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Scientific Assessment of Stratospheric Ozone: 1989

Volume I

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UNITED KINGDOM - DEPARTMENT OF THE ENVIRONMENT
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
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PREFACE

The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer called for convening four assessment panels. This document (Volume I) is the complete report of one of these panels (the Scientific Assessment Panel) convened under the Protocol's review provisions. In the Introduction to this report will be found details concerning the Montreal Protocol assessment and review procedures. This Introduction also contains overviews of the four chapters that comprise this assessment. Chapter 4 on halocarbon ozone depletion and global warming potentials has benefitted extensively from the scientific material and conclusions drawn from the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS).

This latter study was conducted as an international exercise that involved more than 50 scientists during the early part of 1989. The AFEAS was organized and sponsored by fifteen CFC-producing companies from around the world as part of a cooperative effort to study the safety and environmental acceptability of CFC alternatives. Because of the parallelism between the AFEAS study and the analyses performed under Chapter 4, the complete set of research papers prepared under AFEAS has been assembled and is published as the AFEAS Report, an appendix to this scientific assessment. This appendix constitutes Volume II of the World Meteorological Organization Report No. 20.

INTRODUCTION

EXECUTIVE SUMMARY

SCIENTIFIC SUMMARIES

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INTRODUCTION, EXECUTIVE SUMMARY AND SUMMARIES

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I. INTRODUCTION

The present document, *Scientific Assessment of Stratospheric Ozone: 1989*, is a scientific review of the current understanding of stratospheric ozone, prepared by international scientific experts who are leaders in their respective fields. This initial chapter is a summary of its major points.

The aims of this summary section are threefold. The Executive Summary (Section II) is a digest of the key points of the *Assessment* and is directed at government officials, the private sector, and the general public. The Scientific Summaries (Section III) of each of the four chapters contain the major research findings of the *Assessment* and are directed to the scientific community.

In the Appendix, which is found at the end of the report, the numerous contributors to the preparation of the *Assessment* are identified. The success of the *Assessment* rests on the prodigious efforts and dedication of these people.

This introductory section briefly gives the background to the *Assessment*, its scientific scope, and its place in the current discussions of public policies regarding the protection of the stratospheric ozone layer.

Background

The goals, scope, contents, authors, and timetable of the *Assessment* were planned at two international meetings:

- The first was part of a two-day meeting, "Scientific Review of Ozone Layer Modification and its Impact," which was held at The Hague, The Netherlands, 17-18 October 1988. There were about 70 international scientific attendees at this first of a series of meetings sponsored by the United Nations Environment Programme (UNEP). About half of these attendees were involved in the subgroup that focused on defining the scope of the *Assessment* and establishing a scientific steering group (see Section IV for the membership).
- The second meeting occurred on 29 November 1988 at the U.K. Department of the Environment in London. Fourteen scientists attended, coming from eight countries, as well as representation from UNEP and the World Meteorological Organization (WMO). The focus of this Steering Committee was on establishing the structure, authors, and timetable of the *Assessment*.

The preparation of the *Assessment* document occurred over the period from January to June, 1989. Numerous scientists from 25 countries were involved either as authors, contributors, or reviewers (see Appendix). Their professional institutions included universities, government laboratories, and the private sector. A review draft was discussed and evaluated at a review meeting at Les Diablerets, Switzerland on 10-14 July 1989, sponsored by WMO. Forty-three scientists from 14 countries were in attendance and many others participated via mail reviews. Those suggestions and comments have been incorporated into the present final version.

Scientific Scope

The focus of the *Assessment* is on four major current aspects of stratospheric ozone: (1) polar ozone, (2) global trends, (3) theoretical predictions, and (4) halocarbon ozone depleting potentials and global warming potentials. Other ozone-related topics are also included: (i) the trends of stratospheric temperature, stratospheric aerosols, source gases, and surface ultraviolet radiation; and (ii) the oxidizing capacity of the

EXECUTIVE SUMMARY

troposphere as it pertains to the lifetimes of ozone-related chemicals (e.g., the partially halogenated compounds that can serve as shorter-lived substitutes for the long-lived, fully halogenated ozone-depleting gases).

The *Assessment* is an update of the comprehensive "Atmospheric Ozone: 1985" (WMO Report No. 16, 1986) and builds upon the recent "International Ozone Trends Panel Report: 1988" (WMO Report No. 18, in press). It focuses on the results of subsequent recent research and the implications for the stratosphere. The ozone research of the past few years has been remarkable. Several major ground-based and airborne field campaigns have explored the recently discovered Antarctic ozone "hole," as well as the Arctic ozone layer. New laboratory studies of gas-phase and surface-induced chemical processes have provided a better characterization of the polar phenomena. Statistical analyses of hemispheric data sets have revealed significant ozone trends for the first time. Theoretical investigations have aided the interpretation of all these findings. The picture contained in the *Assessment* reveals a new and deeper understanding of the influence of human activities on the Earth's protective ozone layer.

Relation to Public Policy

While the *Assessment* is a scientific document, it also will be useful as essential scientific input to policy decisions regarding the safeguarding of the ozone layer, just as were its predecessor documents (e.g., "Atmospheric Ozone: 1985"). In that regard, one of the most noteworthy applications of the *Assessment* will be the forthcoming international review of the Montreal Protocol on Substances that Deplete the Ozone Layer. Indeed, the above timetable was planned such that the international ozone scientific community can provide that service in the form of the *Assessment*. The Executive Summary of the present document has been written with this need to communicate the state of ozone in mind.

At the meeting in October 1988 at The Hague, UNEP established four panels to review the current scientific, environmental, technical, and economic information relative to possible amendments to the Montreal Protocol. The *Scientific Assessment of Stratospheric Ozone: 1989* is the report of the first of these panels. There are corresponding reports from the three other panels. The main findings of all four reports will be presented to a Working Group meeting in Nairobi, Kenya, on 28 August – 5 September 1989, where the reports will be reviewed. Their integration into a single document will be completed, and the resultant integrated report will serve as key input for considerations of possible draft amendments to the Montreal Protocol.

II. EXECUTIVE SUMMARY

Recent Findings

The past few years have been remarkable insofar as stratospheric ozone science is concerned. There have been highly significant advances in the understanding of the impact of human activities on the Earth's protective ozone layer. Since the last international scientific review (1985), there are four major findings that each heighten the concern that chlorine- and bromine-containing chemicals can lead to a significant depletion of stratospheric ozone:

- **Antarctic Ozone Hole:** The weight of scientific evidence strongly indicates that chlorinated (largely man-made) and brominated chemicals are primarily responsible for the recently discovered substantial decreases of stratospheric ozone over Antarctica in springtime.
- **Perturbed Arctic Chemistry:** While at present there is no ozone loss over the Arctic comparable to that over the Antarctic, the same potentially ozone-destroying processes have been identified in the Arctic stratosphere. The degree of any future ozone depletion will likely depend on the particular meteorology of each Arctic winter and future atmospheric levels of chlorine and bromine.
- **Long-Term Ozone Decreases:** The analysis of the total-column ozone data from ground-based Dobson instruments show measurable downward trends from 1969 to 1988 of 3 to 5% (i.e., 1.8–2.7% per decade) in the Northern Hemisphere (30–64°N latitudes) in the winter months that cannot be attributed to known natural processes.
- **Model Limitations:** These findings have led to the recognition of major gaps in theoretical models used for assessment studies. Assessment models do not simulate adequately polar stratospheric cloud (PSC) chemistry or polar meteorology. The impact of these shortcomings for the prediction of ozone depletion at lower latitudes is uncertain.

Supporting Evidence and Other Results

These and other findings are based upon the results from several major ground-based and aircraft field campaigns in the polar regions, a reanalysis of ground-based ozone data from the past thirty-one years, a reanalysis of satellite ozone and PSC data, laboratory studies of gas-phase and surface-induced chemical processes, and model simulations incorporating these new laboratory data and observations. The highlights and conclusions from these activities in four research areas are summarized below.

Polar Ozone

- *There has been a large, rapid, and unexpected decrease in the abundance of springtime Antarctic ozone over the last decade.*

Beginning in the late 1970s, total column ozone decreases (lately reaching 50%) have been observed by both ground-based and satellite techniques, the latter showing that the loss is a continental-scale phenomenon. Ozonesondes at several stations have shown that the ozone loss occurs between 12 and 24 km, reaching as much as 95% at some altitudes.

- *The weight of scientific evidence strongly indicates that man-made chlorine and bromine compounds are primarily responsible for the ozone loss in Antarctica.*

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The ozone loss over Antarctica is initiated by chemical reactions that occur on the surfaces of PSCs and that convert the long-lived chlorine into chemically more reactive forms. Laboratory studies have provided important evidence that such chemical reactions can occur on PSC surfaces. Furthermore, reactions can also remove reactive nitrogen species, thereby slowing the reformation of the less reactive chlorine compounds. Satellite data show that the frequency of occurrence of PSCs is the highest in the Antarctic stratosphere. Indeed, the abundance of the reactive chlorine compounds is observed to be elevated by 50–100 times in springtime. The observed reactive chlorine and bromine abundances explain a substantial fraction (60–100%) of the rapid ozone loss observed following the return of sunlight to Antarctica in September, 1987.

- *While the onset of the Antarctic ozone hole is linked to the recent growth in the atmospheric abundance of chlorofluorocarbons (CFCs) and to a lesser extent bromine compounds, many of its features are influenced by meteorological conditions.*

Within the strong circumpolar vortex over Antarctica, temperatures are very low during the winter and spring and there is abundant production of PSCs. These special meteorological conditions set the stage for the occurrence of the ozone hole.

The year-by-year variability in the depth of the ozone hole appears to be related, in part, to the Quasi-Biennial Oscillation (QBO), which is a natural oscillation of equatorial stratospheric winds. For example, there was a very deep ozone hole in 1987, but it was substantially less deep in 1988, possibly influenced by the observed temperature extremes between the years, which modulated the abundance of PSCs. Tropospheric weather systems can also influence stratospheric temperatures and water vapor on regional scales, which would in turn influence PSC abundance and ozone changes.

- *The chemical composition of the Arctic stratosphere was found to be highly perturbed.*

The chemical perturbations in the Arctic were similar to those found in Antarctica, namely, an increase in the abundance of the ozone depleting forms of chlorine in association with PSCs. The studies conducted in January and February in 1989 found that the reactive chlorine abundances were enhanced by a factor of 50–100. No unambiguous evidence for ozone loss has yet been identified for the winter of 1988/1989. Readily detectable ozone reductions would be expected during January and February only if high concentrations of reactive chlorine species were maintained for sufficiently long periods in cold, illuminated air. The degree of Arctic ozone depletion will be influenced by the year-by-year timing of the warming of the polar vortex relative to the arrival of sunlight, as well as future chlorine and bromine abundances. In the Antarctic, the warming of the polar vortex always occurs after the arrival of sunlight (hence, ozone depletion), which contrasts with the Arctic, where warming generally occurs prior to the arrival of sunlight, as in 1989.

