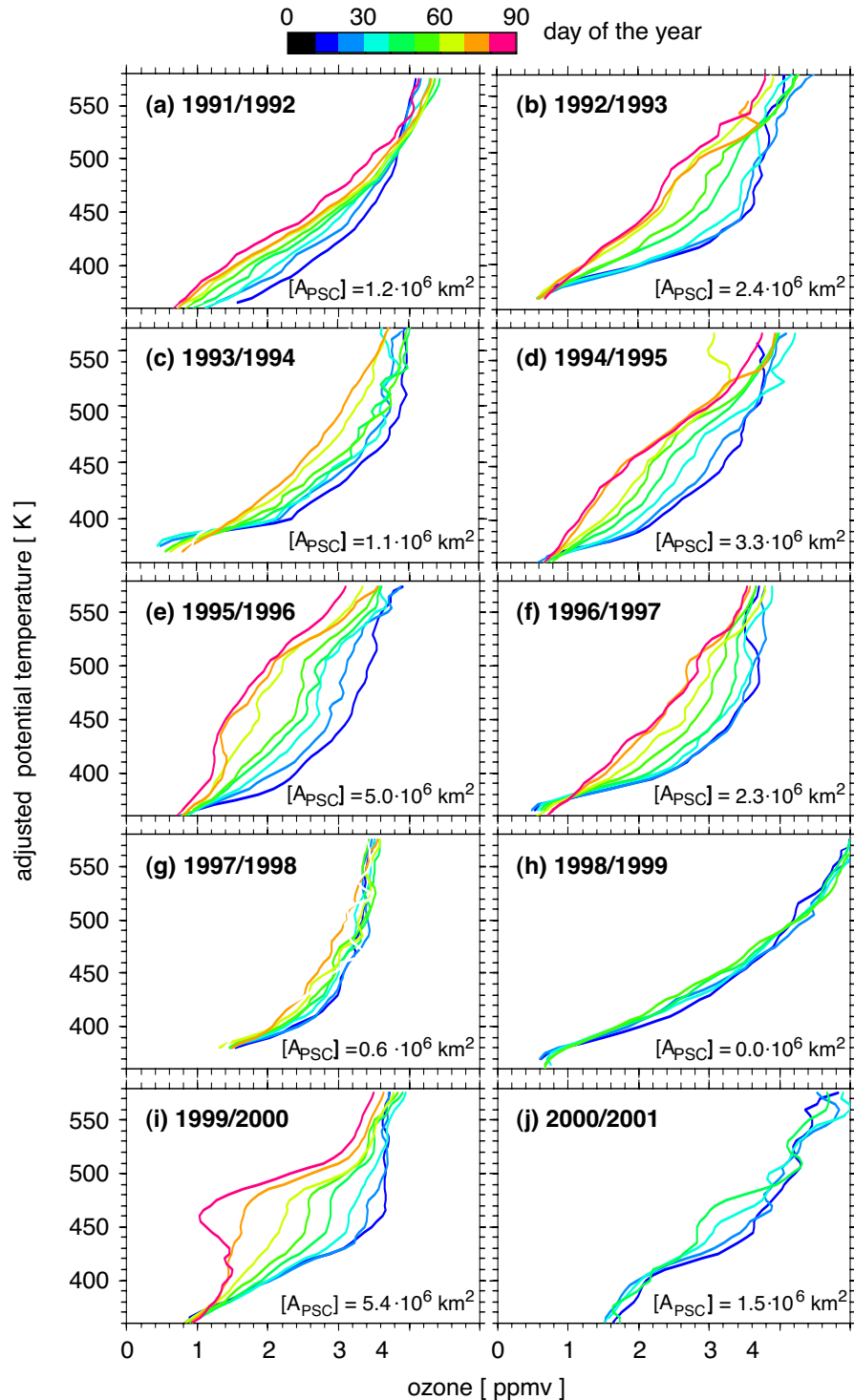


Figure 3-31. The evolution of the average ozone profile inside the Arctic polar vortex in spring-equivalent potential temperature ($e\Theta$) coordinates for various years; see text for a definition of $e\Theta$. The data from all ozonesonde measurements inside the vortex have been averaged into 10-day bins, centered around the day indicated by the color scale. The profiles typically rely on 20 to 50 individual measurements that, in most cases, sample the PV-space homogeneously. The average values for A_{PSC} ($[A_{PSC}]$) from 16 December to 31 March of each winter, between 400 and 550 K, are also given in each panel.

POLAR OZONE

loss is slightly more than in any previous Arctic winter, with 64% local loss in winter of 1995/1996 as the previous record. However, in 1995/1996, ozone loss occurred over a broader vertical region (e.g., ozone loss of more than 1 ppmv occurred between ~ 390 to 530 K in 1995/1996, compared with ~ 420 to 510 K in 1999/2000), and therefore the vertically integrated losses in both years are comparable.

The average value of A_{PSC} (denoted as $[A_{\text{PSC}}]$), averaged from mid-December to end of March between 400 and 550 K potential temperature, is given in Figure 3-31. Figure 3-32 shows the relation between $[A_{\text{PSC}}]$ and the average accumulated ozone loss between 400 and 550 K $\bar{O}_3\text{loss}$. A surprisingly close quantitative relation between both quantities suggests that the chemical loss of ozone in the Arctic stratosphere in a given winter correlates strongly with the parameter $[A_{\text{PSC}}]$. The compactness of the relation shown in Figure 3-32 is currently not fully understood. Many mechanisms that influence Arctic ozone loss, e.g., the degree of denitrification, should correlate well with the parameter $[A_{\text{PSC}}]$. But other meteorological parameters, like the timing of low-temperature periods, which also impact the overall degree of ozone loss, are not expected to correlate with $[A_{\text{PSC}}]$. Figure 3-32 suggests that the effect of variability in these parameters has been relatively limited during the past decade. To reproduce the empirical relation shown in Figure 3-32 is a major challenge for global chemistry transport models.

The ability of models to reproduce the slope of the relation shown in Figure 3-32 is crucial, if models are to be used to predict the impact of climate changes on future ozone losses.

3.3.2.3 EFFECT OF OZONE LOSS ON THE TOTAL OZONE COLUMN

Estimating the total column loss of ozone also requires a good quantification of ozone loss in a broad vertical region. The region above 550 K is of less concern for ozone column loss estimates because it contributes little to the total column amount of ozone, due to the small ozone concentrations at these altitudes. But uncertainties in the ozone loss estimates at altitudes below 400 K make ozone column loss estimates generally less reliable than estimates of local ozone losses near 19-20 km. The ozone column loss has been estimated for all winters since 1993/1994 with the transport model approach. Figure 3-33 shows the difference between ozone columns as measured by the SAOZ UV-visible network in the Arctic (Ny Ålesund, Thule, Scoresbysund, Sodankylä, Salekhard, Zhigansk, and Harestua) and the column of passive ozone in REPROBUS (again, initialized with POAM measurements in early winter) above these stations. In many winters, large deficits of observed ozone compared with passively advected ozone have been observed. These deficits are attributed to chemical loss

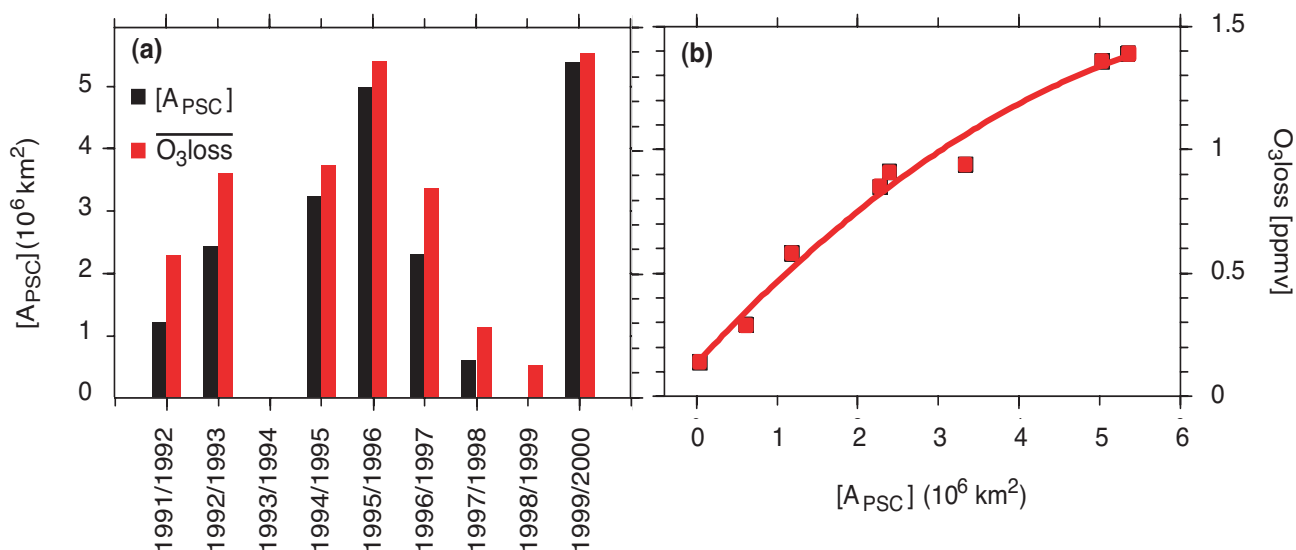


Figure 3-32. (a) Histogram of average values of A_{PSC} ($[A_{\text{PSC}}]$; black bars) and the average value for chemical loss of ozone from mid-January to the end of March, between 400 and 550 K (red bars). When the period of rapid ozone loss overlaps with the vortex break up, the vortex average approach cannot be used to estimate the overall loss of ozone. Those years (1994, 2001) have been omitted. (b) Scatter diagram of average ozone loss versus $[A_{\text{PSC}}]$.

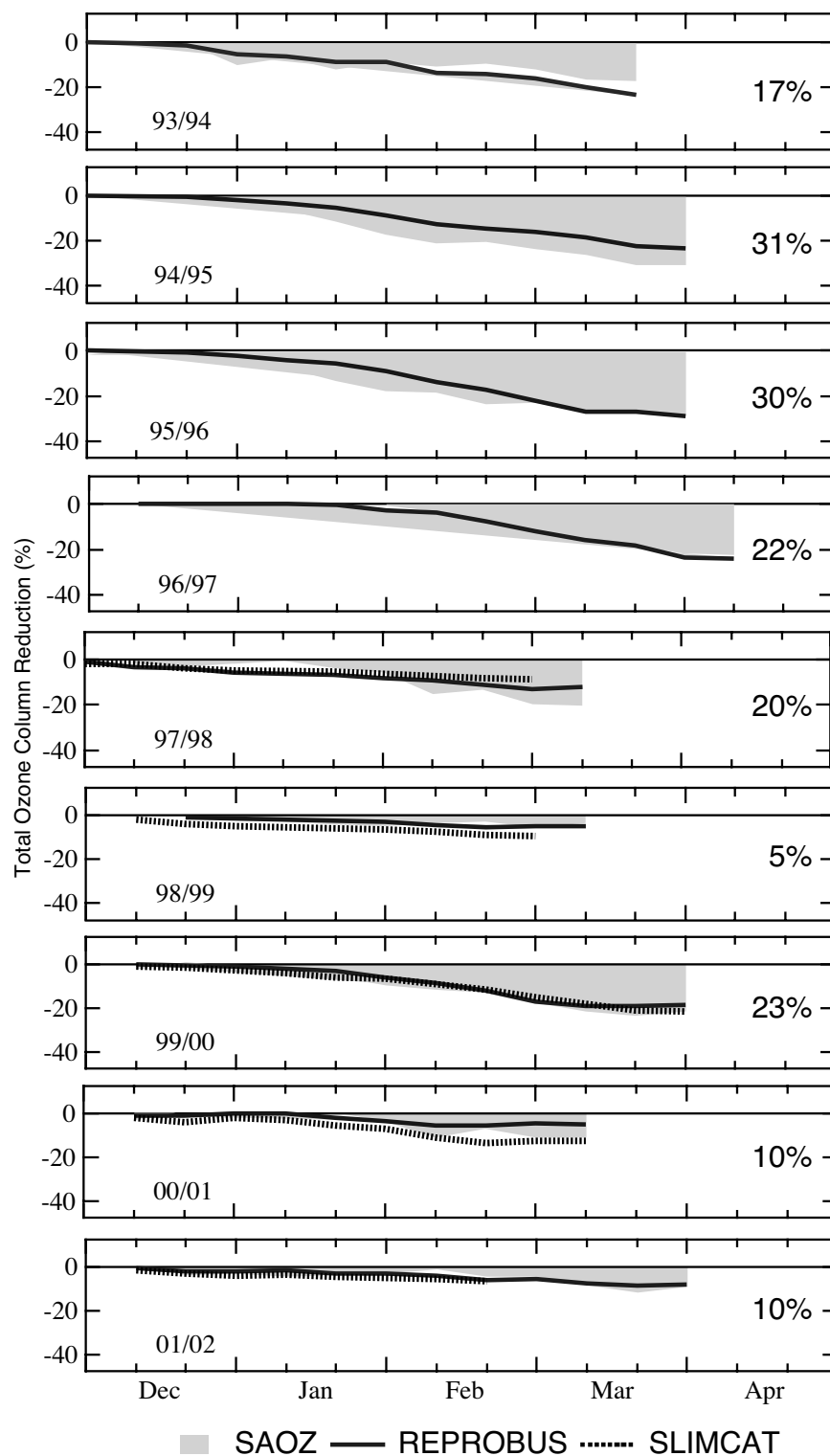


Figure 3-33. Total ozone reduction in the Arctic derived by comparing measurements of the SAOZ network (Ny Ålesund, Thule, Scoresbysund, Sodankylä, Salekhard, Zhigansk, and Harestua) with passive ozone in REPROBUS (gray shaded area) and modeled ozone losses (solid line, REPROBUS; dotted line, SLIMCAT). Written percentages on the right side of each panel are the cumulative SAOZ losses. Reproduced from EC (2001).

POLAR OZONE

of ozone. Associated with persistently low temperatures in the winters of 1994/1995, 1995/1996, 1996/1997, and 1999/2000, large chemically induced ozone reductions of 22 to 31% were observed inside the vortex. The ozone loss during the warmer winter of 1998/1999 was smaller and is hardly significant. In the relatively warm winter of 1997/1998, ozone column losses derived from the transport model approach were still significant (20%). In that winter, temperatures dropped below the PSC threshold only in very limited geographical regions inside the vortex and only during short periods (see Figure 3-30). From the vortex average approach (Figure 3-31) some limited ozone loss in 1997/1998 is also visible, but only below 450 K. During that year Match results at 475 K indicate no significant loss, but results for 450 K and below are not available from Match for that year.

3.3.2.4 CHEMICAL OZONE LOSS IN THE ARCTIC WINTER 1999/2000

The winter of 1999/2000 had the largest potential for PSC formation for at least the last 20 years. Because of the extensive SOLVE-THESEO 2000 campaign during the winter 1999/2000, all basic approaches outlined in Section 3.3.1 were used to study the ozone loss throughout the winter, resulting in a better characterization of the ozone losses in 1999/2000 than in any previous winter and providing a unique opportunity to compare results from the different techniques.

All approaches identified extensive chemical loss of ozone. Figure 3-34a shows the evolution of the vortex averaged ozone loss in a vertical section as determined with the Match approach. Ozone loss started at altitudes above 500 K in mid-January. The largest loss rates of 61 ± 4 ppbv per day (vortex average) were observed at 450 K in early March. Rex et al. (2002a) showed that the vertical structure and the time evolution of the observed ozone loss agree well with the vertical structure and the time evolution of observations of high levels of active chlorine. During the winter of 1999/2000 only approaches that are based on ozonesonde measurements, like Match and the vortex average approach, were able to capture the full extent of the ozone loss, i.e., cover the full altitude range of the loss and the time period from early January to late March in vertical resolution. Comparisons of the results with other approaches are possible for a slightly shorter period and focus on the region close to 450 K. Here the results of all approaches agree very well (see Section 3.3.3).

Figure 3-35 shows the impact of the cumulative ozone loss through the winter on the vortex-averaged vertical ozone profile at the end of March. In a layer of air

around 18 km altitude the degree of chemical ozone destruction reached 70%.

Table 3-2 gives an overview of various estimates for the deficit in the total column amount of ozone due to chemical loss of ozone. The numbers given are the difference between the actually observed column amount of ozone and the column amount of ozone that would have been present at a given day in the absence of chemical ozone loss, dynamics being equal. For comparable time periods the agreement between results from all approaches is within the error bars. The results from the SAOZ/transport model study are generally somewhat higher than the other approaches and have larger uncertainties. The results of the other approaches agree to better than 20%. Figure 3-34c shows the evolution of the total column loss from January through March, as determined by Match. By the end of March, the chemically induced ozone deficit amounted to between 90 and 100 DU. This is roughly the amount of total ozone that has been supplied to the polar vortex by dynamic effects during the same time, and therefore the total ozone column remained relatively constant during January to March (Rex et al., 2002a), which is in contrast to the natural, climatological increase of the Arctic ozone column during this season.

3.3.3 Consistency Between the Different Observational Techniques

Comparisons of the different approaches used to infer Arctic ozone loss are often hampered by the fact that the altitude range, horizontal extent (vortex definition), and time periods used in the various published works are different. These differences are partly unavoidable because of the constraints of the datasets used. But often the datasets can be reanalyzed for certain time periods and regions where they overlap, so that the results can be directly compared.

For winter 1999/2000 basically all approaches can be used to calculate the amount of ozone loss that occurred inside the polar vortex between 20 January and 12 March in the layer of air that subsided from about 475 to 450 K during that time. This subsiding layer of air is indicated in Figure 3-34a by the solid black lines. Figure 3-36 summarizes the accumulated ozone losses as determined for this layer of air with the various techniques. The average of the various estimates is 1.65 ppmv of ozone loss for this specific time period and vertical region. The results from all techniques are within $\pm 20\%$ of this value; all but two are within $\pm 10\%$ of the average.

The winter of 1999/2000 was characterized by relatively weak dynamic activity and perhaps less than average exchange of air across the vortex edge (see

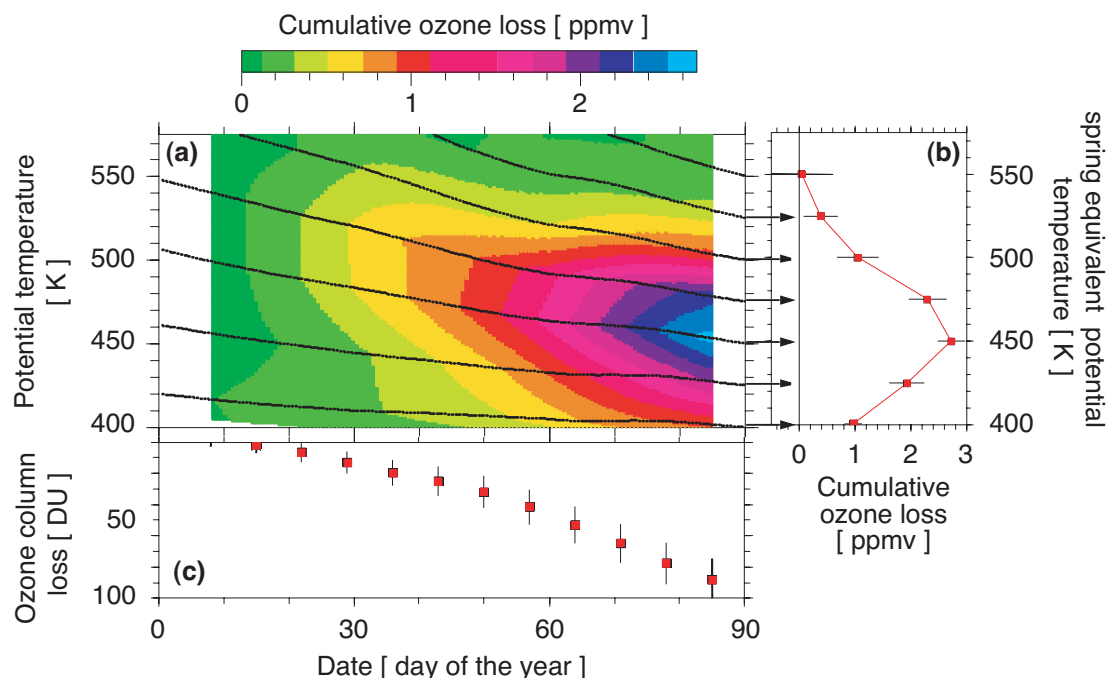


Figure 3-34. (a) Evolution of the cumulative ozone loss in subsiding air masses from March for 1999/2000. The subsidence of air is indicated by the black lines (see text). (b) Profile of the cumulative ozone loss on 26 March 2000 from March. (c) Accumulated chemical ozone loss in the partial column between $\theta = 400$ and 575 K from March. Error bars are 1σ . Reproduced from Rex et al. (2002a).

Section 3.2.1). It is reasonable to assume that for the winter of 1999/2000 the agreement between different techniques to estimate the degree of chemical ozone loss from ozone observations may be better than for dynamically more active winters. However, to investigate this, Harris et al. (2002) reanalyzed data from past winters during the 1990s, using different techniques and datasets, focusing on time periods where the datasets overlap. On the basis of results from many winters, they found an agreement of generally better than 20% between techniques that use explicit transport calculations. Results from tracer relation studies showed slightly larger discrepancies compared with these results, when the initial tracer relation was measured early in fall. This agreement is 25% or better, when the initial tracer relation was measured in midwinter, e.g., in December.

On the basis of these studies, the results from current estimates of the degree of chemically induced Arctic ozone losses appear to have an accuracy of about 20%.

3.3.4 The Effect of Denitrification on Ozone Loss

The effect of denitrification on ozone loss has been quantified (to some extent) in both hemispheres. In the Antarctic (complete) denitrification is shown to cause a

10% increase in the column ozone loss (Brasseur et al., 1997; Portmann et al., 1996).

Evidence for a much more significant impact of denitrification (see Section 3.2.2.3) on Arctic ozone losses in recent cold winters has increased. Observational results indicate that the degree of ozone loss in the Arctic was significantly amplified by denitrification during the winters of 1994/1995, 1995/1996, and 1999/2000. Using model studies, Rex et al. (1997) concluded that in winter 1995/1996, observed ongoing chemical ozone loss in certain air masses more than 1 month after the last exposure to PSCs can only be explained by approximately 80% denitrification in about half of the air masses inside the polar vortex. In that winter the heavily denitrified layer of air was limited to a very narrow vertical region of less than 1 km thickness at about 20 km altitude.

Waibel et al. (1999) presented measurements of denitrification in the Arctic winter of 1994/1995, based on the NO_y -versus- N_2O relation, and used a chemical model to conclude that in the denitrified air masses the degree of ozone loss was enhanced by at least 30% compared with what would have occurred without denitrification. They show that the model results can come close to the observed ozone loss only when the observed denitrification is taken into account.

POLAR OZONE

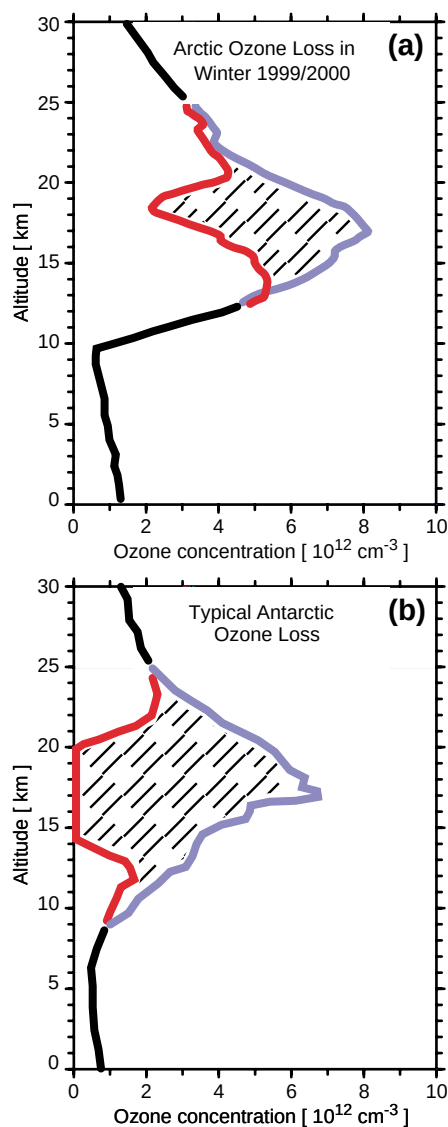


Figure 3-35. Comparison of ozone loss in the Arctic winter of 1999/2000 and typical Antarctic ozone loss. (a) Concentration profile of O_3 during late winter for observations from ozonesondes between 20 and 30 March 2000 in the Arctic (red). The profile of O_3^* (blue), the abundance of O_3 expected in the absence of any chemical loss, was estimated by allowing the early-winter vortex average O_3 profile from ozonesondes to descend by amounts based on cooling rates from the SLIMCAT model. For this calculation, the mixing ratio of O_3 was assumed to be conserved during descent and was converted to concentration in the last step. The profiles are shown for the altitude and pressure the air would have been at on 25 March. The difference between the profile of O_3^* and O_3 is hatched. This is an estimate, based on the vortex average approach, for the accumulated chemical loss of ozone during the winter. The black lines represent a typical late-March ozone profile above and below the vertical region where significant ozone loss occurred. Adapted from Rex et al. (2002a). (b) Illustration of the typical degree of ozone loss in the Antarctic. Typical midwinter (15 July 1997, blue) and late winter (13 October 1997, red) ozone profiles measured inside the Antarctic polar vortex at the Neumayer station at 71°S are shown. This panel is for illustration only, and no attempt has been made to correct for transport effects, which are weaker in the Antarctic compared with the Arctic. Poleward and downward transport between July and October supplies ozone to the Antarctic vortex, and therefore the hatched area in panel (b) is a conservative estimate of the chemical loss.

Table 3-2. Comparisons of chemical loss of column ozone, column $[\text{O}_3^* - \text{O}_3]$ (see Rex et al., 2002a), inside the Arctic vortex for the winter of 1999/2000 as of the indicated date. N/A indicates that data for that date are not available.

Data Source	Method	Reference	Chemical Loss of Column Ozone (DU)		
			5 March 2000	15 March 2000	28 March 2000
OMS balloon	Tracer-tracer (O_3 vs. N_2O)	Salawitch et al. (2002a)	61 ± 14	N/A	N/A
HALOE	Tracer-tracer	Müller et al. (2002)	N/A	84 ± 13	N/A
POAM III satellite	Vortex-averaged descent	Hoppel et al. (2002)	51 ± 11	67 ± 11	N/A
SAOZ network	Transport model	EC (2001)	85 ± 24	98 ± 25	101 ± 30
Ozonesondes	Match	Rex et al. (2002a)	53 ± 11	71 ± 12	88 ± 13

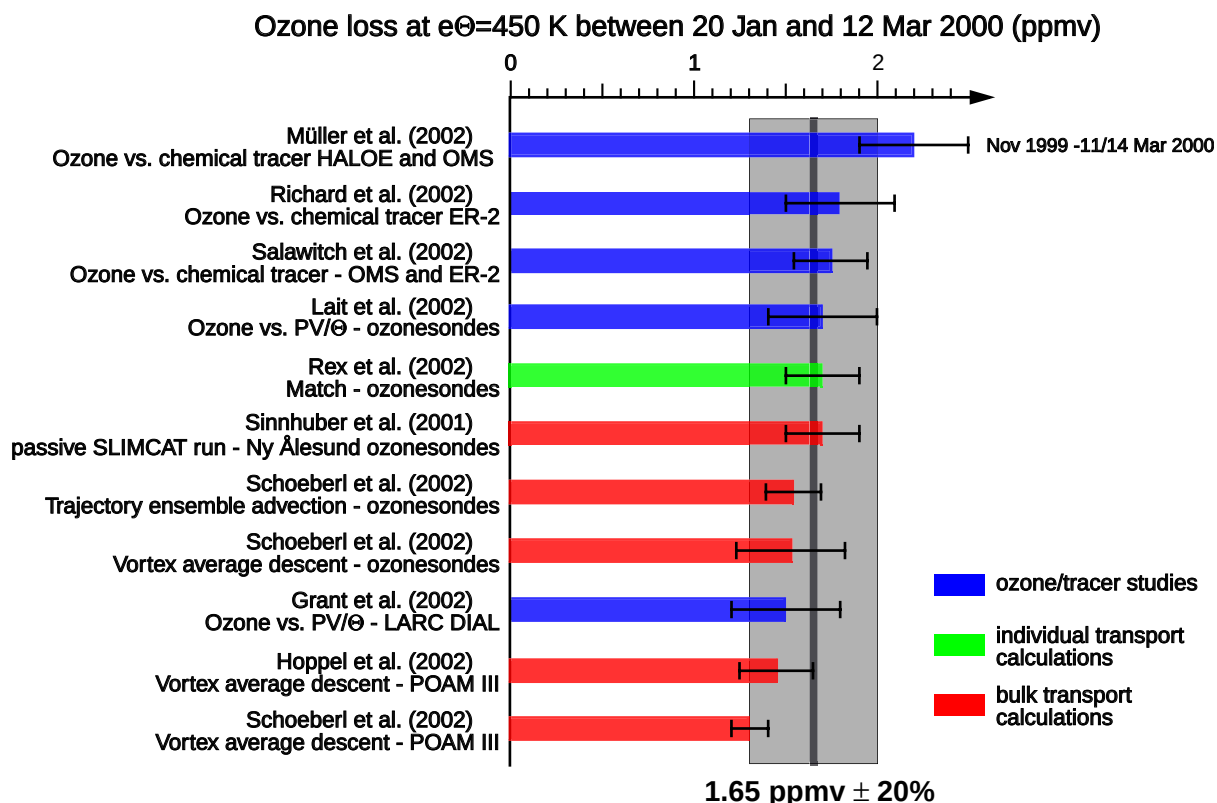


Figure 3-36. Overview of the results of various approaches to estimate the amount of Arctic ozone loss (ppmv) between 20 January and 12 March 2000. The results are stated for the layer of air that subsided from about 475 K at the beginning of the period to 450 K at the end. Results from studies that use the relation between ozone and an inert tracer are plotted in blue; studies that rely on bulk transport calculations are plotted in red; and results from the approach that relies on individual transport calculations are plotted in green. The error bars represent the 2-standard-deviation uncertainty of the loss estimate as estimated by the individual investigators. The average of the various estimates is 1.65 ppmv $\pm$ 20%. (OMS = Observations of the Middle Stratosphere; LARC DIAL = NASA Langley Research Center Differential Absorption Lidar; other acronyms defined in text.) Based on Newman et al. (2002).

Gao et al. (2001b) present measurements of varying degrees of denitrification (also based on the NO_y -versus- N_2O relation) in different areas of the polar vortex, as characterized by fixed ranges of N_2O and potential temperature. Succeeding observations of the rate of ozone loss indicate largest loss rates at the N_2O levels that were most severely denitrified (about 30% larger losses than in less denitrified air). Gao et al. (2001b) show that these differences in the ozone loss rate cannot be explained by differences in solar exposure or initial chlorine activation and, hence, are most likely a result of the denitrification.

These observational studies have shown that denitrification in cold Arctic winters can cause up to a 30% increase in ozone loss at a given altitude, a result that is confirmed by model studies (Chipperfield and Pyle, 1998; Tabazadeh et al., 2000; Drdla and Schoeberl, 2002). The

more pronounced effect of denitrification on ozone loss in the Arctic, compared with the Antarctic, is the result of higher temperatures in the Arctic. In the Antarctic, reactivation of chlorine out of the reforming ClNO_3 reservoir via reactions on cold liquid aerosol particles (e.g., $\text{ClNO}_3 + \text{H}_2\text{O}$) can sustain a high level of active chlorine in spring (Portmann et al., 1996). This is much less effective in the Arctic, since the heterogeneous reaction of $\text{ClNO}_3 + \text{H}_2\text{O}$ is much slower at the higher temperatures typical for the Arctic spring. Therefore, the lifetime of active chlorine is strongly dependent on the rate of formation of ClNO_3 and, hence, the abundance of HNO_3 . The overall effect of denitrification on Arctic column ozone loss depends on the vertical range of severe denitrification. Currently, the effect of denitrification on Arctic ozone is limited to the altitude range of ~ 18 to 21 km, where most parcels are

shown to be severely denitrified in cold winters (Hintsa et al., 1998; Kondo et al., 2000; Fahey et al., 2001). Microphysical studies have shown that the vertical range of severe denitrification in the Arctic lower stratosphere is very sensitive to the temperature (Waibel et al., 1999; Tabazadeh et al., 2001).

It is important to note that current denitrification schemes (e.g., in 3-D CTMs) have difficulties correctly representing the degree of denitrification in cold Arctic winters (e.g., Davies et al., 2002; see also Section 3.2.2.3). In light of the recent results showing that extensive denitrification (up to 80%) occurred in cold Arctic winters and that it had significant impact on the degree of ozone loss in those years, the correct representation of denitrification remains one of the major challenges for 3-D CTMs, when they are used to study the variability of chemical ozone loss in the Arctic (e.g., Chipperfield and Jones, 1999) or to predict future ozone losses in a potentially changing climate.

Dehydration, unlike denitrification, can moderate ozone loss for two reasons (Portmann et al., 1996; Chipperfield and Pyle, 1998). First, in a drier atmosphere it is harder for PSCs to form. Second, heterogeneous reaction rates that lead to active chlorine production drop exponentially with decrease in relative humidity. Sensitivity studies show that dehydration (to the level of ice saturation) in the Antarctic can decrease column ozone loss by about 20% (Portmann et al., 1996; Brasseur et al., 1997). No large-scale model calculations have yet been performed to evaluate the role that dehydration may play in Arctic ozone loss and recovery in the future. However, it is unlikely that climate change in the near future could cause extensive dehydration in the Arctic region. Some air mass trajectory statistical analyses indicate that even a substantial cooling of lower stratospheric temperatures (by 3 to 4 K) is still insufficient to trigger the occurrence of severe dehydration in the Arctic vortex (Tabazadeh et al., 2000).

3.3.5 Model Studies of Arctic Ozone Loss

Model investigation of polar ozone loss was the subject of intense research in recent years. Most studies concentrated on the Arctic region because of the high interannual variability of the Arctic ozone loss in relation to the year-to-year meteorological conditions. Three-dimensional CTMs, which proved to be particularly well fitted to the non-zonal character of the Arctic polar vortex, were used to estimate the overall degree of polar ozone loss for several winters. For more specific studies or highly constrained comparisons between models and ozone loss observations, photochemical box models were used.

3.3.5.1 CHEMICAL TRANSPORT MODELS

Studies using the transport model approach to estimate ozone loss from ozone measurements typically include a comparison with the ozone loss calculated by the chemistry module of the model. Chemical ozone loss inferred from the POAM II and III measurements was compared with that obtained from the REPROBUS model (Deniel et al., 1998, 2000). In the same way, total ozone measurements by the SAOZ network were compared with REPROBUS and SLIMCAT simulations for various Arctic winters from 1993/1994 (Figure 3-33; Goutail et al., 1999; EC, 2001). The agreement between the observed ozone loss and the model result varies from winter to winter. Two points can be seen in Figure 3-33. First, the overall interannual variability of the Arctic ozone loss is reasonably well represented by the models. The models reproduce a large fraction (about 60 to 100%) of the overall Arctic ozone loss. Second, in winters when substantial ozone loss was observed during January (1994/1995, 1995/1996, and 1999/2000), the models fall short of reproducing this January loss. Typically, by the end of January, only about 50% of the observed loss is accounted for by the models. The loss in January is partly why the overall loss at the end of the winter is sometimes underestimated (e.g., 1994/1995). In other winters the January loss contributes only a minor fraction to the overall loss (e.g., 1999/2000) or the model overestimates the loss rate later during the winter, and therefore the overall loss at the end of the winter is better reproduced than the time evolution of the loss (e.g., 1995/1996). Also, in 1995/1996 the simulated vertical distribution of the ozone loss at the end of March differs from that estimated from POAM II measurements, with the model resulting in larger losses at lower altitudes and smaller losses at higher altitudes compared with the observations (Deniel et al., 2000). It appears that a good agreement between observations and modeled total ozone loss at the end of the winter alone may be fortuitous and does not necessarily prove that the ozone loss mechanisms in the model are well reproduced.

Extensive modeling studies were performed as part of SOLVE/THESEO 2000 to estimate the ozone loss in the winter of 1999/2000. Sinnhuber et al. (2000) compared the chemical ozone loss estimated with SLIMCAT with that derived from the model ozone passive tracer and ozonesonde observations at Ny Ålesund (Figure 3-37). They found good agreement between the modeled ozone and observations, both indicating more than 2.5 ppmv ozone destruction by late March, corresponding to 70% ozone loss at the 450 K isentropic level, the largest ozone loss ever produced by SLIMCAT. The reason for the large loss of ozone in the model was extensive formation of

large denitrifying ice particles by the model's microphysical scheme. But the large-scale formation of ice clouds in the model was the result of a cold bias in the UKMO temperature fields used in SLIMCAT and is not consistent with observations during SOLVE/THESEO 2000. A later study performed by Davies et al. (2002) focused on the effect of denitrification on Arctic ozone depletion during the same winter using SLIMCAT and a denitrification scheme based on the formation of large NAT particles (see Section 3.2.2.3). When the model was forced by UKMO analyses, the ozone losses derived inside the vortex were very close to those derived by Sinnhuber et al. When ECMWF temperatures were used that were closer to observations in winter 1999/2000, the modeled active chlorine was in better agreement with ER-2 measurements, but the derived ozone loss was smaller than in observations and in Sinnhuber et al. (2002).

The KASIMA (Karlsruhe Simulation model of the Middle Atmosphere) CTM driven by ECMWF analyses was compared with ozone measurements by a Fourier transform infrared (FTIR) spectrometer and a millimeter wave radiometer in Kiruna for winter 1999/2000. The modeled total ozone loss underestimates the observations by 30% and 20%, respectively (Kopp et al., 2002).

The Langley Research Center (LaRC) Lagrangian chemical transport model (LCTM) was used in conjunction with HALOE and POAM III satellite observations to simulate the large-scale photochemical evolution of the Arctic vortex in 1999/2000 from a vortex ensemble of air mass trajectories using UKMO analyses (Pierce et al., 2002; see also Appendix 3A for satellite data descriptions). The model shows significant denitrification within the vortex in late December and early January. A significant overprediction of the level of chlorine activation is found in early March, but the predicted peak ozone loss rate is in good agreement with that inferred from the Match campaign during the same period. Conversely, it can be concluded that for a realistic level of active chlorine, the model would have significantly underestimated the observed ozone loss rate during that period.

Grooß et al. (2002) report simulations with the Chemical Lagrangian Model of the Stratosphere (CLaMS). This model simulates the dynamics and chemistry of multiple air parcels along their trajectories that are determined from ECMWF winds. The model includes mixing between neighboring air parcels. In this model study, the degree of denitrification was described from observations by using observed relations between NO_y and N_2O and the temperature history based on ER-2 measurements. The simulation was initialized on 10 February, and the ozone loss during the mid-February to mid-March

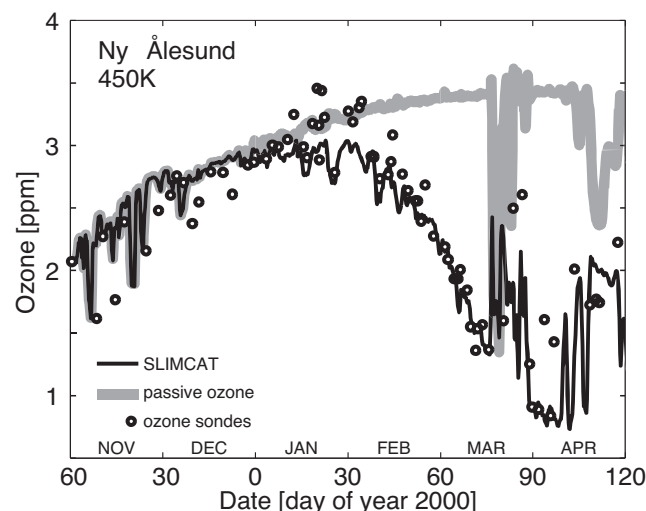


Figure 3-37. Ozonesonde measurements at Ny Ålesund (79°N) compared with the SLIMCAT three-dimensional transport model output for Ny Ålesund at the 450-K isentropic level. Ozone loss is indicated by the difference between the SLIMCAT's passive tracer (gray line) and SLIMCAT's ozone output (black line). Adapted from Sinnhuber et al. (2000).

period (up to 60% at 425 to 450 K) agrees roughly with estimates from observations.

The various 3-D model studies focusing on winter 1999/2000 reveal a consistent picture. The ozone loss after mid-February is well reproduced if the degree of denitrification in the model is correct, whether by coincidence as in Sinnhuber et al. (2000) or because it was specified from observations as in Grooß et al. (2002). Currently, 3-D CTMs are not able to reliably reproduce observed denitrification. This deficit limits the current ability to reliably reproduce the degree of ozone loss in cold Arctic winters.

3.3.5.2 SPECIFIC MODEL STUDIES

Several modeling studies using box models were conducted to compare specific ozone loss observations with model results and test our understanding of the chemical processes involved in the loss. These calculations are performed specifically for the air masses in which the ozone losses have been observed. Hence, the temperature and solar zenith angle history in these studies are much more constrained than in comparisons of vortex-averaged ozone losses. Becker et al. (1998, 2000) performed box model simulations along the trajectories of the Match dataset for 1991/1992 and 1994/1995. This analysis is illustrated in Figure 3-38, which compares the

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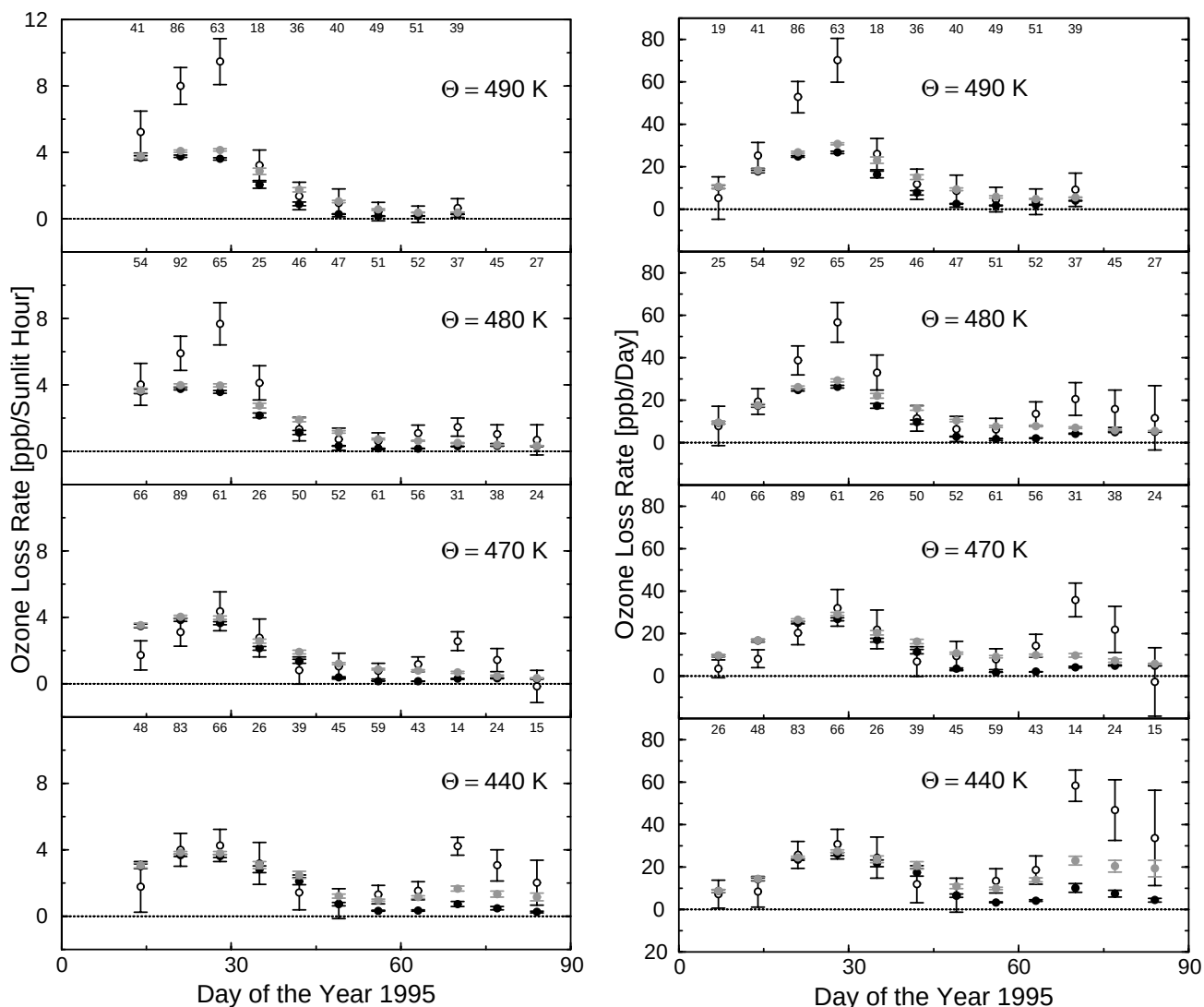


Figure 3-38. Time dependence of the ozone loss rates per sunlit hour (left panels) and the ozone loss rates per day (right panels) at various potential temperature levels in the 1994/1995 Arctic winter. Results of the Match analysis (open black circles) are compared with model results obtained with denitrification (solid gray circles) or without denitrification (solid black circles). Each point was deduced from Match trajectories with less than a ± 7 -day time interval and a ± 10 -K potential temperature interval. The number of matches contributing to each point is specified at the upper edge of each panel. The error bars correspond to the 1σ uncertainty of the linear regression.

ozone loss rates derived from simulations along the Match trajectories with the corresponding Match results at four potential temperature levels between 440 and 490 K for the winter of 1994/1995. It shows that the model underestimates the ozone losses observed by Match in late January by up to a factor of 2 above 475 K. During the other months, the observed losses are also underestimated by the model but within the large uncertainties of the model, mainly linked to the extent of denitrification. Match ozone loss rates were also compared with

SLIMCAT simulations for the winters of 1994/1995 and 1995/1996 (Kilbane-Dawe et al., 2001). The study suggests that Match may have overestimated the ozone loss rates above 525 K in January 1995 because of deficiencies in the ECMWF wind fields close to the top level of the ECMWF assimilation model (the top level has shifted to higher levels since then). In January 1995 at levels below 525 K and in January 1995/1996, SLIMCAT generally underestimated Match ozone loss rates by about 30 to 50%. It was found that the SLIMCAT photochemistry

was least able to reproduce observed ozone losses when low temperatures coincide with high solar zenith angles.

Woyke et al. (1999) used the tracer relation approach to quantify ozone loss in air masses that had been probed by a balloon payload providing observations of ClO, BrO, ozone, and long-lived tracers, on 3 February 1995. They used box model runs constrained by ClO and BrO concentrations observed by the balloon, to calculate the ozone loss throughout January along the back trajectories of the air masses. Using this highly constrained approach, they could explain only half of the observed ozone loss.

These results confirm that ozone losses observed during cold Arctic Januaries are currently not understood.

3.3.6 Quantifying Antarctic Ozone Loss

As emphasized in Section 3.1, Antarctic ozone depletion has been monitored by ground-based and satellite measurements since the mid-1980s. However, relatively few recent studies have concentrated on a detailed quantification of Antarctic ozone loss rates with state-of-the-art approaches to separate chemical loss from dynamical impacts. Hence, our quantitative knowledge of Antarctic ozone loss rates has not been as extensively tested as in the Arctic. The quantification of the accumulated overall ozone loss in the Antarctic is not challenging, because by the end of the winter, ozone is basically completely lost in a broad vertical region.

Hofmann et al. (1997) quantified Antarctic ozone loss from the analysis of 10 years of ozonesonde measurements at the South Pole and made recommendations for the detection of the recovery of the Antarctic ozone. Indicators for recovery include an end to springtime ozone depletion at 22 to 24 km and a 12- to 20-km ozone partial column value of more than 70 DU on 15 September. Bevilacqua et al. (1997) used POAM II ozone observations above Antarctica to derive vortex average ozone loss rates in August and September from 1994 to 1996 in the 450- to 800-K potential temperature range. Significant loss of ozone was found over the whole three-year period, except in 1994, when ozone loss was not observed in August, due to the sampling of the POAM instrument. The largest loss rates were found in September 1996 where they reached 0.1 ppmv/d below 500 K. From the analysis of the temporal evolution of total ozone at the Faraday station together with model calculations, Roscoe et al. (1997) showed that the ozone chemical depletion starts in June at the sunlit vortex edge, and Waters et al. (1999) showed that enhanced abundances of ClO are observed on the sunlit edge of the Antarctic vortex by late May or early June. Ozone loss rates were evaluated above the Antarctic station of Dumont d'Urville (66.4°S, 140°E)

from ozonesonde and lidar measurements on an interannual basis (Godin et al., 2001). Interpretation of the data required careful analysis of PV-equivalent latitude to determine whether each observation was inside, in the edge or outside the vortex at different isentropic levels. Measurements inside the vortex showed complete ozone destruction from 400 to 500 K, with ozone loss rates reaching 0.06 ppmv/d in the late-August to September period.

3.3.7 Model Studies of Antarctic Ozone Loss

The few recent model studies of the Antarctic ozone loss generally point to an agreement between models and observations. The SLIMCAT model was used to study the austral stratosphere in winter and spring 1996 together with ozonesonde measurements from various Antarctic stations (Lee et al., 2000). The model shows very good agreement with measured ozone values, and both the model and observations show that chemical ozone depletion follows the edge of polar night with little mixing poleward until the terminator reaches 80°S. In a follow-up study, Lee et al. (2001) analyzed the isentropic transport processes within the Antarctic polar vortex. Their calculations indicate two distinct regions within the vortex: a strongly mixed vortex core and a broad ring of weakly mixed air that remains isolated from the core between late winter and midspring and where the ozone loss is not complete. This result has an implication for the recovery of Antarctic ozone, since a cooling of the stratosphere could enhance the ozone loss in the edge region and delay the ozone recovery. In another study of Antarctic ozone loss, Wu and Dessler (2001) tested the current understanding of polar ozone chemistry with MLS version 4 measurements of ozone and ClO. By comparing the observed ozone loss estimated from the MLS ozone evolution at 465 K with a modeled ozone loss inferred from the simultaneous ClO measurements and a fixed BrO mixing ratio, they find a good agreement between both methods. However, MLS version 5 data, which has a better vertical definition of the ClO profile, resulted in a significant reduction of the ClO concentrations at 465 K compared with the version 4 data that had been used in Wu and Dessler (2001). This reduction would lead to a reduction in the modeled ozone loss rate in Wu and Dessler (2001). A slight change in the ozone profile in MLS version 5 data compared with version 4 data would also reduce the ozone loss rate deduced from observations. A quantitative study would be required to assess how the conclusions of Wu and Dessler (2001) would change if MLS version 5 data had been used (see Appendix 3A for MLS data description).

3.3.8 Conclusion

Arctic chemical ozone losses during the last decade have been determined by a variety of approaches, and ozone loss rates are now better quantified in the Arctic than in the Antarctic. The uncertainty of state-of-the-art approaches to quantify Arctic ozone losses from ozone observations is below 20% for local losses between 400 and 550 K potential temperature and perhaps somewhat larger for total column loss estimates. Large interannual variability of the Arctic ozone loss, ranging from 0 to 70% loss at about 20 km for individual winters during the past decade, is driven by the variable extent of temperatures low enough for PSC formation in a given winter. Global CTMs reproduce a large fraction (60 to 100%, depending on the winter) of the observed ozone loss in the Arctic and its variability. The largest uncertainties are due to the current unrealistic representation of denitrification processes in 3-D CTMs and unexplained ozone losses during cold Arctic Januarys. These uncertainties currently prevent reliable predictions of future Arctic ozone losses in a potentially changing climate.

3.4 CAUSES OF POLAR STRATOSPHERIC TEMPERATURE TRENDS

3.4.1 Introduction

In the previous Assessment (WMO, 1999), it was recognized that the future development of the ozone layer does not depend just on changes in stratospheric halogen loading but also, very importantly, on a number of other factors connecting chemistry and climate. The observations of temperatures are discussed in Section 3.1.2, and the causes of trends in polar stratospheric temperatures are discussed here: the role of changes in well-mixed greenhouse gases (WMGHGs), ozone, water vapor, and aerosol particles are reviewed. Solar effects are also noted. The onset of low temperatures during the polar winter/spring, their duration, interannual variations, and the statistical significance of trends, over the past two decades, are issues that impact upon our knowledge of the chemistry-climate interactions and the detection and attribution of climate change in the polar stratosphere due to ozone and other greenhouse gases.

Observations, from radiosondes and satellites, have shown a general cooling of the polar lower stratosphere over the last few decades (WMO, 1999; Ramaswamy et al., 2001). For a number of reasons detection and attribution of temperature change in the lower stratosphere may be easier than at the surface (IPCC, 1996).

First, the observed temperature change in the stratosphere is large and the response time of the stratosphere is shorter, compared with the surface. There are relatively good satellite observations of both temperature and the important atmospheric constituents over the last few decades, corresponding to the timing of polar ozone depletion. There are also potentially fewer relatively uncertain mechanisms involved in stratospheric temperature change; many of the large and uncertain surface radiative forcings, such as the anthropogenic sulfate aerosol forcing, are expected to have a minimal effect on stratospheric temperatures. Further, the magnitude of the response in the stratosphere to a given mechanism has been shown to be reasonably well approximated by purely radiative processes, and therefore may be better quantifiable than the surface temperature response (Ramaswamy et al., 2001). However, the WMO (1999) ozone assessment acknowledged that the large variability of temperatures, particularly in the Arctic winter and spring, and a possible stratosphere-wide trend in stratospheric water vapor complicate the attribution issue. It is now recognized that ozone and WMGHG changes cannot be considered in isolation, and there is an increasing acknowledgement that it is important to attempt to quantify the feedbacks between temperature change, chemistry, and stratospheric dynamics, to understand better the stratospheric temperature response.

Since the previous Assessment there has been improved quantification of atmospheric constituent changes and development of more sophisticated stratospheric models, especially coupled chemistry-climate general circulation models. These have provided important insights into our understanding of polar temperature changes in the lower stratosphere.

This section uses the updated lower stratospheric high-latitude temperature trends (discussed in Section 3.1.2) and discusses the recent modeling efforts that have attempted to understand them. It concentrates on the analysis and understanding of past decadal-time-scale trends in the polar lower stratosphere; the upper stratospheric response is often more independent of latitude and is discussed in the global ozone chapter (Chapter 4).

3.4.2 Modeling Techniques

Several different types of model have been adopted for the study of stratospheric temperature change. Two types of commonly used models are briefly assessed here. Figure 3-39 compares the range of model results to observations, and Figure 3-40 shows individual model temperature trends.

3.4.2.1 FIXED DYNAMICAL HEATING (FDH) MODELS

Fixed dynamical heating (FDH) models and seasonally evolving fixed dynamical heating (SEFDH) models (WMO, 1999; IPCC, 2001) employ a method of calculating temperature changes using only a radiative transfer model. They have been shown to agree well with calculations using GCMs (Rosier and Shine, 2000; Ramaswamy et al., 2001), and, compared with these, they are generally faster and allow the use of more sophisticated radiative transfer schemes. In contrast to the FDH technique, SEFDH techniques include a calculation for the time evolution of temperature and have been shown to improve the temperature response in the high-latitude polar stratosphere, compared with GCM integrations (Forster et al., 1997; Rosier and Shine, 2000). This was a region where the equilibrium temperature response calculated with FDH models overestimated the cooling resulting from short-term polar ozone depletion. Both FDH and SEFDH techniques are unable to model the response of atmospheric dynamics.

3.4.2.2 GENERAL CIRCULATION MODELS (GCMs)

The GCM-Reality Intercomparison Project for SPARC (GRIPS) is currently performing an assessment of the performance of current middle-atmosphere GCMs (Pawson et al., 2000). Preliminary analysis of their results suggests that all models have a cold bias, at most levels in the troposphere and stratosphere, which may be indicative of errors in the radiative transfer, or input data (Pawson et al., 2000). This is particularly pronounced at the poles; one of the largest uncertainties remains the parameterization of small-scale gravity waves (see Sections 3.2.1.2 and 3.5.2.1). The upper boundary and vertical resolution may also be important for an accurate simulation (see Section 3.5.2.3). Because of large interannual variability, particularly in the Arctic temperatures (see Sections 3.1.2 and 3.5.2), either many transient integrations or many years of equilibrium experiments need to be performed for statistically significant trend calculations. It must be noted, however, that the real atmosphere has evolved through only one specific realization and that the global observational record spans only ~20 years. Experiments have been performed with both prescribed changes in atmospheric constituents and coupled chemistry-climate GCMs (discussed in more detail in Section 3.5). Although coupled chemistry-climate GCMs allow interaction between radiation, chemistry, and dynamics, they have two main drawbacks when attempting to attribute stratospheric temperature change to a particular cause. First, their complexity makes them

computationally expensive; it is therefore difficult to run them for long enough periods to produce statistically significant trends. Second, their simulation of the ozone change is imperfect; this is to be contrasted with GCMs that employ the ozone trends inferred from observations to determine the temperature response.

3.4.3 Causes of Polar Stratospheric Temperature Trends

This section assesses the role of different mechanisms on polar lower stratospheric temperature trends. A variety of recent model results are compared with the observed temperature trends (discussed in Section 3.1.2; see also Figure 3-9). Figures 3-39 and 3-40 summarize the findings for the lower stratospheric temperature response at 70°N and 70°S to (1) stratospheric ozone changes, (2) WMGHG changes, (3) combined changes in WMGHGs and stratospheric ozone changes, and (4) stratospheric water vapor changes. Annual and seasonal temperature trends are shown at pressures of 50 hPa and 100 hPa. Results are taken from studies by Ramaswamy and Schwarzkopf (2002), Rosier and Shine (2000; updated by M. Bourqui), Langematz et al. (2002), Smith (2001), Butchart et al. (2000), Shindell (2001), Austin (2002), Schnadt et al. (2002), and Forster and Shine (2002). Several factors affect the interpretation of the comparisons of the observations and model simulations presented in this section:

- (1) The satellite measurements comprise radiances from a range of altitudes. This introduces some uncertainty when model results at 50 and 100 hPa are compared with the satellite observations.
- (2) This section examines a single latitude belt in the polar regions where there is a large dynamical variability (see Figure 3-8).
- (3) The polar trends, especially for the winter/spring season, are influenced by the end-year considered for the analysis.

3.4.3.1 OZONE

The stratospheric cooling over Antarctica has been shown previously to be very well correlated with ozone losses (WMO, 1999; Randel and Wu, 1999a). Shine (1986) was the first to show that such a stratospheric cooling could be due to the direct radiative response of the ozone loss. GCM and radiative model studies since then have largely confirmed this early work (Mahlman et al., 1994; Ramaswamy et al., 1996; WMO, 1999). In the NH, studies have also found a correlation between

POLAR OZONE

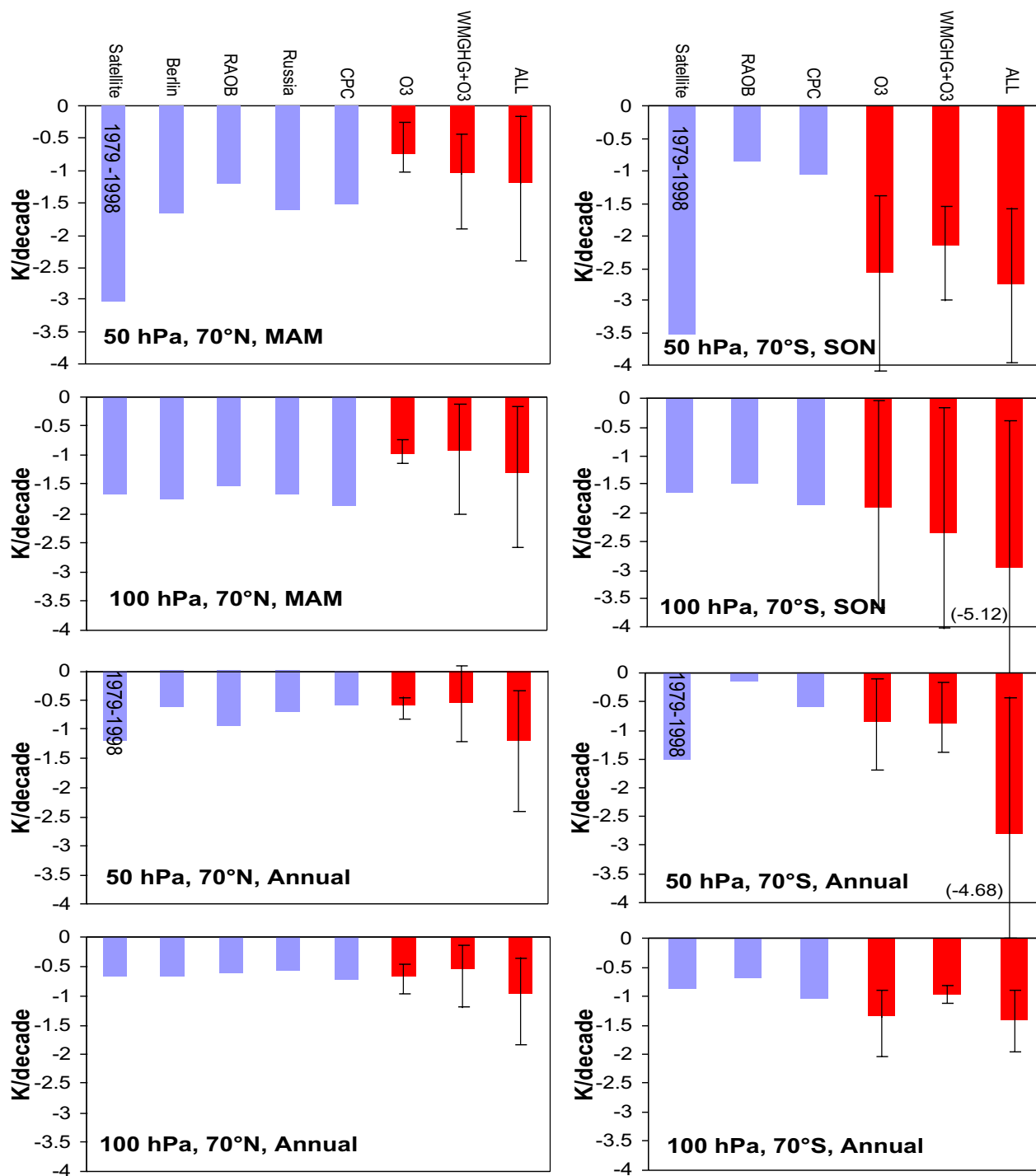


Figure 3-39. Comparison of observed and modeled temperature trends at 70°N and 70°S for the spring seasons and annual averages. Trends are presented at 50 hPa and 100 hPa. Observed trends are represented by blue bars and discussed in Section 3.1.2. All observed trends are significant at, at least, the 1σ level. The average modeled trends from Figure 3-40 are shown as the red bars with the range of model results illustrated by the black “uncertainty bars.” Model trends are shown for ozone changes alone, WMGHG and ozone changes, and “All,” where model estimates of the effects of stratospheric water vapor have been added to the WMGHG and ozone model trends. All observed trends are for 1979-2000 unless otherwise indicated (see Ramaswamy et al. (2001) for details regarding the observational datasets).

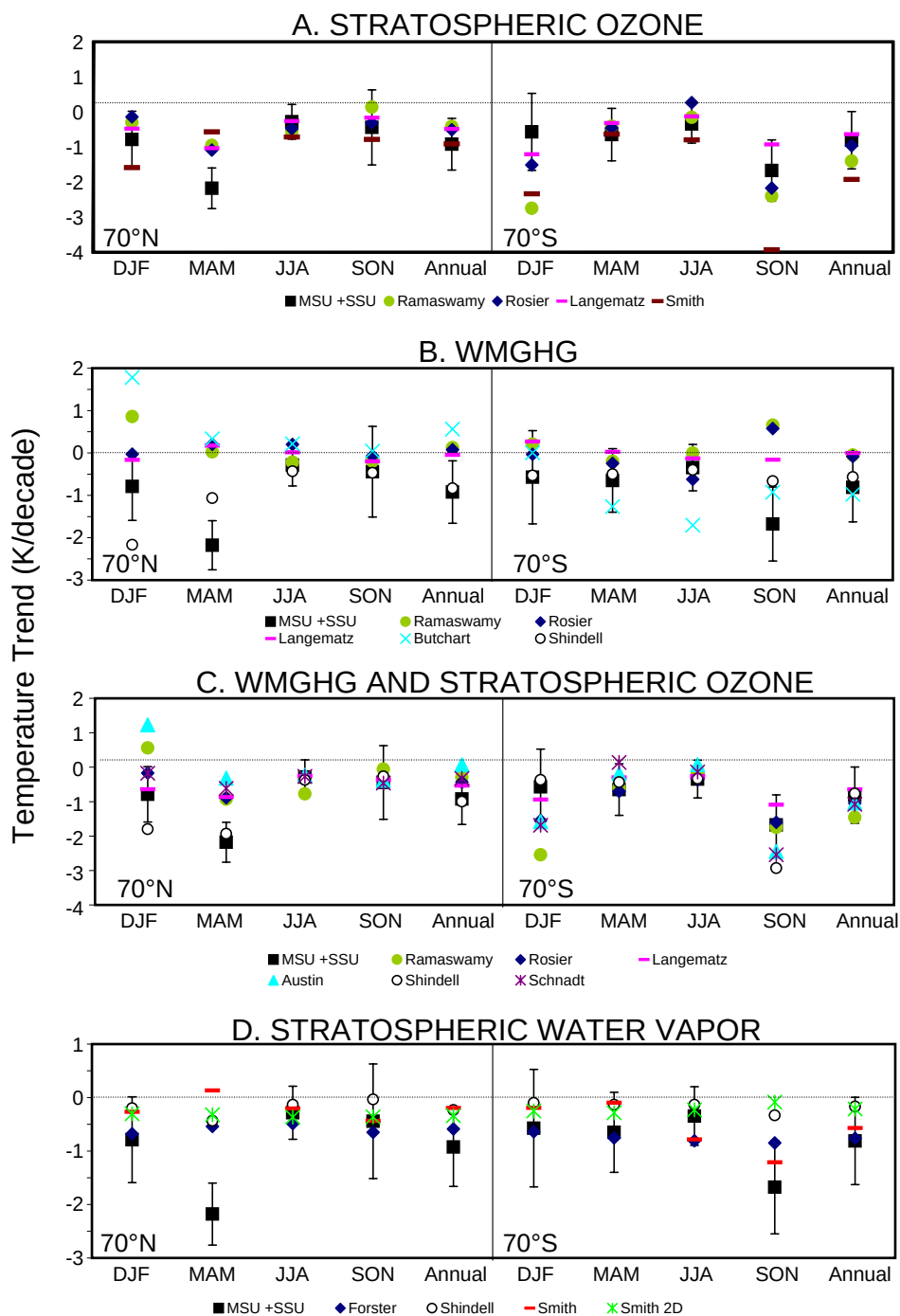


Figure 3-40. The seasonal and annual combined 50- and 100-hPa temperature trends at 70°N and 70°S, corresponding to one-third of the 50-hPa trend added to two-thirds of the 100-hPa trend, using the model-derived trends discussed in this section. The modeled temperature trends are for (a) stratospheric ozone changes; (b) WMGHG changes; (c) WMGHG and stratospheric ozone changes; and (d) stratospheric water vapor changes. On each panel, 2 error bars are plotted for the observed satellite trends, and the horizontal dotted lines indicate the zero trend. References for models are given in Section 3.4.3.

POLAR OZONE

springtime Arctic temperatures and ozone (WMO, 1999; Randel and Wu, 1999a). However, the correlations are not as strong, and the cooling observed during the Arctic winter is not expected from a simple radiative response to the ozone loss (Randel and Wu, 1999a). In addition, reductions of planetary wave driving reduce the strength of the residual circulation, leading to a cooling trend. This also weakens the transport of ozone-rich air to the polar lower stratosphere, and could give larger heterogeneous loss rates. Hence, a correlation of temperature and ozone does not necessarily imply a causal linkage of ozone loss with temperature.

Since the previous Assessment several studies have employed the monthly averaged vertical trend data, based on ozone observations over the period 1979 to 1997 (SPARC, 1998), with most studies employing the combined trend dataset of Randel and Wu (1999b). The results of these prescribed ozone change studies are shown Figure 3-40a for the NH (left panel) and SH (right panel). The calculations presented in the figure had the benefit of more detailed ozone-trend vertical resolution compared with previous work. The ozone dataset employs stratospheric-only trends derived from the Syowa (69°S) and Resolute (75°N) ozonesondes as representative of the polar regions. Figure 3-41 shows an illustration of the annual cycle of model-derived 100-hPa trends from the Berlin model and compares them with trends derived from reanalysis data. It is noted that trends from reanalysis data (Figure 3-41, panel c) must be interpreted with caution (Chapter 5 in WMO, 1999). The Antarctic and Arctic response are discussed separately below.

Antarctic

All model studies report an ozone-induced cooling at 70°S for most seasons, with the largest cooling in all models occurring in September, October, and November (SON) and December, January, and February (DJF) (right panel of Figure 3-40a). Langematz et al. (2002) and Ramaswamy and Schwarzkopf (2002) find that the largest cooling at 100 hPa occurs in DJF not SON (see Section 3.4.4). There is a dynamically induced heating in the middle atmosphere, which adds to the radiative heating owing to more upwelling longwave radiation initiated by the depletion of ozone in the lower stratosphere. This effect is simulated by several models (Kiehl et al., 1988; Mahlman et al., 1994; Ramaswamy et al., 1996; Rosier and Shine, 2000) and is consistent with observations (Ramaswamy et al., 2001), but it is not statistically significant, in either models or observations.

Compared with the observed trends, the Langematz et al. (2002) response underestimates the SON cooling at 50 hPa, but gives a better fit with the MSU-4 observations

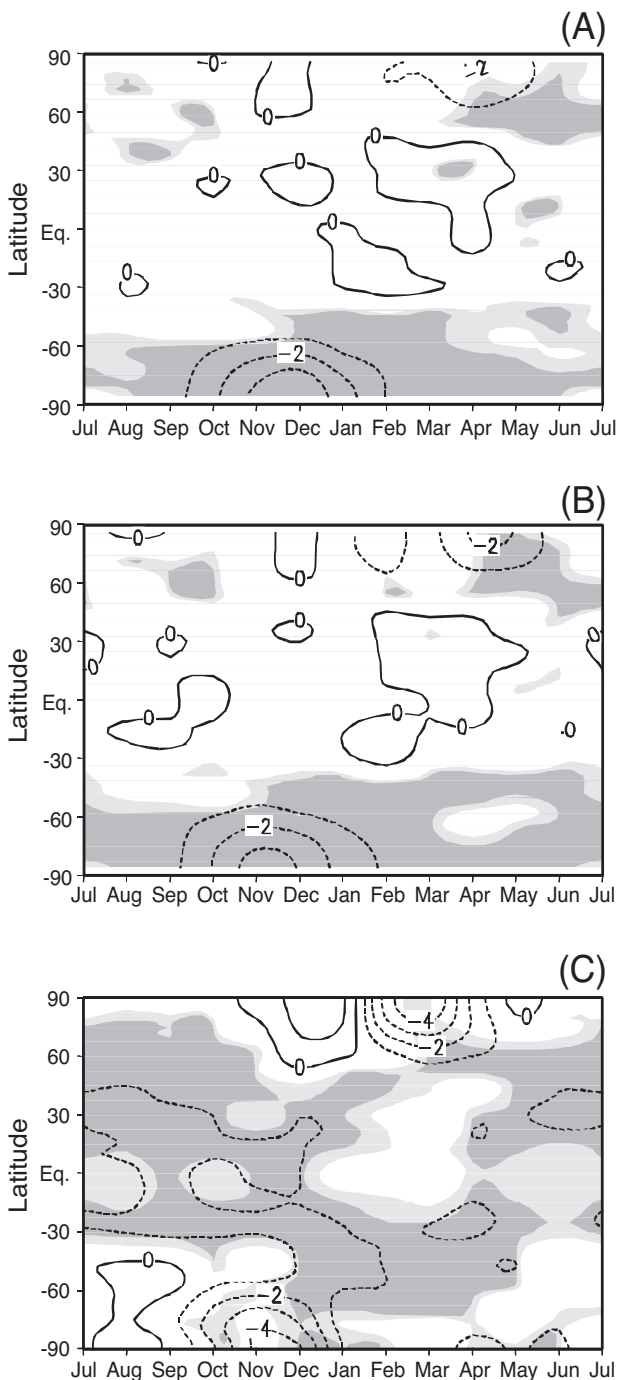


Figure 3-41. Annual cycle of the zonal-mean temperature trend (K/decade) at 100 hPa. (a) Model-derived trends employing the observed 1980 to 2000 ozone trend; (b) same as (a), but with an additional increase in CO₂; and (c) the corresponding 1980 to 2000 linear trend, derived from NCEP reanalysis data. The contour interval is 1.0 K/decade. Dark (light) shaded areas denote regions where the trend is significant at the 99% (95%) confidence level. Adapted from Langematz et al. (2002).

representative of 100 hPa. The other models tend to overestimate the observed spring and summer cooling at 100 hPa, particularly during DJF (see Section 3.4.4). Caution needs to be applied to this satellite-model comparison, because there are uncertainties with regard to the representation of the altitude profile of ozone loss in the models over the winter/spring period, and with regard to the interpretation of seasonal trends at 50 and 100 hPa from satellite data.

Two versions of the same model (Rosier and Shine, 2000, updated; Smith, 2001) produce substantially different trends in SON (Figure 3-40a). Both models are versions of the Reading Intermediate GCM performing 20-year equilibrium experiments. Differences between the simulations are also found in the Arctic (see below), which may imply a difference between the way the ozone trends are implemented and/or differences in the variability of the model.

Arctic

All four models in Figure 3-40a (left panel) find an annually averaged cooling in the Arctic. Three of the four models find the largest cooling in March, April, and May (MAM), which agrees qualitatively well with the satellite data. However, this modeled cooling is only about half the size of the cooling trend in the satellite data. Smith (2001), in contrast, finds a maximum cooling in DJF and smaller cooling in MAM, although differences again may be due to the large variability in the Arctic winter and are of limited significance. When comparing trends, Graf et al. (1998), Waugh et al. (1999), Langematz et al. (2002), and Ramaswamy and Schwarzkopf (2002) make the important point that the large natural variability in the Arctic may mean that the modeled and observed trends are not easily compared (see Figure 3-8).

3.4.3.2 WELL-MIXED GREENHOUSE GASES (WMGHGs)

In general, considering their radiative effects only, WMGHG increases are expected to have a much smaller effect on lower stratospheric temperatures than they do on temperatures above 30 hPa (Forster and Shine, 1997; WMO, 1999; Chapter 4 of this Assessment; Ramaswamy and Schwarzkopf, 2002). This is borne out by the results presented in Figure 3-40b for the NH (left panel) and SH (right panel). The Langematz et al. (2002) trend was derived for CO₂ changes only and has been estimated by taking the difference between the results of their stratospheric-ozone-and-WMGHG experiment and those of their stratospheric-ozone-only experiment. The same

method has been adopted in connection with the Ramaswamy and Schwarzkopf (2002) results. This is in contrast to the updated Rosier and Shine (2000) study where WMGHG effects were studied directly. Few of the modeling studies show significant temperature trends. Some models are seen to cool their annual-mean lower stratospheres in response to WMGHG increases. The magnitude of cooling (~0.3 K/decade) agrees with earlier FDH calculations (e.g., Ramaswamy et al., 2001). For further discussion on the role of WMGHGs in annual-mean trends see Chapter 4.

3.4.3.3 COMBINED CHANGES IN WMGHGs AND STRATOSPHERIC OZONE

Since the previous Assessment (WMO, 1999) several experiments with coupled chemistry-climate models have been performed for different time periods to simulate the combined effect of changes in ozone and WMGHGs. These experiments are discussed in more detail in Section 3.5. Here we only examine how the coupled chemistry-climate modeling studies influence the attribution of high-latitude temperature trends. Results from four coupled chemistry-climate experiments are presented in Figure 3-40c. Temperature trends are also shown for two different prescribed WMGHG and ozone experiments and the updated Rosier and Shine (2000) result, where individual ozone and WMGHG trends have been added.

Antarctic

The agreement between the different models in Figure 3-40c (right panel) is encouraging considering (1) the range of different models employed; (2) the differences between the responses, for models employing the same ozone trend dataset (Section 3.4.3.1); and (3) the large uncertainty in trends derived from transient integrations. Because the overall effect of WMGHG changes on lower stratospheric temperatures is minimal (annual-mean results in Section 3.4.3.2), there is little difference with respect to the annual-mean temperature trends from the stratospheric ozone experiments. Therefore, for all seasons the observed cooling can be explained by either combined WMGHG and stratospheric ozone changes or stratospheric ozone changes alone (see Figure 3-39). Most of the coupled chemistry-climate models and Ramaswamy and Schwarzkopf (2002) tend to overestimate the observed 50- to 100-hPa cooling in SON, although most results are still within the observational uncertainty range. Most of the models presented in Figure 3-40c (right panel) were found to simulate both the annual-mean and SON

POLAR OZONE

change at 50 hPa reasonably well, while all overestimated the 100-hPa trend (not shown). Austin (2002) found that the discrepancies in their model were consistent with systematic biases in the vertical profile of the applied ozone loss. Generally, the models capture Antarctic springtime cooling, but further improvements are needed to simulate the magnitude of the cooling and its vertical extent.

Arctic

The models for the Arctic, like those for Antarctica, are generally consistent with the observed trends, and inter-model differences are generally smaller than the 2σ uncertainty in the observations (left panel of Figure 3-40c). At 50 to 100 hPa, all models underestimate the MAM cooling, which could indicate (1) an underestimate of the ozone-related cooling; (2) a contribution of a missing effect, such as increases in stratospheric water vapor; or (3) an underestimate of the role of natural variability. Some models yield a warming in DJF that is in contrast to the observations, although this may be statistically insignificant in models. In the annual mean, only one of the models (a coupled model) is close to the observations; the rest underestimate the observed cooling.

3.4.3.4 STRATOSPHERIC WATER VAPOR

Since the previous Assessment, a major development has been the burgeoning interest in the role of stratospheric water vapor. Increases in stratospheric water vapor that are roughly twice the expected increase from methane oxidation have now been measured by satellite and ground-based observing systems (see Chapter 4 of this Assessment; Rosenlof et al., 2001; SPARC, 2000). Several recent papers have examined the consequences of this increase for stratospheric temperatures (see Figure 3-40d).

The study of Forster and Shine (1999) used an oversimplified representation of the water vapor change, in both the perturbation and background stratospheric water values (Forster and Shine, 2002) and, perhaps, in its radiative transfer scheme (Oinas et al., 2001). In general, inadequacies of broadband radiative transfer codes are readily accounted for (see Forster et al., 2001; Forster and Shine, 2002). Since the Forster and Shine (1999) study, Smith (2001) (see also Smith et al., 2001) used trends derived from HALOE data over the period 1992 to 1999 to represent better the water vapor change (see also Appendix 3A for HALOE data descriptions). Likewise, Forster and Shine (2002) used an improved representation of the background water vapor and a simulated +1-ppmv water vapor increase, derived from SPARC (2000) data. Shindell

(2001) also modeled the effect on increases in stratospheric water vapor, from methane oxidation, using a coupled chemistry-climate GCM. Although large uncertainties in the water vapor trend remain, these studies indicate a possible cooling of more than 0.5 K/decade at 70°N and 70°S, comparable with that due to ozone (Figure 3-40a). Given the present level of uncertainty in the observational trend analysis and notwithstanding the contribution of WMGHGs and stratospheric ozone to the cooling, one cannot rule out a significant effect due to stratospheric water vapor. There is an indication that a water vapor contribution is required for a quantitative accounting of the observed polar cooling (also see the discussion in Chapter 4).

3.4.3.5 SOLAR CHANGES

Following on from work discussed in the reviews of WMO (1999) and Ramaswamy et al. (2001), van Loon and Labitzke (2000) correlate the solar cycle with stratospheric temperatures and find that the “response” of the Arctic stratosphere depends on the phase of the QBO. During solar maximum, easterly phases of the QBO coincide with a cooler Arctic stratosphere, whereas westerly phases of the QBO give a warmer stratosphere. A model simulation (Cubasch and Voss, 2000) was unable to simulate this response, although their model did not include a modulation of ozone with ultraviolet radiation. Inclusion of this feedback affects the Arctic temperature response (Haigh, 1999; Larkin et al., 2000). Both these modeling studies found a warmer wintertime Arctic stratosphere during solar maximum. Recent studies with coupled chemistry-climate models (Williams et al., 2001; Labitzke et al., 2002) find increased sensitivity of lower stratospheric ozone to the solar cycle, compared with earlier modeling experiments, giving greater consistency with observations (see also EC, 2001). Generally, the latest modeling studies indicate a possible influence of the solar cycle on high-latitude temperatures. However, any effect is still too uncertain to quantify and remains somewhat speculative.

3.4.3.6 VOLCANOES

In the last 20 years the two large volcanic eruptions of Mt. Pinatubo and El Chichón created significant amounts of aerosol in the low-latitude stratosphere. Although several simulations show a low-latitude stratospheric warming, the response at high latitudes is less certain (WMO, 1999). Ramachandran et al. (2000) simulated the Mt. Pinatubo eruption in a GCM and found that the dynamical response to the aerosol forcing led to an

annually averaged cooling at high latitudes of up to 2 K for the 2 years following the eruption. Ramaswamy et al. (2002b) find that the high-latitude simulations of Mt. Pinatubo aerosol effects are affected substantially by the initial conditions in the model ensemble integrations. Timmreck et al. (1999) also found that volcanic aerosol caused a stronger Arctic vortex. Although both model and observations in the Mt. Pinatubo case indicate that polar effects were not statistically significant, the suggestion remains that volcanic eruptions may have contributed to the observed high-latitude stratospheric cooling. Following a volcanic eruption, enhanced ozone loss is expected from heterogeneous chemical reactions on the volcanic aerosol (see WMO, 1999). This ozone loss would cool the stratosphere. Pawson et al. (1999) postulate a stepwise decrease in stratospheric temperatures following volcanic eruptions that may be connected with changes in heterogeneous ozone chemistry (Solomon et al., 1998).

3.4.4 Timing of the Springtime Cooling Trend

Observational evidence shows that the maximum springtime stratospheric cooling trend occurs at roughly the same time as a maximum ozone loss (March in the NH and October–November in the SH (e.g., Randel and Wu, 1999a; see also Figure 3-9). However, most modeling studies of ozone loss and simple radiative arguments would suggest that the maximum cooling lags the ozone loss in the lower stratosphere by a month or more (see Figure 3.41a,b; see also Forster et al., 1997; Ramaswamy et al., 2001; Langematz, 2000; Rosier and Shine, 2000; Graf et al., 1998; Langematz et al., 2002). For example, in Antarctica a number of the models show approximately similar cooling trends in SON and DJF for their stratospheric ozone experiments (Figure 3-40). This is especially true of the 100-hPa level, where radiative relaxation times are longer. The NCEP reanalysis also hints at this feature (Figure 3-41, panel c). This feature is not observed in the satellite record. Graf et al. (1998) investigated whether WMGHG increases could compensate for this lag and found that they could not, at least in their model. Ramaswamy and Schwarzkopf (2002) find that the effects due to ozone and WMGHG over the period 1980 to 2000 in the northern polar region are swamped by the dynamical variability seen in both model and observations. The finding is probably true of the other models (Figure 3-40). Graf et al. (1998) further suggested that the discrepancy could be due to an incorrect modeling of the dynamical response and concluded that, until reasons for this are adequately resolved, it represents a problem in the attri-

bution, of particularly the Arctic cooling, to an anthropogenic cause.

3.4.5 Summary and Conclusions

Generally, modeling studies now demonstrate that the springtime cooling in the Arctic lower stratosphere over the 1980 to 2000 period is, in part, due to stratospheric ozone depletion, but the degree of attribution is hindered by the large dynamical variability in this region. In Antarctica, modeling studies reaffirm that ozone loss is the major cause of the springtime cooling. They also indicate that WMGHG and stratospheric water vapor increases are likely contributors to the annually averaged cooling.

For combined changes in stratospheric ozone and WMGHGs there is generally a reasonable agreement between the various modeling studies; inter-model differences are generally smaller than the uncertainty in observations (the 1σ uncertainty in the observations, if plotted on Figure 3-39, would be substantially larger than the plotted model error bars, which indicate the inter-model range). Including the effects of stratospheric water vapor in models improves the comparison with observations (the “All” scenario of Figure 3-39). However, there is still a large spread in model results, especially for the spring seasons. For the annual mean temperature change, both the agreement between models and the agreement between the satellite and sonde-based observations are encouraging (see Figure 3-39 and Chapter 4).

In summary the cooling of the springtime high-latitude stratosphere is likely influenced to a substantial extent by various mechanisms (WMGHG increases, ozone loss, stratospheric water vapor increases, volcanic eruptions, and natural variability). Attribution of polar temperatures is hampered by the large variability in the polar vortices (see Figure 3-8). This variability not only increases the uncertainty of observational trend analyses, but it also means that either many years of equilibrium studies or many ensemble integrations are needed for reliable statistics. Further, it implies that model studies performed under equilibrium conditions may be inadequate for examination of polar trends, especially in the Arctic, over a time period of two decades. At present, 20 years of an equilibrium GCM run are barely sufficient to resolve temperature changes in the Arctic winter. This would imply that 20-plus-member ensembles would also be needed for transient integrations. Comparison between observations and models, or between different models, is also complicated by uncertainty in the vertical profile of ozone loss, which leads to uncertainty in the temperature response. In models that simulate the chemistry, this

POLAR OZONE

uncertainty could be larger than in those models that prescribe the ozone loss from observations. These coupled-chemistry models are discussed in the next section.

3.5 CHEMICAL-CLIMATE MODELING OF THE PAST AND FUTURE POLAR STRATOSPHERE

3.5.1 Introduction

Section 3.3.2 shows that, while there has been halogen-induced chemical ozone loss in many recent Arctic winters, the extent of this chemical loss in a given year is determined by the meteorological conditions, with severe ozone loss in the colder winters and essentially no loss in the warmer winters. Thus, low temperatures are required to initiate wintertime chemical ozone loss in the Arctic, and the time series of Arctic ozone shown in Figure 3-2 reflects the changes in meteorology much more than it does the changes in halogen loading. This understanding is consistent with the conclusion of Section 3.4.3 (see also Rosier and Shine, 2000; Langematz, 2000) that the observed decrease in Arctic temperature over the last two decades cannot be explained just as a radiative response to the observed ozone decrease (although there is a contribution), and must have occurred for some other reason. In this respect the Arctic is quite different from the Antarctic. In the Antarctic, wintertime temperatures are low enough to initiate severe chemical ozone loss every year, and meteorological variability provides only a small modulation of this loss. The time series of Antarctic ozone shown in Figure 3-2 therefore primarily reflects changes in halogen loading, and the observed late-spring cooling and increased persistence of the Antarctic vortex are understood to be a radiative response to the observed ozone decrease (Section 3.4.3). That this Antarctic cooling is less than the observed Arctic cooling, despite the fact that Antarctic ozone losses are much greater than those in the Arctic, provides further confirmation that the Arctic cooling is a driver of the Arctic ozone decreases (in the presence of anthropogenic halogens), rather than being a response to them.

The difference between the past behavior of Arctic and Antarctic ozone has implications for the future evolution of polar ozone. In the Antarctic, meteorological conditions are so far past the threshold for severe chemical ozone loss that neither natural meteorological variability nor WMGHG-induced climate change are expected to change this situation over the coming decades. Thus, future Antarctic ozone levels are expected primarily to reflect the anticipated decrease in stratospheric halogen loading, as they have reflected the observed increase in

halogen levels in the past. (There is the possibility of more sensitivity for aspects of Antarctic ozone that are closer to threshold conditions, such as ozone losses at the edge of the vortex or in early summer; these may be of more importance for UV impacts than minimum column ozone amounts.) In the Arctic, on the other hand, our expectation for future ozone changes depends on our attribution of the past changes, and in particular on the cause of the observed Arctic cooling over the past two decades. If this cooling represents a forced response to WMGHG changes, then we would expect it to continue in the future and Arctic ozone levels would be expected to decrease further in spite of the decreasing halogen loading. If, on the other hand, the observed cooling represents natural variability, then anything is possible in the future; chemical ozone loss in the Arctic could be essentially zero for the next decade, or it could be severe.

The implication of the above considerations is that we cannot expect future Arctic ozone abundances to follow stratospheric halogen loading, apart from the obvious fact that halogen-induced chemical ozone loss can be expected to become negligible when halogen levels become negligible. Instead, the evolution of Arctic ozone abundances (which reflect both chemistry and transport) will be determined primarily by the evolution of meteorological conditions. In the Arctic, those meteorological conditions are largely determined by dynamical processes (Section 3.2.1), and the effects of WMGHG changes on the lower stratospheric Arctic vortex over the past and through the next few decades are expected to mainly arise from dynamical feedbacks, rather than from direct radiative forcing (Section 3.4). Therefore, in order both to attribute past behavior and predict future behavior of Arctic ozone, it is necessary to use models that are capable of representing those dynamical feedbacks together with a prognostic representation of ozone, namely, coupled chemistry-climate models.

It is important to appreciate what such models can and cannot do. In this respect there is a notable contrast with the CTMs used in Section 3.3. CTMs specify the meteorological conditions (winds and temperatures), and predict the resulting chemical ozone loss without addressing the issue of why those conditions occurred. This prediction is essentially deterministic, because the chemical equations are essentially deterministic; we expect to capture the exact chemical ozone loss on a particular day, within the uncertainties of the calculation. Coupled chemistry-climate models specify the radiative and chemical forcing (WMGHGs, halogens, surface conditions) and predict the resulting state of the chemistry-climate system. However, since the climate system is chaotic and exhibits unforced variability, this prediction

is only stochastic, not deterministic; we do not expect to capture the exact state of the chemistry-climate system on a particular day, or even in a particular year. Therefore, the comparison between such models and observations requires careful thought. On the other hand, chemistry-climate models allow one in principle to draw unambiguous conclusions about the attribution of past changes, and they are the only tool available for prediction of future changes that includes all physical feedbacks.

There are two distinct strategies for assessing the response of a chemistry-climate model to chemical or radiative forcing. The traditional approach is to perform simulations under fixed conditions (so-called “timeslice” experiments) and compare the differences in equilibrium climate resulting from the different forcings. The advantage of this approach is that the simulations can, in principle, be run for a sufficiently long time to obtain good statistics on the differences, which is useful for understanding mechanisms and feedbacks. In this way the unforced variability inherent in the climate system is dealt with explicitly, albeit in an idealized manner. The second approach is to perform simulations under changing conditions (so-called “transient” experiments) over a particular period of time. The advantage of this approach is that it permits a more direct comparison with the real atmosphere, where the forcings are evolving continuously in time. Because of unforced variability, two realizations of the same transient experiment will not evolve in exactly the same way, and an ensemble of experiments is generally required in order to determine a statistically reliable signal.

Yet no matter how good a chemistry-climate model is and how well its climate-change experiments are characterized, the real atmosphere exhibits only a single realization. The best one can expect, even for a perfect model, is that the observations fall within the range of model-predicted behaviors, according to appropriate statistical criteria. Whether this permits a meaningful prediction depends on the relative magnitudes and time scales of the forced signal and the natural noise. As discussed above, we expect the evolution of Antarctic ozone over decadal time scales (past and future) to be a fairly predictable signal, but it is not at all clear whether this is the case in the Arctic. It is known that there is strong interannual variability in the Arctic, extending to multidecadal time scales; even timeslice experiments require several decades of integration to obtain reliable statistics for basic diagnostic quantities (Scaife et al., 2000b). Thus, it is not a priori obvious that even a perfect chemistry-climate model should be able to reproduce the long-term decreases of Arctic ozone observed over the past 20 years, for example.

Chemistry-climate models for stratospheric ozone are probably the most advanced of all chemistry-climate models, but they are still being developed. Early timeslice experiments were performed by Austin et al. (1992) and Pitari et al. (1992) to examine the question of how Arctic ozone might evolve under the conditions of doubled CO_2 expected toward the end of the 21st century, if large halogen abundances were to persist until that time. The results were contradictory, with the former study predicting severe Arctic ozone loss and the latter study predicting only a slight reduction; this at least demonstrated the sensitivity of the response. In the previous Assessment (WMO, 1999, Chapter 12), many of the conclusions were based on the transient experiment of Shindell et al. (1998a), which examined the combined effects of anticipated increasing WMGHGs and decreasing halogens, and predicted increasingly severe Arctic ozone loss over the next couple of decades resulting from Arctic cooling. The stated mechanism for this severe cooling was the dynamical feedback from WMGHG changes, and this represents the key question for the Arctic: namely, are the dynamical feedbacks resulting from WMGHG-induced temperature changes expected to enhance or to reduce the direct radiative stratospheric cooling?

Since the previous Assessment, a number of coupled chemistry-climate models have been developed and run, so there is now considerably more information available than at that time (see Austin et al., 2002). Although these models have improved representations of many processes, they still have many deficiencies, and computational constraints also place severe limitations on the experimental configurations; transient experiments are generally performed singly, not as part of an ensemble, and timeslice experiments are often too short to adequately characterize their variability. In this report, the strategy is therefore adopted of combining the results of the different models, whether the experiments are timeslice or transient, the working assumption being that the differences between the models cover the range of model errors. In this way a current best estimate is obtained of the attribution of past ozone changes in the polar stratosphere and the prediction of future changes over the next half-century.

The models used in the comparisons are indicated in Table 3-3, in order of decreasing horizontal resolution (see Austin et al., 2002). Università degli Studi dell’Aquila (ULAQ) is the only model with a substantial aerosol package and it has reasonably detailed chemistry, albeit diurnally averaged. This model has been run in timeslice mode. Of the other models run in this mode, the Canadian Middle Atmosphere Model (CMAM) and the Middle Atmosphere European Centre Hamburg Model

Table 3-3. Models used in the comparisons. The resolution is given in either degrees latitude $\times$ degrees longitude (grid point models), or as T21, T30, and T32, which are the resolutions in spectral models corresponding to triangular truncation of the spectral domain with 21, 30, and 32 wave numbers, respectively. IS92a refers to scenario IS92a of IPCC (1992), and WMO refers to the halogen scenario indicated in Chapter 11 of WMO (1999).

Model	Horizontal Resolution	No. Levels/ Upper Boundary	GHG/ Halogen Scenarios	Reference
UMETRAC	$2.5^\circ \times 3.75^\circ$	64/0.01 hPa	IS92a/WMO	Austin (2002) (Rayleigh friction version)
CMAM	T32	65/0.0006 hPa	Observations, IS92a/WMO	de Grandpré et al. (2000)
MAECHAM/ CHEM	T30	39/0.01 hPa	IS92a/WMO	See details in Austin et al. (2002)
E39/C	T30	39/10 hPa	IS92a/WMO	Schnadt et al. (2002)
UIUC	$4^\circ \times 5^\circ$	25/1 hPa	Observations	Rozanov et al. (2001)
CCSR/NIES	T21	30/0.06 hPa	IS92a/WMO	Takigawa et al. (1999); Nagashima et al. (2002)
GISS	$8^\circ \times 10^\circ$	23/0.002 hPa	IS92a/WMO	Shindell et al. (1998b)
ULAQ	$10^\circ \times 20^\circ$	18/1 hPa	IS92a/WMO	Pitari et al. (2002a)

(ECHAM) with Chemistry (MAECHAM/CHEM) have reasonably detailed chemistry and a high upper boundary (0.01 hPa and above), while the University of Illinois at Urbana-Champaign (UIUC) model and the ECHAM model with chemistry run at DLR (E39/C) have a much lower upper boundary (1 hPa and below). The Unified Model with Eulerian Transport and Chemistry (UMETRAC), Center for Climate System Research (University of Tokyo)/National Institute for Environmental Studies (Japan) (CCSR/NIES), and GISS have been run in transient mode; UMETRAC and CCSR/NIES have reasonably detailed chemistry, whereas the GISS model has parameterized chemistry.

3.5.2 The Uncertainties in Chemistry-Climate Models

3.5.2.1 TEMPERATURE BIASES

As noted in Section 3.4.2.2, many climate models without chemistry but with a fully resolved stratosphere have a cold bias of the order of 5 to 10 K over Antarctica in the lower stratosphere. This suggests that their residual circulations are too weak (Pawson et al., 2000), i.e., there is too little downwelling in high latitudes and too little upwelling in low latitudes. This cold bias would significantly impact model heterogeneous chemistry and

enhance ozone destruction. The “cold-pole problem” extends to higher stratospheric levels, causing a polar night jet that is too strong and too vertically oriented, whereas the observed polar night jet slopes with height toward the equator in the upper stratosphere. The weaker jet and vertical slope allow waves to propagate into higher latitudes and maintain higher polar temperatures. A potentially important component of climate change is whether these waves will be stronger in the future, since this will likely affect the evolution of ozone (see Section 3.5.2.4). A practical solution applied in some models with a cold bias is to increase the temperatures in the heterogeneous chemistry routines (e.g., Austin et al., 2000) by a fixed amount (e.g., 5 K). The strong polar night jet is also associated with a polar vortex that breaks down later in the spring, particularly in the SH. In a chemistry-climate model this can lead to ozone depletion that continues for longer than observed.

Gravity waves generated by processes other than orographic forcing (e.g., convection) are thought to play an important role in the momentum balance of the stratosphere. Non-orographic gravity wave drag (gwd) schemes have now been developed for climate models (e.g., Medvedev and Klaassen, 1995; Hines, 1997a, b; Warner and McIntyre, 1999), and their use has resulted in a significant reduction in the cold-pole problem relative to simulations that rely on Rayleigh friction to decelerate the

polar night jet (e.g., Manzini and McFarlane, 1998). Two of these schemes have also been shown to produce a QBO when run in a climate model (Scaife et al., 2000a). The latest versions of several coupled chemistry-climate models now employ such schemes: CMAM uses the Medvedev-Klaassen scheme (Medvedev et al., 1998) or the Hines scheme (McLandress, 1998); UMETRAC uses the Warner and McIntyre scheme; and MAECHAM/CHEM uses the Hines scheme (see Austin et al., 2002). The GISS GCM has used a non-orographic gravity wave drag scheme for many years (Rind et al., 1988a, b), which is able to reproduce high-latitude temperatures reasonably well (Shindell et al., 1998b) but does not simulate a QBO in the tropics.

Figure 3-42 shows model temperature biases as a function of height for 80°N and 80°S, which are representative of the polar regions, for the winter and spring seasons. To determine the biases, a 10-year temperature climatology determined from UKMO data assimilation fields (Swinbank and O'Neill, 1994) was subtracted from the mean model temperature profiles applicable to the 1990s. The UKMO temperatures are considered to be about 2 K too high at low temperatures (e.g., Pullen and Jones, 1997; Manney et al., 2002; Pommereau et al., 2002; Knudsen et al., 2002), but this bias is smaller than typical model biases. The upper stratospheric cold-pole problem is particularly noticeable in the south in the UMETRAC (with Rayleigh friction), CCSR/NIES (which also uses Rayleigh friction), and MAECHAM/CHEM results. In the results of the UIUC and ULAQ models, a warm bias is present. For the ULAQ model this is likely to be due to the inclusion of vertical diffusion (in addition to Rayleigh friction). As seen in the UMETRAC results, the winter and spring polar temperature bias can be dramatically reduced by the use of non-orographic gwd. Both UMETRAC and CMAM have very similar biases, within a few K of each other in the seasons investigated. The MAECHAM/CHEM model, which uses the Hines non-orographic gwd scheme, is only a slight improvement on the Rayleigh friction results of UMETRAC and CCSR/NIES. The E39/C model is very similar to the MAECHAM/CHEM model, and gives similar results below 30 hPa, but does not have a non-orographic gwd scheme. At 80°N, temperature biases are somewhat smaller than at 80°S and are sometimes positive. The northern lower stratospheric temperature biases would generally lead to insufficient heterogeneous ozone depletion in early winter but excessive ozone depletion in the more important spring period. In the SH, spring cold biases could lead to more extensive PSCs than observed and delayed recovery in Antarctic ozone.

Some indication of the source of the model temperature biases in the lower stratosphere is given by Figure 3-43, which shows the zonal mean heat flux [$v'T'$] at 100 hPa averaged over the domain 40° to 80°N for January and February plotted against temperature averaged at 50 hPa over the domain 60° to 90°N for February and March. As argued by Newman et al. (2001), the heat flux at 100 hPa is indicative of the wave forcing from the troposphere, and this is highly correlated with lower stratospheric temperature slightly later in the year. Newman et al. (2001) chose a 1-15 March temperature average, but here we choose a longer period for the temperature average to smooth model and atmospheric transients. The model results (Figures 3-43 and 3-44) are in general agreement with observations. Table 3-4 shows results of the linear regression between the two variables (see table caption for explanation of the terms T_0 and β). The results indicate that horizontal resolution may have affected the model results; in general the model regression lines were less steep (smaller β in Table 3-4) as the model resolution decreased, particularly in the NH. This could be because low-resolution models capture the low-amplitude-wave, small-heat-flux case, but have difficulty capturing the large-heat-flux case with its significant potential enstrophy cascade to larger wave numbers. The performance of the models might also depend on the dissipation that the models have at short spatial scales, although this is more difficult to compare. The values of β are generally much smaller in the SH, except for the CCSR/NIES and CMAM models. The implication of these results is that models need higher resolution and non-orographic gwd schemes to improve the relationship between heat flux and temperature in order to reduce their polar temperature biases.

3.5.2.2 THE SIMULATION OF POLAR STRATOSPHERIC CLOUDS

PSCs have a significant impact on stratospheric ozone depletion in polar regions, and recent developments in their understanding are discussed in detail in Carslaw et al. (2001) and in Section 3.2.2. Coupled chemistry-climate models have a variety of PSC schemes with and without sedimentation, but such models have in some cases large climatological temperature biases in the polar regions, as indicated in Section 3.5.2.1. If the models are to be effective, the temperature field must give realistic distributions near the PSC temperature thresholds.

