Modelling
the middle atmosphere
and its sensitivity to
climate change

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Doctoral thesis by
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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 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→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.
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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).

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Andreas Jonsson
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II Revisiting the “Ozone deficit problem” in the middle atmosphere: An investigation of uncertainties in photochemical modelling
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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 mesosphere 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\(_2\)O) and nitrous oxide (N\(_2\)O) 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$_2$O 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
2. The middle atmosphere

UV absorption depends on ozone profile – most absorption in stratosphere. IR emission depends on ozone concentrations and temperature. Change in surface temperature (K) per 10% ozone change at given altitude (km).

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.
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...
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

\[(J_1); \quad O_2 + h\nu \longrightarrow 2O \quad \text{(P1)}\]
\[(J_3); \quad O_3 + h\nu \longrightarrow O_2 + O \quad \text{(P3)}\]
\[(k_2); \quad O_3 + O \longrightarrow 2O_2 \quad \text{(R2)}\]
\[(k_1); \quad O + O_2 + M \longrightarrow O_3 + M \quad \text{(R1)}\]
\[(k_3); \quad O + O + M \longrightarrow O_2 + M \quad \text{(R3)}\]
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

\[
\frac{[O]}{[O_3]} = \frac{J_3}{k_1[M][O_2]}
\]  

(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

\[
\begin{align*}
(k_{33}); \quad O_3 + NO & \rightarrow O_2 + NO_2 \\
(k_{35}); \quad O + NO_2 & \rightarrow O_2 + NO \\
Net: \quad O + O_3 & \rightarrow 2O_2
\end{align*}
\]  

(R33)  

(R35)

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

\[
(k_8); \quad O(^1D) + N_2O \rightarrow 2NO
\]  

(R8)

\(^1\)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 \(k_1\) 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

\[ (k_{57}); \quad \text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \]  

(NO\textsubscript{2} either reacts with atomic oxygen through (R35) or is photolysed through

\[ (J_{10}); \quad \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]  

This means that only the fraction of NO\textsubscript{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\textsubscript{2} photolysis is more important below 40 km, where atomic oxygen is scarce. It follows that the relation between the concentrations of NO\textsubscript{2} and NO molecules can be written as

\[
\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_{33}[O_3] + k_{57}[\text{ClO}]}{k_{35}[\text{O}] + J_{10}} \tag{2}
\]

Even though this simple expression neglects a few less important reactions involving NO and NO\textsubscript{2} conversions, it accurately reproduces the NO\textsubscript{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\textsubscript{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\textsubscript{x} (Cl + ClO) destroys odd oxygen in a cycle similar to the NO\textsubscript{x} cycle above.

\[ (k_{48}); \quad O_3 + \text{Cl} \rightarrow \text{O}_2 + \text{ClO} \]  
\[ (k_{56}); \quad \text{O} + \text{ClO} \rightarrow \text{O}_2 + \text{Cl} \]  
\[ Net : \quad \text{O} + O_3 \rightarrow 2\text{O}_2 \]  

ClO\textsubscript{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

\[
\frac{[\text{ClO}]}{[\text{Cl}]} = \frac{k_{48}[O_3]}{k_{56}[\text{O}] + k_{57}[\text{NO}]} \tag{3}
\]
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 \( \text{HO}_x \) \((\text{H} + \text{OH} + \text{HO}_2)\) 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

\[
(k_{20}); \quad \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(R20)}
\]

\[
(k_{26}); \quad \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2 \text{O}_2 \quad \text{(R26)}
\]

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 \( \text{HO}_x \)-driven odd oxygen loss cycle:

\[
(k_{12}); \quad \text{O} + \text{HO}_2 \rightarrow \text{O}_2 + \text{OH} \quad \text{(R13)}
\]

\[
(k_{12}); \quad \text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \quad \text{(R12)}
\]

\[
(k_{15}); \quad \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad \text{(R15)}
\]

\[
Net: \quad \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2
\]

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:

\[
(k_{12}); \quad \text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \quad \text{(R12)}
\]

\[
(k_{16}); \quad \text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 \quad \text{(R16)}
\]

\[
Net: \quad \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2
\]

The OH concentration at 40-80 km is determined by a fast photochemical balance between (R12) and (R13) and consequently the OH/\( \text{HO}_2 \) ratio can be written as

\[
\frac{[\text{OH}]}{[\text{HO}_2]} = \frac{k_{13}}{k_{12}} \quad \text{(4)}
\]

\( \text{HO}_x \) production and loss rates balance each other in the stratosphere and in the mesosphere up to 75 km. In the stratosphere, \( \text{HO}_x \) production is dominated by
water vapour dissociation through the reaction with $O(^1D)$

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

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

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

The HO$_x$ loss rate is dominated by

$$(k_{24}); \quad OH + HO_2 \longrightarrow H_2O + O_2 \quad (R24)$$

up to 75 km. Thus, the HO$_x$ photochemical steady state equation becomes

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

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

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

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$_2$O (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,
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\(_2\)O 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$_2$O, CH$_4$, N$_2$O, 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 addressed 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 stratosphere 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 mechanisms responsible for the ozone increase. It is shown that the ozone response, both in the stratospheric and mesospheric regions, can be understood primarily 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 temperature 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) stratosphere 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 dependencies, 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) increases 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 result 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 (Fig-
ures 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 wa-
ter 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
(∼25 km). The impact on ozone through increased HO\textsubscript{x} production is also small.
Increased water vapour in the middle atmosphere could however have other sig-
nificant 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\textsubscript{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 chlo-
rine 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 dy-
namical mechanisms necessary to represent changes in circulation (i.e. mainly
the generation, propagation and dissipation of planetary waves) are incorpo-
rated 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 were 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\textsubscript{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\textsubscript{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\textsubscript{2} and overestimate OH in the mesosphere, sometimes referred to as the “HO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2}+M→O\textsubscript{3}+M reaction that controls odd oxygen partitioning.

In Paper IV additional doubled CO\textsubscript{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$_2$O, 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.
References


A Comparison of mesospheric temperatures from the Canadian Middle Atmosphere Model and HALOE observations: Zonal mean and signature of the solar diurnal tide

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Abstract

Currently climate models are being extended to the middle atmosphere in order to investigate climate sensitivity in that region. This paper presents a comparison between the Canadian Middle Atmosphere Model (CMAM) climatology and 9 years of HALOE temperature measurements for the middle atmosphere. The analysis shows an overall agreement throughout the entire middle atmosphere with discrepancies within 10 K and less in various areas for both equinox and solstice conditions. For historical purposes, the analysis also includes a comparison with the CIRA-86 reference model. In this case, the results indicate a significant CIRA-86 warm anomaly in the upper mesosphere over the tropics which is particularly pronounced during equinox. Further analysis of the HALOE sunrise and sunset occultation measurements with the CMAM has revealed the signature of diurnal tides.
1 Introduction

The mesosphere exhibits a greater spatial and temporal variability compared with the stratosphere. It is caused by the impact of growing amplitudes of gravity waves and tides. In particular, at low latitudes in the upper mesosphere the temperature can change by several tens of degrees during a single day, a phenomenon caused by the migrating diurnal solar tide. Satellite temperature measurements in this region and their interpretation are, no doubt, strongly influenced by the presence of these tides and other waves. The contribution of the tidal signature will be dependent upon the type of observation and the nature of the data processing. In this regard, occultation techniques appear powerful in the sense that they, for a given latitude, allow a large number of samples of the atmosphere around the same local time, sunrise(SR) or sunset(SS). This ability to sample specific phases of the tides can be used to identify the tidal signature and allow for its partial removal if required.

The large seasonal and interannual variability of the diurnal tides [Burrage et al., 1985] represents an additional source of uncertainties for model validation purposes. In this study, the analysis will use multi-year climatology datasets to remove this effect as much as possible. We will examine the feasibility of comparing observations throughout the mesosphere with a middle atmosphere model which includes a comprehensive representation of the diurnal tides.

We have analysed nine years (1992-2000) of temperature measurements obtained by the Halogen Occultation Experiment (HALOE) aboard the Upper Atmosphere Research Satellite (UARS). The HALOE measurements are compared with results from the Canadian Middle Atmosphere Model (CMAM) [Beagley et al., 1997] which is a state of the art general circulation model with a vertical domain extending from the surface to the lower thermosphere (∼95km). The version of CMAM used here employs T32 spectral resolution in the horizontal and 50 vertical levels. The model incorporates an interactive representation of ozone that can have a significant impact on the temperature structure of the mesosphere [de Grandpré et al., 2000]. This comparison study also includes an oft-used dataset for the mesosphere from the Cospar International Reference Atmosphere (CIRA-86) [Fleming et al., 1990] to highlight the magnitude of the discrepancies which may exist between different climatologies.

The first part of the study compares zonal and time averaged results from the various datasets. The discrepancies between the model and both climatologies are discussed in the context of tidal motion. Furthermore, the results show that general agreement between HALOE and the CMAM can be obtained when the model data are sampled around the same local time as for the instrument. The second part of the paper shows a comparison of the HALOE and CMAM
sunrise/sunset data which reveal the signature of the diurnal tide.

2 HALOE climatology

HALOE is a solar occultation instrument. We note that, to a large degree, the instrument is self-calibrating and the retrievals depend only on well characterised physical quantities such as cross sections and path length. Furthermore, the temperatures derived should not, generally, have a strong dependence on the retrieval scheme and certainly no dependence on underlying climatologies. Each day HALOE samples 15 sunrises and 15 sunsets along two separate latitude circles. Full latitudinal coverage (typically about 120 degrees) is obtained in about 40 days. A temperature climatology has been derived using the version 19 HALOE temperature retrievals from 1992-2000. Temperature profiles were sorted monthly in five-degree latitude-longitude bins. Monthly mean temperature profiles were then calculated by averaging zonally over the available profiles in each latitude band, including both SR and SS observations. We have restricted the analysis to latitudes with a minimum of 30 SR and 30 SS measurements. Effectively this means that the sparse sampling at higher latitudes excludes the polar regions and parts of the middle latitudes from the climatology.

3 CIRA-86 climatology

The CIRA-86 monthly average temperature profiles in the 20- to 80-km altitude range are a synthesis of observations obtained by the Nimbus 5 selective chopper radiometer (SCR) during 1973-1974 and the Nimbus 6 pressure radiometer modulator (PMR) during 1975-1978. Above 80 km the data set is merged with temperatures derived from the MSIS-83 model. The sampling of the data throughout the mesosphere was generally performed at fixed local time which has introduced biases at various heights. Discrepancies with other instruments due to tidal effects or data processing are discussed in Clancy et al. [1994] and Lawrence and Randel [1996].

4 Mean temperature comparison

The main benefits of the HALOE climatology is that it represents an homogeneous dataset and, as mentioned above, the method is insensitive to calibration errors. The UARS standard pressure levels, on which the HALOE temperature measurements are available, where chosen as the levels for comparison and so
4. Mean temperature comparison

both CMAM and CIRA-86 monthly mean zonally averaged temperature profiles were linearly interpolated onto these levels. Data from a ten year model simulation was used to derive the CMAM monthly mean zonally-averaged temperature profiles.

Figures 1 and 2 show the mean temperature profiles of CMAM, CIRA-86 and HALOE for January and April respectively. The various curves represent area-weighted mean values from 50°N to 50°S derived from the zonal mean temperature fields. The results show that the CMAM temperature profile agrees well with CIRA-86 in the stratosphere in both January and April, with a maximum discrepancy of 6-7 K around 20 km. This cold bias in the lower stratosphere is a common feature of most middle atmosphere models [Pawson et al., 2000] and is attributed to a systematic underestimation of radiative heating rates in the region. Between 35 and 50 km, the model temperatures appear reasonable and lie between HALOE and CIRA-86. In the lower mesosphere, between 50 and 65 km, the CMAM is colder than both sets of observations. Thus there may be a possible model cold bias in this region which could be partially explained by a model ozone deficit in this region [e.g. Figure 2 in de Grandpré et al., 2000]. To assess this, a more detailed analysis of model ozone in this region is necessary. Above 65 km, discrepancies between both CMAM and HALOE and CIRA-86 increase with height and becomes significant. The maximum difference between the CMAM and CIRA-86 temperatures occurs at 80 km and is 15 K in January and 20-25 K in April. In this region, the HALOE climatology is also much colder than CIRA-86. Possible reasons for such discrepancies are discussed below.

Figures 3a and 3b show the latitude-pressure cross-sections of the differences between the HALOE and the CIRA-86 climatologies in January and April. The limited latitudinal coverage of the HALOE observations restricts the comparisons to latitudes between 70°S and 50°N in January and between 55°S and 40°N in April.

The results show that the main source of discrepancies between the HALOE and CIRA-86 datasets is in the upper mesosphere where HALOE is significantly colder. The difference is between 6-12 K at 70-80 km in January and it reaches 25 K in the tropics in April. This is the region and season where the amplitude of the diurnal tide maximises, which suggests that the CIRA-86 climatology may be biased by solar tides. We note that during the equinox, HALOE SR and SS observations at the equator are separated by approximately 12 hours in time, which means that averaging over SR and SS observations should, to some extent, average out the effects of the diurnal tide at that latitude. Figures 3c and 3d compare the HALOE SR temperatures with SR temperatures extracted from the CMAM at the same local time as the HALOE observations. For this
Figure 1. Left: Area-weighted 50°N-50°S “near global mean” temperature profiles of CMAM (solid), CIRA-86 (dash-dotted) and HALOE (dashed) for January. Right: Temperature difference from the CIRA-86 climatology.

Figure 2. Same as Figure 1, but for April.
5. Tidal Analysis

Hervig et al. [1996] have shown that the mean difference between coinciding HALOE SR and SS temperature observations at the equator reveals a vertical wave pattern. In a more recent study, Marsh and Russell [2000] showed that a tidal signature is evident in the HALOE NO observations.

Figure 3e shows the difference between the monthly mean HALOE SR and SS temperature profiles for April. A clear signature of the diurnal tide is evident in these data. A vertical wave pattern is present at equatorial latitudes, with positive temperature anomalies at around 50 and 80 km and a negative anomaly at 60-70 km. The wave amplitude grows with increasing altitude and the wavelength is approximately 30 km. Off the equator, at around 20-50 degrees in both hemispheres the wave pattern shifts phase and the amplitude becomes smaller. These various features are in agreement with theory [Chapman and Lindzen, 1970; Andrews et al., 1987].

Figure 3f shows the difference between CMAM SR and SS temperatures in April. The CMAM simulation of the migrating diurnal tide in the middle atmosphere has been documented by McLandress [1997] and Wu et al. [1998]. There is reasonable qualitative agreement between the CMAM simulation and the observed tidal signature. Below 90 km, each anti-node of the tidal wave pattern simulated by CMAM is present in the HALOE observations. The symmetry of the temperature structure about the equator and the 30-km vertical wavelength

Figure 3. (Next page) (a) Latitude-pressure cross section of the temperature difference (Kelvin) between the HALOE and CIRA-86 climatologies, in January. Contour intervals are 3 K and negative contours are dashed. (b) Same as (a) but for April. (c) and (d). Same as (a) and (b) but for the difference between HALOE and CMAM at SR. (e) Difference between averaged HALOE SR and SS profiles in April. Contour intervals are 2 K up to 10 K and 4 K above 10 K. Negative anomalies are shaded. (f) Same as (e) but for the difference between averaged CMAM SR and SS profiles (synthetic HALOE observations).
are both characteristic features of the (1,1) diurnal Hough mode. The largest discrepancy between the model and observations appears to be in the tropics at about 0.01 hPa where the 30 K positive anomaly in the model is twice as large as that of the observations.

Such discrepancies can be due to several factors. From a model perspective, we cannot rule out the possibility that the model upper boundary at 97 km could affect the result in the mesopause region, although the analysis of McLandress [1997] would seem to preclude a large effect. We note that the model interannual variability may not be well represented. Recent analyses [McLandress, 2002] show that a Quasi-Biennial Oscillation (QBO) may trigger interannual variability in the diurnal tides. In this context, the absence of QBO in the CMAM may well be one of the factors which prevent the model from reproducing a tidal signal of weaker amplitude more in accord with HALOE. From an observational perspective, a monthly analysis of the HALOE data in the above fashion (not shown) indicates that the HALOE data do not appear to exhibit a clear semi-annual behaviour more in keeping with the HRDI data [Burrage et al., 1985]. This aspect requires a more careful statistical analysis which is being pursued.

6 Conclusions

We found agreement between the CMAM model, HALOE and the CIRA-86 temperature climatologies in the stratosphere. In the mesosphere the CMAM temperatures generally agree with the HALOE climatology, and both are colder than the CIRA-86 temperatures in the upper mesosphere, particularly at equinox. In April, the HALOE climatology is up to 25 K colder than the CIRA-86 climatology at 70-80 km.

The difference between HALOE SR and SS temperature observations reveals a clear signature of the solar diurnal tide in the mesosphere, which is in qualitative agreement with the CMAM simulation of the diurnal tide. The phases of the vertically propagating waves match closely although the amplitudes of the diurnal temperature variations as seen in the model for April are up to twice as large as the observations.

Acknowledgements

Our thanks go to all those involved in working with the CMAM atmospheric modelling group. We are particularly grateful to T. Shepherd and C. McLandress of the University of Toronto for valuable comments. We also thank the HALOE
Science team for making the excellent HALOE data set available over the World Wide Web. J. de G and J. C. McC wish to thank NSERC for continuing support.

References


Revisiting the “Ozone deficit problem” in the middle atmosphere: An investigation of uncertainties in photochemical modelling

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Abstract

The scientific understanding of processes related to ozone depletion and climate change in the upper stratosphere and lower mesosphere is compromised by the fact that models tend to underestimate the observed levels of ozone in this region — a problem commonly referred to as the “Ozone deficit problem”. Recently the use of updated photochemical models and improved ozone measurements have led to large reductions in this discrepancy in the 40 km region.

This paper reinvestigates the ozone deficit problem in the upper stratosphere and also examines the ozone budget in the mesosphere. In order to focus on the photochemical aspects of the problem, a comprehensive photochemical box model was constrained by HALOE solar sunset occultation measurements of temperature and several chemical species, such that the key background source gases CH$_4$ and H$_2$O, and the chemical families NO$_y$ and Cl$_y$ in the model are consistent with the observed atmosphere. It is shown that the modelled ozone values can be kept to within 10% of the HALOE observations at 40–55 km. This discrepancy is within the uncertainties of the model and the observations, and is thus in agreement with the current understanding. At 60–75 km, however, the model underestimates the observations by up to 35%, which suggests serious deficiencies in the model and/or the observations, and possibly an important misunderstanding of mesospheric processes.

Careful analyses of model uncertainties that may contribute to the discrepancies have been performed with emphasis on processes that affect the high solar zenith angle simulation of ozone in the model. It has been shown that the use of accurate input solar fluxes measured by SUSIM and the inclusion of multiple scattering processes are essential for the good agreement in the 40-55 km region.

The paper also examines the impact of uncertainties in photochemical rate coefficients on the calculated ozone abundance. Using a Monte Carlo technique, it was shown that the induced 1-sigma ozone uncertainties range from about 6% at 30 km to 20% at 75 km, representing a clear improvement compared to studies based on earlier photochemical data. The reactions contributing most to these uncertainties were identified and listed as a function of altitude. The study also identifies the measurement quality of the HALOE ozone and water vapour to impose severe limitations on the analysis at 70–75 km. This implicates the need for improved measurements of these species in the mesosphere to advance the current understanding of ozone chemistry in this part of the atmosphere.
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1. Introduction and motivation

Ozone is a key element of the middle atmosphere that affects both the chemical and radiative properties of the ambient air. It is a highly reactive molecule that absorbs solar ultraviolet (UV) radiation and is the major heat source of the stratosphere. A realistic calculation of the ozone abundance using photochemical models in middle atmospheric climate studies is therefore crucial for accurate simulations of the distributions of other trace gas species and temperature. Ozone also has non-local effects via changes in the ozone column. For example, stratospheric ozone affects photolysis rates in the troposphere and is an important greenhouse gas affecting the surface climate.

Over the past 20 years several studies have shown that models tend to underestimate ozone observations by 10–30% in the upper stratosphere (WMO, 1995; and references therein) and even more in the mesosphere (Rusch and Eckman, 1985; Clancy et al., 1987). However, more recently model results show much better agreement with observations in the upper stratosphere. WMO (1999) lists a number of studies (Minschwaner et al., 1993; Osterman et al., 1997; Khosravi et al., 1998, Grooß et al., 1999) in which the ozone budget is nearly balanced (or within 10% of the observations) at 40 km. The better agreement in these studies was attributed to a combination of factors; reduction in the modelled concentration of ClO due to the inclusion of a new loss reaction for reactive chlorine and the use of observed methane to constrain the models; the use of ozone observations that appear to be more accurate than previous measurements; deeper penetration of ultraviolet radiation in the O$_2$ absorption cross section wavelengths. Recently, Park et al. (1999) and Natarajan et al. (2002) show similar results, with ozone mixing ratios of 10% or less lower than observations at 40 km. An earlier study in disagreement with these new results is Siskind et al. (1995) in which the calculated ozone mixing ratios are lower by roughly 15–20% than observations at 40 km. This was however partially resolved by an updated model version in Siskind et al. (1998) which calculates approximately 8% more ozone than in Siskind et al. (1995) in the upper stratosphere.

At greater altitudes however, the various studies show contradictory results. While Grooß et al. (1999) and Natarajan et al. (2002) found model-data discrepancies of less than 10% up to ~55 km several other models significantly underestimate ozone observations above 40 km: by up to 35% at 45–60 km (Osterman et al., 1997), by 25% at 48 km (Jucks et al., 1998), by 20–25% at 50 km (Summers et al., 1997), by between 20% at 55 km and 40% at 65 km (Sandor et al., 1997; Sandor and Clancy, 1998), and by between 10% at 40 km and 30% a 60 km (Park et al., 1999). The causes of these disagreements can be divided in
three major factors: (1) the use of different observational datasets, both for the ozone comparison itself and for the constraints of key model parameters, e.g. temperature and background chemical species such as methane (CH$_4$), water vapour (H$_2$O), total inorganic chlorine\textsuperscript{1} (Cl$_x$) and reactive nitrogen\textsuperscript{2} (NO$_y$). In the studies above a variety of satellite, balloon, and ground based measurements were used for the model-data comparisons. (2) The use of different photochemical rate data could possibly explain some of the differences. However, it can be noted that the listed studies are fairly recent and the rate data of reactions important for the ozone budget above 50 km has not changed significantly during the past few years. (3) Finally, a variety of systematic model differences no doubt results in a spread of ozone estimates. Such differences include for example the use of different chemistries, numerical approximations and treatments of radiative transfer processes.

Motivated by the discrepancies between the various model results in the upper stratosphere and in particular the remaining ozone deficit problem in the mesosphere we have in this study examined the influence of various sources of errors that affect the modelled ozone abundance using a comprehensive photochemical box model. A photochemical model includes a large set of reactions, measured reaction rate coefficient and detailed radiative transfer calculations to determine photolysis rates for various species. Errors can enter into the calculations at numerous stages. In this paper model errors are divided in two groups: (1) \textit{Systematic errors}, caused for example by neglected or unknown chemical reactions, by coarse spatial or temporal resolution and by inaccurate treatment of important radiative processes such as O$_2$ and O$_3$ absorption of solar radiation and scattering processes. (2) \textit{Random errors} are defined in this study as those associated with uncertainties in model input parameters, mainly (bimolecular and termolecular) reaction and photodissociation rate coefficients.

In parallel to the model-data comparisons mentioned above a number of papers have discussed the ozone sensitivity to uncertainties in model input parameters. Stolarski \textit{et al.} (1978), Clancy \textit{et al.} (1987) and Chen \textit{et al.} (1997) used photochemical models to derive the uncertainty in calculated ozone values induced from uncertainties in reaction rate coefficients. Butler (1978), Natarajan \textit{et al.} (1986), Dubey \textit{et al.} (1998) and Smith \textit{et al.} (2001) considered uncertainties in both reaction and photodissociation rate coefficients. A general feature in these studies is that uncertainties in estimated ozone concentrations tend to

\textsuperscript{1}Total inorganic chlorine is a term used to describe the total chlorine concentration excluding carbon containing species and includes for the middle atmosphere primarily Cl, ClO, ClONO$_2$, HOCl and HCl.

\textsuperscript{2}Reactive nitrogen in the middle atmosphere includes mainly N, NO, NO$_2$, NO$_3$, N$_2$O$_5$, HNO$_3$, HO$_2$NO$_2$ and ClONO$_2$. 
increase with altitude in the middle atmosphere. As uncertainties in photodissociation rate coefficients are not negligible and can considerably contribute to ozone uncertainties we focus on the latter four studies in the discussion below. They span over more than two decades and show that modelled ozone uncertainties associated with inaccuracies in chemical kinetics have steadily decreased in response to more accurate measurements of photochemical rate data. Butler (1978) estimated the uncertainty in calculated ozone abundance to be 20–25% and 75% at 30 and 50 km respectively. Natarajan et al. (1986) based their calculations on the JPL–83 catalogue (DeMore et al., 1983) and reported 25% and 30–40% 1-sigma uncertainties in simulated ozone values at 37 and 49 km respectively. Dubey et al. (1998) used the photochemical rate data of JPL–94 (DeMore et al., 1994) and found a 22% RMS ozone uncertainty at 40 km. In the work of Smith et al. (2001) the photochemical module was updated from JPL–94 to incorporate the rates of JPL–00 (Sander et al., 2000), whilst the calculated ozone uncertainty was reduced by 3–5% to about 12% at 25–55 km. This estimate neglects however uncertainties in the important photolysis reactions of molecular oxygen and ozone as well as reactions of O with O$_3$ and O$_2$. Neither of the latter studies considered the mesosphere in their analyses. Chen et al. (1997) using JPL–92 (DeMore et al., 1992) reported 1-sigma uncertainties ranging from 10–20% in the stratosphere to 30–40% in the mesosphere, but these are probably low estimates as uncertainties in photodissociation rate coefficients were not included in their analysis. It should be noted that the typical ozone uncertainties in these studies are comparable to the typical model-observation discrepancies summarised earlier in the section.

In recent years new data on reaction rate coefficients and absorption cross sections have been published, new reactions and product branches have been discovered and new approaches for parameterising photolysis in the O$_2$ Schumann-Runge bands (SRB) have been developed. The present model study includes some of this new knowledge and the analysis is extended to the middle mesosphere (75 km). We use a photochemical box model constrained by HALOE (HALogen Occultation Experiment) (Russell et al., 1993) zonal mean observations of temperature and key reactive and long-lived gases and present the calculated ozone profile in comparison with the observations. With this approach our reference model underestimates the ozone observations by 10–20% in the upper stratosphere and by up to 40% in the mesosphere. To test the sensitivity of these results we first investigate the importance of some systematic errors by stepwise including processes, which are included in some of the model studies presented above, but not in others, e.g. methane oxidation chemistry and various radiative processes and approaches, such as multiple scattering and surface albedo effects,
accurate input solar fluxes, interactive ozone for radiative transfer calculations and high temporal resolution of photolysis rate updates. It is shown that the applied model improvements remove up to 10% of the model-observation disagreement in the upper stratosphere, leaving a discrepancy of around 10% in this altitude region. The mesospheric discrepancies can however not be removed by the introduced model improvements, suggesting serious deficiencies in the model chemical scheme and/or photochemical data.

In addition a Monte Carlo sensitivity study has been performed to examine the influence of uncertainties in both reaction rate coefficients and photodissociation rate coefficients on the calculated ozone profile. Several previous studies have suggested changes to specific reaction rate coefficients that could improve the agreement between calculated and observed ozone abundances. In this work the approach is to pinpoint the reactions that contribute most to the ozone uncertainty. This is achieved through a partial least squares (PLS) regression of the input parameters in the Monte Carlo analysis on the resulting ozone distribution.

Furthermore we suspect that the use of different sets of observations to initialise and constrain models in various studies may be an important source for the discrepancies in calculated ozone deficits. Hence we have investigated how uncertainties in the measurements of the source gases used for model constraints affect the calculated ozone uncertainty.

The paper outline is as follows: In section 2 the characteristics of the reference model used in the study is described. Model constraints are discussed in section 3. Section 4 presents the calculated ozone profile from the reference model in comparison with observations and discusses the influence of systematic errors on the resulting discrepancies. This is followed by, in section 5, the results of the Monte Carlo sensitivity study and the PLS regression analysis.

2. Model description

We use an updated version of the photochemical box model presented by Ridal et al. (2001) applied at 30–75 km with 5 km vertical steps. No transport mechanisms between the boxes are considered. However, since the model is applied in a domain where the photochemical lifetime of the odd-oxygen reservoir (O_x=O_3+O) generally is much shorter than the characteristic transport time, this deficiency has little impact on the calculated ozone profile (except at 30 km, as discussed in section 4a). In the model experiments presented here we have chosen a combination of latitude and season for maximum photochemical control (low latitudes in the summer hemisphere).

The reference model uses temperatures from the CIRA climatology (Fleming
et al., 1990) and species are initialised from the output of a coupled chemistry-climate model (de Grandpré et al., 2000). The long-lived source gases CH$_4$ and H$_2$O (with typical chemical lifetimes of months to years in the stratosphere and lower mesosphere) are kept fixed during the simulation. The production of NO$_y$ or Cl$_y$ from nitrous oxide (N$_2$O) and chlorofluorocarbons (CFCs) are not included, and no NO$_y$ or Cl$_y$ loss processes are considered, as they cannot be treated properly without treatment of atmospheric transport processes in the model. This means that NO$_y$ and Cl$_y$ have to be carefully defined at the model initialisation.

Detailed radiative transfer calculations in the UV and visible regions are performed to derive atmospheric transmission. The sphericity of the Earth is taken into account in the calculations, which allows for non-zero transmitted flux at solar zenith angles (SZA) greater than 90 degrees. The solar flux is based on data from Ackerman (1971) for wavelengths at 122–175 nm and from WMO (1986) (referred to as WMO–86 hereafter) for wavelengths at 175–850 nm. The irradiance of the Lyman-alpha line at 121.6 nm is set to 3.82·10$^{11}$ photons cm$^{-2}$ s$^{-1}$, representing near solar minimum conditions (Woods et al., 2000). In addition, the solar flux is corrected for the variation in Earth-sun distance according to Madronich (1993). In January this yields 3.5% greater fluxes at all wavelengths than for the uncorrected solar flux. A climatological mean ozone profile (Brasseur and Solomon, 1986) is used for ozone absorption.$^3$

The model incorporates a majority of the known gas phase chemical reactions and photolysis reactions necessary to derive realistic ozone production and loss rates at extrapolar latitudes in the middle atmosphere. Heterogeneous reactions are not included as they are generally not important in the part of the atmosphere considered in this study. The standard chemical scheme includes 22 species and 84 reactions (see Tables 1–3). Reaction rate coefficients and other photochemical data are based on JPL–97$^4$ (deMore et al., 1997) except when stated otherwise. In particular, O$_3$ absorption cross sections are in accordance with WMO–86, while the O$_2$ absorption cross section in the Schumann-Runge bands (SRB) is parameterised as described by Koppers and Murtagh (1996) and the long-wave tail of the Herzberg continuum is taken from the work of Nicolet and Kennes (1986). The O$_2$ and O$_3$ absorption cross sections for wavelengths 122–175 nm are taken from Ackerman (1971). A 6% yield of HCl from the OH + ClO reaction is used (reactions B42 and B43), as recommended in JPL–00. The chemical reaction scheme generates a system of stiff ordinary differential equations which is solved with a quasi-constant step size variable or-

$^3$The limitations of this approach is discussed in section 4c.

