Doctoral Thesis

Three dimensional chemical transport model study of ozone and related gases 1960-2000

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Publication Date:
2005

Permanent Link:
https://doi.org/10.3929/ethz-a-005181114

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Three Dimensional Chemical Transport Model Study of Ozone and Related Gases 1960-2000

A dissertation submitted to the SWISS FEDERAL INSTITUTE OF TECHNOLOGY (ETH) ZÜRICH for the degree of DOCTOR OF NATURAL SCIENCES presented by CHRISTOPHER ROBERT HOYLE BSc(Hons), University of Canterbury born December 20, 1978 citizen of Vordemwald (AG)

accepted on the recommendation of Prof. Thomas Peter, examiner Prof. Johannes Stähelin, co-examiner Dr. Bram Bregman, co-examiner 2005
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Acknowledgements

There are a lot of people whom I would like to thank for making this project possible. Firstly Thomas Peter, Eugene Rozanov and Johannes Stähelin, for writing the project proposal in the first place, and then for the many hours of discussions over the three years that followed. Thanks especially to Eugene for your patience in explaining the workings of the model (often more than once)! Also to Johannes for your very helpful suggestions with regard to the work in Chapters 4-6, and your thorough reviews of the thesis while I was writing up. I’d also like to thank Tom for providing encouragement, motivation and good ideas when I thought everything was turning to custard.

Thanks to Bram Bregman for your insightful comments on the thesis, and for coming all the way to Zürich for my exam.

Werner Schmutz allowed me to carry out this work at the PMOD/WRC in Davos, and was always ready with advice when it was needed. Tatiana Egorova was a great help when I got stuck with the model and Christof Appenzeller helped arrange access to the ERA-40 data, without which this would have been a really short thesis. With regard to helping me find my way around the ERA-40 archive and extracting the data I needed, I would also like to thank Heini Wernli and Daniel Lüthi.

Thanks also to Dominik Brunner for help with getting hold of the NIWA ozone data and the HALOE data, as well as all those wonderful IDL programs that made life a lot easier.

Christina Schnadt always had very helpful ideas and suggestions during our discussions, regardless of if they were about aircraft emissions, or residual circulation.

I’m very grateful to Petra Forney, for her wisdom of all things administrative at the ETH and also for getting Tom to read his email.

I think Lukas Bäurle, Martin Jonsson, and the other regular visitors to the Châmi Bar on Wednesday nights deserve a mention, Thursday mornings were rather unproductive, but it was well worth it!

Finally I’d like to thank Anja Schilling, for her support during the whole project, listening to me whinge when things were not going well, and especially, when everything was almost finished, for proof reading this thesis so thoroughly.
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Abstract

The stratospheric ozone layer is extremely important, in that it shields terrestrial life forms from harmful levels of solar radiation. Since the 1980’s, it has been known that human activities can have a significant detrimental effect on stratospheric ozone, thus it is vital to understand all processes affecting the abundance of ozone, so that stratospheric ozone may be allowed to return to pre-1980 levels as quickly as possible.

In the past it has been shown that various factors, such as atmospheric circulation, temperature, surface area density of stratospheric sulphate aerosol, and the chlorine loading of the atmosphere all influence the abundance of stratospheric ozone, and play a role in its interannual variability. In order to separate the contribution of these factors to the observed ozone trends, a three-dimensional, off-line Chemical Transport Model (CTM), “MEZON” is applied, simulating ozone variability over the period 1965-2000.

These long term transient model runs are made possible by the use of the newly completed ERA-40 data set from the ECMWF, which provides the circulation, temperature and upper tropospheric humidity data necessary to drive the CTM. Previous data sets have either not covered such an extensive time period, or have not provided data covering most of the upper stratosphere. The experiments performed in this study also provide an interesting test of the suitability of the ERA-40 data for such long CTM integrations.

It is shown that there are some periods where the model reproduces observed ozone values particularly poorly, for example during 1965-1970 in the Antarctic, and in the mid 1970’s, especially in the northern hemisphere. This seems to be related to the temperature and circulation data used to drive the model. In general, ozone trends calculated from modelled ozone fields do not represent the observed trends well. If the influence of the temperature and circulation data on the modelled trends is removed, the remaining portion of the modelled trends reproduces almost all of the observed negative ozone trend. This remaining portion of the modelled trend is related to anthropogenic emissions of ozone depleting substances and variations in stratospheric sulphate aerosol due to volcanic eruptions.

The model reproduces some of the observed features of the long term total ozone record very well, such as the ozone minimum after the eruption of Mt Pinatubo. It is also found that the model only begins to produce ozone losses during times of large stratospheric aerosol loading after about 1980. Before 1980, larger aerosol loadings lead to higher ozone abundances. The greater part of the modelled ozone decrease after the eruption of Mt Pinatubo is found to be dynamical in origin.

Another feature of the observed ozone record, which is also evident in the modelled ozone values, is the large minimum in total ozone, at southern mid latitudes in 1985. This minimum is also present in a model run with “background” aerosol levels, and an atmospheric chlorine loading equivalent to that of the early 1960’s. This implies a dynamical cause of the 1985 ozone minimum.
The instantaneous lifetimes of several ozone depleting substances are calculated from the model results, and correspond well with the WMO reference lifetimes. It is found that the lifetimes of CFC-11 and CFC-12, which have significant sinks in the stratosphere, are quite sensitive to changes in total ozone at tropical to middle latitudes. The lifetimes of CFC-11 and CFC-12 also have a small negative correlation with tropical upward mass flux.

The PSC scheme used in MEZON was extensively updated, and now includes a nucleation barrier to NAT (nitric acid trihydrate) formation, as well as a non-equilibrium NAT growth calculation. The sedimentation of NAT and ice particles is now carried out based upon calculated particle diameters, and denitrification occurs primarily via NAT sedimentation, and not by sedimentation of ice particles containing HNO₃ as previously. These changes allow the model to reproduce observed NAT particle sizes better, and also improve the agreement between modelled and measured gas phase HNO₃ levels.
Zusammenfassung


Verschiedene Faktoren bestimmen die Ozonmenge mit und spielen in ihrer jahreszeitlichen Variabilität unterschiedlich wichtige Rollen. Zu diesen Faktoren gehören die atmosphärische Zirkulation, die Temperatur, die Menge stratosphärischen Schwefelaerosols sowie die Belastung der Atmosphäre mit Chlor. Um den Beitrag der einzelnen Elemente zu den beobachteten Entwicklungen in der Ozonschicht getrennt erfassen zu können, wurde ein dreidimensionales, off-line Modell zur Simulation der atmosphärischen Chemie und der Transportprozesse (Chemical Transport Model, CTM) "MEZON" verwendet, mit dem die Variabilität des Ozon für den Zeitraum von 1965 - 2000 simuliert wurde.


Das verwendete CTM reproduziert einige der beobachteten Charakteristika der lang andauernden Ozonauflaufzeichnungen sehr gut; so zum Beispiel das Ozonminimum nach dem Ausbruch des Vulkans Mount Pinatubo. Zudem wurde festgestellt, dass grosse Mengen
Zusammenfassung


Mit MEZON kann auch die Lebensdauer mehrerer ozonzerstörender Substanzen berechnet werden. Die Resultate passen sehr gut mit den entsprechenden Referenzwerten der WMO zusammen. Dabei zeigt sich, dass die jeweiligen Lebensdauern von FCKW-11 und FCKW-12, die in der Stratosphäre bedeutende Senken haben, sehr sensibel auf Änderungen des Gesamtozons in tropischen bis mittleren Breiten reagieren. Sie haben zudem eine kleine negative Korrelation mit der tropischen aufwärtsgerichteten Strömung.

Der Algorithmus zur Simulation polarer stratosphärischer Wolken (Polar Stratospheric Clouds, PSC), der in MEZON verwendet wird, wurde intensiv überarbeitet und verbessert und enthält jetzt zusätzlich eine Kernbildungs-Barriere für die Bildung von Salpetersäure-trihydrat (Nitric Acid Trihydrate, NAT), sowie eine nicht-Gleichgewicht Wachstums-Berechnung für NAT. Die Sedimentation von NAT und von Eispartikeln wird jetzt basierend auf den Partikeldurchmessern durchgeführt und die Denitrifikation geschieht primär durch die Sedimentation von NAT und nicht mehr durch die Sedimentation von Eispartikeln, die HNO₃ enthalten. Diese Änderungen erlauben dem Modell, die beobachteten NAT-Teilchengrössen besser zu reproduzieren und verbessern zudem die Übereinstimmung zwischen modellierten und gemessenen Mengen an gasförmigem HNO₃.
Chapter 1

Introduction

Ozone is one of the most important gases in the atmosphere, with respect to its influence upon life on Earth. Without ozone to shield the planet from short wave Ultra Violet (UV) radiation (UV-B and UV-C), life would probably not be possible on the surface of the Earth, rather only under water, at depths where the harmful wavelengths of solar radiation are sufficiently attenuated.

Atmospheric ozone is also an important greenhouse gas, playing a role in keeping the surface of the Earth warm enough to support life (Seinfeld and Pandis, 1998). Already these two facts are probably enough to make ozone and the processes affecting its distribution and abundance an important area of research. With the discovery of the Antarctic ozone hole, by Farman et al. (1985), it became indisputably clear for the first time that anthropogenic trace gas emissions can significantly perturb the atmospheric system, and on a global scale.

A swift response to the discovery of the Antarctic ozone hole resulted in the Montreal Protocol (1987) and its Amendments and Adjustments (London, 1990; Copenhagen, 1992; Vienna, 1995; Montreal, 1997; Beijing, 1999;) which caused the rapid decline in production and emissions of the major ozone depleting substances (halogen containing gases which release chlorine and bromine into the stratosphere, hereafter referred to collectively as “ODS”).

Total tropospheric abundances of ODS peaked in 1994 and are now declining (WMO, 1999), however, the decline is so slow that it will take several decades until the ozone layer completely recovers. During the recovery time, the abundance of stratospheric ozone, and in particular ozone over the polar regions, will remain highly sensitive due to the enhanced stratospheric halogen loading. It is, therefore, of utmost importance that we fully understand the processes affecting ozone in order to predict, and if possible minimize or avoid, any future worsening of ozone depletion.

One of the aims of this thesis is to attempt to quantify how much of the past ozone trend can be attributed to a particular process or phenomenon. A three-dimensional Global Chemical Transport Model (CTM), is used to separate the contribution of halogen chemistry, volcanic aerosol and other factors influencing ozone. Such a CTM is an ideal tool for this study, as one can perform experiments which are not possible in the real atmosphere, switching on some processes and switching off others. This permits the separation of the contributions of these processes to ozone trends far more effectively and more convincingly than would be possible by simply constructing correlations between processes and ozone trends. There are also some limitations to this approach, for example that secondary effects such as the influence of volcanic aerosol on temperature (which may lead to changes in stratospheric circulation, or changes in reaction rates) are included in
the meteorological data. This means that it is only possible to separate the contributions of direct effects of volcanic aerosol and increased halogen loading on stratospheric ozone values.

Long term ozone trends have been calculated from both ground based and satellite measurements (see for e.g. Staehelin et al., 2001, and references therein; Wang et al., 2002; Bodeker et al., 2001) and more recently model studies (e.g. Hadjinicolaou et al., 2002; Chipperfield, 2003). Both statistical analysis of measured ozone trends (Mäder, 2004) and estimates of contributions to ozone trends using CTM models (Hadjinicolaou et al., 2002) have shown that the past trend in anthropogenic ODS emissions does not fully explain the observed ozone trends.

There is further uncertainty as to what the main cause of extremely low ozone values after the 1991 eruption of Mt Pinatubo was, with some arguing for a large contribution from enhanced ClO as a result of increased stratospheric aerosol (e.g. Solomon, 1999; Solomon et al., 1996). Other studies (e.g. Hadjinicolaou et al., 1997) show that much of the post-Pinatubo ozone depletion can be explained without including any volcanic impact upon heterogeneous chemistry. The results presented here may help to further quantify the impact of dynamical and chemical processes on ozone.

The circulation and temperature data used to drive the CTM in this study is from the new ERA-40 reanalysis data set, which was completed by the European Centre for Medium Range Weather Forecasts (ECMWF) in 2003. It was hoped that this state of the art data would pave the way for an exciting range of long term CTM experiments, however some deficiencies in the data have come to light during the EU-project CANDIDOZ (Chemical and Dynamical Influences on Decadal Ozone Change) project. There have also been some publications (e.g. van Noije et al., 2004 and Uppala et al., 2005) pointing out that the Brewer Dobson circulation is enhanced in the ERA-40 reanalysis, which can have impacts on the simulation of ozone. The work presented here will help to provide information on the suitability of this data set for use in long term ozone modelling experiments.

The three main issues which will be addressed in this thesis are:

- The calculation of the time evolution of ozone between the years 1965 and 2000 and the separation of the contributions of dynamical, volcanic and anthropogenic processes to ozone variability.
- The calculation of the lifetimes of ODS, and their dependence on the atmospheric general circulation.
- The determination of the cause of the early decline in upper stratospheric HCl, as observed in satellite data.

The second point in this list of aims is important for making predictions about how the recovery of the ozone layer will progress. A more complete understanding of what determines the atmospheric residence times for ODS, combined with predictions about the future state of the atmosphere will result in a more accurate description of the factors that determine how the stratospheric halogen loading will evolve over the next decades. The third point serves a similar purpose, in that by understanding this event, a contribution would be made to the understanding of what processes determine the stratospheric halogen loading. Unless otherwise stated, when ozone is referred to in this thesis, the intended meaning is stratospheric ozone.
The next Chapter gives a brief overview of what is already known about what determines the abundance of ozone, its distribution and chemistry. The CTM which was used in this study, along with the input data and improvements to the model is described in Chapter 3. In Chapter 4, a validation of the model will be presented, and the accuracy with which the model can reproduce the observed atmospheric state will be discussed. Chapters 5 through 7 address the three main points listed above. Finally, in Chapter 8, the performance of a new heterogeneous chemistry parameterization in the model is evaluated and a comparison is made with the original parameterization. A summary and conclusions of the whole project are presented in Chapter 9.
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Chapter 2

Background and Theory

2.1 History and basic chemistry of ozone

The Earth’s atmosphere is believed to have been formed by the out-gassing of volatile compounds, which were trapped within the planet as it condensed from an interstellar cloud of gas and dust about 4.6 billion years ago. It is thought that the early atmosphere mainly consisted of a mixture of carbon dioxide, nitrogen and water vapour (Seinfeld and Pandis, 1998). Oxygen was probably produced by early life forms, and the present abundance of oxygen in the atmosphere is likely to have been reached about 400 million years ago (Seinfeld and Pandis, 1998). As oxygen built up in the atmosphere, ozone formed.

Ozone was discovered around 1840, by C.F. Schönbein, and the following set of reactions governing the basic chemistry of ozone, in a pure oxygen atmosphere, was first proposed by Chapman (1930). Reaction 2.5 was suggested a few years later when it became clear that a further loss mechanism for ozone was required. The formation of ozone begins when molecular oxygen is photolyzed by solar radiation:

\[ \text{O}_2 + h\nu (\lambda<242\text{ nm}) \rightarrow \text{O} + \text{O}. \] (2.1)

An oxygen atom and an oxygen molecule can combine to form ozone or two oxygen atoms can recombine to form molecular oxygen:

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}, \] (2.2)
\[ \text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}. \] (2.3)

Except in the upper atmosphere (above about 100 km altitude), where oxygen atoms are more abundant than oxygen molecules, Reaction 2.2 is by far the dominant pathway. In the reactions above, \( M \) is a third molecule, usually \( \text{N}_2 \), necessary to absorb excess energy.

Ozone photodissociates, at wavelengths \( \lambda \lesssim 1180 \text{ nm} \):

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}, \] (2.4)

but then regenerates readily according to Reaction 2.2. A net destruction of ozone occurs by reaction with atomic oxygen, leading to a loss of odd oxygen (defined as \( [\text{O}_2] = [\text{O}] + [\text{O}_3] \)):
Ozone reaches its peak molecular number density (about $1-6 \times 10^{12}$ molecules cm$^{-3}$) at altitudes between 20 km and 30 km. This band of high ozone concentrations has become known as the "ozone layer". The altitude of the ozone layer is a result of the balance between the production and the destruction of ozone and is influenced by transport processes. With increasing altitude, the photolysis of ozone and molecular oxygen increases, while the density of the atmosphere decreases - and with it, the rate of Reaction 2.2. With decreasing altitude, the photolysis rate of molecular oxygen decreases, also limiting Reaction 2.2 (due to the resultant low concentration of atomic oxygen). In both cases, a reduction in the rate of formation and therefore concentration of ozone results.

This basic chemistry is the key to the importance of ozone. Ozone absorbs solar radiation primarily in the wavelength range 200 nm to 300 nm and almost all the solar radiation in the wavelength range from about 240 nm to about 300 nm is absorbed within the ozone layer. Furthermore, Reaction 2.2 releases thermal energy, causing the characteristic temperature gradient of the stratosphere.

As was mentioned in Chapter 1, ozone is an important "greenhouse gas", along with CO$_2$, CH$_4$, N$_2$O and halogen-containing compounds, which absorb infrared radiation and re-radiate a portion back toward the surface. This keeps the Earth's surface much warmer than it would be in the absence of these gases, which is vital for the existence of present life forms. This property of ozone means that changes in its abundance, especially near the tropopause, may have an effect upon tropospheric climate, with an anthropogenic increase leading to a significant positive radiative forcing, influencing the climate system (Ramaswamy et al., 1992; Lelieveld et al., 1997).

2.2 The natural distribution of ozone

Ozone is not evenly distributed throughout the stratosphere. As well as latitudinal differences in the ozone distribution, there are seasonal effects, and an hemispheric asymmetry. The seasonal and latitudinal distribution of total ozone before it was modified by anthropogenic emissions is shown in Figure 2.1 (from London, 1980).

The major source of stratospheric ozone is in the tropics, where, due to the higher amounts of solar radiation, Reaction 2.1 can proceed most efficiently. The concentration of ozone in the atmosphere is at its highest in the tropical stratosphere, at about 25 km altitude, although total ozone (the sum of a column of ozone over a given point on the Earth's surface) is lower in the tropics than at middle latitudes. From the tropical stratosphere, ozone is transported by the stratospheric mean diabatic circulation towards the middle latitudes and poles. The total ozone field exhibits a general increase towards the poles. The abundance of ozone is always a balance between the supply, either from in situ production (Reactions 2.1, 2.2) or transport, and destruction. Transport of ozone plays the significant role in determining ozone abundances in regions of the atmosphere where the photochemical lifetime of ozone is of a similar magnitude to, or longer than the time scales associated with transport, for example in the winter middle to high latitude stratosphere (Perliski et al., 1989). Stronger poleward and downward transport near the winter pole results in a build up of total ozone at high latitudes during winter, which
peaks in the spring for the northern hemisphere. At the same time, the increased poleward transport of ozone reduces its abundance in the tropics.

In order to describe polar ozone changes, a brief explanation of the polar vortex is necessary. The polar vortex is a dynamical feature of the winter polar atmosphere which has a large influence on ozone. It forms as a result of the latitudinal gradient in ozone heating (Schoeberl et al., 1992), as the polar stratosphere cools in the absence of solar radiation. This cooling leads to a poleward decreasing gradient in isobaric height, and the resulting circulation is perpendicular to the direction of this gradient. Thus the large temperature gradient near the polar terminator results in rapid zonal (west to east) flow, and this “jet” isolates the inner vortex air from the surrounding mid latitude regions.

The polar vortices are disturbed by atmospheric waves. These waves are affected by the topography of the Earth’s surface, as well as by the temperature contrast between land and the oceans. The greater topographical variation in the northern hemisphere leads to more wave disturbance of the northern polar vortex and therefore increased mixing between vortex and out-of-vortex air. There is also an increase in subsidence of air within the vortex. This leads to higher ozone values in the northern hemisphere polar vortex, due to both the increased downward transport of ozone and the fact that the increased wave disturbance of the vortex results in a warmer vortex and less chemical ozone loss in the anthropogenically disturbed stratosphere (Solomon, 1999).

In contrast, there is less wave related disturbance of the Antarctic vortex. This leads to a greater isolation of air within the Antarctic vortex and results in lower ozone abundances due to lower rates of mixing between vortex and out-of-vortex air. Therefore, there is no build-up of ozone in the Antarctic polar vortex during winter. In spring however, as the vortex breaks up, ozone-rich air from outside the vortex mixes in, and there is a sharp increase in the amount of ozone over the Antarctic. Thus, in the undisturbed
atmosphere, total ozone in both hemispheres peaks in the high latitudes in spring and subsequently undergoes a slow decay during summer, due to chemical destruction and the reduced dynamical supply. In both hemispheres, an additional sink of stratospheric ozone is transport into the troposphere.

This picture of the seasonal distribution of ozone has been altered in both hemispheres but especially at high southern latitudes, as a result of anthropogenic ODS emissions (see for example Farman et al., 1985; Solomon, 1990 and Stolarski et al., 1991).

2.3 Ozone loss through catalytic gas-phase reactions

Since the late 1960s, a number of reactions have been discovered, which lead to the catalytic destruction of stratospheric ozone. In an anthropogenically unperturbed atmosphere, the most important of these involve oxides of nitrogen, and atomic hydrogen. The destruction of ozone by atomic hydrogen becomes significant at altitudes above about 40 km (Nicolet, 1970):

\[ \text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2, \]  
(2.6)

\[ \text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2. \]  
(2.7)

The nitrogen oxide catalysed destruction of ozone is most efficient at altitudes around 35-40 km, with the low concentration of oxygen atoms limiting the reaction rate at lower altitudes (Crutzen, 1970):

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2, \]  
(2.8)

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2. \]  
(2.9)

Near the tropopause ozone destruction is dominated by reaction with hydrogen radicals, because this cycle does not involve atomic oxygen (Brasseur and Solomon, 1986):

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2, \]  
(2.10)

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2. \]  
(2.11)

In 1974 Stolarski and Cicerone (1974) suggested that ozone could be catalytically destroyed by reaction with chlorine (Reactions 2.12 and 2.13) and Molina and Rowland (1974) proposed that anthropogenic CFCs were a significant source of chlorine in the stratosphere.

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2, \]  
(2.12)

\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2. \]  
(2.13)

It should be noted that the reactions described in this chapter involving chlorine, occur analogously with bromine.

Reactions 2.12-2.13 are very important, because there has been a rapid increase in the amount of chlorine containing gases in the stratosphere, since the 1960’s. The source
2.3. OZONE LOSS THROUGH CATALYTIC GAS-PHASE REACTIONS

of this chlorine is mostly long lived, anthropogenically produced "source gases", such as the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs) (WMO, 2003). These gases have been produced and emitted since about the 1930s, but significant emissions began in about 1965. They were mainly used as aerosol propellants, foam blowing agents and refrigerants. A further class of halogenated gases, the halons (containing bromine), were used in firefighting systems. The reason most of these gases were useful in industry was that they are insoluble, non-flammable, stable molecules. Because of these properties, they are not broken down, or removed by rain-out in the troposphere, and it is only when they encounter the increased short wavelength radiation in the stratosphere that they are photolyzed, releasing chlorine or bromine atoms.

There are some halogenated gases with significant natural sources, for example CH₃Br, the major source of which is the ocean, and CH₃Cl, which is derived largely from natural sources, both oceanic and terrestrial. The contribution of CH₃Cl to present stratospheric chlorine loading is around 16% (WMO, 2003).

The species involved in the catalytic cycles above can be thought of as belonging to "families" of gases, for example the NOₓ family comprises NO, NO₂, NO₃, N₂O₅ and HNO₄. Similarly, ClOₓ is made up of Cl, ClO, HOCl, Cl₂ and Cl₂O₂ and the HOₓ family contains H, OH, and H₂O₂. Reactions such as those with atomic oxygen and ozone convert between family members. Reactions which link the families are also possible, and are rather important for ozone chemistry, especially those which form the so-called "reservoir species". Reservoir species are relatively unreactive gases and the formation of these temporarily removes species such as ClO from the ozone destruction cycles. For example the formation of nitric acid

\[
\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (2.14)
\]

breaks both the NOₓ and HOₓ ozone destruction cycles, whereas the formation of chlorine nitrate

\[
\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \quad (2.14b)
\]

breaks the ClOₓ and the NOₓ ozone destruction cycles.

Likewise, reaction 2.15 breaks the ClOₓ and HOₓ catalysed ozone destruction cycles:

\[
\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2. \quad (2.15)
\]

Another reservoir species, HCl, is formed by reaction with methane:

\[
\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3. \quad (2.16)
\]

This sequesters chlorine, and indeed, most chlorine is in the form of HCl in the upper stratosphere. HCl is water soluble, and thus can be removed from the atmosphere by rain out, providing a sink of chlorine in the troposphere (Brasseur and Solomon, 1986).

Reservoir species such as ClONO₂, HCl and HOCl can, however, be reactivated by photolysis for example, and cannot therefore be regarded as permanent sinks of ODS.

Short wavelength radiation is also needed in order to release the chlorine or bromine atoms from the ODS, therefore low concentrations of Cl and ClO were expected below altitudes of about 30 km, and Reactions 2.12-2.13 were thus considered to be important for the upper stratosphere only. It was not possible to explain the appearance of the Antarctic ozone hole with the chemistry described above.
2.4 Heterogeneous chemistry

In 1985 Farman et al. (1985) noted that there was a marked decrease in the spring time total ozone values measured over Halley bay, Antarctica, when they compared values from 1957-1973 and values from 1980-1984. They found a similar, but less pronounced effect over the Argentine Islands, and proposed that the reduction of ozone was linked to the build up of CFCs in the atmosphere. Up until this point, it was inferred from model results for low latitudes that the increased chlorine from CFCs would only have a small effect on total ozone over the next decades. The area of ozone affected by the sudden spring-time depletion became known as the Antarctic “ozone hole”.

Measurements showed that the maximum ozone depletion within the area of the ozone hole occurred at altitudes between about 15 km and 25 km. This was unusual, because if the ozone hole was a result of the increased levels of chlorine in the atmosphere, ozone depletion would have been expected to peak at altitudes where there was maximum partitioning of chlorine species into ClO together with high abundances of atomic oxygen. This would put the maximum ozone destruction at altitudes above about 30 km. The highest mixing ratios of NO (which would react with ClO to form Cl and NO₂) also occur at altitudes higher than 30 km.

The observed altitude of the maximum ozone depletion, together with the observation that polar stratospheric clouds (PSC) occur predominantly at altitudes between 10 km and 20 km, prompted Solomon et al. (1986) to propose that Reaction 2.17, occurring on the surface of PSC particles

\[
\text{Cl}^- + \text{ClONO}_2 \xrightarrow{\text{HET}} \text{NO}_5^- + \text{Cl}_2
\]  

(2.17)

could shift the partitioning of chlorine from the reservoir species, to a form which would photolyze rapidly in the sunlit atmosphere. They also suggested a second heterogeneous reaction could be important:

\[
\text{H}_2\text{O} + \text{ClONO}_2 \xrightarrow{\text{HET}} \text{HOCI} + \text{H}^+ + \text{NO}_3^-.
\]  

(2.18)

In sunlight, HOCI is quickly photolyzed, forming OH and Cl. This release of chlorine in a reactive form is termed “chlorine activation”.

These reactions also affect the budget of the NOₓ family, which in turn affects the rate of 2.14b. Predominantly in the Antarctic, but also in the Arctic stratosphere, NO₂ can be temporarily removed via conversion to HNO₃ (denoxification) through Reaction 2.19, which is also an important heterogeneous reaction on cold stratospheric aerosol surfaces (Solomon, 1999) (N₂O₅ forms in the absence of sunlight, via a three-body reaction involving NO₂ and NO₃):

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \xrightarrow{\text{HET}} 2\text{H}^+ + 2\text{NO}_3^-.
\]  

(2.19)

Permanent removal of nitrogen oxides occurs by subsequent uptake of HNO₃ on PSC particles, followed by sedimentation of the particles (denitrification). These particles can evaporate after reaching lower, warmer altitudes, releasing the HNO₃ (re-nitrification). In parts of the polar vortex where NO₂ has been depleted or removed, the rate of chlorine deactivation is reduced, and the catalytic destruction of ozone proceeds more efficiently. As described in Waibel et al. (1999), denoxification is continuous in the Antarctic stratosphere during winter, because the extremely low temperatures are conducive to PSC formation,
and heterogeneous processing of NO₂. The Arctic winter stratosphere however is warmer, denitrification is less common and therefore ozone loss there may be very sensitive to increases in denoxification, or denitrification.

Most of the ozone loss in polar regions during winter and spring occurs via reactions involving the ClO dimer, with an additional contribution from a combined bromine and chlorine cycle (McElroy et al., 1992):

\[
\text{ClO} + \text{ClO} + M \rightarrow \text{ClOOCl} + M \quad (2.20)
\]

\[
\text{ClOOCl} \rightarrow h\nu \rightarrow 2 \text{Cl} + \text{O}_2 \quad (2.20b)
\]

\[
2(\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2) \quad (2.20c)
\]

The ClO dimer cycle was suggested by Molina and Molina (1987), and is most efficient at the low temperatures and relatively high pressures found in the lower polar stratosphere. The Cl-Br cycle was first suggested by Yung et al. (1980):

\[
\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \quad (2.21)
\]

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad (2.21b)
\]

\[
\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2 \quad (2.21c)
\]

and also needs the relatively high BrO and ClO concentrations of the polar winter stratosphere to proceed efficiently.

### 2.5 Other processes related to ozone variability and trends

Although the decline in middle and high latitude ozone correlates well with the increasing atmospheric burden of ODS, it must be kept in mind that processes other than anthropogenically induced ozone destruction may be partly responsible for the observed trends in ozone. Some processes by which ozone trends could be influenced naturally (or at least not directly by human activities) are discussed below. A further point to note is that there are processes which naturally cause a multi-annual variability in ozone values (such as those discussed in the next two sub-sections), and trends must be calculated over a time period long enough that these do not have a significant impact.

#### 2.5.1 The solar cycle

It is well known that solar irradiance undergoes a cycle in its intensity, known as the 11 year solar cycle. Since Reaction 2.1 is dependent on UV radiation, it would be reasonable to expect a correlation between ozone amounts and the solar cycle. There is in fact a small positive correlation, with a 1-2% variation in total ozone, in phase with the solar cycle (Egorova et al., 2004; Staehelin et al., 2001). The variation in solar irradiance can also have an effect on the stratospheric circulation because of changes in the radiative
heating of the stratosphere as a result of the solar influence on ozone production (Hood, 2003). These changes in stratospheric circulation can then influence ozone distributions, thus changes in solar radiation can have both direct and indirect effects on the abundance of stratospheric ozone.

Using the CCM SOCOL, Egorova et al. (2004) found that the tropical stratosphere, at the stratopause, is about 1.2 K warmer during solar maximum than solar minimum. This warming was found to be more than 1.5 K in the high latitude upper stratosphere. The polar night jet (PNJ) was also found to be up to 2 ms\(^{-1}\) stronger in the southern hemisphere during solar maximum than during solar minimum (Egorova et al., 2004).

As well as the 11 year solar cycle, there is a 27 day cycle in solar irradiance, which results from the rotation period of the Sun. The effect of this can be seen in upper stratospheric ozone values, which exhibit a peak to trough difference of 4 - 6\% (WMO, 1999).

