Modelling

the middle atmosphere and its sensitivity to climate change

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Abstract

The Earth's middle atmosphere at about 10–100 km has shown a substantial sensitivity to human activities. First, the ozone layer has been reduced since the the early 1980s due to man-made emissions of halogenated hydrocarbons. Second, the middle atmosphere has been identified as a region showing clear evidence of climate change due to increased emissions of greenhouse gases. While increased CO_2 abundances are expected to lead to a warmer climate near the Earth's surface, observations show that the middle atmosphere has been cooling by up to 2–3 degrees per decade over the past few decades. This is partly due to CO_2 increases and partly due to ozone depletion. Predicting the future development of the middle atmosphere is problematic because of strong feedbacks between temperature and ozone. Ozone absorbs solar ultraviolet radiation and thus warms middle atmosphere, and also, ozone chemistry is temperature dependent, so that temperature changes are modulated by ozone changes.

This thesis examines the middle atmospheric response to a doubling of the atmospheric CO_2 content using a coupled chemistry-climate model. The effects can be separated in the intrinsic CO_2-induced radiative response, the radiative feedback through ozone changes and the response due to changes in the climate of the underlying atmosphere and surface. The results show, as expected, a substantial cooling throughout the middle atmosphere, mainly due to the radiative impact of the CO_2 increase. Model simulations with and without coupled chemistry show that the ozone feedback reduces the temperature response by up to 40%. Further analyses show that the ozone changes are caused primarily by the temperature dependency of the reaction $O+O_2+M \rightarrow O_3+M$. The impact of changes in the surface climate on the middle atmosphere is generally small. In particular, no noticeable change in upward propagating planetary wave flux from the lower atmosphere is found. The temperature response in the polar regions is non-robust and thus, for the model used here, polar ozone loss does not appear to be sensitive to climate change in the lower atmosphere as has been suggested recently. The large interannual variability in the polar regions suggests that simulations longer than 30 years will be necessary for further analysis of the effects in this region.

The thesis also addresses the long-standing dilemma that models tend to underestimate the ozone concentration at altitudes 40–75 km, which has important implications for climate change studies in this region. A photochemical box model is used to examine the photochemical aspects of this problem. At 40–55 km, the model reproduces satellite observations to within 10%, thus showing a substantial reduction in the ozone deficit problem. At 60–75 km, however, the model underestimates the observations by up to 35%, suggesting a significant lack of understanding of the chemistry and radiation in this region.

Acknowledgements

The thesis is done. Piece of cake! It took me only almost eight years...

There have been many ups and downs during this work. Nevertheless I have enjoyed it, both the opportunity to explore exciting new science and the bonuses of being a PhD student of course, such as travelling to exciting places (i.e. conferences) and the rather free management of my time (which in my case I would have probably been better off without).

I have many to thank for helping me to come this far. First and foremost, I would like to mention my three (sic) supervisors at MISU, Donal Murtagh (1998–2001), Kevin Noone (2001–2004) and Jörg Gumbel (2004–2006), who have all contributed in different ways. They have all encouraged my scientific curiosity and supported me in tough times.

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Finally to Matilda, family and friends; thanks for all the support, especially during the past few months. I look forward to be able to spend more time with you from now on.

<div align="right">

Stockholm, December 2005
Andreas Jonsson

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1   Introduction

The middle atmosphere is the region of the atmosphere encompassing the stratosphere from about 10–50 km, characterised by increasing temperatures with height, and the mesosphere from about 50–90 km, where temperature decreases with height.

The stratosphere has received a lot of attention during the past few decades due to the depletion of the Earth's ozone layer. Ozone in the atmosphere protects life at the surface from potentially damaging ultraviolet (UV) radiation, so this has been a significant international concern, addressed by the Montreal Protocol and its Amendments. Ozone depletion is associated with man-made substances, including chlorofluorocarbons (CFCs) and other halogenated hydrocarbons, that are emitted into the atmosphere causing rapid ozone destruction in the stratosphere. Originally this problem was concerned with the upper stratosphere region where the impact of the ozone depleting substances was expected to maximise. Ozone has been reduced at a rate of about 7% decade^{-1} in this region (Newchurch *et al.*, 2003). Since the early 1980s severe ozone depletion has occurred also in the polar regions during late winter and early spring. These reductions have been especially large in the Antarctic where the phenomenon has been called the "ozone hole". Reductions in the vertically integrated ozone column of more than 50% have regularly been observed during the winter-spring period.

The middle atmosphere is also in the focus of current scientific interest as it plays an important role as an indicator of climate change. While the increasing burden of greenhouse gases currently observed in the atmosphere, in particular that of carbon dioxide (CO_2), provides a positive radiative forcing on the surface climate, it generally acts to cool the middle atmosphere. The observed temperature change in the middle atmosphere is substantially larger than in the lower

parts of the atmosphere, particularly in the upper stratosphere and lower meso-sphere regions. These are the regions of interest in this thesis. The observed cooling since the early 1980s is about 0.5 K decade^{-1} in the lower stratosphere and about 2 K decade^{-1} near the stratopause ($\sim$50 km) (Ramaswamy *et al.*, 2001; Shine *et al.*, 2003). In the mesosphere, apart from the mesopause region, negative trends of 2–3 K decade^{-1} have been reported (Beig *et al.*, 2003). These values are typically from a factor of two to an order of magnitude greater than the temperature changes observed at the Earth's surface and in the lower troposphere (IPCC, 2001).

There are several links between ozone depletion and CO_2-induced cooling in the middle atmosphere. Ozone absorbs solar UV radiation and thus constitutes the main heat source throughout most of the middle atmosphere. Although the emissions of ozone depleting substances have been substantially reduced through the Montreal Protocol and its Amendments, steady declines in stratospheric ozone levels was observed during the 1980–2000 period (Fioletov *et al.*, 2002). Thus, ozone depletion has acted to enhance the cooling induced by increased CO_2. About half of the temperature trend in the upper stratosphere is estimated to have been caused by ozone decreases and about half by CO_2 increases (Shine *et al.*, 2003).

As the halogen loading slowly declines in the future, ozone is expected to show signs of recovery. Since gas-phase ozone chemistry is temperature dependent, such that ozone and temperature are anti-correlated, ozone recovery may be accelerated by CO_2 increases, and also, the ozone depletion observed in the past could have been more severe than without the CO_2-induced cooling. In the polar regions it is not quite as simple as that, since polar ozone loss is a highly non-linear process, due to the importance of heterogeneous chemistry on polar stratospheric cloud (PSC) particles. PSCs would be more frequent in a colder climate, so the temperature dependence would be the reverse of that for gas-phase chemistry.

Furthermore, although the ozone concentration maximises in the lower part of the stratosphere, the impact of ozone changes in the upper stratosphere on column ozone trends will be important in the future. Models predict that column ozone should recover in the next few decades, and that ozone levels at extrapolar latitudes could even exceed pre-1980 levels in the second part of the 21st century (WMO, 2003). Much of this effect is expected to come from ozone increases in the upper stratosphere due to CO_2-induced cooling.

In addition to the feedbacks between temperature and ozone, long-lived trace gases such as methane (CH_4), water vapour (H_2O) and nitrous oxide (N_2O) provide important chemical interactions with ozone. Trends in the atmospheric

abundance of these gases, which in many aspects are related to human activity, therefore add further complications to the interpretation and prediction of ozone and temperature trends.

Furthermore, the general circulation of the stratosphere is primarily driven by dissipation of planetary-scale waves originating from the lower atmosphere, and this provides an important link between climate change in the lower atmosphere and the middle atmosphere; changes in transport of both ozone itself and of ozone depleting substances could have a significant effect on the ozone distribution (Rind *et al.*, 1990; Butchart and Scaife, 2001).

In summary, the phenomena of ozone depletion and climate change due to greenhouse gas increase are strongly linked and cannot be completely understood in isolation from each other. This thesis deals with some aspects of the overall problem with a focus on interactions in the upper stratosphere and mesosphere.

1.1 The focus of this work

In order to have confidence in model simulations of future changes to the atmosphere, it is important to first establish that the models used can adequately reproduce key characteristics of the current climate. In **Paper I** the model used for the climate sensitivity studies in **Papers III** and **IV** (see below) was compared to a temperature climatology compiled from satellite observations. Both the long-term mean and fluctuations due to atmospheric tides in the stratosphere and mesosphere were analysed and found to be adequately represented in the model, which gives some confidence in the model's overall performance.

The current understanding of the impact of changes in greenhouse gases and ozone depletion is compromised by the fact that models tend to underestimate the observed ozone concentration in the upper stratosphere and lower mesosphere, commonly referred to as the "Ozone deficit problem". In order to address this problem, a photochemical box model including a comprehensive chemistry scheme and detailed radiative transfer calculations was developed. In **Paper II** the model results were compared to satellite observations in order to estimate the magnitude of the ozone discrepancy. Analyses were performed to assess the importance of various model approximations and observational errors for the estimated ozone deficit.