$^4$More recent photochemical rate data is currently available in JPL–02 (Sander et al., 2003). The impact of differences between JPL–97 and JPL–02 on the results is discussed in section 6.
Table 1. List of bimolecular reactions.

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
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<tr>
<td>B1</td>
<td>$O + O_3$ $\rightarrow$ $O_2 + O_2$</td>
</tr>
<tr>
<td>B2</td>
<td>$O^{(1)D} + O_2$ $\rightarrow$ $O + O_2$</td>
</tr>
<tr>
<td>B3</td>
<td>$O^{(1)D} + H_2$ $\rightarrow$ $OH + H$</td>
</tr>
<tr>
<td>B4</td>
<td>$O^{(1)D} + H_2O$ $\rightarrow$ $OH + OH$</td>
</tr>
<tr>
<td>B5</td>
<td>$O^{(1)D} + N_2$ $\rightarrow$ $O + N_2$</td>
</tr>
<tr>
<td>B6</td>
<td>$O^{(1)D} + HCl$ $\rightarrow$ $OH + Cl$</td>
</tr>
<tr>
<td>B7</td>
<td>$O^{(1)D} + CH_4$ $\rightarrow$ products$^1$</td>
</tr>
<tr>
<td>B8</td>
<td>$O + OH$ $\rightarrow$ $O_2 + H$</td>
</tr>
<tr>
<td>B9</td>
<td>$O + HO_2$ $\rightarrow$ $OH + O_2$</td>
</tr>
<tr>
<td>B10</td>
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<td>B40</td>
<td>$O + HOCl$ $\rightarrow$ $OH + ClO$</td>
</tr>
</tbody>
</table>

*Continued on the next page...*
3. Model constraints

The calculated ozone profile is to a large extent influenced by the choice of model initialisations of NO\textsubscript{y} and Cl\textsubscript{y} as well as the fixed vertical profiles of CH\textsubscript{4} and H\textsubscript{2}O, since these quantities are the sources of the NO\textsubscript{x} (NO+NO\textsubscript{2}), ClO\textsubscript{x} (Cl+ClO) and HO\textsubscript{x} (H+OH+HO\textsubscript{2}) radical species which catalyse ozone loss reactions. Thus we constrain the model abundances of these long-lived tracers.

Table 1. (continued)

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>B41</td>
<td>O + ClONO\textsubscript{2} → NO\textsubscript{3} + ClO</td>
</tr>
<tr>
<td>B42</td>
<td>OH + ClO → HO\textsubscript{2} + Cl</td>
</tr>
<tr>
<td>B43</td>
<td>OH + ClO → O\textsubscript{2} + HCl</td>
</tr>
<tr>
<td>B44</td>
<td>OH + HCl → H\textsubscript{2}O + Cl</td>
</tr>
<tr>
<td>B45</td>
<td>OH + HOCl → H\textsubscript{2}O + ClO</td>
</tr>
<tr>
<td>B46</td>
<td>OH + ClONO\textsubscript{2} → HOCl + NO\textsubscript{3}</td>
</tr>
<tr>
<td>B47</td>
<td>HO\textsubscript{2} + Cl → HCl + O\textsubscript{2}</td>
</tr>
<tr>
<td>B48</td>
<td>HO\textsubscript{2} + Cl → OH + ClO</td>
</tr>
<tr>
<td>B49</td>
<td>HO\textsubscript{2} + ClO → HOCl + O\textsubscript{2}</td>
</tr>
<tr>
<td>B50</td>
<td>Cl + O\textsubscript{3} → ClO + O\textsubscript{2}</td>
</tr>
<tr>
<td>B51</td>
<td>Cl + H\textsubscript{2} → HCl + H</td>
</tr>
<tr>
<td>B52</td>
<td>Cl + H\textsubscript{2}O\textsubscript{2} → HCl + HO\textsubscript{2}</td>
</tr>
<tr>
<td>B53</td>
<td>Cl + NO\textsubscript{3} → ClO + NO\textsubscript{2}</td>
</tr>
<tr>
<td>B54</td>
<td>Cl + CH\textsubscript{4} → HCl + CH\textsubscript{3}\textsuperscript{1)}</td>
</tr>
<tr>
<td>B55</td>
<td>Cl + HOCl → HCl + ClO</td>
</tr>
<tr>
<td>B56</td>
<td>ClO + NO → NO\textsubscript{2} + Cl</td>
</tr>
</tbody>
</table>

\textsuperscript{1)}These products are not included in the reference model.
### Table 2. List of termolecular reactions.

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>$O + O_2 + M \rightarrow O_3 + M$</td>
</tr>
<tr>
<td>T2</td>
<td>$O + O + M \rightarrow O_2 + M$</td>
</tr>
<tr>
<td>T3</td>
<td>$O(^{1}D) + N_2 + M \rightarrow \text{products}^1$</td>
</tr>
<tr>
<td>T4</td>
<td>$H + O_2 + M \rightarrow HO_2 + M$</td>
</tr>
<tr>
<td>T5</td>
<td>$OH + OH + M \rightarrow H_2O_2 + M$</td>
</tr>
<tr>
<td>T6</td>
<td>$O + NO + M \rightarrow NO_2 + M$</td>
</tr>
<tr>
<td>T7</td>
<td>$O + NO_2 + M \rightarrow NO_3 + M$</td>
</tr>
<tr>
<td>T8</td>
<td>$OH + NO_2 + M \rightarrow HNO_3 + M$</td>
</tr>
<tr>
<td>T9</td>
<td>$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$</td>
</tr>
<tr>
<td>T10</td>
<td>$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$</td>
</tr>
<tr>
<td>T11</td>
<td>$ClO + NO_3 + M \rightarrow ClONO_2 + M$</td>
</tr>
</tbody>
</table>

$^1$ These products are not included in the reference model.

### Table 3. List of photolysis reactions.

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>$O_2 + h\nu \rightarrow O + O(^{1}D)$</td>
</tr>
<tr>
<td>P2</td>
<td>$O_2 + h\nu \rightarrow O + O$</td>
</tr>
<tr>
<td>P3</td>
<td>$O_3 + h\nu \rightarrow O_2 + O(^{1}D)$</td>
</tr>
<tr>
<td>P4</td>
<td>$O_3 + h\nu \rightarrow O_2 + O$</td>
</tr>
<tr>
<td>P5</td>
<td>$H_2O + h\nu \rightarrow H + OH$</td>
</tr>
<tr>
<td>P6</td>
<td>$H_2O_2 + h\nu \rightarrow OH + OH$</td>
</tr>
<tr>
<td>P7</td>
<td>$NO + h\nu \rightarrow N + O$</td>
</tr>
<tr>
<td>P8</td>
<td>$NO_2 + h\nu \rightarrow NO + O$</td>
</tr>
<tr>
<td>P9</td>
<td>$NO_3 + h\nu \rightarrow NO + O_2$</td>
</tr>
<tr>
<td>P10</td>
<td>$NO_3 + h\nu \rightarrow NO_2 + O$</td>
</tr>
<tr>
<td>P11</td>
<td>$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$</td>
</tr>
<tr>
<td>P12</td>
<td>$HNO_3 + h\nu \rightarrow NO_2 + OH$</td>
</tr>
<tr>
<td>P13</td>
<td>$HO_2NO_2 + h\nu \rightarrow NO_2 + HO_2$</td>
</tr>
<tr>
<td>P14</td>
<td>$HCl + h\nu \rightarrow Cl + H$</td>
</tr>
<tr>
<td>P15</td>
<td>$HOCl + h\nu \rightarrow Cl + OH$</td>
</tr>
<tr>
<td>P16</td>
<td>$ClONO_2 + h\nu \rightarrow Cl + NO_3$</td>
</tr>
<tr>
<td>P17</td>
<td>$ClONO_2 + h\nu \rightarrow ClO + NO_2$</td>
</tr>
</tbody>
</table>

* For each photolysis reaction $P_n$, the photolysis rate coefficient is referred to as $J_n$ in the text.
to measurements retrieved from the real atmosphere simultaneously with the ozone observation used in the model-observation comparison. For the diurnal model we follow the approach of Crutzen et al. (1995) and Grooß et al. (1999) (referred to as G–99 hereafter) and constrain the model to HALOE satellite observations of temperature, CH$_4$, H$_2$O, NO, NO$_2$ and HCl. This set of key species constitutes a necessary basis for constraining the long-lived reservoirs from which NO$_x$, ClO$_x$ and HO$_x$ species are produced.

HALOE is an occultation instrument onboard the Upper Atmosphere Research Satellite (UARS) providing 15 sunrise and 15 sunset observations along two different latitude circles a day. Hence, for a selected day and latitude the observations allow for a single zonal mean average of each observed constituent to be calculated. Since the observations are available only for the local time of the occultations, short-lived species with significant diurnal variability cannot be constrained continuously by these measurements. Therefore only temperature and the long-lived gases CH$_4$ and H$_2$O are fixed by the HALOE data at the model initialisation. Next, repeated diurnal cycles are integrated where the mixing ratios of NO, NO$_2$ and HCl are replaced by their corresponding HALOE observations at the local time of the measurements. Both NO and NO$_2$ undergoes rapid transitions at high solar zenith angles as a result of rapidly changing incident solar flux. Therefore, instead of replacing NO and NO$_2$ separately the sum of the observed NO and NO$_2$ mixing ratios is inserted in the model with the NO/NO$_2$ ratio given by the model calculation. The effect of these quasi-constraints is that the model NO$_y$ and Cl$_y$ are consistent with the observations. 40 diurnal cycles are calculated after which the model converges to a solution where the diurnal cycles of all species changes insignificantly between subsequent days. With this approach, the zonal mean HALOE data from a single selected day is imposed on the model at each day throughout the simulation, so essentially the model simulates the same day 40 times.

In the present study we use the version 19 HALOE sunset retrievals for 12 January 1994 at 23$^\circ$S and set up the model to simulate this specific time and location. We have chosen to work with sunset occultations as the sunset ozone retrievals are less problematic in the mesosphere than the sunrise retrievals (Natarajan et al., 2005). Because of the limited vertical coverage of some of the HALOE measurements a few assumptions are made. The NO$_2$ and HCl measurements are only available up to about 50 km and are consequently only reset in the model up to this level. We assume a constant Cl$_y$ mixing ratio above 50 km corresponding to the HALOE measurement of HCl at 54 km (3.0 ppbv). This is motivated by the fact that HCl contributes to about 95% of the Cl$_y$ abundance at this level and is therefore a realistic estimate of the Cl$_y$ mixing
ratio for the upper altitudes. Furthermore, the NO mixing ratio is at least one order of magnitude greater than the NO$_2$ mixing ratio above 50 km at sunset (for the latitude and season considered here) and hence constitutes the bulk of the NO$_y$ abundance at this local time. Therefore, the quasi-constraint of the NO mixing ratio above 50 km should be sufficient to ensure an accurate NO$_y$ abundance at the upper levels. We further note that these assumptions should have little effect on the calculated ozone, since above 50 km, HO$_x$ is the dominant source for ozone loss (see e.g. Brasseur and Solomon, 1986; Jonsson et al., 2004). We have chosen not to apply any constraints to ozone as is done in G–99. In a sensitivity study as this, it is crucial that ozone is free to adapt completely unconstrained to the various model perturbations that will be introduced in the following sections.

4. Systematic errors

To investigate the effects of systematic errors on the calculated ozone profile, various processes and model specific numerical approaches which are likely to induce systematic differences between different model studies will be implemented in the reference model presented above. Naturally, all sources of systematic errors cannot be covered. The ozone profile of the converged model at sunset will be presented relative to the HALOE ozone observations and we will therefore in particular examine the importance of processes which affect the model performance at high solar zenith angles, e.g. variations in treatment of radiative processes. However, a few mechanisms that affect the diurnal average ozone budget, will also be treated, e.g. incorporating the methane oxidation chain in the chemical scheme and taking multiple scattering into account in the radiative transfer calculations.

a. Reference model

First a reference run was performed with the model in diurnal mode and constrained by HALOE observations as described in section 3. Figure 1 shows the ozone profile derived by the reference model at sunset for the last day of the simulation and a comparison with the zonal average of the HALOE sunset observations. The uncertainties of the observed zonal averages are indicated by two sets of error bars. The first set (dotted line) represents the average error of the 15 observations in the zonal average, which is less than 1% at 30–45 km, 1–10% at 45–65 km and 10–100% at 65–75 km. However, the zonal mean estimate in the figure represents a more robust estimate of the sunset ozone mixing ratio than a single measurement, since averaging diminishes the impact of instrument
noise. By weighting the individual measurements by the squared inverse of its error in the average, greater weight is given to the more accurate measurements than the less accurate. This method minimises the sum of squared errors of the data points contributing to the mean value and hence produces the best estimate of the mean value. The difference from a standard arithmetic mean is less than 1% at all altitudes except at 75 km where the weighted mean is 4% greater than the corresponding arithmetic mean value. The second set of uncertainty bars (solid line) presented in the figure is the combined error, $E$, of the weighted mean calculated as

$$E^{-2} = e_1^{-2} + e_2^{-2} + \ldots + e_n^{-2},$$  \hspace{1cm} (1)$$

where the $e_i$:s are the errors of the individual measurements.

The model clearly underestimates the observed ozone values at all altitudes except at 30 km. The model result is however within the average error limits of
the observations at 70–75 km and within the uncertainty of the weighted mean at 75 km. Figure 2 shows the details of the discrepancy more clearly. The model underestimation peaks at 40 and 75 km where the discrepancies are about 20% and 40% respectively. Below 35 km the lifetime of odd-oxygen is sufficiently long so that transport of ozone to higher latitudes contributes significantly to the odd-oxygen budget in the real atmosphere. Neglecting this removal process in the model results in a slight overestimation of the observed ozone abundance at 30 km.

The complete diurnal variation of ozone during the final day of the simulation as well as the HALOE zonal mean observations are shown in Figure 3. At 30–50 km the ozone mixing ratio is nearly constant in time due to the long photochemical lifetime of odd-oxygen at these altitudes. The discrepancies between the model and the observations are greater than the maximum diurnal variability at these altitudes. In the mesosphere, rapid ozone photolysis and low air density favour the conversion of ozone molecules into atomic oxygen atoms.

Figure 2. Relative difference between the ozone mixing ratio calculated by the reference model and the HALOE zonal mean observations. The dashed line indicates the zero line.
Figure 3. Diurnal cycle of the ozone mixing ratio at 30–75 km during the last day of the reference model simulation. HALOE zonal mean observations (symbols) are indicated at sunset (the measurements at 30 and 35 km are very close and cannot be distinguished from each other in the figure). Error bars indicate the combined uncertainty of the weighted zonal mean values.
during the day; the time scale for ozone photolysis is generally shorter than the time scale for ozone reformation through reaction T1 (O+O₂+M→O₃+M) in this region (Allen et al., 1984). This leads to significant differences between daytime and nighttime ozone mixing ratios with rapid transitions occurring near sunrise and sunset. In addition, after the initial ozone dip at sunrise due to ozone photolysis, ozone increases in the early morning hours in response to odd-oxygen production from O₂ photolysis, which eventually balances with odd-oxygen loss later in the day. In the mesosphere, odd oxygen loss is provided mainly by HOₓ catalytic cycles and in the afternoon when O₂ photolysis decreases, the HOₓ catalytic cycling tapers off more slowly than the O₂ photolysis causing a decrease in odd-oxygen and ozone.

Figure 4 shows an enlargement of the ozone variations around sunset at 55–75 km. Due to the proximity of the observations to the transition region, the estimated ozone deficit is sensitive to the accuracy and precision of the model calculation at high solar zenith angles. This is in particular the case at 55–65 km where the observations are located near the beginning to half ways through the transition from daytime to nighttime ozone mixing ratios. At these altitudes numerical approximations and coarse temporal resolution around sunset in the model could lead to significant errors in the estimated ozone deficit. An additional uncertainty at mesospheric altitudes is imposed by the variation of local solar times sampled by an occultation measurement, due to the geometry of the observations. For example, assuming that most of the measured signal comes from a layer with a thickness of one scale height (∼7 km), the local solar time varies by about +/–12 minutes along the line of sight of the measurement. This issue is discussed further in section 6.

At 70–75 km the transition to nighttime mixing ratios occurs significantly later than the time of the observation. This is because the atmosphere above a given location on the Earth is illuminated by the sun for a significant time after the surface is shadowed by the Earth’s limb. For increasing altitudes the sun sets at increasingly larger solar zenith angles (and hence later local solar times). For example, at 75 km the sun sets at a local solar zenith angle of 99 degrees, while the occultation measurements (at all altitudes) were collected for solar zenith angles of approximately 90 degrees. From a geometrical viewpoint the model is sunlit some 40 minutes longer at 75 km than at the surface. However, the long optical path through the atmosphere at such extreme zenith angles effectively damps out the transmitted flux in the UV and visible wavelength regions well before the sun disappears behind the Earth’s limb. Nevertheless the ozone mixing ratio at 70–75 km is under daytime photochemical control at the time of the measurement, which should lead to a more robust comparison
Figure 4. Enlargement of Figure 3 around sunset showing the ozone mixing ratios at 55–75 km.
with the observations than at 55–65 km (except for the fact that the observation uncertainties are greater at 70–75 km).

Before we proceed to test the sensitivity of the result, a few comments are needed on the interpretation of the results in Figure 2. This figure shows the relative amount by which the model underestimates or overestimates the observations at specific local solar time. In the stratosphere, where ozone constitutes the major part of the odd-oxygen reservoir and the photochemical lifetime of odd-oxygen is in the order of hours to several days, the calculated ozone abundance at an arbitrary time of day is the integrated result of the net odd-oxygen production minus loss rates over an extended time frame. Hence, an underestimation of the observed ozone abundance at a given local time, e.g. at sunset, suggests an inadequate representation of the diurnal average odd-oxygen budget in the model. This is what is commonly referred to as the “Ozone deficit problem”. Above 60 km, however, ozone contributes to only a minor fraction of the odd-oxygen reservoir and the daytime photochemical lifetime of ozone is much shorter than in the stratosphere, in the order of minutes. This means that by comparison with the HALOE ozone observations at these altitudes we can only assess the models ability to reproduce the observations for local solar times near the time of the measurements. For a complete test of the models diurnally averaged ozone budget in this region, ozone measurements with diurnal coverage would be required, and to rigorously test the odd-oxygen budget, simultaneous observations of atomic oxygen would be necessary. Nevertheless, we present here the comparisons with the HALOE observations up to 75 km as the sunset comparison is interesting in itself.

Next we will test the sensitivity of the modelled ozone deficit. Step by step we will consider photochemical mechanisms and numerical treatments that are likely to affect the results. The result of each case is displayed in Figure 5 and Figure 6. First we examine the importance of the methane oxidation chain on the simulated ozone profile.

**b. The methane oxidation chain**

A large fraction of the water vapour in the middle atmosphere is produced from methane oxidation. The methane oxidation chain is initiated by reactions with O($^1D$), OH and Cl (B7, B20 and B54). The oxidation products are dissociated through a series of reactions yielding the final products CO$_2$, H$_2$O and H$_2$. These reactions are shown in Table 4. In general a model needs to take this chemistry into account in order to produce realistic water vapour abundances. This is essential to achieve realistic HO$_x$ production rates in the model and therefore crucial for deriving accurate odd-oxygen loss rates in the mesosphere where
Figure 5. Relative difference between the modelled ozone mixing ratio and the HALOE zonal mean observation at sunset. The figure includes six modelled cases: (Ref) Reference model (dashed, black); (Ref+CH4) Reference model + methane oxidation chain (dotted, red); (Ref+SUSIM) Reference model + SUSIM solar flux (dot-dashed, green); (Ref+MS) Reference model + multiple scattering (dot-dot-dashed, dark blue); (Ref+J) Reference model + daily updates of the photolysis lookup table (dot-dot-dot-dashed, light blue); (Ref+CH4+SUSIM+MS+J) Reference model + all changes in cases 2–5 (solid, black). See text for more details.

Figure 6. Same as Figure 5, but shows the simulated ozone mixing ratios for the various cases (see legend) relative to the reference model at sunset.
Table 4. List of methane oxidation chain reactions.

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1(^1)</td>
<td>O(^1D) + CH(_4) \rightarrow CH(_3) + OH</td>
</tr>
<tr>
<td>C2(^1)</td>
<td>O(^1D) + CH(_4) \rightarrow CH(_3)O + H</td>
</tr>
<tr>
<td>C3(^1)</td>
<td>O(^1D) + CH(_4) \rightarrow CH(_2)O + H (_2)</td>
</tr>
<tr>
<td>C4</td>
<td>O + CH(_2)O \rightarrow OH + H + CO</td>
</tr>
<tr>
<td>C5(^2)</td>
<td>OH + CH(_4) \rightarrow CH(_3) + H (_2)O</td>
</tr>
<tr>
<td>C6</td>
<td>OH + CH(_2)O \rightarrow H(_2)O + H + CO</td>
</tr>
<tr>
<td>C7</td>
<td>OH + CH(_3)OH \rightarrow H(_2)O + CH(_3)O</td>
</tr>
<tr>
<td>C8</td>
<td>OH + CH(_3)O(_2)H \rightarrow CH(_3)O(_2) + H(_2)O</td>
</tr>
<tr>
<td>C9</td>
<td>OH + CH(_3)O(_2)H \rightarrow CH(_3)O + OH + H(_2)O</td>
</tr>
<tr>
<td>C10</td>
<td>HO(_2) + CH(_3)O(_2) \rightarrow CH(_3)O(_2)H + O(_2)</td>
</tr>
<tr>
<td>C11</td>
<td>CH(_3)O + O(_2) \rightarrow CH(_2)O + HO(_2)</td>
</tr>
<tr>
<td>C12</td>
<td>CH(_3)O(_2) + CH(_3)O(_2) \rightarrow CH(_3)O + CH(_3)O + O(_2)</td>
</tr>
<tr>
<td>C13</td>
<td>CH(_3)O(_2) + CH(_3)O(_2) \rightarrow CH(_2)O + CH(_3)OH + O(_2)</td>
</tr>
<tr>
<td>C14</td>
<td>CH(_3)O(_2) + NO \rightarrow CH(_3)O + NO(_2)</td>
</tr>
<tr>
<td>C15</td>
<td>Cl + CH(_3)O \rightarrow HCl + H + CO</td>
</tr>
<tr>
<td>C16</td>
<td>Cl + CH(_3)OH \rightarrow CH(_2)O + H + HCl</td>
</tr>
</tbody>
</table>

\(^1\) Replacement reactions for B7 in Table 1.
\(^2\) Replacement reaction for B20 in Table 1.

HO\(_x\) species constitute the main sink for odd-oxygen. Even in the middle and upper stratosphere where NO\(_x\) and ClO\(_x\) species generally are more important for the odd-oxygen budget, accurate HO\(_x\) mixing ratios are important because of several couplings between HO\(_x\) species and NO\(_x\) and ClO\(_x\) species and the formation of reservoir species such as HNO\(_3\) and HCl. In this study however the methane oxidation chain was not included in the reference model since the water vapour abundance was constrained by the HALOE observations. We will nevertheless include the complete set of reactions in Table 4 to study potential secondary effects of the methane oxidation chain. Crutzen et al. (1995) showed that including the methane oxidation chain results in less ozone deficit at 35–50 km. We will re-investigate this case and examine the mechanisms behind the ozone increase.

A new model run was performed, identical to the reference run in the previous section, except for the inclusion of the reactions in Table 4. Again the resulting ozone profile was compared to the HALOE zonal mean observation during the final day of the simulation. The comparison is presented in Figure 5,
which also includes the results from the reference run for comparison. Figure 6 shows the induced ozone changes with respect to the reference model. Including the methane oxidation results in minor changes in the calculated ozone profile. The agreement with the observations improves by up to 2% at 35–45 km, while it worsens by up to 1% at 50–65 km. This response is weaker or about half of that reported by Crutzen et al. (1995). In the lower region the greater ozone abundance in the model is a direct effect of 10–15% lower ClO\(_x\) mixing ratios (not shown). This decrease is caused by the inclusion of reaction C15 (Cl+CH\(_2\)O→HCl+H+CO), which provides a significant ClO\(_x\) removal process in addition to B54 (Cl+CH\(_4\)→HCl+CH\(_3\)) and other HCl producing reactions of minor importance which are present in the reference model. The ozone decrease in the upper region is a result of changes in HO\(_x\) chemistry. The primary mechanism for HO\(_x\) production is through water vapour dissociation. However, methane oxidation provides an additional source of HO\(_x\) species. Although significantly weaker than the HO\(_x\) production from water vapour, this mechanism provides 2–3% more HO\(_x\) at 55–60 km (not shown), which explains the slight ozone decrease here. The ClO\(_x\) and HO\(_x\) changes are present at all local times, although the HO\(_x\) increase is slightly more pronounced for high solar zenith angles.

Next the influence of a number of radiative model characteristics on the results will be investigated.

c. Radiative processes

The strong changes in solar forcing around sunrise and sunset produce rapid changes in many short-lived species. Since this time period is the focus of the model-observation comparison in this study, the accuracy of the radiative calculations and the timing of the sunset in the model deserves special attention. We therefore examine a few factors which can influence photolysis rates in the model.

1) Solar flux

An obvious source of uncertainty in photochemical models is the solar flux used, which could explain some of the differences in ozone calculations between different models. Many middle atmospheric models, including this one, adopt the WMO–86 reference spectrum. In this study a correction for the seasonal variation in Earth-sun distance was applied in the reference model, but no correction for the variability in solar flux over the 11-year solar cycle was considered.

The solar flux measurements by the Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) (Brueckner et al., 1993) provide more accurate estimations
of the solar flux in the UV and visible spectrum at 115–410 nm. Furthermore SUSIM retrieves daily measurements simultaneously and from the same satellite platform as the HALOE observations. In this section a new simulation with the reference model is performed for which the solar flux is replaced by the SUSIM flux (version 21 retrievals) where applicable\textsuperscript{5}. Using the SUSIM measurements as input to the model not only provides more credible solar fluxes but also provides a flux that is consistent with the HALOE observations, so that any offset in the solar flux from the long-time mean should be reflected also in the HALOE temperature and species observations, when such physical connections exist. To reduce the noise level in the SUSIM data it was pre-processed to produce a monthly mean solar flux for the month of the HALOE observations.

The SUSIM monthly mean flux from January 1994 is on average 4% greater in the O\textsubscript{2} SRB (175–200 nm), 0.5% greater in the O\textsubscript{2} Herzberg continuum (200–242 nm), 2% smaller in the O\textsubscript{3} Hartley band (200–310 nm) and 4% smaller at 310–410 nm than the corrected WMO–86 flux. It should be noted that changes would have been greater (more positive) by about 3.5% had the WMO–86 flux not been corrected for the seasonal variation in Earth-sun distance. The changed solar flux applied in the new model run yield significant changes to key photolysis rate coefficients and hence affects the ozone simulation. Results from the simulation are shown in Figures 5 and 6. The ozone mixing ratio increases at all altitudes compared to the reference run. The agreement with the observed ozone values improves by 2–3% in the stratosphere and by 3–4% in the mesosphere. In the stratosphere the increase is nearly independent of local time while in the mesosphere it is slightly greater, 5–10%, during daytime than at sunset (not shown). The ozone increases are caused partly by increased O\textsubscript{2} photolysis (providing greater odd-oxygen production), and partly by decreased O\textsubscript{3} photolysis (increasing the O\textsubscript{3}/O\textsubscript{x} ratio). The daytime average increase in the net O\textsubscript{2} photolysis rate coefficient (J\textsubscript{1}+J\textsubscript{2}) is 2–5%, depending on altitude, while the daytime average decrease in the net O\textsubscript{3} photolysis rate coefficient (J\textsubscript{3}+J\textsubscript{4}) is 3% (not shown). In the mesosphere these effects are to some extent counteracted by faster water vapour photolysis. Similar results were reported by Siskind \textit{et al.} (1998) and G–99. Both studies reported ozone increases of up to 4% in the upper stratosphere in response to adopting the solar fluxes given by Lean \textit{et al.} (1997), which is greater than the WMO–86 flux by about 10% near 200 nm.

Next, the importance of multiple scattering and surface reflection effects will be examined.

\textsuperscript{5}The SUSIM flux was applied at 122–410 nm. No changes were applied to the Lyman-alpha flux.
II) **Multiple scattering and surface albedo effects**

The calculation of photolysis rates in the reference model involves deriving the transmitted direct solar flux at any given altitude in a spherical geometry. The model thereby neglects the diffuse flux generated by multiple scattering (MS) in the atmosphere as well as reflections from the surface. MS is commonly not included in photochemical models of the upper stratosphere and mesosphere since the air density in this part of the atmosphere is generally too low for MS to locally affect the total flux of photons. However, the study by Meier *et al.* (1982) shows that the net flux, particularly in the visible wavelength region, increases significantly throughout the atmosphere if MS and surface reflections are taken into account. This is primarily because the direct solar radiation as well as the diffuse flux generated by Rayleigh scattering in the lower atmosphere are reflected from the surface and the underlying atmosphere back into the upper atmosphere.

Lary and Pyle (1991) used a photochemical model to show that the greater net incident flux achieved with MS and surface albedo effects taken into account can lead to ozone increases of up to 10% in the upper stratosphere. Motivated by these results the reference model in the present study is in this section extended to include MS and surface albedo effects in order to examine the sensitivity of the calculated sunset ozone profile to these processes. The results in Meier *et al.* (1982) and Lary and Pyle (1991) apply only to the stratosphere and do not discuss the importance of MS and surface reflections at twilight. The analysis presented here will examine the importance of these processes both in the stratosphere and in the mesosphere. Furthermore, since the model response at twilight is of particular interest in this study, changes in radiative parameters will be discussed for both daytime and twilight conditions.

The reference model was extended with the MS algorithm presented in Meier *et al.* (1982) which in addition to the direct solar flux also describes the contributions from multiply scattered light and reflected diffuse and direct solar radiation from the surface. A surface albedo of 30% was assumed. In this approach the direct solar radiation is derived in a spherical geometry and the reflected and scattered light in a plane parallel approximation. Anderson (1983) shows that this approach yields accurate fluxes for solar zenith angles of up to 92 degrees compared to a fully spherical derivation. This radiative implementation yields substantially greater fluxes in the visible spectrum throughout the stratosphere and mesosphere than in the reference model. Details of the flux changes are presented in Appendix A. Except for the new radiative treatment, the model was constrained and treated as in the reference run.