The areal coverage of PSCs provides a model comparison diagnostic. We use the temperature at 50 hPa as an indicator of likely PSC amounts, and ignore the effect of HNO_3 and sulfate concentrations on the determination

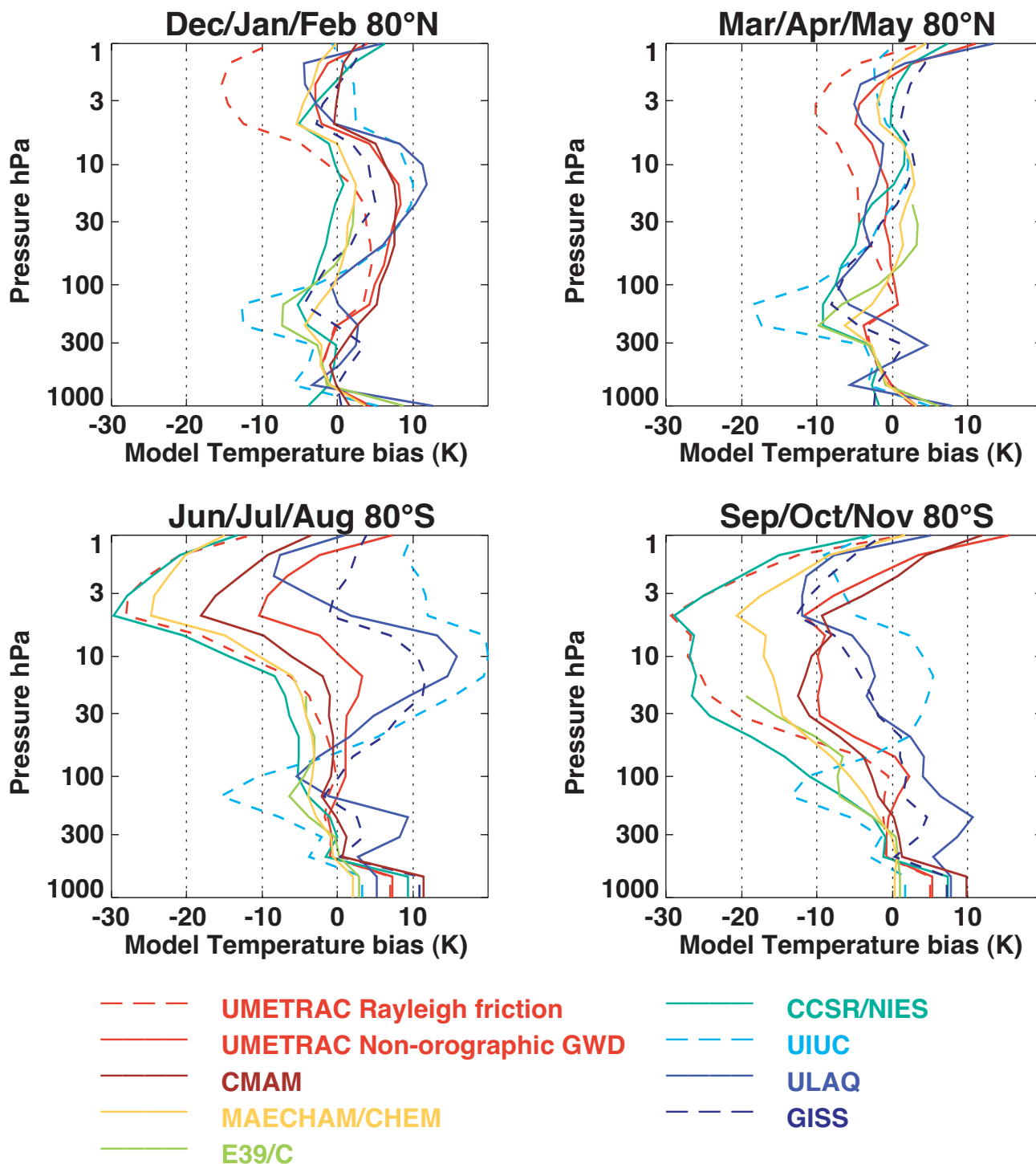


Figure 3-42. Model temperature biases at 80°N and 80°S for the winter and spring seasons, as a function of pressure. To determine the bias, a climatology determined from 10 years of UKMO data assimilation temperatures was subtracted from the model results.

of PSC surface areas (following Pawson and Naujokat, 1997; and Pawson et al., 1999). Figure 3-45 shows for the models and observations the time integral throughout the winter of the PSC area at 50 hPa (A_T). A_T is the sum

throughout the winter of the PSC area (expressed as % fraction of the hemisphere) at 50 hPa. For the ice amount, A_T varies dramatically in the Arctic, between zero and 70% of the hemisphere times days. The models have large

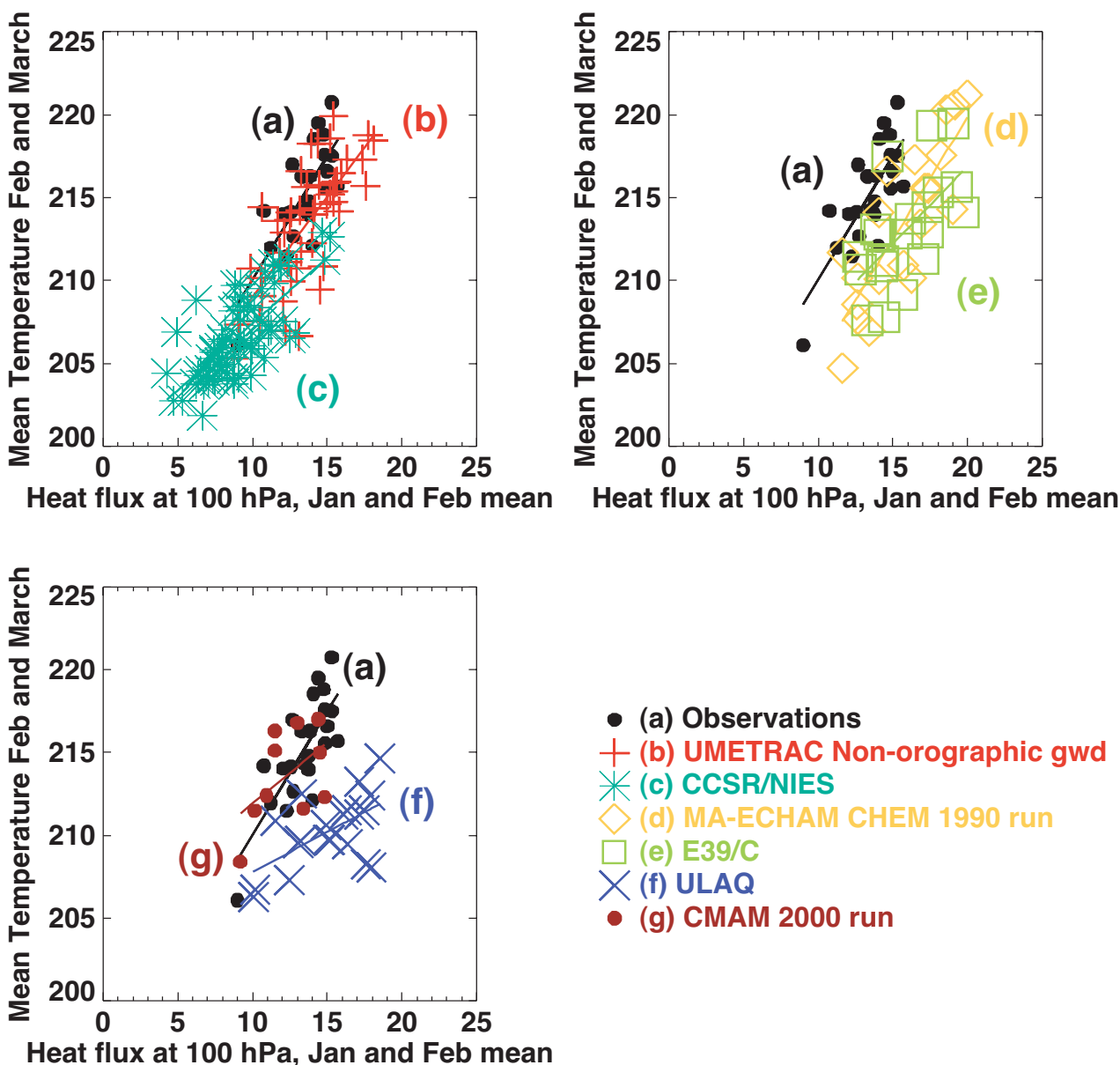


Figure 3-43. Scatter diagrams of the longitudinally averaged (zonal-mean) heat flux (K m/s, averaged for 40° to 80°N, at 100 hPa for January and February) versus temperature (K, averaged for 60° to 90°N, at 50 hPa for February and March) for participating models. The solid lines are linear regression lines between the two variables. The observations are taken from NCEP data.

interannual variability. Arctic NAT also covers a large range, both for different models and in the interannual variability for each simulation. In accordance with their temperature biases, several models have larger areas of NAT than are typically derived from observations. The ULAQ PSCs are in good agreement with observations in both hemispheres, despite a slight positive temperature bias, whereas UMETRAC and CMAM have lower PSC

areas in the Arctic than are derived from observations. In the Antarctic each model has much lower fractional interannual variation for both NAT and ice, but again the results for separate models cover an exceedingly large range for the ice amount. Clearly, the differences between different models will have a profound impact on the amount of chemical ozone depletion calculated. This will be discussed further in Section 3.5.3.

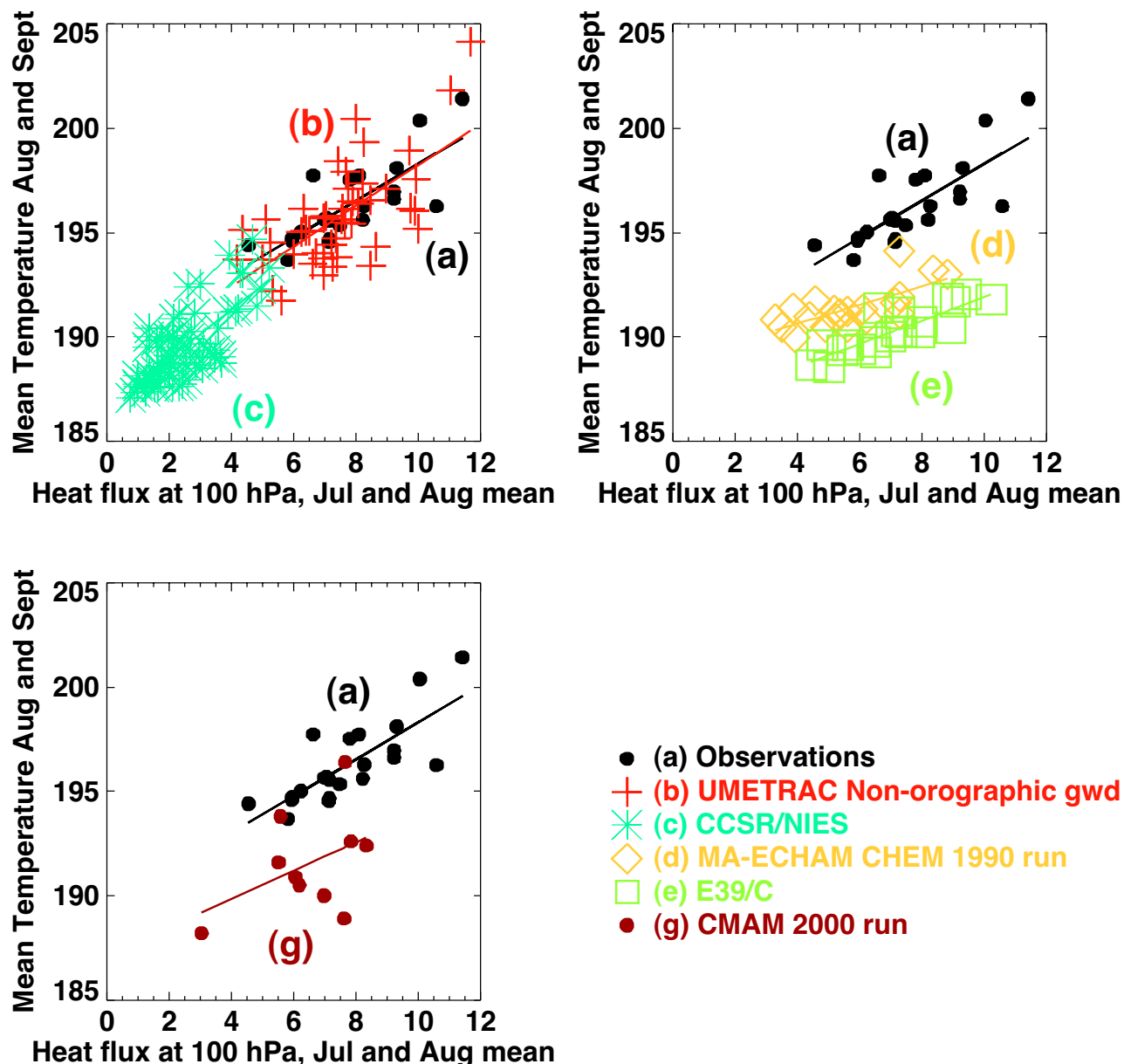


Figure 3-44. As in Figure 3-43, but for heat flux at 40° to 80°S, at 100 hPa for July and August, and temperature at 60° to 90°S, at 50 hPa for August and September.

3.5.2.3 THE POSITION OF THE UPPER BOUNDARY OF THE GCM

There is strong evidence from a number of modeling studies (Garcia and Boville, 1994; Shepherd et al., 1996; Lawrence, 1997; Austin et al., 1997; Rind et al., 1998; Beagley et al., 2000) that the position of the model upper boundary can play a significant role in influencing transport and stratospheric dynamics due to the “downward control principle” (Haynes et al., 1991). The sensitivity of the dynamical fields to the position of the upper

boundary may be larger when non-orographic gwd schemes are used than when Rayleigh friction is used. However, if all the non-orographic gwd that is produced above the model boundary is placed instead in the top model layer, assuming that the upward-propagating waves are not simply absorbed in the top layer, this sensitivity reduces (Lawrence, 1997). Model simulations with an upper boundary as low as 10 hPa have been completed (e.g., Schnadt et al., 2002; Hein et al., 2001; Dameris et al., 1998). Schnadt et al. (2002) show the meridional circulation of the Deutschen Zentrum für Luft- und

Table 3-4. Statistical analysis of the linear regression between the area-averaged temperature (K) at 50 hPa poleward of 60°N for February and March in the NH and 60°S in August and September in the SH, and the heat flux (K m/s) at 100 hPa between 40° and 80°N for January and February in the NH and 40° and 80°S for July and August in the SH. R is the correlation coefficient between the variables, T_0 is the intercept of the line at zero heat flux, and β is the gradient of the line. For ULAQ results in the Southern Hemisphere, the heat flux and temperature are not correlated.

Model/Observations	Northern Hemisphere			Southern Hemisphere		
	R	T_0	β	R	T_0	β
NCEP (observations)	0.77	195.1	1.49	0.78	189.4	0.89
UMETRAC non-orographic gwd	0.74	196.9	1.21	0.66	188.5	0.98
Rayleigh friction	0.67	196.2	1.21	0.51	187.7	0.67
CMAM 2000	0.52	204.5	0.75	0.44	187.2	0.68
MAECHAM/CHEM 1990	0.79	196.3	1.10	0.70	190.0	0.50
E39/C	0.62	198.3	0.93	0.86	186.3	0.56
CCSR/NIES	0.74	199.4	0.80	0.74	186.6	1.17
ULAQ	0.58	203.0	0.48	—	—	—

Raumfahrt (DLR) model. This gives the expected upward motion from the summer hemisphere and downward motion over the winter hemisphere, although modeled meridional circulations are known to extend into the mesosphere (e.g., Butchart and Austin, 1998). Schnadt et al. (2002) argue that it is less important to have a high upper boundary, but more important to have high resolution in the vicinity of the tropopause. At present the evidence appears ambiguous; for example, in the total ozone presented by Hein et al. (2001), insufficient ozone is transported to the North Pole, but there is excessive subtropical ozone transport. This could be related to the cold-pole problem, rather than the position of the upper boundary. While the transport effect on ozone is direct, other considerations are the transport of long-lived tracers such as NO_y and water vapor that have a photochemical impact on ozone. Consequently, it is generally recognized that the upper boundary should be placed at least as high as 1 hPa (e.g., Rozanov et al., 2001; Pitari et al., 2002b); many models are now placing their boundary at about 0.01 hPa (e.g., Shindell et al., 1998b; Austin et al., 2001; Nagashima et al., 2002). In comparison, CMAM (de Grandpré et al., 2000) has an upper boundary somewhat higher (~ 0.0006 hPa) to allow a more complete representation of gwd to reduce the cold-pole problem (Section 3.5.2.1) and to simulate upper atmosphere phenomena.

3.5.2.4 PREDICTIONS OF PLANETARY WAVES

The direct radiative cooling by greenhouse gases at high latitudes in the lower stratosphere causes an increase in the strength of the polar vortex. Planetary wave changes may be a feedback that strengthens or weakens this effect. One proposed planetary wave feedback mechanism (Shindell et al., 2001) works as follows: tropical and subtropical sea surface temperatures increase, leading to a warmer tropical and subtropical upper troposphere via moist convective processes. This results in an increased latitudinal temperature gradient at around 100 to 200 hPa, leading to enhanced lower stratospheric westerly winds that refract upward, propagating tropospheric planetary waves equatorward. This results in a strengthened polar vortex.

The E39/C results (Schnadt et al., 2002) also show a small decrease in planetary wave activity for the period 1960 to 1990. However, results for future simulations differ depending on the model. Without chemical feedback, the Unified Model (UM) (Gillett et al., 2002) predicts a future increase in overall generation of planetary waves, which leads to a greater wave flux to the Arctic stratosphere, and is even able to overcome the radiatively induced increase in the westerly zonal wind so that the overall trend is to weaken westerly flow. This also occurs in the DLR model with chemical feedback (Schnadt et al.,

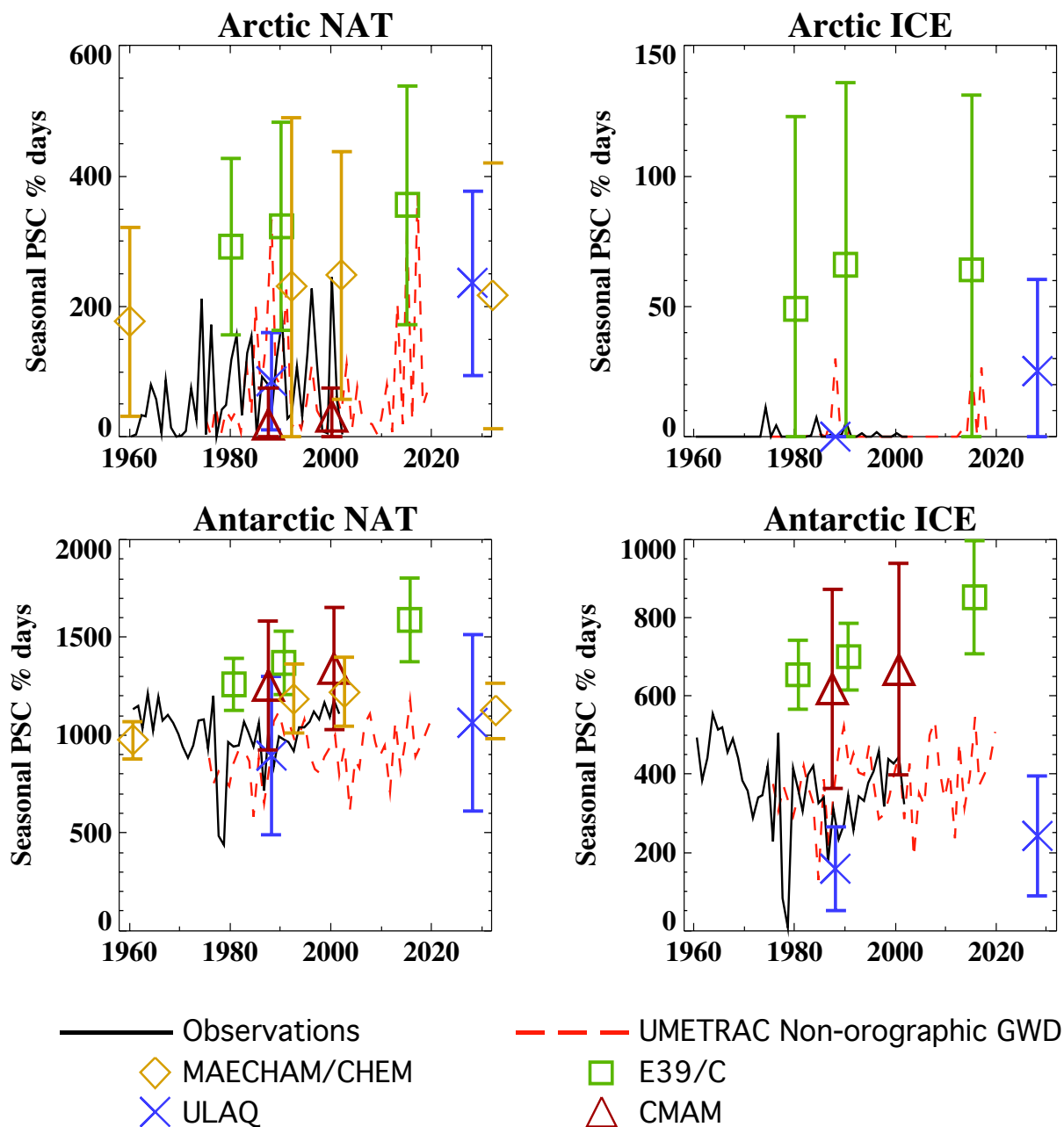


Figure 3-45. Time integral of the percentage area of the hemisphere at 50 hPa covered by temperatures below 195 K (approximate NAT temperature) and below 188 K (approximate ICE temperature) during winter and spring. The error bars for the timeslice runs indicate 95% confidence intervals. For clarity, ULAQ data are plotted 2 years early, and MAECHAM CHEM data for 1990 and 2030 are plotted 2 years late.

2002), whereas in the UM with chemical feedback (UMETRAC) the trend in the heat flux during the period 1975 to 2020 is downward but is not statistically significant. The Center for Climate System Research/National Institute for Environmental Studies (CCSR/NIES) model, of lower resolution than UMETRAC, has systematically

lower heat fluxes but does show a downward trend during the period 1986 to 2050 that is marginally statistically significant. In general, the strengthening of the polar vortex appears to be critically dependent upon the relative importance of changes in wave generation versus wave propagation. These changes are likely to be highly model and

resolution dependent, resulting from the particular wave forcing and drag schemes employed in each climate model. To some degree this sensitivity of the changes in planetary waves to the model simulation reflects similar sensitivities in the atmosphere: for example, in the observations of the last five northern winters, four have been warm with a weaker polar vortex (see Section 3.1.2 and Figure 3-8). As a result, the strengthening of the vortex over the last 20 years noted by some authors (Tanaka et al., 1996; Zurek et al., 1996; Waugh et al., 1999; Hood et al., 1999) will have been modified by recent events.

3.5.2.5 STRATOSPHERIC WATER VAPOR CHANGES

Observations of atmospheric water vapor concentrations have revealed significant increases over the period 1964 to 2000 (Oltmans and Hofmann, 1995; Oltmans et al., 2000; Rosenlof et al., 2001). As discussed further in Chapter 4, these increases are uncertain in magnitude and their causes have not been established.

Increased water vapor directly affects ozone chemistry. It also alters local temperatures by radiative cooling, slowing down the reaction rates of ozone depletion chemistry, which indirectly leads to more ozone. Evans et al. (1998), Dvortsov and Solomon (2001), and Shindell (2001) have studied the effects on homogeneous chemistry. The models all show that increases in water vapor reduce ozone in the upper and lower stratosphere, and increase ozone in the middle stratosphere. The model results differ most in the lower stratosphere where the largest impact on total ozone column occurs. In the model of Evans et al. (1998), lower stratospheric ozone is reduced only in the tropics when water vapor increases, whereas in the other models, ozone reductions extend to midlatitudes or to the poles. Thus, the models of Dvortsov and Solomon (2001) and Shindell (2001) show a slower ozone recovery by about 10 to 20 years, and a 1-2% reduction during the next 50 years due to water vapor increase, assuming that the water vapor increase continues at the current rate. The Evans et al. (1998) model disagrees with these results, presumably due to differences in that model's temperature response to increasing water, which seems to dominate over the chemical impacts.

Water vapor increases also affect heterogeneous chemistry, enhancing the formation of PSCs (see Section 3.2.2). Kirk-Davidoff et al. (1999) calculated a significant enhancement to Arctic ozone loss in a more humid atmosphere. Much of this effect was based on a very large estimate of 6 to 9 K per ppmv radiative cooling induced by increased water vapor. This value has been superseded by newer results showing that the value is almost certainly much smaller, about 1.5 to 2.5 K cooling per ppmv of

water (Section 3.4.3.4). This would in turn imply a reduced role for water vapor in enhancing PSC formation. Tabazadeh et al. (2000) showed that the enhancement of PSC formation due to the addition of 1 ppmv of water vapor is approximately the same as the PSC enhancement due to cooling of about 1 K. This suggests that the radiative impact of water vapor is larger than its effects on chemistry or microphysics but that all these processes should be considered in numerical models. Given the potential for denitrification in the Arctic, and the large ozone losses that could result from a slight cooling there (Tabazadeh et al., 2000), it is important both to understand trends in stratospheric water vapor and to resolve model differences in the radiative impact of those trends.

Model simulations of past water vapor trends do not agree well with observations. In UMETRAC (Austin, 2002), water vapor increases by only about 1% per decade in the stratosphere, despite the inclusion of a methane oxidation scheme. In UMETRAC, the tropical tropopause temperature decreases slightly, counteracting the methane impact. In E39/C (Schnadt et al., 2002), water vapor increases in the lower stratosphere are significantly larger (about 3% per decade) but are still about a factor of 2 to 3 lower than observed. Similar results are also obtained in the GISS model. In general the modeled water vapor trend tends to be driven by methane oxidation and trends in tropical tropopause temperatures, suggesting the need to investigate the microphysics of dehydration and how this is represented in models. (See also Section 4.3.3 of EC (2001).)

3.5.3 Model Assessments

In the Arctic the processes leading to stratospheric ozone depletion may undergo too much natural variability to provide a definite answer to how ozone will actually evolve. Each model may be considered as supplying a single simulation (or range of simulations in the case of the timeslice experiments) of a larger ensemble. Although the mean of the ensemble can be readily computed, the atmosphere may in practice evolve in a manner anywhere within, or even outside, the envelope of the model simulations. In the Antarctic, the dominant processes are less dependent on interannual variability and, hence, the ozone evolution is in principle more predictable.

One of the emphases here has been on spring ozone recovery. In view of the range of results obtained, it is important to define this term carefully. It is here used in two senses: (1) the start of ozone recovery, defined as the date of the minimum spring column ozone as a function of year in the decadal averaged results, and (2) full ozone recovery, defined as the date of the return of the decadal averaged spring column ozone to the value obtained in 1980.

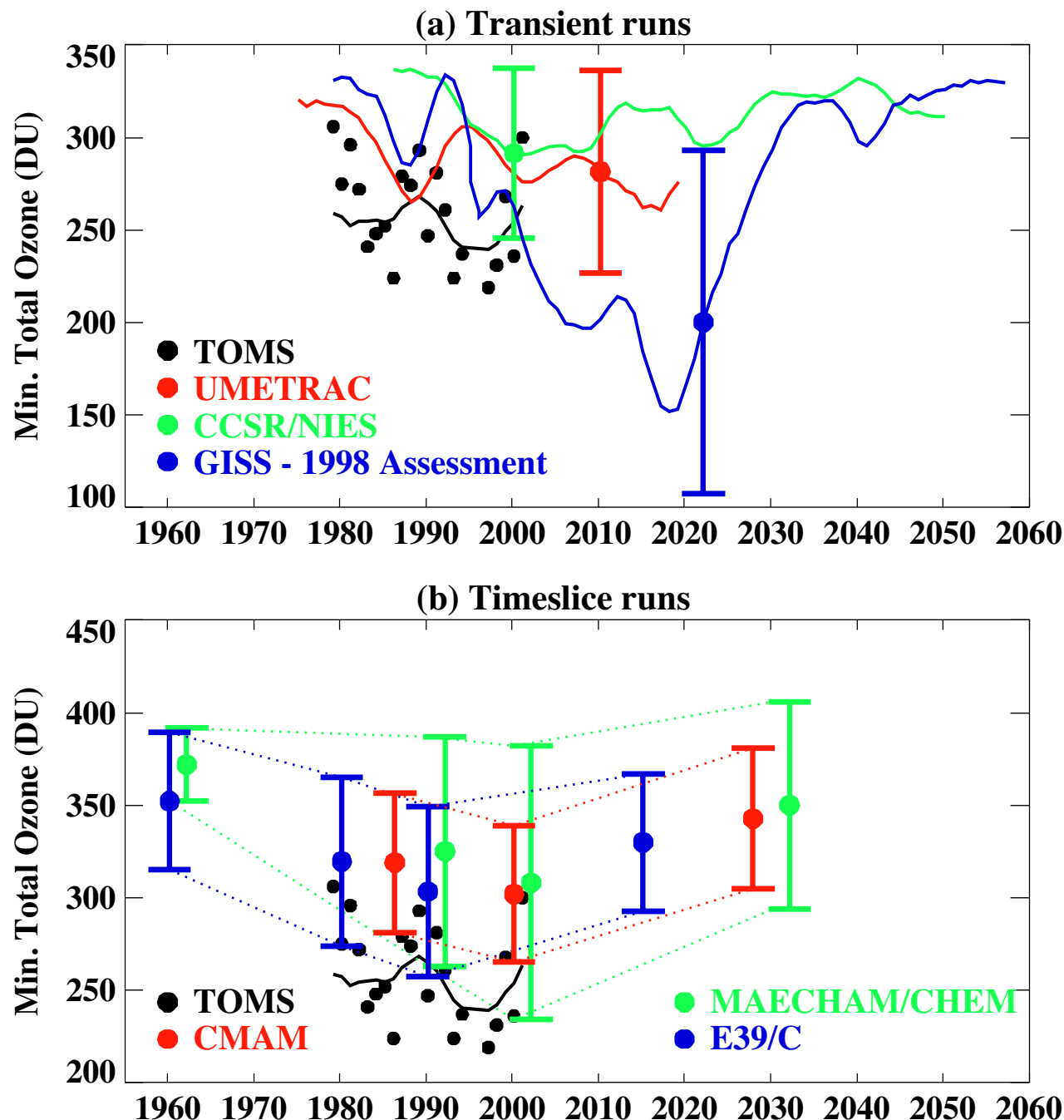


Figure 3-46. Minimum Arctic (March/April) total ozone for the main experiments of this Assessment. (a) Transient runs in comparison with TOMS data. The solid lines show the results of a Gaussian smoothing applied to the individual year's results. The error bars denote twice the standard deviation of the individual years from the smoothed curve. Results from the previous Assessment (the GISS model) are included for comparison. (b) Timeslice runs in comparison with TOMS data. The colored circles and the error bars denote the mean and twice the standard deviation of the individual years within each model sample (10 years for CMAM, 20 years for MAECHAM/CHEM and E39/C). Dotted lines are drawn between the end points of the error bars to assist in estimating trends by eye. For MAECHAM/CHEM only: (1) the values have been plotted 2 years late for clarity, and (2) a standard tropospheric column of 100 DU has been added to the computed stratospheric columns.

3.5.3.1 THE 1960-2000 TIME FRAME: OZONE DEPLETION

As is well established from observations (Section 3.1.1), polar ozone has been decreasing over the last few decades. Figure 3-46 shows the minimum daily ozone throughout the range 60° to 90°N for several of the models of Table 3-3 together with TOMS data. The GISS results are included to provide a comparison with the state of knowledge at the time of the previous Assessment (WMO, 1999). For clarity, the models are separated into two panels according to their mode of simulation (transient or timeslice). For the transient models, a Gaussian low-pass filter is fitted through the results for the individual years, and the error bars denote two standard deviations from the Gaussian filtered curve. For the timeslice experiments, the mean and two standard deviations are plotted, and the dotted lines give an indication of the temporal behavior of the model results. Each model has a large interannual variability, similar to that of the observations, and, hence, detecting a signal is difficult. All the models indicate a slight high bias relative to observations. The trends in the minimum (Table 3-5) are consistent with the observations, although only E39/C, MAECHAM/CHEM, and the observations have statistically significant trends. Averaging the five model results obtained since the previous Assessment gives an Arctic trend that is statistically significant and agrees with observations.

In the Antarctic (Figure 3-47, upper panel), the model runs agree reasonably well with observations for the past and show the steady development of the ozone hole during the period. However, the calculated trends (Table 3-5) depend on the period chosen. CMAM indicates a small trend because the ozone hole was already partially formed in 1987 and the CMAM values for 2000 are higher than observed. The mean trend of the latest five model simulations (Table 3-5) is slightly lower than observed, but if the latest reaction rates for the ClO dimer production (Bloss et al., 2001) had been used, the agreement would have been further improved. While the interannual variability of most of the models is similar to that observed, both CMAM and UMETRAC have a large interannual variability. In the case of UMETRAC, this may to some extent be a product of the non-orographic gwd scheme.

The maximum size of the Antarctic ozone hole during each spring, as given by the area within the 220-DU total ozone contour, is shown in Figure 3-47 (lower panel). The results for GISS, E39/C, and CCSR/NIES are in good agreement with observations, but may indicate a slight underprediction. A much smaller ozone hole is simulated by UMETRAC, but recent model runs with a

revised NO_y distribution consistent with observations show an ozone hole about 50% larger for 1995, which is in close agreement with observations. The size of the ozone hole area for CMAM reflects the bias and large interannual variability noted in Figure 3-47 (upper panel). Errors in the modeling of the size of the ozone hole can have important implications. First, comparisons between models and observations for ozone amounts near 60°S will give poor agreement if the ozone hole area is too small, even though the underlying physics of the model may be correct. Second, a model with a smaller ozone hole may evolve differently from that of the atmosphere due to transport and chemistry effects relating to radiative effects.

3.5.3.2 THE 2000-2020 TIME FRAME: START OF OZONE RECOVERY

The first signs of ozone recovery are expected within the next two decades (Shindell et al., 1998a; Austin et al., 2000; Schnadt et al., 2002; Rosenfield et al., 2002; Nagashima et al., 2002). Two-dimensional (2-D) model simulations (e.g., Rosenfield et al., 2002) indicate a slight delay in Arctic and Antarctic spring ozone recovery following the maximum values in halogen loading. The

Table 3-5. Past trends (1979-2000) in minimum ozone (DU/decade) with 2 σ error bars for participating models and TOMS. The MAECHAM/CHEM results cover the period 1960-2000 (Arctic) and 1960-1990 (Antarctic); the E39/C (ECHAM model with chemistry run at DLR) results cover the period 1960-1990 (Arctic) and 1980-1990 (Antarctic); the CCSR/NIES model results cover the period 1986-2000; and the CMAM results cover the period 1987-2000.

Model/Observations	Northern Trend	Southern Trend
UMETRAC	-6 $\pm$ 22	-80 $\pm$ 31
CMAM	-13 $\pm$ 27	-23 $\pm$ 28
MAECHAM/CHEM	-16 $\pm$ 10	-45 $\pm$ 3
E39/C	-16 $\pm$ 14	-64 $\pm$ 7
CCSR/NIES	-33 $\pm$ 38	-41 $\pm$ 21
Mean (this Assessment)	-17 $\pm$ 12	-51 $\pm$ 11
GISS (1998 Assessment)	-21 $\pm$ 34	-34 $\pm$ 12
TOMS	-21 $\pm$ 16	-59 $\pm$ 12

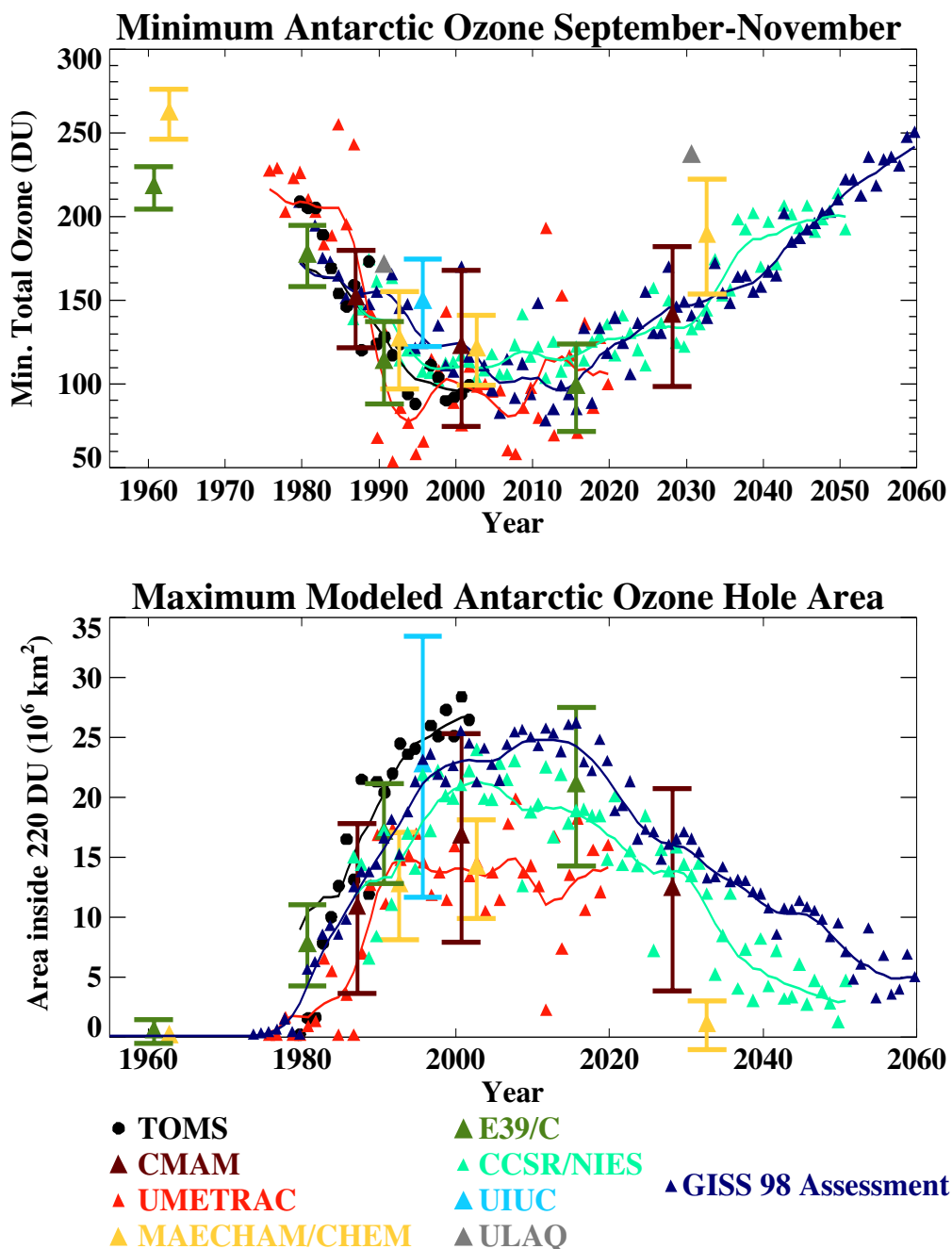


Figure 3-47. Upper panel: Minimum Antarctic total ozone for September to November, as observed by TOMS and as computed by the participating models. For the transient models, the solid lines show the results of a Gaussian smoothing applied to the individual year's results (also plotted). For the timeslice experiments, the mean and twice the standard deviation of the values within each sample are recorded by the colored triangles and the error bars. For MAECHAM/CHEM only: (1) the values have been plotted 2 years late for clarity, and (2) a standard tropospheric column of 40 DU has been added to the computed stratospheric columns. Lower panel: The maximum area of the ozone hole during the period September to November, as given by the 220-DU contour, for TOMS observations and participating models. The TOMS data and transient model results are plotted for each year and with a Gaussian filter applied (solid lines). For the timeslice experiments the means and twice the standard deviations of the model samples are included. For MAECHAM/CHEM only: (1) the values have been plotted 2 years late for clarity, and (2) a standard tropospheric column of 40 DU has been added to the computed stratospheric columns.

GISS model has a larger response than the other models, with the simulation indicating a minimum in the decadal averaged results of about 175 DU compared with almost 100 DU higher in the other transient runs. The date of minimum Arctic ozone, again as indicated by the minimum of the decadal averaged results, varies from 2004 for the CCSR/NIES model to 2019 for the GISS model. UMETRAC indicates a minimum at about the year 2015, but the simulation ends shortly afterwards and the results do not change substantially in the final decade. All three transient runs indicate some delay in the onset of ozone recovery, presumably due to increases in greenhouse gases (GHGs), although such a result is subject to considerable uncertainty because of the large interannual variability. Although the timeslice experiments do not have the temporal resolution to give a precise indication of the timing of future ozone recovery, the E39/C model results (Schnadt et al., 2002) may go against the transient model results by suggesting that increases in planetary waves occur in the Arctic, speeding up ozone recovery. This may be considered the “dynamical effect on chemistry”: increases in planetary waves transport more ozone as well as raise temperatures and decrease heterogeneous chemistry. Therefore, the net effect on ozone is that of the two potentially competing processes of dynamics and radiation. If planetary waves increase, the “dynamical” effect increases ozone and the “radiative” effect decreases ozone, giving a relatively small response. If planetary waves decrease, both the “dynamical” and “radiative” effects are negative, leading to enhanced ozone depletion. To resolve from the timeslice simulations whether increases in GHGs are delaying the onset of ozone recovery would require more results for the period 1990 to 2015.

In the Antarctic, the runs are all in fairly good agreement. Of the transient runs, as in the Arctic, the CCSR/NIES model indicates the earliest start of ozone recovery (2001) followed by UMETRAC (2005) and GISS (2008). The minima in the decadal averaged results are all comparable (109, 86, and 98 DU, respectively). On the basis of the decadal averaged model results this would appear to indicate that ozone recovery would begin earlier in the Antarctic than in the Arctic. Such an earlier start to recovery would also be detectable earlier in observations in Antarctica, because of the smaller interannual variability.

Observations of the size of the ozone hole (Figure 3-47; see also Figure 3-7) do not indicate any clear recovery by October 2001, with interannual variability now dominating over the current trends. For the GISS model the maximum ozone hole is in 2015, whereas for

UMETRAC the maximum occurs in 2007, although any systematic variation is obscured by the large interannual variability noted previously. In contrast the CCSR/NIES results show a peak as early as the year 2002.

3.5.3.3 THE 2020-2060 TIME FRAME: COMPLETE OZONE RECOVERY

Those models that have run beyond the year 2020 indicate some recovery in ozone. Of particular importance is the return to “1980-like conditions,” when the effects of anthropogenic halogen concentrations in the polar regions are negligible. As noted in the previous Assessment (Chapter 12 of WMO, 1999), this recovery would be to a different vertical distribution of ozone, with higher middle and upper stratospheric ozone due to the change in the vertical temperature profile (see Chapter 4). Using a 2-D model, Rosenfield et al. (2002) determined the date for the recovery of total ozone to 1980 levels as a function of day of year and latitude. In the Arctic, this recovery was latest at the end of spring (after 2050) and earliest in autumn (before 2035). Further, the impact of CO₂ increases was shown to accelerate the recovery from that due to chemical changes alone by increasing the downwelling over the poles. In contrast, if methane amounts do not increase at the current rate, ozone recovery could be slowed down in the future by the increased importance of NO_x chemistry (Randeniya et al., 2002). Over Antarctica, downwelling is less important in speeding up the ozone recovery.

Figures 3-46 and 3-47 show similar results for the spring for 3-D models. However, in the Arctic, most models do not show substantial ozone change throughout the period 2020 to 2050, and the low values of the GISS model for the decade 2010 to 2020 are no longer present after 2030 (Figure 3-46). In the Antarctic, the recovery of spring ozone, already under way by 2020, continues in the simulations completed (Figure 3-47). Recovery to 1980-like conditions occurs in the CCSR/NIES and GISS models by about 2045, and perhaps a decade later in the results of Austin et al. (2001). The CCSR/NIES and GISS transient model results suggest a near-monotonic recovery of ozone, but the results of Austin et al. (2001) suggest that ozone could undergo further loss over the period 2025 to 2045. This was identified as due to increases in ice PSCs as the lower stratospheric climate cools (but would need to be confirmed by model simulations with more detailed PSC schemes). Of the timeslice experiments, the MAECHAM/CHEM results indicate a significant (but not “full”) recovery in the Antarctic by 2030, consistent with the transient experiments. In the Arctic this model also simulates full or near-full recovery by 2030.

3.5.3.4 ATTRIBUTION OF MODEL OZONE CHANGES

The contrast between the modeled Antarctic and Arctic ozone behavior is striking in terms of the extent to which the observed behavior can be regarded as a forced response to chlorine loading. There is no question but that this is the case in the Antarctic; the models, despite their various imperfections, together give a clear, statistically significant signal that is in line with the observations. However, this is not the case in the Arctic: although there is a general ozone decrease in the models during the period of chlorine loading, it is not statistically significant. This is partly because of the weaker chemical impact of chlorine loading in the Arctic than in the Antarctic, and partly because of the greater natural variability in the Arctic.

In a coupled chemistry-climate model, the attribution of ozone changes to dynamical and chemical processes may be ambiguous because the dynamical changes themselves may have been caused by chemical changes to the ozone amounts. This is discussed further in Chapter 4. Figure 3-45, illustrating the approximate amounts of PSCs in the model simulations, should in principle reflect the amount of chemical ozone depletion (cf. Figure 3-33). This would suggest, for example, that UMETRAC has slightly less Arctic ozone depletion relative to observations, and this is reflected in the Arctic ozone trend (Figure 3-46; Table 3-5) that is smaller than observed, although the difference is not statistically significant. Also, both MAECHAM/CHEM and E39/C results for PSCs in Figure 3-45 suggest that their chemical ozone depletion is larger than observed in the Arctic, although the net ozone trend is similar to observations. The implication is that transport into the polar regions is enhanced to compensate. However, this does not appear to be consistent with earlier results (e.g., Hein et al., 2001), which if anything indicate reduced transport into the polar regions.

In the Antarctic, many of the models have similar ozone depletion rates, similar amounts of PSCs, and similar ozone trends, when allowance is made for the different periods under consideration (Figure 3-47; Table 3-5). The main exceptions are the GISS model for which PSC diagnostics are not available, and CMAM, which has less ozone depletion than that observed in 2000. These inconsistencies in both hemispheres suggest the need for further investigation of the sizes of the transport versus chemical depletion terms in all the models included herein.

Considering now the future evolution of Arctic ozone, the envelope of ozone variability defined by the timeslice experiments in Figure 3-46b returns to higher values in the future. Thus, the impact of the WMGHGs on Arctic ozone is still uncertain. The two transient exper-

iments performed for this Assessment, shown in Figure 3-46a, are consistent with the timeslice experiments. However, the transient experiment from the previous Assessment falls well outside the envelope of variability defined by the timeslice experiments over the coming several decades, particularly in terms of its lowest values. The prediction of the previous Assessment that changes in WMGHGs could lead to Arctic ozone minima of 100 DU over the coming several decades is not supported by the more recent models. The reason for the difference from the previous Assessment is that the more recent models do not predict the severe decrease in planetary wave drag over the Arctic (leading to essentially Antarctic-like meteorological conditions in the Arctic in some years) predicted by the earlier model. The earlier caveats, including the need for ensemble integrations, should again be borne in mind.

3.5.4 Summary

The main uncertainties of 3-D coupled chemistry-climate models stem from the performance of the underlying dynamical models. Temperature biases lead to errors in the spatial extent of PSCs and the degree of chemical ozone depletion. The model results also suggest significant differences in the transport of ozone to high latitudes, although this is in need of further clarification. At the current stage of model performance, uncertainties in the details of PSC formation and sedimentation are probably less important in simulating ozone amounts than the model temperature biases. Nonetheless, the accurate representation of PSC processes will prove to be increasingly important as temperature biases become smaller by, for example, the inclusion of non-orographic gravity wave parameterizations. Another uncertainty is the amount of aerosol present due to future unpredictable volcanic eruptions. For a large eruption such as that of Mt. Pinatubo, sufficient aerosol would be present to provide additional sites for heterogeneous chemistry and possible severe ozone loss for a period of a few years (see, e.g., Tabazadeh et al., 2002), although this perturbation would not affect the long-term ozone trend. The impact of volcanic eruptions on coupled chemistry-climate model results has not been discussed in this section, but further details may be found in Chapter 4.

For the transient model simulations, the start of ozone recovery, as defined in Section 3.5.3, occurs in the Antarctic within the next decade, depending on the model, and in the Arctic it occurs within the next two decades. In the Antarctic, however, model results suggest that the vertical and horizontal extent of the ozone hole may increase slightly further over the next few years. Thus, the results here suggest that the start of ozone recovery will occur

slightly later in the Arctic than in the Antarctic. Further, since the halogen amounts are thought to have maximized in 2001 (see Chapter 1, Figure 1-7), the start of ozone recovery in the Arctic in the models is delayed by up to almost two decades, probably by greenhouse gas increases. Most of the models come to similar conclusions on this issue, but one of the coupled chemistry-climate model experiments (Schnadt et al., 2002) suggests that greenhouse gas increases would tend to speed up rather than slow down ozone recovery in the Arctic. It should also be recognized that interannual variability on the sub-decadal time scale may still lead to ozone extremes. In the worst-case scenario, therefore, it may take until at least the end of the 2020s before we can be certain that ozone recovery has started in the Arctic. To put this into perspective, most models predict relatively modest changes in future spring Arctic column ozone (under 10%). The one model that does predict a major Arctic ozone change in the near future (described in Shindell et al., 1998a) has lower spatial resolution, simplified ozone transport, and parameterized ozone chemistry. In comparison, the other models have more accurate treatments of these processes.

On the longer time scale, to the middle of the 21st century, model predictions appear to be more uncertain. Hence, although recovery of Antarctic ozone to 1980-like conditions ("full ozone recovery") is to be expected by about 2050, models will need to have a better representation of the water vapor increase than has hitherto been possible, as well as an accurate specification of methane changes, for full confidence in their predictions. Although the results for the Arctic are less certain, since most models indicate relatively modest change in ozone, it is possible that "full recovery" may occur somewhat earlier there.

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Appendix 3A

SATELLITE MEASUREMENTS IN THE ANTARCTIC AND ARCTIC

In this appendix, we update information on satellite instruments that measure ozone and other species that are pertinent to polar ozone issues. We briefly review the status of a variety of ozone and related measurements for the Antarctic and Arctic. Total ozone observations and ozonesondes have been extensively discussed in previous reports, and are further reviewed in Chapter 4 of this Assessment.

Earth Probe (EP) Total Ozone Mapping Spectrometer (TOMS): Data from the TOMS instrument have been extensively used to track Arctic and Antarctic ozone changes. The TOMS data are discussed in Chapter 4, Appendix 4A. The EP/TOMS operational processing configuration has recently been changed in order to apply a correction to a cross-track bias error that has grown since 2000. Although 2001 data are included herein, they are of slightly greater uncertainty (see discussion in the Earth Probes TOMS description in Chapter 4, Appendix 4A).

Microwave Limb Sounder (MLS): MLS observations started in September 1991 with the launch of the Upper Atmosphere Research Satellite (UARS). It gives column and profile data on ozone, ClO, and HNO₃. Recently, the satellite and instrument have experienced problems, and the instrument is turned on only when there are situations of particular interest. In particular, MLS was taken out of standby mode on 31 January 2000 and was operated during the 2-13 February and 27-29 March periods in conjunction with the SOLVE/THESEO 2000 campaign (Santee et al., 2000).

Halogen Occultation Experiment (HALOE): HALOE observations also started in September 1991 with the launch of UARS. HALOE is a solar occultation instrument that makes measurements in the IR at both sunset and sunrise. HALOE measurements are used to retrieve profiles of ozone, HF, HCl, CH₄, H₂O, NO, NO₂, and aerosol extinction. HALOE occultation latitudes are variable over the course of the northern winter, but do not reach the high northern latitudes. During the winter of 1999/2000, the maximum latitude sampled by HALOE was approximately 63°N in mid-March. HALOE typically has difficulty sampling the polar vortex during midwinter, but does sample the vortex edge region in the fall (Pierce et al., 2002).

Global Ozone Monitoring Experiment (GOME): The GOME instrument was launched in 1995 aboard the second European Remote Sensing (ERS-2) satellite. It measures column ozone, NO₂, BrO, and OCIO, and ozone profiles. Details on the GOME instrument can be found in Burrows et al. (1999). The GOME data have been subject to validation exercises (Hansen et al., 1999; Hoogen et al., 1999; Corlett and Monks, 2001; Ionov et al., 2001; Piters et al., 1999; Rathman et al., 1997).

Polar Ozone and Aerosol Measurement (POAM): POAM is a solar occultation instrument that provides ozone, water vapor, NO₂, and aerosol extinction profiles in the polar regions. POAM II was launched in 1993 aboard the French Satellite Pour l'Observation de la Terre (SPOT)-3 satellite. These measurements were interrupted by the failure of the SPOT-3 satellite in November 1996. POAM III was subsequently launched on the French SPOT-4 satellite in March 1998 and is currently operational.

Lucke et al. (1999), Lumpe et al. (2002), and Randall et al. (2002) have published intercomparisons between POAM III and other instruments. Results from POAM III include studies on dehydration (Nedoluha et al., 2000), ozone loss (Randall et al., 2002; Hoppel et al., 2002), and PSCs (Bevilacqua et al., 2002).

Improved Limb Atmospheric Spectrometer (ILAS): ILAS is a satellite instrument that uses the solar occultation technique (Sasano et al., 1999; Nakajima et al., 2002). ILAS was launched onboard the ADvanced Earth Observing Satellite (ADEOS) on 17 August 1996. ILAS made measurements over high-latitude regions from 57°N to 71°N and from 64°S to 88°S from late October 1996 until late June 1997.

ILAS consists of an infrared spectrometer that covers the wavelength region from about 6 to 12 μm. ILAS made vertical profile measurements of ozone, HNO₃, NO₂, N₂O, CH₄, and H₂O from the infrared spectrometer, as well as vertical profiles of aerosol extinction coefficient at 780 nm from the visible spectrometer. Ozone data are validated by correlative and coincident measurements from several instrumental techniques (Sugita et al., 2002). Nitric acid, NO₂, and H₂O data have also been validated (Koike et al., 2000; Kanzawa et al., 2002; Irie et al., 2002).

CHAPTER 4

Global Ozone: Past and Future

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CHAPTER 4

GLOBAL OZONE: PAST AND FUTURE

Contents

SCIENTIFIC SUMMARY	4.1
4.1 INTRODUCTION	4.5
4.2 DESCRIPTION OF PAST CHANGES IN OZONE	4.6
4.2.1 Introduction	4.6
4.2.2 Changes in Total Ozone	4.7
4.2.2.1 Global Ozone: NH and SH Midlatitudes and Tropics	4.7
4.2.2.2 Seasonal Changes in Total Ozone	4.10
4.2.3 Changes in the Vertical Profile of Ozone	4.16
4.2.3.1 Upper Stratosphere	4.16
4.2.3.2 Lower Stratosphere	4.18
4.2.4 Vertical Integral of the Profile Trends vs. Column Trends	4.19
4.2.5 Tropospheric Ozone	4.22
4.2.6 Solar Cycle Effects on Ozone	4.22
4.2.6.1 Column Ozone	4.22
4.2.6.2 Vertical Profile of the Solar Signal	4.24
4.2.6.3 Summary	4.25
4.3 CURRENT UNDERSTANDING OF PAST CHANGES IN STRATOSPHERIC AEROSOL, WATER VAPOR, AND NO ₂	4.25
4.3.1 Stratospheric Aerosol Variability	4.25
4.3.2 Stratospheric Water Vapor Trends	4.27
4.3.3 Trends in Stratospheric NO ₂	4.28
4.4 CURRENT UNDERSTANDING OF PAST CHANGES IN STRATOSPHERIC TEMPERATURE	4.29
4.4.1 Updated Observations of Stratospheric Temperature	4.29
4.4.2 Causes of Past Temperature Changes	4.30
4.4.2.1 Simulated Temperature Trends Due to Observed Ozone Trends	4.31
4.4.2.2 Simulated Temperature Trends Due to Increased WMGG Concentrations	4.33
4.4.2.3 The Role of Trends in Stratospheric Water Vapor	4.34
4.4.2.4 Synopsis of Simulated Temperature Trends	4.35
4.5 CHEMICAL INFLUENCE ON PAST CHANGES IN OZONE	4.37
4.5.1 Chemical Processes that May Contribute to Ozone Changes	4.37
4.5.1.1 Gas-Phase Chemical Processes	4.37
4.5.1.2 Midlatitude Lower Stratospheric Heterogeneous Processes	4.38
4.5.2 Quantifying the Chemical Influence on Ozone: Modeling Tools	4.41
4.5.2.1 2-D Models	4.41
4.5.2.2 3-D Models	4.42
4.5.3 Quantifying the Chemical Influence on Ozone: Model Results	4.43
4.5.3.1 Effects of NO _x - and ClO _x -Related Processes	4.43
4.5.3.2 Effect of Polar Vortex on Midlatitudes	4.45
4.5.3.3 Effect of Water Vapor Trends	4.45
4.5.3.4 Assessment Model Simulations of Past Ozone Changes	4.46

4.6	DYNAMICAL INFLUENCE ON PAST CHANGES IN OZONE	4.52
4.6.1	Introduction	4.52
4.6.2	Dynamical Processes that May Contribute to Ozone Changes	4.54
4.6.2.1	Changes in Planetary-Wave Drag	4.54
4.6.2.2	Effects of Tropospheric Circulation and Tropopause Changes	4.55
4.6.2.3	Hemispheric Variations and Annular Modes	4.56
4.6.3	Statistical Analysis of Observations	4.56
4.6.3.1	Changes in Planetary-Wave Driving	4.56
4.6.3.2	Changes in Tropospheric Circulation and Tropopause Height	4.57
4.6.3.3	Coupling Issues	4.58
4.6.4	Modeling Studies	4.58
4.6.5	Cause of the Dynamical Changes	4.60
4.6.6	Effects of Mt. Pinatubo Eruption	4.61
4.6.7	Conclusions	4.62
4.7	IMPLICATIONS FOR CLIMATE OF UPDATED STRATOSPHERIC OZONE CHANGES	4.62
4.8	FUTURE CHANGES IN OZONE	4.63
4.8.1	Effect of Decreasing Halogens	4.64
4.8.2	Influence of Changing Climate Gases	4.65
4.8.3	Other Stratospheric Influences	4.66
4.8.3.1	Dynamical Effects	4.66
4.8.3.2	Future Effects of Aircraft	4.67
4.8.3.3	Rocket Emissions	4.67
4.8.4	Future Tropospheric Ozone	4.68
4.9	SYNTHESIS OF CURRENT UNDERSTANDING OF PAST AND FUTURE CHANGES IN OZONE	4.70
4.9.1	Discussion of Past Changes	4.70
4.9.2	Discussion of Future Changes	4.72
	REFERENCES	4.72
	APPENDIX 4A: DESCRIPTION OF OZONE DATASETS	4.85
4A.1	Ground-Based Total Ozone Measurements	4.85
4A.2	Satellite Total Ozone Measurements and Merged Datasets	4.85
4A.3	Ozone Profile Measurements	4.88
	APPENDIX 4B: 2-D MODEL SCENARIOS	4.90

SCIENTIFIC SUMMARY

Total Column Ozone

- Global mean total column ozone for the period 1997-2001 was approximately 3% below the pre-1980 average values. Since systematic global observations began in the mid-1960s, the lowest annually averaged global total column ozone occurred in 1992-1993 (5% below the pre-1980 average). These changes are evident in each available global dataset.
- No significant trends in total column ozone have been observed in the tropics (25°N-25°S) for 1980-2000. A decadal variation of total column ozone (with peak-to-trough variations of ~3%) is observed in this region, approximately in phase with the 11-year solar cycle. Total column ozone trends become statistically significant in the latitude bands 25°-35° in each hemisphere.
- There are a number of differences in total column ozone behavior between the two hemispheres:
 - Averaged for the period 1997-2001, total column ozone in the Northern Hemisphere (NH) and Southern Hemisphere (SH) midlatitudes (35°-60°) are about 3% and 6%, respectively, below their pre-1980 average values.
 - The seasonality of total column ozone changes (1997-2001 relative to pre-1980) is different in the NH and SH midlatitudes. Over NH midlatitudes, larger ozone decreases are observed during winter-spring (~4%); summer-autumn decreases are approximately half as large. Over SH midlatitudes, long-term ozone decreases exhibit similar magnitude (~6%) during all seasons.
 - Pronounced negative anomalies are observed in the NH midlatitude time series during 1992-1995 in the winter-spring seasons. Similar anomalies are not seen in the SH midlatitudes.
 - There is a sharp drop in ozone at SH midlatitudes during 1985-1986. A similar drop is not observed in the NH.

Vertical Ozone Distribution

- Ozone profile trends derived from Stratospheric Aerosol and Gas Experiment (SAGE I and SAGE II, version v6.1) data show significant negative trends over latitudes 60°N to 60°S for altitudes ~35-50 km (with extremes near 40 km). Trend maxima of 7-8%/decade over the period 1979-2000 are observed in latitude bands 35°-60° of both hemispheres, with no significant interhemispheric difference. These satellite results are in good agreement with independent Umkehr ozone measurements available over the NH midlatitudes. Ozone decreases in the upper stratosphere (above 25 km) contribute 15-30% to changes in the total column at midlatitudes.
- The updated SAGE data reveal significant negative trends in the small amount of ozone above 30 km extending throughout the tropics, a feature not observed in previous Assessments based on shorter time records.
- Ozonesonde measurements over the NH midlatitudes show that ozone between 20 and 27 km decreased continuously during 1980-2000, while ozone between 10 and 20 km decreased through the early 1990s and was relatively constant thereafter. This behavior is consistent with observed changes in NH midlatitude column ozone.
- The ozonesonde measurements show no trend in tropospheric ozone for 1980 to 2000 for most stations, and the mean trend averaged over all midlatitude stations is also zero.

Ozone-Related Constituents

- Stratospheric aerosol variability over the past 25 years has been dominated by the effects of episodic volcanic eruptions, with subsequent recovery. Following the large eruption of Mt. Pinatubo in 1991, relaxation to a nonvolcanic level continued to at least 1999. There is currently no evidence of a trend in the nonvolcanic aerosol loading over the past 25 years.

GLOBAL OZONE

- Stratospheric water vapor measurements at Boulder, Colorado, U.S. (40°N), for the period 1981-2000 show a statistically significant increase of approximately 1%/year over altitudes 15-28 km. For the shorter period 1991-2001, global satellite measurements covering latitudes 60°S to 60°N show a similar trend of 0.6-0.8%/year for altitudes ~25-50 km, but no significant trend at lower altitudes. This increase in water vapor is substantially larger than can be explained by tropospheric methane (CH₄) trends. Characterization of stratospheric water vapor trends is limited by the lack of global long-term measurements.
- Stratospheric column nitrogen dioxide (NO₂) measurements from Lauder, New Zealand (45°S), for the period 1981-2001, and Jungfraujoch, Switzerland (46°N), for 1985-2001, show statistically significant positive trends of approximately 6%/decade. Transient decreases are also observed following the El Chichón and Mt. Pinatubo volcanic eruptions, which are broadly simulated by models that include heterogeneous chemistry on sulfate aerosols.

Stratospheric Temperature Trends

- Satellite observations indicate that, on an annual and global mean, the stratosphere has cooled over the last two decades. In the lower stratosphere, global and annual mean temperatures for the late 1990s are approximately 1 K lower than values in the late 1970s. Significant annual-mean cooling of the lower stratosphere for the past two decades is found over midlatitudes of both hemispheres (approximately 0.6 K/decade), but no significant trends are observed near the equator. The annual mean temperature trends in the upper stratosphere are larger, with an approximately globally uniform cooling for 1979-1998 of about 2 K/decade near the stratopause (~50 km).
- Modeling studies indicate that changes in ozone, well-mixed greenhouse gases, and stratospheric water vapor can explain the major features of the observed global and annual-mean stratospheric cooling over the past two decades. Cooling due to ozone depletion dominates over the impact of well-mixed greenhouse gases in the lower stratosphere. Upper stratospheric temperature trends are due, roughly equally, to ozone and well-mixed greenhouse gas changes. At 20 km, the observed annual-mean cooling in northern midlatitudes is much larger than that simulated using observed ozone and greenhouse gas changes. In this region increases in water vapor may have been as important as ozone loss in determining the cooling. The inclusion of water vapor generally improves agreement with observations, but uncertainties in the spatial and temporal distribution of its change are large.

Attribution of Past Changes in Ozone

- The vertical, latitudinal, and seasonal characteristics of changes in midlatitude ozone are broadly consistent with the understanding that halogens are the primary cause of these changes, in line with similar conclusions from the 1998 Assessment.
- Assessment models forced by observed changes in halocarbons, source gases, and aerosols broadly reproduce the long-term changes observed in midlatitude total column ozone (35°N-60°N and 35°S-60°S) for 1980-2000, within the uncertainties of the observations and model range. However, the range of model results is large over SH midlatitudes, which is at least partly due to their treatment of the Antarctic ozone hole. In addition, models suggest that the chemical signal of ozone loss following the major eruption of the Mt. Pinatubo volcano in the early 1990s should have been symmetric between hemispheres, but observations show a large degree of interhemispheric asymmetry in midlatitudes.
- There is increased evidence that changes in atmospheric dynamics have had a significant influence on NH midlatitude column ozone on decadal time scales. Natural variability, changes in greenhouse gases, and changes in column ozone itself are all likely to contribute to these dynamical changes. Furthermore, because chemical and dynamical processes are coupled, their contributions to ozone changes cannot be assessed in isolation.
- The observed ozone depletion in the upper stratosphere is consistent with observed changes in anthropogenic chlorine. The vertical and latitudinal profiles of trends in the upper stratosphere are reproduced by photochemical models, but the magnitudes of changes are sensitive to concurrent trends in temperature and other constituents such as CH₄.

- Stratospheric planetary-wave drag drives the wintertime ozone buildup in the extratropics, so the observed decrease in NH planetary-wave drag likely has contributed to the observed decrease in NH total column ozone over the last 20 years. The relationship between planetary-wave drag and ozone is understood, but its quantification in observations is relatively crude.
- There is an observed relationship between total column ozone and tropopause height, and several tropospheric circulation indices. These indices have changed over the last 20 years in the NH in such a way as to imply a decrease in total column ozone. However, the causality of these relationships is not well understood, which makes their extrapolation to long time periods problematic.

Future Changes in Ozone

- The expected decrease in stratospheric chlorine loading over the next 50 years is predicted to lead to an increase in the global total column ozone, although there are differences in the rate of increase between different two-dimensional assessment models. Future ozone levels will also be influenced by other changes in atmospheric composition and by climate change. Because of year-to-year variability it could take as long as a decade to demonstrate a leveling of total column ozone.
- Stratospheric cooling (due mainly to projected carbon dioxide (CO₂) increases) is predicted to enhance future ozone increases in the upper stratosphere. This effect in isolation would substantially hasten the predicted rate of total ozone increase in coming decades. However, a reliable assessment of effects on total column ozone is limited by uncertainties in the lower stratospheric response to these changes.
- Projected increases in methane (CH₄) and nitrous oxide (N₂O) are predicted to have small effects on the rate of increase of global column ozone in the next 50 years, when chlorine changes are the dominant effect. After that time, changes in CH₄ and N₂O become relatively more important.
- Future large volcanic eruptions would be expected to cause transient enhancements of chemical ozone depletion (lasting 3-4 years) but should not alter the overall predicted evolution of ozone.
- Future changes in tropospheric ozone are highly dependent upon the scenario adopted for future emissions of ozone precursors, but all scenarios adopted by the Intergovernmental Panel on Climate Change (IPCC) lead to increases in tropospheric ozone up to 2050. Allowing for climate change leads to smaller increases in tropospheric ozone compared with simulations using present-day climate.

4.1 INTRODUCTION

Concentrations of ozone in the atmosphere can change as a result of both natural processes and human activities, and accurate knowledge of past changes is important both for attribution of causes and for prediction of future changes. Past ozone assessments have documented long-term decreases in stratospheric ozone and have devoted separate chapters to ozone observations, interpretation of past changes, and predictions of future change. In contrast, this chapter takes a comprehensive view of past and future changes in global ozone, combining observational and modeling results. In brief, we seek to address the following questions:

- What have been the changes to stratospheric ozone in the past, and how well do we understand those changes?
- What is our best estimate for stratospheric ozone in the future, and what are the main uncertainties in this estimate?

The bulk of atmospheric ozone is found in the stratosphere, with approximately 90% of the vertically integrated column amount occurring above the tropopause (the “ozone layer”). Long-term changes of stratospheric ozone are related to changes in tropospheric source gases (transported into the stratosphere), to variations in solar radiation and volcanic effects, and to changes in large-scale transport. Changes in tropospheric ozone (which is an environmental pollutant near the surface) are mainly associated with increased urban pollution and biomass burning. Stratospheric ozone has decreased over the last several decades, while tropospheric ozone has increased (at least over Northern Hemisphere (NH) midlatitudes, where long-term observations are available; Logan et al., 1999). In the extratropics the stratospheric decreases greatly outweigh the tropospheric increases in terms of column amount, and therefore observed column ozone changes primarily reflect the stratospheric decreases. Long-term changes in stratospheric ozone are the primary focus of this chapter, and tropospheric ozone is discussed only briefly (in regard to its contribution to past and future column ozone changes). Detailed discussions of tropospheric ozone are included in IPCC (2001); some of those results are highlighted here where relevant.

The distribution of ozone in the atmosphere is maintained by a balance between photochemical production and loss, and by transport between regions of net production and net loss. Understanding long-term changes in ozone, both past and future, requires knowledge of these processes and a quantification of their relative importance and coupling. The basic structure and zonal mean circulation of the stratosphere are summarized in Figure 4-1.

There is an important distinction between the different vertical regions in the stratosphere, which can be characterized by their radiative, dynamical, and transport behavior. The photochemical lifetime of odd-oxygen ($O_x = O + O_3$, where O is atomic oxygen and O_3 is ozone) varies strongly with altitude between these regions (and also with latitude and season; e.g., Garcia and Solomon (1983)). (In the stratosphere, O and O_3 are in a rapidly established equilibrium, and so any analysis of processes that control O_3 should be based on the family O_x .) The lowermost stratosphere (LMS) covers the region between the tropopause and the isentropic surface of about 380 K (about 15 km), and this region is distinct because air can be transported between the troposphere and stratosphere by isentropic transport alone. Above the LMS, between the 380-K surface and about 25 km is the lower stratosphere (LS). In both the LMS and LS, the lifetime of odd-oxygen is long (~months-years), and odd-oxygen will react to chemical changes slowly and be strongly influenced by atmospheric transport. The region between 30 and 50 km is typically referred to as the upper stratosphere (US) based on radiative/dynamical behavior. However, the odd-oxygen photochemical lifetime is relatively short (less than transport time scales) above 25 km, hence dominated by photochemical control, and for simplicity we refer to the region from 25 to 50 km as the US throughout this chapter.

By considering the factors that control the abundance of ozone in the stratosphere, we can classify the three different regions in Figure 4-1 by the complexity of the processes that need to be understood. The US can be

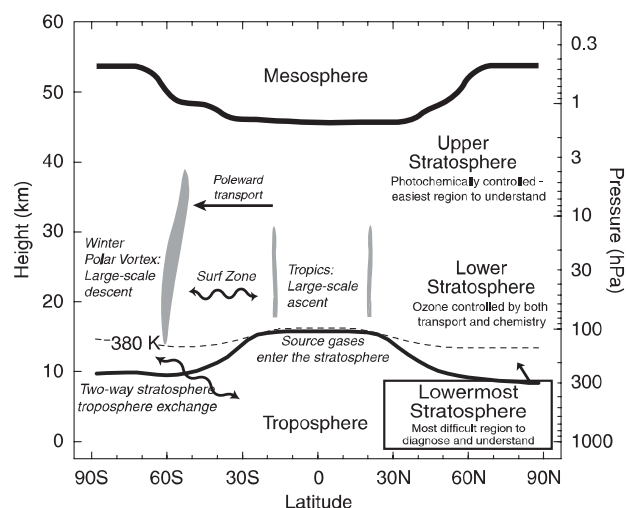


Figure 4-1. Schematic diagram showing the structure of, and transport within, the stratosphere. The three stratospheric regions (LMS, LS, US) discussed in the text are indicated.

regarded as the easiest region to analyze, because ozone there is under direct photochemical control and direct transport effects can be neglected (although transport affects the abundance of ozone-destroying species). The LS and LMS are more difficult to analyze, because both transport and chemistry directly affect ozone. Within these lower altitude regions, the LMS region can be considered more difficult than the LS because it is directly coupled by isentropic transport to the troposphere.

As discussed in the previous Assessment (WMO, 1999), there is strong evidence that the main driver for the upper stratospheric ozone loss near 40 km and the polar lower stratospheric springtime loss is halogen chemistry. In the upper stratosphere, ozone loss occurs through purely gas-phase chlorine chemistry. In the polar lower stratosphere, heterogeneous chemistry in or on polar stratospheric clouds (PSCs) causes the conversion of stable chlorine reservoirs to more active forms. Ozone loss then occurs through reactions involving chlorine and bromine species (see Chapter 3). It is also well established that some of the chemical depletion that occurs during spring in the high latitudes must eventually lead to a decrease (or “dilution”) of ozone at midlatitudes when the polar vortices break down. However, this process is poorly quantified at present. A number of other processes, both chemical and dynamical, have been proposed as contributing to ozone decreases in the midlatitude lower stratosphere. The chemical processes include wintertime transport of chlorine-activated air from the vortex followed by chemical loss, and in situ loss initiated by heterogeneous chemistry on liquid sulfate aerosols. The dynamical processes include changes in planetary-wave driving (and associated stratospheric transport circulation), and changes in tropospheric circulation and in tropopause height. While there is good mechanistic evidence that these processes occur and affect ozone, quantifying their contribution to the long-term change is difficult. Furthermore, the chemical and dynamical contributions are coupled and not truly separable, but rather act synergistically.

Past ozone assessments have focused on estimates of linear trends in ozone, usually determined via a multiple regression analysis (including terms to account for other known sources of periodic variability, such as the solar cycle or quasi-biennial oscillation). The choice of fitting a linear trend was based on the expected response to the approximate linear increases in ozone-depleting substances (ODSs) such as chlorofluorocarbons (CFCs) and halons (prior to the middle 1990s). However, this linear increase in ODS has not continued beyond the middle 1990s (see Chapter 1), and the continued representation of ozone variations as simple linear trends is not

appropriate. The philosophy adopted here is to focus primarily on the observed time series of ozone variations updated through 2001, including their detailed latitude and altitude structure, and use these time variations as fingerprints of the mechanisms that influence change. Linear trends are calculated for some variables, namely, for ozone profile variations (where data availability limits the information in time series), and in comparison of the model results to ozone observations in Section 4.5 (where trends are a useful summary diagnostic). For clarity, we reserve the use of the term “trend” to refer to linear trends calculated over a specific time period (typically determined by regression fit).

The overall layout of this chapter is as follows. Section 4.2 provides an update of observed changes in ozone through 2001, including the latitudinal and temporal changes in column and profile ozone. We focus on global or near-global variability (90°N–90°S or 60°N–60°S), together with specific analyses of the tropics (25°N–25°S) and Northern Hemisphere/Southern Hemisphere midlatitudes (which are defined, somewhat arbitrarily, as latitudes 35°N–60°N and 35°S–60°S). The latitude bands 25°–35°N and S are transition zones, where observations show that decadal ozone trends start to become significant. Tropospheric ozone is briefly discussed, and its role in column ozone is estimated. We also specifically discuss the 11-year solar cycle in ozone evaluated from observations and models; this topic is important for quantifying decadal variability in the relatively short observational record. Sections 4.3 and 4.4 describe the complementary observations of past changes in stratospheric aerosol, water vapor, nitrogen dioxide (NO₂), and temperature, and summarize our understanding of their causes. Section 4.5 describes our current understanding of the chemical influence on ozone changes at midlatitudes, and Section 4.6 discusses the dynamical influences on midlatitude ozone changes. Section 4.7 discusses what effect the observed changes in ozone may have had on climate, and Section 4.8 provides updated estimates of how global ozone may evolve in the future. An overall synthesis of current understanding of past and future global ozone changes is presented in Section 4.9.

4.2 DESCRIPTION OF PAST CHANGES IN OZONE

4.2.1 Introduction

Global and hemispheric-scale variations in stratospheric ozone can be quantified from extensive observational records covering the past 20–30 years. The goal

here is to provide an updated description of interannual variability in ozone over the most recent decades (approximately 1970–2000), with a focus on changes outside of the polar regions (over latitudes approximately 60°N–60°S). There are numerous ways to measure ozone in the atmosphere, but they fall broadly into two categories: measurements of total or column ozone (the vertically integrated amount of ozone above the surface) and measurements of the vertical profile of ozone. There are more independent datasets, longer time series, and better global coverage for total ozone. Regular measurements of total ozone are available from a network of surface stations, mostly in the midlatitude Northern Hemisphere, with reasonable coverage extending back to the 1960s (although geographical coverage is limited before the 1970s). Near-global, continuous total ozone data are available from satellite measurements beginning in 1979. However, changes in availability and calibration of ground-based measurements and satellite datasets, and interruptions in observational records, produce datasets in which the systematic errors are complicated functions of time. Systematic errors of 1% are typical even for the most reliable instruments, whereas interannual changes in global or hemispherically averaged ozone are typically a few percent. The methodology adopted in the past (and used here) is to compare estimates of ozone change from several different and independent techniques (i.e., ground-based and satellite datasets), and use their differences to provide a measure of overall uncertainty. The results indicate an overall good agreement among the different data sources for changes in total ozone, and thus we have reasonable confidence in describing the spatial and temporal characteristics of past changes.

There are fewer independent datasets describing long-term changes in the vertical profile of ozone. Satellite observations are the only dataset with global profile coverage, but they are limited in vertical extent and temporal coverage. Reasonably long time records are available from balloonborne ozonesonde and ground-based Umkehr data, but these are primarily concentrated in NH midlatitudes. Thus, in the case of ozone profile measurements, direct comparison of long records from independent datasets is possible only over NH midlatitudes. Over that region there is reasonably good agreement for long-term changes between the satellite and Umkehr data (in the upper stratosphere), and satellite and ozonesondes (in the lower stratosphere), and this suggests that the satellite data are reliable for global analyses. There is approximate but not exact agreement between trends in NH midlatitude total ozone and the vertically integrated profile changes (from ozonesondes in the lower stratosphere, and satellite/Umkehr in the upper strato-

sphere); the lack of more detailed agreement is probably related to the sparse ozonesonde sampling.

4.2.2 Changes in Total Ozone

4.2.2.1 GLOBAL OZONE: NH AND SH MIDLATITUDES AND TROPICS

Five datasets of zonal and monthly mean total ozone values developed by different scientific teams are examined in this Assessment. These consist of various combinations of ground-based and merged satellite datasets, as described in Fioletov et al. (2002) and summarized in Appendix 4A (p. 4.86). The global and latitudinal structure of total ozone variability is analyzed based on seasonal (3-month average) and zonally averaged time series (on a 5° latitude grid). The ground-based dataset extends in time over ~1965–2001 (depending on latitude, with longer and more reliable records available in the midlatitude NH), and the satellite datasets span 1979–2001. Details of the data analyses are discussed in Fioletov et al. (2002). Briefly, the seasonal cycle of total ozone for each dataset is removed by taking monthly averages for each month of the year for the period 1979–1987, and subtracting these from the original data. Area-weighted ozone deviations are then calculated and expressed as anomalies with respect to the period 1964–1980. For regions with missing data, ozone deviations are assumed identical to the surrounding latitude belt where data are available, prior to area averaging. Systematic differences between the separate datasets of up to 3% are found (for global average ozone), although the deseasonalized total ozone deviations agree to within 0.9% (95% confidence). Overall, each of the total ozone datasets gives similar estimates of large-scale changes; each of the datasets is included in the figures below, and the spread between them gives an estimate of the uncertainty due to measurement technique and sampling.

The total ozone deviations for the 60°S–60°N latitude belt are shown in Figure 4-2 (top), and corresponding results for the global mean (90°S–90°N) are shown in Figure 4-2 (bottom). All five datasets indicate very similar ozone variations, with differences typically less than 0.5%. The global ozone (60°S–60°N or 90°S–90°N) amount shows overall decreasing values between the late 1970s to early 1990s, a relative minimum during 1992–1994, and a slight increase during the late 1990s. A relatively large decadal variation of global total ozone is seen in Figure 4-2, which is likely associated with the 11-year solar cycle (e.g., Chandra and McPeters, 1994; Bojkov and Fioletov, 1995; see further discussion in Section 4.2.6). Figure 4-3 shows the deseasonalized global anom-

GLOBAL OZONE

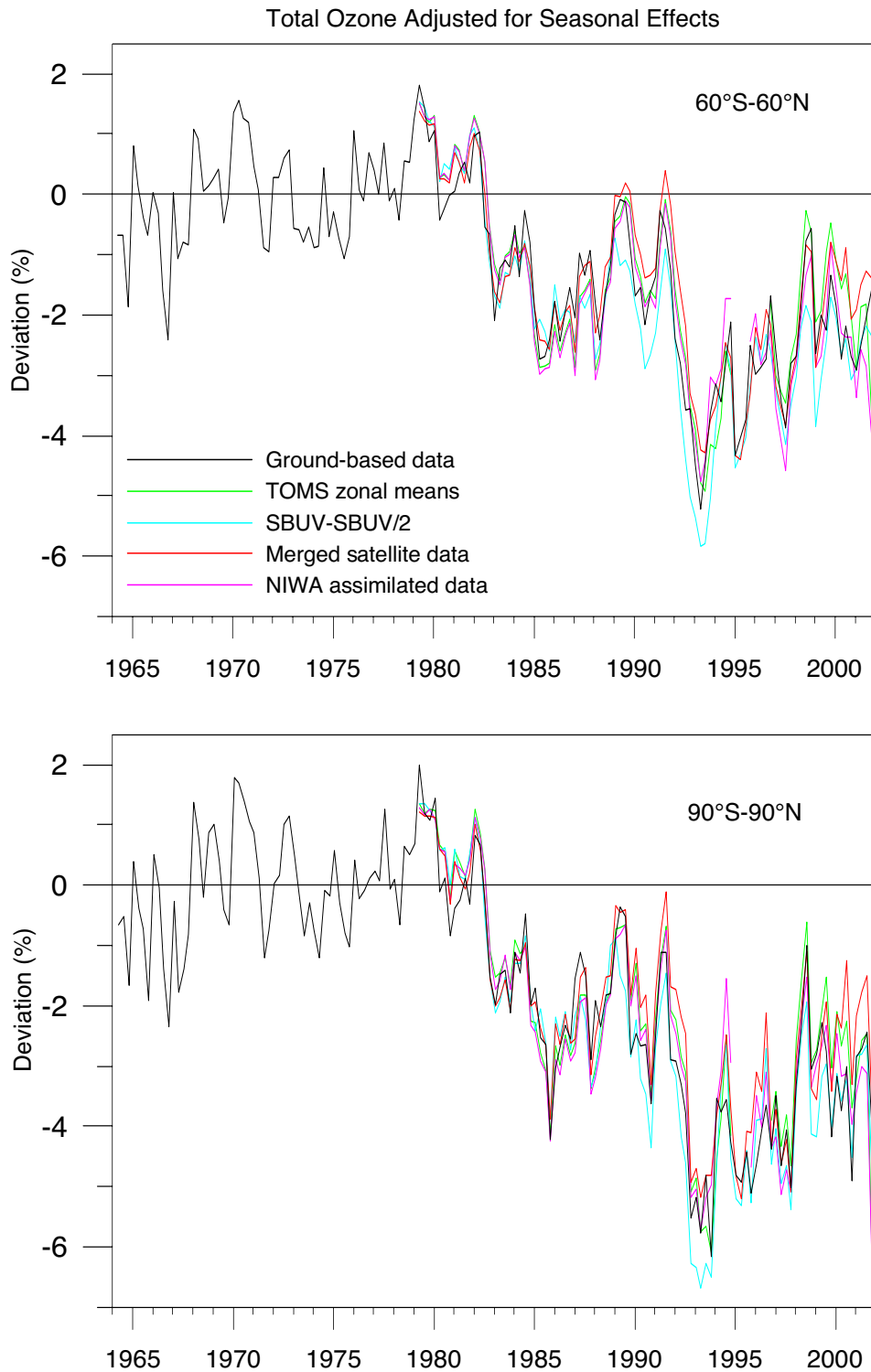


Figure 4-2. Deseasonalized, area-weighted seasonal (3-month average) total ozone deviations, estimated from five different global datasets. Each dataset was deseasonalized with respect to the period 1979-1987, and deviations are expressed as percentages of the ground-based time average for the period 1964-1980. Results are shown for the region 60°S-60°N (top) and the entire globe (90°S-90°N) (bottom). The different satellite datasets cover 1979-2001, and the ground-based data extend back to 1964. TOMS, Total Ozone Mapping Spectrometer; SBUV, Solar Backscatter Ultraviolet; NIWA, National Institute of Water and Atmospheric Research (New Zealand). Adapted from Fioletov et al. (2002).

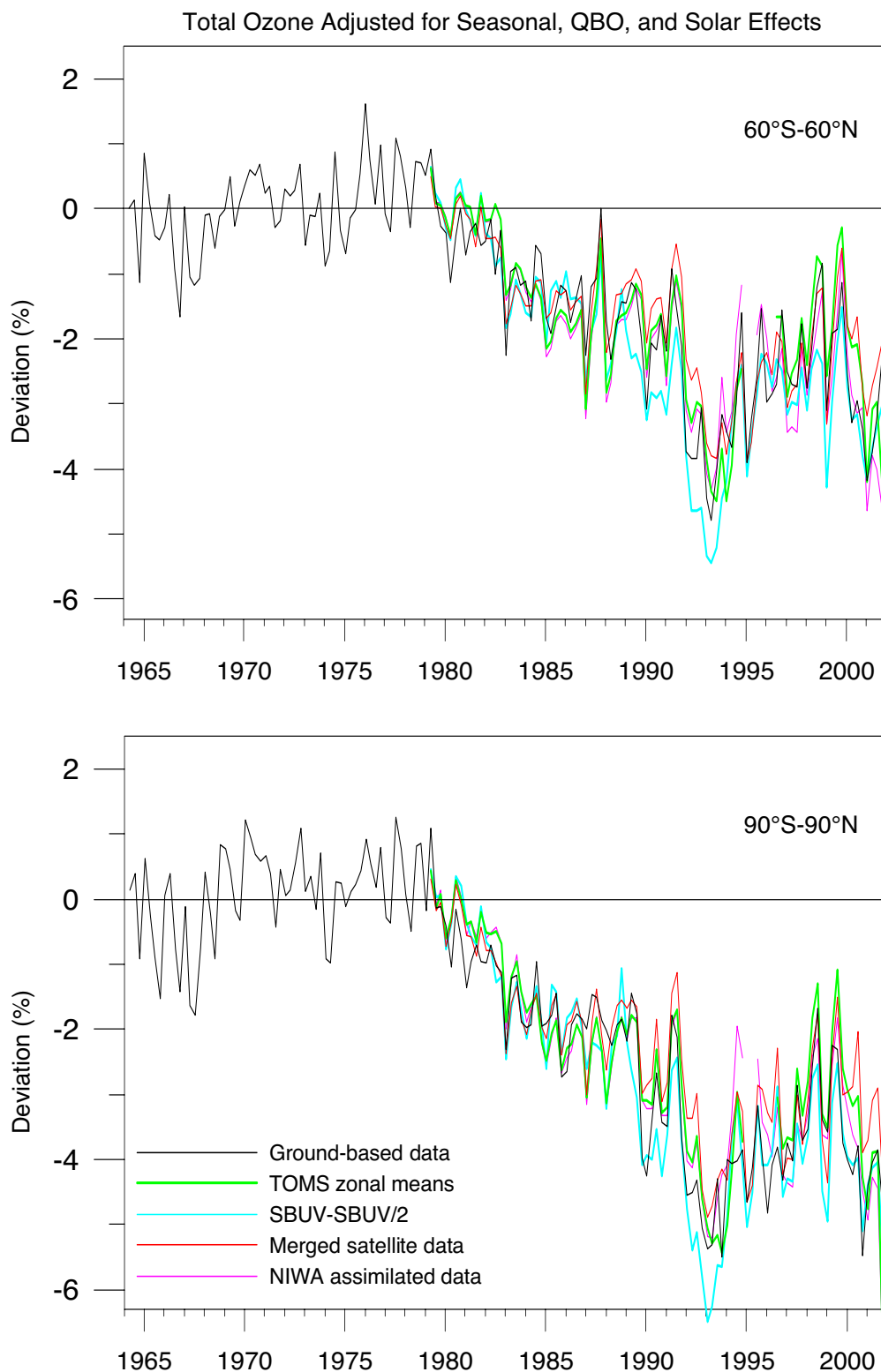


Figure 4-3. Deseasonalized, area-weighted total ozone deviations from five datasets (as in Figure 4-2), adjusted for solar and QBO effects, for the region 60°S-60°N (top) and the entire globe (90°S-90°N) (bottom). The solar and QBO effects were estimated using the ground-based data only and subtracted from all five datasets. Adapted from Fioletov et al. (2002).

GLOBAL OZONE

alies, after statistical removal of the solar cycle and quasi-biennial oscillation (QBO)-related variations (based on standard regression analyses, as discussed in detail in SPARC (1998)). The details of the solar cycle statistical fit, and possible aliasing of solar and volcanic signals in ozone, are discussed in detail in Section 4.2.6. The time series in Figure 4-3 show that the residual global ozone variability can be described by an approximately linear decline from the late 1970s to the early 1990s, a minimum during 1992-1994, increases during the late 1990s, and relatively low values in 2000-2001. The global ozone levels for the years 1998-1999 are similar to those of the early 1980s, but about 2% lower than the late 1970s values. However, the relatively low global ozone values in 2000-2001 suggest caution in interpreting the higher values for 1998-1999. A smoothed version of the global ozone anomalies is shown in Figure 4-4, based on applying four passes of a 13-month running mean to the global anomalies in Figure 4-3. These smoothed time series highlight the low-frequency interannual changes, and provide concise estimates of global ozone changes for comparison with the assessment model results in Section 4.5.

About 40% of global ozone is located in the tropics between 25°N-25°S, and variability in this region over the period 1979-2001 is shown in the middle curves of Figure 4-5. There is a strong decadal variation of total ozone in the tropics, with peak-to-trough variations of approximately 3%, and maxima approximately in phase with the 11-year solar cycle (top panel in Figure 4-5). After statistical removal of the solar signal (bottom curves in Figure 4-5), the residual tropical ozone shows a 1-2% decline in ozone during ~1992-1993, followed by an increase back to pre-1990 values. Significant long-term trends in tropical total ozone have not been observed for the period 1979-2001. H.J. Wang et al. (2002) find weak negative trends ($-1.2 \pm 0.8\%$ /decade) in the tropics (20°N-20°S) using vertically integrated Stratospheric Aerosol and Gas Experiment (SAGE) II ozone (15-50 km) for 1985-2000. Although these trends are different from the near-zero trends derived for column ozone, uncertainty levels do overlap.

Figure 4-6 shows deseasonalized ozone values integrated over the 35°-60°S and 35°-60°N latitude belts. These time series show that ozone levels in the late 1990s are several percent lower than in the late 1970s in the mid-latitudes of both hemispheres, although there is a large degree of year-to-year variability in both cases. Smoothed versions of these time series are shown in Figure 4-7. Time series over NH midlatitudes show an overall decrease in ozone beginning in the early 1980s, pro-

nounced negative ozone anomalies during ~1992-1996, and a partial rebound thereafter. The minimum from ~1992-1996 in the smoothed time series (Figure 4-7) is associated with several individual winters of low ozone over midlatitudes during that time, namely 1991/1992, 1992/1993, and 1994/1995. The large anomalies in 1991/1992 and 1992/1993 have been associated with the Mt. Pinatubo volcanic eruption in June 1991 (e.g., Brasseur and Granier, 1992; Gleason et al., 1993; Hofmann et al., 1994).

Total ozone changes in the midlatitude SH also show a general decline after ~1980 (Figure 4-7), but the time series show a more consistent and gradual decline than in the NH. Net ozone levels in the SH midlatitudes are currently ~6% lower than pre-1980 values. It is especially interesting that the large negative anomalies observed in the NH extratropics during 1992-1996 are not particularly evident in the SH. Furthermore, there are relatively large negative anomalies in the SH during ~1985-1986, which lead to anomalies in the smoothed time series extending over several years (Figure 4-7), with the result that the low-frequency midlatitude variability is quite different between the hemispheres.

4.2.2.2 SEASONAL CHANGES IN TOTAL OZONE

The seasonal changes of total ozone changes over 35°-60°N and 35°-60°S are shown in Figure 4-8, for the time period 1979-2001. A high degree of year-to-year variability is observed during the dynamically active winter and spring periods in each hemisphere: December-January-February (DJF) and March-April-May (MAM) in the NH; June-July-August (JJA) and September-October-November (SON) in the SH. In the NH the largest absolute changes are observed during winter (DJF) and spring (MAM), with maximum deviations during the early to middle 1990s of -6 to -12%. During NH summer (JJA) and fall (SON) the interannual changes show similar time variation (with maximum anomalies during ~1992-1997), but the magnitudes of ozone changes are less (about -3 to -5%). Total ozone changes in the SH midlatitudes in Figure 4-8 show a systematic decline during all seasons, and relatively less seasonal dependence compared with the NH. Although natural variability is highest during SH winter (JJA) and spring (SON), there is relatively little difference for long-term changes between these active seasons and SH summer-fall. Thus the characteristic seasonal signatures of long-term ozone loss are distinct between the NH and SH. Seasonally varying trend calculations are consistent with these time series results, and results for NH and SH midlatitudes are shown in Section 4.5.3.

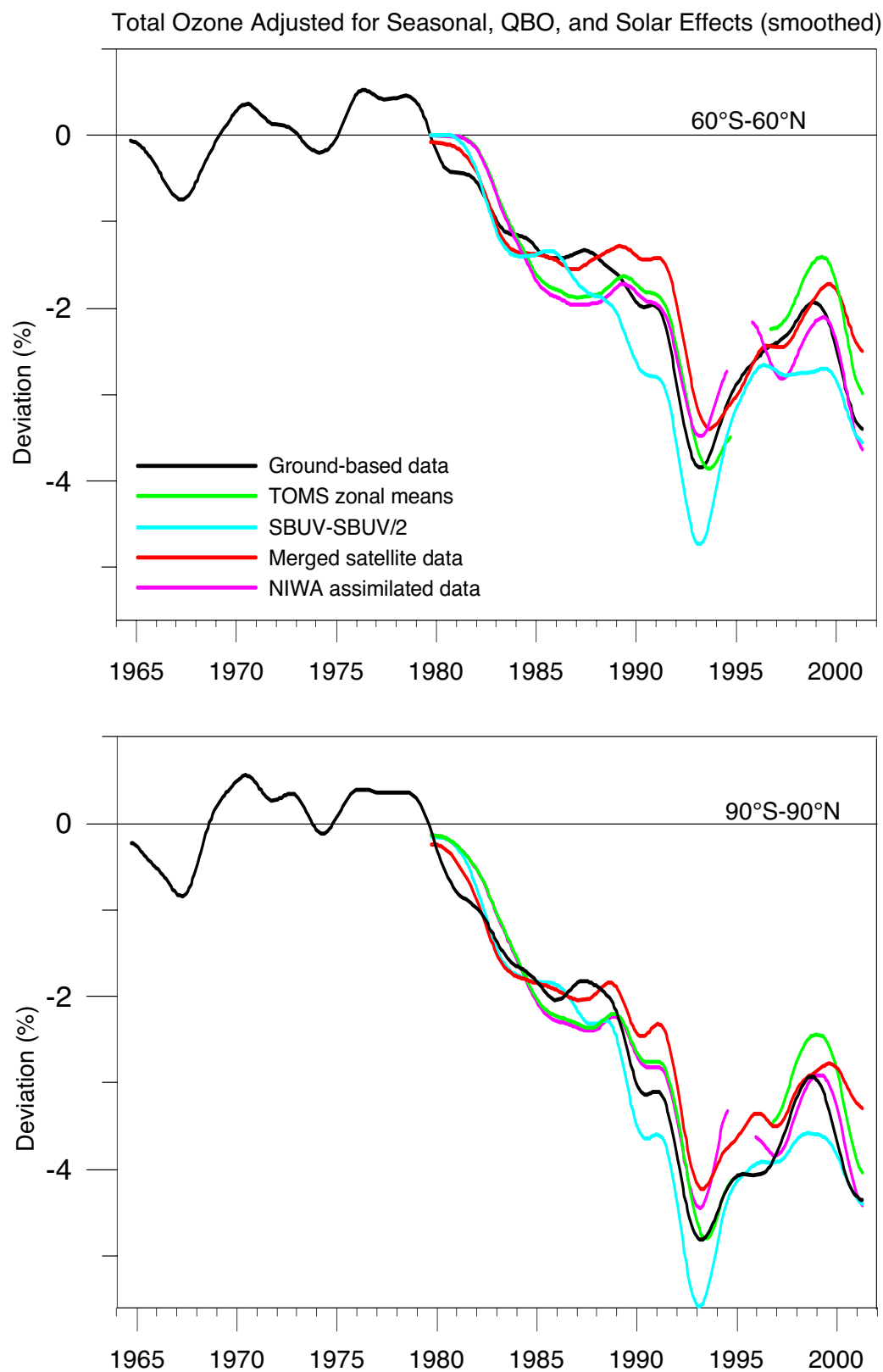


Figure 4-4. Deseasonalized, area-weighted total ozone deviations, adjusted for solar and QBO effects (as in Figure 4-3), smoothed in time using four passes of a 13-month running mean to highlight the lowest frequency interannual variations. Adapted from Fioletov et al. (2002).

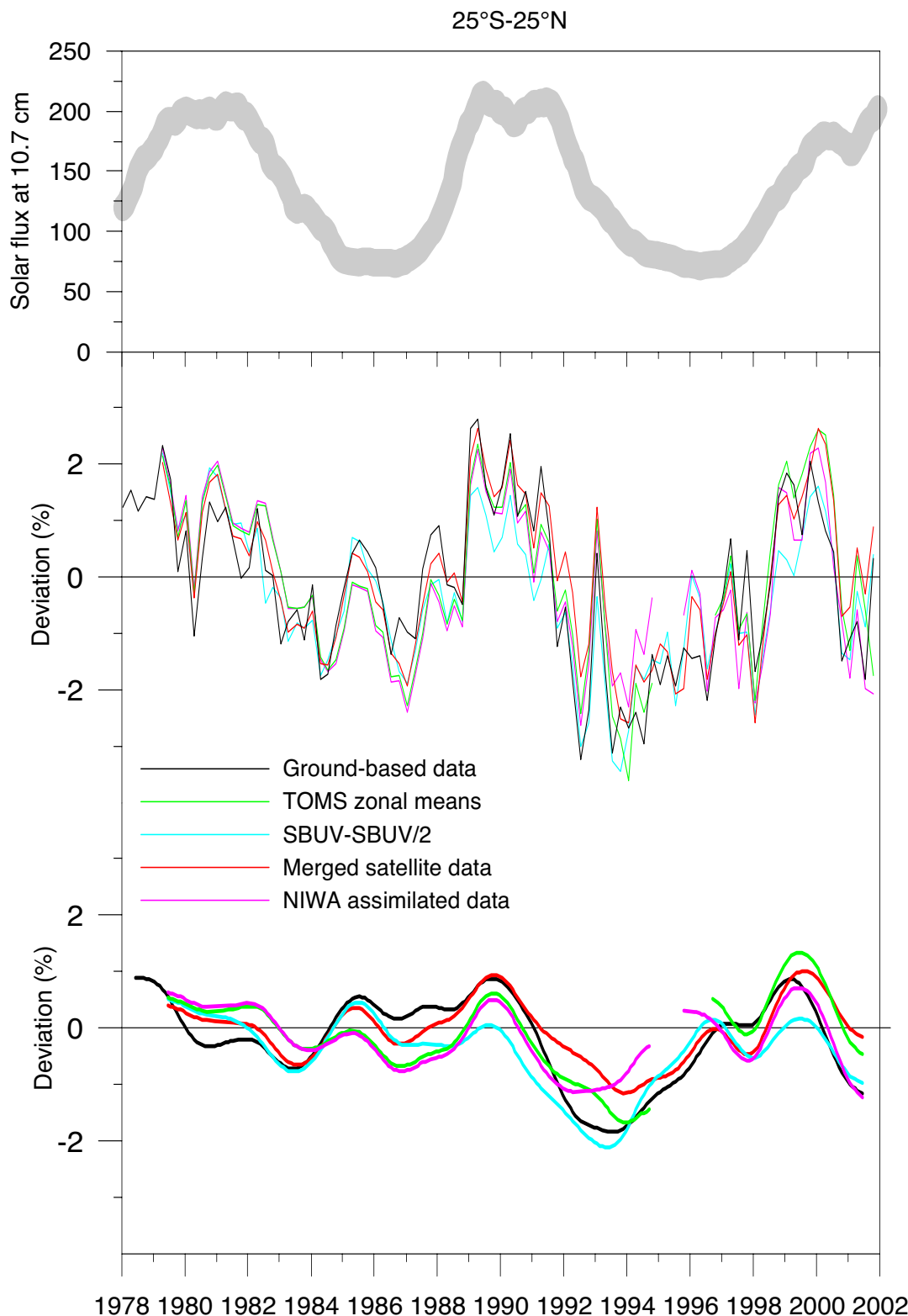


Figure 4-5. Upper curve: The smoothed solar flux at 10.7 cm, shown as a proxy for solar cycle variability. Middle curves: Deseasonalized, area-weighted total ozone deviations from the five datasets for the latitude range 25°S-25°N. Anomalies were calculated with respect to the ground-based data during 1964-1980. Lower curves: Deseasonalized data with the effect of the solar cycle removed by statistical regression, and then smoothed by four passes of a 13-month running mean. Adapted from Fioletov et al. (2002).