In order to predict future changes (and to reproduce the past), transient climate simulations with global models are commonly used. These include a multitude of known climate forcings, e.g. solar input, trends in emissions of CO_2, CFCs, CH_4, N_2O and aerosol loading. However, because of the strong interactions between radiative processes, chemistry and transport, and between different constituents, as mentioned above, an improved understanding of the

role of different processes is often difficult to achieve with this approach. Thus process-based studies are needed to isolate specific aspect of the climate change problem.

In **Papers III** and **IV** a state of the art coupled chemistry-climate model (CCM) was used to examine the middle atmospheric response to a doubling of the atmospheric CO_2 content. **Paper III** focuses on the intrinsic radiative and photochemical impacts of the CO_2 increase on temperature and ozone, while **Paper IV** examines the impacts of changes in the surface climate on the middle atmosphere, which are mainly dynamical in nature. Both of these studies use a process-based approach, i.e. only a single perturbation to the climate system is considered. In **Paper III** the perturbation consists of the specified CO_2 increase and in **Paper IV** the change in sea surface conditions expected for a doubled CO_2 climate is applied to the model lower boundary. Hence, these simulations are not actual predictions of future climate changes, but rather are meant to examine the sensitivity of the atmosphere to the specified forcings. Still, as the CO_2 increase is the strongest known perturbation to the climate system, the results give an indication of what to expect from future changes in the middle atmosphere.

The outline of this thesis summary is as follows. In section 2 the general characteristics of the middle atmosphere are summarised. Then a short review of the variety of models commonly used in atmospheric research is given in section 3. This section also discusses the importance of model validation (**Paper I**) and describes the Canadian Middle Atmosphere Model, which is a CCM used in **Papers III** and **IV**. Thereafter a more detailed summary of the questions pursued in this thesis is presented; section 4 discusses the ozone deficit problem and presents results achieved with a photochemical box model (**Paper II**); section 5 discusses the climate sensitivity of the middle atmosphere, and presents results from **Papers III** and **IV**. The thesis is closed with conclusions and outlook for future research.

2   The middle atmosphere

2.1   Radiative processes

Figure 1 illustrates several important concepts of the ozone layer and its role for climate. Ozone is a strong absorber of UV radiation (panel c) and thus acts to increase the temperature with height in the stratosphere between 15 and 50 km (panel b) where much of the ozone resides (panel a). The layers below and above, the troposphere and mesosphere respectively, are characterised by
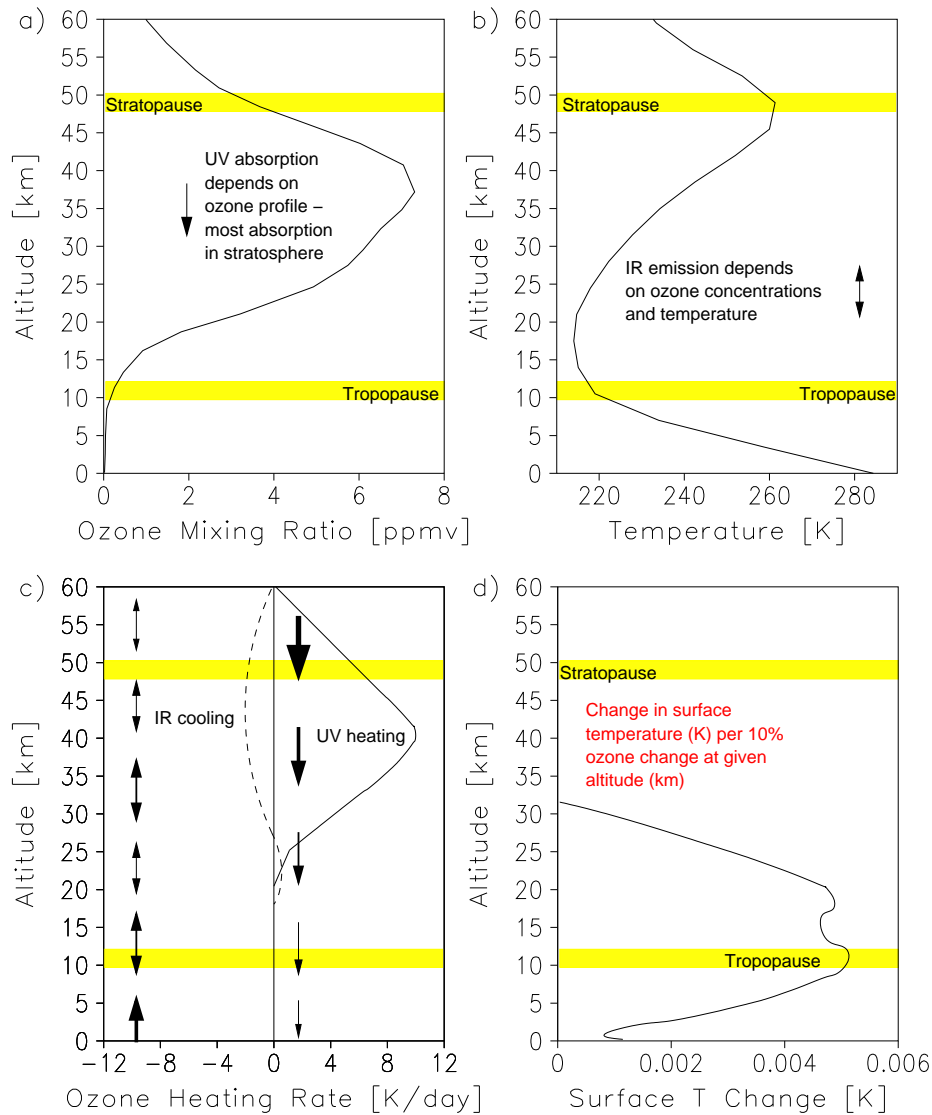
Figure 1. *Vertical profiles and schematics illustrating the role of ozone in climate (from IPCC/TEAP, 2005). (a) Typical mid-latitude ozone mixing ratio profile, based on an update of Fortuin and Langematz (1994); (b) atmospheric temperature profile, based on Fleming et al. (1990); (c) schematic showing the ultraviolet (UV) radiative flux through the atmosphere (single-headed arrows) and the infrared (IR) emission in the 9.6 μm ozone band (double-headed arrows), as well as the heating in the UV (solid curve) and IR (dashed curve) associated with these fluxes; (d) schematic of the change in surface temperature due to a 10% change in ozone concentration in individual 1 km thick altitude layers; The horizontal thick shaded lines in all panels indicate the tropopause and stratopause which separate the troposphere from the stratosphere and the stratosphere from the mesosphere respectively. Reproduced with the permission of the IPCC.*

Radiative Convective Model results after Manabe and Strickler 1964
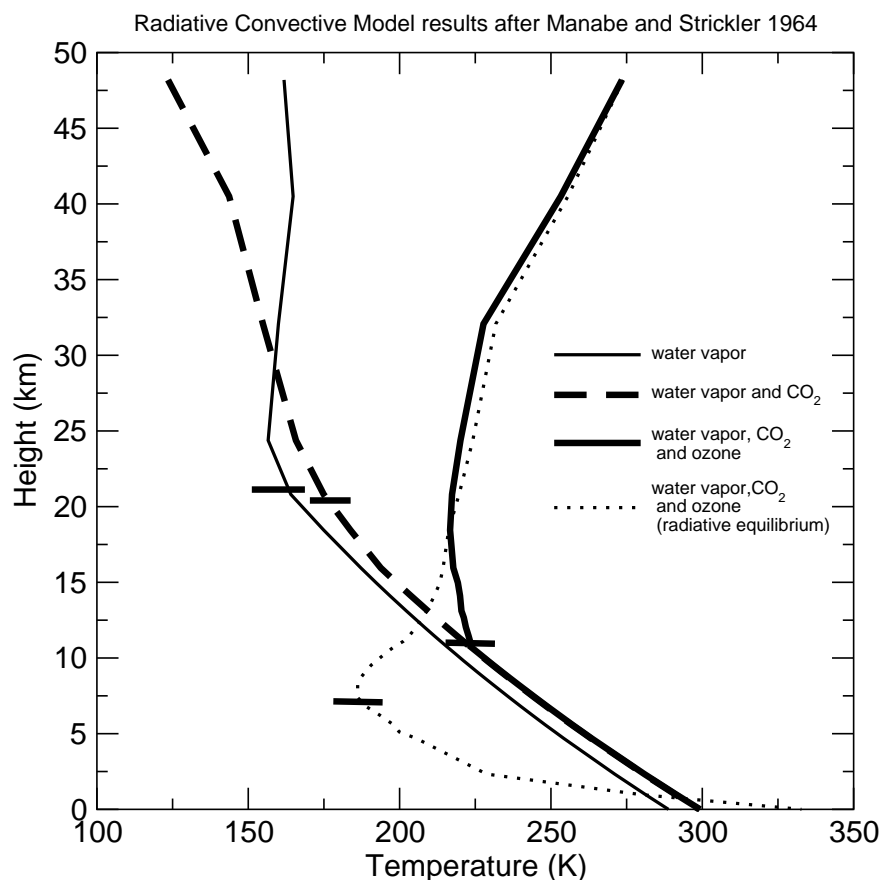
Figure 2. *Global and annual mean radiative equilibrium temperature pro-file (dotted) for an atmosphere containing water vapour, CO_2, and ozone and the corresponding radiative-convective equilibrium temperature (thick solid). Also shown are the radiative-convective equilibrium profiles ob-tained with ozone removed (dashed) and with ozone and CO_2 removed (thin solid). The thick black horizontal bars indicate the location of the lapse-rate tropopause for each profile. Reprinted with permission from Chem. Rev., 2003, 103(12), 4509–4532. Copyright 2003 American Chemical Society.*

decreasing temperatures with increasing height. Ozone is also a greenhouse gas that absorbs in the thermal infrared (IR) (panel c), trapping heat to warm the Earth's surface (panel d). The surface temperature is particularly sensitive to ozone changes in the upper troposphere and lower stratosphere region.

