Three-Dimensional Model Study of the Antarctic Ozone Hole in 2002 and Comparison with 2000

W. FENG AND M. P. CHIPPERFIELD

Institute for Atmospheric Science, School of the Environment, University of Leeds, Leeds, United Kingdom

H. K. ROSCOE

British Antarctic Survey, Cambridge, United Kingdom

J. J. REMEDIOS AND A. M. WATERFALL

EOS, Department of Physics and Astronomy, University of Leicester, Leicester, United Kingdom

G. P. STILLER, N. GLATTHOR, M. HÖPFNER, AND D.-Y. WANG

IMK, Forschungszentrum Karlsruhe, and Universität Karlsruhe, Karlsruhe, Germany

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ABSTRACT

An offline 3D chemical transport model (CTM) has been used to study the evolution of the Antarctic ozone hole during the sudden warming event of 2002 and to compare it with similar simulations for 2000. The CTM has a detailed stratospheric chemistry scheme and was forced by ECMWF and Met Office analyses. Both sets of meteorological analyses permit the CTM to produce a good simulation of the evolution of the 2002 vortex and its breakup, based on O₃ comparisons with Total Ozone Mapping Spectrometer (TOMS) column data, sonde data, and first results from the Environmental Satellite–Michelson Interferometer for Passive Atmospheric Sounding (ENVISAT–MIPAS) instrument. The ozone chemical loss rates in the polar lower stratosphere in September 2002 were generally less than in 2000, because of the smaller average active chlorine, although around the time of the warming, the largest vortex chemical loss rates were similar to those in 2000 (i.e., −2.6 DU day⁻¹ between 12 and 26 km). However, the disturbed vortex of 2002 caused a somewhat larger influence of polar processing on Southern Hemisphere (SH) midlatitudes in September. Overall, the calculations show that the average SH chemical O₃ loss (poleward of 30°S) by September was 20 DU less in 2002 compared with 2000. A significant contribution to the much larger observed polar O₃ column in September 2002 was due to the enhanced descent at the vortex edge and increased horizontal transport, associated with the distorted vortex.

1. Introduction

Since its discovery in the mid-1980s (Farman et al. 1985), the Antarctic ozone hole has been the subject of extensive scientific investigation. Through a large number of observational and theoretical studies, we have a good understanding of the processes that lead to the rapid springtime chemical ozone loss inside the polar vortex (e.g., Solomon 1999; WMO 2003). Numerical modeling studies are able to reproduce the main features of the rapid chemical ozone depletion inside the vortex (e.g., Roscoe et al. 1997). The occurrence of a strong, stable polar vortex with associated cold temperatures and, since the early 1980s, a large chemical loss in spring, was considered a robust, repeatable feature of the stratosphere. However, as discussed in this special issue, the Antarctic ozone hole of 2002 was a significant exception to this pattern. Observations show that the 2002 ozone hole was not only smaller than usual but also split into two on 25 September as a result of a major warming. Although such “sudden stratospheric warmings” are quite common in the Arctic, such a vortex split has not been observed in the Southern Hemisphere (SH; e.g., Simmons et al. 2005; Roscoe et al. 2005). The effect of this sudden warming on polar temperatures is shown in Fig. 1. The minimum temperature in 2002 was around 5 K warmer than 2000 in May–June, similar in July–August, and then again slightly warmer in September. A major warming...
around 25 September 2002 can also be seen in Fig. 1. Such a warming and elongation/split of the polar vortex is expected to lead to very different chemical conditions inside the vortex and a different interaction between the polar latitudes and midlatitudes. The disturbed dynamics of 2002 will also provide a bigger test for the different meteorological analyses and a (so far) unique situation under which to study the chemistry and transport of the SH lower stratosphere (LS).

In this paper, we use the SLIMCAT offline 3D chemical transport model (CTM; Chipperfield 1999) to investigate how well it captures the evolution of the 2002 Antarctic ozone hole and to diagnose the timing and extent of chemical O3 depletion. We compare 2002 with the more typical hole of 2000. We also analyze how ozone loss rates differ in different regions, including the edge region of the vortex. Section 2 describes our 3D model, and section 3 describes the different methods we use to diagnose terms in the ozone budget. Our results are described in section 4, and our conclusions and discussion are presented in section 5.

2. Model

We have used the SLIMCAT offline 3D CTM, which is described in detail by Chipperfield (1999). Horizontal winds and temperatures are specified using meteorological analyses. Vertical advection is calculated from heating rates using the MIDRAD radiation scheme (Shine 1987), and chemical tracers are advected by conservation of second-order moments (Prather 1986). The model has the most important species in the O3, NOy, Cly, Bry, and HOx families along with a CH4 oxidation scheme and long-lived tracers. The model has a detailed gas phase stratospheric chemistry scheme as well as a treatment of heterogeneous chemistry of liquid and solid aerosols (for more information, see Chipperfield 1999). The version used here uses photochemical data from Sander et al. (2000). The model has been widely used in previous studies of stratospheric chemistry (e.g., Chipperfield et al. 1996; Chipperfield and Jones 1999; Chipperfield and Pyle 1998).