Global Trends

- *Several recent analyses of total column ozone data support the conclusion of the 1988 International Ozone Trends Panel (OTP) that there is a downward trend in ozone during winter at mid-to-high latitudes in the Northern Hemisphere over the past two decades.*

The OTP analyzed the re-evaluated data from the ground-based Dobson instruments for the effects of known natural geophysical processes (seasonal variability, the approximately 28-month QBO, and the 11-year solar cycle) and possible human perturbations. After allowing for natural

variability, the analysis showed measurable decreases in the range of 2.3 to 6.2% between 30 and 64°N latitude for the winter months (December - March) between 1969 and 1986, with the larger decreases being at the higher latitudes. This was the first analysis that showed statistically significant downward trends.

The results of model calculations of chlorine-induced ozone loss are broadly consistent with these observed latitudinal and seasonal changes in column ozone, except that the mean values of the observed decreases at mid- and high latitudes in winter are a factor of two to three larger than the mean values of the predicted decreases. This finding suggested that the observed ozone changes may be due, in part, to the increased atmospheric abundances of the CFCs.

Subsequent to the OTP, the results from five new reanalyses of the same OTP data set by three independent analyses, using a variety of statistical models and assumptions, were generally consistent with the earlier result. Zonal mean ozone decreases derived for winter lie in the range 3.2–4.0% over 17 years, when averaged over the latitudes 30–64°N, compared to the value of 4.4% from the OTP analysis. The conclusions were found to be insensitive to the representations used for the QBO and solar cycle, strengthening the belief that the observed trends cannot be attributed to known natural processes.

The extension of the data set beyond that used by the OTP to include 1987 and 1988 does not alter the basic conclusions regarding trends in winter. In addition, no statistically significant zonal trends were found for the summer period (May–August) through 1988. Lastly, within longitudinal sectors, regional differences in the ozone trends were indicated in the Northern Hemisphere, i.e., with the largest changes being observed over North America and Europe and the smallest over Japan.

The present Dobson network and data are inadequate to determine total column ozone changes in the Arctic, tropics, subtropics, or Southern Hemisphere outside of Antarctica. Satellite data can provide the desired global coverage, but the current record is too short to differentiate the effects of natural and human-influenced processes on ozone.

- *Substantial uncertainties remain in defining changes in the vertical distribution of ozone.*

Since the chlorine/ozone theory had predicted that the greatest percentage ozone depletion should occur near 40 km altitude, the OTP looked for indications of such changes in a variety of reanalyzed data sets. The Panel reported that, based on the SAGE satellite data averaged over 20–50°N and S latitudes, ozone near 40 km had decreased by $3 \pm 2\%$ between February 1979–November 1981 and October 1984–September 1987. The SAGE data also indicated a percentage decrease in ozone near 25 km that is comparable in magnitude to that at 40 km. Furthermore, the Panel reported that, based on the Umkehr data from five northern mid-latitude stations, the ozone between 38 and 43 km had decreased by $9 \pm 4\%$ between 1979 and 1986, but this uncertainty range did not account for possible systematic errors. Because the SAGE and Umkehr data records were so short (i.e., less than one solar cycle), no attempt was made to distinguish between solar-induced and human-influenced contributions to these changes.

Adding 15 months of new SAGE data does not change the picture appreciably. Again, no attempt was made to separate the contributions from natural and human-influenced processes. Additionally, a more thorough analysis of data from 10 Umkehr stations in the Northern Hemisphere for the period 1977 to 1987 reports a statistically significant decrease in ozone between 30 and 43 km, the decrease near 40 km being $4.8 \pm 3.1\%$, after allowing for seasonal and solar-cycle effects and correcting the data for aerosol interferences. These losses are somewhat less than those predicted by the chlorine/ozone theory.

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Based on SAGE, Umkehr, and ozonesonde data, there are continuing indications of a stratospheric ozone decrease at 25 km and below. Changes at these altitudes are not predicted by global models based only on gas-phase processes. It is not clear whether this points to missing processes in the models or that these sparse measurements are not representative of the global atmosphere. However, such changes are qualitatively consistent with those required for compatibility with the total column measurements.

- *Recent measurements suggest that the rate of growth in atmospheric methane has slowed somewhat.*

It would appear that the rate of methane increase has been slowing down over the last decade, namely, from 16 to 20 ppbv per year in the early 1980s to 12 to 16 ppbv per year in the late 1980s. For the other trace gases that influence stratospheric ozone and climate (CFCs, nitrous oxide, and carbon dioxide), the observed rates of increase have not changed significantly since the time of the OTP report.

Theoretical Predictions

- *Theoretical models do explain many of the general features of the atmosphere, but new limitations have been recognized.*

Many processes control the distribution of trace gases in the atmosphere. To adequately simulate the atmosphere, models must include representations of numerous radiative, chemical, and small- and large-scale dynamical processes. Current models do indeed reproduce many of the patterns observed, for example, in the ozone column: a minimum in the tropics and maxima at high latitudes in the spring of both hemispheres. Furthermore, the north - south and vertical distributions of the ozone concentration are in general agreement with satellite observations, except for Antarctica. On the other hand, a long-standing discrepancy has been the systematic underestimation of ozone concentrations near 40 km.

Several major shortcomings have been identified recently. None of the assessment models adequately represent polar meteorology or attempt to include heterogeneous processes, i.e., chemical reactions on PSCs. The failure to include these processes would likely lead to an underprediction of ozone loss, both directly at polar latitudes and possibly indirectly at mid-latitudes due to dilution arising from large polar ozone losses.

Furthermore, only a few models include the influence of increasing carbon dioxide abundances and decreasing ozone abundances on temperature, which, in turn, lead to a decrease in the destruction of ozone through lower temperatures in the stratosphere. Hence, while there are still open questions regarding the quantitative treatment of the influence of CO₂ (temperature feedback), the predicted ozone depletions from chlorine- and bromine-containing chemicals are less for those global assessment models used in this report (gas-phase chemistry only) that account for CO₂ increases than the predicted ozone depletions from those models that keep temperatures fixed.

- *Current understanding predicts that, if substantial emissions of halocarbons continue, the atmospheric abundances of chlorine and bromine will increase and, as a result, significant ozone decreases, even outside of Antarctica, are highly likely in the future.*

Several scenarios, which represent a spectrum of possible choices regarding man-made emissions of chlorine- and bromine-containing chemicals, have been used to examine the response of

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stratospheric ozone to atmospheric chlorine and bromine abundances. The predictions for the year 2060 relative to the year 1980 are discussed below for some of those scenarios. In each scenario, it was assumed that the recent trends continue in the atmospheric abundances of methane, nitrous oxide, and carbon dioxide of 15 ppbv, 0.25%, and 0.4% per year, respectively. The scenarios examined and the results predicted are the following:

SCENARIO (1) A freeze of CFCs 11, 12, 113, 114, 115, halons 1211, 1301, and 2402 at 1985 production levels; CCl₄, CH₃CCl₃, hydrochlorofluorocarbon (HCFC) 22 abundances increase at approximately 1 part per trillion by volume (pptv) (1% of today's level), 4 pptv (3% of today's level), and 6 pptv (7.5% of today's level) per year, respectively.

The chlorine loading of the atmosphere is predicted to reach 9.2 ppbv by the year 2060, about three times today's level, and the bromine loading 31 pptv, about two and one half times today's level. For models that did not include the effect of carbon dioxide (i.e., temperature feedback), predicted column ozone reductions were from 1 to 4% in the tropics, and from 8 to 12% at high latitudes in late winter. For models that did include the effect of carbon dioxide, predicted column ozone reductions were from 0 to 1.5% in the tropics and from 4 to 8% at high latitudes in late winter. These predictions do not include the effects of heterogeneous processes, which would increase the predicted ozone depletions, at least in polar regions. Ozone is predicted to decrease by 35–50% at 40 km in models with no temperature feedback, and about 25–40% in models with temperature feedback, and results in stratospheric temperature decreases of 10 to 20 K.

SCENARIO (2) A 50% cut in emissions of CFCs 11, 12, 113, 114, 115, halons 1211, 1301, and 2402 from 1985 production levels by the year 2000; CCl₄, CH₃CCl₃, HCFC 22 increase at approximately 1 pptv, 4 pptv, and 6 pptv per year, respectively, plus a 50% substitution of CFC reductions augmenting HCFC 22 fluxes (used as a surrogate for other HCFCs).

The chlorine loading of the atmosphere is predicted to reach 7.2 ppbv by the year 2060, and the bromine loading 22 pptv. Only models that did not include the effect of carbon dioxide were used to calculate ozone depletions for this scenario. Predicted column ozone reductions were from 1.5 to 3.0% in the tropics, and from 5 to 8% at high latitudes in late winter. These predictions do not include the effects of heterogeneous processes, which would increase the predicted ozone depletions, at least in polar regions. Ozone is predicted to decrease by 25–40% at 40 km (without temperature feedback). Temperature feedbacks are expected to reduce the predicted ozone depletions as in scenario 1.

SCENARIO (3) A 95% cut in emissions of CFCs 11, 12, 113, 114, 115, halons 1211, 1301, and 2402 from 1985 production levels by the year 2000; CCl₄, CH₃CCl₃, HCFC 22 increase at approximately 1 pptv, 4 pptv, and 6 pptv per year, respectively, plus a 50% substitution of CFC reductions augmenting HCFC 22 fluxes.

The chlorine loading of the atmosphere is predicted to reach 5.4 ppbv by the year 2060, and the bromine loading 14 pptv. For models that did not include the effect of carbon dioxide, there was little change in column ozone in the tropics, and a decrease from 2 to 4% at mid-latitudes. For the one model that did include the effect of carbon dioxide, column ozone was predicted to increase by 0–2% at most latitudes. These predictions do not include the effects of heterogeneous processes, which would increase the predicted ozone depletions, at least in polar regions. Ozone is predicted to decrease by 20–30% at 40 km.

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SCENARIO (4) 95% cut in emissions of CFCs 11, 12, 113, 114, 115; halons 1211, 1301, 2402; freeze of CCl_4 and CH_3CCl_3 atmospheric levels constant at 1985; HCFC 22 increase at approximately 6 pptv per year, but no substitution of CFCs with HCFC 22.

The chlorine loading of the atmosphere is predicted to be about 3.6 ppbv by the year 2060, comparable to that of today, and the bromine loading 14 pptv. One model that did not include the effect of carbon dioxide predicted little change of ozone in the tropics and a decrease of up to 4% at high latitudes. These predictions do not include the effects of heterogeneous processes, which would increase the predicted ozone depletions, at least in polar regions.

SCENARIO (5) 100% cut in emissions of CFCs 11, 12, 113, 114, 115; halons 1211, 1301, 2402; and CCl_4 , CH_3CCl_3 , and HCFC 22 by the year 2000.

This calculation was performed to examine the chlorine loading of the atmosphere with time. By the year 2060, the chlorine loading is predicted to be about 1.9 ppbv, significantly less than that of today and approximately the level required to return the Antarctic ozone layer to levels approaching its natural state, assuming that current meteorological conditions continue. Although no model calculations were performed using this scenario, it is likely that all models would predict an increase in global ozone due to the effects of carbon dioxide and methane.