The classic study by Manabe and Strickler (1964) examined the contribution of different radiatively active gases to the shape of the vertical temperature profile in the troposphere and stratosphere. Their results are reproduced in Figure 2. Water vapour is the dominant greenhouse gas in the troposphere followed by CO_2. The figure shows that CO_2 provides an incremental warming effect of about 10 K to that given by water vapour alone, and also acts to cool

the stratosphere. Ozone, while having a relatively much smaller effect in the troposphere, is responsible for the existence of the stratosphere and thus for the reversal of the vertical temperature gradient.

2.2   Temperature climatology

Figure 3 shows the zonal mean temperature distribution in the atmosphere derived from a multitude of observations (see caption). The stratosphere and mesosphere are clearly visible, characterised by increasing and decreasing temperatures with height, respectively. The middle atmosphere is generally controlled by radiative processes, although there are important exceptions as discussed below. The temperature maximum at the stratopause located at around 1 hPa is mainly due to absorption of solar radiation by ozone. It reaches about 260 K on average, and exceeds 280 K at the summer pole. The tropopause temperature minimum of less than 200 K in the tropics near 100 hPa is primarily controlled by adiabatic cooling from tropical upwelling, ozone heating, CO_2 cooling and other radiative processes that involve clouds and water vapour (as discussed above). The general decrease of temperature with height in the mesosphere primarily reflects a decrease in solar absorption by ozone. In the winter stratosphere, the temperature is significantly greater than what is expected from radiative equilibrium considerations alone, and results from adiabatic warming associated with downwelling at high latitudes. The temperature minimum in the summer upper mesosphere is similarly driven by dynamical processes associated with adiabatic ascent. The polar summer mesopause region at 80–100 km is in fact the coldest region on Earth, despite intense solar illumination during the summer season. These low temperatures provide conditions under which noctilucent clouds can form, despite the extreme aridity at these altitudes.

2.3   General circulation

The large-scale circulation of the stratosphere is known as the Brewer-Dobson circulation, after two key discoveries in the middle of the past century. Brewer (1949) suggested that transport into the stratosphere is largely restricted to the tropical tropopause region where the temperatures are low enough to explain the observed low water vapour content in the stratosphere. Dobson (1956) noted that the observed maximum in the ozone column amounts at middle and high latitudes, away from the major ozone photochemical production region in the tropics, are consistent with a poleward flow. These findings are both indications of the general transport patterns in the stratosphere, with rising motion in the tropics and sinking motion in the extratropics, associated with a poleward mass

flux.

This pattern is depicted in Figure 4. The circulation is mechanically driven by dissipation of planetary-scale waves generated in the troposphere by topography, land-sea thermal contrasts and synoptic activity. Because of the asymmetric distribution of these features between the northern and southern hemispheres, planetary waves are stronger in the northern hemisphere. This makes the stratosphere in the Arctic more variable than in the Antarctic, which is the main reason why conditions for which severe ozone depletion occurs mainly in the latter region. Furthermore, because of filtering by stratospheric winds, planetary waves can only propagate into the winter stratosphere, which gives a seasonality in the Brewer-Dobson circulation, with the strongest circulation in the wintertime.
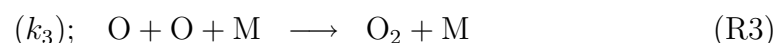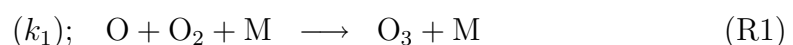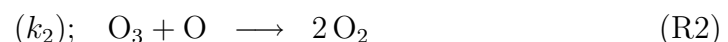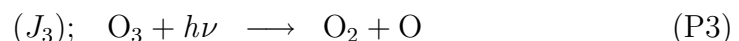
A similar wave-driven circulation exists in the mesosphere, however, extending from pole to pole, with ascending motion at the summer pole and descending motion at the winter pole. In this case the wave forcing comes primarily from gravity waves propagating up from the troposphere. The mesospheric circulation is not shown, but a hint of the pole-to-pole cell can be seen at 30–40 km in Figure 4.
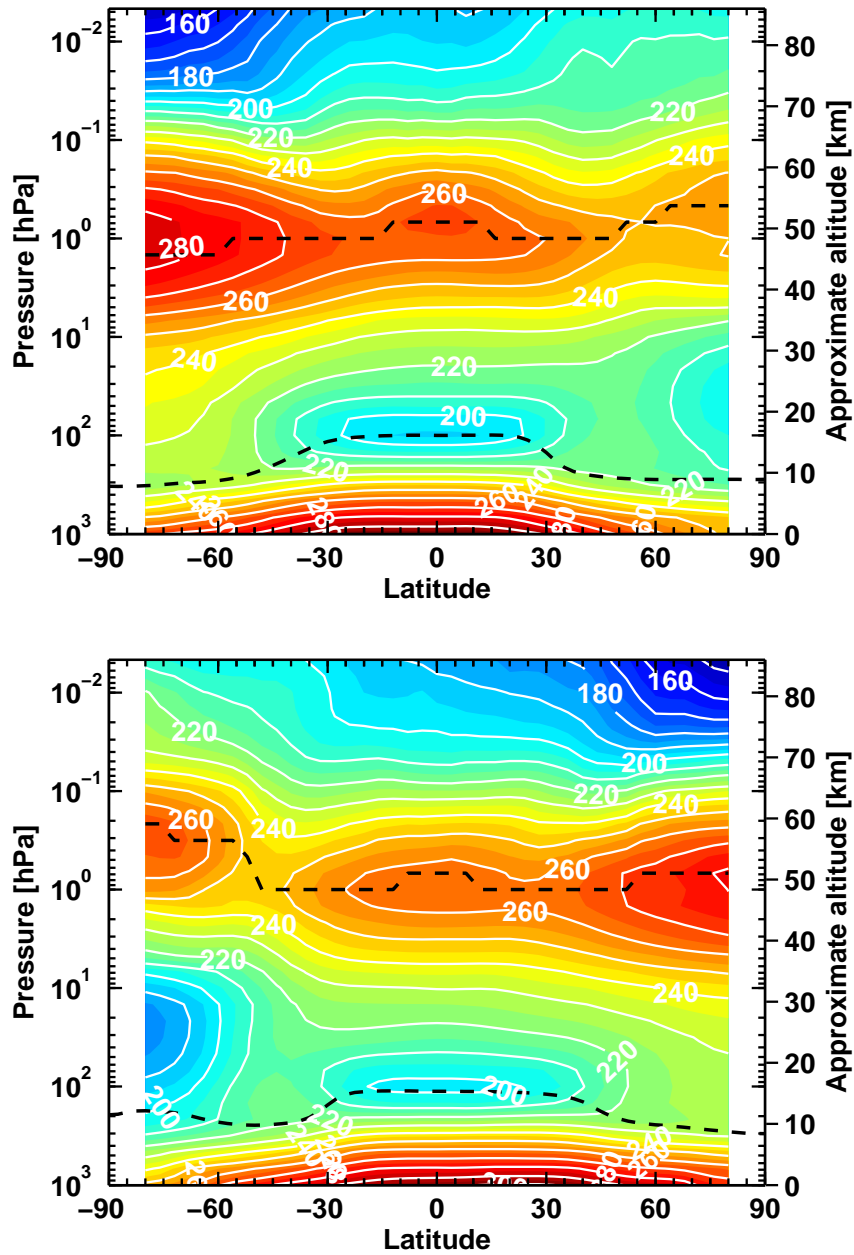
2.4   Ozone chemistry

The ozone distribution in the middle atmosphere is maintained by a balance between transport processes and photochemical production following from O_2 photolysis and loss reactions primarily involving, hydrogen, nitrogen and chlorine radical species. In general the photochemical production and loss terms dominate in the upper stratosphere and lower mesosphere, such that ozone can be thought of as being in a photochemical quasi-steady state in this region. The major reactions relevant for the gas-phase ozone budget at extrapolar latitudes are summarised below. Heterogeneous reactions of importance for polar ozone chemistry are not covered in this discussion.