The ozone deficit versus the HALOE observations with this new model ver-
sion is shown in Figure 5 and the changes compared to the reference model are shown in Figure 6. Taking MS and surface reflections into account removes up to 6% of the discrepancy with the observations at 35–50 km (and increases the ozone surplus at 30 km). No significant changes are present in the mesosphere.

The ozone increase can be understood by considering changes in key photolysis rate coefficients that affect the odd-oxygen budget. The additional flux available with MS and surface reflections enabled, generally leads to faster photodissociation of species, primarily those with absorption cross sections in the visible spectrum. Three photochemical mechanisms responsible for the ozone change in the stratosphere have been identified. These relate to changes in the photolysis rate coefficients of O$_2$, O$_3$ and NO$_2$, which are all key parameters in the odd-oxygen budget. Figure 7 show these coefficients as functions of altitude. Each panel shows the coefficients both with and without MS and surface reflections and for both daytime (SZA=15$^\circ$) and twilight (SZA=90$^\circ$) conditions. Before discussing this figure we note that the photochemical lifetime of odd-oxygen at 35–50 km is in the order of hours to several days. The ozone increase at these altitudes is therefore primarily a result of changes in the odd-oxygen balance during the day, when odd-oxygen production and loss rates are the largest.

O$_2$ photolysis is the primary production mechanism for odd-oxygen. At 15 degrees SZA the net O$_2$ photolysis rate coefficient ($J_1+J_2$) increases by up to 4% in the model domain and, in particular, by 2–3% at 35–50 km, due to flux increases in the Herzberg wavelength region. (see Appendix A). This perturbation in isolation from other changes would yield proportional increases in odd-oxygen and ozone. However, increased solar flux at the lower end of the visible spectrum yields 50–55% greater NO$_2$ photolysis rate coefficients during the day. This leads to lower NO$_2$/NO$_x$ ratios and thereby to slower odd-oxygen loss rates through reaction B24 (O+NO$_2$→NO+O$_2$), which is the rate limiting step of the NO$_x$ catalytic odd-oxygen loss cycle. This mechanism acts to further increase the ozone abundance in the middle stratosphere where NO$_x$ reactions dominate odd-oxygen loss rates. Also, 50–75% greater total flux in the ozone Chappuis absorption band at 450–850 nm (see Appendix A) leads to faster ozone photolysis. At 35–50 km the net ozone photolysis rate coefficient ($J_3+J_4$) increases by 1–6% during the day. This change does not affect the odd-oxygen budget directly, but leads to greater mixing ratios of atomic oxygen, and therefore to faster catalytic odd-oxygen loss rates through atomic oxygen reactions with OH, HO$_2$, NO$_2$ and ClO (B8, B9, B24, and B38). In total the changes induced by increased O$_2$ and NO$_2$ photolysis dominate over the changes induced by changes in ozone photolysis, resulting in the 1–6% ozone improvement shown in Figure 5.
Figure 7. Photolysis rate coefficients of (a) $O_2$ ($J_1+J_2$), (b) $O_3$ ($J_3+J_4$) and (c) $NO_2$ ($J_8$). Left panels show the coefficients with (solid) and without (dashed) multiple scattering and surface reflections for daytime (SZA=15°) and twilight (SZA=90°) conditions as indicated in the figures. Right panels show the relative impact of including the multiple scattering and surface reflection processes.
These conclusions are consistent with Lary and Pyle (1991), although the ozone response presented here (Figure 6) is somewhat weaker than the \( \sim 10\% \) change they reported.

From Figure 7a and b it is also clear that flux increases in the mesosphere are too weak to substantially affect \( O_2 \) and \( O_3 \) photolysis rates. The response in the \( O_2 \) and \( O_3 \) coefficients to the additional flux generated by MS and surface reflections is less than 1\%. These processes are hence not very important for the ozone simulation in this region, as is clearly seen in Figure 6.

Next we will investigate the potential model improvements induced by introducing an interactive ozone implementation, for which photolysis rates are recalculated using simulated ozone mixing ratios instead of climatological ozone values.

III) INTERACTIVE OZONE

The photolysis lookup table in the reference model is pre-calculated using a climatological diurnal average ozone profile. A more accurate approach is to update the photolysis rate coefficients during the simulation using the simulated ozone mixing ratios to recalculate the atmospheric transmission. This would have three important effects. First of all, the dependency on the ozone climatology would disappear. Secondly, all photolysis rate coefficients would be consistent with the calculated ozone profile allowing for interaction between the chemical and radiative parts of the model. A change in the ozone abundance would generate changes in photolysis rates and thus feedbacks on ozone and other species. Finally, the strong diurnal variation in ozone in the mesosphere (Figure 3) would be taken into account and thus would yield different overhead optical thicknesses in the ozone absorption wavelength region for different local times. A completely interactive implementation between chemical and radiative calculations would imply updated photolysis rate coefficients at each time step in the model. This would be much too time consuming, considering the short time steps used in the model used here. Instead the lookup table is recalculated every 24 hours using the complete diurnal variation of the ozone mixing ratio from the previous day.

The calculated ozone profile with this new approach is compared to the HALOE zonal mean observations in Figure 5 and to the reference model in Figure 6. There are no significant changes in ozone compared to the reference run at the lower altitudes but at 45–70 km the ozone mixing ratio is up to 10\% smaller than achieved with the reference model. The maximum change occurs at 60–65 km. The differences are however significantly smaller for moderate solar zenith angles (not shown). For example, at noon the ozone mixing ratio in the
model run with interactive ozone is less than 1% smaller than in the reference model. This suggests that the large differences in ozone at sunset primarily are produced at high solar zenith angles.

This can be explained as follows: The overhead ozone column densities used to derive the local ozone photolysis rate coefficients in the mesosphere are significantly overestimated in the reference model, since diurnal average ozone mixing ratios are used instead of the lower daytime ozone values calculated by the model. For the daytime ozone calculation this has little effect since the overhead atmosphere is optically thin for wavelengths in the ozone absorption cross sections for moderate solar zenith angles. However at large solar zenith angles the optical path through the atmosphere is many times larger than for an overhead sun and mesospheric ozone then causes significant absorption of the solar flux in the Hartley band. The overestimated overhead ozone column densities then lead to unrealistically effective attenuation of the solar flux and hence too low ozone photolysis rates, which explains the greater ozone abundance at twilight in the reference run.

d. Numerical tests

A few important numerical issues regarding the time step of the numerical solver remain to be examined. The rapid changes in ozone and other short-lived species in the mesosphere at high solar zenith angles will not be captured accurately if the time resolution is too coarse. In the reference model, the variable time step around sunset ranges from a 1 to 4 minutes and photolysis rate coefficients are updated from the photolysis lookup table at every time step of the numerical solver. It is assumed that this temporal resolution is sufficient to resolve the chemical changes occurring around the time of the HALOE observations.

A test run was performed to verify this assumption. In this model run the numerical solver was forced to use shorter time steps by decreasing the maximum allowed relative error in the solution by one order of magnitude. The time steps were thus lowered to an interval ranging from 20 seconds to 2 minutes around sunset. This resulted in no significant changes in the calculated ozone profile, regardless of local time. Furthermore, increasing the temporal resolution of the J-value lookup table from 3 minute steps near sunset to 1.2 minute steps affected the sunset ozone profile by less than 1%.

Many models use a much coarser time resolution for photolysis rate updates than adapted in this model study. Forcing the model to limit updates of J-values to 15 minute intervals resulted in up to 15% differences in the ozone mixing ratio during the sunlit morning and late afternoon hours in the mesosphere. At sunset differences were limited to 5%. For moderate solar zenith angles the importance
of frequent updates of J-values is less important because photolysis rates change much more slowly during the mid day. At noon the ozone response to the less frequent J-value updates was below 0.5%.

In conclusion the standard time steps used in the reference model and subsequent runs are sufficient to resolve the rapid chemical changes occurring at high solar zenith angles. This conclusion is however based on that J-values are updated at every time step. 15 minute intervals between J-value updates are sufficient for accurate calculations of daytime ozone but are not sufficient for high solar zenith angle studies of mesospheric ozone.

e. Cumulative effects

Various model improvements have been considered separately in the previous sections. Next, all of these changes were added together in the model to produce the model’s best estimate of the sunset ozone profile. Hence, the methane oxidation chain, the SUSIM flux, interactive updates of photolysis rate coefficients and multiple scattering and surface reflections were all enabled in this model run (referred to as the “best estimate diurnal model run” hereafter).

The results are shown in Figures 5 and 6. Although the individual processes induce rather small changes in the calculated ozone mixing ratio, their cumulative effects are approximately additive above 30 km and yield a significant improvement in the agreement with the observations in the upper stratosphere. An increase of up to about 10% is achieved compared to the reference model in this region, leaving an ozone deficit versus the HALOE observations of approximately 10%. The ozone increase in this part of the model atmosphere is produced through the combined effects of all added processes, except for the interactive ozone implementation, which has only a minor (negative) effect in the stratosphere. In the lower mesosphere, however, the effect of updated photolysis rate coefficients is more important and leads to even greater underestimations of the observed ozone mixing ratios than in the reference model. The mesospheric model-observation discrepancies range from about 10 to 35%, with generally increasing discrepancies with greater altitude.

To examine whether the remaining ozone deficit could be caused by unusually high ozone mixing ratios in the observations or by exceptional abundances of the constrained HALOE gases on the day of the model-observation comparison, the model was also run for several other summer low latitude combinations. These results are shown in Figure 8. The figure shows four comparisons between the model and HALOE observations during the southern hemisphere summer, including the 12 January 1994 comparison shown in Figure 5, and four comparisons during the northern hemisphere summer. It is clear from the figure that
Figure 8. Relative differences between the model and HALOE zonal mean ozone observation at sunset. The data presented was achieved with a model version including the methane oxidation chain, SUSIM solar fluxes, interactive updates of photolysis rate coefficients and multiple scattering and surface reflections enabled as in case 6 of Figure 5. Results are shown for eight different low latitude summer locations as indicated by the legend.

the model underestimation of ozone is a robust result. All cases show similar underestimations of the HALOE observations as in the 12 January 1994 case. Similar consistencies for some of these dates and latitudes were noted by G–99. The differences between individual cases are generally below 10 percentage units at 30–35 km and below 5 percentage units at 40–70 km. At 75 km the variation is greater, presumably due to the larger uncertainties in the HALOE ozone and water vapour measurements at this altitude. The impact of the HALOE measurement uncertainties are discussed in section 5c. Finally it is noted that outside the ±25° latitude band covered by these results, discrepancies are expected to be similar in magnitude judging from earlier work (Khosravi et al., 1998; G–99; Natarajan et al., 2002) that explored the latitude dependence of the ozone deficit problem.

To conclude this section, we note that despite the efforts made here to derive accurate sunset ozone mixing ratios, significant discrepancies with the ozone observations remain in the upper stratosphere. The 10% model underestimation of ozone at 40–55 km is greater than the uncertainties of the HALOE zonal mean values (see section 4a for values). However, while the model underestimation in this region is rather small and could perhaps be explained by systematic errors in the model and measurements which were not covered here, e.g. sensitivity
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to the parameterisation of $O_2$ absorption in the SRB (see section 6b for further
discussion), the large ozone underestimation in the mesosphere is a more serious
problem suggesting deficiencies in the model chemical scheme and photochemical
data. Therefore we will next perform a Monte Carlo analysis to examine the
importance of errors induced in the model by uncertainties in photochemical
rate coefficients.

5. Random errors

The rate coefficients of most photochemical reactions listed in Tables 1–4 were
taken from JPL–97 (deMore et al., 1997). This catalogue lists bimolecular and
termolecular reaction rate coefficients as well as absorption cross sections for
photolysis reactions. For example, bimolecular reaction rate coefficients are
expressed in the Arrhenius form as

$$k(T) = A \exp \left[ \frac{E}{R} \left( - \frac{1}{T} \right) \right], \quad (2)$$

where $T$ is the temperature and $A$ and $E/R$ are measured quantities, or as

$$k(T) = k_{298} \exp \left[ \frac{E}{R} \left( \frac{1}{298} - \frac{1}{T} \right) \right], \quad (3)$$

where $k_{298}$ is the reaction rate coefficient measured at 298 K. Similar expres-
sions exist for termolecular reactions (see the JPL-catalogue for further details).
Most coefficients, including photolysis rate coefficients, are assigned uncertainty
factors that define the upper and lower uncertainty limits of the recommended
values. For bimolecular reactions this is expressed as

$$f(T) = f_{298} \exp \left| \frac{\Delta E}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \right|, \quad (4)$$

where $f_{298}$ and $\Delta E/R$ are listed for each reaction. The upper and lower un-
certainty limits for a given rate coefficient, $k(T)$, are given by $k(T) \cdot f(T)$ and
$k(T)/f(T)$ respectively. As the temperature changes with altitude, both rate
coefficients and uncertainty factors vary with height. For photolysis rate coeffi-
cients a single uncertainty value independent of temperature is given. Although
these upper and lower bounds of the uncertainty intervals were not derived from
rigorous statistical analyses, they represent the current best knowledge of the
uncertainties in the photochemical data that is used in photochemical models.

In this section we will examine the impact of such uncertainties on the mod-
elled ozone mixing ratio. This is achieved through a Monte Carlo (MC) analysis
in which the model is run multiple times with input reaction and photolysis rate coefficients randomly varied within the given uncertainty limits. The resulting ozone variability is a measure of the induced errors. Three important questions will be addressed. (1) What is the magnitude of the induced random errors and can they explain the discrepancies between the modelled and observed ozone mixing ratios presented in the previous section? (2) How do the random errors compare to the systematic errors considered in this study? (3) Which reactions contribute most to the calculated ozone uncertainty? To answer the latter of these questions a statistical analysis based on partial least squares regressions has been performed. In addition a second Monte Carlo analysis has been carried out in which the model constraints of long-lived tracers were varied randomly within the uncertainties of their corresponding HALOE measurements.

**a. Monte Carlo analysis**

1) **Methodology**

For the Monte Carlo analysis the model was run in steady state (SS) mode since simulations of complete diurnal cycles are too time consuming to perform a large number of successive model runs. Except for the fixed solar position in the SS model its implementation of physical and chemical processes are identical to the diurnal model. Furthermore, the version of the SS model used here includes the methane oxidation chain reactions, the SUSIM solar flux as well as MS and surface albedo effects for optimal agreement with the best estimate diurnal model. The model is applied at 23°S on 12 January 1994 and the fixed model profiles of temperature, CH$_4$ and H$_2$O are constrained to the HALOE observations from this time and location. Initialisations of the NO$_x$ and Cl$_x$ mixing ratios are achieved by extracting their corresponding values from the final day of the best estimate diurnal run. Each individual SS model simulation is run for a maximum of 50 days in 5 day intervals. After each such interval, photolysis rates are updated using the calculated ozone abundance and the model is tested for convergence. In general the model converges after 30–40 days, depending on the input parameters selected.

The drawbacks of using a steady state model instead of a full diurnal simulation for the sensitivity analysis are limited for a careful choice of the fixed SZA. Generally, species that are produced during nighttime, e.g. NO$_3$ and N$_2$O$_5$, are underestimated in a steady state model applied at daytime SZAs (Smith, 1995). However, such species do not significantly affect the ozone budget at extrapolar latitudes above 30 km. Several model runs with unperturbed reaction rates and different choices of SZA were performed to find the optimal SZA for reproduction of the diurnal model ozone simulation. It was found that for a SZA of 45 degrees
there is excellent agreement between the SS model and the diurnal model. This SS model run will hereafter be referred to as the MC reference run. Figure 9 shows the calculated steady state ozone mixing ratio profile in comparison with the ozone profile extracted from the diurnal model at 45 SZA as well as with the daytime averaged ozone profile from the diurnal model. The differences are generally within 5%. Furthermore, the short-lived radical species which constitute the main sinks for odd-oxygen, i.e. NO$_2$, ClO, OH and HO$_2$, are also generally within 5% of the diurnal simulation at 45 degrees SZA and within 10–20% of the corresponding daytime averages. It was therefore concluded that the SS model applied at 45 degrees should be accurate enough for the sensitivity studies in this paper.

Figure 10 displays a flow chart describing the MC analysis method. The model is first initialised as described above. Next a set of random reaction and photolysis rate coefficients are produced. As mentioned earlier, the specified uncertainty factors given for each reaction are multiplicative, i.e. for
5. Random errors

Figure 10. Schematic flow chart for the Monte Carlo simulation.
a nominal rate coefficient \( k \) and uncertainty factor \( f \) the upper and lower limits of the uncertainty interval are given by \( k \cdot f \) and \( k / f \) respectively, or \( \exp\{\ln(k) \pm \ln(f)\} \). Therefore it is assumed that the distributions of the random coefficients are lognormal. This assumption was found to be appropriate by Smith (1978) and Stewart and Thompson (1996). The lognormal distribution prevents the calculation of negative values and theoretically allows for positive random values up to infinity. To constrain the random values to always fall within the specified uncertainty interval the following method was used: For each individual reaction a random number \( r \) is generated from a normal distribution with zero mean and its two standard deviation levels at \( \pm \ln(f) \). This ensures that approximately 95% of the generated random values fall between the specified upper and lower uncertainty limits. Random values that fall outside these limits are recalculated until they do not exceed the limits. Next a quasi-lognormal random rate coefficient is given by

\[
k_i = \exp\{\ln(k) + \ln(r)\} = k / r .
\]

This randomisation is applied to all bimolecular, termolecular and photolysis reactions. For \( \text{O}_3 \) photolysis an uncertainty factor of 1.1 was used, although the branching ratios for the products in reactions P3 and P4 (Table 3) are more uncertain. For the \( \text{H}_2\text{O} \) and NO photolysis reactions (P5 and P7), which are important mainly in the mesosphere, uncertainty factors are not listed in the JPL catalogue. \( \text{H}_2\text{O} \) and NO absorb in the SRB wavelength region and were therefore assigned the same uncertainty factor as was specified in the JPL catalogue for P2 (\( \text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \)).

Figure 11 displays a few examples of rate coefficient distributions derived from 2000 random selections using the method described above. One photolysis rate coefficient (P2), one termolecular reaction rate coefficient (T1) and two bimolecular reaction rate coefficients (B13 and B43) are shown at 45 km altitude. For the model temperature at this particular height the uncertainty factors for these four reactions are 1.20, 1.15, 1.35, and 3.19 respectively. The three different types of reactions are treated identically, so the different shapes of the distributions are purely the result of the difference in uncertainty factors. For relatively well known rate coefficients, such as P2 and T1 (Figure 11a and b), the uncertainty interval is nearly symmetric around the reference value and the distribution is hardly distinguishable from the Gaussian shape of a standard normal distribution. For B13 the uncertainty factor is somewhat greater and the lognormal nature of the distribution is visible as a slight skewness of the dis-

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\(^{6}\)Here the functional dependence on temperature in the notation has been omitted for clarity.
5. Random errors

Figure 11. Histograms showing the random distributions for the rate coefficients of (a) the photolysis reaction P2, (b) the termolecular reaction T1, and (c, d) the bimolecular reactions B13 and B43 at 45 km generated from 2000 calculations. The nominal rate coefficients recommended in the JPL-catalogue are indicated by the vertical dotted lines and the upper horizontal axes show the relative deviations of the random values from this reference.
tribution (Figure 11c). The majority of the reactions in Tables 1–4 are known at better or similar accuracy as B13, so most reactions are not very sensitive to the choice of a lognormal distribution function for the random rate coefficients. However, for a few reactions that are associated with large uncertainty factors, e.g. reaction B43 (Figure 11d), the uncertainty interval is strongly asymmetric and the distribution significantly skewed towards the lower values.

After the randomisation of the rate coefficients the model is run for repeated 5 day intervals until convergence is reached. The convergence criterion is fulfilled when the maximum relative change of all species at all altitudes between subsequent 5 day periods is less than 0.1%. After each 5 day period the randomised photolysis rate coefficients are updated to incorporate the simulated ozone profile. When the model has converged, the resulting species concentrations and random rate coefficients are stored and a new run is initialised.

To achieve good statistics from the multiple model runs in the MC analysis, i.e. for the mean and standard deviation of the ozone mixing ratios in successive runs to converge, the model must be run a sufficiently large number of times. In previous studies a wide variety of minimum number of model runs has been used. Clancy et al. (1987) stated that 100 model runs are sufficient for a mesospheric model. However, we note that stratospheric chemistry is more complex and may require a larger set of runs. Natarajan et al. (1986) performed Monte Carlo studies of upper stratospheric ozone and settled for 200 runs while Stolarski et al. (1978) studied ozone sensitivity at 15–60 km and showed that a minimum of 1200 runs is required for these altitudes.

In the present study a series of seven MC simulations were performed, using 20, 50, 100, 200, 500, 1000 and 2000 model runs respectively. Figure 12 illustrates the convergence of the cumulative mean ozone mixing ratio of the seven MC simulations at 30, 45, 60 and 75 km. Figure 13 shows the corresponding cumulative standard deviations. It is clear that the mean converges more quickly than the standard deviation (in relative terms) and also displays an altitude variation, with faster convergence at the lower altitudes. After 100 model runs the variability in the mean between the simulations using 100, 200, 500, 1000 and 2000 runs respectively is 2–5% depending on altitude. Thus, to accurately estimate the mean of the random ozone distribution, a mere 100 model runs should be sufficient for the altitudes considered here.

In this study however we are interested in the variability in the simulated ozone profile. An accurate estimation of the ozone standard deviation is therefore required. From the standard deviation plots we note that the differences between the MC simulations at 100 runs or more are in the order of 20%. To acquire accuracy in the order of 5% or less, at least 1000 model runs would be
required. This estimation is however rather uncertain since at a 1000 runs there are only two simulations available for comparison. To statistically prove how many model runs would be required for 5% accuracy in the estimated standard deviations, a Monte Carlo simulation of Monte Carlo simulations (all using at least 2000 runs) would be required. From the data in Figure 13 we can simply note that the ozone standard deviation converges towards some value and that the uncertainty in the estimated standard deviation in the simulation using 2000 runs appears to be ±5% or less, which should be sufficient for the purpose of this study. It should be noted that the mean and standard deviation would obviously be approached in a different manner, if another set of MC simulations would be performed.

Figure 12. Cumulative mean ozone mixing ratio at (a) 30, (b) 45, (c) 60 and (d) 75 km derived from seven Monte Carlo simulations using 20, 50, 100, 200, 500, 1000 and 2000 model runs respectively. The relative deviations from the cumulative mean value of the entire 2000-run simulation are indicated on the right vertical axes.
Considering the relatively slow convergence of the ozone standard deviation in the MC simulations, we proceed using only the 2000 run simulation for further analysis. In the following section the ozone variability in this simulation is discussed in more detail.

II) Results
Figure 14 shows the ozone distributions from the MC simulation at four different altitudes: 30, 45, 60 and 75 km. Although the input rate coefficient distributions are lognormal, the ozone distributions appear to be near normally distributed. There is no notable skewness in the distributions, except possibly a very weak one at 75 km. This suggests that ozone is controlled mainly by reactions with relatively well known rate coefficients (greater uncertainties result in greater skewness in the lognormal rate coefficient distributions, see Figure 11). This is in disagreement with some previous studies (e.g. Stolarski and Douglass,
Figure 14. Histograms showing the ozone distributions generated from 2000 model calculations with randomised input rate coefficients. Data are shown at (a) 30, (b) 45, (c) 60 and (d) 75 km. The ozone mixing ratio of the MC reference run (using nominal JPL recommendations) is indicated by the vertical dotted lines. The upper horizontal axes show the relative deviations of the random ozone values from the reference run.
Figure 15. Standard deviation of the ozone mixing ratio derived from a MC simulation using 2000 model runs. Values are presented in relative terms as a percentage of the ozone mixing ratio in the MC reference run. Four cases are shown: (P) uncertainties in photolysis rate coefficients only; (B&T) uncertainties in bimolecular and termolecular reaction rate coefficients only; (P+B&T) the combined effect of uncertainties in all reactions; and (P+B&T non-interactive) same as in (P+B&T) but without interactive treatment of photolysis, i.e. J-values were not updated with the calculated ozone profile for this case.

1986; Natarajan et al., 1986; and Chen et al., 1997), that showed greater right hand than left hand standard deviations for the simulated ozone distributions. Presumably, this is mainly because those studies were using older and hence more uncertain rate coefficients.

The widths of the ozone distributions (Figure 14), and hence the uncertainties of the modelled ozone mixing ratios, increase with altitude, in agreement with many previous studies. Figure 15 shows the vertical dependence of the ozone standard deviation derived from several MC simulations. The standard deviation for the general case (solid line), discussed above, increases from about 6% at 30 km to 20% at 75 km, through a plateau with values of 10% at 40–
50 km. This general shape of the vertical variation of the ozone uncertainties was also reported by Chen et al. (1997), and will be discussed further in section 5b. In particular, the sharp decrease in the standard deviation below 40 km is related to the interactive treatment of radiation and chemistry in the model. We made a test simulation identical to the MC simulation described above, but without updating J-values with the calculated ozone profile. The resulting standard deviation is shown in Figure 15 (dotted line). The standard deviation for this simulation is slightly smaller at 40–55 km and slightly larger below 40 km than for the original simulation with interactive J-values. Thus, while allowing the J-values to adjust to ozone changes increases ozone uncertainties above 40 km, it appears as if below 40 km, where overhead ozone absorption becomes significant, there are compensating effects between local and non-local ozone absorption that result in less variability at the lower altitudes. In conclusion, interactive treatment of J-values is important not only for the mean state of the model but also for variability.

To examine the importance of the uncertainties in photolysis rate coefficients relative to the uncertainties in (bimolecular and termolecular) reaction rate coefficients, two additional MC simulations (with interactive J-values) using 2000 model runs were performed, for which only photolysis rate coefficients were perturbed in the first one, and only reaction rate coefficients in the second one. The resulting ozone standard deviations are shown in Figure 15. Most of the ozone uncertainty comes from inaccuracies in the reaction rate coefficients (dash-dotted line), but inaccuracies in photolysis rate coefficients (dashed line) contribute significantly to the overall uncertainty as well, and thus this shows that previous studies ignoring inaccuracies in photolysis rate coefficients are likely underestimating the uncertainties in simulated ozone values. Furthermore, it was found that the variance (squared standard deviation) induced by uncertainties in photolysis rate coefficients and the variance induced by uncertainties in reaction rate coefficients are approximately additive (not shown).

Figures 14 and 15 show that the magnitude of the ozone uncertainty induced by inaccuracies in reaction and photolysis rate coefficients is similar to the ozone discrepancies between the best estimate diurnal model and the HALOE observations described in section 4. For a more careful comparison, Figure 16 shows the ozone deficit derived with the diurnal model together with the one and two standard deviations from Figure 15. The model-observation discrepancy is smaller than the 1-sigma uncertainty up to 55 km and at 60–75 km the magnitude of the modelled ozone deficit exceeds the 1-sigma uncertainty limit while it is smaller than the 2-sigma level. Since the ozone distributions are near normally distributed (Figure 14) about 95% of the model runs in the MC simulation fall
Figure 16. Discrepancy between the best estimate diurnal model and the HALOE observations (solid). Shaded areas denote the one (dark grey) and two (light grey) sigma uncertainties derived from a MC simulation with the SS model incorporating uncertainties in reaction and photolysis rate coefficients.

within the two 2-sigma levels, so these limits represent reasonable upper bounds for the induced model uncertainties. It can be concluded then, that the model underestimation of the HALOE observations could very well be explained by errors in the rate coefficients measurements. We note that the ozone deficit derived by the diurnal model and the MC ozone uncertainties are not comparable in a strict sense since the SS model used for the MC analysis is representative of daytime conditions while the comparison between the diurnal model and the HALOE observations were carried out at sunset. However, in the stratosphere the ozone deficit at sunset is mainly the result of an imbalance in the odd-oxygen budget during the day (when odd-oxygen production and loss rates maximise). For the mesosphere, we have already noted in section 4a that ozone is under daytime photochemical control at 70 and 75 km at the time of the HALOE observations. At 55–65 km, where ozone is more influenced by nighttime chemistry during the HALOE occultations, it is plausible although unlikely, that the chemical constants governing nighttime ozone chemistry are more accurate than for the typical daytime chemistry to such a degree that uncertainties in photochemistry cannot explain the modelled ozone deficit.

In order to identify the key reactions contributing to the overall ozone uncertainty, the next section presents a statistical analysis based on partial least
squares regression. We also defer a general discussion on the vertical shape of the ozone standard deviation profile to that section.

b. Partial least squares regression analysis

Partial least squares (PLS) regression, is an iterative statistical method related to principal components regression (PCR) and multiple linear regression (MLR) (see e.g. Höskuldsson, 1996). The purpose of these methods is to derive statistical models that estimate the values of one or more response variables at the basis of selected linear combinations of a set of explanatory variables or derivatives thereof. In PLS regression, the linear combinations, referred to as latent variables, are formed as to maximise the covariance between the response variable and the explanatory variables. In other words, the method can be used to identify the explanatory variables that correlate best with the response variable, while also describing the maximum variance in the response variable. In our case the response variable could be the ozone concentration and/or any other species concentration we would like to describe with the statistical model. The explanatory variables could be the model input parameters that were varied in the MC analysis, i.e. the reaction and photolysis rate coefficients. In short, a PLS regression of the ozone concentration on the rate coefficient data can reveal which reactions contribute most to the calculated ozone uncertainty, taking into account both the inaccuracies in rate coefficients and the relative importance of the individual reactions for the ozone steady state concentration.

The PLS regression technique has primarily been used in engineering applications. We are not aware of a study where PLS regressions have been used to study middle atmospheric chemistry, although Considine et al. (1999) used a multiple linear regression approach to examine the dominating influential parameters for column ozone trends and middle and high latitude ozone in the lower-most stratosphere. Stewart and Thompson (1996) and Gao et al. (1996) used regression techniques to analyse tropospheric chemistry. PLS regression is a standard method provided by several statistical packages. Here we use the PLS Toolbox to perform the regression analysis. As an example, Figure 17 shows the results of a PLS regression of the MC data at 65 km. The horizontal and vertical axes show the weights on the first and second latent variables respectively. Each data point in the scatter plot represents a photochemical reaction in the model. The interpretation of the figure is that the greater the magnitude of the weight of a data point, the greater the contribution is to the ozone variance. Reactions with positive weights correlate positively with ozone and thus contribute to ozone production, while reactions with negative weights contribute to ozone loss. For the particular case shown in Figure 17, it can be shown that the
Figure 17. Loadings plot for the PLS regression at 65 km. The weight of each explanatory variable (rate coefficient) on the first latent variable (LV1) is plotted against the corresponding weight on the second latent variable (LV2). The analysis is based on 2000 randomisations of the rate coefficients of the reactions in Tables 1–4 and the resulting ozone concentrations derived by the model. Each data point represents a photochemical reaction, while only the ones with a large contribution to the ozone variance are shown by name.

The first latent variable (LV1) explains about 95% of the ozone variance, indicating a high degree of correlation in the data. The second latent variable (LV2) explains about 4% of the ozone variance and thus, only LV1 needs to be considered to explain the majority of the ozone variance. The key reactions contributing to the ozone variance are indicated.