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

- *The impact on stratospheric ozone of the halocarbons (HCFCs and HFCs) that are proposed as substitutes for the CFCs depends upon their chemical removal processes in the lower atmosphere (troposphere).*

Because they contain hydrogen atoms, the HCFCs and HFCs are primarily removed in the troposphere by reaction with the hydroxyl radicals (OH). Although the photochemical theory of tropospheric OH is well developed, it has not been validated experimentally, and the global OH distributions are based on models. Furthermore, the global abundance of OH is influenced by tropospheric composition, which is changing.

The various estimates of the lifetimes of HCFCs and HFCs in the troposphere have an uncertainty of $\pm 50\%$. This contributes an important source of uncertainty in the prediction of the ODPs and GWPs of the HCFCs and HFCs. The fate of the degradation products of the HCFCs and HFCs and their environmental consequences are inferred from data on analogous compounds and hence the specific degradation processes require further study.

- *The values of the ODPs for the HCFCs are significantly lower than those for the CFCs.*

Theoretical predictions performed by different groups using a variety of models have calculated similar, but not identical, values for the ODPs of the HCFCs, as indicated in Table 1 below.

None of the models used for calculating the ODPs are able to simulate the chemical and dynamical processes causing the Antarctic ozone hole. However, relative to CFC 11, the local Antarctic ODPs of HCFCs 22, 142b, and 124 will be larger, perhaps as much as a factor of two or three times greater than those derived from model calculations that do not include heterogeneous chemistry and that cannot simulate polar dynamical processes. The ramifications of polar ozone depletion for ODPs is not currently clear.

Table 1. Range of Ozone Depletion Potentials (ODPs) and halocarbon Global Warming Potentials (GWPs) determined by one-dimensional and two-dimensional models, assuming scaling for HCFC ODPs and GWPs by CH₃CCl₃ derived lifetime (6.3 years)

Species	ODPs		GWP
	1-D Models	2-D Models	1-D Models
CFC-11	1.0	1.0	1.0
CFC-12	0.9–1.0	0.9	2.8–3.4
CFC-113	0.8–0.9	0.8–0.9	1.3–1.4
CFC-114	0.6–0.8	0.6–0.8	3.7–4.1
CFC-115	0.4–0.5	0.3–0.4	7.4–7.6
HCFC-22	0.04–0.05	0.04–0.06	0.32–0.37
HCFC-123	0.013–0.016	0.013–0.022	0.017–0.020
HCFC-124	0.016–0.018	0.018–0.024	0.092–0.10
HFC-125	0	0	0.51–0.65
HFC-134a	0	0	0.24–0.29
HCFC-141b	0.07–0.08	0.09–0.11	0.084–0.097
HCFC-142b	0.05–0.06	0.05–0.06	0.34–0.39
HFC-143a	0	0	0.72–0.76
HFC-152a	0	0	0.026–0.033
CCl ₄	1.0–1.2	1.0–1.2	0.34–0.35
CH ₃ CCl ₃	0.10–0.12	0.13–0.16	0.022–0.026

The HCFCs all have much larger relative ozone depletion potentials during the first 30 to 50 years after their emission into the atmosphere compared to their steady-state ODP values. The transient values depend upon the atmospheric lifetime and their transport time to the region of destruction of the gas. This transient affect is implicitly taken into account by all models calculating atmospheric chlorine abundances and ozone depletion.

- *The steady-state values of the halocarbon GWPs of the HCFCs and HFCs are lower than those of the CFCs.*

The key factors that establish the halocarbon GWP of a HCFC or HFC are its lifetime in the troposphere and its ability to absorb atmospheric infrared radiation. Halocarbon GWP values differ between species due primarily to differences in their lifetimes, since their abilities to absorb infrared radiation are similar. Hence, one of the the largest sources of uncertainty in the calculation of the halocarbon GWPs of the HCFCs and HFCs is quantifying their rate of removal in the troposphere. Calculations by three groups using different models for the halocarbon GWPs of the CFCs, HCFCs, and HFCs yield similar, but not identical, values, as indicated in Table 1.

The HCFCs all have much larger relative global warming potentials during the first 30 to 50 years after their emission into the atmosphere compared to their steady-state halocarbon GWP values.

Implications

The findings and conclusions from the intensive and extensive ozone research over the past few years have several major implications as input to public policy regarding restrictions on man-made substances that lead to stratospheric ozone depletion:

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- The scientific basis for the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer was the theoretical prediction that, should CFC and halon abundances continue to grow, there would eventually be substantial ozone depletion. *The research of the last few years has demonstrated that actual ozone loss due to the CFCs has already occurred, i.e., the Antarctic ozone hole.*
- Even if the control measures of the Montreal Protocol were to be implemented by all nations, today's atmospheric abundance of chlorine (about 3 ppbv) will at least double to triple during the next century. *Assuming that the atmospheric abundance of chlorine reaches about 9 ppbv by 2060, ozone depletions of 0–4% ozone in the tropics and 4–12% at high latitudes would be predicted, even without including the effects of heterogeneous processes.*
- The heterogeneous, PSC-induced chemical reactions that cause the ozone depletion in Antarctica and that also occur in the Arctic represent additional ozone-depleting processes that were not included in the stratospheric ozone assessment models on which the Montreal Protocol was based. Recent laboratory studies suggest that similar reactions involving chlorine compounds may occur on sulfate particles present at lower latitudes, which could be particularly important immediately after a volcanic eruption. *Hence, even with the Montreal Protocol, future global ozone depletions could well be larger than originally predicted.*
- Large-scale ozone depletions in Antarctica appeared to have started in the late 1970s and were initiated by atmospheric chlorine abundances of about 1.5–2 ppbv, compared to today's level of about 3 ppbv. *To return the Antarctic ozone layer to levels approaching its natural state, and hence to avoid the possible ozone dilution effect that the Antarctic ozone hole could have at other latitudes, one of a limited number of approaches is a complete phase-out of all fully halogenated CFCs, halons, carbon tetrachloride, and methyl chloroform, as well as careful consideration of the HCFC substitutes. Otherwise, the Antarctic ozone hole is expected to remain, provided the present meteorological conditions continue.*

III. SCIENTIFIC SUMMARIES

Chapter 1. Polar Ozone

Polar Ozone Trends

The observation of substantial springtime reductions in Antarctic ozone, the Antarctic ozone “hole,” focused world attention on the polar regions. In the few years since the discovery of this phenomenon, a great deal of field and laboratory data have been gathered. Theoretical studies have kept pace with the experimental investigations. This chapter provides a detailed review of the current understanding of the science of polar ozone depletion.

Differences in atmospheric dynamics of the hemispheres cause naturally lower ozone abundances in the Antarctic early spring as compared with the Arctic which should not be confused with the Antarctic ozone hole. Planetary waves are generally weaker in the Southern Hemisphere than in the Northern Hemisphere. The Southern Hemisphere polar winter stratosphere is colder, and the westerly vortex is stronger and more persistent than in the Northern Hemisphere. These factors strongly influence the seasonal and latitudinal variations in ozone in the two hemispheres. The ozone hole is identified not merely with the difference in ozone abundances between the hemispheres or with the latitude gradients, but with a decrease in the ozone abundances found in September and October over the past decade. It is now clear that these decadal trends result from a dramatic drop in total ozone that occurs each September. This unexpected ozone removal results in about a 50% decrease in column abundance by the end of September in recent years, as demonstrated by ground-based measurements from Halley Bay, Syowa, and the South Pole. Ozonesonde and satellite data reveal comparable total column changes, and show that the decreases occur primarily in the height region from about 12 to 24 km, the heart of the polar ozone layer. Further, the satellites demonstrate that the ozone hole extends over broad horizontal scales, at times covering the entire Antarctic continent.

Observed ozone trends in the warmer, winter Northern Hemisphere stratosphere are far smaller than those of Antarctica. Recent analyses suggest that the sub-polar column ozone decreases are largest in the winter and spring, on the order of 5% over the period from 1969 to 1988.

The trend in Antarctic ozone has not been monotonic, but this is not surprising. Inter-annual variations in total ozone occur at all latitudes. One cause of inter-annual variability is the Quasi-Biennial Oscillation (QBO), which is a natural fluctuation of equatorial stratospheric zonal winds and circulation. The mechanisms connecting polar latitude phenomena with the tropical QBO wind oscillation are not well understood.

Polar Stratospheric Chemistry

Hypotheses to explain the ozone hole included halocarbon chemistry, nitrogen chemistry associated with the solar cycle, and dynamical effects. Observations have ruled out the dynamical and solar cycle theories, while a broad range of measurements have been shown to be consistent with the general concepts of the halocarbon theory. The halocarbon theory is based on observations of the widespread occurrence of polar stratospheric clouds (PSCs) in the extremely cold Antarctic lower stratosphere. These provide surfaces on which heterogeneous chemical reactions can take place.

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Satellite data from 1978 to the present provide information regarding the vertical, geographical and seasonal extent of the PSCs. Their frequency in the Antarctic stratosphere is about 10 to 100 times greater than in the Arctic. There is an apparent QBO variation in the occurrence of PSCs during both September and October, as well as increasing numbers of PSC sightings during the Octobers of 1985 and 1987 (years of westerly QBO phase). PSCs may also influence the radiative budget of the polar lower stratosphere, hence affecting the mean circulation and ozone distributions.

Laboratory studies suggest that some PSCs are composed of nitric acid and water, condensing at temperatures considerably warmer than the frost point. As the stratosphere cools, these will be the first types of clouds to form, while water ice clouds will form only at colder temperatures. Field studies have demonstrated that the former contain a substantial amount of nitrate. Laboratory studies have also shown that reactions involving nitrogen oxides and relatively long-lived chlorine species (such as ClONO₂ and HCl) can occur on cloud surfaces. These reactions convert relatively inert chlorine reservoirs to reactive species that photolyze readily, releasing chlorine free radicals which can then destroy ozone. The reactions also tie up nitrogen oxides in the long-lived species, HNO₃, thereby slowing the reformation of chlorine reservoirs such as ClONO₂. This maintains elevated abundances of chlorine free radicals and the associated rapid ozone destruction over notably longer periods than would be possible if the heterogeneous reactions affected only the composition of chlorine species. Both sunlight and extremely cold temperatures are necessary for accelerated ozone loss.

Once liberated, the chlorine rapidly forms chlorine monoxide (ClO), which can then participate in several ozone-destroying catalytic cycles. These involve formation of the dimer of chlorine monoxide as well as reactions of ClO with bromine monoxide (BrO), hydroperoxyl radicals, and atomic oxygen. Laboratory studies have provided most of the rate coefficients and photochemical parameters needed to characterize these cycles, although there are still significant uncertainties in both homogeneous and heterogeneous chemistry.