2.4.1   Oxygen compounds

The most important oxygen reactions, known as the Chapman reactions from the work of Chapman (1930), are

$$(J_1); \quad O_2 + h\nu \quad \longrightarrow \quad 2\,O \tag{P1}$$

$$(J_3); \quad O_3 + h\nu \quad \longrightarrow \quad O_2 + O \tag{P3}$$

$$(k_2); \quad O_3 + O \quad \longrightarrow \quad 2\,O_2 \tag{R2}$$

$$(k_1); \quad O + O_2 + M \quad \longrightarrow \quad O_3 + M \tag{R1}$$

$$(k_3); \quad O + O + M \quad \longrightarrow \quad O_2 + M \tag{R3}$$

Figure 3. *Climatological zonal mean temperatures (Kelvin) for (top) January and (bottom) July. The data was adopted from Randel et al. (2004) using temperatures from UK Met Office (METO) analyses (1000– 1.5 hPa) and a combination of HALOE and MLS data from 1992–1997 above 1.5 hPa (see SPARC, 2002). The dashed lines denote the tropopause (taken from NCEP; see Randel et al., 2000) and stratopause (defined by the local temperature maximum near 50 km) respectively.*
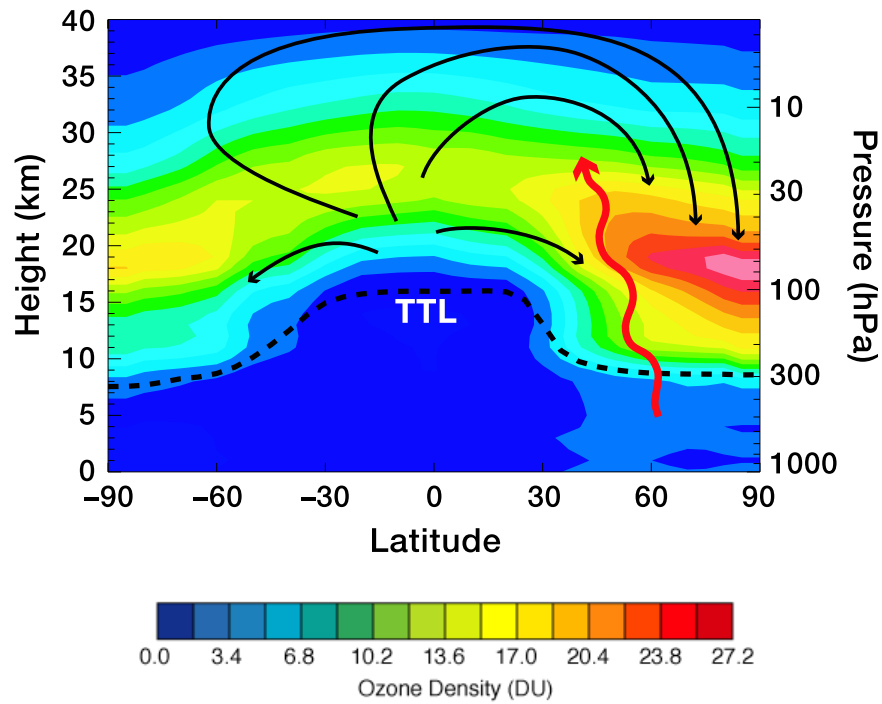
Figure 4. *Meridional cross-section of the atmosphere showing ozone density (colour contours; in Dobson units (DU) per km) during Northern Hemisphere (NH) winter (January to March), from the climatology of Fortuin and Kelder (1998). The dashed line denotes the tropopause, and TTL stands for tropical tropopause layer. The black arrows indicate the Brewer-Dobson circulation during NH winter, and the wiggly red arrow represents planetary waves that propagate from the troposphere into the winter stratosphere. The figure is from IPCC/TEAP (2005). Reproduced with the permission of the IPCC.*

In this scheme[1] atomic oxygen produced from O_2 photolysis (P1) is rapidly converted into ozone through (R1), where M represents a collision partner not affected by the reaction. Ozone itself is photolysed through reaction (P3), establishing a rapid photochemical equilibrium between ozone and atomic oxygen through (R1) and (P3). This is expressed as
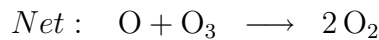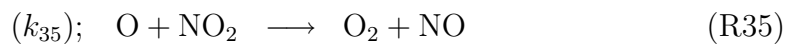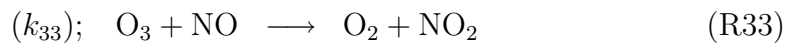
$$\frac{[O]}{[O_3]} = \frac{J_3}{k_1[M][O_2]} \tag{1}$$

where the square brackets indicate concentrations. The quantity $O_x = O + O_3$ is more long-lived and is referred to as *odd oxygen*. The reactions (R2) and (R3) are net loss mechanisms for odd oxygen, while (P3) and (R1) regulate the partitioning between atomic oxygen and ozone. Due to increased ozone photolysis and greater density with altitude (the latter affects the concentration of third bodies, M) ozone decreases rapidly with altitude from the production peak in the middle stratosphere, while atomic oxygen increases, leading to a strong height dependence of the partitioning of odd oxygen.

The Chapman reactions alone cannot explain the observed ozone abundances. Odd oxygen loss also occurs in catalytic reaction cycles, which involve NO_x, ClO_x or HO_x radicals. The following subsections discuss these catalytic cycles in more detail.

2.4.2 Nitrogen compounds

Reactive nitrogen NO_x (essentially $NO + NO_2$) contributes to odd oxygen loss in the stratosphere through the following catalytic reaction cycle

$$(k_{33}); \quad O_3 + NO \quad \longrightarrow \quad O_2 + NO_2 \tag{R33}$$

$$(k_{35}); \quad O + NO_2 \quad \longrightarrow \quad O_2 + NO \tag{R35}$$

$$Net: \quad O + O_3 \quad \longrightarrow \quad 2\,O_2$$

where the net effect of each cycle is to convert one ozone molecule and one oxygen atom into two oxygen molecules. The odd oxygen loss rate is determined by the rate limiting step (R35) and hence not only depends the NO_x concentration but also on the NO_x internal partitioning. NO_x is produced from N_2O via

$$(k_8); \quad O(^1D) + N_2O \longrightarrow 2\,NO \tag{R8}$$

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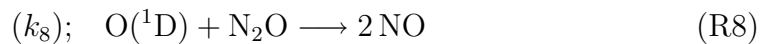
[1] The reaction numbers (listed on the right) here and in the following subsections are the same as given in **Paper III**, with one exception; for clarity, the O_2 and O_3 photolysis reactions are not separated in different product branches in this overview. The parameters k_i and J_i (listed on the left) denote reaction and photolysis rate coefficients respectively.

which in general is followed by (R33). However, around the stratopause, a significant fraction of the NO molecules reacts with ClO through

$$(k_{57}); \quad \text{ClO} + \text{NO} \longrightarrow \text{Cl} + \text{NO}_2 \qquad (\text{R57})$$
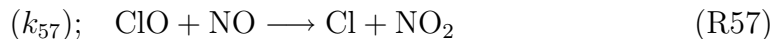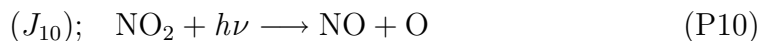
NO_2 either reacts with atomic oxygen through (R35) or is photolysed through

$$(J_{10}); \quad \text{NO}_2 + h\nu \longrightarrow \text{NO} + \text{O} \qquad (\text{P10})$$
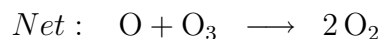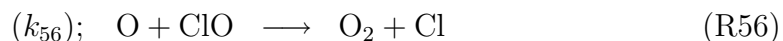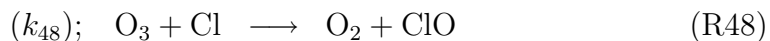
This means that only the fraction of NO_2 molecules that reacts with atomic oxygen through (R35) contributes to a net loss of odd oxygen. Reaction (R35) dominates above 45 km whereas NO_2 photolysis is more important below 40 km, where atomic oxygen is scarce. It follows that the relation between the concentrations of NO_2 and NO molecules can be written as

$$\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_{33}[\text{O}_3] + k_{57}[\text{ClO}]}{k_{35}[\text{O}] + J_{10}} \qquad (2)$$

Even though this simple expression neglects a few less important reactions involving NO and NO_2 conversions, it accurately reproduces the NO_2/NO ratio of comprehensive photochemical models (e.g. the box model used in **Paper II**) to within 10% accuracy at 20-40 km, which is the altitude region where the NO_x contribution to the odd oxygen loss rate has its greatest importance (see e.g. **Paper III**).