Similar regressions have been performed for each model level (not shown), and Table 5 lists the reactions whose uncertainties contribute most to the ozone variance. Results are presented only at 40 km and above, since the PLS regressions are poor below this altitude. This is presumably because the regression technique does not cope well with non-local effects, which can be important in the lower and middle stratosphere. For example, rate coefficient changes can affect ozone both directly, through local chemistry, and indirectly, through...
changes in the overhead amount of absorbing gases.

For ozone production there are three dominating reactions that contribute to the ozone variance: T1 (O+O₂→O₃+M), B18 (OH+HO₂→H₂O+O₂) and P2 (O₂+hν→O+O). Note that O₂ photolysis is divided in two reactions, P1 and P2, where the latter represents photolysis for wavelengths greater than about 175 nm and the former represents photolysis for wavelengths shorter than this limit, which provides excited atomic oxygen atoms O(^1D). Reactions T1 and P2 are large providers of ozone variance at all altitudes in the 40–75 km interval, while the contribution from B18 becomes weaker at 40 and 45 km. As P2 is the single most important odd-oxygen production mechanism in this region and T1 converts atomic oxygen atoms into ozone it is not surprising that these two reactions, with uncertainties in the order of 20% and 15–30% respectively, are large contributors to the calculated ozone uncertainty. Reaction B18 is the most important HOₓ loss reaction throughout the region and has its largest contributions to the ozone uncertainty at altitudes where HOₓ dominates odd-oxygen loss rates, i.e. mainly in the mesosphere. An additional reaction related to HOₓ chemistry (and that correlates positively with ozone) is present at 45–55 km; reaction B5 (O(^1D)+N₂→O+N₂) quenches exited atomic oxygen atoms and thus limits the amount of exited atomic oxygen atoms available for HOₓ production through B4 (O(^1D)+H₂O→OH+OH) which dominates HOₓ production below 60 km. Also, at 40 and 45 km the HCl yield reaction B43 (OH+ClO→O₂+HCl) has a large uncertainty factor (∼3.2) and therefore contributes strongly to the ozone uncertainty there.

On the loss side, the reactions B9 (O+HO₂→OH+O₂), B8 (O+OH→O₂+H), P5 (H₂O+hν→H+OH) and P3 (O₃+hν→O₂+O(^1D)) are the dominating providers of ozone uncertainty at the upper altitudes (60–75 km). Reactions B8 and B9 are the two most important reactions for catalytic odd-oxygen loss, P5 is the dominant source of HOₓ above 60 km and P3 represents the photolysis of ozone at wavelengths shorter than about 310 nm. At 55 km and below, P3 is the single most important contributor to the ozone variance (on the loss side), despite a rate coefficient uncertainty of only about 10%, and B4 (O(^1D)+H₂O→OH+OH) replaces P5 as the most important HOₓ production mechanism. Reactions B8 and B9 contribute weaker amounts to the ozone uncertainty at 50 and 55 km. Reaction B1 (O+O₃→O₂+O₂) appears as a minor contributor at 45 and 50 km and P4 (O₃+hν→O₂+O) (ozone photolysis at wavelengths greater than 310 nm) at 40 and 45 km. At 40 km there is also an influence from NOₓ chemistry, where uncertainties in the catalytic odd-oxygen loss reactions B33 (NO+O₃→NO₂+O₂) and B24 (NO₂+O→NO+O₂) contribute to the ozone uncertainty.
Table 5. Reactions that contribute to calculated ozone uncertainties at altitudes 75, 70, 65, 60, 55, 50, 45 and 40 km as given by PLS regression analyses. For each altitude production and loss mechanisms are given in order of importance. Key contributors are marked with bold font. The uncertainty factors, $f$, for bimolecular and termolecular reactions are temperature dependent, and are given here for the specific model atmosphere in this study.

<table>
<thead>
<tr>
<th>Height</th>
<th>Production</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.</td>
<td>$f$</td>
</tr>
<tr>
<td>75 km</td>
<td>T1</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>B18</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>P2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>B14</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>P1</td>
<td>1.2</td>
</tr>
<tr>
<td>70 km</td>
<td>T1</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>B18</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>P2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>P3</td>
<td>1.1</td>
</tr>
<tr>
<td>65 km</td>
<td>T1</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>B18</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>P2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>P5</td>
<td>1.2</td>
</tr>
<tr>
<td>60 km</td>
<td>T1</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>B18</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>P2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>P5</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>B11</td>
<td>1.45</td>
</tr>
<tr>
<td>55 km</td>
<td>P2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>T1</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>B18</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>B5</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Continued on the next page...
It can be noted that, except for the oxygen reactions T1, P2 and P3, which are important for the ozone uncertainty at all altitudes, HOX reactions have their main impact above 45 km, effects of ClOX reactions are seen mainly at 40 and 45 km and NOX chemistry affects mainly the 40 km level. This reflects the general vertical dependence of the relative contribution of the HOX, ClOX and NOX catalytic odd-oxygen loss cycles to the overall odd-oxygen loss rate (see e.g. Brasseur and Solomon, 1986; Jonsson et al., 2004). However, the uncertainty factors of the individual reactions are important too, as to determine the overall simulated ozone variance. Notably the general increase in ozone standard deviation with altitude in the mesosphere (Figure 15) is caused by increasing uncertainty factors with altitude for the major contributing reactions. Essentially this reflect the temperature dependency of the uncertainty factors; the rate coefficient uncertainties generally increase in magnitude with increasing temperature difference from room temperature (298 K). The same reasoning explains the decrease with altitude in the ozone standard deviation in the stratosphere for the MC simulation without interactive J-values.

<table>
<thead>
<tr>
<th>Height</th>
<th>Production</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No.</td>
<td>$f$</td>
</tr>
<tr>
<td>50 km</td>
<td>P2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>T1</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>B18</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>B5</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45 km</td>
<td>P2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>T1</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>B18</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>B43</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>B5</td>
<td>1.25</td>
</tr>
<tr>
<td>40 km</td>
<td>P2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>T1</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>B43</td>
<td>3.27</td>
</tr>
<tr>
<td></td>
<td>P8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>B18</td>
<td>1.46</td>
</tr>
</tbody>
</table>
Other important uncertainties in photochemical modelling are boundary values or constraints of long-lived source gases. This is investigated in the next section.

c. Uncertainties in model constraints

The zonal mean uncertainties of the HALOE observations of CH$_4$, H$_2$O, HCl, NO, and NO$_2$ are shown in Figure 18. The measurement errors increase with altitude and become larger than 100% towards the upper detection limits of the respective species. However, in the mesosphere, it is mainly the poor quality of the water vapour measurements (which reaches a maximum of about 70% at 75 km) that is of concern for the ozone simulations, as HO$_x$ generally dominates over NO$_x$ and ClO$_x$ as an odd-oxygen sink in this region. Since these measurements have been used to constrain the model in the diurnal simulations that were performed to estimate the ozone deficit versus the HALOE ozone observation, it is relevant to examine the impact of the uncertainties in the model constraints on the ozone calculations. G–99 have studied the ozone sensitivity to uncertainties

![Figure 18. Zonal mean uncertainties (%) for the HALOE observations of CH$_4$, H$_2$O, HCl, NO, and NO$_2$ on the 12 January 1994 at 23°S.](image-url)
in HALOE model constraints, by individually changing the constrained variables to selected upper and lower uncertainty limits respectively. Their results indicate that in the 40 to 55 km region the calculated ozone deficit values are most sensitive to uncertainties in the ozone measurement themselves and to uncertainties in the HALOE temperature data. However, the HALOE uncertainties (in percent) were assumed to be constant with altitude, which is not particularly realistic for the extended vertical model domain used here (Figure 18), and the combined uncertainty for all the model constraints cannot be derived with such a simple approach. Therefore a more rigorous treatment of the HALOE uncertainties has been performed here. We have used the SS model to perform a MC simulation of 2000 model runs, where the model constraints of CH\(_4\), H\(_2\)O, Cl\(_y\) and NO\(_y\) were randomly varied between upper and lower uncertainty limits derived from the HALOE error data in Figure 18. These error estimates may be rather conservative as the use of zonal averaging reduces the statistical errors. For water vapour in particular, random instrument errors dominate over systematic errors throughout the mesosphere (Harries et al., 1996). For simplicity, a uniform distribution function was assumed for the random values. As the SS model uses fixed constraints of Cl\(_y\) and NO\(_y\), and those exact quantities are not measured by HALOE, the HCl measurement uncertainty was used as a proxy for the uncertainty of the model Cl\(_y\) constraint\(^7\), and similarly, the combined\(^8\) measurement uncertainty of NO and NO\(_2\) was used for the model constraint of NO\(_y\). This is reasonable, as HCl and NO+NO\(_2\) in effect constrain Cl\(_y\) and NO\(_y\) in the diurnal version of the model.

Figure 19 shows the resulting ozone standard deviation from the MC simulation. For comparison, the standard deviation for the combined effect of uncertainties in reaction and photolysis rate coefficients from Figure 15 is also shown. The results show that uncertainties in model constraints induce only very small errors in the ozone simulation in the stratosphere (where the 1-sigma uncertainties remain below 2.5%). For the mesosphere, however, the ozone standard deviation increases rapidly with height and supersedes the standard deviation induced by uncertainties in rate coefficients above 70 km, primarily because of the poor quality of the water vapour measurements at those heights. We did not consider uncertainties in the HALOE temperature constraints in this analysis, so the plotted values may be an underestimate as indicated by the work of G–99.

In addition, another MC simulation including both the uncertainties in model constraints and the uncertainties in rate coefficients was performed. The results

\(^7\)The uncertainty value given for HCl at 50 km was applied at all altitudes in the mesosphere, due to the lack of data in that region.

\(^8\)The sum of the absolute errors of NO and NO\(_2\) (given as mixing ratios) were added and then divided by the sum of the NO and NO\(_2\) mixing ratios.
Figure 19. Standard deviation of the ozone mixing ratio derived from a MC simulation using 2000 model runs. Values are presented in relative terms as a percentage of the ozone mixing ratio in the MC reference run. Three cases are shown: (MC) uncertainties in model constraints only; (RC) uncertainties in rate coefficients only; and (MC+RC) the combined effect of uncertainties in model constraints and rate coefficients.

are also shown in Figure 19. The two effects are additive in variance (not shown). The addition of uncertainties in model constraints has little effect on the total model uncertainty in the stratosphere, but leads to up to almost twice as large standard deviations in the mesosphere. We note that with the addition of uncertainties in model constraints, the resulting 1-sigma model uncertainty, ranging from about 6% at 30 km to almost 40% at 75 km, is very similar in magnitude to the discrepancy between the HALOE ozone observations and the best estimate diurnal model results shown in Figure 5. In fact, the modelled ozone deficit values are within 5% of the total standard deviation values shown in Figure 19. In conclusion, the model errors implied by the uncertainties in the rate coefficients and the model constraints are large enough to alone encompass the model-observation discrepancies. This calls for the need of improved measurements of both rate coefficient data, most importantly of those listed in
Table 5, and of mesospheric water vapour abundances.

6. Discussion

The underestimation of the zonal mean HALOE sunset occultation measurements of ozone calculated by the model in this study is around 10% at 40–55 km and ranges between 10 and 35% at 55–75 km with increasing discrepancies for increasing heights. At 40 km the modelled ozone deficit is similar to that reported by Park et al. (1999) but clearly less severe than in some earlier studies, e.g. Rusch and Eckman (1985), Clancy et al. (1987) and Siskind et al. (1995). For a comparable latitude and season to those studied here, G–99 and Khosravi et al. (1998) underestimated HALOE ozone observations at 40 km by about 6 and 5% respectively, and Natarajan et al. (2002) (referred to as N–02 hereafter) reported a deficit versus LIMS ozone measurements of about 7% at this altitude. Both G–99 and N–02 reported slightly better agreements with the observations in the lower mesosphere at 55 km, where the 10% ozone deficit in this study is about 6% greater than in those studies. The fact that G–99 also used HALOE observations for the ozone comparison and for constraints of long-lived tracers, serves as a good illustration of that although using similar approaches, constraints and observation datasets, systematic model differences can yield significantly different results. N–02 also provided a model comparison with HALOE data, for which the ozone deficit at 55 km was about 7%, supporting the slightly greater ozone deficit in the present study at this altitude. N–02 emphasise that their results are in disagreement with the studies by Osterman et al. (1997) and Jucks et al. (1998) who both reported large ozone deficits above 45 km. The results presented in the current study confirm that there indeed exists an ozone deficit problem, although mainly above 55 km.

In the previous sections we have reported on several types of errors that may contribute to the ozone discrepancies between the model and the observations; contributions are made primarily by (1) uncertainties in the HALOE ozone measurements and constraints; (2) systematic model deficiencies; and (3) model uncertainties induced by inaccuracies in photochemical rate data. These three factors are discussed in further detail below.

a. Observation errors

First, it is relevant to ask how accurate the HALOE ozone measurements are. As noted in section 4a, the average error estimates of the version 19 ozone data are typically 1–10% at 45–65 km and 10–100% at 65–75 km for the particular location and time period considered, so the model-observation discrepancies
exceed the quoted measurement uncertainties below about 65 km. However, we note that in an early assessment of the HALOE ozone measurement quality (using the version 17 retrievals) Brühl et al. (1996) derived some general error estimates for the HALOE ozone data in terms of root sum square errors that showed decreasing values from 12% at 31 km to 6% at 55 km, and increasing values above that, to 11% at 65 km, 51% at 72 km and 95% at 80 km. These values are consistent with the error estimates for the version 19 data, used here, in the mesosphere, but they are significantly larger at stratospheric heights. This inconsistency is currently not well understood, and needs to be addressed by further studies, which are being pursued. Using the more conservative error values of Brühl et al. (1996) it is noted that the magnitude of the derived ozone deficit exceeds the measurement errors only at 60 and 65 km. This however disregards the fact that zonal averaging should reduce the impact of instrument noise, which is the main error source above 60 km (Brühl et al., 1996). The robust ozone deficit, with little variation between different dates and latitudes, derived in this study and shown in Figure 8, suggests that in fact the zonal mean HALOE data in the mesosphere are more accurate than the single profile measurement errors indicates, in particular at 65 and 70 km.

An important source of uncertainty in the HALOE ozone retrievals in the mesosphere is associated with the sharp twilight ozone gradients (Figures 3 and 4). Natarajan et al. (2005) introduced correction factors that better take into account the ozone day-night variations along the line of sight of the observed tangent point on the Earth’s limb, leading to substantially improved ozone retrievals. However, the impact is significant mainly for sunrise occultations, for which the retrieved ozone mixing ratios are up to 25% smaller than in the version 19 retrievals. For sunset retrievals (which are relevant in this study) the changes from the version 19 data are a decrease of up to 6% between 1 and 0.1 hPa (about 48–65 km) and an increase of up to 3% between 0.1 hPa and 0.01 hPa (about 65–80 km). No changes to either sunrise or sunset retrievals were suggested at 1 hPa and below. Thus, even with such improved sunset retrievals, the estimated ozone deficit in this study would still be substantial at 60–75 km.

Another occultation instrument, the ACE-FTS (Bernath et al., 2005; Boone et al., 2005) has recently provided twilight measurements of ozone in the mesosphere. In a preliminary comparison study McHugh et al. (2005) report that the ACE-FTS sunset ozone retrievals (version 1) are greater than the HALOE observations by about 0.4 ppmv at 35–70 km (corresponding to a discrepancy of up to 40%), suggestive of even greater model-observation discrepancies in this region. However, the ACE retrievals have not yet been corrected to deal
with the sharp ozone twilight gradients, so some of this bias between ACE and HALOE is expected to be removed when such are taken into account, although large corrections at sunset would not be expected as indicated by the work of Natarajan et al. (2005). Walker et al. (2005) reported ACE-FTS ozone to be on the high side also of SAGE III and POAM III measurements by significant amounts at 40–55 km.

We have also considered the possibility that atmospheric tides may be responsible for some of the high altitude ozone deficit. Tides inflict large temperature and thus density variations in the mesosphere, and may produce non-linear effects (J. C. McConnell, personal communication, 2005). The effects of the diurnal tide on nitrogen oxide and temperature have been observed by HALOE (Marsh and Russell., 2000; Jonsson et al., 2002). However, it seems unlikely that the mesospheric HALOE data at 23°S in January, used in this study, should be substantially affected by the diurnal tide, whose amplitude is at a minimum, both in latitude (Ward et al., 1999) and season (McLandress, 2002) at this location and time.

Regarding model constraints, the results in section 5c show that the HALOE data generally are accurate enough for a useful ozone model-observation comparison at 60 km and below, where the modelled ozone uncertainty induced by errors in the HALOE observations is below 10%. However, the uncertainties increase with altitude and errors in the water vapour constraints alone could explain the ozone deficit at 75 km (keeping in mind that just as for the ozone measurements, the zonal mean data may be more accurate than the single profile uncertainties suggest). ACE-FTS water vapour mixing ratios are greater than those measured by HALOE by up to 30% at 30–70 km (McHugh et al., 2005). Differences are particularly large at 50–65 km, which could imply that the HALOE data are too low in this region. However, we note that the model would have calculated even smaller ozone values in the mesosphere had the model been constrained to greater water vapour values, as that would have provided for more \( \text{HO}_x \) production and thus more odd-oxygen loss. A dry bias of the HALOE water vapour measurements has also been noted in WCRP–SPARC (2000), and a preliminary comparison with EOS-MLS indicate differences of 5–15% in the lower mesosphere, with the HALOE values being lower (Froidevaux et al., 2005).

b. Systematic model errors

Several model deficiencies possibly related to the ozone deficit problem have been analysed in section 4. Other systematic model errors, which were not covered by this study, have been discussed in related publications and are worth mentioning here. For example, the \( \text{O}_2 \) absorption cross section and in particular the
parameterisation of the Schumann-Runge bands (SRB) at about 175–200 nm are important uncertainty factors discussed in several studies. Reviews of such parameterisations can be found in e.g. Siskind et al. (1994) (referred to as S–94 hereafter), Koppens and Murtagh (1996) (referred to as KM–96 hereafter) and Trentmann et al. (2003). G–99 used the widely adopted O$_2$ SRB absorption data from WMO–86, which is based on the parameterisation by Allen and Fredrick (1982). G–99 showed that using the KM–96 parameterisation instead (also adopted in the present study) resulted in an increased ozone deficit at sunset by 2 and 4% at the two top model levels in their study, 50 and 55 km, while changes in the stratosphere were below 1%. On the other hand, they noted a greater sensitivity of the modelled sunset ozone mixing ratio to changes in the O$_2$ absorption cross section in the Herzberg continuum. In the present study, the Herzberg continuum was taken from the work of Nicolet and Kennes (1986). This cross section is 6–17% lower than that of WMO–86 (see e.g. Murtagh, 1988) and generally 5–10% lower than recent JPL recommendations (JPL–97, JPL–00, JPL–02). These two factors could explain part of the smaller ozone deficit shown by G–99, as compared to the results presented here.

Furthermore, for mesospheric heights, KM–96 show that the atomic oxygen production rate (which is proportional to the O$_2$ photolysis rate) using the Allen and Fredrick (1982) parameterisation (or the corresponding WMO–86 cross section) is clearly overestimated compared to line by line (LBL) calculations above 55 km, and particularly so for large SZAs. This was shown also by S–94 and later confirmed by Trentmann et al. (2003). The impact of these differences on ozone is limited for moderate SZAs, typically below 2% for altitudes between 35 and 75 km (S–94). For high solar zenith angles, however, the choice of SRB cross section appears to be more critical. For example, Trentmann et al. (2003) report up to ±30% discrepancies in O$_2$ photolysis rate coefficients between different parameterisations and LBL calculations at 90° SZA. Similar values were reported by KM–96. We note that in the light of this, the uncertainty factor of 1.2 recommended by JPL–97 (and more recently by JPL–00 and JPL–02) for the O$_2$ photolysis rate coefficient may be too low, or at least not representative for the mesosphere and particularly not for high SZAs. In summary, the SRB parameterisation may be an important source of uncertainty in some modelling studies, particularly those addressing questions related to ozone chemistry at high SZAs, such as this one. However, where several parameterisations methods fail to capture the SZA variation in SRB transmittance shown by LBL calculations, the KM–96 method used here is within 4% of the LBL results for any altitude and/or SZA (KM–96). As a result, KM–96 showed that the ozone mixing ratio calculated by a photochemical model using the KM–96 parameteri-
sation is up to about 10% smaller at 55–80 km for a SZA of 85° than when using the WMO–86 SRB cross section. This shows that the impact of the discrepancy between KM–96 and WMO–86 on ozone indicated by G–99 at 50 and 55 km continues to increase at higher altitudes and that using the WMO–86 SRB cross sections may partly mask an ozone deficit in the mesosphere.

A related issue, discussed by S–94 and of particular relevance to this study, is the fact that part of the ozone response to differences in O₂ SRB treatments in the mesosphere is associated with changes in H₂O photolysis. The H₂O absorption cross section overlaps with the SRB and changes by several orders of magnitude in this wavelength region. Treating the H₂O absorption and the O₂ SRB parameterisation separately can introduce large errors in H₂O photolysis rate coefficients as described by S–94. For example, they show that in the stratosphere and for an overhead sun, the H₂O photolysis rate coefficient could be overestimated by more than 50% compared to LBL calculations, depending on the choice of O₂ SRB parameterisation. However, below 60 km HOₓ production is mainly governed by H₂O oxidation by O(^1D)), so the impact on ozone should be relatively small. Above 60 km, where H₂O photolysis dominates HOₓ production, errors in the H₂O photolysis rate coefficient are limited to below 20%. For large SZAs, however, errors are greater. For example, using the parameterisation by Allen and Fredrick (1982) results in an overestimation of the H₂O photolysis rate coefficient by almost a factor of two at 85° SZA in the mesosphere, which likely must lead to underestimated ozone mixing ratios at twilight. For another O₂ SRB parameterisation (Minschwaner et al., 1993), however, errors in H₂O photolysis values are smaller than 10% above 60 km. S–94 present a parameterisation for the H₂O absorption cross section that improves the agreement with the LBL results. This parameterisation, however, is not included in the current study. Unfortunately S–94 give no hint to how well H₂O photolysis is represented in combination with the O₂ SRB parameterisation by KM–96, so it is difficult to estimate to what degree the results presented here could be influenced by inaccuracies in H₂O photolysis rates. In summary, the study by S–94 suggests that errors in HOₓ production and simulated ozone values in the mesosphere with H₂O photolysis rate coefficients derived with standard approaches are rather small for moderate SZAs, while for twilight conditions erroneous H₂O photolysis coefficients could be a large error source for ozone simulations. This will be a key issue to investigate for future research.

c. Random model errors

In the present study photochemical rate data were based on JPL–97 although more recent recommendations are currently available in JPL–00 and JPL–02.
While upgrading bimolecular and termolecular reaction rate coefficient data with these new datasets is straightforward, implementing new photolysis absorption cross sections and parameterisations is a comprehensive task. With the option of updating only the reaction rate data and leaving photolysis rates at the JPL–97 level, it was judged that consistency within the adopted dataset is more important than applying the latest rate modifications, in particular to facilitate meaningful comparisons with other model studies. The possible impacts of differences between JPL–97 and JPL–02 on the calculated ozone discrepancy with the HALOE ozone observations are addressed briefly below. Rate coefficient updates that would affect the ozone budget in the upper stratosphere and mesosphere are few. It should be stressed that the rate coefficients of most reactions in Tables 1–4 are unchanged in the more recent JPL publications; new updates have mainly addressed reactions of importance in the lower and middle stratosphere, many of which are related to NOx. A review is given in WMO (2003).

None of the recommendations for the key reactions of the mesospheric ozone budget (see e.g. Brasseur and Solomon, 1986; Jonsson et al., 2004) were changed in JPL–00. Smith et al. (2001) (referred to as S–01 hereafter) showed that ozone changes due to rate changes between JPL–97 and JPL–00 are limited to below 2% at 25–60 km. From JPL–00 to JPL–02 a few key reactions of importance for the middle atmospheric ozone budget were given new recommendations. For example, a 10% increase in the rate of reaction B49 (HO2 + ClO → HOCl + O2) and decreases in the rate coefficients of the catalytic odd oxygen loss reactions B15 (OH + O3 → HO2 + O2) and B22 (HO2 + O3 → OH + O2 + O2) by less than 10% were suggested, but would mainly affect the ozone budget in the middle and lower stratosphere. Also, a new parameterisation for the O(^1D)-yield from ozone photolysis was given, but judging from the impact of earlier changes to this branch suggests it mainly affects ozone in the lower and middle stratosphere (S–01). JPL–02 also recommends a \( \sim 7\% \) branching ratio for the HCl-yield from the reaction between OH and ClO (B43), while JPL–97 did not include this product branch. This reaction removes reactive chlorine and was shown to reduce the ozone deficit in the study by G–99 by up to 5% in the middle and upper stratosphere, with a maximum effect at 40–45 km. Thus, in the current study, a 6% HCl-yield was used according to JPL–00. Finally a 4% increase in the rate of T1 (O + O2 + M → O3 + M) was suggested in JPL–02. According to the analysis by Jonsson et al. (2004) this should lead to increased ozone by a similar amount in the mesosphere and by slightly less in the upper stratosphere. In summary, this short review of rate coefficient updates since JPL–97 suggests that the new rates should have only a limited effect on the results presented here, and in particular cannot provide an explanation for the substantial ozone deficit at 60–75 km. On
the other hand, the rates of several key reactions of importance for ozone in the middle atmosphere was revised with substantially lower uncertainty factors in JPL–00. This is discussed below.

The ozone uncertainties (1-sigma estimates) associated with inaccuracies in rate coefficients, using uncertainty factors from JPL–97, were in the current study found to be in the order of 10% at 40–55 km and up to 20% at 60–75 km, thus encompassing much of the discrepancy between the modelled and observed ozone mixing ratios noted earlier. These uncertainty values represent a significant improvement, almost by a factor of two, over the uncertainties derived from JPL–92 photochemical data by Chen et al. (1997). S–01 quote a 12% ozone uncertainty throughout most of the stratosphere using JPL–00, which is comparable to the results presented here. However, their values range from 9 to 16% at 35–55 km depending on season and latitude. Significant updates of uncertainty factors in JPL–00 that are of importance for ozone in the upper stratosphere and mesosphere include: decreased uncertainty factors for the reactions T1 (O+O_2+M→O_3+M), B9 (O+HO_2→OH+O_2), B18 (OH+HO_2→H_2O+O_2), B24 (O+NO_2→NO+O_2), and B44 (OH+HCl→H_2O+Cl). There were no improvements for photolysis rates, and furthermore JPL–02 did not introduce any significantly lowered rate uncertainties of importance to this study. In particular, the improved accuracy of the O+O_2+M, the O+HO_2 and the OH+HO_2 reactions, which were all pointed out as major contributors to the overall ozone uncertainty in section 5b (Table 5), implies that the ozone uncertainty values presented in this study would likely decrease further if updated with these new data. As the analysis by S–01 included these improved uncertainty values, and also did not consider either uncertainties in O_2 and O_3 photolysis or uncertainties in reactions of O with O_3 and O_2, it is somewhat of a puzzle why their uncertainty values are not significantly lower than the ones presented here. It is important that this discrepancy is resolved as a robust estimate of typical models errors associated with inaccuracies in photochemical data is important for model-observation comparison studies. We speculate that the entirely different mathematical approach used by S–01 to derive the ozone uncertainties may be partly responsible; they used sensitivity coefficients for each reaction to propagate rate coefficient errors through a pre-calculated model ozone prediction. While a Monte Carlo simulation, as presented in the current study, inherently incorporates non-linearities, S–01 note that non-linear effects are not taken into account and non-local effects can be missed in their sensitivity analysis. Non-linearities, for example through couplings between the HO_x, NO_x and ClO_x families through reactions that form less reactive reservoir species, such as HNO_3, ClONO_2, and HCl, are likely to damp the effect on ozone from rate
coefficient induced changes in HO\textsubscript{x}, NO\textsubscript{x} and ClO\textsubscript{x} species abundances. Thus, neglecting non-linear effects would tend to overestimate ozone uncertainties. Furthermore, it was shown in section 5a in this study that non-local effects can decrease ozone uncertainties caused locally.

The only other study we are aware of that have attempted to identify the major contributing reactions to middle atmospheric ozone uncertainties is Dubey et al. (1998). They based their analysis on JPL–94 rate coefficients and used a similar technique as in S–01. Unfortunately they present results only at 40 km, so a full assessment of the PLS results in the current study is not possible at this time. However, for this particular altitude their analysis is in excellent agreement with the results presented here; the five production reactions of greatest importance for the ozone uncertainty given by the PLS regression analysis, P2, T1, B43, P8 and B18, are pointed out in the same order of importance by Dubey et al. (1998). On the loss side, the five major reactions found in the current study, P3, B33, P4, B24, B44, are found among the six most important contributors in the results of Dubey et al. (1998), with P3 being the most important, but with a different ordering of the following four reactions. These consistencies are encouraging and give some confidence for the PLS analyses at the other altitudes.

A limitation in the Monte Carlo sensitivity study performed in this study is inherent in the particular model setup used, with fixed vertical profiles of NO\textsubscript{y} and Cl\textsubscript{y} and the absence of production and loss reactions for these families. While this approach was used to constrain the background sources of NO\textsubscript{x} and ClO\textsubscript{x} radical species to observed values, it also implies that ozone in the sensitivity study is not sensitive to reactions of NO\textsubscript{y} and Cl\textsubscript{y} formation and destruction. For example, the sensitivity analysis of Chen et al. (1997) reported ozone to be sensitive to N\textsubscript{2}O dissociation by O(1D) in the 30–40 km region. Similarly, uncertainties in the dissociation rates of CFCs are not taken into account in the current study. Consequently, the ozone uncertainties reported here could be somewhat smaller than in more comprehensive models, e.g. coupled chemistry-climate models, in which NO\textsubscript{y} and Cl\textsubscript{y} levels are determined by the interplay between transport and photochemical production and loss. However, it can be noted that both N\textsubscript{2}O and CFCs are dissociated mainly below 40 km, and thus, excluding these processes from the analysis, should not significantly affect the calculated ozone uncertainty values above this level.

A variety of systematic and random errors affecting the ozone abundance in a photochemical box model have been discussed in this paper. It should be stressed that ozone simulations in more comprehensive models are affected also by other types of model errors, including for example deficiencies in ad-
Convection and diffusion processes; these are particularly important in the lower stratosphere and for polar ozone loss. In this study we have not touched upon such issues, as the aim of the study has been to attempt to isolate and analyse uncertainties associated with inaccurate treatment of photochemistry only.