Field Observations

Observations of ClO and BrO in Antarctica have provided a critical test of the halocarbon theory of ozone depletion. *In situ* and remote measurements using two independent techniques have demonstrated that the ClO abundances near 20 km are typically about 1 ppbv in the Antarctic vortex during September, about 100 times greater than theoretical predictions that do not include heterogeneous chemistry. However, these elevated ClO abundances are broadly consistent with modeling studies considering the likely PSC chemistry, frequency, and duration. While there are differences in detail among these studies, all show that a substantial fraction of the observed ozone loss (60–100%) can be explained by the observed ClO and BrO abundances using current measurements of kinetic rates. The Antarctic ozone loss is at present believed to be dominated by the dimer cycle during years when depletion is largest, with bromine reactions contributing about 15–35% and reactive hydrogen contributing about 10–15% to the total chemical loss rate. During years of lower Antarctic ozone depletion (e.g., 1988) and in the Arctic, the bromine chemistry is calculated to be more important. Uncertainties in measurements, model formulation and the potential importance of transport processes currently preclude a fully quantitative evaluation of the consistency between observed rates of ozone change and photochemical mechanisms.

A broad range of ancillary measurements in Antarctica supports and extends our confidence in the understanding of changes in gas-phase composition caused by PSCs. These include: *in situ* measurements of H₂O, NO_y (total reactive nitrogen), NO, particle sizes, and particulate nitrate, as well as long-path measurements of OClO, HCl, HF, ClONO₂, NO₂, and HNO₃. Of particular importance are the observations

of NO_x and H_2O , which show extensive denitrification and dehydration in the Antarctic vortex, believed to result from sedimentation of cloud particles. Denitrification is of particular importance since it controls the amount of nitrogen oxides remaining after PSCs have disappeared, and hence, as mentioned earlier, may strongly affect the rate of reformation of chlorine reservoirs.

Similar chemical measurements have been obtained in the Arctic stratosphere. Satellite and ground-based measurements of steep latitudinal gradients in Arctic NO_2 abundances (the Noxon "cliff") suggest the presence of mechanisms depleting NO_2 in north polar regions. The decrease in NO_2 is qualitatively related to increases in HNO_3 abundances, indicating mechanisms for nitrogen oxides suppression without denitrification (different from that observed in Antarctica). Such an increase could occur, for example, through heterogeneous reactions followed by cloud evaporation. Concentrations of ClO as high as 1 ppbv were observed inside the Arctic polar vortex in the winter of 1989. Enhanced column abundances of ClONO₂ and reduced abundances of HCl and NO_2 also indicated the importance of heterogeneous chemistry similar to that of Antarctica. No unambiguous evidence for ozone loss has yet been identified for the winter of 1989. Readily detectable ozone reductions would be expected to occur only if high concentrations of ClO were maintained for sufficiently long periods in cold, illuminated air. Vortex dynamics during the 1989 winter probably limited these conditions, and are likely to do so in most Northern Hemisphere winter/spring seasons. Thus the Northern Hemisphere ozone trends cannot be unambiguously identified with PSC chemistry, although the observations are qualitatively consistent with such an explanation.

Dynamics

The role of dynamical coupling has been examined in many different studies. Synoptic scale disturbances (tropospheric weather systems) can affect total ozone amounts locally, and may lead to the formation of PSCs. Air may flow through such systems and become chemically perturbed. If there is significant flow of air into and out of the stratospheric polar vortex, ozone amounts may be reduced well outside of the region where heterogeneous chemical reactions on PSCs can occur. Further, some PSCs may be found outside of the denitrified and dehydrated region and may induce chemical perturbations at sub-polar latitudes during winter. Quantitative details are uncertain. Export of air that has undergone ozone depletion may dilute ozone concentrations at lower latitudes when the polar vortex breaks down in the spring. Numerical models indicate that about a 2% change might occur in ozone amounts at mid-latitudes of the Southern Hemisphere due to dilution, and suggest that some fraction of the dilution may remain from one year to the next.

Measurements of the vertical profiles of long-lived tracers such as N_2O and the chlorofluorocarbons in the polar vortices reveal low values compared to those at other latitudes. These apparently result from downward motion and have important implications not only for representations of vortex dynamics but also for chlorine chemical perturbations. For example, measurements indicate only about 0.3 ppbv of total chlorine in the form of chlorofluorocarbons near 20 km at 70°S as compared to 1.0 ppbv at 45°S in about 1987; these imply that the corresponding abundances of reactive chlorine are on the order of 2.2 and 1.5 ppbv, respectively. Thus, the amount of reactive chlorine available for reactions on PSC surfaces in the polar regions is likely to be significantly enhanced compared to lower latitudes.

The stratospheric circulation exhibits variability on a range of time scales. In particular, there is substantial inter-annual variability in the two hemispheres, especially in the Northern Hemisphere. A very deep ozone hole occurred over Antarctica in spring, 1987. The hole was not as deep in 1988, perhaps because dynamics and transport were more vigorous in 1988 than in 1987. Temperatures were also warmer during September 1988 as compared to 1987, which is likely to be the primary cause for a corresponding

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decrease in PSC cloud frequencies in the regions sampled by the SAM II satellite between the 2 years. These factors may yield important differences in heterogeneous chemical perturbations and hence may explain qualitatively the difference in the depth of the ozone hole obtained (with 1988 being much less depleted than 1987). The observed behavior fits general expectations based on QBO behavior since the equatorial winds were strongly westerly near 25 km during October 1987, whereas 1988 was characterized by a transition from westerly to easterly winds. If the current QBO cycle has the average period of about 28 months, winds will remain easterly through October 1989, but change to westerly before September 1990. If the past correlation between the QBO and the ozone hole continues and if the current QBO cycle exhibits a period close to the average, then the ozone depletion should be expected to be relatively modest in 1989 and quite deep in 1990 (note, however, that the QBO period can vary by as much as 8 months so that the measured equatorial winds must be examined before any firm comparisons can be made). The next few years should therefore provide an excellent test of the relationship between the QBO and the Antarctic ozone hole.

Minimum temperatures in the high-latitude Northern Hemisphere stratosphere were unusually low in late January/early February, 1989. PSCs were observed as far equatorward as 50°N. A strong, dynamically induced warming occurred at polar latitudes in mid-February and temperatures rose above the threshold values required for PSC formation. Poleward transport of air rich in ozone and nitrogen oxides is likely to have occurred. This warming of the Arctic vortex probably played an important role in limiting ozone loss during 1989.

On the basis of radiosondes and satellite data, a downward trend in lower stratospheric temperatures has been deduced at high southern latitudes from 1979 through 1987 (note, however, that in 1988 temperatures were much warmer than they would have been if this trend had continued monotonically). The largest changes, about 1K/year, were found in the means for October and for November, while no trend was found in September, when most of the Antarctic ozone loss is observed. The observed time lag between the temperature change and the ozone loss, as well as radiative studies with 1-D, 2-D, and 3-D models, suggest that the temperature trend is the result of the ozone trend rather than its cause (i.e., reduced ozone abundances are predicted to yield smaller solar ultraviolet heating rates and hence colder temperatures).

Future of Polar Ozone

The future depletion of polar ozone depends in large part on mankind's use of halocarbons, although other factors may also contribute. In contrast to its behavior at ground level, increased concentrations of carbon dioxide may cool the stratosphere, perhaps affecting the duration and spatial extent of the PSCs in both hemispheres. Possible changes in climate and in the concentrations of atmospheric methane and nitrous oxide may also affect the processes related to the Antarctic ozone hole. The bulk of the chlorine currently in the stratosphere comes from chlorofluorocarbons that have atmospheric removal times on the order of 50 to 100 years, and hence the ozone hole will likely remain over Antarctica for many decades, even if all production were immediately halted. An examination of the Antarctic springtime column ozone record at several locations permits a rough estimate of the atmospheric chlorine content when the Antarctic ozone hole first became apparent. Assuming no changes in temperature, atmospheric dynamics, or photochemical processes, this provides an indication of the total chlorine abundances required to return the Antarctic ozone layer to levels approaching its natural state. A preliminary analysis of trace gas samples indicates an average age of polar lower stratospheric air of about 5 years. Coupled with the onset of detectable ozone reductions in the late 1970s, this suggests that organic chlorine mixing ratios of roughly the mid-1970s are necessary (corresponding to tropospheric total chlorine mixing ratios of about 1.5–2.0 ppbv, including the 0.6–0.7 ppbv of methyl chloride, which is believed to be of natural origin).

Chapter 2. Global Trends

Introduction

This chapter largely builds upon the Ozone Trends Panel (OTP) report by adding new analyses and updating the database.

Since the 1920s, numerous techniques have been developed and applied to determine total ozone and its vertical distribution. Initially, these measurements were not made for the purpose of determining long-term trends. Fortunately, some of these systems, and only the Dobson spectrophotometer for the last 30 years, have the requisite stability to provide data from which such changes may be detected and quantitatively measured.

For trend determination, short-term random noise is not usually a significant factor, since large amounts of data are averaged. The most important characteristic is stability, i.e., the absence of time-dependent systematic errors. Accuracy is desirable, but continuing systematic errors will not obscure the detection of change.

Determination of the global trends in stratospheric ozone has been based on complementary measurements, from the ground and from satellites. Ground-based instruments can be checked and recalibrated as necessary; they are regarded as capable of long-term stable operation, although this depends on some non-technical factors. Their disadvantages are that they are local systems, and provide few observations in oceanic or remote areas. Satellite-borne instruments obtain global data but, once launched, are not available to checking and are subject to drift. It is thus desirable to have these complementary measurements to provide checks on each other.

Trends in Total Ozone

Existing data on total ozone relies heavily on the Dobson instruments and M83/M124 instruments in the Northern Hemisphere mid-latitudes (30–64°N), so that trends can only be determined in this latitude range. Dobson instruments are referenced to the World Standard instrument, whose calibration is reported to have been maintained within $\pm 0.5\%$ over the past 15 years.

Satellite data are provided by the TOMS/SBUV instruments. They have proven to be very useful to verify consistency and identify erroneous readings in ground-based instruments and to confirm the reliability of the World Standard instrument. An important recent result is the development of a method for using the TOMS/SBUV data themselves to remove the effects of long-term instrumental drift. Although such new data are not used in the following analysis, results of initial testing suggest this has been successful, and that the TOMS data can provide in the future a second, independent source of data on global trends.

The main conclusions of the study of total ozone trends are as follows (± 2 standard error limits are shown):

- *New analyses of the total ozone data set used by OTP produce negative trends whose latitudinal and seasonal patterns are consistent with the earlier results (over the 17-year period from December 1969 through 1986).*

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Zonal mean decadal changes derived using various statistical assumptions lie in the following ranges during winter (December–March): for 30–39°N or 35°N, $-0.9 \pm 0.9\%$ to $-1.7 \pm 0.9\%$; for 40–52°N or 45°N, $-2.0 \pm 0.8\%$ to $-3.0 \pm 1.7\%$; and for 53–64°N or 55°N, $-2.5 \pm 1.9\%$ to $-3.7 \pm 1.8\%$. Analogous changes during summer (May–August) are: for 30–39°N, $-0.4 \pm 0.9\%$ to $-1.1 \pm 0.9\%$; for 40–52°N, $-0.7 \pm 0.6\%$ to $-1.1 \pm 0.8\%$, and for 53–64°N, $-0.1 \pm 0.9\%$ to $-0.7 \pm 0.9\%$. Results of an independent study performed in the USSR lie within the ranges quoted above.