2.4.3   Chlorine compounds

In the upper stratosphere and lower mesosphere, reactive chlorine ClO_x (Cl + ClO) destroys odd oxygen in a cycle similar to the NO_x cycle above.

$$
\begin{aligned}
(k_{48}); \quad \text{O}_3 + \text{Cl} &\longrightarrow \text{O}_2 + \text{ClO} & (\text{R48}) \\
(k_{56}); \quad \text{O} + \text{ClO} &\longrightarrow \text{O}_2 + \text{Cl} & (\text{R56}) \\
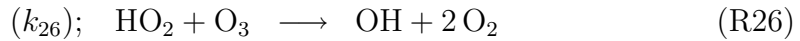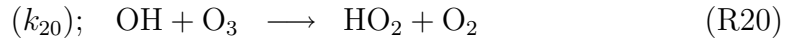Net: \quad \text{O} + \text{O}_3 &\longrightarrow 2\,\text{O}_2 &
\end{aligned}
$$

ClO_x radicals are produced mainly through the degradation of CFCs. The photochemical steady states of Cl and ClO are determined by (R48), (R56) and (R57) and the ClO/Cl ratio is thus expressed as

$$\frac{[\text{ClO}]}{[\text{Cl}]} = \frac{k_{48}[\text{O}_3]}{k_{56}[\text{O}] + k_{57}[\text{NO}]} \qquad (3)$$
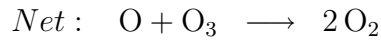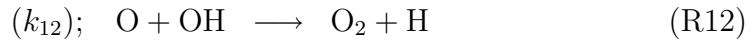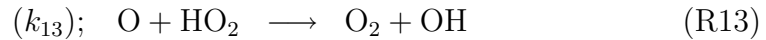
This expression generally reproduces the ClO/Cl ratio of more detailed model calculations (e.g. as in **Paper II**) to within 5% accuracy at 35-75 km.

2.4.4   Hydrogen compounds

Reactive hydrogen or HO_x (H + OH + HO_2) contributes to odd oxygen loss throughout the entire middle atmosphere. In the lower to middle stratosphere, odd oxygen loss occurs predominately through cycles involving ozone, including the reactions

$$(k_{20}); \quad OH + O_3 \quad \longrightarrow \quad HO_2 + O_2 \tag{R20}$$

$$(k_{26}); \quad HO_2 + O_3 \quad \longrightarrow \quad OH + 2\,O_2 \tag{R26}$$

In the upper stratosphere and mesosphere, the concentration of atomic oxygen is such that reactions involving atomic oxygen are more important. Above 40 km, during the day, the following reactions represent the dominating HO_x-driven odd oxygen loss cycle:

$$(k_{13}); \quad O + HO_2 \quad \longrightarrow \quad O_2 + OH \tag{R13}$$

$$(k_{12}); \quad O + OH \quad \longrightarrow \quad O_2 + H \tag{R12}$$

$$(k_{15}); \quad H + O_2 + M \quad \longrightarrow \quad HO_2 + M \tag{R15}$$

$$Net: \quad O + O_3 \quad \longrightarrow \quad 2\,O_2$$

Above 80 km the reaction rate between atomic hydrogen and ozone becomes comparable to that of (R15) and the following odd oxygen loss cycle must be considered:

$$(k_{12}); \quad O + OH \quad \longrightarrow \quad O_2 + H \tag{R12}$$

$$(k_{16}); \quad H + O_3 \quad \longrightarrow \quad OH + O_2 \tag{R16}$$

$$Net: \quad O + O_3 \quad \longrightarrow \quad 2\,O_2$$
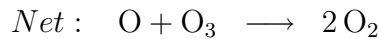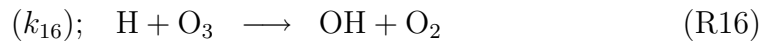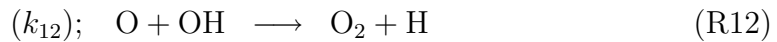
The OH concentration at 40-80 km is determined by a fast photochemical balance between (R12) and (R13) and consequently the OH/HO_2 ratio can be written as

$$\frac{[OH]}{[HO_2]} = \frac{k_{13}}{k_{12}} \tag{4}$$

HO_x production and loss rates balance each other in the stratosphere and in the mesosphere up to 75 km. In the stratosphere, HO_x production is dominated by

water vapour dissociation through the reaction with $O(^1D)$

$$(k_6); \quad H_2O + O(^1D) \longrightarrow 2\,OH \tag{R6}$$

Above 60 km water vapour photolysis takes over as the primary chemical production mechanism.

$$(J_4); \quad H_2O + h\nu \longrightarrow H + OH \tag{P4}$$

The HO_x loss rate is dominated by

$$(k_{24}); \quad OH + HO_2 \longrightarrow H_2O + O_2 \tag{R24}$$
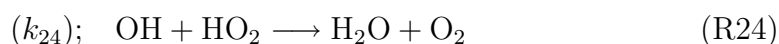
up to 75 km. Thus, the HO_x photochemical steady state equation becomes

$$k_{24}[OH][HO_2] = (J_4 + k_6[O(^1D)])[H_2O] \tag{5}$$

where the first term on the right hand side dominates the expression above 60 km and the second term dominates below 60 km.
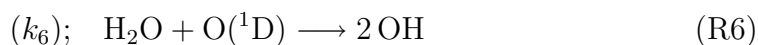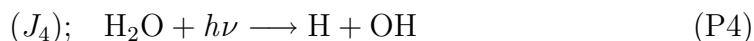
The few sets of reactions presented in the subsections above constitute a necessary basis for a first order understanding of ozone chemistry in the upper stratosphere and mesosphere. In addition, there are several interactions between the NO_x, ClO_x and HO_x families, to form less reactive intermediate compounds, or *reservoir* species, such as HCl, HNO_3 and $ClONO_2$. This was not covered in this brief overview, but is well covered in textbooks (e.g. Brasseur and Solomon, 1986).

2.5   Ozone climatology

Figure 5 shows the ozone distribution in the stratosphere and mesosphere observed from space. The ozone mixing ratio exhibits a maximum of about 10 ppmv (part per million by volume) in the tropics near 10 hPa, due to a local maximum in photochemical production (see **Paper III**). The ozone mixing ratio decreases with altitude in the mesosphere, mainly due to decreased density and increased ozone photolysis. In the lower stratosphere ozone is controlled mainly by dynamical processes and thus ozone isopleths tilt downward from the equator toward the polar regions reflecting the effect of the Brewer-Dobson circulation (see also Figure 4).
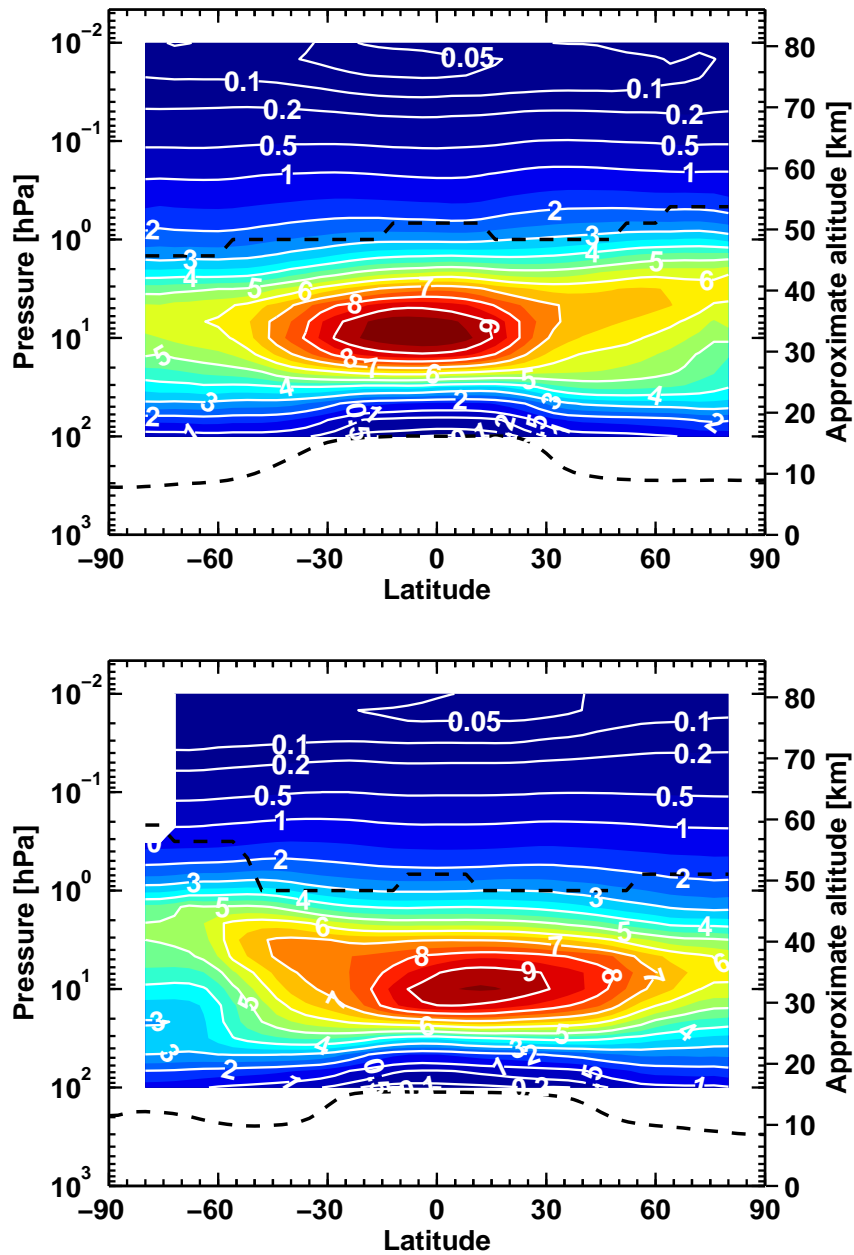
Figure 5. *Climatological zonal mean daytime ozone mixing ratios (ppmv) for (top) January and (bottom) July. The data was adopted from the UARS Reference Atmosphere Project (URAP) climatology (available at* `http://www.sparc.sunysb.edu/html/uars_index.html`*) using a combination of HALOE and MLS data. Contour intervals are 1 ppmv with the addition of 0.5, 0.2, 0.1 and 0.05 ppmv contours in the mesosphere. The dashed lines denote the tropopause and stratopause as in Figure 3.*