### 2.5.2 The Quasi-Biennial Oscillation

The Quasi-Biennial Oscillation (QBO) is another circulation pattern which has a large scale effect on the abundance of ozone (Garcia and Solomon, 1987). The QBO is the reversal in direction of the zonal winds in the tropical stratosphere, which, at altitudes of 15 km to 30 km occurs on a time scale of 26 to 28 months, hence the name quasi-biennial. The QBO is believed to be driven by vertically propagating waves, resulting from unsteady latent heating inside tropical convection. These waves transfer energy into the middle atmosphere, driving the zonal mean winds (Salby, 1995). It was noted by Labitzke (1982) and Holton and Tan (1982) that when the QBO is in its easterly phase, the polar vortex is less isolated and consequently, warmer. When the QBO is in its westerly phase, the polar vortex is less disturbed, more isolated and as a consequence, colder. The latter situation is more favourable for the formation of PSC and therefore could cause a higher degree of ozone depletion within the vortex. Earlier vortex breakup is likely if the middle stratospheric winds are in the opposite direction to the circulation around the vortex, i.e. when the QBO is in its easterly phase.

### 2.5.3 Volcanic aerosol

In the years after recent, large, volcanic eruptions (most notably that of Mt Pinatubo in 1991), unusually low levels of stratospheric ozone have been observed at northern middle latitudes (see for example Gleason et al., 1993; Bojkov et al., 1993).

As a result of large volcanic eruptions, sulphur containing gases, such as H\(_2\)S and SO\(_2\), can be injected into the stratosphere. H\(_2\)S is rapidly converted to SO\(_2\), which is then slowly oxidized to form H\(_2\)SO\(_4\). This takes up water and forms aerosol droplets. There are several ways in which the resulting enhancement of stratospheric aerosol can influence ozone.

The increased aerosol loading can influence the dynamics of the stratosphere. Using a two-dimensional model, Brasseur and Granier (1992) found that the increased aerosol heating in the tropical stratosphere resulted a 10\% strengthening of the meridional circulation, and therefore greater upward transport in the tropics, and a small (less than 3\%) decrease in the tropical total ozone column. In addition, they found that the enhanced meridional circulation increased ozone concentrations by up to about 3\% in the extratropical lower stratosphere.
In contrast, using a three-dimensional General Circulation Model (GCM), Rozanov et al. (2002) found that the increased equator to pole temperature gradient resulted in an intensified polar night jet, and therefore lower ozone values in the northern hemisphere middle and high latitudes.

Both Rozanov et al. (2002) and Al-Saadi et al. (2001) attribute part of modelled decreases in tropical lower stratospheric ozone to increased upwelling bringing more ozone poor air into the lower stratosphere.

The chemistry of the stratosphere can also be influenced as the increased sulphate aerosol provides a greater surface area for heterogeneous reactions such as reactions 2.17, 2.18 and 2.19. As a result of the eruption of Mt Pinatubo, the stratospheric aerosol surface area available for heterogeneous reactions increased dramatically. After the eruption of Pinatubo, the surface area of the aerosol increased from between 0.5-1 μm^2cm^{-3} (McElroy et al., 1992) to about 35 μm^2cm^{-3} at 32 hPa over the equator in November 1991 (Grainger et al., 1995). Aerosol number densities larger than 600 cm^{-3} were observed at 41°N, which reduced to 100-200 cm^{-3} within 30 to 60 days, due to coagulation (Deshler et al., 1992). Aerosol number densities measured by Deshler et al. (1992), in September 1991 over the Antarctic, were greater than 6000 cm^{-3}, although these were attributed to the Cerro Hudson eruption in August 1991. The increases in stratospheric aerosol surface area density from the Pinatubo eruption may have contributed to the exceptionally low northern mid-latitude total ozone values during the subsequent winters of 1992 and 1993. However, Hadjinicolaou et al. (1997) found that even using a CTM with simplified chemistry and no increase in stratospheric aerosol after volcanic eruptions, a substantial portion of the post-Pinatubo ozone depletion could be explained. The residence time (time to decrease to 1/e of the original value) of volcanic aerosols in the stratosphere is around 12-18 months (Staehelin et al., 2001), after which time ozone values should have largely recovered. The increased heterogeneous chemical ozone losses are not believed to be large in the tropics, however they become more important at higher latitudes in winter and spring when temperatures are lower and solar zenith angles are higher (Hofmann et al., 1994), so they should counteract the transport-related ozone increases at mid to high latitudes.

Because of the increase in surface area available for heterogeneous halogen activation reactions, volcanic eruptions should cause more ozone loss when the abundance of halogens in the stratosphere is higher.

2.5.4 Atmospheric circulation and possible changes

As outlined in Section 2.2, atmospheric circulation plays an important role in distributing ozone from regions where it is produced, to other parts of the stratosphere.

There are a number of ways in which the atmospheric circulation can affect the amount of ozone, on scales ranging from regional to hemispheric or global.

It was first noted by Dobson et al. (1929) that the passage of tropospheric weather systems causes day-to-day ozone variability. They found that high total ozone is observed during the passage of a low pressure system and that low total ozone is observed near high pressure systems. One partial reason for these observations is that during the passage of a surface low pressure system, the tropopause pressure is higher than normal, the total mass above a particular point on the surface is increased and therefore so is the total amount of ozone. For a surface high pressure system, the opposite is true (Appenzeller et al., 2000). However, recently it has become clear that "far-range transport" in the
lower stratosphere, related to the high and low pressure systems, may actually contribute as much, if not more, to the correlation between total ozone and surface pressure (Koch et al., 2002, 2005). Through similar effects, there is a relationship between regional total ozone amounts and surface pressure related teleconnection patterns, for example the North Atlantic Oscillation. The North Atlantic Oscillation (NAO) is a regional climate pattern, which strongly influences winter climate in Europe. It is usually defined as the surface pressure difference across the North Atlantic, for example between Ponta Delgada (Azores) and Stykkisholmur (Iceland) as described by Hurrell (1995). When the NAO is in its positive phase, tropopause pressure is higher at high latitudes and lower at low latitudes, and since total ozone correlates with tropopause pressure, this results in higher ozone values at higher latitudes and lower total ozone values at lower latitudes (Appenzeller et al., 2000). From the 1960s, up until the early 1990s, the NAO index showed a continuous increase towards positive values, which may have influenced European total ozone trends (Appenzeller et al., 2000).

A linear regression model was used by Steinbrecht et al. (2001) to investigate the contribution of several factors to interannual variability in February total ozone at Hohenpeissenberg in Germany. They found that around 25% of the long term ozone decline in February at Hohenpeissenberg is related to a more frequent positive phase of the Polar Eurasia tropospheric circulation pattern (negative anomalies of tropospheric geopotential height over Greenland and Arctic Canada coupled to opposite anomalies over Central Europe and North-Eastern China).

In contrast to Appenzeller et al. (2000), no significant influence of the NAO on February total ozone was found by Steinbrecht et al. (2001).

The mixing of ozone poor vortex air into the mid-latitudes may also have a significant impact on ozone trends in the northern mid-latitudes (Bregman et al., 2000; Hadjinicolaou et al., 1997; Knudsen, 1998). This “dilution” of mid-latitude ozone depends upon the amount of ozone destruction within the vortex, and upon the rate at which the ozone depleted air is transported into the mid-latitudes (Knudsen, 1998). Dilution is expected to affect ozone values at lower latitudes up until about November of the same year, but it is not expected that any signal will be carried over into the next year (Hadjinicolaou et al., 1997). However, if there is an increasing amount of dilution every year, it can contribute to a long term seasonal ozone trend. It was shown by Bregman et al. (2002) that it is unlikely that heterogeneous chemistry on subvisible clouds near the tropopause can explain negative ozone trends in the mid-latitude lowermost stratosphere.

On a larger scale, a reduction in the rate of transport of ozone-rich tropical air into the mid-latitudes would result in a decrease in ozone over the mid-latitudes. Such an effect is described by Fusco and Salby (1999), who suggest that much of the mid-latitude trend in ozone, and the inter-annual variability in mid-latitude ozone is linked to trends and variability in the upward Eliassen-Palm (EP) flux from the troposphere. The EP flux is basically a measure of the wave driving of the diabatic circulation. They show that extra-tropical ozone in the winter hemisphere is strongly correlated with average winter-hemisphere EP flux values. An increase in the rate of meridional transport as observed during winter, for example, also leads to a net increase in the production of ozone, as ozone is produced in air which is drawn upwards in the tropics (Fusco and Salby, 1999).

A 20 year CTM run (1979-1998) was carried out by Hadjinicolaou et al. (2002), in which the only inter-annual variability represented in the model was that contained in the meteorological fields. They found that at least half of the observed mid-latitude ozone trend averaged over December to February was reproduced by the model, and that the
2.5. OTHER PROCESSES RELATED TO OZONE VARIABILITY AND TRENDS

Modelled total ozone correlated well with the vertical winter EP-flux at 100 hPa and the NAO. This again suggests a significant contribution of dynamical processes to the observed ozone trend.

El Niño is a shifting of the warmest sea surface temperatures (and consequently the most active convection) from the western Pacific to the eastern and central Pacific. This occurs with an approximate frequency of 3-5 years. El Niño brings with it a change in the surface pressure, known as the Southern Oscillation (the two are often referred to jointly as the El Niño Southern Oscillation, or ENSO). The Southern Oscillation manifests itself as a shifting of the low pressure zone which is usually present over the western Pacific and Indian ocean, to the eastern Pacific. As the diabatic circulation is driven by waves propagating upwards out of the troposphere, the shifting of the major convective cells brought about by ENSO results in a change in the tropical circulation. Effects of the ENSO are also felt in the extra tropics (Salby, 1995).

The effect of the ENSO phenomenon on total ozone was discussed by Brönnimann et al. (2004). They found that observations of unusually high values of total ozone over Europe during 1940-1942 were related to a strong El Niño event which began in autumn 1939 and continued until spring 1942. They suggest that this resulted in a weaker than normal polar vortex, and a strengthened meridional transport, which would have increased transport of ozone to the extratropics. The corresponding increase in descent over the polar areas would have warmed the polar stratosphere and lead to high Arctic total ozone in late winter. Seven other periods during which El Niño may have had a similar but weaker effect on ozone subsequent to 1948 were also identified (Brönnimann et al., 2004).

2.5.5 Climate changes

Further influences on long term ozone trends include a possible future cooling of the stratosphere due to an increase in radiative cooling resulting from a higher stratospheric greenhouse gas burden (Schnadt et al., 2002). A cooling of the Arctic stratosphere could lead to more frequent PSC formation, and more permanent removal of nitrogen species, through sedimentation of PSC particles. It was shown by Waibel et al. (1999) that a cooling of the Arctic stratosphere by only a few degrees, could cause ozone loss greater than that observed in the winter of 1994-1995, even if the total inorganic chlorine loading is similar to values observed around 1980. They found that in particular when taking denitrification into account, the ozone recovery due to reduced chlorine in the stratosphere was mostly offset by more heterogeneous activation of chlorine.

It was suggested by Rex et al. (2004) that about 15 DU of additional ozone loss could be expected per Kelvin cooling of the Arctic stratosphere.

In a modelling experiment Austin and Butchart (1994) showed that a doubled CO₂ climate could lead to lower Arctic vortex temperatures and thus an Arctic ozone hole, however they prescribed planetary wave activity in the model, and noted that increased ozone destruction only occurs when there is no large wave related disturbance of the vortex in winter, and that the risk of a substantial increase in ozone loss was confined to years where the final warming occurred late.

A coupled chemistry-climate model (ECHAM4.L39(DLR)/CHEM) was used by Schnadt et al. (2002) to investigate the effect of a greater stratospheric greenhouse gas burden in 2015. They found that although the increase in greenhouse gas mixing ratios lead to an intensified radiative cooling in the Antarctic, a more persistent vortex and greater ozone loss, the situation was different in the Arctic. Here, the increased greenhouse gas
abundances lead to greater planetary wave activity and hence a more disturbed, warmer vortex. They found that the “dynamical heating” offsets the radiative cooling effect of the greenhouse gases, and therefore the model did not produce a statistically significant temperature change in the Arctic. Further, due to the future reduction in ODS they found that the Arctic ozone spring time depletion was significantly reduced, and the combination of a warmer Arctic vortex with greater planetary wave activity lead to an earlier final warming.

The abundance of water vapour in the stratosphere has been increasing at the rate of about 0.05 ppmv per year over the period 1980 to 2000, and has almost doubled since the 1950’s (Rosenlof et al., 2001). This moistening of the stratosphere is regarded as another source of increased future Arctic ozone loss due to increased PSC abundance (Waibel et al., 1999).

In a model sensitivity study, Chipperfield and Pyle (1998) also showed that an increase in stratospheric water vapour could lead to more frequent PSC and thus greater ozone loss in the Arctic. Increases in stratospheric water vapour could also lead to greater chemical destruction of ozone in the mid-latitudes, due to an elevation of HOx levels (Dvortsov and Solomon, 2001). A decrease in midlatitude ozone, as a result of enhanced stratospheric water vapour was also predicted by Shindell (2001).

2.6 Ozone trend calculations using models

There are many different types of models used in investigating processes affecting the abundance of stratospheric ozone. Here, only experiments involving CTMs will be discussed.

There are several ways in which a CTM may be used to investigate ozone loss. One approach for studies of chemical (ODS related) polar ozone column loss, is to initialize a “passive ozone” tracer at the beginning of a particular winter with observed ozone values, and run the model for the winter, forced by analyzed temperature and wind fields. The passive ozone tracer is similar to ozone in all respects, except that it is not reactive. The total chemical ozone loss at any point during the winter can then be calculated as the difference between the modelled passive ozone and the ozone values observed in reality, or a second, reactive ozone tracer in the model. Using a reactive ozone tracer in the model has the advantage that this can be compared with the observed ozone values, providing some model validation. This was the method used by Lefèvre and Figarol (1998) with the REPROBUS model. A similar approach was used by Sinnhuber et al. (2000), with the SLIMCAT model.

If such model simulations are carried out for several consecutive winters, a seasonal ozone trend could be calculated, however ozone abundances have a high natural variability, and generally a long time period is required to calculate a reliable trend.

Three-dimensional CTMs have mostly been used to simulate short periods of a few months because of the computational expense of such models. However, increasingly, multi-annual transient runs are being performed in order to calculate a long term annual average ozone trend, or global ozone trends (WMO, 2003).

As well as the multiannual model experiments of Hadjinicolaou et al. (1997, 2002) and Chipperfield and Pyle (1998), the main findings of which have been discussed earlier in this chapter, several other long term model experiments have been carried out.

The types of models used in these studies can be divided into two categories, the “off-
line” CTMs, i.e. those which use prescribed circulation and temperature fields, and the
coupled chemistry-climate models (CCM), which calculate the atmospheric circulation
and temperature fields internally. The off-line CTMs have the advantage that they are
compositionally cheap, however, it is not usually possible to directly simulate the effects
of feedback between chemical processes and circulation (e.g. ozone loss and the resulting
cooling of the stratosphere). The simulation of such feedbacks is possible with the CCMs,
however they are computationally much more expensive than the offline CTMs.

Using a CCM with sea surface temperatures, greenhouse gas and halogen concentra-
tions taken from observations, Austin (2002) investigated ozone and temperature trends
from 1980 to 2000. They found that their model reproduced observed annual ozone vari-
ability reasonably well, and that the globally averaged modelled total ozone trend was in
agreement with the observed trend, when the effect of the solar cycle was removed from
the latter. They also reported that a similar model run, with fixed halogen and green-
house gas concentrations did not exhibit any significant ozone trend. The modelled ozone
trends were therefore suggested to be the result of increasing halogen and greenhouse gas
concentrations.

An off-line CTM, SLIMCAT was used by Chipperfield (2003) to study the causes of
changes in ozone in the mid to high latitude lower stratosphere between 1979 and 1998.
The model was forced using circulation and temperature fields from the European Centre
for Medium Range Weather Forecasts (ECMWF) analyses. The model reproduced the
evolution of the high latitude spring time ozone depletion well in both hemispheres from
1980 to the early 1990s, however after 1994 the correspondence with observations was
not as good. It was found that 30-50% of the mid-latitude ozone decreases were due to
heterogeneous chemistry on PSC at high latitudes.

An earlier model study by Chipperfield (1999) indicated that during the period 1991 to
1997, high latitude heterogeneous chemical processes were responsible for a loss of about
2-3% of total ozone at 50°N and about 5% at 50°S.

Using the offline CTM “TM3”, forced by six hourly ECMWF analyzed meteorological
fields, Bregman et al. (2002) investigated the contribution of chlorine activation on sub-
visible ice clouds to the observed decline in northern mid latitude ozone. They performed
two model runs for the year 1996, a base run without subvisible clouds included, and a
second run with the clouds. They found that the additional chlorine activation on the ice
clouds resulted in ozone loss of up to about 4% in the lowermost stratosphere in June,
however, the additional ozone loss was only about 1-2% in December. Although in this
case no multiannual integration was performed, based on the results for 1996 Bregman
et al. (2002) concluded that the additional ozone loss due to chlorine activation on sub-
visible ice clouds was insufficient to explain the observed decline in lower stratospheric
ozone over the northern mid-latitudes.

The University of Illinois at Urbana-Champaign (UIUC) CTM was used by Egorova
et al. (2001) to assess the effect of the Montreal protocol and its amendments on ozone
depletion. They carried out two transient model runs from 1993-2000, one with the
observed increase in CFC emissions, and the other with a 3% annual tropospheric growth
of CFCs (as may have occurred without the Montreal protocol). It was found that by
1999 the Montreal protocol and its amendments had prevented about 1.5% of globally
averaged ozone loss (about 5% in the southern hemisphere). They also noted that CFC
emissions were not chiefly responsible for the modelled inter-annual variability of total
ozone.

Some of the problems of using a CTM forced by assimilated circulation and temper-
nature data are discussed by Douglass et al. (1997, 2003). Douglass et al. (2003) made a comparison between a two year model run using a CTM forced by assimilated circulation data, and a similar run using the same CTM forced by circulation data from a GCM. It was found that the model run using the GCM data reproduced observed tracer fields better than the run using the assimilated data. They suggested that the reason for this is that circulation from a data assimilation system produces excessive upward tropical transport and mixing between the tropics and mid latitudes. Too low tracer gradients between the tropics and mid-latitudes were also reported by Douglass et al (1997) for a seven month CTM run where the model was forced by assimilated circulation fields.

Hall et al. (1999) calculated the "age of air" for several off-line CTMs. The age of air is basically the average time taken for the individual air molecules comprising an air parcel to reach the position of the air parcel, from the tropical tropopause (see for example Hall and Plumb, 1994). Hall et al. (1999) found that for most models the age of air in the lower mid to high latitude stratosphere was too young, implying too rapid upward and poleward transport or mixing.

Although the circulation fields from the ERA-40 reanalysis, which are used to force the model in this study, seem to contain similar effects (see for example van Noije et al., 2004), it may be possible to remove many of the spurious circulation effects by focusing on the difference in tracer fields or trends between two similar model experiments, as is done in Chapter 5.
Chapter 3

General Model Description

The model used in this study is a three dimensional, off-line, atmospheric chemistry transport model (CTM), "MEZON" (Egorova et al., 2003). This type of model has several characteristics which make it ideal for the kind of study performed here.

The fact that simulations are performed in three spatial dimensions has the advantage that processes which are not zonally homogeneous, for example the formation of polar stratospheric clouds, can be modelled more accurately.

Since MEZON is run in off-line mode, that is, with prescribed temperatures and circulation, it is computationally cheaper than a global circulation model (GCM) and multi-year simulations can be carried out more easily. In MEZON's current configuration, a simulation of 40 years takes about 20 days of CPU time. In contrast to a GCM, in a CTM the prescribed meteorological data are calculated from observational data. Thus a particular year of simulation corresponds to a particular year of observations, and the model results can be compared directly with observations for the purpose of validation.

One major disadvantage of running the model in off-line mode, is that any feedback between chemistry and circulation (for example the effect of ozone heating in the stratosphere) can not be simulated. Braesicke and Pyle (2003) carried out three twenty year integrations with the Met Office Unified Model, and found that the observed middle latitude spring-time ozone loss did not produce a large additional feedback on the ozone distribution. However, Randel and Wu (1999) found a significant cooling of the Arctic and Antarctic stratospheres, which corresponds with the spring time ozone loss. This cooling could feedback to cause more ozone loss, through increased heterogeneous halogen activation, or by stabilising the polar vortex, reducing dynamical ozone supply from lower latitudes.

MEZON has a horizontal resolution of $4^\circ$ of latitude by $5^\circ$ of longitude. Vertically, the model atmosphere consists of 24 levels, extending from the Earth's surface, up to 1.0 hPa (about 48 km). MEZON operates on fixed pressure levels and the upper boundaries of the model layers are at 980, 950, 900, 850, 800, 750, 650, 550, 450, 350, 250, 200, 150, 100, 63.1, 39.81, 25.12, 15.85, 10.0, 6.3, 3.98, 2.51, 1.59 and 1.0 hPa, with a surface pressure of 1000 hPa. The initial model time step is two hours, both for chemistry and transport, however in the case of an instable solution, the time step is divided by two and the calculation repeated, until stability is achieved.

The initialization of the model for the 1965-2000 transient runs was carried out by running the model with the circulation and ODS emissions data of 1960, for 10 years of model time. This resulted in a small steady state concentration of ODS in the stratosphere. The model runs were then started from 1965, in order to approximately take into account the time needed for tropospheric emissions to reach the stratosphere. Often
models are initialized with measured fields of key species, however before the satellite era, such an approach is not possible. Experiments with this model have shown that similar initial conditions only produce significant differences in output up to about 5 years after the experiment began.

In previous studies, including a validation of MEZON (Egorova et al., 2003), the model was driven with meteorological fields from the United Kingdom Meteorological Office (UKMO) analysis, which is described by Swinbank and O' Neill (1994).

The transport routine used in the model will be briefly discussed in Section 3.1. The chemistry part of the model and data used as model inputs will be described in sections 3.2 and 3.5 respectively, as it is to these parts of the model that significant changes were made.

3.1 Transport

The advective transport of chemical species in the model is calculated using a "hybrid" scheme, which employs the Prather scheme (Prather, 1986) for vertical transport and a semi-Lagrangian scheme (Williamson and Rasch, 1989) for horizontal transport. The hybrid scheme was designed by Zubov et al. (1999), with the aim of constructing a transport routine which combined an accuracy similar to that of the Prather scheme, with the computational efficiency of a semi-Lagrangian approach. The transport of tracers is calculated using a splitting method, where first the vertical transport is calculated, using the Prather scheme, then the advective horizontal transport is calculated using the semi-Lagrangian scheme. Before and after the semi-Lagrangian transport, the total mass of the tracer is calculated in the model layer. If, after the horizontal transport, the new mass is significantly different to the old, the mass correction of Rasch and Williamson (1990) is applied, in its simplest form. This involves the multiplication of the tracer mixing ratio in all grid boxes in a particular model layer by the ratio of the total mass in the layer before and after the horizontal advection calculation. This method is slightly non-monotonic Zubov et al. (1999). As is shown later, in Chapter 4 and Chapter 7, this "mass fixer" may cause some problems for a few long lived species.

In the MEZON transport routine there is no explicit representation of transport in the planetary boundary layer, and sub-grid scale convection in the troposphere is also not explicitly included. The transport scheme is further described in Egorova et al. (2003).

3.2 Chemistry

The chemistry scheme of MEZON was updated for this study and now includes 192 reactions, 145 of which are gas phase, and 47 of which are photolysis reactions. In addition, the scheme includes 16 heterogeneous reactions, which occur on Nitric Acid Trihydrate (NAT) particles, ice particles and liquid aerosol droplets. The reactions and their rates are listed in Appendix A.

The chemistry scheme is similar to that described in Rozanov et al. (1999) and Egorova et al. (2003), except that it has been extended to include the new species added to the model, and some reaction coefficients have been updated as more up to date data has become available. Reaction coefficients have been taken from DeMore et al. (1997); Sander et al. (2000) and from the IUPAC website (http://www.iupac-kinetic.ch.cam.ac.uk).
3.3 Improvement of the heterogeneous reaction rate parameterization

The parameterization responsible for the calculation of heterogeneous reaction rates on PSC and liquid aerosol particles (hereafter “PSC parameterization”) was extensively updated. The biggest changes were made to the part of the subroutine which calculates the formation and growth of type I PSC particles. The next two sections briefly describe the way PSCs were represented in the model, and in more detail, the improvements that have now been made.
3.3.1 The old parameterization

The previous version of the PSC parameterization was adapted from a parameterization based on the code of Carslaw et al. (1995) which was supplied by Beiping Luo. It represented three types of aerosol - liquid aerosol, type I PSC (here assumed to be Nitric Acid Trihydrate (NAT), and type II PSC (water ice). All three could co-exist. The calculation of heterogeneous reaction rates and sedimentation of PSC particles was confined to regions polewards of 50° and above 150 hPa. PSC particles were not explicitly transported, rather they were effectively evaporated after sedimentation, transported with the gas phase and recondensed in the next time step if the appropriate saturation conditions were met.

The composition of liquid aerosol was calculated without taking into account the lower availability of HNO₃ as a result of NAT formation, or changes in the abundance of H₂SO₄ (due to volcanic activity, for example).

If the temperature dropped below the temperature where NAT is stable, NAT was invoked, with a particle number density of 10 cm⁻³. NAT radii and surface area for the reactions were then calculated assuming that HNO₃ condensed until the particles were in equilibrium with the gas phase. In both old and new versions of the parameterization, the NAT equilibrium vapour pressure is calculated as in Hanson and Ravishankara (1994). The particle size distribution is monodisperse.

The part of the parameterization which deals with PSC II is basically the same in the old and new versions. The amount of water which condenses into the solid particles is calculated assuming equilibrium with the gas phase. If the temperature drops to below the point where ice is possible, ice is nucleated, with a particle number density of 10 cm⁻³. HNO₃ is also condensed until equilibrium with the gas phase is reached. As was the case for NAT particles, all ice particles in the old and new versions of the PSC scheme have the same diameter.

3.3.2 The new parameterization

The key changes in the PSC parameterization are that the assumption of equilibrium between the gas and solid phases in the case of NAT is no longer used, PSC 1 is transported in the model, PSC (or other solid phase clouds) are not artificially limited to certain latitudes or altitudes and ice and NAT can no longer co-exist as separate particles.

NAT is nucleated in a particular model grid box, when a gas phase partial pressure 20 times greater than the equilibrium value (i.e. a saturation of 20) is reached, or exceeded. When this happens, NAT is formed throughout the whole box, with a number density of \(N_{\text{NAT}}^{\text{initial}}\) (in the four long term model runs, a number density of 1×10⁻³ cm⁻³ was used). The particle growth is calculated according to:

\[
\frac{dr^2}{dt} = 2D_g \frac{M}{\rho} (n_{\text{HNO}_3}^{\text{gas}} - n_{\text{HNO}_3}^{\text{NAT}}(\text{H}_2\text{O}, T)),
\]

(3.1)

where \(r\) is the particle radius, \(M\) is the molar mass of NAT (117 g mol⁻¹), \(D_g\) is the gas phase diffusion coefficient, \(n_{\text{HNO}_3}^{\text{gas}}\) is the HNO₃ gas phase partial pressure, and \(n_{\text{HNO}_3}^{\text{NAT}}\) is the vapour pressure over NAT, and \(\rho\) is the density of NAT (1.5-1.6 g cm⁻³).

Therefore, to calculate the change in radius of a NAT particle in a model time step of length \(\Delta t\) one can use:

\[
r^2(t + \Delta t) - r^2(t) = 2D_g \frac{M}{\rho} \left(n_{\text{HNO}_3}^{\text{gas}}(t) - n_{\text{HNO}_3}^{\text{NAT}}(\text{H}_2\text{O}(t), T(t))\right) \Delta t
\]

(3.2)
The gas phase diffusion coefficient of HNO₃ in air, $D_g$, is calculated from:

$$D_g = \frac{(kT)^{\frac{3}{2}}}{p(\sigma_{Air} + \sigma_{HNO₃})^{\frac{3}{2}} \left( \frac{1}{M_{Air}} + \frac{1}{M_{HNO₃}} \right)^{\frac{3}{2}} \frac{3}{\sqrt{8\pi}}},$$  \hspace{1cm} (3.3)

where $p$ is the pressure in Pa, $k$ is the Boltzmann constant, $T$ is the temperature in Kelvin, $\sigma$ is a molecular radius (here taken to be $3.1 \times 10^{-10}$ m for air and $4.74 \times 10^{-10}$ m for HNO₃) and $M$ is the mass of a molecule ($28.86\text{ g mol}^{-1}$ for air and $63.0\text{ g mol}^{-1}$ for HNO₃).

From Equation 3.2, one has the radius of the NAT particles, for use in the heterogeneous reaction rate calculations, and for the sedimentation routine. The mass of condensed NAT, per unit volume, can then be calculated from:

$$m(t) = \frac{4\pi}{3} r^3 \rho.$$  \hspace{1cm} (3.4)

This mass is then removed from the gas phase variables in the model. $N_{NAT}$ (the number density of NAT particles) is transported, as is the mixing ratio of HNO₃ in the solid phase. After a transport step, NAT may have been transported into a box where no NAT has been nucleated. The volume in this box which is filled with NAT particles can be calculated by dividing $N_{NAT}$ after transport, by $N_{NAT}^{\text{init}}$ (the number density of NAT in a box where nucleation occurs) e.g.

$$f = \frac{N_{NAT}}{N_{NAT}^{\text{init}}}.$$  \hspace{1cm} (3.5)

The particle number density $N_{NAT}$ is limited such that it is always less than or equal to $N_{NAT}^{\text{init}}$.

From the equation above, $f$ represents the fraction of the model box which contains NAT. In this fraction of the model box, $N_{NAT}=N_{NAT}^{\text{init}}$, as the number density of NAT should remain the same in the NAT cloud (this procedure avoids a physically unreasonable smearing out over the whole model box). The initial radius of the NAT particle in this microphysical step (before growth) can be calculated from the transported mixing ratio of frozen HNO₃, assuming that this frozen HNO₃ occupies only a fraction $f$ of the model box. The particles are then grown or evaporated using equation (3.2), with an HNO₃ partial pressure given by the average gas phase partial pressure in the model box. If the critical saturation ratio is exceeded by the box average HNO₃ partial pressure, NAT is nucleated in the whole box, and the previously frozen mass is distributed among all particles in the box, before the new radius is calculated using Equation 3.2.

The heterogeneous reaction rates on NAT are multiplied by the fraction of the model box which contains NAT, as the rates should be an average for the model box.

Using this method means that the effective number density of NAT (used in condensation and evaporation calculations) is always equal to the initial number density, i.e. there is no dilution. The transported number density only serves to give us the fraction of the box filled with NAT.

If the radius calculation from Equation (3.2) gives a radius of zero or less (i.e. the particles have evaporated), the condensed mass of NAT is put back into the gas phase and the number density of NAT in the box is set to zero.

Growing the NAT particles using the box average HNO₃ partial pressure is not strictly physically correct. Rather, the gas phase partial pressure in the part of the box containing
NAT particles should be used (as this will be depleted by uptake on NAT). This is unfortunately not possible in this model (and perhaps not in any model) as any uncertainty in either the number of NAT particles in the box, or in the mixing ratio of HNO\textsubscript{3} in the solid phase, can result in a negative gas phase HNO\textsubscript{3} concentration in the part of the model box containing NAT. A further limitation of this method is that all particles are considered to be the same size. On the other hand, this is a simple, and physically reasonable way of representing NAT growth in an Eulerian model, which requires only two extra transport variables.