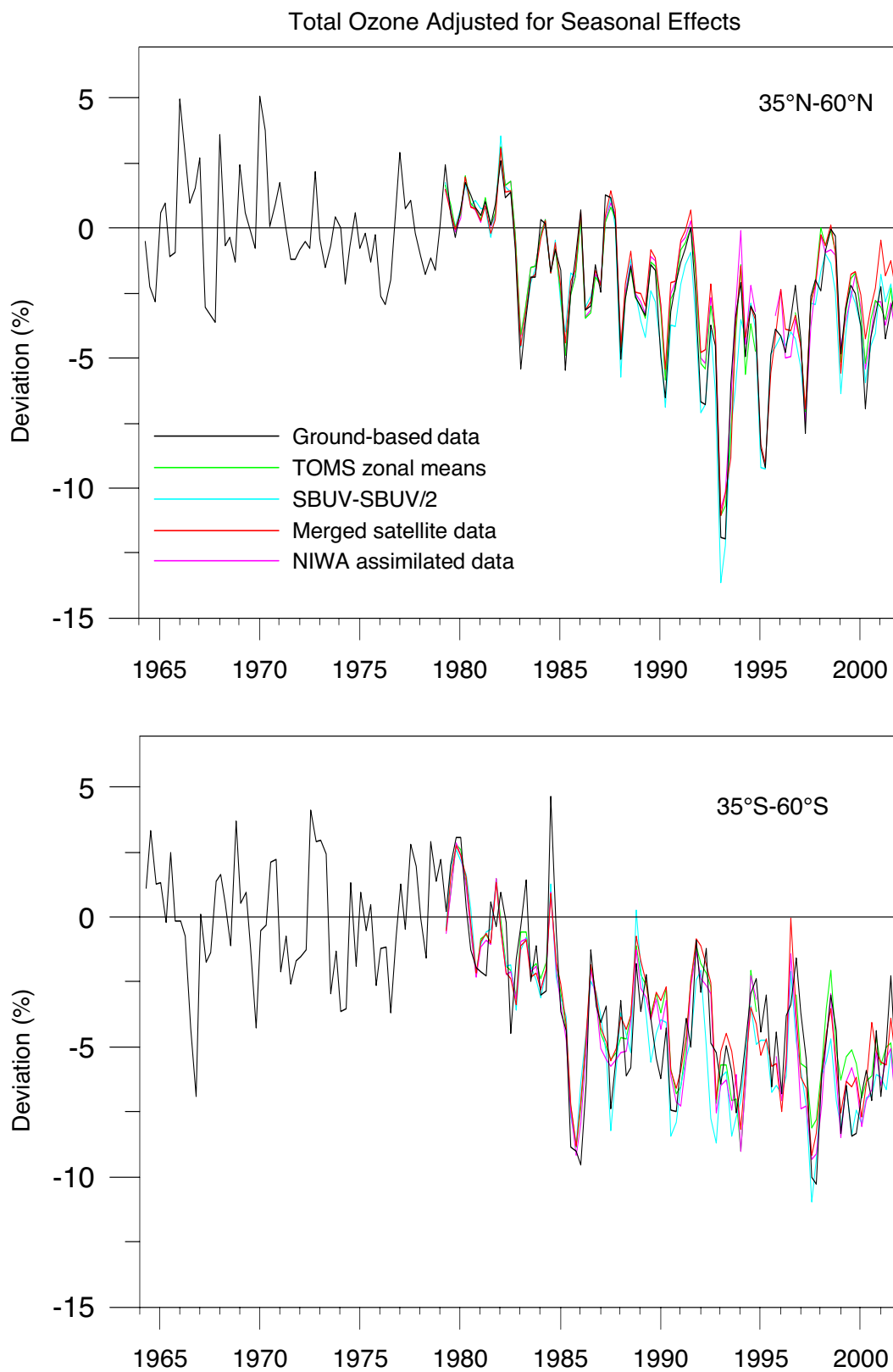


Figure 4-6. Deseasonalized, area-weighted total ozone deviations from five datasets for the latitude bands 35°N-60°N (top) and 35°S-60°S (bottom). Anomalies were calculated with respect to the time average during 1964-1980. Adapted from Fioletov et al. (2002).

GLOBAL OZONE

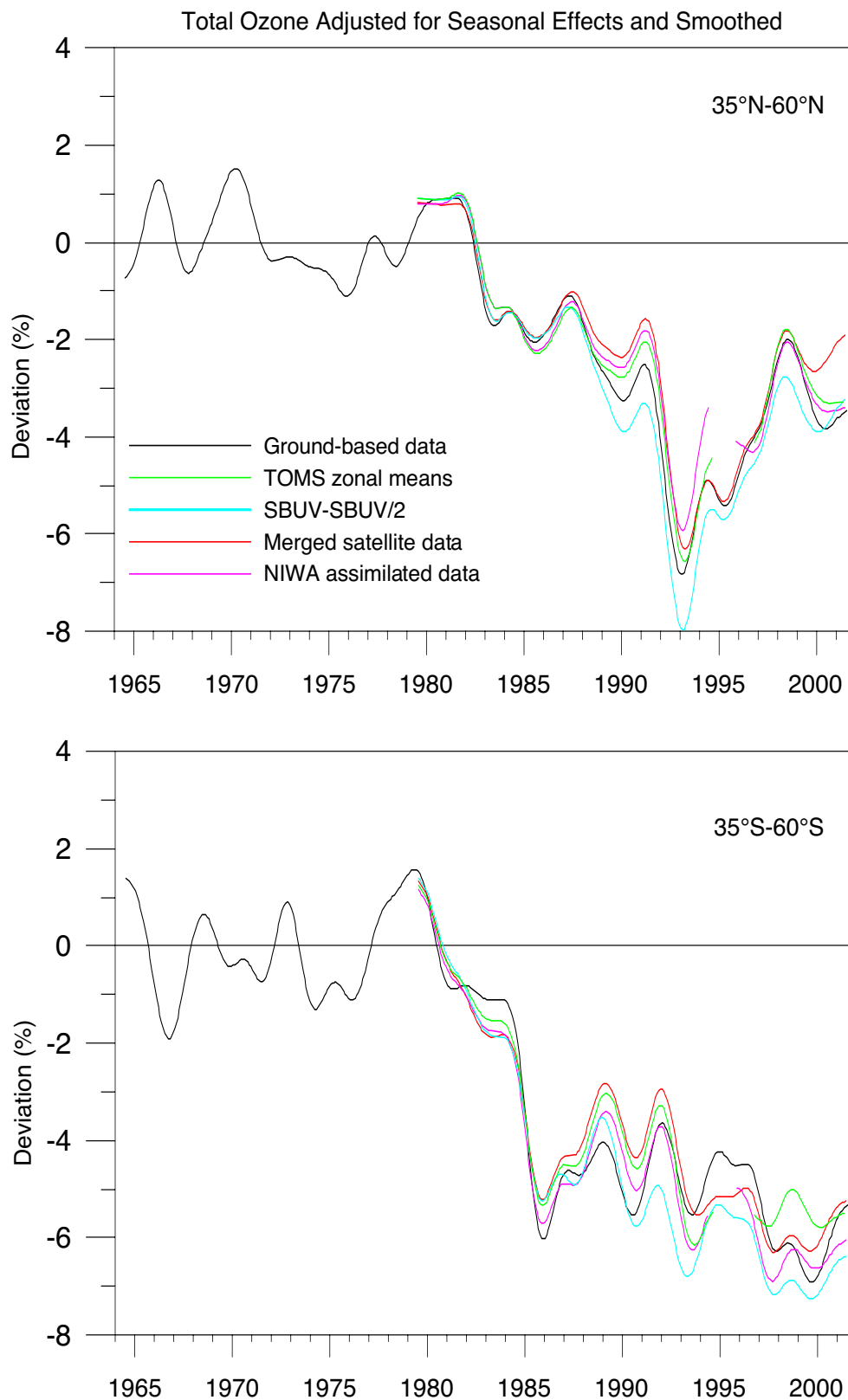


Figure 4-7. Deseasonalized, area-weighted total ozone deviations for the midlatitude regions of 35°N-60°N (top) and 35°S-60°S (bottom) (as in Figure 4-6), but smoothed by four passes of a 13-point running mean. Adapted from Fioletov et al. (2002).

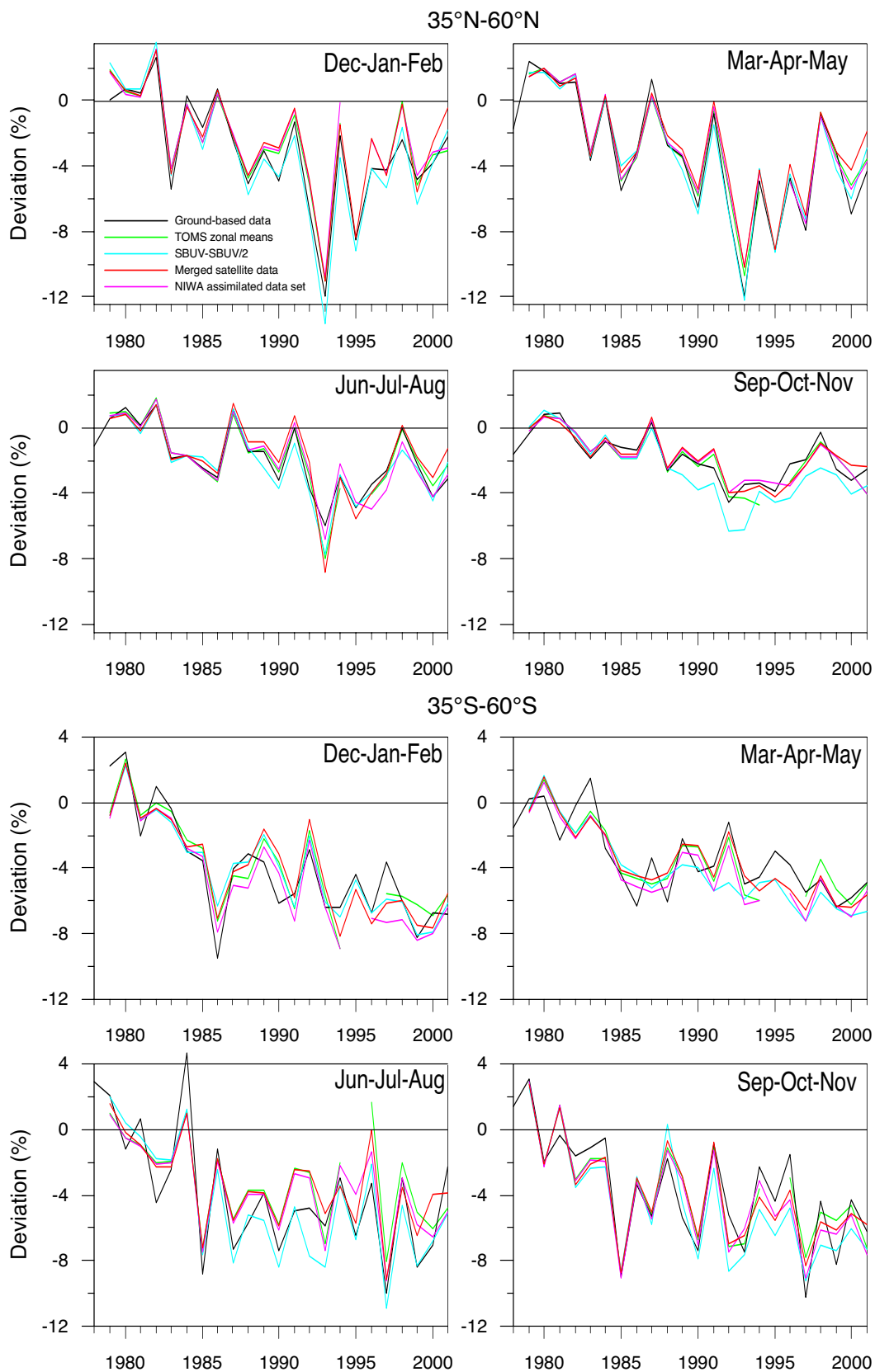


Figure 4-8. Area-weighted total ozone deviations from the 1964-1980 means, calculated for four seasonal averages, for the latitude bands 35°N-60°N (top) and 35°S-60°S (bottom). Adapted from Fioletov et al. (2002).

4.2.3 Changes in the Vertical Profile of Ozone

Changes in the vertical profile of ozone are a key part of the overall fingerprint that helps constrain the understanding of long-term ozone changes. The SPARC (1998) and WMO (1999) Assessments demonstrated that long-term changes in the ozone profile (for the period 1979-1996) have local maxima in the upper stratosphere (centered near 40 km) and lower stratosphere (15-20 km), with a relative minimum around 30 km. A similar result has been discussed by Smyshlyaev and Geller (2001) based on SAGE II measurements incorporated into a data assimilation model. The analyses here focus on updated ozone changes in the upper and lower stratosphere, using both time series and updated trend analyses (the latter are useful to highlight spatial patterns of change in sparse datasets, although the observed time variations are not linear). SAGE I+II data provide near-global measurements covering both regions, whereas the Umkehr and ozonesonde data provide independent information primarily over NH mid-latitudes. Trend calculations reported here use standard statistical analyses (SPARC, 1998).

4.2.3.1 UPPER STRATOSPHERE

SAGE I+II

A meridional cross section of the trends derived from the combined SAGE I (1979-1981) and SAGE II version 6.1 (v6.1) (1984-2000) data is shown in Figure 4-9. The overall pattern is very similar to previous SAGE I+II results that are based on shorter time records (e.g., the 1979-1996 results in WMO (1999)). The largest percentage changes are observed in the upper stratosphere (~35-45 km); maxima are in middle-high latitudes of both hemispheres, with a magnitude of about -5 to -7% /decade for the period 1979-2000. The 2σ uncertainty levels for these trends are of order $\pm 1-3\%$ /decade, depending on location. These trend maxima are slightly less than the WMO (1999) estimates, which are based on SAGE I+II data for 1979-1996. The region of significant negative trends in the upper stratosphere extends throughout the tropics, which is a change from previous results based on shorter time records (SPARC, 1998; WMO, 1999). There are no statistically significant differences between the upper stratospheric trends in the two hemispheres.

Trends derived from the SAGE II v6.1 data record alone (for the shorter period 1984-2000) are shown in

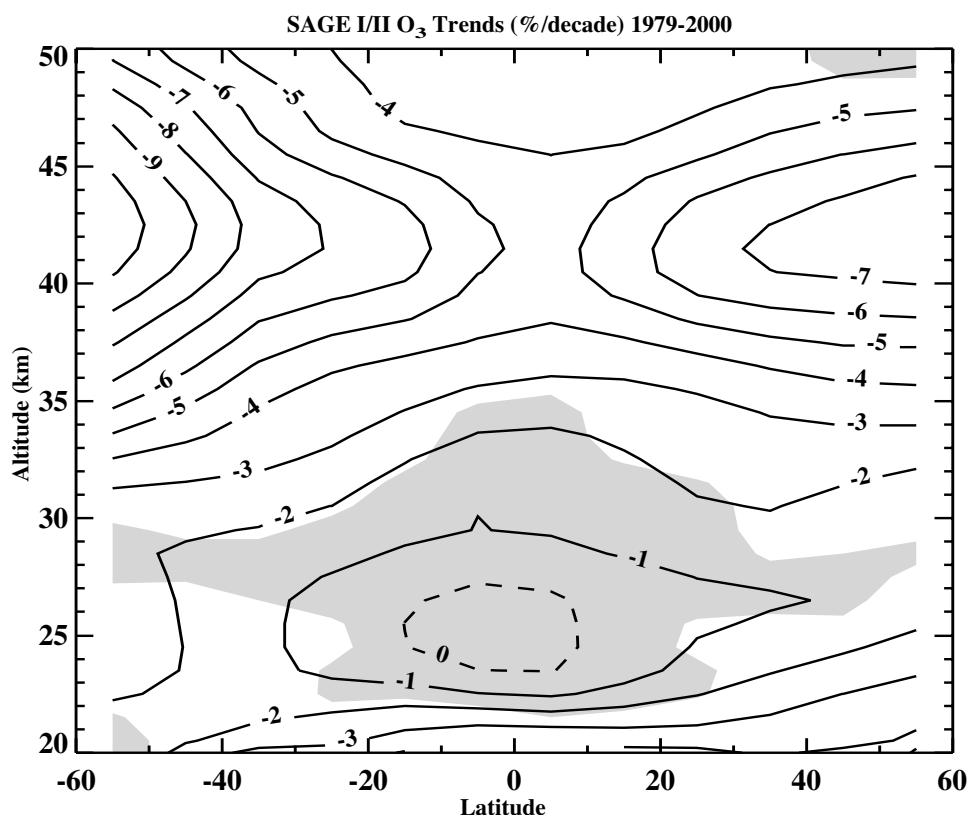


Figure 4-9. Meridional cross section of ozone profile trends derived from the combined SAGE I (1979-1981) and SAGE II (1984-2000) datasets. Trends were calculated in percent per decade, relative to the overall time average. Shading indicates that the trends are statistically insignificant at the 2σ (95%) level. Updated from H.J. Wang et al. (2002).

Figure 4-10. The spatial patterns of the trends are similar to the SAGE I+II record (Figure 4-9), but with smaller negative trends. Significant upper stratospheric trends for the 1984-2000 period extend into the tropics over 35-40 km. Upper stratospheric trends in the SH extratropics are somewhat more negative than those in the NH, but the differences are not statistically significant. At 40 km, the 30°-50°S trends are $-6.9 \pm 2.2\%$ /decade, while those over 30°-50°N are $-6.2 \pm 2.2\%$ /decade (2σ uncertainty). Time series of the SAGE I+II record in the upper stratosphere over 40°-50°N are shown in Figure 4-11 (integrated over 38-43 km, corresponding to Umkehr layer 8). The SAGE II data alone show a step-like change between ~1991 and 1993, with relatively constant ozone over ~1984-1991 and over ~1993-2000. Similar behavior is observed from SAGE data in SH midlatitudes (not shown). Inclusion of the SAGE I data (for 1979-1981) suggests an overall trend of approximately -5 to -7% per decade. Note that while the percentage changes in ozone are relatively high in the upper stratosphere (Figures 4-9 and 4-10), the associated contribution to the total ozone column change is relatively small (the changes over 1979-2000 in Figure 4-11 are less than 2 Dobson units (DU), compared with NH midlatitude column ozone changes of ~10-15 DU for the same period).

Umkehr

Umkehr ozone profile data have recently been reanalyzed using a new retrieval algorithm (Petrovskikh et al., 2001), and these data have been discussed in detail by Bojkov et al. (2002). Although historic Umkehr data are available from 13 sites, only a few have continuous long-term records free from significant discontinuities. Time series and trend analyses of Umkehr data here are estimated using the combination of measurements from Arosa, Switzerland (47°N), Boulder, Colorado, U.S. (40°N), Haute-Provence, France (44°N), and Belsk, Poland (52°N). The vertical structure of trends for the time period 1979-1999 in Figure 4-12 shows a maximum in the upper stratosphere (layer 8 trends of -5 to -7% /decade), a minimum near layer 5, and a separate maximum in the lower stratosphere. The vertical structure and magnitude of the trends are consistent with the SAGE I+II results in Figure 4-9. Umkehr trends for the shorter period corresponding to SAGE II (1984-1999) are smaller than those for 1979-1999 (layer 8 trends of -4 to -5% /decade), similar to the differences between the SAGE I+II and SAGE II-only results.

A time series of the deseasonalized Umkehr anomalies in Layer 8 (38-43 km) is included in Figure 4-11 for

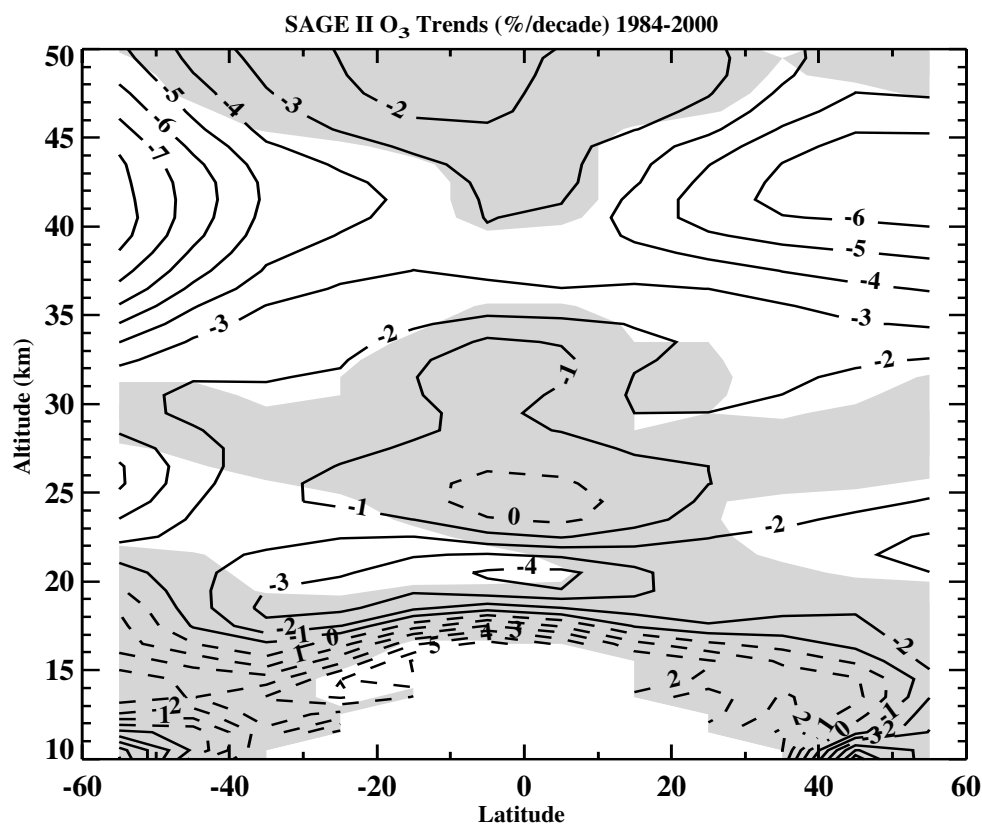


Figure 4-10. Meridional cross section of ozone profile trends derived from SAGE II v6.1 data for the period 1984-2000. Trends were calculated in percent per decade, relative to the overall time average. Shading indicates that the trends are statistically insignificant at the 2σ (95%) level. Updated from H.J. Wang et al. (2002).

GLOBAL OZONE

direct comparison with the SAGE I+II time series. There is a drop in the Umkehr ozone anomalies between 1982 and 1984 (of order $\sim -10\%$ background values), and a similar decrease is found in Nimbus-7 Solar Backscatter Ultraviolet (SBUV) spectrometer data covering 1979-1990 (Figure 3.12 of SPARC, 1998). There is a period of relatively constant Umkehr values over ~ 1984 -1994, and slight decreases after ~ 1995 . These latter decreases are not obvious in the SAGE II data, but direct comparisons of details between these time series are difficult due to the vastly different space-time sampling.

4.2.3.2 LOWER STRATOSPHERE

SAGE I+II

The SPARC (1998) analyses suggested that the SAGE I data are only of sufficient quality for trend studies above 20 km, so trend estimates with the combined SAGE I+II data cover 20-50 km. Trend estimates for 1979-2000 (Figure 4-9) show significant negative trends over the 20- to 25-km altitude region in the extratropics of both hemispheres, with magnitudes of -1 to -3% /decade. These trends are somewhat larger in the NH. The SAGE II data allow analyses to extend downward in altitude to the region of the tropopause (~ 10 km in the extratropics and ~ 16 km in the tropics). For the SAGE II period of 1984-2000, significant negative trends of order -2% /decade are observed in the lower stratosphere over approximately 20-25 km (Figure 4-10). However, significant extratropical trends are not found below ~ 20 km in either hemisphere for the 1984-2000 record.

Ozonesondes

Long records of ozonesonde observations (time series that extend back to at least the early 1970s) are available for 14 stations covering the latitude region 32° - 75° N (SPARC, 1998). Detailed trend analyses of these data for the periods 1970-1996 and 1980-1996 are discussed in SPARC (1998), Logan et al. (1999), and WMO (1999). For both time periods these results reveal significant negative trends that maximize in the lower stratosphere (over pressure levels ~ 200 -50 hPa, or altitudes ~ 12 -20 km). Trends for the period 1980-2000 have been compared with those for 1980-1996 (based on stations in the latitude range 36° - 59° N), and there are notable differences in the trends with the inclusion of 4 additional years of data (Figure 4-13). The difference in trends is largest in the lower stratosphere over ~ 200 -80 hPa (where the 1980-1996 trends are most negative): the mean decrease in stratospheric ozone for 1980-2000 is 5% /decade at 80

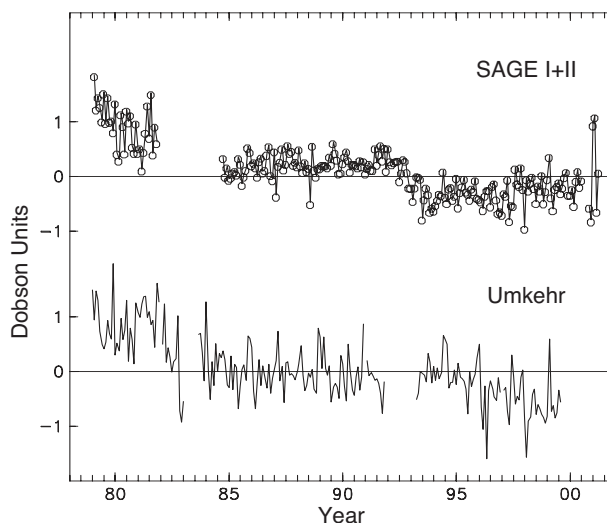


Figure 4-11. Top: Time series showing deseasonalized ozone anomalies over latitudes 40° N- 50° N, derived from SAGE I+II data integrated over altitudes 38-43 km. Bottom: Time series derived from an average of Umkehr measurements at Arosa, Boulder, Belsk, and Haute-Provence, for data in Umkehr layer 8 (approximately 38-43 km).

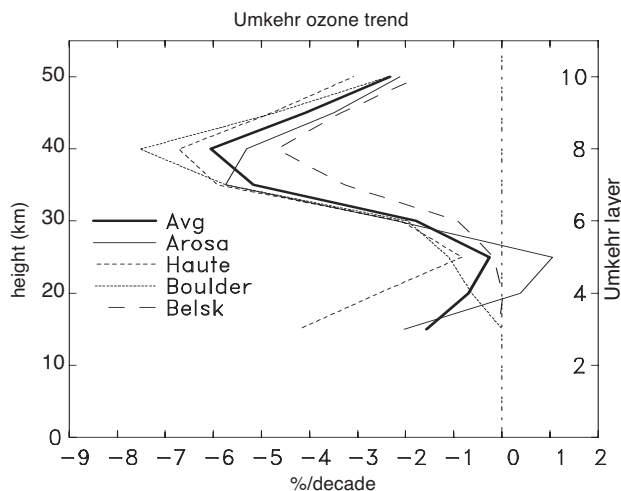


Figure 4-12. Vertical profile of ozone trends derived from Umkehr measurements at Arosa (1979-1999), Haute-Provence (1984-1999), Boulder (1979-1999), and Belsk (1979-1999). The dark line indicates the average trend. The 2σ (95%) uncertainty levels are near $\pm 3\%$ /decade throughout the profile.

hPa, 2.5% /decade smaller than that for 1980-1996. In contrast, there is little change in the trend results for pressure levels near and above 50 hPa (altitudes above ~ 21 km). Comparison of trends for the two periods 1970-1996

and 1970-2000 gives results with similar vertical structure (not shown), but the magnitude of the differences is much less for the longer record.

The reason for the change in the magnitude of the trends as a function of altitude can best be understood by inspection of time series for monthly ozone anomalies. Figure 4-14 shows deseasonalized ozone anomalies for four ~3-km layers spanning the lower to middle stratosphere, derived from the average measurements at three European stations: Hohenpeissenberg, Germany (48°N); Uccle, Belgium (51°N); and Payerne, Switzerland (47°N). Time series at the upper levels (63-40 hPa and 40-25 hPa) show a relatively continuous ozone decline throughout the record. In contrast, ozone in the lower stratosphere (the 158-100 hPa and 100-63 hPa levels) shows a decrease through the early 1990s, with relatively constant levels thereafter. Similar time series results are found for other locations. This flattening of the time series after ~1995 results in the reduced trends in the lower stratosphere for the 1980-2000 period compared with 1980-1996.

The longest continuous ozonesonde record in SH midlatitudes is from Lauder, New Zealand (45°S), covering the period 1986-2000. Figure 4-15 shows a time series of these data in 3-km layers, with similar format to the NH time series in Figure 4-14. While there is substantial interannual variability in these time series (much of it apparently related to the QBO), there are no significant stratospheric trends observed in the Lauder data for 1986-2000. This is somewhat different from the SAGE II trends in Figure 4-10 (showing negative trends over ~22-27 km near the latitude of Lauder), but direct comparisons are difficult in light of the very different space-time sampling. Note also that the lack of trends at Lauder for 1986-2000 is not inconsistent with the column ozone decreases seen

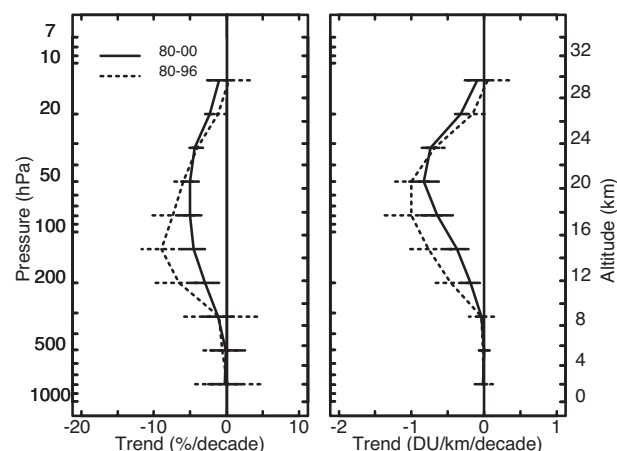


Figure 4-13. Annual mean profile of ozone trends for eight sonde stations located between 36°N and 59°N, for the time periods 1980-1996 and 1980-2000. Trend results are shown in percent per decade (left) and (DU/km/decade) (right). The 2σ error bars are shown.

in Figure 4-6, because much of the column decrease occurs between the pre- and post-1984 periods.

4.2.4 Vertical Integral of the Profile Trends vs. Column Trends

The ozonesonde results show that the largest contribution to interannual column ozone changes (over NH midlatitudes) occurs in the lower stratosphere, over approximately 160-40 hPa (13-23 km). To quantify that result, and directly compare the profile-versus-column ozone changes over NH midlatitudes, Table 4-1 shows the

Table 4-1. Comparison of vertically integrated ozone profile trends (DU/decade) over NH midlatitudes derived from ozonesondes (an average of eight stations over 36°-59°N), zonal mean SAGE I+II (35°-60°N), and zonal mean column ozone (35°-60°N), for the period 1980-2000. Results are calculated for seasonal and annual means. Column ozone trends are calculated from the merged satellite data. The 1σ uncertainty estimates are included in parentheses.

Altitude	Ozone Profile Trends (DU/decade)				
	DJF	MAM	JJA	SON	Annual
25-50 km (SAGE I+II)	-3.8 (0.9)	-2.0 (0.9)	-0.9 (0.9)	-2.1 (0.9)	-1.7 (0.5)
10-25 km (ozonesondes)	-8.5 (3.3)	-13.2 (2.8)	-6.8 (1.8)	-4.1 (1.6)	-8.2 (1.3)
0-10 km (ozonesondes)	+0.9 (0.6)	-0.2 (0.9)	-1.2 (0.9)	-0.2 (0.5)	-0.2 (0.4)
Column (merged satellite)	-9.0 (3.0)	-10.9 (2.8)	-5.9 (2.0)	-4.0 (1.7)	-7.4 (1.2)

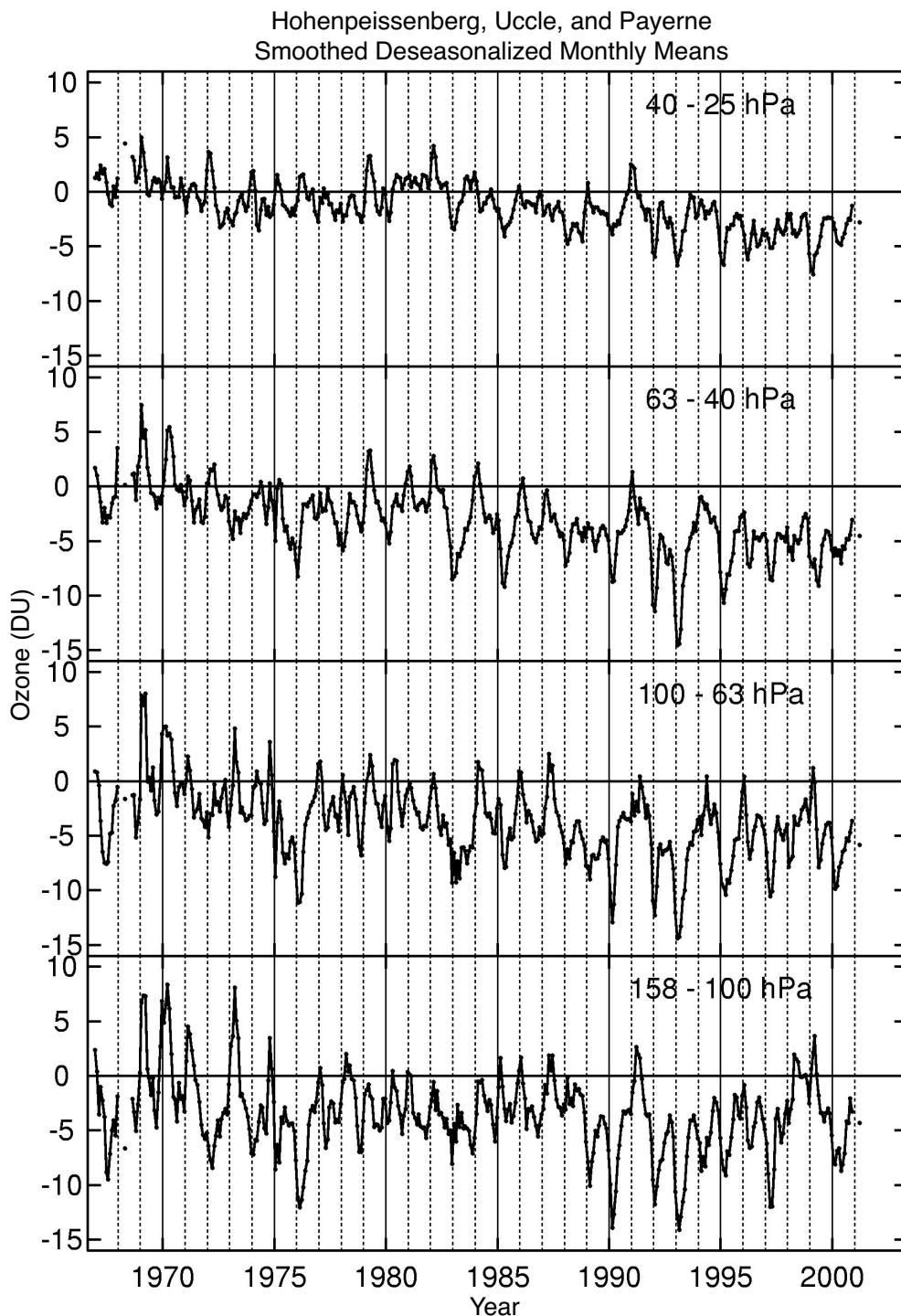


Figure 4-14. Time series of deseasonalized ozone anomalies for four altitude (pressure) layers, each approximately 3 km thick, based on ozonesonde measurements at three European stations (Hohenpeissenberg, Uccle, and Payerne). Anomalies were calculated with respect to 1970-1971.

vertical integral of the profile trends derived from ozonesondes (integrated over 10-25 km), compared with the zonal mean trends derived from the merged satellite data (these results are very similar to trends derived from the other column ozone datasets, as shown in Fioletov et al. (2002)). Also included are the integrated trends from SAGE I+II (over 25-50 km), to quantify the contribution of US ozone losses to the column trends, and tropospheric

ozone trends calculated from ozonesondes integrated over 0-10 km. Trends are calculated from all data for the period 1980-2000 (to directly compare with the ozonesonde results), and both seasonal and annual mean results are shown.

The integrated profile and column ozone trends in Table 4-1 show a number of important features. Ozone trends in the upper stratosphere (>25 km) derived from

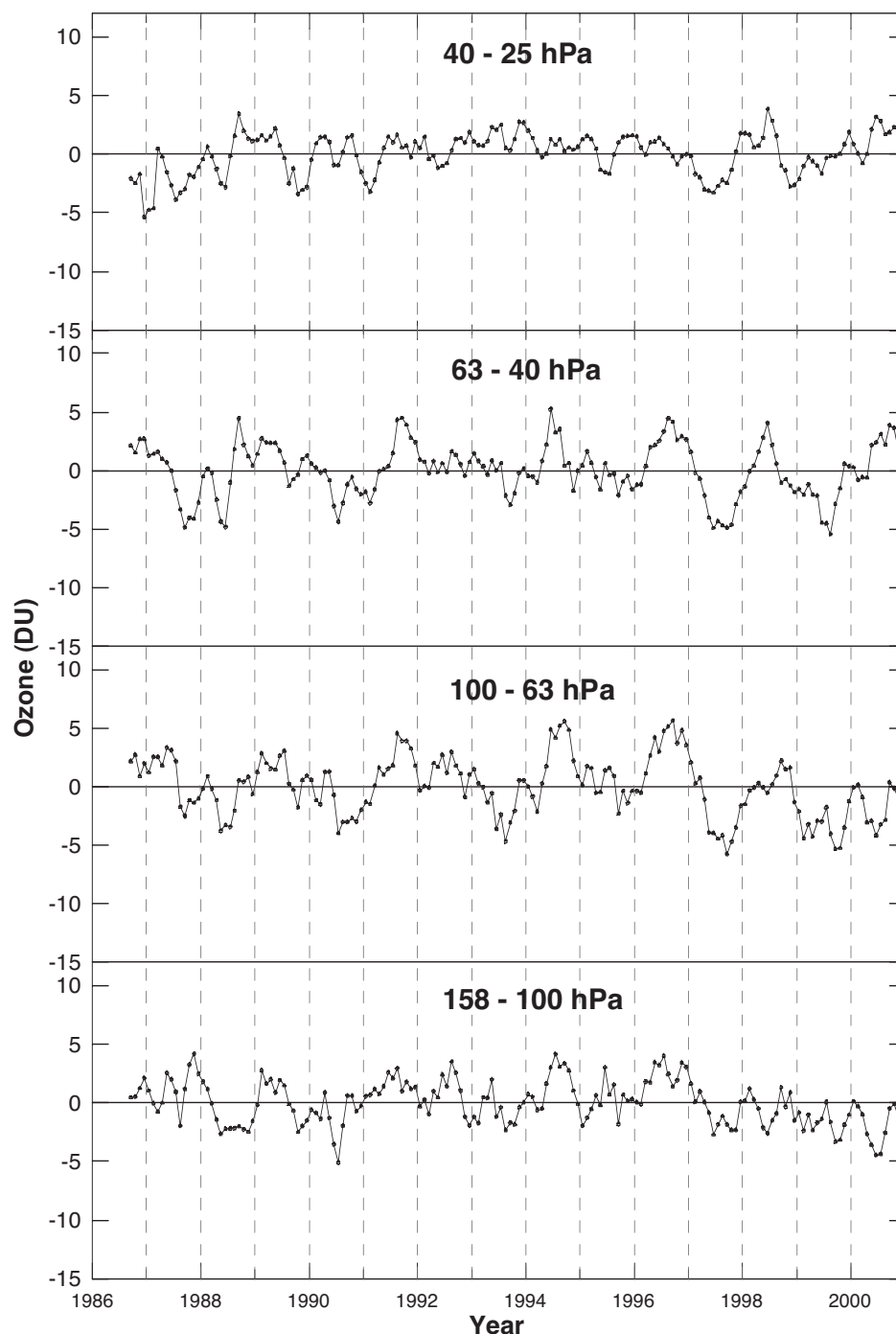


Figure 4-15. Time series of deseasonalized ozone anomalies for four altitude (pressure) layers, each approximately 3 km thick, based on ozonesonde measurements at Lauder, New Zealand.

SAGE I+II data are relatively small (of order ~ -2 -3 DU/decade), and account for a small fraction (15-30%) of the observed column losses. Tropospheric ozone trends do not contribute substantially to the column. There is reasonable agreement between the integrated ozonesonde trends (over 10-25 km) and column trends in terms of seasonality (largest losses in NH winter-spring), but less agreement in terms of magnitude. Partial column trends for 10-25 km calculated from the ozonesonde data are

consistently larger than the total column trends, for most seasons and for the annual mean. The agreement with the total column trends is even worse if the ozone losses above 25 km are included. The reason for the disagreement is not understood, but is likely related to the sparse sampling of the ozonesondes (only eight stations are included in these calculations). Note that the individual ozonesonde profile integrals are constrained to match co-located Dobson measurements, and hence the integrated profile

GLOBAL OZONE

trends will necessarily match the Dobson trends for these eight stations. The fact that the aggregated ground-based data from ~50 stations agree well with the zonal mean satellite data (e.g., Figure 4-6) suggests spatial sampling is at the root of the quantitative imbalances in Table 4-1. In any case, these results show that the major part of NH midlatitude column ozone trends is due to loss in the lower stratosphere (below 25 km), as stated in all previous Assessments.

4.2.5 Tropospheric Ozone

Trends in tropospheric ozone were discussed in detail in the previous Assessment (WMO, 1999), and here we summarize the key points from that report and provide a brief update. Trends in tropospheric ozone are highly variable and depend on region and on the time period considered (e.g., Logan et al., 1999; Oltmans et al., 1998; Tarasick et al., 1995). There were decreases or zero trends at the Canadian stations for 1970-1996, and decreases of -2 to -8%/decade for the mid-troposphere for 1980-1996. The three European stations showed increases for 1970-1996, but trends were close to zero for two stations for 1980-1996, and positive for one. There were increases in ozone for the three Japanese stations for 1970-1996, but trends were either zero or positive for 1980-1996. Time series of ozone given in Logan et al. (1999) and Oltmans et al. (1998) show that much of the increase in ozone in the middle troposphere over Europe occurred before the mid-1980s.

Trends have been calculated for 1970-2000 and for 1980-2000 and compared with those given by Logan et al. (1999) for the periods ending in 1996. The addition of 4 years of data makes the tropospheric trends for 1970-2000 less negative for the Canadian stations, and makes the trends statistically insignificant at Edmonton and Churchill (these stations have data starting in 1973). The extra 4 years of data make the trends for the European and Japanese stations slightly less positive. For the period 1980 to 2000, there is no significant trend in mid-tropospheric ozone for the Canadian stations, the U.S. stations, two Japanese stations, and one European station, Uccle; Hohenpeissenberg, Germany, gives a small decrease in tropospheric ozone, about 4%/decade, and Payerne, Switzerland, an increase of about 8%/decade. The lack of trend shown at most stations for 1980-2000 is responsible for the zero mean tropospheric trend shown in Figure 4-13 for the stations located between 36°N and 59°N.

Updated time series for tropospheric ozone (integrated over 1-10 km) are shown for three stations, in Europe, Canada, and Japan, in Figure 4-16. At Hohenpeissenberg, ozone has been lower in the past few years than the values reached in the mid-1980s and in

1996. All three European stations show continuing ups and downs in the 1990s, but these are not correlated among the stations (unlike for the stratosphere, where the behavior among the three stations is highly correlated). The Canadian stations show interannual variability in the 1990s, but little long-term changes (e.g., Goose Bay in Figure 4-16); at most stations, values are lowest in 1992 and 1993, as they are in the stratosphere. Tarasick et al. (2000) find an increase in tropospheric ozone at all six Canadian stations, but the increase has occurred only since 1993. The Japanese stations (e.g., Tateno in Figure 4-16) show relatively little interannual variability in the 1990s. These results show that tropospheric ozone trends vary considerably depending on location and the time period under consideration.

4.2.6 Solar Cycle Effects on Ozone

Global ozone observations display both a long-term decline and considerable interannual variability on a decadal time scale, which is approximately in phase with the 11-year solar cycle (Figures 4-2 and 4-5). In order to accurately characterize decadal variations in global ozone, and most directly compare them with model results that do not include solar forcing, it is important to quantify the solar cycle effect in the observational record. However, this is difficult for two reasons. First, the global observational record is relatively short, containing only two or three solar cycles (somewhat more for ground-based measurements at a few isolated locations; e.g., Angell (1989)). Second, a complicating factor for the recent record is that the large volcanic eruptions of El Chichón (1982) and Mt. Pinatubo (1991) occurred near the declining phases of the solar cycle in 1982-1984 and 1992-1994, and therefore there is the possibility of aliasing the volcanic and solar effects on ozone (Solomon et al., 1996). In this section the structure of the solar cycle in the updated data record is analyzed, including the most recent solar maximum period during 1999-2001. The availability of data from 1995-2001 provides a new opportunity to distinguish solar from volcanic signals better than was previously possible, as this is a period of no new volcanic activity together with an additional solar maximum. Hence, we present an updated analysis that uses the added years to examine the structure and statistical significance of the estimated solar signal in ozone, and we discuss comparisons with idealized model simulations.

4.2.6.1 COLUMN OZONE

Changes in solar ultraviolet (UV) spectral irradiance directly modify the production rate of ozone in the upper stratosphere (e.g., Huang and Brasseur, 1993), and

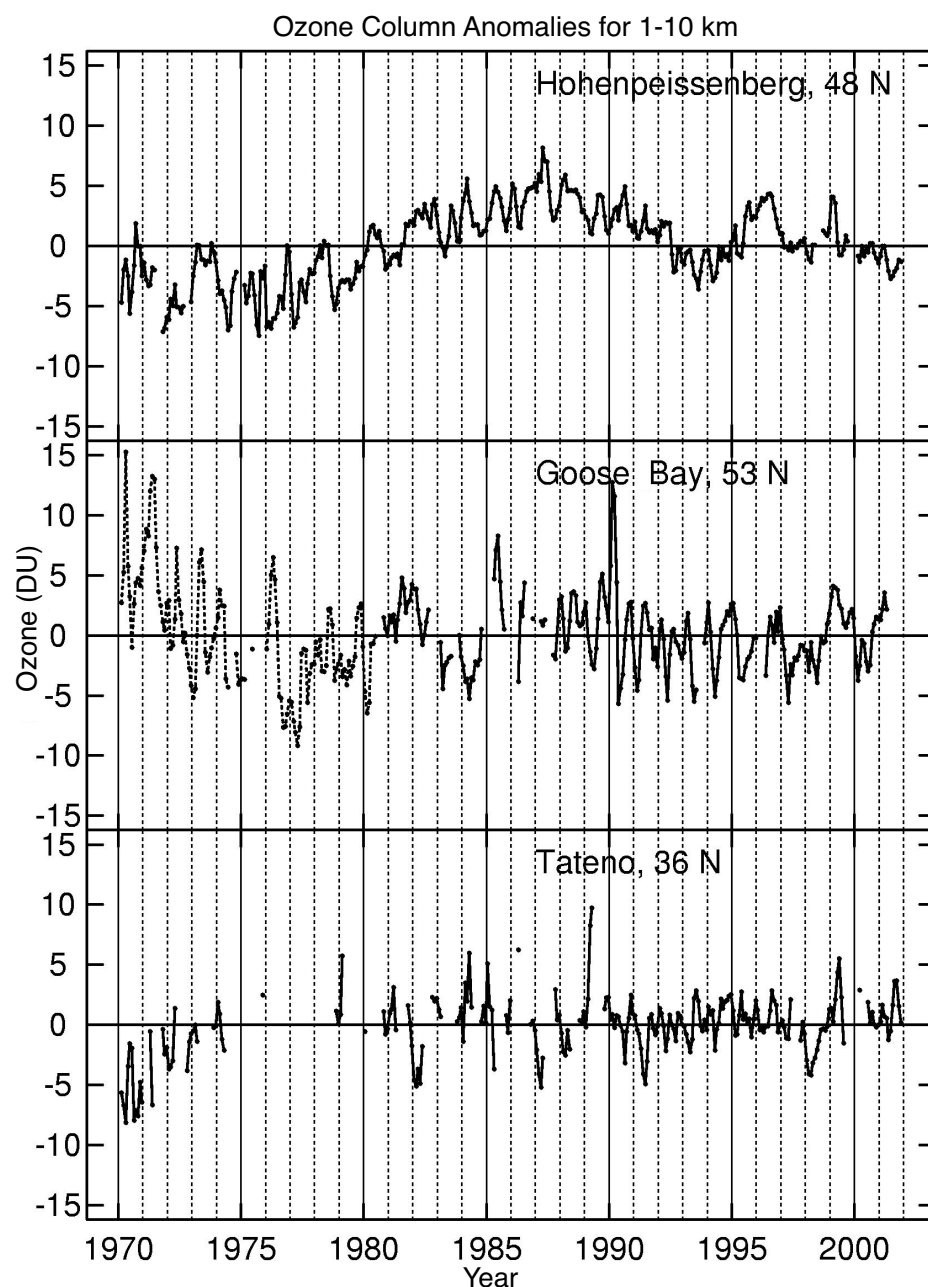


Figure 4-16. Time series of deseasonalized ozone anomalies for tropospheric column ozone, integrated between 1 and 10 km, for Hohenpeissenberg, Germany; Goose Bay, Canada; and Tateno, Japan. The dashed lines in the Goose Bay time series denote measurements by Brewer Mast ozonesondes, which were replaced by electrochemical concentration cell (ECC) measurements (solid lines).

hence it is reasonable to expect a solar cycle variation in total ozone amount. Analyses of ground-based records extending over three to six decades indicate the existence of a decadal time scale variation in column ozone, which is approximately in phase with the solar cycle (e.g., Angell, 1989; Miller et al., 1996; Zerefos et al., 1997). The global satellite records since 1979 show evidence for a decadal oscillation of column ozone with large amplitude at low latitudes (Chandra and McPeters, 1994; Hood et al., 1997; see also Figure 4-5). During at least the last three solar cycles, the decadal oscillation has been approximately in phase with proxies for solar ultraviolet flux,

and statistical representation is typically based on correlation with the 10.7-cm solar radio flux (F10.7).

The latitudinal structure of the solar cycle variation in column ozone derived from several updated datasets is shown in Figure 4-17. Here the solar cycle amplitude is derived from standard regression analyses (e.g., WMO, 1990), using F10.7 as a proxy for solar variability. These results are derived for several updated data including (1) the merged satellite data for 1979-2001, (2) the combined SBUV-SBUV/2 data, (3) the ground-based data for 1979-2001, and (4) the ground-based data for 1964-2001. Results based on the other satellite datasets

GLOBAL OZONE

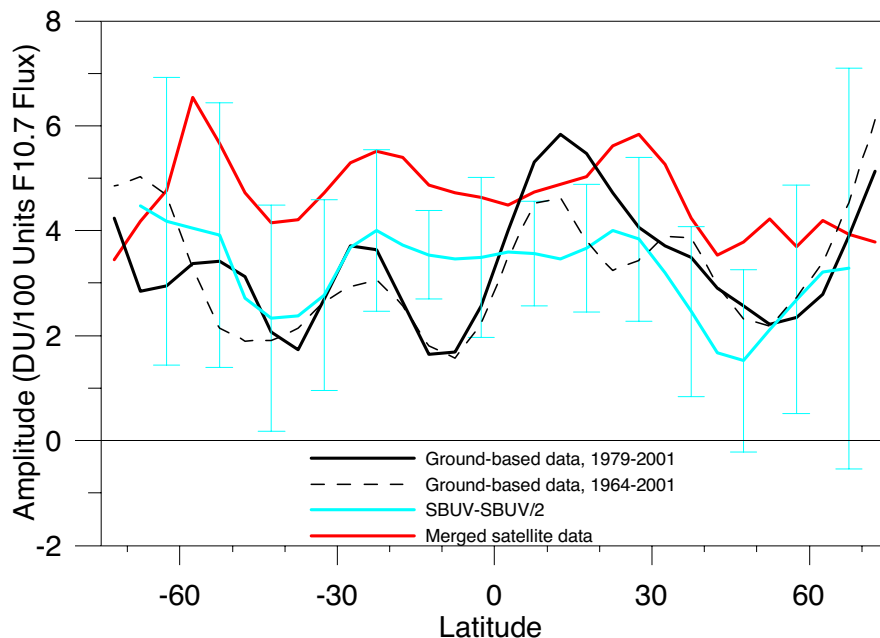


Figure 4-17. Latitudinal structure of the solar cycle regression coefficient calculated from the merged satellite data, SBUV+SBUV/2 data, and ground-based data for the period 1979-2001, and also from the longer record of ground-based data over 1964-2001. Error bars show 2σ regression uncertainty estimates for the SBUV+SBUV/2 results, and uncertainties for the other data are similar (not shown).

for 1979-2000 (which rely heavily on Total Ozone Mapping Spectrometer (TOMS) data) are similar to those from the merged satellite data and are not shown here. The derived solar cycle amplitude in Figure 4-17 from the satellite datasets shows a relatively flat latitudinal structure, with amplitudes in the tropics of approximately 5 DU/(100 units of F10.7) for the merged satellite data and 3.5 DU/(100 units of F10.7) for the SBUV-SBUV/2 data; the larger amplitude in the merged satellite data may be an artifact of the Nimbus-7 TOMS data, as discussed in Appendix 4A. Note that F10.7 varies from ~ 75 to ~ 200 units over a solar cycle (Figure 4-5), and therefore these derived amplitudes should be multiplied by ~ 1.25 to obtain the corresponding column ozone change over a solar cycle (tropical column ozone variations work out to approximately 2-3% between solar maximum and solar minimum). The statistical uncertainty of these fits is relatively large, with 2σ uncertainty levels of order ± 1 -2 DU/(100 units of F10.7) or larger, and the regression fits are most statistically significant in the tropics ($\sim 30^\circ\text{N}$ - 30°S).

The solar cycle amplitudes derived from the ground-based data for both the 1964-2001 and 1979-2001 time periods are similar to each other, and have significantly more latitudinal structure than seen in the satellite data results. Results over the NH (where the ground-based data are most dense) show values roughly consistent with the range of satellite-derived values. However, in the less well sampled SH, the ground-based solar signal is smaller than that derived from the satellite data, ranging from 2 to 3 DU/(100 units F10.7). The similarity of results from the two time periods (1964-2001 and 1979-2001) shows

that an increase of sampling from two solar cycles to three does not strongly influence these empirical estimates.

Solar cycle variations in ozone have been studied in a number of idealized modeling studies (e.g., Huang and Brasseur, 1993; Fleming et al., 1995; Lee and Smith, 2002). While this is (conceptually) a straightforward calculation, given knowledge of the variations in solar spectral irradiance over a solar cycle (e.g., Lean et al., 1997), there are possible dynamical feedbacks in the stratospheric climate system that can complicate the full solar influence. In addition, because there is likely some confusion between direct solar forced and volcanic effects on ozone for recent decades (as demonstrated in the idealized model results in SPARC (1998)), it is useful to perform model simulations with and without realistic aerosol variations to study this influence.

The simulated solar cycle in column ozone shows similarity between different model results, with details depending on the specific model. Fleming et al. (1995) and Lee and Smith (2002) derive a solar signal in column ozone with broad latitudinal structure, and a solar maximum-to-solar minimum amplitude of 1.5-2% (corresponding to 3-5 DU / (100 units of F10.7)), which is in reasonable agreement with observations in Figure 4-17. Lee and Smith (2002) include realistic aerosol effects for 1979-2000, which slightly increases the apparent solar signal in their model, but primarily outside of the tropics.

4.2.6.2 VERTICAL PROFILE OF THE SOLAR SIGNAL

The dependence on altitude of the ozone solar cycle has been investigated using SAGE I+II data by H.J. Wang

et al. (1996) and SPARC (1998). The results show coherent, in-phase ozone variations in the upper stratosphere (~35–45 km), with local variations of ~2–4%/(100 units F10.7), and these values are not substantially changed by the update of the SAGE II data through 2000 (not shown). Similar overall results are obtained from the shorter record of SBUV+SBUV/2 data for 1979–1994 (Chandra and McPeters, 1994; SPARC, 1998), and from analyses of Umkehr data over NH midlatitudes (Miller et al., 1996). The results from both SAGE I+II and SBUV+SBUV/2 measurements show an upper stratospheric solar signal with a minimum in the tropics and maxima in midlatitudes of both hemispheres, which is different from the broad latitudinal structure derived in idealized model simulations (e.g., Huang and Brasseur, 1993). Lee and Smith (2002) have suggested that this pattern arises in the short satellite observational record because of aliasing with volcanic and possibly QBO effects. The SAGE I+II and SBUV+SBUV/2 analyses also suggest a solar signal in the tropical lower stratosphere, which is not simulated in idealized models; SPARC (1998, Section 3.4.2) suggests that signal may arise from volcanic aliasing effects.

4.2.6.3 SUMMARY

Both global observations and idealized model simulations show column ozone variations that are approximately in phase with the 11-year solar cycle. The calculations of Lee and Smith (2002) suggest that volcanic aerosol effects alias onto the solar cycle in column ozone for the 1979–2000 period, but the effect is not excessive in the tropics (<30%), where solar effects are most significant in observations. The amplitude of the modeled response in the tropics is broadly within the range of observations in Figure 4-17, i.e., ~3–5 DU/(100 units F10.7), although there is considerable uncertainty in details of the observed “signal.” In spite of these uncertainties, the decadal variability in column ozone observed in the tropics (and in the global mean) is reasonably consistent with modeled solar variability, and model results suggest that the effect can be approximately isolated during 1979–2000 based on regression analyses. In contrast, there may be large uncertainties in isolation of the solar signal in the extratropics.

4.3 CURRENT UNDERSTANDING OF PAST CHANGES IN STRATOSPHERIC AEROSOL, WATER VAPOR, AND NO₂

Important components of the stratospheric climate system that directly influence ozone (and that are not dis-

cussed explicitly in Chapter 1) include stratospheric aerosol, water vapor, and nitrogen dioxide (NO₂). This section discusses the updated observations and current understanding of long-term changes in these constituents.

4.3.1 Stratospheric Aerosol Variability

Since the late 1970s, stratospheric aerosols have been observed by a variety of ground-based, in situ, and space-based instruments. In this two-decade time period, volcanic eruptions have strongly influenced stratospheric aerosol loading. The eruptions include those of El Chichón (Mexico, 1982) and Mt. Pinatubo (Philippines, 1991), the latter probably having the largest stratospheric impact of any volcano since Krakatau in 1883. On the other hand, stratospheric aerosol loading reached very low levels in the late 1970s, the late 1980s, and from the late 1990s to the present. On this time scale, stratospheric aerosol is perhaps the most variable component of the stratospheric composition. This variability is important because of the role aerosol plays in stratospheric ozone change through heterogeneous chemical processes as well as through aerosol-induced changes in stratospheric circulation.

Figure 4-18 shows a 25-year record of stratospheric aerosol variability based on integrated backscatter from the Fraunhofer Institute for Atmospheric Environmental Research (IFU) lidar (Jäger et al., 1995), together with 17 years of 1020-nm aerosol optical depth measurements by SAGE II. The dominant features are the 1982 eruption of El Chichón and the 1991 eruption of Mt. Pinatubo, which raised the integrated backscatter and aerosol optical depth values to more than 100 times their minimum values observed during this period. The effects of several smaller volcanic eruptions (indicated in the figure) can also be seen. The volcanic aerosols from the large tropical eruptions of El Chichón and Mt. Pinatubo were mixed relatively rapidly throughout the stratosphere, and time series over most of the globe are similar to those in Figure 4-18. With no significant eruptions after 1991, it is clear from Figure 4-18 that the relaxation to a nonvolcanic aerosol level lasted at least until 1999, i.e., more than 8 years. Therefore, with the possible exception of the late 1970s and the last few years, the entire record can be characterized as continual recovery from episodic volcanic injections of aerosol and their gaseous precursors (Bluth et al., 1992). This has made it extremely difficult to infer any long-term trends in aerosols associated directly with human activities or associated with other climate change phenomena. Longer-term measurements from individual stations (such as for the IFU lidar in Figure 4-18) show that current stratospheric integrated backscatter levels are

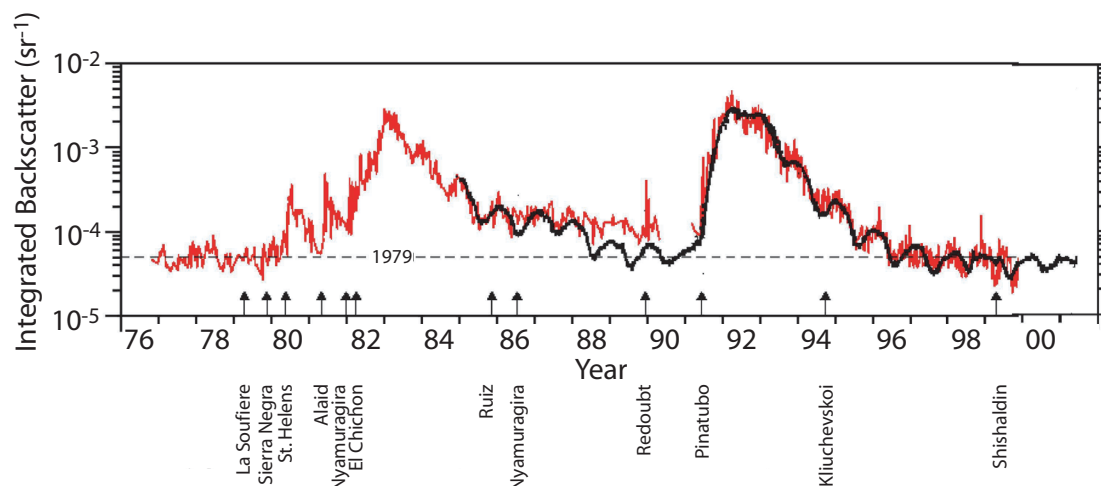


Figure 4-18. Multiyear time series of stratospheric aerosols measured by lidar (694.3 nm) at Garmisch (47.5°N, 11.1°E) in Southern Germany (red curve) and zonally averaged SAGE II stratospheric aerosol optical depth (1020 nm) in the latitude band 40°N–50°N (black curve). Vertical arrows show major volcanic eruptions. Lidar data are given as particle backscatter integrated from 1 km above the tropopause to the top of the aerosol layer. The curve referring to SAGE II data was calculated as optical depth divided by 40. For reference, the 1979 level is shown as a dashed line. Data from Garmisch provided courtesy of H. Jäger (IFU, Germany).

about the same or even less than those observed in the late 1970s, the period commonly considered the nominal stratospheric background period. Although various mechanisms have been suggested (e.g., Hofmann, 1990, 1991), there is currently no compelling evidence of a trend in the nonvolcanic aerosol loading, at least as it is measured by bulk parameters such as extinction or backscatter (Thomason et al., 1997).

The midlatitude records shown in Figures 4-18 reveal a clear annual cycle in addition to the long-term recovery from volcanic eruptions. In the tropics, the record mainly reflects monotonic decreases between volcanic events. However, during the recent clean period, an annual cycle in the column optical depth can be observed. The Climate Monitoring and Diagnostics Laboratory (CMDL) lidar record at Mauna Loa, Hawaii, shows an annual cycle during the current clean period that has been attributed to a transport of new material introduced into the tropics (Barnes and Hofmann, 2001).

Unlike instruments that measure ozone and most other stratospheric species, the instruments that quantify stratospheric aerosol often measure fundamentally different aerosol properties. Rather than measuring number density of a molecule, satellite-based instruments and aerosol lidar measure optical properties that arise from an underlying size distribution and composition that can only be indirectly inferred. As a result, assessing the quality of remotely sensed data and consistency between instruments can be challenging. This problem is illustrated in comparing the SAGE II 1020-nm stratospheric aerosol

optical depth with the IFU integrated backscatter in Figure 4-18 (with the optical depth divided by 40 for comparison). In most time periods the agreement between the two records is very good, because both capture the long-term recovery and the annual cycle. However, in the late 1980s the lidar value is nearly 50% larger than the adjusted SAGE II values. This could reflect the conversion between optical depth and backscatter (an extinction-to-backscatter ratio of 40), though it does not occur in a similar period in the 1990s, or it could reflect limitations in one or both instruments. However, the nature of the measurements makes an objective assessment difficult.

This problem has a direct impact on the assessment of the effect of aerosol on heterogeneous chemical processes and radiative/dynamical processes, and ultimately on ozone. The rates of most heterogeneous reactions are directly related to the aerosol surface area density, whereas extinction (i.e., total scattering plus absorption) is roughly proportional to aerosol volume density. Many models use a climatology of aerosol surface area and volume densities based on satellite observations as either direct input (e.g., Section 4.5.3) or as a verification of an internal simulation. Two long-term, global climatologies are derived from SAGE II and the Halogen Occultation Experiment (HALOE), which both use solar occultation measurements. SAGE II measures aerosol extinction in the visible and near-infrared, where extinction is dominated by scattering, whereas HALOE measures extinction in the infrared where extinction is dominated by aerosol absorption. Surface area and volume

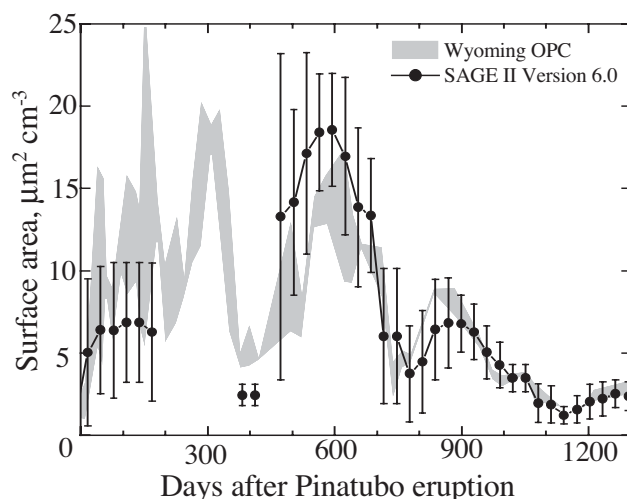


Figure 4-19. Comparison of surface area density inferred from the University of Wyoming optical particle counter (OPC) in Laramie, Wyoming, and that from SAGE II (zonally averaged between 35°N and 45°N). Figure updated from Thomason et al. (1997).

density data from these instruments agree reasonably well with data derived from the in situ optical particle counter (OPC) (Thomason et al., 1997; Hervig et al., 1997; Hervig and Deshler, 1998; Hervig and Deshler, 2002), with differences generally within 30 to 50%. An example of this reasonable agreement is shown in Figure 4-19. On the other hand, comparisons with measurements of aerosol surface area density by the in situ Focused Cavity Aerosol Spectrometer of Denver University are systematically larger than SAGE II estimates by as much as 100%. These differences may reflect the surface area of particles with radii smaller than 100 nm, which are effectively invisible to SAGE II because of their poor scattering efficiency in the visible and near-infrared (J.C. Wilson, University of Denver, personal communication). These differences between inferred surface area densities are large enough to introduce significant uncertainties into modeling of heterogeneous chemistry.

4.3.2 Stratospheric Water Vapor Trends

The recent Stratospheric Processes and their Role in Climate (SPARC) assessment of upper tropospheric and stratospheric water vapor (SPARC, 2000) has provided an extensive review of data sources and quality for stratospheric water vapor, together with detailed analyses of observed seasonal and interannual variability. The longest continuous reliable dataset is at a single location (Boulder, Colorado, U.S.), based on balloonborne frost-point hygrometer measurements, and dates back to 1981.

Over the period 1981-2000, a statistically significant positive trend of approximately 1%/year is observed at all levels between about 15 and 28 km (SPARC, 2000; Oltmans et al., 2000) (Figure 4-20). Increasing water vapor trends of ~2%/year are also found for 19-28 km in balloon measurements made from Washington, D.C., U.S., during 1964-1976 (Oltmans et al., 2000). However, although a linear trend can be fitted to these data, there is a high degree of variability in the infrequent sampling at individual locations, and the increases in either record are neither continuous nor steady. Long-term increases in stratospheric water vapor are also inferred from a number of other ground-based, balloon, aircraft, and satellite datasets spanning ~1980-2000 (Rosenlof et al., 2001), although the sampling uncertainty is high in many cases. Hurst et al. (1999) did not find a significant trend in the quantity $[\text{H}_2\text{O}+2\text{CH}_4]$ in the lower stratosphere from Earth Resources (ER)-2 aircraft measurements between 1993 and 1997, but this result is based on only eight infrequent time samples.

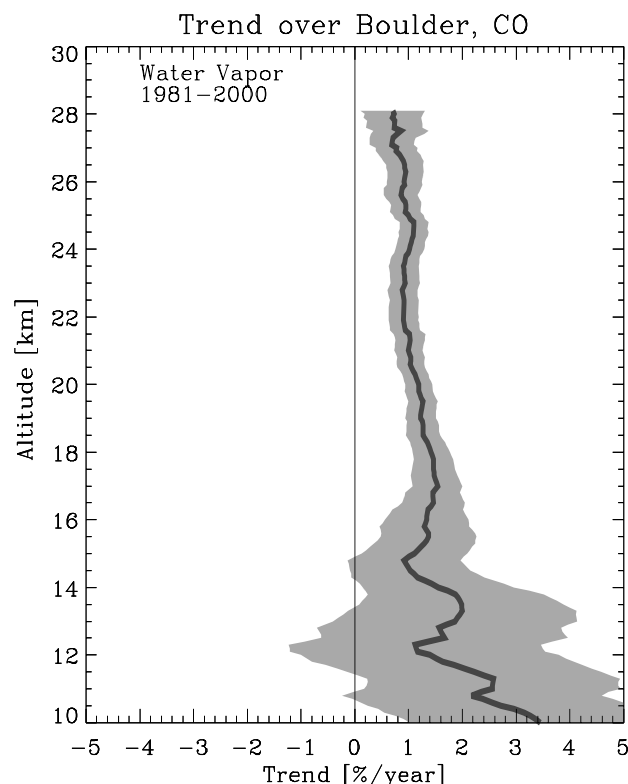


Figure 4-20. Vertical profile of trends in water vapor over Boulder, Colorado, U.S., for the period 1981-2000, expressed in percentage of the long-term means. The solid line is the trend computed at 250-m intervals, and the shaded region is the 95% confidence region. From Oltmans et al. (2000).

Global stratospheric water vapor measurements have been made by the HALOE satellite instrument for more than a decade (Russell et al., 1993). These data show long-term increases over almost the entire stratosphere above 25 km (Nedoluha et al., 1998a; Evans et al., 1998; Randel et al., 1999; C.A. Smith et al., 2000). For the period 1991-2001 the HALOE-derived water vapor trends have a magnitude of ~25 to 45 parts per billion by volume (ppbv) per year, which corresponds to local increases of ~0.6 to 0.8%/year, slightly smaller than the 1981-2000 Boulder balloon measurements. However, the HALOE data do not show significant trends in the lower stratosphere (between 20 and 25 km), which is a curious result given the strong coupling of stratospheric water vapor to the tropical tropopause region. Time series of the HALOE data furthermore show relatively large increases during the period 1991-1996, and a flattening after 1996 (Randel et al., 1999).

Causes of decadal-scale increases in stratospheric water vapor are not well understood at present. A substantial fraction of the stratospheric water vapor budget originates from the oxidation of methane, which accounts for the increase of climatological water vapor with altitude for 20-50 km. However, the observed ~1%/year water vapor increase observed in balloon and satellite observations is more than twice the magnitude that would be expected from observed trends in tropospheric methane alone. A simple explanation for the stratospheric water vapor increase would be an increase in average saturation mixing ratio at the tropical tropopause. However, observations of tropical tropopause temperature do not show a corresponding increase, but rather suggest a small decrease during the period 1979-1998 (Simmons et al., 1999; Randel et al., 2000; Seidel et al., 2001; Zhou et al., 2001a). The inability to explain past changes diminishes our confidence in the projection of future increases in stratospheric water vapor.

4.3.3 Trends in Stratospheric NO₂

Nitrogen dioxide (NO₂) plays a key role in stratospheric ozone chemistry, not only through the NO_x (NO + NO₂) catalytic destruction cycle, but also by interacting with the ClO_x (chlorine radicals) and HO_x (odd hydrogen) families, leading to the formation of important stratospheric reservoirs such as chlorine nitrate (ClONO₂) and nitric acid (HNO₃). Long-term monitoring of all these nitrogen compounds is among the priority tasks of the Network for the Detection of Stratospheric Change (NDSC; see <http://www.ndsc.ws>).

The longest record of column-integrated stratospheric NO₂ is available from measurements made since

1981 at the primary NDSC station of Lauder, New Zealand (45°S, 170°E, 370 m above sea level (asl)). The data (Liley et al., 2000) have been derived from UV-Visible scanning spectrometers that measure sunlight scattered from the zenith sky during sunrise and sunset. The time series at 90° solar zenith angle is continuous from 1981 to the present except for a break of 6 months in 1986. Measurement intercomparisons (Hofmann et al., 1995; Roscoe et al., 1999) have shown that the instruments and analysis procedure meet the standards of the NDSC. Time series of deseasonalized NO₂ anomalies in the sunrise and sunset Lauder measurements are shown in the lower panel of Figure 4-21 for the period 1981-2001. Large episodic decreases of NO₂ are observed following the volcanic eruptions of El Chichón (1982) and Mt. Pinatubo (1991), persisting for 2-3 years in each case. Linear-trend statistical fits to these data (Liley et al., 2000) show an upward trend of $5 \pm 1\%$ /decade over the period 1981-1999; trends extended through 2001 are somewhat larger, i.e., $6 \pm 1\%$ /decade.

Midday NO₂ column abundances have also been derived from the analysis of infrared solar spectra recorded since 1985 at the primary NDSC site of Jungfraujoch, Switzerland (46.5°N, 8.0°E, 3580 m asl). These measurements were made with Fourier transform instruments on clear-sky days during observation campaigns that became more regular and frequent after the NDSC was formalized in 1989. The deseasonalized anomalies from the Jungfraujoch measurements (Figure 4-21) show an overall increase with time, together with a transient NO₂ decrease associated with the Mt. Pinatubo volcanic eruption and its subsequent recovery (De Mazière et al., 1998), similar to that seen at Lauder. Trends calculated from the Jungfraujoch data give a linear rate of increase of $6 \pm 2\%$ per decade for the period 1985-2001 (an update of Mahieu et al., 2000). This trend is in good agreement with the Lauder results, indicating that the stratospheric burden of NO₂ has been evolving similarly in midlatitudes of both hemispheres since the mid-1980s.

The observed trends in stratospheric NO₂ above Lauder and the Jungfraujoch are about twice that of the total reactive nitrogen (NO_y) source gas, nitrous oxide (N₂O), for which surface emissions are known to be increasing the tropospheric concentration by about 3% per decade (WMO, 1999; also Chapter 1 of this Assessment). Model studies (Fish et al., 2000; McLinden et al., 2001) show that much of this difference is largely a result of ozone depletion. The model predictions of McLinden et al. (2001) of a +4.3%/decade trend in NO₂ consist of +2.4%/decade due to the N₂O increase, +2.5%/decade due to ozone depletion, and -0.6%/decade from the halogen

trend's impact on odd-nitrogen partitioning. Changes in the vertical distribution also contributed $+0.4\%/decade$ to the trend in slant-column density. However, this study ignored the effect of H_2O increases, which would decrease the modeled trend by $0.6\%/decade$ (Fish et al., 2000). Overall the observed N_2O increases and decreases in ozone appear sufficient to explain (within uncertainties) an NO_2 trend of $5 \pm 1\%/decade$.

4.4 CURRENT UNDERSTANDING OF PAST CHANGES IN STRATOSPHERIC TEMPERATURE

An evaluation of stratospheric temperature trends is an integral part of understanding ozone trends. Ozone is a key radiatively active gas throughout the stratosphere, and it is important to assess the degree of consistency between observed ozone trends and temperature trends. Furthermore, in the lower (upper) stratosphere halogen-related ozone depletion is generally accelerated (decelerated) by lower temperatures, and therefore quantification of temperature changes is crucial for understanding past and predicting future ozone changes.

4.4.1 Updated Observations of Stratospheric Temperature

An extensive evaluation of stratospheric temperature trends was conducted by the SPARC Stratospheric Temperature Trends Assessment, with results included in WMO (1999), along with some updates in Ramaswamy et al. (2001). We briefly report updated satellite-derived time series, based on Microwave Sounding Unit (MSU) and Stratospheric Sounding Unit (SSU) measurements; the latter are described in detail in WMO (1999). MSU channel 4 provides a measure of the weighted mean temperature for altitudes of 13-22 km, while several different channels of SSU provide temperatures for layers spanning the lower to upper stratosphere, with vertical resolution of about 10-15 km. We also include brief comparisons with temperatures from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalyses (Kalnay et al., 1996), which incorporate both satellite and radiosonde measurements in global analyses. The earlier assessments have discussed other sources of temperature trend data and the reasonable agreement between these and the satellite data.

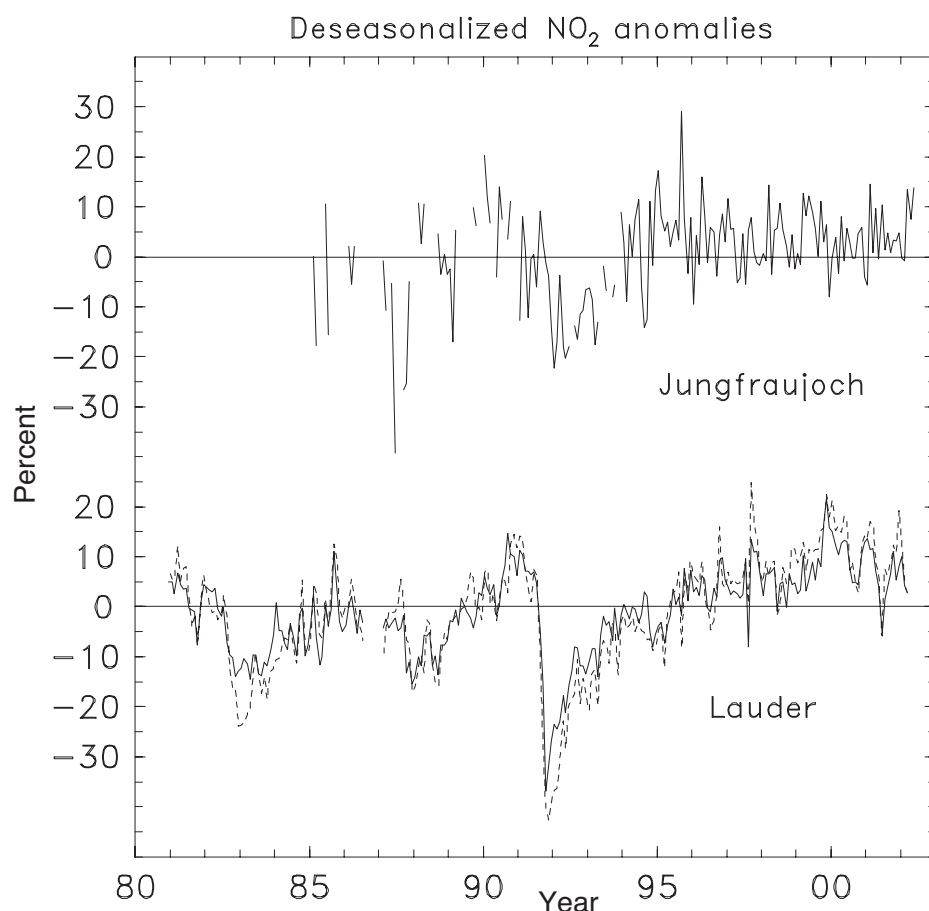


Figure 4-21. Time series of deseasonalized anomalies in slant column measurements of nitrogen dioxide (NO_2) measured at Jungfraujoch, Switzerland ($46^\circ N$), during 1985-2001, and at Lauder, New Zealand ($45^\circ S$), for 1981-2001. Lauder results are shown for measurements made at sunrise (dashed lines) and sunset (solid lines).

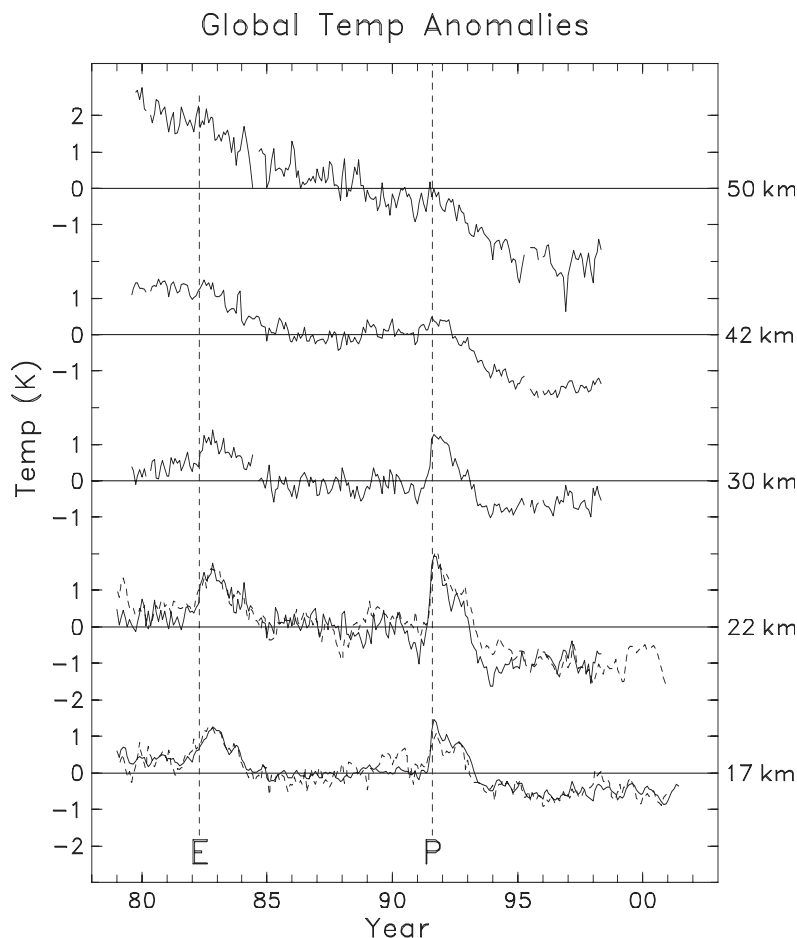


Figure 4-22. Time series of global mean temperature anomalies derived from satellite radiance measurements. The upper four curves (solid lines) are from the Stratospheric Sounding Unit (SSU) channels 47X, 27, 26X, and 15X (top to bottom) and represent mean temperatures for 10- to 15-km layers centered near 50, 42, 30, and 22 km, respectively. The bottom time series (solid line) is a global mean from the Microwave Sounding Unit (MSU) channel 4, which has a peak contribution near 17 km. The dashed lines for the two lower levels show global temperature anomalies derived from the NCEP/NCAR reanalyses, for pressure levels 50 hPa (22 km) and 100 hPa (17 km). The vertical dashed lines indicate the volcanic eruptions of El Chichón (1982) and Mt. Pinatubo (1991).

Time series of global mean temperature anomalies at levels spanning the lower to upper stratosphere are shown in Figure 4-22, based on deseasonalized monthly mean MSU (1979-2001) and SSU (1979-1998) datasets. Globally averaged temperatures in the lower and middle stratosphere (up to about 30 km) show a strong imprint of volcanic eruptions, with warming for 1-2 years following El Chichón (1982) and Mt. Pinatubo (1991) eruptions. Globally averaged temperatures near 17 km show an overall cooling from 1979 to 2001, but the anomalies are relatively constant for the period between the large eruptions; the time series suggest a “step-like” global-scale cooling of approximately 0.5 K following the eruptions. Also included for the lowest two levels in Figure 4-22 are globally averaged anomaly time series derived from the NCEP/NCAR reanalyses for 1979-2000 (100-hPa data plotted at 17 km, and 50-hPa data at 22 km). There is good overall agreement between the thick-layer satellite measurements and the reanalyses time series in the lower stratosphere.

The spatial structure of the annual mean stratospheric temperature trends for 1979-1998 is shown in Figure 4-23. Trends were calculated using a standard regression analysis, including proxies for the QBO and

solar cycle variations, and the two years following the El Chichón and Mt. Pinatubo volcanic eruptions were omitted from the time series to remove any volcanic influences (this has a small effect on the calculated trends, as shown in WMO (1999)). The annual mean trends show a high degree of interhemispheric symmetry. In the lower stratosphere there is statistically significant cooling in the extratropics (20°-60°N and S) of about 0.4 to 0.8 K/decade, which is relatively constant throughout the year (not shown). On the basis of satellite data, the equatorial lower stratosphere exhibits weak cooling (less than 0.4 K/decade), which is not statistically significant. There is a relative minimum in cooling in the middle stratosphere (around 30-35 km). The cooling increases monotonically with height from 35 to 50 km, with maximum values of about 2.5 K/decade near the stratopause (50 km).

4.4.2 Causes of Past Temperature Changes

The previous Assessment (WMO, 1999) concluded that ozone depletion was the dominant cause of global-mean temperature trends in the lower stratosphere. Ozone

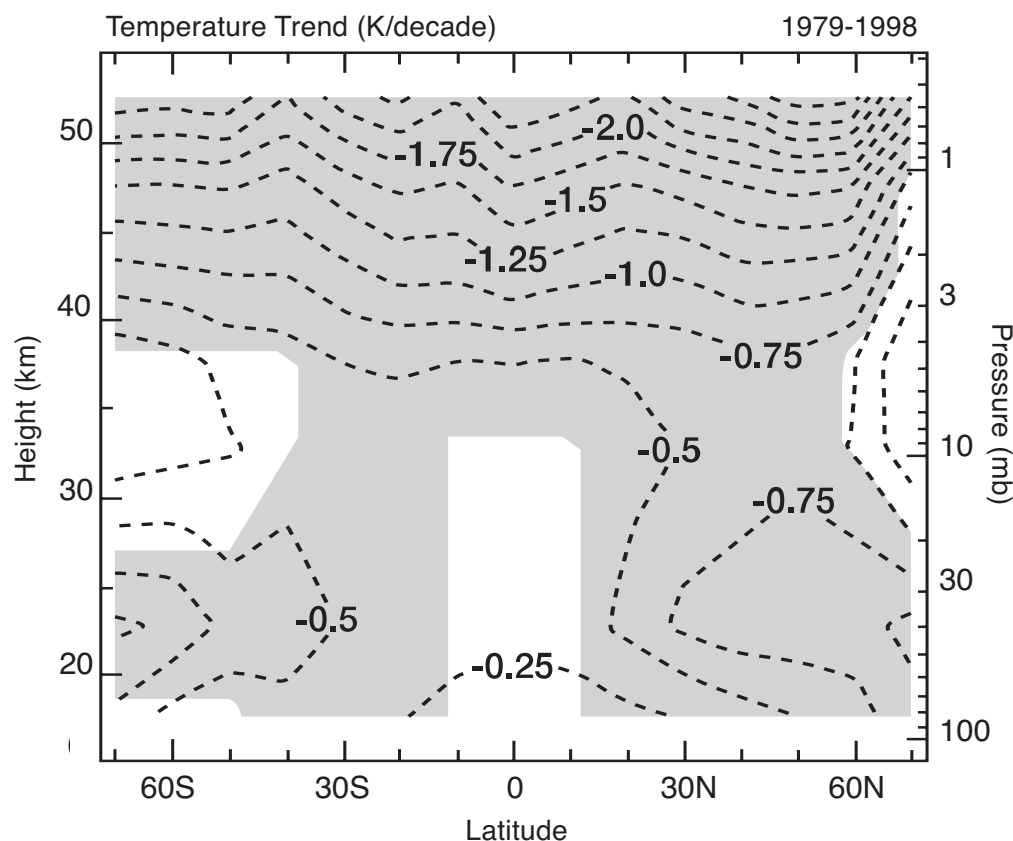


Figure 4-23. Meridional cross sections of trends (K/decade) in stratospheric temperature during January 1979-May 1998, derived from combined SSU and MSU satellite datasets. Shading indicates that the trends are significant at the 2σ level.

depletion and increases in the more well-mixed greenhouse gases (WMGGs) both contributed significantly in the middle and upper stratosphere. It also noted that there was little evidence that changes in tropospheric climate and sea surface temperatures have played a significant role in global-mean stratospheric temperature trends.

There have been significant developments in this area since WMO (1999). First, at the time of WMO (1999), most model studies used rather idealized vertical distributions of ozone change; more refined datasets on the vertical trends in ozone are now in widespread use. Second, several groups have reported simulated temperature trends using coupled chemistry-climate models. Third, much attention has been paid to the potential role of stratospheric water vapor changes on temperature trends.

The analysis here is centered on an intercomparison of available model results that have appeared in the literature or that have used established models. The models range from simple fixed dynamical heating (FDH) models, to two-dimensional (2-D; latitude-height) models, to general circulation models (GCMs) that use imposed ozone trends. The 2-D models and GCMs that incorporate coupled chemistry are discussed in Shine et al. (2002). Table 4-2 lists the contributors to this intercomparison,

together with some model details. More details of these intercomparisons were reported by Shine et al. (2002).

The emphasis of this section is on global-scale temperature changes. Chapter 3 considers polar temperature trends. All plots here include trends from the MSU and SSU data discussed above (Section 4.4.1). They are included on all plots for individual temperature trend mechanisms for reference, but the summary discussion will bring together the information from these individual mechanisms into a coherent picture. The abbreviation WMGG will be used to indicate the longer-lived and more well-mixed greenhouse gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and the halocarbons. For the GCM simulations, the 2σ unforced variability of the global-mean temperature is less than 0.25 K.

4.4.2.1 SIMULATED TEMPERATURE TRENDS DUE TO OBSERVED OZONE TRENDS

Improved analyses of vertical profiles of ozone change over the period from about 1979 to 1997 (e.g., Randel and Wu, 1999; Langematz, 2000) have now been used in models to re-examine the effect of ozone loss on temperature trends (Langematz, 2000; Ramaswamy and

Table 4-2. Contributors to the temperature trend intercomparison. “Timeslice” refers to the calculation of temperature trends by doing steady-state integrations of the model for conditions representative of 2 or more years and calculating the trend from the difference between these simulations. Transient models perform continuous integrations through the given period. The column labeled C refers to whether CO₂ changes are included, O refers to whether other well-mixed greenhouse gases are included, and H refers to whether water vapor trends are imposed. Note that in the absence of imposed water vapor trends, most models will have some water vapor change in response to other perturbations.

Institute	Contributor	Model	Ozone Trend	C	O	H	Experiment	Reference
Univ. of Cambridge, U.K.	P. Braesicke	GCM	Coupled but no changes in trace gases	N	N	N	Transient, obs. SSTs	Braesicke et al. (2002)
Freie Universität, Berlin, Germany	U. Langematz	GCM	Observed trend	Y	N	N	Timeslice	Langematz (2002)
DLR, Germany	V. Grewe, C. Schnadt	GCM	Coupled	Y	N	N	Timeslice	Schnadt et al. (2002)
Imperial College, U.K.	C.A. Smith, J.D. Haigh	2-D	Observed trend	N	N	Y	Timeslice	C.A. Smith et al. (2001)
Imperial College U.K.	C.A. Smith, J.D. Haigh	GCM	–	N	N	Y	Timeslice	Model is Rosier and Shine (2000)
NOAA Aeronomy Laboratory, U.S.	R.W. Portmann, S. Solomon	2-D	Coupled	Y	N	Y	Timeslice	Dvortsov and Solomon (2001)
NOAA GFDL, U.S.	V. Ramaswamy, M.D. Schwarzkopf	GCM	Observed trend	Y	Y	Y	Timeslice	Ramaswamy and Schwarzkopf (2002)
NASA GISS, U.S.	D. Shindell	GCM	Coupled	Y	Y	Y	Transient	Shindell (2001)
Met Office (UKMO), U.K.	J. Austin, N. Butchart	GCM	Coupled	Y	Y	N	Transient	Austin (2002)
Met Office (UKMO), U.K.	N. Butchart	GCM	–	Y	Y	N	Transient	Butchart et al. (2000)
Natl. Inst. of Env. Studies, Japan	T. Nagashima	GCM	Coupled	Y	Y	N	Transient	Nagashima et al. (2002)
Univ. of Reading, U.K.	M. Bourqui, K. Shine	GCM	Observed trend	Y	Y	N	Timeslice	Rosier and Shine (2000)
Univ. of Reading, U.K.	P. Forster	FDH	Observed trend	N	N	Y	Timeslice	Forster et al. (2001)

DLR, Deutsches Zentrum für Luft- und Raumfahrt; NOAA, National Oceanic and Atmospheric Administration; GFDL, Geophysical Fluid Dynamics Laboratory; NASA, National Aeronautics and Space Administration; GISS, Goddard Institute for Space Studies.

Schwarzkopf, 2002; Rosier and Shine, 2000; Smith, 2001; and Forster et al., 2001, who used three different radiation schemes). Figure 4-24 shows the vertical profile of the global and annual mean temperature trends as a function of pressure when only ozone changes are imposed. All models have the same qualitative behavior, with a peak cooling near the stratopause (~1 hPa) exceeding 1 K/decade, a minimum near 10 hPa, and a secondary cooling peak near 80 hPa of about 0.4 K/decade. However, there is a significant amount of disagreement in both the exact size of the cooling and the altitude of the main features, most particularly near 1 hPa. The dominant

reason for these differences seems likely to be the particular radiation codes being used (Forster et al., 2001) and the assumed background climatology of ozone (Ramaswamy and Schwarzkopf, 2002).

The latitudinal structure of annual and zonal mean temperature trends at 50 hPa from observations and models with observed ozone trends is shown in Figure 4-25. It is important to appreciate that whereas dynamical processes exert little direct influence on global-mean temperature at any given level (in the stratosphere), this is decidedly not true of temperatures over particular latitude bands. The general pattern in the GCMs is of a cooling of

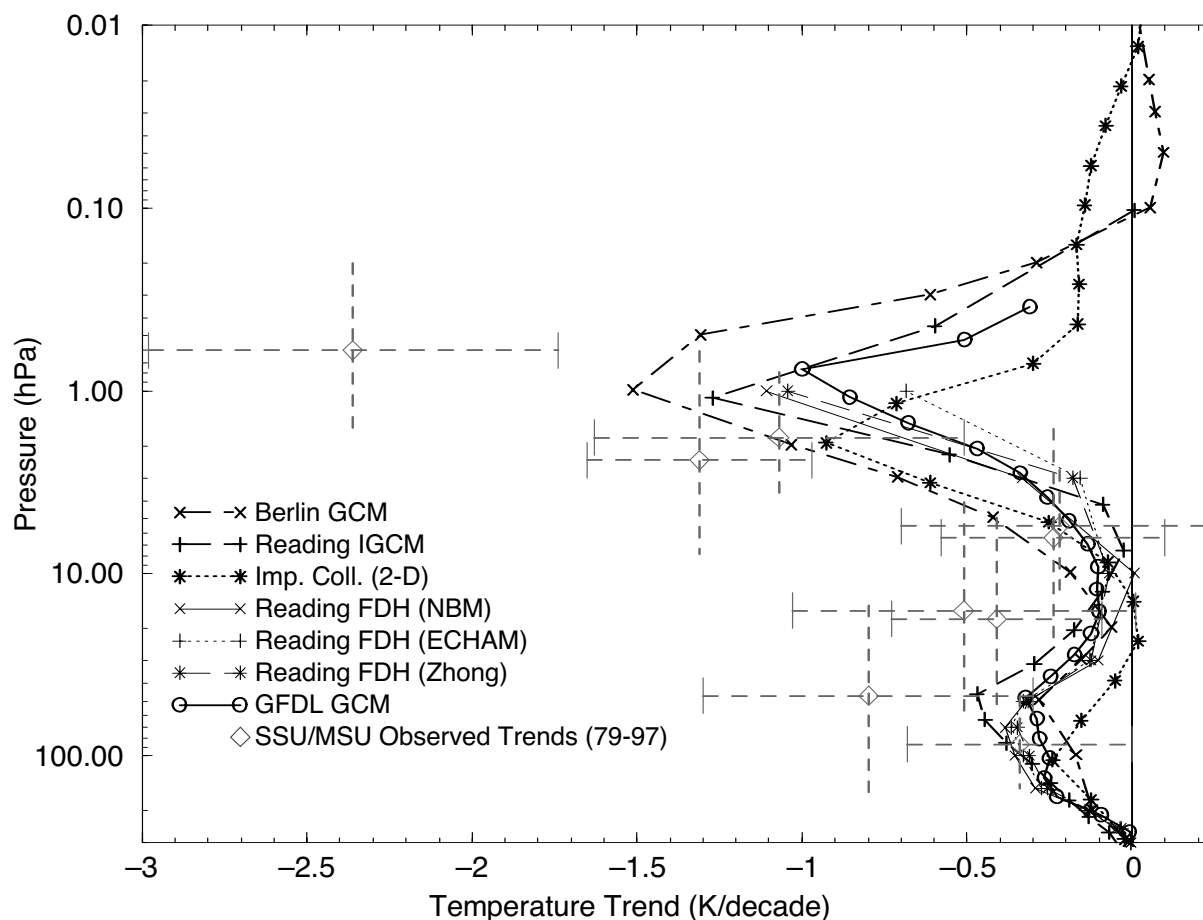


Figure 4-24. Global and annual mean temperature trends for models using imposed height-resolved ozone trends. The observations from MSU and SSU are also shown. The 2σ error bars in the observations are included; the vertical bars are intended to give the approximate altitude range sensed by the particular satellite channel. NBM, ECHAM, and Zhong refer to different radiative transfer codes used in the Forster et al. (2001) fixed dynamical heating model. NBM is a moderately high-resolution narrow band code; ECHAM and Zhong are general circulation model codes.

a few tenths of a Kelvin per decade, which is substantially less than the observed cooling in midlatitudes. At 100 hPa (not shown) the GCMs are in better agreement with observations: the models exhibit midlatitude cooling trends of around 0.3 K/decade, which overlaps the uncertainty levels of the (somewhat larger) observed trends. As a note, there are considerably larger latitudinal gradients in the temperature trends near Antarctica in the FDH models compared with the GCMs in Figure 4-25 (with the exception of the GFDL GCM); as discussed in Rosier and Shine (2000), changes in the GCM model circulation tend to ameliorate the radiatively driven high-latitude cooling.

A further contributor to temperature trends in the lower stratosphere comes from changes in tropospheric ozone concentrations (WMO, 1999); these change the amount of upwelling radiation that can be absorbed by

stratospheric ozone. Sexton et al. (2002), using tropospheric ozone increases derived from a chemical transport model (CTM), found a global mean cooling of about 0.05 K/decade at 50 hPa in recent decades. Although this cooling is smaller than that due to stratospheric ozone loss, it has likely been sustained over many decades; Sexton et al. (2002) estimated a 50-hPa cooling of about 0.5 K from tropospheric ozone changes over the 20th century.

4.4.2.2 SIMULATED TEMPERATURE TRENDS DUE TO INCREASED WMGG CONCENTRATIONS

There is qualitative agreement between the modeled cooling resulting from increases in WMGG concentrations. It generally increases monotonically with height from near zero at 100 hPa to about 0.8 K/decade at the

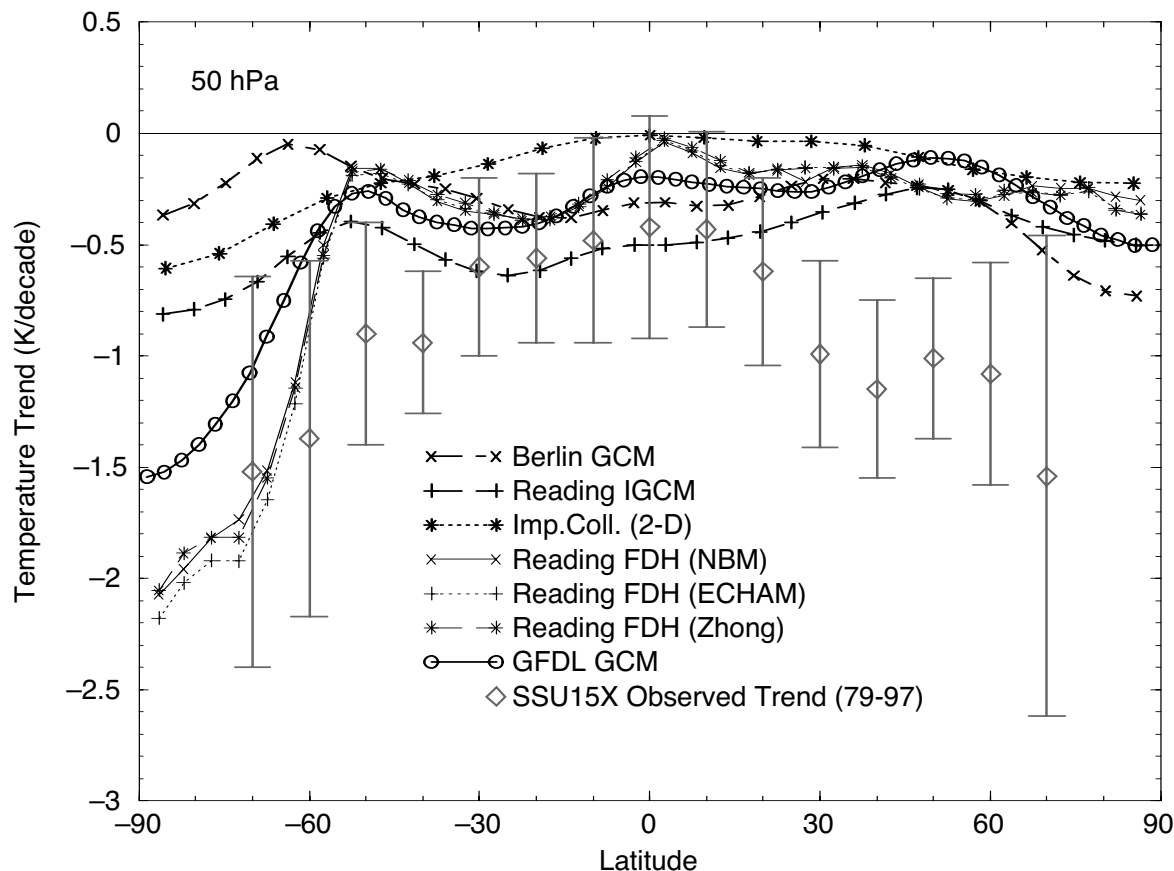


Figure 4-25. Global and zonal mean temperature trends at about 50 hPa for models using imposed height-resolved ozone trends. The observations from SSU channel 15X are also shown. The 2σ error bars in the observations are included. The peak of the SSU channel 15X weighting function is at about 46 hPa. Acronyms as defined in text and in Figure 4-24.

stratopause (not shown, but see Figure 5-24 of WMO (1999)). Between 100 and 10 hPa, there is general agreement between most models, but there is considerable divergence at about 1 hPa, with almost a factor of 4 difference between the model with the most cooling (UKMO, the United Kingdom Meteorological Office model) and that with the least (GISS, the Goddard Institute for Space Studies model). Given that the greenhouse gas changes are fairly linear and well constrained over this period, this divergence is surprising and may be related to the ability of individual radiation codes to simulate heating rates at lower pressures.

The zonal mean cooling at 100 hPa and 50 hPa (not shown) indicates near-zero cooling at all latitudes at 100 hPa and about 0.1 K/decade cooling at 50 hPa in most models. The GISS model gives considerably higher cooling at higher latitudes than other models; it reaches 0.5 K/decade at 60°N and S at 100 hPa and about 1 K/decade at the same locations at 50 hPa.

4.4.2.3 THE ROLE OF TRENDS IN STRATOSPHERIC WATER VAPOR

Observations of increases in stratospheric water vapor (Section 4.3.2) have led to renewed interest in its climatic implications (Forster and Shine, 1999, 2002; Dvortsov and Solomon, 2001; Oinas et al., 2001; Shindell, 2001; C.A. Smith et al., 2001). A major difficulty in comparing estimates of the impact on temperature of stratospheric water vapor changes is in estimating their temporal and geographical variation. Calculations with idealized water vapor changes (i.e., 700 ppbv from a background of 6000 ppbv) adopted by Forster and Shine (1999) and Oinas et al. (2001) are not included here. As noted by Forster and Shine (2002), it is not so much the idealized nature of the change that biases these estimates, but more the idealized background water vapor that is adopted. Both Oinas et al. (2001) and Forster and Shine (2002) demonstrate a strong dependence of the effect of a given perturbation on the assumed background concentrations.