3 Modelling

A central theme in this thesis is the use of numerical models to study the middle atmosphere and its sensitivity to perturbations. In order to adequately represent middle atmospheric processes, as discussed in section 2, models must incorporate atmospheric transport, radiation, and chemistry in a 3-dimensional (3-D) framework. Some of these processes should be coupled in order to account for feedback mechanisms. For example, chemically integrated ozone should be used in the radiation calculations to account for ozone-temperature feedbacks as described in **Paper III**. However, it can sometimes also be useful to use less comprehensive models with a simplified representation of the atmosphere in order to isolate particular processes or phenomena. For example, in **Paper II** a (zero-dimensional) box model is used to examine ozone photochemistry at specific latitudes and heights in the upper stratosphere and lower mesosphere.

The hierarchy of models include box models, 1-dimensional, 2-dimensional and 3-dimensional models. Due to computational limitations lower dimensional models are often used, although this restricts the complexity of the atmospheric processes that can be resolved. A common feature of most of the different model types (except box models) is that the spatial dimensions are discretised in boxes and laws of physics and chemistry are applied to the boxes to simulate local production and destruction of constituents and transport between the boxes. Some of the common model types are reviewed below. At the end of this section the Canadian Middle Atmosphere Model, which is used in **Papers III** and **IV**, is introduced and the importance of model validation is discussed.

3.1 1-dimensional and box models

1-dimensional (1-D) models provide a latitude-longitude averaged representation of the atmosphere. The central "part" in the 1-D framework is the vertical continuity equation, which can be written as

$$\frac{\partial n_i(z)}{\partial t} = P_i(z) - L_i(z)n_i(z) - \frac{\partial}{\partial z}\left[K(z)N(z)\frac{\partial f_i(z)}{\partial z}\right], \qquad (6)$$

where n_i is the concentration of constituent i. The terms P_i and $L_i n_i$ represent the local production and loss rates of species i and the derivative with respect to height, z, on the right hand side of the equation represent vertical transport through mixing processes. f_i is the mixing ratio of species i and N is the atmospheric number density. The mixing ratio relates to the concentration as $f_i = n_i/N$. K is the diffusion coefficient. Molecular diffusion is negligible below the mesopause, so K refers to turbulent mixing processes and circulation effects.

This representation of the vertical distribution of chemical compounds is highly simplified and transport through large-scale circulation cannot be represented explicitly. The diffusion term is a means of incorporating transport on empirical grounds, where the diffusion coefficient is generally derived empirically from observed profiles of trace gases. This 1-D representation of the atmosphere has several problems. First, a single diffusion coefficient is generally not sufficient to adequately represent the vertical distribution of different species, and thus these models are best used in regions of the atmosphere where the P_i and $L_i n_i$ terms dominate over the transport term, i.e. generally in regions controlled by photochemical processes. Part of the problem is that meridional circulation, e.g. through the Brewer-Dobson circulation, affects the vertical distributions of chemical constituents, but cannot be represented in a straightforward way in 1-D models. Despite their limitations, 1-D models provided much of the early understanding of the trace constituents in the atmosphere and were used extensively until the 1980s.

One way to address some of the deficiencies with the incomplete representation of transport processes in 1-D models is to use zero-dimensional models (box models). Box models can be advected along trajectories following the mean wind, and thus are useful tools to study local processes within a moving air parcel in isolation from the effects of transport. Also, several box models can be stacked on top of each other to achieve something similar to a 1-D model, but with the difference that transport between the boxes is not considered. Still, radiative processes interact between the boxes and this approach can thus be used in regions of the atmosphere that are under photochemical control (**Paper II**).

3.2   2-dimensional models

2-dimensional (2-D) models use a zonal mean representation of the atmosphere and thus resolve the vertical and latitudinal spatial directions. The challenge with these models is to adequately represent 3-dimensional phenomena such as winds, waves and dissipation in two dimensions. This thesis does not use this type of model, but WMO (1999, Chapter 7) summarises their general characteristics. Because of the smaller computational load of 2-D models as compared to 3-D models (see below), 2-D models have been used extensively, e.g. for assessments of ozone trends and predictions of long-term future changes in the middle atmosphere in response to trends in chemical species associated with human activity, e.g. CFCs, CH_4 and N_2O (see e.g. WMO, 2003).

Although the longitudinal dimension is not considered in 2-D models most of them include a diurnal component for chemistry. However, some 2-D models have used diurnally averaged chemistry, which has several drawbacks (Smith,

1995). The main disadvantage of 2-D models, however, is that the dynamical forcing (section 2.3) must be parameterised[2]. These models are highly parameterised and can therefore be tuned in an arbitrary and sometimes unphysical manner. Thus, the distribution of source gases important for ozone, e.g. CFCs, CH_4 and N_2O can be quite model dependent. Also, 2-D models may not represent chemical fields well where zonal variability is large, e.g. near the tropopause and in the winter stratosphere.

3.3   3-dimensional models

3-D models include for example general circulation models (GCMs) and chemistry-coupled climate models (CCMs). GCMs are in many aspects similar to numerical weather prediction (NWP) models. But rather than to produce daily forecasts of weather anomalies, GCMs are in general designed to simulate the climatological mean state of the atmosphere and to predict long-term mean changes, ranging over years and decades. GCMs use a three-dimensional representation of large-scale radiative and dynamical processes with a spatial resolution of a few hundred kilometres. Sub-grid processes and phenomena, such as convection and small-scale gravity waves, are parameterised. 3-D models can represent waves and meridional transport on a more physical basis than 2-D models. Tropospheric GCMs have been around since the 1960s while GCMs for the middle atmosphere were introduced in the 1980s. CCMs are interactively coupled GCMs with chemistry and first appeared during the 1990s.

3.4   The Canadian Middle Atmosphere Model

In **Papers III** and **IV** of this thesis a CCM, the Canadian Middle Atmosphere Model (CMAM), is used to study the impact of CO_2 increases on the middle atmosphere. This model is based on a tropospheric GCM for which the lid has been raised to approximately 100 km and the model dynamics, radiation and chemistry have been updated to incorporate processes of importance in the middle atmosphere. For example, the CMAM incorporates the important dynamical coupling between the troposphere and the middle atmosphere through the propagation and dissipation of planetary and gravity waves (as described in section 2.3). It also includes a comprehensive set of chemical reactions to represent middle atmospheric chemistry (as described in section 2.4) and ozone and water vapour are treated interactively between the chemical and radiative parts of the model. More detailed descriptions of the CMAM are given in **Papers III** and **IV**.

---

[2]Numerical prescription of unresolved quantities or processes in terms of resolved quantities.

3.5 Validation

In order to perform predictions of future changes to the atmosphere using models, some level of confidence must be established in how well the models can reproduce the current climate. Thus, model validation is an important aspect of model development. Also, scientific progress is often achieved through the understanding of discrepancies between model results and measurements. Key parameters in CCMs include the temperature, winds, and radiatively active gases such as CO_2, H_2O, CH_4, N_2O, CFCs and ozone. These species can only be well represented in models if atmospheric chemistry is included, and thus many chemical trace species (some of which are mentioned in section 2.4) need to be assessed in the model simulations. Validating models is a non-trivial task in the middle atmosphere, especially in the mesosphere, where observations are limited.

CCMs specify dynamical and chemical forcings but do not specify observed meteorological conditions. Therefore, comparisons with observations must be performed in a statistical manner. This is problematic since the interannual variability in the middle atmosphere can be large and thus a robust climatology can require many years or decades of model simulations and observations. This is particularly a problem when assessing the variable polar regions, as discussed in **Paper IV**. Eyring *et al.* (2005) pointed out that the validation of CCMs requires a process-based approach. By focusing on individual processes, models can be more directly compared to observations than when comparing mean fields of basic model variables, such as temperature, wind and ozone mixing ratios.