The representation of type II PSC is essentially the same as described in Section 3.3.1, except if ice is formed, the NAT calculation is not performed. HNO\textsubscript{3} is assumed to be taken up on the ice particles, until the gas phase HNO\textsubscript{3} reaches the equilibrium value with respect to NAT, and the number density of NAT in a model bin with ice is set to be the same as the number density of ice (i.e. 0.1 cm\textsuperscript{-3}). Reaction rates on liquid aerosol droplets are calculated as the volume weighted average of rates in the part of the model box where solid PSC is present, and the part where there is no solid PSC. If a fraction less than 1 of a model box contains NAT, the calculation of the reaction rates on liquid aerosol is performed twice. For the first calculation, the gas phase HNO\textsubscript{3} is depleted by the amount in the solid phase. For the second calculation, the total HNO\textsubscript{3} is used. The reaction rates for the model box are the average of these calculations, weighted according to the fractions of the box which contain and do not contain NAT.

Aside from this double calculation, the liquid aerosol rates are still calculated as in the previous version of the model.

The amount of H\textsubscript{2}SO\textsubscript{4} in the aqueous phase in stratospheric sulphate aerosol is no longer prescribed, but is calculated from the surface area density of sulphate aerosol (SAD). The SAD data used for the calculation is described in Section 3.5.7. To calculate the H\textsubscript{2}SO\textsubscript{4}(aq), a log normal size distribution was assumed for the aerosol, with \( \sigma = 1.8 \) and a number density of 10 droplets cm\textsuperscript{-3}. Thus the mode radius can be calculated using:

\[
R_{\text{mode}} = \left( \frac{A}{4\pi e^{\frac{\sigma}{2} (\ln N)^2}} \right)^{\frac{1}{2}},
\]

where \( A \) is the aerosol surface area density, and \( N \) is the aerosol droplet number density. The mode radius can then be used to calculate the total volume per cubic centimeter of the lognormally distributed aerosol:

\[
V = \frac{4\pi}{3} (R_{\text{mode}})^3 e^{\frac{3}{2} (\ln N) N}.
\]

And finally the concentration of H\textsubscript{2}SO\textsubscript{4}(aq) is given by:

\[
C = \frac{V \rho}{M_{\text{H}_2\text{SO}_4}},
\]

where \( M_{\text{H}_2\text{SO}_4} = 98.06 \text{ g mol}^{-1} \) is the molar mass of H\textsubscript{2}SO\textsubscript{4}, and \( \rho \) is the density of the aqueous solution, which is calculated assuming its a binary H\textsubscript{2}O/H\textsubscript{2}SO\textsubscript{4} solution.

### 3.4 Sedimentation of PSC

In the old sedimentation routine, the sedimentation of PSC (and other solid cloud particles for that matter) was parameterized using a prescribed sedimentation velocity of
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$13 \times 10^{-3} \text{ms}^{-1}$ for ice particles (corresponding to a particle diameter of about $30 \mu \text{m}$). Denitrification occurred via sedimentation of HNO$_3$ on ice particles. In the revised version, the sedimentation is now calculated according to the size of the cloud particles, assuming a monodisperse size distribution. This allows the sedimentation of NAT, when these particles reach sufficient size. The radii of PSC I particles are taken from the output of the PSC calculation, and the radii for type II PSC are calculated assuming a number density of 0.1 particles cm$^{-3}$, which is the same as the number density used when calculating the heterogeneous reaction rates. The fall velocities for the particles are then calculated from

$$V_t = \frac{1}{18} \frac{D_p^2 \rho_p g C}{\eta},$$  \hspace{1cm} (3.9)

where $D_p$ is the particle diameter, $\rho_p$ is the density of the particle, $g=9.81 \text{ms}^{-2}$ is the gravitational constant, $\eta$ is the viscosity of air, and is given by

$$\eta = 6.45 \times 10^{-7} \text{g cm}^{-1} \text{s}^{-1} \cdot \left(\frac{T}{K}\right),$$  \hspace{1cm} (3.10)

with $T$ being the temperature in Kelvin (Müller and Peter, 1992). In Equation 3.9, $C$ is the Cunningham slip correction factor:

$$C = 1 + \frac{2\lambda}{D_p} \left[1.257 + 0.4 \exp(-\frac{1.1D_p}{2\lambda})\right],$$  \hspace{1cm} (3.11)

where $\lambda$ is the mean free path of air molecules at temperature $T$ and pressure $p$ (Müller and Peter, 1992):

$$\lambda = 0.23 \times 10^{-6} \text{m} \left(\frac{T}{K}\right) \left(\frac{\text{mbar}}{p}\right).$$  \hspace{1cm} (3.12)

Since type I and II PSC are not allowed to coexist in the model, if type II are present, any HNO$_3$ in the solid phase is sedimented with the type II PSC. Cloud particles are allowed to sediment a maximum of one model level per time step. Any HNO$_3$ sedimenting into a level is added to the frozen mass of HNO$_3$ in that level.

### 3.5 Input data

For the 1960 - 2000 transient model simulations, it was necessary to compile new data sets to be used as input for the model, which describe the emissions, or boundary conditions of important trace gases, and meteorological conditions during this time period. These input data are described in the next sections.

#### 3.5.1 Meteorological data

The meteorological data chosen to force the model are part of the new ERA-40 data set, from the ECMWF (Simmons and Gibson, 2000; Uppala et al., 2005). This data set was completed around July 2003, and includes, among other products, the three dimensional winds, and temperatures from September 1957 up until August 2002. Vertically, the data is available on 60 levels, between the ground and 0.1 hPa, and with a horizontal resolution of T159 (approximately $1.1^\circ \times 1.1^\circ$ in the tropics). The ERA-40 re-analysis
data was archived for 00, 06, 12, 18 UTC (Kalberg et al., 2004). The archived data was interpolated to the MEZON horizontal grid, using the program ecgrdb2nc (written by Mark Liniger) and daily mean values were calculated for winds and temperature, before interpolation onto the MEZON vertical grid, in order to construct the meteorological data files to force MEZON. The use of daily data rather than 6 hourly data for the model forcing did not change the results significantly, but reduced the necessary disk space by a factor of 4.

The main advantage that the ERA-40 data set offers over other analysis or reanalysis data sets is the huge time span which it covers, making it possible to also model the ozone trends before anthropogenic chemicals began to have a significant impact upon the ozone layer. Many other data sets only cover a much shorter period of time, for example the UKMO analysis (Swinbank and O’Neill, 1994), which only includes the vertical winds necessary to drive MEZON after 26th of August 1992, or the ERA-15 data set which covers the period 1979 - 1993 (Gibson et al., 1999). The NCEP re-analysis data set covers a similar period of time (1948-present) to the ERA-40 data, but, like the ERA-15 data, it only extends up to 10 hPa. Therefore it was decided that ERA-40 would be the most suitable data to force the model in this study. The ERA-40 data is not, however, without problems. The main deficiency in the ERA-40 data which was noticed during this study was that it seems to produce an excessive rate of upward transport in the tropics, into and within the stratosphere (a problem which is shared by most other circulation data sets produced by data assimilation systems Douglass et al., 2003). This problem is evident from, for example, the “water tape recorder signal” where a particular mixing ratio of water vapour ascends too fast into the stratosphere from the tropopause (see Chapter 4).

The too rapid transport is also discussed by Uppala et al. (2005) and van Noije et al. (2004). According to Uppala et al. (2005), the fast vertical transport is driven by a too strong Brewer-Dobson circulation, which was most likely the result of a forcing of the meridional circulation by repeated corrections of a temperature bias in the background assimilation model. The problem becomes particularly pronounced when satellite radiance data was used in the assimilation (after about 1973). It was also noted by Uppala et al. (2005), that the strong Brewer Dobson circulation caused an overestimation of total maxima over Bismarck from about 1973 to 1978, as well as in 1989/1990, in the reanalysis data set. During these years TOVS (TIROS Operational Vertical Sounder) or VTPR (Vertical Temperature Profile Radiometer) radiance data were used in the assimilation, and ozone was not assimilated.

The production of the ERA-40 reanalysis was organised into streams, the first covering 1989-2002, the second 1957-1972 and the third 1972-1988. Some jumps in upper stratospheric temperatures were noted in overlapping portions of the different streams Uppala et al. (2005). Further, the upper stratospheric temperatures are warm biased early in the reanalysis, in comparison with measurements, oscillate substantially in the middle period, and are cold biased by up to 5 K towards the end of the reanalysis. There is an approximate 10 K cold bias in the Antarctic lower stratosphere in the early years of the reanalysis.

During the testing of MEZON with the ERA-40 circulation data it was noticed that there were several enormous, isolated “spikes” in vertical wind velocities, which produced instabilities in the models transport routine. These were removed, and the excessive vertical transport improved, by averaging the vertical wind velocities. After the vertical wind field for a particular day was read into the model, a 9 point mean was made for each grid point on each model level. In other words, the vertical wind velocity at a particular
point (except the poles) is the mean of itself, and all immediate neighbouring points on a horizontal plane. This “smoothing” was carried out twice and lead to lower amounts of vertical diffusion of the tracers, and a stable transport scheme.

3.5.2 ODS, methane and nitrous oxide lower boundary conditions

The emissions of methane, N₂O and the ODS are included in the model by prescribing the mixing ratios of these species in the planetary boundary layer (PBL). For the ODS, the mixing ratios are taken from WMO (2003), with values every five years from 1960 to 2005. These values were then interpolated to give a monthly PBL mixing ratio. Seasonal cycles in emissions were not included for the long lived ODS, as the troposphere is assumed to be well mixed for time scales similar to those necessary for concentrations corresponding to a particular surface mixing ratio to reach the tropopause. A variable northern to southern hemisphere ratio is imposed on the methyl bromide mixing ratios, in order to account for the seasonal cycle in emissions, which predominantly occurs in the northern hemisphere (Wingenter et al., 1998). PBL mixing ratios for methane and nitrous oxide were taken from the GISS website (http://www.giss.nasa.gov/data/simodel/ghgases/). These data are a combination of ice core measurements and of in situ measurements for more recent times. The PBL mixing ratios used for the ODS, methane and nitrous oxide are shown in Figure 3.1.

3.5.3 CO and NOₓ surface emissions

The lower boundary condition for CO and NOₓ is expressed in the form of emissions at the Earth’s surface. For NOₓ, the emissions are in units of gNOₓm⁻²s⁻¹, and for CO the units are gCOm⁻²s⁻¹. The emissions are based on those used in the model MOZART-2, which are intended to represent the emissions of the early 1990s (Horowitz et al., 2003).

In the MOZART-2 data, emissions from fuel wood burning, fossil fuel combustion and the burning of agricultural waste are based on the emission inventories of the Emission Database for Global Atmospheric Research (EDGAR) v2.0 (Olivier et al., 1996), with seasonality from the Intermediate Model for the Global and Annual Evolution of Species (IMAGES) (Müller, 1992). Biogenic emissions of hydrocarbons from vegetation are taken from the Global Emission Inventory Activity (GEIA) dataset (Guenther et al., 1995), for isoprene and monoterpenes and from Müller (1992) for other species. In the tropics, the spatial and temporal distribution of biomass burning is taken from Hao and Liu (1994) and in the extra tropics from Müller (1992). The MOZART-2 emissions data are described in more detail by Horowitz et al. (2003).

For the year 1990, the MOZART-2 emissions of CO and NOₓ are interpolated onto the MEZON grid, without scaling. For all other years, the emissions are scaled using data from EDGAR-HYDE 1.3 (van Aardenne et al., 2001). The EDGAR-HYDE 1.3 data is on a 1°×1° global grid, and anthropogenic emission values are given at 10 year intervals from 1890-1990, although only 1960-1990 are used here. To scale the data, the EDGAR-HYDE 1.3 data for 1960-1990 was divided by the EDGAR-HYDE 1.3 data for 1990. This gave the pre-1990 emissions as a fraction of the 1990 emissions. These fractions were then interpolated in time to give yearly emission fractions. As the EDGAR-HYDE 1.3 data was only available for 1890-1990, another solution needed to be found for estimating the emissions for 1990 to 2003.
Fig. 3.1: Surface mixing ratios of the ODS, methane and nitrous oxide, used in the model for 1960-2000. Values were taken from WMO (2003). The upper line in the CH$_3$Br plot shows the northern hemisphere values, the lower line represents the southern hemisphere values.

Unfortunately, at this point a mistake was made and instead of accounting for the leveling off of CO and NO$_x$ emissions after 1990, the increasing trend was continued. For 1990-2000, the increase in emissions was taken to be the same as that between 1980 and 1990, and for 2000-2003 the increase was taken to be 3/10 of this. The fractional emissions data was then also regrided onto the MEZON grid. The final emissions files were made by multiplying the anthropogenic part of the MOZART-2 data by the emission fractions. This was then added to the natural emissions from the MOZART-2 data, therefore it is assumed that the natural emissions of CO and NO$_x$ did not change significantly between 1960 and 2003. The MOZART-2 data is monthly data, so the final CO and NO$_x$ emissions
3.5. INPUT DATA

files include a seasonal cycle.

For the conversion of NOx to NO and NO2, a ratio of 9 NO to 1 NO2 is used. The total global annual emissions of NOx and CO are shown in Figure 3.2. The error mentioned above has a negligible influence on the results described in this thesis, since only a very small change in tropospheric OH concentrations is expected, causing a marginal change in the tropospheric lifetimes of some HCFCs.

![Graph showing annual global emissions of NOx and CO from 1960 to 2000.](image)

**Fig. 3.2:** Total annual global emissions of NOx and CO (multiply CO emissions by 10 to get emissions in Tg), used as model input 1960-2003. Note that in reality, the emissions leveled off in the 1990s, and therefore the emissions used in the model after about 1990 are not correct (see text). Pronounced seasonal cycles in the emissions of CO and NOx emissions are evident, due to the seasonal cycles in the major sources, i.e. biomass burning and fossil fuel combustion.

### 3.5.4 NOx emissions from aircraft

The NOx emissions from aircraft are based on the DLR emissions data (Dameris et al., 2005). The emissions are simply converted into the units needed and then regridded onto the MEZON grid, globally and between 1000 hPa and 63 hPa. Figure 3.3 shows the growth in total global emissions of aircraft between 1960 and 2000.

### 3.5.5 Water vapour

The water vapour mixing ratio is prescribed near the tropopause. The value near the tropopause is important for stratospheric chemistry, because it is from here that the water is transported upwards into the stratosphere. The monthly mean water vapour mixing ratio at 100 hPa, from the ERA-40 dataset was downloaded from the ECMWF data server, and used to prescribe the water vapour mixing ratio at this level in the model.
Since the data is on a monthly time scale, the seasonal cycle in stratospheric water vapour is seen in the model output. The values prescribed at 100 hPa are on a two-dimensional grid, i.e. not zonal mean.

3.5.6 Solar cycle

The effect of the 11 year solar cycle on photolysis rates is explicitly included in the model. In order to include the effect of the solar cycle on photochemistry in the model, a “look-up table” of photolysis rates was calculated for all species. This is an annual mean file, containing the photolysis rates for all species, for all atmospherically relevant combination of O2 and O3 columns. During the model run, this table is searched for the O2 and O3 slant column above each model box, and then the photolysis rates for all species in that box are read out. The spectral solar irradiance data for the calculation of the look-up table was taken from the GISS website:
http://www.giss.nasa.gov/data/simodel/solar.irradiance/
and is described by Lean (2000). The solar irradiance data includes the variation during the 11 year solar cycle.

3.5.7 Sulphate aerosol

A representation of the changes in the amounts of stratospheric sulphate aerosol is important for the calculation of heterogeneous chemical reaction rates. The amount of sulphate aerosol in the stratosphere varies substantially with time, as its main source is the oxidation of SO2 injected into the stratosphere during volcanic eruptions. Sulphate aerosol is input into the model in the form of monthly mean, zonal mean surface area density, (SAD) (with units μm² cm⁻²). The data was latitudinally interpolated onto the model grid. The SAD is calculated in four altitude layers (15-20, 20-25, 25-30, 30-35 km) from the zonal mean optical thickness at a wavelength of 550 nm. The optical thickness data is from the GISS webpage (http://www.giss.nasa.gov/data/strataer/) and described by Sato et al. (1993), although the dataset has been extended to the year 2000, and is now provided in the layers stated above, and not as a simple column value. The time evolution of hemispheric mean sulphate aerosol at an altitude of 21 km is shown in Figure 3.4. The huge perturbations resulting from volcanic eruptions can be seen clearly, for
3.6 Brief comparison with other CTMs

It may be useful to include here a brief summary of the features of some similar models, to serve as a comparison with the description of MEZON given above.

The SLIMCAT model is a three-dimensional off-line CTM, which has been used in the studies of Chipperfield (1999); Hadjinicolaou et al. (1997, 2002) and Chipperfield (2003) which were discussed in Chapter 2. It uses isentropic, rather than pressure levels.

SLIMCAT is forced by horizontal winds and temperatures from meteorological analysis or reanalysis data sets (e.g. those of the United Kingdom Meteorological Office (UKMO) or ECMWF ERA-15 and ERA-40), however, the cross-isentropic transport is derived from heating rate calculations. As the vertical motion is calculated “on-line”, the model ozone can be used in the heating rate calculations, allowing for some feedback between ozone heating and transport. In Chipperfield (1999), the model was run with a horizontal resolution of 7.5°× 7.5°, with 12 levels between 335 K and 2700 K (approximately 10 km and 57 km, respectively). The time step used in the chemical integration was 20 minutes, that for transport was 60 minutes. The advection scheme is that which was described by Prather (1986), and some of the species in the model are represented as chemical families. In terms of heterogeneous chemical processes, reactions on stratospheric sulphate particles are represented in the model, as are reactions on ice and NAT particles. NAT formation occurs when NAT is thermodynamically possible, and results in the absorption of all excess (surplus to equilibrium) gas phase HNO₃ onto 10 particles cm⁻³. Ice also forms when low enough temperatures are reached, and excess HNO₃ is taken up by the ice particles. NAT and ice are sedimented assuming particle radii of 1 μm and 10 μm, respectively.

The SLIMCAT model is described in more detail by Chipperfield (1999). Recently the denitrification scheme has been updated as described in Chipperfield et al. (2005).

REPROBUS is an off-line three-dimensional CTM, which is described in detail by Lefèvre et al. (1994). The model is forced by winds and temperatures from ECMWF analyses and has a resolution of 2°× 2°. It extends, in 31 levels, from the ground up to 10 hPa (approximately 30 km). The transport scheme is semi-Lagrangian, and species are
transported as families or separately, with a transport time step of 1 hour. The chemistry time step is 10 minutes.

The heterogeneous chemistry calculation was updated for *LeFèvre and Figarol* (1998), and resulted in all aerosol remaining in the liquid phase down to the ice frost point.

The TM5 model was used by *van den Broek et al.* (2004) to test a new NAT parameterization. This model is a three-dimensional CTM, run in off-line mode. It is based on the TM3 model described by *Bregman et al.* (2000). The TM5 has a vertical domain extending in 33 layers up to 0.2 hPa, and in *van den Broek et al.* (2004) a horizontal resolution of 2° latitude by 3° longitude was used. The model was forced by 6 hourly operational data from the ECMWF, and has chemical and dynamical time steps of 900 seconds. The advection scheme is based on *Prather* (1986) and *Russell and Lerner* (1981). The new NAT scheme described in *van den Broek et al.* (2004) (and in Chapter 8 of this work) takes into account non-equilibrium NAT growth.

A further model, the Stratospheric Chemistry Model 2 (SCTM2) is described by *Rummlukainen et al.* (1999). This three-dimensional CTM is driven by off-line winds from a GCM, however, temperatures from meteorological analyses were used. The model’s resolution is 7.8° of latitude and 10° of longitude and the model consists of 21 levels between the ground and 0.002 hPa (approximately 90 km). SCTM2 uses the Prather scheme for advection, with a time step of 4 hours. The chemistry time step is 10 minutes. Some of the 52 species included in the model are transported in chemical families, some explicitly.

A set of heterogeneous reactions on stratospheric sulphate aerosol or PSCs are included. PSCs form in two of the model levels when prescribed temperatures are reached (197 K at about 18 km and 193 K at about 24 km).

The Goddard Space Flight Center Chemistry and Transport Model (GSFC CTM) was used by *Douglass et al.* (2003), in the study examining tropical lower stratospheric transport that was described in Chapter 2. The GSFC CTM is run off-line and is driven with winds and temperatures from either a GCM, or from a data assimilation system, for example the Goddard Earth Observing System Data Assimilation System (GEOS DAS). There is a 15 minute time step for both transport and photochemistry. The transport routine uses a semi-Lagrangian approach. The model has a horizontal resolution of 2° latitude by 2.5° longitude, and extends from the surface up to about 60 km altitude. The photochemical scheme contains most reactions thought to be significant in the stratosphere and is described by *Kawa et al.* (2002). Below 500 hPa, the CTM ozone is relaxed to a zonal monthly climatology.

Heterogeneous reactions are possible on liquid sulfate, NAT and ice. Growth of the solid particles occurs at equilibrium, and a 1 K nucleation barrier is included for NAT nucleation. The number density of the particles is fixed at 10 cm⁻³ (*Douglass and Kawa*, 1999).

Some details of the models are summarised in Table 3.2. Here it can be seen that in terms of horizontal resolution, MEZON is about in the middle of the range of models. The vertical extent is smaller than that of most other models and the time steps are longer. One reason for the longer time steps is that MEZON uses a semi-Lagrangian advection scheme for horizontal advection, which allows longer time steps without the scheme becoming unstable. Models using the Prather scheme are limited to shorter time steps (or larger grid sizes) in order to ensure stability, especially in polar areas where the model grid is narrower.
3.7. MODEL EXPERIMENTS PERFORMED

<table>
<thead>
<tr>
<th>Model name</th>
<th>Resolution (lat×long)</th>
<th>Approx. vertical extent</th>
<th>Time step (transport/chemistry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEZON</td>
<td>4°×5°</td>
<td>0-48 km</td>
<td>2 hr/2 hr&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>SLIMCAT</td>
<td>7.5°×7.5°</td>
<td>10-57 km</td>
<td>60 min/20 min</td>
</tr>
<tr>
<td>REPROBUS</td>
<td>2°×2°</td>
<td>0-30 km</td>
<td>60 min/10 min</td>
</tr>
<tr>
<td>SCTM2</td>
<td>7.8°×10°</td>
<td>0-90 km</td>
<td>4 hr/10 min</td>
</tr>
<tr>
<td>GSFC CTM</td>
<td>2°×2.5°</td>
<td>0-60 km</td>
<td>15 min/15 min</td>
</tr>
<tr>
<td>TM5</td>
<td>2°×3°</td>
<td>0-60 km</td>
<td>15 min/15 min</td>
</tr>
</tbody>
</table>

Table 3.2: A summary of some key features of the models described in Section 3.6 and references therein. As some models are fairly flexible, their present configuration may be different from that described in this table.<sup>a</sup> The time step used by MEZON is initially 2 hours. If this results in an instability, the time step is divided by two, and the calculation is repeated. This process continues until a stable time step is achieved.

3.7 Model experiments performed

The next chapters provide an evaluation and analysis of several model runs which were carried out with MEZON. These runs are described below:

- **F1-F4**: These model runs were carried out with the aim of separating the contribution of various processes to the observed decline in total ozone, in addition, run F1 was used in the validation of the model (Chapter 4). The time period modelled was January 1965 - December 2000. The first run, F1, included both a realistic variation of stratospheric sulphate aerosol surface area density (SAD), as well as the observed increase in ODS emissions. Run F2 included the variable sulphate aerosol SAD, however, the emissions of ODS were held constant at values typical for the mid 1960s. For run F3, the sulphate aerosol SAD was held constant (at values typical for the late 1990s-2000) and the ODS emissions increase was included. In run F4, both the emissions of ODS and the sulphate aerosol SAD were held constant.

- **F9**: This model run was used to investigate the effect of a mass fixer which was applied to some species in the model. It is a repeat of run F1 for the years 1991-2000, the only difference being that in F9, the mass fixer is turned off for HCl.

- **G1**: This run was similar to F9, however in G1, the mass fixer was turned off for all chlorine containing species.
Seite Leer / Blank leaf
Chapter 4

Model Validation

Before the results of any model experiment can be analyzed, a thorough validation of the model is vital.

In this chapter, the model output is compared with measurements from a variety of sources, both satellite and ground based, with the intention of showing where the model reproduces the observations well, in both a temporal and a spatial sense, and what the weaknesses of the model are.

4.1 Comparison with satellite measurements of total ozone

One of the most useful sets of measurements to compare modelled total ozone with, is the NIWA homogenized TOMS/GOME total ozone data set, which covers the period 1979 up until the end of 2002. This was compiled by the New Zealand National Institute of Water and Atmospheric Research (NIWA) from a combination of TOMS (Total Ozone Mapping Spectrometer) and GOME (Global Ozone Monitoring Experiment) total ozone measurements, which were corrected for drift and offsets (homogenized). Data from TOMS instruments flown on the Nimbus-7, Meteor-3, Earth Probe and ADEOS (Advanced Earth Observing Satellite) satellites were used. The Nimbus-7 and Earth Probe measurements were corrected by comparison with the ground based Dobson spectrophotometer network, and statistical model fits to the Nimbus-7 and Meteor-3 data were used to adjust the Meteor-3 data. The corrections to the ADEOS and GOME data were made in a similar way, in comparison with the adjusted Earth Probe data (Bodeker et al., 2001).

The coverage of the NIWA total ozone data is almost global, except for high latitudes in winter, and for some periods between 1993 and 1996 there are gaps in the data set at all latitudes.

In Figure 4.1, a comparison between modelled zonal mean total ozone (top panel) and zonal mean NIWA total ozone (middle panel) is shown, for 1979-2000. The model reproduces the seasonal and latitudinal distribution of ozone values well. At high northern latitudes there are clear maxima early in the year, then the abundance of total ozone decreases and reaches a minimum in autumn reflecting the interplay between the annual cycle of the Brewer-Dobson circulation and chemical ozone loss in the aging air masses.

The bottom panel of Figure 4.1 shows the percentage difference between the modelled and measured total ozone. This comparison reveals that the seasonal peaks at high northern latitudes are somewhat exaggerated by the model, with local peak values being up to 50% too high.
Fig. 4.1: Top panel: Modelled total ozone, middle panel: NIWA total ozone (measurement), Bottom panel: Percentage difference between modelled ozone and NIWA, i.e. (model-NIWA)/NIWA. Dotted lines indicate lower modelled values than observed. Horizontal dashed lines are drawn at latitudes of 62°, 34° and 0°. The ozone values used in this plot are monthly mean values.
4.1. COMPARISON WITH SATELLITE MEASUREMENTS OF TOTAL OZONE

The low tropical values of total ozone seen in the NIWA data are also evident in the modelled total ozone, although the timing of the seasonal minima is less clear, and the latitudinal band covered by the low values is smaller in the modelled data than in the measurements. The value of the total ozone in the tropical regions is quite well represented in the model, typically within ±10%.

In the southern hemisphere, the model captures the low winter values at high latitudes, and the subsequent spring increase, however, the latter is overestimated, especially in the later part of the model run (after the late 1980s). The southern mid-latitude winter-time peak in total ozone is also overestimated by the model, in some years, and it appears to occur one or two months too early.

The average total ozone from the model results and the NIWA data set, over five latitude bands, is shown in Figure 4.2. The percentage difference between the two is also plotted in the upper part of each panel. Similar plots have been made in the past, e.g. by Chipperfield (2003); Hadjinicolaou et al. (2002, 2005), however only from about 1979 onwards.

The NIWA data coverage is not complete in the high northern latitudes, but the top panel of Figure 4.2 still contains enough information to show that the model generally overestimates total ozone by up to 50% in this region.

There are two features in modelled total ozone during the years before the NIWA data set begins, which look unrealistic. The first is the generally very high total ozone in the 1970s, and the second is the three years of high total ozone between 1975 and about 1980. These features will be investigated in Section 4.2 by comparing the modelled data with Dobson instrument measurements, which are available for the years before satellite observations. The greatest overestimation of total ozone by the model is between 34°N and 62°N, where the differences between the model output and the measurements are between 10% and 40%. There is also a seasonal variation in the differences, which seems to be partly due to a small phase difference between the modelled and measured seasonal cycles. This phase difference may be caused by the too rapid Brewer-Dobson circulation (see Section 4.5).

The model performs best at tropical and mid to high southern latitudes. In these two regions, the observed seasonal variations of total ozone are well reproduced, as are, in general, the actual values. Especially in the mid to high southern latitudes, a seasonal cycle in the differences is apparent, which is again due to to a slight phase shift between observed and modelled data in some years (e.g. 1991-1993). In other years it is due to the overestimation of peak, and underestimation of minimum ozone values (e.g. 1988-1989). The NIWA data is quite sparse at high southern latitudes, but what data there is corresponds well with the model output. Generally, the spring increase in total ozone is well represented, except in the early 1990s. The accuracy of the minimum values is harder to estimate due to a lack of measurement data. There is a wave-like structure in the modelled total ozone, especially in the early part of the plot, which will be looked at in more detail when a comparison is made with Dobson instrument measurements of ozone, in Section 4.2.

There is no obvious effect from the 1991 eruption of Mt Pinatubo in any of the modelled ozone shown in Figure 4.2, however, there is also no particularly pronounced change in the NIWA ozone either. The effect of the Pinatubo eruption will be considered in Section 4.4.

A further comparison between modelled total ozone and NIWA total ozone is shown in Figure 4.3, this time the mean total ozone for March (left column), and October (right
Fig. 4.2: NIWA total ozone (red curves) and modelled total ozone (lower black curves), averaged over five latitude bands (left axis). The top line in each plot is the percentage difference between modelled and measured total ozone, i.e. \((\text{model-NIWA})/\text{NIWA}\) (right axis).
4.2 Comparison with total ozone Dobson measurements

Several long time-series of total ozone measurements are available from specific ground based measurement stations. Although the measurements only represent the ozone col-

Fig. 4.3: Averaged ozone for 1980-1989, March (left column) and October (right column) Top panels: modelled total ozone; middle panels: NIWA total ozone; bottom panels: the percentage difference between the modelled and NIWA total ozone. The contour lines are in steps of 40 DU or 10% deviation. Negative values are represented by dotted lines.

column), averaged over the period 1980-1989. The middle panels show the same for the NIWA data, and the bottom panels show the percentage difference between modelled and measured data. The period 1980-1989 was chosen mainly based on the availability of satellite data without substantial gaps. In March, the model reproduces the total ozone field in the southern hemisphere very well. The observed poleward increase in total ozone from low northern latitudes is also seen in the model data, although it is exaggerated. The longitudinal distribution of total ozone is very well reproduced, only with too high values in the northern hemisphere.

In October, the pattern of the modelled total ozone distribution also corresponds well with the NIWA data. The magnitude of the high southern latitude ozone depletion is close to the observed values, and the high ozone values at southern mid-latitudes are of the correct magnitude. Again, although the geographic pattern of modelled total ozone in the northern hemisphere is similar to the observed pattern, the values are more than 80 DU too high in some areas.

4.2 Comparison with total ozone Dobson measurements
umn above a single point on the Earth's surface, they have the advantage over satellite measurements that they cover a much longer time period. In this section modelled total ozone will be compared with measurements from five stations: Arosa (Switzerland), Bismarck (USA), Sapporo (Japan), Mauna Loa (Hawaii, USA) and Halley Bay (Antarctica). The coordinates of the stations are given in Table 4.1.

Single observations from ground based stations may have uncertainties of up to a few percent, however these random errors are reduced when using mean values (for example monthly means) as is done here. The long term drift in total ozone measurements from the ground based Dobson network is estimated as less than 1% decade\(^{-1}\).

