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# **Ozone–climate interactions**

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## **Preface**

The European Commission supports research on atmospheric ozone and climate since more than 20 years, through its Framework Programmes. The aim is to provide expert scientific advice so that the European Union can meet its commitment to preserving the environment. Moreover, this research has been closely linked to the development of the international regulatory framework, which led to the United Nations Conventions on the ozone (1985) and on climate (1992), as well as the Montreal and Kyoto Protocols (1987 and 1997 respectively). As part of their obligations under these international agreements and in response to the scientific and public concerns about UV radiation increases and climate changes, the European Commission and the Member States support research programmes in these areas. Pertinent results of these programmes are published, for example, in the various documents published in the EC Air Pollution Report series as well the EC Assessments on Stratospheric Ozone and Aviation Impacts on Climate.

Recently, the interactions between atmospheric ozone and climate change have received greater attention. In 2002, on the joint recommendation of the Science Panels on Stratospheric Ozone and UV Radiation and on Atmospheric Chemistry, Research DG, initiated this report which assesses the present state of understanding about ozone-climate interactions and discusses the possible importance of the considerable gaps in our knowledge. The report consists of six chapters which, in addition to introductory and summary statements, treat in detail the effect of changes in stratospheric and tropospheric ozone on climate change as well as the effects of climate change on both atmospheric regions. I am convinced that this report will make a valuable contribution to the international debate about these atmospheric issues.

On behalf of the European Commission, I would like to express my sincere thanks to the authors, the reviewers, the editorial board and the editor for their hard work in preparing this report. I would also like to thank the scientists on whose work the report is based and who have contributed indirectly, to the subject matter of the report.

Anver Ghazi  
Head, Global Change Unit  
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## EUROPEAN REPORT ON OZONE-CLIMATE INTERACTIONS

### *Background*

The coupling between climate change and atmospheric composition results from the basic structure of the atmosphere and the fundamental processes within it. The physical (and hence chemical) composition of the atmosphere is determined by the energy which flows into, out of and within the atmosphere. The principal source of the energy is sunlight at ultraviolet (UV) and visible wavelengths. This incoming energy is balanced by the outgoing emission of infrared (IR) radiation from the earth's surface and the atmosphere. The structure of the stratosphere (stable air with temperature increasing with altitude) is determined mainly by the absorption of UV radiation by stratospheric ozone. The structure of the troposphere (turbulent, with temperature decreasing with altitude) is largely determined by the energy absorbed at or near the earth's surface which also leads to the evaporation of water and the presence of reflecting clouds. Changes in atmospheric composition (whether in ozone (O<sub>3</sub>), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), or aerosol particles) change the radiative properties of the atmosphere and hence the energy balance. Ozone itself absorbs UV and IR radiation and so it has a central and complex role in the earth's energy budget, with a strong coupling between the chemical and physical processes in which it is involved. For example, UV radiation drives much of the atmospheric chemistry so stratospheric ozone depletion indirectly modifies the chemical composition of the troposphere through changes in UV. Further, changes in source gases such as CH<sub>4</sub> and nitrous oxide (N<sub>2</sub>O) affect the chemistry of ozone in both the troposphere and stratosphere.

The potential importance of the coupling between climate change and atmospheric ozone has been recognized for some time. However, it is only recently that atmospheric scientists could even hope to start to capture the full complexity of the most important interactions in their models. For example, global circulation models have often not included detailed, realistic descriptions of the stratosphere, while in the troposphere, the influence of climate change on trace gas emissions or cloud chemistry is not well known. Similarly there has been an insufficient set of measurements to investigate the processes involved. It is a huge field for research and there are many areas with large uncertainties. Climate change will influence the whole atmosphere through changes in chemistry, dynamics, radiation and surface emissions. Further, while it is clear that the upper troposphere and lower stratosphere are especially sensitive to climate change, it is not clear how they will actually respond and what the wider atmospheric implications are.

Traditionally, when considering the role of atmospheric ozone, stratospheric ozone and tropospheric ozone have been considered separately, even though the importance for both regions of what happens in the upper troposphere and lower stratosphere (UTLS) has been well recognised. This approach is reflected, for example, in the respective scientific contents of the WMO-UNEP Scientific Assessments of Ozone and the assessments of the Intergovernmental Panel on Climate Change (IPCC), the essential scientific guides in the development of public policy on ozone depletion and climate change. These assessments have been based on available scientific knowledge and have been concerned, respectively, with how ozone-depleting substances affect stratospheric ozone and what chemical emissions cause tropospheric ozone to increase. Although ozone distribution and changes, and ozone-climate links have partly been included and discussed in the most recent assessments [IPCC, 2001; WMO, 2003], no thorough scientific overview of this problem is presently available.

The aim of this report is to present in a coherent way the present understanding of the interactions between ozone and climate, regardless of the atmospheric region where the processes are taking place and including their consequences for environmental problems such as climate change, ozone depletion and tropospheric pollution. In emphasising these interactions, the report will provide a framework for future strategies in the field of atmospheric research, and for further discussions involving scientists, research agencies and policymakers on the necessary measures to be taken at the interface of the Kyoto Protocol and the Montreal Protocol. The report does not aim to cover all aspects of atmospheric research and, for example, the role of aerosols and other trace gases is included only insofar as it affects, or is affected by, atmospheric ozone. Further this report does not address the important changes that may be occurring at higher altitudes (in the mesosphere), but concentrates on the troposphere and stratosphere.

This summary consists of two further parts: in the next section, the important findings with respect to ozone-climate interactions, presented in chapters 2-5 of the report, are summarised. This is followed by a discussion of some implications for future research, including the improvements needed in climate models and how measurements and data analysis can help to achieve this through an improvement of scientific understanding of the relevant atmospheric processes.

### ***Important aspects of ozone-climate interactions***

The latest scientific knowledge of stratospheric ozone depletion, UV radiation and climate change has been comprehensively described in WMO [2003] and IPCC [2001]. These assessments find that significant changes have occurred in the chemical and physical composition of the atmosphere as a result of increasing trace gas emissions. The amounts of chlorine- and bromine-containing substances have increased in the last decades and, while the total atmospheric content of chlorine is now starting to decline, the bromine content is still increasing. In addition to the well-documented rise in global CO<sub>2</sub> concentrations, CH<sub>4</sub> and N<sub>2</sub>O concentrations have risen over many decades. There have also been significant changes in the emissions of gases which last for shorter times in the atmosphere, such as nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO) and non-methane hydrocarbons (NMHC or VOC). The effect of these changing emissions on their atmospheric concentrations is regional rather than global, and their importance results from their global effect on ozone concentrations and the lifetimes of other greenhouse gases through their effect on the atmospheric concentrations of intermediate species such as the hydroxyl radical (OH). These increases have all been driven by changes in human activities.

There is a clear effect on atmospheric ozone of these changes in emissions. Stratospheric ozone has decreased over the past decades, largely due to chemical depletion by chlorine- and bromine-containing substances. The decreases have occurred principally over polar regions, with smaller decreases over mid-latitudes in both hemispheres. Little change has been seen in the tropics. Tropospheric ozone has increased over the last century, with the largest change (a doubling) occurring over northern mid-latitudes. Since 1985, the rate of increase at these latitudes has slowed. Ozone concentrations are naturally lower in the southern hemisphere, and smaller changes than in the north are thought to have occurred there over the last century. At low latitudes no significant change has been observed. However the observational database at low latitudes and in the southern hemisphere is limited.

These ozone changes have a subsequent impact on UV and climate. Available measurements show that surface UV radiation levels have generally increased with a similar geographic pattern to the observed reductions in stratospheric ozone. Surface UV levels are also strongly influenced by cloud cover, local ground albedo and the atmospheric aerosol content. The estimated doubling in tropospheric ozone since pre-industrial times means that ozone has exerted the third largest radiative forcing (the simplest measure of its impact on climate) after

CO<sub>2</sub> and CH<sub>4</sub>. In contrast, the radiative forcing of the stratospheric ozone decrease is negative – it exerts a small cooling tendency – unlike the positive radiative forcing from the increases in the ozone-depleting substances, principally CFCs. However the full impact of ozone changes is more complicated since ozone is so closely coupled with other atmospheric processes. There are many feedback processes, operating in either direction and involving ozone, climate and UV, which are the subject of this report. Here we summarise those areas where strong climate change/ozone coupling can be found:

### *Stratosphere*

- *Past changes in polar ozone* – The largest depletion of stratospheric ozone has occurred in polar latitudes, over the Arctic and, especially, the Antarctic. The size, timing and extent of the depletions vary from year to year and are determined by the interplay between dynamics and chemistry. The decadal evolution of Antarctic ozone loss has been primarily driven by changes in halogen concentrations, with changing dynamics having possibly been an influence in recent years. In contrast the decadal evolution of Arctic ozone loss has been strongly influenced by changing dynamics and chemistry, with dynamical variability (rather than the change in halogen loading) having been the stronger influence on the variability of chemical ozone loss in the 1990s. This illustrates the sensitivity of polar ozone loss to climate change, whether or not the past changes have themselves been driven by climate change.
- *Past changes in mid-latitude ozone* – Chemical ozone loss has been an important factor in the stratospheric ozone depletion at mid-latitudes and in the observed temperature trends. There has also been a significant dynamic influence on mid-latitude ozone trends through changes in tropopause height (symptomatic of processes in the troposphere and low stratosphere) and in the large-scale stratospheric circulation through changes in wave driving. It is not currently possible to quantify the role of climate change in these dynamical trends. However some climate models calculate significant increases in mid-latitude tropopause height resulting from climate change which are first discernible in the model calculations in the late 1980s.
- *The Tropics* – No significant trend in total ozone has been observed in the tropics to date. However, the processes occurring in the tropics are centrally important in determining stratospheric structure and composition. The tropical tropopause layer, currently poorly understood, largely determines the concentrations of many short-lived species entering the stratosphere (as well as the concentration of water vapour). Furthermore, the tropical troposphere is the critical region for chemical cleansing of the troposphere. Its structure will be sensitive to climate change.
- *Temperature trends in the stratosphere* – A statistically significant cooling has occurred in the lower stratosphere and in the upper stratosphere. The lower stratospheric cooling is attributable largely to the observed ozone reduction there: whether the cooling will continue is uncertain as the expected increase in ozone resulting from decreasing halogens may be offset by dynamical effects. The upper stratospheric cooling will slow down the natural ozone destruction cycles, first offsetting any chlorine-catalysed ozone destruction there and eventually leading to ozone increases compared to pre-ozone hole conditions.
- *Water vapour trend* – Observations indicate that stratospheric water vapour has increased by about 1% per year since 1981. This trend is substantially larger than can be attributed to the observed changes in stratospheric CH<sub>4</sub>. Water vapour enters the stratosphere through the tropical tropopause. The trend in H<sub>2</sub>O is likely to be caused by changes in the tropical UTLS. It cannot be simply due to changing tropical tropopause temperatures, since these have actually decreased, and not increased as would be needed for an H<sub>2</sub>O increase. Water is extremely sensitive to the entry mechanism of air into the stratosphere, and improved understanding of how water enters the stratosphere will significantly improve our understanding of how all constituents enter the stratosphere.

- *Future changes in polar ozone* – The predicted reductions in halogen loading will, on their own, result in reduced ozone losses in polar regions. However climate change will modify polar stratospheric dynamics. The major dynamic factor is the stability of the polar vortices and what impact the changes in tropospheric forcing will have on it. Further, critical processes such as chlorine activation and denitrification are highly temperature sensitive. Most models indicate a slowed recovery of Arctic losses (amid much variability) due to a longer-lived vortex with lower temperatures. However some models indicate enhanced tropospheric forcing, leading to a less stable Arctic vortex with higher temperatures and smaller ozone losses. The impact of changing dynamics on future Antarctic ozone losses is expected to be less than in the north and future ozone losses should follow future halogen levels more closely. However the early warming of the Antarctic in 2002, and its influence on the ozone hole, is unprecedented. A deeper understanding is likely to have important implications for predictions of future ozone losses at both poles.
- *Future changes in mid-latitude ozone* – The influence of halogens in mid-latitudes will decrease over the coming decades. The continuing increases in CH<sub>4</sub> and N<sub>2</sub>O will have an important impact on future stratospheric ozone amounts. For example, increases in CH<sub>4</sub> in the future will tend to increase stratospheric ozone concentrations. Further, radiative cooling of the upper stratosphere by increasing CO<sub>2</sub> and CH<sub>4</sub> is expected to accelerate recovery at high altitudes and eventually lead to enhancements of ozone in the upper stratosphere. Any climate-change induced changes in dynamics will affect future mid-latitude ozone through chemistry and transport.

#### ***Stratosphere-troposphere interface***

- *Stratospheric ozone and radiative forcing* – The radiative forcing by stratospheric ozone depletion (–0.05 to –0.25 Wm<sup>2</sup>) counteracts the radiative forcing from the growth of well-mixed greenhouse gases over the last two decades by 15-20%. However, the sensitivity of climate to radiative forcing by ozone perturbations in the lower stratosphere is higher than indicated simply by its radiative forcing, i.e. the surface temperature change for a given radiative forcing from a change in lower stratospheric ozone is greater than for an identical radiative forcing arising from well-mixed greenhouse gases. Current estimates of radiative forcing due to stratospheric ozone perturbations indicate an important feedback role of water vapour.
- *Ozone/dynamics feedbacks* – Model studies indicate that increasing greenhouse gas concentrations have been a major factor in the observed increase in tropopause height (which is known to affect the ozone column locally). Feedback from stratospheric ozone changes have also been important. These studies imply that a continuing rise in tropopause height is expected even as chemical ozone depletion in the stratosphere becomes smaller, so that there is a direct influence of climate change on stratospheric ozone and UV radiation. The calculated changes are larger at mid-latitudes than at low latitudes. Changes in the Brewer-Dobson circulation (possibly linked to changes in wave propagation from the troposphere) and in synoptic-scale weather patterns (which could influence the frequency of ozone ‘mini-holes’) are also potentially important climate/ozone feedbacks.
- *Ozone flux changes* – The flux of ozone from the stratosphere to the troposphere is a major factor in the tropospheric ozone budget. The flux has decreased during the last decades due to the decrease in stratospheric ozone concentrations. Combination of model calculations and analysis of ozone observations has revealed that the transport of ozone from the stratosphere to the troposphere has been reduced by as much as 30% from the early 1970s to the mid 1990s.
- *Aviation impact* – Aircraft emissions are believed to have changed the chemistry of the upper troposphere. In the current atmosphere the globally averaged ozone increase due to aircraft has been estimated to 0.4 DU, as a global average. This is modest compared to the ozone increase since pre-industrial times. However, aircraft impacts occur mainly in the northern mid-latitudes. The maximum change in zonally averaged ozone column is 1.4 DU, occurring in June. As aircraft emis-

sions are anticipated to increase markedly in the future their impacts on tropospheric ozone are expected to become more significant. A decrease in stratospheric ozone is predicted for a potential fleet of future supersonic aircraft. There are a large number of feedback processes, involving, for example, aerosols, condensation trails and clouds, all requiring more detailed quantification.

### ***Troposphere***

- *Global changes in tropospheric ozone* – Studies of the global tropospheric ozone suggest an annual mean increase of more than 30% since pre-industrial times due to anthropogenic emissions of ozone precursors, namely  $\text{NO}_x$ ,  $\text{CH}_4$ ,  $\text{CO}$  and NMHC. The best estimate of the absolute increase in tropospheric ozone is 9 DU (from 25 to 34 Dobson Units). The uncertainty largely reflects uncertainties in natural emissions of  $\text{NO}_x$  and NMHC.
- *Regional variations in tropospheric ozone* – Tropospheric ozone abundances vary strongly both in time and space, reflecting the short chemical lifetime of from a few days up to a few months. This large regional and temporal variability makes it difficult to use available observations to validate the global budget of tropospheric ozone and to quantify changes since pre-industrial times.
- *Surface ozone changes* – Surface ozone already exceeds air quality standards in many polluted regions, leading to problems for human health and to crop damage. The predicted future increases might be particularly damaging. Increases in ozone and  $\text{NO}_x$  are also likely to affect future biogenic emissions, a potentially important feedback that needs to be assessed.
- *Tropospheric dynamics and ozone* – Although there are limited studies on how changes in dynamics affect tropospheric ozone, climate-induced changes in dynamics are likely to have had only a small impact on the current ozone distribution in the troposphere. However, continued dynamical changes in the future would have stronger effects on the ozone distribution.
- *Tropospheric ozone and radiative forcing* – Changes in tropospheric ozone can impact climate. The radiative forcing (RF) due to the changes calculated since pre-industrial time is in the range from 0.2 to 0.5  $\text{Wm}^{-2}$ . This ranks tropospheric ozone as the third largest contributor among the greenhouse gases to the direct radiative forcing during this period.
- *Ozone changes in the future* – Emissions of ozone precursors are expected to increase in the future, in particular in regions with economic growth and/or population increase (parts of Asia, Africa and Central America). For a range of emission scenarios models have estimated an increase in tropospheric ozone of about 11-21 DU by 2100. The radiative forcing calculated for this increase in tropospheric ozone is in the range 0.4-0.8  $\text{Wm}^{-2}$ . The predicted future forcing is displaced towards lower latitudes compared to present. Tropospheric ozone will remain as an important climate gas for the next hundred years, and in the second half of the 21<sup>st</sup> century it could become the second most important contributor to climate warming after  $\text{CO}_2$ .

### ***UV Radiation***

- *Surface UV radiation* – Measurements and calculations show long-term increases in erythemal irradiance of about 6-14% over the last 20 years. At some sites approximately half of the changes can be attributed to total ozone changes. It is evident that the long-term UV changes are not driven by stratospheric ozone alone, but also by changes in cloudiness, aerosol particles and surface albedo. For example, it is estimated that globally averaged cloudiness increased by about 2% over the past century.
- *UV penetration* – The observed decrease of stratospheric ozone and the resultant increase in UV irradiance has affected the biosphere and biogenic emissions. Such UV increases also lead to an enhanced OH production, which reduces the lifetime of methane and influences ozone, both of which are important greenhouse gases.

## *Climate*

- *Ozone and long-term climate variability* – Statistical and model studies indicate that fluctuations in the strength of the stratospheric polar vortices can influence tropospheric weather patterns and sea surface temperatures. Future changes in stratospheric composition and circulation could thus have an important influence on the distribution and trends of major patterns of climate variability such as the North Atlantic Oscillation.
- *Climate feedback on to the predicted ozone change* – Future changes in tropospheric chemistry will be sensitive to climate-induced changes in humidity, temperature and convection. The climate-change induced increase in humidity is estimated to dampen the increase in tropospheric ozone. The increased humidity will enhance the production and abundance of OH, although the increase in OH is somewhat dampened due to the reduction in ozone. The increased OH concentration will reduce the CH<sub>4</sub> lifetime and hence its growth rate.
- *Climate and emissions* – The radiative forcing due to ozone changes depends on their distribution in space, both vertically and horizontally. In the vertical, the largest forcing is due to changes in the UTLS region, where model estimates of ozone changes deviate considerably. In the horizontal, the radiative forcing from tropospheric ozone to a large extent resembles the pattern of emissions of ozone precursors, although there is a significant export of ozone and precursors from polluted continental regions. The largest contributions to the radiative forcing stem from emissions of precursors in North America, Europe and South East Asia. In Europe the radiative forcing maximizes in the Mediterranean region. Regional forcing by spatially inhomogeneous ozone changes could represent a particularly important chemistry-climate link. Natural emissions of ozone precursors (NO<sub>x</sub>, CO, CH<sub>4</sub> and biogenic VOCs) are important for ozone. Future changes in the emission of these compounds arising from climate changes (e.g. in surface temperature or moisture) will affect global ozone chemistry in the same way as changes in anthropogenic emissions. Lightning is a main source of the ozone precursor NO<sub>x</sub> in the free troposphere. Changes in lightning activity due to climate impact will affect the height profile of ozone in the troposphere, in particular the ozone distribution in the UT region where the climate sensitivity is large.
- *UV and climate* – The radiative forcing due to ozone changes depends on their distribution in space, both vertically and horizontally. In the vertical, the largest forcing is due to changes in the UTLS region, where model estimates of ozone changes deviate considerably. In the horizontal, the radiative forcing from tropospheric ozone to a large extent resembles the pattern of emissions of ozone precursors, although there is a significant export of ozone and precursors from polluted continental regions. The largest contributions to the radiative forcing stem from emissions of precursors in North America, Europe and South East Asia. In Europe the radiative forcing maximises in the Mediterranean region. Regional forcing by spatially inhomogeneous ozone changes could represent a particularly important chemistry-climate link. Climate change will have an important influence on future surface UV irradiance. Any changes in stratospheric ozone will modulate the amount of UV penetrating to the troposphere. Further the transmission through the troposphere will be affected by any changes in other variables such as clouds, aerosols, and local albedo (e.g. snow cover) which will be strongly influenced by climate change. The level of understanding of UV changes and its prediction is high for ozone changes, moderate for aerosols and albedo and low for changes in cloudiness. The level of understanding of the combined effect of all factors is still poor.
- *Regional variations in radiative forcing* – The radiative forcing due to ozone changes depends on their distribution in space, both vertically and horizontally. In the vertical, the largest forcing is due to changes in the UTLS region, where model estimates of ozone changes deviate considerably. In the horizontal, the radiative forcing from tropospheric ozone to a large extent resembles the pattern of emissions of ozone precursors, although there is a significant export of ozone and precursors from polluted continental regions. The largest contributions to the radia-

tive forcing stem from emissions of precursors in North America, Europe and South East Asia. In Europe the radiative forcing maximizes in the Mediterranean region. Regional forcing by spatially inhomogeneous ozone changes could represent a particularly important chemistry-climate link.

### ***Implications for future research***

A basic aim of atmospheric research is an understanding of the processes which control the structure and composition of the atmosphere so as to describe quantitatively how it is affected by human activities. A central part of a research programme is to develop the sophisticated computer models which integrate our present understanding and can be used to explore future scenarios. The recent AIRES in ERA report (EUR 19436) recommended that an integrated European approach should be developed based on the firm foundations of the current successful programme of atmospheric research. Such an approach should include laboratory measurements, instrument development, coordinated field measurements, ground-based observation networks for long-term monitoring, deployment of research aircraft, analysis of satellite data and improvements in theoretical and modelling work. An increasing emphasis should be put on cross-disciplinary studies of the whole earth system. In parallel, integration of European research with international research programmes such as WCRP and IGBP, with European programmes such as GMES, and with research in other countries will be greatly beneficial. The recommendations described in AIRES in ERA are further supported by the findings of this report. In this section we focus on those important aspects of research most relevant to understanding the interactions between ozone and climate change: chemistry-climate models, emissions and measurements (in the laboratory, in process-oriented field activities, and via longer term observations).

### ***Chemistry – climate models***

Good models of the atmosphere are essential tools in the evaluation of different emission scenarios of trace gases and aerosols. The development in the last few years of 3-D general circulation models, including fairly detailed chemistry schemes, has led to renewed interest, and important progress. However, it is clear that these studies are not fully mature. While the central scientific questions are well posed (What is the effect of, say, ozone change on climate, in its broadest sense; what is the effect of climate change on ozone?), crucial details remain to be resolved. Here we describe a few of the major areas where further research would improve our predictive ability.

- *Development of earth system models* – The ‘earth system’ involves a myriad of interacting physical, chemical and biological processes, themselves influenced by economic and social factors. The atmosphere is a crucial component of the earth system, maintaining the air we breathe and the composition which determines, *inter alia*, climate forcing and the penetration of potentially harmful UV radiation. Although models have increasingly included more feedback processes, we are still some way from comprehensive model studies. As a top priority, further development of atmospheric models is required, within the context of the development of sophisticated earth system models, which treat the important processes at a more fundamental level.
- *Transport between troposphere and stratosphere* – The concentrations of many important chemically- and radiatively-active gases, including ozone and water vapour, depend on the transport between troposphere and stratosphere. However the models that have been used for chemistry-climate studies have been principally models of either the stratosphere or the troposphere. This is an important limitation, as the whole atmospheric domain should be considered in a consistent fashion if, for example, the ozone budget is to be well reproduced in a model. Indeed, many of the important interactions involve processes around the tropopause; composition changes around the tropopause can be particularly important for radiative transfer, and hence climate.
- *Including small scale processes* – Models will always be an imperfect representation of the atmosphere, attempting to represent processes down to the smallest scales by averaging over

model domains of a much larger spatial dimension. For example, the modelled impact of local emissions on the regional scale, and hence to the continental and global scales, may well depend on the grid resolution chosen. This will be especially true for chemical processes, like ozone production in the troposphere, which are highly non-linear. Similarly, the modelled impact of global changes on local areas may also be resolution dependent. Nesting of model grids, grid adaptation and coupling of models of different scales are all techniques which have been developed in recent years but remain to be implemented routinely into our global chemistry-climate models.

- *Stratospheric circulation* – A number of important issues are related to this, namely the ability of models to reproduce accurately observed polar temperatures and their inability to reproduce even the sign of the observed trend in tropical tropopause temperatures. The inadequacies in modelling the dynamics of the polar lower stratosphere may, for example, be the reason why the major warming of the Antarctic vortex in 2002 falls outside the climatological expectation of current climate models. Without a successful resolution of such issues, models cannot be expected to predict the future evolution of stratospheric ozone in a changing climate.
- *Chemical composition* – A number of processes which are important for the chemical composition of the atmosphere, particularly in the UTLS, are generally not well modelled. These include convection and lightning, important for both atmospheric transport and NO<sub>x</sub> production. Further a number of new processes need to be included in the models. For example, many of the chemical models have only a limited non-methane hydrocarbon chemistry.
- *Clouds and aerosols* – The treatment of clouds has long been recognised as a limitation of climate models. In the context of chemistry-climate studies more work is required to include any necessary cloud aqueous chemistry and to investigate the role of trace species in cloud nucleation. Aerosols are also important both for chemistry and climate and their description in models needs to be assessed and improved, e.g. by dynamic modelling of mixed aerosols.

### ***Emissions***

Realistic emissions are required for modelling studies of the past and the future, and so it is essential to have good data for anthropogenic and biospheric emissions. Satellite measurements can be combined with inverse modelling and data assimilation techniques to derive present day emissions of a number of important gases with good spatial resolution. Improved understanding of past emissions, and their changes, are required if changes in chemistry and climate in the recent past are to be diagnosed, and attributed, correctly. For example, studies to determine the sensitivity of biogenic emissions to climate parameters such as temperature, UV, surface moisture and, possibly, surface concentrations of ozone and other trace species are required. Understanding past land use changes, and predicting how land use may change in the future is also essential, as is an improved description of the boundary layer. Similarly, predictions of the future evolution of the climate/chemistry system rely on the existence of realistic, authoritative scenarios for the anthropogenic emissions.

### ***Measurements in the field and in the laboratory***

Measurements aimed at understanding these fundamental processes, in the laboratory or the atmosphere, are an essential part of the research strategy as most of the model issues discussed above require additional information and understanding which can only be derived from atmospheric and laboratory measurements. This research strategy will be complex and will involve long-term and global atmospheric observations, field campaigns investigating detailed processes and laboratory measurements. A range of observational platforms is required, from ground-based stations, ships, aircraft, balloons and satellites.

Laboratory studies are fundamental to improved understanding of the changes in ozone and its precursors, other greenhouse gases and aerosol levels. Laboratory studies of heterogeneous reac-

tions on aerosols and ice/water surfaces, as well as of the fate of highly reactive VOCs, including oxygenated compounds, are emerging as priorities for a better understanding of ozone/aerosol/cloud interactions. Interactions between climate change and chemical processes can occur through temperature dependent reactions; detailed knowledge of these temperature dependencies, down to the temperatures of the polar lower stratosphere, is essential.

A range of atmospheric constituents needs to be monitored to understand the changing chemistry-climate system, and so long-term measurements of many chemical species, aerosols and UV radiation, at the surface and at altitude, need to be continued. A significant European component in global observational networks such as the WMO's Global Atmospheric Watch and the Network for the Detection of Stratospheric Change is an essential part of any strategy, and this should be developed in conjunction with GMES. While these should be closely coordinated with satellite observations, they should not be replaced by them as all satellite instruments have limited operational life-times and the ground-based instruments provide continuity as well as invaluable validation.

The hydroxyl radical (OH) is a radical species which is central to tropospheric evolution. Local measurements exist, but direct global measurements do not. Its concentration can be derived from the trend in long-lived gases, like methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ), using a range of modelling techniques, including inverse modelling. Given the central importance of the hydroxyl radical, a strategy for combining, and rationalizing, different approaches needs to be developed.

An important open issue is the explanation of the water vapour trends observed in the stratosphere, for which there is currently no satisfactory quantitative explanation. A combination of model studies, field experiments aimed at an improved understanding of the mechanisms leading to the dehydration of air during its transport into the stratosphere and continued observations of water vapour in the stratosphere are needed to understand the trend and to monitor its future development. The trend analysis should include the monitoring of methane, which is the stratospheric source gas for water vapour. As shown recently in the SPARC water vapour assessment, consistent long-term (i.e. 20 years or more) data sets are most suited for such purposes. It is desirable to combine the global view available from satellites with the long-term stability provided by ground-based network stations and airborne instrumentation, both of which have the advantage that they can be calibrated regularly. Data assimilation will play an important role in combining these different data sets.

The UTLS is a region of the atmosphere which has a particularly strong impact on the radiative balance. Changes in trace gas concentrations in this region affect the radiative forcing and global surface temperatures. The UTLS is also a region of particularly strong variability, sharp transitions and strong gradients in trace gas concentrations. Remote sensing observations from satellites or from the ground available today lack the spatial resolution needed to resolve the gradients in the UTLS. Measurements from airborne platforms are best suited to getting reliable observations in the UTLS with the required resolution necessary for the study of chemical and dynamical processes and the detection of changes in this climate sensitive region. In addition development of new satellite instruments and improvements to retrieval algorithms will provide much better spatial resolution so that processes in the UTLS can be studied on a global scale.

The combined use of coupled climate-chemistry models and long-term measurements is required to simulate past UV, to investigate the relationship between climate signals and UV and to simulate future UV scenarios. Improved descriptions of UV modulation by clouds and aerosols are needed so that the impact of ozone change can be assessed quantitatively, and hence the connection between ozone change and climate. Further the level of physical understanding of UV changes and its prediction is high for ozone changes, moderate for aerosols and albedo and low for changes in cloudiness. The level of understanding of the combined effect of all factors needs to be improved.

Many of the chemistry-climate interactions to be modelled are subtle, with only a small signal (relative to natural variability) and possibly a long time-scale. Detection, or validation by comparison with field measurements, is correspondingly difficult, and work is required to establish suitable 'fingerprints' to identify the impact of the process. The measurement and modelling communities need to be involved together in the development of the measurement strategy by defining the fingerprints. This will also certainly involve an on-going commitment to long-term data records of high quality, from the ground, from airborne platforms and from satellites. Examples include a continued commitment to the ground-based measurements in NDSC and other networks and to the regular *in situ* measurement programmes from in-service commercial aircraft.

Separating dynamical from chemical influences in any observed change is difficult. Meteorological data can be used but other measurements (e.g. tracers with a range of lifetimes) can provide essential diagnostic information. There are to date no satellite observing capabilities for these compounds so maintaining a ballooning or aircraft measurement programme is essential. Changes in the strength of the residual Brewer-Dobson circulation should result in a change of the age of the air. Studies of the past (climatologies, long-term changes) based on global data sets (meteorological and satellite data) are also needed.

#### ***Large scale data sets***

Global data sets will make an increasing contribution to atmospheric science in the coming years with a number of new satellite instruments such as ENVISAT, AURA, CALIPSO and the MetOp series. It will be important to take full advantage of the atmospheric chemistry measurements from these Earth Observing satellites, particularly ESA's ENVISAT which should be operating for the best part of the next decade. In conjunction with the global satellite data sets, data assimilation using the same general circulation/chemistry modelling architecture as used for assessment purposes will be a valuable tool in this regard. Improvements in satellite instrument capabilities means that good tropospheric measurements are now possible, as long as significant work on retrievals and validation continues. Synergistic studies of detailed processes in field campaigns need to be developed in combination with the global data sets.

Meteorological analyses are a vital research tool for model validation and assimilation studies. It is important that their quality continues to be improved, especially in data-sparse regions like the tropics and parts of the southern hemisphere. The use of combined historical data sets will also be important. One important current issue is how the stratospheric polar vortex will evolve as ozone and greenhouse gas concentrations change. A strengthening of the polar vortex is likely to delay the expected recovery of the ozone layer, by providing conditions which are expected to enhance polar ozone loss. However, there is no clear modelling consensus as to whether the vortex will strengthen, or whether on the contrary the frequency of stratospheric warmings will increase. Use of long time series of meteorological data, such as the 40-year reanalysis (ERA-40) currently being produced at the European Centre for Medium-range Weather Forecasts, could be used to validate the models. A reasonable representation of the past would be expected to be a condition for faith in any prediction of the future. In this way historical data sets can be used to investigate the real significance and the robustness of the derived atmospheric trends. Any natural long-term changes in the dynamical structure of the troposphere or stratosphere can enhance or reduce any anthropogenically induced trends.

## INTRODUCTION

Authors

*I.S.A. Isaksen and N.R.P. Harris*

### 1.1 Background

Ozone affects incoming UV radiation from the sun by absorbing UV-B radiation, mainly in the stratosphere, and modulates outgoing IR radiation from the earth. Absorption of solar UV-B radiation initiates the gas phase chemistry in the stratosphere and troposphere responsible for ozone distribution and changes. The ozone chemistry and the interaction of ozone with solar and terrestrial radiation will depend critically on the height distribution and changes in the height profile of ozone. In addition ozone distribution and changes are strongly affected by dynamical processes and changes in such processes.

Changes in atmospheric ozone could have significant negative consequences, either directly, or indirectly through the impact on climate: Increases in damaging UV radiation from stratospheric ozone depletion affect man (skin cancer, cataracts, immune suppression), as well as plants and materials; enhanced ozone levels at the surface due to emission of pollutants affect air quality (impact on human health, inhibit plant growth); changes in ozone levels and distribution could affect weather patterns (e.g. El Niño) through its impact on climate.

Since ozone is not emitted directly, but rather is a secondary compound affected by emission by its precursors ( $\text{NO}_x$ , CO, NMHC,  $\text{CH}_4$ ) in the troposphere, and by ozone depleting substances (CFCs,  $\text{N}_2\text{O}$ , bromine compounds) as well as  $\text{NO}_x$  and  $\text{CH}_4$  in the stratosphere, its presence in the atmosphere is strongly determined by changes in the emission of such compounds. It will further affect the oxidising capacity of the troposphere, and thereby indirectly affect chemically active greenhouse gases like  $\text{CH}_4$  and HCFC. Ozone interaction with climate is complex, since ozone itself is also chemically active with a relatively short tropospheric lifetime. This makes ozone distribution and trends highly variable in space and time, depending on the distribution of the ozone source gases (in the troposphere) and ozone depleting gases (in the stratosphere), and there are strong spatial and temporal variations in radiative forcing from ozone changes.

After the Montreal protocol came into force in 1989 the emissions of the main depleting substances have decreased drastically [WMO, 2003]. This has led to a leveling off in the growth of chlorine loading in the stratosphere [EC, 2001]. Scenarios based on compliance with the Montreal protocol indicate halogen loading to pre-1980 levels by the mid 21<sup>st</sup> century. If no other changes in the stratospheric composition occur it is expected that ozone recovery will occur over approximately the same time period. However, there are significant uncertainties connected to the recovery of the ozone layer. Firstly, ozone recovery will depend strongly on future changes in  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , which are connected with large uncertainties [WMO, 2003; IPCC, 2001]. Secondly, future climate change is likely to lead to changes in stratospheric temperatures and in circulation, which could have significant impact on the ozone recovery. The uncertainty in the stratospheric ozone recovery has also implications for estimates of ozone penetration to the lower atmosphere.

The recent report on stratospheric ozone research in Europe during the period 1996-2000 has given significant contribution to global ozone research. Also, in the IPCC [2001] climate

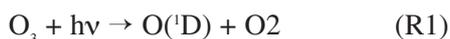
assessment and WMO [2003], ozone assessment some aspects of ozone-climate interactions were discussed. Furthermore, there is increasing international interest in considering ozone in connection with the Kyoto protocol. However, a comprehensive presentation of the problem with focus on the collected understanding of ozone-climate interactions in the troposphere and stratosphere has not yet been made. Therefore, a report, which describes the current understanding and, equally, the uncertainties, which limit our understanding, is now timely, considering in particular that significant progress has been made in different areas of ozone research, including the development of models with improved representation of chemical and dynamical processes in the UTLS (upper troposphere/lower stratosphere) region, global satellite observations of chemical compounds and the development of interactive ozone-climate models. Results from these studies are included in the present report. In the following sections a short summary of ozone chemistry, the distribution of ozone, and its impact on radiation, chemistry, and climate is given.

## 1.2 Ozone chemistry

Tropospheric and stratospheric ozone chemistry is determined by a large number of processes, which interact in a highly non-linear manner due to the emissions of the source gases and the ozone depleting substances, which are unevenly distributed at the Earth's surface. Its formation is furthermore affected by the highly variable short-wave solar (UV-B) radiation. Removal by gas phase reactions, by clouds and precipitation (in the troposphere), and by deposition at the Earth's surface, control the build up of primary and secondary chemical compounds affecting ozone distribution and changes. This leads to highly uneven formation and loss of ozone in the troposphere and stratosphere. Transport processes redistribute the chemical compounds. The impact of transport on the distribution is different for different chemical compounds. Compounds with long chemical lifetime, e.g. methane, are well mixed in the troposphere, while the concentrations of very short-lived compounds, e.g. the hydroxyl radical (OH), are completely determined by chemical production and loss terms. Ozone has a sufficiently short chemical lifetime in the troposphere to strongly affect its distribution. In the lower stratosphere where ozone concentrations are highest, transport processes play a significant role for its distribution.

### *Tropospheric chemistry*

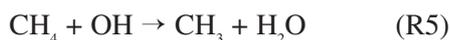
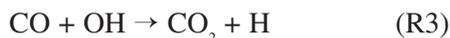
Ozone is a critical compound for oxidation processes in the troposphere, and it is interacting with source gases like  $\text{NO}_x$ , CO, NMHC,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  through its effect on the main oxidation agent OH. The result of the chemical coupling is a pronounced non-linearity in  $\text{O}_3$  changes and changes of the climate gas  $\text{CH}_4$  from emission changes. For instance, Crutzen [1979, 1988] showed that the presence of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) is crucial for  $\text{O}_3$  formation in the troposphere. In remote regions with extremely low  $\text{NO}_x$  levels, precursor emissions lead to ozone loss, while in tropospheric regions with higher  $\text{NO}_x$  levels  $\text{O}_3$  production dominates. Several studies have demonstrated that  $\text{O}_3$  loss takes place in the remote unpolluted troposphere, while it is well documented that net  $\text{O}_3$  formation occurs over polluted and semi polluted regions.  $\text{O}_3$  and OH are strongly linked through a number of key reactions. The chemistry in the free troposphere is initiated through photo-dissociation of  $\text{O}_3$  by solar radiation at wavelength shorter than  $\sim 320$  nanometer (nm), yielding excited state atomic oxygen:



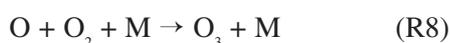
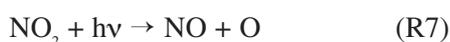
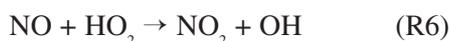
This initial reaction is followed by a reaction leading to the formation of the hydroxyl radical:



OH is a key reaction in the oxidation process in the troposphere, and reaction R2 is followed by a large number of reactions. Of particular importance are the reactions leading to CO and methane oxidation:



Other important reactions are the sequence of reactions leading to ozone, involving nitrogen oxides in the troposphere and in the lowermost part of the stratosphere (or through similar reactions with other peroxy radicals):



The reactions discussed above are the main reactions in the O<sub>3</sub> forming process. A key factor in limiting the O<sub>3</sub> formation in the atmosphere is the efficiency of NO<sub>x</sub> removal. NO<sub>2</sub> has a lifetime of only a few hours to days in the troposphere. Thus, there are large spatial and temporal variations in the NO<sub>x</sub> distribution in the troposphere and thereby in the ozone formation.

Several chemical reactions are involved in the removal of ozone in the troposphere. In addition to chemical reactions, cloud and precipitation through removal of chemical species, and direct surface deposition of ozone affect ozone levels significantly in the troposphere.

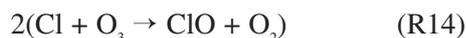
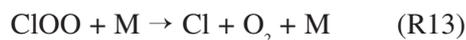
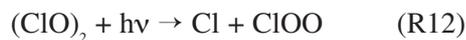
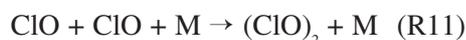
The large inhomogeneities in the ozone production and loss processes, combined with the short chemical lifetime of ozone, particularly in the atmospheric boundary layer, lead to large spatial and temporal variations in ozone. In particular, ozone levels often exceed air quality threshold levels in local and regional polluted areas. The presence of halogens in the surface level over oceans in the polar regions leads to efficient depletion of ozone in the boundary layer during spring months.

### ***Stratospheric ozone chemistry***

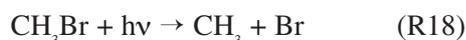
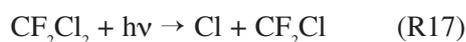
The main ozone formation in the stratosphere is through photo-dissociation of molecular oxygen by UV radiation forming atomic oxygen followed by recombination of atomic oxygen with molecular oxygen. This process occurs mainly at mid and low latitudes above approximately 25 km. Ozone is transported to higher latitudes and lower altitudes. The ozone layer is centered at approximately 15 km (high latitudes) to 25 km (low latitudes). Human activity is first of all affecting the ozone layer through enhancing the loss process through catalytic cycles in the stratosphere of the type:



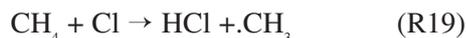
X and XO are chain carriers involving HO<sub>x</sub>, NO<sub>x</sub>, ClO<sub>x</sub> and BrO<sub>x</sub> families, where X=OH, NO, Cl, and Br respectively. In the particular situations when particles are present (e.g. polar stratospheric clouds, volcanic particles), enhanced conversion of inactive inorganic chlorine (HCl, ClNO<sub>2</sub> and HOCl) to active (Cl and ClO) takes place. In the polar vortex where PSCs strongly enhance the levels of ClO the major ozone loss occur via the reactions:



The net effect in the above cycles is the loss of two ozone molecules. Enhanced ozone loss will also occur in the vortex through the reaction between ClO and BrO. The main source gases producing compounds destroying ozone through the above reaction sequences are water vapour, nitrous oxide, CFCs and other chlorinated source gases and halons and other brominated gases through reactions of the type:



All these source gases are changing in the stratosphere, and future changes are likely to have pronounced impact on ozone loss and on ozone trends in the stratosphere. Increases in future methane concentrations, although contributing to the ozone depletion process through formation of odd oxygen, is believed to have an even stronger positive impact on ozone distribution through ozone production in the lower stratosphere, and through its impact on chlorine partitioning through the reaction:



It is therefore clear that understanding past and future ozone changes is strongly linked to our understanding of ozone source gases and ozone depleting substances as well as the chemical interaction between a large number of chemical compounds in the troposphere and stratosphere.