In the present study, SLIMCAT was run for 2002 using both 24-hourly U.K. Met Office (UKMO; Swinbank and O’Neill 1994) and 6-hourly T42 European Centre for Medium-Range Weather Forecasts (ECMWF) analyses (see Table 1). SLIMCAT was also run for 2000 forced by 6-hourly ECMWF T42 analyses. In all cases, the model horizontal resolution was 2.8° latitude × 2.8° longitude, and the runs were initialized from the corresponding day of the same SLIMCAT multiannual simulation that started in 1989. The model had 24 isentropic levels between 335 to 2726 K, resulting in a vertical resolution of ~1.5 km in the lower stratosphere.

3. Diagnosing the O3 budget

A change in O3 can be described by the continuity equation

$$\frac{\partial \text{O}_3}{\partial t} = - \nabla \cdot \text{V} \cdot [\text{O}_3] + \text{P} - \text{L},$$

where $\nabla \cdot \text{V} \cdot [\text{O}_3]$ is the O3 flux divergence, which includes horizontal and vertical transport; V is the flow velocity; P is the photochemical production rate; and L is the chemical loss rate. In this study, the chemical/dynamical contributions to the model O3 budget were diagnosed in a number of ways.

a. Overall net chemical change—Method A

The model contains a “passive odd-oxygen” tracer, which is set equal to the model chemical O3 [$=O(3P) + O(1D) + O_3$] field on 1 July and then advected passively without chemistry. At any point and time after 1 July, the difference between this passive O3 and the model’s chemically integrated O3 tracer is the net chemical O3 change in air that has been advected to that point. In the lower stratosphere, this is essentially the net chemical O3 change. This method has been widely used in model polar studies and gives a direct quantification of the chemical O3 loss (e.g., Lefèvre et al. 1998; Sinnhuber et al. 2000).

b. Chemical loss rates—Method B

The loss of O3 in the polar lower stratosphere is dominated by a few key catalytic cycles (see appendix A

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<th>Table 1. The 3D model experiments.</th>
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and, e.g., Millard et al. 2003). In the model runs, the loss caused by each of these cycles was accumulated over a 24-h period (within each fixed box) and then stored. The sum of these loss cycles then gives the instantaneous loss rate at a given point during a day. Summing these daily values from the date when the passive odd-oxygen tracer was reset gives the overall chemical O₃ loss that has occurred at that point (which differs from method A as the O₃ loss is not transported).

c. Dynamical changes—Method C

In the SLIMCAT model, the transport equations are solved by horizontal and vertical advection schemes. The CTM advection and chemistry schemes conserve mass, although every time a new meteorological analysis field is read in (6 or 24 h) the mass of each grid box is adjusted to equal that diagnosed by the current analyses. During this step, the tracer masses are also adjusted to keep the mixing ratio constant. (Details of this and its effect on the model mass budget will be given in a forthcoming paper (M. P. Chipperfield 2004, unpublished manuscript). Here we calculate the change of divergence of tracer flux (e.g., O₃) before and after the horizontal and vertical advection. The dynamical change used in this paper is the sum of the change of flux divergence of ozone accumulated at each time step at each grid point and saved every day.

4. Results

The majority of the ozone loss associated with the rapid springtime depletion generally extends from ~12 to ~26 km (e.g., WMO 2003). Therefore, here we concentrate on the LS (350–662 K, ~12 to ~26 km), where this occurs. First, we examine whether SLIMCAT can reproduce the O₃ column and profile based on the comparison with Total Ozone Mapping Spectrometer (TOMS), sondes, and Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) observations. Although we expect the changes in ozone to be largely synoptic in origin during the 2002 vortex split itself, we also wish to investigate the model’s ability to simulate O₃ over the period May–October where chemistry will play an important role. Then, we will discuss the O₃ differences and the relative roles of chemistry and transport within the model between 2002 and the other more typical year of 2000.

a. Chemical/dynamical evolution in 2002

Figure 2 shows total column ozone observed by the TOMS for selected days in mid-August, September, and mid-October 2002. The Antarctic ozone hole was displaced westward in mid-September, and the total ozone column around Australia of ~450 Dobson units (DU; 1 DU = 2.89 × 10¹⁶ molecules cm⁻²) was larger than normal. On 22 September, the ozone hole became elongated, and it split into two on 25 September. After that time, the hole remnant near South America weakened and vanished, while the hole remnant southeast of Africa maintained its size and intensity for a few more weeks and recentered close to the pole.