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Start</th>
<th>Run by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arosa</td>
<td>47.0°N</td>
<td>9.7°E</td>
<td>1926</td>
<td>MeteoSwiss</td>
</tr>
<tr>
<td>Bismarck</td>
<td>46.7°N</td>
<td>100.8°W</td>
<td>1957</td>
<td>NOAA-CMDL</td>
</tr>
<tr>
<td>Halley Bay</td>
<td>73.5°S</td>
<td>26.7 °W</td>
<td>1957</td>
<td>BAS</td>
</tr>
<tr>
<td>Mauna Loa</td>
<td>19.5°N</td>
<td>155.6 °W</td>
<td>1957</td>
<td>NOAA-CMDL,MSC</td>
</tr>
<tr>
<td>Sapporo</td>
<td>43.0 °N</td>
<td>141.3 °E</td>
<td>1958</td>
<td>JMA</td>
</tr>
</tbody>
</table>

**Table 4.1:** The locations and year of first measurement for the five total ozone measurement stations used to compare with modelled total ozone. The abbreviations for the institutions which run the stations are as follows: BAS-British Antarctic Survey, JMA-Japan Meteorological Agency, MSC-Meteorological Service of Canada, NOAA-CMDL-National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory.

Total ozone measurement in Arosa began in 1926, and has continued up until the present, making the Arosa total ozone time series the longest in the world (Staehelin *et al.*, 2001).

Measurements at the stations were mostly made with Dobson spectrophotometers, although some of the more recent measurements at Arosa and Mauna Loa were made with Brewer instruments. The data are provided by the institutions listed in Table 4.1, and obtained via the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) website (http://www.woudc.org/).

The measured (lower black line) and modelled (red line) total ozone (left scale) at Arosa are shown in Figure 4.4, along with the percentage difference between the two (upper black line, right scale) and Figures 4.6, 4.8 and 4.10 are similar, except they show total ozone at Bismarck, Sapporo and Mauna Loa respectively.

The percentage deviation of the total ozone values from the monthly mean is also shown for all stations, for both measurements (black line) and modelled values (red line) in Figures 4.5, 4.7, 4.9 and 4.11. In these plots, the total ozone data for each location was deseasonalized and plotted as a deviation from the monthly mean value. The monthly means were calculated over the period 1979-1987 when the correspondence between modelled and measured total ozone values was the best.

In Figure 4.4, a similar overestimation of modelled total ozone as that seen in the 34°N-62°N panel of Figure 4.2 is evident. The percentage difference between measured and modelled values is generally between 10% and 40%, with somewhat higher differences between 1975 and 1980, and also in the late 1960s to early 1970s. The percentage difference between the modelled and the measured total ozone varies over time, with a period of about 14 years.
4.2. COMPARISON WITH TOTAL OZONE DOBSON MEASUREMENTS

Fig. 4.4: A comparison between the total ozone measured at Arosa (47°N, lower black line), and modelled total ozone for model run F1 (red line, full model - see table 5.1 for description of runs). The measurement data is from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC). The top black line shows the percentage difference between model and measurements.

Fig. 4.5: Deseasonalized percentage deviation of total ozone from the monthly mean value calculated for the period 1979-1987, for measurements made at Arosa (black line) and for modelled values (red line).
**Fig. 4.6:** As in Figure 4.4 except for Bismarck.

**Fig. 4.7:** As in Figure 4.5 except for Bismarck.
4.2. COMPARISON WITH TOTAL OZONE DOBSON MEASUREMENTS

When both the offset between the modelled and measured values, as well as the seasonal variation are removed (as described above), it is possible to see where the model reproduces the inter-annual variation of the measured values. In Figure 4.5 the modelled total ozone around 1970 and the mid to late 1970s as well as the late 1980s to early 1990s stands out as being substantially different from the measured values, however in 1970 this difference seems to arise from a model over-representation of an observed inter-annual increase in total ozone. In the mid to late 1970s the modelled and measured time series diverge, and in the late 1980s to the early 1990s the model seems to overestimate observed features. The overestimation of total ozone in the mid to late 1970s and in 1989/1990 were also found in the ERA-40 reanalysis, and were attributed to TOVS or VTPR radiance data causing a too strong Brewer-Dobson circulation, which results in too much ozone transport. Observed ozone reductions in about 1983 and 1992, which may be due to volcanic activity, are both well reproduced by the model.

The same patterns can be seen in total ozone at Bismarck and Sapporo (Figures 4.6 and 4.8 respectively). The high modelled total ozone around 1970 and in the mid to late 1970s is especially obvious at Sapporo.

In the plots of deseasonalized ozone (Figures 4.7 and 4.9) similar features to those in Figure 4.5 are present, in particular the overestimation of the total ozone values in 1970, and the miss-representation of ozone changes in the mid 1970s. The 1992 decrease in total ozone is modelled well.

In Figure 4.9 (Sapporo) in addition to the discrepancies described above, the modelled total ozone was much lower in the late 1960s than in later periods, in contrast to what the measured time series shows. Also, in the early 1990s the modelled total ozone does not decrease as fast as the measured total ozone, and the observed decrease in 1992 is absent from the modelled values.

At Mauna Loa (Figure 4.10) the modelled overestimation of total ozone is less pronounced for much of the time, however the large difference between modelled and measured values in the mid 1970s remains. There is also a period in the 1980s when the model substantially overestimates total ozone at Mauna Loa.

From the deseasonalized time series (Figure 4.11) it can be seen that between 1965 and 1975 the modelled total ozone values at Mauna Loa are unusually low, however the measured values were not. The low total ozone in 1983 was reproduced by the model, although as it occurred during a (unobserved) peak in total ozone, it is only recognizable in the deseasonalized time series. A gradual decrease in total ozone (possibly due to the eruption of Mt Pinatubo) after 1991 is reproduced by the model as is the subsequent increase up until 1995.

From the comparisons made above, it is quite obvious that the large peaks in modelled total ozone seen in the northern hemisphere around 1970 and in the mid-late 1970s in Figure 4.2 were much smaller in reality. The plots of deseasonalized data also indicate that there are several periods when the tendency of the modelled ozone is not the same as that of the measured values.

The comparison between measured and modelled total ozone for Halley Bay is shown in Figure 4.12. Measurements were only made from August until April of the following year because of the necessity of sunlight for measurements using the Dobson instrument. In the other months, occasional measurements were made with moonlight, but the uncertainty in these measurements is rather high, and they have not been included here.

The modelled total ozone at Halley Bay is generally too low up until the mid 1980s. Especially large differences between modelled and measured total ozone are evident in
Fig. 4.8: As in Figure 4.4 except for Sapporo.

Fig. 4.9: As in Figure 4.5 except for Sapporo.
Fig. 4.10: As in Figure 4.4 except for Mauna Loa.

Fig. 4.11: As in Figure 4.5 except for Mauna Loa.
Fig. 4.12: As in Figure 4.4 except for Halley Bay

Fig. 4.13: As in Figure 4.5 except for Halley Bay.
the mid 1970s and mid 1960s. After the mid 1980s the sign of the differences between modelled and measured values changes, and the model generally overestimates the total ozone. In the early part of the modelled period, the disagreement between modelled and measured total ozone appears to come from too much winter and spring time ozone depletion, whereas after about 1990 the overestimation is mostly the result of too high ozone values in late summer. The observed spring time ozone depletion in the 1990s is quite well reproduced by the model, except in the spring of 1997, when the model shows far too little ozone depletion. Again in Figure 4.12 there is a wave-like variability in the differences between modelled and measured values, which indicates that the wave-like features in the 90°S - 62°S panel of Figure 4.2 are not present in the Dobson measurements.

The deseasonalized ozone time series in Figure 4.13 show that the model largely misses the steady decline of total ozone exhibited by the measured values. This is partly because the modelled ozone values over the southern high latitudes were already too low in the late 1960s and early 1970s.

By plotting the deseasonalized temperature at 18km altitude, averaged over 90°S to 62°S (Figure 4.14), it can be seen that the model input temperatures in the late 1960s to early 1970s were exceptionally low. In their description of the ERA-40 data set, Uppala et al. (2005) discussed the fact that the temperatures in the Antarctic lower stratosphere were low biased by up to 10 K in the early years of the reanalysis. One possibility is that the exceptionally low temperatures resulted in more activation of the small amount of chlorine present at this time, resulting in more ozone loss. Another possibility is that the low temperatures are an indication of a problem with the circulation which was used as model input. For example a more stable Antarctic vortex would have resulted in colder temperatures and less dynamical supply of ozone, leading to lower total ozone values.

4.3 Zonal mean ozone profile

The abundance of stratospheric ozone has been measured by the HALOE (Halogen Occultation Experiment) instrument on board UARS (Upper Atmosphere Research Satellite) satellite since October 1991. The March zonal mean ozone profile measured by HALOE (averaged between 1996 and 1999 to avoid any deviations due to the eruption of Mt Pinatubo) is compared with the corresponding modelled profile in Figure 4.15.

The model reproduces the structure of the measured ozone profile well. The magnitude and position of the modelled peak in ozone mixing ratio are close to the observed value. The modelled ozone values are slightly too low in the tropical lower stratosphere, which may be the result of too rapid upward transport of ozone poor tropospheric air in the tropics. The rate of upward transport in the tropical stratosphere will be examined further in Section 4.5.

Figure 4.15 suggests two possible reasons for the too high modelled northern mid-latitude total ozone values. First, the northern hemisphere ozone isopleths extend slightly too far poleward and to lower altitudes in the northern mid-latitude lower stratosphere than the observed values. Again, this could be related to the too fast Brewer-Dobson circulation transporting ozone rapidly northward and down, the shorter transit time resulting in less chemical ozone destruction. Owing to the density profile of the atmosphere the displacement to lower altitudes could lead to higher total ozone values by itself. Second, the ozone mixing ratios are too high by up to 10% in the tropical source region around 35 km altitude. This may be due to a too weak chemical ozone loss in the model.
Fig. 4.14: The deseasonalized model input temperature at 18 km, averaged from $90^\circ$S to $62^\circ$S, plotted as a deviation from the 1979-1987 mean temperature for each month.

Fig. 4.15: Modelled ozone profile for March, averaged between 1996-1999 (top panel). Middle panel: similar profile for HALOE measurements. The difference between the two are shown in the bottom panel, i.e. model minus HALOE. The units for all panels are ppmv and regions where the difference between HALOE measurements and modelled data are smaller than the uncertainty in the measurements are shaded.
in this region of the atmosphere. Such an underestimation of ozone loss could come about if a too rapid vertical transport resulted in lower mixing ratios of NO\textsubscript{2} in the upper tropical stratosphere. Obviously, both of the effects described here could contribute to the larger than observed northern hemisphere total ozone.

### 4.4 Effect of volcanic eruptions

As mentioned in Chapter 2, a significant decrease in total ozone values was observed after the eruption of Mt Pinatubo in 1991, at least in the northern hemisphere. The effect of this eruption on ozone values can be seen more clearly if the total ozone time series is deseasonalized to remove the annual cycle, and if the data is smoothed in order to remove fluctuations in ozone values over small time periods. The data plotted in Figure 4.16 was processed following the method of Fioletov et al. (2002). First, a monthly, zonal mean was calculated for the total ozone data which was gridded on a 4° latitude grid. Next, the data at each latitude were deseasonalized by subtracting the mean of the month obtained from all years between 1979 and 1987, and then the mean of all ozone values at that latitude obtained from the years between 1979 and 1987 was added to these data. The percentage deviation from the mean total ozone value at a particular latitude between 1979 and 1982 was calculated and the area weighted means over three latitude bands were calculated, a three month running mean was applied and finally the processed data were plotted. The solid line in Figure 4.16 represents the modelled total ozone values and the dashed line denotes the NIWA total ozone values. In general there is good correspondence between the modelled and observed total ozone. In particular, the modelled total ozone exhibits the same degree of variability as observed, however, the amplitude of the modelled changes is considerably greater. In the northern hemisphere average (top panel of Figure 4.16) the observed total ozone is extremely low in 1992-1993, and remains low in the subsequent years. This is followed by a slight increase starting around 1996. The minima of modelled total ozone also decrease markedly after 1993 but the peaks remain fairly high. In the central panel (58°S-58°N), total ozone decreases rapidly in 1993, and increases slowly in the subsequent years (except for a second minimum in 1997). The record low in 1993 and subsequent increase is evident in both the modelled and observed values, and has been attributed to the Pinatubo eruption in Fioletov et al. (2002). In the southern hemisphere (bottom panel) the observed values again show a marked minimum in 1993 and a subsequent increase which could be a result of the Pinatubo eruption. The modelled values also exhibit a decline around the same time but remain very variable. Interestingly, the large minimum in total ozone between 1985 and 1986 in the southern hemisphere is very well reproduced by the model, to our knowledge for the first time. This minimum is present, and almost identical in model run F3, in which the aerosol was fixed at background levels. This implies that the minimum is not a result of in situ ozone loss due to heterogeneous reactions on an increased aerosol surface area after the eruption of El Chichón, rather it must be to do with the model circulation input.

A major volcanic eruption can influence stratospheric ozone by causing a change in atmospheric dynamics (and thus altering the production and transport of ozone) or it can have an effect on chemical ozone loss by causing an increase in stratospheric aerosol. The latter possibility would result in an increase in HNO\textsubscript{3} and a decrease in NO\textsubscript{2}, due to an increase in reactions such as 2.17, 2.18 and 2.19. Indeed, a decrease in NO\textsubscript{2} of almost
Fig. 4.16: The percentage deviation of deseasonalized total ozone from pre-1980 mean ozone. The dashed line depicts NIWA data, the solid line shows modelled data. A three month running mean was applied to both data sets.
30% was observed over the Jungfraujoch and a decrease of more than 40% was seen over Lauder (central Otago, New Zealand) after the eruption of Mt Pinatubo (see Figure 4.17). The measurements at Lauder were derived from UV-Visible scanning spectrometer measurements during sunrise and sunset. The uncertainty in the individual measurements for column NO₂ at Lauder is estimated at 0.2×10¹⁶ molecules cm⁻² plus 5% of the observed value (Struthers et al., 2004) and the uncertainty for the Jungfraujoch midday FTIR NO₂ columns is believed to be better than ± 10% (De Mazière et al., 1998).

A similar plot made for the same locations (Figure 4.18), from the model output also shows decreases in the NO₂ column abundance, however, there is much variability in the time series, and the changes in NO₂ after 1991 cannot easily be identified. In order to remove some of the variability from the time series of NO₂, two model runs were used. The first run (F1) was the one used in the rest of this chapter, i.e. including all processes needed in order to reproduce the observed state of the atmosphere. The second run (F3) was identical, except stratospheric aerosol was fixed at "background" levels (i.e. there was no increase in stratospheric aerosol after volcanic eruptions). For a more detailed description of the model runs, see Table 5.1. The difference between the deseasonalized time series was calculated for these two runs, for NO₂, HNO₃ and N₂O₅. This was then expressed as a percentage of the 1979-1987 mean of the values from F3 for each month, and plotted in Figure 4.19. This difference represents the chemical effect of the increased aerosol burden on the NO₂, HNO₃ and N₂O₅ columns.

Some of the expected changes in HNO₃ and NO₂ derived from the numerical simulations can be seen in Figure 4.19. Over the Jungfraujoch, during 1992, there is a 5% enhancement in the HNO₃ column, and an insignificant decrease in the NO₂ column values. Small changes are also to be seen in about 1983, which could be a result of the
Fig. 4.18: The percentage difference between the deseasonalized time series of NO$_2$ and the mean NO$_2$ column, i.e. F1(t)/<F1> (where F1(t) denotes the time series of NO$_2$ from model run F1, and <F1> the average of this time series). The shading indicates the approximate range of data from Figure 4.17.
Fig. 4.19: Time series for HNO$_3$ (solid line), NO$_2$ (dotted line) and N$_2$O$_5$ (dashed line). Calculated as $(F_1(t)-F_3(t))/\langle F_3 \rangle$, to remove the effect of circulation or temperature changes on the species. Shading indicates the approximate range of data from Figure 4.17.
1982 eruption of El Chichón, but in neither year are the changes greatly larger than the other fluctuations in the time series. After about 1999, the stratospheric aerosol loading becomes very low. This causes the increase in NO$_2$ and N$_2$O$_5$ and the decrease in HNO$_3$, which begins around 1999. The variation of N$_2$O$_5$ is larger than that of HNO$_3$ or NO$_2$, and varies in a similar way to the measured values of NO$_2$, although the amplitude of the variation is much smaller. This shows that there is some chemical loss of NO$_x$ in the model, over the Jungfraujoch, after major volcanic eruptions.

The changes in HNO$_3$ and NO$_2$ column values due to volcanic aerosol are much more obvious in Figure 4.18 over Lauder. Again in 1983 there is a decrease in the column abundance of NO$_2$. In Figure 4.17, in 1983, there is also a decrease in NO$_2$ over Lauder, however, it is much larger than the modelled decrease (about 20% less than the year before, compared with the modelled decrease of about 15% shown in Figure 4.18). In Figure 4.19, the decrease in modelled NO$_2$ in 1983 is even smaller, at around 5%. In 1992, the model shows a 12% decrease in NO$_2$ compared with the year before (Figure 4.18 and an approximate 7% decrease in Figure 4.19). In both cases, this is much smaller than the more than 40% reduction which was measured at Lauder. In the modelled data, a large increase in HN$_3$ is also seen in 1992. The modelled decrease in N$_2$O$_5$ in 1983 and 1992 is of a similar magnitude as the observed NO$_2$ decrease.

In the southern hemisphere the model reproduces the changes in NO$_2$ resulting from increases in stratospheric aerosol with the correct timing, and the fact that the decreases in NO$_2$ correspond with increases in HNO$_3$ indicate that the NO$_2$ reductions in the model are a result of increased heterogeneous processing, as expected. The magnitude of the modelled NO$_2$ decreases is much lower than that observed. One possible cause of this is a too low aerosol surface area density. Another possibility is that using monthly mean modelled values results in a damping of the variation in NO$_2$ due to the low daytime values (with potentially less variability) being included in the mean.

From the difference in the percentage deviations shown in Figure 4.18 and Figure 4.19 it is apparent that some of the variability in NO$_2$ values are the result of changes in the model meteorology. For example, the NO$_2$ decrease over Lauder in 1993 is much larger in Figure 4.18 than in Figure 4.19, where the chemical effect was isolated by taking the difference between NO$_2$ values from model run F1 and F3.

Some of this variability could be due to changes in the rate of meridional transport, and therefore changes in the amount of N$_2$O which is photolysed, forming NO$_y$. The rate of transport in the model will be discussed more in the next section.

4.5 The water vapour “tape recorder” as an indication of vertical transport

A good indicator of the rate of upward transport of air in the tropics is the so-called “tape recorder” signal of water vapour. The water vapour mixing ratio varies seasonally at the tropical tropopause, and air which is transported from there up into the stratosphere preserves the water vapour mixing ratio practically equal to the value it had when it crossed the tropopause. Its mixing ratio will change only very slowly as a consequence of methane oxidation (net: CH$_4$ + 2O$_2$ → CO$_2$ + 2H$_2$O). This means that the seasonal cycle in water vapour mixing ratios slowly travels to higher altitudes above the tropopause, with a phase lag at a given altitude which depends on the height above the tropopause and on the mean vertical upwelling of the air in the tropical pipe (Mote et al., 1996).
Fig. 4.20: Top panel: Water vapour mixing ratios measured by HALOE, in ppbv, climatological average for the 1990s, near the equator. From Randel et al. (2001). Bottom panel: the same quantity from model run F1 (full model). The shaded area from the top panel is superimposed to facilitate comparison.
By looking at how long it takes for a particular water vapour mixing ratio to reach a particular altitude in the stratosphere, it is possible to gain information on the rate of upward transport in the tropical stratosphere. The rate of upward transport is important in determining the production and distribution of ozone, as discussed in Chapter 2.

Figure 4.20 shows the modelled water vapour mixing ratio for each month, averaged between 1991 and 2000, and between 10°N and 10°S. This can be compared with a similar plot constructed from HALOE water vapour measurements (top panel of Figure 4.20). The slope of the upward moving values is much greater in the modelled values than in the top panel of Figure 4.20. A particular water vapour mixing ratio takes about 13 months to reach an altitude of 25 km in the HALOE data, whereas it takes about five months in the model. Thus the rate of upward transport in the tropical stratosphere is overestimated in the model, which is either caused by the too fast mean meridional circulation in the ERA-40 data set, as discussed in (Uppala et al., 2005), or by the too rapid diffusive transport of modelled species. This may help to explain some of the too low tropical total ozone values, and the too high extra tropical total ozone values.

4.6 Development of stratospheric CFCs

A further feature of the model which is important for the correct simulation of past ozone depletion, is an accurate representation of the past increase in atmospheric chlorine loading. FTIR measurements of the total CFC-12 column above the Jungfraujoch in Switzerland have been carried out since 1986 (WMO, 2003), as part of the Network for the Detection of Stratospheric Change (NDSC). Part of the NDSC data is publicly available (see http://www.ndsc.wa). Data from 1989-2003 was obtained and monthly means were calculated (for all months during which at least one measurement was made).

In Figure 4.21 the modelled CFC-12 column above the Jungfraujoch is plotted (top line). This compares very well with measured values (upper dotted line, see also Chapter 1 of WMO, 2003) and several features of the inter-annual variability are reproduced by the model, in 1992 and 1996 for example. The major contribution to the total CFC-12 column is from the tropospheric burden (the bottom dotted line in Figure 4.21 shows the modelled column values for altitudes below about 12 km). Most modelled values lie within the uncertainty of corresponding measurements (which have not been plotted, for clarity). Typical values of the measurement uncertainties are around 5%. The two peaks in 1999 and 2000 are significantly larger than the measured values and are not within the uncertainties.

4.7 The influence of a mass fixer

As the analysis of the HCl trend at 55 km altitude was being carried out, a deficiency in the model transport routine was noticed. Basically, the use of a mass fixer which was applied to correct violations of mass conservation, resulting from the semi-Lagrangian transport of certain species, actually resulted in small amounts of mass loss. This problem is illustrated in more detail in Chapter 7, however it is convenient to discuss the implications for total ozone and for the lifetimes of ODS in the present chapter.

A nine year section of the original model run was repeated, with the mass fixer switched off for all chlorine species (run G1). The total ozone values for this run were then plotted along with NIWA total ozone and total ozone from the original model run (F1), in Figure
4.7. THE INFLUENCE OF A MASS FIXER

Fig. 4.21: The total column of modelled CFC-12 above the Jungfraujoch (solid line). The lower dotted line is the column below about 12 km altitude and the upper dotted line shows values from the measurements made on the Jungfraujoch.

4.22. The effect of turning the mass fixer off was an overall reduction in total ozone values. This is because of the larger chlorine values in the stratosphere, as a result of less of the chlorine species being removed from the atmosphere by the mass fixer. Obviously, simply turning the mass fixer off does not necessarily lead to an improvement in the model. It was found that with the mass fixer off, as in run G1, in certain regions of the atmosphere chlorine species are produced by the transport routine. It was for the prevention of this kind of problem that the mass fixer was implemented. The mean reductions in total ozone resulting from the higher chlorine values in run G1, are around 8-10% for most of the regions in Figure 4.22, except at 62°S - 34°S, where the reduction in total ozone is around 20%. Due to the chlorine production when the mass fixer is turned off, an improvement of the mass fixer is likely to result in total ozone values between those from runs F1 and G1. The general variability of total ozone is similar between the two runs, with most of the main features in the F1 total ozone time series being reproduced in the G1 time series. Thus any future improvement in the mass fixer will probably not have a large impact on trends calculated from modelled ozone.

The effect of turning the mass fixer off was also investigated for the lifetimes of CFC-11 and CFC-12. The lifetime of a particular species was calculated from the difference between the total number of molecules of that species in the model before and after the model's chemistry step (for a fuller description of the calculation see Chapter 6). In Figure 4.23, the annual mean lifetimes of CFC-11 and CFC-12 are plotted for run F1 (solid line), and G1 (dotted line). For CFC-11 there is very little difference between the two runs. The lifetime of CFC-12 is somewhat longer in run G1, with the mass fixer turned off, however, the variability is similar to that shown in run F1, so there should again be no
Fig. 4.22: Total ozone averaged over five latitude bands (top to bottom: 62°N-90°N, 34°N-62°N, 34°S-34°N, 62°S-34°S, 90°S-62°S), for run F1 (black line), G1 (red line, mass fixer off for all chlorine species), and NIWA total ozone (green line)
large impact on the results shown in Chapter 6.

![Graph showing lifetime of CFC-11 and CFC-12]

**Fig. 4.23**: Annual mean lifetime of CFC-11 and CFC-12 for model run F1 (solid line) and G1 (dotted line).

### 4.8 Summary

The comparison between the modelled and observed "water vapour tape recorder signal" provides some evidence that the rate of vertical transport in the model is exaggerated. It appears that the time taken for a particular water vapour mixing ratio in the model to be transported from 15 km to 25 km is about half the time taken in reality. This is not a surprise, as the Brewer-Dobson circulation in the ERA-40 reanalysis is known to be too strong (Uppala et al., 2005).

The comparison of modelled total ozone with the NIWA data provides a good overview of the model's performance. During the time period covered by the NIWA data set the model reproduces the observed ozone fields best in the tropics and at southern mid latitudes. The modelled springtime ozone depletion at high southern latitudes matches the measured values quite well, though the measurement data are sparse. The variability of modelled total ozone at high southern latitudes is higher than in the measurements. In the northern hemisphere there is clearly a problem with the magnitude of the total ozone values, the modelled total ozone is significantly greater than that observed. This problem affects the northern mid to high latitudes the most and again points to an
exaggerated Brewer-Dobson circulation in the model. The seasonal cycle of total ozone is well represented in the model, and many of the inter-annual changes in measured total ozone are captured by the model. The spatial distribution of areas of high and low total ozone in the modelled data corresponds well with observations.

From the comparison between modelled total ozone and the total ozone time series at five Dobson instrument measurement stations it is clear that during the 1970s the model does not reproduce the observed values of total ozone well. At high southern latitudes the failure of the model to reproduce observed ozone values in the late 1960s and early 1970s may be due to extremely low temperatures in the model input fields. The wave-like variation in the differences between measured and modelled total ozone is a further interesting feature of the comparison of modelled data with the ground based measurements. A possible explanation for this variation is an over-sensitivity of the model to the 11 year solar cycle. The phase and general timing of the maxima and minima in the variation would support this theory, however, the period of the variation seems a little longer than 11 years. It is also possible that the variation in total ozone is caused by variations in the model circulation data, resulting from the inclusion of different radiance data sets in the ERA-40 reanalysis.

The model reproduces the vertical structure of ozone mixing ratios well in comparison with measured values from the HALOE instrument. It can also be seen that the large modelled northern hemisphere total ozone is the result of a combination of large ozone mixing ratios extending too far poleward from the tropics and lying too low in the stratosphere. This may be caused by an exaggerated meridional poleward and downward circulation in the model. Modelled ozone mixing ratios are around 10% too high in the tropical stratosphere at altitudes of 35 km. These too large ozone mixing ratios most likely indicate a too weak chemical loss of ozone in this region of the model atmosphere, related to an underestimation of NOx concentrations.

The overly active transport and the periods in which sudden, large deviations of modelled total ozone from observed values occur are probably caused by the ERA-40 temperature and wind fields used to drive the model. Stratospheric aerosol also has a substantial inter-annual variability, due to volcanic eruptions, however, the changes in aerosol surface area do not correspond with the years where the largest deviations of modelled total ozone from observed total ozone occur. Therefore, it is unlikely that the large disagreements between modelled and measured total ozone in the 1970s and 1980s are the result of errors in the model’s heterogeneous reaction parameterization. An overestimated total ozone column was also found by Uppala et al. (2005) for years when TOVS or VTPR radiance data was included in the ERA-40 assimilation, i.e. 1973-1979 and 1989/1990. The period 1973-1979 coincides with the first peak of the wave-like variation of total ozone, at least in the northern hemisphere.

Based on the plots of deseasonalized model and measurement total ozone values it may be possible to exclude some years from the trend analysis in Chapter 5 when modelled and measured ozone values are obviously at odds. In any case, caution must be used in the calculation of long term trends in total ozone from the model data. In Chapter 5, data from years before 1979 will be left out of trend calculations.

The model appears to underestimate chemical changes in the lower stratosphere as a result of the increased aerosol surface area after a volcanic eruption. The post eruption decrease in NO2 is better reproduced in the southern hemisphere than in the northern hemisphere. The reason for the underestimation of NO2 depletion after an eruption is not clear, although it could be due to the inclusion of daytime NO2 values in the monthly
mean model data, thus reducing the variability of mean NO$_2$ values. The underestimation may also be due to a too low aerosol surface area density. The model meteorology causes some of the modelled variability in the NO$_2$ values, especially in the northern hemisphere.

The increase in CFC-12 loading over the Jungfraujoch is well represented in the model, so the stratospheric source of chlorine is likely to be correct.

A problem was discovered with a mass fixer used in the model, however, it appears that the influence of this problem on the results presented in other chapters is relatively minor.
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Chapter 5

Trends in Modelled Ozone and their Origin

One of the main aims of this thesis was to separate the contribution of key processes to the ozone trends which were observed over the period 1965 to 2000. Three main factors were considered to have a significant effect on ozone:

- The increasing atmospheric halogen burden
- Changes in atmospheric temperature or circulation
- Increased stratospheric aerosol loading after volcanic eruptions

In order to quantify the influence of each of these processes on stratospheric ozone, four 36 year long transient model runs were performed, beginning with a “reality” model run, including all processes. The three remaining runs were performed omitting one or two processes in each case. The processes included in a particular model run are shown in Table 5.1.

Using this combination of experiments, it should be possible to attribute a part of the observed trend in ozone to each of the processes. It should be noted that the effect of the increasing halogen burden of the atmosphere and the effect of volcanic emissions on ozone calculated from these model runs includes only the direct chemical effect. Any indirect effects, for example changes in ozone abundance due to a change in stratospheric circulation, brought about by volcanic aerosol, are included in the circulation used to force the model and affect all runs.

<table>
<thead>
<tr>
<th>Model run</th>
<th>ODS</th>
<th>Volc. emiss.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>F2</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>F3</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>F4</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 5.1: Processes accounted for in each of the model runs. Here “ODS” means the inclusion of the observed increase in ODS emissions and “Volc. emiss.” is the inclusion of the observed increase in stratospheric aerosol loading after volcanic eruptions. The meteorological data used to force the model was the same in all model runs.
As a result of the poor match between ozone measurements and modelled values in the 1960s and 1970s, which was discussed in Chapter 4, the trend calculations made in this chapter will not include years before 1979.

A good overview of the effect of the different processes on the abundance of ozone can be gained from Figure 5.1. Here the total ozone from all model runs is shown for several latitude bands. After the middle of the 1970s, the ozone depletion due to halogen chemistry becomes evident at all latitudes, from the difference between runs F1 and F2. The most dramatic change can be seen in the 90°S-62°S panel, where after about 1980, the lines for F1 and F2 actually diverge in spring (see 1987 for example) due to the catalytic ozone destruction which takes place when sunlight returns to the Antarctic stratosphere. A further feature which is worth noting is that the amplitude of the seasonal variations in total ozone become smaller in F1 compared with F2 as time progresses. Also, differences in total ozone between model runs with and without volcanic aerosol (for example the difference between F1 and F3) are generally very small, even in the years after the eruption of Mt Pinatubo. This implies that the modelled ozone decreases after major eruptions are mostly dynamical in origin, rather than being related to chemistry on the increased surface area of sulphate aerosols.

The modelled trends in ozone will be discussed in the next section, and the contribution of each of the processes listed above, to the modelled ozone trend will be discussed in sections 5.2 and 5.3. Section 5.5 will cover the apparent increasing trend of total ozone in F2 and F4. The effect on chemical reaction rates of increased stratospheric aerosol after volcanic eruptions will be discussed in Section 5.6 and the decreasing amplitude of the ozone seasonal variations will be examined in Section 5.7.