### 1.3 Ozone distribution and changes

Ozone concentrations in the lower troposphere vary from less than 10 ppbv over remote oceanic regions where the influence of anthropogenic emissions is negligible, and the loss at the surface is significant, to more than 100 ppbv over large regional areas where production is strongly controlled by anthropogenic emission of pollutants. In the upper troposphere, where ozone transport from the stratosphere is a dominant source, typical mixing ratios are of the order of 100 ppbv. The strong variability in ozone in space and time makes it difficult to determine the tropospheric burden from the existing surface observations. Additional information on the height distribution is available from a sparse network of ozonesondes [Logan, 1999] and lidars, and from aircraft measurements (e.g. projects like MOZAIC, CARIBIC, SONEX, POLINAT, NARE, AEROCE). Based on available ozone observations, IPCC [2001] estimates the global tropospheric burden to be about 370 Tg(O<sub>3</sub>), which is equivalent to an average mixing ratio of 50 ppbv. The ozone burden is approximately twice as high in the northern hemisphere as in the southern hemisphere. Possible causes for this could be more lightning activity producing NO<sub>x</sub> or larger emissions of pollutants at northern latitudes.

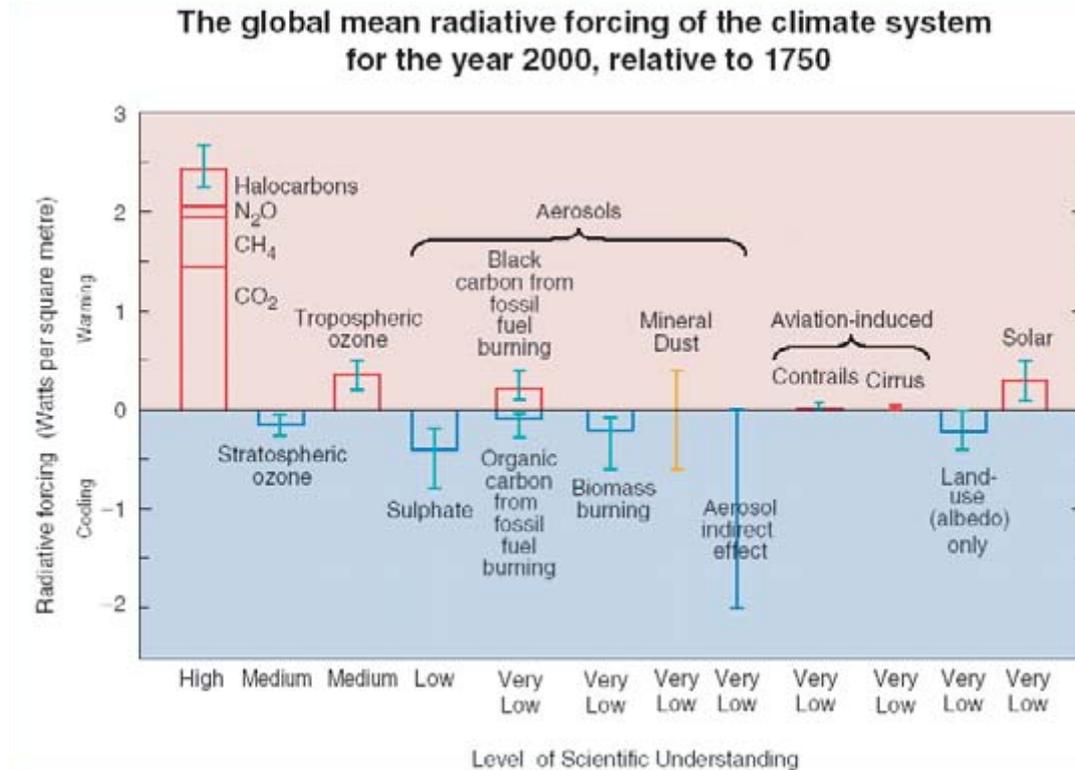
Analysis of observational data, combined with global model studies based on estimated increases in the emission of ozone precursors (NO<sub>x</sub>, CO, CH<sub>4</sub>) since pre-industrial time, indi-

cate a significant enhancement in tropospheric ozone burden at northern latitudes due to human activity. Although there are significant uncertainties connected to the analysis of the early ozone measurements [e.g. Staehelin et al., 2001], there was a significant positive trend in ozone during the 1970s until the mid 1980s at northern mid-latitudes, and changes after about 1985 has been much less. Observations also show large regional differences in the increases, with much smaller increases over North America than over Europe and Japan. Ozone at northern mid-latitudes seems to have increased with at least a factor 2 during the last half of the 20<sup>th</sup> century based on available observations. At low latitudes no significant change in tropospheric ozone is observed. A decline in free tropospheric ozone has been observed at high latitudes since the beginning of the 1980s. This is a likely result of influence from reduced stratospheric ozone.

Stratospheric ozone depletion has been observed over high and mid-latitudes. The largest losses occur in polar regions due to the low temperatures there. These losses were first observed over Antarctica. The Antarctic ozone hole now forms every September. In several recent years rapid losses have occurred in the Arctic. In the warmer mid-latitudes ozone loss is slower. Recent analyses of stratospheric ozone data confirm the now familiar features of the ozone depletion, which has occurred since the 1970s. At mid-latitudes in the northern hemisphere, there has been a statistically significant decline in total ozone in all seasons with larger reductions in winter and spring than in summer and autumn. The loss of ozone at southern mid-latitudes is also statistically significant throughout the year, albeit with a smaller seasonal variation. No statistically significant trends in total ozone have been observed in the tropics.

#### **1.4 Estimates of radiative forcing (RF)**

Ozone plays a central role in the radiative budget of the atmosphere through its interaction with both short wave and long wave radiation. Ozone is of major importance in maintaining the thermal structure in the stratosphere through its absorption of solar radiation in the UV by the Hartley (200-290 nm) and Huggins (290-340 nm) bands and partly in the visible through absorption by the Chappuis (500-700 nm) band. At altitudes above 45 km the Hartley band provides the major heating of the atmosphere, while below 30 km absorption by the Chappuis band dominates. It is believed that stratospheric O<sub>3</sub> is largely responsible for the existence of the tropopause, a nearly isothermal region separating the radiative equilibrated stratosphere from the radiative convectively controlled troposphere. IR radiation is in particular absorbed by ozone in the atmosphere in the 9.6mm wavelength region, with some absorption in the stratosphere in the 14μm wavelength region. Several studies have shown that the strongest impact on climate is for changes of ozone near the tropopause [Wang and Sze, 1980; Lacis et al., 1990; Forster and Shine, 1997; Hansen et al., 1997]. This results from a strong sensitivity to the vertical profile of the ozone change, and in particular to the interaction with thermal infrared radiation. The importance of the UTLS region should be underlined due to the large relative changes in ozone occurring at these heights [Harris et al, 1998]. As the detailed vertical profile of the ozone changes in this region is also relatively uncertain, the climate impact is connected with large uncertainties.



*Figure 1.1* Radiative forcing arising from changes in the atmospheric composition since pre-industrial times [IPCC, 2001], due to changes in greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, halocarbons, tropospheric and stratospheric ozone) and aerosols. The forcings possess a degree of scientific understanding at very different levels. For instance: The levels of understanding of radiative forcing due to changes in ozone (both tropospheric and stratospheric) is considered to be medium; lower than for the other greenhouse gases, but higher than for aerosols.

Radiative forcing has been used as a common tool to compare ozone changes with other component affecting the radiative balance. IPCC [2001] calculated the radiative forcing from the main greenhouse gases, aerosols and from land use change and changes in the solar output between 1750 and 2000 (Figure 1.1). For comparison aviation induced radiative forcing is also included. The figure gives uncertainty estimates and ranks the different radiative forcing estimates with regard to level of scientific understanding.

The increase in tropospheric ozone has led to a positive radiative forcing, with a larger contribution from the thermal infrared radiative forcing component than the solar forcing. Most of the global studies of the radiative effect of the increase in tropospheric ozone are based on models and there are significant differences in the estimate for same column ozone change. Stratospheric ozone depletion has resulted in a negative radiative forcing but the vertical profile is of crucial importance as the solar and thermal infrared radiative forcing have different signs for ozone reduction in the stratosphere. Estimates of radiative forcing for future ozone changes show a large spread due to the large uncertainty in emission scenarios for future emission of ozone precursors. Hansen et al. [1997] used a low resolution GCM to demonstrate that the climate response to ozone perturbations could change significantly when feedback mechanisms like sea ice and cloud coupling are included. The concentration of ozone in the troposphere has increased significantly due to human activities, and its global increase is estimated to give the third largest radiative forcing (RF) since pre industrial time (after CO<sub>2</sub> and CH<sub>4</sub>) [Ramaswamy et al., 2001]. Furthermore, there are large regional variations in RF due to the large regional differences in ozone perturbations. The largest regional RFs are found over the

over polluted regional areas in the northern hemisphere [IPCC, 2001]. Future increases in ozone concentrations could give important contributions to climate forcing, on a regional scale, as well as globally.

## 1.5 Climate-chemistry interactions

The climate has long been known to impact ozone, especially in the stratosphere. Ozone is influenced by climate through the changes in the temperature distribution and by changes in the dynamics of the troposphere and the stratosphere. Before heterogeneous chemical reactions were known to contribute to ozone depletion, it was found that increases in CO<sub>2</sub> would increase the ozone content in the stratosphere, due to a slow down of some gas phase reactions controlling ozone [Groves and Tuck, 1979], but the ozone increase was estimated to be less when chlorine accumulated in the stratosphere as a result of CFC emissions [Isaksen et al., 1980]. After the discovery of the ozone hole and the role of heterogeneous chemical reactions, it has been suggested that emissions of well mixed greenhouse gases (WMGHG) will lead to intensified ozone depletion due to increased activation of halogens on PSCs in the polar region [e.g. Austin et al., 2002]. The reduction in stratospheric ozone as well as the increases in greenhouse gases observed in the lower stratosphere during the last two decades [EC, 2001; WMO, 2003] is believed to be the cause for the significant observed reductions in lower stratospheric temperatures during the last two decades.

Climate change, connected to a rise in tropospheric temperature, in water vapour content and possible changes in dynamics, has been identified in various studies to affect the chemistry by significantly modifying future ozone and methane perturbations [e.g. Granier and Shine, 1999; Stevenson et al., 2000; Johnson et al., 2001]. Coupled climate-chemistry model studies with GCMs are now performed in several research groups, and the ability of models to reproduce the distribution, the changes in distribution of chemical active compounds, and their interactions, are currently being investigated [e.g. Shindell et al., 2001a; Schnadt et al., 2002; Wang et al., 2002a]. These model studies of the coupled stratospheric climate-chemistry recovery of stratospheric ozone as the amount of ozone depleting substances (ODS) decrease reveal large differences in the models and uncertainties in how fast ozone recovery will occur. In addition to the role ozone plays for the radiative budget of the atmosphere, its interactions with other greenhouse gases such as methane and HCFCs affects their lifetime, thus providing an additional indirect impact on climate. On the other hand, changes in climate and ozone caused by anthropogenic emissions will thus mutually influence each other. Although many coupling mechanisms between climate and ozone are understood in principle, the net effect of the impacts of climate change on ozone change and vice versa is only poorly quantified and understood at present.

Modelling activities to improved our understanding and reduce the uncertainty of the effect of climate chemistry interaction represent a large challenge for future studies of climate chemistry interactions. Integrated studies of changes in climate and ozone are thus clearly needed.

## 1.6 Previous assessments of ozone

### *European assessments*

There has been significant progress in stratospheric ozone research in Europe during the last 5 to 10 years, and the European Commission has published two recent assessments on European stratospheric research: European research in the stratosphere, the contribution of EASOE and

SESAME to our current understanding of the ozone layer in 1997, and European research in the stratosphere 1996-2000, Advances in our understanding of the ozone layer during THESEO in 2001. In these studies significant ozone loss was observed and quantified in the Arctic vortex during several winters, and linked to the presence of polar stratospheric clouds. Ground-based ozone and satellite measurements show that there has been a decline in the ozone column during the last two decades, with most of this decline linked to ozone loss in the 14 to 20 km height region. Enhanced increase in surface UV radiation over Europe was detected which is linked to the change in stratospheric ozone. Studies of mid latitude changes are connected to a close interaction between chemistry and dynamics.

Several European groups participated in the model studies in the European assessment of the atmospheric impact of aviation [Brasseur et al., 1998b] using global 3-D CTMs. Conclusions were drawn that aviation has an effect on atmospheric composition and on radiative forcing: aircraft emission of enhance  $\text{NO}_x$  levels in upper troposphere where the lifetime is long and ozone production efficiency (ozone molecules produced to kg of  $\text{NO}_x$  emitted) is high compared to surface emitted  $\text{NO}_x$ . Maximum ozone increases in the upper troposphere in the range 4-8% were obtained for ozone increases in the summer months when photochemical activity was large. Enhancements in ozone at these heights also led to a more efficient effect on radiative forcing than at lower altitudes. The study indicated increases in concentrations of condensation nuclei in the flight corridor. Model studies of the effects of a potential future fleet of supersonic aircraft gave small reduction in ozone levels, and in the level of UV-B radiation reaching the Earth's surface. The studies indicated that emission could become more efficient in perturbing composition and affecting the radiative forcing through a rapid increase in emissions over the coming decades.

### *IPCC climate assessments*

The Intergovernmental Panel on Climate Change (IPCC) has performed two recent assessments where the role of ozone as a climate gas is included.

In the assessment of Aviation and the Global Atmosphere [IPCC, 1999] the atmospheric impact of current, and future fleets of aircraft on the chemical composition is studied, together with the consequence this change could have for the UV flux reaching the Earth's surface, and for climate change. Included in the studies was the effect of a potential future fleet of supersonic aircraft. The assessment also estimated uncertainties related to the calculated impact. Changes in the chemical composition due to  $\text{NO}_x$  emission from aircraft was estimated to give enhanced RF from ozone and reduced RF from methane. Considering the significant uncertainties connected to the model results it was difficult to draw any conclusion with regard to the global impact of  $\text{NO}_x$  emission from aircraft. For supersonic aircraft the dominating contribution to RF was found to be emission of water vapour. Several important areas of uncertainties were identified, which limit our ability to project aviation impact on climate and ozone, and where further research is urgently needed. They include: the role of  $\text{NO}_x$  in changing the ozone and methane concentrations; the ability of aerosols to alter chemical processes; the transport of atmospheric gases and particles in the UTLS region; the climate response to regional forcing and stratospheric perturbations. In addition the scenarios for future emissions (up to 2050) are connected with large uncertainties.

In the IPCC assessment: Climate Change: The Scientific Basis [IPCC, 2001] the relation between atmospheric chemistry and greenhouse gases was discussed. In particular the current distribution and changes from pre-industrial time as well as predictions of future changes of tropospheric ozone are estimated using state of the art atmospheric chemical models (CTMs). Furthermore, RF for the current atmosphere (since 1750) for tropospheric ozone (positive) and for stratospheric ozone (negative) are calculated and compared with RF from other forcing

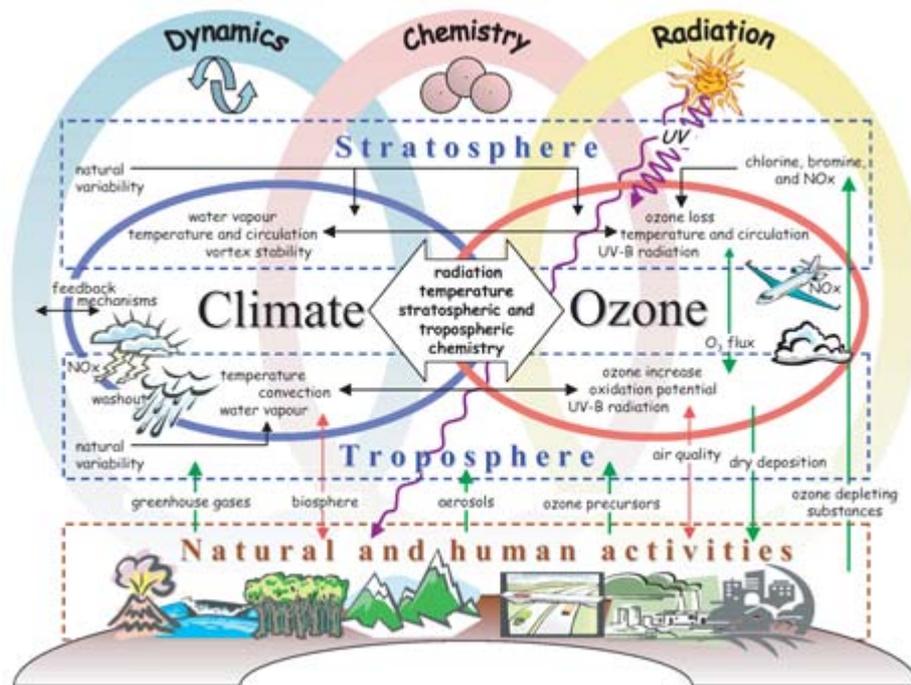
agents. Estimates of future ozone change (over the next century) and thereby of future RF show significant differences due to differences in model estimates, and uncertainties connected to emission scenarios of ozone precursors. The report also discussed chemical processes that were not included in the model studies or feedback processes affecting the atmospheric chemistry: The chemistry affected by changing emission patterns, aerosol interactions with tropospheric O<sub>3</sub> and OH, stratospheric-tropospheric coupling, uncertainties in the tropospheric ozone budget, impacts of physical climate change on atmospheric chemistry, feedbacks through natural emissions. Finally, the need for coupled models including both stratospheric and tropospheric processes as well as coupling atmospheric models with biogeochemical changes and with physical changes in the climate system (water vapour, winds, temperature, convection)

#### ***UNEP/WMO ozone assessment***

UNEP/WMO has recently performed an assessment of stratospheric ozone [WMO, 2003]. It is shown that recent laboratory investigations, atmospheric observations and theoretical and modeling studies have produced results that add to the understanding and strengthen the understanding and the conclusions of changes in the ozone layer and its effects on ultraviolet (UV) radiation of the previous assessment from 1998. Observations show that following a slight decline in total tropospheric chlorine since the mid 1990s stratospheric chlorine levels are at or close to its peak, while bromine levels are still increasing. The spring-time Antarctic ozone depletion has continued to increase during the last decade with increasing impact on UV radiation. In Arctic winters ozone loss is highly variable due to changes in meteorological conditions. In cold years total ozone loss has reached 25 %. There are yearly average ozone losses at northern and southern mid-latitudes of 3 and 6 % respectively. Chemistry climate models have been applied to predict the future recovery of the ozone layer. The prediction is that springtime Antarctic ozone levels will be increasing by 2010 due to decreases in halogen levels. It is found that the prediction of the recovery of the ozone layer in Arctic polar region is connected with large uncertainties. It is however concluded that it is unlikely that there will be sustained low ozone columns as seen in the Antarctic over the next decade when halogen levels are close to their maximum. It is further concluded that the global ozone layer recovery mainly will be linked to the decreasing halogen level with some contribution from other factors. Measurements confirm decreases in ozone column amounts lead to increases in UV radiation. However, the spectral surface UV data records that started in the early 1990s are too short to give a significant long term trend.

#### ***Outline of the report***

Ozone-climate interactions are linked through a complex set of processes involving chemistry, radiation, dynamics and emission of greenhouse gases, ozone precursors and ozone depleting substances. Although the processes are significantly different in the stratosphere and in the troposphere, there is an important link between the two regions through processes in the UTLS region. A schematic presentation of the ozone climate interaction, and how it is affected by processes in the different parts of the atmosphere, is given in Figure 1.2.



*Figure 1.2* Processes determining the ozone climate interactions in the troposphere and the stratosphere. The atmospheric regions are indicated by blue, and source regions by brown dashed boxes. The text inside the climate and ozone circles indicates main processes affected by climate and ozone changes. Text outside the circles indicates natural and human processes affecting the climate chemistry system. Green arrows show the transport of greenhouse gases and black arrows give processes affecting ozone and climate. Greenhouse gases include compounds like  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , CFCs and HFCs; aerosols include sulfate, organic, sea salt and mineral dust particles; ozone precursors include  $\text{NO}_x$ , CO, NMHC,  $\text{CH}_4$ ; ozone depleting substances include CFCs, halons and other bromine compounds, and  $\text{N}_2\text{O}$ . Arrows indicating the impact of enhanced tropospheric ozone levels on air quality, and interaction of climate with the biosphere are given in red. UV radiation indicated by purple arrows affects stratospheric and tropospheric chemistry, as well as humans and the biosphere.

In Chapter 2 the changes in ozone depleting substances and their impact on stratospheric ozone will be presented with further study of how these changes lead to changes in radiative forcing and stratospheric temperatures, and how reductions in ozone columns lead to enhanced penetration of UV fluxes to the troposphere. Chapter 3 will discuss impact of climate change on stratospheric ozone and ozone-climate interactions in the stratosphere, in particular how climate change affects the ozone layer recovery. Chapter 4 will present how changes in tropospheric ozone affect climate, including the interaction with other chemically active greenhouse gases (e.g. methane, HFCs) and changes in the chemistry caused by changes in the ozone column (changes in UV). Chapter 5 will focus on the impact of changes in climate on tropospheric ozone. Climate induced changes affecting ozone are temperature changes, changes in the water content, changes in winds and convection, changes in cloudiness and particles, and changes in land use leading to changes in natural emissions. The summary gives the most important findings with respect to ozone-climate interactions presented in Chapters 2 to 5, followed by a discussion of possible future research topics, like the need for improved climate models and extended measurements and data analysis.

## THE EFFECT OF STRATOSPHERIC OZONE CHANGES ON CLIMATE

Authors

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### 2.1 Introduction

During the past two decades a negative trend in globally averaged total ozone column amount has been observed which is of great concern for the biosphere and human health. It is generally accepted that the release of chlorine- and bromine-containing compounds (halocarbons) into the atmosphere is a major cause for these trends. In addition, the atmospheric concentrations of other so-called well-mixed greenhouse gases, such as CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, have also increased significantly compared to the pre-industrial era. The increase of these greenhouse gases has also influenced stratospheric ozone concentrations by changing dynamical processes in conjunction with the changing temperature structure of the stratosphere (see Chapter 3).

This chapter addresses how stratospheric ozone decrease impacts onto climate change. The interaction between stratospheric ozone change and climate change is very complex and contains various direct and indirect effects and feedback mechanisms. The converse is discussed in Chapter 3. Diagram 2.1 (shown later in this chapter) gives an overview of the components of stratospheric ozone-climate interactions. The major causes of stratospheric ozone depletion and climate change are given at the top in Diagram 2.1. The growth of greenhouse gases, including halogen-containing compounds are inducing climate change and are supplying reactive species causing chemical depletion of ozone. At the bottom of the diagram natural processes, such as volcanic eruptions and variations in solar activity are depicted. They impact on the climate system and stratospheric ozone. Section 2.2 describes past changes in stratospheric ozone and halogen species, including the role of natural processes. Chapter 3 will address the other greenhouse gases.

Stratospheric ozone plays an important role in the short- and long-wave radiation budget of the atmosphere. Changes in stratospheric ozone concentrations directly brings about radiative forcing that leads to climate change by altering temperature. These ozone changes indirectly affect climate by modifying stratospheric dynamical processes. This interaction is indicated in the diagram by the two-way arrow and is described in Sections 2.3 and 2.4. The effects are mutual: changes in temperature and dynamics are in turn affecting stratospheric ozone. This is addressed in Chapter 3. In addition, there are indications that changes in stratospheric dynamics are affecting the troposphere. Section 2.5 will provide an overview of possible links.

Since stratospheric ozone is a major ultraviolet (UV) absorber, its decrease may increase the UV irradiance in the troposphere down to the surface. Both changes in temperature and UV affect chemical processes in the stratosphere and in the troposphere. A two-way arrow in Diagram 2.1 indicates this connection. An important effect of increased UV irradiance is the impact on the biosphere. The arrows indicate damage to primary organic production at the surface and in oceans by increased UV irradiance, which would also affect the production of dimethyl sulphide (DMS) and cloud formation processes. Climate change originally induced by stratospheric ozone

decrease is affecting climate parameters such as cloud, snow, and ice cover. These have a large impact on UV, but also on stratospheric ozone. This complicated relation between stratospheric ozone decrease and UV is addressed in Section 2.6.

The evolution of halogen species is a major issue for the future development of the ozone layer. The Montreal Protocol has led to a worldwide control of all major man-made halocarbons, and it is expected that the halogen loading (especially chlorine) will return to pre-1980 levels some time this century. Section 2.7 describes scenarios on the possible future development of the chlorine and bromine loading.

## **2.2 Past changes in ozone and halogen species**

Observations unequivocally show less global ozone compared to two decades ago, which have been described in previous scientific assessment reports [e.g., IPCC, 2001; WMO, 2003]. This section summarises key aspects of the observed ozone changes and the role of natural and anthropogenic processes.

### **2.2.1 Ozone observations**

Observations of total ozone have been performed since the 1920s [Dobson et al., 1929; Staehelin et al., 2001]. However, it is only since 1960 that the quality, sampling and coverage of ozone data take account of the deduction of trends in global stratospheric ozone. These were reported in several ozone assessments [WMO, 1995, 1999, 2003; IPCC, 2001], and in scientific publications, e.g. Stolarski et al. [1992] and Staehelin et al. [2001]. Satellite measurements have (almost) provided global coverage of total ozone columns since the late 1970s. However, due to the limited lifetime of satellites, the measurements from different satellite instruments have to be homogenised to obtain a consistent series of observations. The satellite observations allow the analysis of total ozone column trends on a global scale. This was performed based on a compilation of six different data sets [Fioletov et al., 2002] to reveal a global and annual average mean decline of total ozone since 1979. The largest negative ozone trends are confined to polar regions during winter and spring (they are stronger in the Antarctic than in the Arctic with -7% per decade at 65°S and -4% per decade at 65°N on a annual mean basis). Statistically significant ozone decreases were also observed at mid-latitudes (of about -2.5% per decade on an annual mean basis), while no significant trends have been found in the tropical region. Figures 2.1a and b show the observed ozone trends at mid-latitudes in both hemispheres and clearly illustrate the ozone decline after 1980 [Fioletov et al., 2002].

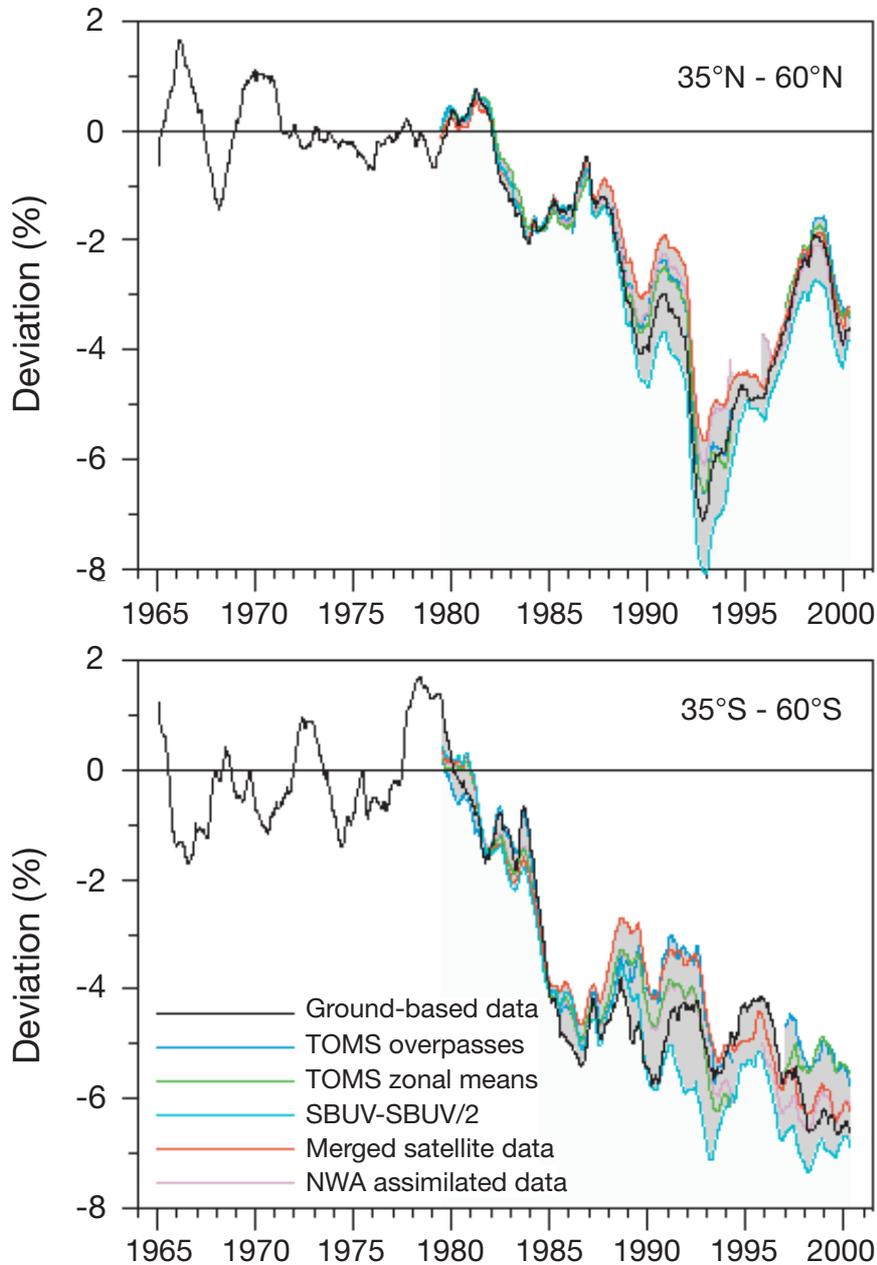


Figure 2.1 Total ozone deviations from the pre-1980 level in percent for the 35-60°S and 35-60°N zones estimated from six data sets (ground-based data, TOMS overpass data, TOMS zonal means, SBUV-SBUV/2 zonal averages, merged TOMS and SBUV-SBUV/2 data, and the National Institute of Water and Atmospheric Research (NIWA) assimilated data, based on TOMS, version 7 and GOME data [Bodeker et al., 2001], with seasonal, QBO, and solar cycle removed. The data are smoothed by 25 months running means. The shaded area indicates the spread of the different data sets [from: Fioletov et al., 2002].

Furthermore, the observed ozone trends are altitude dependent. Observations from satellites, balloons and ground-based stations reveal two broad minima between 1979 and 1996 [e.g. Randel et al., 1999; EC, 2001; Bojkov et al., 2002]: one in the upper stratosphere (peaking at around 40 km) and one in the lower stratosphere (peaking at around 15 km), while there is no trend observed in the middle stratosphere (around 30 km). However, the period viewed is important for trends in ozone in the lower stratosphere in the northern hemisphere. The mean decrease at northern mid-latitude ozonesonde stations at 80 hPa for 1979-2000 is -5% per decade, which is 2.5%

smaller than for 1980-1996 [WMO, 2003]. An extension of the ozone sonde record at Payerne (Switzerland) to 2001 leads to insignificant long-term trends below 15 km [Koch et al., 2002; Weiss et al., 2001].

### **2.2.2 Natural processes**

Besides climate variability (see Chapter 3), important natural processes affecting stratospheric ozone are volcanic eruptions and solar activity. Volcanic eruptions are episodic, whereas solar activity is periodic. In ozone trend analyses over the last 2-3 decades, as those presented in Figure 2.1, these processes have been filtered out. Nevertheless, they have a significant impact on the ozone distribution. Therefore they are discussed in this section.

#### *Volcanic eruptions*

Two major volcanic eruptions occurred during the past two decades; El Chichon in 1982 and Mt Pinatubo in 1991. Both emitted large amounts of sulfur dioxide into the stratosphere, which led to enhanced aerosol particle loading in the stratosphere [Bluth et al., 1992; Solomon, 1999; Robock, 2000]. Low total ozone values were reported for the years following the eruptions of El Chichon and Mt. Pinatubo (see Figure 2.1) [Fioletov et al., 2002; Staehelin et al., 2001].

There have been many modelling studies illustrating that part of the observed low ozone is caused by chemical depletion of ozone involving heterogeneous chemistry on sulfate aerosol particles [e.g. Zerefos et al., 1994; Solomon, 1999; Tabazadeh et al., 2002; WMO, 2003].

In addition to the chemical processes directly altering ozone, an indirect effect of volcanic eruptions is the impact of enhanced aerosol particles on the radiation changing temperature and dynamics and therefore altering transport [e.g. Chandra, 1993]. Based on meteorological analysis of the European Centre for Medium-Range Weather Forecast (ECMWF), recent 3-D model calculations are demonstrating that dynamical processes can explain about half of the negative anomaly in total ozone following the eruption of Mt Pinatubo [Hadjinicolau et al., 2002].

#### *Solar activity*

The solar radiation changes on both short and long (secular) time scales. Changes in the solar UV irradiance are affecting the atmosphere's ozone burden and through radiative and chemical interactions the climate. To understand how a small change in the overall solar irradiance can influence the large scale circulation, we have to understand: (a) the effects of small changes in short-wave heating in the stratosphere; and (b) the changes in the photochemical production and loss of ozone between solar maximum and minimum. Observations of geopotential heights in the stratosphere reveal an 11-year solar signal [Labitzke and Matthes, 2003 and references therein] and there is evidence for a 27-day variation as well. In particular the 11-year cycle influences ozone in the upper stratosphere [WMO, 1999]. In addition, there is observational evidence that the variability in solar activity changes total ozone by a few percent, in particular causing an increase in the tropics at solar maximum [Zerefos et al., 1997; McCormack and Hood, 1997; Solomon, 1999; Hood, 1997; Staehelin et al., 1998; Tourpali et al., 2003]. Modelling studies using global circulation models (GCMs) with enhanced solar irradiance and associated ozone changes derived from photochemical models are finding a consistent dynamical pattern of response: the tropical Hadley cells are weakening and broadening, and the mid-latitude Ferrel cells are moving poleward [Haigh, 1999; Haigh and Williams, 2002; Larkin et al., 2000].

### **2.2.3 Anthropogenic activity**

The increase in well-mixed greenhouse gases ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ) and CFCs through anthropogenic activity has played a major role in the observed ozone trends, which have been described in recent assessments [IPCC, 2001; EC, 2001; WMO, 2003]. In addition to these greenhouse gases, water vapour deserves special attention. It is not only one of the most important greenhouse gases, but there is observational evidence that its concentration in the stratosphere has increased from 4 ppm in 1950 to 6 ppm in 2000 [Rosenlof et al., 2001; SPARC, 2000]. See Chapter 3 for more details.

The increase of greenhouse gases has both direct and indirect effects on ozone. The direct effect is primarily caused by the increase of chlorine radicals by CFCs, that destroy ozone in catalytic reaction cycles [cf. Dessler, 2000; WMO, 1999]. The indirect effect is due to the fact that the growth of well-mixed greenhouse gases is causing a radiative forcing, therefore changing the temperature and consequently changing in the circulation [IPCC, 2001]. Chapter 3 addresses both the direct and indirect effects of increases in well-mixed greenhouse gases and water vapour on ozone. This Section is restricted to the halogen containing species.

*Table 2.1* Reductions in production and consumption (consumption is defined as production plus imports minus exports), prescribed by the Montreal Protocol and its subsequent amendments for different types of ozone depleting substances. While Chlorofluorocarbons (CFCs) are fully halogenated compounds consisting solely of fluorine, chlorine and carbon, Hydrofluorocarbons (HCFCs) contain at least one hydrogen atom. A fraction of the latter class of substance is degraded in the troposphere, which leads to substantially lower ozone depleting potentials (ODPs). Halons are also completely halogenated and carry at least one bromine atom in addition to fluorine or chlorine. As bromine is more reactive towards ozone, the ODPs of Halons are generally larger than those of CFCs or HCFCs. The regulations listed below are those which apply to developed countries. There are exceptions for developing countries, delaying the compliance by 10 years, but with upper limits to allowed consumptions. A total of 183 countries have ratified the original Montreal protocol so far; most of these have also already ratified the London and Copenhagen amendments.

Substance Class	Reference year	Target 1	Target 2	Phase out year
CFC	1986			1996
HCFCs*	1989	2004: 65%	2015: 10%	2030
CCl <sub>4</sub> and CH <sub>3</sub> CCl <sub>3</sub> §	1989			1996
Halons	1986			1994
CH <sub>3</sub> Br#	1991	2001: 50%	2003: 30%	2005

\* The reference amount for HCFCs is the sum of the HCFC consumption in 1989 and 2.8% of the CFC consumption in 1989. There are two more intermediate targets for HCFCs, i.e., 35% in 2010 and 0.5% in 2020.

§ The intermediate targets for CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> were not identical.

# There was a further intermediate target of 75% of the 1991 consumption for the year 1999 for CH<sub>3</sub>Br.

Table 2.1 is listing the major classes of halogen containing compounds, whose production and consumption are regulated by the Montreal Protocol, which was first set up in 1987 and has been amended several times since. The regulations enforced by the protocol have led to a change in the atmospheric trends of most chlorine containing species. While the atmospheric abundances of most compounds listed in Table 2.1 showed a continuous increase in the 1980s; the most important chlorine source gases are now declining in the atmosphere [WMO, 2003]. In the troposphere the maximum chlorine level of about 3600 pptv was reached in 1992-1994, and since then this level declined by about 5% until the year 2000. The current rate of change (for the year 2000) is -22 pptv per year [WMO 2003]. The decrease in tropospheric chlorine has also led to a decrease in stratospheric inorganic chlorine, as illustrated by total column observations of the two major stratospheric inorganic chlorine compounds ClONO<sub>2</sub> and HCl and the total inorganic chlorine (Cly) calculated from these (Figure 2.2).

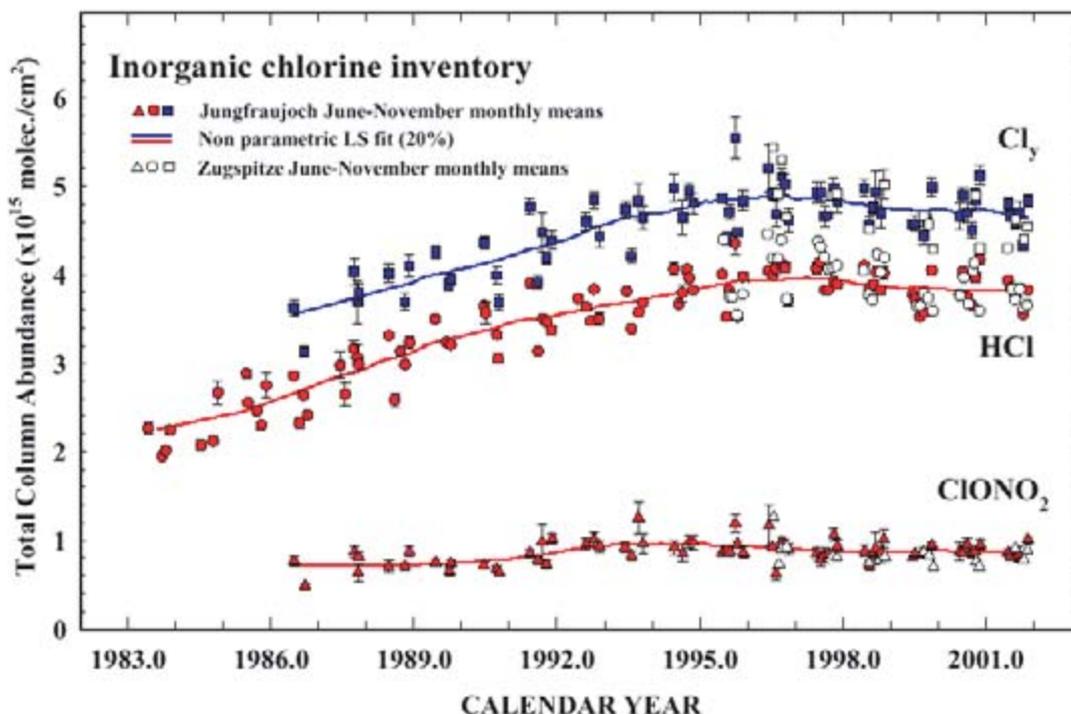


Figure 2.2 Vertical column amounts of HCl and ClONO<sub>2</sub> above the Jungfraujoch (located in the Swiss Alps as part of the NDSC primary station NDSC-ALPS). Only June to November monthly mean vertical column abundances are used in order to avoid large winter-spring variability. The reported Cl<sub>y</sub> includes a ClO background load derived from model calculations (updated from Mahieu et al., [2000]).

Bromine is much more effective than chlorine with regard to chemical ozone loss in the stratosphere. One atom of bromine released into the stratosphere results in 20-100 times the amount of ozone depletion as does one Cl atom. Therefore, although atmospheric bromine levels are only around 20 pptv (compared to a maximum of about 3600 pptv of chlorine) bromine compounds are important ozone depleting substances. Total bromine in halons has increased by a factor of 10 since the late 1970s and the mixing ratios of halons were still increasing in the atmosphere by about 3% per year in 2000 [WMO 2003]. Methyl bromide, however, has begun to decline in recent years [Yokouchi et al., 2002].

Natural organo-iodine gases such as methyl iodide are known to reach the upper troposphere [Blake et al., 1999; Sturges et al., 2000] despite photochemical lifetimes of only a few days. Small column abundances of IO in the stratosphere have been observed or inferred [Wennberg et al., 1997; Pundt et al., 1998; Wittrock et al., 2000], equivalent to stratospheric mixing ratios of, at most, a few tenths of a pptv. Estimates of the stratospheric ozone removal efficiency of iodine relative to chlorine range from 150 to 1000 as cited in WMO [2003], wherein a value of 300 was adopted for the discussion. The effect on stratospheric ozone remains very poorly understood, but is presently thought to be low.

- *The main natural processes leading to changes in stratospheric ozone are solar variability and volcanic eruptions. There is, however, no evidence for long-term changes in these processes. Anthropogenic activity has led to an increase in atmospheric chlorine and bromine loading, which has been identified as a major cause of the observed ozone depletion. While chlorine is now decreasing in the atmosphere, a similar turn-over in bromine has not been reported.*

## 2.3 Radiative forcing

### 2.3.1 *The concept of radiative forcing*

Changes in stratospheric ozone are discussed in this chapter as they can directly alter the climate, e.g. stratospheric and surface temperatures. Stratospheric ozone impacts the climate as it absorbs both incoming solar and outgoing terrestrial radiation. A first measure of the impact of ozone changes on climate, resulting from anthropogenic emissions of ozone precursors, is the radiative forcing (RF) at the tropopause. RF is defined as the change of the radiative flux due to an instantaneous change of the atmospheric radiatively active gases, which in our case is the change of stratospheric ozone concentrations. The atmosphere is not allowed to reach a new equilibrium, except for the stratospheric temperature, which is allowed to obtain a new radiative balance. This is called the “fixed dynamical heating concept” or FDH [cf. IPCC, 2001]. The concept of RF was introduced as a first-order metric of climate change: the equilibrium change in global mean surface temperature ( $\Delta T_s$ ) [K] can be related to a change in the (global and annual mean) RF [ $\text{Wm}^{-2}$ ] by the equation:

$$\Delta T_s = \lambda \text{ RF} \quad (1)$$

where  $\lambda$  is the global mean climate sensitivity parameter [ $\text{K} (\text{Wm}^{-2})^{-1}$ ]. This parameter reflects the translation from RF to surface temperatures, and is usually estimated with a GCM. Figures 2.3 and 2.4 illustrate the consequences for RF and  $\Delta T_s$  from a specific increase in stratospheric ozone, which will be explained later. The calculation of  $\lambda$  is not trivial and depends on assumptions made in GCM integrations. An example is illustrated later.

Sometimes the ‘instantaneous’ radiative forcing is considered, i.e. the radiative forcing without the adjustment of the stratospheric temperatures, also denoted as “fixed temperature” (FT) radiative forcing. The difference between the two concepts, FT and FDH, illustrates the effect of adjusting temperatures in the stratosphere to a new radiative equilibrium.