- *The trends are sensitive to data obtained after October 1982 during periods of anomalies in the ozone patterns.*

If the data are analyzed up to and including October 1982, the summertime trend moves closer to zero by 0.8 to 1.0% per decade. Depending on the details of the statistical model, the analogous change in the wintertime trend is 0.3 to 0.9% per decade less negative.

- *Derived trends for the 17-year period between 1969 and 1986 are insensitive to the statistical treatment of the quasi-biennial oscillation and solar cycle relationships.*

Since the Dobson ozone record approaches 30 years, the trend estimates should be nearly independent of the 11-year solar cycle effect as represented by the F10.7-cm solar flux and the quasi-biennial effect represented by equatorial 50 hPa winds. This is important in that the derived long-term trends are robust to these known natural causes of ozone variability.

- *Extension of the data set into 1988 does not alter the nature of conclusions based on measurements through 1986, although differences in detail exist.*

During winter, derived statistically significant trends are $-1.8 \pm 1.1\%/decade$, $-2.3 \pm 0.9\%/decade$, and $-2.7 \pm 1.2\%/decade$ at latitudes 35°N, 45°N, and 55°N, respectively. Trends derived for summer at 35°N, 45°N, and 55°N are $-0.5 \pm 1.1\%/decade$, $-0.3 \pm 1.0\%/decade$, and $-0.2 \pm 1.2\%/decade$, respectively. None of the summertime trends are statistically significant.

- *Analyses of Dobson measurements from different geographic regions reveal differences in trends.*

Over the period 1969 to 1988, European and North American stations indicate statistically significant wintertime trends of $-2.9 \pm 0.7\%/decade$. Japanese stations indicate a non-significant wintertime trend of $-0.6 \pm 1.0\%$ per decade. Summertime trends vary from $-1.2 \pm 0.7\%$ per decade over North America to $+0.8 \pm 1.2\%$ per decade over Japan.

- *The regional differences in trends derived from the Dobson network are consistent with geographic patterns of ozone change contained in the TOMS/SBUV data sets.*

Data sets now available from satellites are useful in identifying geographic patterns in total ozone changes. However, present satellite data sets have insufficient length for definitive studies of long-term trends.

- *The observed total ozone trends for the winter are more negative than model predictions for the period 1969 through 1986, although there is close agreement between observation and prediction in the summer.*

The observed winter total ozone trends over the latitudes 30 to 60°N ranged from $-1.9 \pm 0.7\%$ per decade to $-2.6 \pm 1.2\%$ per decade among the study groups. Based on the observed trend

uncertainty limits, these changes exceed the theoretical model-calculated winter changes of -0.5 to -1.2% per decade given in the OTP report. The observed summer trends ranged from $-0.6 \pm 0.6\%$ per decade to $-0.8 \pm 0.6\%$ per decade and were consistent within the uncertainty limits with the summer theoretical model calculations of -0.3 to -0.6% per decade.

Trends in Ozone Vertical Distribution

The situation with regard to measurements of the vertical distribution is less satisfactory. Presently, most ground-based observations have been of the Umkehr type, with extensive records at only about 10 stations distributed very non-uniformly over the globe. The observations have a vertical resolution of 11 to 15 km, and are subject to aerosol interference, which can now be corrected for by physical-theoretical methods. The only reliable satellite data are obtained by the SAGE instruments above 25 km. It uses a ratio technique which renders the measurement insensitive to drift. The sampling is 900 profiles a month (two per orbit) with time-varying non-uniform geographical distribution.

The emphasis in the current analysis is first given to the altitude range in the upper stratosphere where the percentage change in ozone concentrations at mid-latitude due to anthropogenic chlorine perturbations is expected to be the largest. The major problem for such an analysis is the scarcity in time and space of the available data base for both satellite and ground-based measurements which precludes any true global evaluation of trends in ozone vertical distributions.

- *Over the regions of maximum density of coincidences (SAGE II minus SAGE I), i.e., 20–50°N and 20–50°S, the comparisons indicate for a 6-year average time period (1980–1986):*
 - an ozone decrease between 35 and 44 km with the maximum ozone change of $-3 \pm 2\%$ occurring at 40 km.*
 - an ozone decrease of $-3 \pm 2\%$ at 25 km and an essentially zero ozone change at 28–33 km and at 45–48 km.*

The only satellite observations that can be used currently for the determination of upper-stratospheric ozone changes are based on the comparison of 33 months (1979–1981) of SAGE I and 3 years (October 1984–December 1988) of SAGE II operations. This analysis constitutes an update of the OTP report by including two more years of SAGE II data, and confirms the previous results. These values represent the changes that occur over this time period and no attempt has been made to correct for solar cycle or any other.

- *Statistically significant negative trends are observed in Umkehr layers 6-7-8 (30–43 km) that correspond to an average ozone change of $-0.4 \pm 0.3\%$ per year at 40 km.*

A trend analysis of Umkehr observations performed at 10 stations in the Northern Hemisphere for the period 1977–1987 has been made on a station-by-station basis using an autoregressive statistical model which accounts for seasonal, solar-cycle and aerosol-induced effects. The latter is of particular importance when considering the high aerosol load in the stratosphere during the year 1982–1983 following the El Chichon volcano eruption.
- *Within the uncertainty limits of SAGE and Umkehr trend results near 40 km, these two independent results are not inconsistent.*

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When corrected for the solar effect on ozone over 6 years, the change in ozone from SAGE observations near 40 km is estimated to be $-0.2 \pm 0.4\%$ per year that is not explained by natural and instrumental variation. When compared to the Umkehr trend of $-0.4 \pm 0.3\%$ per year there is no inconsistency within the margins of error.

- *In the lower stratosphere (15–24 km), the estimated change from a limited network of Northern Hemisphere ozonesonde stations is -0.5% per year $\pm 0.4\%$.*

Analysis of ozonesonde data at nine stations (Canada, Europe, and Japan) with records extending for the three longest ones from 1966 to 1986 has been performed to detect possible trends in ozone concentrations in the lower stratosphere. This analysis leads to some differences in the results for the various stations which probably reflect the differences in the system operation and extent of the data bases as well as varying regional effects.

- *Although at the lower edge, the simulation results are within the error bars of the observed changes in the ozone vertical distributions.*

Calculation of changes in the ozone vertical distribution have been performed in the OTP report using 2-D models for the period 1979–1985. The calculated decreases peak at about -6% at mid-latitudes near 40 km.

- *The ozone decrease observed by SAGE instruments and suggested by Umkehr results in the 40 km region contribute very little to explaining the Dobson year-round total ozone trend of -1.1% per decade.*

The SAGE change of $-3\% \pm 0.2\%$ at 25 km over 6 years, when considered together with the negative Umkehr trend in this height range and the statistically significant, but not globally representative, trend of nearly -0.5% per year observed by ozonesondes between 17 and 24 km, seems to suggest that the stratosphere below 25 km is the prime contributor to the observed total ozone trend at mid-latitude.

Trends in Stratospheric Temperature

The update of the previous temperature trend report (OTP) is based on the stratospheric temperature data set already considered, and updated when possible, and the new Rayleigh lidar data. These lidar data have been compared with the SSU (Stratospheric Sounding Unit) data and the NMC (National Meteorological Center) analyses from 1981 to 1987. Substantial differences are observed, accountable in part by changes in the NOAA satellite series.

The recent finding of a statistical relationship between the stratospheric temperature, the QBO and the 11-year solar cycle has a potential implication for trend determination. The zonal asymmetry of the 11-year solar signal, clearly shown by the radiosonde data up to 30 hPa (24 km), and confirmed by the lidar and rocket data at higher altitudes, leads locally to much larger temperature dependence than the one observed in zonal or global means. Caution must be taken when using local or regional data (for T and O₃ as well) unless the data extend over a long enough period to separate trends from solar activity effects.

In the stratosphere, long-term trends can only be obtained from radiosondes at present. Satellite observations are available for less than a solar cycle:

- *In the lower stratosphere (100–30 hPa), the temperature data over the last 20 years suggest a maximum change of -0.4 K/decade at mid- and low latitudes with larger changes occurring at higher latitudes.*
- *In the upper stratosphere, the satellite data for the period (1985/1986) - (1979/1980) indicate a global temperature change of $-1.5 \pm 1^\circ\text{K}$. It is compatible with the $-3 \pm 4\%$ change in ozone concentration around 40 km as observed by SAGE instruments.*

More work is clearly needed to bring data of different sources into agreement and to understand the causes of the large spatial variability, whether or not it is related to solar activity.

Trends in Tropospheric Source Gases and Ozone

- *For most of the tropospheric trace gases, the observed rates of increase up to the end of 1987 have not changed significantly compared to those in the OTP report, which analyzed data up to the end of 1986.*
- *It would appear that the rate of methane increase has been slowing over the last decade, from 16–20 ppbv per year in the 1980s to approximately 12–16 ppbv per year in the late 1980s.*
- *Trend analysis of surface ozone measurements from ozonesonde and ground-based instruments show variable results.*

The 16 Northern Hemispheric sites show a range of trends from -1.1 to $+3.1\%$ per year. Ten of the Northern Hemispheric sites show statistically significant positive trends; one site shows a statistically significant negative trend. The remaining sites show trends that are not significant. The seven European sites all show statistically significant positive trends, ranging from $+1.1$ to $+3.1\%$ per year. All four Canadian sites show negative trends, from -0.1 to -1.1% per year, only one of which is statistically significant. All three Japanese sites show positive trends, ranging from $+0.9$ to $+2.5\%$ per year, two of which are significant. The four Southern Hemispheric sites show trends ranging from -0.5 to $+0.6\%$ per year, only one of which is significant.

Trends in Stratospheric Aerosols

- *Stratospheric aerosols can produce artifacts in ozone measurements by remote-sensing instruments and, in the case of Antarctic PSCs, have been shown to impact ozone destruction through heterogeneous chemistry. In addition, laboratory studies suggest that heterogeneous processes may occur on the surface of sulfuric acid/H₂O aerosols, which are greatly enhanced after volcanic eruptions. The latter effect could be important in providing a mechanism for ozone destruction on a global scale.*
- *From the standpoint of global trends, global stratospheric aerosol loading, which peaked after the eruption of El Chichon, has generally decreased. Although low in 1989, it has not yet reached the lowest values observed in 1978–1979. The 1989 values have little or no effect on ozone measurements.*

Trends in Surface UV Radiation

The Robertson-Berger meters located in the United States showed no increase in surface ultraviolet radiation over the period 1974 through 1985. The measurements do not contradict the observed downward

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trend in total ozone. The meter is not sensitive to small changes in ozone, and in addition, the system is strongly influenced by cloudiness and sources of pollution.

Chapter 3. Model Predictions

Stratospheric Models

In order to estimate the impact of man-made chemicals on atmospheric ozone, it is essential to develop models that perform long-term predictions. Current models that are used for these predictions include rather detailed schemes for homogeneous chemistry, and to some extent, account for radiative and dynamical feedbacks. Two-dimensional models predict the latitudinal and seasonal changes in ozone and other trace gases. Among the available models for calculating ozone globally, these 2-D models currently include the best representation of homogeneous physical and chemical processes in the middle atmosphere and have been compared extensively with observations of many stratospheric chemical species. However, none of these models properly account for heterogeneous chemistry and polar dynamics. Because of computational requirements and development time, the recently available 3-D models have had only limited applications in assessment studies, but are important in resolving some issues of model formulation and dynamical feedbacks.