5.1 Modelled trends

The trends in modelled total ozone between 1979 and 2000 for run F1 are shown in Figure 5.2. The trends at each latitude and longitude point in Figure 5.2 were calculated by making a linear fit to the total ozone time series at that point, the slope of the fit giving the trend. The calculation of the significance of the trend (shaded area in figure 5.2) was made under the assumption that a linear model of the data is appropriate. The trend was deemed to be statistically significant if it is greater than 2σ. A similar plot (Figure 5.3) was made from the NIWA satellite measurements of total ozone. In both Figures 5.2 and 5.3 large areas of trends are not statistically significant (note that although multiple linear regression models are usually applied to determine long term trends, this is not the method which was used here). The two main exceptions in Figure 5.2 are at high southern latitudes in September to October, and high northern latitudes in September to December. The trend near the south pole in October indicates a mean ozone decline of more than 20 % decade⁻¹, which compares quite well with the decline of 20-30% decade⁻¹ given in Figure 5.3. The area covered by the large negative trends at high southern latitudes in Figure 5.3 is greater than that seen in the modelled ozone data. There is a small (less than -5% decade⁻¹) modelled ozone trend in March, at northern polar latitudes, however it is not statistically significant and is lower than the 5-10% decade⁻¹ decline in the observed total ozone at high southern latitudes in March-April. There is a 5% decade⁻¹ decline in modelled total ozone at northern mid-latitudes in February-April.

Two unexpected features in the modelled total ozone field are the 5% decade⁻¹ decline in tropical total ozone (June-October) and the large (5-15% decade⁻¹) increase in
Fig. 5.1: Comparison of the time series of total ozone from all runs, averaged over five latitude bands. Measured total ozone from the NIWA data set is also shown.
total ozone at high northern latitudes in September-January. Neither of these trends are
seen in the measurements. Although there is no measurement data in Figure 5.3 during
the polar winter, some sign of a positive trend would be seen during late summer, if it
were to correspond with the modelled trends. These spurious modelled trends may be due
to the atmospheric circulation in the model, this possibility will be further investigated
below.

The vertical structure of the modelled ozone trends from 1979-2000 can be seen in
Figure 5.4. Also shown, for comparison, is a plot of the ozone trends derived from SAGE
measurements (Figure 5.5, taken from WMO, 2003). The trends in the SAGE data were
calculated using a multiple regression model, which took into account effects such as
the QBO and the solar cycle. It was found by Harris and Phillips (1998) that the trend
calculation is rather insensitive to inclusion of solar cycle and QBO terms in the statistical
model and that there was only about 10% difference between trends calculated using only
a linear component, or the “full” model. This insensitivity of the trends was attributed
to the relatively long time series of measurements (about 22 years for SAGE) compared with
the time scales of the solar cycle (about 11 years) or the QBO (about 2 years). Therefore
it is reasonable to make a qualitative comparison between Figures 5.4 and 5.5.

The modelled trends in Figure 5.4 were constructed in a similar way as those in Figure
5.2, but from the zonal mean mixing ratio of ozone in model run F1. There are many
significant differences between the trends calculated from the satellite data and those
from the model output. The most obvious difference is the area of positive trend in ozone
mixing ratios in the modelled data, in the upper stratosphere. This lies between about
40°N and 40°S, and extends down to an altitude of about 33 km. In contrast, the trends
in the measurement data depict a decrease in ozone of between 4 and 5% decade⁻¹ in the
upper stratosphere. The negative trends in middle to high latitude ozone above 30 km are
smaller by at least a factor of three in the modelled data than in the observed, reaching
decreases of only 2-3% decade⁻¹, whereas the observed trends are decreases of between
about 7 - 10% decade⁻¹. There are also significant modelled trends in the lower tropical
stratosphere which are not in agreement with the observations, for example the positive
trends between 20 km and 25 km at about 30°N, and the large negative trends centered
at about 25 km altitude and 10°N. In Section 5.3, the contributions to these trends will
be discussed, in an effort to determine where the deviation from the observed trends
originates.

5.2 Influence of ODS and volcanic aerosol

The effects of volcanic aerosol on total ozone can be seen clearly in Figure 5.6, where the
difference in total ozone between run F4 and F2 is plotted for five latitude bands (red
line). Neither of these two runs included an increasing trend in ODS emissions, therefore
they were identical, aside from the stratospheric aerosol being fixed to background levels
in F4 (The surface area densities for the year 2000 were used). Deviations from zero in
Figure 5.6 are thus due to the chemical effect of reactions occurring on volcanic aerosol.

In general, the run including volcanic aerosol (F2), had the higher total ozone. Al¬
tough the eruption of El Chichón in 1984 does not produce any large difference between
the two runs, the effects of the 1991 eruption of Mt Pinatubo are visible in the plots
for the southern polar and middle latitudes as well as in northern hemisphere polar and
mid latitudes. The fact that the volcanic aerosol actually results in more ozone in F2 is
Fig. 5.2: Trends in total ozone from the F1 model run, 1979-2000. The shaded areas show where the trends are statistically significant (i.e. greater than 2σ). The units are % decade$^{-1}$.

Fig. 5.3: Trends in total ozone between 1979-2000, calculated from the NIWA total ozone data set. The units are % decade$^{-1}$ and the shading indicates where trends are statistically significant.
Fig. 5.4: Trends in ozone mixing ratios from the F1 model run calculated between 1979 and 2000. The shading indicates where trends are less than 2σ and therefore not statistically significant. The units are % decade⁻¹.

Fig. 5.5: Trends in ozone mixing ratio calculated from SAGE I and II measurements, from 1979 to 2000. The shading indicates where the trends are not statistically significant. This figure was taken from WMO (2003). The units are % decade⁻¹.
5.3. SEPARATION OF CONTRIBUTION TO TRENDS

probably due to the increased heterogeneous deactivation of nitrogen oxides, which in the low chlorine case may more than compensate for the increased ozone destruction caused by heterogeneous chlorine activation. The effect of volcanic aerosol on the rates of ozone chemistry related reactions is looked at in more detail in Section 5.6.

The change in total ozone due to volcanic aerosol is most marked in the mid-high latitudes, where ozone was of the order of 30 DU higher in F2 than F1 during times with high aerosol loading. At tropical latitudes, the highest enhancement of total ozone is around 4 DU.

The black line in Figure 5.6 shows the difference between runs F3 and F1, both of which included an increasing trend in ODS emissions. An important feature here is that after about 1985 the model run with volcanic emissions included has lower total ozone on average. This must be due to the extra halogen activation on volcanic aerosol, or a reduction in deactivation of active chlorine because of greater N2O5 hydrolysis on volcanic aerosol.

Note that prior to 1980 the difference between the two lines in Figure 5.6 is not very large. Obviously, with increasing chlorine loading, the beneficial effects of volcanic aerosol on modelled ozone are reduced. Due to the increased halogen burden of the atmosphere, after about 1980, large enhancements in the aerosol loading lead to higher amounts of ozone loss. The effect of volcanic aerosol on ozone is most obvious at mid to high latitudes and the increased aerosol loading from the eruptions of Mt Pinatubo and El Chichón had the biggest impact at high southern latitudes in the model runs.

The effect of the increasing trend in ODS emissions can be seen in Figure 5.7. Here, the difference between runs with and without the increasing ODS emissions are plotted, with background stratospheric aerosol (runs F4-F3) and with volcanic aerosol accounted for (runs F2-F1). While the difference between the two lines is again a measure of the effect of volcanic aerosol on total ozone, the values of the individual lines show the effect of ODS on total ozone.

Two lines representing the time series of EEC1 (Effective Equivalent Chlorine) and EESC (Effective Equivalent Stratospheric Chlorine) are included on the 34°S-34°N panel to illustrate the link between the growth of the atmospheric halogen burden and the decline in total ozone. The EEC1 values were calculated from the model input ODS surface mixing ratios (excluding CH3Cl, HALON-2402, CFC-114 and CFC-115), using the weighting factors of Montzka et al. (1999). The EESC values are simply the EEC1 values lagged by six years (WMO, 2003).

The difference between the runs with and without the ODS trend increases with increasing latitude, with the highest differences being polewards of 62°. In the mid-high latitudes there is an extremely strong seasonal cycle in the effect of halogen chemistry on ozone, with the largest ODS related ozone depletion occurring in spring, as expected. The trend in the effect of ODS on ozone is highest in the spring too, illustrated by the fact that the maximum values of the differences increase far more than the minima. This is most obvious in the high southern latitudes. The highest ODS related ozone losses at tropical latitudes occur in the middle of the year.

5.3 Separation of contribution to trends

The total trend in modelled ozone, as shown in Figures 5.2 and 5.4, is the result of a combination of changes in the main processes represented in the model. The contribution
Fig. 5.6: The chemical effect of volcanic aerosol on total ozone values at different latitudes. The red line shows the effect of the aerosol with ODS emissions fixed at 1965 levels. The black line shows the effect of aerosol when increasing ODS emissions are taken into account.
Fig. 5.7: The effect of the increasing ODS emissions on total ozone, for several latitude bands. The black line shows the effect of the increasing emissions when volcanic aerosol is included in the model. The red line shows the effect of the emissions when only background levels of stratospheric aerosol are present. The two thin straight lines on the 34S-34N panel show the increase in EEC1 (top line) and EESC (bottom line).
of each of these processes to the total trend in ozone can be determined by taking the difference between trends of the individual model runs. The total trend in ozone is given by the results of model run F1, and the trend in ozone from F4 should be solely attributable to changes in atmospheric circulation and temperature fields. The contribution to the modelled ozone trend from chemistry on volcanic aerosol is then given by the difference in trend between runs F1 and F3, and the contribution due to the increasing ODS emissions is the difference between the trends in F1 and F2.

The contribution of the key processes to the total trend in zonal mean ozone mixing ratios between 1979 and 1995 is shown in Figure 5.8. This time period was chosen as the observed trend in ozone between 1979 and 1995 can be taken as linear and because of the obvious problems with modelled ozone before 1979, which were shown in Chapter 4.

From panel B of Figure 5.8, one can see that the cause of the areas of statistically significant positive upper stratospheric trend in ozone, in model run F1, are also present in the most basic model run, not including volcanic aerosol or a trend in ODS emissions (F4). This means that these modelled trends are a result either of the circulation and temperature data used in the model, or of some error in the model itself. The same is true for the large negative trends in the lower tropical stratosphere which were shown in Figure 5.4, and which are also present in panel B of Figure 5.8. The positive trends in the lower polar stratosphere which one sees in panel A of Figure 5.8, especially in the northern hemisphere, are again a result of either the model meteorological data or the model itself.

The trends resulting only from the increasing emissions of ODS are shown in panel C of Figure 5.8. The increase in ODS emissions resulted in a decrease in ozone of around 8-10 % decade^{-1} in the upper polar stratosphere. These decreases are similar in magnitude to the trends in SAGE data between 1979 and 2000 (Figure 5.5), however, in run F1 these trends are substantially cancelled by the trends in panel B. The fact that the trends in panel C compare with the SAGE trends so well gives some justification to the suggestion that the errors which produce the incorrect trends in panel A and in Figure 5.4 lie in the meteorological data used in the model, and not in the model itself.

The ODS emissions also result in large negative trends in the lower polar stratosphere, which are again mostly cancelled out by trends shown in panel B. There are no large trends caused by ODS emissions in the lower tropical stratosphere, and in general, the trends in panel C look similar to those seen in the SAGE data in Figure 5.5.

The trend contribution from chemistry on volcanic aerosol (panel D) is small compared with that from the other processes, and has maxima at mid-high latitudes, in the lower stratosphere. The small positive trend in the lower tropical stratosphere, shown in panel D, may be a result of NOx deactivation.

The trends from increasing ODS emissions correspond well with what one would expect, i.e. highest decreases in ozone in the lower stratosphere at high latitudes (especially in the southern hemisphere), as well as the high latitude upper stratosphere, and the tropical upper stratosphere. The inclusion of volcanic aerosol also seems to result in a qualitatively reasonable trend.

The trends shown in panel B are rather unexpected. Several recent papers have pointed out that a substantial portion of at least the observed northern mid-latitude decreasing ozone trend can be explained by changes in stratospheric transport as a result of a reduction in wave forcing (see for example Randel et al. (2002); Hadjinicolou et al. (2002); Fusco and Salby (1999), however, the ozone trends in panel B of Figure 5.8 appear to be consistent with what could be loosely described as an acceleration of meridional
Fig. 5.8: The contribution of key processes to the total modelled linear trend in zonal mean ozone mixing ratios, 1979-1995. Panel A shows the total modelled trend. The shading indicates trends which are statistically significant (greater than 2σ). Panel B shows the trend from circulation and temperature changes, panel C shows the trend due to ODS emissions, and panel D shows the trend due to chemistry on volcanic aerosol. The units are % decade^{-1}. 
transport. These modelled trends could be explained as follows: the ozone mixing ratios are reduced in the tropics, as increasing amounts of ozone poor tropospheric air are transported into the stratosphere, and the mixing ratios at northern mid-latitudes increase with time as an acceleration in the meridional transport and downwelling brings increasing amounts of ozone rich air from the tropical middle stratosphere (and this air has less time to become depleted in ozone during its transport from the tropics). More wave activity could lead to a more disturbed polar vortex, mixing more vortex air with non-vortex air, which could explain the increasing trend in ozone at high southern latitudes. The effect of temperature trends on reaction rates may also explain the positive trends. The changes in circulation and temperature will be looked at in more detail in Section 5.5.

It is also useful to look at the trend in total ozone as a function of month, as the contribution of aerosol and ODS emissions varies during the year. Figure 5.9 is similar to Figure 5.8, except that the trends were calculated for zonal mean total ozone, and plotted as a function of latitude and month. Most of the trends in panel A are not statistically significant, however, there are significant negative trends in the northern low latitudes, southern mid latitudes, and a large positive trend in the northern high latitudes in about September-December. The negative trend around the equator is partly due to temperature or transport processes (see panel B) with a major contribution from ODS emissions (panel C). The small area of statistically significant ozone increase at northern mid latitudes is not related to ODS emissions or volcanic aerosol (both panels C and D show negative trends in this area), but rather to the meteorological data.

The southern high latitude trend looks qualitatively similar to that in Figure 5.3 and is mostly a result of chemistry on aerosols (panel D) and ODS emissions (panel C). Only a small negative contribution is seen in panel B, in about September-November. Also the origins of the positive southern polar trend in panel A (January-September) lie with the model circulation and temperature data.

It is interesting to note that although the chemistry and aerosol included in the model produce ozone losses in the right places (both in a spatial and temporal sense), the resulting negative trends in total ozone are often more than canceled by the trends from circulation and temperature changes. The most obvious example is the huge increasing trend in ozone in panel B, at high southern latitudes during July, and at high northern latitudes during most of the year. The sum of the trends from ODS emissions, volcanic aerosol and transport processes in panel A is then almost positive, and mostly not statistically significant in areas where significant negative trends have been observed in reality.

5.4 Recalculation of trends with only selected months

Based on the comparison of modelled total ozone and Dobson instrument measurements made in Chapter 4, it is possible to identify some years where particularly large differences exist between modelled and measured ozone values. The trends shown in Figures 5.2 and 5.4 can then be recalculated using only data values where there was the best agreement between modelled and measured data. Although this approach should not be used to draw conclusions about what caused observed ozone trends, it is valuable to show that some of the spurious modelled trends are the result of particular months where large deviations occurred between modelled and measured ozone values.

For the recalculation of the trends, three Dobson stations were chosen. These were Arosa, Mauna Loa, and Brisbane (Australia). Where the deseasonalized modelled and
Fig. 5.9: As in Figure 5.8, except for zonal mean total ozone. The shading in panel A shows where trends are significant.
measured total ozone differed by more than 5% for four or more months, the modelled data was deemed to be invalid. Further, single months during which the difference was 20% or more were also removed. The periods of data considered to be valid, as well as the latitude ranges over which the modelled data was filtered with each measurement data set is shown in Figure 5.10.

Fig. 5.10: Dark line segments: months where modelled ozone data was deemed to be valid, for the recalculation of ozone trends. The latitudes indicate where each set of Dobson data was used to filter the modelled data. The stations used were: top line - Arosa, middle line - Mauna Loa, bottom line - Brisbane. The station at Brisbane is run by the Australian Bureau of Meteorology (ABM), and the data was obtained over the WOUDC website.

There are few Dobson stations with long data records in the southern hemisphere, therefore data from the station at Brisbane was used to filter model data for the whole southern hemisphere. The trend in modelled total ozone as a function of latitude and month, calculated from the filtered data is shown in Figure 5.11. When Figure 5.11 is compared with Figure 5.2 (note that the contour intervals are different), some improvement in the northern hemisphere can be seen. The positive trend in total ozone at high northern latitudes is more than halved by filtering the data, bringing the trends closer than those in Figure 5.3. However, the spring time ozone loss in the northern hemisphere is also reduced slightly, and there is an increase in low latitude ozone loss in the northern hemisphere, which does not correspond with the trends in 5.3. In the southern hemisphere, filtering the modelled data removes the positive trend in southern mid-latitude total ozone. The area of statistically significant ozone loss over the southern mid-latitudes is improved, although the negative trend in this area is now too high rather than too low. The positive trend in southern high latitude ozone is not reduced.

A plot similar to Figure 5.4, constructed from filtered data is shown in Figure 5.12. Here, the main difference made by the filtering of the modelled data is that the large area of positive trend in the upper stratosphere in Figure 5.4 is greatly reduced. In the lower tropical stratosphere, some positive ozone trends are created by filtering the data. In the northern hemisphere upper stratosphere, the negative trend is improved slightly in Figure 5.12.

In summary, it is possible to show that some of the modelled ozone trends which do not correspond with measured trends can be eliminated by filtering modelled data. Therefore, at least some of these trends are the result of a few months of poor model performance. As only three Dobson stations were used to perform the filtering of data, it is perhaps not surprising that removing certain data points in the trend calculation did not only
Fig. 5.11: As in Figure 5.2, except calculated using only months shown in Figure 5.10.

Fig. 5.12: As in Figure 5.4, except calculated using only months shown in Figure 5.10.
lead to improvements, but also in some areas, a worsening in the modelled trends. The modelled ozone values which do not correspond well with measurements are likely to be due to the input meteorological data, as the groups of months designated as “invalid” in Figure 5.10 appear to be more or less randomly distributed and are thus unlikely to be caused by a systematic problem in model chemistry for example (which would be more likely to produce a bias in the model). Further, there are no other input data sets used in the model which have a variability which could result in the distribution of “invalid” months shown in Figure 5.10.

A further improvement of modelled ozone trends may be achieved by a more complicated filtering routine, involving more Dobson stations, but there is little value in artificially manipulating data in this fashion. The danger exists that by removing too many data points, any trends calculated are rendered meaningless.

5.5 EP flux, temperature and ozone

In Section 5.3, it was shown that the source of the positive trends in modelled total ozone, especially at mid-latitudes and high southern latitudes is likely to be the circulation and temperature data used to force the model. There are two general possibilities to explain the trends; a “faster” Brewer-Dobson circulation pushes more ozone rich air into the mid and high latitudes (a similar effect could also result from a too high rate of diffusion of transported species) or alternatively, a trend in temperature reduces the efficiency of ozone destruction cycles. From the pattern of decreasing ozone in the lower tropical stratosphere, and increasing ozone in the lower mid-latitude stratosphere as seen in Figure 5.8, the former option appears the likely cause, however, it is still worth looking at the stratospheric temperatures used in the model.

The trend in temperatures between 1979 and 1998 is plotted in Figure 5.13, and can be compared with temperature trends calculated from Stratospheric Sounding Unit (SSU) and Microwave Sounding Unit (MSU) data (Figure 5.14).

In Figure 5.13 there is a statistically significant positive trend in model temperatures over the southern polar areas, and a negative trend in the low to mid-latitude lower stratosphere, and globally in the mid to upper stratosphere. The positive temperature trend in the model temperature data over the polar regions does not correspond with the trend calculated from measurements in Figure 5.14, and neither does the positive trend in the tropical lower stratosphere. The negative upper stratospheric temperature trend in the model data is much larger than in the measurement data, as discussed in Uppala et al. (2005).

This negative trend in the upper stratosphere model temperatures could affect the rate of Reactions 2.12 and 2.13, leading to less chlorine catalysed ozone loss, however, the increase in the rate of activation is only of the order of about 0.25 % decade\(^{-1}\), and is therefore insignificant in comparison with the increase in chlorine loading of the stratosphere over the last few decades. The cooling of the upper stratosphere could however increase the formation rate of ozone via Reaction 2.2 while simultaneously reducing the loss of ozone via Reaction 2.5, thus causing the positive trends in modelled upper stratospheric ozone.

The effect of the warming trends in the mid stratosphere over the poles is harder to judge, because there is a lot of interannual variability in ozone over the polar areas due to dynamical effects, such as vortex strength and wave disturbances.
Fig. 5.13: The trend in zonal mean temperatures used in the model between 1979 and 1998. The units are K decade\(^{-1}\) and the shading shows where the trends are significant.

Fig. 5.14: The trend in zonal mean temperatures between 1979 and 1998, from SSU and MSU satellite data sets. From chapter 4 of *WMO* (2003). The units are K % decade\(^{-1}\) and the shading shows where the trends are significant at the 2\(\sigma\) level.
As discussed in Chapter 2, the EP flux provides a measure of the wave forcing of the mean meridional circulation, and studies such as Fusco and Salby (1999) and Hadjinicolaou et al (2002) find a correlation between mid-high latitude ozone loss and a decreasing interannual trend in wintertime EP-flux. The wintertime mean EP flux at 100 hPa was calculated from the ERA-40 circulation data by Ingo Wohltmann of the Alfred-Wegener-Institut für Polar- und Meeresforschung (AWI). The EP-flux was calculated as the average over each hemisphere, between 75° and 45° latitude, and is shown in Figure 5.15.

In Fusco and Salby (1999) the EP flux was calculated for the NCEP reanalysis data and in Hadjinicolaou et al (2002) for the ERA-15 reanalysis. Both showed a decreasing trend. In Figure 5.15 however, there is a small increasing trend in the EP flux. If this increase in EP-flux signifies an increasing rate of meridional transport, the expected outcome would be an increase in high latitude ozone due to greater dynamical supply and a decrease in lower stratospheric tropical ozone due to greater dilution by ozone poor tropospheric air. Such effects can be seen in panel B of Figure 5.8.

### 5.6 Volcanic aerosol and chemical reaction rates

The chemical destruction of ozone at mid and low latitudes is dominated by several catalytic cycles, as described in Chapter 2. The relative importance of these different cycles is dependent upon the temperature and the abundance of the species involved. The rates of several reaction cycles which are important for ozone loss were calculated for 1992.
and are shown in Figure 5.16, for model run F1, as a function of altitude. Similar plots can be seen in Brasseur and Solomon (1986); Seinfeld and Pandis (1998) and McElroy et al. (1992). It is clear from Figure 5.16 that the most important loss cycle for stratospheric ozone (in the latitude range 62°S-62°N) is the NO$_x$ cycle, with the ClO$_x$ cycle playing the next most significant role, except in the very lowermost stratosphere. This generally agrees with the results of similar studies, however, in Figure 5.16 the altitude where the ClO$_x$ cycle becomes more important than HO$_x$ catalysed ozone destruction is at about 25km, 10 km lower than in Brasseur and Solomon (1986) for example. The main factor which will affect the altitude at which the ClO$_x$ cycle becomes more important than the ozone loss cycle involving OH and HO$_x$ (Reactions 2.10 and 2.11) is the atmospheric chlorine loading, with lower chlorine loadings leading to lower amounts of ozone loss due to the ClO$_x$ cycle in the lower stratosphere (in model run F2, the ClO$_x$ cycle became more important than the cycles involving HO$_x$ at altitudes above about 30km).

**Fig. 5.16:** The reaction rates for several ozone destruction cycles, for model run F1, in 1992. The rates are averaged over 62°S to 62°N. The solid line represents the rate of the slowest ("rate-limiting") step of the NO$_x$ cycle, (Reactions 2.8 and 2.9), the dotted line represents the rate of the slowest step in the ClO$_x$ cycle (Reaction 2.13), and the dashed, and dash dotted lines give the rates of the rate limiting steps in the two HO$_x$ cycles (Reactions 2.6, 2.7 and 2.10, 2.11 respectively).

The differences between the rates of the ozone loss cycles plotted in Figure 5.16 for the different model experiments are shown in Figure 5.17. The left hand panel shows the difference between the rates for the two model runs with the observed increase in ODS emissions, the right hand panel shows the difference for the runs with fixed ODS emissions. The differences in the rates depicted in Figure 5.17 are therefore caused by the change in stratospheric aerosol as a result of the eruption of Mt Pinatubo. As expected, the biggest changes in reaction rates due to the increase in aerosol loading occur in the lower stratosphere, where the bulk of the aerosol exists. The increased aerosol loading causes greater chlorine activation, less chlorine deactivation and therefore increases the rate of the ClO$_x$ cycle in F1. Similarly, the rate of NO$_x$ catalysed ozone loss is reduced,
due to increased N$_2$O$_5$ hydrolysis, which reduces the abundance of NO$_x$. The reduction in NO$_x$ also leads to an increase in HO$_3$, and thus an increase in the efficiency of ozone loss due to Reaction 2.11. The stronger increase in HO$_x$ catalysed ozone destruction in the constant ODS emissions case (right hand panel) may be due to less deactivation of HO$_x$ via reaction with chlorine species.

As discussed above, the most important loss mechanism for ozone in the lower stratosphere is via reaction with NO$_x$. The reduction in NO$_x$ abundance due to hydrolysis of N$_2$O$_5$ on aerosol droplets therefore leads to a reduction in ozone loss. However, the huge increase in chlorine activation, as well as increases in ozone loss involving OH and HO$_2$, in the case where the observed ODS emissions are accounted for (left hand panel), more than compensates for this reduction. Thus, when the chlorine loading of the stratosphere is high, the extra aerosol surface provided by a volcanic eruption leads to a net increase in ozone loss.

When the chlorine loading is low, as in model runs F2 and F4, the importance of ozone loss via the ClO$_x$ catalytic cycle is far less than that involving NO$_x$. In this case the 45% increase in chlorine activation shown in Figure 5.17 is not enough to counteract the decrease in ozone loss due to lower NO$_x$ mixing ratios. The percentage changes in the reaction rates are similar in both panels of Figure 5.17, so the opposite effect on ozone loss in the runs with high and low chlorine loading (shown in Figure 5.6) is a result of the lower significance of the ClO$_x$ cycle in the low chlorine loading case.

![Fig. 5.17: The percentage difference of the rates of various cycles involved in ozone destruction, between the model runs without and with volcanic aerosol, for the case of increasing ODS emissions (left panel) and constant ODS emissions (right panel). The rates were calculated as in Figure 5.16. The solid line represents the rate of the slowest ("rate-limiting") step of the NO$_x$ cycle, (Reactions 2.8 and 2.9), the dotted line represents the rate of the slowest step in the ClO$_x$ cycle (Reaction 2.13), and the dashed, and dash-dotted lines give the rates of the rate limiting steps in the two HO$_x$ cycles (Reactions 2.6, 2.7 and 2.10, 2.11 respectively).](image)

### 5.7 Amplitude of seasonal cycle in ozone

One of the interesting features of Figure 5.1 is that in the tropics and the mid latitudes, the amplitude of the seasonal variation in total ozone decreases with time in run F1, while no such trend is evident for F2. The decreasing trend in the amplitude of seasonal total ozone variations at mid-latitudes is in qualitative agreement with observations, as
is the fact that the decrease in amplitude is due to the faster decline of late winter and spring ozone values than summer values (see for example Staehelin et al., 2001). This is probably a result of polar, ozone poor air masses mixing into the mid-latitudes as described in Hadjinicolaou et al. (1997).

The decreasing amplitude of the seasonal cycle in the tropics is a bit harder to explain. In Figure 5.18, the difference in amplitude of the seasonal variation in total ozone between 34°S and 34°N is plotted for run F2-F1 and F2-F4. The amplitude of the seasonal variation was calculated as the sum of the absolute differences of each monthly mean from the corresponding annual mean total ozone, for each year and for each model run. The differences F2-F1 and F2-F4 are plotted as a percentage of the seasonal variation in F2. In the case of F2-F1, it can be seen that the seasonal variation in total ozone values had a higher amplitude in F2 than in F1 over almost the entire modelled period. The difference between the amplitude of the variation in the two runs increases strongly after about 1980. In contrast to this, there is no obvious trend in the difference in seasonal variation between F2 and F4. The reason for the reduction in seasonal variation of total ozone in F1 must be linked to the ODS emission trend. As was shown in Figure 5.7, the largest ODS related ozone losses at tropical latitudes occurred in the middle of the year, which is also when total ozone is at its highest in the tropics. Thus, the decreasing amplitude of the seasonal variation of ozone in F1 is a result of the decrease in the seasonal maximum. The exact mechanism for this is not clear. The amplitude of the seasonal cycle in measured (NIWA) tropical total ozone does not appear to exhibit any clear trend, although it is of course not possible to say how the amplitude of the seasonal cycle would have developed had there been no substantial ODS emissions.

![Figure 5.18](image)

**Fig. 5.18:** The change in the amplitude of the seasonal variation of total ozone between model runs F2-F1 (solid line) and F2-F4 (dashed line), between 34°S and 34°N. A change in variation of 10 % means that the variation in F1 for example, is 10 percent smaller than in F2.
5.8 Summary

It was found that the effect of an increase in stratospheric aerosol as a result of volcanic activity has changed over the modelled time period. Prior to 1980, model runs with larger aerosol loading had the higher total ozone at mid and high latitudes, probably as a result of NOx deactivation via the hydrolysis of N2O5 on aerosol particles. After about 1980, during periods of high aerosol loading (especially after the eruption of Mt Pinatubo) the situation was reversed, with the higher aerosol loading resulting in a greater ozone loss, due to the increased halogen loading of the atmosphere. A similar effect was discussed by Chipperfield (2003), but there it was found that increased aerosol loadings began to cause greater ozone loss only after the early 1990s.

The model captures the observed decrease in total ozone in the northern midlatitudes well, as can be seen in Figure 4.16. The lowest total ozone values are reached in late 1992 to early 1993, and are around 10% below the pre-1980 mean. On the other hand, in 1992/1993 the maximum difference in total ozone between model runs with and without constant sulphate aerosol, is around 3-4% (see Figure 5.6). Clearly then, heterogeneous chemistry on the volcanically enhanced stratospheric aerosol explains, at most, around half of the ozone reduction after the eruption of Mt Pinatubo. The remaining part of the ozone reduction can be explained by changes in atmospheric circulation caused by the increased amounts of aerosol. Similar findings have been reported by Hadjinicolaou et al. (1997) and Hadjinicolaou et al. (2005), where the decreased ozone after the eruption of Mt Pinatubo was largely reproduced using a CTM which did not account for heterogeneous chemistry on aerosols. The increased aerosol loading was, however, taken into account in the calculation of the meteorological data used to drive the CTM. Also, in Chipperfield (1999) and Chipperfield (2003), where model runs were carried out with and without heterogeneous chemistry on stratospheric aerosol, it was found that a large portion of the post-Pinatubo ozone decrease in the northern mid latitudes could be explained by changes in atmospheric circulation. A significant portion of the decrease was still attributed to heterogeneous chemistry. Therefore, the results presented in this chapter agree with previous studies, in that both circulation changes and heterogeneous chemistry are responsible for the decrease in ozone after the eruption of Mt Pinatubo.