7. Conclusions

This study has aimed to illustrate the importance of some systematic and random errors that affect model calculations of middle atmospheric ozone. The purpose of the performed analyses was to better understand the causes of model underestimations of ozone in the upper stratosphere and mesosphere, commonly known as the “Ozone deficit problem”, reported during the past few decades, and also to investigate possible reasons for discrepancies between different previous studies on the subject. It was shown that a comprehensive photochemical box model constrained by HALOE observations of temperature, CH$_4$, H$_2$O, NO, NO$_2$ and HCl underestimates HALOE ozone observations by 10–40% in the region between 35 and 75 km, with peak values of 20 and 40% at 40 and 75 km respectively. However, with several model improvements, including the addition of methane oxidation chemistry, an improved solar flux from SUSIM observations, making J-values interactive with simulated ozone values, and including an algorithm to take multiple scattering and surface albedo effects into account in the radiative code, the model underestimation of the ozone observations was limited to about 10% at 40–55 km while remaining at between 10 and 35% at 55–75 km. Although the individual effects of the model improvements were small, in the order of a few percent, their cumulative impact was to remove up to 10% of the ozone deficit in the upper stratosphere. The major contribution to this improvement was achieved from the addition of multiple scattering and surface albedo effects in the model, leading on their own to a reduction of up to 6% in the ozone deficit. The use of solar fluxes from SUSIM measurements reduced the ozone deficit by 2–3% in the stratosphere and by 3–4% in the mesosphere. However, in the mesosphere this effect was negated by the addition of interactive J-values, which act to decrease ozone values substantially for high SZAs in the mesosphere. Lastly, the ozone sensitivity to the frequency of J-value updates in the model was studied. It was shown that the adopted high temporal resolution in the model used here, ranging from up to an hour near noon to 1–4 minutes near twilight, is sufficient to resolve the rapid changes in upper stratospheric and mesospheric chemistry around sunrise and sunset. However, a test run using a fixed update frequency of 15 minutes, not uncommon in coupled chemistry-climate models, led to errors in sunset ozone of 5% in the mesosphere and to up to 15% errors during the sunlit morning and late afternoon hours.
The modelled ozone deficit is robust over a variety of model-observation comparisons covering several summer low latitude locations. The magnitude of the model underestimation is in reasonable agreement with other recent studies showing little or no ozone deficit at 40 km. However, the ozone discrepancy in the 60–75 km region confirms the results from some earlier studies showing severe ozone underestimations near 60 km. It has been noted that both the model and observational dataset suffer from large uncertainties in this height region. Both the accuracy of the HALOE ozone measurements at 70–75 km and the model errors induced from uncertainties in the HALOE water vapour model constraint in this region are similar in magnitude as the model-observation discrepancy. Furthermore, errors in O$_2$ and H$_2$O SRB absorption at twilight in the model could be significant.

A Monte Carlo analysis was performed to examine the model uncertainties associated with inaccuracies in photochemical rate data. The model was run 2000 times (for a fixed solar zenith angle) with reaction and photolysis rate coefficients randomly varied between uncertainty limits specified from JPL–97 (deMore et al., 1997). The induced 1-sigma ozone uncertainties range from about 6% at 30 km to 20% at 75 km, with a region of about 10% uncertainty at 40–55 km. This implies that the ozone deficit at 40–55 km could be fully explained by inaccurate rate coefficient data. The uncertainty values are substantially smaller than those achieved in studies using earlier rate data recommendations. Also, it was noted that non-linear and non-local effects affect ozone in the middle atmosphere and appear to result in smaller uncertainty values than in comparable studies where local-linear behaviour was assumed.

A partial least squares (PLS) regression technique was successfully used to examine which reactions contribute most to the calculated ozone uncertainty in the 40–75 km region. The major contributing reactions were listed in a table separately for production and loss mechanisms and sorted in order of importance and as a function of altitude. For ozone production there are three dominating reactions that contribute to the ozone uncertainty throughout the 40–75 km region: O+O$_2$+M→O$_3$+M, OH+HO$_2$→H$_2$O+O$_2$, and O$_2$+h$_v$→O+O. On the loss side, O+HO$_2$→OH+O$_2$, O+OH→O$_2$+H, H$_2$O+h$_v$→H+OH, and O$_3$+h$_v$→O$_2$+O(1D) are the dominating providers of ozone uncertainty at 60–75 km, and the latter reaction is the single most important loss reaction contributing to ozone uncertainties at 40–60 km. Additionally, the following reactions were found to contribute significantly to the ozone uncertainty in the 40–60 km region: O(1D)+N$_2$→O+N$_2$, OH+ClO→O$_2$+HCl, O(1D)+H$_2$O→OH+OH, O+O$_3$→O$_2$+O$_2$, O$_3$+h$_v$→O$_2$+O, NO+O$_3$→NO$_2$+O$_2$, and NO$_2$+O→NO+O$_2$. These results are partly confirmed by a previous study.
which for the 40 km level identified the same reactions to be important for the ozone uncertainty, proving the usefulness of the PLS regression method.

In the current study, the model was constrained to atmospheric background conditions measured by HALOE. A Monte Carlo sensitivity analysis was performed to examine whether errors in the HALOE species measurements propagate to significant errors in the modelled ozone values. The results show that the induced 1-sigma ozone uncertainties are below 5% at 30–55 km, but increases rapidly with altitude to about 30% at 75 km, primarily because of uncertainties in the water vapour measurements. Assuming that differences in observational datasets used for model constraints in different model studies are similar in magnitude as the HALOE measurement uncertainties, an implication of these results is that the choice of model constraints could explain part of the ozone discrepancies between different models.

The results in this paper emphasise that model and observation errors are often large compared to the discrepancy between the model and the HALOE ozone observations and thus sometimes prevent a useful analysis on the causes of the modelled ozone deficit. In particular, for the mesosphere at 60–75 km it has been shown that the modelled ozone uncertainty from the combined effects of uncertainties in model constraints and inaccuracies in photochemical rate data exceeds the ozone model-observation discrepancies.

These limitations have important implications for model development and future measurements. On the modelling side, several improvements to this study could be suggested; for example: (1) to use observed albedos instead of the generic value of 30% for the radiative calculations; (2) to use more recent rate coefficient data; and (3) to examine the twilight ozone sensitivity to the treatment of water vapour photolysis in the mesosphere. Challenges for future satellite missions in the mesosphere include: (1) to provide simultaneous and collocated measurements of temperature, ozone, water vapour and HO$_x$ species; in addition, simultaneous observations of the albedo would be useful; (2) to measure ozone at greater accuracy; and (3) to provide improved measurements of water vapour so as to provide more robust model constraints. Furthermore we have noted that analysis of the odd-oxygen and ozone budgets in the mesosphere would benefit from ozone measurements from different local times (solar zenith angles) and simultaneous observations of atomic oxygen. Although solar occultation instruments, such as HALOE, generally provide very accurate measurements compared to other satellite measurement techniques, analysing mesospheric ozone chemistry only at twilight is associated with many difficulties, as has been shown in this study. As for chemical rate coefficient data, improved measurements of the reactions mentioned above would further help to
improve our understanding of the ozone deficit problem in the mesosphere.

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A. Appendix

Figure 20 illustrates the attenuation of the direct solar flux in the atmosphere as a function of altitude for a solar zenith angle of 15 degrees in January at 23°S. The curves show the solar flux at any given altitude normalised by the unattenuated solar flux at the top of the atmosphere. In panel a the solar flux available for photodissociation processes without considering multiple scattering (MS) and surface albedo effects is shown. The normalised fluxes range between zero and one in this case, indicating zero and complete transmission respectively. Several things can be noted from this figure: (1) Solar radiation with wavelengths in the Schumann-Runge continuum (SRC) below 175 nm is completely absorbed above the domain of the photochemical box model in this study, i.e. above 75 km. An exception is the flux in the Lyman-alpha line at 121.6 nm which penetrates down to 65 km. (2) Absorption of UV radiation in the Schumann-Runge bands (SRB) at about 175–200 nm is highly wavelength dependent, with the shorter wavelengths being absorbed completely in the mesosphere while the longer wavelengths penetrate down to the lower stratosphere. (3) UV radiation with longer wavelengths (200–300 nm) is transmitted largely unattenuated through the mesosphere and is absorbed by the ozone layer at 20–50 km. (4) The absorbing ability of the atmosphere is weak for wavelengths above 310 nm so that a significant fraction of the flux at these wavelengths reaches the ground.

Panel b shows the normalised solar fluxes when MS and surface reflection are taken into account. Panel c shows the absolute difference between the two cases. The scattered and reflected light is added to the direct solar flux, which leads to greater net incident flux for any given altitude. However, the amount of additional flux is a strong function of wavelength. In general MS and surface reflections are more important for wavelengths with weak absorption since strong absorption effectively damps out the contribution from scattered and reflected light. Therefore, a significant increase in the net flux is seen primarily for the visible wavelengths. The flux increase for the visible wavelengths maximises near the ground and decreases asymptotically towards constant but non-zero values above 40 km. This reflects the decrease of the density (and thus concentration of Rayleigh scattering molecules) with altitude. Above 40 km the contribution from locally scattered light is insignificant. The flux increase at these altitudes comprises purely of the contributions from reflected diffuse and direct solar radiation from the surface and the underlying atmosphere. Note that small flux increases are also calculated for UV wavelengths at 200–310 nm. Although these changes are less significant, they are important for ozone chemistry, which to a large extent depend on UV absorption processes. The results in Figure 20 are
Figure 20. (a) The solar flux as a function of height normalised by the unattenuated solar flux at the top of the atmosphere, when multiple scattering and surface albedo are ignored. Data are shown for selected wavelengths through 122–800 nm for typical daytime conditions (SZA=15°) in January at 23°S. The Lyman-alpha flux is labelled A (122 nm). (b) As in panel a but including flux contributions from multiple scattering and surface reflections. (c) Absolute difference between the two cases.
Figure 21. As in Figure 20 but for twilight conditions (SZA=90°).
largely consistent with Meier et al. (1982).

Figure 21 shows in analogy with Figure 20 the normalised fluxes and differences for 90 degrees solar zenith angle. In this case the significantly longer optical path through the atmosphere results in significantly shallower penetration depths of the UV solar fluxes. Most of the visible wavelengths are completely absorbed before reaching the ground in the case when only direct solar radiation is considered (Figure 21, panel a). In the case with MS and surface reflections taken into account (Figure 21, panel b), however, all visible wavelengths show significant fluxes at the surface. As for the overhead sun in Figure 20 it is primarily the visible wavelengths that show significant increases in the net flux (Figure 21, panel c). However, at twilight the increases are approximately an order of magnitude weaker than for the overhead sun case. In the lower part of the model domain this is simply because the incident direct solar flux is much weaker than for an overhead sun. In relative measures the contribution of multiply scattered light to the total flux is actually more important than for lower solar zenith angles. However, because the intensity of the diffuse radiation at the surface is so small in this case the reflected diffuse intensity to the upper stratosphere and mesosphere becomes significantly weaker than for an overhead sun. Also, the fact that there is no reflection of direct solar radiation in the plane parallel model at solar zenith angles of 90 degrees and above contributes to the weaker flux increases.

In conclusion, scattered light contributes significantly to the total flux in the visible spectrum and to some extent also in the near visible part of the UV spectrum. The impact is most pronounced at low solar zenith angles.
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Doubled CO$_2$-induced cooling in the middle atmosphere: Photochemical analysis of the ozone radiative feedback

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Abstract

Simple radiative arguments predict that the impact of CO\textsubscript{2} increases on the stratosphere and mesosphere should be a cooling and that the magnitude of the temperature change should be significantly larger than in the troposphere. Considering the temperature dependence of middle atmospheric gas-phase ozone photochemistry, it is expected that the ozone response will generate a radiative feedback that mitigates the CO\textsubscript{2}-induced cooling. The magnitude and vertical structure of this signal need to be characterised in order to distinguish the impact of future CO\textsubscript{2} changes from other processes affecting the temperature evolution, such as changes in chlorine loading and water vapour trends.

The Canadian Middle Atmosphere Model (CMAM) has been used in a process oriented study to examine the details of radiative and photochemical feedbacks under current and doubled CO\textsubscript{2} conditions at low and middle latitudes. The model was run both with and without interactive chemistry in order to determine the importance of the radiative feedback through ozone changes on the CO\textsubscript{2}-induced cooling signal. Changes in other greenhouse gases, ozone depleting substances or SST’s and sea ice coverage were not considered. The interactive model results show a substantial temperature decrease throughout most of the middle atmosphere with a maximum cooling of 10–12 K at the stratopause. In association with this temperature change, the ozone mixing ratio increases by 15–20\% in the upper stratosphere and by 10–15\% in the lower mesosphere. Results from the non-interactive simulations show that the magnitude of the cooling is overestimated by up to \sim 4.5 K when the ozone radiative feedback is not considered. In spite of the complexity of the ozone chemistry, the ozone increase at 30–70 km can be understood primarily as a result of the negative temperature dependence of the \text{O}+\text{O}_2+\text{M} \rightarrow \text{O}_3+\text{M} reaction that controls odd oxygen partitioning. Additional partial contributions to the ozone increase below 60 km are provided by a decrease in the reaction rate coefficient of the Chapman reaction \text{O}+\text{O}_3 \rightarrow 2\text{O}_2 and by a decrease in the \text{NO}_2 abundance.
1 Introduction

Measurements indicate that the middle atmosphere has been experiencing significant changes over the past few decades. Ozone depletion and temperature decreases are among the most significant observed perturbations in this region, and both phenomena have been well documented [WMO, 1998; Ramaswamy et al., 2001; Beig et al., 2003]. Ozone depletion is primarily attributed to chlorofluorocarbon (CFC) increases, whereas cooling is generally associated with CO$_2$ increases even though the two phenomena are strongly coupled. CFC-induced ozone decreases lead to changes in ozone heating that augment the CO$_2$-induced cooling. Furthermore, ozone chemistry in the stratosphere and mesosphere is temperature sensitive, with the effect that temperature changes are dampened by a radiative feedback through ozone changes. The current estimate is that about half of the cooling since 1980 in the upper stratosphere is caused by ozone decreases and about half by CO$_2$ increases [WMO, 1999, 2003; Shine et al., 2003]. However, this is not a clear separation because CO$_2$-induced cooling results in ozone increases, so ozone has not decreased as much as it would have from CFCs alone.

Extrapolating current temperature trends into the future is problematic since CFCs are expected to decrease which should lead to ozone increases. Furthermore, CO$_2$-induced cooling could disguise the apparent speed of ozone recovery in regions under photochemical control. In order to distinguish between these two effects in future predictions of middle atmospheric changes it is necessary to understand the effect of CO$_2$ increases on ozone and temperature at a detailed level. Some aspects of the couplings between CO$_2$, ozone and temperature have been studied in the past using two-dimensional (2D) models. For example, Fels et al. [1980] used a crude ozone parameterisation in a 2D model with fixed dynamical heating to show that the ozone increases in response to CO$_2$ doubling act to reduce the temperature response by up to 30% with a maximum impact around the stratopause. Haigh and Pyle [1982] and Brasseur and Hitchman [1988] investigated the impact of changes in CFCs and CO$_2$ on ozone and temperature using 2D models with more realistic chemistry. Their results showed substantial increases of ozone in the upper stratosphere in response to CO$_2$ increases, but they noted that the coupled perturbation of CFC and CO$_2$ changes does not behave like a linear combination of the two effects. In later studies [e.g. Roble and Dickinson, 1989; Berger et al., 1993; Akmaev and Fomichev, 1998], 3D models have been adopted to evaluate the thermal response of the middle atmosphere to the doubling of CO$_2$. Akmaev and Fomichev [2000] and Beig et al. [2003] showed the significance of the CO$_2$ forcing for past cooling trends and highlighted the necessity to take into account the radiative forcing from other
constituents. However, these 3D studies did not include interactive ozone.

In recent years, several scenario based model studies have been performed in order to reproduce past temperature trends in the stratosphere [Langematz et al., 2003; Manzini et al., 2003; Shine et al., 2003]. These studies involve models of various complexity: e.g. some models used imposed ozone trends while other used interactive chemistry. Shine et al. [2003] showed that while models reproduced the general features of observed stratospheric temperature trends there remained significant discrepancies. For example at \( \sim 5 \) hPa the mean cooling estimated by the models is greater than that observed by satellite measurements, while at \( \sim 50 \) hPa the measured cooling is greater than that calculated by most models. They noted a potentially important role for water vapour to explain some of these discrepancies. Also, there is a significant spread in results between the various models, indicating that important feedback processes may be missing in some models.

For the mesospheric region Khosravi et al. [2002] have addressed similar issues by analysing climate scenarios using a 2D ozone interactive model which extends to the lower thermosphere. They also presented results from a doubled CO\(_2\) experiment which showed significant changes in ozone and other constituents throughout the mesosphere. However, their analysis did not clearly elucidate the source of the photochemical changes that was presented.

In order to estimate how the middle atmosphere responds to changes in greenhouse gases and other simultaneous forcings, such as trends in chemically active tracers, it is critical to use coupled chemistry-climate models with an extensive vertical domain. However, by the same token, this added complexity makes it a challenge to analyse how chemical, radiative and dynamical processes interact and feed back on one another within such models. A further complication is the presence of couplings between different atmospheric regions. For example, climate changes taking place in the troposphere may impact the middle atmosphere and add to the thermal effects of CO\(_2\) increases within the middle atmosphere. Changes in tropical tropopause temperatures may alter the flux of water vapour into the stratosphere, which ultimately impacts ozone abundances and heating rates. Also, changes in the source and filtering of waves that drive the circulation of the middle atmosphere may be important. The results of recent studies point to the necessity to focus on specific aspects of the problem to better understand the cause of the overall changes obtained.

This study is part of ongoing work to diagnose the impact of increasing greenhouse gas concentrations in the atmosphere using the Canadian Middle Atmosphere Model (CMAM) [Beagley et al., 1997]. This 3D general circulation model, which incorporates an interactive photochemistry module
[de Grandpré et al., 1997, 2000], allows for dynamical, radiative and photochemical interactions making it suitable to study ozone and temperature feedbacks. In this paper we report on a series of idealised model experiments designed to characterise the photochemical and radiative processes which take place in the upper stratosphere and lower mesosphere in response to CO\textsubscript{2} increases. Simulations have been performed for present-day and doubled CO\textsubscript{2} conditions, and both with and without interactive chemistry, in order to estimate the impact of the radiative feedback through ozone changes on the CO\textsubscript{2}-induced cooling. In order to focus on the thermal effects of the CO\textsubscript{2} increase and its photochemical feedbacks, surface conditions were constrained to minimise tropospheric climate changes and their impacts on the middle atmosphere. This was accomplished by using the same sea surface temperatures (SST’s) and sea ice distributions for all model experiments. This approach allows for a quantification of the ozone radiative feedback on the temperature change as well as a detailed analysis of the contributing photochemical mechanisms. Future work [manuscript in preparation, 2004] will investigate the impact of changing the SST’s and sea ice conditions for similar experiments to those studied here. We note that in the winter and spring polar lower stratosphere, the relationship between temperature and ozone can be quite different from that for non-ozone hole conditions because of the added complications of polar stratospheric clouds and heterogeneous chemistry. These conditions are, however, not covered in this paper.

The results indicate that, as expected, the inclusion of interactive chemistry in the model significantly reduces the thermal signal associated with CO\textsubscript{2} doubling in the upper stratosphere and lower mesosphere compared with the results from the non-interactive simulations. In the following analysis we attempt to identify the main photochemical processes responsible for the ozone response to the CO\textsubscript{2} increase. The analysis focuses mainly on the ozone changes in the upper stratosphere and lower mesosphere in the tropics and sub-tropics where ozone is generally under photochemical control. However, both ozone and temperature in the lower stratosphere are affected by the increased optical depth of the overhead atmosphere.

Throughout the middle atmosphere, the local abundance of ozone is generally determined by a nonlinear system of temperature dependent photochemical reactions that govern the production and loss of odd oxygen species \((O_x = O_3 + O + O(1D))\). The dominant reactions include the basic Chapman reactions involving oxygen species as well as catalytic ozone loss cycles which involve radical molecules of the odd nitrogen \((NO_x = NO + NO_2)\), odd chlorine \((ClO_x = Cl + ClO)\) and odd hydrogen \((HO_x = H + OH + HO_2)\) families. 

Haigh and Pyle [1982] estimated the temperature dependence of the dominant
loss reactions in the odd oxygen budget at 40 km. Assuming fixed concentrations of NO\(_x\), ClO\(_x\) and HO\(_x\) species their results indicated that all catalytic loss cycles should contribute to increase the ozone abundance in response to lower temperatures at this altitude. The efficiency of the various odd oxygen loss cycles does not only depend on the temperature dependence of the reaction rate coefficients. It depends also on the abundance and partitioning of the NO\(_x\), ClO\(_x\) and HO\(_x\) radicals and on the concentration of atomic oxygen which is involved in the rate limiting steps of the odd oxygen loss cycles throughout the upper stratosphere. The strong negative temperature dependence of the O+O\(_2\)+M→O\(_3\)+M reaction is a significant factor which affects the partitioning of odd oxygen compounds and in particular leads to less atomic oxygen in the stratosphere and hence slower odd oxygen loss rates [Jucks and Salawitch, 2000]. The relative importance of this reaction mechanism needs to be quantified so that we can better understand the photochemical response of the model to various perturbations independently of other factors that affect the budget of the long lived constituents, such as methane and water vapour.

Our analysis involves using the dominant odd oxygen production and loss reactions to derive analytical expressions for the ozone abundance and change in various altitude regimes. These expressions are used to determine the temperature dependence of various chemical processes and to estimate their relative contributions to the ozone change. We specifically investigate the role of changes in odd oxygen partitioning for the ozone response between 30 and 70 km, and the impact of other factors including changes in the rate of the Chapman odd oxygen loss reaction and changes in the distribution of NO\(_x\), ClO\(_x\) and HO\(_x\) constituents.

The paper is organised as follows. A brief description of the model and experiments is presented in section 2 below. Section 3 shows a comparison of the results from the different experiments and section 4 presents the photochemical analysis to identify the main forcing mechanisms. The summary and conclusions appear in section 5.

## 2 Model Description and Experiments

The Canadian Middle Atmosphere Model (CMAM) [Beagley et al., 1997] is based on the state-of-the-art CCCma GCM [McFarlane et al., 1992; Scinocca and McFarlane, 2004], and includes a comprehensive on-line photochemistry module in which ozone and water vapour interact with the radiation field in the model [de Grandpré et al., 1997, 2000]. The current model version uses the standard configuration described in Austin et al. [2003] and runs at T32 spectral trunca-
2. Model Description and Experiments

Table 1. Model configurations

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Interactive chemistry</th>
<th>CO$_2$ multiplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Off$^a$</td>
<td>1</td>
</tr>
<tr>
<td>A2</td>
<td>Off$^a$</td>
<td>2</td>
</tr>
<tr>
<td>B1</td>
<td>On$^b$</td>
<td>1</td>
</tr>
<tr>
<td>B2</td>
<td>On$^b$</td>
<td>2</td>
</tr>
</tbody>
</table>

$^a$ Radiative calculations are performed using climatological O$_3$ and H$_2$O.

$^b$ Radiative calculations use O$_3$ and H$_2$O derived by the on-line chemical module.

The model uses a gravity wave drag scheme with settings described by McLandress [1998]. It employs the middle atmosphere infrared scheme from Fomichev and Blanchet [1995] and Fomichev et al. [1998], which includes additional processes such as water vapour cooling and the effects of sphericity on solar heating [Fomichev et al., 2004]. The photochemistry module has been updated from earlier versions of the model and now includes 45 species and 135 photochemical processes which are listed in Tables 2 and 3 of the Appendix. The new module includes Cl$_2$ in the list of short lived species and adds new processes related to the oxidation of ClO and BrO by OH. In addition, more recent reaction rate data [Sander et al., 2000] has been incorporated. As the current study focuses on extra-polar processes in the stratosphere and mesosphere, heterogeneous chemistry is not included. A spectral advection scheme is used for the transport of long lived constituents whereas short lived species are treated with the standard family approach [see de Grandpré et al., 2000].

Four multi-year integrations have been performed, for which the important model features are summarised in Table 1. For two of the experiments, one a reference run with current CO$_2$ amounts (1xCO$_2$) and one with doubled CO$_2$ mixing ratios (2xCO$_2$), fixed climatologies of ozone and water vapour were used for radiative calculations. The ozone climatology in these cases is representative of pre-ozone hole conditions and appear in general agreement with CIRA [Keating et al., 1990] in the upper stratosphere and above. For water vapour, a minimum value of 3 ppmv was prescribed throughout the stratosphere-mesosphere domain. The remaining two experiments, one 1xCO$_2$ and one 2xCO$_2$, included full simulations of middle atmospheric chemistry with the associated radiative feedbacks through ozone and water vapour changes on the temperature. The
mixing ratio of CO$_2$ in the model is prescribed to a fixed vertical profile, described in the work of Fomichev et al. [1998], and is scaled to twice its original value for the 2xCO$_2$ simulations. In both 2xCO$_2$ experiments the SST’s and sea ice coverage were the same as those used for the 1xCO$_2$ climate, thereby keeping the tropospheric climate largely unchanged. With this approach the influence from tropospheric climate change on the middle atmosphere is minimised, as discussed in the introduction. All experiments were run for 12 years and analysed over the last 10 years.

3 Results

Before we discuss the model results in detail we note that when the middle atmosphere cools, it contracts, i.e. levels of constant pressure decrease in altitude [see e.g., Roble and Dickinson, 1989; Akmaev and Fomichev, 1998]. This is illustrated by Figure 1. Figure 1a shows the 10-year global mean temperature profiles for the 1xCO$_2$ and 2xCO$_2$ interactive model runs (i.e. experiments B1 and B2, Table 1) in April. Figure 1b shows the temperature decrease as a function of pressure. The associated altitude change, as a function of pressure, is shown in Figure 1c. The contraction becomes significant in the stratosphere above 30 hPa and reaches more than two kilometres at the mesopause. Clearly if the temperature distributions of the various model experiments were to be compared on a height grid, the associated temperature changes would give an apparent reduction of cooling in the stratosphere and an apparent additional cooling in the mesosphere, except near the mesopause. Also, changes in the mixing ratio of chemical species observed on a height grid can be produced by either the atmospheric contraction or by changes in production or loss processes for the given species. In this study all comparisons of model variables are carried out on fixed pressure levels.

Figure 1d shows the change in the total number density that follows from the temperature change. It shows that the CO$_2$-induced cooling implies changes in the number density of up to $\sim$4%. This is important since all chemical reaction rates are proportional to density not just mixing ratio. In particular three-body reactions are very sensitive to the total molecular concentration.

3.1 Temperature and Ozone Response

Figure 2 shows the 10-year zonal mean temperature for January and April and the differences between the 2xCO$_2$ and 1xCO$_2$ simulations with interactive chemistry (experiments B2 and B1, Table 1). The approximate altitudes indicated in
3. Results

Figure 1. Illustration of the thermal shrinking of the middle atmosphere that results from the doubling of CO$_2$. The panels show (a) the 10-year global mean temperature profiles for 1xCO$_2$ and 2xCO$_2$ conditions (interactive experiments B1 and B2) in April, (b) the global average temperature response to the doubling of CO$_2$, (c) the descent of constant pressure levels associated with the temperature change and (d) the relative increase in total molecular number density [$M$] for fixed pressure levels derived from the temperature change.

This and subsequent figures were derived by adopting a constant scale height of 7 km throughout the model domain. The results show, as expected, a substantial cooling for both seasons throughout most of the middle atmosphere with a maximum cooling of $\sim$10 K at the stratopause over the tropics and $\sim$12 K in the polar regions. The cooling induced by the 2xCO$_2$ perturbation leads to a substantial increase in ozone in the upper stratosphere and lower mesosphere. Figure 3 shows the 10-year zonal mean daytime ozone distribution at 100–0.001 hPa for January and April and the relative differences between the 2xCO$_2$ and 1xCO$_2$ cases. We note that daytime averaged data is the appropriate quantity to analyse in order to examine the ozone radiative feedback, since ozone heating occurs only during daylight. The daytime ozone mixing ratio increases throughout most of the model domain with a maximum (rela-
tive) impact in the upper stratosphere where it increases by 15–20%. In the lower mesosphere the ozone increase is rather uniform and is generally 10–15% up to 0.03 hPa (≈70 km). Above 0.03 hPa the ozone changes are large and exhibit significant small-scale latitudinal inhomogeneities. This suggests that these variations are not primarily controlled by the temperature dependence of ozone chemistry, but rather are related to changes in dynamical parameters (although ozone is short-lived compared to the characteristic transport time scale in the upper mesosphere, dynamical processes does impact the ozone distribution through their effects on the more abundant and long-lived oxygen atoms, with which ozone is closely related through a fast photochemical balance). The slight decrease in ozone below 15 hPa (≈30 km) in the tropical region is related to the “self-healing” property of the ozone layer. The greater overhead ozone
abundance above this level for experiment B2, shielding the 200–225 nm production region, reduces the ozone production below. Finally we note that the changes in both ozone and temperature at extra-polar latitudes are statistically significant to the 99% significance level (not shown).

The increase in ozone in the upper stratosphere and lower mesosphere leads to an increase in solar heating and consequently mitigates the cooling induced by the CO$_2$ increase. To illustrate this effect Figure 4a shows the vertical profiles of the 2xCO$_2$ – 1xCO$_2$ temperature differences at the equator for both the non-interactive and the interactive model runs. For the non-interactive cases the magnitude of the cooling in the stratosphere and the lower mesosphere is directly associated with the background temperature profile with increasing cooling response for warmer temperatures. This reflects the fact that in the absence of
other mechanisms, the atmospheric response to a CO$_2$ perturbation is roughly in accord with the cooling to space approximation. These results are consistent with the other studies that used non-interactive models [e.g., Akmaev and Fomichev, 1998; see also review by Beig et al., 2003].

For the interactive experiments the cooling signal is modulated by the contribution from shortwave absorption by ozone. Between 50 and 10 hPa, the greater ozone column above 10 hPa results in a reduction of ozone heating and a $\sim$1 K increase in the predicted cooling. This is due both to the local ozone decrease in the region (see Figure 3) and to the decrease in penetrating solar flux. Above 3 hPa, shortwave absorption by ozone is maximal and the local ozone increase leads to greater ozone heating. The overall temperature response to the doubling of CO$_2$ is reduced by up to $\sim$4.5 K with a maximum impact at $\sim$0.3 hPa, thereby lowering the altitude of the maximum cooling.

A one-dimensional radiative equilibrium (RE) model based on the CMAM libraries has been used to infer the thermal response resulting from the radiative heating associated with the ozone change in the interactive model runs. The RE model was applied at the equator for April conditions and was forced both by a
doubling of CO\textsubscript{2} and by the change in daytime ozone obtained between model runs B1 (1xCO\textsubscript{2}) and B2 (2xCO\textsubscript{2}) using B1 as the reference. For comparison another pair of 1xCO\textsubscript{2} and 2xCO\textsubscript{2} runs was performed with the RE model, using a fixed ozone mixing ratio profile taken from the B1 experiment. Figure 4b shows the results from the RE model and compares it with the CMAM for the same period. The results show that a large fraction of the difference in cooling response between the interactive and non-interactive experiments is associated with the ozone change. Differences between the CMAM and the RE model results occur primarily above 0.03 hPa where the CMAM appears to be less sensitive to the ozone change. However, the discrepancy between the two models in this region simply reflects the fact that the atmosphere is not in radiative equilibrium here. In the CMAM, dynamical sources of heating also affect the temperature distribution [Fomichev et al., 2002]. An investigation of changes in these processes is beyond the scope of this paper.