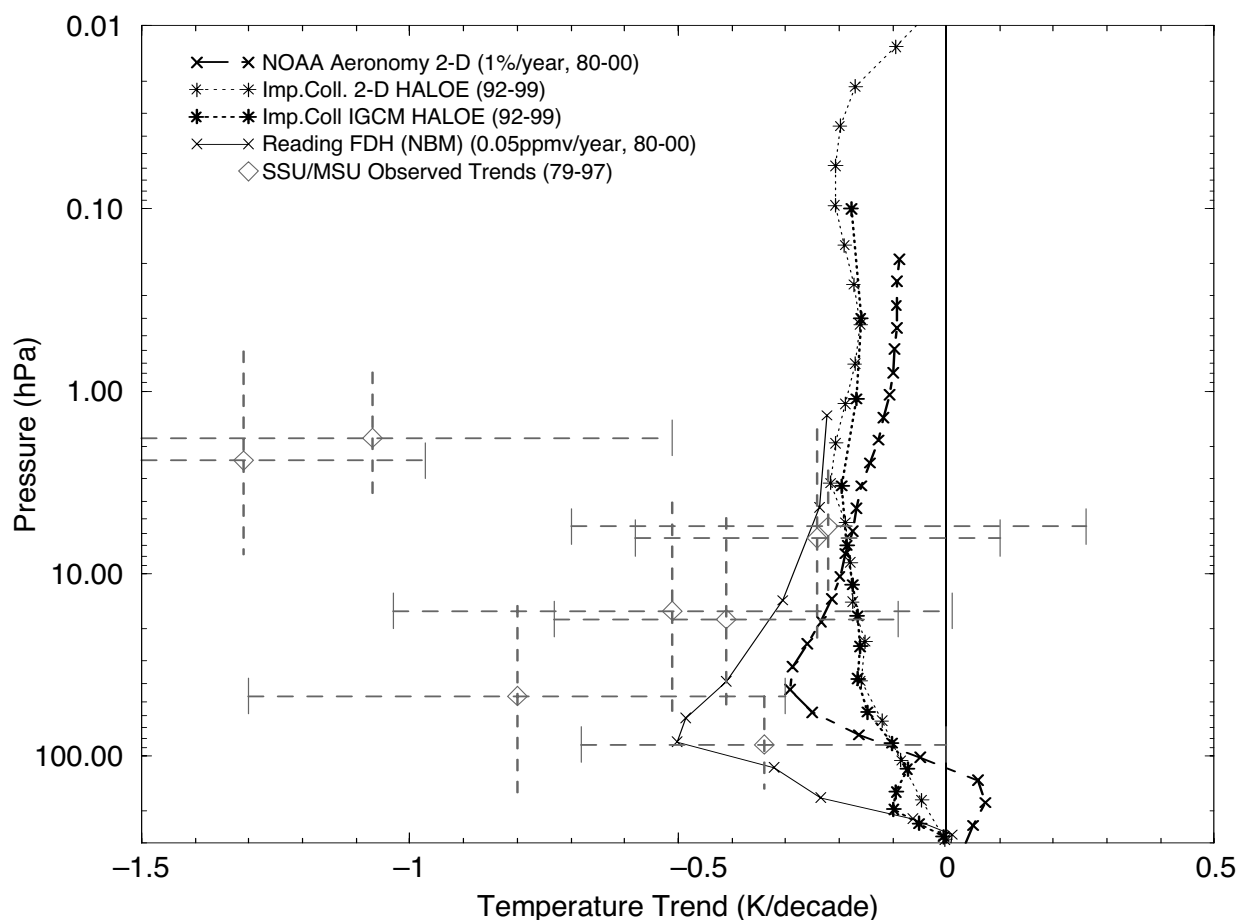


Figure 4-26. Global and annual mean temperature trends for models using imposed water vapor trends. The observations from MSU and SSU are also shown. The 2σ error bars in the observations are included; the vertical bars are intended to give the approximate altitude range sensed by the particular satellite channel. Acronyms as defined in text and in Figure 4-24.

Figure 4-26 shows the vertical profile of the modeled global and annual mean temperature trend, derived for water vapor changes specified ideally (e.g., constant percentage global increases) or derived from HALOE observations. Much of the divergence between the models is likely due to differences in the adopted water vapor trend; this uncertainty is severe. In the mid-to-upper stratosphere the models all produce a cooling of about 0.2 K/decade, but at lower levels there is significant divergence. The latitudinal structure of zonal mean trends at 100 and 50 hPa (not shown) reflects this divergence; furthermore, at mid-to-high latitudes water vapor increases could be causing cooling of order 0.5 K/decade.

4.4.2.4 SYNOPSIS OF SIMULATED TEMPERATURE TRENDS

Figure 4-27 consolidates the above results. An average profile of cooling has been generated from the

imposed observed ozone change calculations and WMGG change experiments. For water vapor, the Imperial College HALOE IGCM trends are used, because these are based on more global observations, albeit for quite short periods. Summing these three components generates the “total” trend.

At 1 hPa, ozone change is the dominant contributor to cooling (1.0 K/decade), with WMGGs at 0.7 K/decade and water vapor much smaller at 0.2 K/decade. Throughout the upper stratosphere, the total model cooling is within the 2σ error bars of the observed cooling. Ozone depletion and increases in WMGGs contribute roughly equally to the temperature trends in this region, although the ozone contribution is more peaked at the stratopause.

At 10 hPa, WMGGs are the dominant cooling mechanism (0.4 K/decade), followed by water vapor (0.2 K/decade) and ozone (less than 0.1 K/decade). There is a significant disagreement with observations. The total

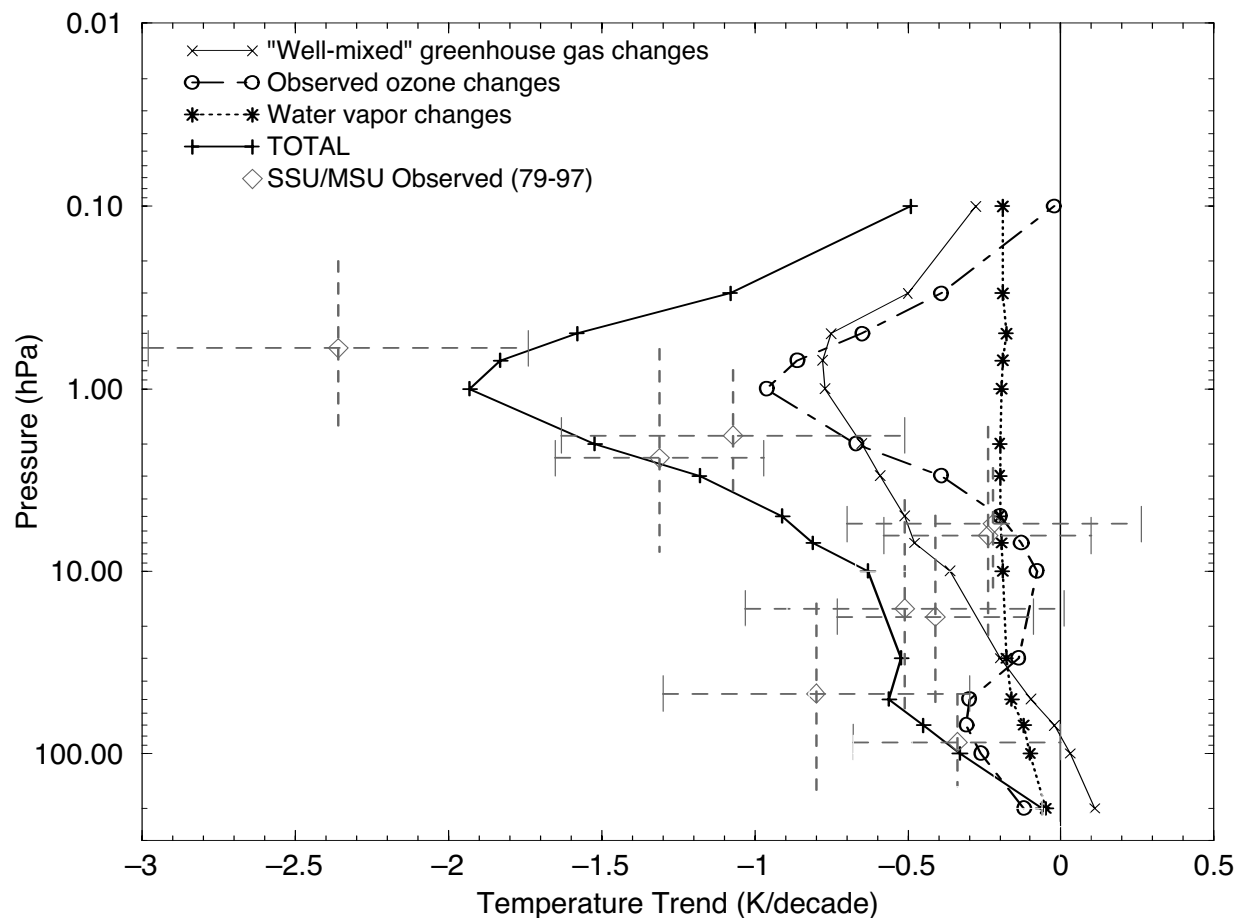


Figure 4-27. Global and annual mean temperature trends from an approximate average of the model results for the imposed height-resolved ozone trends (Figure 4-24) and greenhouse gases; the water vapor results are the trends derived from the HALOE results in Figure 4-26. The observations from MSU and SSU are also shown. The 2σ error bars in the observations are included; the vertical bars are intended to give the approximate altitude range sensed by the particular satellite channel.

model cooling at 5 and 6 hPa is outside the 2σ errors bars of the two SSU channels observing at those altitudes, and indeed, WMGGs alone are toward the edges of these error bars. A similar disagreement was found in the coupled model runs (not shown).

The source of this discrepancy is not clear. If the minimum cooling from any of the contributing models is used (ozone change (zero cooling); WMGGs (0.45 K/decade); and water vapor (less than 0.1 K/decade)), then there would at least be agreement within the error bars at 6 hPa. This would require the water vapor trend for the HALOE period to be unrepresentative of the long-term trend, but it is also possible that there are inaccuracies in the observed ozone trend or the observed temperature trends at these levels.

At 100 hPa, ozone loss is again the dominant cooling mechanism (about 0.3 K/decade) followed by

water vapor (0.1 K/decade) and WMGGs (near zero cooling). The net cooling is within the 2σ error bars of the observations. At 50 hPa, the cooling due to ozone alone is not able to explain the observed trend, and a significant contribution from stratospheric water vapor appears to be needed to achieve agreement.

Considering next the zonal average trends at 50 hPa, in the tropics at least one of the GCMs with imposed ozone trends (Figure 4-25) is within the 2σ error bars of the observations; however, in midlatitudes of both hemispheres, there is a substantial difference between the ozone-induced trend and observations. At 40°N , the gap between the modeled cooling and the observed error bar is about 0.5 K/decade. This difference is more than can be explained by WMGGs alone (most models report a cooling of about 0.2 K/decade, although one model reports 0.4 K/decade) and would need a cooling of about 0.3

K/decade from some other mechanism. Water vapor trends could cause such a cooling, but it requires trends in excess of those deduced from HALOE and more consistent with the trends used in the Reading FDH model (50 ppbv/year). Such a trend would also improve agreement at 50 hPa in the global and annual mean plot (Figure 4-27). In addition, none of the coupled chemistry models (not shown) lie within the 2σ bars of the observations between 30° and 50°N . Another possibility at these latitudes is that part of the cooling trend during 1979-1998 is driven by dynamical causes (this is qualitatively consistent with the observed decreases in NH planetary-wave drag discussed in Section 4.6.3).

For the zonal average trends at 100 hPa, ozone depletion alone can explain the observed trend at all latitudes within the uncertainty of the observations. The WMGG trend is small, and a cooling due to water vapor of several tenths of a Kelvin per decade could be present and would improve the midlatitude agreement with the observations, particularly for those models generating a small ozone-induced cooling.

In summary, there is encouraging agreement between the observed and model temperature trends, particularly in the upper stratosphere. But the degree of agreement is not always good, and the explanations required to improve agreement are not always consistent. In the global annual mean, one way to achieve agreement near 10 hPa would be for the water vapor contribution to be small, and yet at 50 hPa at midlatitudes in the annual zonal means, a significant water vapor contribution is one explanation that would improve agreement with observations.

4.5 CHEMICAL INFLUENCE ON PAST CHANGES IN OZONE

This section discusses the role of chemistry in causing the observed long-term changes in global ozone. Section 4.5.1 discusses updates to our understanding of the important gas-phase and heterogeneous chemical processes. Section 4.5.2 describes the modeling tools that are used to quantify the role of these chemical processes on ozone changes and their key uncertainties. Section 4.5.3 then assesses the role of chemistry in driving extrapolar global ozone changes, based on 2-D and 3-D assessment model simulations compared with the observed ozone changes from Section 4.2.

4.5.1 Chemical Processes that May Contribute to Ozone Changes

In the photochemically controlled US region above about 25 km, ozone trends may be driven by trends in the

gases that provide the sources for reactive radicals (such as N_2O , which produces NO_x , and H_2O , which produces HO_x). Models summarized in WMO (1999) showed that the dominant driver for ozone trends in this region has been the observed trends in reactive chlorine (which are due in turn to the known trends in chlorofluorocarbons). Observed changes in CH_4 , H_2O , and N_2O also have the potential to contribute to chemical ozone changes, but their contributions were estimated to have been relatively small in the past two decades (less than 1% per decade at 40 km). Furthermore, the chemistry of the US is strongly dependent upon temperature, and therefore it is important to consider the feedbacks between ozone depletion and temperature changes in model estimates, and to consider changes in radiatively important gases (especially CO_2 and H_2O ; see, e.g., Evans et al., 1998).

In the LS and LMS, where the chemical lifetime of ozone is comparable to or longer than the transport time scale, both dynamical and chemical processes have the potential to affect ozone and its trends. In particular, changes in chemical loss processes may deplete ozone, but only if they can remove ozone rapidly enough to compete with the seasonally varying transport that moves ozone through this region of the atmosphere. Trends in reactive chlorine may chemically deplete ozone at these altitudes, and can be particularly effective in combination with reactive bromine. Iodine may influence the background concentrations of ozone near the tropopause, but is unlikely to be present in large enough abundances to contribute significantly to the observed trends in the midlatitude ozone column based on the most recent observations.

Ozone in the midlatitude LS and LMS can be affected both by chemical processes occurring locally and by chemical changes occurring in other regions, notably the winter/spring polar vortices, which are then transported to midlatitudes. In this way trends in stratospheric halogens may drive midlatitude ozone trends either by in situ midlatitude chemistry, involving heterogeneous chemistry on liquid sulfate aerosols, or by chlorine activation and/or ozone loss in the polar regions (see Chapter 3) that is then exported to lower latitudes.

4.5.1.1 GAS-PHASE CHEMICAL PROCESSES

Since WMO (1999) there have been many refinements to our understanding of gas-phase reactions including changes in rate coefficients, identification of new and potentially important reaction channels, and reduced uncertainty limits on a host of evaluated rate constants for halogen, HO_x , and NO_x reactions. The discussion in WMO (1999) was based on data summarized in the Jet Propulsion Laboratory (JPL) 1997 recommenda-

GLOBAL OZONE

tion (DeMore et al., 1997). Since then a further recommendation has been published, JPL 2000 (Sander et al., 2000). Here we summarize the main updates (see Table 4-3) and separate the discussion into those updates that were contained in JPL 2000 and those that are more recent. Whereas the implications for ozone trends of the data in JPL 2000 have been assessed (e.g., Section 4.5.3), the full implications for the more recent data have not been determined.

Updates Included in JPL 2000

The discovery of a small hydrogen chloride (HCl) product channel in the hydroxyl radical + chlorine monoxide ($\text{OH} + \text{ClO}$) reaction reported in WMO (1999) has been confirmed by further laboratory studies (Lipson et al., 1999; Wang and Keyser, 2001; Tyndall et al., 2002). The HCl channel substantially impacts model-observation comparisons of atmospheric HOCl/HCl , ClO/HCl , and $\text{ClONO}_2/\text{HCl}$ ratios (Chance et al., 1996; Dubey et al., 1998). However, because of the relatively large dispersion in laboratory results (factor of 2 range in derived rate constant), the magnitude of the HCl channel remains highly uncertain.

Reactions involving NO_x have received substantial attention, motivated in large part by observations of reactive nitrogen partitioning in the summer Arctic (see discussion in Chapter 3). Recent laboratory measurements have led to significant revisions in rate coefficients for $\text{O} + \text{NO}_2$, $\text{OH} + \text{NO}_2 + \text{M}$ (where M is any atmospheric molecule that collides and dissipates the reaction's released energy), and $\text{OH} + \text{HNO}_3$, especially at the low end of the temperature range (Sander et al., 2000; Brown et al., 1999, 2001). The changes in rate coefficients are found to substantially increase NO_x abundance and NO_x -catalyzed O_3 destruction in the lower stratosphere (Portmann et al., 1999).

Updates Since JPL 2000

There is continued uncertainty regarding the $\text{OH} + \text{NO}_2 + \text{M}$ reaction, particularly the reconciliation of low- and high-pressure measurements. The reaction has now been shown to occur via two channels, one producing HNO_3 , the other giving rise to pernitrous acid (HOONO). The laboratory data indicate that HOONO is a relatively weakly bound molecule (Donahue et al., 2001; Golden and Smith, 2000) that decomposes back to $\text{OH} + \text{NO}_2$. This finding is supported by theoretical quantum chemical calculations (Li and Francisco, 2000). Because of its weak bond, HOONO will have a much shorter atmospheric lifetime than HNO_3 , and the fraction of the $\text{OH} +$

NO_2 reaction forming HOONO will not effectively sequester NO_x . Inclusion of the HOONO channel in atmospheric models could potentially affect NO_x levels under high-pressure and/or low-temperature conditions where the HOONO channel takes on its greatest significance.

Another NO_x reservoir, peroxyxynitric acid (HO_2NO_2), has been found to have a photolytic decomposition pathway in the near infrared through excitation to the first vibrational overtone (Roehl et al., 2002). This path serves to substantially increase the rate of HO_x production under high solar zenith angles and may explain observed OH behavior at sunrise in the lower stratosphere (see Chapter 3).

New data on HO_x reactions (Herndon et al., 2001; Nizkorodov et al., 2000) have reduced the uncertainty associated with the rate coefficients of hydroperoxy radicals plus ozone ($\text{HO}_2 + \text{O}_3$) and $\text{OH} + \text{O}_3$. Extensive observations of HO_2/OH ratios in the lower stratosphere have provided stringent tests of the measured rate coefficients and support the results of the newer laboratory studies (Lanzendorf et al., 2001).

For halogen chemistry, several studies have shed new light on the kinetics and mechanism of the $\text{ClO} + \text{HO}_2$ reaction (Nickolaisen et al., 2000; Knight et al., 2000). In contrast to previous work, the recent studies find a different temperature dependence, which implies a slower atmospheric cycling through the catalytic mechanism involving $\text{HO}_2 + \text{ClO}$ and increased importance of longer-lived reservoir species ClONO_2 and HO_2NO_2 formed via reactions of HO_2 and ClO with NO_2 .

Further progress has been made in defining the chemistry of iodine in the stratosphere. Kinetics data have been reported for iodine monoxide (IO) reactions with HO_2 , bromine monoxide (BrO), and IO (Cronkhite et al., 1999; Knight and Crowley, 2001; Rowley et al., 2001; Bloss et al., 2001). The rate coefficient measured for $\text{IO} + \text{HO}_2$ is ~30% higher than that used in the calculations of Solomon et al. (1994). This will slightly increase the (small) calculated impact of iodine species on stratospheric ozone.

4.5.1.2 MIDLATITUDE LOWER STRATOSPHERIC HETEROGENEOUS PROCESSES

In the midlatitude LS, heterogeneous reactions occur mainly on liquid sulfuric acid aerosols. This heterogeneous processing causes the chemical loss of ozone to be dominated by HO_x reactions, with an important contribution from halogen species. Given an accurate knowledge of atmospheric temperature, there are three main limitations on our ability to quantify the importance of

Table 4-3. Changes in the data on gas-phase reactions relevant to stratospheric ozone photochemistry. Minor changes in some of the other reactions are not listed. Reactions for which the most recent revisions were included in JPL 2000 (Sander et al., 2000), and hence in the Assessment model runs in Section 4.5.2, are indicated by “[JPL 2000]” in the final column.

Reaction	Information for 1998 Assessment (WMO, 1999)	Update	Impact	Reference
$\text{OH} + \text{NO}_2 \rightarrow \text{products}$	Few data at lower stratospheric T	Refit of p -dependence at T ; decrease k by ~30%; small yield of short-lived HOONO suggested	Increased NO_x/NO_y and O_3 loss rate in 20-30 km region	Sander et al. (2000), Golden and Smith (2000) [some updates in JPL 2000]
$\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	Few, and scattered, data at low T	Measured over larger T range; increase k by ~20% at low T	Decreased NO_x catalytic cycle between 24 and 36 km	Sander et al. (2000) [JPL 2000]
$\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	Few data at lower T	Improved characterization of p - and T -dependences; increase k by ~50% in lower stratosphere	Increased NO_x/NO_y and O_3 loss rate in 20-30 km region	Sander et al. (2000), Brown et al. (1999), Brown et al. (2001) [JPL 2000]
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	~30% offset between various T -dependent datasets	Better definition of T -dependence; reduced uncertainty	Improved model fit to measured HO_2/OH	Nizkorodov et al. (2000)
$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	Low T -dependence uncertain, possibly nonlinear	Additional low T data; uncertainty reduced	Improved model fit to measured HO_2/OH	Herndon et al. (2001)
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	Scatter in data increases at lower T	No new data; reanalysis increases k at low T by ~7%	Compensates for change in $\text{Cl} + \text{CH}_4$; no impact on ozone	Sander et al. (2000) [JPL 2000]
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	Data variance due to nonlinear T -dependence	No new data; reanalysis increases k at low T by ~7% and reduces uncertainty	Compensates for change in $\text{Cl} + \text{O}_3$; no impact on ozone	Sander et al. (2000) [JPL 2000]
$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	Poorly defined T -dependence, possibly nonlinear	T -dependence better defined and linear; k ~50% smaller at low T	Decreased chlorine catalytic cycle efficiency at low T	Nickolaisen et al. (2000), Knight et al. (2000)
$\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{ClOOC1} + \text{M}$	Large uncertainty at low T	Low T behavior better defined	Increased catalytic efficiency at low T	Sander et al. (2000), Bloss et al. (2001)
$\text{HOCl} + \text{h}\nu \rightarrow \text{OH} + \text{Cl}$	Large uncertainty above 380 nm	Third absorption band identified; extend database to 420 nm	Increased production rate of active chlorine	Sander et al. (2000), Barnes et al. (1998) [JPL 2000]
$\text{IO} + \text{HO}_2 \rightarrow \text{products}$	No data below 298K	Fast reaction; hypoiodous acid (HOI) product observed	Iodine catalytic cycle defined	Knight and Crowley (2001)

T , temperature; p , pressure; k , rate constant.

GLOBAL OZONE

heterogeneous chemistry on midlatitude LS and LMS ozone: variations of the surface area densities of sulfuric acid (H_2SO_4)/ H_2O aerosols of about a factor of 2 in volcanically unperturbed periods (cf. Figure 4-19); estimated uncertainties in the reaction probabilities of 15-30% on cold H_2SO_4 / H_2O aerosols and of factors of 2-3 on ice (Sander et al., 2000); and large uncertainties in how much air is processed through humid, cold conditions close to the local tropopause, i.e., how pervasive cold, dilute H_2SO_4 / H_2O aerosols or subvisible cirrus are in the LMS.

Hydrolysis Reactions on Acidic Droplets

The important hydrolysis reactions of dinitrogen pentoxide (N_2O_5) and bromine nitrate (BrONO_2) on H_2SO_4 / H_2O aerosols have large reaction probabilities that are essentially independent of the temperature and concentration of the droplet solutions. Recently, progress has been achieved in the quantitative understanding of BrONO_2 hydrolysis. Heterogeneous bromine chemistry can potentially enhance OH, suppress the $\text{NO}_x:\text{NO}_y$ ratio, and activate HCl (Hanson and Ravishankara, 1995; Hendricks et al., 1999, 2000). The heterogeneous/homogeneous sequence $\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3$, $\text{HOBr} + \text{h} \rightarrow \text{Br} + \text{OH}$, and $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$ was quantified in calculations by Lary et al. (1996), who found that heterogeneous bromine chemistry in the midlatitude lower stratosphere increased bromine radicals (BrO_x), ClO_x , and HO_x each by about 20%. Erle et al. (1998) provided observational evidence for the presence of BrONO_2 hydrolysis by showing that measurements of BrO and chlorine dioxide (OClO) during winter outside the polar vortex (at temperatures above 200 K) agreed better with photochemical box model calculations when the heterogeneous chemistry of both chlorine and bromine was taken into account.

Chlorine Activation on Cold Aerosol Droplets

At very low temperatures, H_2SO_4 / H_2O droplets in the stratospheric aerosol layer grow into liquid polar stratospheric clouds (PSCs) caused by uptake of HNO_3 (see Chapter 3). At about 200 K, i.e., several degrees above the formation temperature of liquid PSCs, heterogeneous chlorine activation starts (Hanson and Ravishankara, 1995) due to increasing HCl and ClONO_2 solubilities (Carslaw et al., 1997) before the onset of major HNO_3 uptake. It remains an open issue as to what extent such low-temperature processes may also affect LS chemistry at midlatitudes (Michelsen et al., 1999). The requirement of low temperatures concomitant with high inorganic chlorine (Cl_y) is best fulfilled at the midlatitude tropopause, or at high latitudes in winter. Keim et al. (1996)

found enhanced ClO mixing ratios of up to 80 parts per trillion by volume (pptv) peaking about 600 m above the local tropopause at 38°N, and interpreted this as a consequence of the heterogeneous reactions $\text{ClONO}_2 + \text{HCl}$ and $\text{ClONO}_2 + \text{H}_2\text{O}$. These processes would be supported by (1) locally increased water and low temperatures in the vicinity of the tropopause (i.e., high HCl solubility), and (2) enhancements in aerosol surface areas due to high aerosol loading (resulting from the Mt. Pinatubo eruption). The observations of Keim et al. (1996) were corroborated by Borrmann et al. (1997), who also showed a correlation between ClO and aerosol surface area. Because a cooling of 3 K enhances the rate of $\text{ClONO}_2 + \text{HCl}$ by an order of magnitude, the presence of the volcanic aerosols appears to provide an additional enhancement of the rate but is not a necessary requirement.

Currently it is unclear how often situations suitable for chlorine activation directly above the midlatitude tropopause occur. The few available observations seem to provide contradictory results. Regular humidity measurements onboard a commercial airliner within the Measurement of Ozone and water vapor by Airbus In-service Aircraft (MOZAIC) project provide evidence that about 2% of all data above the tropopause show supersaturation with respect to ice (Gierens et al., 1999, 2000). This would turn aqueous sulfuric acid aerosols into dilute solutions (<40 wt% H_2SO_4) highly suited for chlorine activation and should occasionally trigger ice clouds (see below). A recent analysis by J.B. Smith et al. (2001) of ER-2-borne H_2O and ClO observations in the midlatitudes suggests relative humidities decrease strongly within 500 m above the local tropopause (with negligible supersaturation with respect to ice). Therefore, these authors classify cases like the one described by Keim et al. (1996) as exceedingly rare. However, they found 0.8% of measurements in the first kilometer above the local tropopause indicated the presence of enhanced ClO (5 out approximately 660 data points). This value is not so different from the 2% of supersaturation specified by Gierens et al. (1999), and therefore there need not be a contradiction.

Potential Chlorine Activation on Ice Particles

In addition to cold liquid aerosols, ice particles are also a potential host of heterogeneous reactions in the midlatitude LS. Although ice clouds have been observed above the high-latitude tropopause, the different temperature profile at midlatitudes must make the particles less frequent. Borrmann et al. (1997) identified a cirrus event near the local tropopause near Bangor, Maine (45°N), accompanied by ClO mixing ratios ranging between a few and several tens of pptv in the vicinity of the clouds. On

the basis of this measurement, Solomon et al. (1997) included additional very thin (subvisible) ice clouds derived from satellite observations (P.-H. Wang et al., 1996) in their model and suggested that chlorine activation might occur through heterogeneous chemical reactions on aerosol and cloud particles. Bregman et al. (2002) incorporated tropopause ice cloud fields in a 3-D model and found local perturbations in ClO and NO_x to be comparable to the observations of Keim et al. (1996). However, quantitative differences between these studies are substantial, and Bregman et al. (2002) concluded that it would seem unlikely that heterogeneous chemistry on subvisible clouds could explain the observed negative ozone trends in the midlatitude lowermost stratosphere.

A three-year record of continuous lidar observations at the Observatoire de Haute-Provence (OHP, 44°N, 6°E) suggests ice cloud occurrence frequencies in the lowermost stratosphere of 10-20%, with 5% of the cloud top heights observed at least 1 km above the tropopause (Goldfarb et al., 2001). However, this study relies on temperature sonde measurements made 120 km east of OHP, and possible changes in tropopause height over this distance lead to uncertainty in these numbers. Given the contradictory results from the ER-2 and MOZAIC data with respect to extent of ice saturation above the tropopause (see above), the existence and occurrence frequency of ice particles (subvisible cirrus) *above* the midlatitude tropopause remain highly uncertain.

Other Reactions and Surfaces

In the search for other heterogeneous reactions, alternative reaction pathways and reaction partners have been suggested. For example, Drdla et al. (1999) suggested that heterogeneous reactions of formaldehyde (CH₂O) + HNO₃ and nitrous acid (HONO) + HNO₃ (Iraci and Tolbert, 1997; Longfellow et al., 1998) could cause an increase in NO_x of up to 25% in the LMS. Another proposed heterogeneous reaction on sulfuric acid aerosol is carbon monoxide (CO) + HNO₃ (Fairbrother et al., 1997). This reaction could also enhance the NO_x:NO_y ratio, particularly in the LS (Lary and Shallcross, 2000). An assessment of these reactions in long-term modeling studies requires a reduction of the remaining uncertainties in the reaction probabilities.

Soot is another surface that could potentially be important for ozone chemistry in the midlatitude LS. Modeling studies have suggested that ozone could be destroyed on the soot surface, forming O₂, and that NO₂ and HNO₃ could react to form HONO, which photolyzes to yield HO_x (Bekki, 1997; Lary et al., 1999). However, recent laboratory studies and measurements indicate that

soot is likely to have only a negligible impact on ozone chemistry in the lower stratosphere (Choi and Leu, 1998; Gerecke et al., 1998; Kalberer et al., 1999; Strawa et al., 1999; Disselkamp et al., 2000).

4.5.2 Quantifying the Chemical Influence on Ozone: Modeling Tools

Studies of global O₃ changes have used two-dimensional (2-D) latitude-height models or, recently, three-dimensional (3-D) models. These models contain representations of atmospheric transport, radiation, and both gas-phase and heterogeneous chemistry. Some of these processes may be coupled (e.g., chemically integrated ozone being used in the radiation calculation). Alternatively, some models may use fixed fields for certain processes (e.g., transport specified from meteorological analyses). Different models make different approximations, for example, 2-D models approximate the atmosphere as a zonal mean, whereas 3-D models may use a simplified chemistry scheme because of computational costs. Box 4-1 summarizes how well components of these global models are known to reproduce key processes in the stratosphere.

Recent studies have provided more information on the ability of 2-D and 3-D chemical models to quantitatively explain the midlatitude ozone changes. Considine et al. (1999) performed a Monte Carlo study to assess the effects of uncertainties in photochemical data on calculated ozone trends, and found a 46% model uncertainty at the 1σ level. Similar conclusions were obtained by Fish and Burton (1997), who inferred a 50% uncertainty in midlatitude ozone loss rates based upon a quantitative analysis of uncertainties in photochemical data. Both studies argued that, given these large model uncertainties, the discrepancy between the chemically modeled and observed trend could not be used as a critical test of theory. This conclusion remains valid based upon current photochemical uncertainties. Hence, comparisons of observations and numerical models in this Assessment continue to rely upon a broad range of factors in assessing their merits, such as seasonal, latitudinal, and vertical variations in calculated ozone depletion, as well as model-data comparisons for other trace gases such as ClO.

4.5.2.1 2-D MODELS

Two-dimensional radiative-dynamical-chemical models are still a widely used tool for assessing the effects of long-term (many decade) changes in chemical species (e.g., CFCs) on stratospheric ozone. They are computationally inexpensive and can be used for many sensitivity studies. However, these models cannot account for all of

Box 4-1. Components of 2-D and 3-D Chemical Models**Gas-Phase Chemistry**

Most (if not all) stratospheric models use photochemical modules that are based on standard compilations of laboratory data (e.g., JPL 2000; see Section 4.5.1.1). This procedure ensures that results from different models and different runs can be readily compared. All “full chemistry” models contain a complete description of what are believed to be the main species and reactions that control stratospheric ozone. Model-model intercomparisons have shown that, when constrained by the same photodissociation rates, the gas-phase chemical packages from the assessment-type models agree very well (Park et al., 1999; Kawa et al., 1999).

Heterogeneous Chemistry

Modeling the processes that can contribute to changes in ozone in the LS and LMS depends critically on including a realistic treatment of heterogeneous chemistry in the model. For nonpolar studies, the key parameter is the sulfate aerosol surface area density (SAD) and composition. Particularly in the LMS below the maximum in aerosol abundance, the SAD is subject to large uncertainties (of the order of 30%; see Section 4.3.1). For the period perturbed by volcanic eruptions, the inversion of satellite observations to infer aerosol densities below the peak of the aerosol distribution is a source of uncertainty. For diagnostic studies of observed trends, global 2-D and 3-D models can use observations based on satellite data (e.g., SAGE II back to 1984). Outside of this period, global distributions need to be derived from other data.

Temperature

Even with a realistic SAD, model studies have demonstrated that temperatures must be known to better than 2 K to simulate accurately the highly temperature-sensitive Cl-activating heterogeneous chemistry that is critical to ozone loss (see, e.g., Solomon et al., 1998; Tie et al., 1997). Models that use meteorological analyses will almost certainly have more realistic temperatures than 2-D models or GCMs in which they are calculated. However, in the past, meteorological analyses have been far less accurate than this stringent 2-K criterion in the polar vortices of both hemispheres (see, e.g., Manney et al., 1996), although recent analyses show much better agreement (Pommereau et al., 2002). In any case, uncertainties in polar temperatures add to our uncertainties in the ozone depletion in polar regions (see Chapter 3) and thus in the transport of ozone-depleted air to lower latitudes (van den Broek et al., 2000).

Transport

Accurate assessment of the cause of global ozone changes requires models with a realistic treatment of the slow, meridional Brewer-Dobson circulation and eddy transport. Since WMO (1999), a great deal of work has been carried out on comparing models with tracer observations using age-of-air diagnostics (Hall et al., 1999; Park et al., 1999). These studies showed that many 2-D and 3-D models had vertical transport that was too rapid, and hence they underestimated the mean age in the stratosphere derived from observations (see Figure 4-28, p. 4.44). This implies that the models would transport CFCs too rapidly, giving insufficient time for the release of Cl_y , for example, from halogen-containing source gases. This may adversely affect trend calculations, not only through the incorrect Cl_y values in the lower stratosphere, but also because of possible errors in the rate of ozone replenishment through transport. However, the effect of this uncertainty on trend calculations has not been quantified.

the factors that influence interannual variability or trends in atmospheric circulation, though they may capture some of the feedbacks. Also, they are not well suited to the treatment of polar processes, because, for example, they cannot account fully for the dynamics of the polar vortex and its coupling with midlatitudes. For similar reasons they are not well suited to the treatment of transport processes close to the midlatitude tropopause in the LMS. They are probably most reliable in the US and LS, outside of the polar regions (WMO, 1999). Even though the models represent atmospheric zonal means, allowance

can be made for departures from the zonal mean in, for example, the temperature field, which is important for capturing the in situ Cl activation on cold sulfate aerosols (e.g., Solomon et al., 1998; Jackman et al., 1996).

4.5.2.2 3-D MODELS

Three-dimensional models aim to represent the full altitude-latitude-longitude variations in the atmosphere. These models are computationally more expensive than 2-D models, especially when using “full” chemistry. Full-chemistry 3-D models are now used routinely, but gener-

ally for short periods of a few months, e.g., to study seasonal polar ozone loss. However, recently full-chemistry 3-D models have become more widely used for multiannual (or decadal) time scale integrations (e.g., Chipperfield, 1999; Rummukainen et al., 1999; Austin et al., 2000).

Three-dimensional models can be classified into general circulation models (GCMs) and off-line chemical transport models (CTMs) that use winds specified from an external source. When these winds (and temperatures) are taken from meteorological analyses, the model will have a reasonably realistic representation of the atmosphere on a given day, which is useful for interpreting specific observations. However, CTMs are still dependent upon the accuracy of the analyzed temperature fields, and errors of a few degrees may cause substantial errors in calculated ozone losses. The use of analyzed winds may lead to horizontal and vertical winds and temperatures that are not self-consistent. 3-D models (like 2-D models) are also subject to errors in the treatment of the slow, meridional circulation (see Figure 4-28). GCMs calculate their own (self-consistent) winds and temperatures, but they tend to suffer from large uncertainties in the key parameter of calculated polar temperatures (see Chapter 3). Although GCMs should be able to more accurately simulate interactions between the stratosphere and the troposphere than 2-D models, they are still subject to uncertainties, raising questions about the accuracy of some calculated feedbacks to the dynamical fields (see Section 4.6). Furthermore, because 3-D models are relatively new and expensive to use, the exact nature of these models' circulations over long time scales has not been extensively characterized.

4.5.3 Quantifying the Chemical Influence on Ozone: Model Results

Numerical models of the stratosphere have achieved substantial success in simulating many of the observed features of the ozone layer and its depletion. Previous Assessments (e.g., WMO, 1995, 1999) and model intercomparison reports (e.g., Park et al., 1999) showed that both two-dimensional and three-dimensional numerical models could reproduce the general behavior of a wide variety of stratospheric constituents, including reactive species such as nitrogen oxides, source gases such as CFCs, and ozone itself. More than three decades of such comparisons between models and observations, and between differing models of varying complexity, have been a cornerstone of current confidence in the ability of models to represent many key stratospheric processes, albeit with remaining quantitative uncertainties. Here we briefly discuss new information on modeled trends and

distributions of gases other than ozone, to gain insight into the factors that are likely to have affected ozone trends over the past decade. We then discuss current model simulations of past ozone changes.

4.5.3.1 EFFECTS OF NO_x - AND ClO_x -RELATED PROCESSES

Koike et al. (1994), Van Roozendaal et al. (1997), and Liley et al. (2000) presented observations from New Zealand and Europe indicating decreases in NO_2 abundances following the Mt. Pinatubo eruption (see Figure 4-21). These were in general accord with model calculations and support the view that this volcano introduced major perturbations to the photochemistry of the global stratosphere during the period from about 1992 to 1995 (see Section 4.6.6).

A recent study by Froidevaux et al. (2000) examined trends in satellite observations of ClO during the 1990s. Near the 2-hPa level, they showed a positive trend in ClO, which is likely to be caused in part by the trend in Cl_y over this period. However, they also demonstrated that variations in methane (which play a controlling role in the partitioning between ClO and HCl) dominated the changes in observed ClO during this period, as illustrated in Figure 4-29. The observed US methane changes in the mid-1990s (Nedoluha et al., 1998b; Randel et al., 1999) are poorly understood and not included in standard models, raising important questions for the modeled ClO and hence for model-calculated ozone trends in the upper stratosphere.

In the lower stratosphere, the ClO time series presented by Froidevaux et al. (2000) showed enhancements at 22 and 46 hPa following eruption of Mt. Pinatubo, and that perturbation was fairly well reproduced by a 2-D model to which the data were compared. Observations of the ratio of HCl/Cl_y (Webster et al., 2000) provide a separate and important test of the long-term responses of chlorine compounds to variations in sulfate aerosols in the lower stratosphere, since increased ClO is expected to be associated with decreased HCl at those levels. Webster et al. (2000) examined balloonborne and spaceborne data from 1985 to 1994 and argued for an impact on HCl/Cl_y under cold high-aerosol conditions that exceeds current model calculations. However, Dessler et al. (1997) also studied in situ observations of HCl/Cl_y near 50 hPa from aircraft data obtained from 1992/1993 (immediately after Pinatubo) to 1995/1996, showing evidence for chlorine activation close to that predicted by chemical model calculations.

Thus these recent studies have at least qualitatively supported earlier work showing that the observed changes

GLOBAL OZONE

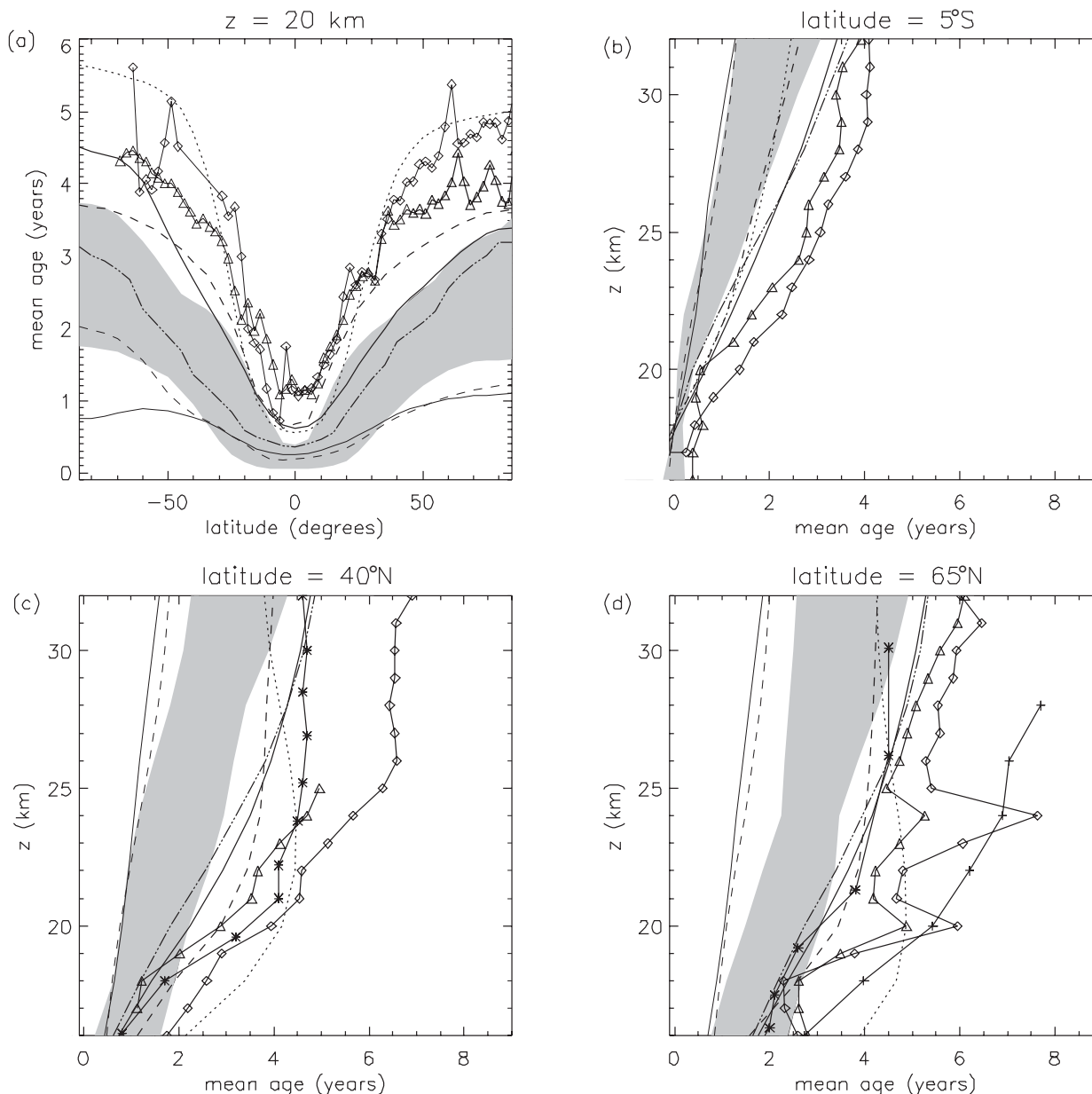


Figure 4-28. Mean age of air estimated from a range of 2-D and 3-D models. In all panels the shaded region indicates the range of mean ages of 17 2-D and 3-D models, not including Harvard-3D (dotted line), MONASH1-3D (heavy solid line), GSFC-2D (heavy dashed line), GSFC-3D (light dashed line), UCI23 (dot-dashed line), and UIUC-3D (light solid line), which are shown separately. The symbols represent observations: mean age from in situ CO_2 (triangles) and in situ SF_6 (diamonds). (a) Latitude profile versus in situ aircraft data. (b) Vertical balloon profiles at 7°N . (c) Balloon flight of September 1996, at 35°N (diamonds and triangles) and SF_6 whole-air samples from 44°N (asterisks). (d) Balloon flight of June 1997, 65°N (diamonds and triangles) and whole-air SF_6 samples at 68°N inside (asterisks) and outside (crosses) the winter polar vortex. From Hall et al. (1999).

in the ClO and NO_x abundances of the lower stratosphere were generally matched by models that included the effects of the Mt. Pinatubo eruption (e.g., Fahey et al., 1993; Solomon et al., 1996). Taken together, the meas-

urements and models continue to provide support for the view that heterogeneous reactions on sulfuric acid aerosols suppress the abundances of NO_x species (mainly through N_2O_5 and BrONO_2 hydrolysis), while enhancing

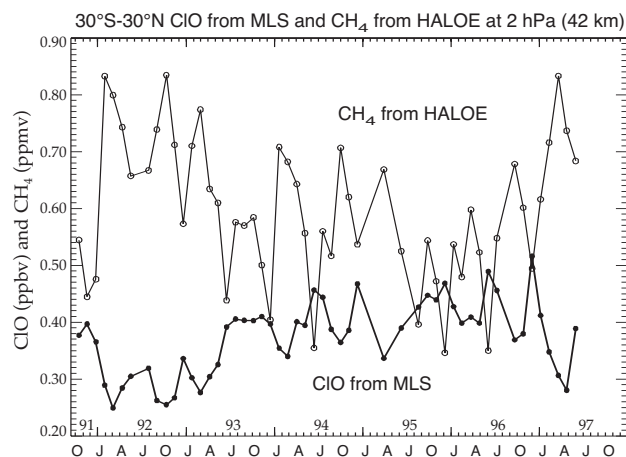


Figure 4-29. Time series of zonal mean abundances of ClO from Microwave Limb Sounder (MLS) data (filled circles) and CH₄ from Halogen Occultation Experiment (HALOE) observations (open circles) for 2 hPa (42 km) and averaged over 30°S–30°N. From Froidevaux et al. (2000).

concentrations of ClO. The net effect of increased sulfuric acid aerosols is an ozone increase above about 25 km, where NO_x dominates ozone losses (Hofmann et al., 1994; Mickley et al., 1997; Solomon et al., 1996), and decrease in the lower stratosphere, where ClO abundances control the impact of halogen chemistry on ozone loss. The changes in stratospheric aerosol content during the 1990s following the massive perturbation of Mt. Pinatubo should therefore be expected to exert a substantial influence on ozone changes during the past decade. Standard models generally include the observed changes in aerosol based upon SAGE observations, as noted (Box 4-1), and hence incorporate a representation of these chemical effects.

4.5.3.2 EFFECT OF POLAR VORTEX ON MIDLATITUDES

Recent model-based studies have attempted to quantify the effect of Arctic polar processing on midlatitude ozone amounts. Knudsen and Grooß (2000) used a seasonal reverse domain filling (RDF) trajectory calculation to study the dilution of ozone-depleted air into northern midlatitudes. They estimated that approximately 40% of the 6.8% decline in midlatitude ozone observed by TOMS between 1979 and 1997 could be accounted for by transport of polar ozone-depleted air into midlatitudes. Other studies have used tracers mapped in equivalent latitude, or discriminated between polar and nonpolar air in 3-D CTMs, to evaluate the connection between polar and midlatitude ozone loss. From the analysis of several

Arctic winters in the late 1990s, Millard et al. (2002) showed that the contribution to the seasonal midlatitude ozone loss from high latitudes was strongly dependent on the meteorological conditions and the stability of the polar vortex. They found the largest contribution to midlatitude ozone loss for winter 1999/2000, with half the midlatitude loss originating north of 60°N. A much smaller contribution was found in the winter 1996/1997, characterized by a strong and pole-centered vortex prior to the final breakup. Using a different model and set of tracers, Marchand et al. (2002) found similar results for the winter 1999/2000. Godin et al. (2002) used a high-resolution model together with ground-based ozone measurements to study the influence of vortex excursions and polar air filaments on midlatitude ozone amounts during several winters, finding the largest impact during 1999/2000 due to the large Arctic ozone loss that occurred that winter coupled with several vortex excursions at the end of the winter.

The accumulated effect of polar vortex loss on midlatitudes has been studied by Chipperfield (1999) using multiannual simulations of the 1990s in a 3-D CTM with full chemistry and horizontal resolution of 7.5° × 7.5°. That study estimated that overall PSC-related depletion processes in or at the edge of the vortex results in 2–3% less ozone at 50°N throughout the year. The effect was larger in the Southern Hemisphere (5% less O₃ at 50°S), reflecting the large losses occurring in the Antarctic.

The fate of ozone-depleted air subsequent to NH polar vortex breakup was studied by Piani et al. (2002). They showed that by the end of June, much of the ozone-depleted air above 420 K has been transported from the polar region to the subtropics. In contrast below 420 K, most of ozone-depleted air remains poleward of 55°N, due to the influence of the upper extension of the tropospheric subtropical jet that provides a transport barrier at lower levels.

4.5.3.3 EFFECT OF WATER VAPOR TRENDS

Observations suggest a positive trend in stratospheric water vapor during the past several decades, which can in turn increase HO_x concentrations and feed back into other chemical cycles involving NO_x and ClO_x. Solomon (1999) and Kirk-Davidoff et al. (1999) also noted the strong dependence of heterogeneous chemistry on water vapor content; the former work emphasized the lowermost stratosphere and temperature variability whereas the latter focused on polar regions. The observed water vapor increases to date substantially exceed the contribution expected from methane oxidation in the lower stratosphere, raising important questions about the source

GLOBAL OZONE

of the increases (see Section 4.3.2). While standard photochemical models do not include this additional water vapor, several modeling groups have carried out specific tests of its likely effects, guided by observations of the magnitude of the water vapor change. Evans et al. (1998) showed that the water vapor trend was unlikely to make a significant contribution to ozone trends in the upper stratosphere (see also WMO, 1999). Dvortsov and Solomon (2001) showed that the observed trend in water vapor could have contributed about 1% to the total column and peak ozone depletions at northern midlatitudes. They argued that this depletion was due to enhancements in HO_x chemistry and to the coupling between HO_x and ClO_x chemistry in the lower stratosphere (which contributed about 0.2%/decade).

Aircraft emissions can potentially affect the composition of the atmosphere. The Intergovernmental Panel on Climate Change (IPCC) Special Report on *Aviation and the Global Atmosphere* (IPCC, 1999) summarized the present understanding and concluded that the 1992 subsonic fleet was responsible for total ozone column changes (at 45°N latitude) of approximately +0.4%, with approximately a quarter of that change occurring in the stratosphere. This impact is likely to increase with future growth in fleet emissions (see Section 4.8.3).

4.5.3.4 ASSESSMENT MODEL SIMULATIONS OF PAST OZONE CHANGES

Within the framework of this Assessment, nine models have performed simulations of past ozone trends in order to test current understanding. The participating 2-D models, which have all been widely used in scientific studies of stratospheric ozone, are listed in Table 4-4. For this Assessment the models were run with the observed surface halocarbon abundances described in Chapter 1 (see Appendix 4B). The surface values of N_2O , CH_4 , and CO_2 were taken from IPCC (2001). (Note that these model runs ignore other drivers of chemical change, such as additional H_2O trend or aircraft emissions.) The models used photochemical data from JPL 2000 (Sander et al., 2000), which is the most recent recommendation available. The aerosol distribution in all models was specified from a monthly climatology based on satellite data, similar to that used in Jackman et al. (1996) and updated by D.B. Considine (NASA Langley Research Center).

The previous Assessment (WMO, 1999) demonstrated that these models simulate many features of the state of the ozone layer prior to the onset of major depletion reasonably well. They are able to reproduce the observed ozone column minimum in the tropics, the inter-hemispheric differences in the ozone maxima in the extra-

tropics, and the general features of the seasonal cycles of both hemispheres. One important difference in the model simulations is that two models (NOCAR and GSFC-INT) incorporate interactive temperature changes due to changes in greenhouse gases (GHGs) (particularly CO_2) and in ozone itself, which result in US cooling of ~1 K/decade. This feedback has a significant effect on simulations of past and future ozone changes in the US, as seen below.

Figure 4-30 shows the annually averaged ozone profile trends for 1980-2000 at northern and southern midlatitudes as calculated by eight of the 2-D assessment models. In the photochemically controlled region above 25 km, there is a large variation in the (maximum) model-calculated trends, which range from around -4 to -5%/decade (NOCAR, GSFC-INT and OSLO) to -8 to -10%/decade for the other models, with observations in the middle (-6 to -7%/decade). The most important difference between the models is the temperature feedbacks included in the NOCAR and GSFC-INT simulations. While the non-interactive models overestimate the observed ozone trends for 40-50 km (probably due in part to the neglect of stratospheric cooling), the interactive model trends are significantly smaller than observations over this region. However, the observed shape of the profile is well reproduced by all the models, and this is controlled by ClO/Cl_y partitioning. Although there is confidence that halogen chemistry is the main driver for the observed trend in the upper stratosphere (WMO, 1999), the model-model differences indicate the important feedback that other changes (especially temperature) have on modulating the ozone depletion.

At lower altitudes the models underestimate the observed NH ozone trends over this period. The model values cluster in the range of -1 to -3%/decade, while the SAGE and ozonesonde trends near 20 km are approximately -3 and -5%/decade, respectively. One caveat is that the ozonesonde trends (derived from an eight-station average) are larger than can be reconciled with the zonal mean column ozone trends, and are likely an overestimate due to limited sampling (see Section 4.2.4). However, the model trends are probably still smaller than observed changes in this region, and because 70-85% of the column trends originate below 25 km (Section 4.2.4), these profile underestimates are the main reason why modeled column ozone changes in NH midlatitude are less than observations (shown below). There may be several reasons for these differences. Part of the model trend underestimate (of order 1%/decade) is likely to be due to the neglect of the observed water vapor trend, and uncertainties in kinetics may also contribute. Further, some recent observations suggest that the bromine content of the low-

Table 4-4. 2-D models participating in simulations of past ozone trends.

Model Name	Institution(s)	Investigators	Temperatures	PSC Scheme	Reference
AER	AER, Inc., U.S.	D.K. Weisenstein, C.J. Scott, M.K.W. Ko	Specified from NCEP analyses	Based on model <i>T</i>	Weisenstein et al. (1998)
MPIC-2D	MPIC, Germany	C. Brühl, J.U. Groo , P.J. Crutzen	Specified from CIRA/MAP data	Based on prescribed <i>T</i> and probability function	Groo et al. (1998)
GSFC	NASA Goddard, U.S.	C.H. Jackman, E.L. Fleming, D.B. Considine	Specified from UKMO analyses	Distribution based on NCEP temperatures	Fleming et al. (1999)
GSFC-INT	NASA Goddard, U.S.	J.E. Rosenfield, D.B. Considine	Calculated by model; interactive with CO ₂ , O ₃ , and H ₂ O	PSC from [ob- served <i>T</i> minus 2 K]	Rosenfield et al. (1997)
NOCAR	NOAA/NCAR, U.S.	R. Portmann, R.R. Garcia, S. Solomon	Calculated above 10 hPa (interactive with CO ₂ , O ₃ , H ₂ O, and CH ₄); NCEP analyses below 10 hPa	NCEP <i>T</i> for PSC	Portmann et al. (1999)
OSLO	University of Oslo, Norway	B. Rognerud	Specified	Based on climatology	Stordal et al. (1985)
RIVM	RIVM, The Netherlands	G. Velders	Climatology (noninteractive)	No solid PSCs	Velders (1995)
SUNY-SPB	SUNY, U.S.; St. Petersburg, Russia	S. Smyshlyaev, M. Geller	Specified from NCEP	Based on NCEP temperatures	Smyshlyaev et al. (1998)
ULAQ	University of L'Aquila, Italy	G. Pitari, E. Mancini	Specified from NCAR dataset	Based on model <i>T</i>	Pitari and Rizi (1993)

AER, Atmospheric and Environmental Research, Inc.; MPIC, Max-Planck-Institut für Chemie; RIVM, Rijksinstituut voor Volksgezondheid en Milieu; SUNY, State University of New York; CIRA, Committee on Space Research (COSPAR) International Reference Atmosphere; MAP, Middle Atmosphere Project.

ermost stratosphere may be larger than estimated in these models that are based on long-lived bromine sources only (Harder et al., 2000). The bromine content of the LMS may be affected by transport of short-lived substances such as bromoform and BrO to the upper troposphere and stratosphere (Ko et al., 1997; Dvortsov et al., 1999; Schauffler et al., 1999; Sturges et al., 2000; Fitzenberger et al., 2000; Pfeilsticker et al., 2000; and Chapter 2). Even if there are no trends in these largely natural sources of Br_y, they could enhance anthropogenic ozone depletion through chemical coupling with Cl_y trends, especially via the ozone-destroying reaction of ClO + BrO. A further reason for the discrepancy in northern midlatitudes may be related to the formulation of the 2-D models, in that they do not accurately simulate polar ozone loss and its transport to midlatitudes. Finally, dynamical contribu-

tions could also contribute to past ozone changes over NH midlatitudes, as discussed in Section 4.6.

Figure 4-31 shows the observed and calculated annual mean column ozone trends as a function of latitude for the period 1980-2000. The largest trends occur at high southern latitudes, associated with the Antarctic ozone hole. The models show a wide variation in their ability to reproduce this feature, with most underestimating the observed trend, though the GSFC and GSFC-INT models produce very large depletions (which extend into SH midlatitudes). In the Arctic, the inter-model differences are smaller and match the observations fairly well near 60°N. The models tend to underestimate the northern midlatitude column ozone loss, consistent with the profile comparisons (Figure 4-30) discussed above. In the tropics, all of the models overestimate the observed

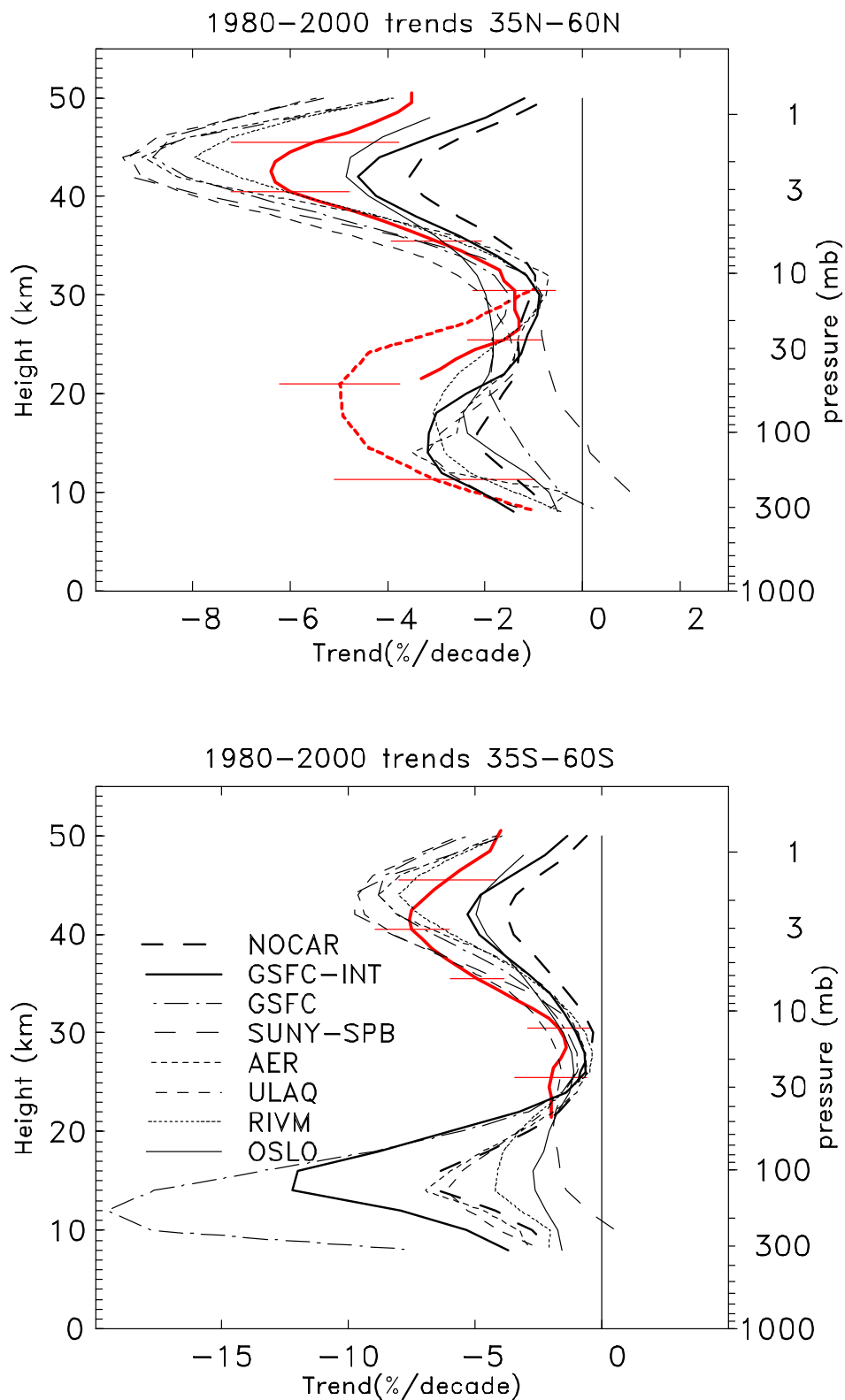


Figure 4-30. Vertical profiles of ozone trends over the period 1980-2000 from observations compared with eight 2-D model calculations for statistics for 35°N-60°N (top) and 35°S-60°S (bottom). The observations are from SAGE I+II (solid red line with 2σ error bars) and averaged ozonesondes (dashed red line; data only available in the NH). The trend units are %/decade calculated with respect to the climatology of each model.

(near-zero) trend, which may be associated with model overestimates of the mixing between the tropical and mid-latitude LS.

Figure 4-32 shows the seasonal variation of the modeled column ozone trends compared with the observations, with results separated for NH and SH midlatitude (35° - 60°) and polar (60° - 90°) regions. In the Antarctic region, most models underestimate the amplitude of the seasonality, because of an underestimation of the spring-time depletion. The two models that produce the largest ozone hole depletions (GSFC and GSFC-INT) substantially overestimate the trend in southern midlatitudes at that time of year. The other models generally reproduce the observed SH midlatitude trends (within the error bars) and its weak seasonality. In the Arctic region, although the models do not capture the same amplitude of seasonal variation as the observations, they do fall within the 2σ uncertainty. At northern midlatitudes the models do a reasonable job of reproducing the magnitude and seasonality of the trend, although the winter-spring maximum is underestimated in most models.

Figure 4-33 compares the smoothed time series of the observed ozone depletion with the 2-D model results, for the near-global average (60° N- 60° S) and for NH and SH midlatitudes. Note that for the 60° N- 60° S average (Figure 4-33, top panel) the observations use the data with the solar cycle statistically removed (Figure 4-4), because these 2-D models do not include a parameterization of the solar cycle. The models all overestimate the decadal ozone changes over 60° N- 60° S (Figure 4-33), because of the overestimate of tropical trends (Figure 4-31). For the

latitude band of 35° - 60° N (Figure 4-33, middle panel), the 2-D models are in broad agreement with many aspects of the observations, but slightly underestimate the decreases. Both the observations and the models display decreases in northern midlatitude ozone following the El Chichón eruption in the early 1980s and the Mt. Pinatubo eruption in the 1990s. However, the magnitudes of the observed changes are larger than most calculations, and there is also an observed dip in the late 1980s that is not simulated by the 2-D models. Chipperfield (1999) noted the important role of polar processing in driving spring-time midlatitude ozone decreases following eruption of Mt. Pinatubo, which may be linked to the underestimate seen in some of the 2-D models in that time period. Also, some of this post-Pinatubo dip may be dynamically induced (see Section 4.6). Current model results are also sensitive to changes in photochemical rates when compared with earlier studies (such as Solomon et al., 1996; Jackman et al., 1996; WMO, 1999). In particular, new data for NO_x reactions (used in the runs presented here) caused reductions in both the calculated trends and in the amplitude of the estimated Mt. Pinatubo perturbation, compared with studies carried out for the previous Assessment (as shown by Portmann et al., 1999). One preliminary run of the NOCAR model using the updated kinetics discussed in Section 4.5.1, but not included in JPL 2000, yielded extremely small changes in calculated midlatitude depletion.

Figure 4-33 (bottom panel) shows the observed and calculated trends for the region of 35° - 60° S. The observations suggest an overall change for the 20 years of about

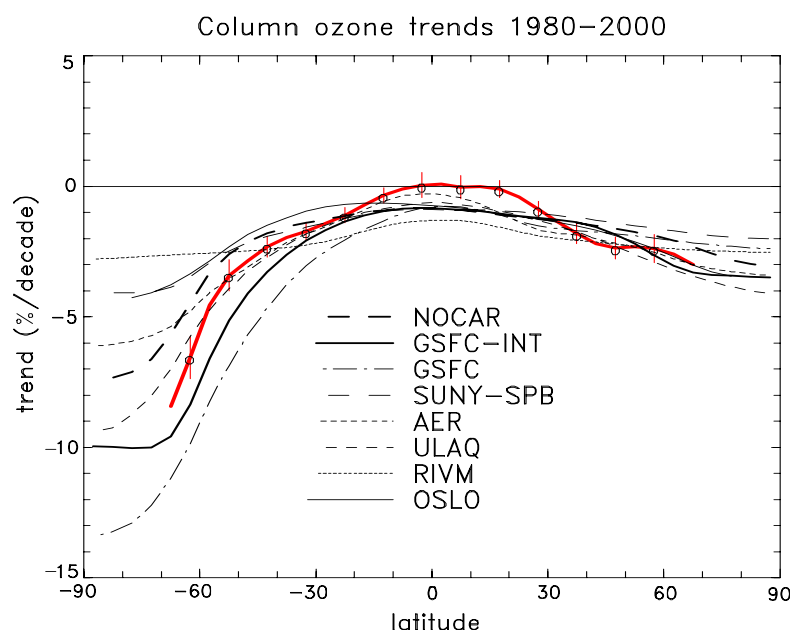


Figure 4-31. Latitudinal profile of annual mean column ozone trends from the merged TOMS+SBUV2 satellite dataset (solid red line) (see Section 4.2) compared with results from eight 2-D models, for 1980-2000. The trend calculations use a standard regression analysis, including a QBO term for the observations but not for the models. The error bars for the observations indicate 2σ uncertainties.

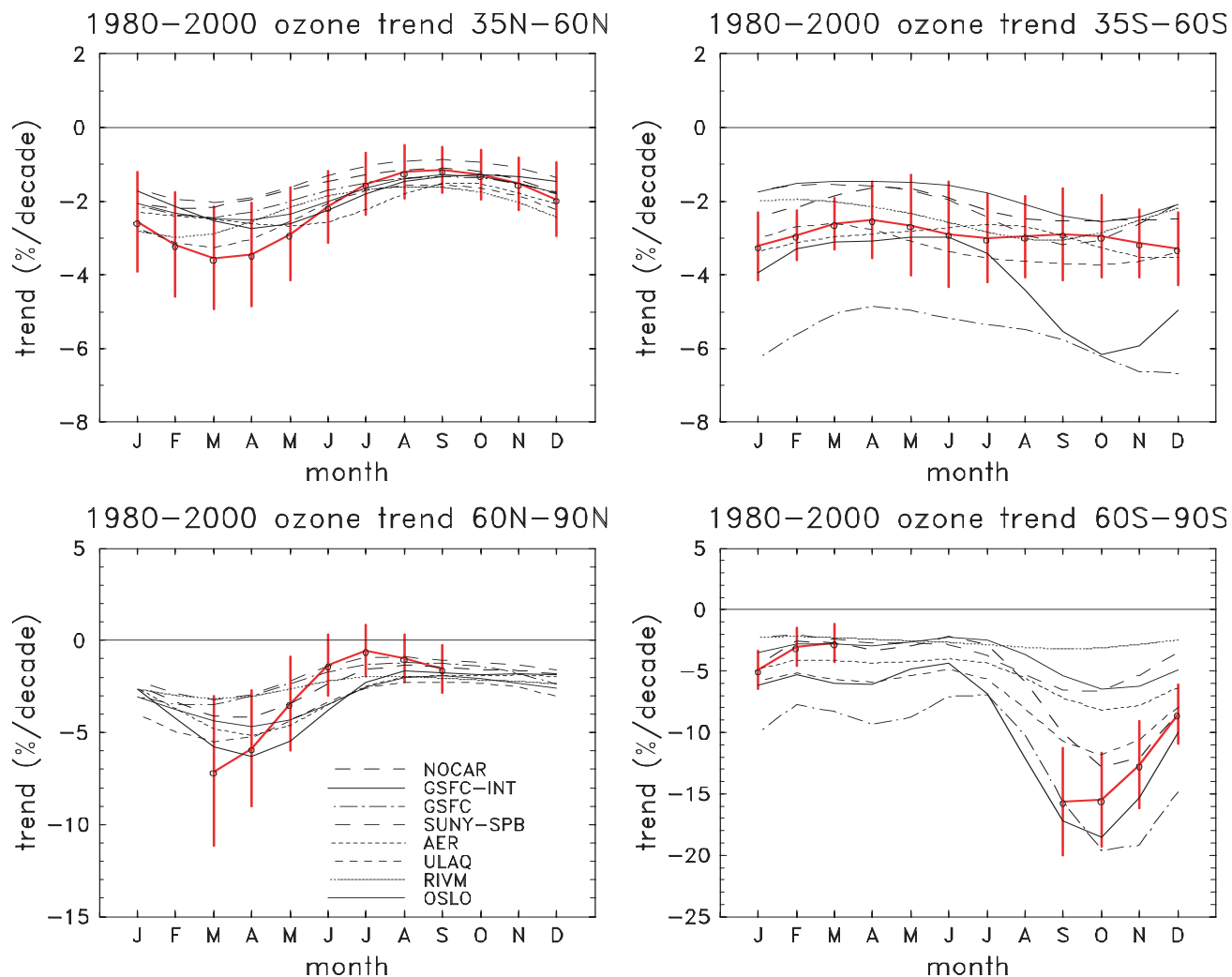
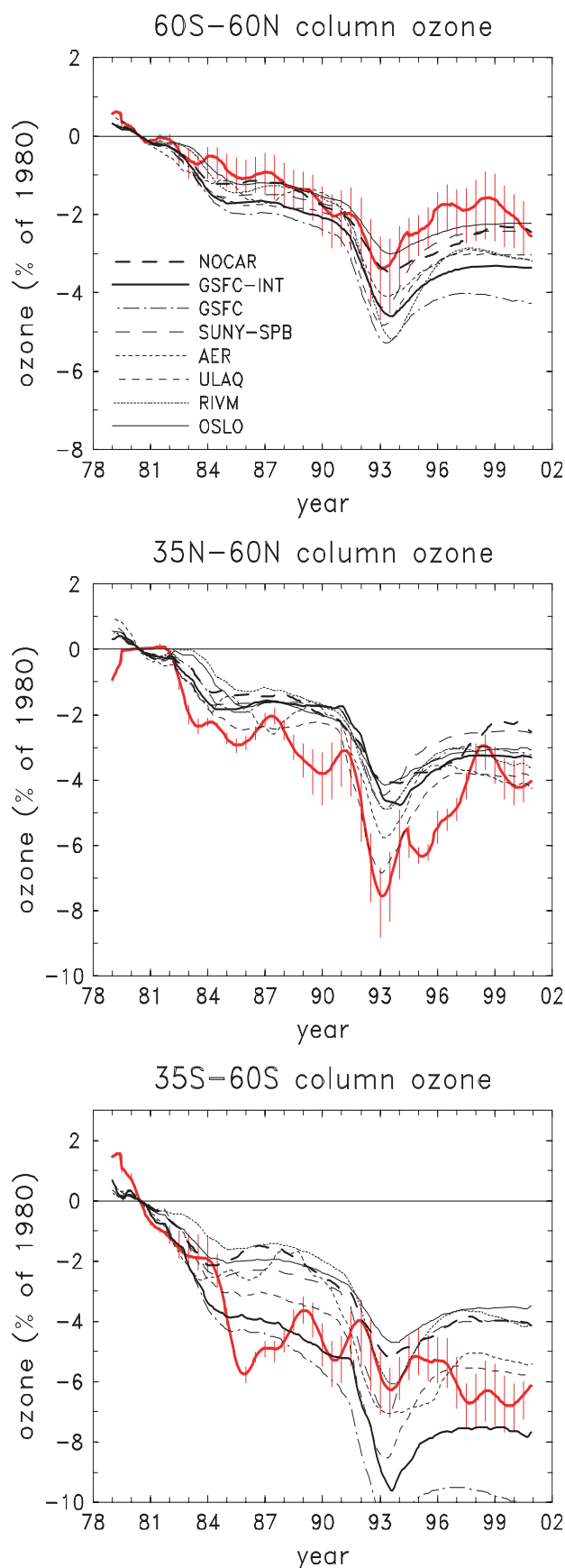


Figure 4-32. Seasonal variation of observed and modeled column ozone trends at 35°N–60°N (top left), 35°S–60°S (top right), 60°N–90°N (bottom left), and 60°S–90°S (bottom right). Observed trends (red lines) were derived from the merged satellite data using a seasonally varying regression model, with error bars denoting 2σ uncertainty estimates.

6%, while the model values range from 4% to 10%. Each of the models displays an ozone decrease in the SH following the eruption of Mt. Pinatubo, approximately similar to the model calculations in the NH, but observations show a much smaller signal. There are relatively large differences of about 2% between the various satellite datasets during that time, implying caution regarding exact details. The largest short-term ozone perturbations for SH midlatitudes are the low values in the mid-1980s, which are not simulated in any model and have not been explained. Closer inspection of the data reveals that the unusual values occurred during a short period (1985–1986), when ozone was low over midlatitudes throughout the SH (see Figure 4-6). The short duration of the pertur-

bation for 1–2 years argues against a solar irradiance-driven mechanism, or attribution to a recurring process such as the El Niño–Southern Oscillation (ENSO) or the QBO. Thus these comparisons show that although SH decadal-scale trends are reasonably well reproduced by some present models (with a wide spread related to different treatments of the Antarctic ozone hole), there are mechanisms for shorter-term interannual variability that are not well simulated by any 2-D model.

As discussed above, it is only very recently that three-dimensional models have been used to study multi-decadal past changes in ozone. Figure 4-34 shows results from a 20-year run of the SLIMCAT 3-D chemical transport model (CTM) (Chipperfield, 1999) over the period



1979–1998. The model was forced by European Centre for Medium-Range Weather Forecasts (ECMWF) meteorological analyses in two separate simulations, one with time-dependent halogen loading and one with constant (1979) halogen loading. Although the atmospheric halogen loading in 1979 itself was well above natural levels, the difference between the two model experiments shows the modeled chemical loss relative to 1980. The 3-D CTM results produce more interannual variability (on the time scale of a few years) than the 2-D models, because of the use of analyzed winds. In the early 1980s and the early 1990s, and again in the late 1990s, the 3-D model with the imposed halogen trend matches much of the observed decreases in column ozone. However, there are periods, during the mid-1980s and mid-1990s, when the model variations differ significantly from the observations. There are still large interannual changes, e.g., related to the low SH ozone in the mid-1980s, that have not been explained.

In summary, the 2-D assessment models generally perform better in simulating the NH changes than the SH changes, both in the polar regions and in midlatitudes. It is likely that the models' ability to simulate the middle latitudes realistically is related to correctly reproducing the polar region. The larger losses in the SH polar region (where the models show large differences) compared with the NH make this connection more critical. In spite of these detailed differences, the overall agreement between the modeled and observed trends in their vertical and latitudinal profiles and seasonal variation support the view of WMO (1999) that increases in halogens are a main driver of the observed changes.

Figure 4-33. Time series of column ozone variations from observations (red lines) and from eight 2-D models for latitude bands of 60°S–60°N (top), 35°N–60°N (middle), and 35°S–60°S (bottom). Changes are calculated in percent with respect to 1980 values for each time series. The observations for 60°S–60°N use results from Figure 4-4, with the solar cycle component removed by statistical regression, whereas the midlatitude observations are from Figure 4-7, with no explicit solar cycle adjustments. The error bars on the observations represent the spread of the different datasets, which provides a minimum estimate of their uncertainty.

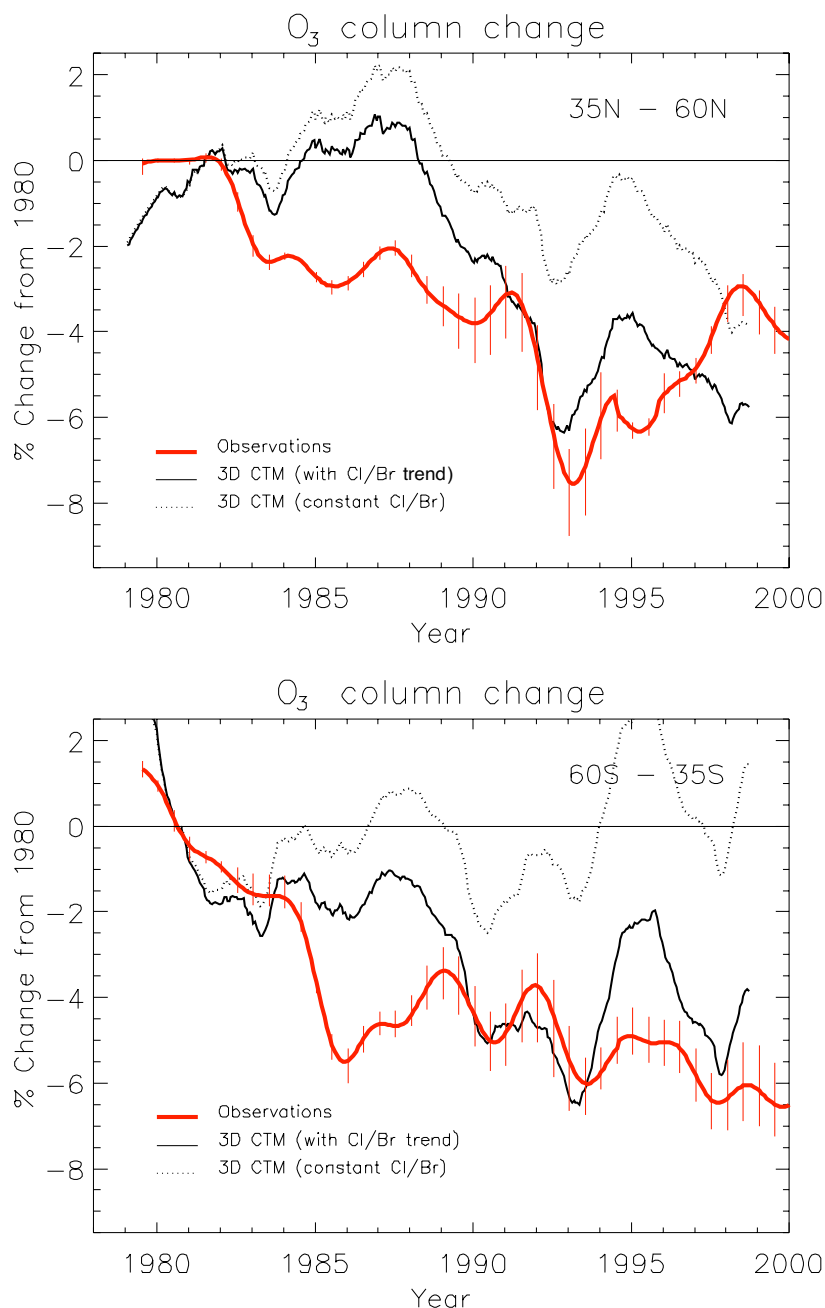


Figure 4-34. Time-series of column ozone change (% change from 1980) from the SLIMCAT 3-D CTM compared with observations (as in Figure 4-33) for 35°N–60°N (top) and 35°S–60°S (bottom). Results from two model simulations are shown: with a halogen trend and with constant (1979) halogen loading.

4.6 DYNAMICAL INFLUENCE ON PAST CHANGES IN OZONE

4.6.1 Introduction

Transport of stratospheric ozone is a key factor influencing its seasonal and interannual variability. The large seasonal cycle in column ozone over the extratropics (in both hemispheres), as seen in Figure 4-35, is due primarily to enhanced transport from the tropical source region during the winter-spring seasons, and the hemispheric differences in ozone amount are mainly a result of

differential transport (larger in the NH). Figure 4-35 also shows that the interannual variability in the winter-spring ozone buildup is greater in the NH than the SH, reflecting the greater dynamical variability of the NH stratosphere. Given the observed large interannual and decadal-scale variability in stratospheric dynamical quantities, it is reasonable to consider a dynamical influence on decadal ozone trends on both regional and hemispheric scales (e.g., Hood and Zaff, 1995).

In WMO (1999), as well as in previous Assessments, the possible influence of long-term changes in

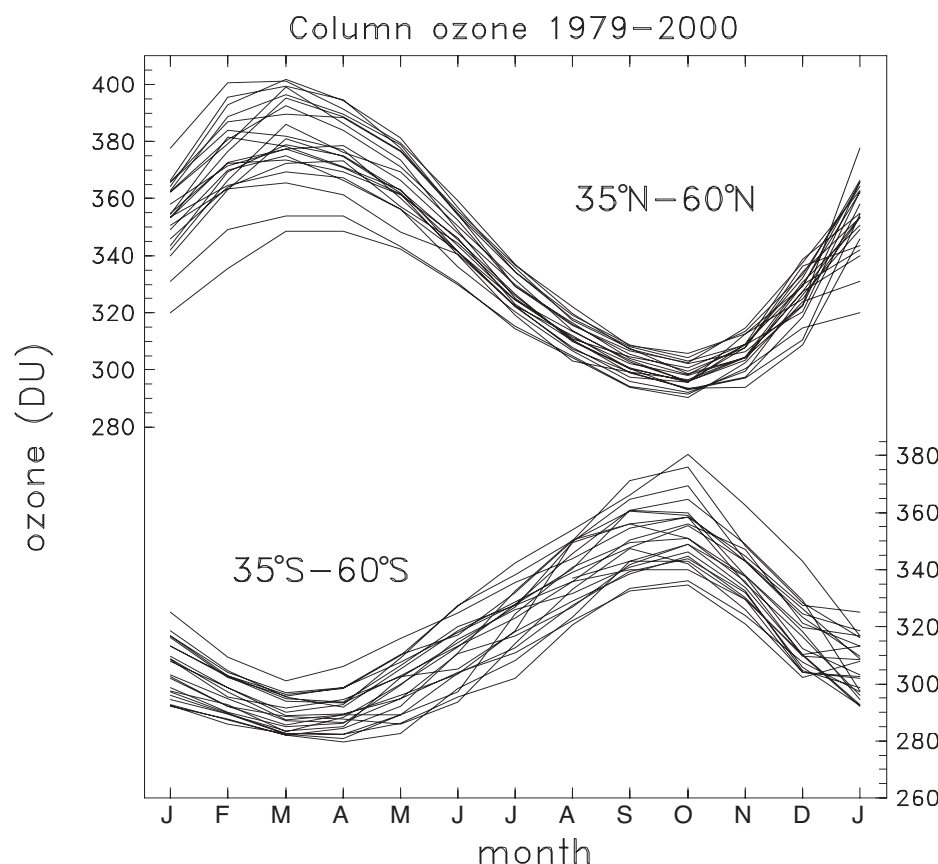


Figure 4-35. Seasonal cycle of total ozone (from the merged satellite dataset) averaged over 35°N–60°N (upper set of curves) and over 35°S–60°S (lower set of curves), with each curve corresponding to a different year in the period 1979–2000.

dynamical processes on ozone changes was discussed. However, the statistical trend analyses presented there did not include explicit dynamical variables (except for the QBO and solar cycle) because of difficulties of interpretation. One particular concern is that establishing the existence of correlations using observations is far from proving cause and effect; sound mechanistic information is also needed. In particular, it is necessary to assess the extent to which the dynamical changes might be a consequence of the ozone changes, rather than a cause. A further problem is that using correlations to attribute causality assumes that linear relationships can represent what are, in reality, complex nonlinear interactions. Although this is a relatively minor issue for periodic signals such as the QBO and solar cycle, it becomes problematic when trying to apply daily or monthly mean correlations to longer time scales.

Recently there has been interest in trying to understand and diagnose the effects of dynamical changes on stratospheric ozone over decadal time scales, and there is now substantially more information available than at the time of the previous Assessment. The relevance of dynamical changes is underlined by related issues such as the unexplained long-term trend in stratospheric water vapor (see Section 4.3.2), and the apparent trend in the

North Atlantic Oscillation (NAO) and other hemispheric-scale meteorological phenomena (Graf et al., 1995; Thompson et al., 2000). Furthermore, the opportunity for long-term dynamical studies on a global scale has been facilitated by the recent availability of meteorological reanalysis products.

The relevant studies may be largely grouped into two categories; neither addresses the cause of the observed dynamical changes. The first consists of modeling studies using observed circulation statistics derived from meteorological analyses to drive the transport in the model. These have been performed in the presence of constant chemical forcing to determine the ozone response to the dynamical forcings alone, and in the presence of a changing chemical forcing so that the two effects can be assessed together. The second category consists of statistical studies that combine mechanistic understanding of the atmosphere with the statistical demonstration of correlations in time series. For such studies the previous caveat about interpreting correlations still holds, both in assessing the results of individual studies and especially in comparing the results from different studies. A simple example makes this point clearly. Increases in both tropopause height and mini-hole frequency have been suggested as being responsible for decreases in ozone over

northern midlatitudes. However, since they are intimately linked (mini-holes occur when the tropopause is exceptionally high), the two influences on ozone cannot be simply added.

This section on dynamical influences is organized as follows. An overview of key dynamical processes associated with midlatitude ozone trends is provided in Section 4.6.2. The statistical analysis of observations is discussed in Section 4.6.3, and the impact of dynamical changes estimated using 3-D chemical transport modeling is detailed in Section 4.6.4. The possibility that the dynamical changes might be the result of the ozone changes is assessed, and the dynamical impact of GHG changes considered, in Section 4.6.5. We note that most of the discussion focuses on the NH because uncertainties in the SH circulation statistics do not permit reliable calculation of trends in dynamical forcing (e.g., Randel et al., 2002).

4.6.2 Dynamical Processes that May Contribute to Ozone Changes

Recent studies of dynamical influence on midlatitude ozone trends have discussed variations and trends in dynamical quantities related to ozone transport. These studies have broadly fallen into topics focused on two processes that although ultimately coupled, are in principle independent:

- Stratospheric planetary-wave drag (PWD), which drives the stratospheric Brewer-Dobson circulation and is a principal dynamical influence on ozone above 20 km although also affecting ozone below 20 km.
- Tropospheric circulation, which affects the ozone distribution in the lowermost stratosphere (up to about 20 km) through both planetary-scale and synoptic-scale disturbances and the location of the tropopause.

Decadal ozone changes induced by these processes can be produced from natural variability, from changes in climate resulting from greenhouse gases, or from ozone depletion itself. The importance of knowing the cause depends on the issue being addressed. To quantify the ozone depletion that can be attributed to ozone-depleting substances such as CFCs and halons, the causes of the dynamical influences on ozone changes are unimportant, as long as they are not a result of the chemical ozone depletion itself. However, to make valid predictions of future ozone levels, it is important to understand the fundamental causes of the dynamical influence on ozone changes. Thus it is useful to distinguish between the identification of dynamical contributions to ozone changes, and their explanation.

The effects discussed above concern the direct impact of transport on ozone. In addition to these purely

dynamical effects, there are chemical and radiative feedbacks between temperature and ozone that are both positive in the lower stratosphere. These chemical and radiative feedbacks may amplify or skew the effect of natural dynamical variability on ozone. It is thus not possible to cleanly separate “dynamical” and “chemical” contributions to ozone changes, attributing a certain fraction to each, because they are nonlinearly coupled. Whether the coupling is a first-order or a second-order effect, and what the causality of the relationship is between dynamics and ozone, has to be assessed on a case-by-case basis.

4.6.2.1 CHANGES IN PLANETARY-WAVE DRAG

The global transport of constituents in the stratosphere can be described in terms of advection by the mean meridional circulation together with eddy transport effects; both of these quantities are first-order terms in the zonal mean continuity equation (Andrews et al., 1987; Mahlman et al., 1980). The stratospheric meridional circulation, known as the Brewer-Dobson circulation (BDC), is primarily driven by mechanical forcing arising from stratospheric (and mesospheric) wave drag, plus seasonal variations in radiative heating. Likewise, large-scale eddy transports are linked to dissipating waves, and hence to stratospheric wave drag, although this linkage is difficult to quantify. This forcing originates from upward-propagating, tropospherically generated waves. Unforced natural variability (i.e., excluding solar variations or volcanic eruptions) arises primarily from dynamics through variability in wave drag, although model results suggest it can be affected by chemical-radiative feedbacks that could change in the presence of anthropogenic forcing (e.g., Shindell et al., 1999; Butchart et al., 2000). Wave-drag variability can be internal to the stratosphere, or can arise from variability in the tropospheric wave sources. The amount of wave drag within the stratosphere is related to the vertical component of the Eliassen-Palm (EP) flux in the lower stratosphere, and this quantity (also referred to as the planetary wave driving) is a convenient proxy used to quantify PWD.

Planetary-wave drag (PWD) is largely restricted to winter and spring for well-understood reasons (Andrews et al., 1987), and drives the spring buildup of extratropical column ozone seen in Figure 4-35. The relationship between PWD and ozone buildup is not simple, but a clear positive correlation has been found in the interannual variability of NH extratropical PWD and total ozone buildup in January (Fusco and Salby, 1999; Randel et al., 2002), as illustrated by Figure 4-36. Such dynamically induced ozone changes would be expected to be seen mainly between midwinter and late summer; each year ozone

essentially returns to photochemical control by the fall (e.g., Chipperfield and Jones (1999) for the polar region), and there is a correlation between winter buildup and summer loss (Fusco and Salby, 1999; Randel et al., 2002). From Figure 4-35 it is evident that this statement applies more to the NH than to the SH, where the late breakup of the vortex does not allow sufficient time for ozone to reach photochemical control before the next year's buildup begins. In contrast, NH ozone exhibits less interannual variability in early fall; indeed the spread of values seen in Figure 4-35 in early fall largely represents the trend shown in Figure 4-8. The fact that the effect of PWD on ozone is seasonal and has essentially no interannual memory suggests (at least for the NH) that decadal changes in PWD can be expected to lead to decadal changes in ozone, all else being equal. For such wave-drag-induced variability, changes in the extratropics should be mirrored (with a negative sign) in the tropics, and this compensation is indeed seen in interannual variability of total ozone (Fusco and Salby, 1999; Randel et al., 2002). Although the basic physics of the connection between PWD and total ozone is well understood, its quantification via correlations is at best a crude measure

of this connection, and this limits our ability to attribute observed changes in total ozone to observed changes in PWD.

4.6.2.2 EFFECTS OF TROPOSPHERIC CIRCULATION AND TROPOPAUSE CHANGES

The tropospheric circulation also affects the ozone distribution, with the direct effects confined to the lowermost stratosphere. The relationship between midlatitude tropopause height and total ozone is well documented (e.g., Bojkov et al., 1993), with roughly a 20-DU decrease for every 1-km increase in tropopause height (Hoinka et al., 1996), independent of season. Day-to-day changes in tropopause height at a given location are associated with the passage of synoptic-scale baroclinic disturbances in the upper troposphere and lowermost stratosphere, which affect ozone through the depth of the lowermost stratosphere (e.g., Salby and Callaghan, 1993; Vigliarolo et al., 2001). Longer-term changes are associated with planetary-scale circulation anomalies, such as the NH annular mode (see next section), which elevate the tropopause at certain longitudes and lower it at others. However, the effect of tropospheric circulation on total

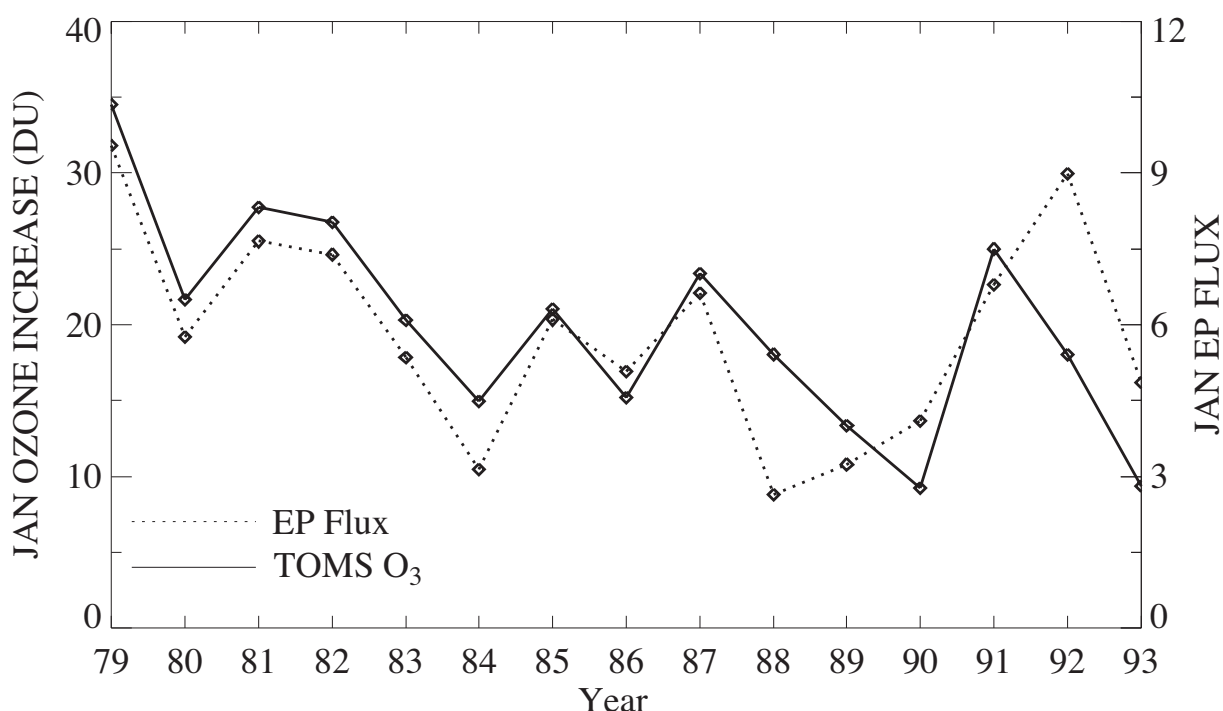


Figure 4-36. Upward Eliassen-Palm (EP) flux at 100 hPa (a measure of the stratospheric planetary wave driving) during January (in normalized units) averaged over 20°-90°N (dashed), compared with the January increase in total ozone over the same latitude range (solid). The regression of TOMS ozone with EP flux has a correlation coefficient of 0.74. Adapted from Fusco and Salby (1999). Randel et al. (2002) showed that the strong positive correlation extends over 1979-2000.

GLOBAL OZONE

ozone, and its relation to tropopause height, is much less well understood than the effect of PWD on total ozone. In particular, the relationship between tropopause height and total ozone mentioned above applies to single stations and is mainly associated with reversible transport; there is no reason to expect it to apply in the zonal mean, or on longer time scales (e.g., seasonal or interannual) over which ozone transport is irreversible.

4.6.2.3 HEMISPHERIC VARIATIONS AND ANNULAR MODES

Both hemispheres exhibit natural variability in PWD, manifested in “strong-vortex” and “weak-vortex” conditions in the stratosphere. The associated modes of variability evident in statistical analyses show out-of-phase behavior between the polar and midlatitude regions, which is primarily zonally symmetric (i.e., annular). These hemispheric patterns are referred to as the NH and SH annular modes (NAM and SAM). The stratospheric NAM and SAM are observed to be coupled to similar tropospheric structures, in both observations (Thompson and Wallace, 1998, 2000) and GCM simulations (Shindell et al., 1999), and there is a strong observed correlation between NAM index and both midlatitude tropopause height and total ozone during the winter-spring period (Brönnimann et al., 2000). The stratosphere-troposphere coupling occurs on sufficiently rapid time scales that the relevant mechanisms must be dynamical, through wave-mean-flow interaction (Baldwin and Dunkerton, 1999), although the specific mechanisms are far from clear (see Section 4.6.5). In the troposphere the NAM is closely associated with the North Atlantic Oscillation (NAO), and some studies have used the NAO as a dynamical proxy for ozone variability (e.g., Appenzeller et al., 2000).

4.6.3 Statistical Analysis of Observations

4.6.3.1 CHANGES IN PLANETARY-WAVE DRIVING

In the NH, there have been long-term changes in various meteorological indicators over the past 30 years or so, which together paint a fairly consistent, albeit incomplete, picture. The Arctic wintertime vortex has been getting colder and stronger (Graf et al., 1995; Pawson and Naujokat, 1999; Thompson et al., 2000), and more persistent (Vaughan et al., 1999). Any dynamically induced component of these changes requires a weakened meridional circulation, which at least over the last 10 years (the length of the relevant data record) is consistent with variations in long-lived trace gases in the middle and upper stratosphere (Nedoluha et al., 1998b; Randel et al., 1999). A weakened meridional circulation requires a decrease in

stratospheric wave driving, which has been documented in several studies (Fusco and Salby, 1999; Newman and Nash, 2000; Zhou et al., 2001b; Randel et al., 2002). However, it should be cautioned that these results are quite sensitive to the months and time period considered. For example, Newman and Nash (2000) report significant negative trends in wave driving for January-February (1979-1999), whereas Hu and Tung (2002) do not find the decrease (over 1968-1998) to be statistically significant for November-January. Randel et al. (2002) analyzed data during 1979-2000 for each month separately, and find the wave driving to increase during November and December and to decrease during January and February (with only January near statistical significance) (Figure 4-37). This seasonal variation is consistent with the Arctic early-winter warming and late-winter cooling seen over the same period at 100 hPa (Langematz et al., 2002). A weakened meridional circulation implies a decrease in the NH extratropical winter-spring buildup of ozone, in both polar and midlatitudes, through a decrease in ozone transport.

Because of the seasonality of the winter-spring buildup of ozone, with any interannual memory (in ozone) being largely erased by the return to photochemical control by early fall (Figure 4-35), there is some justification for extending interannual correlations to decadal time scales. This would only be strictly appropriate if the inter-

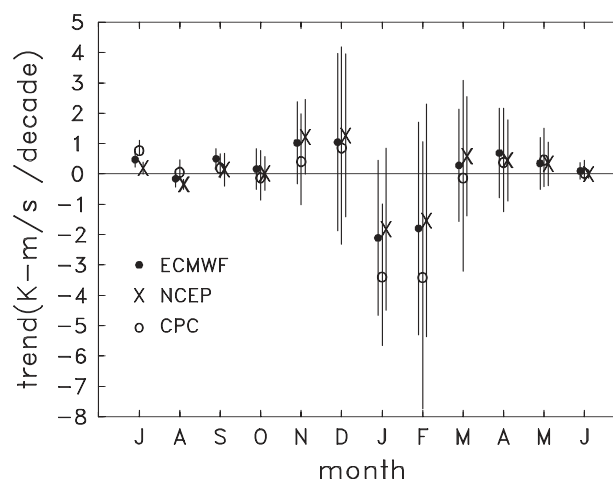


Figure 4-37. Linear trends in monthly averaged NH eddy heat flux ($\overline{v'T'}$) statistics at 100 hPa (proportional to the upward EP flux), calculated for the period 1979-2000. Results for each month were calculated based on meteorological analyses from the European Centre for Medium-Range Weather Forecasts (ECMWF), the NCEP Climate Prediction Center (CPC), and the NCEP/NCAR reanalyses. Error bars denote $\pm 2\sigma$ uncertainty. From Randel et al. (2002).

annual correlations were established in the presence of constant chemical forcing (e.g., Cl_y), which is not the case. With this caveat, the extent of the resulting wave driving contribution to midlatitude ozone trends in winter-spring then depends entirely on the extent of the changes in wave driving for the period in question. Between 1979 and the period 1990-1993, the extent and statistical significance of wave driving changes is particularly sensitive to the last year chosen, because of the especially large variability in wave driving during 1990-1993 (see Figure 4-36), and the estimated impact on ozone is accordingly highly variable (Fusco and Salby, 1999; Randel et al., 2002). Over the longer period 1979-2000, Randel et al. (2002) find that decreases in wave driving (Figure 4-37) may account for ~30% of the observed changes to total ozone in the January-March period.

4.6.3.2 CHANGES IN TROPOSPHERIC CIRCULATION AND TROPOPAUSE HEIGHT

Observations have shown that the NH extratropical tropopause has generally risen in altitude over recent decades. Radiosonde measurements over both Europe and Canada show an increase in altitude of about 300-600 m over the past 30 years, the exact amount depending on location (Forster and Tourpali, 2001; Steinbrecht et al., 2001). Consistent increases are also seen both in the ECMWF reanalysis for 1979-1993 (Hoinka, 1999) and in the NCEP-NCAR reanalysis for 1968-1997 (Thompson et al., 2000); although not all longitudes show an increase, it is present in the zonal mean. An increase in zonal-mean tropopause height is qualitatively consistent with a decrease in stratospheric planetary-wave drag via a weakened meridional circulation (Thuburn and Craig, 2000), but Steinbrecht et al. (1998) found little correlation between changes in monthly mean tropopause height and in lower stratospheric temperatures, arguing against this mechanism. Rather, they found a very strong correlation with mid-tropospheric temperatures, suggesting that the observed tropopause height changes are mainly caused by changes in tropospheric circulation. Moreover, an analysis of ozone profile changes over Payerne, Switzerland (Weiss et al., 2001), found that the tropopause height changes are correlated with significant ozone changes throughout the lowermost stratosphere, but not above, suggesting that they are primarily associated with the observed higher frequency of subtropical intrusions due to synoptic-scale disturbances (Reid et al., 2000; Bojkov and Balis, 2001), rather than with a change in the meridional circulation. However, because of our poor understanding of what controls the zonal-mean midlatitude tropopause height, it is not at all clear that the corre-

lations obtained for month-to-month variability can be extended to decadal time scales. The seasonality characterizing PWD influences does not apply to tropospheric dynamical processes, which affect ozone year-round.