The changes in reaction rates, due to the increased aerosol loading in 1992, were calculated for several important ozone destruction cycles. It was found that the increase in aerosol resulted in an approximate 20% decrease in the rate of ozone loss via the NOx cycle, and an approximate 45% increase in the rate of the ClOx cycle, in the lower stratosphere. The increase in aerosol loading also resulted in increases in the rates of ozone loss via reactions with HOx species.

Trends in total ozone and in ozone mixing ratios were calculated from the results of four model runs. The ozone trends from the run which was designed to reproduce the observed ozone trends (F1) were compared with trends calculated from measurement data between 1979 and 2000. In terms of the zonally averaged trend in total ozone, as a function of month and latitude, the model reproduces the observed decrease in southern high latitude ozone, in the spring. The model does not reproduce the observed decrease in northern hemisphere high latitude ozone particularly well. There are also areas of positive ozone trends at high latitudes in both hemispheres in the model results, which are not present in the measurements. Similarly, for the comparison of zonal mean ozone mixing ratios as a function of latitude and altitude, there are areas of positive trend, which are not present in the trends calculated from the SAGE measurements (in the middle - upper
5.8. SUMMARY

The observed decrease in high and mid latitude stratospheric ozone is partially reproduced in model run F1.

For both the trends in ozone mixing ratios and the total ozone trends, it was found that the source of the spurious trends was either the circulation data used to force the model, or some trend-producing error in the model itself. The former explanation seems more likely, as in Chapter 4 it was shown that there were particular years where the modelled ozone values were markedly different from the observed values. Partly for this reason, the trend calculations were only carried out for years between 1979 and 1995, however, there may be other years during this time period for which the circulation data has resulted in smaller errors in the calculated ozone distribution, which nevertheless cause incorrect trends to be calculated. It was shown that some of the errors in the modelled ozone trends could be improved in some areas by filtering out months in the modelled data which were particularly different from observations, but this approach also resulted in worse trends in other areas (for example the mid-low latitudes of both hemispheres in Figure 5.12).

An interesting finding from the analysis of the contribution to the modelled trends was that the trend in ozone due to the chemical effects of an increase in ODS emissions reproduced the observed trends very well, except in the lower, extra-tropical stratosphere. If the trends caused by the circulation data had been negligible, the modelled ozone would have exhibited the same general trends as are present in observational data, in most of the atmosphere. The contribution to the modelled ozone trend from the circulation data however, cancels most of the trend from the additional ODS emissions. The trends in extra-tropical ozone due to ODS emissions, shown in Figure 5.9 are also very close to the observed trends. The contribution of volcanic aerosol to the negative trend in high latitude spring time ozone was found to be about 16% for the southern hemisphere and 20% for the northern hemisphere.

The upper stratospheric temperatures used in the model input have a much larger negative trend than observed temperatures, as also described by Uppala et al. (2005) in their evaluation of the ERA-40 data set. This may have contributed to the increase in ozone in this region, in the model run where no ODS emissions trend or volcanic aerosol was included. Likewise, an increase in the rate of the meridional circulation may have contributed to the decrease in tropical total ozone in this model run, and to the increases in mid-latitude ozone, especially in the northern hemisphere.
Chapter 6

ODS Lifetimes

Integrating a CTM over the period 1965-2000 provides an opportunity to examine the evolution of the lifetimes of long-lived ODS during the years when the atmospheric burden was rapidly increasing, and later when the burden began to stabilise. First, however, it is useful to examine the concept of lifetime, methods of calculating it and the sources of uncertainties.

6.1 Definition of the atmospheric lifetime

The lifetime of an atmospheric species is basically the time necessary to remove all molecules of that species from the atmosphere. The lifetime can be derived from the equation governing the atmospheric burden of a particular species,

$$\frac{dB(t)}{dt} = E(t) - \int L n \, dV. \quad (6.1)$$

Here $B(t)$ is the burden, and is defined by $\int n(x, y, z, t) \, dV$, where $n(x, y, z, t)$ is the number density of the species at a particular point, and $x, y, z$ are the Cartesian coordinates in the longitudinal, latitudinal and vertical directions respectively, and $t$ represents time. The emission rate of the species, at the surface, is given by $E(t) = \int E(x, y, 0, t) \, dx \, dy$ and the loss frequency is given by $L(x, y, z, t)$, so that $Ln$ is then the loss rate, which when integrated over the volume of the atmosphere ($dV=dx\,dy\,dz$), gives the total atmospheric loss rate.

If Equation 6.1 is rewritten as

$$\frac{dB(t)}{dt} = E(t) - \frac{B(t)}{\tau(t)}, \quad (6.2)$$

then $\tau$ is the instantaneous lifetime:

$$\tau(t) = \frac{B(t)}{\int L n \, dV}. \quad (6.3)$$

If the boundary conditions of emissions are time-dependent, Equation 6.3 can be used to calculate the “instantaneous” or “transient” lifetime. In the case where the atmospheric burden is constant in time, the left hand side of Equation 6.2 is zero and the species is said to be in “steady state”. In this case the resulting lifetime is the “steady state lifetime”. For gases with lifetimes of a few years or longer, instantaneous lifetimes are often reported as annual averages, to avoid seasonal changes in the lifetimes.
6.1.1 Steady state and instantaneous lifetimes

The instantaneous lifetime is not necessarily the same as the steady state lifetime, as the latter depends upon the history of emissions at the surface. As there is a lag between emission at the surface and mixing into the stratosphere, if emissions are increasing in time, there will be a proportionally smaller abundance of a species in the stratospheric sink region, leading to a longer lifetime WMO (1999).

The steady state lifetime is a good representation of the removal time of a species if the atmospheric burden really is in steady state, however, for the majority of ODS, this is not the case. It is, however, also interesting to investigate the effect of changes in emissions and ozone abundance on lifetime, something for which the instantaneous lifetime is more useful. Therefore, the main focus of this chapter will be on the instantaneous lifetime.

6.2 Calculation of lifetimes and sources of uncertainty

The loss rate \( L_n \) and the burden \( B \) can be output from atmospheric models, therefore Equation 6.3 can be used to calculate the lifetimes of ODS. In this study, the total number of molecules of a particular species in the model atmosphere was summed before and after the chemistry step of the model integration. The difference between these two values is the loss per model time step and is mostly due to photolysis for long-lived species such as CFC-11 and CFC-12. The instantaneous lifetimes were thus calculated for every model time step, and were output as monthly mean values at the end of each month.

The reference lifetimes for ODS in WMO (1995) (with the exception of CFC-11) were taken as the average of steady state values from a range of models in Kaye et al. (1994). All but one of the models were two-dimensional. The range of the modelled lifetimes in Kaye et al. (1994) was quite large for some species (between 40 and 60.8 years for CFC-11, for example), and a number of reasons for the differences were proposed.

One of the most obvious possible sources of error in model calculated lifetimes is the calculation of photolysis rates. For long-lived species, photolysis in the stratosphere represents the major sink. The photolysis rate is the integral of the product of the solar flux, the absorption cross section and the quantum yield of a species over all relevant wavelengths, and all these parameters have an associated uncertainty. The unattenuated solar flux has an uncertainty of about 5% WMO (1999), and the columns of \( O_2 \) and \( O_3 \) above each point in the model atmosphere contribute further uncertainty when the attenuated flux is calculated. Thus, the loss rates at a particular point in space and time will differ between models. Further, the distribution of a species (and therefore its abundance in the sink region) is dependent upon transport in the model, as is the loss rate itself, as the \( O_3 \) column used to calculate the photolysis rate is also partly dependent upon model transport. The effect of differing model transport on lifetimes calculated by the models in Kaye et al. (1994) was estimated as about 30%.

A different method for calculating instantaneous lifetimes involves using measurements of the distribution of each species in the stratosphere. Photolysis rates are calculated using measured \( O_2 \) and \( O_3 \) columns. This method was used by Minschwaner et al. (1998) to calculate lifetimes for CFC-12 and \( N_2O \). Here the uncertainties resulting from the dependence of the distributions of ODS, \( O_2 \) and \( O_3 \) on modelled transport are eliminated, however, those from the photolysis rate calculation remain, as well as some uncertainty in the measured distributions of each species.

The reference lifetimes for ODS in WMO (1999) were reviewed, mainly as a result of
6.3 Average modelled ODS lifetimes

The instantaneous lifetimes of several ODS from model run F1 were averaged over 11 year periods, and are presented in Table 6.1, in comparison with the WMO reference steady-state lifetimes. The 11 year means of the modelled lifetimes were calculated for two periods, 1980-1990 and 1990-2000. With the exception of HCFC-141b, all the modelled lifetimes between 1980 and 1990 are of equal length to, or longer than, the corresponding 1990-2000 lifetimes. As shown in Figure 3.1, the surface mixing ratio of HCFC-141b was negligible in 1980-1990, so not too much should be read into this deviation from the general pattern of decreasing lifetimes. In general the agreement of the modelled lifetimes with the reference lifetimes is satisfactory, especially for shorter lived species such as H-2402, CH₃Cl and H-1211. Longer lived species such as CFC-11, and CFC-114 have systematically underestimated lifetimes in the model (approximately 13% and 8% too short respectively.) This is likely to be a result of the overly vigorous upward transport described in Section 4.5, as an increased rate of transport reduces the time taken for a species to travel from the emission region (the Earth's surface) to the part of the atmosphere where it undergoes photolysis (the stratosphere).

The modelled lifetime of CFC-12 is around 30% larger than the WMO reference lifetime of 100 years. A possible reason for this is that the absorption cross sections used for CFC-12 in the model are from the IUPAC recommendations, and not from DeMore et al. (1997), the data which is used in many other models. The IUPAC data was used in this experiment as it was published in 2000, and was therefore thought to be more up to date than that of DeMore et al. (1997). There are some differences between the absorption cross sections in the two data sets, and this may have lead to the shorter lifetime of CFC-12 in the model. Previous estimates of the lifetime of CFC-12 have ranged from 100 to 180 years (Volk et al., 1997).

The fact that the modelled lifetimes become shorter with time is related to ozone abundance, and changes in ODS emissions, and possibly also changes in atmospheric transport. These factors are looked at in more detail in the following sections.
### Table 6.1: Reference steady state lifetimes from WMO (2003) and 10 year mean instantaneous modelled lifetimes. The modelled lifetimes are from run F1.

<table>
<thead>
<tr>
<th>Industrial or common name</th>
<th>Chemical formula</th>
<th>Reference lifetime</th>
<th>Modelled instantaneous lifetime 1990-2000</th>
<th>Modelled instantaneous lifetime 1980-1990</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11</td>
<td>CCl₃F</td>
<td>45</td>
<td>37</td>
<td>39</td>
</tr>
<tr>
<td>CFC-12</td>
<td>CCl₂F₂</td>
<td>100</td>
<td>130</td>
<td>140</td>
</tr>
<tr>
<td>CFC-113</td>
<td>CCl₂F₂CCl₂F₂</td>
<td>85</td>
<td>65</td>
<td>71</td>
</tr>
<tr>
<td>CFC-114</td>
<td>CClF₂CCl₂F₂</td>
<td>300</td>
<td>260</td>
<td>280</td>
</tr>
<tr>
<td>CFC-115</td>
<td>CClF₂CF₃</td>
<td>1700</td>
<td>1200</td>
<td>1300</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>CHClF₂</td>
<td>12</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>CH₃CCl₂F</td>
<td>9.3</td>
<td>8.0</td>
<td>7.7</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>CH₃CCl₂F₂</td>
<td>17.9</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>H-1211</td>
<td>CBrClF₂</td>
<td>16</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>H-1301</td>
<td>CBrF₃</td>
<td>65</td>
<td>46</td>
<td>50</td>
</tr>
<tr>
<td>H-2402</td>
<td>CBrF₂CBrF₂</td>
<td>20</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>Methyl bromide</td>
<td>CH₃Br</td>
<td>0.7</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>CCl₄</td>
<td>26</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>Methyl chloroform</td>
<td>CH₃CCL₃</td>
<td>5.0</td>
<td>4.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Methyl chloride</td>
<td>CH₃Cl</td>
<td>1.3</td>
<td>1.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

6.4 Lifetime changes due to emissions and ozone abundance

As pointed out by Kaye et al. (1994), there are two main reasons that the instantaneous lifetime of a species may change over time. The first of these (discussed in Section 6.1.1) is that the instantaneous lifetime depends upon the history of emissions of the species at the Earth’s surface. The second reason is that through ODS related ozone destruction, the minimum altitude where significant photolysis of the ODS can occur is reduced, leading to a shorter path between emission and destruction zones, and consequently, a shorter lifetime.

In Figure 6.1, the annual mean of the instantaneous lifetimes calculated for CFC-12 during model runs F1 and F2 is plotted. The lifetime of CFC-12 during the 1970s and 1980s is longer in F1 than in F2, due to the steady increase in the CFC-12 surface mixing ratio during this time (dashed line). The slow decrease in the difference in lifetimes must be due to the greater rate of ozone loss in F1 than in F2, as was shown in panel C of Figure 5.8. As the surface mixing ratio in F1 begins to decrease around 1990, the ratio of the tropospheric burden to the stratospheric burden decreases and the lifetime of CFC-12 becomes smaller in F1 than in F2.

The minimum altitude at which significant photolysis of an ODS occurs is determined by the wavelengths of solar radiation necessary to photolyse that species and how much these wavelengths are attenuated by the atmosphere. The total number of molecules of modelled ODS destroyed per second was calculated (for run F1), zonally averaged and plotted as a function of latitude and altitude in Figure 6.2. Long lived species such as CFC-11, CFC-12 and CCl₄ are mostly destroyed by photolysis in the stratosphere. The main area where photolysis of the longest lived species in Figure 6.2 (CFC-12) occurs is at about 35km altitude, whereas a shorter lived species such as CCl₄ is mainly photolyzed at a considerably lower altitude (about 25km). The main sink of HCFC-142b is via reaction...
6.4. LIFETIME CHANGES DUE TO EMISSIONS AND OZONE ABUNDANCE

Fig. 6.1: Yearly mean instantaneous lifetimes of CFC-12 for model runs F1 (solid line) and F2 (dotted line). The dashed line shows the surface mixing ratio of CFC-12 in run F1.

Fig. 6.2: The number of molecules of a particular ODS photolyzed as a function of altitude and latitude, in run F1. The units are molecules cm\(^{-3}\)s\(^{-1}\). Top left panel: CFC-11, top right panel: CFC-12 bottom left panel: CCl\(_4\) bottom right panel: HCFC-142B. The contours are drawn at \(1 \times 10^{-5}, 5 \times 10^{-5}, 1 \times 10^{-4}\ldots 1,2,3\ldots\). The data is averaged over 1990-1999.
with tropospheric OH, therefore the region where the most destruction of this species occurs is at a far lower altitude than for the other species in Figure 6.2.

The effect of ozone loss has on the altitude at which a particular species is photolyzed can be seen by looking at Figures 6.2 and 6.3. The number of molecules of each ODS destroyed at a particular point in the model atmosphere, as a percentage of the total number destroyed, was calculated for both run F1 and F2. The percentage difference between these values for the two runs was plotted in Figure 6.3. The values in Figure 6.3 are only really meaningful in areas where the number of destroyed molecules of ODS is significant (between about 20 km and 35 km altitude for CFC-11 for example). The only difference in input data for the runs F1 and F2 is the amount of ODS in the lower troposphere.

In Figure 6.3 one can see that, especially for the shorter lived species with significant stratospheric sinks (e.g. CFC-11 and CCl₄), the lower abundance of stratospheric ozone lead to more photolysis at lower altitudes. There was also a corresponding decrease in photolysis at higher altitudes, due to the lower mixing ratios of ODS being transported into the upper stratosphere.

![Graph showing percentage difference in photolysis for different ODS species](image)

**Fig. 6.3:** The percentage difference (F1-F2) between the percentage of the total photolysis of a particular ODS at a given latitude and altitude. The species are (from the left) CFC-11, CFC-12 (top row) and CCl₄, HCFC-142b (bottom row). The data is averaged over 1990-1999.

This shifting of the photolysis altitude, as mentioned above, must lead to a shorter lifetime of ODS in the stratosphere, as the distance between source and sink regions decreases. The task of quantifying exactly how much reduction in lifetime is caused by a given reduction in column ozone can be addressed as follows: During the time that the increase in the emissions of a particular ODS is linear, one may expect a relatively constant ODS lifetime (whereas an exponential increase in emissions would result in a
steadily increasing lifetime). While the ODS emissions increase, the ozone abundance in the stratosphere will also decrease, due to a higher stratospheric chlorine loading. In this case, any change in lifetime of a particular ODS in run F1, relative to run F2 should be a result of a change in ozone abundance. This is only a good method for species destroyed primarily by photolysis. The lifetimes of CFC-11 and CFC-12 in run F1 were subtracted from the lifetimes in F2 and were plotted against the difference in total ozone (F1-F2) (averaged between 62°S and 62°N) between the two runs. The results are shown in Figure 6.4, where the slope of a linear fit is also given. Only months between 1975 and 1990 were used, when the increase in CFC-11 and CFC-12 surface mixing ratios was linear in the model. It was found that a 10 DU reduction of total ozone between 62°S and 62°N results in a lifetime shortening of approximately 3.7 years and 0.8 years for CFC-12 and CFC-11 respectively. This corresponds to about 3% of the total modelled lifetime for CFC-12 and about 2% of the modelled lifetime for CFC-11. Conversely, an increase in the mean ozone column would result in longer lifetimes.

![Fig. 6.4: The difference in monthly mean lifetimes of CFC-11 and CFC-12 between model runs F1 and F2 (F1-F2), as a function of the difference in total ozone averaged over 62°N and 62°S (F1-F2). Both calculated linear trends are significant at the 2 σ level.](image)

6.5 Lifetime changes due to circulation

A further possible cause of changes in ODS lifetimes is a change in the rate of transport between the emission and sink regions. A faster transport of ODS into the stratosphere would result in shorter lifetimes. This concept was investigated by Butchart and Scaife (2001), who found that a 3% decade⁻¹ increase in troposphere to stratosphere transport...
could increase ODS removal rates, bringing forward the ozone recovery predicted for 2050 by five years. Given the results presented in Figure 6.2, the question arises whether or not different species, undergoing the bulk of their photolysis at different altitudes, may also differ in their sensitivity to transport changes. Further, it may be possible that the lifetimes of two different species do not always vary in phase, according to changes in transport. This latter point would seem to be supported by Figure 6.5, where the monthly mean instantaneous lifetimes of CFC-11 and CFC-12 are plotted. During several periods, but especially in 1997 - 1999, the lifetimes show different tendencies. Such short term changes in lifetime must be due to changes in atmospheric circulation. Increases in upward transport and meridional transport in the lower stratosphere, for example, could result in a shorter lifetime for CFC-11 and an increase in the lifetime of CFC-12.

![Fig. 6.5:](image)

**Fig. 6.5:** The deviation of the monthly mean lifetime from the mean lifetime over 1970-2000, for CFC-11 (solid line) and CFC-12 (dotted line).

In order to further investigate the dependence of ODS lifetime on atmospheric circulation, the correlation between the zonal mean upward mass flux and the global instantaneous lifetime of four ODS was plotted (Figure 6.6). The highest negative correlations (implying greater upward mass flux and therefore shorter lifetimes) are evident at altitudes around 18-20 km, for CFC-11, CFC-12 and CCl₄. The correlation is worse in most areas for HCFC-142b, as the primary sink of this species is in the troposphere. There does not appear to be any systematic change in the altitude of highest correlation based on the lifetime of the species. Rather the mass flux at, or just above the approximate altitude of the tropical tropopause has the largest influence on the lifetime. Even here, the correlation between lifetime and upward mass flux is not very strong, indicating that there is not, in general, a simple relationship between the two.

In the long term, it is evident from Figure 6.5 that the lifetimes of CFC-11 and CFC-12 vary in a similar way. The positions of the highest correlations in Figure 6.6 show that the atmospheric region where upward transport contributes the most to the lifetime is similar for both CFC-11 and CFC-12.

Finally, an attempt was made to quantify the effect of a change in upward mass flux on the lifetimes of CFC-11 and CFC-12. Annual mean, zonal mean upward mass flux through
6.5. LIFETIME CHANGES DUE TO CIRCULATION

Fig. 6.6: The correlation between upward mass flux and global mean instantaneous lifetime. Panel 1: CFC-11; panel 2: CFC-12; panel 3: CCl₄; panel 4: HCFC-142b. The correlations were calculated with lifetime lagging mass flux by one month.

an altitude of about 24 km was calculated, and from this a latitudinal weighted mean of the data between 28°N and 28°S was made. Annual mean lifetimes were also calculated. If these timeseries of tropical mass flux and lifetimes were plotted against each other, the resulting relationship would still contain the effect of ozone loss on lifetimes. This can be avoided by taking the difference between mass flux from a particular year, and the immediately preceding year, doing the same for lifetimes, and plotting these values against each other, as the change in lifetime due to ozone loss should be relatively small from one year to the next. This procedure was carried out for run F1 and the same procedure was applied to data from run F2 as a comparison. A linear trend was calculated and is shown in Figure 6.7, for the lifetimes from model run F2. The slope of the fit to the data in this figure is approximately the same when calculated with CFC-11 lifetimes from run F1, however, the magnitude of the slope is almost 20% larger for CFC-12 lifetimes from F1. Because of the need for the changes in ODS emissions at the surface to be linear so as not to interfere with the mass flux-lifetime relationship, only about 14 data points could be calculated for run F1, which is not really enough points to determine the relationship between mass flux and lifetime well. In Figure 6.7, about 33 points were possible, as the ODS emissions were constant, and all years could be used. The relationship between mass flux and lifetime was much less compact at levels above and below 24 km, especially for CFC-12. Even in Figure 6.7, the relationship is much more compact for CFC-11 than CFC-12.

From Figure 6.7, a change in lifetime of 0.34 years (0.6 years) per percent change in tropical upward mass flux can be inferred, for CFC-11 (CFC-12). This means that the
3% decade\(^{-1}\) increase in mass flux, which was predicted by Butchart and Scaife (2001), as a result of increased greenhouse gases in the atmosphere, would cause an approximate 14% (9%) reduction in the lifetime of CFC-11 (CFC-12) by 2050. It is interesting to note that the effect of a change in circulation on these two species is indeed different, with CFC-11 being more sensitive to changes in lower stratospheric, tropical upward mass flux. There is also a far better correlation between changes in the lifetime of CFC-11 and changes in the mass flux, than is the case for CFC-12.

![Graph showing the relationship between changes in upward mass flux at about 24km altitude, averaged between 28°S-28°N, and the global instantaneous lifetime of CFC-11 and CFC-12.]

Fig. 6.7: The relationship between changes in upward mass flux at about 24km altitude, averaged between 28°S-28°N, and the global instantaneous lifetime of CFC-11 and CFC-12.

### 6.6 Summary

The aim of this chapter was the investigation of changes in the lifetimes of ODS over the last decades, and the causes of these changes. It was shown that the model is capable of reproducing realistic lifetimes for the modeled ODS species. For most of the modelled species whose main sink region is in the stratosphere, the modelled lifetime is shorter than the WMO reference lifetimes. This can likely be attributed to a too rapid upward transport in the tropics. The shorter lived species, which are mostly destroyed within the troposphere, have modelled lifetimes very close to the WMO reference lifetimes.

The lifetimes, especially of the longer-lived ODS, exhibit a negative trend overall. This is partly due to decreasing emissions in the 1990s, for species such as CFC-11 and CFC-12, but also due to a loss of stratospheric ozone. In the 1990s, a higher percentage of each ODS is photolyzed in the lower stratosphere in model run F1 than in run F2. There is also less of each ODS photolyzed in the upper stratosphere in run F1 than in run F2. Because
the only difference between these two runs is in the emissions of ODS, the difference in photolysis altitude must be a result of the lower ozone abundance in run F1. An increase in photolysis of a species at a lower altitude leads to a shorter lifetime. By plotting the decrease in ODS lifetime in model run F1 relative to that in run F2, against the difference in total ozone between the two runs, a lifetime change per 10 DU ozone loss (or increase) was calculated for the two most important anthropogenic sources of stratospheric chlorine (CFC-11 and CFC-12). These values were approximately 3% change in lifetime for CFC-12 per 10 DU change in total ozone, and 2% per 10 DU for CFC-11. The ozone values used in the calculation were the zonal mean total ozone averaged over 62°S to 62°N.

Although the lifetimes of CFC-11 and CFC-12 do not appear to be highly correlated with zonal mean upward mass flux, a reasonably compact relationship was found between the lifetimes and zonal mean tropical upward mass flux at approximately 24 km altitude, especially for CFC-11. This implies a change in the lifetime of CFC-11 of 0.34 years (or 0.9%) per percent change in mass flux. The lifetime of CFC-12 was less sensitive to changes in mass flux, with a lifetime change of approximately 0.6 years (or 0.5%) per percent change in mass flux.

During work on the model experiments described in Chapter 7, it was found that the model's transport scheme is not entirely conservative. The effect of this on the lifetimes of ODS, and on the ozone column was investigated in Chapter 4. It was found that the behaviour of the annual mean lifetimes of CFC-11 and CFC-12 over time are almost identical when the mass fixer is turned off and when it is turned on, however there is a slight offset in the lifetime. Since the trends in lifetime, and the interannual variability remain the same, it is unlikely that the problems with the transport routine have a significant impact on the conclusions of this chapter.
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Chapter 7

The Unexpected Decrease in Upper Stratospheric HCl

The abundance of HCl observed by HALOE shows a steady increase in the upper stratosphere (around 55 km) until 1997, at which point it abruptly begins to decrease. This was described by Anderson et al. (2000), who suggested that the decrease was the beginning of the reduction of upper stratospheric chlorine. However, it was pointed out by Waugh et al. (2001), that 1997 was at least two years early for total chlorine in this region of the atmosphere to reach its peak, as the tropospheric abundance of chlorine has only been declining since about 1993-1994, and the total chlorine abundance at 55 km altitude (ClT) corresponded to the tropospheric abundance lagged by approximately six years, at least during the time that the tropospheric and stratospheric increases were close to linear. Further, the HCl values at 55 km increased again after 2000.

At 55 km altitude, around 95% of total chlorine is in the form of HCl, therefore HCl makes a good proxy for total chlorine (Waugh et al., 2001). In this chapter the behaviour of HCl at 42 km is examined. At this altitude the proportion of total chlorine in HCl is much less than 95% (around 2/3 of total chlorine is in HCl at 42 km in the model), however, the behaviour of HCl mixing ratios and total chlorine mixing ratios is still nearly identical.

Several options were investigated by Waugh et al. (2001) to try to reproduce the decline in ClT, using a two-dimensional model. They considered low frequency changes in transport, chlorine partitioning, anomalous build-up of organic chlorine at 55 km as well as tropospheric rain out of inorganic chlorine, but they found no proof that any of these could explain the measurements.

The vertical domain of MEZON does not extend up to 55 km, but the HCl decrease in HALOE measurements is also present at lower altitudes. The global mean HCl mixing ratio at an altitude of approximately 42 km, from version 19 HALOE data, is plotted in Figure 7.1 (bold line), along with the same for the F1 (ODS emission trend included) model run (dotted line). In order to construct this plot, the HALOE data was interpolated onto the model grid, where data existed. When the global means were calculated, a latitudinal weighting was applied, and the model data was only included in the average for grid points where HALOE data also existed. This masking of the model data was carried out so that any bias in the HALOE data, due to incomplete latitudinal coverage, would also be included in the model data. The decrease in HCl after 1997 is evident in the HALOE data, and also in the model results, although in the model it begins a year later, in 1998. The model greatly overestimates the amplitude of the decrease, as well as the fluctuations in mixing ratio prior to 1998.
Fig. 7.1: Global mean HALOE measurements of HCl mixing ratio at approximately 42 km (bold line) and global mean modelled HCl mixing ratio at 42 km (dotted line).

For further confirmation of the trend in the HALOE data, a comparison is plotted with column measurements made at the Jungfraujoch in Switzerland (vertical stripes in Figure 7.2). The column amount of HCl over the Jungfraujoch exhibits a leveling off after about 1998, with periods of very low HCl, followed by an increase of the values after about 2000. Therefore the HCl column observed above the Jungfraujoch displays a time line that is quite similar to the values observed by HALOE in the upper stratosphere. One can not quantitatively compare ground based column measurements of HCl with a time series of HCl measurements for 42 km altitude, however, the fact that both the data sets exhibit similar trends is encouraging.

The possibility that the change in HCl values was due to a change in the latitudes where HALOE measurements were made, was also considered. HALOE HCl at 55 km was plotted, averaged over 90°S-26°S, 22°S-22°N and 26°N-90°N. The decrease after 1998 was visible in each of these three regions (not shown). Thus it appears that a geographical shift in HALOE measurements is not an explanation for the HCl decrease.

The question remains whether or not the sudden decrease in HCl in the model results and in observational data is a result of the same phenomenon. It is possible that the timing of the tropospheric peak in modelled total chlorine is slightly different to the observed peak, or that the lag between tropospheric and stratospheric chlorine abundances is shorter than observed. Either of these situations could cause the stratospheric HCl loading in the model to decrease earlier than expected, causing the decline in HCl after 1998. A comparison with the results of the F2 model run shows that this is not the case (Figure 7.2). If the decrease in HCl had been a result of the decrease in ODS emissions, it should not be present in the F2 model run, as the emissions were held constant.

In panel A of Figure 7.2, the surface mixing ratio of total chlorine (smooth dashed line) and the HCl mixing ratio at 42 km (solid line) is plotted for the F1 model run. In panel B, the same values for the F2 model run are shown. Although the decrease in upper stratospheric HCl seems much less obvious in the data from the F2 run, the same pattern is evident, and the peak to peak percentage decrease is of similar magnitude in the two experiments. As there was no decrease in the boundary layer abundance of total chlorine in the F2 run, the decrease at 42 km could not have been caused by the turnaround of stratospheric chlorine loading. A change in chlorine partitioning is also not the cause of
the decrease, as the behaviour of total chlorine (fluctuating dashed lines in Figure 7.2) mimics that of HCl.

The behaviour of \( \text{Cl}_T \) in the model’s upper stratosphere must then be the result of a change in atmospheric circulation or transport, however, it is not clear if this change which caused the decreasing HCl in the modelled data is real, or if it is due to some artificial effect in the circulation data which was used to force the model. This will be investigated further in the next section.

![Figure 7.2: Surface mixing ratios of total chlorine (dotted lines) and HCl mixing ratios at 42 km altitude (solid lines) for model runs F1 (panel A) and F2 (panel B). The dashed lines show total chlorine at 42 km altitude and the vertical stripes indicate the measurement and uncertainty range of FTIR HCl measurements at Jungfraujoch in Switzerland.](image)

### 7.1 Possible causes of the modelled decline in HCl

The cause of the decline in HCl at 42 km in the model needs to be determined before it is possible to draw any conclusions as to what happened in the real atmosphere. As pointed out above, a repartitioning of chlorine into species other than HCl can be ruled out, as the sum of the mixing ratios of all chlorine containing species represented in the model also decreases in a similar way to HCl (which contains the majority of chlorine at this altitude). One species not accounted for in the sum of the chlorine containing
species is atomic chlorine, but the conversion of a substantial fraction of HCl into atomic chlorine over a period of a few years is, due to the reactivity of this species, a very unlikely scenario.

The only loss process for total chlorine included in the model is a parameterized form of rain-out of HCl in the lower troposphere. An increase of tropospheric HCl removal may contribute to a HCl decrease in the stratosphere.