An important prerequisite for prediction models is that they represent with sufficient accuracy the present distributions of trace gases. The 2-D models involved in the present assessment generally reproduce the patterns observed in the ozone column, with a minimum in the tropics and maxima at high latitudes in the spring of both hemispheres. The meridional distribution of local ozone is also in good agreement with the satellite observations. However, important discrepancies have also been noted: in particular, the models systematically underestimate ozone concentrations near 40 km, where they should accurately represent the physical and chemical processes controlling ozone. Calculated and observed distributions and seasonal variations of species such as nitrous oxide, methane, nitric acid, nitrogen oxides, and chlorine monoxide are in qualitative agreement, although substantial quantitative differences are found in certain cases.

The recent intercomparison of stratospheric models (1988, Virginia Beach) has highlighted many specific differences in the models, but has not yet resolved their causes. For example, the photodissociation rates were compared using specified ozone and temperature fields and found to differ among models by a factor of 2 or more in many instances. Follow-up studies examining the detailed radiative transfer in the models are continuing. Tests of the model circulation using synthetic tracers with specified chemistry has revealed substantial differences in the rate of upward motion in the tropical stratosphere. In spite of these individual differences, the calculated distribution of ozone is in good agreement between the models, and may demonstrate the robustness of the ozone photochemistry in these models.

Important Issues in Ozone Modeling

Modeling the polar regions is an especially challenging task because of the difficulty both in simulating the physics and chemistry of polar stratospheric clouds (PSCs) and in modeling the dynamical processes controlling the distribution of tracers and temperature of the high-latitude lower stratosphere in winter. The model predictions in this assessment do not include the effects of heterogeneous processes involving chlorine and nitrogen-containing chemicals on the surface of particles in PSCs. These processes are known to increase the abundance of the chlorine radical, ClO, which plays an important role in reducing ozone in

the Antarctic atmosphere. In several models, exploratory studies including these effects were performed, and showed substantially enhanced ozone depletion at high latitudes during winter and smaller changes in neighboring mid-latitudes for much of the year. Additional studies, including some of these 2-D models and other 3-D models, have shown that the transport of ozone-depleted air from the Antarctic region today can account for ozone reductions at mid-latitudes of several percent.

Laboratory studies suggest that heterogeneous processes on the natural background aerosols (Junge layer, which can be perturbed by volcanic eruptions) could also contribute to enhanced chlorine-catalyzed ozone destruction over much of the globe. Several model studies have examined the effects of parameterized heterogeneous reactions on sulfuric acid aerosols and have shown the potential for additional ozone depletion. Because of uncertainties in the laboratory data on rate constants for these reactions under stratospheric conditions, only sensitivity studies can be made at present.

Stratospheric temperature perturbations resulting from changes in CO₂ or tropospheric climate will in turn affect the photochemistry of ozone. In the upper stratosphere for the scenarios described below, increased CO₂ and reduced ozone both lead to temperature reductions near the stratopause of 10–20 K by the year 2060. This significant cooling is a robust feature of simulations; it leads to a reduced rate of ozone photochemical loss and hence moderates the ozone depletion due to chlorine. In the lower stratosphere, a particularly difficult region to model, smaller temperature changes are predicted. If the lower stratosphere cools significantly (2–4 K) in the future, then reduced chemical loss predicted by the models with homogeneous chemistry would lead to an increase in ozone concentrations that must be considered along with other perturbations. Such changes in stratospheric temperatures could be accompanied by changes in the circulation. A number of the models used in this assessment include radiative feedbacks, and some attempt to account for circulation feedbacks.

Scenarios for Atmospheric Composition

The composition of the atmosphere will depend on the rate at which halocarbons and other trace gases will be emitted in the future. Several scenarios have been considered in this assessment in order to examine the impact of possible control policies. Their details are specified in Table 2. None of the individual scenarios is intended to be a prediction of the future atmospheric composition; the range is only illustrative of different strategies for halocarbon control. They are used to define a range of chlorine and bromine loadings to the atmosphere and to study the consequent response of stratospheric ozone.

The predictions given here should be interpreted with caution in the light of the models' successes and limitations discussed above. Thus, given that the broad features of the present atmosphere are in general reproduced satisfactorily, it is then the broad features of the predictions that should be given most credence. For example, predictions of ozone and temperature changes near 40 km, as well as that of global chlorine loading, are probably more robust than detailed latitudinal behavior, especially in view of the models' lack of PSC chemistry.

1-Reference Scenario. In the reference scenario (A1), the fluxes of the CFCs (11, 12, 113, 114, 115) and halons (1211, 1301, 2402) controlled under the Montreal Protocol were held constant at their estimated 1985 production levels. The concentration of additional halocarbons and other chemically and radiatively important gases were assumed to increase at rates consistent with presently observed trends: CCl₄ at +1 pptv/yr (+1%/yr in 1985); CH₃CCl₃ at +4 pptv/yr (+3%/yr in 1985); CH₄ at +15 ppbv/yr (+0.9%/yr in 1985); N₂O at +0.25%/yr; CO₂ at +0.4%/yr. For HCFC-22 the current estimated emissions (140 Gg/yr in 1985) and growth rate in emissions (5%/yr of the 1985 emission rate) were chosen to be consistent with the

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Table 2. Scenarios for halocarbon abundances

1985 Conditions				
Gas	Mixing Ratio (pptv)	Flux (Gg/yr)	Gas	Mixing Ratio
CFC-11	220	350	CCl ₄	100 pptv
CFC-12	375	450	CH ₃ CCl ₃	130 pptv
CFC-113	30	150	CH ₃ Cl	600 pptv
CFC-114	5	15	CH ₃ Br	10 pptv
CFC-115	4	5		
halon 1211	1.5	5	N ₂ O	306 ppbv
halon 1301	1.7	8	CH ₄	1600 ppbv
HCFC-22	80	140	CO ₂	345 ppmv

Scenario Definitions					
Scenario	CFC cut (1996–2000)	CFC-22 Surrogate	CFC-22 Growth	CCl ₄ Growth	CH ₃ CCl ₃ Growth
A1	0%	—	+7 Gg/yr/yr	+1 pptv/yr	+4 pptv/yr
B1	50%	50%	+7 Gg/yr/yr	+1 pptv/yr	+4 pptv/yr
C1	85%	50%	+7 Gg/yr/yr	+1 pptv/yr	+4 pptv/yr
D1	95%	50%	+7 Gg/yr/yr	+1 pptv/yr	+4 pptv/yr
D2	95%	50%	+7 Gg/yr/yr	fix (1985)	fix (1985)
D3	95%	0%	+7 Gg/yr/yr	fix (1985)	fix (1985)
E1	100%	50%	+7 Gg/yr/yr	+1 pptv/yr	+4 pptv/yr
E2	100%	50%	+7 Gg/yr/yr	fix (2000)	fix (2000)
E3	100%	50%	+7 Gg/yr/yr	cut (2000)	fix (2000)
E4	100%	50%	+7 Gg/yr/yr	cut (2000)	cut (2000)
E5	100%	0%	+7 Gg/yr/yr	cut (2000)	cut (2000)
E6	100%	0%	fix (2000)	cut (2000)	cut (2000)
E7	100%	0%	cut (2000)	cut (2000)	cut (2000)
E8	95%	0%	cut (2000)	cut (2000)	cut (2000)
E9	85%	0%	cut (2000)	cut (2000)	cut (2000)
E10	100%	50% cut (2030)	cut (2030)	cut (2000)	cut (2000)

Total Chlorine Abundance, Summed Over All Halocarbons (ppbv)

Year	A1	B1	C1	D1	D2	D3	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10
1985	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98	2.98
2000	4.52	4.41	4.33	4.31	4.07	3.98	4.30	4.30	4.30	4.30	4.21	4.21	4.21	4.22	4.26	4.30
2030	7.09	5.93	5.12	4.89	4.17	3.66	4.77	4.29	4.09	3.52	2.98	2.84	2.58	2.72	3.01	3.38
2060	9.16	7.15	5.75	5.35	4.15	3.55	5.15	4.19	3.87	3.30	2.67	2.27	1.95	2.18	2.64	2.13
2090	10.72	8.09	6.25	5.73	4.05	3.42	5.47	4.03	3.64	3.07	2.41	1.88	1.55	1.84	2.43	1.59

limited atmospheric observations (+6 pptv/yr in 1985). Many of the models used in the assessment had specified temperature distributions and were therefore unable to include the radiative impact on stratospheric temperatures of CO₂ increases or ozone changes.

In this reference scenario (A1), the chlorine loading of the atmosphere increases from 3.0 ppbv in 1985 to 4.5 ppbv in the year 2000, to 7.1 in the year 2030, and to 9.2 in the year 2060. The bromine loading increases from 13 pptv in 1985 (10 pptv CH₃Br; 1.5 pptv halon 1211; 1.7 pptv halon 1301) to 31 pptv in the year 2060 (10 pptv CH₃Br; 3 pptv halon 1211; 18 pptv halon 1301). For models that did not contain the carbon dioxide effect, reductions in column ozone from 1980 to 2060 ranged from 1% to 4% in the tropics and from 8% to 12% at high latitudes in late winter. For models that included the carbon dioxide effect, the corresponding ozone reductions were less: 0% to 1.5% in the tropics and 4% to 8% in high latitudes in late winter. Ozone reductions at 40 km were about 35–50% in models with no temperature feedback and about 25–40% in models with temperature feedback, resulting in temperature decreases of 10–20 K. No heterogeneous chemistry was included in these models. When methane increases are suspended in 1985, ozone column reductions are larger in all latitudes and seasons by about 3%. Methane increases lead to increases in ozone by conversion of active chlorine (Cl, ClO) into inactive chlorine (HCl) and further by contributing to the direct production of ozone by “smog chemistry” in the lower stratosphere and troposphere. Many of the differences in the model results occur in the lower stratosphere where it is more difficult to predict the impacts of radiative and chemical forcing.

2-Scenarios with CFC Reductions. Several scenarios were considered in which emissions of CFCs and halons were reduced between 1995 and the year 2000, with 50% of the total CFC reduction augmenting the HCFC-22 budget. The increase in carbon tetrachloride and methyl chloroform are taken from the reference scenario. When CFC emissions are cut by 50% (B1), the chlorine loading in the year 2060 reaches 7.2 ppbv and the bromine loading is 22 pptv. The corresponding reductions in column ozone by 2060 are about 65% of those calculated for the reference scenario: 1–3% in the tropics and 5–8% at high latitudes in late winter for models without temperature feedback. Ozone reductions at 40 km are also less than in A1, 25–40% (without temperature feedback). No heterogeneous chemistry was included in these models.