Notwithstanding these concerns, several studies have attempted to estimate the dynamical contribution to total ozone trends by statistical regression against tropopause height or tropospheric circulation indices that are correlated with it. Steinbrecht et al. (1998) analyzed Hohenpeissenberg, Germany, ozonesonde data for 1967-1997 and found that about 25% of the trend in total ozone could be attributed to tropopause height changes. Forster and Tourpali (2001) used 11 ozonesonde stations in Europe and Canada from 1970 to 1997 and found that about one-third of the observed ozone change below 20 km could be associated with the change in tropopause height, which is consistent with the Steinbrecht et al. (1998) result. Both studies concerned annual-mean changes, since the correlation between tropopause height and total ozone exists at all times of the year. Weiss et al. (2001) studied changes in the ozone profile at Payerne for 1967-2000 and showed that the tropospheric dynamical influence on the calculated ozone trend is essentially confined to the lowermost stratosphere (below about 20 km), and its magnitude depends strongly on the period considered (Figure 4-38).

During the winter-spring period, there is a strong correlation between the NAM and various tropospheric circulation indices including tropopause height. Thus, Thompson et al. (2000), Appenzeller et al. (2000), and Steinbrecht et al. (2001) used NAM-like dynamical proxies in statistical trend analyses of total ozone during the winter-spring period and found consistent results to those found using tropopause height, namely, ~1/3 of the observed total ozone trend being statistically associated with the dynamical changes. The relationship between wintertime total ozone, tropopause height, and mid-tropospheric temperature is illustrated by Figure 4-39. Using global dynamical proxies such as the NAM removes the concern about the statistical correlations being dominated by local dynamical effects, and Thompson et al. (2000) showed using hemispheric data that virtually all the spatial structure of tropopause height and total ozone trends during January-March for 1979-1993 is related to the NAM.

Other tropospheric dynamical indicators have also been used: Hood et al. (1999) used 330-K potential vorticity and meridional wind shear from NCEP-NCAR reanalyses for 1979-1998 as dynamical proxies and argued that 40% of the February total ozone trends and 25% of the March trends could be attributed to dynamical changes. So there appears to be a consensus between the

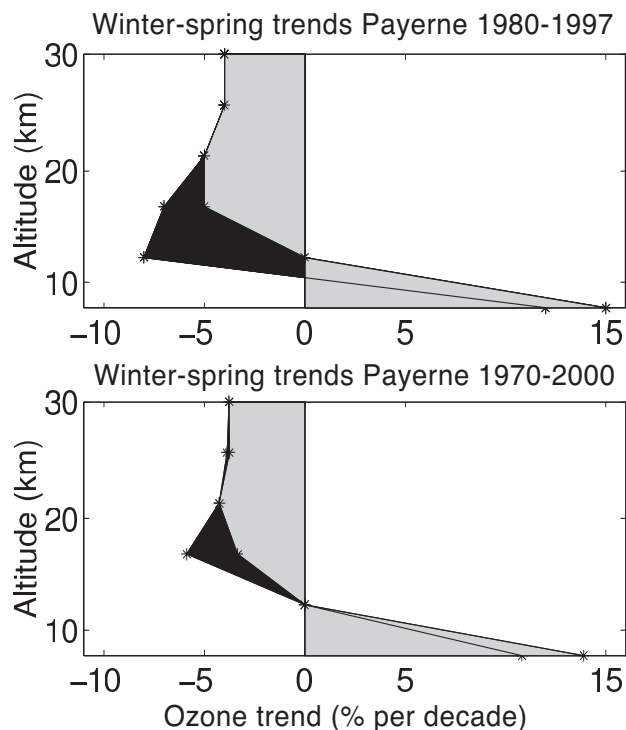


Figure 4-38. Payerne winter-spring ozone sounding trends for 1980-1997 (top) and for 1970-2000 (bottom). On the basis of a statistical analysis, the observed trends can partly be explained by dynamical changes (solid area), while the remaining trend (shaded area) is attributed to anthropogenic (chemical) ozone depletion. From Weiss et al. (2001).

different statistical studies that for decadal time scales, a significant fraction (20-40%) of the observed NH mid-latitude total ozone change is associated with changes in tropospheric circulation. The fact that these different dynamical proxies give reasonably consistent results is not very surprising, however, given the strong correlation between the various meteorological indices.

4.6.3.3 COUPLING ISSUES

An important question to address is whether the recent trends in wave driving and in tropopause height are somehow linked, especially since they lead to similar estimates of the dynamical contribution to total ozone changes. Given the expected association between the NAM and PWD at stratospheric altitudes, the stratosphere-troposphere coupling apparent in the NAM would then imply a connection between wave driving and tropopause height. However, Waugh et al. (1999) found no particular correlation between the NAM index and either the total wave driving or the persistence of the Arctic vortex. Furthermore, the tropopause height trends

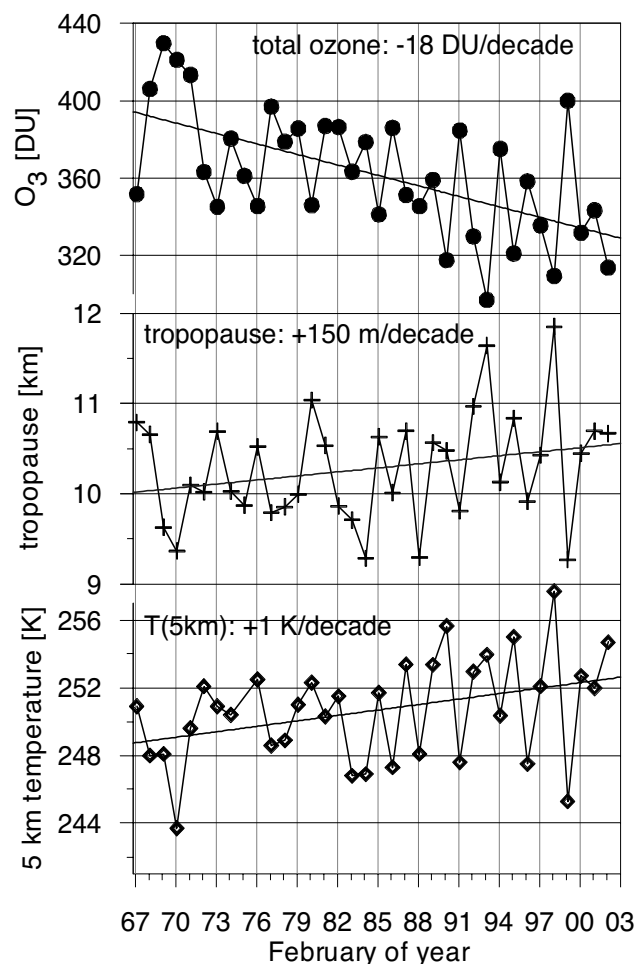


Figure 4-39. February monthly means of total ozone (top), tropopause height (middle), and temperature at 5-km altitude (bottom), at Hohenpeissenberg (47.8°N, 11.0°E). Updated from Steinbrecht et al. (2001) through February 2002.

exist in all seasons, suggesting that although they might lead to PWD changes during winter-spring, the converse cannot be true. So while there is a certain self-consistency between the various dynamical trends, without a clear mechanism connecting the NAM, PWD, and tropopause height, any such connection in the context of long-term trends remains speculative. This question will probably not be answerable until the origin of the changes in the individual dynamical quantities has been identified. Having said that, it would seem unlikely that the statistical effects of wave driving and tropopause height (or NAM) on ozone could simply be added.

4.6.4 Modeling Studies

Another way to estimate the contribution of dynamical changes to ozone changes is by using CTMs driven

by the observed wind and temperature fields. This has recently become possible on a multiannual basis because of the advance in CTM capabilities (Chipperfield, 1999). Hadjinicolaou et al. (1997), using parameterized ozone chemistry, and Chipperfield (1999), using full chemistry, found that the variations in NH midlatitude total ozone in the early 1990s can be largely accounted for by circulation changes alone, including the aftermath of the Mt. Pinatubo volcanic eruption (Figure 4-40). There is, however, a chemical feedback, in that colder winters lead to more polar chemical ozone loss, which is transported to midlatitudes. Hadjinicolaou et al. (1997) identified significant PSC-induced ozone losses both in the polar region and at midlatitudes, especially during the cold winters of 1996 and 1997. Chipperfield (1999) identified a long-term 2-3% reduction at 50°N from polar processing, and

about a 1% reduction from direct midlatitude Cl activation reaching 3% in 1992/1993. Nevertheless a contribution to the very low total O₃ anomaly seen in 1993, relative to the years 1992 and 1994, was attributed to circulation changes (possibly the result of the eruption of Mt. Pinatubo itself), as illustrated in Figure 4-40. From a similar integration covering the 20-year period of 1980-1998, Hadjinicolaou et al. (2002) further argued that at least half of the observed NH midlatitude trend from December through February during this period could be accounted for by dynamical forcing (Figure 4-41), and that the modeled total ozone was strongly correlated with both the NAM and stratospheric wave driving. Hadjinicolaou et al. (2002) furthermore found that the latitudinal and seasonal characteristics of the dynamically induced modeled ozone decrease were consistent with observations,

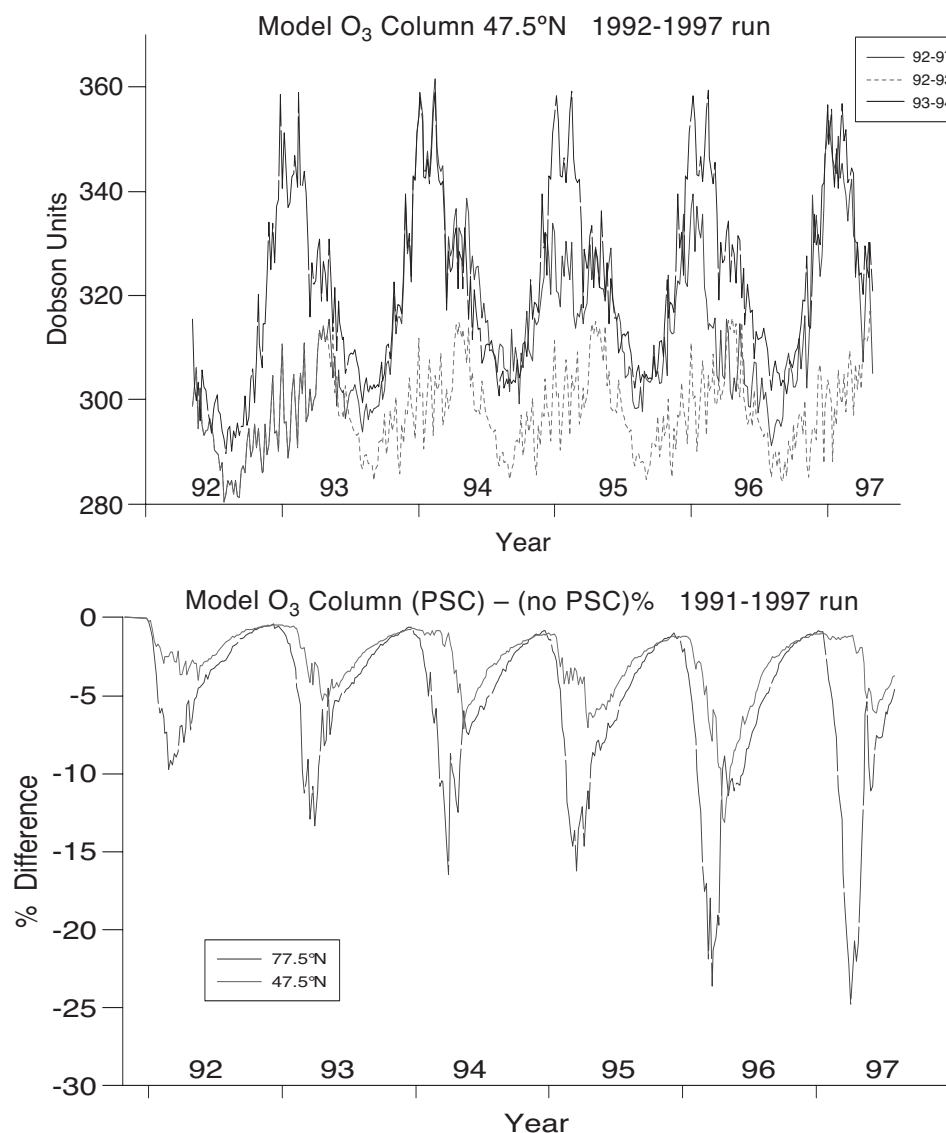


Figure 4-40. Results from a 3-D CTM with parameterized O₃ chemistry. Top panel: Zonal mean column ozone (DU) at 47.5°N for three experiments: annually varying meteorological forcing, repeated 1992/1993 forcing, and repeated 1993/1994 forcing. The interannual variability in ozone is controlled by the meteorological variability. Bottom panel: Difference in zonal mean column O₃ at 47.5°N and 77.5°N between two runs (with annually varying meteorology): one run included the effects of PSCs and the other did not. The colder winters show a larger difference. From Hadjinicolaou et al. (1997).

GLOBAL OZONE

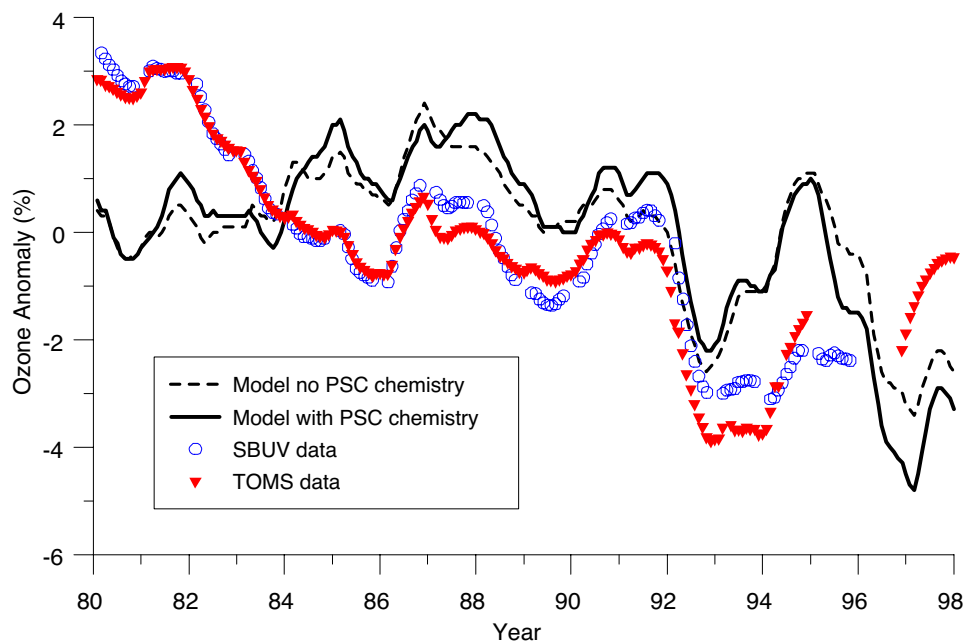


Figure 4-41. Anomaly of column ozone at 30°N-60°N for 1980-1998 from 3-D model simulations with parameterized ozone chemistry compared with satellite data. The chemical forcing is held constant in time, so the modeled trend in ozone is dynamically induced. From Hadjinicolaou et al. (2002).

although the vertical structure was not particularly close. Results from the parameterized ozone runs of Hadjinicolaou et al. (2002) can be compared with the full-chemistry 3-D simulations shown in Figure 4-34, which use constant halogen loading. This shows that dynamical variations do produce much of the short-term variability, but the largest contribution to the modeled trend with time-dependent halogen loading is due to halogen chemistry, rather than dynamics. It should be noted that the CTM results are further from observations in the SH than in the NH, and in particular do not match the decadal-scale variability well. This is perhaps because of the poorer quality of the analyzed winds and temperatures in the SH.

A complementary approach to that of CTMs is using stratosphere-only dynamical-chemical models with explicit representation of planetary waves, driven by observed forcing at the tropopause. This approach was used by Kinnersley and Tung (1998) to study Arctic ozone, and by Fusco and Salby (1999) to study midlatitude ozone. Both studies confirmed the large effect of interannual variations in wave driving on total ozone. Fusco and Salby (1999) found results consistent with those of Hadjinicolaou et al. (1997), including the latitudinal structure of the ozone trends.

4.6.5 Cause of the Dynamical Changes

The question then arises as to why the dynamical changes have occurred. This can ultimately only be answered with GCMs. The first question to resolve is whether chemical ozone depletion might somehow have caused the circulation changes. There has been signifi-

cant attention paid to stratospheric cooling induced by ozone losses (see Section 4.4), but considerably less to associated dynamical feedbacks.

With regard to stratospheric PWD, there is no clear mechanism that would predict ozone loss leading to a decrease in PWD. In contrast to the effect of PWD on ozone, which is clear (if difficult to accurately quantify), the effect of the zonal-wind and temperature structure on PWD is not well understood. Chen and Robinson (1992) and Limpasuvan and Hartmann (2000) have argued that stronger vertical shear of the zonal wind in high latitudes reduces the strength of stratospheric PWD (although they disagree on the details of the mechanism), whereas Hu and Tung (2002) argue for precisely the opposite effect. These studies appeal to different physical mechanisms than does the study of Shindell et al. (1999), which focuses on the zonal wind (not its vertical shear) in subtropical (not high) latitudes. In any case, the seasonality of the relation between NH PWD and ozone means that spring-time ozone depletion cannot be used to explain reduced wintertime PWD. Although Langematz et al. (2002) find a reduction in stratospheric PWD from their imposed ozone changes, this reduction is not statistically significant and only amounts to about one-fourth of the observed PWD changes. Thus although a contribution from the dynamical feedback from ozone changes cannot be excluded, it appears that other factors must contribute to changes in PWD.

With regard to tropospheric circulation changes, it is more difficult to draw conclusions, partly because of our more limited understanding of the tropopause region.

The observed lower stratospheric cooling attributable to ozone decreases would be expected to raise tropopause height on radiative grounds alone. Although this direct effect has not been quantified, Thuburn and Craig (2000) removed all the stratospheric ozone in an idealized GCM experiment and found the extratropical tropopause rose by only 1 km, which suggests that the observed ozone losses of several percent could not account for a rise of 300–600 m. Furthermore, as noted earlier, the observed increase in tropopause height appears to be statistically associated with tropospheric warming, rather than with stratospheric temperature changes (Steinbrecht et al., 1998). Recent GCM studies confirm this: Langematz et al. (2002) found no significant change in mid-tropospheric circulation (including the NAM) arising from imposed ozone changes; Shindell et al. (2001) found an increase in the NAM index, but not of sufficient magnitude to account for the observed change; Santer et al. (2002) found that observed ozone changes had a small positive (but statistically insignificant) effect on tropopause height changes over the past 20 years. Thus, it appears that although the ozone decreases may have led to changes in tropospheric circulation (including tropopause height) that are qualitatively consistent with the observed changes, they are of insufficient magnitude, implying that other factors must contribute. However, it should be noted that most GCMs cannot resolve the observed tropopause height changes, so they must be inferred by interpolation (see Santer et al., 2002), and furthermore the observed ozone changes are not well quantified close to the tropopause.

The subsequent question is whether the circulation changes might be the result of GHG-induced climate change. On the basis of radiative balance, the expected tropospheric warming and stratospheric cooling should lead to an increase in tropopause height at midlatitudes, and to a strengthened meridional temperature gradient in the upper troposphere/lower stratosphere. The GCM study of Santer et al. (2002) showed a mean extratropical tropopause pressure decrease of 3 hPa/decade resulting from changes in WMGGs; this corresponds to an extratropical tropopause height increase of about 120 m/decade, which is roughly consistent with observed changes over recent decades. Perlwitz and Graf (1995) proposed that these changes would act to weaken NH stratospheric PWD, and Shindell et al. (1999, 2001) indeed found such a dynamical feedback in their GCM study of the response of the stratosphere to GHG forcing. However, other GCM studies come to the opposite conclusion; for example, Butchart and Scaife (2001), Schnadt et al. (2002), and Langematz et al. (2002) found that GHG-induced changes lead instead to stronger PWD and a more intense Brewer-Dobson circulation (BDC). Caution is

also warranted because the trend in the NAM index seems to have dropped substantially in the last 5 years or so, and the recent behavior may well be a manifestation of natural variability. As Hartmann et al. (2000) emphasize, the fact that the NAM is a mode of atmospheric variability means that it can be affected by even a relatively small external forcing, and its response may be highly sensitive. It also makes secular changes difficult to separate from natural low-frequency climate variability, because they bear the same fingerprint.

4.6.6 Effects of Mt. Pinatubo Eruption

The volcanic eruption of Mt. Pinatubo in June 1991 produced an increase in stratospheric aerosols that persisted for several years (e.g., Figure 4-18) and that significantly perturbed stratospheric circulation and chemistry. There was a decrease in tropical ozone for several months following the eruption, attributed to a transient increase in tropical upwelling (Schoeberl et al., 1993). Large ozone decreases were observed in NH extratropics for several years following the eruption, primarily during the winter-spring seasons (largest in 1992/1993), as documented in ozonesonde and satellite data (Kerr et al., 1993; Hofmann et al., 1994; Gleason et al., 1993). Smoothed time series of NH midlatitude ozone anomalies suggest the Mt. Pinatubo effect persisted during approximately 1992–1996 (Figure 4-7). However, although the Mt. Pinatubo aerosol was transported into the extratropics of both hemispheres and covered much of the globe by early 1992, column and profile ozone measurements in SH midlatitudes (Figures 4-6 and 4-15) do not show a pronounced ozone decrease comparable to that seen in the NH. This lack of a SH Mt. Pinatubo signal in ozone is curious, in light of the 2-D model simulations that suggest a chemical signal of comparable magnitude between hemispheres (Figure 4-33).

The NH extratropical ozone losses following eruption of Mt. Pinatubo have been characterized as primarily a chemical depletion in several modeling studies (Brasseur and Granier, 1992; Tie et al., 1994; Kinnison et al., 1994; Rosenfield et al., 1997) and in WMO (1995, 1999). The evidence for a chemical mechanism is provided by observations of increases in stratospheric HNO_3 and decreases in NO_2 following the eruption (e.g., Koike et al. (1994); see also Figure 4-21), enhanced ClO in the lower stratosphere (Fahey et al., 1993; Froidevaux et al., 2000), together with the observed vertical profile of ozone changes (decreases in the lower stratosphere over 12–22 km, and increases above 24 km; Hofmann et al. (1994)). The lack of a corresponding Mt. Pinatubo ozone signal in SH midlatitudes is even more puzzling in light of the large perturbations in stratospheric NO_2 that were observed at Lauder, New

Zealand (Figure 4-21). These NO_2 anomalies are evidence of anomalous chemistry acting on the Mt. Pinatubo aerosol in SH midlatitudes, which would be expected to lead to increased ClO and associated ozone losses.

The model simulations of Hadjinicolaou et al. (1997) called into question a purely chemical mechanism for NH midlatitude ozone loss, because they simulated a post-Mt. Pinatubo decrease in a CTM based solely on analyzed meteorological fields (Figures 4-40 and 4-41). Results in the 3-D CTM calculations shown in Figure 4-34 suggest a contribution of roughly 50% from chemistry and 50% from dynamics for the NH midlatitude ozone decrease, consistent with the recent coupled chemistry GCM study of Al-Saadi et al. (2001). The dynamical contribution to midlatitude ozone loss arises from reduced transport, and the relation to the volcanic aerosols has been studied in several idealized models. Observations show that the volcanic aerosols act to warm the tropical stratosphere (Figure 4-22), persisting for several years. Robock and Mao (1992), Graf et al. (1994), and Kirchner et al. (1999) argued that the change in the zonal winds implied by thermal wind balance would then reduce the PWD in the NH winter, essentially putting the atmosphere into a high-NAM-index state. This dynamical feedback is expected to operate only in the NH during winter-spring, because of the strength and sensitivity of PWD, and to be much weaker in the SH. The decrease in PWD leads to a weaker BDC during several NH winters following the eruption, causing less midlatitude ozone from transport effects, and also colder temperatures in the lower stratosphere (which can enhance chemical loss preferentially in the NH). The overall effect on ozone would be a combination of dynamical and chemical effects, with an inter-hemispheric asymmetry. Although these model results are suggestive, the causal relationships are difficult to quantify in observations because of natural variability of the winter stratosphere, and quantified understanding of the global response to the eruption of Mt. Pinatubo is an ongoing research topic.

4.6.7 Conclusions

There is now evidence based on both empirical/observational and modeling studies that a sizable fraction of the trends in total column ozone reported over northern midlatitudes during the past 20 or so years has occurred as a result of decadal changes in atmospheric dynamics. It is hard to quantify this fraction accurately, partly because of the large uncertainty (due mainly to interannual climate noise) in both the observed ozone changes and the estimated dynamical changes, reflected in the sensitivity of the trends to the length of the record, and partly because

the effects are not really separable because of nonlinear feedbacks. There is no doubt that this has occurred on a regional basis, with, for example, the reported ozone trends over mainland Europe being significantly enhanced by long-term changes in dynamics. There is now much stronger evidence than at the time of the previous Assessment (WMO, 1999) that the same is true for the Northern Hemisphere as a whole. The available evidence suggests that the dynamical feedbacks from ozone changes (whether chemical or dynamical) probably act in the same sense as the observed changes, but are of insufficient magnitude to account for them. The cause of the dynamical changes is, at the present time, unknown; neither greenhouse-gas forcing nor natural variability can be excluded.

4.7 IMPLICATIONS FOR CLIMATE OF UPDATED STRATOSPHERIC OZONE CHANGES

This section presents a brief update of the understanding of the impact of changes in stratospheric ozone on climate. IPCC (2001) presented a detailed review of recent work on the climate impact of tropospheric ozone changes; this is not a topic of this section.

IPCC (2001) gave a central estimate of $-0.15 \pm 0.1 \text{ W m}^{-2}$ for the radiative forcing due to stratospheric ozone loss over the period 1979-1997 and included an extensive discussion of the forcing/response relationship for stratospheric ozone changes. Forster et al. (2001) computed the ozone radiative forcing using the Randel and Wu (1999) ozone trends and three different radiative transfer schemes. They estimate a forcing of between -0.08 and -0.15 W m^{-2} , which is on the low side of the IPCC estimate. Hansen et al. (2000) and Hansen and Sato (2001) estimate a forcing of $-0.1 \pm 0.1 \text{ W m}^{-2}$; this more recent estimate is less negative than their previous estimate of -0.2 W m^{-2} because the more recent ozone trend estimates they use show more middle-stratospheric ozone loss than they had used in their earlier estimates. Schnadt et al. (2002), using ozone trends derived from their coupled chemistry-climate model, estimate a 1980-1990 forcing of -0.02 W m^{-2} ; this smaller value may be related to that model's underestimation of the Northern Hemisphere midlatitude ozone loss. Bengtsson et al. (1999) performed time-dependent GCM experiments including observed changes in stratospheric ozone for the period 1979-1997. They found that the ozone reductions in that period lead to a clear cooling, not only in the lower stratosphere, but also in the troposphere. In their model the relative cooling effect was larger in the upper than in the lower troposphere. They point out that this reduces the upper tropospheric warming by the well-mixed greenhouse gases,

resulting in an upper tropospheric temperature change in better agreement with observations.

Over the past 20 years, stratospheric ozone changes may have offset about 20% of the forcing due to well-mixed greenhouse gases, consistent with the values reported in WMO (1999); because the ozone change has been concentrated in this period, the offset since the 19th century is much smaller, about 5%.

An area of recent interest is the degree to which radiative forcing is a useful predictor of climate change; earlier work was discussed in Section 10.3 of WMO (1999). A key unresolved issue is whether the surface temperature response to a given ozone radiative forcing is the same as that due to an identical forcing from, for example, changes in carbon dioxide. If we take r to be the ratio of the global-mean surface temperature response for a global-mean ozone (or any other) radiative forcing to the global-mean surface temperature response for the same global-mean radiative forcing but due to carbon dioxide, then, as discussed by Shine (2000), there is little agreement among available GCM results. Hansen et al. (1997) imposed stratospheric and tropospheric ozone changes on their model and found a value of r of about 0.7 to 0.8 (for simulations including cloud feedbacks). Christiansen (1999), using idealized ozone changes, found r to be near unity for lower stratospheric ozone changes but 1.4 for upper stratospheric ozone changes. Forster and Shine (1999), using observed stratospheric ozone changes, found r to be 1.4. More recently, Stuber et al. (2001) obtained a value of r of 1.8 for idealized stratospheric ozone changes, as a result of a strong stratospheric water vapor feedback in their model. Joshi et al. (2002) provide a comparison of three different GCMs (including that of Stuber et al. (2001)) using the Stuber et al. (2001) perturbation. They found that r varies from 1.25 to 1.8, but interestingly for all three models, the lower stratospheric ozone perturbation generated the largest value of r amongst a range of other climate perturbations.

Hence there remains a lack of consensus as to whether the climate is more or less sensitive to a given radiative forcing due to stratospheric ozone changes than it is to the same radiative forcing due to carbon dioxide changes, but there is now some indication that it may be more sensitive. This will act to modestly enhance the relative importance of stratospheric ozone changes on climate, relative to what would be inferred from radiative forcing alone.

4.8 FUTURE CHANGES IN OZONE

Following the controls on halogen-containing source gases due to the Montreal Protocol (and its

Amendments), the stratospheric loading of chlorine and bromine should decrease in the coming decades (see Chapter 1). Accordingly, over the time scale of the next 50 years, the stratospheric ozone layer is expected to “recover” from the effects of halogen-induced depletion. However, because of other atmospheric changes, future ozone levels may differ from those in the past. These other changes include the radiative effects (stratospheric cooling) of increased GHGs, the chemical effects of certain GHGs (e.g., CH₄), dynamical changes, and changes to the aerosol loading. There are many ways of defining the recovery of stratospheric ozone. These include: a decrease (or reversal) of the rate of ozone decline, an increase in column ozone (or ozone at some specific altitude), a return to some past ozone level, or a reestablishment to a new “unperturbed” level. Under certain plausible scenarios, it is possible that stratospheric ozone will not return to 1980 levels and indeed may not stabilize within the next century.

The detection of recovery will require long time series of high-quality observations. Weatherhead et al. (2000) estimated the length of ozone datasets needed to detect a statistically significant increasing trend in ozone. Even assuming no external perturbations (e.g., from volcanoes), Weatherhead et al. (2000) estimate at least 15 years of observations will be required. This estimate also assumes that no interruptions occur in the time series (e.g., due to data gaps and instrument changes). These calculations show that the unequivocal detection of recovery will not be made in the near future and emphasize that long-term observations should be obtained.

The stratospheric 2-D models used to interpret past changes in ozone in Section 4.5 have also been used to predict the future evolution of ozone over the time period 2000-2050. WMO (1999) discussed the issue of future ozone and presented a number of 2-D model calculations. These calculations focused on the sensitivity of the rate of recovery to different halocarbon scenarios. In this Assessment the impact of different halocarbon scenarios on the decrease in the stratospheric halogen loading is discussed in Chapter 1. Here we take the baseline halocarbon scenario (Table 4B-2 in Appendix 4B) and use the chemical models to investigate the expected evolution of stratospheric ozone under expected GHG changes, and the sensitivity of this to changes in CH₄, N₂O, and CO₂ from these scenarios. (Note that the models do not simulate possible future changes to tropospheric ozone; see Section 4.8.4.) Table 4B-1 (Appendix 4B) lists the model experiments performed. The two standard GHG scenarios, runs MA2 and MB2, are taken from IPCC (2001) scenarios A2 and B2, respectively (Table 4B-3 in Appendix 4B). IPCC (2001) described four scenario families that made dif-

GLOBAL OZONE

ferent assumptions about economic and social development. These scenarios are all considered to be “equally likely,” and here we have chosen two to illustrate the different sensitivity of CH_4 and N_2O changes. The 2-D model runs assumed constant aerosol loading based on the actual 1997 values. Six sensitivity runs were performed to investigate $\pm 20\%$ changes in the rate of change of CH_4 , N_2O , and CO_2 from 2000 onward. Finally, the impact of volcanic eruptions was considered by assuming episodic eruptions (i.e., a repeat of the 1979-2000 aerosol loading) and a constant, enhanced loading corresponding to 1993.

4.8.1 Effect of Decreasing Halogens

Figure 4-42 shows the predicted evolution of global and midlatitude ozone from the 2-D models for run MA2. The models generally predict a local minimum in column ozone in about 2000, followed by a steady increase. There is, however, a large spread in the predicted time at which global ozone returns to 1980 levels, ranging from 2025 until after 2050. The figure can be compared with Figure 12-6 from WMO (1999), where the model runs were based on a “maximum allowed production” halocarbon scenario, and none of the models predicted a return to the 1980 global ozone level before the end of the simulations in 2050. Updates to chemical kinetics, especially key NO_x reactions, are probably an important contributor to the overall more rapid increase in the simulations presented here. Note that the two interactive models (NOCAR and GSFC-INT) have the more rapid rates of predicted column ozone increases in Figure 4-42, due primarily to changes in the US discussed below. This more rapid ozone increase due to the effect of increasing CO_2 was also present in the coupled 2-D model studies of Rosenfield et al. (2002).

Figure 4-43 shows the predicted evolution of ozone in the upper stratosphere (38-43 km). The two models that include temperature feedbacks from increasing GHGs (GSFC-INT and NOCAR) show a significantly faster increase in ozone. In contrast, the models that use fixed climatological temperatures show a more gradual increase, and by 2050 the predicted ozone is still less than 1980 values. An additional run was performed with the NOCAR model (NOCAR2) that used fixed CO_2 after 2000, thereby keeping upper stratospheric temperatures effectively constant. The difference in temperature between these two runs in the US was about 6 K by 2050. Figure 4-43 shows that this NOCAR2 run exhibits a much slower rate of increase, in line with the other fixed-temperature 2-D models, highlighting the importance of temperature changes on future US ozone. The cooling

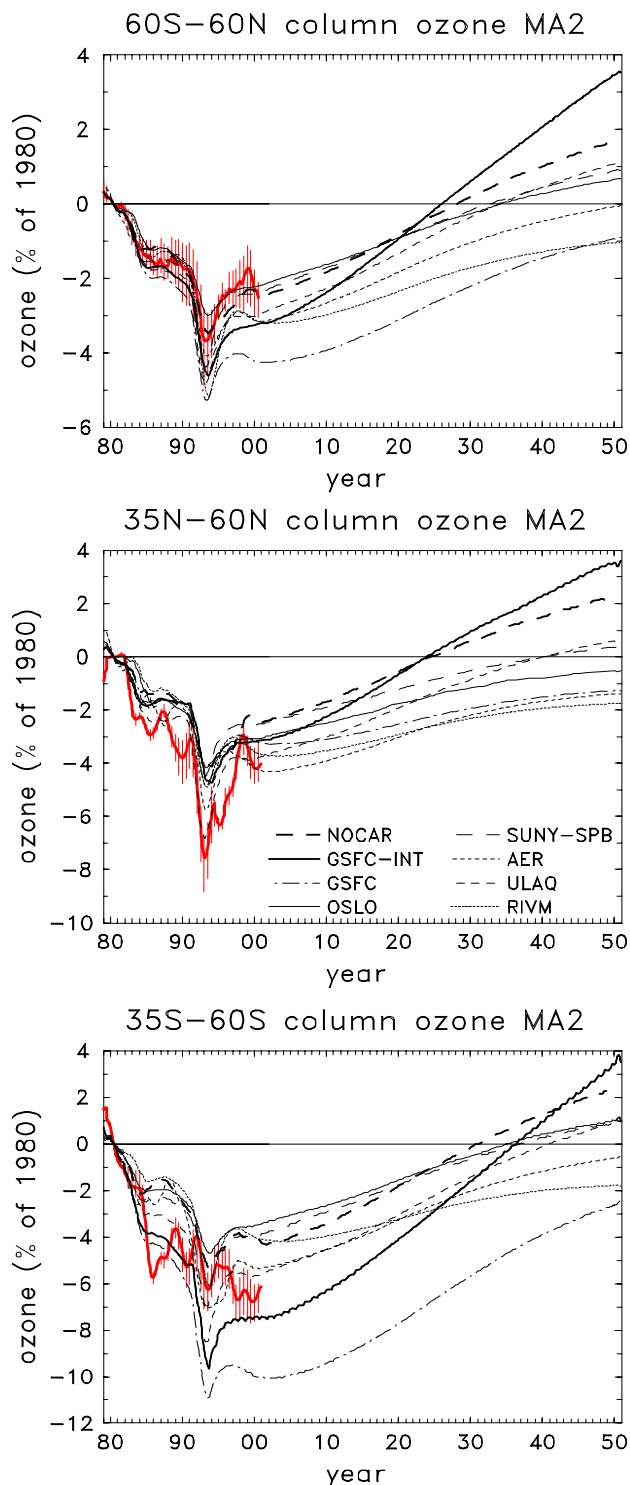


Figure 4-42. Predicted future evolution of column ozone averaged over latitude bands 60°S - 60°N (top), 35°N - 60°N (middle), and 35°S - 60°S (bottom), from a suite of eight 2-D models. Results are shown for GHG scenario MA2. The plots also include the model results and observations of past trends (red lines) prior to 2000 (see Section 4.5.3).

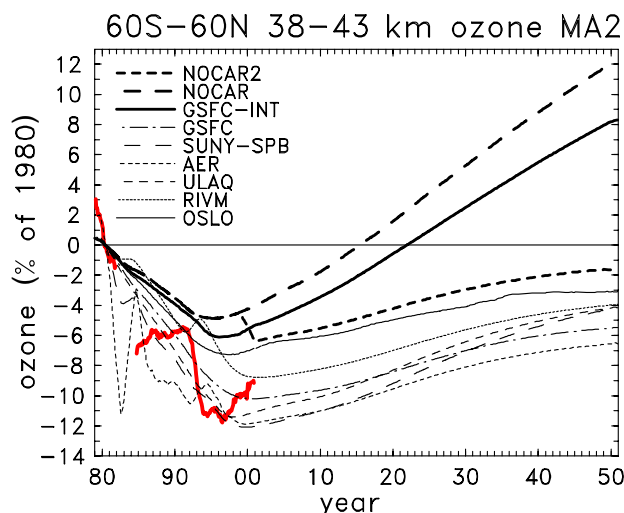


Figure 4-43. Predicted future evolution of US ozone (38-43 km), averaged over latitudes 60°S-60°N from the eight 2-D models shown in Figure 4-42. An additional model run (labeled NOCAR2) used the NOCAR model but with fixed CO₂ after 2000 (with CO₂ set to 1980 values, accounting for the discontinuity near 2000). The models used GHG scenario MA2. The plots also include the model results and observations (SAGE I+II; red lines) of past changes prior to 2000 (see Section 4.5.3).

not only has the direct effect on the rates of chemical reactions, but also can lead to circulation changes that in turn will affect the US abundance of, for example, CH₄ and NO_y. However, the dominant effect is likely to be the decreased rate of ozone-destroying gas-phase chemical reactions due to colder temperatures. This is a well-understood feedback (e.g., Haigh and Pyle, 1979) that is captured by the NOCAR and GSFC-INT models. However, these models underestimate the observed depletion in the late 1990s, and so their predicted increase starts from too high a value. For the models with fixed temperatures, the predicted increase in CH₄ should also tend to increase O₃ near 40 km (by increasing the rate of conversion from ClO to HCl). Therefore, other factors (e.g., the increase in NO_x, from N₂O, or the increase in HO_x) are apparently exerting a dominant influence by 2050.

4.8.2 Influence of Changing Climate Gases

The IPCC scenarios given in Table 4B-3 in Appendix 4B show a range in the predicted evolution of CH₄, N₂O, and CO₂ under different assumptions. The effect of this uncertainty in CH₄ and N₂O on the future evolution of ozone has been investigated using one representative model (which uses fixed temperatures). A

decrease (increase) in the rate of CH₄ growth increases (decreases) the time for O₃ recovery to 1980 levels. However, the effect of a 20% change in CH₄ is to shift the recovery by only about 2 years. This uncertainty in the growth of CH₄ essentially covers the range of all IPCC (2001) scenario families except B1, which predicts a CH₄ growth some 85% less than the A2 scenario. In contrast, a decrease (increase) in the rate of N₂O growth decreases (increases) the time for recovery, but again the effect is small. For N₂O the various IPCC scenarios represent a variation in N₂O growth of +8% to -50% compared with A2. Therefore, for both gases the modeled direct chemical sensitivity of the rate of recovery to the range in the IPCC scenarios is smaller than the inter-model differences (and uncertainties). Uncertainties in CO₂ could lead to a large uncertainty in future O₃ through the important feedback discussed in Section 4.8.1.

A recent 2-D model study by Randeniya et al. (2002) supports and extends the analysis presented here, as well as that of WMO (1999), on the direct chemical effects of future N₂O and CH₄ increases. These authors based model runs from 2000 to 2100 on two IPCC scenarios with different rates of N₂O increase and both an increase and decrease in CH₄. (Note, however, that their model ignored the effect of temperature feedbacks from GHG increases.) Figure 4-44 shows the calculated percent annual change in ozone at 45°N for 2000-2100 from

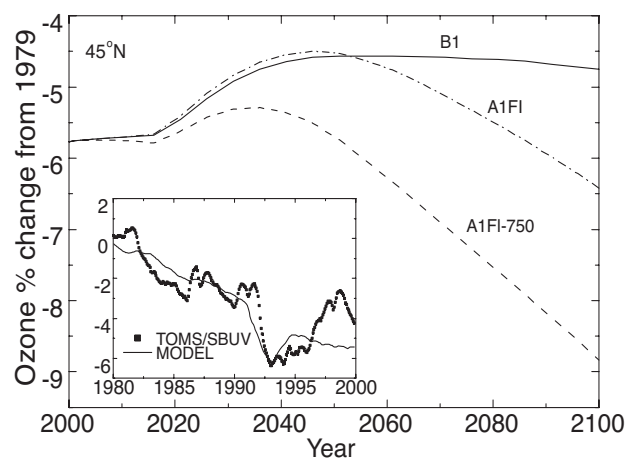


Figure 4-44. Percent change in annual average stratospheric ozone at 45°N from 1979 levels for the period 2000-2100 calculated with a 2-D model and a range of GHG scenarios. The GHG scenarios are based on IPCC (2001) scenarios B1 and A1F1, with a third scenario based on A1F1 but with reduced CH₄ emissions (labeled by A1F1-750). The insert shows modeled and observed ozone changes from 1980 to 2000. From Randeniya et al. (2002, Figure 2).

GLOBAL OZONE

their study. In agreement with the fixed-temperature models shown here, that study found that ozone increases between about 2000 and 2050. However, different behavior could occur at longer time horizons. Increasing levels of N_2O in the 21st century should be expected to increase NO_x , which will lead to enhanced ozone loss in the middle stratosphere. Moreover, as chlorine abundances decline, such increasing NO_x would no longer form ClONO_2 in the lower stratosphere and could hence lead to substantial ozone loss. Only when both N_2O is assumed to stop increasing and methane is assumed to decrease in the latter half of the 21st century does their model predict a stabilized ozone layer. This study makes clear that the large perturbations in NO_x , ClO_x , and HO_x that could occur in conjunction with various possible future scenarios for N_2O , CFCs, and CH_4 in the latter half of the 21st century may complicate long-term ozone changes, and could even prevent a return to 1980 levels. However, as Section 4.8.1 shows, the strong influence of CO_2 on cooling the upper stratosphere means that the coupled radiative effects of future CO_2 increases also need to be considered, which will tend to increase ozone over this time period.

Figure 4-45 shows the sensitivity of global ozone to different aerosol scenarios. Assuming an enhanced, but constant, aerosol loading causes lower O_3 values throughout the period 2000-2050. The largest difference occurs early in the 21st century with an additional decrease of 2%. As chlorine in the atmosphere declines, the additional effect of the enhanced aerosol loading decreases, and by 2050 the difference compared with the background aerosol is an additional 1% global loss. The episodic aerosol scenario also shows this behavior; the transient ozone depletion associated with a Mt. Pinatubo-size eruption is largest in the early 21st century (additional 2.5% loss in 2013, compared with additional 1.5% loss in 2034).

4.8.3 Other Stratospheric Influences

4.8.3.1 DYNAMICAL EFFECTS

As discussed in Section 4.6, two dynamical influences appear to have contributed to NH midlatitude ozone decreases over 1980-2000: a decrease in wave driving and an increase in tropopause height. These mechanisms likewise have the potential to influence future ozone. If the past dynamical changes represent natural variability, then one cannot extrapolate past dynamical trends, and ozone recovery could be either hastened or delayed by dynamical variability. If, on the other hand, the past dynamical changes represent the dynamical response to GHG-induced climate change, then one might expect these

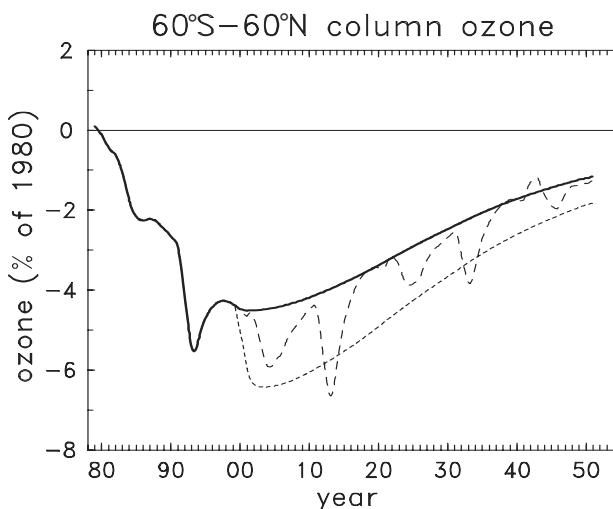


Figure 4-45. Predicted evolution of global column ozone (60°S–60°N) for one representative model for the MA2 scenario, which assumes a constant 1997 aerosol loading (solid line) along with results from sensitivity experiments that assume a constant 1993 aerosol loading (dotted line) and an episodic loading that repeats the 1979-2000 values (dashed line).

changes to increase in magnitude in the future. This would decrease future ozone levels and delay ozone recovery.

Unfortunately, our ability to predict future dynamical influences is very poor, for two reasons. First, dynamical processes affecting ozone exhibit significant temporal variability and are highly sensitive to other aspects of the atmospheric circulation. This means that the GHG-induced signal is inherently difficult to isolate or to represent accurately in GCMs, while the climate noise is relatively high (especially in the NH). Second, coupled chemistry GCMs, which are the tools needed to address this question, are still in their infancy (see Chapter 3). As discussed in Section 4.6.5, predictions of GHG-induced dynamical changes by such models do not even agree on the sign of the changes: some models predict weakened PWD, which would decrease midlatitude (and polar) ozone via reduced transport, while others predict strengthened PWD. Note that these dynamical changes would also affect the lifetime of stratospheric pollutants, with stronger PWD leading to a reduced lifetime (Butchart and Scaife, 2001). (This latter effect acts on the several-year time scale associated with the BDC, in contrast to the effect of PWD on ozone transport, which is essentially instantaneous.) Thus, the direct effect of PWD on ozone transport (no matter what its sign) would be reinforced over decadal time scales by altered chemical ozone loss arising from PWD-induced change in stratospheric chlorine loading.

4.8.3.2 FUTURE EFFECTS OF AIRCRAFT

Future subsonic and potential supersonic aviation have been calculated to impact atmospheric ozone. The IPCC Special Report on *Aviation and the Global Atmosphere* (IPCC, 1999) summarized the present understanding regarding future aviation emission levels and their effect on ozone. Model calculations were performed for forecasted (to 2015) and projected (to 2050) increases in NO_x emissions (1.7 Tg in 1992, 4.1 Tg in 2015, 7.2 Tg in 2050) from subsonic aviation. The calculated impacts increase with fleet emissions, rising from +0.4% to +1.2% (total column change at 45°N latitude) between 1992 and 2050. The impact is primarily confined to the troposphere, with approximately 25% of the change occurring in the stratosphere.

The impact on column ozone of a potential fleet of supersonic aircraft was estimated by IPCC (1999) and Kawa et al. (1999). The estimated effect on column ozone (at 45°N latitude) in 2050 of a combined supersonic and subsonic fleet is -0.4% relative to no aircraft and -1.5% relative to a 2050 subsonic-only fleet, with all the supersonic-induced change occurring in the stratosphere. For the presumed emission levels of NO_x , the predicted decrease in ozone is dominated by the influence of aircraft-emitted H_2O on odd-hydrogen abundances.

Aircraft impact studies conducted since the IPCC (1999) report have examined the sensitivity of model predictions to changing model parameterizations and input parameters. Schoeberl and Morris (2000) employed a trajectory model to evaluate the transport of subsonic and supersonic aircraft exhaust into the stratosphere. Their simulations indicate that there is less upward diffusion of supersonic emissions than found in Kawa et al. (1999) and that subsonic emissions do not significantly penetrate the 380-K potential temperature surface (i.e., they are confined to the lowermost stratosphere). The trajectory model results point to possible excessive diffusion in the global models. However, the sensitivity of ozone change to the reduced transport remains to be explored.

The importance of meteorological conditions on the calculated impacts of supersonic aircraft has been examined by Rogers et al. (2000). Three-dimensional model calculations were performed identically to those used in the IPCC Assessment, except that the model was forced with an annually varying meteorological analysis. The varying meteorology results in a calculated O_3 perturbation that exhibits interannual variability that is of similar magnitude (i.e., 50 ppbv) to the dispersion found among the models used in the IPCC (1999) and Kawa et al. (1999) assessments. This finding strengthens arguments presented in IPCC and Kawa et al. regarding the

substantial influence of model transport differences on the ozone impact computations.

The impacts of supersonic aircraft on stratospheric sulfate and PSC abundances have also received further scrutiny. Kärcher et al. (2000) have coupled a detailed analytical formulation for the near-field aerosol plume to a far-field plume model and a 2-D global aerosol model. Predicted changes in sulfate aerosol surface area density due the operation of a supersonic fleet using the detailed microphysical treatment are similar to the earlier IPCC estimates. The Kärcher et al. analysis indicates that the sulfur-to-sulfate conversion efficiency and emission index of particulate organic matter are the most important parameters affecting large-scale cloud and chemical impacts.

The effects of supersonic NO_x and H_2O emissions on PSC formation have been examined by Considine et al. (2000) using a PSC parameterization formulated for inclusion in a global 3-D chemistry and transport model. The increased levels of polar NO_x and H_2O arising from the aircraft emissions are found to induce an earlier onset of PSC formation, denitrification, and dehydration in the Southern Hemisphere polar vortex. Resulting increases in active chlorine are calculated to produce approximately 1% decreases in lower stratospheric vortex O_3 concentrations.

It should also be noted that increases in the use of other types of aircraft or other routes, not considered in the Assessments discussed above, might lead to significant emissions in the stratosphere. In particular, a large increase in the use of small “executive” jets or introduction of near-supersonic commercial jets could affect stratospheric ozone. Also, increased use of subsonic polar routes could have important implications for the stratosphere. The potential effects of these will need to be assessed in more detail.

4.8.3.3 ROCKET EMISSIONS

Additional modeling and observation results have been reported on rocket combustion emissions and plume wake chemistry since the previous Assessment (WMO, 1999), in which it was concluded that stratospheric accumulation of chlorine and alumina exhaust from current launch activities leads to small (<0.1%) global column ozone decreases. The new data support this conclusion. They also reveal new chemical and physical processes that could influence future estimates of ozone loss associated with rocket launches.

Large (~100%) ozone loss has been observed and characterized in the local wakes of Delta II (Ross et al., 2000) and Atlas IAS (Ross et al., 1999a) rockets powered by a combination of solid propellant ($\text{NH}_4\text{ClO}_4/\text{Al}$;

GLOBAL OZONE

ammonium perchlorate/aluminum) and liquid propellant (LOX/kerosene; liquid oxygen/kerosene). The cumulative ozone losses in the Delta II and Atlas IIAS wakes are comparable with those observed in solid-propellant-only Titan IV rockets, even though the total solid rocket motor (SRM) emissions are a factor of 9 and 11 greater for the Titan IV rocket than for the Delta and Atlas rockets, respectively.

This apparent nonlinear scaling of ozone loss with total SRM emissions is not predicted by plume wake models because the LOX/kerosene emissions are not expected to destroy ozone locally. To explain the observations, it has been suggested that exhaust products of the hydrocarbon-fueled engines of the Delta and Atlas rockets, possibly soot, catalyze ozone depletion. This suggestion remains to be tested because suitable gas and particle emission data for LOX/hydrocarbon-fueled rocket engines are not available. In situ particle number density and composition measurements made recently in an enormous aerosol cloud at 20 km altitude were linked to a Soyuz rocket launch 12 days earlier (Newman et al., 2001). These measurements constitute the first stratospheric data on emissions from a hydrocarbon-fueled rocket.

Danilin et al. (2001a) investigated the global implications of large, local ozone loss due to chlorine and alumina emissions from the current Space Shuttle (SRM/LOX-hydrogen) fleet. They modeled the accumulation of ozone losses in two Shuttle wakes (followed by dilution) and found this immediate wake effect not to be globally significant relative to the ozone loss on the longer time scale of plume dispersion and mixing with ambient background air globally. The relative significance of ozone loss accumulated in the plume on intermediate time scales (i.e., greater than 2 days) has not been evaluated.

The impact of alumina particles on ozone depletion is calculated to increase with surface area density (Danilin et al., 2001b). Particle measurements in SRM wakes have revealed a trimodal size distribution, in general agreement with rocket plume wake models (Ross et al., 1999b). However, the fraction of particle mass contained in the smallest (i.e., submicron) size modes differs by more than a factor of 5 between data obtained from large Titan IV and Shuttle SRMs (Ross et al., 1999b) and from a small Athena II SRM (Schmid et al., 2002). The large variance may reflect real differences between the emissions of large and small SRMs or differences in measurement techniques. In either case, because particle surface area density is most influenced by the submicron particle modes, the variance between the results of Ross et al. and Schmid et al. adds significant uncertainty to the predicted global impact of SRM emissions. Assuming the Schmid et al. particle distribution with its larger number

of submicron particles for the larger SRMs would result in the ozone impacts from emitted alumina and chlorine being roughly comparable. Alternatively, assuming the Schmid et al. distribution only for small SRMs would imply that ozone loss relative to total SRM emission varies inversely with SRM size, a feature not included in models.

The effect of plume-wake processing on the reactivity of rocket-emitted alumina particles and the associated ozone loss has yet to be fully explored. The reactivity depends strongly on the composition of the wake particles. Some insight into the composition of rocket particles has been gained from measurements of H₂O vapor and CO₂ in the lower stratospheric wake of an Athena II SRM (Gates et al., 2002). These data show that a fraction of the H₂O emissions condensed onto particles and remained condensed for more than 40 minutes after launch, long beyond when temperatures rose above the estimated frost point. Gates et al. (2002) argue that, for this to occur, the water surface layer of the particles is either coated with HNO₃ or combined with HNO₃ to form nitric acid trihydrate (NAT). In either case, the HNO₃ would serve to inhibit evaporation of the volatile aerosol component. Popp et al. (2002) measured ~30 parts per billion (ppb) HNO₃ in the Athena II wake, likely sufficient to explain the observed persistence of condensed volatiles. It is not clear if HNO₃ is produced during SRM combustion, during intense chemical processing in the plume wake, or by a combination of the two processes. In any case, the Athena II observations indicate that SRM plume wake particles are more complex and likely to be more reactive than previously considered.

Space launch activity has undergone substantial growth over the last decade (60% increase per decade; FAA, 2000). If this growth rate is realized through SRM use and is sustained over the next several decades, the associated ozone depletion from stratospheric chlorine and particle injection might become significant. Under some plausible scenarios, ozone loss due to rockets may become greater than that due to chlorofluorocarbons by the year 2050. However, recent technology developments indicate that growth in hydrocarbon engine emissions may exceed growth in SRM emissions. The change in calculated ozone impact resulting from SRM replacement by hydrocarbon engines cannot be confidently estimated at this time.

4.8.4 Future Tropospheric Ozone

The future evolution of tropospheric ozone was considered in some detail in the recent Third Assessment Report (TAR) of the Intergovernmental Panel on Climate Change (IPCC, 2001), and here we focus primarily on the

results presented therein. Research groups involved in 3-D tropospheric chemistry modeling were invited to participate in the TAR through a model intercomparison activity. Ten different models submitted results for both the year 2000 (Y2000), and for one scenario for the year 2100 (Y2100). The groups were asked to run with a standard set of emissions for NO_x , CO, and volatile organic compounds (VOCs) for 2000 and for abundances of long-lived gases; the standard simulation for 2000 provided the baseline from which changes in greenhouse gases were calculated.

The model simulations for 2000 were tested by comparison with the seasonal cycle of ozone at five locations (20°N-75°N) for 700, 500, and 300 hPa, and the simulation for CO was compared with surface concentrations from five sites (40°S-80°N). The models captured the broad seasonal patterns for CO and ozone, but there was a wide dispersion among the models for both gases. Most models were within 30% of the ozone observations. However, it should be noted that there were large variations in the calculation of the present-day tropospheric ozone budget. In particular, there is disagreement between models on the sign of the net photochemical production, possibly driven by differences in the calculated flux of ozone from the stratosphere.

A large number of scenarios for future emissions were developed for the IPCC Assessment, but only one of these, designated the Special Report on Emissions Scenarios (SRES) A2p, was used for the Y2100 standard calculation; a CH_4 abundance of 4.3 parts per million by volume (ppmv) was specified for Y2100. The TAR notes that the SRES scenarios assume few controls on CO, NO_x , and VOCs, and that A2p has overall the highest emissions. It was chosen so that once the response of ozone and OH to these extreme emissions was understood, other scenarios and intermediate years could be interpolated with some confidence.

The increase in the tropospheric column of ozone from Y2000 to Y2100 calculated by the ten 3-D models was 16.6 to 26.5 DU, and the TAR adopted a best estimate of 22 DU. Although the increases in the tropospheric ozone column given by the various models were rather consistent, the spatial and vertical distributions of the ozone changes varied considerably from model to model. A footnote added in proof to the TAR notes that these “tropospheric” column changes erroneously included the lower stratosphere, and that the troposphere-only changes are 25-33% less, or about 16 DU. The present-day column of tropospheric ozone is about 34 DU, so the calculated increase is a substantial fraction of the current amount in

the troposphere, and it is a few percent of the total column of midlatitude ozone.

The TAR used the standard Y2000 and Y2100 calculations, along with three other cases (Y2000 with a 10% increase in CH_4 , Y2100 with no increase in NO_x emissions, and Y2100 with no increase in NO_x , VOC, and CH_4) to define simple linear relationships for the absolute change in tropospheric ozone and the relative change in OH as a function of the CH_4 abundance, and the emission rates for NO_x , CO, and VOC. These relationships were then used to estimate the evolution of six different emission scenarios from 2000 to 2100. The changes in the tropospheric ozone column for 2000 to 2100 for the six scenarios are from -4 to +22 DU, whereas the changes for 2000 to 2050 are from 4 to 15 DU. Clearly, the scenario selected for the Y2100 model study represents an extreme case.

The calculations that were carried out for the TAR did not allow for changes in stratospheric ozone, nor did they allow for changes in climate. Calculations with the coupled ocean-atmosphere-chemistry model at the Hadley Centre (U.K.) have shown that the increases predicted for tropospheric ozone and CH_4 by 2100 are smaller in simulations that allow for climate change than in those that do not (Johnson et al., 2001). Trace gas emissions were taken from the same scenario, A2, as in the TAR, but CH_4 was calculated based on emissions. In the control run, ozone at 650 hPa increased from 40 ppbv to 65 ppbv at midlatitudes, whereas in the run with changing climate, ozone increased to only 49 ppbv. The increase in CH_4 was from 1.67 ppmv in 1990 to 3.65 ppmv in 2100 in the control run, but to only 3.23 ppmv in the climate change run. Most of the difference for both gases occurred after 2040. The main causes for smaller changes in ozone and CH_4 in the climate change run were (1) an increase in photochemical destruction of ozone caused by higher water vapor, and (2) a decrease in the CH_4 lifetime caused by the higher temperatures increasing the rate coefficient for $\text{OH} + \text{CH}_4$, and by higher OH.

While these results indicate that estimates of future tropospheric ozone may be reduced in a future climate, there are other feedbacks that may result in higher tropospheric ozone levels. For example, increased deep convection in a future climate could lead to increases in NO_x production by lightning (e.g., Toumi et al., 1996). Climate change may also lead to increases in temperature-dependent emissions (e.g., isoprene) or changes in the flux of ozone from the stratosphere, resulting in additional increases in tropospheric ozone. Current uncertainties in our knowledge about such feedbacks hinder our ability to predict future changes.

4.9 SYNTHESIS OF CURRENT UNDERSTANDING OF PAST AND FUTURE CHANGES IN OZONE

Table 4-5 summarizes the important processes that we believe have contributed to the observed past changes in global ozone, our estimated level of scientific understanding of these processes, and their likely importance in causing the observed trend in column ozone. Our level of scientific understanding is given on a scale from low to high. The impact on global ozone is rated from negligible to important. The table also summarizes the processes that will affect the future evolution of the ozone layer, an estimate of the likely importance of that process, and a measure of our confidence in that prediction. The stated confidence ranges from high to low. The importance for column ozone ranges from minor to important.

4.9.1 Discussion of Past Changes

There is very high confidence that gas-phase chlorine chemistry is the main driver of ozone trends in the upper stratosphere. This is based on overall reasonable agreement between observed and modeled ozone trends in the upper stratosphere, in terms of vertical profile (Figure 4-30) and latitudinal structure (e.g., WMO, 1999, Figure 6-20). Although there are substantial inter-model differences in the magnitude of the trends near 40-45 km for the simulations examined here (Figure 4-30), these are strongly related to differences in modeled temperature trends in the upper stratosphere, and also to changes in constituents such as CH_4 (although a quantitative analysis of these effects is beyond the scope of this Assessment). In the upper stratosphere, lower temperatures cause a slow down of the gas-phase chemical loss reactions due to chlorine, while CH_4 controls the ClO/HCl partitioning (as is apparent in observations in Figure 4-29), and therefore larger CH_4 trends lead to smaller ozone trends. Note that long-term global observations of upper stratospheric CH_4 over 1979-2000 are unavailable to compare and constrain the model results. Upper stratospheric CH_4 measurements from HALOE during 1991-2000 show substantial interannual variability and changes in “trends” that are not well understood at present (Randel et al., 1999), and these are difficult to extrapolate to the longer 1979-2000 period. Although the processes responsible for upper stratospheric ozone losses are reasonably well understood, the contribution to column ozone trends is relatively small: only 15-30% of the extratropical column ozone losses for 1980-2000 originate at altitudes above 25 km.

In the lower stratosphere, there is fairly high confidence that halogen-related chemistry is responsible for a large fraction of the midlatitude ozone trends. This is

based on the fact that 2-D and 3-D models with imposed halogen trends are able to approximately simulate the latitudinal, vertical, and seasonal characteristics of observed midlatitude ozone trends. There are important caveats to this attribution, because the 2-D models all overestimate observed ozone trends in the tropics and underestimate the magnitude and seasonality of trends in the midlatitude NH, and there is relatively large inter-model variability for trend calculations in the midlatitude SH. The underestimate of NH midlatitude trends during winter-spring may be due to a number of factors: effects of water vapor trends and uncertainties in bromine amount and chemical reaction rates, lack of detailed polar vortex chemistry and mixing to midlatitudes in 2-D models, and the contribution of dynamically induced ozone changes in observations. Also, the precise mechanisms for the decadal-scale ozone changes that occur in the models are not simply isolated, and the relative importance of polar processing (and export to midlatitudes) versus in situ activation awaits clarification. The overestimates of tropical ozone trends may be related to relatively weak dynamical isolation of the tropics in many models (Hall et al., 1999; see also Figure 4-28), and the large inter-model variability in SH extratropics is associated with simulation of the Antarctic ozone hole and transport out of the vortex.

Although the models are able to approximately simulate the 20-year trends in midlatitudes, both 2-D and 3-D simulations are less successful at simulating the actual time series of midlatitude ozone. This is particularly the case in the SH, where models overestimate SH ozone losses after the eruption of Mt. Pinatubo and miss substantial ozone declines observed during the middle 1980s. Variability in the wave-driven Brewer-Dobson circulation contributes to interannual ozone changes in the lower stratosphere during winter and spring, and this factor is relatively more important in the NH where wave driving is stronger and highly variable. Although the contribution of this process to decadal ozone trends is difficult to quantify, it probably accounts for 30% or less of the observed NH trends during 1979-2000.

The lowermost stratosphere is the region where the ozone trends, and their causes, are least certain. Long records of ozonesonde data are limited to relatively few stations over NH midlatitudes. The role of chemistry is difficult to quantify because of low temperatures and occasionally high humidity. This makes the role of heterogeneous chemistry on aerosols and cirrus particles uncertain. Dynamics plays a relatively large role for ozone variability in the lowermost stratosphere. This region is sensitive to the Brewer-Dobson circulation (from above), and empirical studies over NH midlatitudes show strong relationships between ozone and changes in tropo-

Table 4-5. Summary of understanding of past long-term midlatitude stratospheric ozone changes and expected importance in the future.

Influence	Process	Level of Scientific Understanding (LOSU) ^a	Region of Local Change	Contribution to Past Column Changes and Sign of Forcing ^b	Likely Importance for Future Column Change Over Next 50 Years
Chemical CFCs, halons, and other Cl/Br source gases	Cl _y /Br _y processing from vortex Cl _y T-dependent gas-phase chemistry in US	Medium Very high	Tropopause-30 km 25-50 km	Important; negative Important; negative	Decreasing over time Decreasing over time
	Cl _y /Br _y gas-phase chemistry in LS/LMS	High	Tropopause-25 km	Important; negative	Decreasing over time
	N ₂ O ₅ + H ₂ O on sulfate aerosol	High	Tropopause-30 km	Important; negative	Decreasing over time
	Cl _y processing on cold liquid aerosol	Medium	Tropopause-20 km	Important; negative	Decreasing over time
CH ₄	CH ₄ chemistry	High	Tropopause-50 km	Minor; positive	Minor
	HO _x chemistry	High	Tropopause-20 km and 30-50 km	Minor; negative	Minor
	Effect on H ₂ O and heterogeneous chemistry	Medium	Tropopause-20 km	Minor; negative	Minor
	NO _y chemistry	Very high	25-45 km	Minor; negative	Increasing over time
N ₂ O	HO _x and heterogeneous chemistry	Medium	Tropopause-50 km	Minor; negative	Unknown
H ₂ O	NO _x , HO _x , aerosols	Medium	Tropopause-20 km	Minor; positive	Minor
Aircraft	Cl _y , alumina, soot	Medium	Tropopause-50 km	Negligible; negative	Minor
Dynamical and radiative					
Stratospheric planetary waves	Transport	Medium	15-30 km	Important; positive, negative	Important
Tropospheric circulation	Stratosphere-troposphere exchange and LMS dynamics ^c	Medium-low	Tropopause-20 km	Important; positive, negative	Important
Radiatively active species (CO ₂ , CH ₄ , N ₂ O, H ₂ O) GHG direct effect ^d	Thermal structure	Medium-high	Tropopause-50 km	Minor; positive (US), negative (LS/LMS)	Important
Other					
Solar irradiance	Modulation of photolysis rates	Medium	Tropopause-50 km	Negligible; positive, negative	Minor
Volcanoes	Heterogeneous chemistry	Medium	Tropopause-25 km	Important; negative	Transient; possibly large
Tropospheric O ₃ precursors	RO ₂ -NO _x chemistry	Medium	Surface-tropopause	Minor; positive	Important

^a The meaning of LOSU for dynamical influences is different from that used for the chemical influences. The relevant physics and mechanisms of the stratospheric planetary wave forcings are well understood. However, it is hard to quantify their past effect in the real atmosphere. For tropospheric circulation changes, uncertainties come from our lack of clear understanding of the mechanisms controlling tropopause height. For direct GHG changes, uncertainties come from factors influencing how well the changes in H₂O near the tropopause are known. For future changes, the LOSU for all processes is limited by the quality of predictive models.

^b The meaning of "forcing" for the effects of stratospheric planetary waves and tropospheric circulation on ozone is different than for chemical forcings. Here "forcing" is used in the sense that decadal changes in these dynamical properties of the atmosphere have occurred that can cause decadal changes in ozone. The possible causes of these dynamical changes are discussed in Section 4.6.

^c Tropopause height is a proxy for LMS dynamics.

^d GHG direct effect means the radiative impact of changes in GHGs and any consequent changes in the thermal structure of the atmosphere GHG effect. The direct greenhouse effect of GHGs is a forcing in the same way as the chemical forcings are defined, namely, an increase in atmospheric concentrations of certain gases as a result of anthropogenic activity has an effect on the atmosphere that can, in principle, be separated and determined.

spheric circulation and tropopause height (forcing from below). The interrelationships between ozone and circulation parameters in the lowermost stratosphere are poorly quantified at present, and estimates of circulation effects on decadal changes in ozone are highly uncertain.

Overall, the balance of evidence still suggests that increases in halogens have been the most important driver for long-term changes in global ozone. However, compared with previous Assessments, the longer observation time series now available have emphasized other factors, such as dynamical variability, which modulate ozone in the lower part of the stratosphere.

4.9.2 Discussion of Future Changes

Over the next 50 years the stratospheric burden of chlorine is expected to return to the same level as that which existed in 1980 (Chapter 1). Accordingly, the reversal of the halogen forcing of the observed past trends in global ozone is expected to lead to an ozone increase. However, a number of other factors may affect the rate and extent of this recovery from the halogen-induced depletion.

In the upper stratosphere, where past trends have been due to chlorine chemistry, ozone is expected to return to 1980 values well before 2050. Coupled 2-D model calculations suggest that a cooling of the stratosphere (due to GHG increases) will significantly increase US ozone through a slowdown of the gas-phase chemical loss reactions (Figure 4-43). Without this cooling, similar models predict that US ozone would not have returned to 1980 levels by 2050, highlighting the important impact of this feedback.

In the lower stratosphere, the decrease in stratospheric chlorine will also lead to a recovery from the observed depletion of the past two decades. Although bromine has also contributed to LS O₃ changes, the reduction in chlorine is expected to dominate future trends. A range of 2-D models indicate that NH and SH midlatitude column ozone (which is dominated by the LS) will return to 1980 levels between 2025 and 2050, although there is a large uncertainty in this timing (Figure 4-42). The models that include the effect of stratospheric cooling on gas-phase chemistry indicate that this will also significantly accelerate the rate of column ozone increase in this period. An important caveat to these predictions is that the 2-D models examined here do not include a detailed treatment of polar processes and mixing to midlatitudes. Heterogeneous processing of chlorine species in the polar vortex may significantly affect midlatitude ozone, and over the next decade or so stratospheric cooling could enhance polar ozone loss (see Chapter 3). Therefore, in

the near future continued midlatitude ozone losses may still be observed.

Midlatitude ozone will be most susceptible to enhanced chemical loss by volcanic eruptions in the next 20 years or so while stratospheric chlorine levels remain high. During this period, a large eruption, similar in magnitude to that of Mt. Pinatubo in 1991, may cause a similar transient decrease in column ozone that lasts a few years. Predicted changes in N₂O and CH₄ will have a relatively small impact on column ozone over the next 50 years.

Any future changes in stratospheric circulation and transport could have the potential to affect global column ozone. At present it is not possible to predict what these changes may be and therefore what effect they may have on column ozone. This is a major limitation on our predictive capability.

Beyond 2050 the stratosphere will return to one in which halogens play less of a role in controlling the distribution of ozone. Ozone trends may then be dominated by trends in other gases that produce chemical species known to catalytically destroy ozone (e.g., H₂O, N₂O, and CH₄). For example, under some possible scenarios, future increases in N₂O may lead to enhanced loss due to enhanced NO_y chemistry. However, it seems that the radiative cooling of future increased GHGs, which will lead to increased US ozone, may dominate. In the future low-halogen atmosphere, the cooling of the stratosphere will also have less leverage to destroy ozone through polar processing. Combined with the fact that model studies predict an increase in tropospheric ozone by 2100, it seems likely that by the end of this century the atmosphere may contain more ozone than in the recent past.

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Appendix 4A

DESCRIPTION OF OZONE DATASETS

A brief description of the various observational ozone datasets used in this Assessment is included here. More detailed discussions can be found in the *Report of the International Ozone Trends Panel: 1988* (WMO, 1990) and previous Assessments.

4A.1 Ground-Based Total Ozone Measurements

Three types of ground-based instruments are used for long-term monitoring of total ozone content. Their characteristics and performance have been discussed in numerous WMO Assessments (e.g., WMO, 1995, 1999), and therefore only a brief description is provided here. The longest records of continuous reliable measurements are available from stations equipped with Dobson spectrophotometers. The first regular Dobson measurements started in the 1920s, and a worldwide network of Dobson instruments was established in the 1950s and early 1960s. Recent intercomparisons show that at present Dobson instruments at main sites agree with the World Standard Dobson 83 within 0.5% (WMO, 1995, 1999).

The Brewer spectrophotometer, developed in the early 1980s, can measure total ozone with approximately the same uncertainty as the Dobson spectrophotometer. All Brewer instruments are calibrated against the traveling standard Brewer instrument, and the traveling standard is calibrated against the Brewer triad at Toronto (Kerr et al., 1997). The Dobson and Brewer calibrations are independent, and the fact that there is no systematic difference between the two types of instruments adds to confidence in the data quality.

Filter ozonometers are widely used in the former Soviet Union countries, and long-term reliable records are available from 1972. This instrument is less accurate than the Dobson and Brewer instruments, and the calibration is traceable to the Dobson reference. Filter ozonometer observations are important for estimations of long-term ozone variations over vast regions where no Dobson and Brewer data are available and where observations from several stations can be averaged to reduce the random errors (Bojkov et al., 1994).

Total ozone data available from the World Ozone and Ultraviolet Radiation Data Center (WOUDC) were used here, including stations with reliable data and without any major calibration problems in their records. Fioletov et al. (1999) presented a recent review of the ground-based network performance. Data are available from 45 stations with continuous records starting before 1983 (WMO, 1999), and a larger set (up to 109 stations) was used to estimate zonal and global ozone averages for the period 1979-2001, following the methodology described in Bojkov and Fioletov (1995).

4A.2 Satellite Total Ozone Measurements and Merged Datasets

TOTAL OZONE MAPPING SPECTROMETER (TOMS)

In a TOMS measurement, ozone is derived using the “backscattered albedo,” the ratio of the radiance backscattered from the Earth-atmosphere system to the extraterrestrial solar irradiance. The solar irradiance is measured using an onboard diffuser plate. Instrument change should cancel when using this ratio, except for change in the diffuser plate itself, something that proved to be a problem for Nimbus-7 (N7). This was solved by using a triple diffuser for the Meteor-3 (M3) and Earth Probe (EP) instruments. All the TOMS datasets used for this report have been processed using the version 7 (v7) algorithm. Each TOMS instrument has had unique hardware problems, but in-orbit calibration techniques have been used to maintain the relative calibration of each instrument to approximately 1%/decade accuracy. For long-term trend determination there is the additional uncertainty of the relative calibration of EP TOMS, M3 TOMS, and N7 TOMS.

GLOBAL OZONE

NIMBUS-7 TOMS: NOVEMBER 1978 TO APRIL 1993

The absolute accuracy of the Nimbus-7 (N7) TOMS instrument depends on the radiometric calibration that was performed pre-launch, using standard lamps and laboratory diffuser plates. The time-dependent (in-orbit) calibration is maintained by a technique in which the ratio of two long-wavelength channels (non-ozone sensitive) is stabilized. Although instrument changes in N7 TOMS were becoming significant by the end of its life, the calibration was maintained to within $\sim 1\%$ /decade. This is supported by a comparison with a network of 39 Dobson stations that have nearly complete coverage over the entire N7, M3, EP period (McPeters and Labow, 1996). This comparison showed that the drift of N7 TOMS relative to this Dobson network was less than 0.5% /decade, with an average offset of 0.83% .

It is strongly suspected that there is an error in the N7 TOMS data due to “togglings.” In approximately 1983, N7 TOMS began to exhibit small errors in the synchronization of the chopper wheel and the electronics. The instrument appeared to “toggle” between two possible states, and when the calibration was set, one of the two states had to be chosen as the “correct” state. It now appears that the incorrect choice was made, resulting in an error of somewhat less than 1% between 1982 and 1988. This error has little effect on the overall trends for this instrument, but because of the accident of its timing it is likely that it increases the apparent amplitude of any solar cycle term in a regression model. This error will be corrected when these data are reprocessed with a v8 algorithm.

METEOR-3 TOMS: AUGUST 1991 TO DECEMBER 1994

The absolute calibration of the Meteor-3 (M3) TOMS instrument was explicitly set to be the same as that of the N7 TOMS instrument. During the period of overlap when both instruments were operating (8/91-4/93) a normalization factor was derived for the M3 instrument based on a subset of the data for which strict match-up criteria in space and time were met. This makes the M3 dataset a consistent extension of the N7 dataset rather than a totally independent dataset.

The time dependence of M3 TOMS was independently maintained. This was the first instrument to have a triple diffuser assembly: a cover diffuser, a working diffuser that was used weekly, and a reference diffuser that was exposed only a few times a year. This approach was very successful; the well-protected reference diffuser showed no detectable signs of degradation after years of operation. (The same is true of the Earth Probe diffuser after more than 5 years in space.) Precession of the orbit of the Meteor-3 spacecraft led to periods of lower quality data when the orbit was near the terminator, but the effect of these missing data on long-term changes should be minimal since these periods are distributed evenly through the data record.

EARTH PROBE TOMS: JULY 1996 TO DECEMBER 2000

The pre-launch radiometric calibration procedure used for the Earth Probe (EP) TOMS instrument was described in detail by MCPeters et al. (1998). Comparison of EP TOMS ozone with that from the 39 Dobson stations through April 2000 shows an average difference of 1.5% . However, a wavelength calibration performed on the QuikTOMS instrument infers that there were small wavelength errors in the EP instrument, which will reduce the EP TOMS ozone values by about 0.5% when a planned reprocessing is done. This will bring the difference with the Dobson measurement down to about 1% , and make the EP data consistent with N7 to within about 0.2% , well within the expected calibration errors of the two instruments.

As with the M3 instrument, EP maintains its time-dependent calibration using a triple diffuser plate. The calibration appears to have been very stable through 1999, but in 2000 artifacts began to appear in the TOMS data related to the look angle. By the summer of 2000, ozone when measured to the left of the orbital track was on average 6 DU lower than when measured to the right of the orbital track. Analysis showed that this cross-track bias was caused by real changes in the optical properties of the scan mirror. The principle that instrument errors should cancel in the radiance-to-irradiance ratio works to some extent, but the angle of the scan mirror when it is viewing the diffuser plate is quite different from when it is looking at the Earth, leading to residual error. It is expected that this scan angle-dependent error will be corrected when the data are next reprocessed. The EP TOMS data should be fully usable for analysis of long-term change through the end of 1999, and an empirical scan bias correction has been derived that should make the EP data usable through the end of the year 2000. However, by 2001 the changes in the optical properties of the scan mirror have become so large that the EP data should not be used for trend determination at this time.

SOLAR BACKSCATTER ULTRAVIOLET (SBUV, SBUV/2)

The long-term collection of total ozone measurements from the Solar Backscatter Ultraviolet (SBUV) spectrometer began with its launch on the NASA Nimbus-7 (N7) spacecraft in 1978. With the demonstrated success of this instrument, the National Oceanic and Atmospheric Administration (NOAA) adopted it (with some modifications) for launch on the NOAA afternoon operational satellite series beginning in 1985, and designated it SBUV/2. Thus far, the NOAA series has included NOAA-9, -11 and -14; NOAA-16 was launched in late 2000. The SBUV retrieval algorithm provides both total ozone and the vertical distribution of ozone in ~5-km-thick layers, and the data here use the version 6 backscatter ultraviolet (BUV) retrieval discussed in Chapter 1 of the SPARC/IOC report (SPARC, 1998). The differences in total ozone between instruments are approximately 1 to 2%. The temporal overlap of instruments can be used to account for calibration biases between instruments, and Miller et al. (2002) have derived a continuous, intercalibrated dataset incorporating measurements from Nimbus-7 (11/78 to 2/85), NOAA-9 (3/85 to 12/88 and 1/94 to 12/95), NOAA-11 (1/89 to 12/93 and 7/98 to 12/00), and NOAA-14 (1/96 to 6/98). The separate time periods for NOAA-9 and -11 data result from the precession of the satellite orbits, and the corresponding loss of BUV measurements as the orbit drifts from local day to night.

There can be substantial biases in the SBUV/2 retrieved ozone for measurements made at very high solar zenith angle (SZA), and the gridded analyses used here only included data for SZA up to 80°. For the “normal” afternoon orbit of SBUV/2, this results in a loss of data at high southern latitudes during local winter (data are unavailable poleward of ~55°S). However, the combination of this SZA cutoff and the orbital drifts of NOAA-9 and -11 results in increased data loss at high southern latitudes for some years, namely, 1988, 1992, 1993, and 1998, when winter data are unavailable poleward of ~45°S. This undersampling by the SBUV+SBUV/2 data is one potential source of difference with the other datasets over SH midlatitudes.

MERGED TOMS+SBUV/2

The Goddard merged ozone dataset was derived using measurements from six satellite instruments: the Nimbus-7 TOMS and SBUV; the NOAA-9, -11, -14, and -16 SBUV/2; and the Earth Probe TOMS. The D-pair (306 nm–311 nm) measurements from SBUV and SBUV/2 instruments were used to stabilize their calibrations as a function of time. The overlaps of these instruments with N7 and EP TOMS were used to establish the relative calibration of each instrument. These were then all adjusted to the first 2 years of EP TOMS as a reference. During this process it was discovered that the N7 TOMS exhibited time-dependent calibration shifts, in part due to a 1.5-DU error in 1984 when the instrument went into the “toggling” mode. The N7 TOMS calibration has been adjusted for these calibration shifts, leading to a deduced trend over its lifetime that is smaller than that shown in previous studies. The data, and information about how they were constructed, can be found at http://code916.gsfc.nasa.gov/Data_services/merged.

NIWA ASSIMILATED DATASET

The National Institute of Water and Atmospheric Research (NIWA) assimilated total ozone dataset is derived from combining measurements obtained by TOMS instruments flown on the Nimbus-7, Meteor-3, Earth Probe, and ADEOS (Advanced Earth Observing Satellite) satellites, together with the Global Ozone Monitoring Experiment (GOME) instrument flown on the European Remote Sensing (ERS)-2 satellite (Burrows et al., 1999). A description of these datasets and their homogenization is provided in Bodeker et al. (2001). Briefly, comparisons between TOMS data and measurements from the ground-based Dobson spectrophotometer network were used to remove offsets and drifts in the Nimbus-7 and Earth Probe satellite data. Statistical model fits to the Nimbus-7 and Meteor-3 differences were used to adjust the Meteor-3 TOMS data. Adjusted Earth Probe TOMS data were similarly used to correct ADEOS TOMS data and GOME data.

COMPARISON OF COLUMN OZONE DATASETS

Some systematic differences between the separate total ozone datasets described above were found. Figure 4A-1 shows the 1979–1987 annual mean percentage differences between the zonal averages estimated from four satellite datasets and the ground-based data as a function of latitude. All datasets agree to within 1% of the ground-based data at 40°–50°N. However, larger differences of 2–4% are seen in the tropics and the Southern Hemisphere for the TOMS, SBUV-SBUV/2, and merged satellite datasets (the NIWA dataset uses adjustments to fit the ground-based data, and hence

GLOBAL OZONE

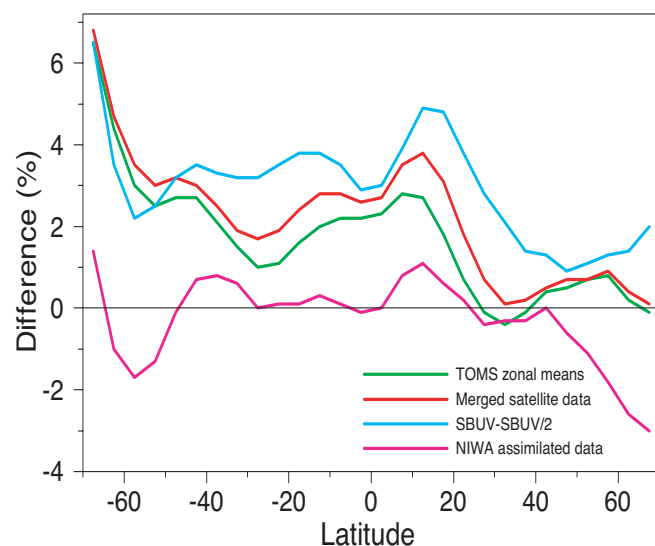


Figure 4A-1. The difference between total ozone zonal means estimated from four datasets and ground-based data, as a function of latitude for the period 1979-1987. Monthly means calculated from the ground-based data have been subtracted from the monthly means of each of the other four datasets, and annual averages calculated; results expressed in percent of the ground-based means. From Fioletov et al. (2002).

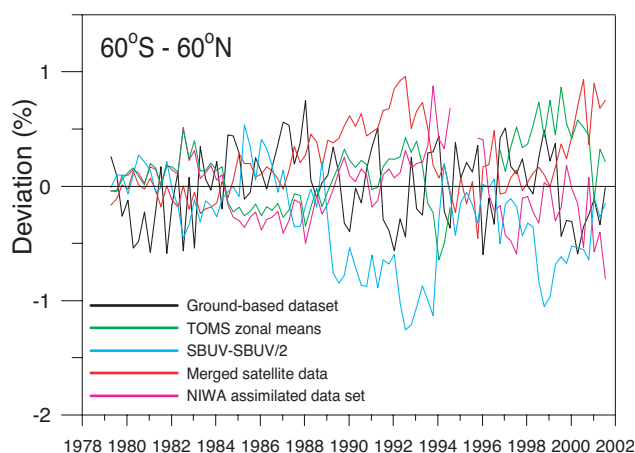


Figure 4A-2. Differences between the five estimates of deseasonalized ozone anomalies over 60°N-60°S (shown in Figure 4-2) and their average. The average of all five estimates was calculated for each season, and then subtracted from all five datasets. Updated from Fioletov et al. (2002).

the mean differences are small). Satellite data are 5-6% higher than ground-based measurements over the Antarctic. For the entire 60°S-60°N zone the area-weighted differences between the other datasets and ground-based zonal averages are the following: 1.5% higher for the TOMS, 2.1% higher for the merged satellite dataset, 0% for the NIWA assimilated dataset, and 3% higher for the SBUV-SBUV/2 dataset.

Deseasonalization removes systematic differences between the datasets, and the deseasonalized total ozone deviations agree to within a root mean square (rms) difference of 0.6-0.8 % (depending on the dataset) over the 1979-2001 period. However, the differences vary in time, as shown in Figure 4A-2, where the individual data records are compared with the average of all five datasets. The range of differences is typically ~1%, but can be as high as 2% at certain times (notably 1991-1993). The SBUV-SBUV/2 dataset is on the low end of the ensemble for much of the period after 1989.

4A.3 Ozone Profile Measurements

Long-term ozone profile datasets include satellite, ground-based Umkehr, and ozonesonde (balloon) measurements. The satellite data are near-global, whereas the Umkehr and ozonesonde measurements are taken at only a few stations, mostly located in northern midlatitudes. The primary satellite data source is derived from the Stratospheric Aerosol and Gas Experiment (SAGE I and SAGE II) measurements, which cover the altitude region ~15-50 km. Although ozone profile information is also available from SBUV-SBUV/2 satellite measurements, there are important uncertainties in the long-term calibration and changes associated with orbital precession of the NOAA-9 and -11 spacecraft, and therefore a homogeneous long-term profile dataset useful for trend analyses is not available at present. Detailed descriptions and intercomparisons of the SAGE, Umkehr, and ozonesonde measurement techniques and instruments can be found in SPARC (1998), and only brief summaries are provided here.

SAGE I

The SAGE measurement technique (McCormick et al., 1989) is based on solar occultation, with ozone profile measurements obtained at sunrise and sunset on each of 14 orbits per day. This technique provides high vertical resolution (~ 1 km) and very small long-term drifts resulting from instrument calibration. However, spatial sampling is limited, and it takes approximately one month to sample the latitude range 60°N to 60°S . SAGE I ozone profile data cover the time period February 1979 to November 1981. A difficulty in combining the SAGE I and SAGE II data for trend studies arises from an apparent error in the reference altitude for SAGE I. An empirical altitude correction has been applied to the SAGE I data in an attempt to remove this bias (H.J. Wang et al., 1996).

SAGE II

SAGE II ozone profile data commenced in November 1984 and continue to the present (December 2002). The analysis here used SAGE II version 6.1 (v6.1), which was released in March 2002. It includes a new algorithm for altitude registration, which results in a large reduction in the scatter in the transmission profile. There is evidence that the vertical resolution has been significantly improved over previous versions and is now approximately 0.75 km; v6.1 is placed on a 0.5-km altitude grid. The species separation and inversion in v6.1 is similar to that used in v5.96 (the basis for the SAGE II ozone data in WMO (1999), but v6.1 incorporates an aerosol model that improves the ozone retrievals in the presence of enhanced aerosol (H.J. Wang et al., 2002). The primary change to v6.1 was the method of estimating the species errors, which now include terms for the Rayleigh scattering and aerosol model uncertainties. In general, the ozone results are of good quality down to the tropopause. The data analyzed here exclude time periods of enhanced aerosol extinction following the eruption of Mt. Pinatubo in June 1991.

UMKEHR OZONE PROFILE MEASUREMENTS

Ground-based measurements use the Umkehr technique for measuring the profile of ozone concentration. It consists of observing a series of ultraviolet wavelengths of solar radiation, some of which are strongly absorbed by atmospheric ozone. A sequence of radiance measurements is made as the Sun rises or sets, and information about the ozone profile is obtained from an inversion algorithm applied to the measurements (e.g., Mateer and Deluisi, 1992). A new Umkehr retrieval algorithm (ALG-99) has been developed by Petropavlovskikh et al. (2001), with results discussed extensively in Bojkov et al. (2002). ALG-99 utilizes latitudinally and seasonally dependent first-guess ozone profiles. Unlike previous versions, the new first-guess profiles do not depend on total ozone, and therefore the influence of the total ozone trend on the retrieval has been largely reduced.

Relatively long records of Umkehr measurements (exceeding 15-20 years) are available from 13 stations. However, time series from many stations have significant discontinuities resulting from occasional changes in instrumentation. Careful analysis of the individual time series in addition to station histories suggests that the long-term data are of sufficient quality at only a relatively few stations. The results here are based on data from Arosa, Switzerland (47°N); Belsk, Poland (52°N); Boulder, Colorado, U.S. (40°N); and Haute-Provence, France (44°N).

OZONESONDES

A network of stations provides ozone profile information from balloonborne sondes, which measure ozone from the ground to about 30 km, with a vertical resolution of ~ 150 m. Details of ozonesonde measurements and data processing are discussed in SPARC (1998). One important detail is that each sonde profile is normalized to coincident total ozone measurements, and the amount of data available for trend analyses depends on the chosen limits of this normalization factor (SPARC, 1998; Logan et al., 1999). Data are available to the end of 2000 for all the stations used in the SPARC (1998) analysis, which include 14 locations spanning the latitude range 32°N - 75°N . The Uccle dataset has been reprocessed since the SPARC study. The ozonesondes at Uccle switched from Brewer Mast to electrochemical concentration cell (ECC) sondes in March 1997, with a transition period during which both sondes were used, to allow adjustment for any discontinuity in the dataset.

Appendix 4B

2-D MODEL SCENARIOS

Table 4B-1. Definition of the 2-D model scenarios. All model runs used the halocarbon scenario described in Table 4B-2 below. IPCC refers to IPCC (2001).

Scenario	Period	Motivation	CH ₄	N ₂ O	CO ₂	Aerosol
MC2	1979-2000	Best past trend	IPCC	IPCC	IPCC	D. Considine
MA2	2000-2050	Control A2	IPCC A2	IPCC A2	IPCC A2	Background
MB2	2000-2050	Control B2	IPCC B2	IPCC B2	IPCC B2	Background
MLCH4	2000-2050	Low CH ₄	0.8 × A2 increase post-2000	IPCC A2	IPCC A2	Background
MHCH4	2000-2050	High CH ₄	1.2 × A2	IPCC A2	IPCC A2	Background
MLN2O	2000-2050	Low N ₂ O	IPCC A2	0.8 × A2	IPCC A2	Background
MHN2O	2000-2050	High N ₂ O	IPCC B2	1.2 × A2	IPCC B2	Background
MLCO2	2000-2050	Low CO ₂	IPCC A2	IPCC A2	0.8 × A2	Background
MHCO2	2000-2050	High CO ₂	IPCC A2	IPCC A2	1.2 × A2	Background
MEPI	2000-2050	Episodic aerosol	IPCC A2	IPCC A2	IPCC A2	Episodic
MENH	2000-2050	Enhanced background aerosol	IPCC A2	IPCC A2	IPCC A2	Enhanced

Table 4B-2. Halocarbon scenario used in the 2-D model calculations. This scenario is essentially the same (except for a few small deviations) as the baseline scenario Ab described in Tables 1-13 and 1-16 of Chapter 1.

Time	CFC-11	CFC-12	CFC-113	CFC-114	CFC-115	CCl ₄	CH ₃ CCl ₃	HCFC-22	HCFC-141b	HCFC-142b	Halon-1211	Halon-1202	Halon-1301	Halon-2402	CH ₃ Br	CH ₃ Cl
1950	0.39	5.81	0.19	1.13	0.00	34.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.02	483.42
1955	2.96	14.59	0.53	2.39	0.00	41.16	0.05	0.25	0.00	0.00	0.00	0.00	0.00	0.00	7.09	492.78
1960	9.16	29.81	1.18	3.63	0.00	51.13	1.44	1.28	0.00	0.00	0.00	0.00	0.00	0.00	7.26	510.97
1965	23.26	59.14	2.44	4.90	0.00	63.63	4.59	3.82	0.00	0.10	0.00	0.00	0.00	0.00	7.44	528.77
1970	52.62	114.74	4.93	6.37	0.12	75.36	15.96	10.11	0.00	0.21	0.02	0.00	0.00	0.01	7.66	540.55
1975	105.99	203.64	9.84	8.14	0.50	85.04	39.20	21.17	0.00	0.30	0.12	0.00	0.04	0.04	7.93	546.48
1980	162.26	295.85	19.52	10.28	1.33	93.03	78.53	36.72	0.00	0.36	0.42	0.01	0.24	0.11	8.20	549.05
1985	205.27	382.18	36.72	12.64	2.91	99.62	105.68	56.32	0.00	0.51	1.04	0.02	0.74	0.20	8.55	550.10
1990	256.34	474.07	67.97	15.36	5.06	105.67	124.91	81.33	0.00	1.24	2.27	0.03	1.66	0.31	8.95	550.51
1995	270.62	524.80	83.23	16.18	7.49	103.66	108.63	111.78	2.09	5.27	3.25	0.04	2.33	0.42	9.40	550.68
2000	262.64	540.48	81.70	16.38	8.97	97.94	49.81	140.15	10.81	10.61	3.97	0.05	2.82	0.41	9.31	550.72
2005	250.66	541.09	78.01	16.41	9.15	92.25	21.85	172.56	23.71	18.91	4.14	0.02	3.17	0.37	8.81	550.72
2010	236.07	522.50	73.87	16.27	9.15	80.13	10.79	180.55	34.65	24.28	3.76	0.01	3.40	0.31	8.44	550.72
2015	218.15	497.02	69.68	16.07	9.13	66.11	5.67	168.54	39.14	26.12	3.19	0.00	3.52	0.26	8.44	550.72
2020	198.88	472.78	65.70	15.84	9.10	54.55	2.75	141.32	36.78	24.67	2.59	0.00	3.56	0.21	8.17	550.72
2025	179.90	449.72	61.95	15.59	9.07	45.01	1.22	110.25	30.68	21.49	2.05	0.00	3.52	0.17	8.17	550.72
2030	162.01	427.79	58.41	15.34	9.04	37.13	0.51	84.70	24.33	18.19	1.59	0.00	3.44	0.13	8.17	550.72
2035	145.52	406.92	55.07	15.09	9.01	30.64	0.21	65.05	18.85	15.20	1.22	0.00	3.33	0.10	8.17	550.72
2040	130.51	387.08	51.93	14.84	8.98	25.28	0.08	50.08	14.38	12.56	0.93	0.00	3.19	0.08	8.17	550.72
2045	116.94	368.20	48.96	14.60	8.95	20.85	0.03	38.03	10.80	10.26	0.70	0.00	3.04	0.06	8.17	550.72
2050	104.72	350.24	46.16	14.36	8.92	17.21	0.01	26.56	7.55	8.06	0.52	0.00	2.88	0.05	8.17	550.72

Table 4B-3. GHG scenarios (from IPCC, 2001). Scenarios A2 and B2 were used in the model runs. CO₂ is from the Integrated Science Assessment Model (ISAM) reference CO₂ scenario (p. 807 of IPCC, 2001).

Time	CH ₄ (ppbv)				N ₂ O (ppbv)				CO ₂ (ppmv)			
	IS92a	A2	B1	B2	IS92a	A2	B1	B2	IS92a	A2	B1	B2
1970	1420	1420	1420	1420	295	295	295	295	326	325	325	325
1980	1570	1570	1570	1570	301	301	301	301	338	337	337	337
1990	1700	1700	1700	1700	308	308	308	308	354	353	353	353
2000	1810	1760	1760	1760	319	316	316	316	372	369	369	369
2010	1964	1861	1827	1839	328	325	324	323	393	390	388	388
2020	2145	1997	1891	1936	339	335	333	328	418	417	412	408
2030	2343	2163	1927	2058	350	347	341	333	446	451	437	429
2040	2561	2357	1919	2201	361	360	349	338	476	490	463	453
2050	2793	2562	1881	2362	371	373	357	342	509	532	488	478

CHAPTER 5

Surface Ultraviolet Radiation: Past and Future

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CHAPTER 5

SURFACE ULTRAVIOLET RADIATION: PAST AND FUTURE

Contents

SCIENTIFIC SUMMARY	5.1
5.1 INTRODUCTION	5.5
5.2 CURRENT UNDERSTANDING OF FACTORS AFFECTING SURFACE UV RADIATION	5.5
5.2.1 Dependence of UV on Geophysical Variables	5.5
5.2.1.1 The Extraterrestrial Solar Spectrum	5.6
5.2.1.2 Dependence of UV on Ozone and Other Trace Gases	5.6
5.2.1.3 Dependence of UV on Clouds	5.6
5.2.1.4 Dependence of UV on Aerosol Scattering and Absorption	5.7
5.2.1.5 Dependence of UV on Surface Albedo	5.8
5.2.1.6 Dependence of UV on Altitude	5.8
5.2.1.7 Angular Dependence of UV	5.9
5.2.1.8 Dependence of UV Under Water	5.9
5.2.2 Daily Forecasting of Ozone and UV	5.10
5.2.3 Remaining Questions and Uncertainties	5.11
5.3 AVAILABLE RESOURCES FOR STUDYING SURFACE UV RADIATION	5.11
5.3.1 Ground-Based Measurements	5.11
5.3.1.1 Spectroradiometers	5.11
5.3.1.2 Broadband Filter Radiometers	5.12
5.3.1.3 Narrowband Multifilter Radiometers	5.13
5.3.1.4 Data Quality and Databases	5.13
5.3.1.5 Instrument Intercomparisons	5.14
5.3.2 Radiative Transfer Models and Model Validation	5.15
5.3.3 Satellite Estimates and Validation	5.16
5.3.4 Statistical Modeling	5.19
5.4 UV CLIMATOLOGY, TEMPORAL CHANGES, AND TRENDS	5.20
5.4.1 Ground-Based UV Measurements	5.20
5.4.2 Estimates from Satellite Data	5.22
5.4.3 Estimates from Radiative Transfer Models	5.23
5.4.4 Estimates from Ground-Based Ancillary Data	5.23
5.5 EXPECTATIONS OF UV IN THE FUTURE	5.25
5.5.1 Links with the Recovery of the Ozone Layer	5.25
5.5.2 Factors Related to Climate Change	5.28
REFERENCES	5.31
APPENDIX 5A: SPECTRAL DATA AVAILABLE FROM DATABASES	5.43
5A.1 World Ozone and Ultraviolet Radiation Data Centre (WOUDC)	5.43
5A.2 European Ultraviolet Database (EUUVDB)	5.44
APPENDIX 5B: INTERNET ADDRESSES FOR UV SITES	5.45
5B.1 General UV Information	5.45
5B.2 International UV Projects	5.45
5B.3 Radiative Transfer Codes	5.45

5B.4	Extraterrestrial Spectra	5.45
5B.5	General UV Index Information	5.46
5B.6	Internet Sites with UV Information by Country	5.46

SCIENTIFIC SUMMARY

Important Confirmations of Previous Results

- Additional measurements have confirmed that decreases in column ozone lead to increases in surface ultraviolet (UV) radiation. The relationship has been further documented from existing and new sites. Spectral data records from 65 stations are now available in international data centers. Episodes with elevated UV irradiance associated with low total ozone continue to occur.
- There is clear evidence that the long-term UV changes are not driven by ozone alone, but also by changes in cloudiness, aerosols, and surface albedo. The relative importance of these factors depends on local conditions.
- Enhanced values of UV radiation continue to be observed at high latitudes in the Southern Hemisphere under the Antarctic ozone hole. Highest biologically weighted UV doses under the ozone hole are typically not observed in October when maximum ozone depletion occurs, but in November and early December when solar elevations are higher and low ozone values still prevail. Changes in the duration and spatial extent of the Antarctic ozone hole are therefore more important for Antarctic UV levels than the annual ozone minimum.

New Findings

- Satellite estimates of surface UV radiation from the Total Ozone Mapping Spectrometer (TOMS) dataset have been compared with ground-based measurements at several more sites since the previous Assessment. In general the estimates capture short-term and long-term variability. However, the estimates are systematically higher than ground-based measurements at many sites. The differences in monthly average erythemal (“sunburning”) UV irradiance range from about 0% at some clean sites and up to 40% in the Northern Hemisphere. The fact that the agreement is better at the cleaner sites suggests that the differences are due to aerosols and/or pollutants near the ground.
- New algorithms have been developed that produce UV maps with improved spatial (down to 1 km) and/or temporal resolution (down to 30 minutes). These algorithms take into account the effects of clouds, surface albedo, topographical features, and aerosols by using information from other satellite and ground datasets, in addition to satellite column ozone data. The detailed maps have contributed to a better understanding of the geographical and temporal variability in surface UV radiation and have enabled specific UV impact studies. The achievable agreement between the results of such algorithms and ground-based measurements for monthly averages is within $\pm 5\%$.
- The length of ground-based spectral UV measurement has reached more than 10 years for some sites. It has been shown that a record of 10 years is still too short to derive statistically significant trends.
- UV increases associated with the ozone decline have been observed by spectral measurements at a number of sites located in Europe, North America, South America, Antarctica, and New Zealand.
- Calculations based on pyranometer (total irradiance), total ozone, and other meteorological measurements have been used to reconstruct surface UV irradiance at several mid- to high-latitude sites. Pyranometer and other meteorological data serve as proxies for parameters affecting UV other than ozone. The reconstructed datasets, which extend backward in time to as early as the 1960s at some sites, show long-term increases in erythemal irradiance of about 6-14% over the last 20 years. At some sites approximately half of the changes can be attributed to total ozone changes. It is believed that the increases of UV irradiance derived from the ground-based reconstructed data are clear indicators of the long-term changes that have occurred since the 1980s. However, these reconstructions contain several assumptions on the nature of radiative transfer, are not measurements of UV irradiance, and are not representative on a global scale.
- The reconstructed datasets show that the number of hours of UV levels above certain threshold values has increased at some northern midlatitude sites since the 1970s. For example, in Toronto the number of hours per year with the UV Index above 7 has doubled.