The concept of radiative forcing is used to compare the influence of several factors impacting the troposphere – surface system (see Chapter 1). A positive forcing, which is produced for instance by an increase of the well-mixed greenhouse gases, and tropospheric ozone, warms the surface. A negative forcing, which can arise from a decrease in stratospheric ozone and from an increase in most types of aerosol particles, cools the surface. For stratospheric ozone losses (taking into account typical profile changes) RF is  $-0.006$  to  $-0.012 \text{ Wm}^{-2} \text{ DU}^{-1}$ , which is about a factor of five smaller than the RF resulting from tropospheric ozone changes, which is discussed in Chapter 4.

### 2.3.2 *Stratospheric ozone changes and radiative forcing*

The sign and magnitude of RF due to stratospheric ozone changes strongly depends on the altitude where the changes occur. This is illustrated in Figure 2.3. Here, results are shown of radiative forcing calculations assuming ozone increases of 10 DU at different altitudes for clear sky mid-latitude summer conditions, using the FDH and FT concepts, explained earlier. The Figure clearly illustrates that RF is particularly sensitive for ozone changes in the vicinity of the tropopause.

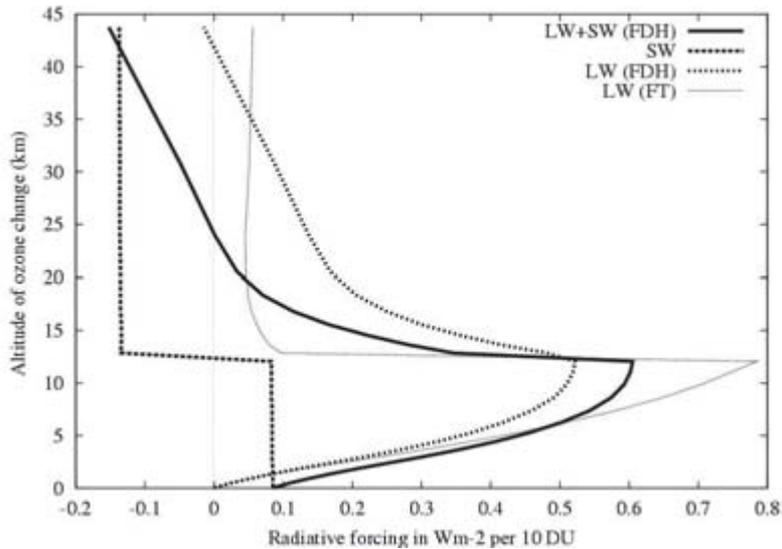


Figure 2.3 Ozone sensitivity curve in a clear sky mid-Latitude summer atmosphere in terms of radiative forcing per 10 DU ozone increase at given altitude. Shown are the total (solid line), the long-wave (dotted line), and the short-wave (dashed line) radiative forcing using the fixed dynamical heating (FDH) concept. The thin line represents the long-wave forcing using the fixed temperature (FT) concept (updated from Van Dorland and Fortuin, [1994]). The difference between FDH and FT represents the effect of taking into account stratospheric temperature changes.

For stratospheric ozone losses the RF is opposite to that shown in Figure 3.3; the short-wave radiative forcing is positive due to less absorption of solar radiation by ozone, so that more reaches the troposphere. In the long-wave region, mainly through the 9.6 and 14  $\mu\text{m}$  bands, stratospheric ozone loss results in a negative RF, since more long-wave radiation emits to space than in the situation without any ozone loss. In the FT concept, the long-wave forcing is quite small, about  $-0.004 \text{ Wm}^{-2} \text{ DU}^{-1}$ . When the adjustment of the lower stratospheric temperature to a new equilibrium is allowed (FDH case), the long-wave RF for stratospheric ozone depletion is below  $-0.014 \text{ Wm}^{-2} \text{ DU}^{-1}$ . This is the reason why net RF (FDH) is negative for ozone loss in the lower stratosphere directly above the tropopause.

The maximum total RF (short and long wave) is found for ozone changes in the tropopause region. To account for the time lag between forcing and stratospheric response, Forster et al. [1997] developed the concept of the “Seasonally Evolving Fixed Dynamical Heating” (SEFDH). The difference in radiative forcing due to (observed) stratospheric ozone changes between both concepts is usually within 5% when an annually averaged RF is considered.

Considering the RF by stratospheric ozone changes, the observed ozone depletion in the lower stratosphere may have offset the well-mixed greenhouse gas-induced RF by 2-11%. This range in offset is based on the sum of the RF of  $2.78 \text{ Wm}^{-2}$  due to well-mixed greenhouse gases and tropospheric ozone (with an uncertainty of about 12%), and a range in RF due to stratospheric ozone losses of  $-0.05$  to  $-0.25 \text{ Wm}^{-2}$  [IPCC, 2001]. Note that when considering only the last two decades, the RF due to stratospheric ozone depletion counteracts the RF from the growth of well-mixed greenhouse gases by 15-20% [WMO, 2003].

The response of the global mean surface temperature to local ozone perturbations is illustrated by Figure 2.4, which shows the global surface temperature changes resulting from constant absolute ozone increases of 10 DU at different altitudes (perturbations similar to those in Figure 2.3) and on a constant relative increase (10% of the background) at different altitudes [Forster

and Shine, 1997]. Similar to the results shown in Figure 2.3, the largest temperature response to absolute ozone perturbations is found close to the tropopause. To translate the RF (in Figure 2.3) to surface temperature changes (in Figure 2.4) the sensitivity parameter,  $\lambda$  has to be calculated.

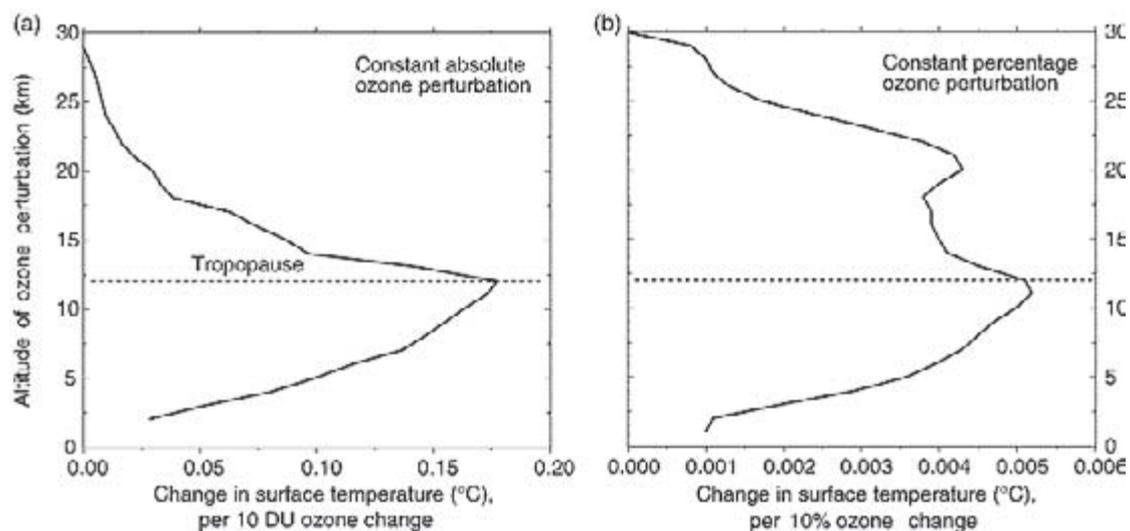


Figure 2.4 Dependence of the surface temperature response on the height and type of ozone perturbation; (a) shows the sensitivity to a constant absolute change (10 DU), while (b) shows the sensitivity to a constant percentage change (10%). The model tropopause is at 12 km. From Forster and Shine [1997].

While the value of  $\lambda$  was assumed to be independent of the species causing the forcing, there was a large discrepancy in the actual value of  $\lambda$  in different models [IPCC, 2001]. In addition, model results by Ponater et al. [1999], and similar results obtained with a simplified GCM by Hansen et al. [1997], question whether  $\lambda$  is really independent of the forcing species.

One example of a factor influencing  $\lambda$  is water vapour, demonstrated by a model study: using an online calculation of RF within the ECHAM4 GCM [Stuber et al., 2001b], the impact of ozone perturbations (with a RF of  $1 \text{ Wm}^{-2}$ ) was systematically studied by Stuber et al. [2001a]. They found an unusual high  $\lambda$  value for ozone perturbations in the lower stratosphere, which is 1.8 times the value associated with an equivalent  $\text{CO}_2$  perturbation. In contrast, ozone perturbations in the upper troposphere showed an unusual small  $\lambda$  of 0.7 times of the  $\text{CO}_2$  value. The calculated  $\lambda$ 's are significantly higher than previous calculations [IPCC, 2001]. They explained this behaviour by feedback processes with stratospheric water vapour: in the case of an ozone perturbation in the lower stratosphere, the primary temperature response is such that due to a higher cold point (minimum) temperature, more water vapour is transported from the tropical troposphere into the stratosphere. The opposite is true for the ozone perturbation in upper troposphere. Thus the impact of ozone perturbations is amplified by a coupling with water vapour. These results indicate that  $\lambda$  is variable within one model, while in previous model studies  $\lambda$  was found to be an approximate constant within one model [IPCC, 2001]. Further, the results appear to be valid for different GCMs [Joshi et al., 2003; see also Sausen et al. 2002; and Chapter 4].

The role of water vapour is described in more detail in Chapter 3. Currently, we do not fully understand the reasons for this special behaviour.

- The radiative forcing by stratospheric ozone depletion ( $-0.05$  to  $-0.25 \text{ Wm}^{-2}$ ) counteracts the radiative forcing from the growth of well-mixed greenhouse gases over the last two decades by 15-20%. However, the climate sensitivity parameter is particularly high for ozone perturbations in the lower stratosphere, i.e. the surface temperature change for a given radiative forcing from

stratospheric ozone is greater than for an identical radiative forcing arising from well-mixed greenhouse gases. Current estimates of radiative forcing due to stratospheric ozone perturbations indicate an important role of water vapour.

## 2.4 Impact on the stratosphere: thermal and dynamic changes

As reported in the review-paper by Ramaswamy et al. [2001], global and annually averaged stratospheric temperatures have decreased during the past three decades, based on observations from a variety of instruments and platforms. Radiosonde and satellite data indicate a statistically significant cooling trend in the lower stratosphere (~50-100 hPa) over the period 1979-1994 of ~0.6 K decade<sup>-1</sup>. For the period prior to 1980 the radiosonde data indicate a substantially weaker cooling trend. The strongest cooling occurs in the polar lower stratosphere during late winter/spring in both hemispheres (~3-4 K per decade). This trend is observed in the Antarctic since the early 1980s and in the Arctic since the early 1990s. However, the dynamical variability in these regions is large, particularly in the Arctic. Lidar and rocket data generally show a cooling of the middle and upper stratosphere (~30-50 km) of 1-2 K per decade since ~1970, with the magnitude increasing with altitude. Satellite data indicate a cooling trend in the upper stratosphere (above ~40 km) in the 60°S-60°N region over the period 1979-1994 (up to ~3K per decade near 50 km).

The global and annual stratospheric temperature decrease is illustrated in Figure 2.5, as well as the calculated temperature changes from the changes in well-mixed greenhouse gases, ozone and water vapour, as an average of different models. The model simulations indicate that the depletion of lower stratospheric ozone is a major cause of the observed global-mean lower stratospheric cooling trend over the period 1979-1997 (~0.5 K per decade at 100 hPa, ~1 K per decade at 50 hPa); the contribution by the well-mixed greenhouse gases is smaller than the contribution by ozone.

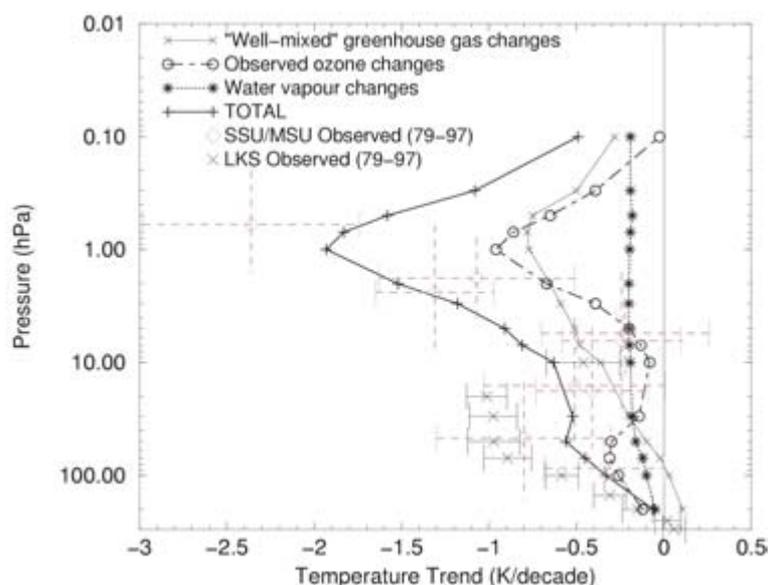


Figure 2.5 Global and annual mean temperature trends from an average of models results for imposed height-resolved ozone trends and greenhouse gases. The water vapour results are the Imperial College IGCM HALOE trends. The satellite trends from MSU and SSU, and the radiosonde trends from Lanzante et al. [2003] are also shown (LKS). The 2-sigma error bars in the observations are included; the vertical bars are intended to give the approximate altitude range sensed by the particular satellite channel (from Shine et al., [2003]).

Figure 2.5 also illustrates that the observed temperature trends in the lower stratosphere are several K per decade more negative than those calculated by the models using the observed ozone trends. This result is in agreement with other GCM studies [Austin et al., 2001; Langematz et al., 2000, 2003; Rosier and Shine, 2000]. Other effects must be considered to fully explain the discrepancy. For example, it might be (partially) due to the observed increase in lower stratospheric water vapour [Rind and Lonergan, 1995; Forster and Shine, 1999], which has recently been reported [SPARC, 2000]. See Chapter 3 for more details about water vapour changes.

In the upper stratosphere both well-mixed greenhouse gases and ozone contribute in an important manner to the cooling [see also Forster and Shine, 1997; Langematz et al., 2003]. In the upper stratosphere the observations indicate a cooling trend of about 2 K per decade (at 1 hPa), which is confirmed by the models (Figure 2.5).

Stratospheric ozone depletion does not always lead to cooling of the stratosphere. Model simulations of the response to the observed lower stratospheric ozone loss in middle and high latitudes indicate a radiative-dynamic feedback leading to a warming of the middle and upper stratospheric regions, especially during spring [Ramaswamy et al., 2001]. This is corroborated by Antarctic radiosonde observations which indicate a warming trend at ~30 hPa during spring, above the altitudes of the observed ozone depletion where a strong temperature decrease has been observed [Ramaswamy et al., 2001].

Langematz et al. [2003] recently studied the effect of ozone and CO<sub>2</sub> changes on stratospheric dynamics. The observed intensification and lifetimes of the polar vortices in spring are captured by their GCM but with smaller amplitude than observed. Their results suggest that ozone decreases in the polar regions were responsible for enhanced cooling of the polar winter upper stratosphere by a weakening of planetary wave activity and of the meridional residual circulation. A model study of Braesicke and Pyle [2003] demonstrates that mid-latitude ozone loss in the lower stratosphere can also extend the lifetime of the polar vortex in spring. Further this study found that there is no radiative-dynamical amplification of a small change in lower stratospheric ozone at mid-latitudes.

The observed spring-time breakdown of the lower stratospheric polar vortex has been delayed in recent decades, in which stratospheric ozone depletion and subsequent temperature decrease is a major cause [Waugh et al., 1999; Zhou et al., 2000]. A causal linkage to ozone depletion is stronger for the southern hemisphere, while in the northern hemisphere dynamic forcing may also play an important role.

- *The depletion of stratospheric ozone is a major contributor to the observed global-mean lower and upper stratospheric temperature trends over the period 1979–1990.*
- *A stronger and extended prolongation of the polar vortex into spring-time is partly caused by ozone depletion in the lower stratosphere. In the northern hemisphere dynamic forcing may additionally play an important role.*

## **2.5 Impact on the troposphere**

### **2.5.1 Dynamical coupling**

The dynamics of the stratosphere and the troposphere are coupled. Therefore, stratospheric ozone changes not only lead to climate change in the stratosphere but possibly also, via downward coupling, in the troposphere.

The existence of a dynamical coupling between the stratosphere and the troposphere is illustrated by the existence of modes of atmospheric variability that comprise both the troposphere and the stratosphere in mid- and high latitudes of both hemispheres [Hartmann et al., 2000]. These modes are longitudinally symmetric and often referred to as the northern and southern hemisphere annular mode (NAM and SAM). The extent to which these modes contribute to the circulation at a certain moment is given by their indices. A high index mode generally corresponds with strong westerly winds both in the polar stratosphere (i.e. a strong polar vortex) and in the troposphere. How the NAM relates to the well-known modes of the North Atlantic Oscillation (NAO) and the Pacific-North American pattern is still subject of discussion [Wallace, 2000; Ambaum et al., 2001; Wanner et al., 2001]. The annular modes are also referred to as the Arctic Oscillation (AO) and Antarctic Oscillation (AAO).

Baldwin and Dunkerton [1999] have presented evidence for a downward propagation of the NAM index from the stratosphere into the troposphere. Kodera and Kuroda [2000], however, find that the vertical structure of the NAM differs considerably depending on whether it is initiated by a downward propagation of zonal wind anomalies from the stratosphere, or whether it is produced in the troposphere. The first process preferentially occurs in February and March, while the latter occurs in November and December. Thompson et al. [2002] show the existence of a strong relationship between surface temperature extremes in several northern mid to high latitude cities and the strength of the Arctic polar vortex.

In the last three decades the dynamical indices exhibited a positive trend, corresponding to a stronger westerly circulation; for the NAM this trend is shown in Figure 2.6. The corresponding tropospheric circulation change is explaining a large part of the observed warming during NH winter over continents in this period [Thompson et al., 2000]. In addition, Thompson and Solomon [2002] argue that recent trends in the southern hemisphere tropospheric circulation and surface temperatures over Antarctica are consistent with the positive trend in the SAM-index. However, the linkage is weak, and the temperature trend in the troposphere maximises in southern hemisphere summer (December-January), instead of winter.

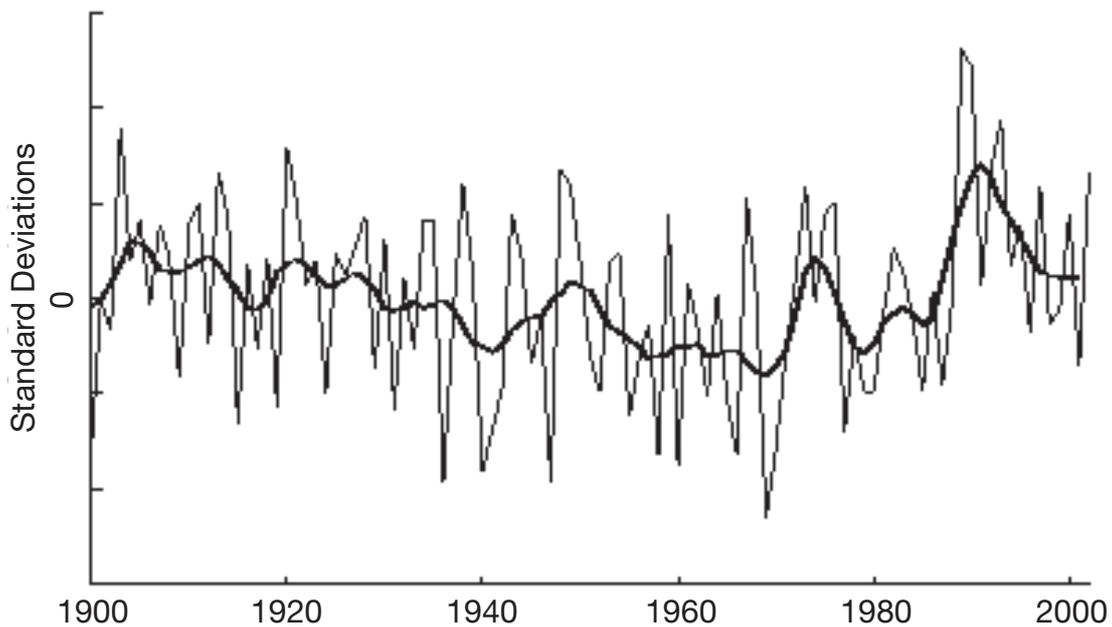


Figure 2.6 January–March means of standardised daily AO index, 1900-2002. Vertical tickmarks are one standard deviation of the daily index. [Source D. Thompson: [www.atmos.colostate.edu/ao/Figures](http://www.atmos.colostate.edu/ao/Figures)]

The increases in the NAM and SAM indices are possibly due to increasing greenhouse gases and ozone depletion. Both changes lead to a colder polar winter stratosphere, a larger meridional temperature gradient in the stratosphere, and, consequently, a stronger polar vortex (see Chapter 3). On the other hand, Hu and Tung [2002] argue that greenhouse gas growth enhances the meridional temperature gradient in the subtropics, and not in the polar regions. By downward propagation, the stronger vortex westerly winds could then lead to stronger westerlies in the troposphere.

Model simulations of the NAM response to increasing greenhouse gases generally show an increase in the NAM index, but this is not true for all models, and the magnitude and character of the changes vary across the models [IPCC, 2001]. The stratospheric ozone decrease has produced a NAM like winter-time response in one model [Volodin and Galin, 1998], but has been found to be relatively unimportant in other models [Graf et al., 1995; Shindell et al., 1999]. The model results leave the question open as to whether a fully resolved stratosphere is needed to accurately model anthropogenic climate change [IPCC, 2001].

The mechanism of downward propagation from the stratosphere to the troposphere is still poorly understood. One possibility is the existence of a meridional cell, by which meridional motions in the stratosphere and the troposphere can induce surface pressure variations and, hence, variations in the NAM index. Using ECMWF re-analysis northern hemispheric data, Sigmond et al. [2003] showed that during winter, low frequency meridional wind variations in the stratosphere generally precede those in the troposphere, by about one day, thus leading to surface pressure and tropospheric zonal wind variations. Another possible mechanism of the downward coupling is the anomalous refraction of upward propagating planetary waves [Hartmann et al. 2000]. It is also possible that the annular modes are just statistical constructs, rather than physically existing modes [Ambaum et al., 2001]. In this case, the NAO, and other more regional climate patterns, would drive the variability and would be more physically meaningful. This does not preclude that there is downward-propagating coupling between the stratosphere and the troposphere. In fact, Ambaum and Hoskins [2002] and Orsolini and Reyes [2003] demonstrate connections between the NAO, a strengthened polar vortex and uplifted polar tropopause, with strong impact on column ozone variability. In addition, Christiansen [2002] argues that the NAM is a physical mode and not only a product of mathematical methods.

- *Stratospheric ozone depletion is changing the stratospheric circulation. There is statistical evidence that these changes propagate downwards into the troposphere, but understanding of the dynamical mechanisms involved, and cause and effect relations is still lacking.*

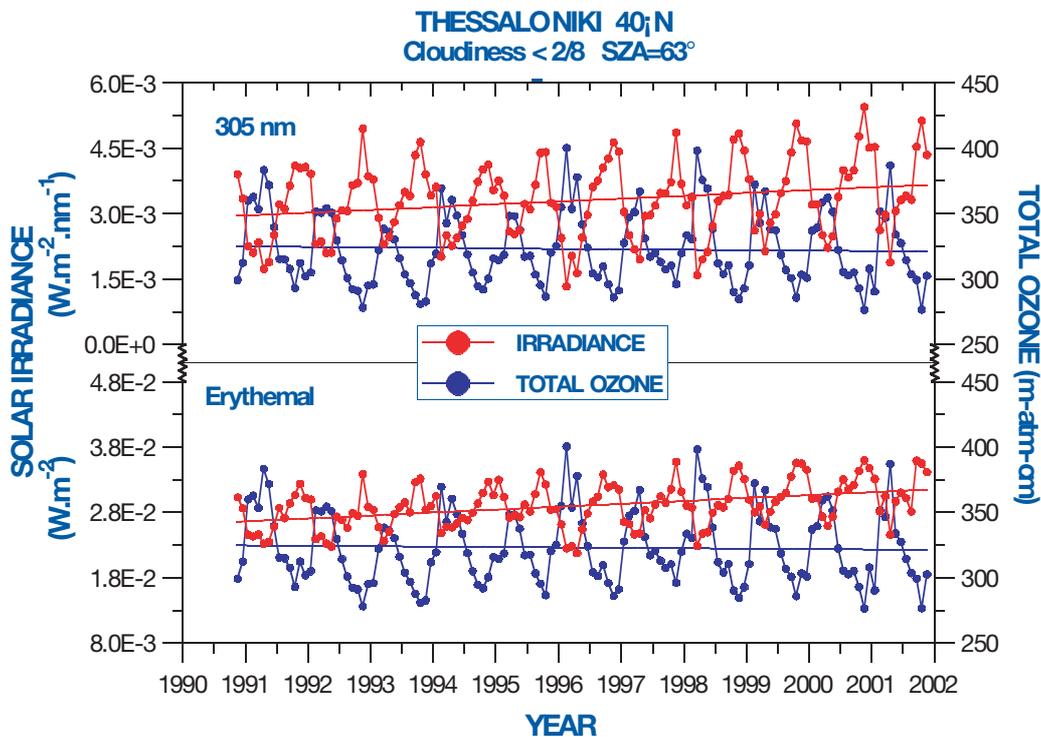
### **2.5.2 Changes in UV radiation**

The major absorber of UV-B radiation in the earth's atmosphere is stratospheric ozone [Chapter 5, WMO, 2003]. It has been well established by numerous measurements at many sites all over the globe that decreases in column ozone lead to increases in surface ultraviolet radiation [WMO, 1999]. Spectral data records from more than 65 stations are now available in international data centers [Kerr et al., 2003]. Presently there are two major databases, where interested scientists can obtain data: the World Ozone and Ultraviolet radiation Data Centre (WOUDC) operated by the Meteorological Service of Canada (MSC) in Toronto, Canada (<http://www.msc-smc.ec.gc.ca/woudc/>) and the European UltraViolet DataBase (EUVDB) in Helsinki, Finland (previously called SUVDAMA-database, <http://www.muk.uni-hannover.de/EDUCE> [Seckmeyer, 2000]).

There is clear evidence that the long-term UV changes are not driven by ozone alone [e.g. Seckmeyer et al., 1994; Zerefos, et al. 2002]. Major other factors are clouds, aerosol particles and ground albedo. All these parameters are strongly altered by climate change [IPCC, 2001] to which stratospheric ozone depletion also contributes. To complicate the interaction, stratospheric ozone itself is strongly influenced by climate change (see Chapter 3).

Enhanced values of UV radiation are continuously observed at high latitudes in the southern hemisphere below the Antarctic ozone hole. Highest biologically weighted UV doses below the ozone hole are typically not observed in October when maximum ozone depletion occurs, but in November and early December when solar elevations are higher and low ozone values still prevail [Diaz et al., 2001; Booth et al. 2001]. Changes in the duration and spatial extent of the Antarctic ozone hole are therefore more important for Antarctic UV levels than the annual ozone minimum [Kerr et al., 2003]. In the Arctic high-elevated UV levels have been observed especially in late winter and early spring due to very low total ozone events [Blumthaler et al., 2001]. Episodes with elevated UV irradiance associated with low total ozone are occurring regularly in mid-latitudes as well [e.g. Seckmeyer et al., 1997; Fioletov et al., 2001].

Direct observations of UV changes are now available from several sites for clear sky conditions. One example is the data set from Thessaloniki, Greece. Figure 2.7 shows the time series of UV irradiance at 305 nm for low cloudiness (< 2/8 cloud cover) conditions, updated to 2002, with an observed trend of 3.5% over the past decade, after removing changes caused by other local factors [Zerefos et al., 2002]. Since ozone has decreased during the 1990s [Zerefos et al., 1998], Figure 2.7 demonstrates how stratospheric ozone depletion has a great impact on UV irradiance. Another example for measured increases of UV irradiance due to ozone decline is the increase in peak UV values in response to decreasing ozone at Lauder, New Zealand [McKenzie et al., 1999]. It should be noted that the length of spectral UV measurement is still too short to derive statistically significant trends [Weatherhead et al., 1998, 2000] due to a combination of variability and autocorrelation in datasets.



PERIOD: 1990-2002			
IRRADIANCE	MEAN	SLOPE	%/decade
305 nm	3.3	0.065	19.7
Erythemal	29.0	0.450	15.5

Figure 2.7 Updated version of the inverse long-term relationship between increases in 305 nm irradiance, the erythemal dose and the decrease in total ozone under clear skies over Thessaloniki [from Zerefos and Meleti, private communication].

Calculations based on pyranometer (total irradiance), total ozone, and other meteorological measurements have been used to reconstruct surface UV irradiance at several mid- to high latitude sites [Krzyscin, 1996; Fioletov et al., 1997, 2001; McArthur et al., 1999; Bodeker et al., 2000; Kaurola et al., 2000; Gantner et al., 2000; Den Outer et al., 2000; Diaz et al., 2000, 2003; Chubarova et al., 2002]. Pyranometer and other meteorological data are used as additional proxies for UV in addition to ozone. The reconstructed data sets, which extend backwards in time at some sites to the early 1960s, show long-term increases in erythemal irradiance of about 6-14% over the last 20 years. For example, in Toronto the number of hours per year with the UV index (the number of hours of UV levels) above 7 has doubled. At some sites approximately half of the changes can be attributed to total ozone changes. Based on these analyses, the increases of UV irradiance derived from the ground-based reconstructed total ozone data are clear indicators of the long-term changes that have occurred since the 1980s.

An increase in UV irradiance impacts tropospheric chemistry, the biosphere and primary organic production (see Diagram 1). It increases the production of the O('D) radical through photo-dissociation of ozone, which in turn produces the OH radical after reaction with water vapour. The global concentrations and distribution of OH control the lifetime and distribution of the chemically active climate gas CH<sub>4</sub> and of the precursors of tropospheric O<sub>3</sub>, for example CO and non-methane hydrocarbons (see Chapter 4). A possible trend in OH is thus important for climate change. However, stratospheric ozone change is not the only factor that influences tropospheric OH. Changes in other chemically active climate species mentioned above also influence OH (see Chapter 4). Even negative OH trends were reported [Prinn et al., 2001], suggesting a minor influence of stratospheric ozone depletion or counterbalancing impacts. However, recent data and modelling analysis of methyl chloroform questions these trends and imply that tropospheric OH remained relatively constant in time over the past decades [Krol et al., 2003].

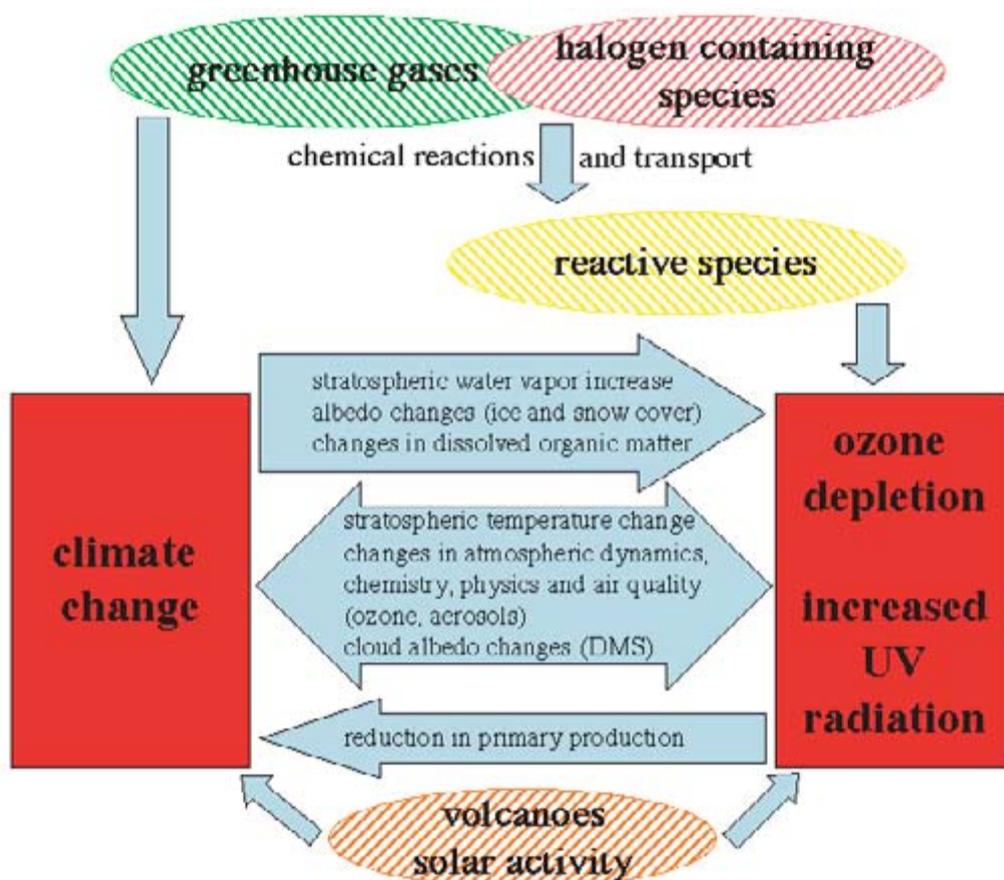


Diagram 2.1 Summary of the stratospheric ozone – climate interactions described in Chapters 2 and 3.

Recent studies confirmed that UV increases have adverse effects on photosynthesis of plants, and can reduce the productivity of oceanic phytoplankton. The latter effect reduces the oceanic sink for carbon in the atmosphere. UV increase can also influence the production of dimethyl sulphide, which is a condensation nucleus of importance on climate [WMO, 2003]. However, the impact on the biosphere is not discussed within this report.

As mentioned earlier, next to the direct effect of stratospheric ozone depletion on UV irradiance, it contributes to changes in other climate parameters, such as aerosol particles, cloudiness and surface albedo (snow and ice cover). Snow cover can increase surface UV irradiance by more than 50% [Degünther et al., 1998; Schwander et al., 1999]. Decreases in sea ice cover over the northern hemisphere have occurred and are likely to continue [IPCC, 2001; Robock, 2000]. Although UV irradiance above the surface is enhanced by snow covered areas, a decrease in sea ice and snow cover will result in an increase of UV dose for organisms living under water and on land areas previously covered by snow.

Aerosol particles of various types have important effects on UV-B transfer in the troposphere, especially in the lower troposphere, because they alter actinic fluxes and enter other important radiation-chemistry interactions [Zerefos et al., 2002].

It is thought that cloudiness has increased by about 2% over the past century and is likely to continue increasing in future [IPCC, 2001], which may significantly impact surface UV irradiance. It is very likely, however, that cloudiness will increase in some regions and decrease in others. Chen et al. [2002] and Wielicki et al. [2002] report unexplained decreases in cloud cover in the tropics.

Finally, more frequent weather extremes, related to climate change may have caused higher UV irradiance during dry spells, damaging some biological species.

As discussed in the previous Sections, it is not possible to quantify the contribution of stratospheric ozone depletion to changes in all these climate parameters and thus to UV changes. Nevertheless, the biological impact of these changes might exceed those caused directly by the expected changes in stratospheric ozone.

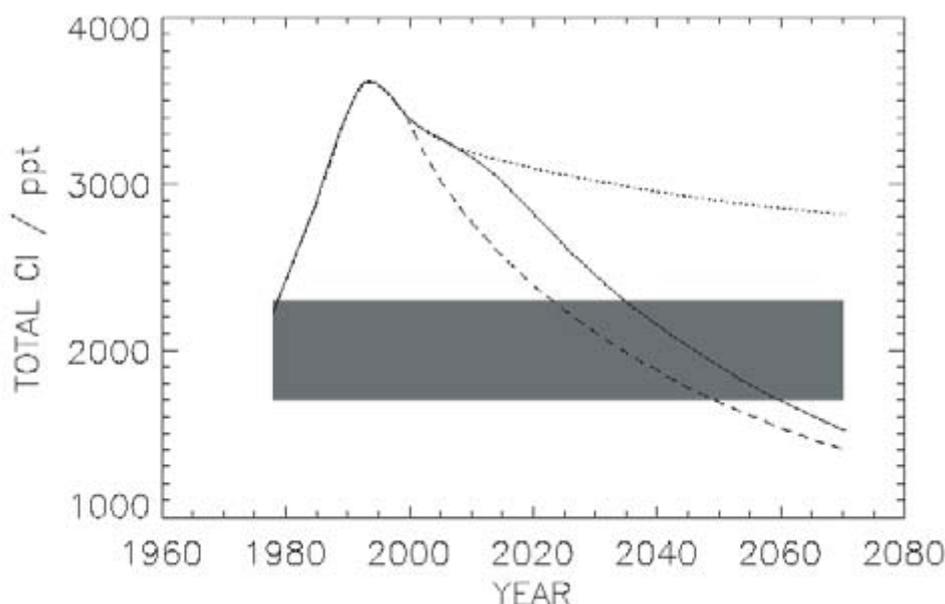
It should be emphasised that the known feedback mechanisms do not end here. Both the changing UV and the changed atmospheric composition are thought to change the biogenic emissions, which in turn influence the climate and stratospheric ozone.

- *Measurement and calculations show long-term increases in erythemal irradiance of about 6-14% over the last 20 years. At some sites approximately half of the changes can be attributed to total ozone changes. It is evident that the long-term UV changes are not driven by stratospheric ozone alone, but also by changes in cloudiness, aerosol particles and surface albedo. For example, it is estimated that cloudiness increased by about 2% over the past century.*
- *The observed decrease of stratospheric ozone and the resultant increase in UV irradiance has affected the biosphere and biogenic emissions. Such UV increases lead to an enhanced OH production, which reduces the lifetime of methane and influences ozone, both of which are important greenhouse gases.*
- *Climate change will have an important influence on future surface UV irradiance. Any changes in stratospheric ozone will modulate the amount of UV penetrating to the troposphere. Further the transmission through the troposphere will be affected by any changes in other variables such as clouds, aerosols, and local albedo (e.g. snow cover) which will be strongly influenced by climate change.*

- *The level of understanding of UV changes and its prediction is high for ozone changes, moderate for aerosols and albedo and low for changes in cloudiness. The level of understanding of the combined effect of all factors is still poor.*

## 2.6 Future changes in halogen species

Future changes in halogens species, well-mixed greenhouse gases ( $N_2O$ ,  $CH_4$ ,  $CO_2$ ) and water vapour are crucial for the development of the ozone layer in the 21<sup>st</sup> century. In a constant climate the ozone layer would recover to pre-1980 levels, mainly driven by the decline of the inorganic chlorine abundance. In order to estimate when this will happen, the future evolution of tropospheric chlorine needs to be known. Engel et al. [2002] considered three different scenarios. Figure 2.8 shows the evolution of total chlorine in the troposphere based on these three assumptions. The grey area indicates the range of chlorine levels in 1980 estimated for the troposphere (upper end) and stratosphere (lower end). Even if all emissions were stopped immediately it would take about 20 years until tropospheric chlorine levels would drop below the 1980 values, whereas this would never happen if the emissions remained at the levels assumed for the year 2000. As the transport of air (and thus the propagation of the chlorine loading) from the troposphere to the stratosphere takes some time (which can be characterised by the age of the air), stratospheric total chlorine loadings were lower than the tropospheric levels in the 1980s, whereas they will most probably be higher by the middle of the 21<sup>st</sup> century. It will therefore take much longer for stratospheric chlorine levels to return to pre-ozone hole values than for tropospheric ones [Engel et al., 2002].



*Figure 2.8* Calculated evolution of tropospheric chlorine based on tropospheric trends of CFCs-11, -12, -113, HCFC-22,  $CCl_4$ , and  $CH_3CCl_3$  measured by NOAA-CMDL (updated from e.g. Elkins et al. [1993], and Montzka et al., [1996] and three different future emission scenarios: a) emissions stop in the year 2000 (dashed line); b) the base scenario given in WMO [1999] (solid line) and c) the emissions remain at the level assumed for the year 2000 in the base scenario (dotted line). The decay of chlorine species is calculated based on the best estimate of atmospheric lifetimes given in WMO [1999]. The grey shaded area depicts the range of total chlorine present in 1980 in the troposphere (upper limit) and the stratosphere (lower limit). The stratospheric chlorine levels for 1980 are based on mean age derived from stratospheric observations of  $SF_6$  and  $CO_2$  (see Engel et al., [2002] for details).

Assuming emissions as given in the base scenario (see Figure 2.8), stratospheric total chlorine levels should return to pre-ozone hole values (the period before 1980) around 2055, and in the troposphere by around 2035. The validity of this estimate depends crucially on the international adherence to the regulations of the Montreal Protocol and its subsequent amendments. Note that these calculations do not take into account possible changes in atmospheric dynamics. If the main transport patterns in the atmosphere change under the influence of a changing climate, as discussed in Chapter 3, this could lead to differences in the future evolution of chlorine loading.

Although there are no indications that the well-mixed greenhouse gases and water vapour will decline, their future development is uncertain, and so are the estimates of future ozone recovery, which are described in Chapter 3.

As halogen input from compounds regulated under the Montreal Protocol begin to decrease, the relative importance of other halogen source gases (e.g. shorter lived compounds) may increase and could lead to a delay of the ozone recovery. It is notable, for instance, that whilst atmospheric chlorine levels have begun to decline, there has been no turnover in atmospheric bromine reported so far, although the rate of increase has slowed in recent years. This is largely due to continuing release from the existing large reservoirs of the long-lived man-made halon gases, and to ongoing emission of short-lived bromine containing constituents. In the future, a decrease in most anthropogenic bromine gases is expected, but it is unknown whether emissions of natural bromine source gases will change.

A number of relatively short lived (lifetimes of hours to a few months) halocarbon gases of (partly) natural origin exist in the atmosphere, that may impact not only the marine boundary layer, but also the upper tropospheric and lower stratospheric ozone (see also Chapter 5). As these gases are short-lived only a part of the halogen content can reach the stratosphere. Under changing climatic conditions, however, changes in tropospheric transport patterns (see section 2.5) and troposphere-stratosphere exchange (see Chapter 5) could alter the fraction that reaches the stratosphere, thereby providing a coupling mechanism between stratospheric ozone chemistry and climate change [WMO, 2003]. Climate change might also change the natural emission rates of some of these gases, either by effects on the biosphere, or through changes in exchange processes with the atmosphere.

Of particular interest are brominated compounds such as the longer-lived methyl bromide (lifetime about 0.7 years), and the shorter-lived gases bromoform, dibromomethane and mixed bromochlorocarbons. Coincident observations of these gases and BrO in the upper troposphere point to the possibility of bromine-ozone chemistry in this region [Pfeilsticker et al., 2000]. There is the hypothesis that additional inorganic bromine in the upper troposphere and lower stratosphere (UTLS) derives from the atmospheric breakdown of short-lived organobromines. Indeed, both Dvortsov et al. [1999] and Nielsen and Douglass [2001] singled out bromoform as an important source of inorganic bromine in the UTLS region.