When the CFC emissions are reduced by 85% (C1), the chlorine and bromine loadings in 2060 are 5.5 ppbv and 14 pptv, respectively. The reductions in column ozone are approximately 50% of those calculated in the reference scenario. No heterogeneous chemistry was included in these models.

When the CFC emissions are reduced by 95% (D1), the chlorine and bromine loadings in 2060 are 5.4 ppbv and 14 pptv, respectively. The reductions in column ozone at mid- to high latitudes are approximately 40–50% of those calculated in the reference scenario: very little change in the tropics and 2–4% at mid-latitudes for models without temperature feedback. Ozone reductions at 40 km are 20–30%. In the one model that includes the CO₂ effect, modest ozone column increases, 0–2%, are found at most latitudes. No heterogeneous chemistry was included in these models.

Further reductions in chlorine loading were considered by freezing concentrations of methyl chloroform and carbon tetrachloride (D2). When CFC emissions were also cut by 95%, the chlorine loading at 2060 was reduced to 4.2 ppbv. The reductions in column ozone were about 30% of that in the reference scenario, corresponding to about 60% of those calculated in the similar case when CCl₄ and CH₃CCl₃ were assumed to increase. If, in addition, the 95% cutback in CFC emissions is not compensated for by increased emission of HCFC-22 (D3), the chlorine loading at 2060 is reduced further to 3.6 ppbv, but the calculated ozone columns are not significantly different: little change in the tropics and a decrease of up to 4% at high latitudes. This change in chlorine loading, from 4.2 to 3.6 ppbv, has little effect on column ozone because

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it is associated with changes in HCFC-22 abundance. In these current assessment models, HCFC-22 does not release a large fraction of its chlorine in the middle stratosphere where chlorine-catalyzed loss of ozone is most important. No heterogeneous chemistry was included in these models.

Examination of chlorine loading. Thus far, in all of the scenarios (A-D) the tropospheric mixing ratio of chlorine, when summed over all halocarbons (i.e., chlorine loading), is well above the 1985 levels of 3 ppbv by the end of the scenarios in 2060. It is interesting to note what different combination of halocarbon reductions could possibly yield a chlorine loading of less than 3 ppbv by 2060, and also whether chlorine levels prior to the onset of the Antarctic ozone hole (at most 2 ppbv) could be achieved by 2060 with any combination of freezes or cuts in halocarbon emissions in the year 2000. Additional scenarios (E) in Table 2 explore the range of chlorine loading assuming that emissions of all halocarbons can be completely eliminated by 2000, except for CH_3Cl . Only a complete cut in emissions of CFCs, HCFC-22, CCl_4 , and CH_2Cl_2 results in chlorine loading less than 2 ppbv by 2060, although a combination of cuts and reductions in emissions (including low levels of CFC emissions) can give values below 3 ppbv. If the time frame is extended to 2090, there is a slightly greater range of emission restrictions that will result in 2 ppbv of atmospheric chlorine. Model assessments of these scenarios were not performed since the ozone perturbations would be dominated by the increases in CH_4 , N_2O , and CO_2 rather than the chlorine abundances.

Changes in Ultraviolet Radiation at the Surface

The changes in UV radiation at the surface have been calculated both for the observed changes in ozone column over the past decade and for the predicted changes in the future. The ultraviolet spectrum has been averaged to account for DNA damage, for plant damage, and for the Robertson-Berger meter's response. The TOMS data normalized to Dobson was used to define the change in the column over the past decade (0 to -4% in the tropics, -4 to -8% in northern high-latitude winter, and -8 to -30% at high southern latitudes from March through December). The calculated UV doses for DNA and plant damage increased by 2-5% in the Northern Hemisphere, by 2-10 % between 30 and 60°, and by 10-60 % under the Antarctic ozone hole. Predictions for 2060 from a model with fixed temperatures and circulation, neglecting heterogeneous chemistry, were used to illustrate future ozone perturbations (reference scenario A1 yielding a chlorine loading of 9.2 ppbv in 2060, 1-4% reduction in tropical total ozone, and 8-12% reduction at high latitudes). The largest absolute increase in average UV dose for the 1960-2060 period is predicted to occur in the springtime at mid-latitudes, and values may be sensitive to systematic latitudinal differences in cloud cover. The greatest relative increase, 20-40 %, occurs at high latitudes in early spring. For the scenario in which CFC emissions are cut by 95% in year 2000 (chlorine loading of 5.4 ppbv), the calculated increases in UV dose are half as large.

Chapter 4. Halocarbon Ozone Depletion and Global Warming Potentials

Concern over global environmental consequences of fully halogenated chlorofluorocarbons (CFCs) has sparked interest in the determination of the potential impacts on stratospheric ozone and climate of halocarbons, both chlorinated and brominated. In particular, the recent search for replacement compounds for the CFCs has primarily focused on several hydrogen-containing halocarbons (HCFCs, HFCs) which need to be closely examined. The kinetics and degradation mechanisms of many of these compounds (CFCs, HCFCs, HFCs, and halons) in the troposphere, their potential relative effects on stratospheric ozone, and their potential relative effects on global climate have been evaluated.

Halocarbon Oxidation in the Atmosphere

The halocarbons containing hydrogen atoms (HFCs and HCFCs), which have been proposed for substitutes for CFCs, react with the OH radical and are primarily removed in the troposphere by this process. The rate constants for attack of OH on these compounds are well defined ($\pm 20\%$ at relevant temperatures) and this reaction is the major loss process for these molecules in the atmosphere.

There are virtually no experimental data available concerning the subsequent reactions occurring in the atmospheric degradation of HFCs and HCFCs. By analogy with similar chemical species, it is predicted that the major products formed from the reactions of the OH radical with HFCs and HCFCs under tropospheric conditions are halogen-substituted carbonyl compounds and hydrogen halides. Based on the available knowledge of gas-phase chemistry, only four of the possible products appear to be potentially significant carriers of chlorine to the stratosphere: CClFO , CF_3CClO , $\text{CClF}_2\text{CO}_3\text{NO}_2$, and $\text{CCl}_2\text{FCO}_3\text{NO}_2$. Physical removal processes (to the liquid phase) will probably reduce this potential, but tropospheric removal pathways for the carbonyl compounds, especially the physical processes, are not well understood and require further study.

The oxidizing efficiency of the troposphere is determined by the abundance of OH radicals. However, quantitative validation of photochemical models by direct experimental measurement of the tropospheric OH concentrations has not been satisfactorily achieved. Global budgets and distributions of methyl chloroform and ^{14}CO have been used to estimate a volume-averaged global OH concentration of $6(\pm 2) \times 10^5$ molecule cm^{-3} . The budget and lifetime of methyl chloroform calculated using OH fields predicted by models is in general agreement with these results.

The calculated lifetimes of HFCs and HCFCs range from 0.25–40 years with an uncertainty of $\pm 50\%$. These are shorter than the lifetimes for the fully halogenated CFCs.

Ozone and ozone precursors (CH_4 , CO , NO_x , and non-methane hydrocarbons) can influence OH concentrations in the troposphere and hence could indirectly influence the lifetime of halocarbons. Model calculations indicate that, if man-made emissions of ozone precursors continue to increase, ozone concentrations are anticipated to grow throughout the Northern Hemisphere. The magnitude of the predicted ozone increase will depend on the detailed assumptions made concerning future emissions of ozone precursors. Model calculations indicating future tropospheric ozone increases as large as 50% also indicate future OH concentrations could decrease by as much as 25%. This would lead to increased lifetimes for many molecules removed by hydroxyl radical chemistry.

Ozone Depletion Potentials

Ozone Depletion Potentials (ODPs) have been defined as the ratio of steady-state calculated ozone column changes for each unit mass of a gas emitted into the atmosphere relative to the depletion for a mass unit emission of CFC-11. This definition provides a single-valued estimate of the cumulative ozone depletion for a gas, relative to CFC-11 on an equal mass basis.

One-dimensional and two-dimensional global atmospheric models have determined ODPs for a number of halocarbons, including CFCs, other chlorinated compounds, several potential replacement hydrohalocarbons, and several brominated compounds. Table 3 gives the range of calculated ODPs from one-dimensional and two-dimensional models for the CFCs, HCFCs, HFCs, plus CCl_4 and CH_3CCl_3 . Although 2-D models have generally a sounder physical basis, there are no real differences between the 1-D and

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Table 3. Range of Ozone Depletion Potentials (ODP) determined by one-dimensional and two-dimensional models, assuming scaling for HCFC ODPs by CH_3CCl_3 observed lifetime (6.3 years)

Species	1-D Models ^a	2-D Models ^b
CFC-11	1.0	1.0
CFC-12	0.9–1.0	0.9
CFC-113	0.8–0.9	0.8–0.9
CFC-114	0.6–0.8	0.6–0.8
CFC-115	0.4–0.5	0.3–0.4
HCFC-22	0.04–0.05	0.04–0.06
HCFC-123	0.013–0.016	0.013–0.022
HCFC-124	0.016–0.018	0.018–0.024
HFC-125	0	0
HFC-134a	0	0
HCFC-141b	0.07–0.08	0.09–0.11
HCFC-142b	0.05–0.06	0.05–0.06
HFC-134a	0	0
HFC-152a	0	0
CCl_4	1.0–1.2	1.0–1.2
CH_3CCl_3	0.10–0.12	0.13–0.16

^a1-D models from AER, LLNL, DuPont, and IAS.

^b2-D models from AER, LLNL, University of Oslo, and DuPont.

2-D results. In general, the ODPs for fully halogenated compounds, such as the CFCs, are much larger than those for the hydrogenated halocarbons, which include the potential replacement compounds considered.

Table 4 gives the ODPs determined for several brominated halocarbons from calculations by two models. These compounds should be compared to each other, because of the strong dependence of bromine effects on ozone to background chlorine levels. Bromine Ozone Depletion Potential (BODPs) are used for relative comparisons with Halon-1301, which has the longest lifetime and largest ODP, as the reference.

Although the calculated ODPs agree reasonably well among models, many uncertainties still exist. None of the models used for calculating ODPs include the chemical and dynamical processes causing the seasonal ozone losses over Antarctica. Another uncertainty lies in the model-calculated OH, which is a major source of uncertainty for both lifetimes and ODPs of the HCFCs.

Because of the apparent special chlorine processing and dynamics within the polar winter vortex, local Antarctic ODPs are expected to be larger than those shown in Table 3. Insofar as the observed long-lived tracer distributions, such as CFC-11 in the polar vortex, suggest that much of the total chlorine may be available there, then an upper limit on Antarctic ODPs can be determined by calculating the relative amounts of chlorine transported through the tropopause by the different gases. These chlorine loading potentials (CLPs) determined using assumed reference lifetimes (which generally agree with those in the models used here) can be as large as a factor of two to three times the derived ODP values (c.f., Tables 3 and 5). The ramifications of polar ozone depletion for global ozone depletion potentials (ODPs) are not currently clear.