SURFACE ULTRAVIOLET RADIATION

- Snow cover can increase surface UV irradiance by more than 50%. The presence of snow several kilometers away from the observing site may still lead to significant enhancement. Three-dimensional radiative transfer models have shown that the region of significance (defined by increases of UV irradiance by more than 5%) can extend beyond a radius of 40 km.
- In the Antarctic, ozone depletion has been the dominant factor for increases in UV irradiance. The future evolution of UV radiation is therefore expected to follow the ozone recovery. However, because of changes in other influencing factors, such as changes in cloud cover, aerosols, or snow/ice cover, UV radiation may not return exactly to pre-ozone-hole values.
- Elsewhere, including the Arctic, the impact of other influencing factors can be comparable to the impact of ozone depletion. The large uncertainties in future changes of these prevent reliable predictions on the future evolution of UV irradiance. Furthermore, climate-change-induced trends in cloudiness, aerosols, and snow/ice cover are expected to be seasonally and geographically dependent, leading to differences in future UV irradiance in different parts of the world.
- The 2001 Intergovernmental Panel on Climate Change report (IPCC, 2001) states that decreases in sea ice cover over the Northern Hemisphere have occurred and are likely to continue. Furthermore, increases in global cloud cover are likely. Such changes lead to decreases in UV irradiance over large areas of the globe. Quantitative estimations of these effects and their regional dependence cannot yet be made. Although UV irradiance above the surface is enhanced by snow-covered areas, a decrease in sea ice and snow cover will result in an increase of UV dose for organisms living under water and on land areas previously covered by snow.

Advances in Our Understanding

- The effects of climate change on surface UV irradiance are twofold. The first effect is indirect and results from climate changes that influence total ozone. The second effect is direct and results from changes in other climatic variables such as clouds, aerosols, and snow cover.
- Spectral irradiance and actinic flux calculated by several radiative transfer models agree to within 2% when input assumptions are properly chosen. For cases when the Sun is close to the horizon and for shorter wavelengths, the relative standard deviations are somewhat higher (5%), but then irradiance is very small.
- The influence of tropospheric aerosols on UV irradiance may be larger than previously thought, and may affect large areas of the globe. This result is based on studies on the reduction of UV irradiance by aerosols using ground-based instruments and aircraft missions.
- Three-dimensional radiative transfer models have improved the understanding of atmospheric scattering and absorption processes. These models are used to study the effects of inhomogeneous features such as broken and scattered clouds, and nonuniform surface albedo.
- Advances have been made in the understanding of the penetration of UV radiation under water that have allowed the estimation of the underwater UV environment on a global scale using combined satellite datasets.
- A reanalysis of TOMS satellite data with respect to the influence of changes in cloudiness over Europe has confirmed the result found previously by ground-based measurements showing that pyranometric irradiance at the ground has decreased in recent decades. Thus it can be concluded that UV increases due to ozone are partly masked by the increased cloudiness in some regions.
- Uncertainties of ground-based UV measurements are now found to be greater than those estimated in the previous Assessment. A rigorous uncertainty analysis for spectroradiometric solar UV measurements has been performed. For a typical well-maintained instrument it has been shown that uncertainties are as high as $\pm 12.7\%$ at 300 nm and

SURFACE ULTRAVIOLET RADIATION

$\pm 6.3\%$ for erythemally weighted irradiance. Major reasons are uncertainties related to calibration standards and wavelength uncertainties. Deviations of about 5-10% between well-maintained instruments and between measurements and models have been seen at recent intercomparisons. In general, broadband instruments have even higher uncertainties than spectroradiometers.

- Better calibration methods have been developed that result in smaller deviations among spectroradiometers. New instruments have been developed and existing instruments have improved with regard to stability, wavelength alignment, and angular response.
- The extraterrestrial solar UV spectrum can be retrieved by Langley plot analysis of ground-based measurements at very clean sites. New studies have shown that these retrievals agree with space-based measurements to within 3%.

5.1 INTRODUCTION

A major concern regarding a decrease in stratospheric ozone is the consequential increase of solar ultraviolet (UV) radiation passing through the atmosphere and reaching the Earth's surface. Ozone absorbs radiation strongly in the UV, and the presence of ozone and oxygen in the stratosphere results in the absorption of nearly all solar radiation below 290 nm. Thus virtually all UV-C radiation (200-280 nm) does not reach the troposphere or the Earth's surface. Solar UV-B radiation (280-315 nm) is significantly absorbed by atmospheric ozone, whereas only a small fraction (less than 3%) of UV-A radiation (315-400 nm) is absorbed by ozone. Accurate measurement of spectral UV has historically been a difficult task. The fact that irradiance varies by many orders of magnitude over a relatively short wavelength range (290-320 nm) requires that useful instruments have a wide dynamic range and a high degree of spectral purity and accuracy. Also the long-term stability of UV instruments and their absolute calibration standard are still difficult to maintain. Consequently, good quality routine spectral measurements did not start until the late 1980s, and these longer records are few in number.

Solar UV radiation that reaches the ground is influenced by many complicated scattering and absorption processes in the atmosphere and at the Earth's surface. These processes must be understood in order to describe fully the characteristics of the current climatology of surface UV radiation on a global scale and to project it to the past and future. Section 5.2 presents findings since the previous Assessment (WMO, 1999) that have improved the understanding of radiative transfer (RT) processes defining the magnitude, wavelength dependence, and angular distribution of UV radiation at and above the Earth's surface and under water or ice. Section 5.2 also discusses the UV Index, a direct application of our understanding of the processes defining surface UV. Section 5.3 discusses resources that are applied to understand and quantify RT processes. These resources include ground-based measurements of surface UV radiation and other pertinent variables; satellite-based measurements of extra-terrestrial solar flux, ozone, cloud cover, and reflectivity; RT computer models; and statistical models that quantify dependencies of UV radiation on scattering and absorption. Assessment of the effectiveness and accuracy of these resources (also Section 5.3) includes intercomparisons of different ground-based instruments, intercomparison of RT models, and comparisons of the surface measurements with satellite estimates and RT model results.

In addition to an assessment of recent findings described in the scientific literature, this chapter provides the link between ozone depletion as assessed in earlier

chapters of this report and the impacts of increases of surface UV radiation that are assessed in the most recent United Nations Environment Programme (UNEP) "Effects Panel" report (UNEP, 2002). In general, aquatic and terrestrial biological systems (including human beings), material degradation, and pollution photochemistry are sensitive to UV radiation, and in most of the cases the sensitivity increases with decreasing wavelength. The wavelength dependence of the sensitivity of a particular biological system to UV radiation is defined by an action spectrum, and the erythema (sunburning) action spectrum as standardized by the Commission Internationale de l'Éclairage (CIE; McKinlay and Diffey, 1987) is often used. Studies on impacts of UV radiation require knowledge of the present UV climatology (including average and extreme values) and any changes that have occurred in the past. Results of studies showing that there have been past changes in UV (caused by changes in ozone as well as changes in other variables such as clouds, aerosols, and snow cover) are given in Section 5.4. Section 5.5 presents estimates of future surface UV radiation determined from predictions of ozone changes given in earlier chapters. Effects of other climatological changes, as determined and discussed in the recent Intergovernmental Panel on Climate Change (IPCC) report (IPCC, 2001), that may directly influence surface UV radiation in the future are also discussed in Section 5.5.

5.2 CURRENT UNDERSTANDING OF FACTORS AFFECTING SURFACE UV RADIATION

Since the previous Assessment (WMO, 1999), available resources have been applied to advance our understanding of processes that affect surface UV radiation and have recently been reviewed (e.g., Taalas et al., 2000a; Blumthaler and Taalas, 2001). New research results regarding the dependencies of UV on geophysical variables are presented in Section 5.2.1. Following that is a discussion on the UV Index forecast (Section 5.2.2), which is a direct application of our knowledge and resources. Validation of these daily forecasts allows an ongoing opportunity to assess the accuracy of our resources. Finally, Section 5.2.3 briefly summarizes aspects regarding surface UV radiation that we do not fully understand.

5.2.1 Dependence of UV on Geophysical Variables

One of the main objectives for making good quality measurements of surface UV radiation is to understand the dependencies of UV on absorption and scattering processes that occur in the atmosphere and at the Earth's

SURFACE ULTRAVIOLET RADIATION

surface. In principle, if the spatial distribution of all absorbers and scatterers within the atmosphere and at the Earth's surface were fully known, it would be possible to determine the wavelength dependence and angular distribution of surface UV radiation by model calculations. In practice, the complicated distribution of the predominant variables (clouds, ozone, aerosols, and surface albedo) and their interactive impact on UV irradiance makes detailed calculations on a global scale an extremely difficult task.

5.2.1.1 THE EXTRATERRESTRIAL SOLAR SPECTRUM

Accurate knowledge of the solar spectrum is important for studying surface UV, since it is used in RT models that are ultimately compared with measurements. At the time of the previous Assessment (WMO, 1999) several satellite measurements were available showing agreement to within $\pm 3\%$ (Cebula et al., 1996). Appendix 5B (Section 5B.4) lists Internet sites that provide information on measured extraterrestrial spectra.

Knowledge of the stability of solar irradiance at UV wavelengths is important because it drives many geophysical processes, including the formation of stratospheric ozone. It could also be used as a reference standard for UV measurements. Changes in solar irradiance from 1700 to present were determined by Fligge and Solanki (2000). Their model assumes that solar irradiance variations on time scales from days to centuries are due only to the changing distribution of solar surface magnetic features. The study determined an increase of solar spectral irradiance at solar activity cycle minimum since the Maunder minimum (year 1700) of 3.0% for wavelengths less than 300 nm and 1.3% for the band 300-400 nm. The total (all wavelengths) and the visible irradiance showed an increase of about 0.3%. Rozema et al. (2002) note that a past long-term increase in solar UV-C radiation would lead to an increase in the production of stratospheric ozone that would reduce surface UV-B irradiance.

5.2.1.2 DEPENDENCE OF UV ON OZONE AND OTHER TRACE GASES

The effects of the absorption of atmospheric ozone on surface UV radiation were well understood at the time of the previous Assessment (WMO, 1999), and there has been no major change in our knowledge since then. The wavelength dependence of the sensitivity in UV irradiance to ozone had been fairly well established both by observations and comparison of observations with RT models (e.g., Fioletov et al., 1997; Bodhaine et al., 1998), and these relationships continue to be confirmed (e.g., Bartlett and Webb, 2000; Casale et al., 2000; Cho et al.,

2000; Miyauchi et al., 2000). Further work has been done regarding the effects of variations of the vertical distribution and the temperature of ozone (Sabziparvar et al., 1998; Krzyścin, 2000; Lapeta et al., 2000). These effects could influence surface UV should there be a long-term change in the vertical profile or effective column temperature of ozone; however, the effects are relatively small compared to past or expected future long-term changes in total ozone.

The effects of sulfur dioxide on surface UV were shown to be negligible on a global scale but could be significant at sites near local pollution sources or continuous volcanic activity (Fioletov et al., 1998), or over wider areas in the aftermath of major volcanic eruptions. Other gases that absorb in the UV (e.g., nitrogen dioxide, nitric acid, and formaldehyde) are not significant under natural conditions, but could be significant under heavy pollution situations.

5.2.1.3 DEPENDENCE OF UV ON CLOUDS

Clouds have more influence on surface UV irradiance than any other atmospheric variable. Although important, cloud effects on UV irradiance are difficult to quantify. The effect of clouds on UV is understood in principle. However, in practice the necessary parameters used to calculate local cloud effects are rarely available, and if they were, the complexities of cloud geometry need to be specified in sufficient detail and require the use of three-dimensional (3-D) model calculations.

Under overcast conditions, clouds decrease the irradiance measured at the surface (Josefsson and Landelius, 2000; Renaud et al., 2000). However, enhancements of up to 25% can occur under broken cloud conditions (Estupiñán et al., 1996; Sabburg and Wong, 2000; Weihs et al., 2000), or if there are reflections from cloud decks below high-altitude observation sites such as Mauna Loa Observatory (McKenzie et al., 2001b). Even for large cloud fractions, the reduction in irradiance can be small if the clouds do not obscure the direct beam. Thus, one of the most important parameters is whether or not the Sun is obscured (Grant and Heisler, 2000; Schwander et al., 2002). For individual sites, this poses difficulties for satellite products. When a histogram of cloud transmission is plotted as a function of cloud amount, a bimodal distribution typically results (e.g., Seckmeyer et al., 1997; McKenzie et al., 1998b; McKenzie et al., 2001b), with a lower peak resulting from conditions when cloud obscures the Sun, and a higher peak corresponding to conditions where clouds do not block the Sun. Since the Sun can be unobscured even for large cloud fractions, or obscured even for small cloud fractions, the quantification of cloud

effects can become problematic (e.g., Udelhofen et al., 1999; Matthijsen et al., 2000). There are also complications when the scattering of radiation by clouds enhances effects such as absorption by ozone (e.g., Fioletov et al., 1997, 2002) or scattering by aerosols (e.g., Erlick et al., 1998; Mayer et al., 1998b) within the cloud.

The presence of scattered or broken clouds poses difficulties for comparisons between ground-based measurements and satellite estimates of surface UV irradiance. In this situation direct solar radiation is either obscured or not obscured by a cloud at the ground-based measurement site, whereas the satellite measures an average cloud amount over its footprint.

Ground-based measurements of cloud cover are now available at several sites using automated all-sky imagery (Sabburg and Wong, 2000). Although in some cases high thin clouds may not be distinguishable in all-sky images, these continuous records of the spatial distribution of clouds used in parallel with UV irradiance measurements offer the potential to understand and quantify cloud effects more accurately.

5.2.1.4 DEPENDENCE OF UV ON AEROSOL SCATTERING AND ABSORPTION

Aerosols are highly variable over space and time. They attenuate UV flux through the atmosphere to an extent that is mostly described by the aerosol optical depth (AOD) and the average column value of the single scattering albedo (ω_0), which is the ratio of scattering to extinction (where extinction = scattering + absorption). The wavelength dependence of the AOD is generally assumed to be proportional to $\lambda^{-\alpha}$, where λ is wavelength, and α is the Angstrom coefficient. Measurements of AOD at visible and UV-A wavelengths using sunphotometry are routinely carried out (e.g., Schmid et al., 1997, 1999). Currently the worldwide Aerosol Robotics Network (Holben et al., 1998) is the best source of information on aerosol particle size, optical depth, and single scattering albedo. Significant progress has been made recently in the measurement and quantification of the effects of aerosols at UV-B wavelengths.

One of the objectives of the Photochemical Activity and Solar Ultraviolet Radiation (PAUR) campaign held in Greece during June 1996 and the PAUR II campaign in Greece and Italy during May-June 1999 was to study the optical properties of aerosols. The AOD in the UV was shown to be approximately inversely proportion to wavelength (i.e., $\alpha = 1.0 \pm 0.5$), and values of ω_0 between 0.84 and 0.98 were determined by comparing model results with the measurements (Marenco et al., 1997; Kazantzidis et al., 2000; Kylling et al., 1998). A variety of atmos-

pheric gaseous and particulate concentrations were measured with radiative and optical characteristics of the atmosphere during the PAUR II campaign (Zerefos et al., 2002). Kouvarakis et al. (2002) found that the AOD and single scattering albedo correlated well with surface measurements of ammonium sulfate, indicating the key role that this gas plays in radiative forcing in the area. Variations of calcium originating from the Sahara also correlated well with AOD measurements. The campaigns also studied how changes in stratospheric ozone might influence tropospheric photochemistry through changes in the UV environment (Jonson et al., 2000; Zerefos et al., 2001; Balis et al., 2002; Hofzumahaus et al., 2002; Zanis et al., 2002). These impacts are discussed in the Effects Panel report (UNEP, 2002).

Wenny et al. (2001) studied the variations in AOD at 317, 325, 332, and 368 nm from July through December 1999 using a multifilter radiometer near Asheville, North Carolina, and found the mean optical depth was 0.33 at 368 nm and increased to 0.40 at 317 nm, indicating a value of about 1 for α . The study used an RT model to investigate the reduction in erythral UV irradiance relative to a baseline case with AOD = 0.2 and $\omega_0 = 1.0$. When the AOD was increased to 1.3, maximum reduction in UV was 44% for $\omega_0 = 0.75$, 29% for $\omega_0 = 0.90$, and only 18% for $\omega_0 = 1.0$. Vermeulen et al. (2000) have developed a method for retrieving the scattering and microphysical properties of atmospheric aerosols (including ω_0) from measurements of solar transmission, aureole, and angular distribution of the scattered and polarized sky light in the solar principal plane.

It has been shown by ground-based measurements that large reductions of UV-B occur under absorbing aerosols such as smoke from biomass burning (e.g., Ilyas et al., 2001; Kirchhoff et al., 2001), forest fires (e.g., McArthur et al., 1999), or desert dust (di Sarra et al., 2002a). Recent work suggests that anthropogenic aerosols that absorb in the UV region may play a more important role in attenuating UV irradiances than has been assumed previously (Jacobson, 2001).

Comparisons between satellite-derived UV and ground-based spectral measurements have revealed inconsistencies in satellite-derived UV that are probably related to the inability of the satellite sensors to correct for boundary layer extinctions. Ground-based estimates of regional UV irradiances suffer from a similar inability to correct for horizontal inhomogeneities in boundary layer extinction as well as inhomogeneities in the troposphere and stratosphere. Only at the cleaner sites is there good agreement within the experimental errors. At continental sites in the Northern Hemisphere, the satellite-derived UV

SURFACE ULTRAVIOLET RADIATION

estimations are too large (McKenzie et al., 2001a; Fioletov et al., 2002).

Gröbner et al. (2001) made a comparison of AODs determined by seven Brewer spectrophotometers and a Li-Cor spectrophotometer at Huelva, Spain, between 1 and 10 September 1999. For all instruments, measurements of AOD at 306, 310, 313.5, 316.7, and 320 nm agreed to within ± 0.03 over a range of AOD between 0.2 and 0.6 at 306 nm. These results suggest that the existing Brewer network can be used to determine UV AODs, an important consideration for extending the coverage of ground-based measurements for studying scattering/absorption processes and long-term trends. Routine measurements of AOD in the UV using Brewer instruments have been reported (e.g., Meleti and Cappellani, 2000; Kerr, 2002).

5.2.1.5 DEPENDENCE OF UV ON SURFACE ALBEDO

The presence of snow cover surrounding an observing site increases UV irradiances (McKenzie et al., 1998a; Minschwaner, 1999; Herman and McKenzie et al., 1999; Krotkov et al., 2001; Chubarova et al., 2002; Fioletov et al., 2002), even when the snow is several kilometers away (Degünther et al., 1998; Degünther and Meerkötter, 2000b; Weihs et al., 2001). Recently developed RT models have shown that certain snow distributions can cause significant (defined as being $>5\%$) increases of surface UV irradiance even if the snow is farther than 40 km from a site (Degünther et al., 1998; Ricchiazzi and Gautier, 1998; Smolskaia et al., 1999; Lenoble, 2000; Mayer and Degünther, 2000). Models have also been used to study the complicated interactions between snow enhancements combined with atmospheric scattering and absorbing processes (Aoki et al., 1999; Renaud et al., 2000; Krotkov et al., 2001).

Snow enhancements between 8% and 39% for surface UV at 324 nm were reported in the previous Assessment (Herman and McKenzie et al., 1999). Increases are greater at Arctic sites surrounded by uniform snow cover and less at urban sites or sites near open water (Fioletov et al., 2002). Site-specific enhancements are attributable to increases in the “regional” albedo, which represents a spatial average around the site. The regional albedo may be determined from the snow enhancement values (Schwander et al., 1999; Krotkov et al., 2001; Chubarova et al., 2002) and is a function of the age and depth of snow as well as the terrain and other features around the site. Measurements of UV irradiance (320–325 nm) made at Syowa, Antarctica (Aoki et al., 2000), were compared with those made at four Japanese sites (Sapporo, Tsukuba, Kagoshima, and Naha) for the

same values of total ozone and solar zenith angle (SZA). Values at Syowa were observed to be about 60% higher than the upper limit of values seen over Japan (Takao et al., 1999), making the albedo enhancement an important consideration when combined with low total ozone values seen under the Antarctic ozone hole.

Information regarding the average albedo in the satellite field of view is important for space-based estimates of surface UV (Krotkov et al., 2001). When snow depth information is used as input to estimate regional albedo, better agreement between ground-based measurements and satellite estimates is achieved, particularly under cloudy conditions (Arola et al., 2002; Krotkov et al., 2002). However, day-to-day knowledge of regional albedo on a global scale remains a challenge.

Combining measurements with RT model results can be used to derive estimates for unknown input parameters by statistical fitting procedures. When aerosol optical depth is relatively low (and thus the effect of inaccurately known optical characteristics of aerosols is small), regional albedo of partly snow-covered terrain can be derived (Schwander et al., 1999; Gröbner et al., 2000; Weihs et al., 2001). Values of regional surface albedo in the range of 0.3 to 0.9 were determined, depending on local conditions of topography and snow coverage.

5.2.1.6 DEPENDENCE OF UV ON ALTITUDE

Since the previous Assessment (WMO, 1999), the dependence of UV irradiance on altitude has been further quantified. In practice the altitude dependence of UV irradiance is itself dependent on differences in surface albedo, boundary layer extinctions by aerosols, and tropospheric ozone concentrations. Therefore the dependence is not represented by a single value (Seckmeyer et al., 1997). Even when these effects are ignored, it has been found that at higher altitude the dependence of UV irradiance on SZA and wavelength changes. In general, for erythemally weighted UV, irradiances in clean conditions increase between 5 and 10% per kilometer (McKenzie et al., 2001b; Zaratti et al., 2002; Schmucki and Philipona, 2002), with the greatest increase occurring at SZA ~ 60 – 70° . To model the dependence correctly at Mauna Loa Observatory, it was necessary to consider the effects of sky irradiance scattered from below the observatory (McKenzie et al., 2001b). In mountainous regions the vertical gradient in some instances can be larger (up to 50% per kilometer) because of local effects such as increasing albedo with altitude and high concentrations of ozone or aerosols in the lower troposphere (Seckmeyer et al., 1997). Larger altitude gradients in the free tropo-

sphere have also been measured from aircraft under polluted situations over Greece (Varotsos et al., 2001).

5.2.1.7 ANGULAR DEPENDENCE OF UV

Ground-based measurements of UV irradiance are generally made with a horizontal diffuse surface that would ideally follow a response proportional to the cosine of the angle from normal (vertical) incidence. In many cases the collection efficiency of the diffuser falls below the cosine function for large SZA, and calculations are made to adjust (usually increase) the measured irradiance (Bais et al., 1998a; Chubarova and Nezval, 2000; Fioletov et al., 2002). The adjustments depend on the angular distribution of incident radiation and are complex functions of SZA, wavelength, total ozone, ozone distribution, aerosol, and cloud amounts. The relationships of measured to adjusted values are corrected by use of RT models.

For many biological and photochemical processes, actinic fluxes rather than cosine-weighted irradiances are more appropriate. However, such measurements have not been generally available until quite recently (Hofzumahaus et al., 1999, 2002; Shetter and Müller, 1999). Recent progress has been made in converting irradiances to actinic fluxes, offering the prospect of deriving historical changes of actinic flux from the extensive existing database of irradiance measurements (Kazadzis et al., 2000; McKenzie et al., 2002; Webb et al., 2002). It was found that the most important parameters defining the relation between actinic flux density and global UV irradiance are the ratio of direct to global irradiance, whether or not the Sun is obscured, and the description of the angular distribution of the diffuse radiation. Under clear skies, retrieved spectral actinic flux densities agree with model calculations to within $\pm 5\%$ for a variety of aerosol conditions. The assumption of an isotropic distribution of the diffuse radiation can lead to a wavelength-dependent overestimation of actinic flux densities from 10 to 15%, depending on SZA, especially in atmospheres with high aerosol content (Kazadzis et al., 2000).

A campaign to measure spectral global UV irradiance and actinic flux at the ground, supported by ancillary measurements used to characterize the atmosphere, was carried out in August 2000 at Nea Michaniona, in northern Greece (Webb et al., 2002). It was established that the ratio of actinic fluxes (F) to horizontal irradiance (E) is between 1.4 and 2.6 for UV wavelengths. This ratio is a function of wavelength, SZA, and the optical properties of the atmosphere. Both the wavelength and SZA dependency of the ratio decrease when the scattering in the atmosphere increases and the direct beam proportion of global irradiance decreases, as expected.

5.2.1.8 DEPENDENCE OF UV UNDER WATER

The underwater UV environment is an important consideration for studies of the sensitivities of aquatic (both freshwater and saltwater) species to UV radiation (de Mora et al., 2000). These effects are discussed extensively in the UNEP Effects Panel report (UNEP, 2002). There have been recent spectral measurements of UV under fresh water (e.g., Sommaruga and Psenner, 1997; Laurion et al., 1997; Bukaveckas and Robbins-Forbes, 2000; Markager and Vincent, 2000) and salt water (e.g., Booth and Morrow, 1997; Kuhn et al., 1999). Measurements of UV penetration into seawater using a biochemical deoxyribonucleic acid (DNA) dosimeter combined with a spectroradiometer have been reported (Boelen et al., 1999). In general, these measurements show that there is wavelength-dependent absorption by water in the UV that increases with decreasing wavelength. The underwater absorption has strong dependence on the abundance of dissolved organic matter that has wide temporal and spatial variability. A sensitivity study conducted by RT modeling has shown that the main parameters controlling levels of the most harmful UV-B radiation underwater for clear-sky conditions are the SZA, seawater bio-optical properties, and total ozone amount (Vasilkov and Krotkov, 1997). Attenuation of UV-B irradiance and DNA dose rate with water depth is primarily controlled by the total seawater absorption coefficient and its spectral dependence.

Estimates of UV radiation penetration into the ocean waters are now available on a global scale by combining Total Ozone Mapping Spectrometer (TOMS) satellite estimates of UV irradiance at the ocean surface with the SeaWiFS (Sea-viewing Wide Field-of-view Sensor) satellite ocean-color data and using a model to define seawater optical UV properties (Vasilkov et al., 2001). Weekly maps of underwater UV irradiance and DNA-weighted exposure are calculated using monthly-mean SeaWiFS chlorophyll and diffuse attenuation coefficient products, daily SeaWiFS cloud fraction data, and daily maps of TOMS-derived surface UV irradiance. The final products include global maps of weekly-average UV-B irradiance and DNA-weighted daily exposures at depths of 3 m and 10 m, and depths where the UV-B irradiance and DNA-weighted dose rate at local noon are equal to 10% of their surface values.

Global mapping of underwater UV radiation creates many new challenges. The challenges are mostly related to larger uncertainties in physical input parameters caused by biological processes within the oceans. Vasilkov et al. (2002) discuss the problems encountered in the assessment of the underwater UV irradiance from

SURFACE ULTRAVIOLET RADIATION

space-based measurements, and propose approaches to overcome the difficulties by combining different satellite datasets (TOMS, SeaWiFS, and Moderate Resolution Imaging Spectroradiometer (MODIS)). Both SeaWiFS and MODIS provide some estimate of seawater optical properties in the visible. Currently, the problem of accurate extrapolation of visible data to the UV spectral range is not solved completely, and there are only a few available measurements. Vasilkov et al. (2002) propose to parameterize UV absorption by oceanographic constituents empirically by using bio-optical measurements from a variety of ocean waters. Another problem is the lack of reliable data on pure seawater absorption in the UV. Laboratory absorption measurements of the middle UV for both pure water and pure seawater are required (Fry, 2000).

The transmission of UV radiation through sea ice is reduced by absorption and scattering processes that occur within and on top of the ice. UV radiation is strongly absorbed by both colored dissolved organic matter and particulate organic matter, including ice algae. Scattering occurs above the ice by snowcover, within the ice, and from interstitial brine (Vasilkov et al., 1999). Consequently, the transmission changes during the season, either declining by an order of magnitude as a highly scattering turbid brine layer develops on top of the ice, and as ice algal communities bloom (Trodahl and Buckley, 1990; Perovich et al., 1998), or increasing if snow melt ponds form on top of the ice, thereby reducing albedo and scattering (Belzile et al., 2000). In the latter case, the under-ice spectrum becomes enriched in UV-B relative to photosynthetically active radiation, and may exacerbate UV-B effects.

5.2.2 Daily Forecasting of Ozone and UV

Forecast of the UV Index is a direct application of the resources used to study UV radiation and the knowledge of the dependencies of surface UV on absorption and scattering processes. Forecast values of total ozone are used as input to RT models or statistical models. Most of the agencies that currently produce forecasts of the UV Index had been doing so by the time of the previous Assessment (WMO, 1999) in accordance with the international definition and standardization (WMO, 1994, 1997). Although many agencies provide UV Index forecasts on their web pages, only a few have published their methodology (Burrows et al., 1994; Long et al., 1996; Burrows, 1997; Bais et al., 1998b; Lemus-Deschamps et al., 1999). Many countries have adopted and/or modified the above methodologies to produce their own UV Index

forecasts. Further information regarding the UV Index can be found on Internet sites listed in Appendix 5B (Section 5B.5).

With the increase of computing speeds, more countries moved from empirical forecasts of the UV Index to using RT models that can be very specific or can make several assumptions to increase output speed. These models provide the UV irradiances at the surface under clear skies with known column ozone amount and aerosol type and content. The difficulty in the forecast of UV Indices lies in the forecast of the ozone amount and the transmission of UV radiation through the atmosphere in the presence of clouds and aerosols. Our inability to estimate accurately the aerosols at a specific location introduces further uncertainty in UV Index calculations, and a recent study by Krzyścin et al. (2001) has addressed this issue. Comparisons of model predictions with measured UV Indices under cloudless conditions (De Backer et al., 2001) showed that models generally overestimate the UV Indices, owing to lack of aerosol information. Inclusion of clouds in UV forecasts is a double problem, because clouds must be accurately forecast and their transmittance properties must be accurately known.

There have been two approaches to address the cloud problem. In the absence of a comprehensive weather forecasting model, empirical relations between forecast cloud types and observed UV amounts provide the necessary means of producing a UV Index forecast. These relations may include variable amounts of aerosols and the inherent elevation of the site, thus making the relationships unique to a particular site. The second approach is to use a numerical weather prediction model (NWP) such as that from National Centers for Environmental Prediction (NCEP), the United Kingdom Meteorological Office (UKMO), or the European Centre for Medium-Range Weather Forecasts (ECMWF). These models provide the necessary cloud parameters, shortwave radiation information, and snow cover (i.e., albedo) information to derive a better estimate of the UV Index forecast. Research must be conducted to make sure that the NWP's cloud fields and transmittances are validated by observations.

The forecasts of ozone used to produce the UV Index forecasts have been determined using two methods: persistence of satellite-observed ozone amounts, and using NWP meteorological variables to make ozone forecasts via statistical regressions (Bais et al., 1998b; Plets and Vynckier, 2000). The former procedure works well for one-day forecasts year round in the tropics and during summer poleward of the tropics. The latter method is required when ozone variability is large and statistical

correlations between ozone variations and variations in the meteorological parameters are greater.

Recently, forecasting centers (e.g., NWP mentioned above and the Koninklijk Nederlands Meteorologisch Instituut (KNMI)) have been assimilating ozone into their forecast models. These models require a much better depiction of ozone in the atmosphere for their radiation calculations. At NCEP, the Solar Backscatter Ultraviolet Spectrometer (SBUV2) ozone profile and total column information is assimilated into the global NWP model. Accurate forecasts of the global ozone field are available out to 5 days. Ozone forecasts are useful for forecasting UV, as well as for the a priori ozone estimates (total and profile) required by ozone retrieval algorithms. The quality of this a priori value greatly affects the derived value (Bhartia et al., 1996). Thus positive feedback between observation and model forecast is created.

5.2.3 Remaining Questions and Uncertainties

Remaining uncertainties in our understanding of the radiative transfer processes that define surface UV radiation include the following:

- A lack of knowledge of aerosol absorbing and scattering processes that results in observed differences between some of the satellite estimates and ground-based measurements of surface UV irradiance.
- A lack of knowledge of aerosol optical depths and aerosol single scattering albedo values on a global scale. Differences in these variables from one geographic location to another may lead to differences in the bias between ground-based measurements and satellite estimates from one site to another.
- The extent to which inhomogeneities of terrain, surface reflectivity, or persistent geophysical features surrounding an individual site influence ground-based measurements. The inhomogeneities also affect how well a single point measurement is representative of an extended region (Chubarova et al., 2002; Fioletov et al., 2002). These uncertainties, plus the fact that the geographic distribution of ground-based sites is not uniform, make the determination of global UV climatologies and long-term trends solely from ground-based networks a difficult, if not impossible, task.
- The combined effects of clouds and surface albedo in the derivation of satellite estimates of surface UV.
- The combined effects of clouds, aerosols, and tropospheric absorbing gases on ground-based and satellite measurements. Some of these processes have

been established in case studies, but their importance is not quantified on global and regional scales.

5.3 AVAILABLE RESOURCES FOR STUDYING SURFACE UV RADIATION

Surface UV radiation is studied by using several types of resources that have been developed and applied by many research groups. These resources include ground-based instruments, RT models, satellite instruments, and statistical models. Ground-based instruments that measure surface UV irradiance include spectroradiometers, broadband radiometers, and narrowband multifilter instruments. RT models calculate surface UV using a model atmosphere with the solar spectrum and several scattering and absorbing geophysical parameters as input. Satellite instruments measure geophysical variables and use RT models to calculate surface UV irradiance on a global scale. Statistical models are used to determine dependencies of surface UV irradiance on scattering and absorbing variables.

5.3.1 Ground-Based Measurements

The measurement of solar UV radiation received at the Earth's surface is technically demanding. Usually, the quantity measured is the irradiance on a horizontal surface using a detector with a cosine response. This means, for example, that radiation at 60° from the zenith has only half the weighting of that from the zenith direction.

Three categories of UV sensors are in widespread usage: (1) spectroradiometers designed to measure the spectrum of UV at UV-A (315-400 nm) and UV-B (280-315 nm) wavelengths at spectral resolutions of 1 nm or better, (2) broadband sensors designed to measure biologically weighted UV irradiance, in most cases the erythemally weighted (or "sunburning") UV irradiance, and (3) multifilter instruments where the irradiance is measured through several narrowband (~2- to 10-nm bandwidth) filters and the full spectrum can be recovered using RT models.

5.3.1.1 SPECTRORADIOMETERS

Since the previous Assessment (WMO, 1999) there have been a number of developments on UV spectroradiometers with the introduction of new instrument types and improvements of existing UV instrumentation. A dual-prism spectrograph (UV-rotating shadowband spectroradiometer) that makes continuous and nearly simultaneous spectral measurements of direct, diffuse, and total horizontal irradiance using an array detector has recently

SURFACE ULTRAVIOLET RADIATION

been introduced (Harrison et al., 1999; Lantz et al., 2002). Compared with conventional scanning spectroradiometers, these array instruments measure spectra much faster, thus creating new opportunities to investigate fast-changing atmospheric variables such as clouds. Also a high-resolution (0.1 nm) 1-m Czerny-Turner double grating spectroradiometer with 10^{-10} out-of-band light rejection has been developed and is in operation in the U.S. Department of Agriculture (USDA) monitoring network (Bigelow et al., 1998; Lantz et al., 2002).

The need to correct for the cosine error (McKenzie et al., 1992; Seckmeyer and Bernhard, 1993; Gröbner et al., 1996) is now more widely recognized. More spectroradiometers have been equipped with diffusers that represent the cosine response better than previously used collectors (Bernhard and Seckmeyer, 1997; Bais et al., 2001a). In addition, methods to correct measurements made by instruments with known angular response have been developed and applied to existing data records (Bais et al., 1998a; Fioletov et al., 2002).

Wavelength shifts in measured spectra can contribute significantly to the overall error budget, particularly at wavelengths less than 300 nm where the spectral gradient is large from absorption by ozone. Emphasis has been given in recent years to develop improved wavelength drives with increased thermal stability and reproducibility (e.g., Gröbner et al., 1998). With the implementation of these developments, the wavelength scale of many spectroradiometers can be aligned to within ± 0.02 nm, which is acceptable for long-term trend detection. Also methods for post-correction of wavelength shift by correlating the Fraunhofer structure in measured spectra with the same structure in reference spectra have been further refined and tested (Bais et al., 2001a; De la Casinière et al., 2001).

The temperature dependence of the responsivity of Brewer instruments in the U.S. Environmental Protection Agency (EPA) network has been characterized (Weatherhead et al., 2001). It was shown that temperature dependence varies from instrument to instrument and can result in errors up to $\pm 10\%$ in some cases. However, with knowledge of the temperature dependence it is possible to partly correct existing data records.

A comprehensive list of spectroradiometer specifications based on requirements of UV research is given by Seckmeyer et al. (2001). This report contains guidelines for instrument characterization such as spectral sensitivity, stray light determination, wavelength alignment, angular response, and other parameters that influence the quality of data measured by spectral UV instruments. The dominating factors in the uncertainty budget of spectroradiometers are uncertainties related to the radiometric calibration

(e.g., uncertainty of calibration standards), deviation from the ideal angular response (the cosine error), instrument drift, and wavelength misalignment (Bernhard and Seckmeyer, 1999). Uncertainties arising from an instrument's spectral bandpass (the slit function) and stray light, which were historically a problem, are of less importance with state-of-the-art instruments that use high-quality double monochromators and a resolution smaller than 1 nm.

5.3.1.2 BROADBAND FILTER RADIOMETERS

Instruments that measure irradiance over a wide wavelength range (>10 nm) are called broadband instruments. Many of these instruments are designed to measure the erythemally weighted irradiance as defined by the Commission Internationale de l'Éclairage (CIE) (McKinlay and Diffey, 1987). From measurements of the erythemally weighted irradiance, the UV Index (WMO, 1994) can be directly calculated. Since the previous Assessment (WMO, 1999) research efforts have focused on the calibration of these instruments and the analysis of data, with little instrument development.

No broadband instrument precisely matches the erythral spectrum. Examinations of broadband instruments by independent laboratories have revealed that variation of individual instruments from the specifications offered by manufacturers can result in calibration errors between 10 and 20% (Bodhaine et al., 1998; Leszczynski et al., 1998; Landelius and Josefsson, 2000). The conversion from individual detector-based units to standardized units (e.g., the UV Index) depends on the wavelength dependence of the radiation, and at the Earth's surface this dependence is characterized mainly by the SZA and total ozone. Thus, the absolute calibration of a broadband detector depends on these parameters. Often this dependence is determined using RT model results to convert from detector weighted units to erythemally weighted units or by comparing measurements of a broadband detector for a considerably long time with a co-located spectroradiometer (Mayer and Seckmeyer, 1996; Blumthaler, 1997; Bodhaine et al., 1998; Lantz et al., 1999).

Significant changes in the responsivity of broadband detectors have been noted during routine operation (Weatherhead et al., 1997; Silbernagl and Blumthaler, 1998; Borkowski, 2000). These changes are difficult to detect without careful examination of the instruments (Lantz et al., 1999; di Sarra et al., 2002b). Furthermore, it was found that changes of internal relative humidity or temperature are responsible for short-term variations of sensitivity by more than 10% in some instruments (Huber et al., 2002). Therefore, stability for these instruments (as

well as for other UV instrument types) should be verified by careful, periodic characterization and calibration.

5.3.1.3 NARROWBAND MULTIFILTER RADIOMETERS

Narrowband multifilter radiometers are less expensive and require less maintenance than spectroradiometers, yet, if well calibrated, can produce valuable information. Their bandwidths range from about 2 nm to 10 nm, and some are equipped with an automated shadowband to retrieve direct Sun irradiance. As with any radiometric measurement, regular calibrations are essential. Recent repeat measurements of the spectral response of 34 multifilter radiometers before and after 6 to 12 months of field use revealed mean spectral shifts of less than 0.04 nm for all channels (Gao et al., 2001). Multifilter radiometers measure all wavelengths (typically from four to seven channels) in less than 1 second as opposed to scanning spectroradiometers that usually require several minutes to complete a scan. This rapid and nearly simultaneous sampling of all wavelengths is useful for studying variations in UV irradiance caused by rapidly changing cloud and aerosol conditions. Radiometers that measure direct Sun can retrieve aerosol optical depth (Wenny et al., 2001; Slusser et al., 2002) as well as track the instrument's radiometric stability in the field (Bigelow and Slusser, 2000). Radiometers that measure global irradiance only, as well as those measuring global and direct Sun irradiances, can retrieve column ozone (Slusser et al., 1999; Gao et al., 2001). Several methods have been successfully implemented to construct a complete spectrum from multifilter measurements (Fuenzalida, 1998; Min and Harrison, 1998). Combining multifilter measurements with concurrent measurements of a scanning radiometer allows the derivation of spectra at high temporal resolution, thus blending the strengths of both instrument types (Thorseth and Kjeldstad, 1999); however, rigorous intercomparisons with spectroradiometers are still sparse.

5.3.1.4 DATA QUALITY AND DATABASES

Scientific objectives, such as the detection of trends in UV radiation and investigations into radiative transfer processes, require UV data of known quality that are attainable only with carefully maintained and well-characterized instruments. The improvement of data quality has remained a vital goal in recent years, and progress has been made toward achieving this since the previous Assessment.

Many new stations have started regular spectral UV observations since the previous Assessment. However, the geographic distribution of these stations is weighted more toward continents in the Northern Hemisphere and

less over oceans and large regions of the Southern Hemisphere. The existing nonuniform distribution is not adequate to make measurements of long-term trends that are representative of global coverage.

Currently there are two major databases where interested scientists can obtain data: the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) operated by the Meteorological Service of Canada (MSC) in Toronto, Canada, and the European UltraViolet DataBase (EUVDB) in Helsinki, Finland (called Scientific UV Data Management (SUVDAMA) in the previous Assessment). Appendix 5A gives a list of stations and data that are currently available. Since the contents of these databases are rapidly changing, the interested reader is referred to the database websites given in Appendix 5A as well as other websites listed in Appendix 5B.

Most of the spectroradiometers deployed today are radiometrically calibrated with tungsten halogen standard lamps that are traceable to standards maintained by national standards laboratories. The calibration uncertainty of these lamps is still one of the most prominent sources of error in solar UV radiometry. Standard lamps can abruptly change by up to 1% in the radiation output at unpredictable intervals (Bernhard and Seckmeyer, 1999). In addition, irreversible changes of 10% or more have been seen by several investigators. These are connected to visible changes in the lamp's filaments. Such lamps can no longer be used for calibration purposes. Lamp comparisons further suggest that even standards of the same calibration laboratory may disagree with each other beyond their stated accuracy, and deviations exceeding 4% have been observed at UV wavelengths (Bernhard and Seckmeyer, 1999; Kiedron et al., 1999). National standards laboratories usually provide calibration points in increments of 5 to 50 nm, and interpolation to wavelengths between these points may lead to errors of the order of 0.5 - 1%. New interpolation procedures have recently been developed to reduce this effect (Huang et al., 1998). In order to diminish uncertainties related to transportation of radiometers between calibration in the laboratory and deployment on site, new field calibration units have been developed in recent years (Seckmeyer et al., 1996, 1998; Early et al., 1998; Bais et al., 2001b).

Assessment of the comparability of lamp standards currently used at different stations in Europe has been initiated by the Joint Research Centre (JRC) of the European Commission. A set of carefully selected and seasoned lamps is circulated among the nine participating institutes, which report their spectral irradiance output based on comparative measurements with the local calibration standards. The results of the first round indicate differences of up to 9% between the calibration standards of different

SURFACE ULTRAVIOLET RADIATION

laboratories (Gröbner et al., 2002). The average root mean square (rms) difference of all the lamps to the mean is 2.0, 1.8, and 1.7% at 300, 330, and 360 nm, respectively, which is within the expected uncertainty estimates of the lamp calibration certificates. A series of measurements with the same stationary spectroradiometer of JRC proved that the lamps were stable to within 0.6% during the entire period of the exercise, giving confidence to the differences encountered and to the feasibility of the method.

As an alternative to standard lamps, it has been proposed that the Sun can be used as a long-term reference to monitor instrument stability and as a calibration source, since its irradiance is stable to within $\pm 0.5\%$ at UV-A and UV-B wavelengths. This is done with the Langley plot technique using instruments that are able to perform both direct and global measurements at clean sites where the diurnal variability of ozone and aerosol extinction is small (Bais, 1997; Slusser et al., 2000; Gröbner and Kerr, 2001; Kerr, 2002). Ground-based measurements of direct solar irradiance (using absolute lamp-based calibrations) are extrapolated to zero air mass and compared with an extra-terrestrial solar spectrum (e.g., Cebula et al., 1996). It has been shown that lamp-based Langley extrapolation measurements of the solar spectrum performed with a Brewer spectrophotometer under ideal conditions at Mauna Loa Observatory (3397-m altitude) are consistent with satellite measurements to the 2-3% level for wavelengths greater than 305 nm (Gröbner and Kerr, 2001). A similar comparison of Langley and lamp-based calibrations was performed at the same observatory with a UV multifilter rotating shadowband radiometer. Differences between 0 and 7% were found, with largest deviations at the shortest wavelengths (Slusser et al., 2000), and drifts in sensitivity of the instruments of the order of 1% per year were detected (Bigelow and Slusser, 2000). An important prerequisite for these extrapolation measurements is that atmospheric conditions remain constant. Therefore such calibrations can only be performed at very clean sites, where aerosols do not influence UV irradiance. Also reliable calibrations cannot be made at wavelengths less than 305 nm, where the signal is strongly attenuated by ozone.

New techniques have been pursued to uncover errors in spectral measurements. For example, analyzing ratios of spectra sampled throughout a day enables the detection of errors in the data acquisition of instruments and the determination of wavelength shifts (Bernhard et al., 1998; Seckmeyer, 2000). Standardized methods to mark data with reduced accuracy or to flag scanning spectral UV measurements that are distorted by clouds have been developed (Vasaras et al., 2001). The WOUDC now flags data before adding them to the database, and other data centers are currently developing data-flagging algo-

rithms for the detection of spectral distortion, wavelength error, and the presence of clouds.

Since the previous Assessment, more systematic work to determine the uncertainty of UV measurements has been completed. Bernhard and Seckmeyer (1999) present a general procedure to calculate the uncertainty budget of spectroradiometers depending on instrument specifications, calibration uncertainties, and atmospheric conditions. The method can be applied to most types of spectroradiometers deployed worldwide. For well-characterized spectroradiometers, erythema irradiance can be measured within an uncertainty of $\pm 6\%$ ($\pm 2\sigma$). A substantial reduction in this uncertainty would require more accurate calibration sources and improved methods to correct for instrument drifts. Below 300 nm, the most important sources of error are typically wavelength misalignment and photon noise. Thorough uncertainty estimates for actinic flux spectroradiometers (i.e., instruments with isotropic rather than cosine-weighted angular response) have also been performed recently (Hofzumahaus et al., 1999). According to Hofzumahaus et al. (1999), the total uncertainty of photolysis frequencies due to uncertainties in the measurement of the spectral actinic UV flux lies in the range of 5-7% and is dominated by the $\pm 4\%$ ($\pm 2\sigma$) uncertainty of the irradiance standard. This result is similar to the uncertainty estimate for global irradiance measurements.

In 1994, WMO established a scientific advisory group to provide guidance for UV measurements performed within the Global Atmosphere Watch program. Guidelines for site quality control of UV monitoring (Webb et al., 1998) and recommended specifications for spectroradiometers measuring solar ultraviolet radiation (Seckmeyer et al., 2001) have been drafted. Both publications are considered as working documents that will evolve when new technologies or new objectives for UV spectroradiometry emerge.

5.3.1.5 INSTRUMENT INTERCOMPARISONS

Since the beginning of the 1990s, periodic inter-comparisons of spectroradiometers from different organizations have become an international practice for assessing the quality of UV radiation measurements. Although the stability and the absolute accuracy of individual instruments can be sufficiently maintained using various calibration methods, intercomparison with other independently maintained instruments is an important method that provides uniform quality assurance and data quality. Intercomparisons also provide the opportunity for effective interaction between participating scientists in order to exchange new ideas and findings.

Results of three intercomparisons have been reported since the previous Assessment. The SUSPEN (Standardization of Ultraviolet Spectroradiometry in Preparation of a European Network) intercomparison held in Greece in July 1997 (Bais et al., 2001a) included 19 spectroradiometers from 15 countries. In August 1997 an intercomparison of 10 spectroradiometers operated in Germany (Seckmeyer et al., 1998) took place. In September 1997 the fourth North American Intercomparison of Ultraviolet Monitoring Spectroradiometers (including narrowband filter radiometers) was held near Boulder, Colorado. It included 11 instruments from 9 U.S. agencies (Lantz et al., 2002). Results of these intercomparisons showed that agreement of about $\pm 5\text{--}6\%$ (1σ) was typically achieved, with some dependence on wavelength, zenith angle, and observing conditions. Agreement improves with the application of corrections (e.g., wavelength shift and cosine error) to the data and is generally better at longer wavelengths.

The descriptions above represent gross summaries only. The behavior of the individual instruments can only be judged from more detailed information found in the references. Although the intercomparisons have shown that a considerable number of instruments still show large deviations, overall improvement has been achieved as a result of the knowledge gained through the intercomparison exercises.

Previous comparisons and assessments of the operation of broadband instruments have shown the need to examine their performance regularly (e.g., Johnsen and Moan, 1991; DeLuise et al., 1992; Weatherhead et al., 1997). In this context an intercomparison campaign involving 39 erythral radiometers and two well-calibrated and maintained spectroradiometers was organized in 1999 at the University of Thessaloniki, Greece (Bais et al., 2001b). The campaign was combined with laboratory investigation of the spectral and angular response of the participating instruments. From the comparisons of broadband with the spectroradiometric measurements, new calibration factors were derived, with differences from the original values ranging between -10% and $+25\%$. For about half of the instruments the differences were smaller than about $\pm 10\%$, but only a few agreed with the spectroradiometer to better than $\pm 5\%$. These deviations depend on the time elapsed between the two subsequent calibration checks and on the individual characteristics of each instrument. The large deviations found for many of the instruments suggest that the calibration of broadband detectors should generally be checked more frequently, either in comparison with a spectroradiometer, or against another instrument of similar type.

5.3.2 Radiative Transfer Models and Model Validation

Radiative transfer (RT) models allow the calculation of radiation fluxes (direct, global, sky radiance distribution) as functions of geophysical variables and SZA. Most common models are one-dimensional (plane-parallel or pseudo-spherical) with scattering on spherical particles and polarization effects neglected. Several of these models are freely available for public use (Internet sites given in Section 5B.3 of Appendix 5B): the “library for Radiative transfer” (libRadtran, formerly known as uvspec) (Mayer et al., 1997; Kylling et al., 1998); the Tropospheric Ultraviolet Visible (TUV) model (Madronich and Flocke, 1997); the Santa Barbara Discrete-ordinate Atmospheric Radiative Transfer (SBDART) model (Ricchiazzi et al., 1998); the Streamer model (Key, 1999); and the System for Transfer of Atmospheric Radiation (STAR) model (Ruggaber et al., 1993, 1994). However, these one-dimensional models cannot be used to study situations with nonuniform spatial distributions of scattering or absorbing parameters.

Comparison of measurements of spectral UV surface fluxes with numerical RT simulations greatly facilitates the interpretation of measurements. Also, the quality and internal consistency of measurement methods may be checked using numerical simulations. In addition, RT calculations are required for estimating surface UV radiation from satellite data and for making forecasts of spectral surface UV radiation and the UV Index. In order to use RT simulations for these purposes, the validity of the simulations must be assured. However, validation of UV RT models for real atmospheric cases is a complicated task. At best the validation includes a model intercomparison in combination with observations for some well-defined cases. This combined approach has been pursued in the Scientific UV Data Management (SUVDAMA) project (van Weele et al., 2000).

The SUVDAMA model intercomparison (with 12 participating codes) established benchmarks for six real cloud-free atmospheric cases with different ozone column, air density profile, SZA, aerosol loading, surface albedo, and location. The benchmarks give the spectral surface UV irradiance between 295 and 400 nm with 0.5-nm steps and with a standard deviation of 2% between the modeled spectral irradiances. For cases with the Sun close to the horizon and for the shortest wavelengths, the relative standard deviations are somewhat higher (5%), but then irradiance is very small. Remaining differences between model results relate to the translation of the ancillary data and other fixed input parameters into the optical properties that are needed in the RT algorithms. Examples

SURFACE ULTRAVIOLET RADIATION

include the parameterization of aerosol optical properties, interpolation of the ozone absorption cross section as a function of wavelength and temperature, and the discretization of the atmosphere into vertical homogeneous layers. Comparison of the benchmarks with the observations showed differences, within $\pm 13\%$ over the whole spectral UV range for four out of six cases, mainly due to uncertainty in the input parameters and assumptions on instrument characteristics such as slit function and wavelength alignment.

Atmospheric and ground parameters are usually horizontally inhomogeneous, especially for cloudy cases. These nonuniformities must be addressed by using three-dimensional (3-D) models, which require significant computational time and are therefore restricted to a subset of conditions only. In recent years, 3-D RT models have become available, which use either the Monte Carlo method (e.g., Cahalan et al., 1994) or the spherical harmonics discrete ordinate method (Mueller and Crosbie, 1997; Evans, 1998). These models allow the study of effects of three-dimensional clouds (O'Hirok and Gautier, 1998a, b; Marshak et al., 1999; Degünther and Meerkötter, 2000a; Meerkötter and Degünther, 2001) or of inhomogeneous surface albedo (Degünther et al., 1998; Degünther and Meerkötter, 2000b; Kylling et al., 2000).

The first intercomparison of 3-D radiation codes has been performed. Differences between the 3-D model calculations are in the range $\pm 5\text{--}10\%$, which is comparable with the uncertainties typically associated with UV measurements. However, such a complete description of the atmosphere is usually not available when UV measurements are to be compared with results of model calculations. Therefore, the uncertainty of the calculated irradiance is much higher, even under clear-sky conditions (Weihs and Webb, 1997a, b; Schwander et al., 1997). For well-characterized conditions, agreement to within about $\pm 5\text{--}10\%$ can be obtained between observations and model calculations. When some input parameters are not known, differences higher than $\pm 20\%$ are found (Koepke et al., 1998; De Backer et al., 2001).

5.3.3 Satellite Estimates and Validation

The understanding of RT processes forms the scientific basis for estimating surface UV irradiance from satellite measurements. Since the previous Assessment (WMO, 1999), advances have been made in our understanding and application of the required processes. The Total Ozone Mapping Spectrometer (TOMS) UV algorithm (Eck et al., 1995; Herman et al., 1996; Krotkov et al., 1998) has been modified to improve cloud attenuation estimates and to introduce the enhancement of surface

irradiance caused by the high albedo of snow (Herman et al., 1999; Krotkov et al., 2001, 2002). The method has been adapted to the Global Ozone Monitoring Experiment (GOME), the European UV spectrometer on the second European Remote Sensing Satellite-2 (ERS-2) (Peeters et al., 1998). Li et al. (2000) have proposed an alternative parameterization for deriving surface irradiance from TOMS total ozone and TOMS 380-nm reflectivity or Advanced Very High Resolution Radiometer (AVHRR) visible data. Mayer et al. (1998a) have modified the TOMS UV algorithm to estimate the surface actinic flux giving photolysis rates for atmospheric chemistry models.

Polar-orbiting UV spectrometers (e.g., TOMS, GOME) are able to make measurements of atmospheric properties at a given location once per day. This together with a relatively coarse spatial resolution affects their ability to estimate the total daily exposure to UV radiation because of the high temporal and spatial variability of cloud cover. It has been shown that for accurate retrievals, several cloud images per day are required (Martin et al., 2000; Meerkötter and Bugliaro, 2002; Verdebout and Vogt, 2002). Different methods have been proposed that draw cloud transmission information from other satellites or datasets with higher spatial and/or temporal resolution. Lubin et al. (1998) used Earth Radiation Budget Experiment (ERBE) hourly cloud and surface albedo data resolved at 100 km to determine a 5-year climatology; Matthijsen et al. (2000) generated a multiyear dataset over Europe using the International Satellite Cloud Climatology Project (ISCCP) dataset (~ 15 km, every 3 hours); and Verdebout (2000) retrieved cloud optical thickness and surface albedo from METEOSAT (~ 5 km over Europe, half-hourly) to generate UV maps over Europe. AVHRR data (between one and five images per day with ~ 1 -km resolution) have been used to map the surface UV radiation over Antarctica (Lubin et al., 1994), the Moscow region, Russia (Rublev et al., 1997), and parts of Europe (Meerkötter et al., 1997) as shown in Figure 5-1 (from Simon et al., 2000). These methods use the TOMS, GOME, or Television Infrared Observation Satellite (TIROS) Operational Vertical Sounder (TOVS) derived total column ozone and various ancillary information such as digital elevation models, aerosol climatologies, or gridded surface visibility observations as inputs to RT models that estimate surface UV irradiance.

Accurate knowledge of cloud transmittance is critical for satellite UV estimates. The TOMS and GOME instruments can measure UV cloud reflectivity, R , and estimate cloud transmission, C_T , by the simple expression $C_T \sim 1 - R$, with a correction for ground reflectivity (Eck et al., 1995; Herman and Celarier, 1997; Herman et al., 2001a; Krotkov et al., 2001). Alternately, C_T for plane-parallel

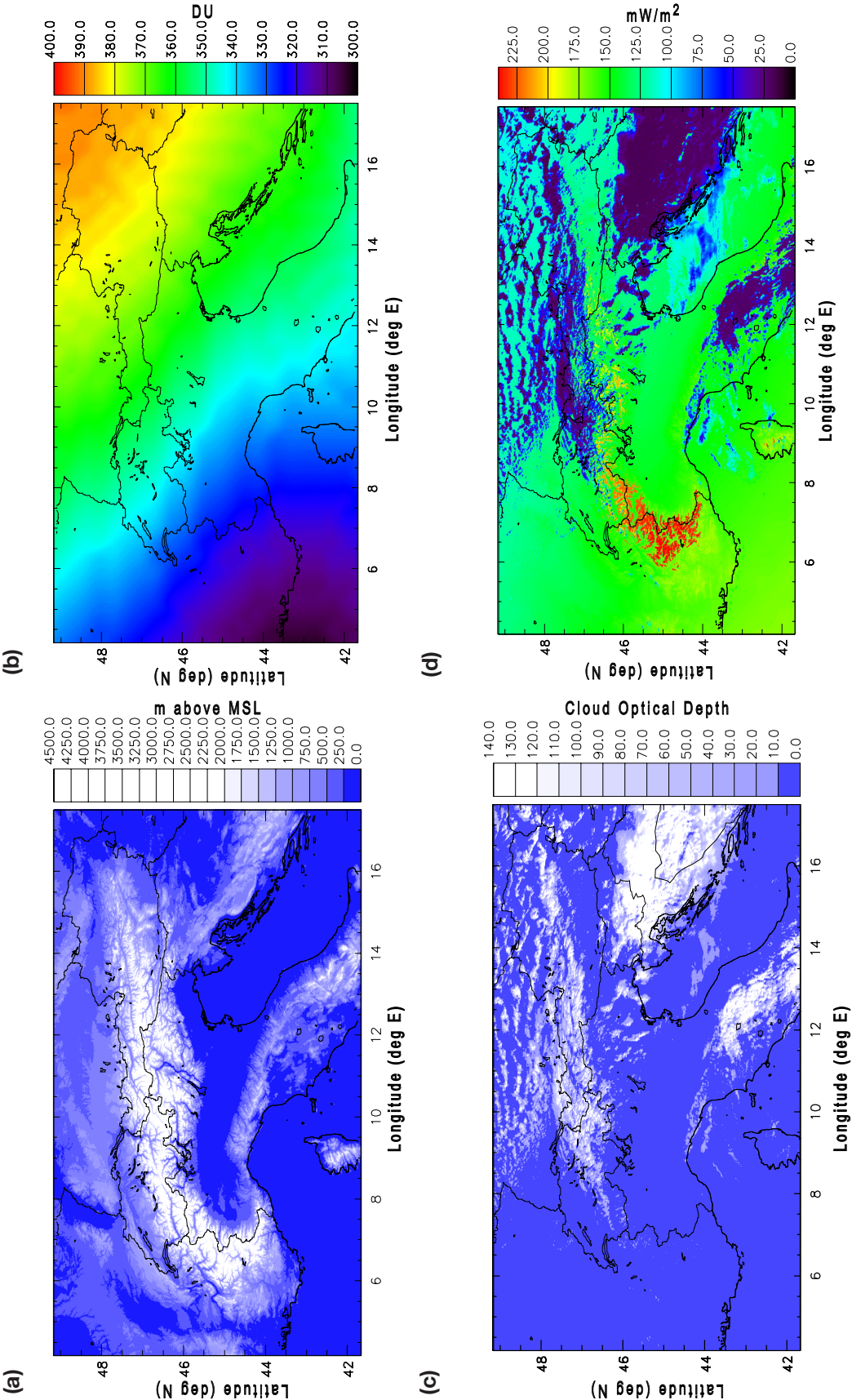


Figure 5-1. A region in Central Europe including the Alps: (a) surface elevation in meters above mean sea level, (b) horizontal distribution of the GOME (Global Ozone Monitoring Experiment) total ozone column amount in Dobson units (DU) on 15 April 1997, (c) horizontal distribution of cloud optical depth as derived from NOAA/AVHRR (Advanced Very High Resolution Radiometer) data on 15 April 1997, and (d) high-resolution map of the erythemal dose rates in milliwatts per square meter (mW m⁻²). From Simon et al. (2000).

SURFACE ULTRAVIOLET RADIATION

cloud can be estimated by radiative transfer inversion of the satellite-measured “top of atmosphere radiance.” The latter approach is applicable to UV, visible, and infrared sensing instruments, since the C_T spectral dependence is included in the RT model (Meerkötter et al., 1997; Krotkov et al., 2001; Verdebout, 2000). There have been a number of studies where satellite estimates of C_T compared with ground-based measurements often show good agreement, but reveal systematic errors in the presence of snow (Kalliskota et al., 2000; Arola et al., 2002). A method to improve satellite cloud reflectivity estimates with snow on the ground has been developed by including snow depth information (Krotkov et al., 2002), and this method is to be considered for future satellite algorithms.

Under cloud-free conditions the accuracy of satellite UV data is limited mainly by an imperfect knowledge of the highly variable aerosol properties. TOMS UV two-channel reflectivity data are used to correct for absorbing aerosols at a known altitude by forming the aerosol index (AI; Krotkov et al., 1998). The effect of aerosols on satellite UV estimates over large areas is largest in tropical regions where there are major dust plumes (e.g., the Saharan plume) and smoke plumes (e.g., Africa and South America) from biomass burning. There the reductions in surface UV irradiance are frequently as much as 50% (Herman et al., 1999). However, the TOMS AI technique does not have the sensitivity to detect absorbing or non-absorbing aerosols close to the ground that are often present in urban atmospheres (Dickerson et al., 1997; Torres et al., 1998; Herman et al., 1999; Jacobson, 1999). When the aerosol effects are estimated using measured optical depths and single scattering albedos between 0.95 and 0.98, the clear-sky differences are usually reduced to within the instrument uncertainty. However, when near-surface atmospheric visibility data are used, UV irradiance reductions as large as 10% are found in some parts of Europe (corresponding to visibility values of ~10 km) (Verdebout, 2000), and even higher reduction could be expected in some cases. Simultaneous measurements of aerosol optical properties and surface UV irradiance are required to quantify local satellite biases for such areas. The aerosol problem is smaller at midlatitudes in the Southern Hemisphere because of clearer air compared with the same latitudes in the Northern Hemisphere (McKenzie et al., 2001a).

The accuracy and precision of satellite estimates have been assessed through comparisons between satellite and ground-based data and are reported either in papers describing the satellite-based methods or in dedicated publications (Kalliskota et al., 2000; Wang et al., 2000; Herman et al., 2001b; McKenzie et al., 2001a; Arola et al., 2002; Chubarova et al., 2002; Fioletov et al., 2002;

Slusser et al., 2002; Wuttke et al., 2002). The observed differences of noontime irradiance values between ground-based measurements and TOMS satellite estimates can be ± 20 -30% rms and are caused by temporal and spatial cloud variation. However, the rms differences are reduced for daily integrals averaged over longer periods (e.g., $\pm 4\%$ for May, June, July, and August monthly mean values at Toronto; Fioletov et al., 2002). McKenzie et al. (2001a) compared ground-based measurements from cross-calibrated spectrometers with UV estimated from TOMS instruments over several years at four midlatitude sites. There is reasonable agreement in the day-to-day variability of UV derived by both methods; however, the TOMS data overestimate monthly erythema doses by about 15% in Toronto, 24% in Thessaloniki, and 38% in Garmisch-Partenkirchen. At the pristine Southern Hemisphere site, Lauder, New Zealand, the average agreement is within 3%. Fioletov et al. (2002) reported similar comparisons at 10 sites in Canada. At 9 of the 10 sites TOMS overestimates the ground-based measurements from 7 to 16%. The only site with agreement to within 2% is at Saturna, located on the Canadian west coast where there is predominantly clean maritime air. Chubarova et al. (2002) showed that TOMS estimates are about 10% larger than a long-term (1979-2000) record of broadband measurements made at Moscow State University. The reasons for the large differences at northern midlatitudes may be attributed to absorption in the lower troposphere by aerosols and/or other pollutants that are not properly considered in the TOMS retrievals.

Part of the observed differences reflects the fact that the estimates and measurements are not of the same thing. There is always a mismatch between satellite-based and ground-based data acquisition. The satellite-derived value represents a single large-area average compared with the near-continuous local irradiance measured by a ground-based instrument. Lubin et al. (1998) have shown that daily doses can be estimated from satellite data obtained only at local noon with knowledge of the course of the SZA throughout the day. For all cloud cases Martin et al. (2000) have shown that the uncertainty in daily doses reconstructed from a single ground-based near-noon measurement is at least $\pm 25\%$, and reduces to $\sim \pm 5\%$ for monthly doses.

Another important consideration is that there are site-specific biases caused by the persistence of local geophysical variables (McKenzie et al., 2001a, b; Chubarova et al., 2002; Fioletov et al., 2002). These include variations in altitude around the site, the persistence of local cloud patterns, or persistent patterns of nearby albedo. The 38% bias between TOMS and Garmisch-Partenkirchen ground-based UV data (reported by

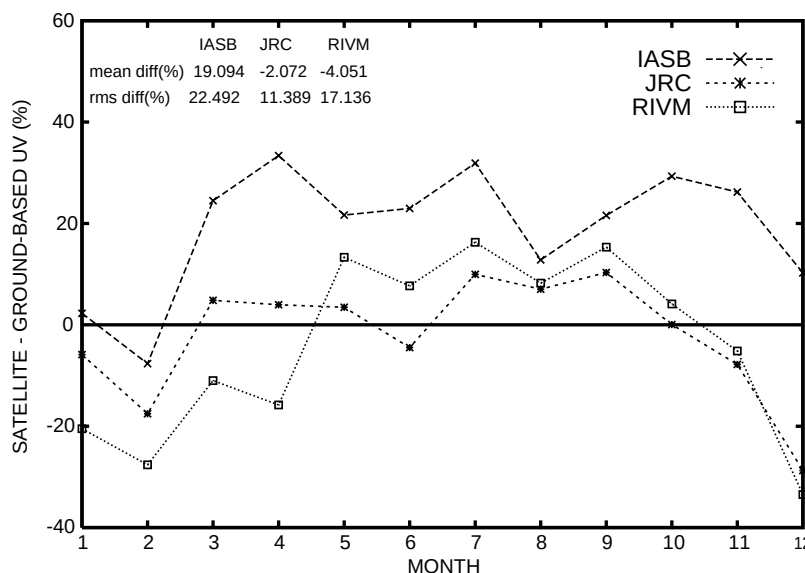


Figure 5-2. Percentage difference between ground-based and satellite-based monthly erythemal irradiance in 1997 predicted by three different satellite algorithms: from the Institut d'Aéronomie Spatiale de Belgique (IASB), the European Commission Joint Research Centre (JRC), and the National Institute of Public Health and the Environment of the Netherlands (RIVM). The algorithm of IASB shows a systematic bias with respect to ground-based data, whereas the algorithms of JRC and RIVM show improved agreement for the mean erythemal yearly dose. However, the latter two algorithms show a seasonal dependence, which is not well understood yet. Adapted from Arola et al. (2002).

McKenzie et al., 2001a) was not seen when METEOSAT or AVHRR data were used (Arola et al., 2002). The algorithm developed by the Institut d'Aéronomie Spatiale de Belgique (IASB) uses TOMS data, but shows a mean difference of 19% (Figure 5-2). The reason for the difference between the original TOMS algorithm and the IASB algorithm is not known. The algorithm of JRC based on METEOSAT and GOME data, and the algorithm of RIVM (National Institute of Public Health and the Environment, Netherlands) based on TOMS ozone and ISCCP data, show a smaller difference between satellite estimates and ground-based measurements at Garmisch-Partenkirchen as well as other sites (Figure 5-2). This leads to the conclusion that some satellite algorithms give better estimates of surface erythemal UV radiation than others. In addition there are systematic seasonal variations between satellite and ground-based results that are not understood yet. A novel method to understand such differences better has been proposed by Wuttke et al. (2002). It has been shown that the use of the full spectral information of both the satellite algorithm and the ground-based measurements helps to identify the reasons for deviations. Such an improved understanding has been used to develop an improved algorithm that shows less deviation when compared with ground-based measurements.

5.3.4 Statistical Modeling

The main geophysical variables that affect surface UV radiation are ozone, clouds, aerosols (both absorbing and nonabsorbing), and surface albedo. Total ozone measurements and ancillary data have been used with measurements of surface UV irradiance to develop statistical relationships that define the dependence of UV on the

scattering and absorbing variables. Previous applications of statistical models include the UV Index forecast (e.g., Burrows et al., 1994) and the derivation of total ozone from UV measurements (Fioletov et al., 1997).

Recent studies (Krzyzscin, 1996; Fioletov et al., 1997, 2001; McArthur et al., 1999; Bodeker et al., 2000; Kaurola et al., 2000; Gantner et al., 2000; den Outer et al., 2000; Diaz et al., 2000, 2002; Chubarova et al., 2002) have shown that surface UV radiation can be estimated by using measurements of total ozone (ground-based or satellite) with other ground-based data (such as global solar radiation measured with pyranometers). Total ozone values determine the spectral absorption features in the UV-B, and the ancillary data quantify the scattering processes that have weak wavelength dependence (clouds, aerosols, and surface albedo).

There have been a number of approaches for the use of statistical models. In some of these models, daily integrals of wavelength interval or erythemally weighted UV irradiance are statistically related to measurements of global radiation and other atmospheric variables (Diaz et al., 2000, 2002; Gantner et al., 2000); in others (Kaurola et al., 2000; den Outer et al., 2000) the daily integrals are compared with model results. Relationships as functions of total ozone, SZA, and other variables allow hour-by-hour comparisons (Bodeker et al., 2000; Fioletov et al., 2001). The neural network technique has also been applied to datasets of total ozone, global pyranometer information and other weather observations (Janouch, 2000; Schwander et al., 2002).

Good-quality spectral UV irradiance measurements have been available for about 10 years. These data are used with total ozone and ancillary data taken over recent

SURFACE ULTRAVIOLET RADIATION

years to establish statistical relationships that determine the dependence of ground-based spectral UV radiation on total ozone and the ancillary data. The statistical relationships are then used with measurements of total ozone and ancillary data to estimate UV radiation at other sites and at times when spectral UV radiation was not measured. These estimates can be extrapolated backward in time to as early as the 1960s, prior to the onset of ozone depletion. Figure 5-3 shows an example of statistical model results compared with ground-based spectral UV irradiance measurements and TOMS UV satellite estimates for summer months at Toronto (Fioletov et al., 2002). This figure demonstrates the good agreement between the ground-based estimates and spectral measurements for the overlap period (1989-1997). Also, the year-to-year variability of the ground-based estimates extended backward is similar to that of the satellite estimates, although there is a bias between satellite and ground-based results as discussed earlier.

5.4 UV CLIMATOLOGY, TEMPORAL CHANGES, AND TRENDS

The main objectives for taking long-term systematic measurements of surface UV radiation are to establish a global climatology of UV, both average and extreme values, and to quantify any long-term changes that may have occurred as a result of changes in stratospheric ozone or other variables. This information is of interest to members of the “effects” community, who focus research studies on the response of biological systems (including human beings), materials, and pollution photochemistry to changes in the UV environment. Some ground-based spectral datasets are available to establish average values and variability of UV at specific sites; however, these datasets are relatively short in duration and have sparse and nonuniform spatial coverage over the globe. They are also representative of areas that are small in size and defined by specific local conditions. Understanding and quantifying the radiative transfer processes (Section 5.2) has allowed the extension of these datasets, both in time and space, with a good degree of certainty. Global coverage has been achieved by the use of satellite data, and the temporal extension backward in time has been achieved by using satellite measurements with RT models, as well as ancillary ground-based data with RT and statistical models.

5.4.1 Ground-Based UV Measurements

Difficulties involved in the routine operation and maintenance of accurately calibrated ground-based UV instruments have limited the length of reliable data records

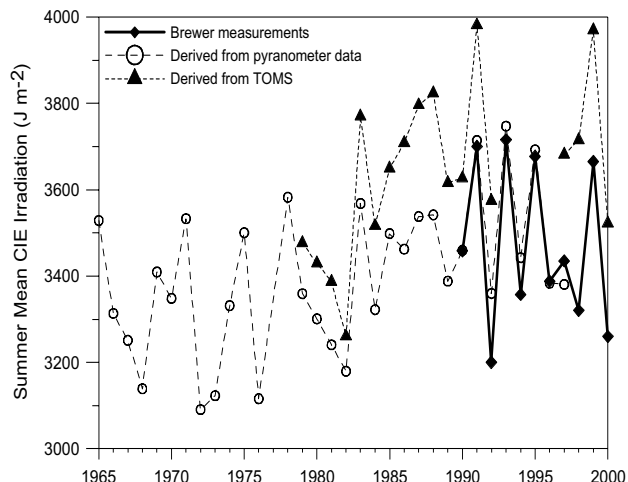


Figure 5-3. Time series of Toronto summertime (May-August) mean daily ground-based and satellite-based erythemal irradiation estimates compared with ground-based measurements. The estimated values using ground-based total ozone and pyranometer data agree very well with the measurements during the overlap period (1989-1997). The satellite estimates follow the year-to-year variability of the ground-based measurements; however, there is a bias as discussed in the text. Similar year-to-year variability is captured by both the satellite-based and ground-based estimates extrapolated backward in time. Adapted from Fioletov et al. (2002).

to about the past 10 years. It is recognized that 10-year records are not of adequate length to carry out long-term trend analyses (Weatherhead et al., 1998, 2000) because of a combination of variability and autocorrelation in datasets. However, some recent studies have used ground-based measurements to identify shorter term changes in surface UV radiation (McKenzie et al., 1999; Frederick et al., 2000; Zerefos, 2002). Also there has been some work done in using the data to develop specific climatologies of UV radiation at some sites (Ilyas et al., 1999; Cede et al., 2002).

An increase in peak UV values in response to decreasing ozone at Lauder, New Zealand, is shown in Figure 5-4 (from McKenzie et al., 1999, 2000). The trend has not continued in the last two austral summers, and ozone amounts at this site have been slightly higher than in the summer of 1998/99. Furthermore, both summers were rather cloudy over the period that is most critical for this analysis. It should be noted that year-to-year variability in cloud cover can have a significant effect even for peak irradiances and that the analysis of peak values cannot be automatically transferred to average values.

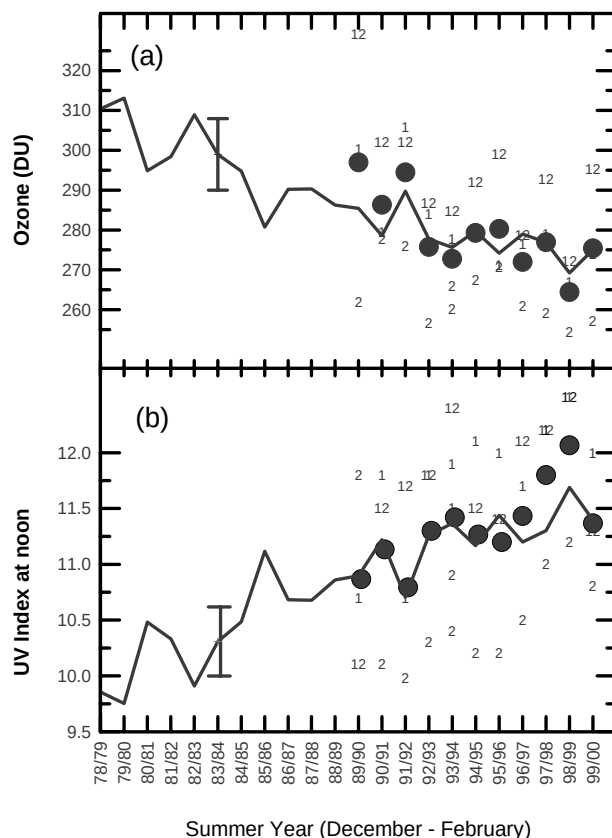


Figure 5-4. (a) Mean total ozone and (b) noontime UV Index at Lauder, New Zealand, for summers (December to February) from 1978/79 to 1999/2000. The solid line in (a) shows observed summertime ozone values that have occurred since the 1970s, and the solid line in (b) shows the expected values of clear-sky UV. The symbols (from 1989/90 on) show measured summertime values of ozone and peak UV Index, both derived from spectral UV irradiance measurements. The plot also shows the values from each contributing month, labeled by the month number. Two-sigma error bars are shown for reference. Adapted from McKenzie et al. (1999, 2000).

Data analysis for the summer of 2000/01 has not yet been finalized because of uncertainties in the National Institute of Standards and Technology (NIST) irradiance scale provided by the irradiance standards laboratories involved. It is likely that the entire dataset will eventually be reanalyzed taking historical changes in lamp irradiance scales into account better. However, it is not expected that the conclusions of the paper will change as a result of that reanalysis.

Routine spectral ultraviolet irradiance measurements made at Reading, England, since 1993 (Bartlett and Webb, 2000), along with total ozone measurements from

a nearby site, demonstrated the inverse relationship between ozone and UV-B. Global radiation measurements suggest that from 1993 to 1997 cloud conditions did not change systematically. A decline in ozone of 5.9% and a corresponding increase in erythral UV of 4.3% were seen, although these changes should not be considered statistically significant trends. Also, solar UV irradiance spectra (290–325 nm) have been measured at Rome and Ispra, Italy, since 1992 (Casale et al., 2000). Correlation coefficients between irradiance at 305 nm and total ozone at Rome were -0.61 ($\text{SZA} = 47^\circ$) and -0.75 (66°) and at Ispra, -0.55 and -0.76 . Seasonal analysis showed higher negative correlation with short-term ozone changes (related with weather patterns) during spring and winter, while in summer the long-term changes (time period greater than 2 years) and seasonal changes (between 2 years and 1 month) in ozone were dominant.

Time series of UV irradiance at 305 and 325 nm for Thessaloniki, Greece, for 1990–1997 were reported in the previous Assessment (Zerefos et al., 1997, 1998; Herman and McKenzie et al., 1999) for low-cloudiness ($2/8$ cloud cover) conditions. These series have been updated to 2001 (Zerefos, 2002) and are shown in Figure 5-5. Both ozone and sulfur dioxide (SO_2) have decreased during the 1990s (Zerefos et al., 1998). However, the observed increase in irradiance of 16.3% per decade at

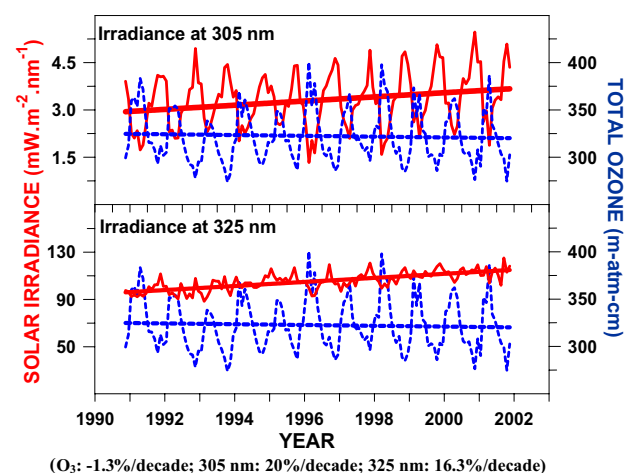


Figure 5-5. Time series of low-cloudiness ($2/8$ cloud cover) monthly mean values of total ozone and solar UV irradiance (63° SZA for 305 and 325 nm) measured at Thessaloniki, Greece (40°N), between 1990 and 2001. These time series are extensions of those reported in the previous Assessment (Herman and McKenzie et al., 1999; Zerefos et al., 1997). The observed temporal increase at 325 nm is attributable to causes other than ozone, because ozone absorbs weakly at this wavelength.

SURFACE ULTRAVIOLET RADIATION

325 nm cannot be caused by the decrease of these gases, since they both absorb weakly at this wavelength. The increase must be caused by long-term changes in other factors, such as aerosols that are associated with the decrease in SO_2 at the observing site.

The spectral UV irradiance records of the U.S. National Science Foundation (NSF) UV radiation monitoring network operating at Ushuaia (Argentina) and Palmer, McMurdo, and South Pole (Antarctica) have increased in length and are now more than 10 years long. Recent analyses of the records have been carried out (Sobolev, 2000; Booth et al., 2001; Diaz et al., 2001). Although the NSF dataset spans roughly 10 years, it is still too short for statistically robust trend detection. At all Antarctic sites, changes in erythemal and DNA-weighted UV are generally positive for the months from September to December, with largest increases typically observed in November. However, trends in monthly averages of daily erythemal and DNA-weighted doses are not significant at the 2-sigma level because of the large year-to-year variability in total column ozone, related to the interannual variability of the ozone hole. Compared with ozone variability, the year-to-year fluctuation in other factors such as cloud cover is of minor importance for interannual UV changes at Antarctic network sites.

The highest UV levels on record observed at McMurdo, Palmer Station, and the South Pole by the NSF network instruments occurred in the austral spring of 1998. UV levels in 1999, 2000, and 2001 were generally lower. The record-size ozone hole in 2000 led to enhanced UV levels at all austral network sites during September, and some extreme events at Ushuaia during October. The observed increases during September are small in absolute

terms because of the low solar elevations prevailing during this month. At all austral network sites, UV values in November 2000 were close to the minimum values on record because of the early closing of the ozone hole.

Yearly maximum erythemal UV levels at austral network locations were observed during recent years in November and early December, 1 to 2 months after the period of maximum ozone depletion. This pattern is explained by the combination of smaller SZA later in the year and the relatively low stratospheric ozone concentrations that still prevail in November. Figure 5-6 demonstrates that peak levels of daily erythemal UV dose in November and December at austral sites exceed those seen during the summer at San Diego (Booth et al., 2001). The large enhancements in November and December suggest that changes in the duration of the ozone hole have a greater influence on biologically relevant UV levels than does the depth of minimum total ozone typically observed at the end of September and beginning of October (Diaz et al., 1994).

5.4.2 Estimates from Satellite Data

The UV trends calculated from the Nimbus-7 TOMS satellite data (1979-1992) were reported in the previous Assessment (Herman et al., 1996; Herman and McKenzie et al., 1999; Ziemke et al., 2000). Follow-on TOMS missions (Meteor-3, Advanced Earth Observing Satellite (ADEOS), and Earth Probe) have extended the TOMS UV record, with an 18-month gap in 1995-1996 (Herman et al., 1999). Extensions of the trends calculated on a global scale and presented in the previous Assessment are not yet available.

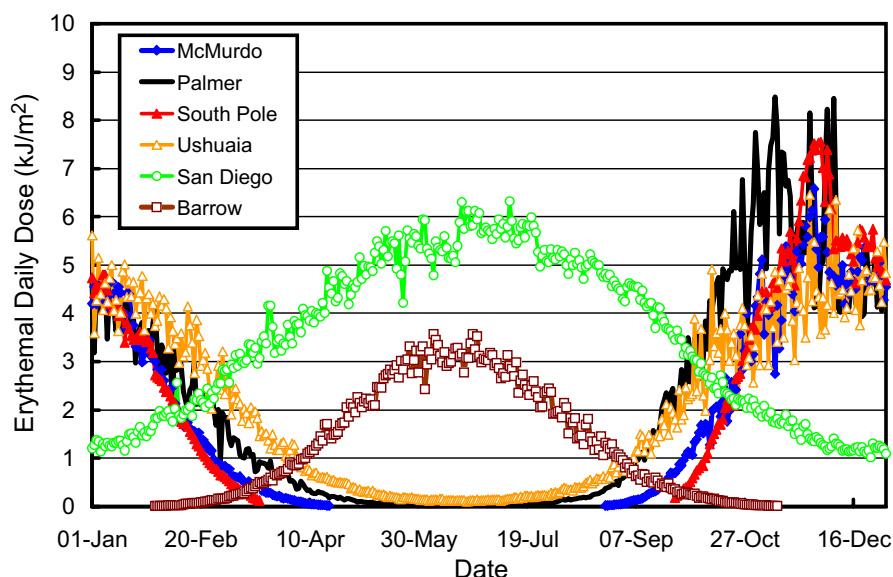


Figure 5-6. The maximum daily dose of erythemal irradiance (in kilojoules per square meter) measured at stations in the National Science Foundation (NSF) UV monitoring network. Peak values occur at austral sites in middle to late spring when the combination of higher Sun angles and low values of total ozone still prevail from an extended breakup of the Antarctic ozone hole. The peak values at these high-latitude sites exceed those at significantly lower latitudes during summer (e.g., San Diego).

Both the TOMS-derived and TOMS/ERBE-derived global UV climatologies have documented the seasonal surface UV variability in different regions in the world caused by cloudiness, ozone, UV-absorbing aerosols, and surface albedo (Lubin and Jensen, 1995; Lubin et al., 1998; Herman et al., 1999, 2001a, b). In addition, inter-annual variability associated with the quasi-biennial oscillation has been observed (Herman et al., 2000). These datasets permit us to identify the areas and periods where particularly high levels of UV radiation can be expected in cases of low ozone events and low amounts of cloud cover (e.g., parts of South America, Africa, and Australia). Year-to-year variations of UV values in March are up to $\pm 35\%$ over Europe because of highly variable ozone and cloudiness. There have also been changes in UV irradiance associated with long-term systematic changes in cloudiness (Herman et al., 2001a), with large regions of cloud-induced increases over Europe and parts of North America, as well as some small but well-defined regions of UV decrease over the oceans near South America and Antarctica. This represents significant progress in understanding since the previous Assessment (WMO, 1999). At that time the decrease of UV due to the increase in cloudiness over Europe was identified from ground-based measurements of total (pyranometric) radiation but was not found in the satellite estimates.

Trends in snow cover and/or albedo can also affect UV trends at high latitudes. The effects of these forcings on UV trends are significant, but their relative contribution varies geographically and seasonally. Vinnikov et al. (2002) found a statistically significant decrease in sea ice cover over the Northern Hemisphere, whereas sea ice cover has increased in the Southern Hemisphere. Thus it is expected that UV irradiance has decreased in some areas of the Northern Hemisphere and has increased in some areas of the Southern Hemisphere. These conclusions can be drawn from our understanding of the radiative transfer, but ground-based observations are lacking, especially over oceans. Satellite estimations of UV in these areas and seasons are complicated by the difficulties in distinguishing between snow/ice and cloud albedo.

Whereas the effects of UV-absorbing aerosols on surface UV irradiance have been investigated (Krotkov et al., 1998; Herman et al., 1999), their effects on UV-irradiance trends have not been estimated. In some situations, there are indications that aerosol effects are an important source of error (McKenzie et al., 2001a). In the tropics, there does not appear to be a long-term trend in dust aerosol amounts, even though biomass burning in South America has caused some increases in smoke (Herman et al., 1997), which considerably absorbs UV radiation. Absorbing aerosol trends at middle and high

latitudes may be affected by industrial activity. If so, they would contribute to long-term changes in UV amount. The current TOMS UV algorithm accounts for absorbing and scattering aerosol effects, and could be used for extended trend estimates by combining the Nimbus-7/TOMS and Earth-Probe/TOMS data.

5.4.3 Estimates from Radiative Transfer Models

Sabziparvar et al. (1999) have calculated the climatology of surface UV radiation using the discrete-ordinate RT model of Stamnes et al. (1988) modified by Forster (1995). Calculations were made for daily doses of UV-B (280-315 nm) and UV-A (315-400 nm), and weighted with various biological action spectra. Calculations were performed for the four midseason months: January, April, July, and October. Clear-sky and aerosol-free irradiance values were calculated using TOMS total ozone averages as input. All-sky conditions were calculated using average cloud distributions measured by the International Satellite Cloud Climatology Project (Rossow and Schiffer, 1991) and aerosol optical depth of 0.1 at 400 nm. Figure 5-7 shows the annual average of daily dose calculations for erythemally weighted UV irradiance.

The same RT model was used by Sabziparvar et al. (1998) to calculate changes in surface UV radiation due to changes in ozone (both stratospheric and tropospheric) and tropospheric aerosols since preindustrial times (1850). Decreases in erythemally weighted irradiance of up to 9% were calculated for tropical regions as a result of increases in tropospheric ozone. Decreases in erythemally weighted irradiance of 4-8% from increased tropospheric ozone were calculated north of 20° in the Northern Hemisphere during July. Increases of erythemal irradiance of 70% at southern high latitudes in October and 10% at northern high latitudes were calculated as a result of stratospheric ozone depletion. Effects of increases in absorbing aerosols and sulfate aerosols were also considered, and it was concluded that an increase in aerosols has decreased erythemally weighted UV by up to 7% locally and 2% on a global average. The study does not include long-term changes in cloud cover or surface albedo.

5.4.4 Estimates from Ground-Based Ancillary Data

Gantner et al. (2000) reconstructed noontime irradiance values at 300, 305, 310, and 320 nm for clear-sky and no-snow conditions at Hohenpeissenberg going back to 1968. Statistical dependencies of irradiance on total ozone were determined from measurements taken

SURFACE ULTRAVIOLET RADIATION

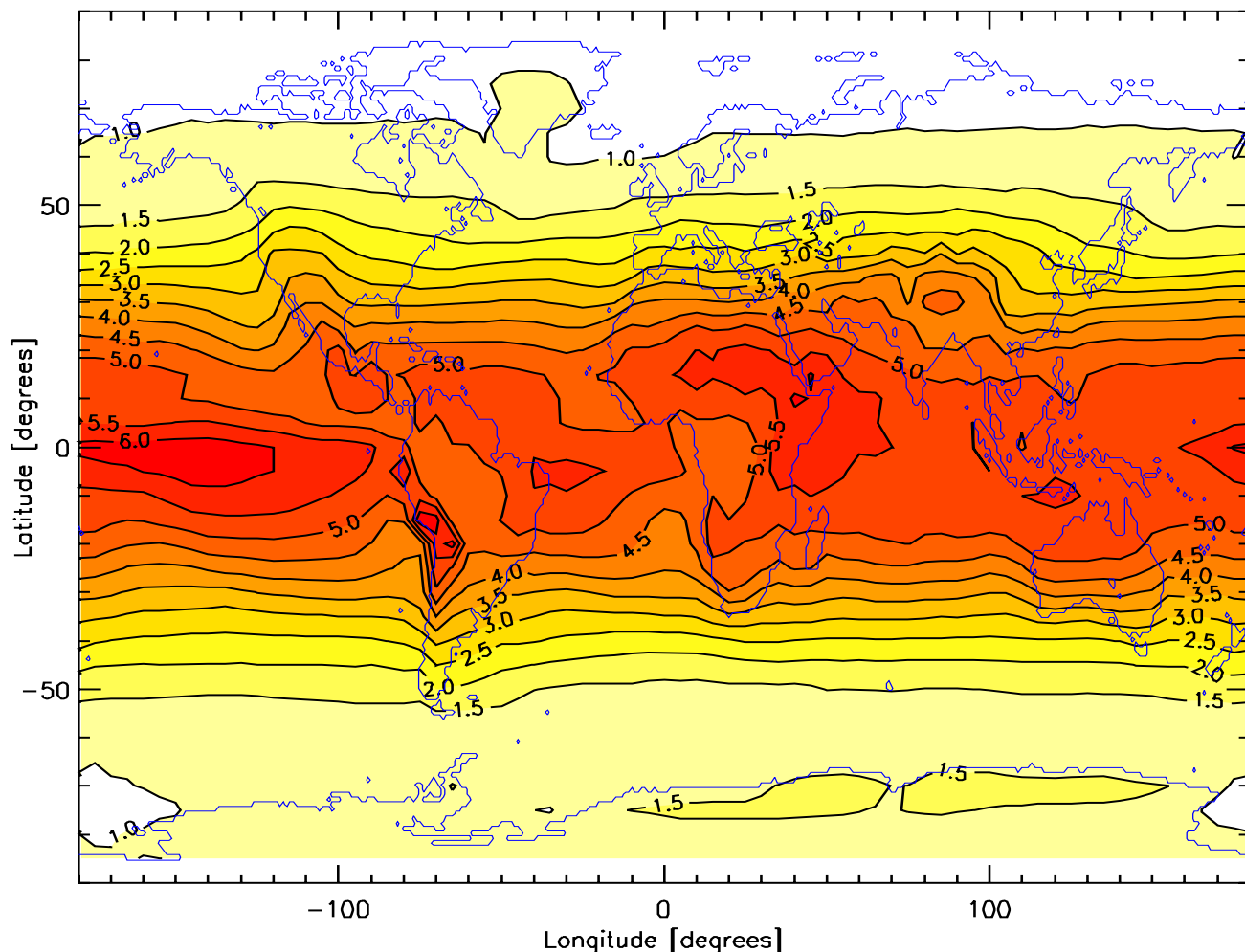


Figure 5-7. Climatology of annual average erythemal dose (in KJoule/(m² day)). Values are computed from total ozone and cloud satellite data. Adapted from Sabziparvar et al. (1999).

between 1990 and 1997 when spectral UV, total ozone, and global and diffuse radiation data are available, and the relationships were used to extrapolate estimates of UV irradiance backward in time. For all months between March and September, statistically significant long-term increases in clear-sky noontime values of UV were found that increase with decreasing wavelengths.

The studies by Kaurola et al. (2000) (using data from Norrköping, Sweden; Jokioinen, Finland; and Belsk, Poland) and den Outer et al. (2000) (using data from Bilthoven, Netherlands) took another approach to reconstruct past UV data that includes effects of clouds and other scattering processes. RT models were used to calculate clear-sky daily integral values of erythemally weighted UV irradiance and global solar irradiance (280–4000 nm) using total ozone, other meteorological data, and the daily variation of SZA as input. The ratio of the daily integral of pyranometer measurements to the mod-

eled clear-sky integral was used to quantify scattering processes that are related statistically to variations in UV observed in recent years. The relationships were used to estimate daily UV values under all weather conditions backward in time to 1979 using pyranometer data and satellite total ozone data, or to the 1960s if ground-based total ozone measurements were available. In general, the reconstructed datasets show that erythemally weighted UV has increased since the 1970s and that the increases and year-to-year temporal variations are consistent with satellite estimates for the same sites (Kaurola et al., 2000).

Diaz et al. (2000, 2002) demonstrated a method that calculates the daily integral of UV radiation (at specific wavelength intervals, broadband or biologically weighted irradiance) from daily average total ozone, daily average SZA (for daylight hours), and the daily integral of broadband measurements (UV-B, biologically weighted UV, or global solar pyranometer). A multilinear

regression model was used to fit the daily UV values as a function of the three measured independent variables, and regression coefficients were determined using data from South Pole, Antarctica; Ushuaia, Argentina; and San Diego, U.S. It was shown that monthly averages of UV irradiance between 303 and 308 nm can be predicted to an accuracy of 4-5% using broadband radiation data. The method was applied to TOMS total ozone data and pyranometer data from South Pole and Barrow, Alaska. The regression was determined using data from 1993 to 1998, and results of the regression were used to estimate UV radiation (303-308 nm) back to October 1979. Significant increases (~300%) were found for the month of October at South Pole and lower values (between 90% and 120%) for April at Barrow between 1979 and 1996.

Results of statistical models described by Fioletov et al. (1997, 2001) and McArthur et al. (1999) establish empirical dependencies of UV radiation (both at individual wavelengths and spectral intervals) on SZA, total ozone, global solar radiation, dewpoint temperature, and snow cover. The relationships were determined from observations at six sites in Canada (Edmonton, Winnipeg, Churchill, Toronto, Montreal, and Halifax) where total ozone, spectral UV irradiance, and global solar irradiance (pyranometer) measurements have been made since the early 1990s. It was shown that monthly mean values of erythral irradiance for summer months (May-August) can be estimated from the ancillary data with a standard error (1-sigma) of 4.2%. The statistical relationships have been used to estimate hourly UV irradiance values dating back to the mid 1960s at Toronto, Churchill, and Edmonton when both total ozone and pyranometer data are available (Fioletov et al., 2001). The hourly values were integrated to make daily total and noontime (within 1 hour of noon) values, and monthly averages of the daily and noontime values were determined. Monthly average daily UV doses for summer months (May, June, July, and August) predicted from the ancillary data agree with simultaneous spectral measurements with an rms difference of 3.3%. This agreement is better than the 4% rms difference for summer monthly ground-based spectral measurements and satellite estimates (Fioletov et al., 2002). Trends in UV for individual wavelengths and weighted spectral intervals were determined for the period from 1979 to 1997 and are shown in Figure 5-8. It is of interest to note that trends in the daily integrated values and noontime values are essentially the same. The annual trend values at wavelengths of 310 nm or less and for the erythemally weighted UV are all statistically significant to the 2-sigma level.

In addition to the estimation of past hour-by-hour UV irradiance, the ancillary data can be used to quantify

and distinguish between trends in UV that are caused by factors other than long-term changes in total ozone. Figure 5-8 shows that Churchill had statistically significant trends at all wavelengths, including those with insignificant ozone absorption (325 nm). The positive trend of about 7% per decade at 325 nm is due to the combined effect of an increase of days with snow cover (causing an increase in UV irradiance by about 2% per decade) and a decrease in hours of cloudiness (causing an increase of about 5% per decade) that occurred at Churchill over the period (1979-1997). The 11% per decade increase of erythemally weighted irradiance was found to consist of +2% per decade from increasing snow cover, +5% per decade from decreasing clouds, and +4% per decade from decreasing ozone.

A continuous UV time series made up of irradiance measurements from recent years (1990s) and of irradiance estimates using ancillary data from earlier years (as early as the mid-1960s) is useful to quantify extreme events that are pertinent to some biological studies. Fioletov et al. (2001) demonstrated that the incidence of extreme events has increased since 1970 by showing that the number of hours per year the UV Index is above a threshold value has increased at Toronto, Edmonton, and Churchill (Figure 5-9). This is in accordance with the findings for an alpine site (Seckmeyer et al., 1997), which concluded the same with the support of the ancillary measurements made at Hohenpeissenberg.

5.5 EXPECTATIONS OF UV IN THE FUTURE

Just as the climatology of surface UV radiation has changed in the past, there will likely be changes over the next several decades. The future evolution of UV irradiance will depend on changes in total ozone as well as other atmospheric variables that are influenced by changes in climate. Quantification of predicted changes in total ozone, influenced both by halogen chemistry as well as other climate variables, is discussed and presented in previous chapters in this Assessment. Here we address the changes in UV irradiance that are likely to occur over the next 50 years, both as a result of the expected recovery of the ozone layer (Section 5.5.1) and variations driven by other variables influenced by climate change that directly affect surface UV irradiance (Section 5.5.2).

5.5.1 Links with the Recovery of the Ozone Layer

It is well known that a reduction in total ozone column leads to increased levels of surface UV irradiance if other factors remain constant. This relationship has

SURFACE ULTRAVIOLET RADIATION

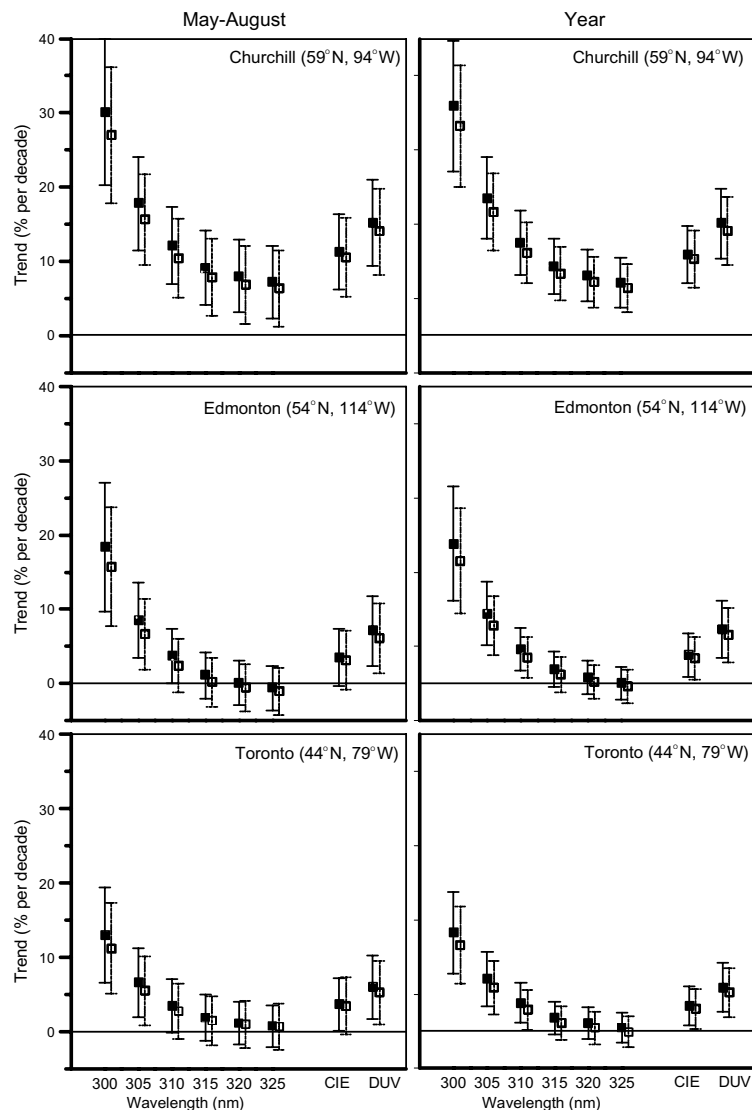


Figure 5-8. Trends in UV irradiance at 300, 305, 310, 315, 320, and 325 nm, and trends in erythemally (CIE) and DNA weighted irradiance for 1979-1997, for May-August and year-round, at Churchill (58.75°N), Edmonton (53.55°N), and Toronto (43.75°N), with 2σ error estimates indicated. Solid squares are trends in daily integrals, and open squares are trends from values within ±1 hour of solar noon. Adapted from Fioletov et al. (2001).

been clearly demonstrated and reported in previous Assessments (WMO, 1992, 1995, 1999).