- *Based on our best estimates about future emissions of halogen containing species, it is expected that stratospheric chlorine levels should return to pre-ozone hole values sometime between 2050 and 2060, which is 15-25 years later than the expected return of tropospheric chlorine to pre-ozone hole values, based on IPCC scenarios. Due to possible changes in atmospheric circulation, continued emissions and a possible influence of short-lived species, as well as the expected increase in greenhouse gas concentrations, this may not necessarily mean a recovery of the ozone layer by that time.*

## 2.7 Conclusions

Stratospheric ozone is an important radiative gas, and changes in stratospheric ozone have both direct and indirect impacts on climate. Two important direct effects involve temperature and UV

irradiance. The observed decrease in stratospheric ozone is a major cause for the observed stratospheric temperature decrease and tropospheric UV irradiance increase. Important indirect effects are related to changes in chemical and dynamic processes both in the stratosphere and troposphere, and to feedback processes induced by these changes. There is statistical evidence of downward propagation of stratospheric dynamic changes into the troposphere, where they influence weather patterns. In addition, climate change induced by changes in stratospheric ozone affects climate variables, such as clouds, aerosol particles, snow and ice cover, which in turn affect stratospheric ozone.

Table 2.2 summarises the complex impact of stratospheric ozone changes on climate. Applying the IPCC [2001] terminology, the direct impacts have a “medium” level of scientific understanding, except for temperature changes in the lower stratosphere, which have a low level of understanding, partly because of the influence of water vapour. All indirect impacts and feedback mechanisms have a “very low to low” level of scientific understanding.

*Table 2.2* Summary of the impact of stratospheric ozone changes on several climate related processes. The uncertainties of the impacts are outlined in the different section of the chapter. Note the large vertical variability of the response of stratospheric ozone decrease on both stratospheric and surface temperatures (see section 2.3). The level of understanding is “low-to-medium” for the stratospheric temperature changes, ‘very low-to-low’ for changes in dynamics, and in UV-B and the biogenic production.

Parameter	Impact of stratospheric ozone decrease	
	Impact	Sign
Stratospheric temperatures		
- upper stratosphere	Large	-
- middle stratosphere	Small	±
- lower stratosphere	Medium-to-large	-
Surface temperatures with respect to ozone decrease in the:		
- upper stratosphere	Small	±
- middle stratosphere	Small	-
- lower stratosphere	Medium-to-large	-
Stratospheric dynamics	Medium-to-large	Not applicable
Tropospheric dynamics	Medium-to-large	Not applicable
Tropospheric ozone	Medium	±
Surface UV-B	Medium-to-large	+
Biogenic production	Medium-to-large	-

The stratospheric ozone – climate interaction is just one part of the changing climate system. Other processes affecting the climate system will have impacts on this interaction. Understanding these impacts is a necessity to predict future ozone amounts and distributions, which is a great challenge for future research.

#### *Acknowledgements*

We thank R. Salawitch, K. Carslaw, Y. Orsolini, R. Müller, M. Prather, D. Lee, and a number of other anonymous reviewers for their valuable and constructive comments that have greatly improved this chapter. We are grateful to R. Zander and K. Shine for providing their results. We also thank M. van Weele and P. van Velthoven for their comments.



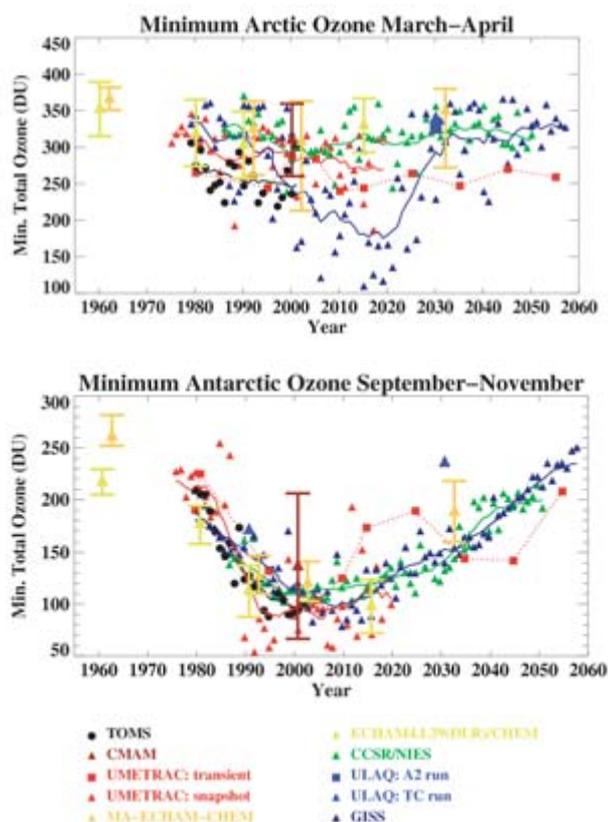
## THE EFFECT OF CHANGES IN CLIMATE ON STRATOSPHERIC OZONE

Authors

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### 3.1 Background

A key science issue is the timing and the “end point” of the ozone recovery irrespective of the Montreal Protocol which yields the central question: How will climate change influence stratospheric ozone? In particular, will climate change affect the recovery of the ozone layer? To answer these questions requires a detailed understanding of relevant dynamical, physical and chemical processes. The current uncertainties in predicting the further development of the ozone layer are clearly illustrated in Figure 3.1 which compares the evolution of Arctic and Antarctic ozone concentrations from several state of the art coupled chemistry-climate models (CCMs) [Austin et al., 2003; see also Section 3.8].



*Figure 3.1* Minimum Arctic (March/April) and Antarctic (September/October/November) total ozone calculated from different coupled chemistry-climate models. The solid lines show running decadal averages for transient model simulations, the symbols with bars indicate the mean and two standard deviations for multi-year time slice runs. For comparison, the TOMS observations (black dots) are included [WMO, 2003].

The concentrations of CFCs in the troposphere have now started to decrease (see Chapter 2) which should cause a decline of stratospheric chlorine concentrations in coming years. Without climate change this would be expected to lead to a recovery of stratospheric ozone concentrations with the most dramatic effects, like the ozone hole, disappearing when chlorine levels return to their natural level. Future changes in bromine contents, particularly in the lower stratosphere, could complicate this expected recovery of the ozone layer. However stratospheric ozone is influenced by a variety of dynamical, physical, and chemical processes. The increase of greenhouse gases (including ozone and CFCs) affects both tropospheric and stratospheric temperatures directly via changes in heating and cooling rates, leading to a warming of the troposphere and an overall cooling of the stratosphere. Long-term observations clearly indicate these temperature changes. The temperature changes influence ozone by changing the rate of chemical reactions. Furthermore, lower temperatures in the stratosphere lead to increased Polar Stratospheric Cloud (PSC) occurrence and more ozone destruction due to heterogeneous chemistry. Increases of natural methane emissions caused by tropospheric warming could also raise stratospheric water vapour concentrations leading to a higher temperature threshold for PSC existence, and thus more PSCs. Atmospheric winds are also affected by temperature changes, for example the strength of the polar stratospheric vortex would be stronger if the stratosphere cooled. Changes in stratospheric dynamics alter transport processes, not only in the stratosphere, but also in the troposphere. The vertical exchange of air masses between the stratosphere and the troposphere is also affected with consequences for the residence time of trace gases (e.g. CFCs) and for the ozone concentration and distribution in the stratosphere.

Further warming of the troposphere due to the greenhouse effect may change the dynamics of the troposphere including the forcing and upward propagation of planetary waves which will change stratospheric dynamics, e.g. the Brewer-Dobson circulation. The Brewer-Dobson circulation is driven to a large extent by wave forcing. This conversely affects the transport of atmospheric tracers including ozone. Stratospheric planetary wave drag drives the winter-time ozone build up in the extra-tropics, i.e. changes in wave activity would lead to changed transport.

There is also statistical evidence for a relationship between the strength of the stratospheric polar vortex in northern winter and the index of the tropospheric North Atlantic Oscillation (NAO) (i.e. potential vorticity (PV) values larger than climatological mean values are connected with a positive index of the NAO). Furthermore, a statistical relationship has been found between total ozone and tropopause pressure, but the physical mechanisms behind this relationship is not yet entirely clear (see Section 2.8). Observed increases in tropopause height at European stations during recent years (decades) seems to be linked to long-term changes in the atmosphere's dynamical structure, related to the NAO. These dynamical changes, whether related to anthropogenic changes or not, contribute significantly to the decrease in total ozone over Europe but lead to a smaller decrease over the North Atlantic ocean.

These various statements indicate that there are key uncertainties, which currently make it difficult to give reliable answers to the questions about ozone recovery. In this chapter, the mechanisms by which climate change may impact ozone concentrations are discussed along with uncertainties and requirements for future investigations.

## 3.2 Changes in stratospheric constituents

### 3.2.1 Well-mixed greenhouse gases ( $CO_2$ , $CH_4$ , $N_2O$ )

A detailed description of recent changes of well-mixed greenhouse gases (WMGHGs) can be found in IPCC [2001]. Atmospheric concentrations of these gases have increased significantly since 1750 ( $CO_2$ : 31%;  $CH_4$ : 150%;  $N_2O$ : 16%). Emissions are still increasing and there is no indication of a future reduction of their atmospheric concentrations. Future emission scenarios cover a wide range and although climate models generally predict a continued warming of the troposphere and cooling of the stratosphere, large uncertainties remain. Therefore the question still remains as to which way and how strong the atmosphere will react. There are a lot of direct and indirect effects via radiation transfer and chemical processes which will result in dynamic (temperature) changes of the atmosphere. Although well-mixed in the troposphere, these gases are not necessarily well-mixed in the stratosphere. They have distinct vertical profiles and a time lag compared to tropospheric values which is important for the atmospheric radiation budget. Radiation transfer strongly depends not only on the vertical distribution; furthermore, changes in the radiation budget are also dependent on the altitude at which changes occur.  $CO_2$  mainly affects temperature, whereas  $CH_4$  and  $N_2O$  also have a direct effect on chemistry.

- *The rate of future enhancement of WMGHG emissions, particularly of  $CO_2$  is uncertain. The question still remains as to how strong the stratosphere will cool down due to future emissions.*

### 3.2.2 Water vapour

An assessment of upper tropospheric and stratospheric water vapour distribution and trends was published by SPARC [2000, see Chapter 2]. A brief summary was given by Kley and Russell III [2001]. A considerable amount of data has been collected, mainly by the radiosonde network (world-wide) and from satellite instruments (in particular HALOE on UARS, since 1991). But there is only one nearly continuous time-series of stratospheric water vapour of about 20 years duration from Boulder [Oltmans and Hofmann, 1995; Oltmans et al., 2000] (see Figure 3.2). An approximately 1 ppm rise of stratospheric water vapour is found at this location since 1980, a dramatic increase in relation to the current stratospheric mixing ratios of typically 4-6 ppmv [e.g. Rosenlof et al., 2001]. Currently, it is not clear if there is a global trend. Simultaneously, an increase of about 0.5 ppmv has been observed for methane mixing ratios in the troposphere which can explain, at most, half of the increase in stratospheric water vapour. Attribution of the rest of the trend is still an open question. Processes which determine the water vapour distribution could have changed due to the greenhouse effect, e.g. the Brewer-Dobson circulation; the wave induced mixing in the stratosphere; the upward extension of tropospheric circulation in the lowest few kilometres of the stratosphere; convection; cirrus properties. If a model demonstrates a trend, it is usually because their tropical tropopause warms, but this is not observed and is therefore probably due to incorrect physics. This indicates deficiencies in the modelling of chemistry-climate interactions and currently makes it difficult to make reliable predictions of future trends.

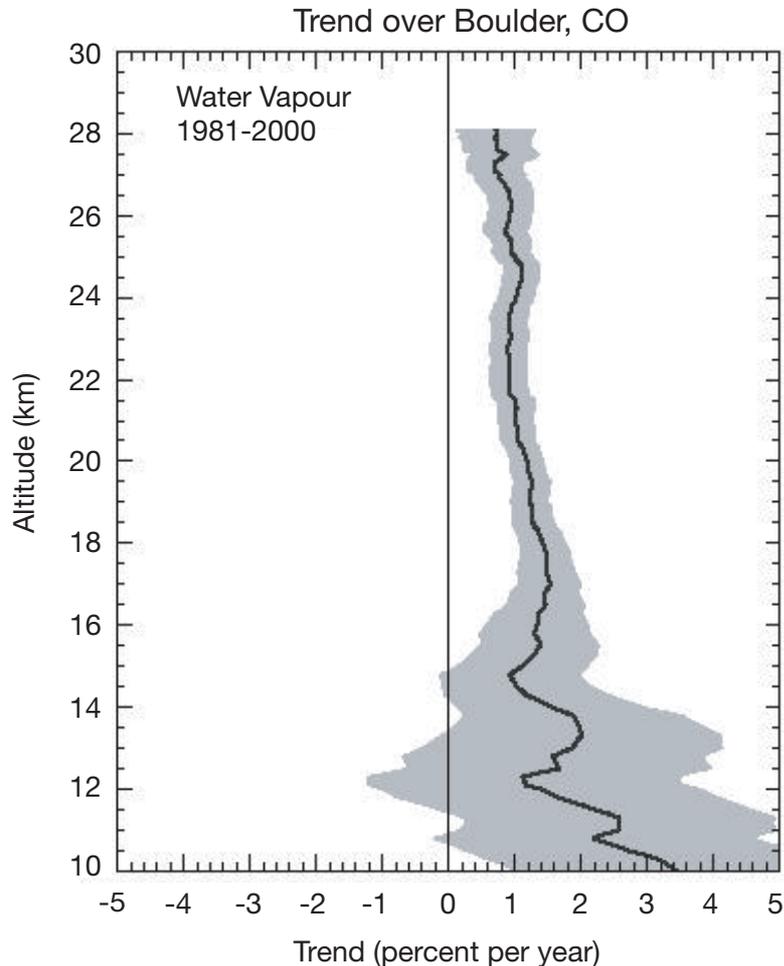


Figure 3.2 Water vapour trend in percent per year as a function of height, for the period 1981-2000, determined from measurements at Boulder.

- *The recent increase of stratospheric water vapour is not understood in detail. Models are not able to reproduce the observed trend which indicates gaps in the knowledge of related processes. Therefore estimates of future trends are currently highly unreliable.*

### 3.2.3 Ozone

Ozone is also an important greenhouse gas. Changes in ozone concentrations are spatially variable, not only in the vertical but also in the horizontal. The radiative role is more complex than for the WMGHGs. During the last three decades tropospheric ozone has increased at most of the European stations [SPARC, 1998; WMO, 2003]. In the stratosphere, ozone has decreased globally (see Chapter 2 and Figure 3.8), in particular over the Antarctic in spring-time (the “ozone hole”). The latter changes caused a reduction of the south polar stratospheric temperatures during this season [e.g. Randel and Wu, 1999]. One point which requires further investigation is that tropospheric ozone increases should cool the stratosphere as well and could be a large feedback in the future [WMO, 2003].

- *The impact of enhanced tropospheric ozone concentrations on stratospheric dynamics and radiation is not clear.*

### 3.2.4 Aerosols

Other anthropogenic forcing mechanisms in the atmosphere could also play a role in future ozone trends. An example is the potential climate forcing of tropospheric aerosols, and the link of tro-

ospheric sulphur with lower-stratospheric sulphuric aerosols [Pitari et al., 2002]. Not only heterogeneous chemical reactions on or within the particles are important, but also radiation changes due to aerosols. They can strongly influence dynamical processes, e.g. disturb the circulation patterns and the temperature, which themselves impact chemical processes. An increase of the lower-stratospheric sulphuric aerosols may be expected as a result of globally and regionally changing emissions of sulphur dioxide in future years, mainly as a consequence of rapidly growing anthropogenic sulphur emissions in developing countries [IPCC-SRES, 2000; IPCC-TAR, 2001]. Changes in stratospheric aerosol loading will have an impact on the ozone layer (see Chapter 5). Model simulations indicate that a significant increase in the surface area density of sulphuric acid aerosol in the lower stratosphere enhances ozone depletion (Figure 3.3), via heterogeneous chemistry and consequent modification of the relative weights of  $\text{NO}_x$ ,  $\text{HO}_x$ ,  $\text{Cl}_x$ , and Brx catalytic cycles for ozone depletion. Pitari et al. [2002] have calculated that the impact of this aerosol surface area density change on global ozone is about  $-0.3\%$ . This is smaller than the calculated global ozone change produced by increasing polar ozone depletion, due to stratospheric cooling forced by future climate changes, but is still of the same order of magnitude [e.g. Austin et al., 2003].

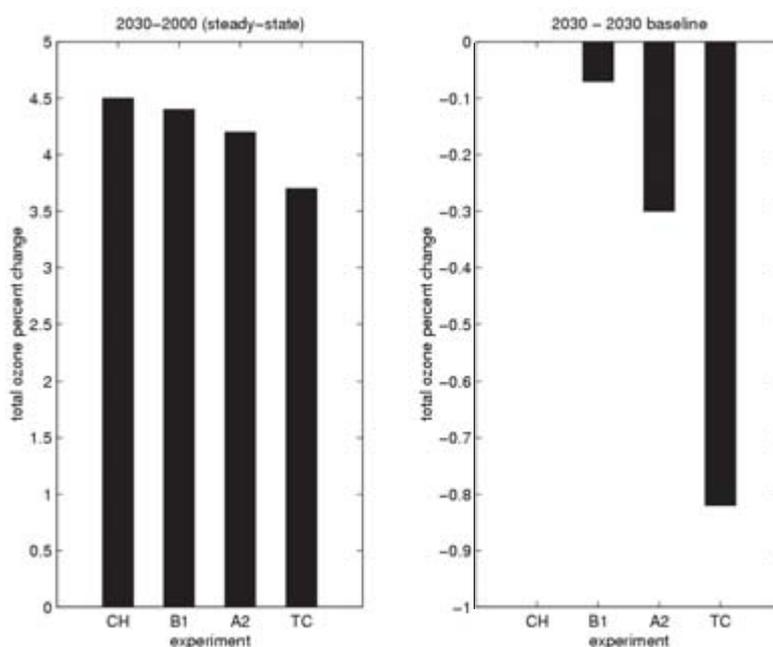


Figure 3.3 Calculated steady-state total ozone column changes ( $90^{\circ}\text{S}$ - $90^{\circ}\text{N}$  global annual mean) for different future scenarios in 2030 with respect to 2000 (left panel) and for 2030 with respect to the “CH” case (right panel). “CH” refers to update of chemistry boundary conditions in future years, while aerosol, temperature and circulation are kept unchanged with respect to 2000; cases “B1” and “A2” are as “CH” but also include update of  $\text{SO}_2$  surface fluxes according to IPCC emission scenarios B1 and A2, respectively (i.e., lower and upper limit emissions respectively). Case “TC” is as “A2” including in addition climate forced changes of temperature and circulation [from Pitari et al., 2002].

- An impact of the potential increase of sulphuric acid aerosols due to changing emissions of  $\text{SO}_2$  and carbonyl sulphide (COS) on stratospheric ozone is expected, the strength of which is uncertain.

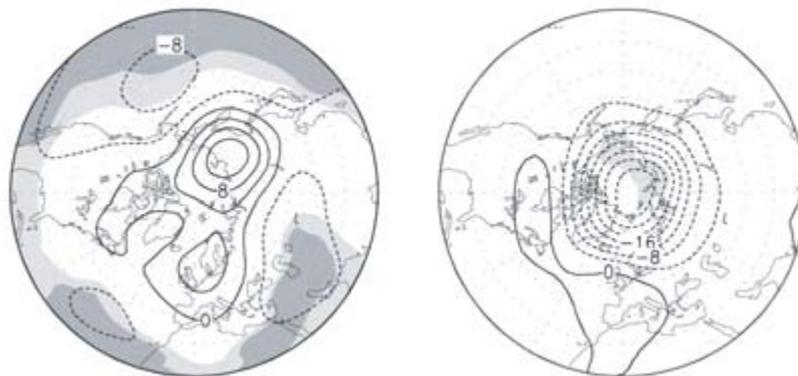
### 3.3 Changes in stratospheric temperature and circulation

Over the last few decades the stratosphere has exhibited a long-term cooling trend due to a combination of WMGHG, ozone and water vapour changes. A comprehensive assessment of stratospher-

ic temperature trends was presented in WMO [1999] and Ramaswamy et al. [2001] with trends updated in WMO [2003]. Updated satellite and radio-sonde trends are summarised in Figures 2.7 and 3.5 [from Shine et al., 2003]. The annual mean trend is for a statistically significant lower stratospheric cooling in the extra-tropics and high latitudes of greater than 0.4 K per decade. Above the lower stratosphere the temperature trend is less dependent on latitude: there is a relative minimum in cooling of the middle stratosphere (around 35 km) with a maximum in cooling at the stratopause of around 2.5 K per decade. Outside the polar regions and lower stratosphere, the trends are found to be largely independent of season. In the southern polar lower stratosphere the largest trends are seen during spring, largely as a result of ozone depletion [WMO, 2003].

However the high dynamical variability during northern winter and spring makes the determination of significant changes (trends) difficult there [see Chapter 3 in WMO, 2003]. During the 1990s, several cold polar winters, including the winters of 1994/95 and 1995/96 and the cold spring in 1997, were followed by two relatively disturbed and warm winters (1997/98 and 1998/99). In the Decembers of 1998 and 2001, two unusually early major stratospheric warmings occurred [Naujokat et al., 2002]. Inclusion of these recent years significantly impacts the long-term trend estimates for the Northern Hemisphere [WMO, 2003]. Consistent with the temperature change, the annual mean change in the geostrophic zonal wind component shows an increase throughout the lower stratosphere north of 50°N and a decrease equator-wards [Langematz et al., 2003].

A further issue of stratospheric change discussed in the recent literature is the possibility of alterations in the intensity and the lifecycle of the stratospheric polar vortices [e.g. Waugh et al., 1999; Newman and Nash, 2000; Hu and Tung, 2002; Randel et al., 2002; Section 2.5.4 in EC, 2001]. Figure 3.4 shows the decadal trend at about 30 hPa geopotential height, derived from the Berlin stratospheric analyses [Langematz et al., 2003] for January (left panel) and March (right panel) for the years 1979-2000. While in mid-winter an increase in geopotential height is observed from mid- to high latitudes, spring is characterised by a zonally symmetric decrease of up to 30 dam over the North Pole, indicating an intensification of the northern hemisphere polar vortex in spring. In contrast to January, this change pattern is robust and locally statistically significant at the 95% significance level. An estimate of the polar vortex breakdown date according to Waugh et al. [1999] using the Berlin analyses, shows an increase of the polar vortex lifetime of 8 days between the periods 1976-1985 and 1990-2001. This result is qualitatively consistent with the analysis of Zhou et al. [2000], but the values are smaller. Here, it must be recalled that Zhou and co-workers employed NCEP data and for a different period. The prolonged vortex is an important issue because it can strongly influence and enhance processes like denitrification. Moreover, Rex et al. [2002] analysed temperature changes of the Arctic vortex and found that the coldest Arctic winters are getting colder, which is of course related to the intensification of the vortex circulation.



*Figure 3.4* Northern hemisphere decadal geopotential height change at 30 hPa for January (left panel) and March (right panel), derived from the Berlin stratospheric analyses for the period 1979-2000 (contour interval 4 dam per decade). Shaded areas denote regions where the results are significant at the 99% (dark grey) and 95% (light grey) levels [from Langematz et al., 2003].

Much less clear is whether the observed lower stratospheric cooling trend will continue into the future and whether it will lead to a more stable polar winter vortex over the Arctic. Changes of the strength of the polar vortex would also alter the conditions for propagation and refraction of planetary waves, which itself would influence the dynamics of the polar vortex. A stable Arctic vortex would imply more PSCs, which could yield substantial spring-time ozone depletion, similar to what is observed in the Antarctic ozone hole. While most winters in the 1990s had a very cold and stable Arctic vortex and substantial Arctic ozone depletion was observed, e.g. in the European campaigns EASOE (1991/92) and SESAME (1994/95), the vortex was warmer and less stable in some of the most recent winters (e.g. 1998/99, 2001/02). Long-term data, e.g. from the Berlin group, show a strong non-linear connection between the quasi-biennial oscillation (QBO) of equatorial winds, the 11-year solar activity cycle (see Section 2.3), and the stability of the Arctic vortex [Labitzke and van Loon, 1994, 2000]. Although this complicated non-linear connection is of paramount importance for the year to year variability of polar winter and spring temperatures, our understanding of the underlying processes is poor. Predictions of the future development of the Arctic vortex (e.g. most current model simulations) cannot be reliable, as long as the predictive tools cannot describe the observed past.

Over the next century, carbon dioxide increases will continue to cool the stratosphere, especially above 30 km. However in the lower stratosphere, the slight cooling from CO<sub>2</sub> could be partially offset by the warming of decreasing halocarbons and ozone recovery. Further tropospheric ozone increases may be expected to continue to cool the stratosphere. The largest uncertainty is due to the unknown future of the stratospheric water vapour trend in the lower stratosphere. As the causes of the water vapour trend in the lower stratosphere are largely unknown, future water vapour scenarios cannot be calculated and its effect on future stratospheric temperatures remains open.

- *Mean stratospheric temperatures are decreasing, particularly those during cold Arctic winters. Changes in the strength and the temperature of the polar vortices (i.e., prolongation and cooling) have been detected. The future development in the lower stratosphere is highly uncertain, especially in the northern hemisphere. This is one of the largest uncertainties in predicting the recovery of the stratospheric ozone layer.*

### **3.4 Changes in the utls region, stratosphere-troposphere exchange, tropopause height, planetary wave activity**

A well known and well documented example of the interaction of the troposphere and the stratosphere, is the effect of tropospheric weather systems on lower stratospheric ozone (and other parameters of the lower stratosphere), where high total ozone is associated with tropospheric cyclones with a low tropopause, and low total ozone with anti-cyclones with a high tropopause [e.g. Steinbrecht et al., 1998; Appenzeller et al., 2000; Weiss et al., 2001].

Data from a variety of sources indicate an unprecedented warming of the Earth's surface over the last 30 years by about 0.1 K per decade globally, and by about 0.6 K per decade over Europe (annual mean; IPCC [2002]). Radiosonde data from Central Europe, e.g. Hohenpeissenberg, show a warming of about 0.6 K per decade throughout the troposphere. The entire lower stratosphere at northern mid-latitudes, however, has been cooling by about 0.5 K per decade over the last 20 years (see Figure 3.5). At least over central Europe, these changes go hand in hand with an increase of the tropopause height, e.g. by around 120 m per decade (annual mean) at Hohenpeissenberg (Figure 3.6). Similar values are found at other northern hemisphere stations [Forster and Tourpali, 2001]. Weiss et al. [2001] studied ozone profiles at

Payerne (Switzerland) from 1967-2000 and showed that the tropopause height changes are correlated with ozone changes in the lowermost stratosphere, but not above. They found that the dynamical influence on calculated ozone trends is clearly confined to the lowermost stratosphere. Ambaum and Hoskins [2002] outlined how an intensified polar vortex could induce a lifting of the Arctic tropopause. They showed that when the polar vortex is stronger than normal, the total ozone column decreases over much of the Arctic, in association with a higher than normal tropopause. Santer et al. [2003] showed that changes in tropopause height may be a useful “fingerprint” of anthropogenic effects on climate. They analysed long time series from NCEP and ERA reanalyses and found an overall increase of tropopause height which is primarily thermally driven, and is an integrated measure of the anthropogenically-forced warming of the troposphere and a cooling of the stratosphere. The basic mechanism between ozone abundance and tropopause altitude still remain in question: is it the shrinking/expanding of the tropopause height because of low/high pressure systems, or is it caused by changes in the frequency of the advection of air masses of tropical origin? Possibly, these two processes are not independent, i.e., a high pressure system could lead to advection of air from the (sub) -tropics to the extra-tropics.

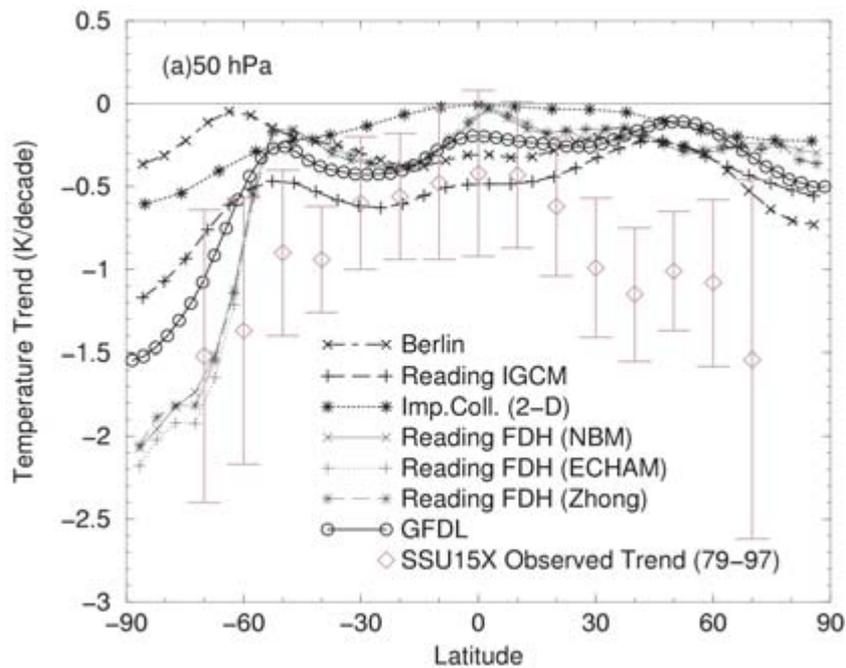
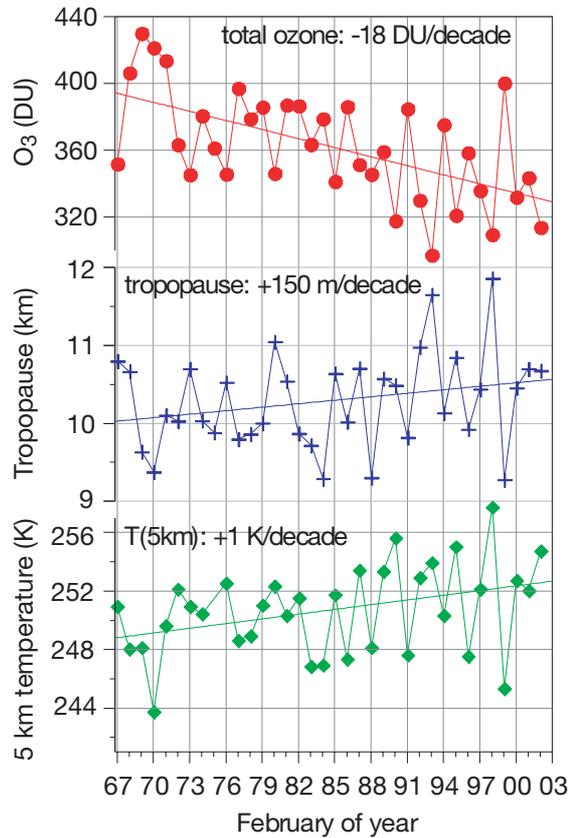


Figure 3.5 Annual and zonal mean temperature trends at 50 hPa for models using imposed height resolved ozone trends. The trend from SSU Channel 15X is also shown. The 2-sigma error bars in the observations are included. The peak of the SSU Channel 15X weighting function is at about 46 hPa [from Shine et al., 2003].



*Figure 3.6* Inter-annual variability and long-term trends in February monthly means of total ozone (top), tropopause height (middle) and temperature at 5 km altitude (bottom) over Hohenpeissenberg. The high correlation between 5 km temperature and tropopause height on inter-annual and decadal time scales points to a very strong link between these parameters. At the same time a strong anti-correlation is evident between total ozone and tropopause height, again on inter-annual and longer time-scales. It is estimated that about two thirds of the long-term total ozone decrease over Hohenpeissenberg is caused by anthropogenic chlorine, one third is attributed to the observed increase of tropopause height [updated from Steinbrecht et al., 1998].

Possible climate dynamical contributions discussed in the recent literature include not only the long-term changes in the position of the tropopause [Steinbrecht et al., 1998; Appenzeller et al., 2000; Wong and Wang, 2000; Forster and Tourpali, 2001; Steinbrecht et al., 2001], but also a long-term change of the preference of climate patterns [Appenzeller et al., 2000; Thompson et al., 2000], a long-term change in the large scale diabatic circulation (related to a change of the northern hemisphere upward propagating wave activity, Fusco and Salby [1999]) or a change of isentropic transport of ozone from the tropics [e.g. Reid et al. 2000]. It is clear that these possible changes are not independent of each other [Staehelin et al., 2002].

- *There is evidence that changes in tropopause height are related to climate change. It contributes to ozone variability and therefore to regional ozone trends. Future impacts cannot be assessed since the basic mechanisms are not understood in detail.*

The time-scale for the removal of CFCs from the stratosphere might be determined by the rate at which air is transported from the troposphere into the stratosphere, which obviously will affect the recovery of stratospheric ozone. In a doubled CO<sub>2</sub> climate simulation, Rind et al. [2001] showed that the tropical transport from the troposphere into the stratosphere is enhanced by 30% due to an increase in the stratospheric subtropical residual circulation. They ascribed this change, not to an increase in the planetary wave energy or Eliassen-Palm flux, but to a change in the

refraction of the wave energy in the upper troposphere, leading to increased Eliassen-Palm flux convergence in the lower stratosphere. Butchart and Scaife [2001] calculated with a climate model an increase of mass exchange between the troposphere and the stratosphere of 3% per decade in the first half of the twenty-first century due to increased greenhouse gas concentrations. This effect is mainly caused by enhanced planetary wave activity in the stratosphere. This of course would also impact the transport within the stratosphere itself.

- *Ozone is transported to mid- and high latitudes by the diabatic circulation which is driven by tropospheric wave activity. Climate change related changes in the forcing and propagation of planetary waves will therefore modify the ozone distribution. The strength of the impact is currently undefined.*

A region of special interest is the tropical tropopause. A number of papers [e.g. Sherwood and Dessler, 2000, 2001] argued that the division between the troposphere and the stratosphere, particularly in the tropics, cannot be defined as an infinitely thin line, but occurs over a layer that is several kilometres thick. Therefore the lower latitude region between the 150 and 70 hPa pressure layers is named tropical tropopause layer (TTL). The TTL can be thought of as a transition layer between the upper troposphere and the lower stratosphere. It determines the entry level value of many short-lived chemical species as well as water vapour to the stratosphere. Changes in the TTL are important since they cause changes, for example in fluxes of water vapour and short-lived substances, which are highly significant for the stratosphere. The current knowledge of the transport mechanisms across the TTL is still incomplete. This strongly limits the ability to predict future changes of stratospheric composition.

- *It is expected that future changes in the TTL will alter the fluxes of water vapour and other trace gases from the upper troposphere into the lower stratosphere. The sign of this change is unknown.*

A detailed description of dynamical processes, which may contribute to stratospheric ozone change, are discussed in detail in WMO [2003, Chapter 4.6]. It includes the effects of changes in planetary wave drag, the effects of tropospheric circulation and tropopause changes as well as hemispheric variations and annular modes.

### **3.5 Impact of climate change and dynamics on chemistry**

The structure and dynamics of the stratosphere, including the transport of chemical substances, have strong impacts on chemical processes. The inter-annual variability in the winter/spring ozone distribution is much larger in the northern hemisphere than in the southern hemisphere, reflecting the greater dynamical variability of the northern hemisphere stratosphere. Changes of the dynamics, i.e. variability and trends, have direct consequences for chemical processes. One example is the detected delay in the breakdown of the polar vortices in spring-time in both hemispheres (prolongation of the vortices), which extends the cold winter season and therefore the chemical ozone loss.

An extraordinary dynamic situation was observed in the Antarctic stratosphere in September 2002, which has surprised the scientific community. A major stratospheric warming was generated by enhanced planetary wave activity, which produced a split of the polar vortex into two smaller vortices. Much higher temperatures and, therefore, reduced chemically induced ozone losses were detected in the south polar region than is usual (Figure 3.7). Comparable events are normally found only in winter in the northern hemisphere and have not been observed in the southern hemisphere during the last 25 years, e.g. in the NCEP analyses. Although a plausible explanation for the origin of this unusual strong planetary wave activity in the southern hemi-

sphere cannot currently be given, it illustrates impressively the strong impact of dynamics on polar ozone abundances.

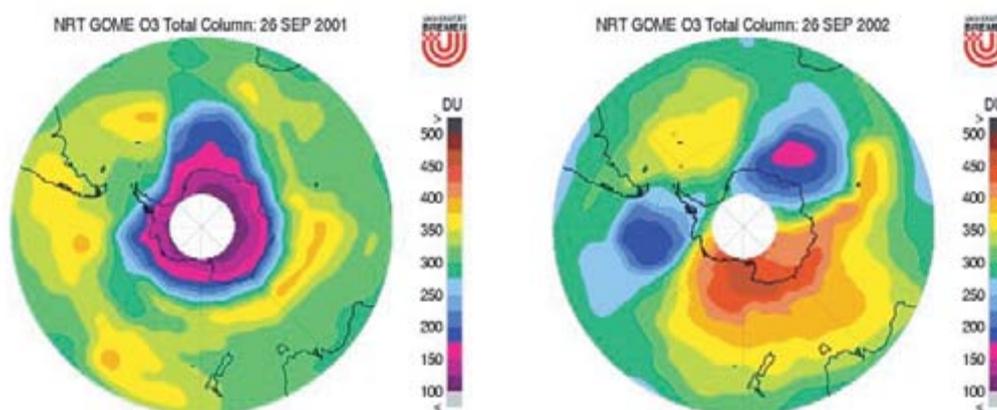


Figure 3.7 Total ozone columns (in DU) over Antarctica in September 2001 (left) and 2002 (right) as measured from the GOME instrument on satellite ERS-2 (pictures provided from the IUP, University Bremen). White coloured areas indicate data gaps.

- *The dynamic situation in the Antarctic stratosphere in spring-time of the year 2002 impressively shows the interactions of dynamical and chemical processes on ozone, even in the southern hemisphere. The possibility of a major warming event in the southern hemisphere has not been seen by any model to date, which points to gaps in our understanding of stratospheric dynamics.*

During summer, significant decreases of stratospheric temperature due to WMGHGs are most obvious since atmospheric dynamics play a minor role. Therefore the impact of temperature changes on natural chemistry (e.g.  $\text{NO}_x$  and  $\text{HO}_x$  chemistry) can be identified more easily: cooling of the stratosphere yields an increase in ozone which is caused by simple gas phase reactions [WMO, 2003]. In the WMO assessment, it was also emphasised that the strongest effect of future stratospheric cooling was to accelerate the expected recovery of ozone in the upper stratosphere. Predictions from 2-D models, which include stratospheric cooling due to enhanced WMGHG concentrations, show ozone in the  $60^\circ\text{N}$ - $60^\circ\text{S}$  band rising above its 1980 value by approximately 2030 [WMO, 2003].

- *Expected radiative cooling of the middle and upper stratosphere tends to accelerate the recovery of ozone in these altitude regions.*

### 3.6 Past changes in polar ozone

Arctic ozone loss during winter is strongly related to the occurrence of PSC particles and aerosols, as well as the duration of the polar vortex. PSCs and aerosols influence the ozone budget in the Arctic due to both direct and indirect effects on the halogen compounds involved in ozone-destroying catalytic cycles. Heterogeneous chemical reactions on or within the particles convert relatively non-reactive chlorine compounds (such as  $\text{ClONO}_2$  and  $\text{HCl}$ ) into reactive species that can enter into the ozone-destroying catalytic cycles. The duration of the ozone-destroying catalytic cycles is extended if sedimentation of large nitric acid-containing PSC particles occurs during winter (so called denitrification). Such denitrification increases the lifetime of reactive chlorine species because it slows down chlorine deactivation. The significance of denitrification for ozone depletion in the Arctic and the high sensitivity to temperature changes has been demonstrated, e.g. by Rex et al. [1997] and Waibel et al. [1999], who concluded that

increased denitrification in future colder winters may delay the recovery of ozone until later in the century.

For both effects, the composition and phase of the PSCs determining the rate of heterogeneous reactions and controlling the process of denitrification are themselves controlled by meteorological conditions (i.e. temperature). As the Arctic polar vortex is generally warmer and less persistent, episodes of denitrification have been sporadic compared to the Antarctic. However during several Arctic winters in the 1990s the conditions were suitable for widespread PSC formation (see [Section 3.3 in EC, 2001] for an overview of the PSC measurements). Recently, Mann et al. [2002] showed with a particle trajectory model coupled to the 3-D chemistry transport model (CTM) SLIMCAT that selectively nucleated PSC particles Nitric Acid Trihydrate (NAT) need about 8 days to grow to large particles (NAT-rocks) which were observed during the SOLVE THESEO-2000 campaign [Fahey et al., 2001] causing substantial denitrification in the Arctic stratosphere. Such a long growth time can only be achieved in conditions in which the cold pool of the temperature field is concentric with the polar vortex. Thus, these barotropic conditions seem to be a prerequisite for the growth of large NAT particles to denitrify the lower Arctic stratosphere substantially. The evolution of these large NAT particles and their effect on denitrification can be calculated by models (such as that used by Mann et al. [2002]) provided the nucleation rate of NAT particles can be defined. The nucleation mechanism for low number density NAT clouds is uncertain, but needs to be defined in order to make reliable predictions of denitrification. Some nucleation mechanisms have been suggested but remain to be fully evaluated [Fueglistaler et al., 2002a, b; Dhaniyala et al., 2002].

Widespread and persistent denitrification was observed in the winters 1994/95, 1996/97 and 1999/2000. For 1994/95 conditions, Waibel et al. [1999] have achieved good agreement with single balloon observations, employing a quasi 3-D model and prescribed NAT particle number densities. Denitrification at the scale observed leads to increased ozone loss and consequently the strongest ozone losses in past Arctic winters has been quantified by different approaches for these denitrified winters. In 1999/2000 ozone loss reached 70% at some altitudes and the vertically integrated loss in the total column amounted to about 30% in 1994/95, 1996/97, and 1999/2000. Little or no significant ozone loss was observed in the warmer winters of 1997/98 and 1998/99 (see [Section 3.5 in EC, 2001] for an overview of the approaches to determine ozone loss and the quantified ozone losses during the winters in the 1990s).

Comparisons of the calculated model ozone losses (3-D CTMs or box models) show that under certain conditions the rate of chemical ozone loss is underestimated by current chemical models if realistic halogen abundances are assumed [e.g. Rex et al., 2000]. The largest discrepancies are reported for cold twilight conditions in late January, nearly independent of chlorine activation rates in the models [e.g. Becker et al., 1998]. The reason for the discrepancy is not understood. In contrast to this underestimation of the ozone loss, some models tend to overestimate the observed loss in winters in conditions that are marginal for PSC formation (e.g. 1997/98) [Guirlet et al., 2000] as a result of an apparently unrealistic modelled chlorine activation.

A substantial fraction of the inter-annual changes of total ozone column arises from year-to-year dynamic variability in ozone transport. On the other hand, modifications of the dynamics, e.g. vortex stability (persistence), or the temperature field, directly influence the chemical ozone loss. The relative influences of transport and chemistry on Arctic ozone during the 1990s has been investigated in a multi-annual integration of the SLIMCAT 3-D CTM [Chipperfield and Jones, 1999]. The results show that inter-annual differences in ozone are dominated by dynamical variations and that those conditions which lead to larger chemical depletion (i.e. a cold stable vortex) are also those which lead to low ozone columns through transport. Recently, a number of observationally based studies [e.g. Andersen and Knudsen, 2002] concluded that inter-annual variability in chemical loss and dynamical supply of ozone are about equally important for the overall variability of the late winter Arctic ozone column (Figure 3.8). Moreover, the coupling between

vortex concentricity and the rate of denitrification is another example of dynamical-chemical coupling. These results emphasise the important changes that may occur to Arctic ozone through dynamical changes (e.g. induced by changes in greenhouse gas loading) despite recovery from halogen-induced ozone loss.