The SLIMCAT 3D CTM integrations reproduce the key features of the observed O₃ distribution (Figs. 3 and 4). In particular, the runs forced by ECMWF and UKMO analyses successfully reproduce the general structure of the vortex minimum and extravortex ozone maximum. However, the model forced by ECMWF analyses underestimates the column by about ~25 (inside the vortex) to ~50 DU (outside the vortex). The run forced by UKMO analyses also underestimates the TOMS-observed column but, compared to the ECMWF-forced run, tends to have less O₃ inside the vortex and more in the extravortex maximum.

Recently, first results for ozone profiles from the ENVISAT–MIPAS instrument (Fischer and Oelhaf 1996; Harris 2000) derived at the Institut für Meteorologie und Klimaforschung (IMK) have become available (Glatthor et al. 2005). Using a nonoperational self-standing retrieval algorithm, a self-consistent dataset independent from the European Space Agency (ESA) operational product covering the periods from 18 to 28 September and 11 to 13 October 2002 was generated. A description of the retrieval strategy is given in von Clarmann et al. (2003), while the application to ozone retrieval for the relevant period is described in Glatthor et al. (2005). More details of the MIPAS retrievals are given in appendix B. Figure 5 compares O₃ at 20 km with model run EC02. There is good agreement between the model and observations relating to the single vortex on 18 September and the split vortex on 26 September. On 18 September, the MIPAS data provide a very good coverage of the vortex showing low ozone in the outer vortex and depleted but slightly higher ozone in the core. For 26 September, the MIPAS data are in excellent agreement with the split vortex at this altitude as calculated by the CTM. The data and model also agree well on the filamentary structure between the African remnant of the vortex and the southern part of Africa.

Figure 6 compares MIPAS O₃ profiles with run EC02 at two locations on both 18 and 26 September. On 18 September, both profiles are inside the polar vortex. On 26 September, the profile at 77°S, 41°E is inside, while that at 77°S, 166°E is outside. The model results show the profiles of both the chemically integrated O₃ and the model passive O₃ tracer, which was reset to the model chemical O₃ on 1 July 2002. In the lower stratosphere for the profiles inside the vortex, the effect of the modeled chemical loss is evident (e.g., 2 ppmv loss near 18 km), while for the profile outside the vortex, there is essentially no difference in the profiles (i.e., no chemical loss). Moreover, the modeled chemical loss is very small above 25 km, which confirms our approach to concentrate our column diagnostics on the lower
stratosphere. Below 34 km, the model chemical O$_3$ agrees well with the observed profiles within the estimated uncertainty in stratosphere. Inside, this agreement clearly requires the modeled chemical loss to be reasonable, and, based on these profiles, the model has a realistic balance between transport and chemical loss. However, above 35 km the model underestimates the MIPAS observations by $\sim$1.5 ppmv. Figure 7 is a similar comparison with O$_3$ sonde profiles available from Neumayer (71°S, 352°E) during the sudden warming event (Koenig-Langlo and Marx 1997). On 19 September, Neumayer was inside the vortex and was still inside the vortex on 22 September though the vortex was elongated. Neumayer was outside the vortex on 25 September because of the vortex split. Again, the model reproduces the O$_3$ profiles in the lower stratosphere at this location during this period, including profiles that have been subjected to large chemical loss.

b. Comparison of 2002 with 2000

In this section, we compare the simulations for 2002 with a similar one (initialized by the same multiannual CTM run) for 2000 (run EC00). Figure 8 compares re-
results from run EC00 with TOMS observations on two days in September. For this more typical situation, the model reproduces the main features of the column O$_3$ distribution very well. As in 2002, however, the model forced by ECMWF analyses does underestimate column O$_3$ inside the vortex by $\sim 25$ DU in places and in the collar region by up to 50 DU.

1) CHLORINE ACTIVATION

On 25 September 2002, the polar vortex split into two. This is clearly visible at 450 K (Fig. 9), where there is a strong vortex edge, but the abnormal polar vortex is evident throughout almost the whole stratosphere (not shown). In contrast, in 2000 the stratospheric polar vortex was more typical and stable and essentially covered the Antarctic continent. The distribution of active chlorine (ClO$_x$) follows the vortex location (Fig. 9) and on 25 September 2002, it is elongated over the Antarctic continent. On this day, there are two small and separate areas with temperature below 195 K. Furthermore, the minimum temperature in 2002 (190 K) is warmer than in 2000 (184 K) (Fig. 1).