There has been a significant amount of work done to predict the future of the ozone layer based on considerations of the reduction of atmospheric chlorine and bromine compounds as well as the interactions with climate change. Previous chapters in this Assessment discuss these future ozone scenarios in detail. Future UV levels as a result of changes in ozone have been predicted (Taalas et al., 2000b; Reuder et al., 2001), but, because surface UV radiation is dependent on the many complex scattering and absorbing processes discussed previously in this chapter, prediction of future UV radiation is more difficult and leads to deviating results about the probable UV levels over the coming decades.

Chapter 4 of this Assessment presents results of several two-dimensional (2-D) models that simulate the

decline of total ozone between 1979 and 2000 and project its recovery using several halogen and climate change scenarios between 2000 and 2050. The derived ozone projections do not include polar effects (e.g., increased occurrence of polar stratospheric clouds) and their influence at higher latitudes. The results have been used with RT model calculations to estimate future UV irradiance over the next 50 years. Monthly values of total ozone at 5° latitude intervals were averaged from the output of seven 2-D model runs for the MA2 scenario (described in Chapter 4) and used as input to the RT model used by NASA to estimate surface UV irradiance from TOMS satellite data (Herman et al., 1996, 1999; Krotkov et al., 1998, 2001). Monthly values for noontime erythemal irradiance were determined using the total ozone from Chapter 4, and noontime SZA at the middle of each month, for clear skies and low (3%) albedo. Figure 5-10 shows

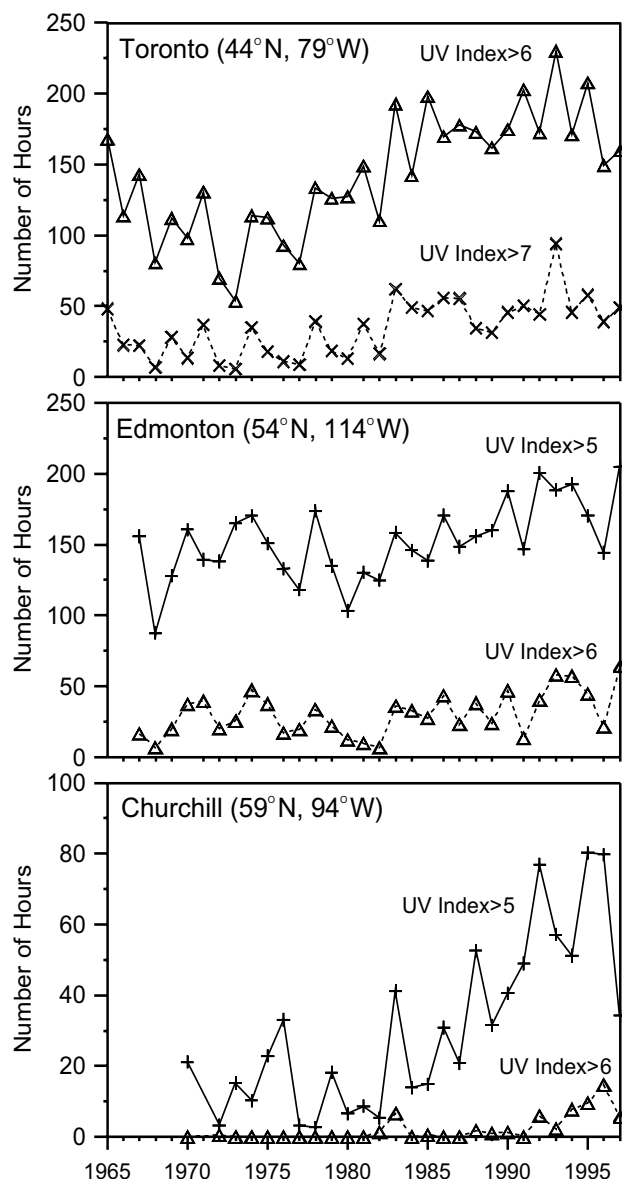


Figure 5-9. The number of hours per year that the UV Index exceeded 6 and 7 at Toronto, 5 and 6 at Edmonton, and 5 and 6 at Churchill. These numbers are determined from reconstructed erythemal UV irradiance determined from total ozone and other ancillary data. Adapted from Fioletov et al. (2001).

the departure (in percent) of these clear-sky calculations of noontime erythemally weighted UV from the 1980 mean values for the period from 1979 to 2050 for the months of January, April, July, and October.

Results of the 2-D model calculations (Figure 5-10) indicate that generally there will be small changes in UV radiation over the next decade. However, in the longer term (next 50 years) UV levels will return to values sim-

ilar to those that were present in 1980, provided that all other factors (clouds, snow cover, aerosols, etc.) are assumed to remain constant. It should be stressed that this assumption is an unlikely scenario. Past changes of surface UV that are associated with changes other than total ozone have occurred at some sites, as illustrated in Figure 5-5 (Thessaloniki) and Figure 5-8 (Churchill). It should further be emphasized that there have been many surprises in the occurrence of extreme events in the past due to the complex and nonlinear behavior of the atmosphere. These surprises cannot be included in such a projection.

Impacts of greenhouse gases and halogenated species on future UV levels have been studied by Taalas et al. (2000b). The UV scenarios are based on ozone predictions from 3-D chemistry-climate calculations carried out by three different models that were discussed in Chapter 3: the Goddard Institute for Space Studies (GISS; Shindell et al., 1998) model, the U.K. Meteorological Office (Austin et al., 2000) model, and the German Aerospace Institute model.

Figure 5-11 shows results of future erythemal UV levels relative to 1979-1992 averages calculated using the GISS model ozone predictions for April in the Northern Hemisphere and October in the Southern Hemisphere (from Taalas et al., 2000b). For the Northern Hemisphere in April there are enhancements up to 90% at 70°N calculated for the 2010-2020 time period that reduce to <25% in 2040-2050. For the Southern Hemisphere in October the enhancements are up to 100% over Antarctica for the 2010-2020 period and reduce to <50% by 2040-2050. Maximum increases in the annual (not shown) northern high-latitude UV doses were estimated to be up to 14% in 2010-2020, and reduce to 2% in 2040-2050 because of the expected recovery of the ozone layer. At southern high latitudes, 40% annual maximum enhancements are expected during 2010-2020 that reduce to 27% by 2040-2050.

The following points should be noted regarding the rather large deviations stated above, particularly for the Arctic. First, the above values (Figure 5-11) are relative to the period 1979-1992. Since the models indicate that we are nearing minimum ozone values in 2002 (Chapter 3), deviations relative to today's values are appreciably less than those stated above for the 2010-2020 period and are negative for the 2040-2050 period. Second, the deviations are spatially dependent, and the values stated above are at places where the maxima are predicted to occur. When UV levels are averaged from 60°N to 90°N, the GISS model agrees reasonably well with other models (Taalas et al., 2000b). Finally, the GISS prediction of minimum UV levels for the Northern Hemisphere would be higher than those of other 3-D models, since the GISS

SURFACE ULTRAVIOLET RADIATION

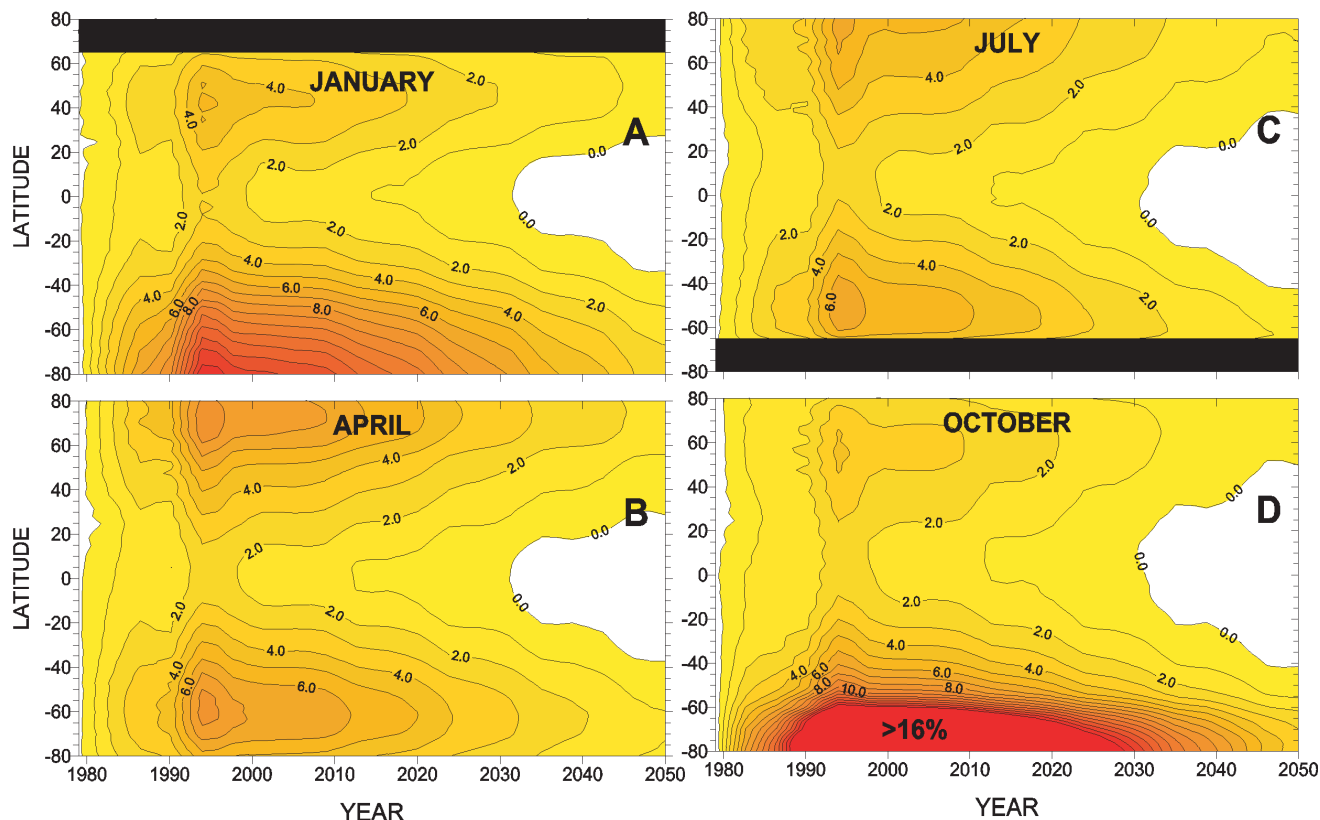


Figure 5-10. Calculations of the departures (in percent) from 1980 UV noontime clear-sky irradiance levels between 1979 and 2050 for the months of (a) January, (b) April, (c) July, and (d) October. The average of seven model runs calculating total ozone from the MA2 scenario discussed in Chapter 4 were used as input to the TOMS radiative transfer model (Herman et al., 1996, 1999; Krotkov et al., 1998, 2001). These results show that UV levels will have insignificant variation over the next 10 years and will return to nearly the same levels as those present in 1980 by 2050. It should be stressed that these calculations assume all variables other than total ozone remain constant, which is unlikely.

model predicts the lowest ozone levels for the Arctic (Chapter 3).

5.5.2 Factors Related to Climate Change

The effects of climate change on surface UV radiation are twofold. The first (indirect) effects are caused by changes in climate that affect total ozone. The consequential changes in total ozone are addressed in Chapters 3 and 4 of this Assessment, and the impact of these changes on surface UV radiation are discussed in Section 5.5.1 above. The second effects of climate change on UV are direct effects (e.g., changes in clouds, aerosols, snow cover, etc.) and those are discussed in this section.

The recent IPCC report (IPCC, 2001) lists many factors that are likely to change due the increased emission of greenhouse gases. Many of these factors have already started to change or are likely to have changed in

the past. In addition to these feedbacks that are already discussed in previous chapters (e.g., the higher likelihood of polar stratospheric clouds and their associated role in enhancing the chemical destruction of ozone), there are other factors related to climate change that are directly influencing UV irradiance at the Earth's surface.

In Section 5.2.1.5 it is discussed that snow albedo leads to a significant enhancement of UV irradiance above the surface due to multiple scattering. The IPCC report (IPCC, 2001) states that the sea ice cover in the Northern Hemisphere has reduced significantly and is likely to reduce more in the future. In addition, the snow cover and the extent of glaciers in mountainous areas have been decreasing. Consequently, it can be predicted that UV irradiance above the surface will decrease in these areas for seasons where snow cover or sea ice is reduced. Although UV irradiance above the surface is enhanced by snow-covered areas, a decrease in sea ice and snow cover

SURFACE ULTRAVIOLET RADIATION

will result in an increase of UV dose for organisms living under water and on land areas previously covered by snow. According to the IPCC report (2001), the largest reductions of snow albedo will be at high latitudes in spring and

summer, and consequently surface UV irradiance will likely be reduced by the decrease in albedo at high latitudes in spring and summer in some areas of the Northern Hemisphere.

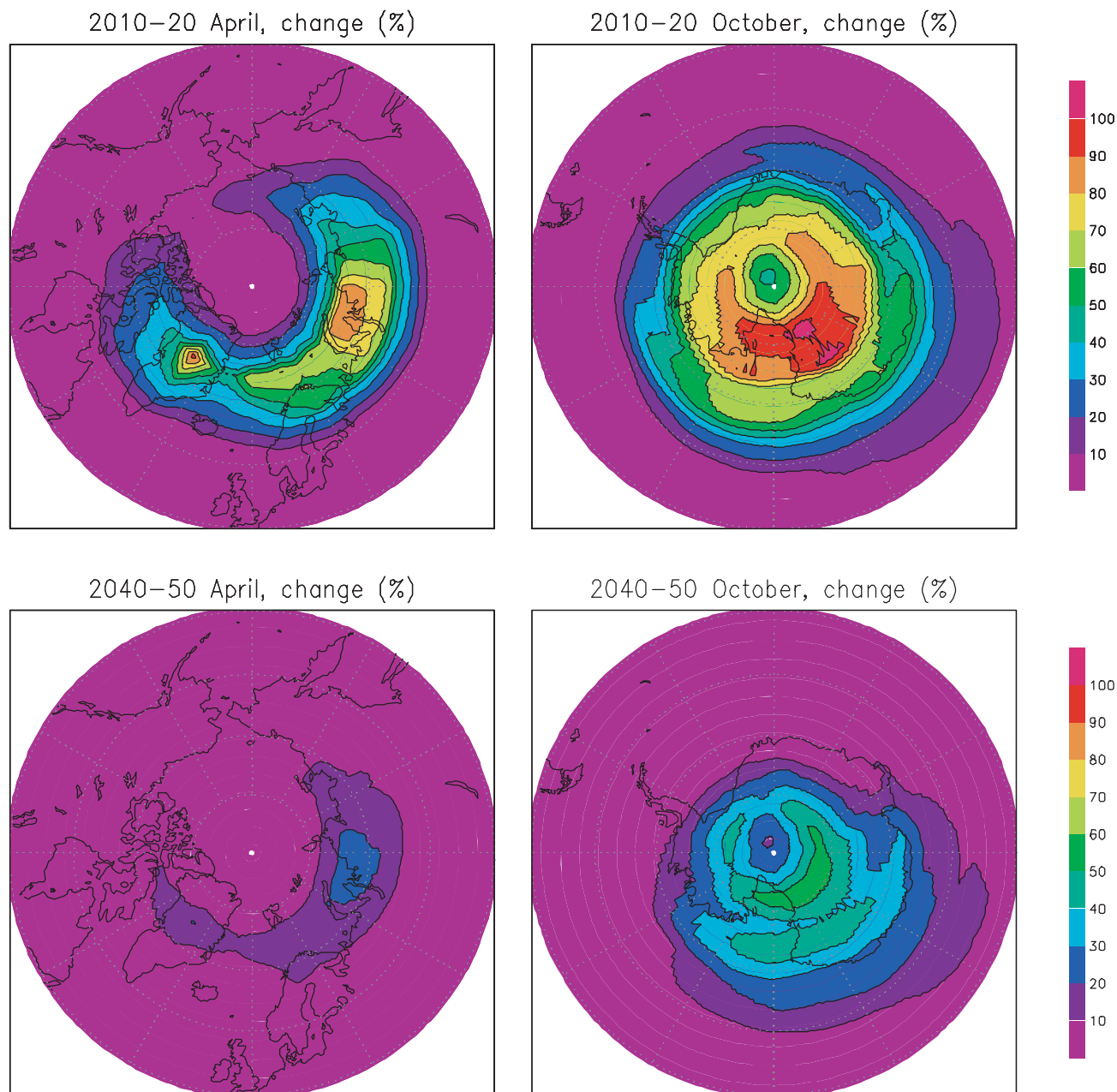


Figure 5-11. Results of erythemal UV changes due to ozone changes predicted by the Goddard Institute for Space Studies (GISS) 3-D chemistry-climate model for April in the Northern Hemisphere and October in the Southern Hemisphere. Future increases of greenhouse gases are expected to delay the recovery of the ozone layer (Chapter 3), and the resulting enhanced UV values at high latitudes are predicted to persist for about two more decades. The indicated changes are relative to the time period 1979-1992, so the changes relative to present-day levels are less than those shown for 2010-2020 and would likely be negative for 2040-2050. Adapted from Taalas et al. (2000b).

SURFACE ULTRAVIOLET RADIATION

Table 5-1. Factors related to climate change that influence UV irradiance at the surface globally. Regional changes are expected to be over a much larger range than the numbers given here. Also the relative importance of the factors may be different in different regions (e.g., snow cover would become a major factor in mountainous areas). It should be emphasized that there have been many surprises in the occurrence of extreme events in the past due to the complex and nonlinear behavior of the atmosphere. These surprises cannot be included in such a projection.

	Correlation with UV Change	Predicted Change in Globally Averaged Erythmal UV from Present	
		2010	Long Term
Major Factors			
Stratospheric ozone	Negative	0 to −3%	Figure 5-10
Cloudiness	Negative	±1%	Negative
Aerosols	Negative	±3%	Negative
Tropospheric ozone	Negative	±1%	−2 to +7%
Minor Factors			
Aviation (IPCC, 1999)		±1%	±1%
Ozone profile		±1%	±1%
Stratospheric temperature	Negative	Positive	Positive
Snow cover and sea ice	Positive	Negative in some areas and seasons	
Tropospheric temperature	Negative	Negative	Negative
Weather extremes		Positive peak values	

Another statement of the IPCC 2001 report has an impact on surface UV: it is thought that cloudiness has increased by about 2% over the past century and is likely to continue increasing in the future. The effects of clouds on UV irradiance depend both on their amount and type. The observed increase of cirrus clouds in the Northern Hemisphere is likely to reduce UV irradiance slightly. However, this increase would lead mainly to a redistribution of UV radiance from the direct beam to diffuse. More important is the likely increase of overall global cloudiness over the next century. The effect of this increase will lead to a reduction of surface UV globally. However, it should be noted that it is very likely that cloudiness will increase in some regions and decrease in others. Recent results by Chen et al. (2002) and Wielicki et al. (2002) demonstrate unexplained decreases in cloud cover in the tropics. These changes will have a great influence on the UV irradiance locally, possibly exceeding those caused by changes in ozone.

Weather extremes may occur more frequently than they have in the past century. In the future, climate episodes of high precipitation might alternate with extremely dry episodes in many parts of the Earth. Higher UV irradiance can be expected during dry spells than during wet spells, and this may be problematic for some biological species. At present it is not possible to predict

these changes quantitatively. Nevertheless the biological impact of these changes might exceed those caused by the expected changes in stratospheric ozone.

Aerosol effects on surface UV radiation may be larger than previously thought, and may affect large areas of the globe because of the following:

- (1) Many anthropogenic aerosols absorb in the UV (Jacobson, 1999).
- (2) Altitude gradients of UV irradiance are generally larger than expected (Lenoble et al., 2002; McKenzie et al., 2001b; Seckmeyer et al., 1997). The relatively high altitude gradients could be partly explained by the attenuation of UV irradiance by aerosols near the ground.
- (3) Satellite estimates of surface UV-B irradiance are too large over large areas of the globe, possibly caused by a widespread influence of the aerosols that is not accounted for in the satellite estimates (McKenzie et al., 2001a; Fioletov et al., 2002).

Over the first half of the 20th century, aerosol extinction increased (Liu et al., 1991; Sabziparvar et al., 1998). In recent years aerosol extinction has started to decrease with a cleaner troposphere in some areas (e.g., Krzyścin and Puchalski, 1998; Zerefos et al., 1998). What might happen in the future is open to conjecture,

depending on the disparate forcings of increased population, increased awareness of environmental issues, and reduced reliance on fossil fuels. However, it is now likely that UV radiation at the ground will increase in the coming years, before the expected recovery of the ozone layer might take place.

The IPCC report on impacts of aviation on the atmosphere (IPCC, 1999) considered changes in UV that could result from increased aviation activity both in the upper troposphere and lower stratosphere. These changes were generally found to be less than $\pm 1\%$ due to effects that influence UV negatively or positively.

Table 5-1 shows a summary of factors related to climate change that influence UV irradiance at the surface on a global scale. An attempt has been made to quantify changes that may occur both in the shorter term (next 10 years) and longer term (to 2050). It should be emphasized that the UV changes are expected to be larger in certain areas under specific situations (e.g., by changing pollution, cloud cover, or surface albedo).

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Appendix 5A

SPECTRAL DATA AVAILABLE FROM DATABASES

5A.1 World Ozone and Ultraviolet Radiation Data Centre (WOUDC) ^a

Station	Name	Instrument	Country	Institute ^b	Lat. (°N)	Long. (°E)	Start Date
7	Kagoshima	Brewer	Japan	JMA	31.5	130.5	1/01/91
12	Sapporo	Brewer	Japan	JMA	43.02	141.3	1/01/91
14	Tateno	Brewer	Japan	JMA	36.02	140.07	1/01/90
18	Alert	Brewer	Canada	MSC	82.47	-62.35	6/09/95
21	Edmonton (Stony Pl.)	Brewer	Canada	MSC	53.52	-114.13	3/19/92
24	Resolute	Brewer	Canada	MSC	74.69	-95.01	3/14/91
31	Mauna Loa	Brewer (double)	United States	MSC	19.5	-155.6	1/01/98
31	Mauna Loa	Brewer	United States	MSC	19.5	-155.6	3/24/97
31	Mauna Loa	Bentham	United States	NIWA	19.5	-155.6	11/01/97
65	Toronto	Brewer	Canada	MSC	43.75	-79.5	3/01/89
76	Goose Bay	Brewer	Canada	MSC	53.15	-60.51	1/01/97
77	Churchill	Brewer	Canada	MSC	58.72	-94.1	3/30/92
95	Taipei	Brewer	Taiwan	CWBT	24.99	121.49	3/06/92
101	Syowa	Brewer	Japan	JMA	-69.03	-39.55	1/01/93
111	Amundsen-Scott	Biospherical ^c	Antarctica	NSF	-89.96	-24.8	1/01/91
190	Naha	Brewer	Japan	JMA	26.17	127.65	1/01/91
199	Barrow	Biospherical ^c	United States	NSF	71.32	-156.6	1/01/91
239	San Diego	Biospherical ^c	United States	NSF	32.45	-117.11	1/01/92
241	Saskatoon	Brewer	Canada	MSC	52.08	-106.74	1/01/91
256	Lauder	Bentham	New Zealand	NIWA	-45.03	169.68	1/01/94
261	Thessaloniki	Brewer	Greece	AUTH	40.52	22.97	10/01/89
268	Arrival Heights	Biospherical ^c	Antarctica	NSF	-77.83	166.67	1/01/89
290	Saturna Island	Brewer	Canada	MSC	48.75	-123.16	10/03/90
292	Palmer	Biospherical ^c	Antarctica	NSF	-64.75	-64.05	1/01/91
301	Ispira	Brewer (double)	Italy	JRC-EC	45.8	8.63	1/01/01
306	Chengkung	Brewer	Taiwan	CWBT	23.07	121.34	1/02/92
307	Obninsk	Brewer	Russia	IEM-SPA	55.09	35.97	5/06/93
319	Montreal (Dorval)	Brewer	Canada	MSC	45.45	-73.78	3/06/93
320	Winnipeg	Brewer	Canada	MSC	49.87	-97.27	7/06/92
321	Halifax (Bedford)	Brewer	Canada	MSC	44.65	-63.67	7/02/92
331	Poprad-Ganovce	Brewer	Slovakia	SHMI	49	20.29	1/01/94
332	Pohang	Brewer	Korea	KMA	36	129.35	1/27/94
338	Bratts Lake (Regina)	Brewer	Canada	MSC	50.18	-104.74	1/01/95
339	Ushuaia	Biospherical ^c	Argentina	NSF	-54.85	-68.31	1/01/90
353	Reading	Optronics	United Kingdom	UMIST	51.42	0.96	1/27/94

^a Website: <http://www.msc-smc.ec.gc.ca/woudc/>

^b JMA, Japan Meteorological Agency; MSC, Meteorological Service of Canada; NIWA, National Institute of Water and Atmospheric Research; CWBT, Central Weather Bureau of Taiwan; NSF, National Science Foundation; AUTH, Aristotle University of Thessaloniki; JRC-EC, Joint Research Centre-European Commission; IEM-SPA, Institute of Experimental Meteorology-Scientific Production Association; SHMI, Slovak Hydrometeorological Institute; KMA, Korea Meteorological Administration; UMIST, University of Manchester Institute of Science and Technology.

^c Data from Biospherical Instruments are also available via the website <http://www.biospherical.com/nsf>

SURFACE ULTRAVIOLET RADIATION

5A.2 European Ultraviolet Database (EUVDB) ^a

No.	Station Name	Instrument	Country	Institute ^b	Lat. (°N)	Long. (°E)	Start Date
1	Sonnblick	Bentham	Austria	BOKU	47.05	12.97	Feb. 96
2	Vienna	Bentham	Austria	BOKU	48.23	16.35	Mar. 98
3	Uccle, Brussels	Jobin & Yvon	Belgium	IASB	50.80	4.36	Mar. 93
4	Jokioinen	Brewer	Finland	FMI	60.81	23.50	Apr. 95
5	Sodankylä	Brewer	Finland	FMI	67.37	26.63	Apr. 90
6	Villar St. Pancrace	Jobin & Yvon	France	USTL	44.90	6.65	Sep. 99
7	Villeneuve d'Asq	Jobin & Yvon	France	USTL	50.37	3.01	Apr. 97
8	Neuherberg	Bentham	Germany	BfS	48.22	11.58	Jan. 01
9	Offenbach	Bentham	Germany	BfS	50.10	8.75	Jul. 01
10	Hohenpeissenberg	Brewer	Germany	DWD	47.80	11.02	Jan. 95
11	Lindenberg	Brewer	Germany	DWD	52.22	14.12	Jan. 95
12	Potsdam	Brewer	Germany	DWD	52.36	13.08	Jan. 95
13	Garmisch-Partenkirchen	Bentham	Germany	IFU	47.48	11.07	Apr. 94
14	Zugspitze	Bentham	Germany	IFU	7.42	10.98	Apr. 94
15	Thessaloniki	Brewer	Greece	LAP	40.52	22.97	Oct. 89
16	Lampedusa		Italy	ENEA	35.50	12.60	Feb. 98
17	Ispra	Brewer	Italy	JRC	45.81	8.63	Jan. 92
18	Rome	Brewer	Italy	URO	41.90	12.52	Feb. 92
19	Andøya	Bentham	Norway	NILU	69.48	16.02	Feb. 98
20	Trondheim	Optronic	Norway	NTNU	64.43	10.47	Mar. 97
21	Tromsø	Brewer	Norway	UT	69.66	18.93	May 94
22	Belsk	Brewer	Poland	IGFPAS	51.83	20.78	Jan. 93
23	Azores	Brewer	Portugal	MI	38.66	-27.22	
24	Funchal (Madeira Is.)	Brewer	Portugal	MI	32.64	-16.89	Jan. 97
25	Lisbon	Brewer	Portugal	MI	38.77	-9.15	Jun. 00
26	Penhas Douradas	Brewer	Portugal	MI	40.42	-7.55	
27	Izana	Brewer	Spain	INM	28.49	-16.50	Jan. 95
28	Norrköping	Brewer	Sweden	SMHI	58.58	16.15	Sep. 91
29	Vindeln	Brewer	Sweden	SMHI	64.23	19.77	Jul. 96
30	De Bilt	Brewer	Netherlands	KNMI	52.10	5.18	Jan. 94
31	LSO (Bilthoven)	Dilcon	Netherlands	RIVM	52.12	5.20	Jan. 96
32	Reading	Optronics	United Kingdom	UMIST	51.45	-0.93	Jan. 94

Only permanent stations are listed; campaign data are not included.

Data from Neuherberg, Offenbach, Lampedusa, Andøya, Azores, and Penhas Douradas will be submitted in the coming months.

^a Website: <http://www.muk.uni-hannover.de/EDUCE>

^b BOKU, Universität für Bodenkultur Wein; IASB, Institut d'Aéronomie Spatiale de Belgique; FMI, Finnish Meteorological Institute; USTL, Université des Sciences et Technologies de Lille; BfS, Bundesamt für Strahlenschutz; DWD, Deutscher Wetterdienst; IFU, Atmosphärische Umweltforschung; LAP, Laboratory of Atmospheric Physics; ENEA, Ente per le Nuove Technologie l'Energia e l'Ambiente; JRC, Joint Research Centre, European Commission; URO, University of Rome; NILU, Norsk Institutt for Luftforskning; NTNU, Norges Teknisk-Naturvitenskapelige Universitet; UT, University of Tromsø; IGFPAS, Institute of Geophysics, Polish Academy of Sciences; MI, Institute of Meteorology, Portugal; INM, Instituto Nacional de Meteorologia; SMHI, Swedish Meteorological and Hydrological Institute; KNMI, Koninklijk Nederlands Meteorologische Instituut; RIVM, Rijkinstituut voor Volksgezondheid en Milieu; UMIST, University of Manchester Institute of Science and Technology.

Appendix 5B

INTERNET ADDRESSES FOR UV SITES

5B.1 General UV Information

WMO UV radiation page	http://titan.srrb.noaa.gov/UV/
TOMS (Ozone and UV satellite data)	http://toms.gsfc.nasa.gov/
NSF UV monitoring network, U.S.	http://www.biospherical.com/NSF/
USDA UV-B monitoring and research program	http://uvb.nrel.colostate.edu/
NIWA, New Zealand	http://www.niwa.co.nz/services/uvozone/
EPA, U.S.	http://www.epa.gov/uvnet/ and http://oz.physast.uga.edu/
EPA SunWise School Program	http://www.epa.gov/sunwise/
WMO Ozone Bulletins	http://www.wmo.ch/web/arep/ozone.html
Center for International Earth Science Information Network (CIESIN), U.S.	http://sedac.ciesin.columbia.edu/ozone/
Atmospheric Sciences Research Center, U.S.	http://uvb.asrc.cestm.albany.edu/
World Radiation Centre	http://wrdc-mgo.nrel.gov/

5B.2 International UV Projects

World Ozone and UV Data Center	http://www.msc-smc.ec.gc.ca/woudc/
European Cooperation in the field of Scientific and Technical research (COST-713)	http://159.213.57.69/uvweb
SUVDAMA, European Commission	http://www.ozone.fmi.fi/SUVDAMA/
EDUCE, European Commission	http://www.muk.uni-hannover.de/EDUCE/
Thematic Network For Ultraviolet Measurements	http://metrology.hut.fi/uvnet/
QASUME, European Communities	http://lap.physics.auth.gr/qasume/

5B.3 Radiative Transfer Codes

Tropospheric Ultraviolet Visible (TUV) library for Radiative Transfer (libRadtran)	http://www.acd.ucar.edu/TUV/ http://www.libradtran.org/
System for Transfer of Atmospheric Radiation (STAR)	http://www.meteo.physik.uni-muenchen.de/strahlung/uvrad/ Star/STARinfo.htm
Fast and Easy Radiative Transfer (FASTRT)	http://zardoz.nilu.no/~olaeng/fastrt/fastrt.html
Santa Barbara DISTORT Atmospheric Radiative Transfer (SBDART)	http://arm.mrcsb.com/sbdart/

5B.4 Extraterrestrial Spectra

Solar Ultraviolet Spectral Irradiance Monitor (SUSIM)	http://wwwsolar.nrl.navy.mil/susim_atlas_data.html
Solar Stellar Irradiance Comparison Experiment (SOLSTICE)	http://lasp.colorado.edu/solstice/ and http://www-uars.gsfc.nasa.gov/cdrom_main.html
McMath/Pierce at Kitt Peak	ftp://ftp.noao.edu/fts/fluxat/

SURFACE ULTRAVIOLET RADIATION

5B.5 General UV Index Information

“UV-Index for the public,” COST-713	http://www.bag.admin.ch/strahlen/nonionisant/pdf/e/dossier-cost.pdf
EPA, U.S.	http://www.epa.gov/sunwise/uvindex.html
NOAA/EPA, U.S.	http://www.cpc.ncep.noaa.gov/products/stratosphere/uv_index/index.html
University of Vienna, Austria	http://www-med-physik.vu-wien.ac.at/uv/uv_online.htm
The UV Index Sun Awareness Program, Canada	http://www.msc-smc.ec.gc.ca/uvindex/index_e.html
World Health Organization (WHO)	http://www.who.int/inf-fs/en/fact133.html
Intersun/WHO	http://www.who.int/peh-uv/

5B.6 Internet Sites with UV Information by Country

Argentina	http://www.conae.gov.ar/caratula.html and http://www.meteofa.mil.ar
Australia (BOM)	http://www.bom.gov.au/info/about_uv.html
Australia (ARPANSA)	http://www.arpansa.gov.au/is_uvindex.htm
Australia (SunSmart)	http://www.sunsmart.com.au/
Austria (University Vienna)	http://www-med-physik.vu-wien.ac.at/uv/uv_online.htm
Austria (University Innsbruck)	http://www.uibk.ac.at/projects/uv-index/
Canada	http://www.ec.gc.ca/ozone/
Czech Republic	http://www.chmi.cz/meteo/ozon/o3uvb-e.html
European Commission (JRC)	http://ecuv.jrc.it/
Finland	http://www.fmi.fi/research_atmosphere/atmosphere_2.html
France	http://www.securite-solaire.org/
Germany (DWD)	http://www.uv-index.de/
Germany (BfS)	http://www.bfs.de/uvi/index.htm
Greece	http://lap.physics.auth.gr/uvindex/
Italy	http://www.lamma.rete.toscana.it/previ/eng/uvhtm/uvnew0.html
Japan	http://www.shiseido.co.jp/e/e9708uvi/html/
Mexico	http://www.sima.com.mx/tlmsn_valle_de_mexico/uv-index.asp
New Zealand	http://www.niwa.co.nz/services/uvozone/
Norway	http://uvnett.nrpa.no/uv/
Poland	http://www.imgw.pl/
Portugal	http://www.meteo.pt/uv/uvindex.htm
Spain	http://infomet.am.ub.es/uv_i_ozo/uvi.html
Sweden	http://www.smhi.se/weather/uvindex/sv/uvprog.htm
Switzerland	http://www.bag.admin.ch/strahlen/nonionisant/uv/d/index.php
United States	http://www.cpc.ncep.noaa.gov/products/stratosphere/uv_index/

TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER

Lead Author:
D.W. Fahey

A draft of this component of the Assessment was reviewed and discussed by the 74 scientists who attended the Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002). In addition, subsequent contributions, reviews, or comments were provided by the following individuals: A.-L.N. Ajavon, D.L. Albritton, S.O. Andersen, P.J. Aucamp, G. Bernhard, M.P. Chipperfield, J.S. Daniel, S.B. Diaz, E.S. Dutton, C.A. Ennis, P.J. Fraser, R.-S. Gao, R.R. Garcia, M.A. Geller, S. Godin-Beekmann, M. Graber, J.B. Kerr, M.K.W. Ko, M.J. Kurylo, G.L. Manney, K. Mauersberger, M. McFarland, G. Mégie, S.A. Montzka, R. Müller, E.R. Nash, P.A. Newman, S.J. Oltmans, M. Oppenheimer, L.R. Poole, G. Poulet, M.H. Proffitt, W.J. Randel, A.R. Ravishankara, C.E. Reeves, R.J. Salawitch, M.L. Santee, G. Seckmeyer, D.J. Siedel, K.P. Shine, C.C. Sweet, A.F. Tuck, G.J.M. Velders, R.T. Watson, and R.J. Zander.

TWENTY QUESTIONS AND ANSWERS ABOUT THE OZONE LAYER

Contents

	page
INTRODUCTION	Q.1
I. OZONE IN OUR ATMOSPHERE	
Q1. What is ozone and where is it in the atmosphere?	Q.3
Q2. How is ozone formed in the atmosphere?	Q.4
Q3. Why do we care about atmospheric ozone?	Q.5
Q4. Is total ozone uniform over the globe?	Q.6
Q5. How is ozone measured in the atmosphere?	Q.7
II. THE OZONE DEPLETION PROCESS	
Q6. What are the principal steps in stratospheric ozone depletion caused by human activities?	Q.8
Q7. What emissions from human activities lead to ozone depletion?	Q.10
Q8. What are the reactive halogen gases that destroy stratospheric ozone?	Q.13
Q9. What are the chlorine and bromine reactions that destroy stratospheric ozone?	Q.16
Q10. Why has an “ozone hole” appeared over Antarctica when ozone-depleting gases are present throughout the stratosphere?	Q.18
III. STRATOSPHERIC OZONE DEPLETION	
Q11. How severe is the depletion of the Antarctic ozone layer?	Q.21
Q12. Is there depletion of the Arctic ozone layer?	Q.23
Q13. How large is the depletion of the global ozone layer?	Q.25
Q14. Do changes in the Sun and volcanic eruptions affect the ozone layer?	Q.26
IV. CONTROLLING OZONE-DEPLETING GASES	
Q15. Are there regulations on production of ozone-depleting gases?	Q.28
Q16. Has the Montreal Protocol been successful in reducing ozone-depleting gases in the atmosphere?	Q.30
V. IMPLICATIONS OF OZONE DEPLETION	
Q17. Does depletion of the ozone layer increase ground-level ultraviolet radiation?	Q.32
Q18. Is depletion of the ozone layer the principal cause of climate change?	Q.34
VI. STRATOSPHERIC OZONE IN THE FUTURE	
Q19. How will recovery of the ozone layer be detected?	Q.36
Q20. When is the ozone layer expected to recover?	Q.37
ADDITIONAL TOPICS	
• Understanding Stratospheric Ozone Depletion	Q.9
• Heavier-Than-Air CFCs	Q.12
• Global Ozone Dobson Network	Q.15
• The Discovery of the Antarctic Ozone Hole	Q.20
• Replacing the Loss of “Good” Ozone in the Stratosphere	Q.24

INTRODUCTION

Ozone is a very small part of our atmosphere, but its presence is nevertheless vital to human well-being.

Most ozone resides in the upper part of the atmosphere. This region, called the stratosphere, is more than 10 kilometers (6 miles) above Earth's surface. There, about 90% of atmospheric ozone is contained in the "ozone layer," which shields us from harmful ultraviolet light from the Sun.

However, it was discovered in the mid-1970s that some human-produced chemicals could destroy ozone and deplete the ozone layer. The resulting increase in ultraviolet radiation at Earth's surface can increase the incidences of skin cancer and eye cataracts.

Following the discovery of this environmental issue, researchers focused on a better understanding of this threat to the ozone layer. Monitoring stations showed that the abundances of the ozone-depleting chemicals were steadily increasing in the atmosphere. These trends were linked to growing production and use of chemicals like chlorofluorocarbons (CFCs) for refrigeration and air conditioning, foam blowing, and industrial cleaning. Measurements in the laboratory and the atmosphere characterized the chemical reactions that were involved in ozone destruction. Computer models employing this information could then predict how much ozone depletion was occurring and how much more could occur in the future.

Observations of the ozone layer itself showed that depletion was indeed occurring. The most severe and most surprising ozone loss was discovered to be over Antarctica. It is commonly called the "ozone hole" because the ozone depletion is so large and localized. A thinning of the ozone layer also has been observed over other regions of the globe, such as the Arctic and northern middle latitudes.

The work of many scientists throughout the world has provided a basis for building a broad and solid scientific understanding of the ozone depletion process. With

this understanding, we know that ozone depletion is occurring and why. And, most important, it has become clear that, if ozone-depleting gases were to continue to accumulate in the atmosphere, the result would be more ozone layer depletion.

In response to the prospect of increasing ozone depletion, the governments of the world crafted the 1987 United Nations Montreal Protocol as a global means to address a global issue. As a result of the broad compliance with the Protocol and its Amendments and Adjustments and, importantly, the industrial development of more "ozone-friendly" substitutes for the now-controlled chemicals, the total global accumulation of ozone-depleting gases has slowed and begun to decrease. This has reduced the risk of further ozone depletion. Now, with continued compliance, we expect recovery of the ozone layer in the late 21st century. International Day for the Preservation of the Ozone Layer, 16 September, is now celebrated on the day the Montreal Protocol was agreed upon.

This is a story of notable achievements: discovery, understanding, decisions, and actions. It is a story written by many: scientists, technologists, economists, legal experts, and policymakers. And, dialogue has been a key ingredient.

To help foster a continued interaction, this component of the *Scientific Assessment of Ozone Depletion: 2002* presents 20 questions and answers about the often-complex science of ozone depletion. The questions address the nature of atmospheric ozone, the chemicals that cause ozone depletion, how global and polar ozone depletion occur, and what could lie ahead for the ozone layer. A brief answer to each question is first given in italics; an expanded answer then follows. The answers are based on the information presented in the 2002 and earlier Assessment reports. These reports and the answers provided here were all prepared and reviewed by a large international group of scientists.¹

¹ A draft of this component of the Assessment was reviewed and discussed by the 74 scientists who attended the Panel Review Meeting for the 2002 ozone assessment (Les Diablerets, Switzerland, 24-28 June 2002). In addition, subsequent contributions, reviews, or comments were provided by the following individuals: A.-L.N. Ajavon, D.L. Albritton, S.O. Andersen, P.J. Aucamp, G. Bernhard, M.P. Chipperfield, J.S. Daniel, S.B. Diaz, E.S. Dutton, C.A. Ennis, P.J. Fraser, R.-S. Gao, R.R. Garcia, M.A. Geller, S. Godin-Beekmann, M. Graber, J.B. Kerr, M.K.W. Ko, M.J. Kurylo, M. McFarland, G.L. Manney, K. Mauersberger, G. Mégie, S.A. Montzka, R. Müller, E.R. Nash, P.A. Newman, S.J. Oltmans, M. Oppenheimer, L.R. Poole, G. Poulet, M.H. Proffitt, W.J. Randel, A.R. Ravishankara, C.E. Reeves, R.J. Salawitch, M.L. Santee, G. Seckmeyer, D.J. Siedel, K.P. Shine, C.C. Sweet, A.F. Tuck, G.J.M. Velders, R.T. Watson, and R.J. Zander.

I. OZONE IN OUR ATMOSPHERE

Q1: What is ozone and where is it in the atmosphere?

Ozone is a gas that is naturally present in our atmosphere. Each ozone molecule contains three atoms of oxygen and is denoted chemically as O_3 . Ozone is found primarily in two regions of the atmosphere. About 10% of atmospheric ozone is in the troposphere, the region closest to Earth (from the surface to about 10-16 kilometers (6-10 miles)). The remaining ozone (90%) resides in the stratosphere, primarily between the top of the troposphere and about 50 kilometers (31 miles) altitude. The large amount of ozone in the stratosphere is often referred to as the “ozone layer.”

Ozone is a gas that is naturally present in our atmosphere. Because an ozone molecule contains three oxygen atoms (see **Figure Q1-1**), it has a chemical formula of O_3 . Ozone was discovered in laboratory experiments in the mid-1800s. Ozone’s presence in the atmosphere was later discovered using chemical and optical measurement methods. The word ozone is derived from the Greek word *ozein*, meaning “to smell.” Ozone has a pungent odor that allows ozone to be detected even in very low amounts. Ozone will rapidly react with many chemical compounds and is explosive in concentrated amounts. Electrical discharges are generally used to make ozone for industrial processes including air and water purification and bleaching of textiles and food products.

Ozone location. Most ozone (about 90%) is found in the stratosphere, a region that begins about 10-16 kilometers (6-10 miles) above Earth’s surface and extends up to about 50 kilometers (31 miles) altitude (see **Figure Q1-2**). The stratosphere begins at higher altitudes (16 kilometers) in the tropics than in the polar regions (10 kilometers). Most ozone resides in the stratosphere in what is commonly known as the “ozone layer.” The remaining ozone, about 10%, is found in the troposphere, which is the lowest region of the atmosphere between Earth’s surface and the stratosphere.

Ozone abundance. Ozone molecules have a relatively low abundance in the atmosphere. In the strato-

sphere near the peak of the ozone layer, there are up to 12,000 ozone molecules for every *billion* air molecules (1 billion = 1000 million). Most air molecules are either oxygen (O_2) or nitrogen (N_2) molecules. In the troposphere near Earth’s surface, ozone is even less abundant, with a typical range of 20 to 100 ozone molecules for each billion air molecules. The highest surface values are a result of ozone formed in air polluted by human activities.

As an illustration of the low relative abundance of ozone in our atmosphere, one can consider bringing all the ozone molecules in the troposphere and stratosphere down to Earth’s surface and uniformly distributing these molecules into a gas layer over the globe. The resulting layer of pure ozone would have a thickness of less than one-half centimeter (about one-quarter inch).

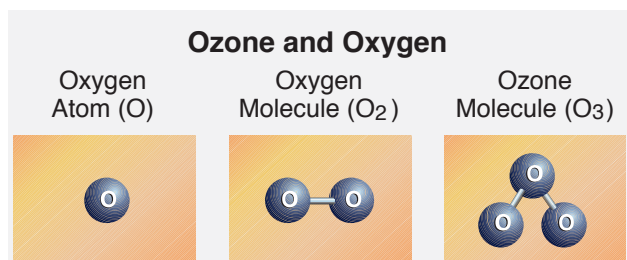


Figure Q1-1. Ozone and oxygen. A molecule of ozone (O_3) contains three oxygen (O) atoms bound together. Oxygen molecules (O_2), which constitute 21% of Earth’s atmosphere, contain two oxygen atoms bound together.

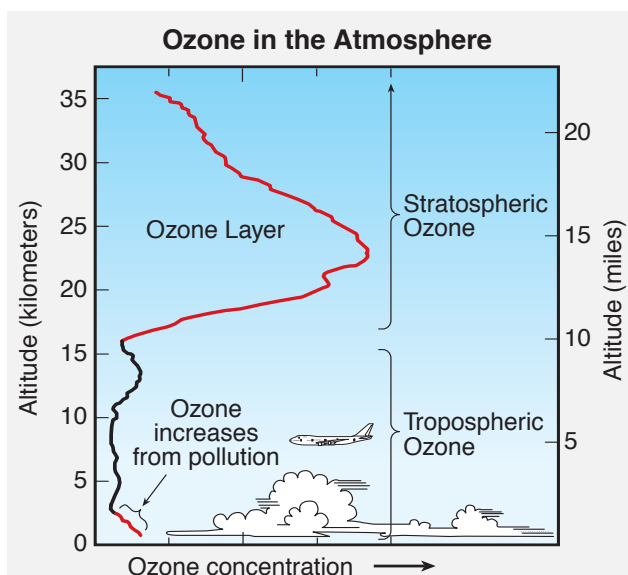


Figure Q1-2. Atmospheric ozone. Ozone is present throughout the lower atmosphere. Most ozone resides in the stratospheric “ozone layer” above Earth’s surface. Increases in ozone occur near the surface as a result of pollution from human activities.

TWENTY QUESTIONS

Q2: How is ozone formed in the atmosphere?

Ozone is formed throughout the atmosphere in multistep chemical processes that require sunlight. In the stratosphere, the process begins with the breaking apart of an oxygen molecule (O_2) by ultraviolet radiation from the Sun. In the lower atmosphere (troposphere), ozone is formed in a different set of chemical reactions involving hydrocarbons and nitrogen-containing gases.

Stratospheric ozone. Stratospheric ozone is naturally formed in chemical reactions involving ultraviolet sunlight and oxygen molecules, which make up 21% of the atmosphere. In the first step, sunlight breaks apart one oxygen molecule (O_2) to produce two oxygen atoms ($2 O$) (see **Figure Q2-1**). In the second step, each atom combines with an oxygen molecule to produce an ozone molecule (O_3). These reactions occur continually wherever ultraviolet sunlight is present in the stratosphere. As a result, the greatest ozone production occurs in the tropical stratosphere.

The production of stratospheric ozone is balanced by its destruction in chemical reactions. Ozone reacts con-

tinually with a wide variety of natural and human-produced chemicals in the stratosphere. In each reaction, an ozone molecule is lost and other chemical compounds are produced. Important reactive gases that destroy ozone are those containing chlorine and bromine (see Q8).

Some stratospheric ozone is transported down into the troposphere and can influence ozone amounts at Earth's surface, particularly in remote unpolluted regions of the globe.

Tropospheric ozone. Near Earth's surface, ozone is produced in chemical reactions involving naturally occurring gases and gases from pollution sources. Production reactions primarily involve hydrocarbon and nitrogen oxide gases and require sunlight. Fossil fuel combustion is a primary pollution source for tropospheric ozone production. The surface production of ozone does not significantly contribute to the abundance of stratospheric ozone. The amount of surface ozone is too small and the transport of surface air to the stratosphere is not effective enough. As in the stratosphere, ozone in the troposphere is destroyed in naturally occurring chemical reactions and in reactions involving human-produced chemicals. Tropospheric ozone can also be destroyed when ozone reacts with a variety of surfaces such as those of soils and plants.

Balance of chemical processes. Ozone abundances in the stratosphere and troposphere are determined by the *balance* between chemical processes that produce and destroy ozone. The balance is determined by the amounts of reacting gases and by how the rate or effectiveness of the various reactions varies with sunlight intensity, location in the atmosphere, temperature, and other factors. As atmospheric conditions change to favor ozone-production reactions in a certain location, ozone abundances will increase. Similarly, if conditions change to favor reactions that destroy ozone, its abundances will decrease. The balance of production and loss reactions combined with atmospheric air motions determines the global distribution of ozone on time scales of days to many months. Global ozone has decreased in the last decades because the amounts of reactive gases containing chlorine and bromine have increased in the stratosphere (see Q13).

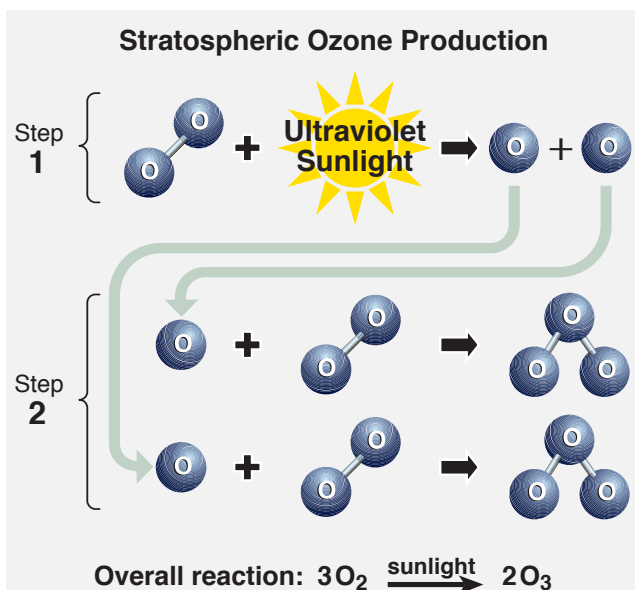


Figure Q2-1. Stratospheric ozone production. Ozone is naturally produced in the stratosphere in a two-step process. In the first step, ultraviolet sunlight breaks apart an oxygen molecule to form two separate oxygen atoms. In the second step, these atoms then undergo a binding collision with other oxygen molecules to form two ozone molecules. In the overall process, three oxygen molecules react to form two ozone molecules.

Q3: Why do we care about atmospheric ozone?

Ozone in the stratosphere absorbs some of the Sun's biologically harmful ultraviolet radiation. Because of this beneficial role, stratospheric ozone is considered "good ozone." In contrast, ozone at Earth's surface that is formed from pollutants is considered "bad ozone" because it can be harmful to humans and plant and animal life. Some ozone occurs naturally in the lower atmosphere where it is beneficial because ozone helps remove pollutants from the atmosphere.

All ozone molecules are chemically identical, with each containing three oxygen atoms. However, ozone in the stratosphere has very different environmental consequences for humans and other life forms than ozone in the troposphere near Earth's surface.

Good ozone. Stratospheric ozone is considered "good" for humans and other life forms because it absorbs ultraviolet (UV)-B radiation from the Sun (see **Figure Q3-1**). If not absorbed, UV-B would reach Earth's surface in amounts that are harmful to a variety of life forms. In humans, as their exposure to UV-B increases, so does their risk of skin cancer (see **Q17**), cataracts, and a suppressed immune system. The UV-B exposure before adulthood and cumulative exposure are both important factors in the risk. Excessive UV-B exposure also can damage terrestrial plant life, single-cell organisms, and aquatic ecosystems. Other UV radiation, UV-A, which is not absorbed significantly by ozone, causes premature aging of the skin.

The absorption of UV-B radiation by ozone is a source of heat in the stratosphere. This helps to maintain the stratosphere as a stable region of the atmosphere with temperatures increasing with altitude. As a result, ozone plays a key role in controlling the temperature structure of Earth's atmosphere.

Protecting good ozone. In the mid-1970s, it was discovered that some human-produced gases could cause stratospheric ozone depletion (see **Q6**). Ozone depletion increases harmful UV-B amounts at Earth's surface. Global efforts have been undertaken to protect the ozone layer through the regulation of ozone-depleting gases (see **Q15** and **Q16**).

Bad ozone. Ozone is also formed near Earth's surface in natural chemical reactions and in reactions caused by the presence of human-made pollutant gases. Ozone produced by pollutants is "bad" because more ozone comes in direct contact with humans, plants, and animals. Increased levels of ozone are generally harmful to living systems because ozone reacts strongly to destroy or alter many other molecules. Excessive ozone exposure reduces crop yields and forest growth. In humans, ozone exposure can reduce lung capacity; cause chest pains, throat irritation, and coughing; and worsen pre-existing health conditions related to the heart and lungs. In addition, increases in tropospheric ozone lead to a warming of Earth's surface (see **Q18**). The negative effects of increasing tropospheric ozone contrast sharply with the positive effects of stratospheric ozone as an absorber of harmful UV-B radiation from the Sun.

Reducing bad ozone. Reducing the emission of pol-

lutants can reduce "bad" ozone in the air surrounding humans, plants, and animals. Major sources of pollutants include large cities where fossil fuel consumption and industrial activities are greatest. Many programs around the globe have already been successful in reducing the emission of pollutants that cause near-surface ozone production.

Natural ozone. Ozone is a natural component of the clean atmosphere. In the absence of human activities on Earth's surface, ozone would still be present near the surface and throughout the troposphere and stratosphere. Ozone's chemical role in the atmosphere includes helping to remove other gases, both those occurring naturally and those emitted by human activities. If all the ozone were to be removed from the lower atmosphere, other gases such as methane, carbon monoxide, and nitrogen oxides would increase in abundance.

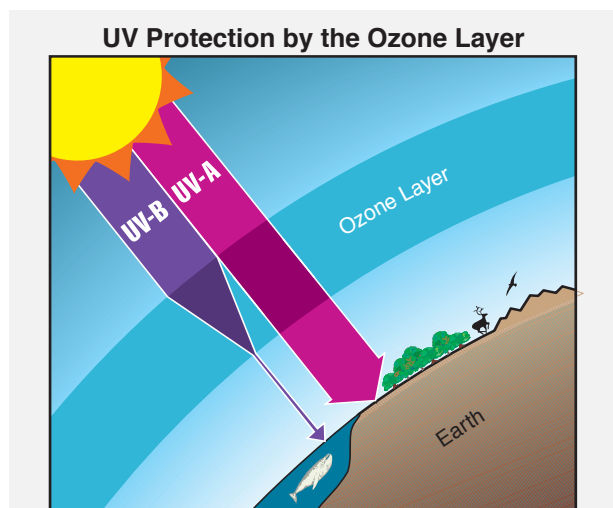


Figure Q3-1. UV-B protection by the ozone layer.

The ozone layer resides in the stratosphere and surrounds the entire Earth. UV-B radiation (280- to 315-nanometer (nm) wavelength) from the Sun is partially absorbed in this layer. As a result, the amount reaching Earth's surface is greatly reduced. UV-A (315- to 400-nm wavelength) and other solar radiation are not strongly absorbed by the ozone layer. Human exposure to UV-B increases the risk of skin cancer, cataracts, and a suppressed immune system. UV-B exposure can also damage terrestrial plant life, single-cell organisms, and aquatic ecosystems.

TWENTY QUESTIONS

Q4: Is total ozone uniform over the globe?

No, the total amount of ozone above the surface of Earth varies with location on time scales that range from daily to seasonal. The variations are caused by stratospheric winds and the chemical production and destruction of ozone. Total ozone is generally lowest at the equator and highest near the poles because of the seasonal wind patterns in the stratosphere.

Total ozone. Total ozone at any location on the globe is found by measuring all the ozone in the atmosphere directly above that location. Total ozone includes that present in the stratospheric ozone layer and that present throughout the troposphere (see **Figure Q1-2**). The contribution from the troposphere is generally only about 10% of total ozone. Total ozone values are often reported in *Dobson units*, denoted “DU.” Typical values vary between 200 and 500 DU over the globe (see **Figure Q4-1**). A total ozone value of 500 DU, for example, is equivalent to a layer of pure ozone gas on Earth’s surface having a thickness of only 0.5 centimeters (0.2 inches).

Global distribution. Total ozone varies strongly with latitude over the globe, with the largest values occurring at middle and high latitudes (see **Figure Q4-1**). This is a result of winds that circulate air in the stratosphere, moving tropical air rich in ozone toward the poles in fall and winter. Regions of low total ozone occur at polar latitudes in winter and spring as a result of the chemical destruction of ozone by chlorine and bromine gases (see **Q11** and **Q12**). The smallest values of total ozone (other than in the Antarctic in spring) occur in the tropics in all seasons, in part because the thickness of the ozone layer is smallest in the tropics.

Natural variations. The variations of total ozone with latitude and longitude come about for two reasons. First, natural air motions mix air between regions of the stratosphere that have high ozone values and those that have low ozone values. Air motions also increase the vertical thickness of the ozone layer near the poles, which increases the value of total ozone in those regions. Tropospheric weather systems can temporarily reduce the thickness of the stratospheric ozone layer in a region, lowering total ozone at the same time. Second, variations occur as a result of changes in the balance of chemical production and loss processes as air moves to new locations over the globe. Reductions in solar ultraviolet radiation exposure, for example, will reduce the production of ozone.

Scientists have a good understanding of how chemistry and air motion work together to cause the observed large-scale features in total ozone such as those seen in **Figure Q4-1**. Ozone changes are carefully monitored by a large group of investigators using satellite, airborne, and ground-based instruments. The analysis of these observa-

tions helps scientists to estimate the contribution of human activities to ozone depletion.

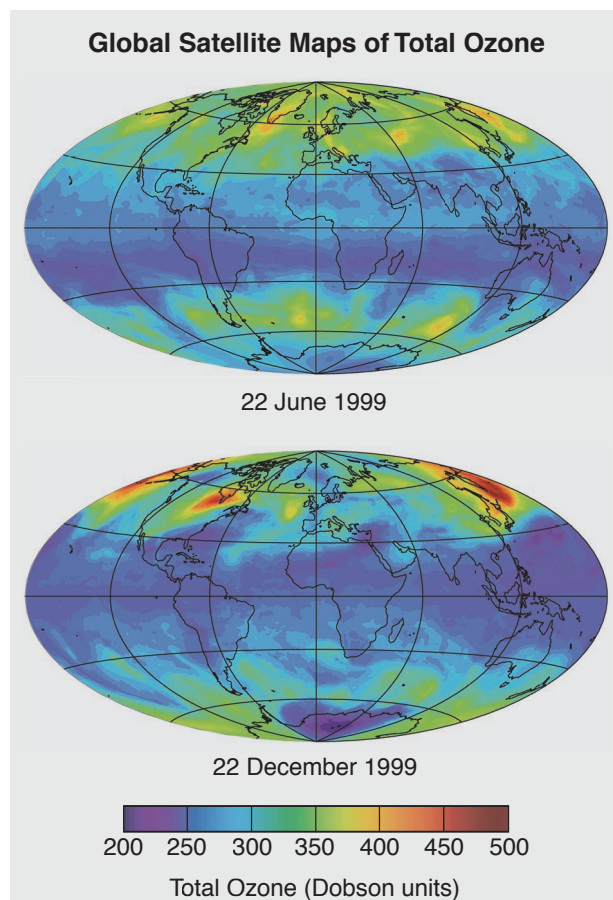


Figure Q4-1. Total ozone. A total ozone value is obtained by measuring all the ozone that resides in the atmosphere over a given location on Earth’s surface. Total ozone values shown here are reported in “Dobson units” as measured by a satellite instrument from space. Total ozone varies with latitude, longitude, and season, with the largest values at high latitudes and the lowest values in tropical regions. Total ozone at most locations varies with time on a daily to seasonal basis as ozone-rich air is moved about the globe by stratospheric winds. Low total ozone values over Antarctica in the 22 December image represent the remainder of the “ozone hole” from the 1999 Antarctic winter/spring season (see **Q11**).

Q5: How is ozone measured in the atmosphere?

The amount of ozone in the atmosphere is measured by instruments on the ground and carried aloft in balloons, aircraft, and satellites. Some measurements involve drawing air into an instrument that contains a system for detecting ozone. Other measurements are based on ozone's unique absorption of light in the atmosphere. In that case, sunlight or laser light is carefully measured after passing through a portion of the atmosphere containing ozone.

The abundance of ozone in the atmosphere is measured by a variety of techniques (see **Figure Q5-1**). The techniques make use of ozone's unique optical and chemical properties. There are two principal categories of measurement techniques: *direct* and *remote*. Ozone measurements by these techniques have been essential in monitoring changes in the ozone layer and in developing our understanding of the processes that control ozone abundances.

Direct measurements. Direct measurements of atmospheric ozone abundance are those that require air to be drawn directly into an instrument. Once inside an instrument, ozone can be measured by its absorption of ultraviolet (UV) light or by the electrical current produced in an ozone chemical reaction. The latter approach is used in the construction of "ozonesondes," which are light-weight ozone-measuring modules suitable for launching on small balloons. Small balloons ascend far enough in the atmosphere to measure ozone in the stratospheric ozone layer. Ozonesondes are launched weekly at many locations around the world. Direct ozone-measuring instruments using optical or chemical detection schemes are also used routinely on board research aircraft to measure the distribution of ozone in the troposphere and lower stratosphere. High-altitude research aircraft can reach the ozone layer at most locations over the globe and can reach farthest into the layer at high latitudes in polar regions. Ozone measurements are also being made on some commercial aircraft.

Remote measurements. Remote measurements of ozone abundance are obtained by detecting the presence of ozone at large distances away from the instrument. Most remote measurements of ozone rely on its unique absorption of UV radiation. Sources of UV radiation that can be used are the Sun and lasers. For example, satellites use the absorption of UV sunlight by the atmosphere or the absorption of sunlight scattered from the surface of Earth to measure ozone over the globe on a near-daily basis. A network of ground-based detectors measures ozone by the amount of the Sun's UV light that reaches Earth's surface. Other instruments measure ozone using

its absorption of infrared or visible radiation or its emission of microwave or infrared radiation. Total ozone amounts and the altitude distribution of ozone can be obtained with remote measurement techniques. Lasers are routinely deployed at ground sites or on board aircraft to detect ozone over a distance of many kilometers along the laser light path.

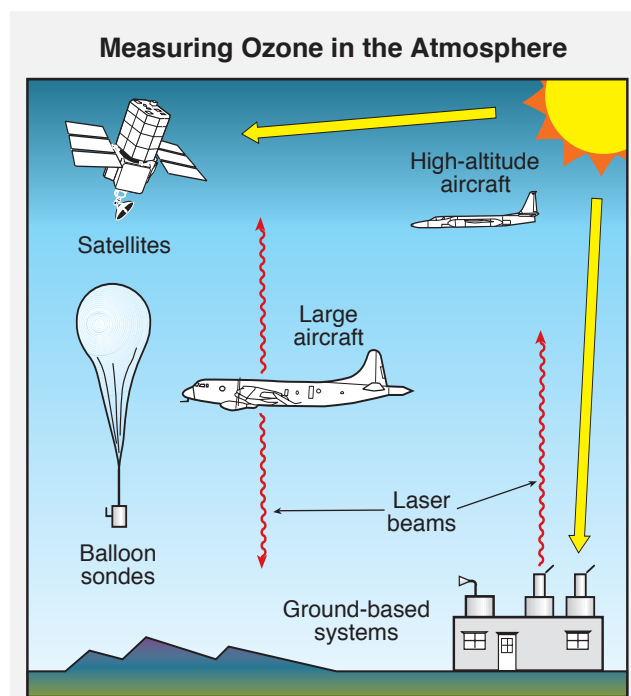


Figure Q5-1. Ozone measurements. Ozone is measured throughout the atmosphere with instruments on the ground and on board aircraft, high-altitude balloons, and satellites. Some instruments measure ozone directly in sampled air and others measure ozone remotely some distance away from the instrument. Instruments use optical techniques with the Sun and lasers as light sources or use chemical reactions that are unique to ozone. Measurements at many locations over the globe are made weekly to monitor total ozone amounts.

II. THE OZONE DEPLETION PROCESS

Q6: What are the principal steps in stratospheric ozone depletion caused by human activities?

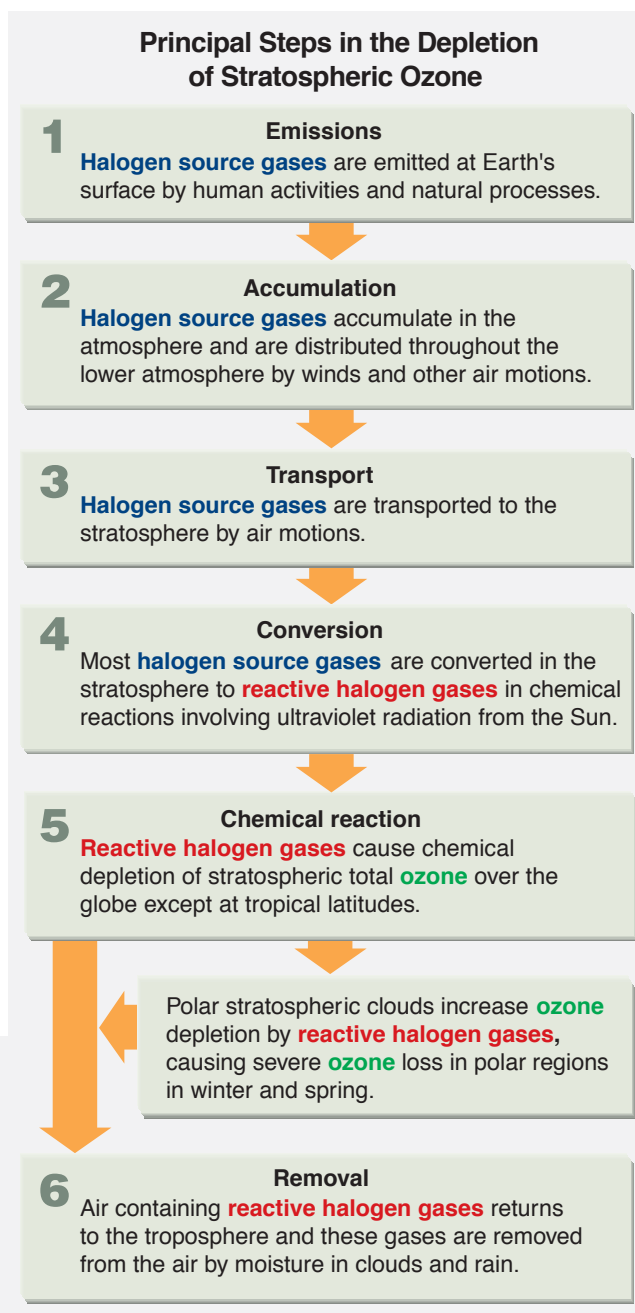
The initial step in the depletion of stratospheric ozone by human activities is the emission of ozone-depleting gases containing chlorine and bromine at Earth's surface. Most of these gases accumulate in the lower atmosphere because they are unreactive and do not dissolve readily in rain or snow. Eventually, the emitted gases are transported to the stratosphere where they are converted to more reactive gases containing chlorine and bromine. These more reactive gases then participate in reactions that destroy ozone. Finally, when air returns to the lower atmosphere, these reactive chlorine and bromine gases are removed from Earth's atmosphere by rain and snow.

Emission, accumulation, and transport. The principal steps in stratospheric ozone depletion caused by human activities are shown in **Figure Q6-1**. The process begins with the *emission* of halogen source gases at Earth's surface (see Q7). Halogen source gases include manufactured gases containing chlorine or bromine that are released to the atmosphere by a variety of human activities. Chlorofluorocarbons (CFCs), for example, are important chlorine-containing gases. These source gases *accumulate* in the lower atmosphere (troposphere) and are eventually *transported* to the stratosphere. The accumulation occurs because most source gases are unreactive in the lower atmosphere (troposphere). Small amounts of these gases dissolve in ocean waters.

Some emissions of halogen gases come from natural sources (see Q7). These emissions also accumulate in the troposphere and are transported to the stratosphere.

Conversion, reaction, and removal. Halogen source gases do not react directly with ozone. Once in the stratosphere, halogen source gases are chemically *converted* to reactive halogen gases by ultraviolet radiation from the Sun (see Q8). These reactive gases chemically destroy ozone in the stratosphere (see Q9). The average depletion of total ozone attributed to reactive gases is estimated to be small in the tropics and up to about 10% at middle latitudes (see Q13). In polar regions, the presence of polar stratospheric clouds greatly increases the abundance of the most reactive halogen gases (see Q10). This results in ozone destruction in polar regions in winter and

Figure Q6-1. Principal steps in stratospheric ozone depletion. The stratospheric ozone depletion process begins with the emission of halogen source gases at Earth's surface and ends when reactive halogen gases are removed by rain and snow in the troposphere and deposited on Earth's surface. In the stratosphere, the reactive halogen gases, namely chlorine monoxide (ClO) and bromine monoxide (BrO), destroy ozone.



spring (see *Q11* and *Q12*). After a few years, air in the stratosphere returns to the troposphere, bringing along reactive halogen gases. These gases are then *removed* from the atmosphere by rain and other precipitation and deposited on Earth's surface. This removal brings to an end the destruction of ozone by chlorine and bromine atoms that were first released to the atmosphere as components of halogen source gas molecules.

Tropospheric conversion. Halogen source gases with short lifetimes (see *Q7*) undergo significant chemical conversion in the troposphere, producing reactive

halogen gases and other compounds. Source gas molecules that are not converted accumulate in the troposphere and are transported to the stratosphere. Because of removal by precipitation, only small portions of the reactive halogen gases produced in the troposphere are also transported to the stratosphere. Important examples of gases that undergo some tropospheric removal are the HCFCs, which are used as substitute gases for other halogen source gases (see *Q15* and *Q16*), bromoform, and gases containing iodine (see *Q7*).

Understanding Stratospheric Ozone Depletion

Scientists learn about ozone destruction through a combination of laboratory studies, computer models, and stratospheric observations. In *laboratory studies* scientists are able to discover and evaluate individual chemical reactions that also occur in the stratosphere. Chemical reactions between two gases follow well-defined physical rules. Some of these reactions occur on the surfaces of particles formed in the stratosphere. Reactions have been studied that involve a wide variety of molecules containing chlorine, bromine, fluorine, and iodine and other atmospheric constituents such as oxygen, nitrogen, and hydrogen. These studies show that there exist several reactions involving chlorine and bromine that can directly or indirectly cause ozone destruction in the atmosphere.

With *computer models*, scientists can examine the overall effect of a large group of known reactions under the chemical and physical conditions found in the stratosphere. These models include winds, air temperatures, and the daily and seasonal changes in sunlight. With such analyses, scientists have shown that chlorine and bromine can react in catalytic cycles in which one chlorine or bromine atom can destroy many ozone molecules. Scientists use model results to compare with past observations as a test of our understanding of the atmosphere and to evaluate the importance of new reactions found in the laboratory. Computer models also enable scientists to explore the future by changing atmospheric conditions and other model parameters.

Scientists make *stratospheric observations* to find out what gases are present in the stratosphere and at what concentrations. Observations have shown that halogen source gases and reactive halogen gases are present in the stratosphere at expected amounts. Ozone and chlorine monoxide (ClO), for example, have been observed extensively with a variety of instruments. Instruments on the ground and on board satellites, balloons, and aircraft detect ozone and ClO at a distance using optical and microwave signals. High-altitude aircraft and balloon instruments detect both gases directly in the stratosphere. For example, these observations show that ClO is present at elevated amounts in the Antarctic and Arctic stratospheres in the winter/spring season, when the most severe ozone depletion occurs.

TWENTY QUESTIONS

Q7: What emissions from human activities lead to ozone depletion?

Certain industrial processes and consumer products result in the atmospheric emission of “halogen source gases.” These gases contain chlorine and bromine atoms, which are known to be harmful to the ozone layer. For example, the chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), once used in almost all refrigeration and air conditioning systems, eventually reach the stratosphere where they are broken apart to release ozone-depleting chlorine atoms. Other examples of human-produced ozone-depleting gases are the “halons,” which are used in fire extinguishers and which contain ozone-depleting bromine atoms. The production and consumption of all principal halogen source gases by human activities are regulated worldwide under the Montreal Protocol.

Human-produced chlorine and bromine gases.

Human activities cause the emission of *halogen source gases* that contain chlorine and bromine atoms. These emissions into the atmosphere ultimately lead to stratospheric ozone depletion. The source gases that contain only

carbon, chlorine, and fluorine are called “chlorofluorocarbons,” usually abbreviated as CFCs. CFCs, along with carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3), are the most important chlorine-containing gases that are emitted by human activities and destroy stratospheric ozone

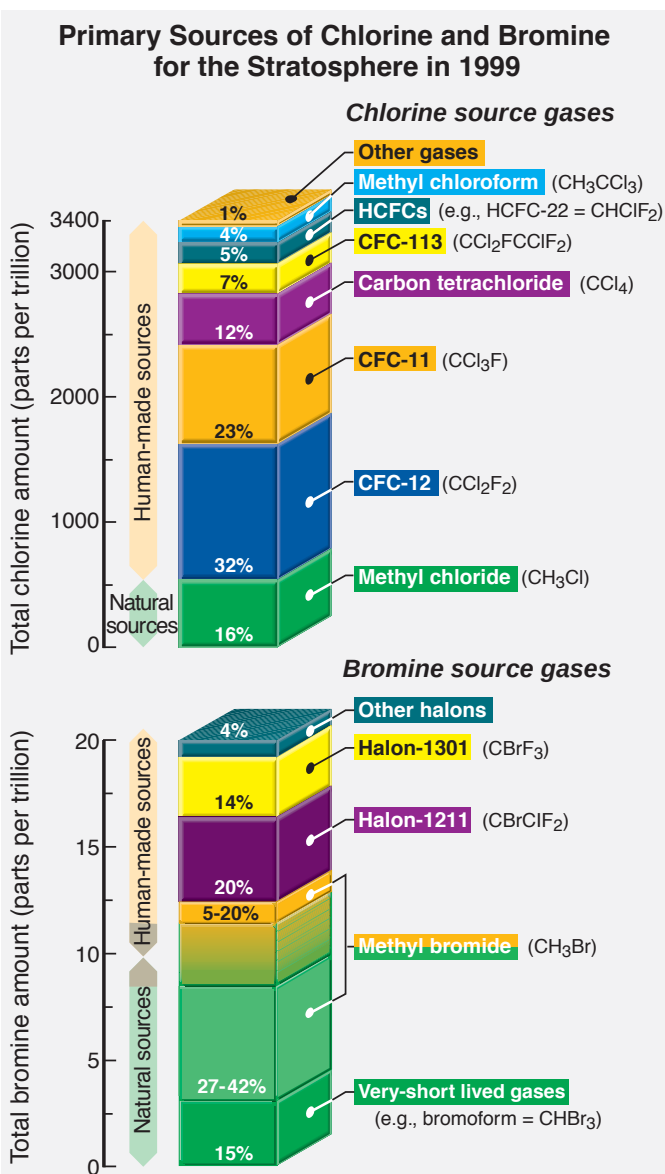


Figure Q7-1. Stratospheric source gases. A variety of gases transport chlorine and bromine into the stratosphere. These gases, called halogen source gases, are emitted from natural sources and human activities. For chlorine, human activities account for most that reaches the stratosphere. The CFCs are the most abundant of the chlorine-containing gases released in human activities. Methyl chloride is the most important natural source of chlorine. For bromine that reaches the stratosphere, halons and methyl bromide are the largest sources. Both gases are released in human activities. Methyl bromide has an additional natural source. Natural sources are a larger fraction of the total for bromine than for chlorine. HCFCs, which are substitute gases for CFCs and also are regulated under the Montreal Protocol, are a small but growing fraction of chlorine-containing gases. The abundance scale shows that the amount of chlorine in the stratosphere is greater than that of bromine by about 170 times. (The unit “parts per trillion” is a measure of the relative abundance of a gas: 1 part per trillion indicates the presence of one molecule of a gas per trillion other molecules.)

Table Q7-1. Atmospheric lifetimes, emissions, and Ozone Depletion Potentials of halogen source gases.^a

Halogen Source Gas	Lifetime (years)	Global Emissions in 2000 (gigagrams per year) ^b	Ozone Depletion Potential (ODP)
Chlorine			
CFC-12	100	130-160	1
CFC-113	85	10-25	1
CFC-11	45	70-110	1
Carbon tetrachloride	26	70-90	0.73
HCFCs	1-26	340-370	0.02-0.12
Methyl chloroform	5	~20	0.12
Methyl chloride	1.3	3000-4000	0.02
Bromine			
Halon-1301	65	~3	12
Halon-1211	16	~10	6
Methyl bromide	0.7	160-200	0.38
Very short-lived gases	Less than 1	^c	^c

^a Includes both human activities and natural sources.

^b 1 gigagram = 10⁹ grams = 1000 metric tons.

^c No reliable estimate available.

(see **Figure Q7-1**). Chlorine-containing gases have been used in many applications including refrigeration, air conditioning, foam blowing, aerosol propellants, and cleaning of metals and electronic components. These activities have typically caused the emission of halogen-containing gases to the atmosphere.

Another category of halogen source gases contains bromine. The most important of these are the “halons” and methyl bromide (CH₃Br). Halons are halogenated hydrocarbon gases originally developed to extinguish fires. Halons are widely used to protect large computers, military hardware, and commercial aircraft engines. Because of these uses, halons are often directly released into the atmosphere. Halon-1211 and Halon-1301 are the most abundant halons emitted by human activities (see **Figure Q7-1**). Methyl bromide, used primarily as an agricultural fumigant, is also a significant source of bromine to the atmosphere.

Human emissions of chlorine- and bromine-containing gases have increased substantially since the middle of the 20th century (see **Q16**). The result has been global ozone depletion with the greatest losses occurring in polar regions (see **Q11** to **Q13**).

Natural sources of chlorine and bromine. There are two halogen source gases present in the stratosphere that have large natural sources. These are methyl chloride (CH₃Cl) and methyl bromide (CH₃Br), both of which are emitted by oceanic and terrestrial ecosystems. Natural sources of these two gases contribute about 16% of the chlorine currently in the stratosphere, and about 27-42% of the bromine (see **Figure Q7-1**). Very short-lived gases containing bromine, such as bromoform (CHBr₃), are also released to the atmosphere by the oceans. The estimated contribution of these gases to stratospheric bromine (about 15%) is uncertain at this time. Changes in the natural sources of chlorine and bromine since the middle of the 20th century are not the cause of observed ozone depletion.

Lifetimes and emissions. After emission, halogen source gases are either removed from the atmosphere or undergo chemical conversion. The time to remove or convert about 60% of a gas is often called its atmospheric “lifetime”. Lifetimes vary from less than 1 year to 100 years for the principal chlorine- and bromine-containing gases (see **Table Q7-1**). Gases with the shortest lifetimes (e.g., the HCFCs, methyl bromide, methyl chloride, and the very short-lived gases) are significantly destroyed in the troposphere, and therefore only a fraction of the emitted gas contributes to ozone depletion in the stratosphere.

The amount of a halogen source gas present in the atmosphere depends on the lifetime of the gas and the amount emitted to the atmosphere. Emissions vary greatly for the principal source gases, as indicated in **Table Q7-1**. Emissions of most gases regulated by the Montreal Protocol have decreased since 1990, and emissions from all regulated gases are expected to decrease in the coming decades (see **Q16**).

Ozone Depletion Potential. The halogen source gases in **Figure Q7-1** are also known as “ozone-depleting substances” because they are converted in the stratosphere to reactive gases containing chlorine and bromine (see **Q8**). Some of these reactive gases participate in reactions that destroy ozone (see **Q9**). Ozone-depleting substances are compared in their effectiveness to destroy stratospheric ozone using the “Ozone Depletion Potential” (ODP), as listed in **Table Q7-1**. A gas with a larger ODP has a greater potential to destroy ozone over its lifetime in the atmosphere. The ODP is calculated on a “per mass” basis for each gas relative to CFC-11, which has an ODP defined to be 1. Halon-1211 and Halon-1301 have ODPs significantly larger than CFC-11 and most other emitted gases. This results because bromine is much more effective overall (about 45 times) on a per-atom basis than chlorine in chemical reactions that destroy ozone in the stratosphere. The gases with small

TWENTY QUESTIONS

ODP values generally have short atmospheric lifetimes. The production and consumption of all principal halogen source gases by humans are regulated under the provisions of the Montreal Protocol (see *Q15*).

Fluorine and iodine. Fluorine and iodine are also halogen atoms. Most of the source gases in *Figure Q7-1* also contain fluorine atoms in addition to chlorine or bromine. After the source gases undergo conversion in the stratosphere (see *Q6*), the fluorine content of these gases is left in chemical forms that do not destroy ozone. Iodine is a component of several gases that are naturally emitted from the oceans. Although iodine will participate in ozone destruction reactions, these iodine-containing

gases are largely removed in the troposphere by natural processes before the gases can reach the stratosphere.

Other gases. Other gases that influence stratospheric ozone abundances also have increased in the stratosphere as a result of human activities. Important examples are methane (CH_4) and nitrous oxide (N_2O), which react to form water vapor and reactive hydrogen and nitrogen oxides, respectively, in the stratosphere. These reactive products also participate in the production and loss balance of stratospheric ozone (see *Q2*). The overall affect of these other gases on ozone is much smaller than that caused by increases in chlorine- and bromine-containing gases from human activities.

Heavier-Than-Air CFCs

CFCs and other halogen source gases reach the stratosphere despite the fact they are “heavier than air.” All the principal source gases are emitted and accumulate in the lower atmosphere (troposphere). Air containing the emitted halogen gases is in continual motion as a result of winds and convection. Air motions ensure that the source gases are horizontally and vertically well mixed throughout the troposphere in a matter of months. It is this well-mixed air that enters the lower stratosphere from upward air motions in tropical regions, bringing with it source gas molecules emitted from a wide variety of locations on Earth’s surface.

Atmospheric measurements confirm that halogen source gases with long atmospheric lifetimes are well mixed in the troposphere and are present in the stratosphere (see *Figure Q8-2*). The amounts found in these regions are consistent with the emissions estimates reported by industry and government. Measurements also show that gases that are “lighter than air,” such as hydrogen (H_2) and methane (CH_4), are also well mixed in the troposphere, as expected. Only at altitudes well above the troposphere and stratosphere (above 85 kilometers (53 miles)), where much less air is present, do heavy gases begin to separate from lighter gases as a result of gravity.

Q8: What are the reactive halogen gases that destroy stratospheric ozone?

Emissions from human activities and natural processes are large sources of chlorine- and bromine-containing gases for the stratosphere. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases also containing chlorine and bromine. Important examples of the reactive gases that destroy stratospheric ozone are chlorine monoxide (ClO) and bromine monoxide (BrO). These and other reactive gases participate in “catalytic” reaction cycles that efficiently destroy ozone. Volcanoes can emit some chlorine-containing gases, but these gases are ones that readily dissolve in rainwater and ice and are usually “washed out” of the atmosphere before they can reach the stratosphere.

Reactive gases containing the halogens chlorine and bromine lead to the chemical destruction of stratospheric ozone. Halogen-containing gases present in the stratosphere can be divided into two groups: *halogen source gases* and *reactive halogen gases*. The source gases are emitted at Earth’s surface by natural processes and by human activities (see Q7). Once they reach the stratosphere, the halogen source gases chemically convert to form the reactive halogen gases.

Reactive halogen gases. The chemical conversion of halogen source gases, which involves ultraviolet sunlight and other chemical reactions, produces a number of reactive halogen gases. These reactive gases contain all of the chlorine and bromine atoms originally present in the source gases.

The most important reactive chlorine- and bromine-containing gases that form in the stratosphere are shown in **Figure Q8-1**. Away from polar regions, the most abundant are hydrogen chloride (HCl) and chlorine nitrate (ClONO₂). These two gases are considered *reservoir*

gases because they do not react directly with ozone but can be converted to the most reactive forms that do chemically destroy ozone. The *most reactive* forms are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). A large fraction of available stratospheric bromine is generally in the form of BrO whereas usually only a small fraction of stratospheric chlorine is in the form of ClO. In polar regions, the reservoirs ClONO₂ and HCl undergo a further conversion on polar stratospheric clouds (see Q10) to form ClO. In that case, ClO becomes a large fraction of available reactive chlorine.

Reactive chlorine observations. Reactive chlorine gases have been observed extensively in the stratosphere with both direct and remote measurement techniques. The measurements from space at middle latitudes displayed in **Figure Q8-2** are representative of how chlorine-containing gases change between the surface and the upper stratosphere. Available chlorine (see red line in **Figure Q8-2**) is the sum of chlorine contained in halogen source gases and

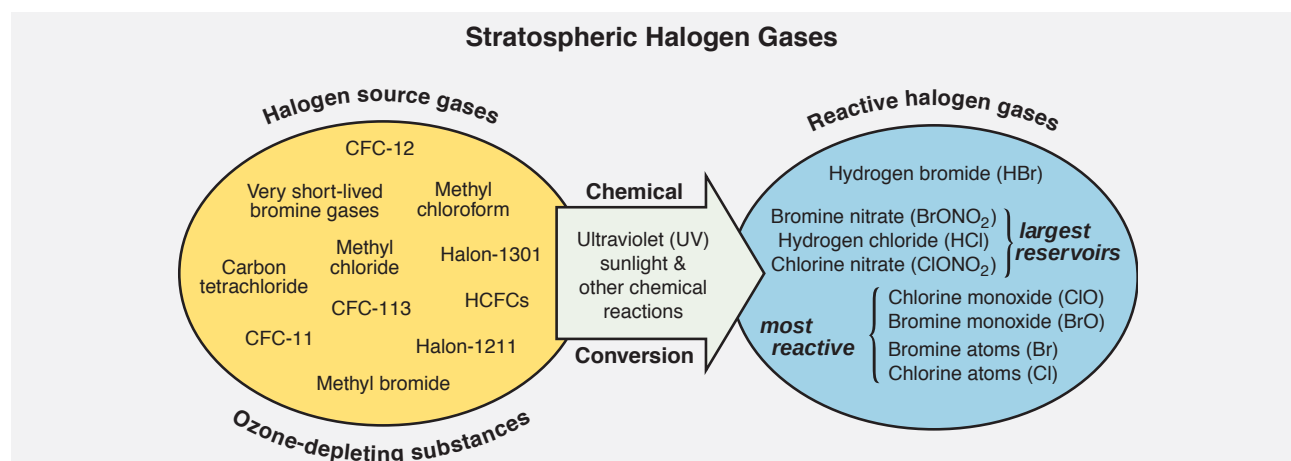


Figure Q8-1. Conversion of halogen source gases. Halogen source gases (also known as ozone-depleting substances) are chemically converted to reactive halogen gases primarily in the stratosphere. The conversion requires ultraviolet sunlight and a few other chemical reactions. The short-lived gases undergo some conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases. Some reactive gases serve as reservoirs of chlorine and bromine whereas others participate in ozone destruction cycles.

TWENTY QUESTIONS

the reactive gases HCl , ClONO_2 , ClO , and other minor gases. Available chlorine is constant within a few percent from the surface to 47 kilometers (31 miles) altitude. In the troposphere, available chlorine is contained almost entirely in the source gases described in *Figure Q7-1*. At higher altitudes, the source gases become a smaller fraction of available chlorine as they are converted to reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of reactive chlorine gases.

In the altitude range of the ozone layer, as shown in *Figure Q8-2*, the reactive chlorine gases HCl and ClONO_2 account for most of available chlorine. ClO , the

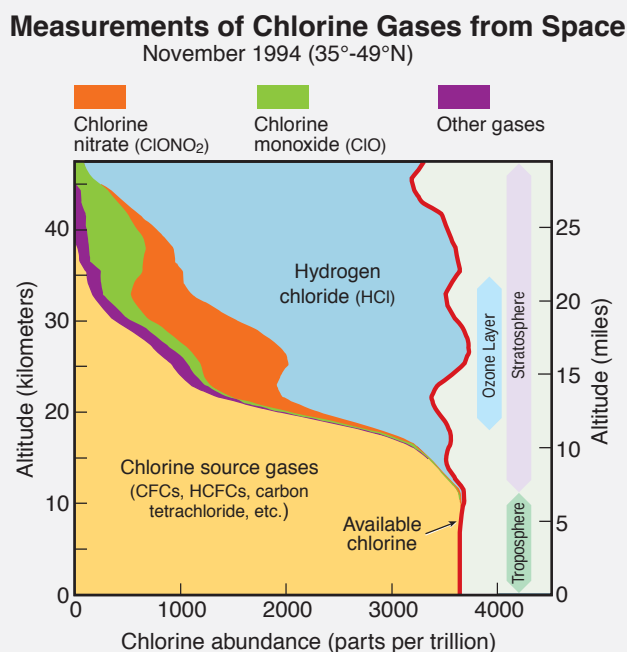


Figure Q8-2. Reactive chlorine gas observations.

Reactive chlorine gases and chlorine source gases can be measured from space. These abundance measurements made over midlatitudes, for example, show that chlorine-containing source gases are present in the troposphere and that reactive chlorine gases are present in the stratosphere. In the stratosphere, reactive chlorine gases increase with altitude and chlorine source gases decrease with altitude. This results because the source gases are converted to reactive gases in chemical reactions involving ultraviolet sunlight. The principal reactive gases formed are HCl , ClONO_2 , and ClO . The sum of reactive gases and source gases gives available chlorine, which is nearly constant with altitude up to 47 km. In the ozone layer, HCl and ClONO_2 are the most abundant reactive chlorine gases. (The unit “parts per trillion” is defined in the caption of *Figure Q7-1*.)

most reactive gas in ozone depletion, is a small fraction of available chlorine. This small value limits the amount of ozone destruction that occurs outside of polar regions.

Reactive chlorine in polar regions. Reactive chlorine gases in polar regions in summer look similar to the altitude profiles shown in *Figure Q8-2*. In winter, however, the presence of polar stratospheric clouds (PSCs) causes further chemical changes (see *Q10*). PSCs convert HCl and ClONO_2 to ClO when temperatures are near minimum values in the winter Arctic and Antarctic stratosphere. In that case, ClO becomes the principal reactive chlorine species in sunlit regions and ozone loss becomes very rapid. An example of the late-winter ClO and ozone distributions is shown in *Figure Q8-3* for the Antarctic stratosphere. These space-based measurements show that ClO abundances are high in the lower stratosphere over a region that exceeds the size of the Antarctic continent (greater than 13 million square kilometers or 5 million square miles). The peak abundance of ClO exceeds 1500 parts per trillion, which is much larger than typical mid-latitude values shown in *Figure Q8-2* and represents a large fraction of reactive chlorine in that altitude region. Because high ClO amounts cause rapid ozone loss (see *Q9*), ozone depletion is found in regions of elevated ClO (see *Figure Q8-3*).

Reactive bromine observations. Fewer measurements are available for reactive bromine gases than for reactive chlorine, in part because of the low abundance of bromine in the stratosphere. The most widely observed bromine gas is bromine monoxide (BrO). The measured abundances are consistent with values expected from the conversion of the bromine-containing source gases such as the halons and methyl bromide.

Other sources. Some reactive halogen gases are also produced at Earth’s surface by natural processes and by human activities. However, because reactive halogen gases are soluble in water, almost all become trapped in the lower atmosphere by dissolving in rainwater and ice, and ultimately are returned to Earth’s surface before they can reach the stratosphere. For example, reactive chlorine is present in the atmosphere as sea salt (sodium chloride) produced by evaporation of ocean spray. Because sea salt dissolves in water, this chlorine is removed and does not reach the stratosphere in appreciable quantities. Another ground-level source is emission of chlorine gases from swimming pools, household bleach, and other uses. When released to the atmosphere, this chlorine is rapidly converted to forms that are soluble in water and removed. The Space Shuttle and other rocket motors release reactive chlorine gases directly in the stratosphere. In that case the quantities are very small in comparison with other stratospheric sources.

Satellite Observations in the Lower Stratosphere

30 August 1996

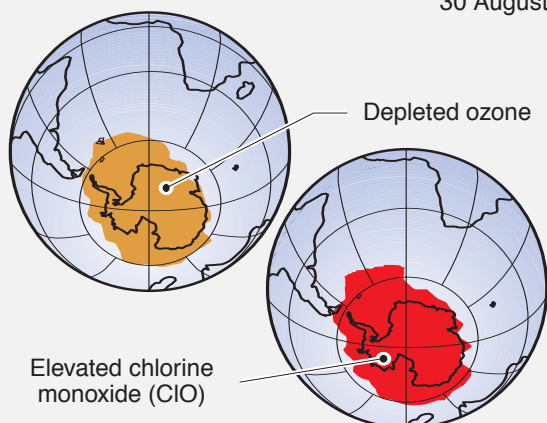


Figure Q8-3. Antarctic chlorine monoxide and ozone. Satellite instruments monitor ozone and reactive chlorine gases in the global stratosphere. Results are shown here for Antarctic winter for a narrow altitude region within the ozone layer. In winter, chlorine monoxide (ClO) reaches high values (1500 parts per trillion) in the ozone layer, much higher than observed anywhere else in the stratosphere because ClO is produced by reactions on polar stratospheric clouds. These high ClO values in the lower stratosphere last for 1 to 2 months, cover an area that at times exceeds that of the Antarctic continent, and efficiently destroy ozone in sunlit regions. Ozone values measured simultaneously within the ozone layer show very depleted values.

Volcanoes. Volcanic plumes generally contain large quantities of chlorine in the form of hydrogen chloride (HCl). Because the plumes also contain a considerable amount of water vapor, the HCl is efficiently scavenged by rainwater and ice and removed from the atmosphere. As a

result, most of the HCl in the plume does not enter the stratosphere. After large recent eruptions, the increase in HCl in the stratosphere has been small compared with the total amount of chlorine in the stratosphere from other sources.

Global Ozone Dobson Network

The first instrument for routine monitoring of total ozone was developed by Gordon M. B. Dobson in the 1920s. The instrument measures the intensity of sunlight at two ultraviolet wavelengths: one that is strongly absorbed by ozone and one that is weakly absorbed. The difference in light intensity at the two wavelengths is used to provide a measurement of total ozone above the instrument location.

A global network of ground-based, total ozone observing stations was established in 1957 as part of the International Geophysical Year. Today, there are about 100 sites distributed throughout the world (from South Pole, Antarctica (90°S) to Ellesmere Island, Canada (83°N)), many of which routinely measure total ozone with Dobson instruments. The accuracy of these observations is maintained by regular calibrations and intercomparisons. Data from the network have been essential for understanding the effects of chlorofluorocarbons (CFCs) and other ozone-depleting gases on the global ozone layer, starting before the launch of space-based ozone-measuring instruments and continuing to the present day. Because of their stability and accuracy, the Dobson instruments are now routinely used to help calibrate space-based observations of total ozone.

Pioneering scientists have traditionally been honored by having units of measure named after them. Accordingly, the unit of measure for total ozone is called the “Dobson unit” (see Q4).

Q9: What are the chlorine and bromine reactions that destroy stratospheric ozone?

Reactive gases containing chlorine and bromine destroy stratospheric ozone in “catalytic” cycles made up of two or more separate reactions. As a result, a single chlorine or bromine atom can destroy many hundreds of ozone molecules before it reacts with another gas, breaking the cycle. In this way, a small amount of reactive chlorine or bromine has a large impact on the ozone layer. Special ozone destruction reactions occur in polar regions because the reactive gas chlorine monoxide reaches very high levels there in the winter/spring season.

Stratospheric ozone is destroyed by reactions involving *reactive halogen gases*, which are produced in the chemical conversion of *halogen source gases* (see **Figure Q8-1**). The most reactive of these gases are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). These gases participate in three principal reaction cycles that destroy ozone.

Cycle 1. Ozone destruction Cycle 1 is illustrated in **Figure Q9-1**. The cycle is made up of two basic reactions: $\text{ClO} + \text{O}$ and $\text{Cl} + \text{O}_3$. The net result of Cycle 1 is to convert one ozone molecule and one oxygen atom into two oxygen molecules. In each cycle chlorine acts as a *catalyst* because ClO and Cl react and are reformed. In this way, one Cl atom participates in many cycles, destroying many ozone molecules. For typical stratospheric conditions at middle or low latitudes, a single chlorine atom can destroy hundreds of ozone molecules before it reacts with another gas to break the catalytic cycle.

Polar Cycles 2 and 3. The abundance of ClO is greatly increased in polar regions during winter as a result of reactions on the surfaces of polar stratospheric cloud (PSC) particles (see **Q10**). Cycles 2 and 3 (see **Figure Q9-2**) become the dominant reaction mechanisms for polar ozone loss because of the high abundances of ClO and the relatively low abundance of atomic oxygen (which limits the rate of ozone loss by Cycle 1). Cycle 2 begins with the self-reaction of ClO. Cycle 3, which begins with the reaction of ClO with BrO, has two reaction pathways to produce either Cl and Br or BrCl. The net result of both cycles is to destroy two ozone molecules and create three oxygen molecules. Cycles 2 and 3 account for most of the ozone loss observed in the Arctic and Antarctic stratospheres in the late winter/spring season (see **Q11 and Q12**). At high ClO abundances, the rate of ozone destruction can reach 2 to 3% per day in late winter/spring.

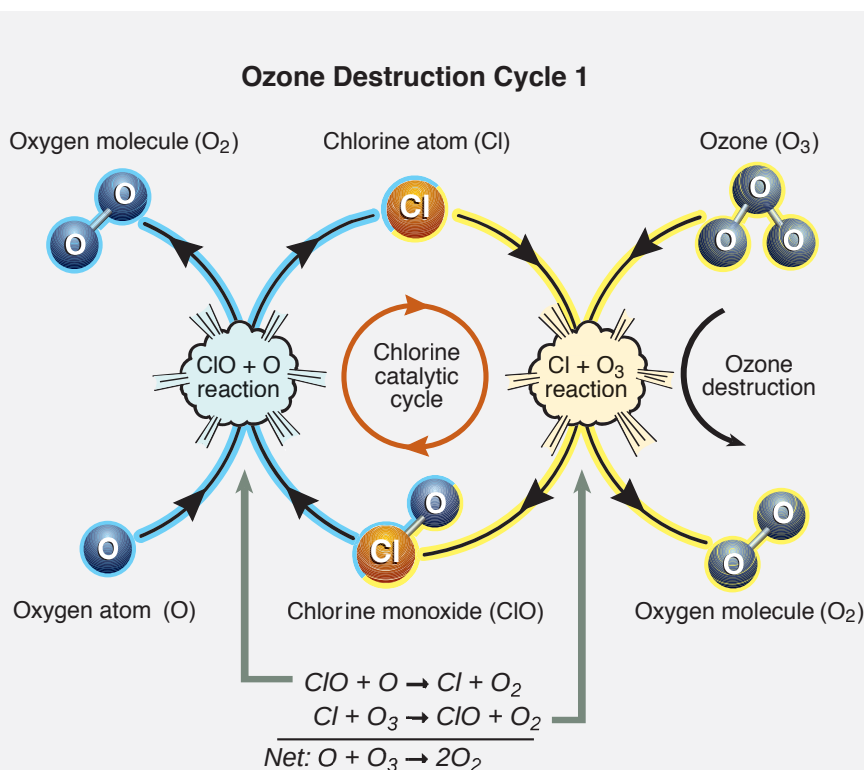
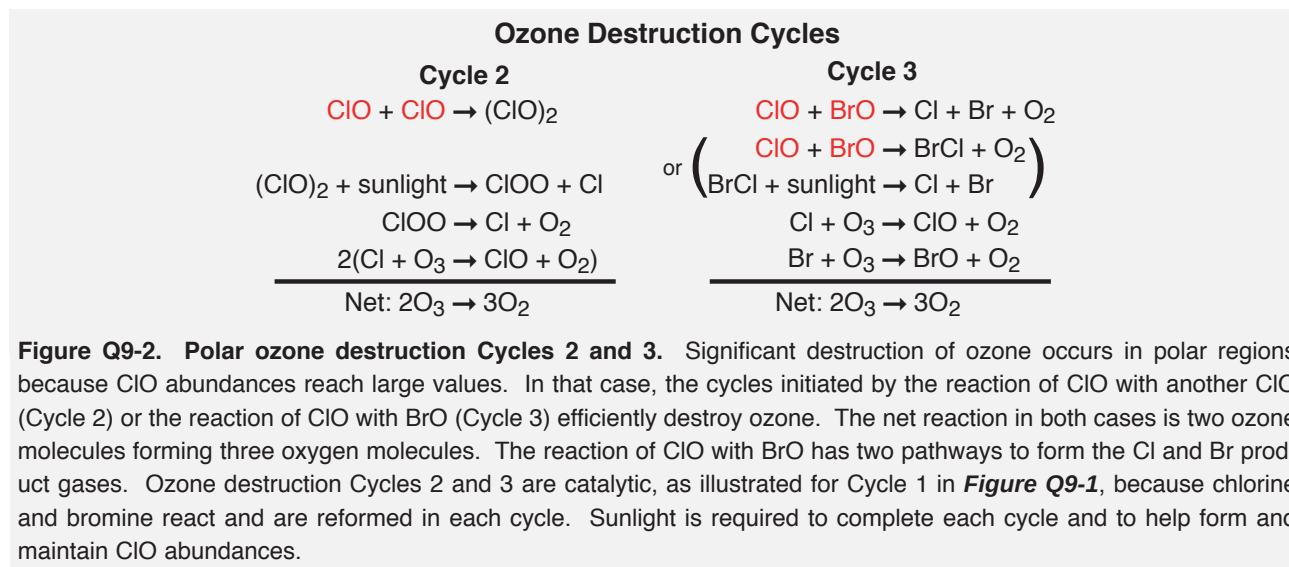


Figure Q9-1. Ozone destruction Cycle 1. The destruction of ozone in Cycle 1 involves two separate chemical reactions. The net or overall reaction is that of atomic oxygen with ozone, forming two oxygen molecules. The cycle can be considered to begin with either ClO or Cl. When starting with ClO, the first reaction is ClO with O to form Cl. Cl then reacts with (and thereby destroys) ozone and reforms ClO. The cycle then begins again with another reaction of ClO with O. Because Cl or ClO is reformed each time an ozone molecule is destroyed, chlorine is considered a catalyst for ozone destruction. Atomic oxygen (O) is formed when ultraviolet sunlight reacts with ozone and oxygen molecules. Cycle 1 is most important in the stratosphere at tropical and middle latitudes where ultraviolet sunlight is most intense.