In summary the results show that the incorporation of interactive chemistry in the CMAM has an important damping effect on the cooling produced by the 2xCO\textsubscript{2} perturbation. The ozone increase responsible for the negative radiative feedback occurs primarily in the upper stratosphere and lower mesosphere where odd oxygen is generally under photochemical control. This suggests that these changes should be understood in terms of the photochemical processes that control the ozone abundance in this region, rather than through changes in dynamical processes. In the following section we will investigate in detail the causes for the simulated ozone changes to better understand the link between temperature and ozone.

4 Analysis

In this section, we analyse the ozone change and its causes in detail in the 30–70 km height region. We examine the temperature dependence of the various chemical processes that control the ozone abundance in this region in order to identify the reactions and photochemical parameters responsible for the ozone change. The analysis involves assuming that odd oxygen is photochemically controlled and solving the odd oxygen steady state equation for the ozone concentration. This allows us to analytically estimate both the ozone change in response to the simulated cooling and to quantify the major contributing parameters.

The analysis is divided into three sub-sections. In the first sub-section we review the major production and loss mechanisms of the odd oxygen budget and set up some necessary equations to be used later in the paper. It is noted
that several important characteristics of middle atmospheric ozone chemistry are fundamentally different above and below 60 km. Therefore the analysis is performed separately in the following two sub-sections for the two main altitude regions, the middle mesosphere (MM) defined as the 60–70 km height interval, and the upper stratosphere and lower mesosphere (USLM) region, at 30–60 km. Throughout the analysis, results are shown for the month of January.

4.1 Odd Oxygen Photochemical Steady State

The primary chemical production mechanism for odd oxygen in the middle atmosphere is photodissociation of molecular oxygen. Chemical loss occurs either through the Chapman reactions or through catalytic odd oxygen destruction cycles involving NO\(_x\), ClO\(_x\) or HO\(_x\) radicals. The temperature dependence of molecular oxygen photodissociation is weak, and hence the dominating mechanisms for the simulated ozone increase are likely to be found in the various odd oxygen loss cycles.

The major cycles relevant for ozone in the 30–70 km region are summarised below. The most important reactions for a pure oxygen atmosphere are [Chapman, 1930]

\[
\begin{align*}
O_2 + h\nu & \xrightarrow{J_1} 2O \quad \text{(P1)} \\
O_3 + h\nu & \xrightarrow{J_3} O_2 + O \quad \text{(P3)} \\
O_3 + O & \xrightarrow{k_2} 2O_2 \quad \text{(R2)} \\
O + O_2 + M & \xrightarrow{k_1} O_3 + M \quad \text{(R1)}
\end{align*}
\]

Reactions P1 and R2 constitute net production and loss mechanisms for odd oxygen, while P3 and R1 regulate the partitioning between atomic oxygen and ozone within the odd oxygen family. In the stratosphere and lower mesosphere, odd oxygen loss also occurs in catalytic reaction cycles,

\[
\begin{align*}
O_3 + X & \rightarrow O_2 + XO \\
O + XO & \rightarrow O_2 + X \\
\text{Net} : & \quad O_3 + O \rightarrow 2O_2
\end{align*}
\]

where X represents OH, NO or Cl radicals (reaction pairs R20–R13, R33–R35 and R48–R56 in Table 2). For these cycles, the reaction involving atomic oxygen is rate limiting throughout most of the stratosphere. In the upper stratosphere
4. Analysis

and mesosphere the following cycle is also important:

\[
\begin{align*}
O + OH & \xrightarrow{k_{12}} O_2 + H \quad (R12) \\
H + O_2 + M & \xrightarrow{k_{18}} HO_2 + M \quad (R18) \\
O + HO_2 & \xrightarrow{k_{13}} O_2 + OH \quad (R13)
\end{align*}
\]

Net : \[2O \longrightarrow O_2\]

Two more catalytic HO\(_x\) cycles, R16–R12 and R20–R26, contribute to odd oxygen destruction, but are only of minor importance in the 30–70 km region. The photochemical rate of change of odd oxygen (\(d[O_x]/dt\)) during the day can be written as

\[
\frac{d[O_x]}{dt} = 2J_1[O_2] - 2k_2[O][O_3] - 2k_{35}[NO_2][O] - 2k_{56}[ClO][O] - k_{12}[OH][O] - k_{20}[OH][O_3] - k_{13}[HO_2][O] - k_{26}[HO_2][O_3] - k_{16}[H][O_3] + \text{other small terms} \tag{1}
\]

where square brackets indicate concentrations. The first term on the right hand side of the equation represents the rate of odd oxygen production through O\(_2\) photolysis and the following negative terms denote the net loss of odd oxygen from the Chapman loss reaction (R2) and the NO\(_x\), ClO\(_x\) and HO\(_x\) catalytic cycles. Figure 5a shows the 10-year zonal mean daytime averages of the loss terms in (1) at 100–0.01 hPa at the equator. Figure 5b shows that odd oxygen production and loss rates balance at 30–70 km, which illustrates the photochemical steady state of the region. Figure 5c compares the relative contributions from the Chapman loss reaction (O\(_x\)) and the NO\(_x\), ClO\(_x\) and HO\(_x\) catalytic cycles to the overall odd oxygen loss rate. HO\(_x\) chemistry is completely dominant for the odd oxygen loss rate in the mesosphere down to about 60 km where the ClO\(_x\) cycle and the Chapman loss reaction start to contribute. The importance of the HO\(_x\) reactions decreases with decreasing altitude and at about 45 km the O\(_x\), NO\(_x\), ClO\(_x\) and HO\(_x\) families contribute roughly equal amounts to the total odd oxygen loss rate. Below, at 25–45 km, the NO\(_x\) cycle is the main loss process for odd oxygen although the O\(_x\), ClO\(_x\) and HO\(_x\) reactions contribute significantly also in this region. The relative contributions from the various loss cycles in the 30–70 km region do not change dramatically with latitude except for the ClO\(_x\) cycle. Its relative contribution reaches \(~50\%) at high latitudes in the 40–50 km region where the peak in the ClO\(_x\) distribution occurs (not shown).
Figure 5. (a) The dominating odd oxygen ($O_x$) loss rate terms at the equator in January. (b) Same as in (a) but rates are accumulated by families ($O_x$, $NO_x$, $ClO_x$ and $HO_x$). Also shown are the total chemical loss rate and the odd oxygen production rate. (c) The relative contribution from each family to the total odd oxygen loss rate. All rates are daytime averages and were derived for current $CO_2$ conditions (model experiment B1).
Figure 6. Relative difference (%) in the zonal and monthly mean daytime mixing ratios of (a) atomic oxygen and (b) odd oxygen $O_x$ ($O_3 + O + O(\text{^1D})$) between the 2xCO$_2$ and 1xCO$_2$ interactive model experiments (B2-B1) for January. Contour intervals are 5% and negative values are shaded.

The analysis of (1) will be divided into two key altitude regions; above and below 60 km. The primary reason for this distinction is the dominant role of the HO$_x$ loss cycle (R12–R13–R16) above this level, which leads to a significantly simplified version of (1) and, hence, a more straightforward analysis. Also the odd oxygen family undergoes a fundamental transition around this altitude. The daytime partitioning of odd oxygen in ozone and atomic oxygen is generally controlled by ozone photolysis and recombination through P2, P3 and R1. This is expressed by:

$$R = \frac{[O]}{[O_3]} = \frac{J_2 + J_3}{k_1^* [O_2]}$$

(2)

where $k_1^* = k_1 [M]$ is the second order equivalent reaction rate coefficient corresponding to $k_1$. In the stratosphere, ozone is the most abundant form of odd oxygen and is therefore controlled by the odd oxygen budget through (1). In the mesosphere, however, strong ozone photolysis and low molecular density favour the conversion of ozone molecules into atomic oxygen atoms. In the middle and upper part of the mesosphere, atomic oxygen is several orders of magnitude more abundant than ozone. In this region the odd oxygen budget determines the atomic oxygen concentration, and ozone assumes a fast photochemical steady state with the more abundant atomic oxygen atoms through reactions P2, P3 and R1. Consequently an ozone change can be understood as resulting from either a change in the odd oxygen budget or a change in odd oxygen partitioning.

Figure 6 shows the relative changes in the 10-year zonal mean daytime O and O$_x$ mixing ratios between the interactive 2xCO$_2$ and 1xCO$_2$ experiments at 100–0.01 hPa. The ozone increase in the middle atmosphere (Figure 3) is
accompanied by a 5–10% decrease in atomic oxygen and hence a concomitant decrease in the O/O_3 ratio. We also note that the relative change in odd oxygen mimics the behaviour of ozone in the stratosphere where ozone dominates the odd oxygen reservoir. Analogously, above 70 km where oxygen atoms dominate the odd oxygen reservoir, the odd oxygen change reflects the change in atomic oxygen.

4.2 The Middle Mesosphere

In this section we analyse the temperature dependence of the ozone budget at 60–70 km. We first note from Figures 3 and 6 that the ozone mixing ratio increases by ∼10% in this region while the relative change in odd oxygen is small (<5%) and mostly negative. This suggests that in this part of the atmosphere the ozone increase is primarily a result of changes in odd oxygen partitioning rather than changes in odd oxygen production or loss rates.

To investigate this hypothesis, we follow the steps outlined by Allen et al. [1984] to derive an analytic equation for the daytime ozone concentration. These steps involve noting that the odd oxygen loss rate in this region is dominated by the HO_x reactions R12 and R13 and consequently that the odd oxygen steady state concentration is determined primarily by the HO_x abundance and its partitioning. The HO_x budget above 60 km is controlled primarily by water vapour photolysis through reactions P4 and P5 and by the HO_x loss reaction between OH and HO_2 (R24). Furthermore, the ratio of OH and HO_2 is determined by the fast photochemical balance between R12 and R13. With these assumptions and by combining (2) and (1) the following expression can be derived:

\[
[O_3] = J_1[O_2] \times \frac{k_1^*[O_2]}{J_2 + J_3} \times \left\{ \frac{k_{24}}{k_{12}k_{13}(J_4 + J_5)[H_2O]} \right\}^{\frac{1}{2}}
\]

The first factor in this equation represents the rate of odd oxygen production through O_2 photolysis. The second factor describes the O_3/O ratio. The third factor involves parameters which determine the HO_x abundance and the rate of odd oxygen destruction through the catalytic HO_x reactions R12 and R13.

Allen et al. [1984] showed that this equation, although approximate, accurately reproduces instantaneous daytime ozone values at 70 km calculated by a one-dimensional photochemical-diffusive model applied at 38°N for summer solstice conditions. We have tested whether (3) can reproduce the CMAM results at any latitude in the MM region by substituting the parameters in (3) for monthly averaged daytime zonal mean fields diagnosed from the 10-year model data. The analysis shows that the ozone concentration calculated by the ana-
lytical expression is generally within 10% of the modelled values at extra-polar latitudes at 64–67 km. Below this region and towards higher latitudes, the reaction of water vapour with O(\(^{1}\)D) (R6) becomes increasingly more important for HO\(_x\) production, and the neglect of this reaction in the balance represented by (3) results in overestimated ozone values compared to the model results. Above 67 km the analytical expression underestimates the modelled values, primarily because of a [HO\(_x\)] overestimation that results from the neglect of the HO\(_x\) loss reactions between H and HO\(_2\) (R18 and R19) in the HO\(_x\) budget.

Given that (3) can reproduce the modelled ozone abundance at extra-polar latitudes at 64–67 km, we have conducted an analysis of the parameters in (3) to determine which photochemical processes contribute to the ozone change forced by the 2xCO\(_2\) perturbation in this region. The reaction rate coefficient \(k^*_1\) has a strong negative temperature dependence with the potential to significantly increase the \(O_3/O\) ratio in response to the 6–8 K cooling in the MM region (Figure 2c). Figure 7 shows that the relative increase in \(k^*_1\) between the 1xCO\(_2\) and 2xCO\(_2\) interactive model runs is of the same order of magnitude as the ozone change itself, i.e. \(\sim 10\%\) throughout the region, and therefore from (3) is the main driver of the ozone increase. A significant fraction of the increase in \(k^*_1\) is due to its implicit dependence on the number density, which increases in response to the cooling of the atmosphere (see Figure 1). Figure 8 shows the zonal mean change in [M], and indicates that the change in number density contributes about 30% of the increase in \(k^*_1\). For the \(O_2\) and \(O_3\) photodissociation rate coefficients (\(J_1\) and \(J_2 + J_3\)), the change in the MM region is below 1%.

The potential for variations in the remaining parameters in (3) (\(k_{12}, k_{13}, k_{24}, J_4, J_5\) and \([H_2O]\)) to affect the ozone abundance is weakened by the square root dependence of the ozone concentration on these parameters. The odd hydrogen reaction rate coefficients \(k_{12}\) and \(k_{13}\) both have weak negative temperature dependencies which result in slightly faster odd oxygen destruction in the cooler 2xCO\(_2\) atmosphere, an effect which to a large extent is cancelled by the somewhat stronger negative temperature dependence of \(k_{24}\), which acts to decrease the HO\(_x\) abundance. Changes in the water photodissociation rate coefficient (\(J_4 + J_5\)) are insignificant.

The water vapour abundance could potentially be an important factor since it controls the HO\(_x\) abundance. A change in the tropical tropopause temperature would change the freeze-out properties of the tropopause cold trap, leading to a change in the influx of water from the troposphere into the stratosphere. This effect will be studied in a separate paper [manuscript in preparation, 2004], where changes in SST’s and sea ice distribution are included, thus providing for the impact of tropospheric climate change on the middle atmosphere. In
Figure 7. Relative difference (%) in the zonal and monthly mean daytime reaction rate coefficient $k_{1}^{*} (O+O_2+M\rightarrow O_3+M)$ between the 2xCO$_2$ and 1xCO$_2$ interactive model experiments (B2-B1) for January. Contour intervals are 3% and negative values are shaded.

The experiments considered here, however, this impact has deliberately been minimised by keeping the tropospheric climate largely unchanged. In this case, changes in the water vapour mixing ratio are small (less than $\sim$5%) and not statistically significant throughout the region of interest (30–70 km).

To compare the importance of the individual parameters in (3) for the overall ozone increase we take the logarithmic differential of (3), keeping only the major terms, to achieve an equation expressing the relative contribution from each parameter to the overall ozone change:

\[
\frac{df_{O_3}}{f_{O_3}} = \frac{dk_{1}^{*}}{k_{1}^{*}} - \frac{1}{2} \frac{dk_{12}}{k_{12}} - \frac{1}{2} \frac{dk_{13}}{k_{13}} + \frac{1}{2} \frac{dk_{24}}{k_{24}} - \frac{1}{2} \frac{df_{H_2O}}{f_{H_2O}} + \frac{1}{2} \frac{d[M]}{[M]} \]

(4)

Here $f_{O_3}$ and $f_{H_2O}$ are the volume mixing ratios of ozone and water vapour and $[M]$ is the air number density. Equation (4) is essentially a linearisation of (3) around the ozone steady state of the 1xCO$_2$ reference experiment. Each term in the equation represents the relative change in the various parameters between
the 1xCO$_2$ and the 2xCO$_2$ model runs.

Figure 9 shows both the individual terms on the right-hand side of (4) (full lines with symbols) and their sum (dashed line) as well as the modelled relative increase in the ozone mixing ratio (dotted line) at 67 km. Individual terms were computed from the zonal daytime average data of the interactive 1xCO$_2$ and 2xCO$_2$ model runs at 67 km. The reasonably close agreement of the simulated ozone increase and the change predicted by the simplified analytical expression, both in magnitude and latitudinal variation for all latitudes except for the winter high latitudes, confirms that the approximations made so far are valid to first order and that equation (4) may be used to further examine the contributions from the individual terms.

The results show that the change in $k_1^*$ totally dominates the ozone increase at this level. The remaining five parameters in (4) all contribute less than 2.5% to the ozone change. Furthermore the contribution from these minor parameters tend to cancel each other out, so that their cumulative contribution is only about 1%. Thus, our conclusion is that the major part of the ozone increase registered in the 60–70 km region for a doubling of CO$_2$ is caused by a faster rate of the odd oxygen partitioning reaction R1. It can also be noted that, since $k_1^*$ is linear in [M], the overall dependence of the ozone mixing ratio on the density is expressed
Figure 9. The relative difference (%) in daytime ozone mixing ratio between the 2xCO$_2$ and 1xCO$_2$ interactive model experiments (B2-B1) at 67 km (dotted) is compared to the relative change predicted by the analytical expression (3) (dashed). The full lines with symbols (see legend) show the contributions to the ozone change from each of the terms listed in equation (4). The analysis is shown for January.

by $f_{O_3} \sim [M]^{3/2}$ and thus the total contribution of the density change ($\sim 3-4\%$, Figure 8) to the ozone increase is $(3/2) \times (d[M]/[M]) \sim 5\%$. In other words, the density increase explains about half of the ozone increase in the region, whereas the remaining increase results from the temperature change.

4.3 The Upper Stratosphere and Lower Mesosphere

Allen et al. [1984] derived an analytical expression for the ozone concentration at 50 km by switching the dominating HO$_x$ production mechanism in (3) from water photolysis (P4 and P5) to water oxidation by O($^1$D) (R6). We note that although this yields an accurate representation of the HO$_x$ balance at this altitude and although HO$_x$ chemistry dominates odd oxygen loss rates at this level (see Figure 5c), neglect of the contributions from the NO$_x$, ClO$_x$ and the Chapman loss reactions yields significantly smaller odd oxygen loss rates than calculated by the model. Hence, we have performed a more detailed analysis based on the most important loss terms in (1) to analyse the USLM (30-60 km)
Figure 10. Relative difference (%) between the primary odd oxygen production and loss rates defined by (5). All rates were derived for January and for current CO\textsubscript{2} conditions (model experiment B1). Contour intervals from -100% to 100% in 10% steps. Negative contours are dashed.

By noting from Figure 5a that the contributions from reactions R16, R20 and R26 to the odd oxygen loss rate in the USLM region are small compared to the dominant terms, (1) can be simplified to

\[
\frac{d\text{[O\textsubscript{x}]}}{dt} = 2J_1\text{[O\textsubscript{2}]} - 2k_2\text{[O][O\textsubscript{3}]} - 2k_{35}\text{[NO\textsubscript{2}][O]} - 2k_{56}\text{[ClO][O]} - 2k_{12}\text{[OH][O]} \tag{5}
\]

For simplicity we have assumed a fast photochemical balance between OH and HO\textsubscript{2} through reactions R12 and R13 in order to represent the HO\textsubscript{x} odd oxygen loss rate as a single term. This approximation is valid only above 40 km, but does not introduce significant errors to our analysis below this altitude since HO\textsubscript{x} is the least important family for odd oxygen destruction at 30–40 km. As shown in Figure 10, (5) describes the photochemical balance of odd oxygen reasonably well throughout the 30–70 km region. With the exception of middle and high latitudes in the winter stratosphere, where odd oxygen is not photochemically controlled, production and loss rates are generally equal to within 10%. Having verified the validity of (5) at the altitudes of interest, we anticipate that the
reactions that result in the ozone increase in experiment B2 should either be present in (5) or indirectly affect the parameters therein.

Assuming photochemical steady state for odd oxygen and substituting (2) into (5) yields a quadratic equation for the ozone concentration

\[
0 = J_1[O_2] - R k_2[O_3]^2 - R k_{35}[NO_2][O_3] - R k_{56}[ClO][O_3] - R k_{12}[OH][O_3]
\]

This equation can be solved for the ozone concentration if \([NO_2]\), \([ClO]\) and \([OH]\) are known. However these species depend on the ozone abundance itself. Instead we choose to apply differentials to (6) and solve for the differential ozone abundance, in the same fashion as in the middle mesosphere analysis. This yields an equation describing the sensitivity of ozone to the various parameters in (6) and (2). Differences between the interactive 1xCO\(_2\) and 2xCO\(_2\) model results can then be used to diagnose the modelled ozone change. Applying differentials to (6) and solving for the relative change in ozone mixing ratio yields

\[
\frac{df_{O_3}}{f_{O_3}} = \frac{1}{A} \left\{ \frac{J_1[O_2] dJ_1}{R [O_3] J_1} - \frac{k_2[O_3]}{A} \left( \frac{dk_2}{k_2} + r \right) \right\}_{L_1} \\
- \frac{k_{35}[NO_2]}{A} \left( \frac{dk_{35}}{k_{35}} + \frac{df_{NO_2}}{f_{NO_2}} + r \right)_{L_2} \\
- \frac{k_{56}[ClO]}{A} \left( \frac{dk_{56}}{k_{56}} + \frac{df_{ClO}}{f_{ClO}} + r \right)_{L_3} \\
- \frac{k_{12}[OH]}{A} \left( \frac{dk_{12}}{k_{12}} + \frac{df_{OH}}{f_{OH}} + r \right)_{L_4}
\]

where

\[
A = 2k_2[O_3] + k_{35}[NO_2] + k_{56}[ClO] + k_{12}[OH]
\]

and

\[
r = \frac{d(J_2 + J_3)}{J_2 + J_3} - \frac{dk_1^*}{k_1^*}
\]

The first term in (7), denoted \(P\), expresses the contribution to the overall ozone change from changes in the odd oxygen production rate. The following four terms, denoted \(L_1\), \(L_2\), \(L_3\) and \(L_4\), includes the contributions from changes in the Chapman \((O_x)\), NO\(_x\), ClO\(_x\) and HO\(_x\) odd oxygen loss cycles respectively.
Figure 11. Relative difference (%) in the zonal and monthly mean daytime reaction rate coefficient $k_2$ $(O_3+O\rightarrow 2O_2)$ between the 2xCO$_2$ and 1xCO$_2$ interactive model experiments (B2-B1) for January. Contour intervals are 5% and negative values are shaded.

The relative changes within each cycle are weighted by the relative strength of the respective loss cycles.

We note that none of the reaction rate coefficients of the HO$_x$, NO$_x$ and ClO$_x$ cycles, $k_{12}$, $k_{35}$ and $k_{56}$, exhibit strong temperature dependencies. All three coefficients increase by 1–3% between the interactive 1xCO$_2$ and 2xCO$_2$ model runs and their contribution to the overall ozone change is therefore limited. The Chapman loss reactions rate coefficient ($k_2$), on the other hand, has a strong positive temperature dependence that leads to a substantial reduction in the Chapman odd oxygen destruction rate. Figure 11 shows a general decrease in $k_2$ of 20–30% in the USLM region which contributes significantly to the odd oxygen increase in the region.

Figure 12 shows the relative changes in the NO$_2$, ClO and OH mixing ratios. The mixing ratio of NO$_2$ has decreased by roughly 10–15% at 30–50 km which contributes to a smaller odd oxygen loss rate in this region. The NO$_2$ response is somewhat larger at higher altitudes, but of less importance for the odd oxygen budget as HO$_x$ chemistry dominates odd oxygen loss rates above 50 km (see Figure 5c). The NO$_2$ decrease is primarily a result of an overall NO$_y$ (NO$_x$+
Figure 12. Relative difference (%) in the zonal and monthly mean daytime mixing ratios of (a) NO$_2$, (b) ClO and (c) OH between the 2xCO$_2$ and 1xCO$_2$ interactive model experiments (B2-B1) for January. Contour intervals are 5% and negative values are shaded.
Figure 13. Same as Figure 12a but showing the relative change in the (diurnal average) NO$_y$ mixing ratio.

HNO$_3$ + HNO$_4$) decrease of similar magnitude (Figure 13), but there is also a contribution from a 15–20% decrease in the rate coefficient for the NO+O$_3$ reaction (R33). Two photochemical mechanisms contribute to the decrease in NO$_y$. First, O(1D) decreases below 40 km in response to the greater overhead ozone column, which leads to slower NO$_x$ production in the tropics below 10 hPa from N$_2$O oxidation by O(1D) (R8). Second, above the NO$_y$ peak at ~3 hPa, the NO$_y$ mixing ratio is affected by increased photochemical loss. Nitrogen atoms produced by NO photolysis (P9) are either lost through

$$\text{N} + \text{NO} \xrightarrow{k_{31}} \text{N}_2 + \text{O}$$  \hspace{1cm} (R31)

or recycled through

$$\text{N} + \text{O}_2 \xrightarrow{k_{28}} \text{NO} + \text{O}$$  \hspace{1cm} (R28)

The latter reaction has an extremely temperature dependent rate coefficient, which decreases by ~40% in response to the CO$_2$-induced cooling and thereby increases the fraction of nitrogen atoms lost through R31. This effect has also been noted by Rosenfield and Douglass [1998].

For ClO and OH the changes are generally too small to have significant im-
pacts on the odd oxygen budget. The OH mixing ratio is nearly unchanged above 40 km, where the HO\textsubscript{x} cycle is of importance. The ClO mixing ratio displays a maximum change of 5 to 15\% at low latitudes in the upper stratosphere. Although this increase coincides with the peak altitude of the ClO\textsubscript{x} odd oxygen loss cycle (see Figure 5b), this change has only a limited effect on the odd oxygen balance since the ClO\textsubscript{x} cycle contributes only about one fifth of the overall odd oxygen loss in this region.

Each of the loss rate terms in (7) also includes a common term \( r \) that expresses the changes in the parameters controlling the atomic oxygen abundance. Hence, we note that, although none of the Chapman odd oxygen partitioning reactions (P2, P3 and R1) add or remove odd oxygen, changes in their rate coefficients \((J_2, J_3 \text{ and } k_1^*)\) indirectly affect the odd oxygen budget by altering the rate of odd oxygen loss through a change in the atomic oxygen concentration. Notably the large relative increase in \( k_1^* \) is expected to decrease the atomic oxygen concentration and thereby slow down odd oxygen loss rates.

Finally we note that although neither of the O\textsubscript{2} and O\textsubscript{3} photodissociation coefficients \((J_1 \text{ and } J_2 + J_3)\) have a strong temperature dependence, the change in these parameters cannot be neglected. Below the stratopause the change in overhead ozone column between the 1xCO\textsubscript{2} and 2xCO\textsubscript{2} cases becomes significant and induces substantial changes to the O\textsubscript{2} and O\textsubscript{3} photodissociation coefficients, which must be included in order for (7) to balance.

Equation (7) should be interpreted similarly to (4), as a linearisation of the ozone steady state equation, in this case (6), around the ozone steady state of the 1xCO\textsubscript{2} reference experiment. Taking each relative change term in (7) to be the diagnosed 2xCO\textsubscript{2} – 1xCO\textsubscript{2} relative difference allows us to estimate the relative contribution to the overall ozone change from the various parameters controlling the ozone budget.

The calculated ozone change in percent as well as the contributions from the five production and loss terms \((P, L_1, L_2, L_3 \text{ and } L_4)\) are shown in Figure 14. The results are presented at six different model pressure levels in the USLM region. Furthermore each panel shows for comparison the ozone change produced by the model. The analytical expression (7) accurately reproduces the modelled ozone difference at all six levels. Not only is the magnitude of the change correct, but also most of the latitudinal variations are captured. The discrepancies between model and equation at winter high latitudes, of increasing magnitude with decreasing altitude, occur primarily because odd oxygen is not under photochemical control in this region, as indicated in Figure 10.

The results show that regardless of altitude all odd oxygen loss mechanisms act to increase the ozone mixing ratio in response to the cooling, in agreement
Figure 14. The relative difference (%) in daytime ozone mixing ratio between the $2x$CO$_2$ and $1x$CO$_2$ interactive model experiments (B2-B1) (plus signs) is compared to the ozone change predicted by the analytical expression (7) (squares) at pressure levels corresponding approximately to (a) 59, (b) 53, (c) 48, (d) 43, (e) 37 and (f) 32 km. Also shown are the contributions to the ozone change from changes in odd oxygen production and loss mechanisms (see legend and equation (7) for details). All data are shown for January.
with Haigh and Pyle [1982]. At 59 km the ozone increase is explained almost exclusively by slower HO$_x$ catalytic reactions, as would be expected from the dominance of HO$_x$ chemistry at this altitude (see Figure 5c). At 53 km the temperature dependence of the Chapman loss reaction becomes a significant factor and at 48 km this reaction explains about half of the ozone increase. At the lower levels most of the ozone increase is a result of slower NO$_x$ catalytic reactions, but with a significant contribution also from the Chapman loss reaction. The influence of changes in the ClO$_x$ cycle peaks at 43 and 48 km, particularly at high latitudes. Odd oxygen production rates in the model are largely unchanged in the mesosphere (59 and 53 km). In the stratosphere, however, we note that greater overhead UV filtering by ozone in the 2xCO$_2$ experiment leads to a reduction in odd oxygen production through O$_2$ photolysis, which thereby limits the ozone increase induced by the slower odd oxygen loss rates.

The relative contributions to the ozone increase from the four loss cycles to a large extent reflects their relative importance for the overall loss rate as a function of latitude and height (see Figure 5c). This suggests that much of the decrease in odd oxygen loss rates is governed by the common term $r$, which includes the parameters controlling the steady state abundance of atomic oxygen (i.e. $k_1^*$, $J_2$ and $J_3$). To illustrate the importance of the increase in $k_1^*$, relative to changes in the other parameters in (7), for the overall ozone increase we rewrite (7) as

$$\frac{df_{O_3}}{f_{O_3}} = \frac{1}{A} \left( \frac{J_1 [O_2]}{R [O_3]} \right) \frac{dJ_1}{L_1} - \frac{k_2 [O_3]}{f_{O_3}} \frac{dk_2}{k_2}$$

$$+ \left( \frac{dJ_2}{k_{35}} + \frac{dJ_3}{k_{35}} \right) \frac{df_{NO_2}}{A}$$

$$+ \left( \frac{dJ_4}{k_{56}} + \frac{dJ_3}{k_{56}} \right) \frac{df_{ClO}}{A}$$

$$+ \left( \frac{dJ_5}{k_{12}} + \frac{dJ_3}{k_{12}} \right) \frac{df_{OH}}{A}$$

$$- \left( 1 - \frac{k_2 [O_3]}{A} \right) \frac{d(J_2 + J_3)}{J_2 + J_3}$$
where we have used (8) and (9) to isolate the effects of the atomic oxygen controlling parameters in the terms $L_5^*$ and $L_6^*$. In Figure 15 we have plotted the individual terms in (10) as well as the net analytical and modelled ozone changes. The results show that the increase in $k_1^*$ (term $L_6^*$) is the major factor behind the ozone increase throughout the USLM region. At 59 km $L_6^*$ is completely dominant and at 53 km it explains more than 80% of the ozone increase. At 48, 43 and 37 km the increase in $k_1^*$ explains about two thirds of the ozone increase with the remaining contribution coming mainly from the Chapman and NO$_x$ terms ($L_1^*$ and $L_2^*$ respectively). The Chapman contribution is clearly generated by the strong decrease in $k_2$, while the contribution from the NO$_x$ term is primarily a result of the NO$_2$ decrease (see Figure 12). At these altitudes we also note the increasing impact of changes in O$_2$ and O$_3$ photodissociation rate coefficients. However, the contributions from the terms P and $L_5^*$ are similar in magnitude and have opposite signs, so that much of the decrease in odd oxygen production (term P) is counteracted by a decrease in ozone photolysis (term $L_5^*$). The impact of decreases in P2 and P3 on the odd oxygen budget is indirect: they lead to a decrease of the atomic oxygen concentration, which in turn results in slower odd oxygen loss rates. At 32 km the ozone increase is significantly smaller than above and the relative importance of $L_6^*$ not as dominant. Throughout the USLM region the contributions from the ClO$_x$ and HO$_x$ terms ($L_3^*$ and $L_4^*$ respectively) are generally below 2%, showing that the impact of the HO$_x$ and ClO$_x$ cycles in Figure 14 is primarily a result of the decrease in atomic oxygen concentration.