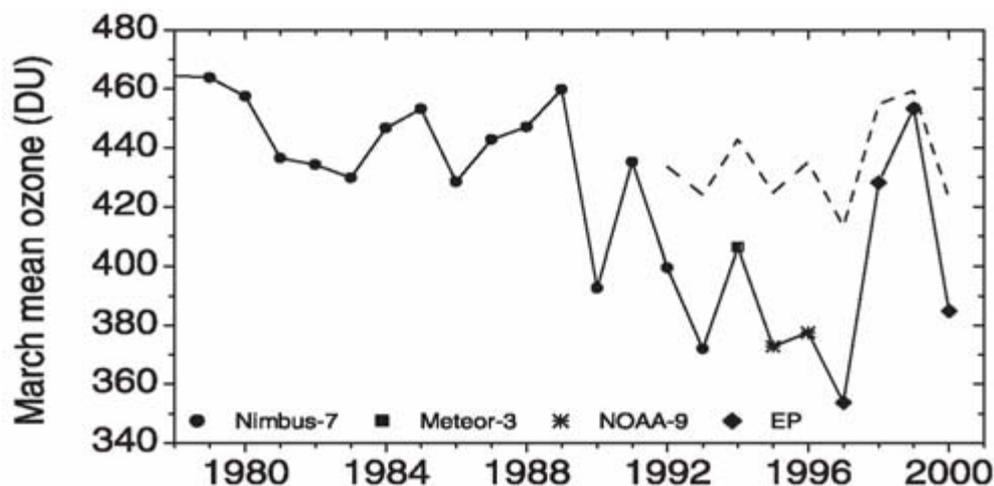


Figure 3.8 Total March monthly mean ozone in the region 63°-90°N (solid line) from various satellite instruments as indicated [update from Newman et al., 1997]. The sum of the total ozone and the 63°-90°N mean vortex depletion (dotted line), is also shown for the years 1992-2000. For details see Andersen and Knudsen [2002].

- Polar ozone abundances are determined by chemical and dynamical processes. Both processes are strongly coupled to climate variability/changes. The degree of dynamical variability is underestimated by currently employed CCMs related to the “cold bias” problem. For polar ozone, the process of denitrification, which depends non-linearly on temperature, has been identified as one of the largest uncertainties with regards to future ozone prediction, particularly in the northern hemisphere. A realistic physical representation of denitrification in CTMs and CCMs is currently missing.

### 3.7 Mid-latitude ozone loss changes

The observed trends of total ozone in northern mid-latitudes confirm that the strongest decline and the largest variability occur during winter and spring [e.g. Fioletov et al., 2002].

The largest relative ozone decline is found from ground-based lidar and satellite observations in the upper stratosphere around 42 km altitude, where the annual mean depletion reaches about -7% per decade [SPARC, 1998]. Long-term measurements, for example at Hohenpeissenberg, show that this trend persists up to the present (Figure 3.9). Ozone depletion at these altitudes is fairly well understood and occurs through gas phase reactions involving anthropogenic chlorine. Agreement between models [e.g. Jackman et al., 1996] and observations is good. Models predict ozone recovery to even above 1980 levels by roughly 2040. Upper stratospheric chlorine levels are expected to decrease and ozone destruction cycles are expected to slow down due to the expected (and already observed) CO<sub>2</sub> cooling in the upper stratosphere [e.g. Rosenfield et al., 2002]. It remains to be seen from the observations whether and when the predicted recovery will start.

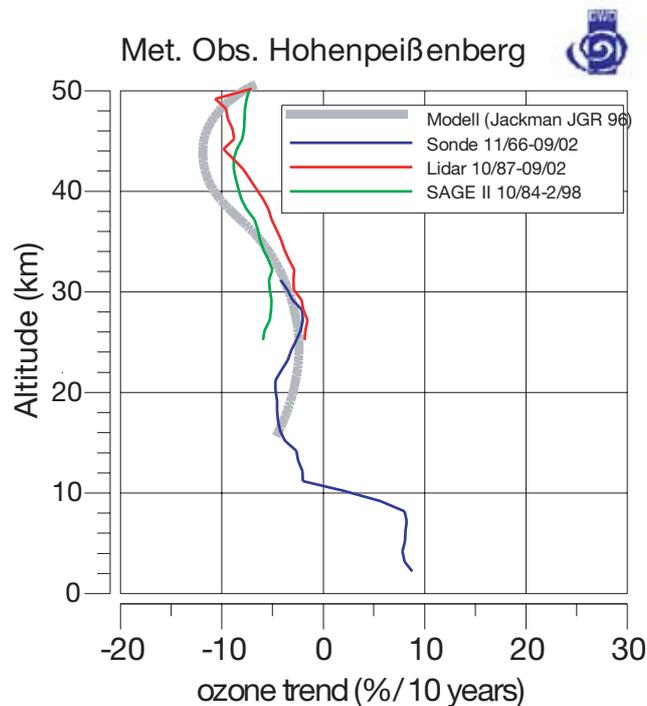


Figure 3.9 Vertical profiles of annual mean ozone trend (in percent per decade) as observed by lidar and sondes at Hohenpeißenberg (47.80°N, 11.02°E), by SAGE II within  $\pm 5^\circ$  latitude and  $\pm 10^\circ$  longitude near Hohenpeißenberg, and as modelled by a 2-D model.

- *Upper stratospheric ozone changes are determined by changes in halogen abundances and changes in temperature due to enhanced greenhouse gas concentrations. In future, both effects will likely result in positive ozone changes.*

In the lower stratosphere, one important factor in addition to chemical processes influencing mid-latitude ozone concentration is the transport of air from sub-tropical or polar latitudes into mid-latitudes. For example, Bojkov and Balis [2001] observed an increase of extremely low total ozone episodes at mid- and polar latitudes from October to December over the Atlantic/European region since the 1980s, indicating an increase of air intrusions with low ozone concentration. However a recent analysis of the ozonesonde record of Payerne (Switzerland) showed that the frequency of southerly advection was less pronounced during recent years, yielding an insignificant ozone trend in the lowermost stratosphere when considering the entire period of 1970-2001 [Koch et al., 2002]. Advection of ozone-poor air through either the sub-tropical transport barrier, as for example identified in airborne and satellite observations [Offermann et al., 1999; Riese et al., 1999], or across the edge of the stratospheric polar vortices in winter, by so-called streamers, may decrease the mid-latitude ozone concentration. To assess the possible contribution of streamer transport to the observed mid-latitude ozone loss, their nature has been investigated and possible changes during the past have been quantified from observations and model studies [e.g. Orsolini and Grant, 2000; Krüger, 2002]. For example, it was shown that the frequencies of sub-tropical streamers are much higher in winter than in summer. There are indications that the streamer events found in the lower stratosphere are mainly forced from the troposphere and are not directly related to the dynamics of the polar vortex [Eyring et al., 2002]. The future development of mid-latitude ozone concentrations may be influenced by possible changes in streamer frequencies and/or the location of maximum streamer activity. First estimates analysing results of a fully coupled CCM showed no statistically significant changes in the frequencies of subtropical streamers [Eyring et al., 2002], but more detailed investigations are necessary before definite conclusions can be made.

- *Variability and trends of lower stratospheric ozone in mid-latitudes are much less understood. It is largely affected by transport from (sub-) tropical and polar latitudes, which both may be influenced by climate change.*

As discussed in Chapter 4 of EC [2001] there have been many studies investigating the magnitude and cause of the observed mid-latitude decline in stratospheric ozone. Whereas progress has been made in the understanding of the chemical processes involved (nitrogen and chlorine gas phase chemistry and heterogeneous reactions on cold aerosols), the relative importance of chemical and dynamical processes on the ozone trend is still unclear. The proxies used to separate chemical from dynamical changes are correlated with each other and possible feedbacks between different mechanisms acting on different scales are difficult to quantify. In general, it is a very difficult question to unravel from model studies and/or observations to what degree changes in dynamics, induced by chemically depleted ozone, are responsible for the apparent strong “dynamics only” effect.

In a recent study, Hadjinicolaou et al. [2002] have examined the time period 1979-1998 to discriminate the dynamically driven trend from the chemically driven trend by using the 3-D CTM SLIMCAT with ECMWF analyses and a simplified parameterised ozone chemistry including no inter-annual variability. The model integration reproduces many of the observed features in mid-latitudes, especially in the mid 1980s and early 1990s. As these features and the calculated trend arise from changes in the meteorology, Hadjinicolaou et al. [2002] conclude that the dynamically driven model trend accounts for about half of the observed northern mid-latitudes trend from December to February. As they also found a strong correlation of the modelled ozone column at northern mid-latitudes with the vertical winter EP-flux at 100 hPa and with low-frequency atmospheric variability such as the North Atlantic Oscillation (NAO) index they suggest that changes in the intensity of the winter-time circulation are connected not only to the inter-annual variability, but also to the downward winter/spring ozone trend during 1979-1998 over the northern middle latitudes.

In recent years, the relation of long-term changes in the stratosphere with tropospheric (meteorological) patterns or climatic indices, particularly the NAO and the AO (Arctic Oscillation) has been investigated in detail. The NAO index is defined as the surface pressure difference between the Azores and Iceland [e.g. Hurrell et al., 2003]. The AO is the leading empirical orthogonal function (EOF) of the northern hemisphere wintertime sea level pressure field and is correlated with the NAO [e.g. Thompson and Wallace, 1998]. The NAO describes the dominant large scale climate variability over the North Atlantic/European area. Positive NAO phases are related to higher winter temperatures in Europe than usual, whereas negative NAO phases have an opposite relationship. The preferred occurrence of negative phases in the 1960s and 1970s and positive phases in the NAO in the 1980s and 1990s has also led to an increase of days with a high tropopause over Europe [Appenzeller et al., 2000]. Due to the link between total ozone and tropopause pressure (see Section 3.4), this also results in an increase of days with low ozone in the lower stratosphere, from the tropopause to about 20 km. A number of studies indicate that for central Europe roughly one third of the observed long-term decline in total ozone is thus related to the observed long-term change in dynamical structure of the atmosphere [Peters et al., 1996; Hood et al., 1999; Appenzeller et al., 2000]. A clear example is given in Figure 3.10 which shows total winter ozone over Arosa, Switzerland (right scale) and the normalised winter NAO index (left scale). For the long-term total ozone winter trends in Arosa, the dynamic impact, related to the NAO, accounts for up to 25% of the observed total ozone winter trends. Orsolini and Limpasuvan [2001] analysed 20 years of TOMS observations and found that low ozone episodes, or ozone mini-holes, appear more frequently over the European-Atlantic area in the high NAO phase. Since the NAO index shows a tendency to higher values in the last 25 years (Figure 3.10) it is suggested that the more frequent ozone mini-holes observed in recent years are connected with the modulation of tropospheric storm tracks by the NAO [e.g. Orsolini and Limpasuvan, 2001]. The mechanism of ozone mini-hole formation is fairly well understood through lifting of isentropes and pole-ward advection of ozone-poor air in the lower stratosphere.

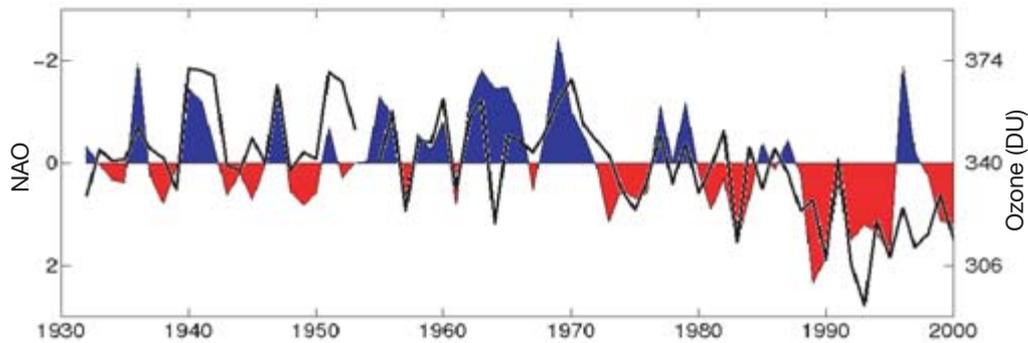


Figure 3.10 Total ozone in winter over Arosa, Switzerland (black line; in DU, right scale) and the normalised NAO index (colour coded; left scale - inverted axis). Adapted from Appenzeller et al. [2000].

While tropospheric warming and stratospheric cooling are consistent with changes expected from increasing well-mixed greenhouse gases and decreasing stratospheric ozone [Ramaswamy et al., 2001] and while some climate models indicate a stronger NAO from increasing greenhouse gases [Shindell et al., 2001a], we still lack the understanding of the underlying mechanisms. In particular it is unclear whether the observed long-term change in the NAO variability is a manifestation of anthropogenic climate change.

- *Correlation patterns between the troposphere and the stratosphere have been identified. Stratospheric variability and ozone distribution have been shown to correlate with modes of tropospheric variability, such as the NAO. The relations to climate change are undetermined.*

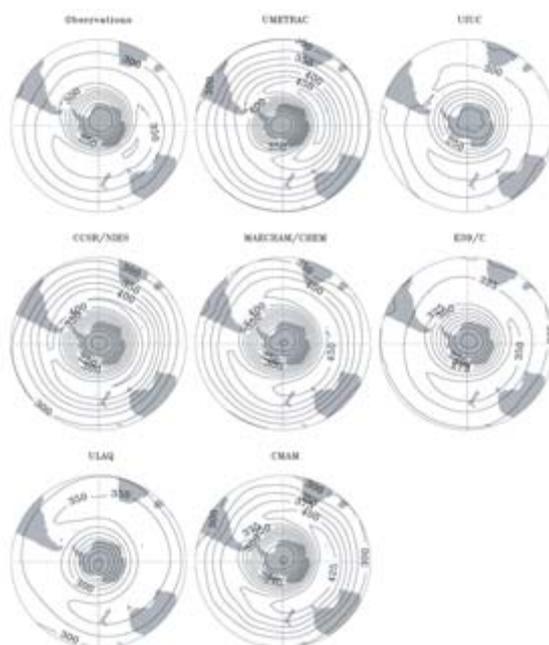
### 3.8 Modelling of ozone-climate interactions, climate impact on ozone recovery

While the impact of climate change on ozone can only be adequately simulated by coupled chemistry-climate models (CCMs) considering a wide range of chemical, dynamical and radiative feedback processes, pure climate model studies using prescribed changes of atmospheric composition allow the study of the impact and importance of individual atmospheric species on climate. Shine et al. [2003] compared temperatures from various modelling studies with the observed trends (Figures 2.7 and 3.5). Although obvious differences remain between individual modelling studies (up to a factor of 4 at the stratopause) the average model trend from a combination of WMGHGs, ozone and stratospheric water vapour changes is found to agree reasonably well with the observations. In the lower stratosphere combined WMGHG changes and ozone changes cannot explain all of the observed cooling, which is perhaps indicative of a stratospheric water vapour induced cooling. In the mid stratosphere, models consistently over-estimate the observed cooling. This may indicate a problem with the satellite derived temperature trends in this region: the small temperature trend in the mid stratosphere does not seem to fit with the expected  $\text{CO}_2$ -induced cooling and small ozone change. This could indicate that the ozone trends are positive in this region or that we are missing an as yet unknown localised warming mechanism. However both these seem unlikely and this discrepancy could indicate problems with the uncorroborated satellite trend.

The occurrence of changes in stratospheric dynamical processes as a result of climate change can be investigated with GCMs and CCMs, respectively. Analyses are required which separate the fraction of direct impacts of climate change on ozone from those of purely chemically induced ozone changes. This task is a great challenge due to complicated feedback mechanisms of physical, dynamical, and chemical processes. Recently, for the first time, fully coupled CCMs have tried to simulate the impacts of recent and future greenhouse gas and halogen changes on ozone depletion and recovery [Austin et al., 2003].

The employed CCMs cover a wide range of time-scales of integration and vary considerably in complexity. Specific diagnostics have been used to examine the agreement and differences between individual models and observations. The examination of model results with observations, particularly long-term and global observations as provided by ground-based stations and satellites, is the basis for the detection and attribution of model deficiencies, which is important for the assessment of the consistency of model predictions. Since individual model simulations with coupled chemistry-climate models consume large amounts of computer time, it is not possible to establish sets of sensitivity simulations with each model to estimate their particular uncertainties. Currently, each model system can only be run for a very small number of model scenarios. Therefore one way to check the reliability of CCM results is to compare scenario calculations of different models which assume similar boundary conditions.

Many models indicate a significant cold bias at high latitudes, particular in the southern hemisphere during winter and spring which strongly influences polar chemistry, especially through the formation of PSCs. Another unsolved problem is that none of these models is able to reproduce the observed water vapour trend in the (lower) stratosphere. As a result of the widely differing modelled polar temperatures and water vapour mixing ratios, different amounts of PSCs are simulated which in turn result in varying ozone values in the models (Figure 3.11). Additionally, it must be noted that none of the currently available (chemistry-) climate models have ever simulated a major stratospheric warming event in the southern hemisphere (see Section 3.5). If all models fail to reproduce such an extreme event, this points to further deficiencies in the models which might be related to an inadequate representation of planetary wave activity, i.e. the forcing mechanisms in the troposphere and the upward propagation into the stratosphere.



*Figure 3.11* Monthly mean total ozone (DU) over the southern hemisphere for the month of October for the current atmosphere for 8 different chemistry-climate models. The observations (upper left) are taken from a range of satellite data for the period 1993-2000. The model climatologies are as follows: UMETRAC: mean 1980-2000, CMAM: 2000 run, MAECHAM/CHEM: 2000 run, E39/C: 1990 run, CCSR/NIES: mean 1990-1999, UIUC: 1995 run, ULAQ: 1990 run. For details see Austin et al., [2003].

Nevertheless, the available CCMs have been employed to determine the possible future behaviour of ozone (see Figure 3.1). The differences in the model predictions give an indication for the degree of uncertainty of such estimates. All models predict eventual ozone recovery, but they give a range of results concerning its timing and extent. In the Antarctic, the models mostly agree with each other

suggesting that stratospheric ozone columns in spring-time (ozone hole) have probably reached almost the lowest values although the vertical and horizontal extent of depletion may increase slightly over the next few years which would increase the UV impact. For the Arctic it is much more difficult to determine the start of ozone recovery since inter-annual variability due to dynamical processes will tend to mask the signal. On the other hand, the question still remains as to whether climate change will lead to a decrease in stratospheric temperature in northern winter (due to radiative cooling caused by enhanced greenhouse gas concentrations) or if this effect is reduced or over-compensated for by dynamical heating (due to enhanced activity of planetary waves generated in a warmer troposphere). This open question is a central point for further investigations of the recovery of the ozone layer and emphasises the importance of the feedback between climate change and atmospheric chemistry. Possible changes in future TTL and in the Brewer-Dobson circulation will have important consequences for the dynamics and chemistry of the stratosphere, not only for the recovery of the ozone layer. Therefore it is necessary to continue long-term observations, particularly in the tropics, to get a more reliable data base which is also necessary to check the models.

An important climate forcing mechanism to be taken into account in future CCM simulations is the interaction of tropospheric and stratospheric aerosols with solar and terrestrial radiation. It is necessary to include realistic simulations of the various physical processes affecting the distribution of different aerosol components (source location, strength, and trends; removal mechanisms; vertical and horizontal transport; microphysics) and then use detailed radiative transfer codes. Future growth of sulphur emissions in developing countries may partially compensate for the tropospheric warming due to increasing greenhouse gases.

The expected improvements of our knowledge of dynamical, physical and chemical processes and their feedback will certainly produce further developments of the models. Therefore the next generation of CTMs and CCMs might produce results related to the recovery of the ozone layer which may be outside of the bandwidth of current model assessments.

- *Current model simulations with respect to future development of the stratospheric ozone layer show large uncertainties, particularly for the Arctic region. Key issues which currently limit the reliability of prognostic studies include realistic representations of stratospheric water vapour concentrations (trends), polar temperatures in particular in the UTLS region, the process of denitrification, and the diabatic circulation.*

### 3.9 Conclusions

There is a strong need for further development of CTMs and CCMs and comparison with all available observations and analyses. The examination of models should concentrate more on process studies. The comparison of model results and measurements carried out so far has focussed mainly on specific dynamical or chemical parameters. This should be seen as a first step, helping to identify the deficiencies and uncertainties of the distinct models. In a next step the investigation of processes should be the centre of interest. Therefore data products expected from satellite measurements, especially ENVISAT (with the instruments MIPAS, SCIAMACHY, and GOMOS) should help to identify further model deficiencies. The synergistic use of specific dynamical and chemical values and parameters which are measured or estimated globally at the same time and space will yield a new quality of consistent data products which will help to improve the understanding of atmospheric processes, especially of feedback mechanisms of dynamical and chemical processes. To guarantee the quality of data products derived from satellite instruments strong validation with ground-based, balloon, and aircraft measurements is required. This is an essential task, not only during the commissioning phase, but also continuously during the whole satellite mission. Further development of the models is necessary, in particular with respect to the improvement of parameterisations of physical, dynamical, and chemical processes, transport algorithms, the interaction of aerosols and clouds, and heterogeneous

chemistry on cirrus clouds. The aim is to reduce/remove known systematic errors of temperature (“cold bias”), age of air, clouds, water vapour, and distribution of trace gases.

A key for a more reliable prediction of climate change and ozone is stratospheric water vapour. As long as we do not understand the stratospheric water cycle and water vapour trends, predictions of the future development of ozone and climate are very uncertain.

One issue that needs further attention in future work is the question of the significance and the robustness of the derived stratospheric trends. Any natural long-term change in the dynamical structure of the troposphere (e.g. the NAO index) or the stratosphere (e.g. the prolongation of the polar vortices) can enhance or reduce any anthropogenically induced trend. This is particularly true for the long-term total ozone trends in the North Atlantic/European region, as shown above. On the other hand it must be considered that the NAO/AO, certainly the dominant pattern, accounts for only 30% of the total winter-time geopotential variance over the Atlantic-European region. Hence other climate patterns ought to be taken into account in estimating regional ozone trends and variability (e.g. various blocking phenomena). In contrast to northern hemisphere mid-latitudes, polar latitudes are very sensitive to the specific years included in the trend calculation. This is most likely due to the large inter-annual dynamical variability during northern winter, which masks or enhances a possible anthropogenic trend. The other region of higher sensitivity is the tropical stratosphere, where trend estimates from different data sets diverge more than for other regions [Ramaswamy et al., 2002]. The decadal trend in the tropical lower stratosphere, calculated from NCEP/NCAR-Reanalyses between 1979 and 2000, exceeds  $-1\text{K}$  per decade significantly for some months [Langematz et al., 2003] and has increased compared to the period 1979-1996 [Langematz, 2000]. Whether this result is unique to the data set used for the analyses or can be confirmed by other data sets, such as the currently compiled European Re-analysis data set, ERA-40, will be the subject of future studies.

Table 3.1 summarises the impact on stratospheric ozone of several climate related processes which has been partly discussed in this Chapter and in Chapter 5. In general, the level of scientific understanding of these processes is low.

Process / Activity	Impact on global stratospheric ozone resulting from climate change	
	Impact	Sign
Human activity - fossil fuel related emissions	Small	o
- biomass burning related emissions	Small	o
Natural emissions - soil $\text{N}_2\text{O}$	Medium	-
- lightning $\text{NO}_x$	Small	-
- $\text{CH}_4$	Medium	-
- $\text{SO}_2$ , COS ( $\rightarrow$ sulphate aerosols)	Medium	-
Heterogeneous chemistry on PSCs	Large	-
Denitrification	Large	-
Climate induced changes in stratosphere-troposphere exchange	Large	$\pm$
Climate induced changes in stratosphere-troposphere teleconnection patterns	Medium to large	$\pm$
Climate induced changes in planetary wave forcing and propagation	Large	-
Change of vortex temperature and dynamics	Large	-

Table 3.1 Potential impact on stratospheric ozone levels of several climate related processes.



## CLIMATE IMPACT OF TROPOSPHERIC OZONE CHANGES

Authors

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### 4.1 Background

#### 4.1.1 Introduction

The present chapter focuses on the changes in tropospheric ozone and their impact on climate. Research on tropospheric ozone started about 150 years ago, very soon after its discovery. Having received wide interest as an indicator of clean air in cities during the second half of the 19<sup>th</sup> century, tropospheric ozone regained the attention of European scientists and environmental policy makers in the early 1970s as an air pollutant, because its mixing ratio was found to increase well above toxic levels during photochemical smog episodes, which had first been observed in southern California. More than a decade ago evidence was presented that the ozone background in the lower troposphere over Europe had increased by a factor of two or more since the beginning of the 20<sup>th</sup> century [Volz and Kley, 1988]. The trend seemed to become less pronounced in the nineties, although no clear picture emerged from the many data sets of the different ozone monitoring networks that had been established, especially in the upper troposphere.

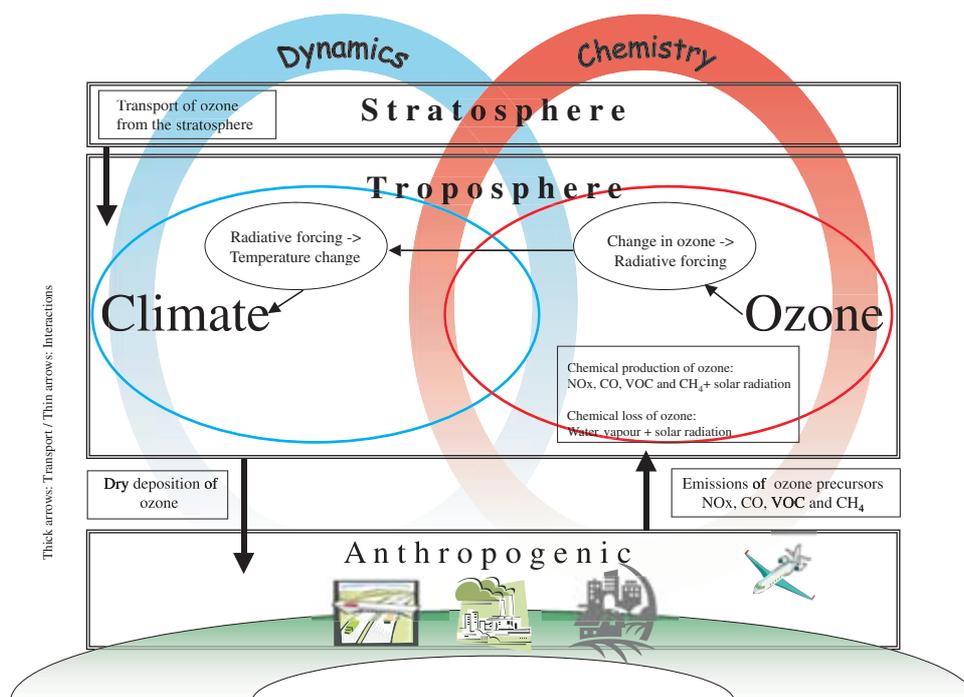


Figure 4.1 Processes governing the budget of tropospheric ozone and processes through which changes in tropospheric ozone impacts the climate

It is now well recognised that the large increase in the background tropospheric ozone concentrations during the previous century is mainly due to anthropogenic emissions of gases leading to ozone formation, the so-called ozone precursors (NO<sub>x</sub>, CO, CH<sub>4</sub> and Volatile Organic Compounds

(VOCs), see Figure 4.1). Tropospheric ozone influences the radiative balance of our planet, both by absorbing solar radiation and, more importantly, by acting as a greenhouse gas (GHG) through absorption and re-emission of infrared radiation from the Earth's surface. As a result, the ozone increase in the troposphere has led to trapping of radiation in the troposphere, yielding a positive radiative forcing (see Chapter 1 for definition, and see Figure 4.1). Recent calculations show that the increase in tropospheric ozone represents the third largest positive radiative forcing since pre-industrial time [IPCC, 2001]. In this way the ozone increase has had a significant climate warming impact (see Figure 4.1). In addition tropospheric has an indirect climate impact as it decreases the concentration methane, through its chemical influence on OH.

Ozone has an atmospheric residence time in the order of weeks to a few months, depending on altitude, geographical location and time of the year. As a consequence, changes predominantly occur downwind of the industrial regions. The complexity of atmospheric chemistry, often critically depending on a variety of atmospheric conditions, leads to a large variability in space and time of the ozone levels.

- *Tropospheric ozone has increased and is expected to continue to increase in certain regions due to anthropogenic emissions of ozone precursors.*
- *Tropospheric ozone absorbs terrestrial as well as solar radiation resulting in a positive radiative forcing when ozone concentrations increase.*
- *Due to its short lifetime changes in the concentrations and the subsequent radiative forcing and climate effects are all very difficult to quantify accurately.*

#### 4.1.2 Budget of tropospheric ozone

Quantifying the impact of natural and anthropogenic ozone as a climate gas requires quantitative understanding of the processes that control its abundances (see Figure 4.1). This is more complex for tropospheric ozone than for long-lived greenhouse gases. The concentration of long-lived greenhouse gases in the troposphere can be determined from a limited number of measurement stations at the ground. This is not the case for ozone, which varies very significantly in space and time throughout the troposphere.

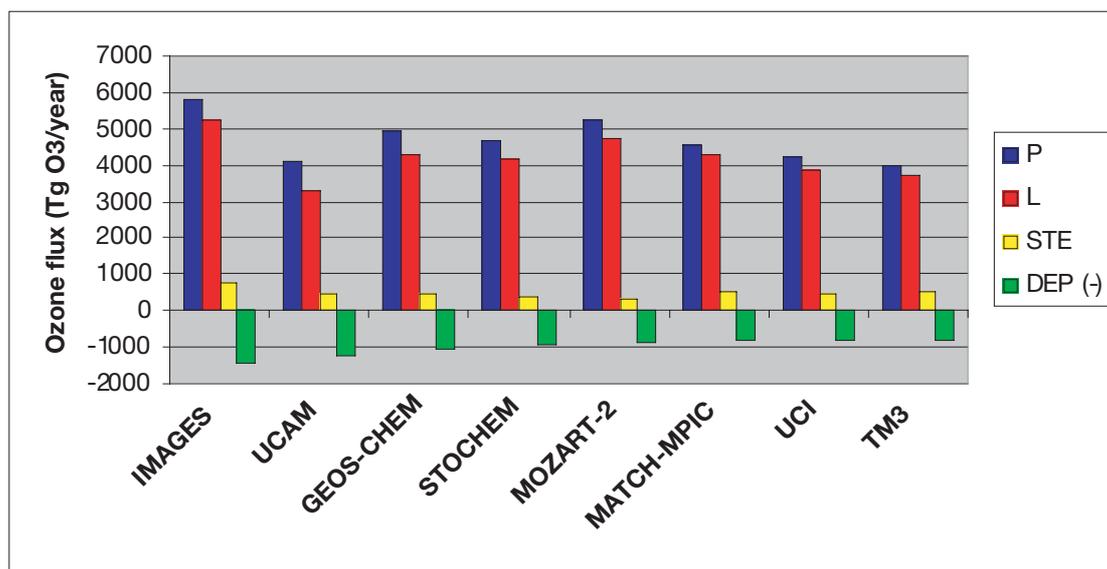


Figure 4.2 Tropospheric ozone budget based on 8 global chemistry transport models (CTM). The figure shows the chemical production (P) and loss (L), the Stratosphere-Troposphere Exchange (STE) and the surface deposition (DEP). See text for further discussion. The numbers represent global averages for 1990 conditions.

Ozone is formed *in situ* in the troposphere in photochemical reactions. It is also transported into the troposphere from the stratosphere, where the concentrations are much higher than in the troposphere. The chemical production in the troposphere is counteracted by other reactions that destroy ozone. Finally, ozone is also removed from the troposphere by deposition at the ground, most efficiently by vegetation. The total amount of ozone in the troposphere, which is about 370 Tg(O<sub>3</sub>) [Park et al., 1999], is only slowly varying, and the amount for a given year (for example) is almost maintained as a near balance between the production and loss processes described above.

The influx of stratospheric ozone into the troposphere is very difficult to quantify. Based on observed correlations with other gases it has been estimated to be about 475 Tg(O<sub>3</sub>)yr<sup>-1</sup> [Murphy and Fahey, 1994]. The uncertainty is large, and in current chemistry transport models (CTMs) the ozone influx from the stratosphere ranges from about 420 to 790 Tg(O<sub>3</sub>)yr<sup>-1</sup> (from Figure 4.2). The ozone concentrations have decreased in the stratosphere over the last decades due to emissions of ozone depleting substances (see Chapter 2). Thus the influx has been reduced. In a recent study, which is based on a combination of model calculations and analysis of ozone observations, it has been estimated that the transport of ozone from the stratosphere to the troposphere has been reduced by as much as 30% from the early 1970s to the mid 1990s [Fusco and Logan, 2003].

The magnitude of the surface deposition sink is difficult to establish from observations, and the range in the CTM calculations is again large, ranging from 670 to 1640 Tg(O<sub>3</sub>)yr<sup>-1</sup>. The difference between the flux from the stratosphere and the destruction at the surface is balanced by the net chemical production (NCP), which varies from 70 to 880 Tg(O<sub>3</sub>)yr<sup>-1</sup> in current models. This shows that, from current CTM studies, it is not possible to accurately quantify the relative importance of stratospheric input, deposition at the surface and net chemical production in the global tropospheric ozone burden. Therefore, the evaluation of the mutual impact of tropospheric ozone and climate on each other remains a difficult task.

NCP of tropospheric ozone is the difference between chemical production (P) and chemical loss (L), which are typically one order of magnitude larger than the NCP (chemical production and loss: each ~4000-6000 Tg(O<sub>3</sub>)yr<sup>-1</sup>). Chemical production of ozone occurs (see Chapter 1) when NO reacts with a peroxy radical (HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>, or RO<sub>2</sub> - a peroxy radical derived from a VOC other than methane). For this reason, hydrocarbons and nitrogen oxides are called ozone precursors. Ozone is chemically destroyed in the troposphere in a catalytic cycle involving OH and HO<sub>2</sub>, and in a pathway involving the reaction of O(<sup>1</sup>D), a product of ozone photodissociation, with H<sub>2</sub>O. There are other minor loss processes; reaction of O<sub>3</sub> with hydrocarbons, and NO<sub>y</sub> (the sum of NO and its atmospheric oxidation products) losses, which represent an indirect sink of O<sub>3</sub>. A chemical loss of ozone in the Arctic winter/spring has been identified, involving halogen radicals and aerosols [e.g. Platt and Moortgat, 1999]. The contribution to the global loss is probably small. NCP also has a distinct distribution: it peaks in the polluted boundary layer, but is negative over much of the oceans and in the lower-mid free troposphere, before becoming positive again in the upper troposphere. This distribution mainly reflects the concentration fields of NO<sub>x</sub> (typically a C-shaped profile, with maxima in the boundary layer and in the upper troposphere) and H<sub>2</sub>O.

The large spatial variability in ozone abundances in the troposphere reflects the wide range of scales in the distributions of ozone precursors. The representation of all the relevant scales in global models is a major challenge. For example, urban, biomass burning and aircraft plumes (and convection) are small scale phenomena which cannot be fully resolved in global models. Since the ozone chemistry is strongly non-linear, the crude parameterisation of such

processes in global CTMs makes it difficult to establish reliable regional and global budgets for tropospheric ozone.

- *The content of ozone in the troposphere is maintained as a balance between transport from the stratosphere, deposition at the ground and in situ chemical production and loss. Figures representing these processes can be established by use of chemistry-transport models. The crude parameterisation of certain processes (in particular small scale processes) in global CTMs makes it difficult to establish an accurate global budget for tropospheric ozone.*
- *Increased chemical production due to emissions of ozone precursors is not the only process that has changed the content of ozone in the troposphere. Combination of model calculations and analysis of ozone observations has revealed that the transport of ozone from the stratosphere to the troposphere has been reduced by as much as 30% from the early 1970s to the mid 1990s.*

## **4.2 Ozone precursors: anthropogenic emissions and concentrations**

Most of the ozone in the troposphere is formed as a result of emissions of precursor gases, both natural and anthropogenic emissions. Since anthropogenic emissions are acknowledged as being the main driver behind the increase in tropospheric ozone since pre-industrial time, they are our main concern here. The magnitude, variability and trends of anthropogenic emissions of ozone precursors are described in this section. Natural emissions of ozone precursors are described in Chapter 5, as changes in natural emissions of ozone precursors can occur as a result of climate changes.

- *Anthropogenic emissions are acknowledged as being the main driver behind the increase in tropospheric ozone since pre-industrial time.*

### **4.2.1 Methane ( $\text{CH}_4$ )**

Methane is one of the major greenhouse gases. In addition, like other hydrocarbons, its oxidation in the presence of significant amount of  $\text{NO}_x$  and sunlight leads to photochemical production of ozone. The total emission of methane has been estimated to be about 600 Tg of  $\text{CH}_4$  per year. About 60% of it is of anthropogenic origin with the most important sources being related to fossil fuel use, ruminants and agriculture. Its global burden is of the order of 5000 Tg of  $\text{CH}_4$  and its lifetime is about 9 years [IPCC, 2001].

The tropospheric distribution of methane is relatively well characterised, especially through surface measurements in global monitoring networks (vertical gradients are very small in the troposphere). Ice core measurements indicate that pre-industrial levels of methane were about 40% of the present-day levels. This appears to match well the estimated fractions of anthropogenic (60%) and natural (40%) emissions.  $\text{CH}_4$  levels have been increasing since pre-industrial time. However, the increase seems to have been slowing down in the last two decades (see Figure 4.3) [Dlugokencky et al., 1998]. The exact causes for this apparent long-term decline in the  $\text{CH}_4$  growth rate have not yet been clearly identified. There are also some large year-to-year fluctuations of the growth rate superimposed on the declining trend. The explanations put forward for these fluctuations invoke inter-annual variations in biomass burning, gas, coal, or wetlands emissions, or in the OH sink (see Chapter 5). Note that even the largest of these inter-annual fluctuations corresponds to an annual change in the atmospheric  $\text{CH}_4$  burden of less than 1% of the total burden.

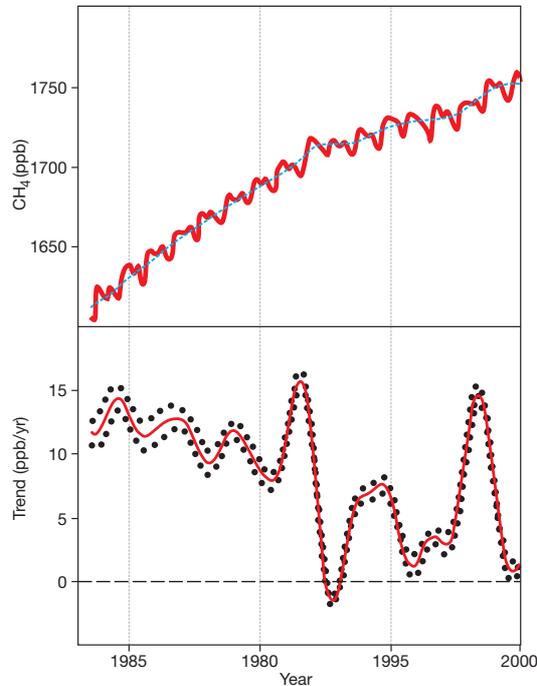


Figure 4.3 CH<sub>4</sub> mixing ratio (upper panel) and growth rate (lower panel).

- Methane is a greenhouse gas yielding a radiative forcing. In addition emissions of methane leads to an indirect radiative forcing through formation of ozone which takes place in the presence of NO<sub>x</sub>.
- An observed upward trend and inter-annual variations in the growth rate are influenced by the history of emissions and removal of methane by OH. Anthropogenic emissions account for 60% of the total emissions.

#### 4.2.2 Carbon monoxide (CO)

Presently most of the direct emissions of CO are man-made (almost evenly distributed between emissions from biomass burning and fossil fuel). The other important anthropogenic source of CO is the oxidation of hydrocarbons, in particular methane, emitted during industrial activities. As a result the northern hemisphere contains about twice as much CO as the southern hemisphere. Even within the northern hemisphere there are large gradients, due to the relatively short lifetime (1-2 months) and heterogeneous emission patterns. Its global burden is estimated to be about 360 Tg [IPCC, 2001].

As pointed out for ozone in the previous section, there are uncertainties in establishing the distribution and the budget of CO because of the spatial and temporal variations (see Figure 4.4) and the lack of observations to resolve the variability. It is worth noticing that satellite retrieval of the CO column have been achieved with Measurement of Air Pollution from Satellite (MAPS) and Interferometric Monitor for Greenhouse gases/Advanced earth Observing System (IMG/ADEOS) data [Clerbaux et al., 1998; Connors et al., 1999]. These data, along with the satellite observations with Measurements Of Pollution In The Troposphere (MOPITT), should help to reduce some of the uncertainties. Surface observations have shown that CO increased slowly on a global scale until the late 1980s. Then, there has been a decrease of about 2% per year for the period 1991-1997 [Novelli et al., 1998], possibly due to decrease in motor vehicle emissions as a result of catalytic converters. A trend in OH would also impact the trend in CO.

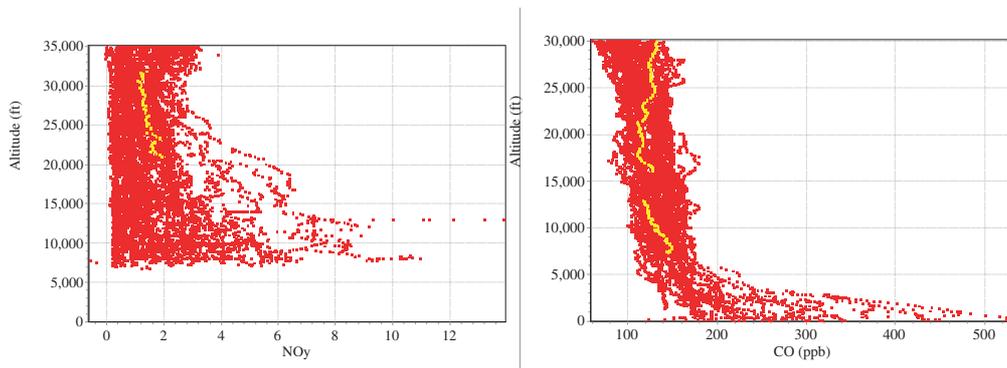


Figure 4.4 Vertical profiles of NO<sub>y</sub> (left) and CO (right) over Frankfurt in spring 2002, collected by the EC funded MOZAIC project [Source: P. Nedelec and A. Volz-Thomas, MOZAIC data base].

- CO contributes to generation of tropospheric ozone. The majority of direct emissions are anthropogenic. An increasing trend during much of the previous century was followed by a slight decline over the final decade, possibly due to decrease in motor vehicle emissions as a result of catalytic converters.

#### 4.2.3 Volatile Organic Components (VOC)

As for CH<sub>4</sub>, VOCs (including non-methane hydrocarbons), produce ozone in the presence of NO<sub>x</sub> and sunlight (Figure 4.1). In general the natural emissions are larger than the anthropogenic. However, this is only true for global budgets and for the VOC group as a whole. The fraction of anthropogenic emissions varies considerably between individual species and also geographically. The largest anthropogenic sources are from motor vehicles due to evaporation and incomplete fuel combustion, as well as biomass burning. VOCs include a large number of species, most with a very short lifetime. Their global distributions and budgets are only poorly known from a sparse network of observations. Anthropogenic emissions occur in heavily populated and industrialised regions where natural emissions are relatively low. Consequently they have a major impact on ozone formation on local and regional scales.