Paper I is the outcome of an effort to assess the CMAM model performance. In this paper the model temperature was compared to two datasets derived from observations; the CIRA–86 temperature climatology and the mean temperature fields obtained by the HALogen Occultation Experiment (HALOE) instrument on the Upper Atmosphere Research Satellite (UARS). The results show that the model reproduces the mean HALOE observations adequately (within 10 K) in the upper stratosphere and mesosphere. It was also shown that the CIRA–86 dataset, has a warm anomaly in the upper mesosphere over the tropics compared to the HALOE data, which is particularly pronounced during equinox.

Also, a process-based approach was used to examine the model simulation of atmospheric solar diurnal tides, which were diagnosed from the same set of HALOE observations. HALOE is a solar occultation instrument and thus observes the atmosphere as the sun rises and sets behind the Earth's limb. Computing the differences between the sunrise and sunset temperature measurements thus allows to identify diurnal variations, such as the diurnal tide. The study shows that the model tidal structure resembles the observed pattern with alter-

nating positive and negative anomalies in the tropical upper stratosphere and mesosphere, and weaker anomalies in the subtropics and middle latitudes (Figures 3e and f, **Paper I**). The vertical wavelength of the tropical wave pattern is approximately 30 km, in good agreement with the observations. However, the tropical wave amplitude in the upper mesosphere is about twice as large as in the observations. Possible explanations for this discrepancy are discussed. The tidal analysis also suggests that the CIRA–86 warm anomaly in the upper mesosphere tropics may be caused by tidal influences.

4   The Ozone deficit problem

The scientific understanding of the impact of changes in greenhouse gases and ozone depletion in the upper stratosphere is compromised by the fact that CCMs tend to underestimate the ozone concentration in this region, a problem known as the "Ozone deficit problem". Discrepancies of several tens of percent have been reported. Significant efforts have been made over the past two decades to address this important modelling problem. In particular, revisions of the ozone chemistry in the region have been suggested. For example, substantial changes to the chemical rate coefficients of the O_x and HO_x chemistry that dominate ozone production and loss rates in the upper stratosphere and mesosphere have been proposed. Also, some studies have looked for new mechanisms for ozone production other than that following from photolysis of O_2 (see section 2.4).

However, recent model simulations, some of which use specialised photochemical box models, indicate that the use of current chemical reaction rate data and recent satellite ozone observations results in rather good agreement between models and ozone observations in the 40 km region, thus cancelling the need for substantial revisions of the reaction schemes and rate coefficients. Some of these results also indicate close agreements with the ozone observations at 55 km, while several other studies, however, report significant model underestimations in the lower mesosphere.

In **Paper II** the ozone deficit problem is revisited using a comprehensive photochemical box model. The model is constrained by HALOE observations of key variables of the background atmosphere such as temperature and long-lived tracers, thereby isolating the chemical aspects of the problem from possible model deficiencies in atmospheric transport. The study also assesses various model and observational errors, and uses a statistical approach to identify which reactions are the most uncertain and thus affect the uncertainty in the model ozone calculation the most. The model produces ozone values that are approximately 10% below the HALOE observations in the 40–55 km region (e.g. Figure 8, **Pa-**

per II), and thus confirms the recent findings indicating a significant reduction in the ozone deficit problem in the upper stratosphere. However, at 60–75 km the model underestimates the observations by up to 35% suggesting that some problems with the current understanding of mesospheric processes still exists. For this region it is noted that uncertainties in the analysis are large. The measurement errors for both ozone and water vapour (the latter is used for model constraints) are substantial. The paper goes on to discuss the importance of various model uncertainties, induced from numerical approximations and lack of implemented processes as well as the importance of inaccuracies in the measured chemical rate coefficients used to integrate the model chemistry. It is shown that uncertainties in the rate coefficients propagate to produce uncertainties in the simulated ozone values ranging from about 6% at 30 km to about 20% at 75 km. The paper finally suggests improvements to measurements and models that are needed to improve the understanding of the mesospheric ozone deficit.

5   Climate change in the middle atmosphere

Climate change due to increases of CO_2 and other greenhouse gases in the atmosphere is potentially one of the most severe environmental problems of today. Naturally, the focus has been primarily on the warming at the Earth's surface and the associated effects in the troposphere. However, since the global mean stratosphere and lower mesosphere are close to radiative equilibrium (see e.g. Fomichev *et al.*, 2002), changes in radiatively active gases have a more direct impact on the climate in those regions than in the troposphere. This should lead to a stronger and more detectable climate change signal in the middle atmosphere. As discussed in section 1, this has been confirmed by observations, which show substantial temperature trends over the past few decades in the middle atmosphere. While the CO_2 increase acts to warm the troposphere it acts to cool most of the middle atmosphere. The latter is because CO_2 emits IR radiation to space and thus is the main heat loss process for the region.

Although the direct radiative impact of the CO_2 increase is the dominating effect throughout most of the middle atmosphere, there are several other aspects of climate change in this region that are important. For example, the temperature response in the middle atmosphere can be modulated by locally induced changes in the residual circulation and by photochemical feedbacks via changes in the ozone abundance. In addition, the middle atmosphere could be affected by changes taking place in the troposphere, for example through changes in atmospheric wave generation and propagation or through adjustments of the

characteristics of the tropical tropopause and thereby of middle atmospheric water vapour.

In **Papers III** and **IV** some aspects of the climate change problem in the middle atmosphere have been address by analysing the middle atmospheric response to a doubling of the atmospheric CO_2 content, using the CMAM. The CO_2 abundance in the atmosphere has already risen by about 30% since the pre-industrial level of about 280 ppmv, so a doubling is not an unreasonable perturbation to investigate. The impact of CO_2 doubling on the middle atmosphere has been investigated by several modelling groups, and reviews of some of the results can be found in the introduction sections of **Papers III** and **IV**. However, many of the earlier results were achieved with 2-D models and 3-D models without the necessary dynamical, radiative and photochemical interactions that are implemented in the CMAM.

The CMAM was run for several integrations with different configurations in order to isolate two aspects of the CO_2 impact; the change in atmospheric CO_2 content and the associated changes in sea surface conditions (sea surface temperatures and sea ice distribution) were implemented separately as well as together (see Table 1, **Paper IV**, for further details). As the CMAM, like most other middle atmosphere CCMs, does not have an interactive ocean model coupled to it, sea surface conditions must be specified. For this study the sea surface conditions for the doubled CO_2 climate were taken from a model simulation with the coupled atmosphere-ocean GCM that CMAM is based upon. As the surface temperature effectively controls the temperature throughout much of the troposphere, through convection and other processes that transport heat vertically, changing the surface temperatures in the model can be thought of as perturbing the climate throughout the troposphere. The separation of the intrinsic radiative effect of the CO_2 increase and the effect of changes in the troposphere is possible since the two effects are approximately additive. This is shown in **Paper IV** (Figure 9, **Paper IV**).

5.1   Radiative-photochemical response

Paper III examines the radiative-photochemical response to CO_2 doubling in the extrapolar regions. For this, the model simulations with CO_2 increase but without changes in sea surface conditions were analysed. In addition, identical model runs without interactive chemistry (Table 1, **Paper III**) were used to quantify the impact of the ozone radiative feedback on temperature changes. The model response to the CO_2 doubling shows, as expected, a cooling throughout the middle atmosphere with a maximum temperature decrease of 10–12 K near the stratopause (Figure 2, **Paper III**). Due to the temperature dependency

of gas-phase ozone chemistry, ozone increases by 15–20% in the upper strato-
sphere and by 10–15% in the lower mesosphere (Figure 3, **Paper III**). These
values are in agreement with earlier studies. The additional heating from the
ozone increase, primarily through increased absorption of solar UV radiation
but also through decreased IR cooling (this is shown in **Paper IV**), leads to
a net temperature response that is up to 4.5 K weaker than without the ozone
radiative feedback (Figure 4, **Paper III**). The difference accounts for up to 40%
of the total response, which shows that interactive chemistry and the negative
feedback on temperature provided by ozone changes are important and must be
considered in predictions of future climate change in the middle atmosphere.

A secondary focus of **Paper III** is to examine the photochemical mecha-
nisms responsible for the ozone increase. It is shown that the ozone response,
both in the stratospheric and mesospheric regions, can be understood primar-
ily from changes in the rate of a single three-body reaction, $O+O_2+M \rightarrow O_3+M$
(R1). The rate coefficient of this reaction, k_1, has a strong negative temper-
ature dependency (Figure 7, **Paper III**). Above about 60 km (where atomic
oxygen dominates the odd oxygen reservoir) changes in k_1 have a direct impact
on ozone; decreased temperatures lead to a faster rate of (R1) and thus to more
ozone production.

Below 60 km (where ozone dominates the odd oxygen reservoir) the impact
of the temperature-induced changes in k_1 is indirect. It is sometimes quoted that
the strong ozone sensitivity to temperature changes in the (extrapolar) strato-
sphere is due to the temperature dependence of the ozone loss rate through the
Chapman $O+O_3$ reaction and the catalytic ozone destruction cycles. This is
true, but the statement is somewhat confusing. Although the rate coefficients of
the NO_x cycle and the Chapman loss reaction have significant temperature de-
pendencies, the major mechanism is through changes in the rate of (R1), which
is not part of these cycles, but mainly acts to control the abundance of atomic
oxygen in the stratosphere. As the temperature decreases, the rate of (R1) in-
creases and thus the abundance of atomic oxygen decreases. In general, the rate
limiting reactions of the NO_x, ClO_x and HO_x catalytic cycles are the reactions
including atomic oxygen and therefore the catalytic cycling runs slower, and as
a results both odd oxygen and ozone increase. Hence, the initial mechanism is
through changes in (R1), while the decreased odd oxygen loss rate is manifested
through the Chapman reaction and the various catalytic cycles.