More information about the origin of the changes in upper stratospheric HCl can be gained from Figure 7.3. Here the global average total chlorine is plotted for runs F1 and F2 (top and bottom panels respectively). In both model runs, an area of low total chlorine mixing ratios appears during 1997 and 1998, at altitudes between about 5 km and 20 km altitude, and then propagate upward during the next years until they reach the upper stratosphere. A number of low total chlorine mixing ratio features also appear along the upper boundary of the model. As these areas of low total chlorine appear in the middle of the model atmosphere, where there are no prescribed loss processes, the possibility of a mass conservation (or "continuity") violation must be considered. To address this possibility, two passive tracer experiments were carried out, the results of which can be seen in Figure 7.4. In the first experiment, a region of the model atmosphere in the tropics was initialized with a passive tracer mixing ratio set to 1 ppmv. This tracer was then transported from January 1996 until December 2001, and the total number of molecules of the tracer in the model atmosphere was recorded as a monthly mean, each month. The data was deseasonalized and plotted as a percentage relative to the mean value over the five years (dash-dotted line in Figure 7.4). There were no sources or sinks for this tracer and after some initial changes in total mass during 1997 (large gradients

![Figure 7.3: Global mean total chlorine for run F1 (top panel) and run F2 (bottom panel). The units are ppbv, and a dotted line is drawn at an altitude of 42 km.](image_url)
7.1. POSSIBLE CAUSES OF THE MODELLED DECLINE IN HCL

can lead to problems with the model transport), the tracer was conserved to within about 10% over the remaining four years (only these latter four years are plotted in Figure 7.4). In the second experiment, a passive tracer was initialised everywhere in the atmosphere,

![Graph showing the deviation of tracer concentrations from the mean over time.](image)

**Fig. 7.4:** Top solid line: HCl at 42 km from model run F1 (displaced from zero for clarity). The dashed line shows the deviation of the total number of molecules of a passive tracer from the 1996-2000 mean, at 42 km. The dotted line shows the deviation from 1996-2000 mean of the total number of molecules of the tracer in the whole atmosphere. The dashed-dotted line shows the same value, for a second tracer, initialised around the equatorial tropopause. The triple dot dashed line, offset from the zero line by +20 for clarity, shows the mixing ratio deviation at 42 km, of an inert tracer, with the mass fixer switched off.

with a mixing ratio of 1 ppm, and was transported from January 1996 until December 2000. The mixing ratio in the lower troposphere was held constant, as it is for HCl. The total number of molecules of this tracer were plotted in a similar way to the first tracer and are shown by the dotted line in Figure 7.4. The total number of molecules of this tracer show a decrease in 1998, which could be linked to the appearance of low chlorine mixing ratios in the lower stratosphere at this time. The number of molecules of this tracer at 42 km altitude (dashed line) shows very similar behaviour to the HCl mixing ratio from model run F1.

The mass conservation fixer described in Section 3.1, was applied to the second tracer, but not the first. This fixer is designed to correct any mass loss arising on a particular horizontal level of the model, from the use of the semi-Lagrangian transport scheme for horizontal advection, as the semi-Lagrangian scheme is not completely mass conservative. Ironically, the tracer to which the fixer was not applied exhibits fewer fluctuations in the total number of molecules in the model atmosphere (i.e. better mass conservation). A final mass conservation experiment was run, where an inert tracer was initialized in the whole model atmosphere at a mixing ratio of 1 ppmv, and was transported from 1997-2000, without using the mass fixer. The time series of the total number of molecules in this experiment is shown by the triple dot-dashed line in Figure 7.4, and has been offset from zero by +20, for clarity. It is evident that without the mass fixer on, the model is capable of preserving a homogeneously initialised tracer almost perfectly for four years.
Because of the problems with the mass fixer, the last ten years of model run F1 were re-run, and the total chlorine distribution re-evaluated. Figure 7.5 shows the global mean total chlorine time series as a function of altitude (similar to Figure 7.3). The top panel of Figure 7.5 shows total chlorine for an experiment where the mass fixer was turned off for HCl, but left on for other chlorine containing species. The most notable difference between this plot and the top panel of Figure 7.3 is that the low chlorine values at the models upper boundary are no longer present. The low chlorine values at 10-20 km altitude are, however, still present. The bottom panel of Figure 7.5 shows total chlorine for a model run where the mass fixer was turned off for all chlorine containing species. Here, even the areas of low total chlorine between 10-20 km in 1998 appear to be gone. Finally, the

![Figure 7.5](image)

**Fig. 7.5:** Global mean total chlorine for a model run with the mass fixer turned off for HCl, but on for all ODS (top panel) and for a run with the mass fixer off for HCl and all ODS (bottom panel). The units are ppbv and a dotted line is drawn at 42 km.

time series of total chlorine at 42 km altitude was replotted in Figure 7.6, for the two experiments just described. The development of total chlorine mixing ratios with time is similar between the two experiments, with the values for the experiment with the mass fixer switched off for all chlorine containing species being slightly higher in general. The decrease in total chlorine starts in 1996, about two years earlier than in model run F1. This is also about the same time that the surface mixing ratios of total chlorine in the model begin to decline, although from Figure 7.5 there appears to be no link between the decline of the surface and upper stratospheric mixing ratios. After 1998, a similar decrease as that in run F1 is to be seen in Figure 7.6.

In Figure 7.6, the total chlorine mixing ratios at 42 km are larger than those at the surface. This implies some violation of mass conservation and is not necessarily a surprising result, as the model was run in these last two experiments without any checking of mass
conservation during the transport calculation. The isolated peaks in total chlorine mixing ratios at about 10 km and 42 km in the lower panel of Figure 7.5 are also symptoms of the same problem. As well as a problem with the mass fixer in the model, it could be that by interpolating the ERA-40 winds onto the model grid, some areas of divergence or convergence were created. Because of the sensitivity of the mixing ratio of HCl or total chlorine to any lack of mass conservation, there is little point in continuing the search for the cause of the total chlorine decline in the model until the mass conservation of the transport routine has been improved.

![Graph showing total chlorine mixing ratios over time](image)

Fig. 7.6: Total chlorine mixing ratios at 42 km altitude, for a model run with the mass fixer turned off for HCl (dotted line) and for all chlorine species (solid line). The straight solid line shows boundary layer mixing ratios of total chlorine for these model runs. The dashed line shows global mean total chlorine from run F1.

### 7.2 Summary

At first it appeared as if the variation of total chlorine in MEZON represented the decline in HALOE HCl (despite starting a year too late, in 1998 instead of 1997 as it did in the HALOE measurements), however, at least some of the modelled variation in HCl was the result of a mass fixer used in the model. Switching off this mass fixer resulted in an improvement in the conservation of a passive tracer. Part of the model run F1 was repeated to check if total chlorine values still behaved in a similar way to those from the HALOE observations, even when the mass fixer was turned off. The result of these experiments is not conclusive. The total chlorine values in the upper stratosphere still exhibit a decline, although this decline begins two years earlier when the mass fixer is turned off (with the fixer off, the decline begins in 1996, a year earlier than in the HALOE measurements). The decline in upper stratospheric HCl in MEZON has been shown not to be a result of a change in chlorine partitioning in the model. Further, the modelled reduction in upper stratospheric chlorine does not appear to be a result of the turn around in model surface mixing ratios, which also occurred in 1996. The fact
that the upper stratospheric total chlorine reaches values that are higher than the surface mixing ratios points to further problems with model transport, therefore the reasons for the modelled variability in total chlorine will not be pursued further.

It should be pointed out at this stage that the possible effects of the mass fixer problem on results in the rest of this thesis were also considered. The monthly mean lifetimes of several ODS changed slightly when the mass fixer was turned off for these species, but there were only small changes in annual mean values. The atmospheric HCl levels in the model were slightly increased. The effect of this increase in chlorine loading was a small decrease in total ozone. Both of these effects are discussed in Chapter 4. Although turning the mass fixer off improved the transport of a passive tracer, it appears that it results in mass creation for certain other species. Therefore turning the fixer off is not a simple solution resulting in an automatic improvement in model performance. Further experiments must be carried out to ascertain the effect of this fixer on species with spatial gradients in mixing ratio and to determine any necessary changes to the model's transport routine. Operating the model with the mass fixer off and with it on, appears to cause two extremes of behaviour in the transport routine, for different model species i.e. small amounts of mass loss and creation respectively. As was shown in Chapter 4, the lifetimes of CFC-11 and CFC-12 are not greatly different in model runs with the mass fixer off and runs with it on, and the trends in lifetime are very similar in both cases. Apart from the small reduction in total ozone which resulted from turning the mass fixer off, the ozone values exhibit a very similar behaviour and trend to the ozone in runs with the fixer turned on. Improvement of the transport routine and mass conservation is thus unlikely to affect the conclusions of this thesis.
Chapter 8

The New PSC Parameterization

The role of polar stratospheric clouds in ozone loss has been known since 1986 (Solomon et al., 1996). The importance of these clouds is twofold: they provide a surface for the heterogeneous activation of chlorine (via reactions 2.17 and 2.18) and they provide a surface for the uptake of HNO$_3$. This removes nitrogen oxides from the atmosphere, pushing the partitioning of chlorine species into active forms, thus enhancing ozone destruction.

Studies such as Rex et al. (2004) have shown that the degree of ozone loss in the Arctic is closely related to $V_{PSC}$, the volume within which temperatures are low enough that PSCs could potentially form. Tabazadeh et al. (2000) suggested that widespread denitrification could increase future Arctic ozone loss by up to 30% and Waibel et al. (1999) found that for the Arctic winter of 1994-1995, local modelled ozone loss was increased by 55% in air parcels with active denitrification with respect to air parcels with no denitrification. Clearly, it is then important that PSC formation, growth and sedimentation processes, as well as reaction rates on PSCs are well represented in CTMs used in studies of polar ozone loss.

In the past, CTMs have not been able to reproduce observed denitrification (WMO, 2003). One of the difficulties in constructing an effective parameterization of PSC processes for a model, is the validation of the scheme. Measurements of many quantities such as HNO$_3$, NO$_y$, particle size and particle number density are necessary to compare with the model output. In the Arctic winter of 1999-2000, measurements were carried out by two major field experiments, the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE) and the Third European Stratospheric Experiment on Ozone (THESEO 2000). The results of this field campaign and others have been very useful for the improvement of the representation of PSC processes in CTMs (Chipperfield et al., 2005). Measurements made during the SOLVE/THESEO 2000 campaign will be used in this chapter to validate the new PSC scheme which has been implemented in MEZON.

In the next section of this chapter, the approaches of several groups to the problem of representing PSC in models will be examined. In Section 8.2, the differences between the approach used in MEZON (described in Chapter 3) and a similar method described by van den Broek et al. (2004) will be discussed. In Section 8.3, results from the new parameterization in MEZON will be compared with measurements and results from the old parameterization. In Section 8.4 conclusions will be drawn.
8.1 Representation of PSC in models

Until recently, PSC processes have been parameterized in a highly simplified manner in CTMs. The NAT and ice saturation temperatures were determined by using the formulations of, for example, Hanson and Mauersberger (1988) and Marti and Mauersberger (1993) respectively, and the appropriate types of PSC were invoked either below this temperature (Chipperfield, 1999; Davies et al., 2002) or once a specified supersaturation ratio was reached (Koike et al., 2002; Douglass and Kawa, 1999). HNO₃ and H₂O were then condensed from the gas phase until a saturation ratio of 1, or equilibrium was achieved, hence this method is known as the "equilibrium" approach. A similar method was used in previous versions of MEZON (see Section 3.3.1). PSC was not transported (although it was allowed to sediment), and the existence of PSC was reassessed after every time step. Often, the size of the PSC particles was prescribed, and sedimentation occurred at a prescribed velocity (Chipperfield, 1999; Lefèvre et al., 1994).

There are a number of problems with the simplified representation of PSC. Obviously, basing sedimentation velocities on a single, prescribed particle size for ice particles, and one for NAT particles is a less than optimal approach. NAT particle diameters of up to 10 μm-20 μm were reported by Fahey et al (2001), and the difference in fall velocity between such large particles, and freshly nucleated NAT is enormous.

The assumption of equilibrium between the gas and solid phases also breaks down for larger particle sizes, although an equilibrium based calculation will be reasonably accurate for a population of particles with diameter up to about 9 μm, about five days are needed to reach a diameter of 20 μm (Carslaw et al., 2002). Further, gas phase HNO₃ will never fully equilibrate with rapidly sedimenting solid particles (McKinney et al., 2004).

The problem of a fixed PSC size was addressed by Considine et al (2000), who represent the condensed mass in PSCs in their model as a population of particles with a lognormal size distribution. Either the number density and the sigma value for the distribution are prescribed by the user (which results in a variable median radius), or the sigma value and the median radius are prescribed. The latter case results in a variable number density. The scheme still uses the equilibrium approach, however supersaturation ratios of 1.4 and 10 respectively must be reached before ice or NAT are nucleated. Particles (or rather condensed mass) are transported in the model wind fields. In Considine et al. (2000), type 1 PSC was taken to be supercooled ternary sulphate (STS), therefore due to the small sizes of STS particles, denitrification occurred primarily through the co-condensation of NAT onto ice particles followed by sedimentation. In a later study with the same PSC scheme, Considine et al. (2003) set the composition of type 1 PSC to NAT for some model runs, which allowed denitrification in the absence of ice. They found that with this configuration, the model reproduced the observed denitrification better than was the case when type 1 PSC was assumed to be STS.

A version of the SLIMCAT CTM used in studies assessing the effect of denitrification on ozone depletion (Davies et al., 2002) and the sensitivity of ozone loss to low temperatures in the Arctic winter (Chipperfield et al., 2005) does not take non-equilibrium PSC growth into account. PSC is assumed to form at NAT and ice equilibrium temperatures, and the radii of the resulting particles, and sedimentation rates are prescribed. There are two options for the scheme, which differ in their treatment of NAT and ice. The first possibility is that NAT condenses onto 10 μm radii ice particles, which nucleated below the frost point. Denitrification is effectively due to sedimentation of NAT on ice. In the second configuration, no ice is formed by the model, and the NAT particles are repre-
8.1. REPRESENTATION OF PSC IN MODELS

presented by a bimodal distribution, with radii of 0.5 \( \mu \text{m} \) and 6.5 \( \mu \text{m} \). Denitrification in this case is mostly due to the larger particles, which have a prescribed sedimentation velocity of 1100 m d\(^{-1}\). It was found that the version of the scheme where large NAT particles were allowed to form produced the best correspondence with measurements. This was also the version of the denitrification scheme used by Chipperfield et al. (2005) to investigate the variation in Arctic chemical ozone loss and its correlation with low temperatures.

A different approach to the problem of including a realistic PSC scheme in a Eulerian model was developed by Carslaw et al. (2002) and used by Mann et al. (2002) and Mann et al. (2003) to determine factors controlling Arctic denitrification. Their method was to develop a Lagrangian particle model, where the growth and sedimentation of many thousands of individual particles within the polar vortex is simulated. Three different particle nucleation mechanisms were evaluated by Davies et al. (2005), these were: nucleation at a constant rate when the temperature is less than the NAT or NAD (nitric acid dihydrate) equilibrium temperature; ice mediated nucleation; and a variable nucleation rate based on super saturation, temperature or other factors. They concluded that direct nucleation of NAT or NAD on synoptic ice clouds was unlikely. After nucleation, the particles were advected and grew or evaporated according to the HN\(_3\) vapour pressure at their location. The gas phase HN\(_3\) was advected by a version of the SLIMCAT model which only included four tracers (NO\(_x\), non-denitrified NO\(_x\), H\(_2\)SO\(_4\), and H\(_2\)O). When the particles took up HN\(_3\), it was removed from the model grid, and when the particles evaporated, HN\(_3\) was returned to the model grid (Mann et al., 2003). This denitrification scheme was then coupled with the full chemistry version of SLIMCAT by Davies et al. (2005).

A relatively simple, computationally efficient representation of PSC was included in the TM5 CTM by van den Broek et al. (2004). Their method accounts for non-equilibrium PSC growth. NAT particles are nucleated with an initial number density of \( 5.75 \times 10^{-5} \) cm\(^{-3}\) and an initial radius of 0.1 \( \mu \text{m} \), when temperatures are lower than the NAT equilibrium temperature. NAT is only allowed to exist north of 50°N, and at temperatures of 200 K or lower. The particles are transported as tracers, using a number of size bins. Either a fixed radius in a size bin is assumed (resulting in a variable number density) or the number density is fixed, allowing the radius of the particles to vary. If the number density is fixed, particles are put into the next larger or smaller size bin depending on the radius of the particles. If the radius is fixed, a number density threshold is specified as the criteria for transfer of mass between size bins.

Probably the most realistic of the schemes described here is that of Carslaw et al. (2002). However, this is relatively expensive in terms of CPU time, and is complex as it involves coupling two models (the PSC scheme and a regular CTM). The aim of the present study was to produce a simple, yet physically based parameterization of PSC processes, which could be easily included in an Eulerian CTM and used in multi-annual integrations.

As it turns out, there are some similarities between the scheme of van den Broek et al. (2004) and the one developed for MEZON. This will be discussed further in the next section.
8.2 Comparison of the new MEZON PSC scheme and that of van den Broek

Both the PSC parameterization of van den Broek et al. (2004) (hereafter “TM5 scheme”) and the new MEZON scheme described in 3.3.2 account for the non equilibrium growth and evaporation of NAT particles, which is a rather new idea in CTMs. In contrast to the TM5 scheme, the existence of NAT particles is not constrained to geographical or temperature limits in MEZON. NAT is allowed to exist anywhere that it is thermodynamically stable, growing, or where it is in the process of evaporating. A nucleation barrier requiring a supersaturation ratio of 20 is included in MEZON, however, NAT forms at the NAT equilibrium temperature in the TM5 scheme. Probably the most important difference lies in how the particle sizes are represented (monodisperse in MEZON) and transported. As large particles fall much faster than smaller particles, it is likely that particles in a particular air parcel have quite different sizes and origins. It could be argued in this case that the more realistic approach would be to preserve size information by binning the particles, rather than distributing the mass equally among all particles. On the other hand, many more tracers (representing each size bin) are required to do this.

In the TM5 scheme, only the mass in each size bin is transported. It was noted by van den Broek et al. (2004) that the properties (i.e. size) of NAT in each bin could be calculated exactly by transporting not only the mass, but also the number density. This is the approach chosen with the new MEZON scheme, however, as predicted by van den Broek et al. (2004), transporting two related tracers which are allowed to have different model gradients is perilous, as a situation can occur where for example the number density at a particular grid point is zero, while the mass is not. As it turns out, this does occur in the new MEZON PSC scheme, and when this occurs, the non zero variable is simply set to zero. Typically, the number of boxes containing PSC needing such a correction is of the order of 0.1 % - 8 % per time step.

Although there may be some room for future improvement, the new MEZON PSC scheme is far more physically based than the old one. Below the new scheme is evaluated, by comparison with the old equilibrium scheme, and measurements.

8.3 Scheme validation

The starting point for the comparison of the performance of the old and new PSC schemes in MEZON will be the CLAES (Cryogenic Limb Array Etalon Spectrometer) measurements of gas phase HNO₃ over the Arctic and Antarctic in 1992. The CLAES instrument is part of the UARS satellite which was launched in 1991 and measured concentrations of several trace gases, including HNO₃, from the 1/10/1991 - 5/5/1993. The vertical lines in Figure 8.1 show the uncertainty range of the CLAES HNO₃ measurements, taken from Figure 5.5.13 of Park et al. (1999). The top panel shows the HNO₃ at approximately 80°N, at an altitude of 20 km. There is little difference between the HNO₃ in model runs with the old PSC scheme (dotted line) and the new scheme (solid line), which both underestimate the measurements. Given that there was little solid phase HNO₃ in either of the model runs (dashed line for the old scheme, dash dotted line for the new scheme), the underestimation in gas phase HNO₃ is obviously not due to too active denitrification. The model underestimation of HNO₃ is at its largest during the northern hemisphere summer. The bottom panel of Figure 8.1 shows the same quantities as the upper panel, but for the
8.3. SCHEME VALIDATION

Antarctic. Again the model underestimates summer time gas phase HNO₃. Denitrification is much more active in the Antarctic winter than in the northern hemisphere, with uptake of HNO₃ onto PSC starting some time in April for the old scheme, and a month later for the new scheme. The depletion of the gas phase occurs too quickly in the old scheme, with the more gradual decline in the new scheme matching the measurements much better. The fate of the HNO₃ taken up onto PSC particles is rather different, depending on which PSC scheme was used. In the old scheme, most of the NAT does not sediment significantly and is not, therefore, permanently removed from the atmosphere (dashed line in the lower panel of Figure 8.1). In contrast, the larger particles formed by the new scheme sediment rapidly and remove HNO₃ from the atmosphere (the dashed dotted line in Figure 8.1 indicates a far smaller amount of HNO₃ still present as NAT at the 20 km level). This has an impact upon the gas phase HNO₃ in spring. In model runs with the old PSC scheme, it increases very quickly as the PSCs evaporate, whereas with the new scheme, the replenishment of HNO₃ takes much longer.

![Figure 8.1: HNO₃ volume mixing ratios at 20 km altitude and (top panel) 80°N, (bottom panel) 80°S. The CLAES error range is given by the vertical bars, averaged between 75° and 80°. The solid line shows gas phase HNO₃ for run F1, the dotted line shows the same, for the same model using the old PSC representation. The dashed line shows the mixing ratio of HNO₃ in solid form, for the old PSC scheme, the dash dotted line shows solid HNO₃ in the model with the new PSC scheme. A similar figure is shown in Park et al. (1999). Abscissae tick marks indicate the end of the month, model data points are monthly means and plotted at the middle of each month.](image-url)
Fig. 8.2: Diameter of NAT particles for three different days, on the 430 K level in the old and new PSC schemes. This figure is similar to Figure 2 of Carslaw et al. (2002).
Fig. 8.3: Diameter of modelled NAT particles for three different days, on the 420-440 K level. From Figure 2 of Carslaw et al. (2002). The red lines show the flight path of the ER-2.
The size of NAT particles which are formed by the PSC scheme is very important, as it determines the sedimentation velocity of the particles, and therefore the rate of denitrification. The diameters of NAT particles formed by the old and new PSC schemes are shown for three days during the Arctic winter of 1999/2000, on the 430K potential temperature level, in Figure 8.2. The particle sizes were calculated for the old scheme based on the prescribed number density of NAT used in the old model. It should be noted that in the old PSC scheme, the actual particle size was not used to determine the sedimentation velocity, instead this velocity was set to a single prescribed value for ice particles. Denitrification only occurred via sedimentation of HNO₃ which had condensed on ice particles, in the old scheme. It is still worthwhile to compare the NAT diameters generated by the two schemes, in order to show that had the old scheme used the actual sizes of the NAT particles which formed, denitrification would have been too weak. The largest particles formed by the old scheme had diameters of less than 1 μm, and therefore would have had fall velocities of the order of 70 m day⁻¹ had the particle size been used in the sedimentation velocity calculation. In contrast, on the 20th of January, particles formed by the new scheme grew to between 11μm and 12 μm, and had sedimentation velocities of around 2.4 km day⁻¹. The particle sizes generated by the new scheme are in far better agreement with those found by Carslaw et al. (2002) from their model (Figure 8.3), which in turn corresponded very well with particle sizes observed by the NO₃ instrument on board the ER-2 aircraft during flights on the three days considered here. Particle sizes as large as 12-14μm are shown in Figure 8.3, for the 20th of January. On the 3rd of February the largest particles are around 10 μm in diameter, whereas the particles generated by the new PSC scheme in MEZON are only reach about 2 - 4 μm, however, still much larger than the 0.6 - 0.8 μm diameter particles generated by the old scheme. By the 26th of February, the maximum particle sizes were approximately 6 μm for the model of Carslaw et al. (2002), 1-2 μm for the new MEZON PSC scheme, and 0.8 - 0.1 μm for the old MEZON PSC scheme.

The horizontal extent of the PSC shown in Figure 8.2 is also different for the two schemes. This is partly due to the nucleation barrier built into the new scheme, and partly due to the fact that transport of PSC is possible in the new scheme. The area where PSC exists in the model with the new PSC scheme corresponds well with the PSC area in 8.3, whereas the old scheme generally produces too small PSC areas.

The mixing ratios of gas phase HNO₃ on the 430 K level, in the Arctic, during three periods of February and March 2000 are plotted in Figure 8.4, for both the new and the old PSC scheme. In this winter, the vortex average temperature sank below the NAT saturation temperature in about mid December (Newman et al., 2002), allowing plenty of time for denitrification before February.

Clearly the denitrification in the new scheme is much stronger than in the old scheme, leading to a depletion of the gas phase by 5 ppb already in early February. A similar difference between the two schemes is seen later in February, but by the end of March, the HNO₃ gas phase mixing ratios are similar for both schemes. This may be because of mixing between vortex and lower latitude air, or because of increasing photolysis of HNO₃ (Santee et al., 2000).

During the 2nd - 4th of February, the new scheme produces gas phase HNO₃ values about 3 ppb lower than those measured by the MLS (Microwave Limb Sounder), shown in Figure 8.5, however, it overestimates the mixing ratios in the areas east of Greenland, and north of Scandinavia by about 2 ppb. The old scheme almost exactly reproduces the high HNO₃ mixing ratios east of Greenland, however, it overestimates the mixing ratios
north of Scandinavia by 4-5 ppb. On the 9th - 11th of February, the overestimation of HNO₃ mixing ratios, by the old scheme, east of Greenland lies at about 5-6 ppb, while the new scheme only overestimates the mixing ratios by about 1-2 ppb. At the end of March, both schemes show similar values, and are close to the measured values. From this comparison, it appears that the new scheme is better able to reproduce the observed levels of denitrification in the Arctic vortex, however, the effects are spread out, and localised areas of non denitrified air are not sustained.

**Fig. 8.4:** The gas phase HNO₃ mixing ratio, for simulations with the old and the new PSC schemes, on the 465K level.
8.4 Summary

The new PSC scheme is a definite improvement on the old scheme. The formation, growth, and sedimentation of NAT particles are calculated in a more physically reasonable way than in the old scheme. The amount of denitrification calculated by the model using the new scheme is not in perfect agreement with measurements, however, the agreement could be improved in the future by carrying out sensitivity studies on parameters such as the nucleation barrier (presently set to a saturation ratio of 20) and the initial nucleated number density (currently $1 \times 10^{-3}$ cm$^{-3}$).

Whereas the old PSC scheme does not produce substantial permanent denitrification even in the southern polar vortex, the new scheme does. The particle diameters produced by the new scheme for the northern winter of 1999/2000 are in far better agreement with aircraft measurements than those calculated by the old scheme. Areas of gas phase HNO$_3$ depletion, which were observed by the MLS in February 2000, are better reproduced by the model using the new PSC scheme, although the effects of this depletion are too smoothed out, and observed air masses with relatively little HNO$_3$ depletion are not reproduced well by the model using the new PSC scheme. This may be improved by using a higher model resolution.
Chapter 9

Conclusion

A three-dimensional offline CTM, “MEZON”, was used to study the changes in ozone and ODS for the period 1965-2000. This is one of the first CTM simulations carried out over such a long time period, using the new ERA-40 reanalysis data. Before the 36 year transient model runs were started, various changes and improvements were made to the model. A total of 13 new ODS were added to the chemical scheme, in order to facilitate the simulation of the lifetime of these species. The model’s PSC and aerosol schemes were also improved, the latter to enable the simulation of the effect of a varying amount of stratospheric sulphate aerosol on ozone.

In terms of horizontal resolution, MEZON is about in the middle of the range when compared with contemporary models. The vertical extent also compares well with similar models. The chemical and transport time steps used in MEZON are significantly longer than most other models. This is partly because models using the Prather advection scheme for horizontal advection require short time steps in order to remain stable, however, the hybrid scheme applied in MEZON does not have this limitation. In the future, it may be interesting to increase the horizontal resolution of MEZON to 2° latitude by 2° longitude, in order to investigate the effect on the quality of the model results.

The ERA-40 reanalysis project was completed during this study (around July 2003) and MEZON was adapted to use this newly available circulation and temperature data. Various other long term input data sets were also created in preparation from the 36 year transient runs, these included surface mixing ratios for CH$_4$, N$_2$O and the ODS, as well as sulphate aerosol surface area density and tropopause water mixing ratios.

During the first experiments using the ERA-40 data in MEZON, several problems were noticed with the new circulation data. Large fluctuations in vertical wind velocities caused instabilities in the model transport calculation. This was solved by smoothing the vertical winds on each horizontal level with two applications of a 9 point running mean. Other deficiencies in the circulation data, which were noticed during the model validation have been confirmed by other groups.

It was noted that the upward transport in the tropics, and the meridional transport or dispersion, is too strong in MEZON, using the ERA-40 circulation data. This can be seen, for example, in a comparison of the modelled water vapour “tape recorder” signal with measured values. In the modelled values, a particular water mixing ratio that was at approximately 15 km altitude, in the tropics, reaches an altitude of approximately 31 km a year later. Measurements from HALOE show that an altitude of only 22 km is attained in reality. An unrealistically enhanced Brewer-Dobson circulation in the ERA-40 data was also reported by van Noije et al. (2004). It was further suggested by van Noije et al. (2004) that this exaggerated Brewer-Dobson circulation would result in increased ozone mixing.
ratios in the lower extra-tropical stratosphere, something that was also observed during the validation of MEZON results, especially in the northern hemisphere. These too-large lower stratospheric ozone mixing ratios, along with an apparent downward displacement of the ozone mixing ratio isopleths, are the cause of the high bias in northern hemisphere total ozone in MEZON.

During the mid 1970s, total ozone was greatly overestimated by MEZON, in comparison with measurements from several Dobson spectrophotometer stations. An overestimation in total ozone was also found in the ERA-40 reanalysis data, for years when VTPR or TOVS radiance data was assimilated, but no ozone data was assimilated Uppala et al. (2005). During the period 1972-1978, radiance data from the VTPR was used in the reanalysis, from 1979 onwards this was replaced by TOVS and other data sets. Before 1972 no satellite radiance data was assimilated. It was suggested by Uppala et al. (2005) that the enhanced Brewer-Dobson circulation, which was especially apparent during years when satellite radiance data was assimilated, was the result of a forcing of the meridional circulation by temperature corrections applied repeatedly in the stratosphere during the assimilation. These corrections were necessary because of temperature differences between the assimilation model's stratosphere and measured temperatures calculated from the radiance data. It is possible that the especially high modelled total ozone in the 1970s is related to the use of these first satellite radiance data in the assimilation.

Despite periods of poor correspondence between MEZON modelled ozone and measurements, much of the observed ozone variability was reproduced by the model. The seasonal cycle of ozone, as well as the geographic pattern of areas of high and low total ozone were simulated well. In most of the comparisons between Dobson measurements of total ozone and modelled values, the decrease in total ozone after the eruption of Mt Pinatubo was very well reproduced by the model.

The effect on total ozone of an increase in stratospheric sulphate aerosol after volcanic eruptions was found to be quite sensitive to the chlorine loading of the atmosphere. In model runs with ODS emissions fixed at 1960s levels, the enhanced aerosol surface area after the eruption of Mt Pinatubo actually resulted in an increase in total ozone, probably due to the removal of NO\textsubscript{x} via the N\textsubscript{2}O\textsubscript{5} hydrolysis on the aerosol droplets. In model runs where the observed trend in ODS emissions was accounted for, the greater aerosol surface area resulted in greater ozone loss, for eruptions occurring after about 1980. In this case, the rate of the ClO\textsubscript{x} ozone destruction cycle increased enough to counteract the reduction of the rate in NO\textsubscript{x} catalysed ozone loss. However, even after the eruption of Mt Pinatubo, most of the modelled ozone loss was found to be dynamical in origin, rather than being a result of chemistry occurring on the increased amount of stratospheric aerosol.