Sunlight requirement. Sunlight is required to complete and maintain Cycles 1 through 3. Cycle 1 requires sunlight because atomic oxygen is formed only with ultraviolet sunlight. Cycle 1 is most important in the stratosphere at tropical and middle latitudes where sunlight is most intense.

In Cycles 2 and 3, sunlight is required to complete the reaction cycles and to maintain ClO abundances. In the continuous darkness of winter in the polar stratospheres, reaction Cycles 2 and 3 cannot occur. It is only in late winter/spring when sunlight returns to the polar regions that these cycles can occur. Therefore, the greatest destruction of ozone occurs in the partially to fully sunlit periods after midwinters in the polar stratospheres. The sunlight needed in Cycles 2 and 3 is not sufficient to form ozone

because ozone formation requires ultraviolet sunlight. In the stratosphere in the winter/spring period, ultraviolet sunlight is weak because Sun angles are low. As a result, ozone is destroyed in Cycles 2 and 3 in the sunlit winter stratosphere but is not produced in significant amounts.

Other reactions. Atmospheric ozone abundances are controlled by a wide variety of reactions that both produce and destroy ozone (see Q2). Chlorine and bromine catalytic reactions are but one group of ozone destruction reactions. Reactive hydrogen and reactive nitrogen gases, for example, are involved in other catalytic ozone-destruction cycles that also occur in the stratosphere. These reactions occur naturally in the stratosphere and their importance has not been as strongly influenced by human activities as have reactions involving halogens.

TWENTY QUESTIONS

Q10: Why has an “ozone hole” appeared over Antarctica when ozone-depleting gases are present throughout the stratosphere?

Ozone-depleting gases are present throughout the stratospheric ozone layer because they are transported great distances by atmospheric air motions. The severe depletion of the Antarctic ozone layer known as the “ozone hole” forms because of the special weather conditions that exist there and nowhere else on the globe. The very cold temperatures of the Antarctic stratosphere create ice clouds called polar stratospheric clouds (PSCs). Special reactions that occur on PSCs and the relative isolation of polar stratospheric air allow chlorine and bromine reactions to produce the ozone hole in Antarctic springtime.

The severe depletion of stratospheric ozone in Antarctic winter is known as the “ozone hole” (see Q11). Severe depletion first appeared over Antarctica because atmospheric conditions there increase the effectiveness of ozone destruction by reactive halogen gases (see Q8). The formation of the Antarctic ozone hole requires abundant reactive halogen gases, temperatures low enough to form polar stratospheric clouds (PSCs), isolation of air from other stratospheric regions, and sunlight.

Distributing halogen gases. Halogen source gases emitted at Earth’s surface are present in comparable abundances throughout the stratosphere in both hemispheres even though most of the emissions occur in the Northern Hemisphere. The abundances are comparable because

most source gases have no important natural removal processes in the lower atmosphere and because winds and warm-air convection redistribute and mix air efficiently throughout the troposphere. Halogen gases (in the form of source gases and some reactive products) enter the stratosphere primarily from the tropical troposphere. Atmospheric air motions then transport them upward and toward the poles in both hemispheres.

Low temperatures. The severe ozone destruction represented by the ozone hole requires that low temperatures be present over a range of stratospheric altitudes, over large geographical regions, and for extended time periods. Low temperatures are important because they allow polar stratospheric clouds (PSCs) to form.

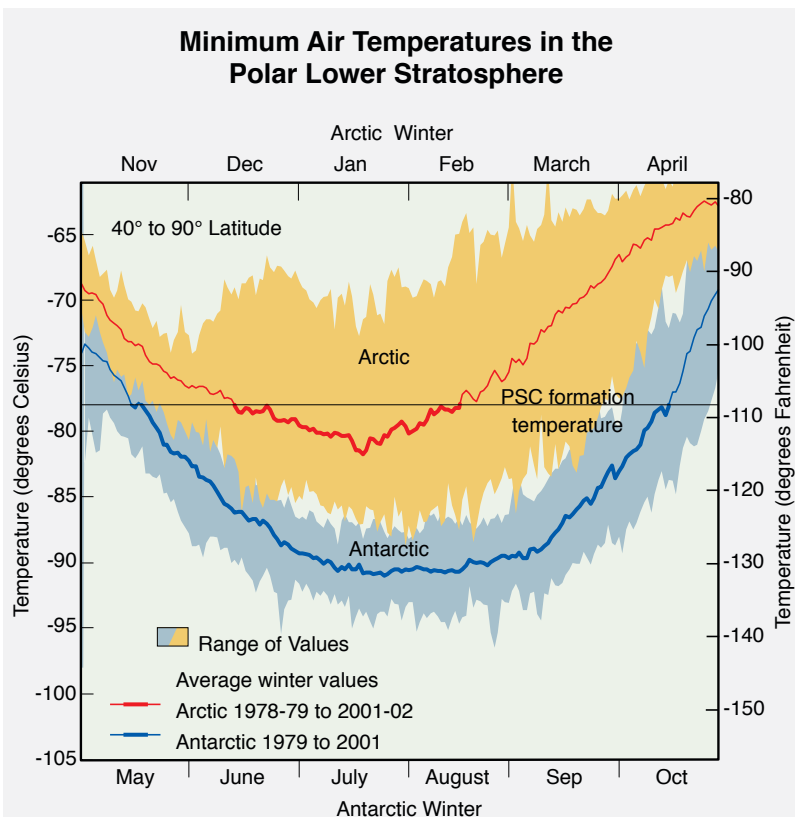


Figure Q10-1. Arctic and Antarctic temperatures. Stratospheric air temperatures in both polar regions reach minimum values in the lower stratosphere in the winter season. Minimum values over Antarctica reach -90°C in July and August in an average year. Over the Arctic, minimum average values are near -80°C in January and February. Polar stratospheric clouds (PSCs) are formed when winter temperatures fall below the formation temperature (about -78°C). This occurs on average for weeks to months over both poles (see heavy red and blue lines). Reactions on PSCs cause the highly reactive chlorine gas ClO to be formed, which increases the destruction of ozone. The range of minimum temperatures found in the Arctic is much greater than in the Antarctic. In some years, PSC formation temperatures are not reached in the Arctic, and significant ozone depletion does not occur. In the Antarctic, PSCs are formed over many months, and severe ozone depletion now occurs in each winter season.

Reactions on the surfaces of the cloud particles initiate a remarkable increase in the most reactive halogen gases (see below and Q8). Temperatures are lowest in the stratosphere over both polar regions in winter. In the Antarctic winter, minimum temperatures are generally lower and less variable than in the Arctic winter (see **Figure Q10-1**). Antarctic temperatures also remain below the PSC formation temperature for much longer periods during winter. This occurs, in part, because there are significant differences between the hemispheres in the distributions of land, ocean, and mountains at middle and high latitudes. The winter temperatures are low enough for PSCs to form for nearly the entire Antarctic winter but usually only for part of every Arctic winter.

Isolated conditions. Air in the polar stratospheric regions is relatively isolated from other stratospheric regions for long periods in the winter months. The isolation comes about because of strong winds that encircle the poles, preventing substantial motion of air in or out of the polar stratospheres. The isolation is much more effective in the Antarctic. Once chemical changes occur in the low-temperature air as a result of the presence of PSCs, the changes remain for many weeks to months.

Polar stratospheric clouds (PSCs). Polar stratospheric clouds cause changes in the abundances of reactive chlorine gases. Reactions occur on the surfaces of PSC particles that convert the reservoir forms of reactive chlorine gases, ClONO_2 and HCl , to the most reactive form ClO (see **Figure Q8-1**). ClO increases from a small fraction of available reactive chlorine gases to nearly all that is available (see Q8). With increased ClO , additional catalytic cycles involving ClO and BrO become active in the chemical destruction of ozone when sunlight is available (see Q9).

PSCs form when stratospheric temperatures fall below about -78°C (-108°F) in polar regions. As a result, PSCs are often found over vast areas of the winter polar regions and over a significant altitude range. At low polar temperatures, nitric acid (HNO_3) and sulfur-containing gases condense with water vapor to form solid and liquid PSC particles. At even lower temperatures, ice particles also form. PSC particles grow large enough and are numerous enough that cloud-like features can be observed from the ground under certain conditions, particularly when the Sun is near the horizon (see **Figure Q10-2**). PSCs are often found near mountain ranges in polar regions because the motion of air over the mountains can cause local cooling of stratospheric air.

When temperatures warm in spring, PSCs no longer form and the production of ClO ends. Without continued ClO production, ClO amounts decrease as other chemical reactions reform ClONO_2 and HCl . As a result, the intense period of ozone depletion ends.

PSC removal. Once formed, PSC particles move downward because of gravity. The largest particles move down several kilometers or more in the stratosphere during the low-temperature winter/spring period. Because most PSCs contain nitric acid, their downward motion removes nitric acid from regions of the ozone layer. That process is called *denitrification*. With less nitric acid, the highly reactive chlorine gas ClO remains chemically active for a longer period, thereby increasing chemical ozone destruction. Because PSC formation temperatures are required (see **Figure Q10-1**), denitrification occurs each winter in the Antarctic and in some, but not all, Arctic winters.

Arctic Polar Stratospheric Clouds



Figure Q10-2. Polar stratospheric clouds. This photograph of an Arctic polar stratospheric cloud (PSC) was taken from the ground at Kiruna, Sweden (67°N), on 27 January 2000. PSCs form during winters in the Arctic and Antarctic stratospheres. The particles grow from the condensation of water along with nitrogen and sulfur gases. Because the particles are large and numerous, the clouds often can be seen with the human eye when the Sun is near the horizon. Reactions on PSCs cause the highly reactive chlorine gas ClO to be formed, which is very effective in the chemical destruction of ozone.

TWENTY QUESTIONS

Discovering the role of PSCs. The formation of PSCs has been recognized for many years from ground-based observations. However, the geographical and altitude extent of PSCs in both polar regions was not known fully until PSCs were observed by a satellite instrument in the late 1970s. The role of PSCs in converting reactive chlorine gases to ClO was not understood until after the

discovery of the Antarctic ozone hole in 1985. Our understanding of the PSC role developed from laboratory studies of their surface reactivity, computer modeling studies of polar stratospheric chemistry, and direct sampling of PSC particles and reactive chlorine gases, such as ClO, in the polar stratospheric regions.

The Discovery of the Antarctic Ozone Hole

The first decreases in Antarctic ozone were observed in the early 1980s over research stations located on the Antarctic continent. The observations showed unusually low total overhead ozone during the late winter/early spring months of September, October, and November. Total ozone was lower in these months compared with previous observations made as early as 1957. The early-published reports came from the British Antarctic Survey and the Japan Meteorological Agency. The results became more widely known in the international community after they were published in the journal *Nature* in 1985 by three scientists from the British Antarctic Survey. Soon after, satellite measurements confirmed the spring ozone depletion and further showed that in each late winter/spring season starting in the early 1980s, the depletion extended over a large region centered near the South Pole. The term “ozone hole” came about from satellite images of total ozone that showed very low values encircling the Antarctic continent each spring (see *Q11*). Currently, the formation and severity of the Antarctic “ozone hole” are documented each year by a combination of satellite, ground-based, and balloon observations of ozone.

III. STRATOSPHERIC OZONE DEPLETION

Q11: How severe is the depletion of the Antarctic ozone layer?

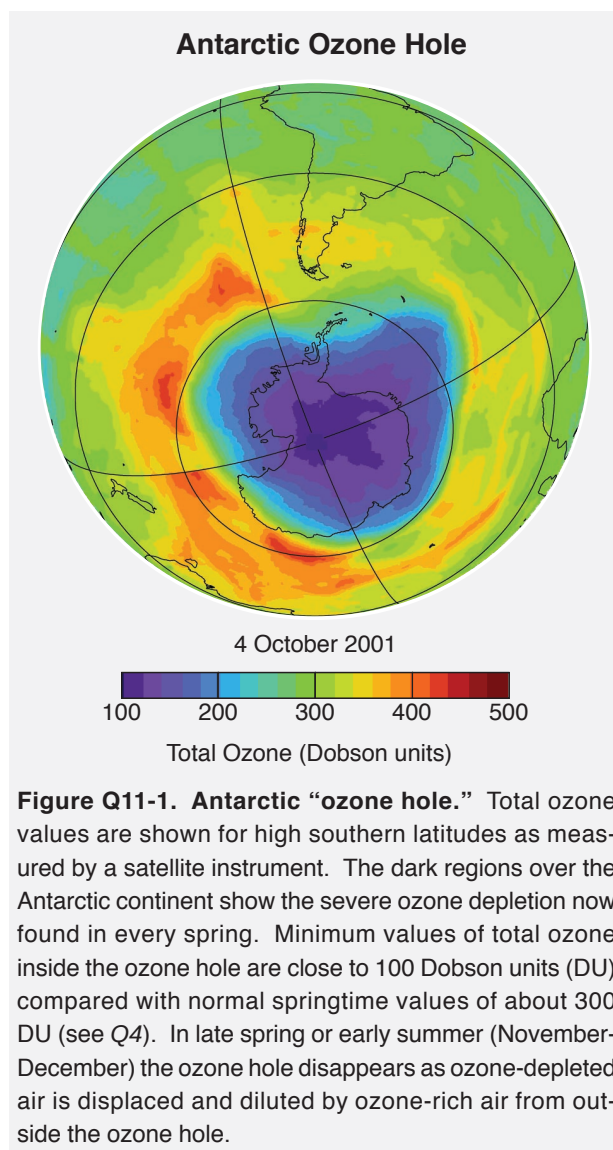
Severe depletion of the Antarctic ozone layer was first observed in the early 1980s. Antarctic ozone depletion is seasonal, occurring primarily in late winter and spring (August–November). Peak depletion occurs in October when ozone is often completely destroyed over a range of altitudes, reducing overhead total ozone by as much as two-thirds at some locations. This severe depletion creates the “ozone hole” in images of Antarctic total ozone made from space. In most years the maximum area of the ozone hole usually exceeds the size of the Antarctic continent.

The severe depletion of Antarctic ozone known as the “ozone hole” was first observed in the early 1980s. The depletion is attributable to chemical destruction by reactive halogen gases, which increased in the stratosphere in the latter half of the 20th century (see Q16). Conditions in the Antarctic winter stratosphere are highly suitable for ozone depletion because of (1) the long periods of extremely low temperatures, which promote PSC formation and removal; (2) the abundance of reactive halogen gases, which chemically destroy ozone; and (3) the isolation of stratospheric air during the winter, which allows time for chemical destruction to occur (see Q10). The severity of Antarctic ozone depletion can be seen using images of total ozone from space, ozone altitude profiles, and long-term average values of polar total ozone.

Antarctic ozone hole. The most widely used images of Antarctic ozone depletion are those from space-based measurements of total ozone. Satellite images made during Antarctic winter and spring show a large region centered near the South Pole in which total ozone is highly depleted (see **Figure Q11-1**). This region has come to be called the “ozone hole” because of the near-circular contours of low ozone values in the images. The area of the ozone hole has reached 25 million square kilometers (about 10 million square miles) in recent years, which is nearly twice the area of the Antarctic continent. Minimum values of total ozone inside the ozone hole have fallen as low as 100 Dobson units (DU) compared with normal springtime values of about 300 DU (see Q4). The mass of ozone destroyed over the Antarctic each season has reached an estimated 80 megatons, which is about 3% of the global ozone mass (1 megaton = 1 billion kilograms = 2.2 billion pounds).

Altitude profiles of Antarctic ozone. Ozone within the “ozone hole” is also measured using balloonborne instruments (see Q5). Balloon measurements show changes within the ozone layer, the vertical region that contains the highest ozone abundances in the stratosphere. At geographic locations where the lowest total ozone values occur in ozone hole images, balloon measurements show that the

chemical destruction of ozone is complete over a vertical region of several kilometers. **Figure Q11-2** shows an example of such depletion with balloon measurements



TWENTY QUESTIONS

made over South Pole, Antarctica, on 2 October 2001. The altitude region of total depletion (14-20 kilometers) in the profile corresponds to the region of lowest winter temperatures and highest ClO abundances. The average South Pole ozone profiles for the decades 1962-1971 and 1992-2001 (see **Figure Q11-2**) show how reactive halogen gases have changed the ozone layer. In the 1960s, the ozone layer is clearly evident in the October average profile. In the 1990s, minimum average values in the center of the layer have fallen by 90% from the earlier values.

Long-term total ozone changes. Low winter temperatures and isolated conditions occur each year in the Antarctic stratosphere. As a result, significant spring ozone depletion has been observed every year since the early 1980s. In prior years, the amounts of reactive halogen gases in the stratosphere were insufficient to cause significant depletion. Satellite observations can be used to examine the average total ozone abundances in both polar regions for the last three decades (see **Figure Q12-1**). In the Antarctic, average values decreased steadily through the 1980s and 1990s, reaching minimum values that were 37%

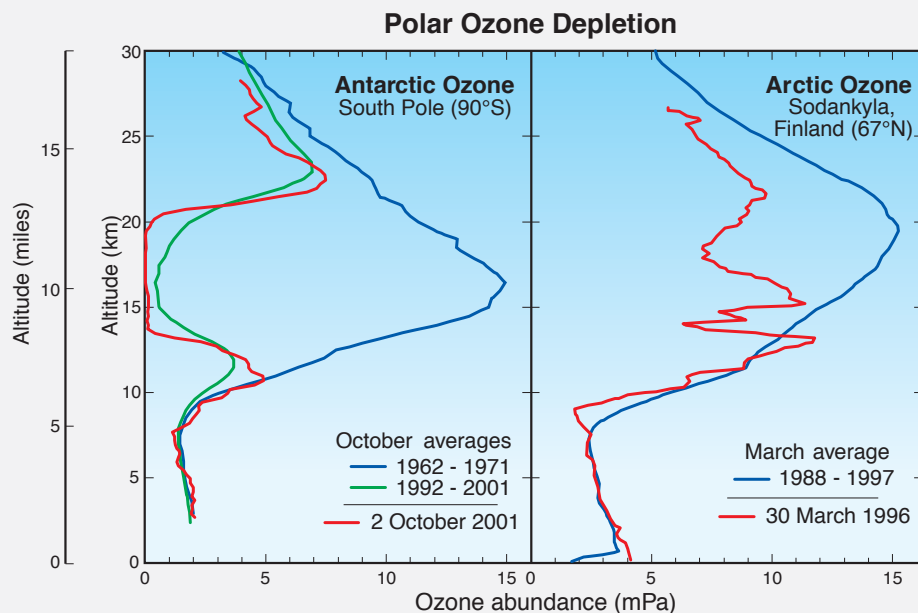
less than in pre-ozone-hole years (1970-1982). The year-to-year changes in the average values reflect variations in the meteorological conditions, which affect the extent of low polar temperatures and the transport of air into and out of the Antarctic winter stratosphere. However, essentially all of the ozone depletion in the Antarctic in most years is attributable to chemical loss from reactive halogen gases.

Restoring ozone in spring. The depletion of Antarctic ozone occurs primarily in the late winter/spring season. In spring, temperatures in the lower polar stratosphere eventually warm, thereby ending PSC formation and the most effective chemical cycles that destroy ozone (see **Q10**). The transport of air between the polar stratosphere and lower latitudes also increases during this time, ending winter isolation. This allows ozone-rich air to be transported to polar regions, displacing air in which ozone has been severely depleted. This displaced air is diluted at lower latitudes with more abundant ozone-rich air. As a result, the ozone hole disappears by December and Antarctic ozone amounts remain near normal until the next winter season.

Figure Q11-2. Arctic and Antarctic ozone distribution.

The stratospheric ozone layer resides between about 10 and 50 kilometers (6 to 31 miles) above Earth's surface over the globe. Long-term observations of the ozone layer from small balloons allow the winter Antarctic and Arctic regions to be compared. In the Antarctic at the South Pole, halogen gases have destroyed ozone in the ozone layer beginning in the 1980s. Before that period, the ozone layer was clearly present as shown here using average ozone values from balloon observations made

between 1962 and 1971. In more recent years, as shown here for 2 October 2001, ozone is destroyed completely between 14 and 20 kilometers (8 to 12 miles) in the Antarctic in spring. Average October values in the ozone layer now are reduced by 90% from pre-1980 values. The Arctic ozone layer is still present in spring as shown by the average March profile obtained over Finland between 1988 and 1997. However, March Arctic ozone values in some years are often below normal average values as shown here for 30 March 1996. In such years, winter minimum temperatures are generally below PSC formation temperatures for long periods. (Ozone abundances are shown here with the unit "milli-Pascals" (mPa), which is a measure of absolute pressure (100 million mPa = atmospheric sea-level pressure).)



Q12: Is there depletion of the Arctic ozone layer?

Yes, significant depletion of the Arctic ozone layer now occurs in some years in the late winter/spring period (January–April). However, the maximum depletion is generally less severe than that observed in the Antarctic and is more variable from year to year. A large and recurrent “ozone hole,” as found in the Antarctic stratosphere, does not occur in the Arctic.

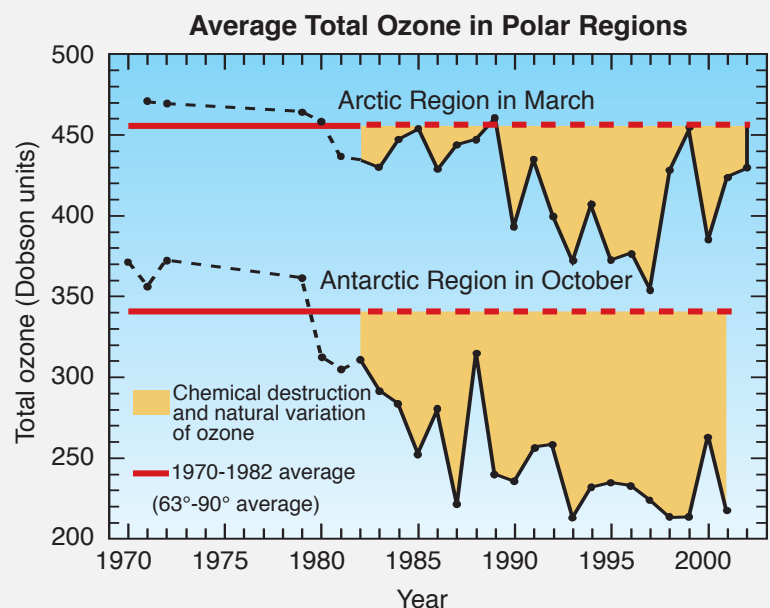
Significant ozone depletion in the Arctic stratosphere occurs in cold winters because of reactive halogen gases. The depletion, however, is much less than occurs in every Antarctic winter and spring. Although Arctic depletion does not generally create persistent “ozone hole”-like features in Arctic total ozone maps, depletion is observed in altitude profiles of ozone and in long-term average values of polar ozone.

Altitude profiles of Arctic ozone. Arctic ozone is measured using balloonborne instruments (see Q5), as in the Antarctic (see Q11). Balloon measurements show changes within the ozone layer, the vertical region that contains the highest ozone abundances in the stratosphere. **Figure Q11-2** shows an example of a depleted ozone profile in the Arctic region on 30 March 1996, and contrasts the depletion with that found in the Antarctic. The 30 March spring profile shows much less depletion than the 2 October spring profile in the Antarctic. In general, some reduction in the Arctic ozone layer occurs each winter/spring season. However, complete depletion each year over a broad vertical layer, as is now common in the Antarctic stratosphere, is not found in the Arctic.

Long-term total ozone changes. Satellite observations can be used to examine the average total ozone abundances in the Arctic region for the last three decades and to contrast them with results from the Antarctic (see **Figure Q12-1**). Decreases from the pre-ozone-hole average values (1970–1982) were observed in the Arctic beginning in the 1980s, when similar changes were occurring in the Antarctic. The decreases have reached a maximum of 22%, but have remained smaller than those found in the Antarctic since the mid-1980s. The year-to-year changes in the average Arctic and Antarctic average ozone values reflect annual variations in meteorological conditions that affect the extent of low polar temperatures and the transport of air into and out of the polar stratosphere. The effect of these variations is generally greater for the Arctic than the Antarctic. In almost all years, most of the Arctic ozone decrease (about 75%) is attributable to chemical destruction by reactive halogen gases.

Arctic vs. Antarctic. The Arctic winter stratosphere is generally warmer than its Antarctic counterpart (see **Figure Q10-1**). Higher temperatures reduce polar stratospheric cloud (PSC) formation, the conversion of reac-

Figure Q12-1. Average polar ozone. Total ozone in polar regions is measured by well-calibrated satellite instruments. Shown here is a comparison of average springtime total-ozone values found between 1970 and 1982 (solid red line) with those in later years. Each point represents a monthly average in October in the Antarctic or in March in the Arctic. After 1982, significant ozone depletion is found in most years in the Arctic and all years in the Antarctic. The largest average depletions have occurred in the Antarctic in the last decade. Natural variations in meteorological conditions influence the year-to-year changes in depletion, particularly in the Arctic. Essentially all of the decrease in the Antarctic and usually most of the decrease in the Arctic each year are attributable to chemical destruction by reactive halogen gases. Average total ozone values over the Arctic are initially larger each winter/spring season because more ozone is transported poleward in the Northern Hemisphere each season than in the Southern Hemisphere.



TWENTY QUESTIONS

tive chlorine gases to form ClO, and, as a consequence, the amount of ozone depletion (see *Q10*). Furthermore, the temperature and wind conditions are much more variable in the Arctic from winter to winter and within a winter season than in the Antarctic. Large year-to-year differences occur in Arctic minimum temperatures and the duration of PSC-forming temperatures into early spring. In a few Arctic winters, minimum temperatures are not low enough for PSCs to form. These factors combine to cause ozone depletion to be variable in the Arctic from year to year, with some years having little to no ozone depletion.

As in the Antarctic, depletion of ozone in the Arctic is confined to the late winter/spring season. In spring, temperatures in the lower stratosphere eventually warm, thereby ending PSC formation and the most effective chemical cycles that destroy ozone. The subsequent trans-

port of ozone-rich air into the Arctic stratosphere displaces ozone-depleted air. As a result, ozone layer abundances are restored to near-normal values until the following winter.

High Arctic total ozone. A significant difference exists between the Northern and Southern Hemispheres in how ozone-rich stratospheric air is transported into the polar regions from lower latitudes during fall and winter. In the northern stratosphere, the poleward and downward transport of ozone-rich air is stronger. As a result, before the onset of ozone depletion in the 1980s, total ozone values in the Arctic were considerably higher than in the Antarctic in winter and spring (see *Figure Q12-1*). The Arctic values have remained higher to the present day because of the greater depletion of Antarctic ozone.

Replacing the Loss of “Good” Ozone in the Stratosphere

The idea is sometimes put forth that humans could replace the loss of global stratospheric ozone, called “good” ozone, by making ozone and transporting it to the stratosphere. Ozone amounts reflect a balance in the stratosphere between continual production and destruction by mostly naturally occurring reactions (see *Q2*). The addition of chlorine and bromine to the stratosphere from human activities has increased ozone destruction and lowered “good” ozone amounts. Adding manufactured ozone to the stratosphere would upset the existing balance. As a consequence, most added ozone would be destroyed in chemical reactions within weeks to months as the balance was restored. So, it is not practical to consider replacing the loss of global stratospheric ozone because the replacement effort would need to continue indefinitely, or as long as increased chlorine and bromine amounts remained.

Other practical difficulties in replacing stratospheric ozone are the large amounts of ozone required and the delivery method. The total amount of atmospheric ozone is approximately 3000 megatons (1 megaton = 1 billion kilograms) with most residing in the stratosphere. The replacement of the average global ozone loss of 3% would require 90 megatons of stratospheric ozone to be distributed throughout the layer located many kilometers above Earth’s surface. The energy required to produce this amount of ozone would be a significant fraction of the electrical power generated in the United States, which is now approximately 5 trillion kilowatt hours. Processing and storing requirements for ozone, which is explosive and toxic in large quantities, would increase the energy requirement. In addition, methods suitable to deliver and distribute large amounts of ozone to the stratosphere have not been demonstrated yet. Concerns for a global delivery system would include further significant energy use and unforeseen environmental consequences.

Q13: How large is the depletion of the global ozone layer?

The ozone layer has been depleted gradually since 1980 and now is about an average of 3% lower over the globe. The depletion, which exceeds the natural variations of the ozone layer, is very small near the equator and increases with latitude toward the poles. The large average depletion in polar regions is primarily a result of the late winter/spring ozone destruction that occurs there annually.

Stratospheric ozone has decreased over the globe since the 1980s. The depletion, which in the period 1997-2001 averaged about 3% (see **Figure Q13-1**), is larger than natural variations in ozone. The observations shown in **Figure Q13-1** have been smoothed to remove regular ozone changes that are due to seasonal and solar effects (see **Q14**). The increase in reactive halogen gases in the stratosphere is considered to be the primary cause of the average depletion. The lowest ozone values in recent years occurred following the 1991 eruption of Mt. Pinatubo, which increased the number of sulfur-containing particles in the stratosphere. The particles remain in the stratosphere for several years, increasing the effectiveness of reactive halogen gases in destroying ozone (see **Q14**).

Observed ozone depletion varies significantly with latitude on the globe (see **Figure Q13-1**). The largest losses occur at the highest southern latitudes as a result of the severe ozone loss over Antarctica each winter/spring period. The next largest losses are observed in the Northern Hemisphere, caused in part by winter/spring losses over the Arctic. Air depleted in ozone over both polar regions spreads away from the poles during and after each winter/spring period. Ozone depletion also occurs directly at latitudes between the equator and polar regions, but is smaller because of smaller amounts of reactive halogen gases present there.

Tropical regions. There has been little or no depletion of total ozone in the tropics (between about 20° latitude north and south of the equator in **Figure Q13-1**). In this region of the lower stratosphere, air has only recently (less than 18 months) been transported from the lower atmosphere. As a result, the conversion of halogen source gases to reactive halogen gases is very small. Because of the low abundance of reactive gases, total ozone depletion in this region is also very small. In contrast, stratospheric air in polar regions has been in the stratosphere for an average of 4 to 7 years, and the abundance of reactive halogen gases is much larger.

Seasonal changes. The magnitude of global ozone depletion also depends on season of the year. In the period pre-1980 to 1997-2001, average total ozone decreased by about 3% in northern middle latitudes (35°N-60°N) and about 6% at southern middle latitudes (35°S-60°S). The seasonality of these changes is different in the two hemispheres. In the Northern Hemisphere, larger decreases are observed in winter/spring (4%) than in summer/autumn (2%). In the Southern Hemisphere, the decreases are about the same (6%) during all seasons.

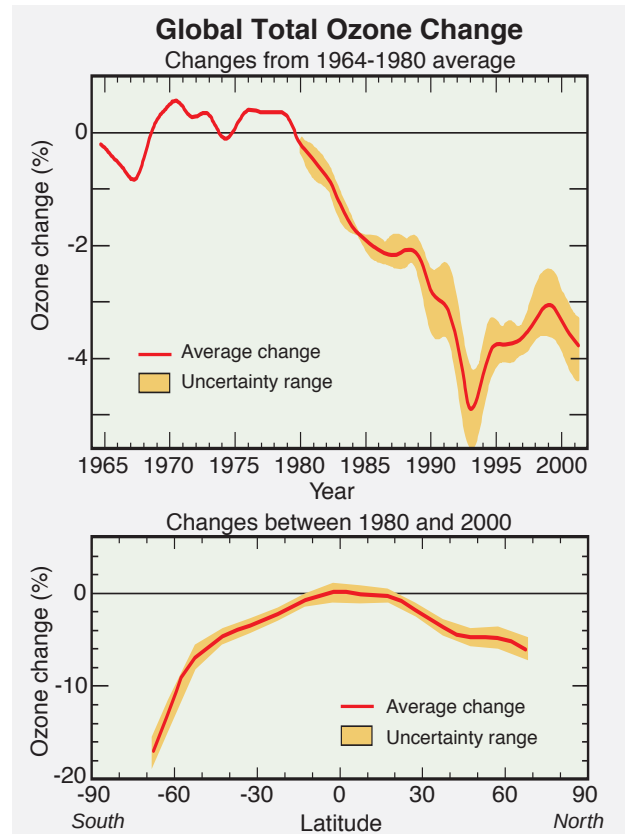


Figure Q13-1. Global total ozone changes. Global total ozone values decreased by an average of a few percent in the last two decades, as measured by satellite instruments. In the top panel, global ozone changes are compared with average global ozone found in the period of 1964 to 1980. Between 1980 and 2000, the largest decreases occurred following the volcanic eruption of Mt. Pinatubo in 1991. In the 1997 to 2001 period global ozone was reduced by about 3% from the 1964-1980 average. In the bottom panel, ozone changes between 1980 and 2000 are compared for different latitudes. The largest decreases have occurred at the highest latitudes in both hemispheres because of the large winter/spring depletion in polar regions. The losses in the Southern Hemisphere are greater than those in the Northern Hemisphere because of the greater losses that occur each year in the Antarctic stratosphere. Long-term changes in the tropics are much smaller because reactive halogen gases are not abundant in the tropical lower stratosphere.

TWENTY QUESTIONS

Q14: Do changes in the Sun and volcanic eruptions affect the ozone layer?

Yes, factors such as changes in solar radiation, as well as the formation of stratospheric particles after volcanic eruptions, do influence the ozone layer. However, neither factor can explain the average decreases observed in global total ozone over the last two decades. If large volcanic eruptions occur in the coming decades, ozone depletion will increase for several years after the eruption.

Changes in solar radiation and increases in stratospheric particles from volcanic eruptions both affect the abundance of stratospheric ozone, but they have not caused the long-term decreases observed in total ozone.

Solar changes. The formation of stratospheric ozone is initiated by ultraviolet (UV) radiation coming from the Sun (see **Figure Q2-1**). As a result, an increase in the Sun's radiation output increases the amount of ozone in Earth's atmosphere. The Sun's radiation output and sunspot number vary over the well-known 11-year solar cycle. Observations over several solar cycles (since the

1960s) show that global total ozone levels vary by 1 to 2% between the maximum and minimum of a typical cycle. Changes in solar output at a wavelength of 10.7 cm, although much larger than changes in total solar output, are often used to show when periods of maximum and minimum total output occur (see **Figure Q14-1**). Since 1978, the Sun's output has gone through maximum values around 1969, 1980, and 1991, and is currently near a maximum value in 2002.

Over the last two decades, average total ozone has decreased over the globe. Average values in recent years

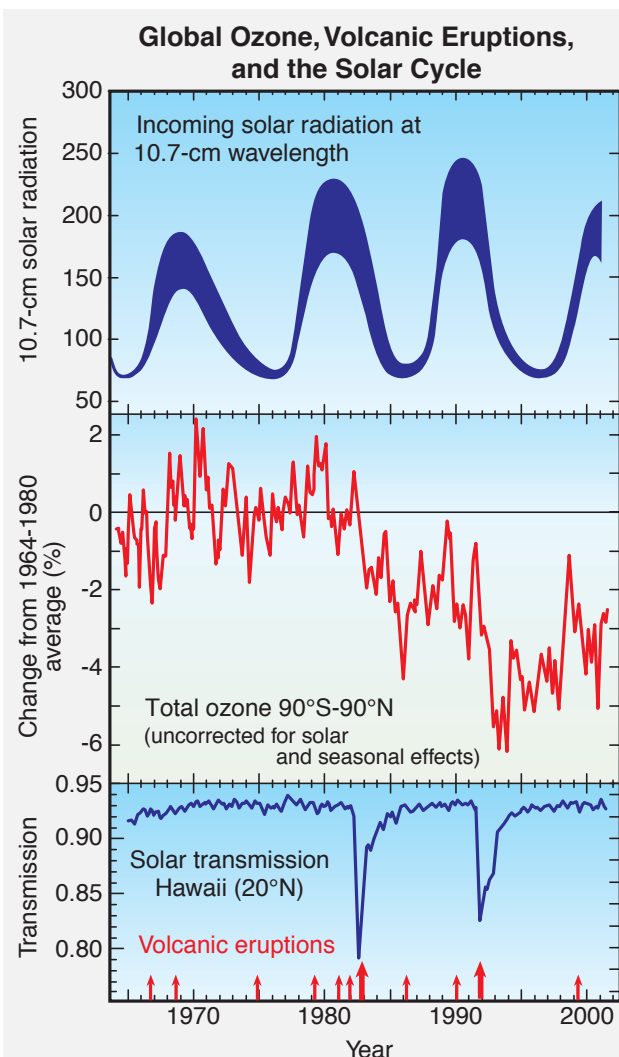


Figure Q14-1. Solar changes and volcanoes. Total ozone values have decreased beginning in the early 1980s (see middle panel). The ozone values shown have not been smoothed for solar and seasonal effects as they were in **Figure Q13-1**. Incoming solar radiation, which produces ozone in the stratosphere, changes on a well-recognized 11-year cycle. Solar radiation at 10.7-cm wavelength is often used to show the times of maximum and minimum solar output (see top panel). A comparison of the top and middle panels indicates that the cyclic changes in solar output cannot account for the long-term decreases in ozone. Volcanic eruptions occurred frequently in the 1965 to 2002 period. The largest recent eruptions are El Chichón (1982) and Mt. Pinatubo (1991) (see large red arrows). Large volcanic eruptions are monitored by the decreases in solar transmission to Earth's surface that occur because new particles are formed in the stratosphere from volcanic sulfur emissions (see bottom panel). These particles increase ozone depletion but do not remain in the stratosphere for more than a few years. A comparison of the middle and bottom panels indicates that large volcanic eruptions also cannot account for the long-term decreases found in global total ozone.

show a 3-4% depletion from pre-1980 values (see **Figure Q14-1**). The ozone values shown have not been smoothed for solar and seasonal effects as they were for **Figure Q13-1**. Over the same period, changes in solar output show the expected 11-year cycle but do not show a decrease with time. For this reason, the long-term decreases in global ozone cannot result from changes in solar output alone. Most discussions of long-term ozone changes presented in this and previous international scientific assessments account for the influence of the 11-year solar cycle.

Past volcanoes. Large volcanic eruptions inject sulfur gases directly into the ozone layer, causing new sulfate particles to be formed. The particles initially form in the stratosphere above the volcano location and then spread globally as air is transported within the stratosphere. The presence of volcanic particles in the stratosphere is shown by observations of solar transmission through the atmosphere. When large amounts of particles are present in the stratosphere, transmission of solar radiation is reduced. The large eruptions of El Chichón (1982) and Mt. Pinatubo (1991) are recent examples of events that temporarily reduced transmission (see **Figure Q14-1**).

Laboratory measurements and stratospheric observations have shown that chemical reactions on the surface of volcanically produced particles increase ozone destruction by increasing the amounts of the highly reactive chlorine gas, chlorine monoxide (ClO). Ozone depletion increases as a consequence of increased ClO. The most recent large eruption was that of Mt. Pinatubo, which

resulted in up to a 10-fold increase in the number of particles available for surface reactions. Both El Chichón and Mt. Pinatubo reduced global ozone for a few years (see **Figure Q14-1**). After a few years, the effect of volcanic particles diminishes as volcanically produced particles are gradually removed from the stratosphere by natural air circulation. Because of particle removal, the few large volcanic eruptions of the last two decades cannot account for the long-term decreases observed in ozone over the same period.

Future volcanoes. Observations and atmospheric models indicate that the record-low ozone levels observed in 1992-1993 resulted from the relatively large number of particles produced by the Mt. Pinatubo eruption, combined with the relatively large amounts of halogen gases present in the stratosphere in the 1990s. If the Mt. Pinatubo eruption had occurred before 1980, changes to global ozone would have been much smaller than observed in 1992-1993 because the abundance of halogen gases in the stratosphere was smaller. In the early decades of the 21st century, the abundance of halogen gases will still be substantial in the global atmosphere (see **Figure Q16-1**). If large volcanic eruptions occur in these early decades, ozone depletion will increase for several years. If an eruption larger than Mt. Pinatubo occurs then ozone losses could be larger than previously observed and persist longer. Only later in the 21st century when halogen gas abundances have declined will the effect of volcanic eruptions on ozone be lessened.

IV. CONTROLLING OZONE-DEPLETING GASES

Q15: Are there regulations on the production of ozone-depleting gases?

Yes, the production of ozone-depleting gases is regulated under a 1987 international agreement known as the “Montreal Protocol on Substances that Deplete the Ozone Layer” and its subsequent Amendments and Adjustments. The Protocol, now ratified by over 180 nations, establishes legally binding controls on the national production and consumption of ozone-depleting gases. Production and consumption of all principal halogen-containing gases by developed and developing nations will be significantly reduced or phased out before the middle of the 21st century.

Montreal Protocol. In 1985, a treaty called the *Convention for the Protection of the Ozone Layer* was signed by 20 nations in Vienna. The signing nations agreed to take appropriate measures to protect the ozone layer from human activities. The Vienna Convention supported research, exchange of information, and future protocols. In response to growing concern, the *Montreal Protocol on Substances that Deplete the Ozone Layer* was signed in 1987 and ratified in 1989. The Protocol established legally binding controls for developed and developing nations on the production and consumption of halogen source gases known to cause ozone depletion. National consumption of a halogen gas is defined as the amount that production and imports of a gas exceed its export to other nations.

Amendments and Adjustments. As the scientific basis of ozone depletion became more certain after 1987 and substitutes and alternatives became available for the principal halogen source gases, the Montreal Protocol was strengthened with Amendments and Adjustments. These revisions added new controlled substances, accelerated existing control measures, and scheduled phaseouts of the production of certain gases. The initial Protocol called for only a slowing of chlorofluorocarbon (CFC) and halon production. The 1990 London Amendments to the Protocol called for a phaseout of the production of the most damaging ozone-depleting substances in developed nations by 2000 and in developing nations by 2010. The 1992 Copenhagen Amendments accelerated the date of the phaseout to 1996 in developed nations. Further controls on ozone-depleting substances were agreed upon in later meetings in Vienna (1995), Montreal (1997), and Beijing (1999).

Montreal Protocol projections. The future stratospheric abundances of effective stratospheric chlorine can be projected based on the provisions of the Montreal Protocol. The concept of effective stratospheric chlorine accounts for the combined effect on ozone of chlorine- and bromine-containing gases. The results are shown in **Figure Q15-1** for the following cases:

- No Protocol and continued production increases of 3% per year (business-as-usual scenario).
- Continued production as allowed by the Protocol’s original provisions agreed upon in Montreal in 1987.
- Restricted production as outlined in the subsequent Amendments and Adjustments: London, 1990; Copenhagen, 1992; and Beijing, 1999. (The city names and years signify where and when the agreements were made.)
- Zero emissions of ozone-depleting gases starting in 2003.

In each case, production of a gas is assumed to result in its eventual emission to the atmosphere. Without the Montreal Protocol, continued production and use of CFCs and other ozone-depleting gases are projected to have increased effective stratospheric chlorine tenfold by the mid-2050s compared with the 1980 value. Such high values likely would have increased global ozone depletion far beyond that currently observed. As a result, harmful UV-B radiation would have increased substantially at Earth’s surface, causing a rise in excess skin cancer cases (see lower panel of **Figure Q15-1** and **Q17**).

The 1987 provisions of the Montreal Protocol would have only slowed the approach to high effective chlorine values by one or more decades in the 21st century. Not until the 1992 Copenhagen Amendments and Adjustments did the Protocol projections show a *decrease* in future effective stratospheric chlorine values. Now, with full compliance to the Montreal Protocol and its Amendments and Adjustments, use of the major human-produced ozone-depleting gases will ultimately be phased out and effective stratospheric chlorine will slowly decay, reaching pre-ozone-hole values in the mid-21st century.

Zero emissions. Effective chlorine values in the coming decades will be influenced by emissions of halogen source gases produced in those decades as well as the emission of currently existing gases that are now being used or stored in various ways. Some continued

production and consumption of ozone-depleting gases is allowed, particularly in developing nations, under the 1999 Beijing agreements. As a measure of the contribution of these continued emissions to the effective chlorine value, the “zero emissions” case is included in **Figure Q15-1**. In this hypothetical case, all emissions of ozone-depleting gases are set to zero beginning in 2003. The reductions in effective stratospheric chlorine beyond the values expected for the 1999 Beijing agreement would be significantly smaller than most earlier changes, as shown.

HCFC substitute gases. The Montreal Protocol provides for the transitional use of hydrochlorofluorocarbons (HCFCs) as substitute compounds for principal halogen source gases such as CFC-12. HCFCs differ chemically from most other halogen source gases in that they contain hydrogen (H) atoms in addition to chlorine and fluorine atoms. HCFCs are used for refrigeration, for blowing foams, and as solvents, which were primary uses of CFCs. HCFCs are 1 to 15% as effective as CFC-12 in depleting stratospheric ozone because they are chemically removed primarily in the troposphere. This removal partially pro-

ducts stratospheric ozone from the halogens contained in HCFCs. In contrast, CFCs and many other halogen source gases are chemically inert in the troposphere and, hence, reach the stratosphere without being significantly removed. Because HCFCs still contribute to the halogen abundance in the stratosphere, the Montreal Protocol requires the production and consumption of HCFCs to end in developed and developing nations by 2040.

HFC substitute gases. Hydrofluorocarbons (HFCs) are also used as substitute compounds for CFCs and other halogen source gases. HFCs contain only hydrogen, fluorine, and carbon atoms. Because HFCs contain no chlorine or bromine, they do not contribute to ozone depletion. As a consequence, the HFCs are not regulated by the Montreal Protocol. However, HFCs (as well as all halogen source gases) are radiatively active gases that contribute to human-induced global warming and climate change as they accumulate in the atmosphere (see Q18). HFCs are included in the group of gases listed in the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC).

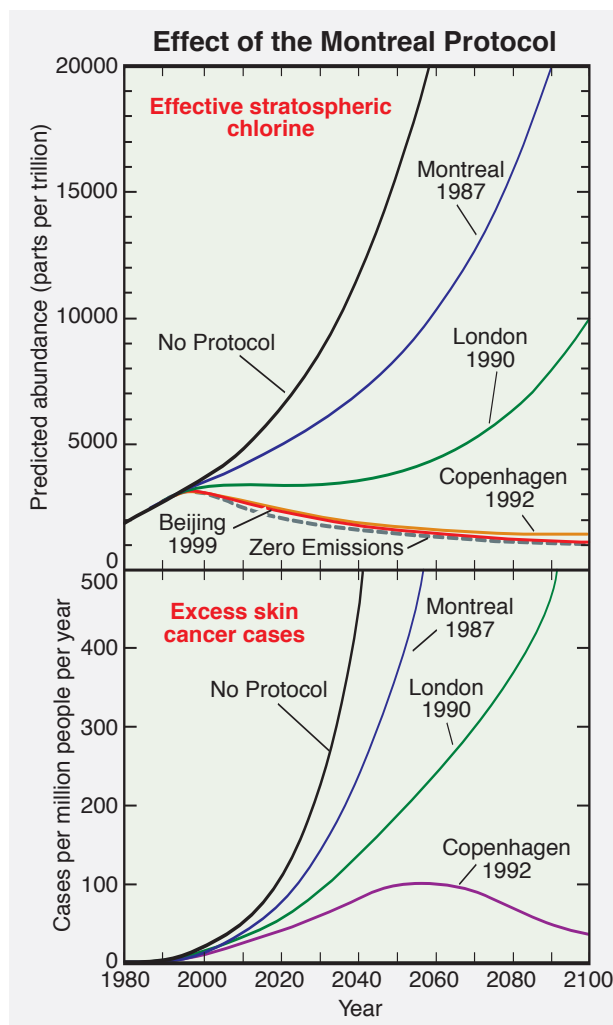


Figure Q15-1. Effect of the Montreal Protocol. The purpose of the Montreal Protocol is to achieve reductions in stratospheric abundances of chlorine and bromine. The reductions follow from restrictions on the production and consumption of manufactured halogen source gases. Predictions for the future abundance of *effective stratospheric chlorine* are shown in the top panel assuming (1) no Protocol regulations, (2) only the regulations in the original 1987 Montreal Protocol, and (3) additional regulations from the subsequent Amendments and Adjustments. The city names and years indicate where and when changes to the original 1987 Protocol provisions were agreed upon. Effective stratospheric chlorine as used here accounts for the combined effect of chlorine and bromine gases. Without a Protocol, stratospheric halogen gases are projected to have increased significantly in the 21st century. The “zero emissions” line shows stratospheric abundances if all emissions were reduced to zero beginning in 2003. The lower panel shows how excess skin cancer cases (see Q17) would increase with no regulations and how they will be reduced under the Protocol provisions. (The unit “parts per trillion” is defined in the caption of **Figure Q7-1**.)

Q16: Has the Montreal Protocol been successful in reducing ozone-depleting gases in the atmosphere?

Yes, as a result of the Montreal Protocol, the total abundance of ozone-depleting gases in the atmosphere has begun to decrease in recent years. If the nations of the world continue to follow the provisions of the Montreal Protocol, the decrease will continue throughout the 21st century. Some individual gases such as halons and hydrochlorofluorocarbons (HCFCs) are still increasing in the atmosphere, but will begin to decrease in the next decades if compliance with the Protocol continues. By midcentury, the effective abundance of ozone-depleting gases should fall to values present before the Antarctic “ozone hole” began to form in the early 1980s.

Effective stratospheric chlorine. The Montreal Protocol has been successful in slowing and reversing the increase of ozone-depleting gases in the atmosphere. An important measure of its success is the change in the value of *effective stratospheric chlorine*. Effective chlorine is based on measured or estimated abundances of both chlorine- and bromine-containing gases in the stratosphere. The two groups of gases are not simply added together, because bromine gases are much more effective on a per-atom basis than chlorine in depleting ozone (see *Q7*). Instead, the amounts for bromine gases are multiplied by a factor that accounts for their greater effectiveness and then added to the total amount of chlorine. Bromine atoms are much less abundant in the stratosphere than chlorine (see *Figure Q7-1*), but are about 45 times more effective than chlorine in chemically destroying ozone molecules. Increases in effective chlorine in the past decades have caused stratospheric ozone depletion. Accordingly, ozone is expected to recover in the future as effective chlorine values decrease.

Effective stratospheric chlorine changes. In the latter half of the 20th century up until the 1990s, effective chlorine values steadily increased (see *Figure Q16-1*). The values shown were calculated using halogen source gas abundances obtained from measurements, historical estimates of abundance, and future projections of abundance. As a result of the Montreal Protocol regulations, the long-term increase in effective chlorine slowed, reached a peak, and began to decrease in the 1990s. This small and continuing decrease means that the potential for stratospheric ozone depletion has begun to lessen as a result of the Montreal Protocol. The decrease in effective chlorine is projected to continue throughout the 21st century if all nations continue to comply with the provisions of the Protocol. Once halogen gas emissions from human activities have ceased, the decrease in effective chlorine will continue as natural destruction processes gradually reduce halogen gas abundances in the global atmosphere. Significant reduction requires decades because the lifetimes of halogen source gas molecules in the atmosphere range up to 100 years (see *Table Q7-1*).

Individual halogen source gases. Reductions in effective chlorine follow directly from decreases in the emission of individual halogen source gases. The regulation of human-produced halogen source gases under the Montreal Protocol is considered separately for each class of one or more gases

and is based on several factors. The factors include (1) the effectiveness of each class in depleting ozone in comparison to other halogen source gases; (2) the availability of suitable substitute gases for domestic and industrial use; and (3) the impact of regulation on developing nations.

The change in atmospheric abundance of a gas in response to regulation also depends on a number of factors that include (1) how the gas is used and released to the atmosphere; (2) how rapidly the gas is chemically destroyed in the atmosphere; and (3) the total amount of the gas that has accumulated in the atmosphere.

Methyl chloroform and CFCs. The largest reduction in the abundance of a halogen source gas has occurred for methyl chloroform (CH_3CCl_3). As shown in *Figure Q16-1*, atmospheric methyl chloroform values dropped abruptly as a result of the provisions of the Montreal Protocol that reduced global production to near zero. Atmospheric abundances subsequently dropped rapidly because methyl chloroform has a short atmospheric lifetime (about 5 years). In addition, methyl chloroform is used mainly as a solvent and therefore has no significant long-term storage reservoir, as do refrigerants, for example. The reduction in effective chlorine in the 1990s came primarily from the reduction in methyl chloroform abundance in the atmosphere. Significant emissions reductions have also occurred for the chlorofluorocarbons CFC-11, CFC-12, and CFC-113 starting in the 1990s. As a result, the atmospheric increases of these gases have slowed, and CFC-11 and CFC-113 abundances have decreased slightly (see *Figure Q16-1*). Because of longer lifetimes in the atmosphere (see *Table Q7-1*), CFC abundances decrease more slowly than methyl chloroform as their emissions are reduced.

HCFC substitute gases. The Montreal Protocol allows for the use of hydrochlorofluorocarbons (HCFCs) as short-term substitutes for CFCs. As a result, the abundances of HCFC-22, HCFC-141b, and HCFC-142b continue to grow in the atmosphere (see *Figure Q16-1*). HCFCs are desirable as CFC substitutes because they are partially destroyed in the troposphere by chemical processes, thus reducing the overall effectiveness of their emissions in destroying stratospheric ozone. Under the Montreal Protocol, HCFC production will reach zero in developed nations by 2030 and in developing nations by 2040. Thus, the future projections in *Figure Q16-1* show HCFC abundances reaching a peak in the first decades of the 21st century and steadily decreasing thereafter.

Halons. The atmospheric abundances of Halon-1211 and Halon-1301 are significant fractions of all bromine-containing source gases (see **Figure Q7-1**) and continue to grow despite the elimination of production in developed nations in 1994 (see **Figure Q16-1**). The growth in abundance continues because substantial reserves are held in fire-extinguishing equipment and are gradually being released, and production and consumption are still allowed in developing nations. Release of stored halons could keep atmospheric halon abundances high well into the 21st century.

Methyl chloride and methyl bromide. Both methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are unique among halogen source gases because a substantial fraction of their sources are associated with natural processes (see

Q7). The average atmospheric abundance of methyl chloride, which is not regulated under the Montreal Protocol, is expected to remain nearly constant throughout this century. At century's end, methyl chloride is expected to account for a large fraction of remaining effective stratospheric chlorine because the abundances of other gases, such as the CFCs, are expected to be greatly reduced (see **Figure Q16-1**). The abundance of methyl bromide, which is regulated under the Protocol, is projected to decrease in the first decades of this century as a result of production phaseouts in developed and developing countries. In the remaining decades of the century, methyl bromide abundances are expected to be nearly constant.

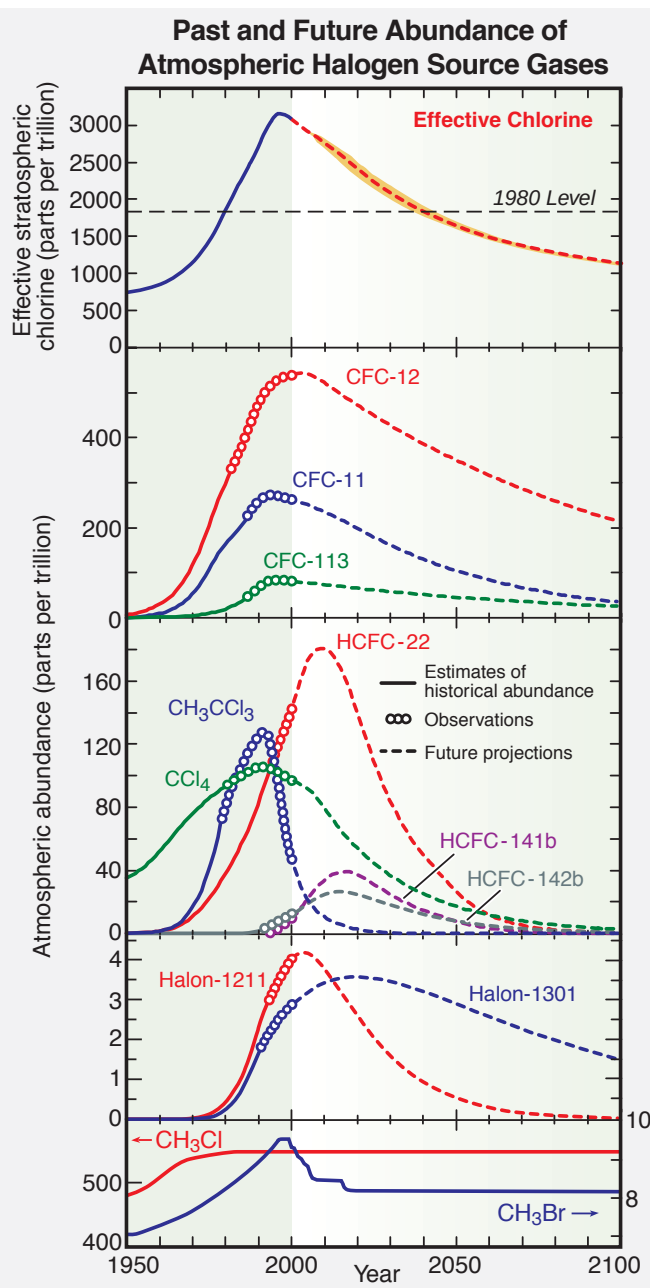


Figure Q16-1. Halogen source gas changes. The rise in effective stratospheric chlorine values in the 20th century has slowed and reversed in the last decade (top panel). Effective chlorine values combine the measured or projected abundances of chlorine-containing gases with those of bromine-containing gases in a way that properly accounts for the greater effectiveness of bromine in depleting stratospheric ozone. As effective chlorine decreases in the 21st century, the potential for ozone depletion from halogen gases will also decrease. The decrease in effective chlorine values is a result of reductions in individual halogen source gas emissions. The emissions decreased because of the Montreal Protocol, which restricts production and consumption of manufactured halogen gases. The changes in the atmospheric abundance of individual gases are shown in the lower panels using a combination of direct atmospheric measurements, estimates of historical abundance, and future projections of abundance. The increases of CFCs, along with those of CCl_4 and CH_3CCl_3 , have either slowed significantly or reversed in the last decade. HCFCs, which are being used as CFC substitutes, will continue to increase in the coming decades. Some halon abundances will also grow in the future while current halon reserves are being depleted. Smaller relative decreases are expected for CH_3Br in response to restrictions because it has substantial natural sources. CH_3Cl has large natural sources and is not regulated under the Montreal Protocol. (See **Figure Q7-1** for chemical names and formulas. The unit “parts per trillion” is defined in the caption of **Figure Q7-1**.)

V. IMPLICATIONS OF OZONE DEPLETION

Q17: Does depletion of the ozone layer increase ground-level ultraviolet radiation?

Yes, ultraviolet radiation at Earth's surface increases as the amount of overhead total ozone decreases, because ozone absorbs ultraviolet radiation from the Sun. Measurements by ground-based instruments and estimates made using satellite data have confirmed that surface ultraviolet radiation has increased in regions where ozone depletion is observed.

The depletion of stratospheric ozone leads to an increase in surface ultraviolet radiation. The increase occurs primarily in the ultraviolet-B (UV-B) component of the Sun's radiation. UV-B is defined as radiation in the wavelength range of 280 to 315 nanometers. Changes in UV-B at the surface have been observed directly and can be estimated from ozone changes.

Surface UV-B radiation. The amount of ultraviolet radiation reaching Earth's surface depends in large part on the amount of ozone in the atmosphere. Ozone molecules in the stratosphere absorb UV-B radiation, thereby significantly reducing the amount of this radiation that reaches Earth's surface (see Q3). If total ozone amounts are reduced in the stratosphere, then the amount of UV radiation reaching Earth's surface generally increases. This relationship between total ozone and surface UV radiation has been studied at a variety of locations with direct measurements of both ozone and UV. The actual amount of UV reaching a location depends on a large number of additional factors, including the position of the Sun in the sky, cloudiness, and air pollution. In general, surface UV at a particular location on Earth changes throughout the day and with season as the Sun's position in the sky changes.

Long-term surface UV changes. Satellite observations of long-term global ozone changes can be used to estimate changes in global surface UV that have occurred over the past two decades. These changes are of interest because UV radiation can cause harm to humans and other life forms (see Q3). The amount of UV that produces an "erythema" or sunburning response in humans is often separately evaluated. UV-B radiation is a large component of sunburning UV. Long-term changes in sunburning UV at a location can be estimated from the changes in total ozone at that location. The results show that average sunburning UV has increased by up to a few percent per decade between 1979 and 1992 over a wide range of latitudes (see *Figure Q17-1*). The largest increases are found at high polar latitudes in both hemispheres. As expected, the increases occur where decreases in total ozone are observed to be the largest (see *Figure Q13-1*). The smallest changes in sunburning UV are in the tropics,

where long-term total ozone changes are smallest.

UV Index changes. The "UV Index" is a measure of daily surface UV levels that is relevant to the effects of UV on human skin. The UV Index is used internationally to increase public awareness about the detrimental effects of UV on human health and to guide the need for protective measures. The Index is essentially a measure of erythema, of which UV-B is a principal component. The daily maximum UV Index varies with location and season, as shown for three locations in *Figure Q17-2*. The highest daily values generally occur at the lowest latitudes (tropics) and in summer when the midday Sun is closest to overhead. Values in San Diego, California, for example, normally are larger year round than those found in Barrow, Alaska, which is at a higher latitude. At a given latitude, UV Index values increase in mountainous regions. Winter and fall values become zero in periods of continuous darkness at high-latitude locations.

An illustrative example of how polar ozone depletion increases the maximum daily UV Index is shown in *Figure Q17-2*. Normal UV Index values for Palmer, Antarctica, in spring were estimated from satellite measurements made during the period 1978-1983, before the appearance of the "ozone hole" over Antarctica (see red dotted line). In the last decade (1991-2001) severe and persistent ozone depletion in spring has increased the UV Index well above normal values for several months (see thick red line). Now spring UV Index values in Palmer (64°S) sometimes equal or exceed normal values measured in San Diego (32°N) in spring.

Other causes of long-term UV changes. The intensity of surface UV-B may also change as a result of other human activities or climate change. Long-term changes in cloudiness, aerosols, pollution, and snow or ice cover will cause long-term changes in surface UV-B. At some ground sites, measurements indicate that long-term changes in UV-B have resulted from changes in one or more of these factors. The impact of some of the changes can be complex. For example, a change in cloud cover usually results in a reduction of UV-B radiation below the cloud layer, but can increase radiation above the layer (in mountainous regions).

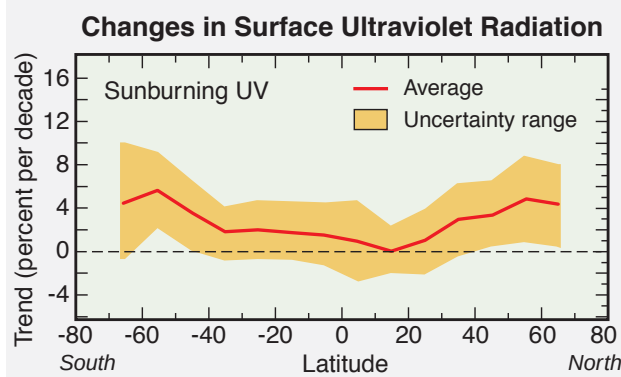
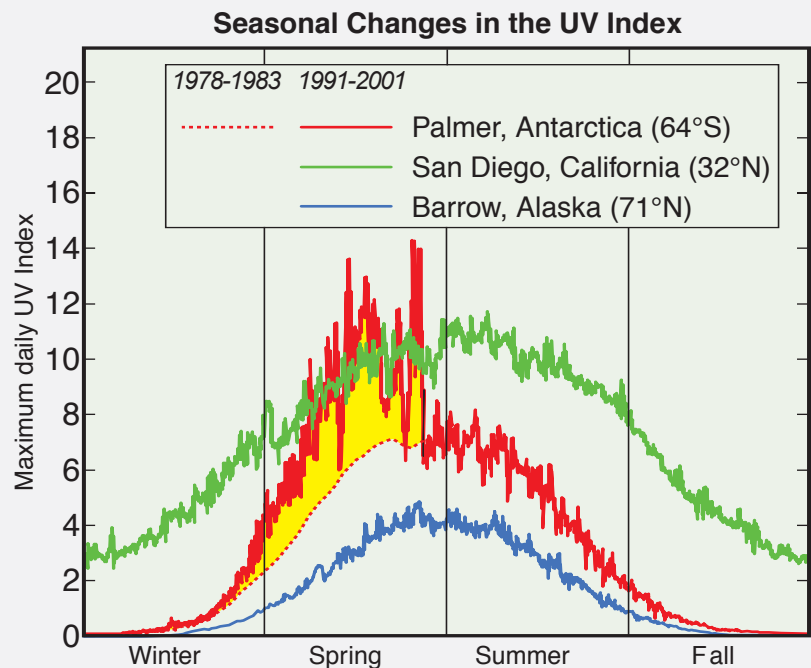


Figure Q17-1. Changes in surface UV radiation. Ultraviolet (UV) radiation at Earth's surface that causes sunburning has increased over the globe between 1979 and 1992. Also known as "erythemal radiation," sunburning UV is harmful to humans and other life forms. The increase shown here is estimated from observed decreases in ozone and the relationship between ozone and surface UV established at some surface locations. The changes in ultraviolet radiation in the tropics are estimated to be the smallest because observed changes in tropical ozone have been the smallest.

UV changes and skin cancer. Skin cancer cases in humans increase with the amount of sunburning UV reaching Earth's surface. Atmospheric scientists working together with health professionals can estimate how skin cancer cases will change in the future. The estimates are based on knowing how sunburning UV increases as total ozone is depleted and how total ozone depletion changes with effective stratospheric chlorine (see Q16). Estimates of future excess skin cancer cases are shown in **Figure Q15-1** using future estimates of effective chlorine based on the 1992 Montreal Protocol provisions. The cases are those that would occur in a population with the UV sensitivity and age distribution such as that of the United States. The cases counted are those in *excess* of the number that occurred in 1980 before ozone depletion was observed (about 2000 per million population). The case estimates include the fact that skin cancer in humans occurs long after the exposure to sunburning UV. The results show that, with current Protocol provisions, excess skin cancer cases are predicted to increase in the early to middle decades of the 21st century. By century's end, with the expected decreases in halogen source gas emissions, the number of excess cases is predicted to return close to 1980 values. Without the provisions of the Protocol, excess skin cancer cases would be expected to increase unchecked throughout the century.

Figure Q17-2. Changes in UV Index. The maximum daily UV Index is a measure of peak sunburning UV that occurs during the day at a particular location. UV-B, which is absorbed by ozone, is an important component of sunburning UV. The UV Index varies with latitude and season as the Sun's path through the local sky changes. The highest values of the maximum daily UV Index occur in the tropics where the midday Sun is highest throughout the year and where total ozone values are lowest. For comparison, the figure shows that the UV Index is higher in San Diego than in Barrow throughout the year. Index values are zero at high latitudes when darkness is continuous. The effect of ozone depletion on the Index is demonstrated by comparing the Palmer and San Diego data in the figure. Normal values estimated for Palmer are shown for the 1978-1983 period before the "ozone hole" occurred each season (see red dotted line). In the last decade (1991-2001), Antarctic ozone depletion has led to an increase in the maximum UV Index value at Palmer throughout spring (see yellow shaded region). Values at Palmer now sometimes equal or exceed those measured in spring in San Diego, which is located at a much lower latitude.



TWENTY QUESTIONS

Q18: Is depletion of the ozone layer the principal cause of climate change?

No, ozone depletion itself is not the principal cause of climate change. However, because ozone is a greenhouse gas, ozone changes and climate change are linked in important ways. Stratospheric ozone depletion and increases in global tropospheric ozone that have occurred in recent decades both contribute to climate change. These contributions to climate change are significant but small compared with the total contribution from all other greenhouse gases. Ozone and climate change are indirectly linked because ozone-depleting gases, such as the chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and halons, also contribute to climate change.

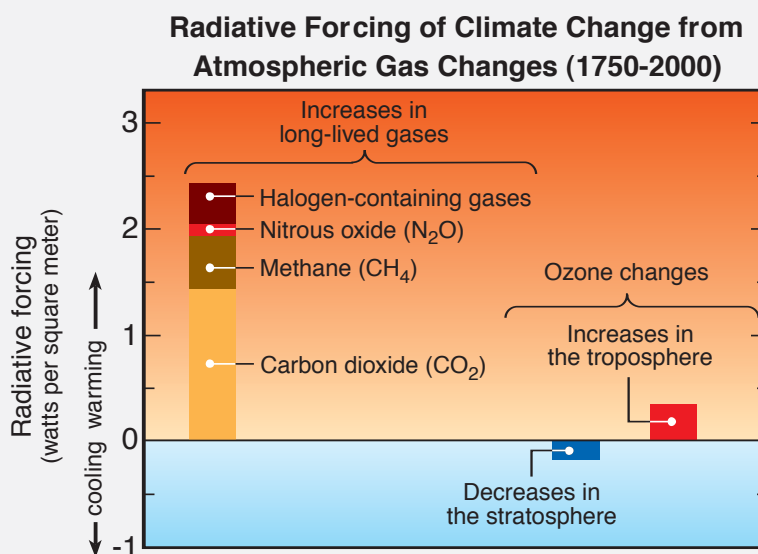
Ozone depletion is not the major cause of climate change, but ozone changes are linked to climate change in important ways.

Radiative forcing of climate change. Human activities have led to the accumulation in the atmosphere of several long-lived and radiatively active gases known as “greenhouse gases.” Ozone is a greenhouse gas, along with carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and halogen source gases. The accumulation of these gases changes the radiative balance of Earth’s atmosphere. The balance is between incoming solar radiation and outgoing infrared radiation. Greenhouse gases generally change the balance by absorbing outgoing radiation, leading to a warming at Earth’s surface. This change in Earth’s radiative balance is called a *radiative forcing of climate change*. If the total forcing from all gases becomes large enough, climate could change in significant ways. A summary of radiative forcings resulting from the increase in long-lived

greenhouse gases is shown in **Figure Q18-1**. All forcings shown relate to human activities. Positive forcings lead to *warming* and negative forcings lead to *cooling* of Earth’s surface. The accumulation of carbon dioxide is the largest forcing term. Carbon dioxide concentrations are increasing in the atmosphere primarily as the result of the burning of coal, oil, and natural gas for energy and transportation. The atmospheric abundance of carbon dioxide is currently about 30% above what it was 150 years ago in preindustrial times.

Stratospheric and tropospheric ozone. Changes in stratospheric and tropospheric ozone both represent radiative forcings of climate change. Stratospheric ozone absorbs solar radiation, which heats the stratosphere and affects air motions and chemical reactions. Stratospheric and tropospheric ozone both absorb infrared radiation emitted by Earth’s surface, effectively trapping heat in the atmosphere below. Overall, the depletion of stratospheric ozone represents a negative radiative forcing. In contrast,

Figure Q18-1. Climate change from atmospheric gas changes. Human activities since 1750 have caused increases in the abundances of several long-lived gases, changing the radiative balance of Earth’s atmosphere. These gases, known as “greenhouse gases,” result in *radiative forcings*, which can lead to climate change. The largest radiative forcings come from carbon dioxide, followed by methane, tropospheric ozone, the halogen-containing gases (see **Figure Q7-1**), and nitrous oxide. Ozone increases in the troposphere result from pollution associated with human activities. All these forcings are positive, which leads to a warming of Earth’s surface. In contrast, stratospheric ozone depletion represents a small negative forcing, which leads to cooling of Earth’s surface. In the coming decades, halogen gas abundances and stratospheric ozone depletion are expected to be reduced along with their associated radiative forcings. The link between these two forcing terms is an important aspect of the radiative forcing of climate change.



increases in tropospheric ozone due to surface pollution represent a positive radiative forcing. The radiative forcing due to tropospheric ozone increases is larger than that associated with stratospheric ozone depletion. Both forcing terms are significant, but are small in comparison with the total forcing from all other greenhouse gases.

Halogen source gases. An indirect link between ozone depletion and climate change is the radiative forcing from halogen source gases. These gases, which include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and halons (see **Figure Q7-1**), are radiatively active in the atmosphere before they are chemically converted in the stratosphere. As a group, they represent a significant positive radiative forcing. Once converted, they form reactive halogen gases, which chemically destroy ozone. In the coming decades, halogen gas abundances and their associated positive radiative forcings are expected to decrease (see *Q16*). With reduced halogen gases, stratospheric ozone depletion and its associated negative radiative forcing will also be reduced. This link between these two forcing terms is an important aspect of the radiative forcing of climate change.

HFCs. The radiative forcing of halogen-containing gases in **Figure Q18-1** also includes that of the HFCs, which do not cause ozone depletion. The HFCs are

increasing in the atmosphere because of their use as substitute gases for the CFCs and other halogen gases. HFCs are not regulated under the Montreal Protocol, but are included in the group of gases listed in the Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC).

Climate change. Certain changes in Earth's climate could affect the future of the ozone layer. Stratospheric ozone is influenced by changes in temperatures and winds in the stratosphere. For example, low temperatures and strong polar winds both affect the extent and severity of winter polar ozone depletion. While Earth's surface is expected to warm in response to the positive radiative forcing from carbon dioxide increases, the stratosphere is expected to cool. Indeed, a small cooling of the lower stratosphere has occurred since the 1970s. A cooler stratosphere would extend the time period over which polar stratospheric clouds (PSCs) are present in polar regions and, as a result, might increase winter ozone depletion. These changes could delay the recovery of the ozone layer. In the upper stratosphere at altitudes above PSC formation regions, a cooler stratosphere is expected to increase ozone amounts. Changes in atmospheric composition that lead to a warmer climate may also affect the balance of production and loss processes of stratospheric ozone (see *Q20*).

VI. STRATOSPHERIC OZONE IN THE FUTURE

Q19: How will recovery of the ozone layer be detected?

Scientists expect to detect the recovery of the ozone layer with careful comparisons of the latest ozone measurements with past values. Changes in total overhead ozone at various locations and in the extent and severity of the Antarctic “ozone hole” will be important factors in gauging ozone recovery. Natural variations in ozone amounts will limit how soon recovery can be detected with future ozone measurements.

Recovery factors. Detecting the recovery of the ozone layer will rely on comparisons of the latest ozone values with values measured in the past. Because of its importance, ozone likely will be measured continuously in the future using a variety of techniques and measurement platforms (see Q5). In the ozone comparisons, scientists will look for improvements in certain factors related to the distribution of ozone. These factors include the following:

- A lessening of the decline in global ozone, either in total ozone or ozone at specific altitudes in the stratosphere.
- An increase in global total ozone amounts toward values found before 1980 when halogen source gas abundances in the atmosphere were much lower than today.
- A sustained reduction in the maximum size of the Antarctic “ozone hole.”
- A sustained increase in the minimum value of ozone found in the Antarctic ozone hole.

- Less ozone depletion in Arctic winters during which temperatures are below polar stratospheric cloud (PSC) formation temperatures.

As the ozone layer approaches full recovery, scientists expect to observe improvements in all these factors.

Natural factors. Global total ozone is influenced by two important natural factors, namely, changes in the output of the Sun and volcanic eruptions (see Q14). The evaluation of ozone recovery must include the effects of these natural factors. The solar effect on ozone is expected to be predictable based on the well-established 11-year cycle of solar output. Volcanic eruptions are particularly important because they increase ozone depletion caused by reactive halogen gases, but cannot be predicted. The occurrence of a large volcanic eruption in the next decades when effective stratospheric chlorine levels are still high (see **Figure Q16-1**) may obscure progress in overall ozone recovery by temporarily increasing ozone depletion. The natural variation of ozone amounts will also limit how easily small improvements in ozone abundances can be detected.

Q20: When is the ozone layer expected to recover?

The ozone layer is expected to recover by the middle of the 21st century, assuming global compliance with the Montreal Protocol. Chlorine- and bromine-containing gases that cause ozone depletion will decrease in the coming decades under the provisions of the Protocol. However, volcanic eruptions in the next decades could delay ozone recovery by several years and the influence of climate change could accelerate or delay ozone recovery.

Halogen source gas reductions. Ozone depletion caused by human-produced chlorine and bromine gases is expected to gradually disappear by about the middle of the 21st century as the abundances of these gases decline in the stratosphere. The decline will follow the reductions in emissions that are expected to occur under the provisions of the Montreal Protocol and its Adjustments and Amendments (see **Figure Q16-1**). The emission reductions are based on the assumption of full compliance by the developed and developing nations of the world. The slowing of the increases in the atmospheric abundances of several halogen gases and the substantial reduction of one principal halogen gas, methyl chloroform, has already occurred. Natural chemical and transport processes limit the rate at which halogen gases can be removed from the stratosphere. The atmospheric chemical lifetimes of the

halogen source gases range up to 100 years (see **Table Q7-1**). Chlorofluorocarbon-12 (CFC-12), with a lifetime of 100 years, will require about 200 to 300 years before it is removed (less than 5% remaining) from the atmosphere (see **Figure Q16-1**).

Ozone predictions. Computer models of the atmosphere are used to assess past changes in global ozone and predict future changes. Two important measures of ozone considered by scientists are global total ozone averaged between 60°N and 60°S latitudes, and minimum ozone values in the Antarctic “ozone hole.” Both measures show ongoing ozone depletion that began in the 1980s (see **Figure Q20-1**). The range of model predictions shows that the lowest ozone values are expected to occur before 2020 and that substantial recovery of ozone is expected by the middle of the 21st century. The range of predic-

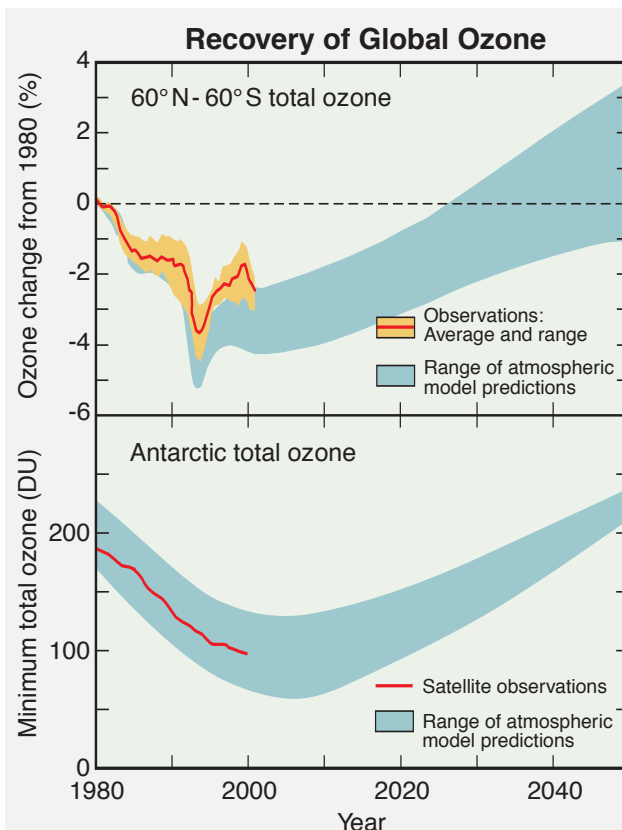


Figure Q20-1. Global ozone recovery predictions. Observed values of global total ozone (top panel) and minimum total ozone over Antarctica (bottom panel) have decreased beginning in the early 1980s. As halogen source gas emissions decrease in the early 21st century, ozone values are expected to increase and recover toward pre-1980 values. Atmospheric computer models that account for changes in halogen gases and other atmospheric parameters can be used to predict how ozone amounts will increase. These model results show that recovery is expected to be significant by 2050, or perhaps earlier. The range of model predictions comes from the use of several different models that have different assumptions about the future climate and composition of the atmosphere. These assumptions are an attempt to account for estimated differences in atmospheric composition and other parameters between 1980, before the “ozone hole” began, and 2050.

TWENTY QUESTIONS

tions comes from several computer models of the atmosphere that have different assumptions concerning the future climate and composition of the atmosphere. Some of these models indicate that recovery of total ozone may possibly come well before midcentury.

A different atmosphere in 2050. By the middle of the 21st century, halogen amounts in the stratosphere are expected to be similar to those present in 1980 before the onset of the ozone hole (see *Figure Q16-1*). However, other aspects of the global atmosphere will not be the same in 2050 as in 1980. The ozone recovery evaluations in *Figure Q20-1* attempt to take these differences into account. For example, since 1980 human activities have increased the abundance of important greenhouse gases, including carbon dioxide, methane, and nitrous oxide. The accumulation of these gases is expected to cause warmer surface temperatures and colder stratospheric temperatures. Colder temperatures may accelerate ozone

recovery in the upper stratosphere (about 40 kilometers (25 miles) altitude). Colder winter temperatures over polar regions will increase the occurrences of polar stratospheric clouds (PSCs) and chemical ozone destruction (see *Q10*). Water vapor increases that have occurred in the stratosphere over the last two decades also will lead to increased PSC occurrences and associated ozone destruction. A cooler, wetter polar stratosphere could delay ozone recovery beyond what would be predicted for the 1980 atmosphere. Increased methane and nitrous oxide abundances due to human activities also cause some change in the overall balance of the chemical production and destruction of global stratospheric ozone. Finally, an outcome not included in models is the occurrence of one or more large volcanic eruptions in the coming decades. In that case, stratospheric particles may increase for several years, temporarily reducing global ozone amounts (see *Q14*) and delaying the recovery of the ozone layer.

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APPENDIX B

MAJOR ACRONYMS AND ABBREVIATIONS

AASE	Airborne Arctic Stratospheric Expedition
ADEOS	Advanced Earth Observing Satellite
AER	Atmospheric and Environmental Research, Inc. (United States)
AFEAS	Alternative Fluorocarbons Environmental Acceptability Study
AGAGE	Advanced Global Atmospheric Gases Experiment
AI	aerosol index
ALE	Atmospheric Lifetime Experiment
AO	Arctic Oscillation
AOD	aerosol optical depth
ATMOS	Atmospheric Trace Molecule Spectroscopy
AVHRR	Advanced Very High Resolution Radiometer
AWI	Alfred Wegener Institute (Germany)
BDC	Brewer-Dobson circulation
BL	boundary layer
BUV	Backscatter Ultraviolet (spectrometer)
CARIBIC	Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container
CARMA	Community Aerosol and Radiation Model for Atmospheres
CCSR	Center for Climate System Research (University of Tokyo)
CFC	chlorofluorocarbon
CICERO	Centre for International Climate and Environmental Research, Universitetet i Oslo (Norway)
CIE	Commission Internationale de l'Éclairage (France)
CIRES	Cooperative Institute for Research in Environmental Sciences (United States)
CLAES	Cryogenic Limb Array Etalon Spectrometer
CLAMS	Chemical Lagrangian Model of the Stratosphere
CMAM	Canadian Middle Atmosphere Model
CMDL	Climate Monitoring and Diagnostics Laboratory (NOAA)
CNR-IFA	Consiglio Nazionale della Ricerca-Istituto di Fisica dell'Atmosfera (Italy)
CNRM	Centre National de Recherches Météorologiques (France)
CNRS	Centre National de la Recherche Scientifique (France)
CONICET	Consejo de Investigaciones Científicas y Técnicas
CPC	Climate Prediction Center (NCEP)
CSIRO	Commonwealth Scientific and Industrial Research Organisation (Australia)
CTM	chemical transport model
DLR	Deutsches Zentrum für Luft- und Raumfahrt (Germany)
DMS	dimethyl sulfide
DMSO	dimethyl sulfoxide
DOAS	Differential Optical Absorption Spectroscopy
DSCD	differential slant column density
DSIR	Department of Scientific and Industrial Research (South Africa)
DU	Dobson unit
EC	European Commission
ECC	electrochemical concentration cell (ozonesonde)

ACRONYMS

ECD	electron capture detector
ECHAM	European Centre Hamburg Model
ECMWF	European Centre for Medium-Range Weather Forecasts (United Kingdom)
EECI	effective equivalent chlorine
EESC	effective equivalent stratospheric chlorine
ENSO	El Niño-Southern Oscillation
EP	Earth Probe
EPA	Environmental Protection Agency (United States)
ER-2	Earth Resources-2 (aircraft)
ERBE	Earth Radiation Budget Experiment
ERS-2	European Remote Sensing-2 (satellite)
ETH	Eidgenössische Technische Hochschule (Swiss Federal Institute of Technology) (Switzerland)
EU	European Union
EUVDB	European Ultraviolet Database
FC	fluorocarbon
FDH	fixed dynamical heating (model)
FSSP	forward scattering spectrometer probe
FTIR	Fourier transform infrared
FUB	Freie Universität Berlin (Germany)
GAGE	Global Atmospheric Gases Experiment
GAW	Global Atmosphere Watch
GCM	general circulation model
GC-MS	gas chromatograph-mass spectrometer
GFDL	Geophysical Fluid Dynamics Laboratory (NOAA)
GHG	greenhouse gas
GISS	Goddard Institute for Space Studies (NASA)
GOME	Global Ozone Monitoring Experiment
GRIPS	GCM-Reality Intercomparison Project for SPARC
GSFC	Goddard Space Flight Center (NASA)
GWD	gravity wave drag
GWP	Global Warming Potential
HALOE	Halogen Occultation Experiment
HBFC	hydrobromofluorocarbon
HC	hydrocarbon
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFE	hydrofluorinated ether or hydrofluoroether
hPa	hectoPascal
IASB	Institut d'Aéronomie Spatiale de Belgique (Belgium)
IFU	Institute for Atmospheric Environmental Research (Germany)
IGAC	International Global Atmospheric Chemistry
ILAS	Improved Limb Atmospheric Spectrometer
IPCC	Intergovernmental Panel on Climate Change
IR	infrared
IROE-CNR	Istituto di Ricrea sulle Onde Elettromagnetiche del Consiglio Nazionale della Ricerche (Italy)
ISAMS	Improved Stratospheric and Mesospheric Sounder
ISCCP	International Satellite Cloud Climatology Project
IUPAC	International Union of Pure and Applied Chemistry

JMA	Japan Meteorological Agency (Japan)
JPL	Jet Propulsion Laboratory (NASA)
JRC	Joint Research Centre (Italy)
KASIMA	Karlsruhe Simulation Model of the Middle Atmosphere
KNMI	Koninklijk Nederlands Meteorologisch Instituut (The Netherlands)
LaRC	Langley Research Center (NASA)
LCTM	Lagrangian chemical transport model
LLNL	Lawrence Livermore National Laboratory (United States)
LMS	lowermost stratosphere
LS	lower stratosphere
M3	Meteor-3 (satellite)
MAECHAM/CHEM	Middle Atmosphere European Centre Hamburg Model with Chemistry
MASP	Multiangle Aerosol Spectrometer Probe
MATCH	Model of Atmospheric Transport and Chemistry
MBL	marine boundary layer
MD	mass deficiency
MIT	Massachusetts Institute of Technology (United States)
MLS	Microwave Limb Sounder
MODIS	Moderate Resolution Imaging Spectroradiometer
MOZAIC	Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
MOZART2	Model for Ozone and Related Chemical Tracers, version 2
MPAE	Max-Planck-Institut für Aeronomie (Germany)
MPIC	Max-Planck-Institut für Chemie (Germany)
MSA	methanesulfonic acid
MSC	Meteorological Service of Canada
MSU	Microwave Sounding Unit
N7	Nimbus-7 (satellite)
NAD	nitric acid dihydrate
NAM	NH annular mode
NAO	North Atlantic Oscillation
NASA	National Aeronautics and Space Administration (United States)
NAT	nitric acid trihydrate
NCAR	National Center for Atmospheric Research (United States)
NCEP	National Centers for Environmental Prediction (NOAA)
NDSC	Network for the Detection of Stratospheric Change
NH	Northern Hemisphere
NIES	National Institute for Environmental Studies (Japan)
NIST	National Institute of Standards and Technology (formerly NBS, United States)
NIWA	National Institute of Water and Atmospheric Research (New Zealand)
NMHC	nonmethane hydrocarbon
NOAA	National Oceanic and Atmospheric Administration (United States)
n-PB	n-propyl bromide
NPL	National Physical Laboratory (United Kingdom)
NPLS	nonparametric least-square fits
NSF	National Science Foundation (United States)
NWP	numerical weather prediction
NWS	National Weather Service (NOAA)

ACRONYMS

ODP	Ozone Depletion Potential
ODS	ozone-depleting substance
OGI	Oregon Graduate Institute (United States)
OHP	Observatoire de Haute-Provence (France)
OMS	Observations of the Middle Stratosphere
OPC	optical particle counter
PAN	peroxyacetyl nitrate
PAUR	Photochemical Activity and Solar Ultraviolet Radiation
PEM-Tropics	Pacific Exploratory Mission in the Tropical Pacific
PFC	perfluorocarbon
PGI	product gas injection
POAM	Polar Ozone and Aerosol Measurement
POLARIS	Photochemistry of Ozone Loss in the Arctic Region in Summer
ppb	parts per billion
ppbv	parts per billion by volume
ppm	parts per million
ppmv	parts per million by volume
ppt	parts per trillion
pptv	parts per trillion by volume
PSC	polar stratospheric cloud
PV	potential vorticity
PWD	planetary-wave drag
QBO	quasi-biennial oscillation
RAF	radiation amplification factor
RDF	reverse domain filling
RIVM	Rijksinstituut voor Volksgezondheid en Milieu (National Institute of Public Health and the Environment) (The Netherlands)
rms	root mean square
RT	radiative transfer
SAD	surface area density
SAGE	Stratospheric Aerosol and Gas Experiment
SAM	SH annular mode
SAM	Stratospheric Aerosol Measurement
SAOZ	Système d'Analyse par Observation Zénithale
SBDART	Santa Barbara Discrete-ordinate Hemispheric Radiative Transfer
SBUV/SBUV2	Solar Backscatter Ultraviolet (spectrometer)
SCD	slant column density
SeaWiFS	Sea-viewing Wide Field-of-view Sensor
SEFDH	seasonally evolving fixed dynamical heating (model)
SGI	source gas injection
SH	Southern Hemisphere
SIO	Scripps Institution of Oceanography (United States)
SOLVE	SAGE III Ozone Loss and Validation Experiment
SPARC	Stratospheric Processes and Their Role in Climate (WCRP)
SPOT	Satellite Pour l'Observation de la Terre (satellite)
SRES	Special Report on Emissions Scenarios (IPCC)
SRM	solid rocket motor
SSA	stratospheric sulfate aerosol
SSU	Stratospheric Sounding Unit

STAR	System for Transfer of Atmospheric Radiation
STE	stratosphere-troposphere exchange
STRAT	Stratospheric Tracers of Atmospheric Transport
STREAM	Stratosphere-Troposphere Experiments by Aircraft Measurements
STS	supercooled ternary solution
STT	secondary tropical tropopause
SUNY	State University of New York (United States)
SUSPEN	Standardization of Ultraviolet Spectroradiometry in Preparation of a European Network
SUVDAMA	Scientific UV Data Management
SZA	solar zenith angle
2-D	two-dimensional
3-D	three-dimensional
TAR	Third Assessment Report (IPCC)
TEAP	Technology and Economic Assessment Panel (UNEP)
THESEO	Third European Stratospheric Experiment on Ozone
TIROS	Television Infrared Observation Satellite
TOMS	Total Ozone Mapping Spectrometer
TOVS	TIROS Operational Vertical Sounder
TRACE-P	Transport and Chemical Evolution over the Pacific
TT	tropical tropopause
TTL	tropical tropopause layer
TTT	thermal tropical tropopause
TUV	Tropospheric Ultraviolet Visible
UARS	Upper Atmosphere Research Satellite
UCI	University of California at Irvine (United States)
UEA	University of East Anglia (United Kingdom)
UH	University of Heidelberg (Germany)
UIUC	University of Illinois at Urbana-Champaign (United States)
UK	United Kingdom
UKMO	United Kingdom Meteorological Office
ULAU	Università degli Studi dell'Aquila (Italy)
UM	unified model
UMETRAC	Unified Model with Eulerian Transport and Chemistry
UN	United Nations
UNEP	United Nations Environment Programme
US	upper stratosphere
USDA	United States Department of Agriculture
UT	University of Tokyo (Japan)
UT	upper troposphere
UV	ultraviolet
VOC	volatile organic compound
WCRP	World Climate Research Programme
WMGHG	well-mixed greenhouse gas
WMO	World Meteorological Organization
WOUDC	World Ozone and Ultraviolet Radiation Data Centre (Canada)

APPENDIX C

MAJOR CHEMICAL FORMULAE AND NOMENCLATURE FROM THIS ASSESSMENT

HALOGEN-CONTAINING SPECIES

Cl	atomic chlorine	Br	atomic bromine
Cl ₂	molecular chlorine	Br ₂	molecular bromine
ClO	chlorine monoxide	BrO	bromine monoxide
ClO _x	chlorine radicals	BrO _x	bromine radicals
OCIO	chlorine dioxide	OBrO	bromine dioxide
ClOO	chloroperoxy radical		
Cl ₂ O ₂ , ClOOCl	dichlorine peroxide (ClO dimer)		
ClONO	chlorine nitrite, nitryl chloride		
ClONO ₂ , ClNO ₃	chlorine nitrate	BrONO ₂ , BrNO ₃	bromine nitrate
HCl	hydrogen chloride (hydrochloric acid)	HBr	hydrogen bromide
HOCl	hypochlorous acid	HOBr	hypobromous acid
Cl _y	inorganic chlorine	Br _y	inorganic bromine
CCl _y	organic chlorine	CBr _y	organic bromine
BrCl	bromine chloride	BrOOCl	bromochloroperoxide
F	atomic fluorine	I	atomic iodine
F ₂	molecular fluorine	I ₂	molecular iodine
		IO	iodine monoxide
		OIO	iodine dioxide
		IONO ₂	iodine nitrate
HF	hydrogen fluoride (hydrofluoric acid)	HI	hydrogen iodide
		HOI	hypoiodous acid
SF ₆	sulfur hexafluoride		
SF ₅ CF ₃	trifluoromethylsulfurpentafluoride		
NF ₃	nitrogen trifluoride		

HALOCARBONS

CHLOROFLUOROCARBONS (CFCs)

CFC-11	CCl ₃ F
CFC-12	CCl ₂ F ₂
CFC-13	CClF ₃
CFC-113	CCl ₂ FCClF ₂
CFC-113a	CCl ₃ CF ₃
CFC-114	CClF ₂ CClF ₂
CFC-114a	CCl ₂ FCF ₃
CFC-115	CClF ₂ CF ₃

HYDROCHLOROFLUOROCARBONS (HCFCs)

HCFC-21	CHCl ₂ F
HCFC-22	CHClF ₂
HCFC-31	CH ₂ ClF
HCFC-123	CHCl ₂ CF ₃
HCFC-124	CHClF ₂ CF ₃
HCFC-141b	CH ₃ CCl ₂ F
HCFC-142b	CH ₃ CClF ₂
HCFC-225ca	CHCl ₂ CF ₂ CF ₃
HCFC-225cb	CHClF ₂ CF ₂ CClF ₂
HCFC-243cc	CH ₃ CF ₂ CFCl ₂

CHEMICAL FORMULAE

HYDROFLUOROCARBONS (HFCs)

HFC-23	CHF_3	HFC-245cb	$\text{CH}_3\text{CF}_2\text{CF}_3$
HFC-32	CH_2F_2	HFC-245ca	$\text{CH}_2\text{FCF}_2\text{CHF}_2$
HFC-41	CH_3F	HFC-245ea	$\text{CHF}_2\text{CHFCHF}_2$
HFC-125	CHF_2CF_3	HFC-245eb	$\text{CH}_2\text{FCHFCF}_3$
HFC-134	CHF_2CHF_2	HFC-245fa	$\text{CHF}_2\text{CH}_2\text{CF}_3$
HFC-134a	CH_2FCF_3	HFC-263fb	$\text{CH}_3\text{CH}_2\text{CF}_3$
HFC-143	CH_2FCHF_2	HFC-272ca	$\text{CH}_3\text{CF}_2\text{CH}_3$
HFC-143a	CH_3CF_3	HFC-281ea	$\text{CH}_3\text{CHFCH}_3$
HFC-152	$\text{CH}_2\text{FCH}_2\text{F}$	HFC-365mfc	$\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_3$
HFC-152a	CH_3CHF_2	HFC-356mcf	$\text{CH}_2\text{FCH}_2\text{CF}_2\text{CF}_3$
HFC-161	$\text{CH}_3\text{CH}_2\text{F}$	HFC-356mff	$\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$
HFC-227ea	$\text{CF}_3\text{CHFCF}_3$	HFC-338pcc	$\text{CHF}_2\text{CF}_2\text{CF}_2\text{CHF}_2$
HFC-236cb	$\text{CH}_2\text{FCF}_2\text{CF}_3$	HFC-43-10mee	$\text{CF}_3\text{CHFCHFCH}_2\text{CF}_3$
HFC-236ea	$\text{CHF}_2\text{CHFCH}_2\text{CF}_3$	HFC-458mfcf	$\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_3$
HFC-236fa	$\text{CF}_3\text{CH}_2\text{CF}_3$	HFC-55-10mcff	$\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_3$

HALONS

Halon-1202	CBr_2F_2	Halon-1301	CBrF_3
Halon-1211	CBrClF_2	Halon-2402	$\text{CBrF}_2\text{CBrF}_2$

CHLOROCARBONS

CH_3Cl	methyl chloride, chloromethane
CH_2Cl_2	methylene chloride, dichloromethane
CHCl_3	chloroform, trichloromethane
CCl_4	carbon tetrachloride
C_2HCl_3	trichloroethene, trichloroethylene
C_2Cl_4	tetrachloroethene, perchloroethene
$\text{CH}_3\text{CH}_2\text{Cl}$	chloroethane
$\text{CH}_2\text{ClCH}_2\text{Cl}$	1, 2 dichloroethane
CH_3CCl_3	methyl chloroform
$\text{C}_2\text{H}_2\text{Cl}_4$	tetrachloroethane
C_4Cl_6	hexachlorobutadiene
COCl_2	phosgene, carbonyl chloride

IODOCARBONS

CH_3I	iodomethane, methyl iodide
CH_2I_2	diiodomethane
$\text{CH}_3\text{CH}_2\text{I}$	iodoethane, ethyl iodide
$\text{CH}_3\text{CHICH}_3$ (i-C ₃ H ₇ I)	2-iodopropane, isopropyl iodide
$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ (n-C ₃ H ₇ I)	1-iodopropane, n-propyl iodide

OTHERS

CHBr_2Cl	dibromochloromethane
CH_2BrCl	bromochloromethane
CHBrCl_2	bromodichloromethane
CH_2BrI	bromoiodomethane
CHBrF_2	bromodifluoromethane
CH_2ClI	chloroiodomethane

BROMOCARBONS

CH_3Br	methyl bromide, bromomethane
CH_2Br_2	methylene bromide, dibromomethane
CHBr_3	bromoform, tribromomethane
$\text{CH}_2\text{BrCH}_2\text{Br}$	1,2 dibromoethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (n-C ₃ H ₇ Br)	1-bromopropane, n-propyl bromide, n-PB
$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{Br}$	bromoacetone

FLUOROCARBONS

CF_4	tetrafluoromethane, carbon tetrafluoride
C_2F_6 , CF_3CF_3	perfluoroethane
C_3F_8 , $\text{CF}_3\text{CF}_2\text{CF}_3$	perfluoropropane
c-C ₃ F ₆	perfluorocyclopropane
C_4F_{10}	perfluorobutane
c-C ₄ F ₈	perfluorocyclobutane
C_5F_{12}	perfluoropentane
C_6F_{14}	perfluorohexane
COF_2	carbonyl fluoride
TFA	trifluoroacetic acid (CF_3COOH)
CF_3COF	trifluoroacetyl fluoride

CF_3I	trifluoromethyl iodide, trifluoroiodomethane
$\text{CF}_3\text{CF}_2\text{I}$	iodopentafluoroethane
COCIF	chlorofluorocarbonyl
CF_3COCl	trifluoroacetyl chloride
SF_6	sulfur hexafluoride
SF_5CF_3	trifluoromethylsulfurpentafluoride

 OTHER SPECIES

O	atomic oxygen	H	atomic hydrogen
O(³ P)	atomic oxygen (ground state)	H ₂	molecular hydrogen
O(¹ D)	atomic oxygen (first excited state)	OH	hydroxyl radical
O ₂	molecular oxygen	HO ₂	hydroperoxyl radical
O ₃	ozone	H ₂ O	water
O _x	odd oxygen (O, O(¹ D), O ₃) or oxidant (O ₃ + NO ₂)	H ₂ O ₂	hydrogen peroxide
		HO _x	odd hydrogen (H, OH, HO ₂ , H ₂ O ₂)
		HDO	deuterated water
N	atomic nitrogen	HNO ₂ , HONO	nitrous acid
N ₂	molecular nitrogen	HOONO	pernitrous acid
N ₂ O	nitrous oxide	HNO ₃	nitric acid
NO	nitric oxide	HNO ₄ , HO ₂ NO ₂	peroxynitric acid, pernitric acid
NO ₂	nitrogen dioxide	CH ₃ OONO ₂	methylperoxynitrate
NO ₃	nitrogen trioxide, nitrate radical	PAN	peroxyacetylnitrate (CH ₃ C(O)OONO ₂)
N ₂ O ₅	dinitrogen pentoxide	RONO ₂	alkyl nitrates
NO _x	nitrogen oxides (NO + NO ₂)	NAD	nitric acid dihydrate (HNO ₃ ·2H ₂ O)
NO _y	total reactive nitrogen (usually includes NO, NO ₂ , NO ₃ , N ₂ O ₅ , ClONO ₂ , HNO ₄ , HNO ₃)	NAT	nitric acid trihydrate (HNO ₃ ·3H ₂ O)
		NAP	nitric acid pentahydrate (HNO ₃ ·5H ₂ O)
S	atomic sulfur	H ₂ S	hydrogen sulfide
SO ₂	sulfur dioxide	CS ₂	carbon disulfide
SO ₄	sulfate	COS, OCS	carbonyl sulfide
H ₂ SO ₄	sulfuric acid		
CH ₃ SCH ₃	DMS, dimethyl sulfide		
CH ₃ S(O)CH ₃	DMSO, dimethyl sulfoxide		
CH ₃ SO ₃ H	MSA, methanesulfonic acid		
C	carbon atom		
CO	carbon monoxide		
CO ₂	carbon dioxide		
NMHC	nonmethane hydrocarbon	CH ₂ O, HCHO	formaldehyde
CH ₄	methane	CH ₃ COCH ₃	acetone
C ₂ H ₆	ethane	CH ₃ OOH	methyl hydroperoxide
C ₃ H ₈	propane	CH ₃ COO	methyl peroxy radical
C ₂ H ₄	ethylene, ethene	CH ₃ C(O)OO	acetyl peroxy radical
C ₂ H ₂	acetylene, ethyne	RO	alkoxy radicals
		RO ₂	organic peroxy radicals