5.2   Response to changes in tropospheric climate

In **Paper IV** model results including both the CO_2 increase and the associated
changes in tropospheric climate are considered. The study reports on the overall

changes in temperature, ozone and water vapour in the middle atmosphere (Figures 5, 6, 7, **Paper IV**). With the exception of a tropospheric warming of about 2–4 K, the temperature and ozone responses are similar to that achieved without changes in sea surface conditions, as reported in **Paper III**, since the radiative-photochemical response in the middle atmosphere generally is much stronger than the impacts from tropospheric changes. For water vapour, however, the changes are quite different when tropospheric effects are taken into account. In response to the warmer sea surface temperatures the model tropopause becomes warmer and higher. The tropical tropopause cold trap thus allows for more water vapour input into the stratosphere. This leads to a relatively uniform water vapour increase throughout the stratosphere of about 0.3–0.4 ppmv. However, this has no noticeable effect on the global mean radiative cooling above 30 hPa ($\sim$25 km). The impact on ozone through increased HO_x production is also small. Increased water vapour in the middle atmosphere could however have other significant effects. For example, it has been suggested that trends in the tropical tropopause temperature could lead to changes in the occurrence of noctilucent clouds in the summer mesopause region.

Another outcome of **Paper IV** is an important negative result. The study addresses the question whether changes in wave flux from the troposphere could affect the circulation of the stratosphere and thus adiabatic heating rates and temperatures in the polar regions. For this purpose, model simulations including the changes in sea surface conditions (and the associated tropospheric changes), but without a doubling of the atmospheric CO_2 content, are used. However, although the analysed model datasets are 30 years long, the large interannual variability in the polar regions prevents the detection of a significant response. Polar temperatures are extremely important for the degree of ozone depletion occurring at the poles since the polar stratospheric clouds that facilitate chlorine activation form only at very low temperatures. The possibility that climate change could have an impact on ozone loss in the polar regions through changes in wave propagation has thus been a subject of much interest lately. It has been speculated that such effects could result in polar ozone depletion in the Arctic as severe as observed in the Antarctic. However, there is currently no consensus between models on even the sign of the simulated temperature changes in the Arctic (Austin *et al.*, 2003). The version of the CMAM used for **Paper III** and **IV** does not include heterogeneous chemistry and thus does not permit a full analysis of changes in polar ozone chemistry. On the other hand, the dynamical mechanisms necessary to represent changes in circulation (i.e. mainly the generation, propagation and dissipation of planetary waves) are incorporated in the model. Previous model studies have indicated both increased and

decreased ozone loss during the polar winter, due to circulation changes (e.g. Shindell *et al.*, 1998; Schnadt and Dameris, 2003). However, many of these results where achieved with relatively short model runs, ranging from 5–30 years in length. The results of **Paper IV** show that a clear impact of tropospheric climate change on the polar regions in the middle atmosphere cannot be concluded. The study emphasises the need for longer model integrations in order to achieve a statistically significant signal.

6 Conclusions and outlook

In this thesis I have used atmospheric models to examine certain features of the middle atmosphere climatology and response to human-induced perturbations. In particular the impact of a doubling of CO_2 and the associated changes in sea surface conditions on the middle atmosphere were studied using a coupled chemistry-climate model. Also, a photochemical box model was developed and used to examine the ozone budget in the upper stratosphere and lower mesosphere.

In **Paper I** it was shown that the Canadian Middle Atmosphere Model (CMAM) is capable of reproducing some general features of the observed middle atmospheric temperature structure. The CMAM was compared to CIRA–86 and HALOE temperature data. The model reproduced the HALOE zonal mean temperatures in the middle atmosphere (to within 10 K) as well as fluctuations around the mean state in terms of atmospheric (diurnal) tides. Analysis of the HALOE sunrise and sunset solar occultation measurements and synthetic observations extracted from the model revealed a clear signature of the solar diurnal tide in the model and in the observations. The results also indicated a substantial warm bias in the commonly used CIRA–86 temperature climatology in the upper mesosphere near equinox, possibly related to tides. This study serves to show the capability and suitability of the model to perform process/prediction studies of the middle atmosphere.

In **Paper II** a detailed examination of the ozone budget and its uncertainties in the upper stratosphere and mesosphere was performed. The results confirmed the current understanding that the long-standing ozone deficit problem in the upper stratosphere has been substantially reduced with the use of current rate coefficient recommendations and recent satellite data; the model used in **Paper II** calculated ozone concentrations that were 10% below HALOE observation at 40–55 km. However, at 60–75 km the discrepancies between the model and the observations were larger, up to 35%. Unfortunately the uncertainties in both model input parameters and the HALOE observations were too large

in this region for a definite attribution of this discrepancy. Possible candidates were discussed, including the parameterisation of the Schumann-Runge bands for O_2 photolysis, uncertainties in water vapour photolysis and inaccuracies in chemical rate coefficients.

There are some important implications of this study for future measurements. To improve our understanding of mesospheric ozone chemistry, improved accuracy of both ozone and water vapour measurement are needed. New generations of satellite instruments are currently in orbit. For example, initial results from the solar occultation ACE-FTS (Bernath *et al.*, 2005) instrument indicate that they could be useful for a similar study as in **Paper II**. However, the ACE-FTS retrievals are still being developed, so this lies in the future. Also, additional measurements of HO_x species and atomic oxygen would be very useful to more completely assess the ozone and odd oxygen budgets in the mesosphere.

Furthermore, a partial least squares regression analysis was successfully used in **Paper II** to identify the measured chemical rate coefficients that contribute most to the uncertainty in the model ozone calculations. These reactions are listed in **Paper II** and should be the primary targets for new kinetic measurements.

It is worth noting that in parallel to the ozone deficit problem and with the increasing availability of measurements from the mesosphere, another chemical modelling puzzle has appeared on the horizon, possibly related to the ozone deficit problem. While photochemical models tend to underestimate ozone, they also underestimate HO_2 and overestimate OH in the mesosphere, sometimes referred to as the "HO_x dilemma" (see e.g. Jucks *et al.*, 1998; and references therein). However this topic lies outside the scope of this study, but is an issue that needs to be resolved by future research, and that can possibly shed some light on the mesospheric ozone deficit obtained in **Paper II**.

In **Paper III** the CMAM was used to examine the response of the middle atmosphere to a doubling of the CO_2 mixing ratio. Model simulations with and without interactive chemistry were performed, and the results emphasised the importance of the negative radiative feedback through ozone changes on the calculated temperature changes. The CO_2 increase led to a substantial temperature decrease throughout most of the middle atmosphere, which however, was up to 40% smaller when ozone was treated interactively than when a fixed ozone climatology was used. A photochemical analysis showed that the ozone feedback is mainly associated with the $O+O_2+M{\rightarrow}O_3+M$ reaction that controls odd oxygen partitioning.

In **Paper IV** additional doubled CO_2 experiments were performed, but now with the changes in the sea surface conditions associated with tropospheric

warming taken into account. Notable differences from the results presented in **Paper III**, are related to mechanisms by which the middle atmosphere is coupled to the troposphere. For example, the tropopause was warmer and higher in the doubled CO_2 simulations with surface condition changes taken into account, which led to an increased influx of water vapour into the stratosphere through the tropical tropopause region. It was also shown that the radiative-photochemical response of the middle atmosphere and the response to tropospheric changes are approximately additive, and that the ozone radiative feedback occurs not only through increased solar heating, but also through decreased IR cooling.

Also, the paper addressed some statistical issues regarding the model's internal variability. Although some recent studies have indicated that climate change could lead to changes in the circulation of the stratosphere and to changes in polar temperatures and polar ozone loss, in **Paper IV** a statistically significant response to changes in sea surface conditions could not be achieved for the polar regions in the stratosphere. This is despite the fact that the analysis was based on 30-year model datasets, which is longer than used in most other doubled CO_2 studies. Thus it was concluded that longer simulations are needed to establish with certainty how tropospheric climate change affects temperatures and ozone in the polar stratosphere.

Finally, a word on current developments with the CMAM. In 2006 a new WMO ozone assessment report is due to be published. CMAM is taking part in this significant effort to assess our understanding of ozone depletion and climate change in the stratosphere. Currently, CMAM is running multi-year transient scenarios of the past and future, ranging from 1960 to 2050, including many important forcings, such as CO_2, CH_4, N_2O, CFCs and sea surface changes. Several ensembles of such simulations will be performed in order to improve the statistical significance of the atmospheric response. I hope that the work presented in this thesis will make the interpretation of these new simulations more straightforward and enlightening.

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