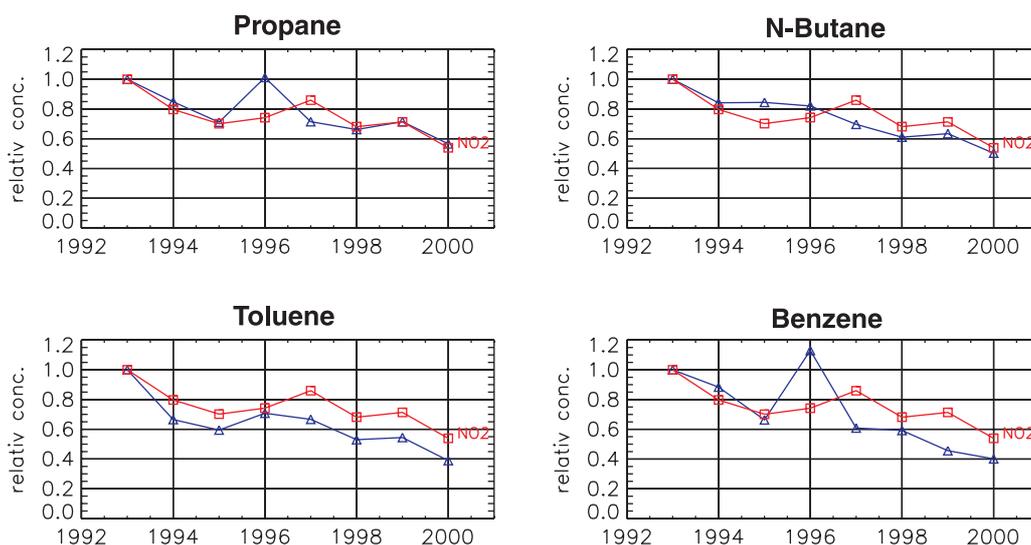


Figure 4.5 Winter medians (Jan-March) of selected hydrocarbons (blue) and NO<sub>2</sub> (red) at Waldhof from 1993-2000. The NO<sub>2</sub> data are 24-hour samples and only from those days when hydrocarbon samples were collected. All data are relative to the medians in 1993 [Solberg et al., 2002].

A few VOCs, such as ethane and acetone, have lifetimes long enough to impact ozone formation on a hemispheric scale. Data for ethane are most comprehensive. Ethane levels increased in Europe in the 1950s and through most of the 1980s [Ehhalt et al., 1991]. Since then they have been decreasing (-2.7% per year in the column at Jungfraujoch [Mahieu et al., 1997] somewhat weaker trends in Arizona/US and New Zealand). Figure 4.5 shows that the decrease in ethane is accompanied by similar negative trends in other VOC components (and NO<sub>2</sub>) in the 1990s at a rural German station (20-50% decline in the period 1993-2000). This is indicative of covariance in the VOC and NO<sub>x</sub> sources in this region.

- A wide range of VOCs contribute to ozone formation in the troposphere. On a global scale the natural emissions dominate, but on local and regional scales anthropogenic emissions produce significant amounts of ozone. The largest anthropogenic sources are from motor vehicles and biomass burning.

#### 4.2.4 Nitrogen oxides (NO<sub>x</sub>)

Nitrogen oxides catalyse ozone formation in the troposphere. The lifetime ranges from about one to up to ten days, and there is an extremely large spatial and temporal variability in the concentrations of NO<sub>x</sub> (see for example profiles of NO<sub>y</sub>, a group of species strongly correlated to NO<sub>x</sub>, from MOZAIC in Figure 4.4), ranging from a few pptv in remote oceanic regions to a few hundred ppbv in polluted urban regions. The global distribution and budget of NO<sub>x</sub> is thus very difficult to establish, although column abundances of NO<sub>2</sub> are now measured from satellite platforms. The Global Ozone Monitoring Experiment (GOME) satellite data show maxima of NO<sub>2</sub> over industrialised regions in North America, Europe and Asia (Figure 4.6). It is important to note that in polluted situations surface layers contribute most to the total columns, and in this altitude region derivation of satellite data is often difficult due to e.g. clouds and aerosols. Potential future retrievals of NO<sub>x</sub> profiles from satellite observations are of extreme importance for the understanding of ozone budget since NO<sub>x</sub> is a major driver of ozone chemical production in the troposphere.

The major anthropogenic source of NO<sub>x</sub> is fossil fuel combustion (approximately 33 Tg(N) per year), with 40% from the transportation sector. The emissions and concentrations (see Figure 4.5) have been slowly decreasing in Europe since the early 1990s. However, emissions were increasing in south-east Asia in the 1980s, and are possibly still increasing, although there are indications that the emissions of some greenhouse gases are now reduced in this region. Another anthropogenic source, which is more uncertain, is biomass burning which can be seen in the satellite data over Africa in Figure 4.6. However, parts of the emissions from biomass burning and soils are of anthropogenic origin (see also Chapter 5).

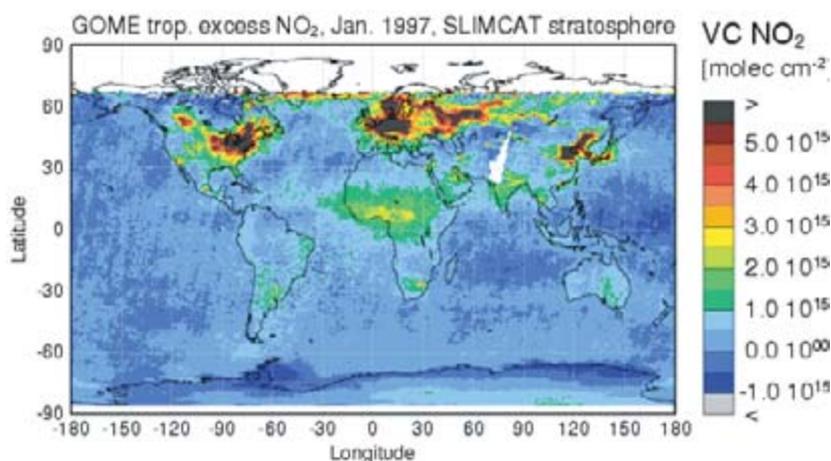


Figure 4.6 Global distribution of the tropospheric NO<sub>2</sub> column derived from the GOME instrument (TROPOSAT Annual Report 2001). The stratospheric SLIMCAT model has been used to remove the stratospheric part of the column.

- $NO_x$  play a special role in formation of tropospheric ozone since they catalyse ozone production. The major anthropogenic source is fossil fuel combustion with approximately 40% from the transport sector.  $NO_x$  is short-lived and there is a large spatial variability in the concentration and the ozone formation.

#### 4.2.5 Aircraft emissions

Aircraft are the only anthropogenic source that emits outside the planetary boundary layer. This increases the effect of species with a short atmospheric lifetime like  $NO_x$ . The primary emissions of aircraft are  $CO_2$  and  $H_2O$  as direct product of the combustion of kerosine. Due to its rather long lifetime (many decades) the location or altitude of the  $CO_2$  emission is of negligible importance for the associated climate impact. In the case of water vapour emissions location matters. In particular, water vapour emissions from a large fleet of supersonic aircraft would have a noticeable climate impact [IPCC, 1999].

Beside the primary emissions, aircraft also emit various other species like  $NO_x$ , VOCs, sulphur components or soot (at rates at least two orders of magnitude smaller than the primary emissions). With respect to an impact on ozone the aviation  $NO_x$  are of particular interest. At cruise altitude the life time of  $NO_x$  is at least an order of magnitude larger than close to the surface. Therefore, significantly more ozone can be produced per  $NO_x$  molecule released by aircraft than by  $NO_x$  from surface emissions. In addition the lifetime of ozone produced in the upper troposphere is significantly longer than at lower altitudes, making the potential ozone change larger.

Several 3-D inventories of these emissions exist for the period around 1992 [Baughcum et al., 1996; Schmitt and Brunner, 1997; Gardner, 1998]. All have similar total amounts and geographical and vertical distributions. Figure 4.7 shows the zonal mean aircraft  $NO_x$  emissions according to the DLR-2 inventory [Schmitt and Brunner, 1997]. Obviously, a large fraction of the emissions occurs at cruise altitude (10-12 km ~260-190 hPa) in the northern extra-tropics. The global mean emissions are 0.56 Tg N per year.

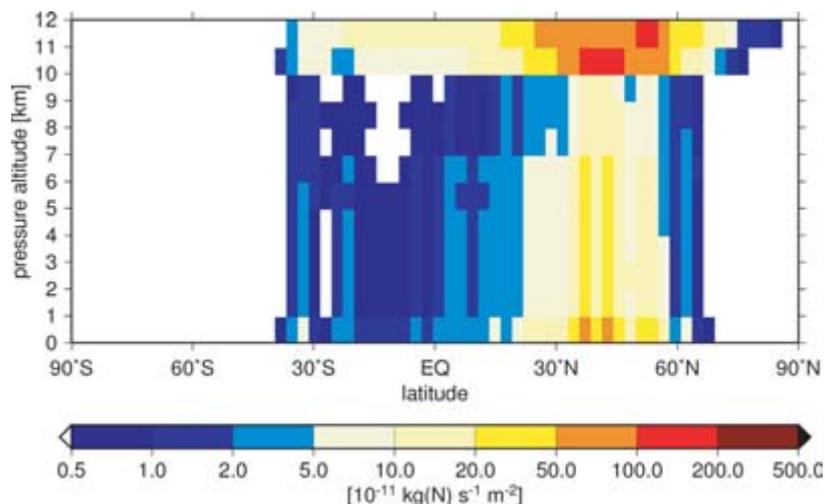


Figure 4.7 Zonal mean aircraft  $NO_x$  emissions according to the DLR-2 inventory for the year 1992. Note that the contour scaling is approximately logarithmic.

- Climate impacts of aircraft through formation of ozone from  $NO_x$  emissions are important as the emissions take place in a region with large climate impact of ozone changes and because  $NO_x$  has a long lifetime in this region.

#### 4.2.6 Future emissions

The future distribution of ozone, and thus its impact on climate, will be controlled by the evolution of emission strengths of ozone precursors, which is very uncertain. In the few next years, and

perhaps decades, it is likely that certain trends in emission patterns of ozone precursors will persist. For example, it is likely that the shift in growth of emissions of  $\text{NO}_x$ , CO and VOC from north America and Europe to southern and eastern Asia will continue. This will in turn significantly affect the spatial distribution of ozone. This is in contrast with long-lived GHGs, as shifting the location of their emissions has little impact on their distribution.

IPCC have developed several scenarios for GHG emissions, including ozone precursors, until 2100 (IPCC SRES – Special Report on Emission Scenarios). One of the scenarios has been used by the global tropospheric ozone modelling community to estimate the ozone distribution, and the resulting radiative forcing, in the year 2100 [the OxComp study, Prather and Ehhalt, 2001]. The scenario chosen, A2p [see IPCC/SRES; and IPCC, 2001, Annex II] has the highest emissions of ozone precursors throughout most of the 21<sup>st</sup> century. Therefore, the results of the OxComp calculations, which are used to discuss the future impact of tropospheric ozone on climate in this chapter (see Sections 4.3.2 and 4.4.1), should be regarded as upper estimates of this impact.

In the scenario adopted in OxComp [Prather et al., 2001] anthropogenic  $\text{NO}_x$  and CO emissions increase by a factor 3.4 and 2.4, respectively, from 2000 to 2100. Relative increases in north America (1.8 for  $\text{NO}_x$  and 1.6 for CO) and Europe (2.0 and 2.0) are lower than the global average, whereas the increases in India (5.9 and 4.4), south-east Asia (5.7 and 4.6), Africa (7.7 and 6.0) and South America (8.7 and 6.5) are substantially higher.

Aircraft emissions are assumed to grow particularly rapidly during the next decades. IPCC [1999] provided several scenarios which correspond to the IS92 IPCC scenarios for greenhouse gas emissions. Until 2050 air traffic increases by factors of 3.6 to 10.1 relative to 1990 if only the FSEG scenarios are considered. The EDF scenarios assume a more rapid growth. (For definition of the scenarios, see [IPCC, 1999]). The corresponding  $\text{NO}_x$  emissions grow less rapid due to improved aircraft efficiency and cleaner engines. In the case of the FSEG scenarios the factors range from 2.0 to 5.7. Note that these growth factors only cover a 60 year period, i.e. the aircraft emissions increase faster than the total anthropogenic emissions.

- *Future emissions of ozone precursors are of course uncertain. In the next few decades it is likely that the current shift in surface emissions of  $\text{NO}_x$ , CO and VOC from Europe and north America to southern and eastern Asia will continue. Aircraft emissions are assumed to grow particularly rapid during the next decades.*
- *IPCC has developed several scenarios for the current century. One of these, A2p, which has the highest emissions of ozone precursors throughout most of the century, has been chosen for studies of future ozone and its climate implications discussed in this chapter.*

### 4.3 Distribution and trends of tropospheric ozone

Surface measurements made in the tropics in the late 19<sup>th</sup> century suggest fairly constant mixing ratios of only 5-10 ppbv throughout the year [Pavelin et al., 1999]. There are valid questions about the quantitative reliability of early surface ozone measurements [e.g. Lefohn et al., 2001]. However, they represent the only observational constraints on pre-industrial ozone levels. The lack of global information on pre-industrial tropospheric  $\text{O}_3$  distributions is, therefore, the major uncertainty in the evaluation of the climate impact of changes in this key gas [Mickley et al., 2001; Hauglustaine and Brasseur, 2001; Shindell and Faluvegi, 2002].

To understand and quantify the impact of changes in tropospheric ozone on climate, it is therefore necessary to use models that describe complete global distributions, both for the pre-industrial and present atmosphere. The modelling intercomparison exercise conducted by Kanakidou et al. [1999] describes the state-of-the-art in global model resolutions, chemical scheme and per-

formances. However, joint scientific efforts are necessary in the future to combine observations and model results to establish and assess trends in ozone leading up to the current distribution.

- *Due to the large spatial variations in tropospheric ozone a global distribution of its concentration is difficult to establish. Thus one has to rely also on models to establish the global tropospheric ozone distribution and its trend. A joint observational and modelling effort is still needed to quantify changes in tropospheric ozone and the subsequent climate impact.*

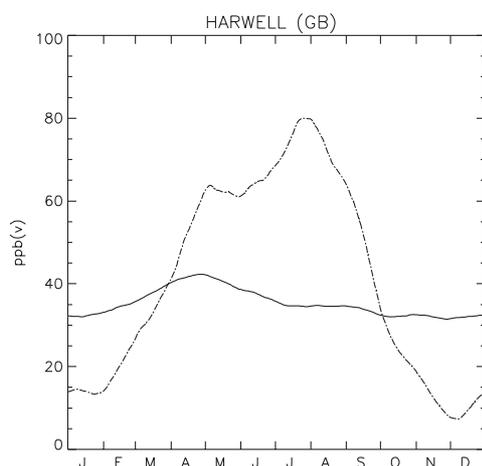
#### **4.3.1 Observed changes in tropospheric ozone**

Due to the relatively short residence time of ozone in the troposphere the concentration of ozone is varying strongly within the troposphere on a global scale. As opposed to e.g. other well mixed greenhouse gases, as CO<sub>2</sub>, observations are therefore needed at many locations and at many altitudes.

##### *Surface ozone*

Even within Europe the surface ozone concentrations are spatially varying to a large extent. A north-west to south-east gradient in current surface ozone concentrations can be observed in Europe [Scheel et al., 1997]. Similarly, a gradient towards higher concentrations from west to east in the United States [Logan et al., 1999] has been found. Current background ozone concentrations over Europe are between 19-27 ppbv on the Continent and 32 ppbv on the western European border [Scheel et al., 1997]. Levels of 35 ppbv are reported for unpolluted air masses at ground-level Mace Head (north-western Ireland) [Simmonds et al., 1997] and for the European Alps (Arosa, 1840 m asl) [Pochanart et al., 2001]. In the lower free troposphere over continental Europe (Jungfraujoch, 3,580 m asl), current background ozone levels are at 40 ppbv [Schuepbach et al., 2001]. In the Mediterranean regions background values are up to 60 ppbv, but in polluted areas ozone concentrations are often much higher. Not only the ozone concentrations, but also their seasonal cycle varies [Schuepbach et al., 2003].

Many factors control the variations in surface ozone, including emissions of ozone precursors, solar radiation to drive the photochemistry, moisture and transport processes. There is some observational evidence (see Figure 4.8) that ozone is formed as a result of ozone precursors during summer (the high NO<sub>x</sub> percentiles in Figure 4.8), whereas ozone is reduced during winter, notably by emissions of NO<sub>x</sub> and subsequent titration of ozone [Solberg, 2001]. This is most clearly demonstrated at locations at the outskirts of the major emission regions, experiencing the contrast between relatively clean and polluted air masses.



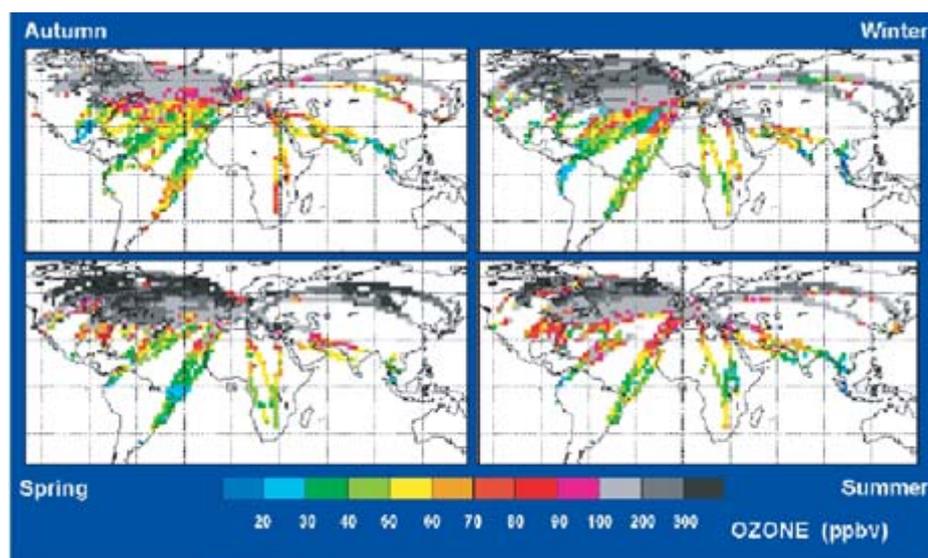
*Figure 4.8* Seasonal cycles of ozone at Harwell, UK, as a function of the NO<sub>x</sub> emissions integrated along back trajectories from the time of measurement. The solid curve represents back-

ground conditions and the dash-dotted curve polluted air masses (the lowest 25% and the highest 10% of the integrated  $\text{NO}_x$  emissions, respectively) [from Solberg et al., 2002].

Observed surface ozone concentrations in Europe show an increase by more than a factor of two over the 20<sup>th</sup> century [Staehelin et al., 1994; see also WMO, 1999; IPCC; 2001]. Ozone records dating back to the late 19<sup>th</sup> century are few, and the evidence for a positive trend in lower tropospheric ozone is strongest in Europe due to the first historical, quantitative ozone record at Montsouris (Paris). Volz and Kley [1988] established 11 ppbv as the observed background level at this site; the value is rather close to the 15 ppbv measured on the island of Rügen in northern Germany in the 1950s [Feister and Warmbt, 1987]. On the other hand, emissions of some of the ozone precursors declined during the last approximately two decades of the 20<sup>th</sup> century. As a consequence, observed summer ozone concentrations have generally decreased after the mid 1980s [e.g. Roemer, 2001], while winter ozone levels have increased [e.g. Schuepbach et al., 2001]. Similar trends in the seasonal ozone concentrations are observed in the northern United States [NARSTO, 2000]. These observed trends in the seasonal variations of ozone are consistent with reductions in emissions of  $\text{NO}_x$  over the last few decades.

#### *Free troposphere ozone*

More important than the surface concentrations of ozone are the concentrations at higher levels, where changes lead to a stronger forcing of the climate. Current experimental work in Europe [e.g. Zanis et al., 2000] and the northern United States [e.g. Wang et al., 2002b] based on measurements from high elevation surface sites and aircraft campaign measurements, suggest that in the lower free troposphere over large continental regions NCP (see Section 4.1.2) is positive, especially during the transition from winter to spring. An analysis of ozone sonde data in the mid troposphere (around 5 km altitude) showed that northern hemispheric seasonal variations are quite similar spatially, with a maximum in ozone between April and September [Logan et al., 1999]. This maximum is caused by efficient photochemical ozone formation in summer, possibly also by strong STE during spring.  $\text{NO}_x$  emissions from lightning, which are most efficient over continents in summer, may contribute significantly to the chemical production.



*Figure 4.9* Seasonal climatologies of  $\text{O}_3$  established from MOZAIC data collected in the altitude region 9-12 km between September 1994 and August 1996. The seasons specified in the panels refer to the northern hemisphere.

In the upper troposphere ozone observations of long-range Airbus A340 cruises from the long term program MOZAIC (Figure 4.9, from the 10-12 km altitude region) display a seasonal

variation in the northern hemispheric mid-latitudes with maximum concentrations in the late winter and spring. The peak concentrations over Europe are somewhat lower than over eastern north America and eastern Asia. However, Law et al. [2000] suggest that the magnitude of the maximum concentration depends on the position of the particular flight level where the measurements were collected relative to the height of the tropopause which is governed by the position of the large planetary scale ridge and trough pattern in the upper troposphere (ridge over Europe, trough over eastern north America and eastern Asia). In tropical areas, O<sub>3</sub> concentrations generally decrease toward the Equator and show less seasonal variation. At low latitudes the seasonal cycle is determined predominantly by the insolation since the direction of stratosphere-troposphere exchange is from the troposphere into the stratosphere. Hence, the influence of ozone originating from the stratosphere is very small throughout the year. The ozone concentration is thus mainly varying in line with photochemical destruction (which dominates the NCP) that minimizes on the winter and maximizes on the summer side of the Equator.

Outside the equatorial region, the seasonal variation in biomass burning emissions is an important factor. In the southern hemisphere, spring (northern hemisphere autumn) it is the dry season, when large-scale burning of biomass occurs in south America, Africa and Indonesia, which releases ozone precursors into the atmosphere. There is convective uplift of O<sub>3</sub> and its precursors from biomass burning regions into rather stable haze layers which can exist for many days and be transported large distances [Garstang et al., 1996; Diab. et al, 1996]. Due to the meteorological conditions, the biomass burning pollution is transported over large parts of the southern hemisphere. The influence by biomass burning between August and November has been observed in the seasonal cycle as seen in ozonesonde data at 500 hPa and 300 hPa [Logan et al., 1999].

Ozonesondes offer the longest record of free tropospheric ozone. Since 1970 observations are available weekly from a limited number of stations in a latitude range at mid to high latitudes in the northern hemisphere. Most stations show an increase in mid-tropospheric ozone from 1970 to 1980 [Logan, 1999]. Since then the changes are less clear. At some stations the increase continued in the period 1980-1996 (one in Europe, one in Japan), other stations had a significant decrease (all four Canadian stations), whereas other stations had no significant trend.

#### *Total ozone columns*

Full global observations of tropospheric ozone can only be obtained using satellites. There are no direct satellite observations of ozone in the troposphere. However, the tropospheric ozone columns have been obtained indirectly, by subtracting the stratospheric burden from the total column [Fishman et al., 1990; Fishman and Brackett, 1997]. Nevertheless, these observations show some interesting features. The lowest ozone concentrations are found over the tropical Pacific Ocean, due to photochemical loss under low NO<sub>x</sub> and high water vapour conditions. In contrast, a plume high in ozone rises from the continents to fill up the troposphere between south America and Africa over the latitude range 0°-20°S during austral spring. However, the largest ozone columns are clearly seen at mid-latitudes in the northern hemisphere, especially during spring and summer, when solar radiation stimulates production of ozone following the anthropogenic emissions of precursors.

- *Concentrations of tropospheric ozone vary strongly in space and with time of the year. Anthropogenic impact on tropospheric ozone has been possible to establish from long-term in situ ozone records and observation campaigns, when combined with observations of ozone precursors. For example, NO<sub>x</sub> has been demonstrated to yield ozone production during summer and ozone loss during winter conditions.*

- *A strong increase in surface ozone has been observed over Europe since the late 19th century. At mid and high latitudes in the northern hemisphere there was an increase in mid tropospheric ozone in the 1970s, according to ozone sonde observations. Since then there has been a continued increase in some regions, but a decreasing or not significant trend in others.*

#### **4.3.2 Modelling and interpretation**

Over the last 10 years, there has been a considerable effort devoted to the calculation of pre-industrial tropospheric ozone distribution and associated radiative forcing of climate. For this purpose, studies have used global 3-D CTMs [e.g., Chalita et al., 1996; Berntsen et al., 1997; van Dorland et al., 1997; Stevenson et al., 1998; Hauglustaine and Brasseur, 2001]. These studies generally calculate more pre-industrial ozone than observed with the Schonbein technique. In order to match these sparse observations, several studies have forced ozone to match pre-industrial levels in their radiative forcing calculations [Kiehl et al., 1999; Mickley et al., 2001; Shindell and Faluvegi, 2002]. Under these assumptions, radiative forcings reaching values as high as  $0.7 \text{ Wm}^{-2}$  are calculated.

As an example, Figure 4.10 illustrates the pre-industrial and present-day ozone surface mixing ratios simulated for January and July conditions [Hauglustaine and Brasseur, 2001]. The distributions were calculated with the state of the art global 3-D CTM of the troposphere, MOZART. The model calculates the ozone distribution by taking into account emissions of ozone precursors (natural emissions in the pre-industrial and in addition anthropogenic emissions in the present day case). The chemical reactions impacting ozone as well as transport of chemical constituents are described. The meteorology that drives the transport of chemical species is assumed to be the same in both cases. Thus no interactions between the chemistry on one hand and the transport or climate change on the other is taken into account. The pre-industrial levels over the continents in the northern hemisphere range from a minimum value of 5-15 ppbv in January, associated with chemical loss and dry deposition, to a summer value reaching 10 ppbv in Europe and 20 ppbv in the central United States. In the southern hemisphere the pre-industrial mixing ratios over the ocean range from only 4-8 ppbv in January to values of 10-20 ppbv in July. The present day distributions clearly emphasise a strong impact of anthropogenic activities on ozone levels at a global scale. Maximum O<sub>3</sub> mixing ratios reaching 50-60 ppbv are calculated over polluted regions (i.e., northern America, Europe, and south-east Asia) during summer in the northern hemisphere. This corresponds to an increase of a factor of 3-5 from pre-industrial levels. The background ozone levels calculated over the ocean in the southern hemisphere have also increased by 5-10 ppbv in comparison to pre-industrial values.

The calculated pre-industrial ozone levels appear to be very sensitive to assumptions made for natural emissions of NO and hydrocarbons. The NO soil emissions represent a main surface source of NO<sub>x</sub> at mid-latitudes in the northern hemisphere for pristine conditions, and assumptions on their pre-industrial level are crucial regarding simulated surface ozone. The situation is also complex in tropical regions where recorded pre-industrial ozone levels at the surface indicate very low values of only 5 ppbv. The calculated ozone levels in the tropics crucially depend on assumptions made for biomass burning emissions of ozone precursors by natural fires. The observed regional variability of O<sub>3</sub> trends is related to the transport of key precursors, particularly reactive nitrogen, CO and NMHCs. However, the chemistry of O<sub>3</sub> production is non-linear, so that increased emissions of NO<sub>x</sub> do not necessarily lead to linear responses in O<sub>3</sub> concentrations over all ranges of likely values [e.g., Klonecki and Levy, 1997; Fiore et al., 2002]. Further, the relationship of precursor emissions to O<sub>3</sub> increase may also vary in time. The study by Wang and Jacob [1998] suggest that the O<sub>3</sub> production efficiency per mole of nitrogen oxide emitted has decreased globally by a factor of 2 since pre-industrial times.

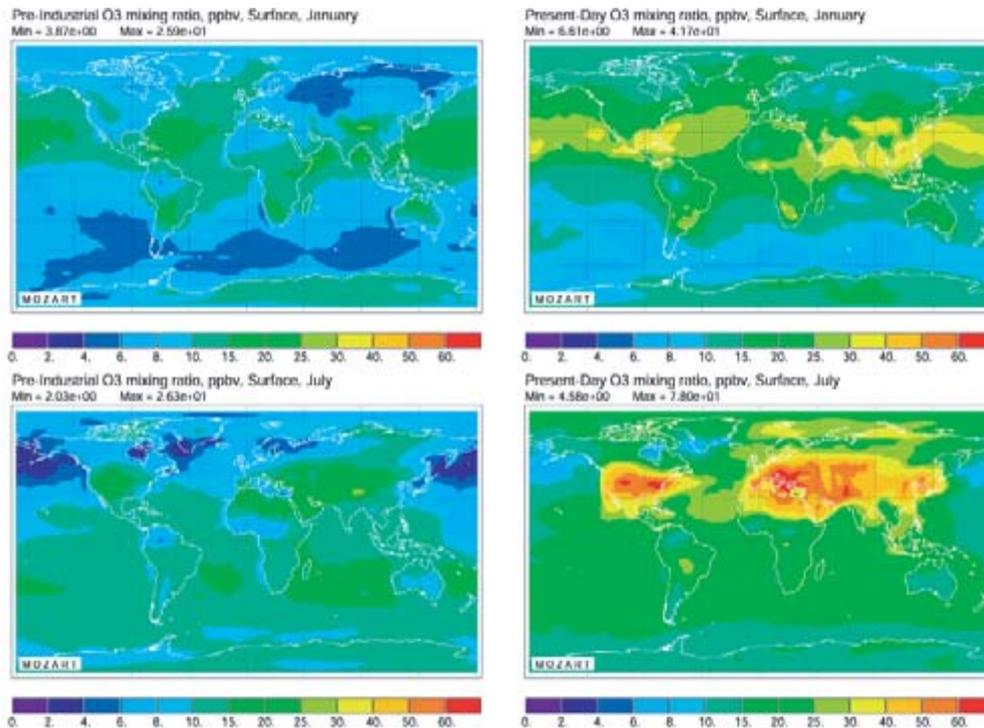


Figure 4.10 Surface distribution of ozone in January and July for pre-industrial and present day conditions in ppbv [Hauglustaine and Brasseur, 2001].

A recent survey of CTM studies provides global average increases in integrated tropospheric ozone ranging from 7 to 13 DU (Dobson Unit =  $2.687 \times 10^{16}$  molecules  $\text{cm}^{-2}$ ) from pre-industrial to present [IPCC, 2001]. These results are summarised in Table 4.1. The spread among the various models clearly stresses the uncertainty on the pre-industrial ozone level estimates associated mainly with assumptions made on natural emission of precursors and on the magnitude of the ozone input from the stratospheric reservoir. The associated radiative forcings of climate range from 0.28 to 0.49  $\text{Wm}^{-2}$  and reflects this uncertainty. The spread among the models is similar when normalised forcing (radiative forcing per ozone change,  $\text{Wm}^{-2}\text{DU}^{-1}$ ) is considered, pointing to uncertainties also in the calculations of the radiative forcing for a given ozone change.

Several recent studies have also used global models and ozonesonde measurements to examine the ozone trend from pre-industrial to present based on historical reconstructions of ozone precursor surface emissions [Berntsen et al., 2000; Lelieveld and Dentener, 2000; Shindell and Faluvegi, 2002]. These studies emphasise the dominant contribution of stratosphere-troposphere exchanges on the ozone trend at high latitudes, of industrial and fossil fuel emissions at northern mid-latitudes, and the important role played by natural emissions in the tropics. All these various contributions and their time evolution have to be adequately considered in order to simulate the past evolution of tropospheric ozone. The adequacy of the meteorological fields used to transport ozone and its precursors is also essential in order to try to represent the inter-annual variability. The study by Shindell et al. [2001b] suggests, however, that the impact of climate change from pre-industrial to present is minor as far as the tropospheric ozone change is concerned.

Table 4.1 Global integrated tropospheric ozone increase from pre-industrial to present (DU), associated radiative forcing of climate ( $\text{Wm}^{-2}$ ), and corresponding normalised forcing ( $\text{Wm}^{-2}\text{DU}^{-1}$ ) based on global CTM studies. The right-hand column specifies the type of chemistry and

the type of model used. The term “intermediate” denotes a first generation CTM with lower degree of complexity in its representation of transport or physical processes. Note that Berntsen et al. [1997] reported two values, as two different radiative forcing calculations were performed.

<b>Study</b>	<b>Tropospheric O3 change</b>	<b>Net radiative forcing</b>	<b>Normalised forcing</b>	<b>Note</b>
Lelieveld and van Dorland [1995]	9.4	0.49	0.052	Intermediate CTM (NMHCs)
Chalita et al. [1996]	...	0.28	...	Intermediate CTM (NMHCs)
Levy et al. [1997]	9.5	...	...	Parameterised chemistry
Berntsen et al. [1997]	7.6	0.28	0.037	NMHCs included
Berntsen et al. [1997]	7.6	0.31	0.041	NMHCs included
Van Dorland et al. [1997]	8.1	0.38	0.047	Intermediate CTM (NMHCs)
Wang and Jacob [1998]	11.0	...	...	Intermediate CTM (NMHCs)
Brasseur et al. [1998a]	...	0.37	...	Intermediate CTM (NMHCs)
Stevenson et al. [1998]	8.7	0.29	0.033	NMHCs included
Haywood et al. [1998]	7.9	0.31	0.039	Parameterised chemistry
Roelofs et al. [1997]	7.2	0.42	0.058	NMHCs not included, GCM
Kiehl et al. [1999]	8.4	0.32	0.038	Based on observations
Mickley et al. [1999]	12.6	0.44	0.035	Some NMHCs included (GCM)
Berntsen et al. [2000]	9.6	0.34	0.036	NMHCs included
Lelieveld and Dentener [2000]	7.7	0.42	0.054	NMHCs included
Shindell et al. [2001b]	7.5	0.32	0.042	NMHCs not included, GCM
Hauglustaine and Brasseur [2001]	8.9	0.43	0.048	NMHCs included
<b>Mean</b>	<b>8.9 ± 1.4</b>	<b>0.36 ± 0.06</b>	<b>0.043 ± 0.008</b>	

Emissions of ozone precursors are expected to increase significantly in the future. This is particularly the case in regions where rapid economic growth or population increase are expected (i.e.,

south-east Asia, south and central America, Africa). Several studies have pointed out the potentially important impact of Asian emissions on the background level of pollutants over the Pacific and northern United States [Berntsen et al., 1996, 1999; Jaffe et al., 1999; Jacob et al., 1999; Mauzerall et al., 2000]. In the tropics, pollutants are rapidly transported to the upper troposphere where subsequent redistribution through long transport can take place [Grewe et al., 2001; Hauglustaine et al., 2001]. Other studies have also illustrated how background ozone levels over Europe are affected by long-range transport of pollution from Northern America [Li et al., 2002]. Estimates of future ozone levels have been performed with several models and under various emission scenarios [Chalita et al., 1996; van Dorland et al., 1997; Stevenson et al., 1998, 2000; Brasseur et al., 1998a; Hauglustaine and Brasseur, 2001; Grewe et al., 2001].

Recently, an intercomparison exercise of future ozone levels has also been performed by 11 global models [Prather et al., 2001]. The simulated surface ozone levels in 2100 under the IPCC SRES A2 scenario indicate large increases along the southern edge of Asia from Arabia to eastern China, in Africa and Central America [OxComp, Prather et al., 2003]. The changes in tropospheric column ozone from the OxComp study are shown in Figure 4.11. The largest increase in ozone abundance occurs near the tropopause at 40°N. Some models tend to concentrate this increase in the tropics and others push it to high latitudes. These changes are likely to affect significantly the background ozone concentrations in most pristine regions and to represent a sizeable increment towards violation of air quality standards over the next decades [Hauglustaine and Brasseur, 2001; Prather et al., 2003] and also to yield a significant climate impact (see Section 4.4.1). The globally averaged increases in ozone between 2000 and 2100 in the OxComp study was in the range 11-21 DU.

Aircraft emissions are believed to have changed the chemistry of the upper troposphere due to their emissions in this region (see Section 4.2.5). In the current atmosphere the ozone increase due to aircraft has been estimated to 0.4 DU, as a global average (results from the state of the art Oslo CTM2). This is modest compared to the ozone increase since pre-industrial times. However, aircraft impacts are restricted to certain latitude bands. The maximum change in zonally averaged ozone column is 1.4 DU, occurring in June. As aircraft emissions are anticipated to increase markedly in the future (see Section 4.2.6) their impacts on tropospheric ozone are expected to be significant.

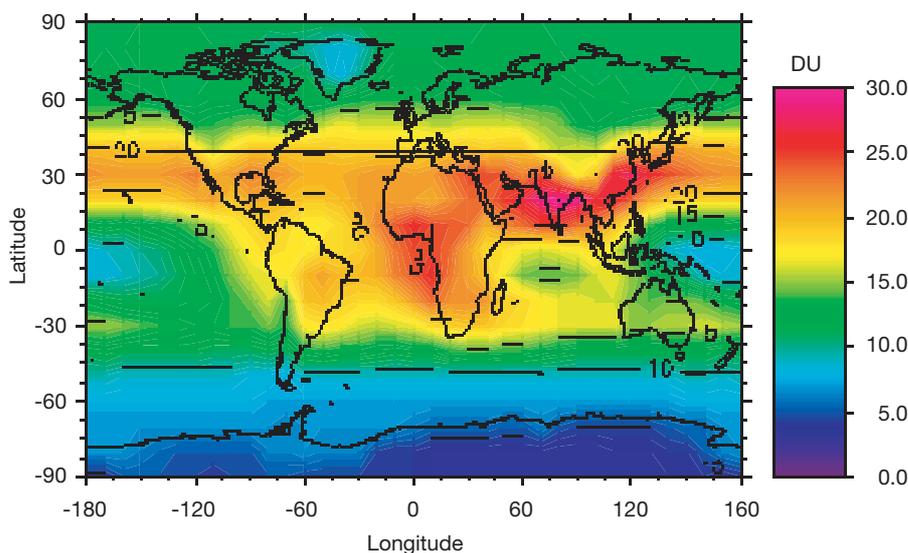


Figure 4.11 Changes in tropospheric ozone columns (DU) from year 2000 to 2100, as calculated by the 11 models in OxComp. The results shown are averages for all the models. (based on results in Gauss et al. [2003]).

- *Due to a lack of observational data for pre-industrial and even to some extent current ozone, models are used to establish changes in tropospheric ozone up till present time to assess the radiative forcing and the climate impact. A recent survey of CTM studies provides global average increases in integrated tropospheric ozone ranging from 7 to 13 DU.*
- *The ozone increase due to aircraft has been estimated to 0.4 DU, as a global average. This is modest compared to the ozone increase since pre-industrial times. However, aircraft impacts are restricted to certain latitude bands. The maximum change in zonally averaged ozone column is 1.4 DU.*
- *Future changes in tropospheric ozone have been calculated with several models and for several scenarios for emissions of ozone precursors. A recent model intercomparison study has applied the IPCC A2p scenario introduced above. The range of changes in global average ozone from 2000 to 2100 was estimated to 11-21 DU.*

#### **4.4 Climate impact of current and future changes in tropospheric ozone**

A first measure of the impact of ozone resulting from anthropogenic emissions of ozone precursors on climate is the associated change in the radiative energy flux through the tropopause (the boarder region between the troposphere and the stratosphere), called the radiative forcing. The concept of radiative forcing is introduced since as a first approximation, changes in surface temperature are proportional to changes in the radiative forcing (see Chapter 2).

In this chapter the radiative forcing associated with changes in tropospheric ozone is discussed first in Section 4.4.1 followed by a discussion on the changes in temperatures associated with the radiative forcing, in Section 4.4.2.

##### **4.4.1 Ozone changes and radiative forcing**

Changes in tropospheric ozone impacts climate *directly* through the radiative forcing, as explained above. Also, ozone changes impacts climate *indirectly* through chemical reactions that changes the concentrations of other radiatively active gases, in particular methane. These direct and indirect forcings are subjects of the following two subsections.

###### **4.4.1.1 Direct radiative forcing**

The fact that ozone is radiatively active in the long-wave as well as the shortwave spectral region results in a different radiative forcing (RF) dependency on atmospheric and surface conditions as compared to pure greenhouse gases on one hand and aerosols on the other. Due to its long-wave characteristics, mainly through the 9.6 and 14  $\mu\text{m}$  bands, the RF is critically dependent on the temperature contrast between the surface and the altitude of ozone change [Forster and Shine, 1997; Van Dorland et al., 1997]. This property is shared with the well-mixed greenhouse gases. The short-wave forcing is sensitive to surface albedo, cloud cover and solar zenith angle via both the amount of solar radiation on a horizontal plane and the path length through the atmosphere, as for aerosols. The role of clouds is twofold: it masks the greenhouse effect of tropospheric ozone, but it enhances the shortwave effect [Roelofs, 1999]. The net effect is that in the global and annual mean the RF is reduced by about 13% given the current distribution of clouds [Van Dorland et al., 1997].

Several studies of global tropospheric ozone change, and subsequent changes in the radiative forcing, since pre-industrial times have been performed. These studies give an increase in global yearly ozone mean of more than 30% (from 25 to 34 Dobson Units) with corresponding radiative forcings (RF) in the range from 0.2 to 0.5  $\text{Wm}^{-2}$  (Table 4.1). Recent estimates of radiative forcing have been mostly based on output from CTMs [e.g. Hauglustaine et al., 1994; Chalita et

al., 1996; Forster et al., 1996; Berntsen et al., 1997; Van Dorland et al., 1997, Brasseur et al., 1998a, Haywood et al., 1998; Stevenson et al., 1998; Hauglustaine and Brasseur, 2001]. Roelofs et al. [1997] used the fully interactive tropospheric chemistry/climate European Centre Hamburg Model (ECHAM4) to compute the RF due to tropospheric ozone changes. Portmann et al. [1997] and Kiehl et al. [1999] combined an ozone climatology based upon satellite measurements of the tropospheric column content [from Fishman and Brackett, 1997] with a model calculation to derive estimates of the ozone RF for the tropics and for the globe, respectively. Mickley et al. [2001] found that the RF could be significantly larger due to uncertainty in estimates of pre industrial ozone levels. They obtain an instantaneous global yearly mean RF due to ozone changes of 0.72-0.80  $Wm^{-2}$  and this would make ozone at least as important as methane as a greenhouse gas when considering increases by human activities.

The geographical distribution of the RF due to tropospheric ozone changes is much more inhomogeneous than that of the well-mixed greenhouse gases. Most studies show that the annual mean RF reaches a peak over north Africa due to a coincidence of relatively large ozone increases with the region where those changes are most effective due to a warm surface, high surface reflectance and cloudless skies [Van Dorland et al., 1997; Berntsen et al., 1997]. Many studies show distinct peaks in the seasonal cycle of the ozone forcing: most pronounced is the high RF at the northern hemisphere subtropical belt in July/August (Figure 4.12). A secondary maximum is found in the tropical region in autumn due the effects of biomass burning.

Tropospheric ozone levels are projected to increase further in future. The IPCC Special report on Scenarios developed 4 “marker scenarios” which represent different demographic, economical and technological developments. The so called A2 scenario represents the extreme range of emissions and results in the highest emissions of all 4 scenarios. The other scenarios are far less extreme. The older emission scenario IS92a results in emissions that are less than scenario A2 but more than scenario A1 with relatively low emission increases between 2000 and 2100. By using the IS92a scenario, Van Dorland et al. [1997], have calculated a 70% ozone change between 1990 and 2050 as compared with pre-industrial to 1990. This would result in a radiative forcing of 0.83  $Wm^{-2}$  and 0.66  $Wm^{-2}$  in 2050 (from pre-industrial time) for the annual mean northern hemispheric and global average respectively. Brasseur et al. [1998a] and Hauglustaine and Brasseur [2001] found for the same time horizon a comparable global mean RF of 0.63  $Wm^{-2}$  and 0.69  $Wm^{-2}$ , respectively, while the model of Stevenson et al. [1998] yields a lower RF of 0.48  $Wm^{-2}$  in 2100 due to temperature and associated humidity increases resulting in lower projected ozone levels.