5 Summary and Conclusions

In this paper, as part of an ongoing study of chemistry and climate change interactions, a middle atmosphere model with interactive chemistry has been used to investigate the impact of a doubling of the CO$_2$ mixing ratio on the middle atmosphere temperature distribution. Sensitivity experiments with and without interactive ozone and for present-day and 2xCO$_2$ conditions have been performed to examine the importance and chemical details of the ozone radiative feedback.

The results of the interactive model runs show a substantial cooling throughout much of the middle atmosphere with a maximum cooling of $\sim$10 K at the
Figure 15. As Figure 14, except that the contributions to the ozone change from the rate coefficients of the odd oxygen partitioning reactions $R1$ (crosses), $P2$ and $P3$ (triangles) are shown separately from the remaining parameters of the Chapman ($O_x$), $NO_x$, $ClO_x$ and $HO_x$ cycles. See legend and equation (10) for details.
stratopause over the tropics and \( \sim 12 \) K in the polar regions. Associated with the lower temperatures is an increase in the daytime ozone mixing ratio by up to \( \sim 20\% \) in the upper stratosphere (30–50 km) and by 10–15\% in the lower half of the mesosphere (50–70 km), which acts to reduce the CO\(_2\)-induced cooling by up to \( \sim 4.5 \) K through enhanced ozone heating. Because of the increase in overhead ozone column, less UV radiation penetrates down to the lower stratosphere, which leads to ozone decreases below 30 km in the tropics and subtropics.

The ozone increase simulated by the model at 30–70 km was shown to be caused by changes in the temperature dependent chemical reactions that control the odd oxygen abundance and partitioning in this region. In the middle mesosphere at 60–70 km, odd oxygen changes were small (<5\%) and the ozone increase is caused by a shift in odd oxygen partitioning resulting from a \( \sim 10\% \) increase in the \( \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \) reaction rate coefficient \( (k_1^*) \). A 3–4\% number density increase produced by the cooling induced contraction of the middle atmosphere is responsible for about 30\% of the rate increase.

In the upper stratosphere and lower mesosphere at 30–60 km, the analysis of the temperature dependence of the odd oxygen photochemical steady state is more complex due to the variety of chemical loss cycles involved. However, it is possible to perturb the odd oxygen steady state equation to achieve an approximative analytical expression for the relative ozone change as a function of changes in odd oxygen production and loss rates, which reproduces the modelled ozone increase at these altitudes. The results show that the increase in ozone is forced by slower odd oxygen loss rates. The fractional contribution to the overall ozone change from the odd oxygen loss cycles (Chapman \( (\text{O}_x) \), NO\(_x\), ClO\(_x\), HO\(_x\)) varies with altitude and to a large extent reflects the relative importance of the different cycles as a function of altitude. Hence, the ozone increase in this region is primarily explained by less effective HO\(_x\) odd oxygen destruction at 50–60 km, by slower rates of the Chapman odd oxygen loss reaction \( \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2 \) at 45–50 km and by slower NO\(_x\) catalytic cycling below 45 km.

Our analysis also shows that the slower odd oxygen loss rates are not primarily controlled by the temperature dependence of the reaction rate coefficients of the odd oxygen loss cycles, but are mainly the result of a shift in odd oxygen partitioning. The increase in the \( k_1^* \) reaction rate coefficient reduces the atomic oxygen abundance, and because the major odd oxygen loss rates at 30–60 km are all proportional to the atomic oxygen concentration, this leads to slower odd oxygen loss rates. About two thirds of the ozone increase in the 30–60 km region can be explained by this effect. The remaining ozone increase is induced primarily by a decrease in the reaction rate coefficient of the Chapman reaction \( \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2 \) and by a decrease in the NO\(_2\) abundance.
Acknowledgements

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# Appendix

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<td>$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$</td>
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<td>R2</td>
<td>$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$</td>
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<td>$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$</td>
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<td>Br + HO$_2$ → HBr + O$_2$</td>
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<tr>
<td>R76</td>
<td>Br + OClO → BrO + ClO</td>
</tr>
<tr>
<td>R77</td>
<td>BrO + O → Br + O$_2$</td>
</tr>
<tr>
<td>R78</td>
<td>BrO + OH → Br + HO$_2$</td>
</tr>
<tr>
<td>R79</td>
<td>BrO + OH → HBr + O$_2$</td>
</tr>
<tr>
<td>R80</td>
<td>BrO + HO$_2$ → HOBr + O$_2$</td>
</tr>
<tr>
<td>R81</td>
<td>BrO + NO → Br + NO$_2$</td>
</tr>
<tr>
<td>R82</td>
<td>BrO + NO$_2$ + M → BrONO$_2$ + M</td>
</tr>
<tr>
<td>R83</td>
<td>BrO + ClO → Br + OCIO</td>
</tr>
<tr>
<td>R84</td>
<td>BrO + ClO → Br + Cl + O$_2$</td>
</tr>
<tr>
<td>R85</td>
<td>BrO + ClO → BrCl + O$_2$</td>
</tr>
<tr>
<td>R86</td>
<td>BrO + BrO → 2 Br + O$_2$</td>
</tr>
<tr>
<td>R87</td>
<td>HBr + OH → Br + H$_2$O</td>
</tr>
<tr>
<td>R88</td>
<td>BrNO$_2$ + M → HNO$_3$ + HOBr</td>
</tr>
<tr>
<td>R89</td>
<td>CH$_3$Br + OH → Br + CO + 2H$_2$O</td>
</tr>
<tr>
<td>R90</td>
<td>CH$_4$ + OH → CH$_3$O$_2$ + H$_2$O</td>
</tr>
<tr>
<td>R91</td>
<td>CH$_4$ + Cl → HCl + CH$_3$O$_2$</td>
</tr>
<tr>
<td>R92</td>
<td>CH$_3$O$_2$ + HO$_2$ → CH$_3$OOH + O$_2$</td>
</tr>
<tr>
<td>R93</td>
<td>CH$_3$O$_2$ + NO → CH$_2$O + NO$_2$ + HO$_2$</td>
</tr>
<tr>
<td>R94</td>
<td>CH$_3$O$_2$ + ClO → CH$_2$O + Cl + HO$_2$</td>
</tr>
<tr>
<td>R95</td>
<td>CH$_3$O$_2$ + CH$_3$O$_2$ → 2 HO$_2$ + 2 CH$_2$O</td>
</tr>
<tr>
<td>R96</td>
<td>CH$_3$OOH + OH → CH$_3$O$_2$ + H$_2$O</td>
</tr>
<tr>
<td>R97</td>
<td>CH$_2$O + O → CO + OH + HO$_2$</td>
</tr>
<tr>
<td>R98</td>
<td>CH$_2$O + OH → CO + H$_2$O + HO$_2$</td>
</tr>
<tr>
<td>R99</td>
<td>CH$_2$O + Cl → CO + HO$_2$ + HCl</td>
</tr>
<tr>
<td>R100</td>
<td>CO + OH → CO$_2$ + H</td>
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</tbody>
</table>

*For each reaction Rn, the reaction rate coefficient is denoted $k_n$ in the text.*
Table 3. Table of Photolysis Reactions

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>$\text{O}_2 + h\nu \rightarrow 2\text{O}$</td>
</tr>
<tr>
<td>P2</td>
<td>$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^{1}\text{D})$</td>
</tr>
<tr>
<td>P3</td>
<td>$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}$</td>
</tr>
<tr>
<td>P4</td>
<td>$\text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{OH}$</td>
</tr>
<tr>
<td>P5</td>
<td>$\text{H}_2\text{O} + h\nu \rightarrow 2\text{H} + \text{O}$</td>
</tr>
<tr>
<td>P6</td>
<td>$\text{H}_2\text{O} + h\nu \rightarrow \text{H}_2 + \text{O}(^{1}\text{D})$</td>
</tr>
<tr>
<td>P7</td>
<td>$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$</td>
</tr>
<tr>
<td>P8</td>
<td>$\text{N}_2\text{O} + h\nu \rightarrow \text{O}(^{1}\text{D}) + \text{N}_2$</td>
</tr>
<tr>
<td>P9</td>
<td>$\text{NO} + h\nu \rightarrow \text{N} + \text{O}$</td>
</tr>
<tr>
<td>P10</td>
<td>$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$</td>
</tr>
<tr>
<td>P11</td>
<td>$\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}$</td>
</tr>
<tr>
<td>P12</td>
<td>$\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2$</td>
</tr>
<tr>
<td>P13</td>
<td>$\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO}_3$</td>
</tr>
<tr>
<td>P14</td>
<td>$\text{HNO}_3 + h\nu \rightarrow \text{NO}_2 + \text{OH}$</td>
</tr>
<tr>
<td>P15</td>
<td>$\text{HNO}_4 + h\nu \rightarrow \text{NO}_2 + \text{HO}_2$</td>
</tr>
<tr>
<td>P16</td>
<td>$\text{CFC11} + h\nu \rightarrow 3\text{Cl} + \text{products}$</td>
</tr>
<tr>
<td>P17</td>
<td>$\text{CFC12} + h\nu \rightarrow 2\text{Cl} + \text{products}$</td>
</tr>
<tr>
<td>P18</td>
<td>$\text{HCl} + h\nu \rightarrow \text{Cl} + \text{H}$</td>
</tr>
<tr>
<td>P19</td>
<td>$\text{HOCl} + h\nu \rightarrow \text{Cl} + \text{OH}$</td>
</tr>
<tr>
<td>P20</td>
<td>$\text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_3$</td>
</tr>
<tr>
<td>P21</td>
<td>$\text{Cl}_2\text{O}_2 + h\nu \rightarrow 2\text{Cl} + \text{O}_2$</td>
</tr>
<tr>
<td>P22</td>
<td>$\text{OCIO} + h\nu \rightarrow \text{ClO} + \text{O}$</td>
</tr>
<tr>
<td>P23</td>
<td>$\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$</td>
</tr>
<tr>
<td>P24</td>
<td>$\text{CH}_3\text{Br} + h\nu \rightarrow \text{OH} + \text{BrO} + \text{CO} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>P25</td>
<td>$\text{HBr} + h\nu \rightarrow \text{Br} + \text{H}$</td>
</tr>
<tr>
<td>P26</td>
<td>$\text{HOBr} + h\nu \rightarrow \text{Br} + \text{OH}$</td>
</tr>
<tr>
<td>P27</td>
<td>$\text{BrO} + h\nu \rightarrow \text{Br} + \text{O}$</td>
</tr>
<tr>
<td>P28</td>
<td>$\text{BrONO}_2 + h\nu \rightarrow \text{Br} + \text{NO}_3$</td>
</tr>
<tr>
<td>P29</td>
<td>$\text{BrCl} + h\nu \rightarrow \text{Br} + \text{Cl}$</td>
</tr>
<tr>
<td>P30</td>
<td>$\text{CH}_4 + h\nu \rightarrow 2\text{HO}_2 + \text{CO} + \text{H}_2$</td>
</tr>
<tr>
<td>P31</td>
<td>$\text{CH}_4 + h\nu \rightarrow 2\text{HO}_2 + \text{CO} + 2\text{H}$</td>
</tr>
<tr>
<td>P32</td>
<td>$\text{CH}_3\text{OOH} + h\nu \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{OH}$</td>
</tr>
<tr>
<td>P33</td>
<td>$\text{CH}_2\text{O} + h\nu \rightarrow \text{CO} + \text{H} + \text{HO}_2$</td>
</tr>
<tr>
<td>P34</td>
<td>$\text{CH}_2\text{O} + h\nu \rightarrow \text{CO} + \text{H}_2$</td>
</tr>
<tr>
<td>P35</td>
<td>$\text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O}$</td>
</tr>
</tbody>
</table>

*a For each photolysis reaction Pn, the photolysis rate coefficient is denoted $J_n$ in the text.*
References


References


Response of the middle atmosphere to CO$_2$ doubling: Results from the Canadian Middle Atmosphere Model

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Abstract

The Canadian Middle Atmosphere Model (CMAM) has been used to examine the middle atmosphere response to CO$_2$ doubling. The radiative-photochemical response induced by doubling CO$_2$ alone and the response produced by changes in prescribed SSTs are found to be approximately additive, with the former effect dominating throughout the middle atmosphere. The paper discusses the overall response, with emphasis on the effects of SST changes, which allow a full tropospheric response to the CO$_2$ forcing. The overall response is a cooling of the middle atmosphere that maximizes near the stratopause. The cooling leads to an ozone increase in the upper stratosphere and lower mesosphere that provides a radiative feedback on the temperature decrease through both increased solar heating and decreased infrared cooling, with the latter accounting for up to 15% of the total effect. Changes in global mean water vapor cooling are negligible above $\sim$30 hPa, despite significant increases in the water vapor abundance. Near the polar summer mesopause, the temperature response is weak and not statistically significant. The main effects of SST changes are a warmer troposphere, a warmer and higher tropopause, cell-like structures of heating and cooling at low and middle latitudes in the middle atmosphere, warming in the summer mesosphere, water vapor increase throughout the domain, and O$_3$ decrease in the lower tropical stratosphere. No noticeable change in upward propagating planetary wave activity in the extratropical winter/spring stratosphere and no significant temperature response in the polar winter/spring stratosphere have been found.
1. Introduction

The observed increase in atmospheric CO$_2$ concentrations represents the single most significant anthropogenic perturbation to the climate system. Most attention naturally focuses on the associated warming effects in the troposphere. In the middle atmosphere, the enhanced infrared emission associated with the CO$_2$ increase acts instead to cool the region, particularly at the stratopause where the temperature maximizes. Indeed, a cooling of the middle atmosphere in recent decades has been well documented (Ramaswamy et al. 2001; Beig et al. 2003).

There are several reasons why it is important to understand the effects of increased CO$_2$ on the middle atmosphere. First, it is quite possible that climate change can be more easily detected in the middle atmosphere, because the relevant physical processes are so much simpler than in the troposphere. In contrast to the troposphere, the middle atmosphere is close to being in global-mean radiative balance at all altitudes below the mesopause (e.g., Fomichev et al. 2002). Thus, global-mean temperature changes provide an excellent tool for attribution (e.g., Shine et al. 2003). Furthermore, the uncertainty in tropospheric climate change associated with cloud and water vapor feedbacks is not a major issue in the middle atmosphere. On the other hand, measurements in the middle atmosphere are subject to considerable uncertainties and are of relatively short duration (WCRP-SPARC 2002). Middle atmosphere climate change is also significantly affected by anthropogenically induced ozone depletion (WMO 2003), which has itself acted to cool the stratosphere (Shine et al. 2003). Although this last point represents a complication for attribution, it also provides a second important motivation for understanding the effects of increasing CO$_2$ on the middle atmosphere – namely, to help distinguish the effects of ozone-depleting substances, which is a separate attribution problem.

Because ozone and temperature are so strongly coupled in the middle atmosphere, a complete understanding of middle atmosphere climate change requires accounting for the ozone radiative feedback. Furthermore, because the troposphere strongly affects the stratosphere through dynamical forcing from upward propagating waves, it is necessary to account for changes in this dynamical forcing. This suggests the need to use a three-dimensional coupled chemistry climate model (CCM), with an accurate representation of stratospheric ozone chemistry. A particular issue concerns the predicted effect of increased CO$_2$ levels on the Arctic stratosphere, which has potentially significant implications for Arctic ozone (WMO 2003). Such predictions appear to be very sensitive and non-robust. A recent comparison of several CCMs (Austin et al. 2003) found that some models predicted an increase in stratospheric wave forcing, some a decrease, and some not much of a change. Thus, there is no current consensus on
even the sign of the expected CO$_2$-induced changes in the Arctic stratosphere. While some of the differences between different models may reflect differences in the models themselves, they may also be the result of insufficiently long integrations.

While the preferred tool for attribution and prediction of climate change is ensembles of transient simulations, with the different forcings included incrementally as well as together, computational constraints currently make this a severe challenge for CCMs. Thus, there is much to be learned from performing simulations under doubled CO$_2$ conditions. Although idealized equilibrium simulations cannot reproduce the complexity of the real atmosphere which is evolving slowly to increasing greenhouse gases, such studies can be used to identify robust processes and feedbacks that can then be used to test hypotheses in transient simulations.

It is useful to consider two distinct aspects of the response to CO$_2$ doubling – the intrinsic middle atmosphere response, and the middle atmosphere response to the change in tropospheric climate. The former is primarily radiative-photochemical in nature, driven by the CO$_2$ induced cooling, while the latter is primarily dynamical in nature, driven by the upward propagating waves and their induced circulation. One reason to distinguish these two aspects of the full response is that the former should be robust, while the latter can be expected to depend on details of the change in tropospheric climate which may be more model dependent. For example, Rind et al. (2002) studied 2$\times$CO$_2$ effects for two different sets of the sea surface conditions (sea surface temperatures and sea ice distribution, referred to hereafter simply as SSTs for short), and pointed out the importance of the SST distribution for the middle atmosphere response to doubled CO$_2$.

Sigmond et al. (2004) separated the tropospheric and middle atmosphere effects by doubling CO$_2$ in the troposphere and middle atmosphere separately, as well as together. They found that the combined response was equal to the sum of the separate responses, confirming the idea that the two aspects of the response are largely distinct. Schmidt et al. (2005, manuscript submitted to J. Climate) instead separated the radiative-photochemical and dynamical effects by controlling the SSTs. This is essentially equivalent to the Sigmond et al. (2004) approach because if only the SSTs are changed, then the middle atmosphere response to doubled CO$_2$ is driven by the change in the troposphere alone.

In this paper, we report on doubled CO$_2$ simulations with the Canadian Middle Atmosphere Model (CMAM). The significance of interactive ozone chemistry and photochemical analysis of the ozone radiative feedback in the CMAM under doubled CO$_2$ conditions have been presented by Jonsson et al. (2004). To min-
Table 1. Model Simulations

<table>
<thead>
<tr>
<th>Experiment</th>
<th>CO₂ Multiplier</th>
<th>SST Changes</th>
<th>Run Length (years)</th>
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</thead>
<tbody>
<tr>
<td>B1</td>
<td>1</td>
<td>none</td>
<td>15+15</td>
</tr>
<tr>
<td>B2</td>
<td>2</td>
<td>none</td>
<td>15+15</td>
</tr>
<tr>
<td>C1</td>
<td>1</td>
<td>yes</td>
<td>15</td>
</tr>
<tr>
<td>C2</td>
<td>2</td>
<td>yes</td>
<td>15+15</td>
</tr>
</tbody>
</table>

* In this paper, the term “SST” is used as a shorthand for both sea surface temperature and sea ice distribution. The SST changes are those associated with a doubled CO₂ climate.

imize the influence of tropospheric climate change on the middle atmosphere, only experiments with SSTs corresponding to 1×CO₂ conditions were used in that study. In this companion study, we discuss the overall effect of CO₂ doubling in the middle atmosphere, with emphasis on the effects of SST changes.

2. Model Description and Experimental Setup

The Canadian Middle Atmosphere Model (CMAM) is based on the Canadian Center for Climate Modeling and Analyses (CCCma) general circulation model (GCM) (McFarlane et al. 2005, manuscript to be submitted to Atmos.-Ocean) and includes a comprehensive on-line photochemistry module in which ozone and water vapor interact with the radiation field in the model. The dynamical core and the chemistry and radiative schemes of the CMAM are described by Bea- gley et al. (1997), de Grandpré et al. (1997, 2000), and Fomichev et al. (2004), respectively. A detailed description of the model version used in the current study is given by Jonsson et al. (2004). The model runs at T32 spectral truncation with 65 vertical layers extending from the surface up to 0.00067 hPa (∼ 97 km). It includes comprehensive tropospheric physics, realistic radiative schemes with non-local thermodynamical equilibrium treatment in the mesosphere, and orographic and non-orographic gravity wave drag schemes. The photochemistry module is active from 410 hPa up to the model lid and includes 45 species and 135 photochemical processes. A spectral advection scheme is used for the transport of long-lived constituents whereas short-lived species are treated with the standard family approach.

Several multi-year numerical experiments have been performed (Table 1). B1 is a control run for the current CO₂ amount (1×CO₂) and C2 represents the full 2×CO₂ experiment with the CO₂ concentration in the atmosphere doubled and the SSTs prescribed for the 2×CO₂ climate. The two other experiments (C1
and B2) represent artificial conditions which, in fact, would not to occur in the real atmosphere: $1\times\text{CO}_2$ with modified SSTs (C1), and $2\times\text{CO}_2$ with unchanged SSTs (B2). These two experiments have been used to assess the impact of changes in the troposphere on the middle atmosphere. Experiments B1, B2, and C2 are referred to as the control, atmospheric CO$_2$ doubling, and (full) CO$_2$ doubling experiments, respectively, hereafter. These three experiments consist of two separate 15-year simulations, referred to as subsets S$_1$ and S$_2$ hereafter. Detailed diagnostics were only saved for subset S$_2$. If not stated otherwise, the analysis presented in this paper is performed for the combined 30-year datasets.

The mixing ratio of CO$_2$ in the model is prescribed to a fixed vertical profile: it is 348 ppmv below $\sim$85 km and decreases above as described by Fomichev et al. (1998). The CO$_2$ mixing ratio is scaled to twice its original value for the $2\times\text{CO}_2$ experiments. The SST distribution for the $2\times\text{CO}_2$ climate has been taken from a separate transient simulation with a coupled atmosphere-ocean CCCma GCM (Boer et al. 2000) that has a tropospheric component that is nearly identical to the CMAM.

3. Control Simulation and Radiative Forcing

To study the model response to CO$_2$ doubling, we have analyzed changes in temperature, O$_3$, and water vapor fields. Figures 1, 2, and 3, respectively, present 30-year monthly mean distributions of these three fields for the control run for a representative month in each season. They provide the reference point to which the subsequent perturbation experiments will be assessed.

The model reproduces the main characteristics of observed climatologies, but also has some biases discussed below. Comparison of the temperature field (Fig. 1) with the HALOE measurements (Hervig et al. 1996) indicates a robust and widespread cold bias throughout the upper stratosphere and mesosphere which reaches 15–20 K on average above $\sim$0.1 hPa. This model bias is partially attributed to the absence of both chemical and near-infrared CO$_2$ heating in this version of the model (Fomichev et al. 2004). Comparison of the daytime ozone mixing ratio (Fig. 2) with the combined HALOE-MLS ozone climatology (WCRP-SPARC 2002) indicates a model ozone deficit of 10–20% between 10 and 0.1 hPa throughout the year which exceeds 20% in the upper stratosphere high latitude regions, similar to that reported in previous versions of the model (de Grandpré et al. 2000). The model ozone deficit is partially responsible for the model cold bias below 0.1 hPa. Throughout the middle atmosphere, the water vapor (Fig. 3) is generally biased low compared to observations, and in particular, the maximum in the lower mesosphere is $\sim$1.5 ppmv lower than reported in WCRP-SPARC (2000). This bias is mainly the result of too low
temperatures at the tropical tropopause (near 90 hPa in the CMAM), where the model is colder by $\sim 2$ K than observations (WCRP-SPARC 2002).

Distributions of solar, infrared and net radiative heating rates produced by the model for the $1\times CO_2$ case are shown in Figs. 4a-c for January. The region between the tropopause and $\sim 70$ km, except near the winter pole, is close to radiative equilibrium conditions, i.e., the net radiative heating (Fig. 4c) is close to zero in this region. When $CO_2$ is doubled in the model, this quasi-steady state is disturbed. Figure 4d shows the initial forcing induced by the $CO_2$ doubling. This term is defined as the difference between the infrared heating rates calculated for the $2\times CO_2$ and $1\times CO_2$ cases (B2 and B1, respectively) at the very first model time step after the $CO_2$ concentration has been doubled. The doubling of $CO_2$ leads to a decrease of infrared cooling in the troposphere and, hence, provides a positive initial forcing. This forcing would lead to the greenhouse warming and a warmer sea surface if the model had an interactive ocean. In the middle atmosphere, the initial forcing exhibits the positive and

Figure 1. Zonal and monthly mean temperature (K) averaged over 30 years for (a) January, (b) April, (c) July, and (d) October for the $1\times CO_2$ case (control experiment B1). Contour intervals are 10 K.
negative features of the infrared heating shown in Fig. 4b but with only $\sim$30% of the strength.

4. Full Response to Doubled CO$_2$

The atmosphere responds to the forcing shown in Fig. 4d by changing temperature, ozone, water vapor, and other fields until the initial forcing is entirely compensated and a new quasi-equilibrium energy balance is reached. The full response to CO$_2$ doubling (including the associated changes in SSTs) for temperature, daytime ozone and water vapor is shown in Figs. 5, 6 and 7, respectively.

In general, the simulated changes are statistically significant throughout most of the domain.

The troposphere warms by $\sim$2–4 K and the middle atmosphere cools by up to $\sim$10–12 K (Fig. 5) with a maximum impact near the stratopause. The overall vertical structure of the thermal response in the middle atmosphere reflects
the background temperature distribution (Fig. 1), with stronger cooling where temperatures are higher as expected on radiative grounds. Some significant latitudinal structure is also apparent. At the stratopause, there are cooling maxima at the summer pole (where temperatures are highest) and at the winter pole (where in the absence of sunlight the ozone radiative response does not counteract the cooling). It is noteworthy that there is no significant response near the polar summer mesopause where the initial forcing is positive (Fig. 4d). This is consistent with the fact that no noticeable trends have been observed in this region for the past few decades (Beig et al. 2003).

In response to the cooling of the middle atmosphere, the O₃ mixing ratio increases by 10–20% between 30 and 70 km (Fig. 6). Jonsson et al. (2004) showed that the ozone increase in this region can be understood primarily as a result of the negative temperature dependence of the O + O₂ + M → O₃ +
The statistically significant relative increase of $\text{O}_3$ near 75 km and decrease near the tropical tropopause are mainly associated with the SST changes and will be discussed in section 6.

The water vapor increase (Fig. 7) is mainly associated with a warmer sea surface, which allows for a warmer troposphere and, as a result, leads to a moister troposphere. There is also a small but statistically significant increase of $\sim 0.3$–$0.4$ ppmv in the stratosphere and lower mesosphere which is caused by enhanced water vapor input from the troposphere due mainly to a warmer tropical tropopause (see section 6b for further discussion).

Changes in temperature and radiatively active gases such as ozone and water vapor lead to a new quasi-equilibrium energy balance. Figure 8 shows changes in the radiative energy budget induced by the $\text{CO}_2$ doubling for January. The
initial infrared forcing of up to 3 K day$^{-1}$ (Fig. 4d) is partially compensated by a change in infrared heating (Fig. 8b) through an adjustment of the temperature field and partially by an increase in solar heating (Fig. 8a) due to the ozone increase. The net radiative heating (Fig. 8c) is largely unchanged in the middle atmosphere below $\sim$70 km and south of 50°N, indicating that the model response is radiative-photochemical in this region. Dynamical effects occur mainly over the winter pole and near the model top and are mainly related to SST changes. Figure 8d shows changes in the individual components of the globally averaged radiative energy budget. Due to the strong overlapping of spectral lines in the lower atmosphere, contributions from different gases can only be isolated above $\sim$30 hPa. In this region, O$_3$ absorption dominates the solar heating, whereas noticeable contributions to the infrared cooling are provided by the 15 µm CO$_2$, 9.6 µm O$_3$, and rotational H$_2$O bands. As seen in Fig. 8d, the residual (i.e.,
equilibrated) CO$_2$ cooling is compensated by not only an increase in solar heating but also by a decrease in the 9.6 $\mu$m O$_3$ band cooling. Near the stratopause, the effect of the infrared O$_3$ band exceeds $\sim$0.1 K day$^{-1}$ or about 15% of the change in solar heating. This is less than the radiative feedback of up to 0.4 K day$^{-1}$ due to the 9.6 $\mu$m O$_3$ band found by Akmaev and Fomichev (1998) from simulations without interactive chemistry. The change in the 9.6 $\mu$m O$_3$ band contribution can be explained by the counteracting effects of the temperature decrease and the ozone increase. The temperature decrease results in a reduction of infrared cooling, whereas the ozone increase tends to increase the 9.6 $\mu$m O$_3$ band cooling. Changes in the water vapor contribution to the energy budget were found to be negligible above $\sim$30 hPa despite significant increases in the water vapor abundance.
5. Additivity of the Radiative-Photochemical and Dynamical Responses

To simulate the doubled CO$_2$ climate, two forcings have been applied to the model: (1) the CO$_2$ concentration in the atmosphere was increased and (2) the SSTs were modified to a state representative of doubled CO$_2$ conditions. The impact of CO$_2$ alone is mainly radiative-photochemical in the middle atmosphere, as shown by Jonsson et al. (2004), i.e., the temperature changes can be understood primarily as a result of CO$_2$-induced cooling and photochemical feedback. The effect of changes in SSTs dominates in the troposphere but also produces some effects in the middle atmosphere. In order to analyze the impact of changes in SSTs on the middle atmosphere separately from the effect of increased CO$_2$, the impacts of the two forcings need to be additive in this region. An analysis for additivity is presented in Fig. 9 for January. The top two panels of Fig. 9 show the individual effects of the atmospheric CO$_2$ increase.
Figure 8. Heating rate (K day\(^{-1}\)) difference (experiments C2-B1) for January. Panels (a), (b), and (c) show solar, infrared, and net radiative heating, respectively. Contour intervals are 0.5 K day\(^{-1}\). Positive area is shaded. Panel (d) shows globally averaged values for: Solar heating; IR, (total) infrared heating; CO\(_2\), 15 \(\mu\)m CO\(_2\) band; O\(_3\), 9.6 \(\mu\)m O\(_3\) band; and H\(_2\)O, rotational H\(_2\)O band. The data shown are based on zonal and monthly mean values averaged over 15 years (subset S\(_2\)).

(Fig. 9a, B2-B1) and the changes in SSTs (Fig. 9b, C1-B1), respectively. From comparison of Fig. 9a and Fig. 9b, it is clear that the radiative-photochemical response dominates in the middle atmosphere. The full effect of CO\(_2\) doubling which includes both CO\(_2\) increase and SST changes (C2-B1) is shown in Fig. 9c.