Table 4. Ozone Depletion Potentials for brominated compounds as calculated in the LLNL one-dimensional model and University of Oslo two-dimensional model

Species	ODP ^a		BODP ^b	
	LLNL	Oslo	LLNL	Oslo
Halon-1301	13.2	7.8	1.0	1.0
Halon-1211	2.2	3.0	0.17	0.38
Halon-1202	0.3		0.02	
Halon-2402	6.2	5.0	0.5	0.64

^aRelative to CFC-11, shown for historical purposes. Values will be underestimates if account is taken of polar effects. Assumed upper stratospheric Cl₂ mixing ratio is 3 ppbv in the LLNL model and 4.5 ppbv in the Oslo model.

^bBromine Ozone Depletion Potentials (BODPs) defined relative to Halon-1301, the longest lived brominated gas.

Table 5. Maximum relative Chlorine Loading Potential (CLP) for examined CFCs, HCFCs, HFCs, and other chlorinated halocarbons based on reference species lifetimes chosen to be compatible with available atmospheric measurements and modeling studies

Species	Reference ^a Lifetime (yrs)	Chlorine Loading Potentials ^b
CFC-11	60.0	1.0
CFC-12	120.0	1.5
CFC-113	90.0	1.11
CFC-114	200.0	1.8
CFC-115	400.0	2.0
HCFC-22	15.3	0.14
HCFC-123	1.6	0.016
HCFC-124	6.6	0.04
HFC-125	28.1	0
HFC-134a	15.5	0
HCFC-141b	7.8	0.10
HCFC-142b	19.1	0.14
HFC-143a	41.0	0
HFC-152a	1.7	0
CCl ₄	50.0	1.0
CH ₃ CCl ₃	6.3	0.11

^aLifetimes (e-folding time) are based on estimates used in scenario development in Chapter 3 summary for the CFCs and from the analysis in Ozone Depletion section for the HCFCs and HFCs.

^bChlorine Loading Potential is defined as the maximum chlorine transported across the tropopause per mass emitted relative to the same for CFC-11. It is proportional to lifetime and the number of chlorine atoms per molecule. It is inversely proportional to molecular weight.

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The time-dependent relative ozone depletion values differ from the steady-state ODP values. The time-dependent values depend on the atmospheric lifetime and the transport time to the region of destruction of the gas. The shorter the stratospheric lifetime, the sooner the gas will impact stratospheric ozone and hence the higher the transient relative ozone depletion. An example of this behavior is shown by the HCFC-123 curve in Figure 1. It has a shorter lifetime than CFC-11; its relative ozone depletion is largest soon after emission. Other gases in this category include HCFC-141b and CH_3CCl_3 . Species such as HCFC-22, HCFC-124, and HCFC-142b have somewhat longer time constants in the stratosphere. Their relative ozone depletions build slowly to values (based on their time constants) as large as 0.2 and then decay slowly with time to the derived ODP value. Relative ozone depletion values for HCFCs are greater than ODP values even after 30 to 50 years. Time-dependent relative ozone depletions for CFCs with lifetimes longer than CFC-11 show a monotonic increase to the ODP value. As shown for a pulse injection in Figure 2, the ratio of the cumulative calculated depletion of HCFC-22 or HCFC-123 to the cumulative depletion of CFC-11 is equal to the ODP for these species. Therefore, the ODP is the cumulative response; as discussed above, the transient response of relative ozone depletion may be larger than the ODP value at early times after emission.

Several of the halocarbons indicate a strong latitude dependence in their ODP values and a generally weaker seasonal variation. In particular, ODPs for species such as CFC-12, HCFC-22, HCFC-124, and HCFC-142b, which have greatly different stratospheric loss patterns than CFC-11, produce strong latitudinal gradients in ODPs, with the largest ODPs near summer poles and smallest values in the tropics. The effects of heterogeneous chemistry and polar dynamics could modify these findings.

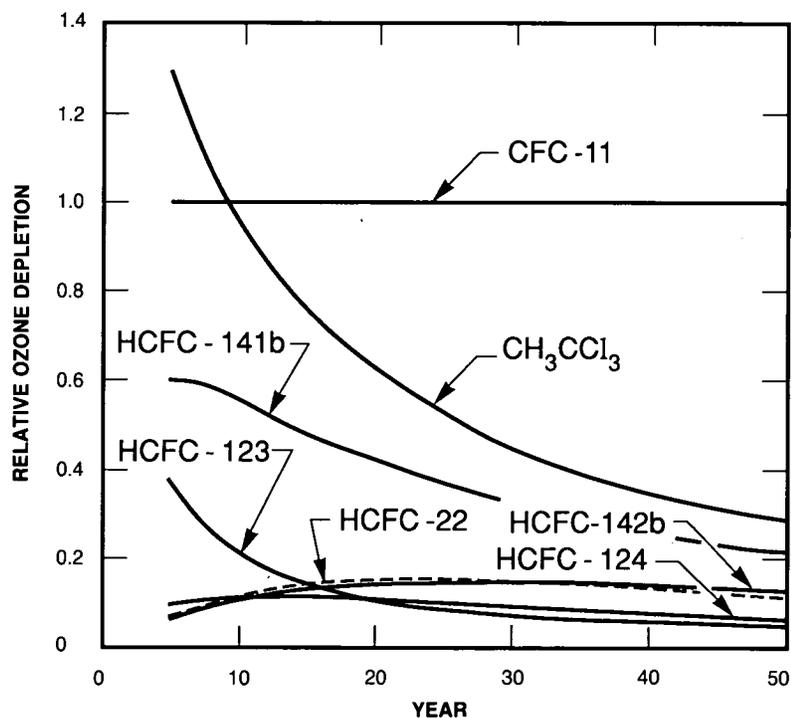


Figure 1. Calculated time-dependent change in relative ozone column depletion following a step change in emission of halocarbons (LLNL 1-D model).

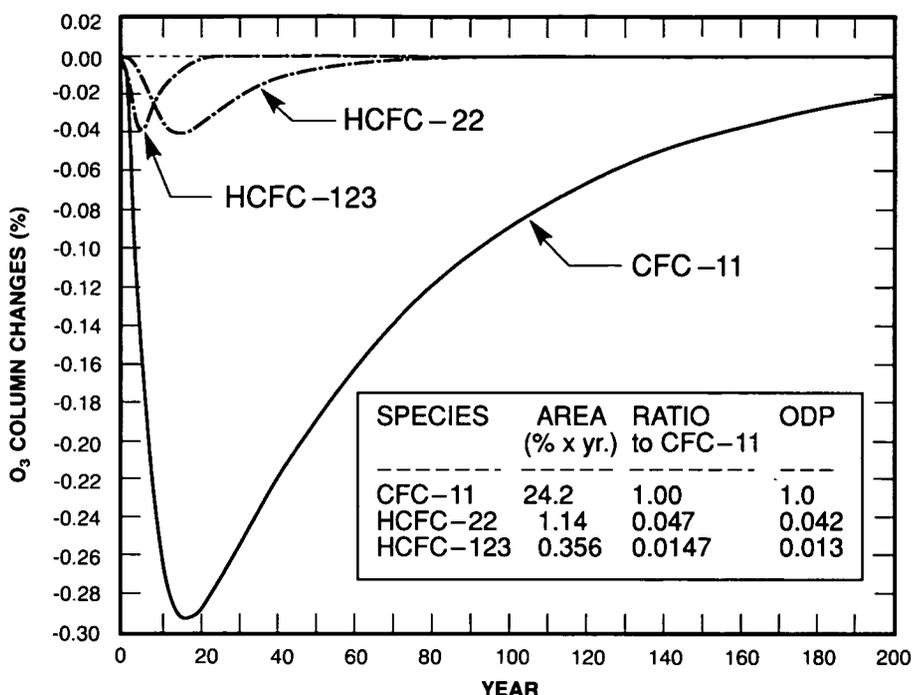


Figure 2. Calculated column ozone change following a pulsed input of 5×10^9 kg (for one year) of specified gas (DuPont 1-D model).

Sensitivity analyses indicate that ODPs are affected to only a minor degree ($\leq 20\%$) by assumed variations in background levels of N_2O , CH_4 , CO_2 , CO , total stratospheric chlorine, and total stratospheric bromine.

Halocarbon Global Warming Potentials

Halocarbon Global Warming Potential (GWP) is defined as the ratio of the calculated steady-state net infrared flux change forcing at the tropopause for any halocarbon for each unit mass emitted relative to the same for CFC-11. This definition quantifies the relative cumulative greenhouse warming per unit mass emitted.

Changes in the infrared fluxes in the surface troposphere system have been calculated for a number of these gases using a line-by-line radiative transfer model (GFDL). In addition, radiative forcing and surface temperature changes for these gases have been calculated using two one-dimensional radiative-convective models (AER and DuPont).

Halocarbon GWPs have been calculated from these results and scaled to a reference set of lifetimes (see Table 6). Agreement of ratio values is good, although direct radiative forcing values for individual gases differ systematically among models (between line-by-line and band models).

Halocarbon GWPs for fully halogenated compounds are larger than those for the hydrogenated halocarbons. Fully halogenated CFCs have halocarbon GWP values ranging from 1.0 to 7.5, whereas HCFCs and HFCs range from 0.02 to 0.7.

EXECUTIVE SUMMARY

Table 6. Halocarbon Global Warming Potentials (Halocarbon GWPs) scaled relative to reference set of halocarbon lifetimes.

Species	Reference ^a Lifetime (Yrs)	AER ^b	DuPont ^b	GFDL ^b
CFC-11	60.0	1.0	1.0	1.0
CFC-12	120.0	3.4	2.8	3.0
CFC-113	90.0	1.4	1.4	1.3
CFC-114	200.0	4.1	3.7	
CFC-115	400.0	7.5	7.6	7.4
HCFC-22	15.3	0.37	0.34	0.32
HCFC-123	1.6	0.020	0.017	0.017
HCFC-124	6.6	0.10	0.092	
HFC-125	28.1	0.65	0.51	
HFC-134a	15.5	0.29	0.25	0.24
HCFC-141b	7.8	0.097	0.087	0.084
HCFC-142b	19.1	0.39	0.34	0.35
HFC-143a	41.0	0.76	0.72	
HFC-152a	1.7	0.033	0.026	0.028
CCl ₄	50.0	0.34	0.35	
CH ₂ Cl ₂	6.3	0.022	0.026	

^aLifetimes are based on estimates used in scenarios development (Chapter 3 summary) for CFCs and from the analysis in the Ozone Depletion section for HCFCs and HFCs.

^bAER and DuPont results are based on surfaced temperature perturbations calculated using radiative-convective models. The GFDL results are based on line-by-line determined radiative forcing.

Halocarbon GWP values differ between species because of differences in infrared absorbances and differences in lifetimes. The range of absorbances is approximately a factor of 4, while the lifetimes vary by a factor of 250. Thus, the range of 600 among the halocarbon GWP values is primarily a result of differences in lifetimes.

Halocarbon GWP values are nearly insensitive to changes in background concentrations of CO₂, CH₄, and N₂O. Minor effects ($\leq 20\%$) do result from influences on chemical lifetimes, but these do not affect the relative radiative forcing.

Calculated time-dependent relative global warmings for halocarbons are initially on order unity, but decrease or increase depending on whether their lifetimes are shorter or longer than that of the reference gas. At long lifetimes the relative global warmings asymptotically approach halocarbon GWP values.