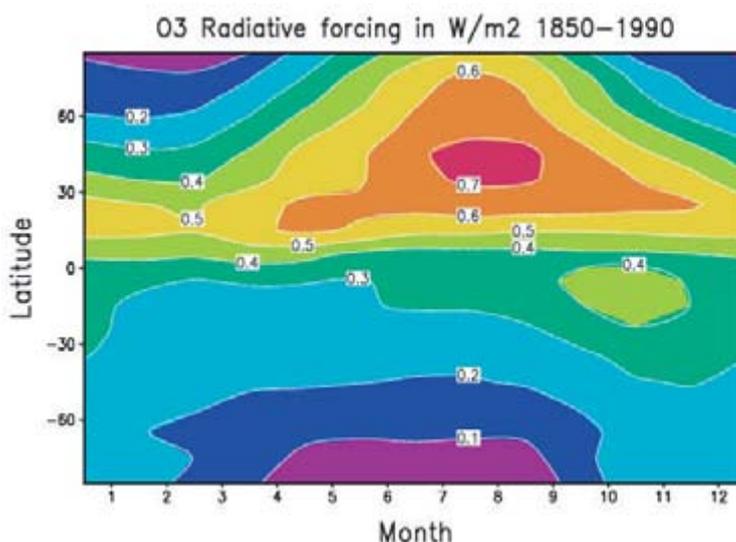


Figure 4.12 Radiative forcing due to changes in tropospheric ozone from pre-industrial to present conditions [Van Dorland et al., 1997].

The projected tropospheric ozone maximum for the 21<sup>st</sup> century shifts significantly southward as a result of increasing industrial activities in countries with emerging economies (see Section 4.3.2). Concurrently there is a shift in the time of the year of the ozone maximum from July/August for the period 1850-1990 to August/September for the period 1990-2050. As a follow up of the OxComp study for year 2100, radiative forcing has been estimated for the ozone distributions calculated in the intercomparison [Gauss et al., 2003]. The geographical distribution of the forcing reflects the estimated ozone changes, but is amplified over desert regions with high surface albedo (Figure 4.13). The range of the forcing as calculated in the Gauss et al. [2003] study is 0.40-0.78 Wm<sup>-2</sup>, associated with the simulated tropospheric ozone increase from present day to 2100.

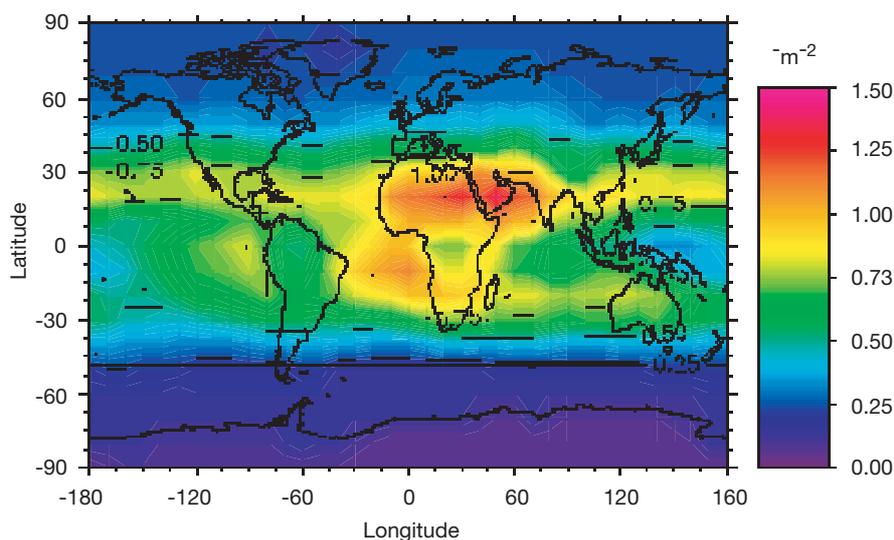


Figure 4.13 Radiative forcing due to changes in tropospheric ozone from 2000 to 2100 (average of 11 models in Gauss et al., [2003]).

- Several studies have yielded an increase in global yearly mean of tropospheric ozone since pre-industrial times of more than 30% (9 Dobson Units) with corresponding radiative forcings in the range from 0.2 to 0.5 Wm<sup>-2</sup>. This ranks ozone as the third most important greenhouse gas in this time period after CO<sub>2</sub> and CH<sub>4</sub>.
- A recent model intercomparison study which applied the IPCC A2p scenario calculated radiative forcing due to changes in ozone between 2000 and 2100 to be in the range 0.40 to 0.78 Wm<sup>-2</sup>.
- The geographical distribution of the radiative forcing due to tropospheric ozone is much more inhomogeneous than that of the well-mixed greenhouse gases, more like the forcing due to aerosols.

#### 4.4.1.2 Indirect radiative forcing

The hydroxyl radical, OH, which removes methane and other GHG from the atmosphere, is produced from ozone and water vapour in the troposphere, in the presence of solar radiation. The impact of the ozone precursors (CH<sub>4</sub>, CO, VOC and NO<sub>x</sub>) on climate thus has an indirect climate effect by their impact on OH, in addition to their impact through production of ozone [see e.g. Lelieveld et al., 1993, 1998; Johnson and Derwent, 1996; Fuglestvedt et al., 1996, 1999]. This can partly be viewed as an indirect effect of changes in tropospheric ozone. It is important to notice, however, that the ozone precursors in addition influence the OH concentrations through reactions not involving ozone. Only part of their indirect climate effect therefore involves ozone in an explicit manner. Any regulatory action aimed at reducing tropospheric ozone must, however, take these processes into consideration.

Table 4.2 Impacts of ozone precursor gases on the radiative forcing. + denotes a positive RF, - a negative RF. \* denotes low NO<sub>x</sub> conditions, see text.

Source gas	Tropospheric Ozone	Methane and other gases removed by OH
CH <sub>4</sub>	+	+
CO	+ (- *)	+
NMVOC	+ (- *)	+
NO <sub>x</sub>	+	-

Table 4.2 summarises the impact of the ozone precursors on the radiative forcing. As previously shown, CH<sub>4</sub>, CO, VOC and NO<sub>x</sub> lead to an increase in ozone and a positive (marked as + in Table 4.2) radiative forcing. The exceptions are effects of CO and VOC (perhaps also CH<sub>4</sub>) in regions of extremely low NO<sub>x</sub>, where they can result in ozone reductions and a negative (marked as -) radiative forcing (hence the \* in Table 4.2). This effect has only a weak impact on the global radiative forcing. CH<sub>4</sub>, CO and VOCs react with OH and therefore reduce OH and impose a positive radiative forcing. An opposing effect is the production of OH from the increase in ozone. This is usually a somewhat weaker effect, yielding an overall positive radiative forcing due to the impact on OH. The role of NO<sub>x</sub> is different since it increases OH also in the first place (by shifting the HO<sub>2</sub>/OH balance towards higher values of OH), yielding a negative radiative forcing from NO<sub>x</sub>. Wild et al. (2001) found that this effect dominated over the positive forcing due to production of ozone, yielding an overall slightly negative radiative forcing for NO<sub>x</sub> when integrated over 100 years.

- *The ozone precursors (CH<sub>4</sub>, CO, VOC and NO<sub>x</sub>) have an indirect climate effect by their impact on OH, in addition to their impact through production of ozone. For CH<sub>4</sub>, CO and VOCs this forcing is positive, working in the same direction as the ozone forcing. For NO<sub>x</sub> the indirect forcing opposes the ozone forcing.*

#### 4.4.2 Climate impact of tropospheric ozone change on temperature

Different climate models have different values for the global mean climate sensitivity parameter  $\lambda$  (see Chapter 2). The current range for  $\lambda$  is 0.4 to 1.2 K (Wm<sup>-2</sup>)<sup>-1</sup> [Ramaswamy, 2001]. The sensitivity represents the amalgamation of all feedback processes in the model, and the wide range reflects differences in model parameterisations, mainly relating to clouds and sea-ice. A further concern is that within a given model, whilst  $\lambda$  is approximately constant for the well-mixed greenhouse gases, it does vary somewhat for more spatially heterogeneous forcings, such as changes in ozone and aerosols.

Because ozone has a relatively short lifetime (from a few days at the surface in the tropics to several months in the upper troposphere), its distribution has changed due to anthropogenic activities in a spatially heterogeneous way. For ozone changes, the largest radiative forcings are produced for changes at tropopause levels, because of the low temperatures in this region [Lacis et al., 1990; Brasseur et al., 1998b]. For a given change in ozone, the largest forcings are seen over hot, cloud-free high albedo land, or areas of low, warm cloud with a high, cold tropopause (i.e. sub-tropical deserts and oceanic stratocumulus regions) [Gauss et al., 2003].

There have been only a few studies concerning the impact of tropospheric ozone changes on climate using GCMs [Hansen et al., 1997; Bintanja et al., 1997; Christiansen, 1999; Ponater et al., 1999; Stuber et al., 2001a, b; Grewe et al., 2002; Sausen et al., 2002; Joshi et al., 2003]. The GCMs used were of varying complexity, and the experiments generally considered only highly idealised ozone changes [apart from Ponater et al., 1999; Stuber et al., 2001a]. Hansen et al. [1997] found that  $\lambda$  was strongly influenced by cloud feedbacks, and was most sensitive to lower tropospheric ozone changes. Bintanja et al. [1997] found that  $\lambda$  depended on the latitudinal distribution of the

radiative forcing, mainly due the ice-albedo feedback. Consequently, climate was more sensitive to ozone changes at high latitudes. Christiansen [1999] also looked at climate sensitivity and the vertical structure of ozone changes, but found much less variation with height than Hansen et al. [1997]. Differences were attributed to the different treatment of cloud feedbacks in the two models. Stuber et al. [2001a, b] found that for ozone changes in the lower and mid-troposphere  $\lambda$  was similar to the value found for  $\text{CO}_2$ , but a lower sensitivity was found in the upper troposphere. In contrast, a higher sensitivity was found for ozone changes in the lower stratosphere: this was related to a strong feedback with lower stratospheric water vapour. However, the feedback from  $\text{H}_2\text{O}$  on ozone through chemistry was no included. Joshi et al. [2003] have attempted to build a consensus view, by comparing results from the same experiments performed by 3 GCMs: the University of Reading, ECHAM4/DLR, and LMD models. All of these models found that for global ozone changes just below the tropopause,  $\lambda$  was reduced by 16-37% compared to the equivalent forcing from  $\text{CO}_2$ , whereas  $\lambda$  was increased by 23-80% for ozone changes in the lower stratosphere (see Figure 4.14). There was a lack of consensus between the models about the sensitivity of the extra-tropics compared to the tropics. Overall, this study suggested that for the same magnitude radiative forcing, tropospheric ozone was  $\sim 25\%$  less effective in generating a climate response, compared to  $\text{CO}_2$ . The reason for this appears to be that increases in upper tropospheric ozone cause reduced dynamic coupling between the surface and the upper troposphere. Furthermore this ozone increase appears to reduce the cold point temperature at the tropical tropopause and hence reduces the water vapour transport to the stratosphere. However, in one of the experiments reported by Sausen et al. [2002] (experiment ON-LT), ozone changes in the boundary layer generate a 60% larger climate response than for an equivalent  $\text{CO}_2$  forcing. Clearly, this could be important, as some of the largest observed increases in tropospheric ozone have been observed in this region.

Folland et al. [1998] used the Met Office Hadley Centre GCM to consider the individual impacts of a variety of anthropogenic forcings over the second half of the twentieth century, including the simulated change in tropospheric ozone. These authors found that the increase in tropospheric ozone generated a distinctive signature (tropospheric warming and lower stratospheric cooling), as compared to the response for the well-mixed greenhouse gases (tropospheric warming and upper stratospheric cooling).

Clearly, studies of the climate change in response to a given radiative forcing resulting from changes in tropospheric ozone are only in their beginning, representing a future research challenge. Potentially, even surprises may arise from fully interactively coupled CTMs due to new modes of the system.

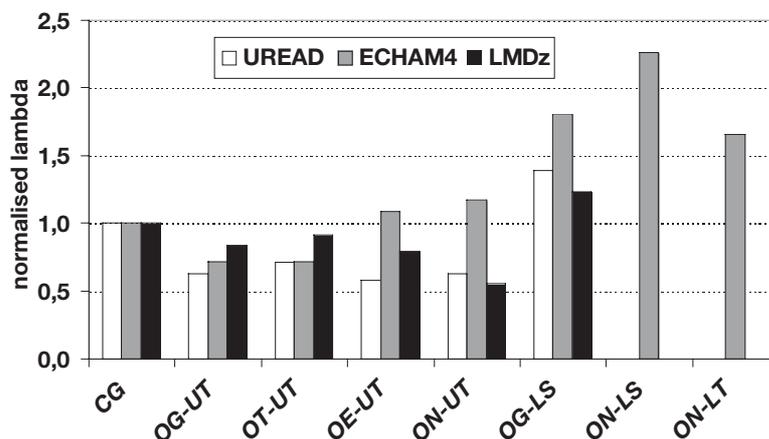


Figure 4.14 Normalised climate sensitivity parameters  $\lambda/\lambda_{\text{CO}_2}$  as simulated by 3 different models (UREAD, ECHAM4, LMDz) for various experiments (CG:  $\text{CO}_2$  added globally, vertically homogeneous; OG-UT: ozone added globally in the upper troposphere, i.e. in the levels just below the thermal tropopause; OT-UT: ozone added equator-ward of  $30^\circ$  in the upper troposphere; OE-UT: ozone added pole-ward of  $30^\circ$  in the upper troposphere; ON-UT: ozone added northwards of  $30^\circ\text{N}$

in the upper troposphere; *OG-LS*: ozone added globally in the lower stratosphere (in levels that are everywhere higher than the tropical tropopause); *ON-LS*: ozone added northwards of 30°N in the lower stratosphere; *ON-LT*: ozone added northward of 30°N in the planetary boundary layer). The figure is adopted from Sausen et al. [2002] and from Joshi et al. [2003].

- For ozone changes, the largest radiative forcings are produced for changes at tropopause levels, because of the low temperatures in this region. In addition, the climate response to a given radiative forcing depends on the altitude of the ozone change.
- There have been only a few studies concerning the impact of tropospheric ozone changes on climate using GCMs. A recent study build on results from three different models suggested that for the same magnitude radiative forcing, tropospheric ozone was in general ~25% less effective in generating a climate response, compared to CO<sub>2</sub>, with a range from ~50% less effective to ~50% more effective than CO<sub>2</sub> depending on altitude and latitude region of ozone change.

## 4.5 Conclusions

Tropospheric ozone influences the radiative balance of our planet, both by absorbing solar radiation and, more importantly, by acting as a greenhouse gas (GHG) through absorption and re-emission of infrared radiation from the Earth's surface. Thus ozone plays an important role in the climate system. It is now well recognised that the large increase in the background tropospheric ozone concentrations during the previous century is mainly due to anthropogenic emissions of ozone precursors. The ozone increase in the troposphere has lead to trapping of radiation in the troposphere, yielding a positive radiative forcing. Recent calculations show that the increase in tropospheric ozone represents the third largest positive radiative forcing since pre-industrial time (within the uncertainty rage 0.2–0.5 Wm<sup>-2</sup>). In this way the ozone increase has had a significant climate warming impact.

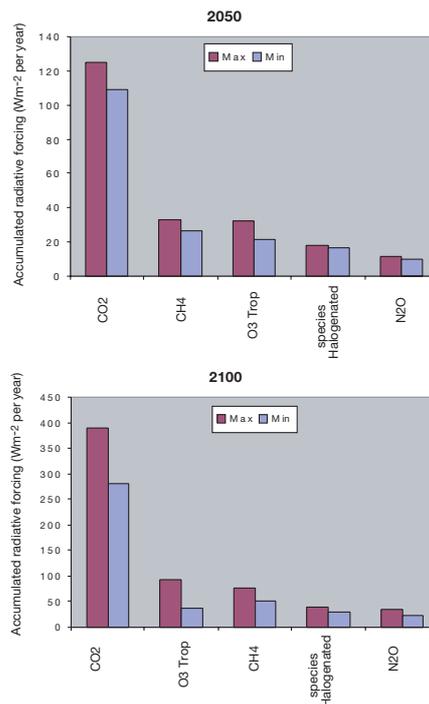


Figure 4.15 Accumulated radiative forcing (in Wm<sup>-2</sup> per year) due to greenhouse gases from 2000 to 2050 (upper panel) and 2100 (lower panel). The results are based on instantaneous radiative forcing scenarios (in Wm<sup>-2</sup>) for each 10 years between 2000 and 2100 estimated in IPCC [2001] for tropospheric ozone, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and a range of halogenated greenhouse gases (CFCs, HCFCs, HFCs, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and SF<sub>6</sub>). The numbers have been accumulated for this report.

Emissions of ozone precursors are expected to increase significantly in the future. This is particularly the case in regions where rapid economic growth or population increase is expected (i.e., south-east Asia, South and Central America, Africa). Thus tropospheric ozone caused by anthropogenic emissions will continue to contribute to climate warming during this century. According to scenarios established in IPCC [2001] the global radiative forcing due to ozone will range from 0.4 to 1.0  $\text{Wm}^{-2}$  in 2050 and from 0.2 to 1.3  $\text{Wm}^{-2}$  in 2100. Climate change is as a first approximation proportional to the accumulated forcing up to a given point in time. The accumulated forcing due to tropospheric ozone is given in Figure 4.15, up till 2050 as well as 2100. It is compared to the accumulated forcing due to other greenhouse gases, again based on scenarios for radiative forcing given by IPCC [2001]. The maximum as well as the minimum values are given for each greenhouse gas, representing an uncertainty range. The results show that tropospheric ozone will continue to be an important climate gas in the next hundred years, and perhaps be the second most important contributor to climate warming after  $\text{CO}_2$ .

- *The increase in tropospheric ozone represents the third largest positive radiative forcing since pre-industrial time. Tropospheric ozone will continue to be an important climate gas in the next hundred years, and perhaps be the second most important contributor to climate warming after  $\text{CO}_2$ .*



## IMPACT OF CLIMATE CHANGE ON TROPOSPHERIC OZONE

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### 5.1 Background

Several studies, summarised in IPCC [2001] and in Chapter 4, have shown that global tropospheric ozone has increased by between 7 and 12 DU (or 20-33 %) since the pre-industrial era, mostly in the northern hemisphere. Background ozone concentrations in the lower troposphere over Europe may have increased by a factor of 2-3 since the end of the 19<sup>th</sup> century [Volz and Kley, 1988]. These changes have been attributed to increases in surface emissions of ozone precursors, i.e. methane, nitrogen oxides, carbon monoxide and hydrocarbons. Such increases are mostly related to human activities linked to industrialisation, agricultural practices and land-use changes. During the next decades, it is expected that surface emissions related to human activities will continue to increase, with limited changes in temperate regions and large changes in developing countries in tropical regions.

However, climate change will also lead to a wide set of changes, not only in anthropogenic surface emissions, but also in climate-sensitive natural emissions; gas-phase and heterogeneous chemical processes; deposition processes; transport; and removal of chemical species (see Figure 5.1). This chapter discusses possible impacts of changes in climatic patterns on the different processes that determine the global distribution of ozone in the troposphere. Because of the complexity of the interactions and the scarcity of observations (especially over long time series), this chapter reports mostly on studies using comprehensive global model simulations to estimate the impacts of the various processes.

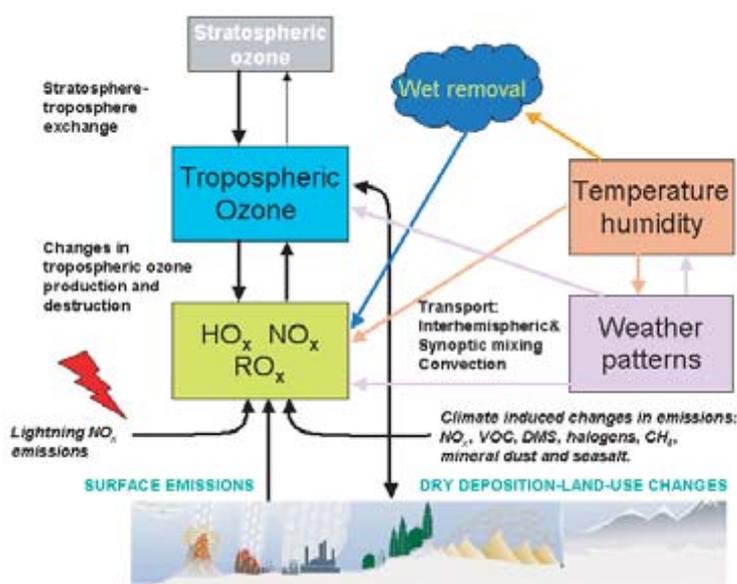


Figure 5.1 Schematic description of the chemical and physical processes discussed in the chapter.

Most of the possible impacts discussed in this chapter are rather speculative and inherently difficult to quantify, since they are based on an incomplete knowledge of the possible climate related processes that may impact ozone concentrations. Therefore this chapter will discuss a number of processes that have been identified as important for the current tropospheric ozone budget. Then attempts are made to estimate the impact of climate change on the distribution of tropospheric ozone. A qualitative expert judgement using the qualifications *small-medium-large*, meaning <1%, 1-5%, >5% change relative to present-day concentrations for different altitude levels in the troposphere will be provided. This chapter also proposes an estimation of the sign of the change possible.

## 5.2 The impact of climate change on ozone precursor emissions and sinks

This section considers the sources and sinks of the precursor gases that control the global distribution of ozone in the troposphere through chemical interactions, i.e. methane, nitrogen oxides, carbon monoxide, volatile organic compounds (VOCs) and aerosols. Anthropogenic emissions of ozone precursor gases are described in more detail in Chapter 4. In this section, focus is more particularly on natural emissions because they are most likely to be affected by climate change and, in particular, changes in vegetation, rainfall and surface temperatures. The sensitivity of some human-activity related emissions and of ozone surface deposition to climate change is also discussed. The potential impact of these climate-induced changes on the tropospheric ozone distribution is briefly discussed. It should be noted that the distinction between human-related and natural emissions is not always well defined. For example, emissions related to biomass burning have both natural and anthropogenic components.

### 5.2.1 Human-activity related emissions

#### *Fossil fuel related emissions*

Climatic changes have the potential to affect human activities such as energy consumption for heating and transport, agriculture, forestry, and the survival of human settlements in endangered climatic zones (e.g. those in coastal settlements, arid regions or permafrost regions). Since most of these activities generate emissions of ozone precursors, climate-induced activity changes will be accompanied by changes in emissions of precursor gases. The effect of temperature increases on the evaporative emissions of anthropogenic non-methane-volatile organic compounds (NMVOCs) is potentially important. Current evaporative emissions account for about half of all NMVOC emissions. Since the influence of temperature on evaporation processes is expected to be exponential, clearly this process may be important. However the magnitude of such changes will depend on how, and to what extent, we introduce emissions reductions and how well we are able to respond and adapt to climate change, and hence abate the increase of e.g. NMVOCs emissions.

Therefore there is little quantitative information on the climate related change of these emissions and its potential effects on ozone. Emission scenarios, such as those developed in the IPCC Special Report on Emission Scenarios (SRES) so far have not considered a climate impact on anthropogenic emissions [J. Olivier, personal communication, 2002] since the first-order effects were considered to be *small*.

It should also be noted that changes in the concentrations of ozone precursors, such as nitrogen oxides due to changes in anthropogenic emissions, could influence the importance of natural emissions through non-linear chemistry.

- *First-order impacts of climate change on ozone through changes in fossil-fuel related emissions are expected to be small, and the sign of the ozone change cannot be identified.*

### *Biomass burning emissions*

There is an important link between climate and land-use related emissions, through the strong relationship of land-use changes and biomass burning, i.e. the burning of plant material, which represents a major source of trace gases and aerosols at the global scale [e.g. Crutzen and Andreae, 1990]. Biomass burning accounts for about 50% of the global emissions of CO, 21% of NO<sub>x</sub>, and 8% of CH<sub>4</sub> [Granier et al., 2000]. Biomass burning may contribute about 5% of the total aerosol mass emitted into the atmosphere, but the actual contribution to the aerosol fraction smaller than 1 micrometer may be much higher. A number of studies have been devoted to the influence of biomass burning on tropospheric ozone. Marufu et al. [2000] estimated that globally, biomass burning contributes 9%, or 29 Tg to total tropospheric ozone amounts. Schultz et al. [1999] found experimental evidence for the large-scale impact of biomass burning on tropospheric ozone and ozone precursor concentrations, and estimated the enhancement of ozone over the south Pacific in austral spring to be 7-8 ppbv throughout the troposphere. Galanter et al. [2000] and Granier et al. [2000] concluded that biomass burning contributes more than 15% and 18%, respectively, of surface tropospheric ozone concentrations in the tropics throughout the year. Measurements of surface CO concentration at various stations in the northern hemisphere show a significant year-to-year correlation with the estimated area burned in boreal forest fires over the 1990s [Wotawa et al., 2001].

The majority of fires occur in the tropical latitudes and are believed to be human-induced [Andreae, 1991]. They are related to domestic cooking and heating, agricultural waste burning, and the clearing of forested land. However fire is also a natural factor in the self-regulation of ecosystems [e.g. Oliver and Larson, 1996; Skinner et al., 2000]. For example, fires induced by lightning strokes are estimated to ignite about 10% of the vegetation fires in boreal and temperate forests, but these fires may account for up to 37% of the burned area due to their remoteness [Korovin and Romanovich, 1996]. Current estimates of emissions from vegetation fires are very uncertain due to the lack of systematic long-term monitoring of fire occurrence and amount of biomass burnt. Earlier emission inventories [e.g. Hao and Liu, 1994] relied on the use of burned area statistics and plausible assumptions on the amount of vegetation burned and the related emission factors. These inventories are estimated to be uncertain by at least a factor of two [Schultz, 2002]. In addition, the timing of these fires is uncertain and there is no information on the inter-annual variability. Very recently, satellite observations have been used to address these issues by using aerosol optical density [Duncan et al., 2002a], active fire counts [Schultz, 2002], or burned areas [Barbosa et al., 1999; Hölzemann et al., 2002]. Unfortunately, due to the rather short lifetime of satellites, their different orbital characteristics, and the current disagreement between different satellite sensors, it is not yet possible to assess the longer-term trends of global fire occurrence and to detect a possible impact from recent climate change.

The dominant natural factors controlling the amount of biomass burned in a given year are the amount of fuel available (i.e. plant litter, twigs, small stems), the soil and vegetation dryness, temperature, and wind speed [Bond and Van Wilgen, 1996]. Changes in these parameters lead to the large inter-annual variability of fire occurrence, which can be observed from space and in regional field studies. For example, Barbosa et al. [1999] estimate an inter-annual variability of biomass burning emissions in Africa of 30% for the period 1981-1991, and Wotawa et al. [2001] report a factor of 10 range in the burnt area in boreal forests in North America and Russia over the 1990s. Climate change may lead to prolonged dryness in some regions, which would change the statistics towards more frequent years with high fire occurrence. In addition, changes in lightning activity may lead to intensified burning in temperate and boreal regions. Simulations with a global general circulation model suggest a 44% increase in lightning activity under 2xCO<sub>2</sub> conditions, which would almost lead to a doubling of the burnt area in the US [Price and Rind, 1994; Flannigan et al., 2000]. Skinner et al. [2000] report that the burned area in some regions of Canada has tripled between 1980 and 2000, which may be related to changes in weather patterns. Fire emissions from tropical regions are expected to be less affected by climate change as most fires result from human-induced controlled burns in these regions.

Climate change might also modify the extent and intensification of individual fires, which complicates the assessment of its impact. Furthermore in many regions, policy-driven fire suppression strategies play a significant role. For example, forest management in the US has led to far fewer fires over the recent decades, but also to the build-up of large reservoirs of available bio-fuel, which bears the risk of fewer but larger and more intense fires in the future.

- *Biomass burning, which displays a large spatial and temporal variability, has a strong influence on the current global ozone burden. The influence of climate-induced changes in biomass burning on tropospheric ozone may be medium to large. However the sign and strength of the impact may vary regionally.*

### 5.2.2 Natural emissions and sinks

Natural emissions of compounds can significantly affect the distribution of tropospheric ozone. These processes include emissions of: (i) nitrous oxide and nitrogen oxides from soils; (ii) nitrogen oxides from lightning; (iii) methane from wetlands; (iv) hydrocarbons from vegetation; (v) various gases from the oceans; and (vi) particles by physical processes. This section also considers dry deposition of ozone at the surface. As seen in the previous chapters, nitrogen oxides and nitrous oxide play a key role in the determination of the photochemical production of ozone.

#### 5.2.2.1 Natural sources of oxidised nitrogen.

##### **Emissions by soils**

Soils are an important source of oxidised nitrogen due to the microbial production of nitrous oxide ( $N_2O$ ) and nitric oxide (NO). The emitted NO is involved in fast (~minutes) chemical transformations resulting in a net emission flux of nitrogen oxides ( $NO_x = NO + NO_2$ ). The production of  $NO_x$  depends on biogeochemical and physical soil properties and is tightly linked to land-use management. The actual flux of reactive nitrogen into the atmosphere over vegetation depends on the interactions between turbulent transport, chemistry and the subsequent uptake of the reaction products within the canopy.

Global estimates of soil NO surface emissions to the atmosphere range between 9.7 Tg (N) per year [Potter et al., 1996] and 21 Tg (N) per year [Davidson and Kinglerlee, 1997]. Estimates that include the role of canopy deposition are about 50% smaller [Yienger and Levy, 1995; Ganzeveld et al., 2002a]. These emissions control the  $NO_x$  budgets in remote and rural areas, while the fossil fuel source of about 33 Tg (N) per year dominates the  $NO_x$  budget in industrialised areas. It is thought that there is a significant anthropogenic component in NO soil emissions, induced by the use of fertilizer, which may at present amount to 50% of all soil NO emissions. Current estimates of the influence of soil on global tropospheric ozone amount to 10%, or 5 ppbv [Lelieveld and Dentener, 2000]. Ganzeveld et al. [2002a] estimated that the tropospheric ozone burden increased by about 5% for an increase of soil NO<sub>x</sub> emissions of about 10 Tg (N) per year.

Soil NO and  $N_2O$  are largely produced by nitrification and denitrification processes, which are influenced by soil environmental conditions [Conrad, 1996] such as soil temperature, moisture, fertility and vegetation cover. For example, a 10°C rise in soil temperature produces a 2-5 fold increase in NO emission rates [Williams and Fehsenfeld, 1991; Valente and Thornton, 1993]. Short-term changes in soil moisture after a rainfall event can influence soil behaviour to the extent that production of NO can revert to NO consumption [Davidson, 1991] or, in contrast, result in a large pulse of NO emissions [Davidson, 1992; Meixner and Engster, 1999]. One of the specific land-use practices, biomass burning, results in a temporary reduction in the plant and microbial sink of soil inorganic nitrogen, favouring the conditions for NO production [e.g. Verchot et al., 1999]. In addition, changes in vegetation cover, for example due to deforestation, are expected to result in a decrease in the canopy deposition [Kirkman et al., 2002] and consequently in a more significant contribution, by soil-biogenic NO emissions, to the atmospheric  $NO_x$  budget.

These examples illustrate that there is no straightforward extrapolation of climate and land-use induced impacts on soil-biogenic NO and N<sub>2</sub>O fluxes. For example, there might be a short-term increase in the soil NO emissions due to a temperature change, but the long-term effect may be reduced due to a depletion of the substrates that are involved in the relevant microbiological processes.

A promising approach to assess the impact of anticipated future climate, land use and land cover conditions on soil-biogenic NO and N<sub>2</sub>O emissions, is the use of process-based soil nitrogen emission models [e.g. Li et al., 1992]. These models consider, to some extent, the short- and long-term variabilities in biogeochemical processes and emission fluxes as functions of the controlling environmental parameters such as temperature, soil moisture and vegetation dynamics. The models provide a tool to assess the impact of climate change, land cover and land use changes on soil-biogenic NO<sub>x</sub> emissions on short as well as on long time-scales. Moreover the process models can be used to identify the key parameters that are mainly responsible for the changes in the soil-biogenic NO<sub>x</sub> emissions.

- *The magnitude and potential climate induced changes of soil NO<sub>x</sub> emissions, and their relevance to O<sub>3</sub> concentrations indicates a highly uncertain medium impact on global O<sub>3</sub>.*

### **Emissions by lightning**

The production of NO in a lightning discharge is generally believed to take place according to the Zel'dovich and Raizer [1966] mechanism of N<sub>2</sub> and O<sub>2</sub> dissociation and subsequent NO formation in the hot (~4500K) lightning channel. Due to rapid cooling of the air heated by a lightning stroke the NO produced by lightning is preserved. Subsequently, in the atmosphere NO<sub>2</sub> will quickly form due to the photostationary steady state involving ozone, NO, and NO<sub>2</sub>.

NO<sub>x</sub> production from lightning is important for the ozone budget in the troposphere because of the high altitude and relatively clean conditions in which it is released. Unfortunately, the amount of thermo-chemical production of NO<sub>x</sub> in lightning discharges is poorly known. Recent estimates of the global lightning NO<sub>x</sub> production rate converge at a range of 2-20 Tg (N) per year [Lawrence et al., 1995; Price et al., 1997]. This can be compared to the emissions from fossil fuel combustion of about 33 Tg (N) per year [IPCC, 2001]. Lelieveld and Dentener [2000] estimate that at present, O<sub>3</sub> produced by lightning in various continental regions contributes 10-35% of the tropospheric ozone concentrations, with a tropospheric average of 26%. Grewe et al. [2001] estimate this input to be 5-20%. Another 3-D model study indicates an increase in global tropospheric ozone of 12%, if NO<sub>x</sub> production from lightning is doubled from 5 Tg (N) per year to 10 Tg (N) per year [Brasseur et al., 1996].

The estimate of the impact of NO<sub>x</sub> emissions from lightning requires three pieces of information: (1) the lightning frequency; (2) the energy and amount of NO<sub>x</sub> produced per flash; and (3) the vertical distribution of the produced NO<sub>x</sub>.

Lightning arises from the breakdown of the charge separation in thunderstorms and requires the co-existence of liquid water, ice crystals and hail or graupel. The global frequency of lightning flashes was first estimated by Brooks [1925] to be of the order of 100 s<sup>-1</sup>. More recent observations with the Optical Transient Detector [Christian et al., 1996] show a global average of about 40 s<sup>-1</sup>. Lightning is much more frequent over land than over the oceans. The ratio is about 50:1 except for a few regions, which appear to be linked to continental outflow, where this ratio increases to about 10:1. There is a distinct seasonal and diurnal cycle with most flashes occurring during the northern hemisphere summer (about 1.5-2 times more than in winter [Orville and Spencer, 1979]) and during the afternoon.

Most current parameterisations of lightning NO<sub>x</sub> in the global CTMs that are used to simulate the distribution of tropospheric ozone typically rely on the work of Price and Rind [1992], who para-

meterise the flash frequency as a function of the maximum cloud top height raised to the 5<sup>th</sup> power, as a surrogate for the maximum updraft velocity in convective clouds. This yields a global flash frequency distribution which is consistent with the model physics and also gives reasonable global NO<sub>x</sub> production rates in CTM simulations. However the use of average thunderstorm properties is obviously a very crude approximation. Pickering et al. [1998] define three standard vertical NO<sub>x</sub> production profiles based on several observations and results from a cloud resolving transport model. By using the parameterisation of Pickering [1998], Meijer et al., [2001] demonstrated that the scaling of lightning with model convective precipitation gave the best agreement with observation from several aircraft campaigns such as EULINOX, POLINAT2, and SONEX. Recently, Kurz and Grewe [2002] published a new parameterisation of the flash frequency based on the mean updraft velocity in convective regions. This approach yields a good representation of the geographical and seasonal distribution of lightning flashes without the artificial distinction between land and ocean surfaces that was necessary in the Price and Rind [1992] parameterisation.

Field observations of NO<sub>x</sub> concentrations in or around active thunderstorm anvils provide another way for estimating the NO<sub>x</sub> production rate from lightning [Huntrieser et al., 1998 and references therein]. Although it is difficult to distinguish between the NO<sub>x</sub> produced from lightning and the NO<sub>x</sub> that is transported from the boundary layer in the cloud updraft, measurements show typical mixing ratio enhancements between 0.4 and 2 ppbv in the thunderstorm anvil [Huntrieser et al., 1998]. Unfortunately the extrapolation of these measurements to global estimates (0.3-22 Tg (N) per year) does not provide a better constraint than the theoretical studies.

Very little is known about climate induced changes in the variability and trends of lightning occurrence. As mentioned before, there is a close link between the hydrological cycle and lightning. Price and Rind [1994] use a climate model to predict a 5-6% increase in global lightning activity per degree Celsius global warming, with much larger regional and temporal changes. Stenke and Grewe [2002] find even larger changes of 14% per degree Kelvin. With the current range of expected global mean surface temperature increase over the period 1990 to 2100 of 1.5-5.8 K [IPCC, 2001], this would result in a 7.5-60% increase in lightning activity. This is corroborated by the consistent prediction of increased precipitation and intensity of the rainfall events in tropical and mid-latitude regions by five regional climate models in IPCC [2001]. Clearly, given the very important contribution of lightning-induced NO<sub>x</sub> to the global ozone budget, such an increase may have important consequences for the ozone budget.

- *Given the 10-25% contribution of lightning NO<sub>x</sub> to tropospheric ozone concentrations, and the likelihood of a high sensitivity of lightning to climate change, we expect the related increase of O<sub>3</sub> to be medium-to-large.*

#### 5.2.2.2 Natural emissions of methane

IPCC [2001] indicates that a 10% increase in CH<sub>4</sub> leads to a 1.5% increase in ozone. About 40% of the 600 Tg CH<sub>4</sub> emitted per year is of natural origin. The major natural sources are wetlands, which release between 90–240 Tg CH<sub>4</sub> per year [Matthews and Fung, 1987; Cao and Dent, 1995; Potter, 1997; Walter and Heimann, 2000] to the atmosphere. Inverse modelling-derived estimates hint at the upper half of this range [Hein et al., 1997; Houweling et al., 2000]. Key factors that determine the wetland methane emissions are the (seasonally varying) wetland area, the water table level, temperature, and a variety of soil and vegetation characteristics. Recent studies [Walter et al., 2001; Dlugokencky, 2001] suggest increased wetland emissions during relatively warm and wet years, which may partly explain the enhanced growth rate of CH<sub>4</sub> during the 1997-1998 El Niño, and, to a lesser extent, the reduced growth-rate after the Mt Pinatubo eruption. A study by Warwick et al. [2002] showed that meteorological dynamics could have a significant impact on both the local and global surface growth rates of methane.

Process modelling [Walter and Heimann, 2000] suggests a dependency on temperature of wetland emissions of the order of 20% per K. Using this relationship, a climate induced temperature increase of 2°C would result in about 40 Tg CH<sub>4</sub> per year higher emissions, which at steady state, would roughly correspond to a 10% increase in methane concentrations and an increase of global tropospheric ozone by 1.5%. However, more research is needed to corroborate these relationships. Systematic flux measurements are urgently lacking for some, especially tropical, wetland ecosystems [Walter and Heimann, 2000]. Linkage of wetland modelling and ecosystem modelling [Kaplan, 2001] may provide better tools to make flux estimates, and the application of remote sensing-derived products may improve the input to emissions models. Such satellite observations would consist of surface properties such as soil moisture or inundated areas. It is expected that, in the near future, column integrated methane mixing ratios from satellite experiments, such as SCIAMACHY on board ENVISAT in combination with inverse modelling may improve our knowledge and our capabilities in the quantification of the natural sources of methane.

The relatively unstable methane hydrates are natural gas locked within ice-like material at the bottom of oceans and in permafrost. Changes in ocean temperature or circulation or sudden melting of permafrost could release this methane to the atmosphere, contributing to a “runaway greenhouse” and substantial influence on atmospheric chemistry. Clearly, if the amounts of methane are large, it will have a large influence on ozone. However, it is not possible to quantify the effect since it is highly uncertain if, and to what extent, this process will happen.

- *Climate induced increases of CH<sub>4</sub> emissions could have a medium-to-large positive influence on O<sub>3</sub> concentrations.*

#### 5.2.2.3 Emissions of biogenic VOCs

Plants emit a wide range of highly reactive VOCs. At sufficiently high levels of NO<sub>x</sub>, the degradation of these compounds leads to a large photochemical production of ozone. In areas with low NO<sub>x</sub> levels, these VOCs reduce ozone levels. Another important impact of VOC emissions is the enhanced conversion of NO<sub>x</sub> into reservoir species such as organic nitrates (e.g. PAN), increasing the effective lifetime of NO<sub>y</sub>. On the global scale, increased biogenic VOC emissions would result in higher CO production and concentrations, and in a decreased oxidising capacity of the atmosphere. Whereas globally averaged OH concentrations would decrease, it is expected that upper tropospheric and lower stratospheric OH and HO<sub>2</sub> levels will increase because of the large relative contribution of oxygenated VOCs like acetone to the total production of HO<sub>x</sub> in this region of the atmosphere [Müller and Brasseur, 1999]. Isoprene emissions also have a significant effect on global ozone levels. Wang and Shallcross [2000] used a 3-D CTM to perform simulations with and without isoprene emissions. They found that ozone over marine locations increased by 4 ppbv, and by 8-12 ppbv over mid-latitude land areas when isoprene emissions were included. Houweling et al. [1998] and Poisson et al. [2000] estimated that including non-methane hydrocarbons (NMHCs) (both biogenic and anthropogenic) in a global model increases the tropospheric O<sub>3</sub> burden by about 17%, twice the 8% increase reported by Wang et al. [1998].

The emission rates of the biogenic VOCs (BVOCs) are highly variable among different plant species and are also strongly dependent on meteorological conditions. A major difficulty in estimating the global BVOC emissions arises from the very high biodiversity of the main source regions (tropical forests), since the emissions from only a small fraction of the total number of species have been measured. One of the most important natural VOCs is isoprene (C<sub>5</sub>H<sub>8</sub>), whose emissions depend on levels of photosynthetically-active radiation (PAR) and temperature. Figure 5.2 displays the normalised isoprene emissions using the model of Guenther et al. [1995]. At low light levels, the isoprene emission is linearly proportional to the PAR flux. The isoprene emission increases with temperature to a maximum at about 312 K and then decreases rapidly above this threshold temperature.

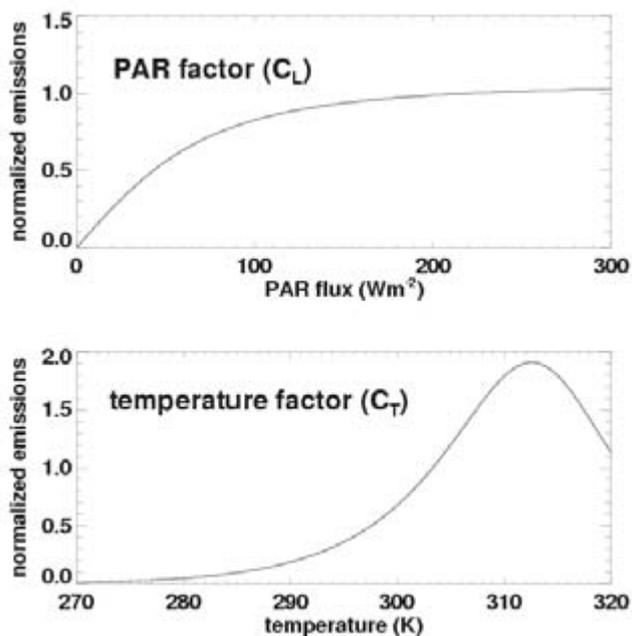


Figure 5.2 Dependence of emissions on photosynthetically-active radiation (PAR) and temperature (based on Guenther et al. [1995]).