Figure 9d presents a statistical test for additivity of the radiative-photochemical and dynamical responses. Here, the sum of the individual effects of the increase of atmospheric CO\(_2\) and the SST changes are subtracted from the full model response to CO\(_2\) doubling (i.e., (C2-B1)-[(B2-B1)+(C1-B1)]). From Fig. 9d it is clear that additivity is a valid assumption throughout most of the model domain. Moreover, in regions where the radiative-photochemical and dynamical responses are not additive, the magnitude of the non-additivity...
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The model response to the changes in SSTs for temperature, daytime ozone and water vapor for the four different months is shown in Figs. 10, 11, and 12, respectively. In the troposphere, where convective processes dominate in establishing the overall thermal structure, a warmer sea surface inevitably
leads to an increase in temperature – here by $\sim 2–4$ K throughout most of the region (Fig. 10). The warmer sea surface implies enhanced evaporation from the oceans and, as a result, a considerable increase in the tropospheric water vapor abundance (Fig. 12). The warmer and moister troposphere in the full CO$_2$ doubling experiment (Figs. 5 and 7) is mainly associated with the SST changes (cf., Figs. 5 and 10, and Figs. 7 and 12).

Comparing Fig. 10a and Fig. 9b we see that the model thermal responses to the SST changes are similar for 2$\times$CO$_2$ and 1$\times$CO$_2$ conditions. This is what one would expect if the radiative-photochemical and dynamical responses to CO$_2$ doubling are additive. The impact of changes in SSTs on the middle atmosphere is relatively small and localized. Apart from the tropospheric temperature increase, the main features outside of the polar regions are: cooling just above the tropopause in the tropics and extratropics by up to 1–2 K during
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all seasons, warming of the mid-latitude summer upper mesosphere by up to 4 K in January and by more than 1 K in July, and cell-like structures of heating and cooling (of up to 1–2 K) in the tropical and mid-latitude upper stratosphere and mesosphere. All of these features agree qualitatively with results obtained by Sigmond et al. (2004) and Schmidt et al. (2005, manuscript submitted to *J. Climate*) for the middle atmosphere response to the SST changes associated with doubling of CO$_2$. Figure 10 also shows considerable changes in the polar regions which are generally not statistically significant or have only a marginal statistical significance of 90%. Exceptions are the Southern Hemisphere (SH) summer and the Northern Hemisphere (NH) lowermost stratosphere. The model response near the tropopause and in the polar regions is discussed in detail in sections 6b and 6c, respectively.

The warm regions at middle and high latitudes in the summer mesosphere (Figs. 10a and 10c) are associated with changes in the residual pole-to-pole circulation. An examination of the residual circulation of the mesosphere and upper stratosphere (not shown) reveals that the SST changes associated with
doubled CO\textsubscript{2} (experiment C2) moderate the changes in the circulation resulting from the CO\textsubscript{2} changes alone (experiment B2). B2 has a generally stronger pole-to-pole flow during solstices (than the control experiment B1) that results from changes in gravity wave drag associated with the changes in middle atmosphere winds. The impact of SST changes alone reduces this change in the mesosphere by slowing the summer mesospheric ascent. The warm regions in the summer mesosphere are consistent with adiabatic heating resulting from the slower ascending branch of the residual circulation. The slower ascent also results in a higher atomic oxygen concentration in this region which can at least partially explain the higher ozone concentration in the summer mesosphere near 75 km (Fig. 11). Given the long solar illumination during the polar summer, this ozone increase provides radiative heating of up to \(\sim 1\) K day\(^{-1}\) (not shown), adding to the adiabatic heating associated with the slower ascent in the region.

Downward control diagnostics (Haynes et al. 1991) (not shown) confirm that
the changes in the residual circulation in the mesosphere are mainly due to changes in parameterized gravity wave drag (GWD). In particular, there is a slower ascent over the SH summer pole. A similar, but weaker, effect occurs in the NH summer mesosphere, which results in a weaker temperature response than for the SH counterpart (cf., Figs. 10a and 10c). The change in GWD is an indirect response to CO$_2$ doubling since the parameterized gravity wave source, which is specified at the ground, remains effectively constant in all experiments. Thus, the mesospheric change in GWD is possible only by changes in the filtering of the parameterized waves by the resolved winds. The stronger equator-to-pole temperature gradient (warming in the upper tropical troposphere and cooling above the extratropical tropopause, Figs. 10a and 10c) generates stronger mid-latitude tropospheric westerlies (by up to \( \sim 5 \text{ m s}^{-1} \) at middle latitudes near 15 km, not shown). These stronger westerlies filter more of the eastward propagating (parameterized) gravity waves, which results in less eastward drag in the upper mesosphere. There is no such effect in the winter mesosphere because these waves are absorbed by the stratospheric winter westerlies.

In reality, we can expect the gravity wave source spectrum to change under doubled CO$_2$ conditions. However, given our current state of knowledge it is not possible to predict the nature of this change. With the source spectrum essentially fixed, the gravity wave response is strongly constrained (Shepherd and Shaw 2004). On the other hand, we do not expect the response to be very dependent on the specific gravity wave drag parameterization used (McLandress and Scinocca 2005).

The cell-like structures above \( \sim 30 \) km at low latitudes in Fig. 10 are attributed to changes in the semi-annual oscillation (SAO) brought about by changes in resolved equatorial waves and parameterized GWD. Although the exact reason for these changes is unknown, it is most likely linked to changes in upward-propagating equatorial waves generated by the deep convection parameterization (Horinouchi et al. 2003). Changes to the resolved wave forcing would then feed back on the parameterized GWD, producing further changes to the SAO in the mesosphere. Because of the dependence of these changes to the SAO on unconstrained aspects of the deep convection and GWD parameterizations, the changes may well be model dependent and consequently not reproducible in general.

The response of the daytime O$_3$ mixing ratio to changes in SSTs (Fig. 11), although statistically significant throughout much of the middle atmosphere, is in general very weak. Two features stand out: a decrease of up to \( \sim 25\% \) around the tropical tropopause, and a near pole-to-pole layer of up to \( \sim 50\% \) increases around 75 km. Both these features are present throughout the year. While
the relative impact on the ozone mixing ratio is large near 75 km, the absolute changes are small as they occur in the ozone mixing ratio minimum (Fig. 2). Therefore these changes do not significantly modify the energy budget of the region except, as mentioned above, in the polar summer mesosphere where solar heating increases by up to 1 K day$^{-1}$. The ozone increases in this region result from increased downward transport of atomic oxygen from higher levels. The ozone decrease near the tropical tropopause results primarily from the upward shift of the tropopause but also reflects an enhanced two-cell diabatic circulation in the lower stratosphere (see section 6b for further analysis), as is confirmed by increased ozone mixing ratios above the tropopause in the extratropics. This change takes place well below the ozone number density peak at $\sim$25–30 km, so column ozone changes are small, being generally below 10 Dobson units for extra-polar latitudes (not shown). Two minor features in the ozone response plots are also worth mentioning. First, the broad region of small (less than 5%) negative changes between 40 and 70 km is a response to increased HO$_x$ mixing ratios, which in turn results from increased water vapor (Fig. 12). Second, the $\sim$5% increase at 30–40 km at low latitudes results partly from increased O$_2$ photolysis caused by the ozone decrease in the layer above (“self-healing” effect) and partly from a reduction of catalytic cycling of odd oxygen due to decreases in the NO$_x$ abundance in the region, presumably resulting from increased tropical upwelling.

In response to the SST changes, the water vapor mixing ratio (Fig. 12) increases throughout the model domain, thus explaining most of the water vapor change in the full CO$_2$ doubling experiment C2 (Fig. 7). There is a large increase of up to $\sim$100% in the troposphere (cf., Figs. 3 and 12) and a small, but statistically significant, increase of $\sim$0.3–0.4 ppmv in the middle atmosphere. The uniformity of the water vapor increase in the middle atmosphere suggests an enhanced inflow of water vapor from the troposphere. This is analyzed in detail in section 6b.

\textit{a. Importance of Integration Length}

An important question that arises in analysis of small signals, such as those in Figs. 10, 11, and 12, is how many years of simulation are required to confidently distinguish the signal from the internal variability of the model. This question, however, is not a trivial one to answer and a full investigation of the problem lies outside the scope of this paper. Most previous model studies have relied on 10 year datasets or less to diagnose the middle atmosphere response to CO$_2$ doubling. Scaife et al. (2000) argues from analysis of observations that 10 years are generally sufficient to characterize the mean state of the variable winter
Figure 13. Effect of changes in SSTs on temperature (K, experiments C2-B2) in January for (a) subset $S_1$ and (b) subset $S_2$ of the 30-year dataset. Dark/light shading: 99/90% statistical significance. The data shown represent zonal and monthly mean values averaged over 15 years. Contour intervals are 2 K with the addition of $\pm 0.5$ and $\pm 1$ K contours.

hemispheres. However, we note that detection of the model response to a small perturbation should require longer datasets, since the signal to noise ratio of such a problem is much smaller. Figure 13 shows the temperature response to changes in SSTs in January for the two 15-year subsets ($S_1$ and $S_2$). Features away from the polar winter region that are present in the 30-year dataset (Fig. 10a) are also present in both 15-year subsets, indicating that these features are robust and, hence, are indeed a direct result of processes associated with changes in SSTs. For the winter polar region, however, the diagnosed temperature changes for subsets $S_1$ and $S_2$ are dramatically different. Subset $S_2$ (Fig. 13b) shows a considerable cooling throughout the middle and upper stratosphere and warming in the upper mesosphere, with both signals being statistically significant at the 90% level. Subset $S_1$ (Fig. 13a) shows changes of the opposite sign in the same regions, which are below the 90% significance level in most of the stratosphere and above this level in the mesosphere. The combined 30-year dataset (Fig. 10a) shows a much smaller response which, in addition, is not statistically significant in most of the polar winter region. This implies that 15 years are not enough to capture the models interannual variability in the polar winter region. Also, since the response for the two subsets are indicated to have a high statistical significance (90–99%) in parts of the polar winter region, it appears that the student’s t-test used here may not be an appropriate tool for identifying physical changes at high latitudes. The student’s t-test assumes that the sampled populations (in our case zonally averaged monthly mean temperatures) are independent and normally distributed. It is not obvious that these assumptions are valid, partic-
ularly in the Arctic wintertime. The studies by Yoden et al. (2002) and Taguchi and Yoden (2002) indicate that temperature distributions in the polar regions may be highly skewed or even bimodal.

Figure 14 shows the temperature distributions for the B1, B2 and C2 experiments at three different locations: the polar winter upper stratosphere (left panels), the tropical lower stratosphere (middle panels), and the mid-latitude summer upper mesosphere (right panels). For each experiment and region, the means for both subsets and for the combined 30-year dataset are indicated by the vertical lines and the arrow along the top axes. The polar upper stratosphere is clearly the most variable region of the three, with temperatures ranging over 30–50 K. For the tropical lower stratosphere and the mid-latitude upper mesosphere, the 30-year mean temperatures are well defined and the distributions for the various experiments are in general well separated, with little overlap. For the polar upper stratosphere region, however, the 30-year temperature distributions for the B2 and C2 experiments overlap over several tens of degrees and show close mean values. Consequently, the t-test for the 30-year dataset shows no significant difference between B2 and C2 in this region (Fig. 10a).

Due to the limited sample sizes, it is not straightforward to attribute the shape of the 30-year histograms in Fig. 14 to a certain distribution law. There is, however, no obvious indication that the distributions should be dramatically non-Gaussian in nature, nor can one say that the temperatures in the winter polar region are less normally distributed than those in the other two regions. Figure 14 also illustrates that the two 15-year subsets are characterized by their own mean and variability. In particular the mean temperature in the polar upper stratosphere in experiment C2 (Fig. 14, bottom left) differs substantially between the two subsets, explaining the opposite sign in the model temperature response in this region (Fig. 13).

b. Effects on the Tropopause

The tropopause pressure and temperature were diagnosed by an interpolation scheme based on Reichler et al. (2003), but using the cold point instead of the lapse rate definition. Comparing mean changes using both variants of the diagnostic showed little difference except over the Antarctic during southern winter and spring where the cold point definition is not applicable.

A doubling of CO$_2$ without modified SSTs (experiment B2) has a minor impact on the tropopause altitude, approximated here by the geopotential height, averaged over all months and years of the simulation (Fig. 15a, dashed curve). The tropical tropopause temperature increases by about 0.5 K (Fig. 15b, dashed curve). This change appears to be due primarily to the direct radiative effect
Figure 14. Histograms of latitudinally averaged zonal mean temperature for January at 70°N-90°N, 43 km (left); 15°S-15°N, 21 km (center); and 30°S-60°S, 81 km (right) for \(1\times CO_2\) (experiment B1, top row); \(2\times CO_2\) (experiment B2, middle row); and \(2\times CO_2\) with modified SSTs (experiment C2, bottom row). The dark shading denotes data from the second 15-year subset (subset \(S_2\)); the combined light and dark shading denote the full 30-year dataset. The arrow at the top of each panel denotes the mean of the 30-year dataset; the two thin lines on either side are the means of the respective 15-year subsets.
Figure 15. (a) Tropopause height (km) and (b) tropopause temperature (K) differences induced by the CO$_2$ doubling with (solid curves, experiments C2-B1) and without (dashed curves, experiments B2-B1) taking into account changes in SSTs. Zonal and annual mean values averaged over 30 years are shown. The shading represents the standard error of the difference between the means.

of the CO$_2$ increase. Strong overlapping of the spectral lines in the tropopause region makes it difficult to separate individual contributions of the radiatively active species, which include CO$_2$, water vapor and O$_3$. However, the change in water vapor and ozone near the tropical tropopause in experiment B2 (not shown) is relatively small whereas CO$_2$ acts as a source of both longwave and shortwave heating in the tropical tropopause region (e.g., Gettelman et al. 2004) and provides a positive initial forcing from CO$_2$ doubling (Fig. 4d).

Inclusion of the SST changes (experiment C2) results in an increase in water vapor exceeding 50% in most of the troposphere compared to B2 (cf., Figs. 3 and 12). The warmer sea surface increases the convective available potential energy and hence the convective activity. In this model experiment (C2) the annual and zonal mean tropopause undergoes an increase in altitude of about 700 meters (geopotential height) in the tropics, about 600 meters in the NH and about 400 meters in the SH extratropics (Fig. 15a, solid curve). The asymmetry between the NH and SH originates from the asymmetry in the SST changes between the two hemispheres, with the larger changes occurring in the NH (not shown).

The mean tropical tropopause temperature increases by over 1 K compared to the control experiment (Fig. 15b, solid curve). This is in spite of the fact that
Figure 16. (a) Annual mean residual upwelling difference induced by the CO$_2$ doubling (experiments C2-B1) vs. latitude at 18 km (dash), 20 km (solid), and 22 km (dash-dot). (b) Annual cycle of tropical (30$^\circ$S-30$^\circ$N; negative curves) and extratropical (positive curves) mean temperature, with global mean subtracted, at 50 hPa: model experiment B2 (atmospheric CO$_2$ doubled) is shown by the dashed curves and model experiment C2 (full 2xCO$_2$ experiment) is shown by the solid curves. Zonal mean values averaged over 30 years are shown. The shading represents the standard error of the difference between the means and the standard error of the mean for panels a and b, respectively.

there are concurrent cooling effects. In particular, ozone decreases by about 15% at the tropopause compared to B2 (Fig. 11), and the tropical upwelling associated with the diabatic circulation increases (Fig. 16). It is likely that additional water vapor around the tropopause increases solar heating and is also acting to trap infrared radiation which leads to enhanced warming of the tropopause compared to B2. The water vapor increase in the lower tropical stratosphere is about twice as large as in B2 and amounts to 20% more than in the control experiment B1 (cf., Figs. 3 and 7).

The results on the tropopause height and temperature are consistent with Seidel et al. (2001) regarding the mechanisms controlling the tropopause. Seidel et al. (2001) have shown using radiosonde data that the tropical tropopause height is mainly associated with the temperature of the underlying troposphere, whereas the tropopause temperature is associated with the temperature and pressure of the lower stratosphere.

An interesting feature of the full doubled CO$_2$ experiment (C2) is the layered
water vapor structure in the tropical lower stratosphere seen in the C2-B1 and C2-B2 difference fields (Figs. 7 and 12, respectively). This reflects changes in the annual cycle of tropical tropopause temperatures. During the warm phase of the cycle more water vapor is transported into the stratosphere compared to the B1 and B2 experiments. During the cold phase (northern winter) the additional water vapor is much smaller. So the difference field has a water vapor maximum moving upward from the tropopause starting in late northern summer and dissipating in the upper tropical stratosphere during the course of a year.

There is little difference in the tropical upwelling between B2 and the control experiment B1 (not shown). In contrast, the upwelling in the tropical lower stratosphere increases by over 10% between 16 km and 20 km (geopotential height) in the full 2×CO₂ experiment (C2). Part of this increased upwelling is due to an increase in the height of the tropospheric Hadley circulation, which can be seen at 18 km (Fig. 16a, dashed curve). At the 18 km level there is evidence of a single upwelling maximum near the equator flanked by two regions of descent. A similarly shaped upwelling change is also found at 16 km (not shown) but with a much larger amplitude, suggesting that it is part of the Hadley circulation. At 20 km (Fig. 16a, solid curve) there is a broad increase of upwelling across the tropics, with larger values occurring away from the equator, which appears to be a feature of an enhanced Brewer-Dobson circulation. At 22 km (Fig. 16a, dash-dot curve) the upwelling change is negligible near the equator, but peaks in the subtropics of both hemispheres. This pattern is consistent with increased wave drag outside of the “tropical pipe”, which would result in an upwelling increase maximizing near the edge of the pipe (Plumb and Eluszkiewicz 1999).

The change in the Brewer-Dobson circulation can also be seen in the seasonal evolution of tropical and extratropical temperatures at 50 hPa (Fig. 16b). Compared to B2, in the C2 experiment the tropical mean temperature is colder relative to the global mean on this pressure surface and the extratropical mean temperature is warmer, which indicates an intensification of the Brewer-Dobson circulation. The difference between B2 and B1 (not shown) is much smaller and not statistically significant. The difference between C2 and B2 for both the tropical and extratropical mean temperatures during the NH summer and fall is smaller and has a lower statistical significance than during the NH winter and spring: the standard error bars of the two curves nearly overlap in the NH summer and fall as indicated by the shaded regions in Fig. 16b. The more pronounced temperature difference during the NH winter and spring suggests that there is an intensification of NH wave drag and the associated branch of the Brewer-Dobson circulation. This is consistent with the asymmetry in the
6. Effect of the Change in SSTs

SST changes between the NH and SH mentioned above. An additional indication of an enhanced two-cell diabatic circulation in the lower stratosphere tropics and extratropics can be seen in the annual mean ozone distribution (ozone decreases in the tropical lower stratosphere and increases above the extratropical tropopause, Fig. 11). Intensification of the Brewer-Dobson circulation in response to greenhouse gas increase has also been diagnosed from mass flux analysis (Butchart and Scaife 2001).

c. Planetary Rossby Waves in the Extratropical Stratosphere

A question of obvious importance to the stratospheric circulation and polar temperatures is the extent to which the forcing from extratropical planetary Rossby waves propagating out of the troposphere will change with doubled CO$_2$ and modified SSTs. This dynamical feedback to the radiative changes could in principle aggravate, mitigate, or even reverse the stratospheric cooling expected on radiative grounds. Austin et al. (2003) identified this process as a key uncertainty in future predictions of Arctic ozone, with not even the sign of the changes being clear. Figure 17 shows histograms of the vertical component of the Eliassen-Palm (EP) flux ($F_z$) averaged from 40° to 80° at 100 hPa (∼16 km) for the months when the breakup of the polar vortex occurs. As with the temperature histograms shown in Fig. 14, the combined 30-year dataset is denoted by the total shaded area. The differences in the time mean $F_z$ in the SH for the 30-year datasets (denoted by the arrows) are statistically insignificant (the significance level is below 80%). While the difference between the B1 and C2 experiments in the NH is significant at the 95% level, the relative change is small (less than 5%). Thus, in these experiments, we are unable to detect much of a change in stratospheric planetary wave forcing.

A useful means of highlighting the relationship between stratospheric planetary wave forcing and polar temperatures in the lower stratosphere was proposed by Newman et al. (2001). Figure 18 shows such a result but using the months, pressure levels, and latitude ranges employed in Figs. 4 and 5 of Austin et al. (2003). Overall there is good qualitative agreement between the observations and the 1×CO$_2$ (experiment B1) results, which gives us confidence in the ability of the CMAM to simulate this aspect of the stratospheric circulation. Manzini et al. (2003) illustrated the utility of this diagnostic for separating the radiative and dynamical aspects of stratospheric climate change; radiative changes correspond to a shift in the intercept of the straight line fit with the vertical axis, which we denote $T_{pole}(0)$ and which represents the combined effects of radiation and gravity-wave drag, while changes in large-scale dynamical forcing correspond to changes in the location of the points along this
Figure 17. Histograms of the latitudinally averaged vertical component of the Eliassen-Palm flux (m²s⁻²) at 16 km for January/February/March from 40°N-80°N (left) and September/October/November from 40°S-80°S (right) for 1×CO₂ (experiment B1, top row), 2×CO₂ (experiment B2, middle row), and 2×CO₂ with modified SSTs (experiment C2, bottom row). The dark shading denotes data from the second 15-year subset (subset S₂); the combined light and dark shading denote the full 30-year dataset. The arrow at the top of each panel denotes the mean of the 30-year dataset; the two thin lines on either side are the means of the respective 15-year subsets. \[ F_z \text{ used here is equivalent to } F_z/(a \rho_o) \text{ used by Andrews et al. (1987) in equation 3.5.3, p. 128.} \]

line. Similarly with Manzini et al. (2003), we find the relationship between resolved wave forcing and polar temperatures to be much better defined in the SH than in the NH. Thus we focus on the SH.

If we compare Fig. 18e and Fig. 18f we do not see a noticeable change in \( T_{pole}(0) \), which is consistent with the fact that CO₂ has not changed between these two simulations. However, comparing these 2×CO₂ results to those in Fig. 18d for the 1×CO₂ case, we see a change in \( T_{pole}(0) \) of several degrees. The sign of the temperature change is in agreement with the cooling that occurs in the stratosphere that results from increased CO₂. The robustness of this change
in $T_{pole}(0)$ is in contrast to the high degree of variability in this region of the atmosphere and the fact that our 30-year dataset is probably not long enough to accurately determine the means, as seen by the histograms of $\bar{v'}T'$ and $\bar{T}_{pole}$ shown along the horizontal and vertical axes of Fig. 18. This shows that process-oriented diagnostics such as this wave-drag/temperature relation may provide a more reliable attribution of atmospheric change than individual fields.

7. Summary and Conclusions
The Canadian Middle Atmosphere Model (CMAM) has been used to study the effects of CO$_2$ doubling on the middle atmosphere. The radiative-photochemical impact on the atmosphere has already been studied by Jonsson et al. (2004). In this companion paper we have presented the overall effect of CO$_2$ doubling on the middle atmosphere, with an emphasis on analyzing the impacts produced by changes in the troposphere.

Four different model experiments were performed. In addition to a control run and a doubled CO$_2$ experiment with sea surface conditions (i.e., sea surface temperatures and sea ice distribution, referred to as SSTs for short) appropriate for a doubled CO$_2$ climate, a doubled CO$_2$ experiment without changes in SSTs and an experiment with modified SSTs but with unchanged CO$_2$ were also performed. The latter two experiments, which are physically unrealizable, were performed to investigate the relative impact on the middle atmosphere of radiative-photochemical effects and those effects produced by modified SSTs (and hence a modified tropospheric climate). Our results show that to a first approximation the radiative-photochemical impact and the response to SST changes are

Figure 18. (Next page) Scatter plots of heat flux ($\bar{v'}T'$) at 100 hPa ($\sim$16 km) versus zonal mean temperature ($\bar{T}$) at 48 hPa ($\sim$21 km). Top row: Northern Hemisphere for the three 30-year simulations: a) 1×CO$_2$ (experiment B1), b) 2×CO$_2$ (experiment B2), and c) 2×CO$_2$ with modified SSTs (experiment C2). $\bar{v'}T'$ is for January/February and is averaged from 40° to 80°; $\bar{T}$ is for February/March and is averaged from 60° to the pole. Bottom row: same but for the Southern Hemisphere, where $\bar{v'}T'$ (multiplied by -1) and $\bar{T}$ are for July/August and August/September, respectively. The straight line is the linear best fit through the points. The correlation coefficient ($r$) and the slope of the best-fit line ($b$) are plotted in the top left corner of each panel. Histograms of the distributions of $\bar{v'}T'$ and $\bar{T}$ are shown along the horizontal and vertical axes, respectively. The plus marks denote the observations taken from NCEP assimilations for the years 1970 to 2000; the corresponding correlation coefficient and slope of the best fit line (not drawn) are denoted by the subscript “obs”.

additive and therefore can be analyzed separately.

Analysis of the radiative energy budget has shown that in response to CO₂ doubling the net radiative heating remains largely unchanged in the middle atmosphere below \( \sim 70 \) km, except poleward of \( \sim 50^\circ \) in the winter hemisphere. This reflects the radiative-photochemical nature of this region of the atmosphere. Dynamical effects occur mainly in the upper mesosphere and also over the winter pole in the upper stratosphere and mesosphere, and are mainly related to the SST changes. The initial forcing induced by CO₂ doubling is partially compensated by a change in infrared cooling through an adjustment of the temperature field, and partially by an increase in solar heating due to ozone changes. The ozone radiative feedback occurs through both an increase in solar heating and a decrease in the 9.6 \( \mu \)m band cooling, with the latter providing up to 15% of the total effect. Changes in the water vapor contribution to the radiative balance, which appear to be a dominant component in the troposphere and also important in the lower stratosphere, are negligible above \( \sim 30 \) hPa on a globally averaged basis.

For the case of CO₂ doubling with SST changes taken into account, the troposphere warms by \( \sim 2–4 \) K and the middle atmosphere cools by up to \( \sim 10–12 \) K. There is no significant response near the polar summer mesopause, in accordance with observations over the past few decades (Beig et al. 2003). This occurs since there is positive CO₂ radiative forcing in this region (due to the heat exchange between this cold region and the relatively warm layers below), but the doubling of CO₂ also leads to a strengthening of the summer-to-winter pole circulation in the mesosphere, with stronger upwelling over the summer pole which produces adiabatic cooling and mitigates the positive radiative forcing near the mesopause.

Much of the temperature change in the middle atmosphere can be understood in terms of the radiative-photochemical response. The impact of SST changes on middle atmospheric temperatures are generally localized and smaller in amplitude. The main impacts are: (1) a warmer and higher tropopause during all seasons, (2) cooling just above the tropopause by up to 1–2 K, (3) warming of the middle latitude summer upper mesosphere by up to 4 K in January and by more than 1 K in July, and (4) cell-like structures of heating and cooling (of up to 1–2 K) alternating with height in the tropical and middle latitude upper stratosphere and mesosphere.

The increased height of the tropopause is clearly attributed to SST changes, while the warming of the tropopause results from enhanced radiative heating in the lower stratosphere. The cooling regions just above the tropopause are partly related to the tropopause height shift and, in the tropics (where the cooling
region is broader both vertically and latitudinally), partly related to adiabatic cooling resulting from enhanced upwelling in the tropical branch of the Brewer-Dobson circulation. The latter appears to be due to enhanced Rossby wave drag at low latitudes.

The higher temperatures at middle and high latitudes in the summer upper mesosphere result from decreased adiabatic cooling associated with a slower ascending branch of the mesospheric residual circulation. This change is caused by weakened westerly gravity wave drag in the summer hemisphere which results from enhanced critical level filtering of eastward propagating waves by the strengthened tropospheric westerlies. The cell-like structures of heating and cooling at low latitudes reflect a change in the vertical structure of the semi-annual oscillation (SAO). It is important to note, however, that both the warmer summer mesosphere and the SAO changes appear to be related to changes in the parameterized gravity wave forcing and, hence, depend to some extent on the model’s gravity wave drag scheme. Since the source spectrum for gravity wave parameterizations cannot at present be constrained by observations, the choice of spectrum is somewhat arbitrary. In addition, the gravity wave source was kept effectively constant in our experiments. The robustness of the parameterized gravity-wave feedbacks under climate change is an important issue for future research.

In addition to the changes discussed above, the model predicts substantial changes in the polar regions of the stratosphere in response to changes in SSTs. However, comparison of the temperature response and significance levels for two 15-year subsets of our 30-year dataset has shown that these results appear to be robust only away from the polar winter region. There, the inter-annual variability is too large for 15-year simulations to accurately characterize the model response. It was also shown that the student’s t-test applied at winter high latitudes can yield misleading signals of statistical significance. Further studies are required to bring clarity to this issue. Analysis of planetary Rossby waves in the extratropical stratosphere has shown no noticeable change in upward propagating planetary wave activity and, consequently, no significant thermal effect in the polar winter stratosphere.

In the full 2×CO₂ experiment, the ozone mixing ratio increases by 10–20% between 30 and 70 km, which is a response to lower temperatures as described by Jonsson et al. (2004). As a result of the modified SSTs, ozone also increases in a thin layer around 75 km and decreases near the tropical tropopause. The thin layer in the mesosphere results from increased downward transport of atomic oxygen from higher levels in the model. While the relative change in ozone near 75 km is large, the absolute change is very small. The ozone decrease
near the low latitude tropopause results primarily from the upward shift of the
tropopause, but also reflects an enhanced two-cell diabatic circulation in the
lower stratosphere.

The warming of the lower atmosphere leads to more water vapor in the tro-
posphere. There is also a small but statistically significant water vapor increase
of $\sim$0.3–0.4 ppmv in the stratosphere and lower mesosphere, resulting from the
warmer (and higher) tropical tropopause, and hence less effective freeze drying
of air entering from the troposphere.

This study has several limitations. First, there is no heterogeneous chemistry
and hence no severe polar ozone loss. Thus, changes in polar temperatures are
only indicative of potential chemical ozone loss in the polar lower stratosphere.
This eliminates the ozone radiative feedback that would delay the breakdown of
the polar vortex under conditions of high chlorine loading (Manzini et al. 2003).
Second, by forcing the CMAM with SSTs obtained from a coupled (transient)
simulation with a tropospheric GCM, any feedback on surface climate arising
from stratospheric changes or from interactive ozone is strongly damped. In
order to properly investigate such changes, CMAM would need to be coupled
to a dynamical ocean model. On the other hand, the set-up in the current
study allows a separate attribution of the radiative-photochemical response of
the middle atmosphere to CO$_2$ increases, and the dynamical response to changes
in tropospheric climate. Finally, by running the CMAM under fixed forcings,
and only those associated with CO$_2$ increases, the results do not represent a
quantitative prediction of future climate. Rather, they provide an understanding
of the response of future climate to certain specific forcings, and the statistical
challenges associated with such attribution. Results from these simulations will
be important for attributing the behavior of transient simulations performed
with CMAM or other CCMs under both greenhouse gas and halogen forcings.

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