The difference in the reaction rates of various ozone destruction cycles were examined for a model run accounting for enhanced aerosol after the eruption of Mt Pinatubo, and for a run where the aerosol surface area density was fixed at "background" levels. It was found that in the lower stratosphere, the rate of the ClO\textsubscript{x} catalysed ozone loss increased by around 40%, while the rate of the NO\textsubscript{x} cycle decreased by around 20%.

The decrease in column amounts of NO\textsubscript{2} in MEZON after the eruption of Mt Pinatubo are slightly underestimated with respect to the observed decrease over Lauder and the Jungfraujoch. In the southern hemisphere, the decrease in NO\textsubscript{2} observed after the eruption of El Chichón is well captured by the model. When the influence of the input circulation and temperature data is removed, the magnitudes of the modelled column decreases of NO\textsubscript{2} are reduced even further. The decrease over the Jungfraujoch becomes almost imperceptible, while about half of the decrease over Lauder remains. Some of the
underestimation in the column NO₂ decreases may have come from the use of monthly mean data in the model as the abundance, and therefore probably also the variability of NO₂, is greatly reduced during the day time.

One very interesting result is MEZON’s reproduction of a pronounced minimum in total ozone, which occurred at southern low to middle latitudes in 1985. This decrease was noted by Fioletov et al. (2002), and was also described in WMO (2003), however, as far as we know, no explanation has yet been put forward. It was suggested by Fioletov et al. (2002) that the feature has a strong dynamical component, as its magnitude was decreased when the natural components of ozone variation were removed. The fact that this minimum in total ozone was also present and of almost exactly the same magnitude, in a further model run with background levels of aerosol in MEZON, shows that the influence of chemistry on aerosol droplets does not play a role. It is interesting to note that in two simulations with the coupled chemistry climate model (CCM) SOCOL, Martin Schraner was also able to reproduce the 1985 minimum in ozone in one case, but not in the other. The two simulations differed in the data set used to calculate the surface area of stratospheric sulphate aerosol (Schraner, personal communication, 2005). The model SOCOL uses MEZON as its chemistry module and as it has been found that the ozone minimum is not a result of chemistry in MEZON, this leaves only the possibility that it is a result of the influence of variations in sulphate aerosol on atmospheric circulation.

One of the aims of this work was to calculate the contribution of various processes to the observed ozone trend. Based on the information gained in the model validation, certain periods of the 36 year transient model runs could be removed from the ozone trend calculation. Linear trends in total ozone and in ozone mixing ratios were calculated for 1979-2000, and compared with trends calculated from measured ozone abundances. It became clear that MEZON did not reproduce the observed trends particularly well in many regions. Specific problems were for example the upper stratosphere, where the modelled trend in ozone was positive, while the observed trend was negative; high southern latitudes during early winter, where the modelled trend in total ozone was large and positive; and the high northern latitudes, where a large positive trend was also produced by the model.

The separation of contributions to the modelled trend was carried out over the period where the observed ozone trend should be roughly linear, i.e. 1979-1995. It was found that the chemical effect, on modelled total ozone, of the increasing emissions in ODS corresponded very well with the observed negative trend in total ozone in the extratropics. Likewise, the contribution from increases in stratospheric sulphate aerosol after volcanic eruptions also produced a negative contribution to the ozone trends. In contrast, the trends in total ozone from circulation and temperature were often large and positive. Thus it appears that the reason that the overall modelled trend in total ozone was so far from the observed trend is related to the circulation and temperature data used in the model.

A similar result was found for trends in ozone mixing ratios; the trend as a result of ODS emissions and volcanic aerosol was negative, and corresponded well with measurements except in the lower extra-tropical stratosphere, however, the trend attributed to the circulation and temperature input lead to an unrealistic overall ozone trend. The positive trend in upper stratospheric ozone, for example, was a result of the large positive contribution from the temperature and circulation data to the overall ozone trend.

It was found that some of the overall modelled trends in ozone could be brought into better agreement with measured trends, by comparing modelled data with Dobson in-
instrument measurements and filtering out certain months where the disagreement between modelled and measured ozone was especially large.

It may be possible to attribute the positive upper stratospheric trend in ozone mixing ratios to an anomalous stratospheric temperature trend in the ERA-40 reanalysis data. It was noted by Uppala et al. (2005) that in the early years of the reanalysis, the temperature data was high biased in comparison with measurements. In the later years, this situation had changed to a low bias. The resulting negative temperature trend is much larger than that in measured temperatures, and may have lead to enhanced ozone production.

Some of the increase in mid and high latitude ozone, and the corresponding decrease in tropical total ozone may be the result of an increasing trend in the rate of meridional transport in the ERA-40 circulation data. There appears to be a small increasing trend in the winter average EP-flux, which is a proxy for the wave driving of the meridional circulation, and therefore the rate of ozone transport from the tropics to the extra-tropics (Fusco and Salby, 1999).

The results of the separation of the contribution to the modelled ozone trends imply that the negative ozone trends calculated from observations are almost entirely related to the increase in ODS emissions.

The instantaneous lifetimes of several ODS were calculated during this study. The modelled lifetimes correspond well with the reference lifetimes given in WMO (2003), however, in general lifetimes of ODS with significant stratospheric sinks, such as CCl4, CFC-11 and CFC-114 are underestimated. This is a result of the too rapid upward transport in the tropics. The lifetime of CFC-12 is overestimated in MEZON, and this may be a result of the absorption cross sections used to calculate the photolysis rate. It would be interesting to substitute the cross sections from DeMore et al. (1997) for the IUPAC cross sections which are currently used in MEZON, to determine what effect this has on the modelled lifetime of CFC-12.

It was shown that the lifetimes of CFC-11 and CFC-12 are sensitive to the abundance of ozone between 62°N and 62°S, and that a 10 DU decline in mean total ozone in this region results in a reduction in the CFC-11 lifetime of approximately 2% and a reduction in the CFC-12 lifetime of approximately 3%.

A loose correlation between upward mass flux at 24 km, averaged over 28°S and 28°N, and lifetime of CFC-11 and CFC-12 was also found. This implied a reduction in lifetime of 0.9% for CFC-11 and 0.5% for CFC-12, per percent increase in upward mass flux.

Another of the subjects of this study was the determination of the causes of the early reduction in HCl mixing ratios in the upper stratosphere, followed by the increase in HCl after about 2000. At first it appeared as if the model could reproduce this decline and subsequent increase, but it was found that a deficient "mass fixer", used to ensure mass conservation during the semi-Lagrangian advection step, was actually resulting in a small amount of mass loss, which then appeared to result in the HCl decline near the upper boundary of the model. Experiments with passive tracers showed that the model transport was nearly completely conservative for tracers without strong gradients, when the mass fixer was switched off. A further model run with the mass fixer turned off for HCl resulted in small amounts of HCl creation in the stratosphere. Further model validation experiments determined that the effects of this mass fixer on other parts of this work are negligible, but it will not be possible to determine whether or not the model can reproduce the early decline in HCl mixing ratios until this problem is solved. Improving this mass fixer is clearly an important future task.

While MEZON was being prepared for the 36 year transient runs, the PSC and aerosol
scheme was extensively updated. This included changes to enable the calculation of reaction rates on sulphate aerosol droplets as a function of surface area density. The surface area density data was provided as a model input and included the increases in surface area density following volcanic eruptions. The calculation of the formation and growth of NAT particles was improved to include a nucleation barrier, and account for non-equilibrium particle growth. Further, NAT particles are now transported in the model and sedimentation rates are calculated based on particle diameter. The result is a larger amount of permanent denitrification, rather than a simple uptake of HNO₃ onto PSC particles. This results in a more delayed recovery of HNO₃ levels in the Antarctic spring, which corresponds better with measurements. The diameters of the NAT particles calculated by the new scheme are in better agreement with observations from the SOLVE/THESEO campaign during the Arctic winter of 1999/2000 than the diameters calculated by the old NAT scheme. A possible future improvement of the MEZÓN PSC scheme would be the preservation of NAT particle size information by binning the particles according to diameter, rather than assuming a mono-disperse size distribution. This would, however, result in more tracers which would need to be transported and therefore an increase in the necessary CPU time.
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Appendix A

Chemical Reactions

The reactions included in the model chemical scheme are listed below, along with rate constants, where applicable.

A.1 Bimolecular reactions

The Arrhenius parameters for all bimolecular reactions used in the model are given in Table A.1. The rate constant, $k$, can be calculated from equation A.1

$$k = Ae^{-\frac{E}{R} \frac{1}{T}}, \quad \text{(A.1)}$$

where $-E/R$ is the negative of the “activation energy” divided by the ideal gas constant (8.314 JK$^{-1}$mol$^{-1}$), $A$ is the “pre-exponential factor”, both from Table A.1 and $T$ is the temperature in Kelvin.

Table A.1: Bimolecular reactions

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<th>Reaction</th>
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<td>$O^1D + N_2 \rightarrow O + N_2$</td>
<td>$1.8 \times 10^{-11}$</td>
<td>110</td>
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<td>$O^1D + O_2 \rightarrow O + O_2$</td>
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<td>$NO + HO_2 \rightarrow OH + NO_2$</td>
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<td>$NO + ClO \rightarrow Cl + NO_2$</td>
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Bimolecular reactions (continued from previous page.)

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<th>E/R</th>
<th>Number</th>
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### Bimolecular Reactions (continued from previous page)

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<td>-1775.0</td>
<td>RCH3</td>
</tr>
<tr>
<td>CH3O2 + NO → CH3O + NO2</td>
<td>3.0 × 10^{-12}</td>
<td>280.0</td>
<td>RCH5</td>
</tr>
<tr>
<td>CH3O + O2 → CH2O + HO2</td>
<td>3.9 × 10^{-14}</td>
<td>-900.0</td>
<td>RCH6</td>
</tr>
<tr>
<td>CH3O + OH → HCO + H2O</td>
<td>1.0 × 10^{-11}</td>
<td>0.0</td>
<td>RCH7</td>
</tr>
<tr>
<td>CH3O + O → HCO + OH</td>
<td>3.4 × 10^{-11}</td>
<td>-1600.0</td>
<td>RH7a</td>
</tr>
<tr>
<td>HCO + O2 → CO + HO2</td>
<td>3.5 × 10^{-12}</td>
<td>140.0</td>
<td>RCH10</td>
</tr>
<tr>
<td>Cl + CH2O → HCl + HCO</td>
<td>8.1 × 10^{-11}</td>
<td>-30.0</td>
<td>RCH11</td>
</tr>
<tr>
<td>CH3 + HO2 → CH2O H + O2</td>
<td>3.8 × 10^{-13}</td>
<td>800.0</td>
<td>RCH13</td>
</tr>
<tr>
<td>CH3O2H + OH → CH3O2 + H2O</td>
<td>3.8 × 10^{-12}</td>
<td>200.0</td>
<td>RCH14</td>
</tr>
<tr>
<td>CH3O2 + CH3O2 → CH3O + CH3O</td>
<td>0.875 × 10^{-13}</td>
<td>190.0</td>
<td>RCH20</td>
</tr>
<tr>
<td>CH3O2 + CH3O2 → CH2O + H2O</td>
<td>1.625 × 10^{-13}</td>
<td>190.0</td>
<td>RCH21</td>
</tr>
<tr>
<td>H2 + O → OH + H</td>
<td>8.8 × 10^{-12}</td>
<td>-4200.0</td>
<td>RT06</td>
</tr>
<tr>
<td>NO3 + OH → NO2 + HO2</td>
<td>2.2 × 10^{-11}</td>
<td>0.0</td>
<td>RT07</td>
</tr>
<tr>
<td>NO3 + HO2 → NO2 + OH + O2</td>
<td>2.8 × 10^{-12}</td>
<td>0.0</td>
<td>RT08</td>
</tr>
<tr>
<td>NO3 + HO2 → HNO3 + O2</td>
<td>7.0 × 10^{-13}</td>
<td>0.0</td>
<td>RT09</td>
</tr>
<tr>
<td>CH3O + NO3 → CO + HO2 + HNO3</td>
<td>6.0 × 10^{-13}</td>
<td>-2058.0</td>
<td>RT10</td>
</tr>
<tr>
<td>O + HOCI → OH + ClO</td>
<td>1.7 × 10^{-13}</td>
<td>0.0</td>
<td>RT11</td>
</tr>
<tr>
<td>Cl + HOCl → OH + Cl2</td>
<td>2.5 × 10^{-12}</td>
<td>-130.0</td>
<td>RT12</td>
</tr>
<tr>
<td>O1D + Cl2 → ClO + Cl</td>
<td>2.8 × 10^{-10}</td>
<td>0.0</td>
<td>RT13</td>
</tr>
<tr>
<td>Cl + Cl2O2 → Cl2 + Cl + O2</td>
<td>1.0 × 10^{-10}</td>
<td>0.0</td>
<td>RT14</td>
</tr>
<tr>
<td>NO3 + Cl → NO2 + ClO</td>
<td>2.4 × 10^{-11}</td>
<td>0.0</td>
<td>RT15</td>
</tr>
<tr>
<td>NO3 + ClO → NO2 + Cl + O2</td>
<td>4.7 × 10^{-13}</td>
<td>0.0</td>
<td>RT16</td>
</tr>
<tr>
<td>O + HCl → OH + Cl</td>
<td>1.0 × 10^{-11}</td>
<td>-330.0</td>
<td>RT17</td>
</tr>
<tr>
<td>OH + Cl2 → HOCI + Cl</td>
<td>1.4 × 10^{-12}</td>
<td>-900.0</td>
<td>RT18</td>
</tr>
<tr>
<td>BrO + OH → HO2 + Br</td>
<td>7.5 × 10^{-11}</td>
<td>0.0</td>
<td>RT19</td>
</tr>
<tr>
<td>H + NO2 → OH + NO</td>
<td>4.0 × 10^{-10}</td>
<td>-340.0</td>
<td>RT20</td>
</tr>
<tr>
<td>O1D + O3 → O2 + O + 0</td>
<td>1.2 × 10^{-10}</td>
<td>0.0</td>
<td>RT21</td>
</tr>
<tr>
<td>CCl3F + O1D → ClO</td>
<td>2.0 × 10^{-10}</td>
<td>0.0</td>
<td>RF16</td>
</tr>
<tr>
<td>CCl2F2 + O1D → ClO</td>
<td>1.1 × 10^{-10}</td>
<td>0.0</td>
<td>RF17</td>
</tr>
<tr>
<td>CCl2FClClF2 + O1D → ClO</td>
<td>2.0 × 10^{-10}</td>
<td>0.0</td>
<td>RF18</td>
</tr>
<tr>
<td>CCl2F2CClF2 + O1D → ClO</td>
<td>9.8 × 10^{-11}</td>
<td>0.0</td>
<td>RF19</td>
</tr>
<tr>
<td>CCl2F2CF3 + O1D → ClO</td>
<td>5.0 × 10^{-11}</td>
<td>0.0</td>
<td>RF20</td>
</tr>
<tr>
<td>CHClF2 + O1D → ClO</td>
<td>7.2 × 10^{-11}</td>
<td>0.0</td>
<td>RF21</td>
</tr>
<tr>
<td>CH3CCl2F + O1D → ClO</td>
<td>1.8 × 10^{-10}</td>
<td>0.0</td>
<td>RF22</td>
</tr>
<tr>
<td>CH3CClF2 + O1D → ClO</td>
<td>1.6 × 10^{-10}</td>
<td>0.0</td>
<td>RF23</td>
</tr>
<tr>
<td>CF2ClBr + O1D → BrO</td>
<td>1.0 × 10^{-10}</td>
<td>0.0</td>
<td>RF25</td>
</tr>
</tbody>
</table>

Continued on next page.
Bimolecular reactions (continued from previous page.)

<table>
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<th>A-factor</th>
<th>-E/R</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF_3Br + O_3D \rightarrow BrO</td>
<td>4.0 \times 10^{-11}</td>
<td>0.0</td>
<td>RF26</td>
</tr>
<tr>
<td>CBrF_2BrF_2 + O_3D \rightarrow BrO</td>
<td>8.8 \times 10^{-11}</td>
<td>0.0</td>
<td>RF27</td>
</tr>
<tr>
<td>CH_3Br + O_3D \rightarrow HBr + CH_2O</td>
<td>1.8 \times 10^{-10}</td>
<td>0.0</td>
<td>RF28</td>
</tr>
<tr>
<td>CCl_4 + O_3D \rightarrow ClO</td>
<td>3.0 \times 10^{-10}</td>
<td>0.0</td>
<td>RF29</td>
</tr>
<tr>
<td>CHClF_2 + OH \rightarrow H_2O</td>
<td>1.0 \times 10^{-12}</td>
<td>-1600.0</td>
<td>RF30</td>
</tr>
<tr>
<td>CH_3CCl_2F + OH \rightarrow H_2O</td>
<td>1.7 \times 10^{-12}</td>
<td>-1700.0</td>
<td>RF31</td>
</tr>
<tr>
<td>CH_3ClIF_2 + OH \rightarrow H_2O</td>
<td>1.3 \times 10^{-12}</td>
<td>-1800.0</td>
<td>RF32</td>
</tr>
<tr>
<td>CH_3Br + OH \rightarrow H_2O</td>
<td>4.0 \times 10^{-12}</td>
<td>-1470.0</td>
<td>RF34</td>
</tr>
<tr>
<td>CH_3CICH_2Cl + OH \rightarrow H_2O</td>
<td>1.8 \times 10^{-12}</td>
<td>-1550.0</td>
<td>RF35</td>
</tr>
<tr>
<td>CH_3Cl + OH \rightarrow H_2O</td>
<td>4.0 \times 10^{-12}</td>
<td>-1400.0</td>
<td>RF36</td>
</tr>
<tr>
<td>CHClF_2 + Cl \rightarrow HCl</td>
<td>1.5 \times 10^{-12}</td>
<td>-2430.0</td>
<td>RF37</td>
</tr>
<tr>
<td>CH_3CCl_2F + Cl \rightarrow HCl</td>
<td>1.8 \times 10^{-12}</td>
<td>-2000.0</td>
<td>RF38</td>
</tr>
<tr>
<td>CH_3CClF_2 + Cl \rightarrow HCl</td>
<td>1.4 \times 10^{-12}</td>
<td>-2420.0</td>
<td>RF39</td>
</tr>
<tr>
<td>CH_3Br + Cl \rightarrow HCl</td>
<td>1.5 \times 10^{-11}</td>
<td>-1060.0</td>
<td>RF41</td>
</tr>
<tr>
<td>CH_2CCl_3 + Cl \rightarrow HCl</td>
<td>2.8 \times 10^{-12}</td>
<td>-1790.0</td>
<td>RF42</td>
</tr>
<tr>
<td>CH_3Cl + Cl \rightarrow HCl</td>
<td>3.2 \times 10^{-11}</td>
<td>-1250.0</td>
<td>RF43</td>
</tr>
</tbody>
</table>

A.2 Termolecular reactions

Termolecular reactions are reactions of the form

\[ A + B \rightleftharpoons [AB]^* \xrightarrow{M} AB, \]  

and the rate constants are given by:

\[ k_0(T) = k_0^{300} \left( \frac{T}{300} \right)^{-n} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}. \]  

Similarly, the limiting high pressure rate constant can be calculated from:

\[ k_\infty(T) = k_\infty^{300} \left( \frac{T}{300} \right)^{-m} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. \]  

The effective second-order rate constant for a particular temperature and pressure is then given by:

\[ k_f([M], T) = \left( \frac{k_0(T)[M]}{1 + \frac{k_0(T)[M]}{k_\infty(T)}} \right)^{0.6} \left\{ 1 + \left[ \log_{10}\left( \frac{k_0(T)[M]}{k_\infty(T)} \right) \right]^2 \right\}^{-1}. \]  

The parameters \( k_0(300), n, k_\infty(300) \) and \( m \) for the calculation of rate constants of termolecular reactions used in the model are listed in Table A.2.
### A.4 Photolysis reactions

Photolysis reactions used in the model are given in Table A.4.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_2 \rightarrow O + O )</td>
<td>RO1</td>
</tr>
</tbody>
</table>

Continued on next page.
Photolysis reactions (continued from previous page.)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_3 \rightarrow \text{O}_2 + \text{O}$</td>
<td>RO2</td>
</tr>
<tr>
<td>$\text{O}_3 \rightarrow \text{O}_2 + \text{O}^1\text{D}$</td>
<td>RO3</td>
</tr>
<tr>
<td>$\text{NO} \rightarrow \text{O} + \text{N}$</td>
<td>RN1</td>
</tr>
<tr>
<td>$\text{NO}_2 \rightarrow \text{NO} + \text{O}$</td>
<td>RN5</td>
</tr>
<tr>
<td>$\text{HNO}_3 \rightarrow \text{NO}_2 + \text{OH}$</td>
<td>RN11</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}$</td>
<td>RN14</td>
</tr>
<tr>
<td>$\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$</td>
<td>RN15</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$</td>
<td>RN16</td>
</tr>
<tr>
<td>$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^1\text{D}$</td>
<td>RN17</td>
</tr>
<tr>
<td>$\text{HNO}_4 \rightarrow \text{NO}_2 + \text{HO}_2$</td>
<td>RN20</td>
</tr>
<tr>
<td>$\text{ClNO}_3 \rightarrow \text{Cl} + \text{NO}_3$</td>
<td>RN23</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$</td>
<td>RH8</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$</td>
<td>RH18</td>
</tr>
<tr>
<td>$\text{HOC}_1 \rightarrow \text{Cl} + \text{OH}$</td>
<td>RC9</td>
</tr>
<tr>
<td>$\text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}$</td>
<td>RC12</td>
</tr>
<tr>
<td>$\text{Cl}_2\text{O}_2 \rightarrow \text{Cl} + \text{Cl}$</td>
<td>RC15</td>
</tr>
<tr>
<td>$\text{BrO} \rightarrow \text{Br} + \text{O}$</td>
<td>RB19</td>
</tr>
<tr>
<td>$\text{BrNO}_3 \rightarrow \text{BrO} + \text{NO}_2$</td>
<td>RB20a</td>
</tr>
<tr>
<td>$\text{BrNO}_3 \rightarrow \text{Br} + \text{NO}_3$</td>
<td>RB20b</td>
</tr>
<tr>
<td>$\text{BrCl} \rightarrow \text{Br} + \text{Cl}$</td>
<td>RB21</td>
</tr>
<tr>
<td>$\text{HOBr} \rightarrow \text{Br} + \text{OH}$</td>
<td>RB22</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2$</td>
<td>RCH8</td>
</tr>
<tr>
<td>$\text{CH}_2\text{O} \rightarrow \text{HCO} + \text{H}$</td>
<td>RCH9</td>
</tr>
<tr>
<td>$\text{CO}_2 \rightarrow \text{CO} + \text{O}$</td>
<td>RCH12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}_3\text{H} \rightarrow \text{CH}_3\text{OH} + \text{OH}$</td>
<td>RCH15</td>
</tr>
<tr>
<td>$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$</td>
<td>RT01</td>
</tr>
<tr>
<td>$\text{O}_2 \rightarrow \text{O}^1\text{D} + \text{O}$</td>
<td>RT02</td>
</tr>
<tr>
<td>$\text{ClNO}_3 \rightarrow \text{ClO} + \text{NO}_2$</td>
<td>RT03</td>
</tr>
<tr>
<td>$\text{HCl} \rightarrow \text{Cl} + \text{H}$</td>
<td>RT04</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{F} \rightarrow \text{Cl} + \text{Cl} + \text{Cl}$</td>
<td>RF01</td>
</tr>
<tr>
<td>$\text{CCl}_2\text{F}_2 \rightarrow \text{Cl} + \text{Cl}$</td>
<td>RF02</td>
</tr>
<tr>
<td>$\text{CCl}_2\text{FCClF}_2 \rightarrow \text{Cl} + \text{Cl} + \text{Cl}$</td>
<td>RF03</td>
</tr>
<tr>
<td>$\text{CCIF}_2\text{CCIF}_2 \rightarrow \text{Cl} + \text{Cl}$</td>
<td>RF04</td>
</tr>
<tr>
<td>$\text{CCIF}_2\text{CF}_3 \rightarrow \text{Cl}$</td>
<td>RF05</td>
</tr>
<tr>
<td>$\text{CHClF}_2 \rightarrow \text{Cl}$</td>
<td>RF06</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CCl}_2\text{F} \rightarrow \text{Cl} + \text{Cl}$</td>
<td>RF07</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CClIF}_2 \rightarrow \text{Cl}$</td>
<td>RF08</td>
</tr>
<tr>
<td>$\text{CF}_2\text{ClBr} \rightarrow \text{Cl} + \text{Br}$</td>
<td>RF10a</td>
</tr>
<tr>
<td>$\text{CF}_3\text{Br} \rightarrow \text{Br}$</td>
<td>RF11</td>
</tr>
<tr>
<td>$\text{CBrF}_2\text{CBrF}_2 \rightarrow \text{Br} + \text{Br}$</td>
<td>RF12</td>
</tr>
<tr>
<td>$\text{CH}_2\text{Br} \rightarrow \text{CH}_3 + \text{Br}$</td>
<td>RF13</td>
</tr>
<tr>
<td>$\text{CCl}_4 \rightarrow \text{Cl} + \text{Cl} + \text{Cl}$</td>
<td>RF14</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CCl}_3 \rightarrow \text{Cl} + \text{Cl} + \text{Cl}$</td>
<td>RF15</td>
</tr>
<tr>
<td>$\text{CH}_3\text{Cl} \rightarrow \text{CH}_3 + \text{Cl}$</td>
<td>RF45</td>
</tr>
</tbody>
</table>
A.5 Heterogeneous reactions

The heterogeneous reactions which occur on sulphate aerosol, PSC I and PSC II are given in Table A.5.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O_5 \xrightarrow{\text{HET}} HNO_3 + HNO_3$</td>
<td>SHS1</td>
</tr>
<tr>
<td>$ClNO_3 \xrightarrow{\text{HET}} HOCL + HNO_3$</td>
<td>SHS2</td>
</tr>
<tr>
<td>$BrNO_3 \xrightarrow{\text{HET}} HOBr + HNO_3$</td>
<td>SHS3</td>
</tr>
<tr>
<td>$ClNO_3 + HCl \xrightarrow{\text{HET}} Cl_2 + HNO_3$</td>
<td>HS1</td>
</tr>
<tr>
<td>$HOCl + HCl \xrightarrow{\text{HET}} Cl_2 + H_2O$</td>
<td>HS2</td>
</tr>
<tr>
<td>$HOBr + HCl \xrightarrow{\text{HET}} BrCl + H_2O$</td>
<td>HS3</td>
</tr>
</tbody>
</table>

On sulphate aerosol

On PSC I

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O_5 \xrightarrow{\text{HET}} HNO_3 + HNO_3$</td>
<td>SHP1</td>
</tr>
<tr>
<td>$ClNO_3 \xrightarrow{\text{HET}} HOCL + HNO_3$</td>
<td>SHP2</td>
</tr>
<tr>
<td>$ClNO_3 + HCl \xrightarrow{\text{HET}} Cl_2 + HNO_3$</td>
<td>HP1</td>
</tr>
<tr>
<td>$HOCl + HCl \xrightarrow{\text{HET}} Cl_2 + H_2O$</td>
<td>HP2</td>
</tr>
</tbody>
</table>

On PSC II

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O_5 \xrightarrow{\text{HET}} HNO_3 + HNO_3$</td>
<td>SHP4</td>
</tr>
<tr>
<td>$ClNO_3 \xrightarrow{\text{HET}} HOCL + HNO_3$</td>
<td>SHP5</td>
</tr>
<tr>
<td>$BrNO_3 \xrightarrow{\text{HET}} HOBr + HNO_3$</td>
<td>SHP6</td>
</tr>
<tr>
<td>$ClNO_3 + HCl \xrightarrow{\text{HET}} Cl_2 + HNO_3$</td>
<td>HP4</td>
</tr>
<tr>
<td>$HOCl + HCl \xrightarrow{\text{HET}} Cl_2 + H_2O$</td>
<td>HP5</td>
</tr>
<tr>
<td>$HOBr + HCl \xrightarrow{\text{HET}} BrCl + H_2O$</td>
<td>HP6</td>
</tr>
</tbody>
</table>

A.6 Other reactions

There are also some reactions with rate constants calculated via other methods:

$HNO_3 + OH \xrightarrow{\text{M}} NO_3 + H_2O$, the rate constant of which is calculated as follows:

$$k_0(T) = 6.5 \times 10^{-34} \left( \frac{1.335 \times 10^3}{T} \right)$$  \hspace{1cm} (A.7)

$$k_\infty(T) = 2.7 \times 10^{-17} \left( \frac{2.19 \times 10^3}{T} \right)$$  \hspace{1cm} (A.8)

The rate constant for a particular temperature and pressure is then given by:

$$k_f([M], T) = \left( \frac{k_0(T)[M]}{1.0 + \frac{k_0[M]}{k_\infty}} \right)$$  \hspace{1cm} (A.9)

The reaction $O + N \rightarrow NO$ is pressure dependent with the rate constant:

$$k([M]) = 1.5 \times 10^{-17} + 2.383 \times 10^{-13}([M] 4.196 \times 10^{-20}).$$  \hspace{1cm} (A.10)
Likewise, for the reaction $\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$,

$$k([M]) = 1.5 \times 10^{-13} + 9.0 \times 10^{-14}([M] 4.196 \times 10^{-20}). \quad (A.11)$$

Finally, $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}$, with rate constant

$$k([M], T) = 4.1 \times 10^{-14}([M] 4.196 \times 10^{-20}) \text{EXP} \left(\frac{1.0 \times 10^3}{T}\right). \quad (A.12)$$
Appendix B

Abbreviation List

ADEOS Advanced Earth Observation Satellite
CANDIDOZ Chemical and Dynamical Influences on Decadal Ozone Change
CCM Coupled Chemistry-Climate Model
CFC Chlorofluorocarbon
CLAES Cryogenic Limb Array Etalon Spectrometer
CPU Central Processing Unit
CTM Chemical Transport Model
ECMWF European Centre for Medium-Range Weather Forecasts
ENSO El Niño/Southern Oscillation
EP-flux Eliassen-Palm flux
ERA ECMWF Re-Analysis
EU European Union
FTIR Fourier Transform Infrared Spectroscopy
GCM General Circulation Model
GISS Goddard Institute for Space Studies
GOME Global Ozone Monitoring Experiment
HALOE Halogen Occultation Experiment
HCFC Hydrochlorofluorocarbon
IUPAC International Union of Pure and Applied Chemistry
MEZON Model for investigating ozone trends
MLS Microwave Limb Sounder
MSU Microwave Sounding Unit
NAO North Atlantic Oscillation
NAT Nitric Acid Trihydrate
NCEP National Centers for Environmental Prediction
NIWA National Institute of Water and Atmospheric research
ODS Ozone Depleting Substance
PBL Planetary Boundary Layer
PNJ Polar Night Jet
PSC Polar Stratospheric Cloud
QBO Quasi-Biennial Oscillation
SAGE Stratospheric Aerosol and Gas Experiment
SOCOL modeling tool for studies of SOLar Climate Ozone Links
SSU Stratospheric Sounding Unit
TIROS Television Infra-Red Observation Satellite
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>TOMS</td>
<td>Total Ozone Mapping Spectrometer</td>
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<tr>
<td>TOVS</td>
<td>TIROS Operational Vertical Sounder</td>
</tr>
<tr>
<td>UKMO</td>
<td>United Kingdom Meteorological Office</td>
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<tr>
<td>UV</td>
<td>Ultra Violet</td>
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<tr>
<td>VTPR</td>
<td>Vertical Temperature Profile Radiometer</td>
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<tr>
<td>WMO</td>
<td>World Meteorological Organization</td>
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