Other important classes of VOCs emitted by plants are monoterpenes, sesquiterpenes, alcohols, aldehydes and ketones. Although it has generally been assumed that monoterpene emissions are only controlled by temperature, an increasing number of field data show that emissions from some plant species are controlled by both temperature and PAR, in a similar way to isoprene emissions. The complexity and the insufficient understanding of the associated processes restrict the accuracy of the quantification of all of these natural emissions.

The quantification of the impact of climate change on future BVOC emissions and their corresponding effect on ozone levels remains complex. The most important effect might be a large increase in the emission rates as a direct result of the higher temperature. Changes in cloudiness might have an important impact as well on isoprene emissions through their dependence on PAR levels. In addition, the areas of tropical forest will change in response to the climatic effects and human induced-deforestation. In consequence, the BVOC emissions will decrease if the areas of forest are reduced. More complex effects might arise from changes in the proportion of high-isoprene emitters in the different ecosystems. Finally, changes in plant metabolism and therefore in the emissions might result from increased exposure of vegetation to high levels of ozone or other pollutants, although little is known on this topic.

A modelling study by Sanderson et al. [2002], using the coupled GCM HadCM3 [Gordon et al., 2000], and including the chemistry model STOCHEM [Collins et al., 2000], the interactive vegetation model TRIFFID [Cox, 2001], and the isoprene emission model of Guenther et al. [1995], considered the effect of a warmer climate with increased levels of CO<sub>2</sub> (2090s; 712 ppmv) on isoprene emissions. The area of tropical forest had reduced in response to climate change, mainly in the Amazonia region. Despite this reduction in forest area, more isoprene (27%) was emitted globally compared to the present day due to the greater temperature, causing an increase in ozone levels of up to 10 ppbv in, for example, central Amazonia and the eastern USA. If vegetation changes are ignored, isoprene emissions in the 2090s have increased by 34% and the ozone levels in some areas increase by as much as 20 ppbv. In some locations with small vegetation changes, significant ozone increases were observed.

- *Climate induced changes of biogenic VOC emissions may be regionally substantial. The effect on global ozone may be medium-to-large and the sign will be mostly positive.*

#### 5.2.2.4 Oceanic emissions of sulphur containing gases

Oceans emit particulate precursor gases such as the sulphur containing the gases dimethyl sulphide (DMS), carbonyl sulphide (COS), and carbon disulphide (CS<sub>2</sub>). The main fate of DMS emissions in the atmosphere is oxidation to SO<sub>2</sub> and further to sulphate aerosol. Charlson et al. [1987] postulated a feedback mechanism between sulphate produced from DMS and clouds, which initiated much research on DMS. DMS may lead to changes in aerosol and cloud occurrence, which in turn may influence tropospheric ozone concentrations through heterogeneous chemistry and by influencing photolysis rates. These aspects are further discussed in Section 5.2.2.5.

It is likely that the distribution of plankton blooms, and thus the DMS emissions, will change due to a climate-induced change of ocean surface temperatures. This is corroborated by the analysis of long-term atmospheric DMS concentration measurements which were shown to be caused by variations of the oceanic source [Sciare et al., 2000] and correlated with an ENSO signal. The influence of climate change on biologically related DMS emissions has not yet been evaluated. However, the influence of increasing wind speeds in a future climate on DMS emissions has been evaluated by IPCC [2001], using wind speed information from the NCAR climate model. Globally DMS fluxes increase by about 6% due to an increase of winds. As discussed in Section 5.3.2, a few studies infer that the effect of clouds on tropospheric ozone is of the order of 5%, and the influence of DMS chemistry on cloud cover and cloud chemistry should be substantially smaller. Therefore, only very large changes of DMS emissions would significantly perturb cloud- and aerosol chemistry. The contribution of the biogenic emissions of COS and CS<sub>2</sub> to the sulphate burden in the troposphere is negligible compared to that of DMS. However these components are important for the stratospheric sulphate layer (see Chapters 2 and 3). At present, there are insufficient measurements available to evaluate a potential climate-emission link for these gases.

- *The influence of changing DMS and corresponding changing aerosol abundances on tropospheric ozone is expected to be low.*

#### 5.2.2.5 Climate induced changes of particulate emissions and heterogeneous chemistry

Jacob [2000] showed that, in general, ozone and its precursors HO<sub>x</sub> and NO<sub>x</sub> can be influenced by heterogeneous chemistry. The reaction of N<sub>2</sub>O<sub>5</sub> on wet aerosol and cloud droplets leading to HNO<sub>3</sub> is relatively well documented. It provides an important removal mechanism for NO<sub>x</sub> in the global troposphere, and significantly reduces the global tropospheric OH and O<sub>3</sub> concentrations by the order of 10% [Dentener and Crutzen, 1993].

Barrie et al. [1988] showed the occurrence of heterogeneous halogen reactions in the Arctic involving bromine from sea-salt, leading to an almost complete O<sub>3</sub> destruction in the boundary layer. Likewise, similar chemistry has been observed over the Dead Sea [Matveev et al., 2001] and the Great Salt Lake [Stutz et al., 2002]. High tropospheric BrO concentrations have been observed from the GOME satellite over large areas over both polar regions [Richter et al., 2002].

The production of sea-salt aerosol increases strongly with wind speed and may increase in the future by as much as 75% [IPCC, 2001]. Emissions of sea-salt lead to increases of inorganic halogens concentrations in the marine boundary layer. The loss of HNO<sub>3</sub> on these particles is very efficient, as it occurs with an accommodation coefficient ( $\gamma$ ) greater than 0.1 [Ten-Brink, 1998; Guimbaud et al., 2002].

Dickerson et al. [1999] found evidence for missing heterogeneous chemistry in the tropical marine boundary layer ozone budget. Vogt et al. [1996] calculate at steady state a destruction of

ozone amounting to 20-40% from sea-salt halogens. However, the chemistry of these reactions is complex, and not well understood. Furthermore, there may be synergies of sea-salt halogen chemistry and increasing emissions of acidifying anthropogenic emissions, e.g. those of ship exhaust [Keene, personal communication, 2002].

- *Chemical cycling of inorganic halogens from sea-salt will probably increase in the future. It can be tentatively estimated that there could be a medium negative impact of climate change on ozone from halogen activation in the marine boundary layer.*

Mineral dust emissions may increase by about 10% [IPCC, 2001], taking into account changes in wind-speed and soil moisture from the climate model of Dai et al. [2001], however this estimate is extremely uncertain.

Reactions of O<sub>3</sub> and its precursors on mineral dust may be important, since several studies report low ozone concomitant with elevated dust concentrations [e.g. Balkanski et al., 2002] However, conclusive experimental evidence for the importance of these reactions is lacking. A model study by Dentener et al. [1996] estimated an ozone loss of 2-10% by reactions of O<sub>3</sub>, NO<sub>x</sub> and HO<sub>2</sub> on mineral aerosol over source regions. Recent laboratory experiments [Hanisch and Crowley, 2001a, b, 2002] confirm the rapid HNO<sub>3</sub> uptake and have shown that uptake of O<sub>3</sub> on aerosols is significant. Recent global modelling [Bauer et al., 2002] accounting for uptake of O<sub>3</sub>, HNO<sub>3</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, shows decreases of tropospheric O<sub>3</sub> ranging from 10-30% in the tropics and northern sub-tropics. A large part of this decrease was caused by efficient uptake of HNO<sub>3</sub> on mineral dust.

- *Climate induced increase of mineral aerosol concentrations is expected to have a small and regionally medium negative impact on future ozone concentrations.*

#### 5.2.2.6 Natural emissions of organohalogen gases

A number of organohalogens of natural, or partly natural origin exist in the atmosphere; the emissions and concentrations of which may respond to changes in climate via changes in the biosphere, oceanic emissions, and atmospheric removal processes and transport.

Methyl chloride (CH<sub>3</sub>Cl) contributes some 15% of total tropospheric organic chlorine (CCl<sub>y</sub>) [WMO, 2003]. However, its main effect is on stratospheric ozone. It appears to be predominantly of marine and terrestrial natural origin which could be influenced by changes in temperature, rainfall, vegetative cover, biogenic productivity, and sea level rise. Other more minor organochlorine gases of natural origins also exist, such as chloroform. A potential impact of a climate induced change of emissions has not been quantified.

Similarly, methyl bromide is the largest carrier of bromine to the stratosphere, but has both natural and anthropogenic origins. It affects both stratospheric and potentially upper tropospheric ozone (see Chapters 2 and 3). A number of other brominated gases such as bromoform, dibromomethane and mixed bromochloromethanes of predominantly natural origin affect the upper troposphere and stratospheric ozone [WMO, 2003]. This is discussed in Chapter 2.

Short-lived organoiodine compounds of natural origin (diiodomethane, bromoiodomethane, etc.) have been measured in clean marine air at coastal locations, as have the iodine radicals IO and OIO resulting from their photochemical breakdown [Carpenter, 2001; Allan, 2001]. It is believed that similar iodine chemistry occurs over the open ocean, although the origins of the organic precursors (biological versus photo-chemical) in the open ocean are a matter of debate. Models indicate that iodine chemistry can result in up to 13% of the available ozone being destroyed per day in marine air [McFiggans, 2000]. Any climate impact on coastal or open ocean marine productivity or marine photochemistry might therefore affect marine background ozone. A small amount of methyl iodide can reach higher altitudes [Bell, 2002], having a small effect on stratospheric ozone [Pundt, 1998; Wittrock, 2000].

- *Short-lived organohalogen emissions predominantly affect the marine boundary layer. Climate induced changes of organohalogen emissions cannot be quantified, although any changes will have a negative impact on tropospheric ozone.*

### 5.2.3 Dry deposition

Dry deposition, which is the irreversible removal of gases and aerosols at the Earth's surface, provides an important sink for ozone and some precursor gases. IPCC [2001] and Figure 5.3 indicate that dry-deposition is of comparable magnitude to stratosphere-troposphere exchange. Ganzeveld and Lelieveld [1995] evaluated two different parameterisations of ozone removal in a Global Circulation Model and found maximum differences in monthly mean ozone deposition fluxes of 10-50%.

Differences in surface concentrations were generally smaller associated with negative feedbacks in ozone concentrations through dry deposition and chemistry. However, O<sub>3</sub> was found to be influenced by about 5% up to a height of 2 km. Removal of ozone at the surface is most effective over vegetated surfaces, where it is largely controlled by stomatal uptake [e.g. Baldocchi et al., 1987; Kerstiens and Lenzian, 1989; Wesely and Hicks, 2000] and the amount of biomass. Soil uptake can also play a role, especially for canopies with a relatively small amount of biomass. The role of surface wetness is not well understood since measurements show significant uptake of ozone by wet canopies, whereas deposition models assume reduced uptake for wet surfaces based on the low solubility of ozone [e.g. Fuentes et al., 1992]. Several measurement campaigns have shown a decrease as well as increases in the uptake of ozone but the underlying mechanisms that explain these increases/decreases are not yet well understood. This is also due to the complex chemical interactions in the water film covering the vegetation including the co-deposition of other chemical compounds, e.g. SO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and fluids being exuded from the vegetation. This means that only empirical representations of the uptake by wet surfaces have been developed and used in various modelling studies. The low solubility of ozone also partly explains the observed small deposition velocities over the oceans [McKay et al., 1992] and snow and ice surfaces [Galbally and Roy, 1980; Wesely et al., 1981].

Anticipated changes in the dry deposition fluxes of ozone associated with climate change are expected to be controlled by changes in surface cover and land use due to the important role of surface cover for ozone dry deposition. In addition, an important feature will be how increases in the ambient CO<sub>2</sub> concentration and moisture exchange will affect stomatal exchanges and thereby ozone dry deposition velocities. For instance Ganzeveld et al. [2002b] calculate in Amazonia a smaller removal of ozone during the day due to deforestation, whereas during the night O<sub>3</sub> removal increases by larger soil uptake. Moreover, the potential impact of exceeding critical levels of exposure to ozone and critical loads of acidity and nitrogen deposition on plant physiology should be included in such analyses.

The analysis of the potential impacts of land cover and land use changes on the dry deposition processes is limited by the lack of understanding of underlying mechanisms that control dry deposition especially over snow and ice, soils, oceans and wet vegetation. Moreover, the complex interactions between the meteorology and the dry deposition process require the use of explicitly coupled meteorological, atmospheric and biogeochemistry models to assess the impact of anticipated future climate and associated land-cover and land-use changes on ozone dry deposition.

- *Climate change and land-use induced changes in deposition of ozone and precursor gases could have a medium influence of an unknown sign on O<sub>3</sub> abundances, mainly in the boundary layer.*

### 5.2.3 Wet deposition

Ozone precursor gases like H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>O, and HNO<sub>3</sub>, are efficiently scavenged by rain and snow. Similarly ozone depleting inorganic halogen gases are subject to washout. Climate change is likely to lead to an increase of precipitation and of the intensity of the rainfall events in tropical and mid-latitude regions [IPCC, 2001], which may in turn influence ozone concentrations.

Unfortunately, there is little information available on the effect of the impact of wet deposition on ozone abundances and the effect of climate induced precipitation changes on the ozone is difficult to assess. Current model parameterisations are crude and there are only few measurements available for evaluation of such processes. Lawrence and Crutzen [1998] have evaluated the effects of an additional removal by gravitational settling of  $\text{HNO}_3$  in ice-crystals. They found a substantial influence of 20-50% on free tropospheric  $\text{NO}_x$  abundances; the effect on ozone was calculated to be less than 10%. Dentener et al. [2002] used 15 years of ECMWF data in an off-line model, and evaluated the individual effect of inter-annual rainfall variability on tropospheric ozone to be smaller than 1%. Grewe et al. [2001] analysed climate chemistry simulations and found that a change in precipitation and circulation (from 1992 to 2015) led to changes of  $\text{NO}_y$  and  $\text{O}_3$  concentrations mainly in tropical regions of the order of -10%. The changes were attributed to a modification in the wash-out patterns.

- *Therefore the effect of climate change through changes in precipitation amounts, patterns and intensity is probably negative and small-medium to regionally large.*

### 5.3 Impact of climate change on tropospheric chemistry

This section focuses on the impact of climate changes on the mechanisms of ozone formation and loss in the troposphere. The distribution of most of the chemical species in the troposphere depends on the distribution of OH, which is the most efficient oxidising compound. Therefore, the distribution of OH and ozone are tightly linked. The following sub-sections discuss the impact of climate change on OH distributions and on methane, and the impact on the net photochemical production of ozone.

#### 5.3.1 Impact of climate change on the oxidation capacity of the troposphere

The main oxidant removing trace gases from the atmosphere is the hydroxyl (OH) radical. The production of the OH radical in the troposphere occurs through the photo-dissociation of ozone, yielding  $\text{O}(^1\text{D})$ , of which a few percent react with  $\text{H}_2\text{O}$  to produce OH radicals. The photo-dissociation reaction of ozone is very sensitive to changes in the UV irradiance [WMO, 1999]. Calculations of UV irradiance suggest that this quantity has increased since the early 1980s by 6-14% at more than 10 sites distributed over mid- and high latitudes of both hemispheres. These results are consistent with spectral ultraviolet irradiance measurements and estimates from satellite observations. The UV radiation at the surface depends on several factors (zenith angle as well as clouds, airborne fine particles, surface albedo, total ozone, etc.), and the complicated spatial and temporal distributions of these variables and their interactions limit our ability to describe fully the UV field at the global scale.

Different methods have been used to determine the global average OH concentration. Previous studies of OH variability have focused on the role of changing stratospheric ozone [e.g. Bekki et al., 1994] and changing surface emissions [e.g. Karlsdottir and Isaksen, 2000]. Only very few studies have been devoted to the role of meteorological variability, for example, Fuglestad et al. [1995] looked at the effect of UV fluxes, temperatures and water vapour on tropospheric ozone in a 2-D CTM. The important role of humidity on OH has been considered in several studies [Toumi et al., 1996; Johnson et al., 1999; Stevenson et al., 2000; Grewe et al., 2001]. Grewe et al. [2001] calculated that higher humidity increased OH, and led to changes in  $\text{NO}_y$  partitioning, with a higher proportion present as  $\text{HNO}_3$ . The higher solubility of  $\text{HNO}_3$  compared to other  $\text{NO}_y$  compounds generated an increased washout of  $\text{NO}_y$ , and a reduction in upper tropospheric  $\text{NO}_y$  and ozone. Stevenson et al. [2000] found that climate change has a negative feedback on both ozone and methane, mainly due to increases in the fluxes through the reactions  $\text{O}(^1\text{D})+\text{H}_2\text{O}$  and  $\text{CH}_4+\text{OH}$ , respectively. The ozone changes due to climate change are driven mainly by increases in humidity; the methane changes reflect increases in both humidity and temperature, as the  $\text{CH}_4+\text{OH}$  reaction is strongly temperature dependent.

The lifetime of methane, a greenhouse gas, as well as an ozone precursor has been discussed in IPCC [2001]. The methane lifetime is mostly determined by the OH concentrations in the lower tropical troposphere, where temperature and humidity are large. Johnson et al. [2002] used a climate model to show that a substantial part of the variability of the observed recent methane growth rates could be associated with meteorological variability. A strong link to the El Niño Southern Oscillation (ENSO) and the model water vapour was demonstrated. In a similar study, Dentener [2002] used the ECMWF ERA15 re-analysis and calculated a  $0.24 \pm 0.06\%$  per year change in OH for the period 1979-1993. This trend can be compared to the study of Krol et al. [2001], who used methylchloroform measurements to derive a trend of  $0.46\% \pm 0.6\%$  per year. A large part of the calculated change of OH could again be explained by meteorological variability and more specifically humidity. Variability of precipitation rates and clouds were of smaller significance for global OH.

- *A link between meteorological variability, especially absolute humidity, and oxidation capacity has been demonstrated. Increased humidity will probably increase OH concentrations.*

### 5.3.2 Impact of climate change on global production and loss rates of ozone

As detailed in Chapter 4, ozone chemical production occurs when NO reacts with a peroxy radical. Ozone is chemically destroyed in the troposphere mainly through the reaction of O(<sup>1</sup>D) (following the photolytic destruction of ozone) and H<sub>2</sub>O, and its reaction with HO<sub>2</sub> and OH. As indicated in the previous chapter, present-day net chemical production (NCP) is difficult to quantify, as it is a relatively small residual (~70-600 Tg (O<sub>3</sub>) per year) of two large terms. NCP also has a distinct distribution: it peaks in the polluted boundary layer, but is negative over much of the oceans and in the lower-mid free troposphere, before becoming positive again in the upper troposphere. This distribution mainly reflects the concentration fields of NO<sub>x</sub> (typically a C-shaped profile) and H<sub>2</sub>O (decreasing exponentially with height). All of these chemical production and loss terms will be affected by climate change. Only a few groups have quantitatively addressed the impact of climate change on future ozone budgets using 3-D chemistry-climate models. Grewe et al. [2001] used the ECHAM3/CHEM model to simulate 1992 and 2015 atmospheres, and found that climate change reduced tropospheric ozone and NO<sub>y</sub>, through increases in temperature and humidity. This study also found that changes in precipitation patterns, particularly in the tropics, had a strong influence on HNO<sub>3</sub> concentrations, and hence NO<sub>x</sub> and ozone. Three other groups [Stevenson et al., 2000; Johnson et al., 2001; Zeng and Pyle, 2002] have used different chemistry models, but the same climate model (the UK Met. Office Hadley Centre model) to analyse the global ozone budget in detail. These studies used the SRES A2 scenario at the end of the 21<sup>st</sup> century, and compared a simulation with a fixed climate to one with a changed climate. Under the A2 scenario, global mean surface temperatures rise by 3.5 K between 1990 and 2100, and by ~5 K in the upper troposphere. Accompanying increases in specific humidity are between 15 and 84%, with the larger values in the upper troposphere. Table 5.1 summarises climate change impacts on the ozone budget.

Flux	Stevenson et al. [2000]	Johnson et al. [2001]	Zeng and Pyle [2002]
O <sub>3</sub> chemical production	6%	0%	+20%
O( <sup>1</sup> D)+H <sub>2</sub> O	+21%	+15%	+40%
O <sub>3</sub> chemical destruction	+10%	+4%	+37%
Net Chemical Production	-31%	-35%	-50%

Table 5.1 Difference in percentage change from 2000 to 2100 (A2 scenario) when climate change is included, relative to a fixed underlying climate.

In these studies, Zeng and Pyle [2002] included an increase of 10% in lightning  $\text{NO}_x$  emissions; the other studies kept this  $\text{NO}_x$  source fixed. Johnson et al. [2001] performed two 110-year integrations, and included the impact of climate on  $\text{CH}_4$  interactively. Climate change effects (higher temperatures and humidities) reduced 2100  $\text{CH}_4$  levels compared to the other studies that used prescribed values. This tends to reduce methoxy and peroxy radical concentrations, and hence  $\text{O}_3$  production. All three studies found that the  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  flux was the most sensitive to climate effects, and that although chemical production generally increased, chemical destruction increased by more, resulting in a large reduction in NCP. The Zeng and Pyle model appears to be more sensitive to climate change, and also predicts large increases in stratosphere-troposphere exchange. A more comprehensive description of climate change and STE is discussed in Chapters 2 and 3, and in the next section.

Climate change might also be accompanied by significant changes in cloud cover and lifetime [IPCC, 2001], which should affect tropospheric photochemistry and, in particular, ozone. Clouds cover on average about half of the earth's surface, and 5-10% of the volume of the troposphere is occupied by clouds. Lelieveld and Crutzen [1990] suggested a large effect of absorption and reaction of ozone and precursor gases in liquid water cloud droplets. Using 3-D models coupled with comprehensive aqueous phase chemistry schemes, the global effect of clouds on  $\text{O}_3$  has been estimated to be of the order of -3% to -7% [Dentener, 1993; Liang and Jacob, 1997]. Since our knowledge of aqueous phase chemical reactions is rather incomplete, these estimates remain very uncertain. The uncertainties in the effects of clouds on actinic fluxes are probably larger [Jacob, 2000]. Actinic fluxes are typically higher above clouds and lower below, compared to cloud-free conditions. The resulting effects on ozone concentrations have been estimated to range from -5% to +4%, and scale non-linearly with cloud amounts [Matthijssen, 1995]. This is corroborated by Brasseur et al. [2002], who found an increase in  $\text{O}_3$  production rates in the upper troposphere by 15% when clouds are considered.

- *Climate change induced changes in meteorology (more particularly in humidity) are likely to lead to large changes in net and gross  $\text{O}_3$  chemical production and losses. Therefore the negative effect on  $\text{O}_3$  is likely to be large. The highly uncertain effect of cloud changes on tropospheric ozone decrease is believed to be small.*

## 5.4 Impact of climate changes on the transport of ozone

### 5.4.1 Uncertainties on the present $\text{O}_3$ budget

Tropospheric ozone is influenced by chemical processes involving its precursors, weather patterns and, more importantly, by the influx of stratospheric ozone which is partly linked to the strength of the general circulation. The exact magnitude of the net flux of stratospheric ozone into the troposphere is still highly uncertain, as already discussed in Chapter 4. Theoretical studies, and measurements [e.g. Murphy and Fahey, 1994] tend to find values around 450 Tg  $\text{O}_3$  per year. Present day tropospheric ozone budgets derived from global chemistry-transport models [IPCC, 2001] indicate stratospheric ozone fluxes differing by up to a factor of three. Figure 5.3 (updated from IPCC [2001] using current CTMs) illustrates how sensitive tropospheric ozone budgets derived from CTMs are to the magnitude of the stratospheric flux. It indicates that the difference between the flux from the stratosphere and the destruction at the surface is balanced by the net *in-situ* photochemical production, which varies from 70 to 600 Tg  $\text{O}_3$  per year, as previously mentioned in Section 4.2. Tropospheric ozone in models with high stratospheric fluxes is expected to be much more sensitive to changes in stratospheric ozone or in stratosphere-to-troposphere exchange. These differences suggest that the uncertainty in the magnitude of the stratospheric flux results in further uncertainties in the tropospheric ozone budget, making it difficult to determine whether the troposphere is a chemical source or sink of ozone. Resolving this issue is critical to our ability to predict the tropospheric ozone response to climate changes.

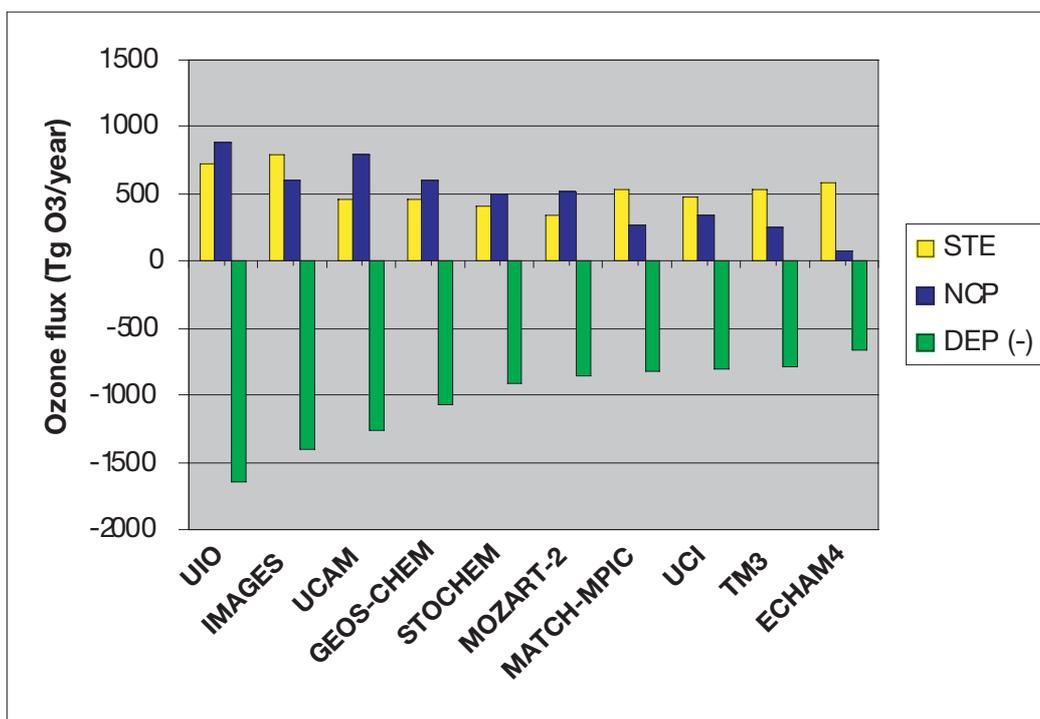


Figure 5.3 The tropospheric ozone budgets for 1990 conditions for a sample of global 3-D CTMs and CCMs are shown. STE = net ozone flux from the stratosphere, NCP = net photochemical production, DEP = - surface deposition. References: UiO: Gauss [personal communication, 2003]; IMAGES: Müller and Brasseur [1995]; UCAM: Zeng and Pyle [2002]; GEOS-CHEM: Bey et al. [2001a]; STOCHEM: Johnson et al. [2001]; MOZART2: Horowitz et al. [2002]; MATCH-MPIC: von Kuhlmann et al. [2002]; UCI: Wild and Prather [personal communication, 2002]; TM3: van Weele [personal communication, 2001]; ECHAM4: Roelofs and Lelieveld [2000].

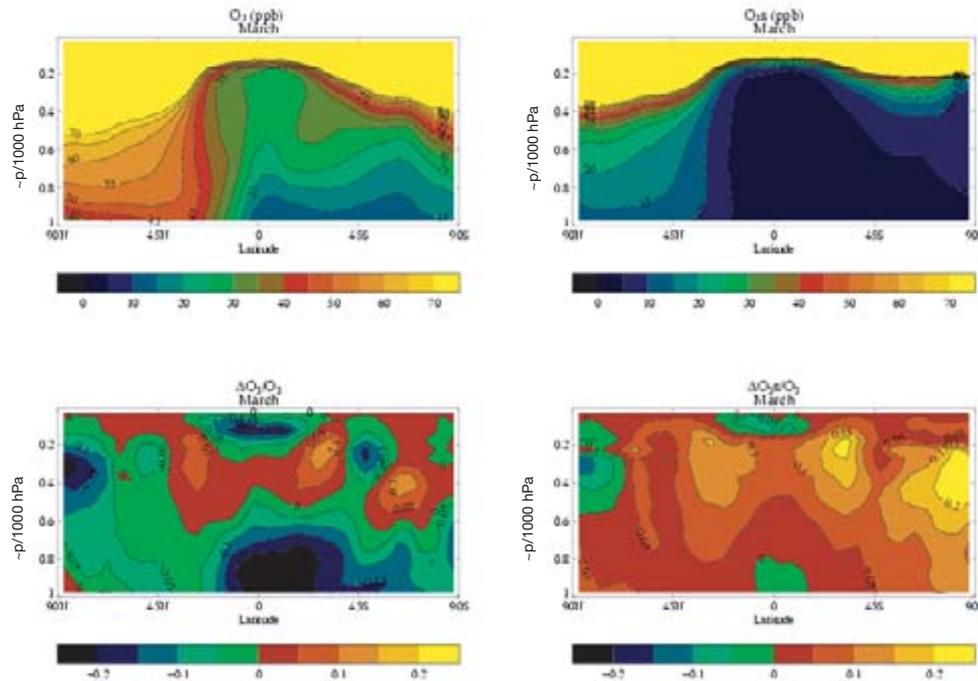
#### 5.4.2 Impact of stratospheric ozone changes on tropospheric ozone

Stratospheric ozone influences the tropospheric ozone chemistry in two ways. The first is indirectly through controlling the flux of ultra-violet radiation and affecting the ozone loss rate and the oxidising capacity of the troposphere. This effect is evaluated in Chapter 3. It also directly serves as a source of ozone through the influx of stratospheric ozone into the troposphere. This source is not expected to remain constant in the future, but to vary depending on the stratospheric concentration of ozone and the strength of the transport between the troposphere and the stratosphere.

The flux of air through the tropopause is determined by the downward control principle. It is expected [e.g. Butchart and Scaife, 2001] that this flux will increase in a warmer climate. Collins et al. [2003] used an online tropospheric CTM with detailed ozone chemistry within the climate model HadAM4, to investigate the influence of climate change on the stratosphere-troposphere exchange of ozone. The stratospheric ozone concentrations were held constant for this experiment to isolate the changes due solely to transport. Fixing the stratospheric ozone concentrations is inconsistent with a dynamically changed stratosphere but the effect of this was found to be small [Collins et al., 2003]. The study found an increase between 1990s and 2090s of over 30% in the net downward flux of ozone across the 200 hPa surface. However, this greater influx did not give rise to a higher tropospheric ozone burden because in the warmer, more humid climate, the increased ozone destruction more than compensated for (see Figures 5.4a and 5.4c). It was possible to trace the influence of the stratospheric ozone by the use of a theoretical stratospheric ozone ( $O_3s$ ) tracer [Roelofs and Lelieveld 1997]. The  $O_3s$  tracer is produced in the stratosphere at the same rate as the normal ozone but has no tropospheric production, and is therefore only exposed to destruction. In spite of the increased ozone destruction rate in the 2090s, the  $O_3s$  trac-

er concentration increased throughout the troposphere (see Figures 5.4b and 5.4d). This implies that in a future climate (assuming no changes in the stratospheric ozone distribution), the stratosphere will have a greater impact on the tropospheric ozone distribution than at present. The largest impact in this study was in the sub-tropical upper troposphere, which would have implications for the radiative forcing from tropospheric ozone.

The study here focused on changes in the temporally and spatially averaged ozone concentrations. Climate change may also affect the frequency and intensity of deep stratospheric intrusion events that reach the lower troposphere. Combined stratosphere-troposphere chemistry models are currently being developed to address stratosphere-troposphere exchange in a consistent framework.



*Figure 5.4* Simulated zonal mean ozone concentrations (a: top-left) and stratospheric ozone tracer concentrations (b: top-right) averaged over 1991-1994. Zonal mean changes between 1991-1994 and 2090-2094 in  $O_3$  (c: bottom-left) and stratospheric  $O_3$  tracer (d: bottom-right). Changes are expressed as a fraction of the 1991-1994 total ozone, from simulations with the STOCHEM model [Collins et al., 2003]. The vertical axis is a hybrid pressure coordinate approximately equal to pressure/1000 hPa.

- *Stratospheric ozone is expected to recover in the future, and climate change will probably increase the ozone downward flux. The effect on ozone will probably be large and positive.*

### 5.4.3 Impact of changes in weather patterns on tropospheric ozone

Weather patterns of local and synoptic scales affect the global distribution of tropospheric ozone by providing pathways for the transport of ozone and its precursors from the boundary layer to the free troposphere. Convection in the tropical and mid-latitude regions is an important pathway for lifting ozone and related species from the boundary layer to the free troposphere [Jacob et al., 1993; Horowitz et al., 1998; Taguchi et al., 2002; Duncan et al., 2002b]. It affects in particular the redistribution of species due to biomass burning emissions. In the mid-latitude regions, another efficient pathway for the vertical transport of ozone and related species out of the boundary layer to the middle and upper troposphere is provided by warm conveyor belts associated with frontal systems [Bethan et al., 1998; Stohl and Trickl, 1999; Yienger et al., 2000; Bey et al., 2001b; Donnell et al., 2001]. Because warm conveyor belts

originate most frequently over the eastern seaboard of North America and Asia [Stohl, 2001] (which include large urban agglomerations), they have been shown to be especially efficient in exporting anthropogenic emissions to the Pacific and Atlantic Oceans. Once ozone has been transported out of the boundary layer and reaches the upper levels of the troposphere, the large scale weather features determine its fate and ozone can then travel over thousand of kilometres [e.g. Schultz et al., 1998; Staudt et al., 2001; Duncan et al., 2002b]. At the present time, a clear picture of the chemical and physical fate of these polluted plumes transported by large scale features is still missing.

Larger-scale weather patterns associated with the North Atlantic Oscillation (NAO) and El Niño Southern Oscillation (ENSO), for example, also contribute significantly to the global distribution of tropospheric ozone. Using a long-term record of ozonesonde observations, satellite measurements and a 15-year model simulation, Peters et al. [2001] concluded that the ENSO signal is the most important component of inter-annual variability in the tropical tropospheric column. Sudo and Takahashi [2001] and Chandra et al. [2002] used 3-D global models to examine how the ENSO-induced meteorological changes (such as changes in convective activity, large scale dynamics and precipitation) affect the distribution of ozone in the southern hemisphere. They concluded that about half of the ozone increase observed over Indonesia and the equatorial western Pacific in 1997 can be attributed to changes in meteorological effects alone (i.e. without considering changes in ozone precursor emissions). No evaluation of the possible impact of changes of large-scale weather conditions associated with the ENSO can be proposed, since predictions of changes in ENSO differ among current general circulation models.

It can also be noted that an increase in the meridional residual circulation such as predicted by Grewe et al. [2002] would lead to a larger impact of ozone precursor tropical sources (including a potentially increased lightning source; Section 5.2.2.1) on mid-latitude ozone concentrations.

Li et al. [2002] used a 3-D global model to investigate the trans-Atlantic transport of ozone. They found that episodes of ozone transport from North America to the western coast of Europe occur frequently in the model, through low-level westerly flows associated with the Icelandic low located between Iceland and the British Isles. They subsequently established a strong correlation (especially in spring) between the NAO and the occurrence and magnitude of such transport events. Creilson et al. [2002] used tropospheric ozone residuals and also found such correlations. They suggest that increases in spring tropospheric ozone during the positive phase of the NAO could be due to a stronger ozone transport via the westerlies over the northern edge of the Azores high. Although our understanding of the processes contributing to the NAO is still too limited, there is increasing evidence that the observed changes in the NAO could result from anthropogenic activities [IPCC, 2001].

A better understanding of the effects of weather patterns on tropospheric ozone distributions is clearly needed for assessing the impact of future climate change. Changes in weather patterns will certainly affect the global distribution of tropospheric ozone, but at the moment, a quantitative understanding of such changes is not available. Assessment of the influence of natural variability of weather patterns on ozone, can give information on the effect of climate-induced changes. As an example, Liu et al. [2002] examined the inter-annual variability of continental outflow from East Asia due to the changes in weather patterns. They found that the dominant patterns for continental outflow are similar over various years but they observed a significant variability related to El Niño. For example, spring 2001 (corresponding to a La Niña period) was characterised by unusually frequent cold fronts passing over the Pacific Rim and strong convection in South East Asia, which, in turn, lead to unusually strong boundary layer outflow and convective outflow in the upper troposphere.

- *Climate induced changes in weather-patterns may influence tropospheric ozone. However, at present, a quantification of this is not possible.*

## 5.5 Conclusions

Climate change affects a number of processes which all act together to determine the global budget of ozone. The possible impacts discussed in this chapter are rather speculative, inherently difficult to quantify, and based on an incomplete knowledge of the possible climate related processes that may impact ozone concentrations. Therefore, when using the IPCC [2001] definition, the level of scientific understanding can be considered as low-to-very-low. As indicated in the table below which summarises the different sections of the chapter, we have tried to estimate the impact of different processes on the ozone budget as small (<1%), medium (1-5 %) or large (>5%). Finally, it should be pointed out that climate change cannot be seen in isolation, as the future world is likely to face other challenges at the same time (population pressure, water shortage, etc.). These could potentially change emission sources, for example, beyond the assumptions of future climate scenarios that are available today.

Process/activity	Impact on global tropospheric ozone resulting from climate change	
	Impact	sign
Human activity-fossil fuel related emissions	Small	o
Biomass burning	Medium to large	±
Soil NO <sub>x</sub>	Medium	o
Lightning NO <sub>x</sub>	Medium-to-large	+
Natural CH <sub>4</sub> emissions	Medium-to-Large	+
Natural VOC emissions	Medium-to-large	+
Oceanic emissions of sulphur containing gases	Small	o
Heterogeneous chemistry on sea-salt	Medium	-
Heterogeneous chemistry on mineral dust	Small-medium	-
Organohalogens	Unknown	-
Changes in dry deposition	Medium	o
Changes in wet deposition	Small-medium	-
Effect of meteorology on O <sub>3</sub> production and loss	Large	-
Cloudiness	Small	-
Climate induced changes in stratosphere-troposphere exchange	Large	+
Changes in weather patterns	Unknown	o

*Table 5.2* Summary of the impact on tropospheric ozone levels of several climate related processes. The uncertainties of the impacts are indicated in the different sections of the chapter. The level of scientific understanding and of the quantification of these impacts is considered as low to very-low.

## GLOSSARY

AAO	Antarctic Oscillation
AEROCE	Atmosphere-Ocean Chemistry Experiment
AO	Arctic Oscillation
CARIBIC	Civil Aircraft for Remote Sensing and In-situ Measurements in Troposphere and Lower Stratosphere based on the Instrumentation Container Concept
CCM	Chemistry-Climate Model
CCSR/NIES	Centre for Climate System Research (NIES = ???)
CFC	Chlorofluorocarbon
CMAM	Canadian Middle Atmosphere Model
COS	Carbonyl Sulphide
CTM	Chemistry Transport Model
DMS	Dimethyl Sulphide
DLR	Deutsches Zentrum für Luft und Raumfahrt
DU	Dobson Units
EASOE	European Arctic Stratospheric Ozone Experiment
ECHAM	European Centre Hamburg Model
ECMWF	European Centre for Medium Range Weather Forecasts
ENSO	El Niño Southern Oscillation
ENVISAT	Environmental satellite
EOF	Empirical Orthogonal Function
ERA	ECMWF Re-Analyses
ERS-2	European Research Satellite 2
EULINOX	European Lightning Nitrogen Oxides Project
EUVDB	European UltraViolet DataBase
FDH	Fixed Dynamical Heating Concept
FT	Fixed Temperature
GCM	Global Circulation Model
GEOS-CHEM	Goddard Earth Observing System atmospheric Chemistry model
GHG	Greenhouse gases
GOME	Global Ozone Monitoring Experiment (on ERS-2)
GOMOS	Global Ozone Monitoring by Occultation of Stars (on ENVISAT)
HALOE	Halogen Occultation Experiment
HCFC	Hydrofluorocarbon
IMAGES	Intermediate Model of the Annual and Global Evolution of Species
IMG/ADEOS	Interferometric Monitor for Greenhouse gases/Advanced earth Observing System
IPCC	Intergovernmental Panel on Climate Change
IR	InfraRed
MAECHAM/CHEM	Middle Atmosphere ECHAM model with chemistry
MAPS	Measurement of Air Pollution from Satellite
MATCH	Model of Atmospheric Transport and Chemistry
MIPAS	Michelson Interferometer for Passive Atmospheric Sounding (on ENVISAT)
MOPITT	Measurements Of Pollution In The Troposphere
MOZART	Model of Ozone and Related Chemical Tracers
MSC	Meteorological Service of Canada
NAM	Northern Hemisphere Annular Mode
NAO	North Atlantic Oscillation
NARE	North Atlantic Regional Experiment
NAT	Nitric Acid Trihydrate

NCAR	National Center for Atmospheric Research (Boulder, CO, USA)
NCEP	National Centre for Environmental Prediction
NCP	Net chemical production
NMHC	Non-Methane Hydrocarbon
NMVOC	Non-Methane Volatile Organic Compound
ODP	Ozone Depleting Potential
OxComp	Tropospheric Oxidant Model Comparison
PAR	Phytosynthetically-Active Radiation
POLINAT	Pollution from Aircraft Emissions in the North Atlantic Flight Corridor
PSC	Polar Stratospheric Clouds
PV	Potential Vorticity
QBO	Quasi-Biennial Oscillation
RF	Radiative Forcing
SAGE	Stratospheric Aerosol and Gas Experiment
SAM	Southern Hemisphere Annular Mode
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (on ENVISAT)
SEFDH	Seasonally Evolving Fixed Dynamical Heating
SESAME	Second European Stratospheric Arctic and Mid-latitude Experiment
SLIMCAT	Semi-Lagrangian Model of Chemistry and Transport
SOLVE	SAGE III Ozone Loss and Validation Experiment
SONEX	NASA SASS ozone and nitrogen oxide experiment
SPARC	Stratospheric Processes And their Role in Climate
SRES	Special Report on Emissions Scenarios (IPCC)
STE	Stratosphere-Troposphere Exchange
STOCHEM	Stochastic Transport and Atmospheric Chemistry Model
TAR	Third Assessment Report (IPCC)
THESEO	Third European Stratospheric Experiment on Ozone
TOMS	Total Ozone Monitoring Spectrometer
TRIFFID	Top-down Representation of Interactive Foliage and Flora Including Dynamics
TROPOSAT	The Use and Usability of Satellite Data for Tropospheric Research
TTL	Tropical Tropopause Layer
UARS	Upper Atmosphere Research Satellite
UCAM	University of Cambridge
UCI	University of California, Irvine
UIUC	University of Illinois at Urbana-Champaign
UMETRAC	Unified Model with Eulerian Transport and Chemistry
ULAQ	University of L'Aquila
UTLS	Upper Troposphere Lower Stratosphere
UV	Ultraviolet
VOC	Volatile Organic Compound
WMGHG	Well-Mixed Greenhouse gases
WMO	World Meteorological Organisation
WOUDC	World Ozone and UltraViolet radiation Data Centre

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