The temperatures below 195 K before mid-Septem-
ber allow polar stratospheric clouds (PSCs) to transform reservoir chlorine from HCl and ClONO₂ to active species that can destroy O₃ in sunlight (e.g., ClO). Because of the temperature differences between 2000 and 2002, and the sudden warming in 2002, the impact of PSC chemistry should be somewhat different. Observations of PSCs from MIPAS did not reveal any PSC activity from 16 September 2002 onward. We have diagnosed PSC occurrence in the model based on the equilibrium formation of nitric acid trihydrate (NAT). With the ECMWF temperatures, except for the brief possibility of NAT near 430 K on 6 October, the last model day of PSC occurrence was 24 September. However, this assumes that NAT forms at the equilibrium NAT point and depends on the model HNO₃ field, which in turn depends on the modeled sedimentation. In any case, the model shows a large reduction in PSC (NAT) occurrence around 16 September, in accord with the MIPAS observations. Figures 10a,b show the modeled distribution of ClOₓ at 450 K from early May to the end of October for 2000 and 2002. Activation starts about 15 days earlier in 2000 compared to 2002. The year 2000 is characterized by the typical enhanced values of ClOₓ of over 2.7 ppbv, which extend to mid-September. Deactivation then occurs until mid-October. Figures 10c,d show the modeled inorganic chlorine (Clₓ) during the two winters. The maximum Clₓ values in 2000 are larger than in 2002, although Clₓ does in-
crease to 3 ppbv near the pole in late August/September, indicating ongoing descent. Overall, in 2002 the extent of chlorine activation is less due to both less Cl$_2$ and less heterogeneous processing. There are smaller maximum values at high latitudes, and a more rapid deactivation follows the major warming in late September. The latitudinal gradients are also weaker, although, interestingly, the equatorward extent of the activated air (i.e., 0.3 ppbv contour) is similar to 2000 and in both cases reached about 50°S [equivalent latitude (EL)].

2) ACCUMULATED MODELED O$_3$ CHANGE

The CTM’s passive O$_3$ tracer can be used to examine the evolution of polar ozone in the absence of chemical loss. Figure 11 shows the column values for the start and end of September in 2000 and 2002. On 1 September 2000, even without chemical change since 1 July, the passive O$_3$ indicates relatively low ozone with column values around 225 DU near the pole. During September, these values increase slightly, although the minimum is still around 250 DU. This evolution in 2000 is caused by the weak vertical transport associated with the strong, cold vortex in this typical SH winter/spring. In contrast, the passive O$_3$ column inside the vortex on 1 September 2002 is slightly larger than in 2000. Moreover, this column increases significantly during September as the vortex distortion and associated adiabatic warming cause diabatic cooling and stronger descent. On 30 September 2002, the region of O$_3$ column above 375 DU is much greater than in 2000. This variability is analogous to that seen in the Arctic, where the lowest springtime O$_3$ columns associated with a cold, stable vortex are a result of both chemical loss and weak transport (e.g., Chipperfield and Jones 1999).

We now consider the O$_3$ budget for the larger Southern Hemisphere region. Figure 12a shows the accumulated lower-stratospheric modeled ozone change from 1 July for 30°–90°S. In both years, poleward of 30°S, ozone clearly decreases from 1 July, and it generally begins to recover after early October. The average column ozone change was about 40 DU for 2000 until early October but was only 20 DU in 2002.
3) LOWER-STRATOSPHERIC CHEMICAL OZONE LOSS

Based on the methods described in section 3a, we have derived the corresponding chemical ozone loss since 1 July for the same equivalent latitude regions as Fig. 12a. Figure 12b shows the accumulated change in the LS partial column caused by chemistry. The difference between this figure and Fig. 12a (above) is therefore caused by transport processes, which are generally more important at lower latitudes. There is smaller overall chemical depletion poleward of 30°S in 2002 compared to 2000 by about 20 DU in early November.

4) SEPTEMBER CHEMICAL OZONE LOSS RATE

Figure 13 shows the chemical O₃ loss rates as a function of equivalent latitude in September, when most of the rapid polar depletion occurs. In 2000 the chemical loss in the polar region increases during early Septem-
Fig. 7. Comparison of ozonesonde observations from Neumayer (71°S, 352°E) with model run EC02 on 19, 22, and 25 Sep 2002. Data courtesy of AWI.

Fig. 8. Total column ozone (DU) for 10 and 25 Sep 2000 observed by (left) TOMS and (right) modeled by SLIMCAT (run EC00). A tropospheric contribution has been added to the model values assuming an O₃ mixing ratio of 25 ppbv between the bottom model level and the surface.
ber (with increasing insolation) to a maximum loss of over 3.2 DU day\(^{-1}\). This value is very similar to that estimated by, for example, Hofmann et al. (1997). After this time, the loss rate declines as ClO is deactivated. In 2002, the loss rates in early September are generally less than those of 2000 in the polar region. However, during the period just before the warming in late September, O\(_3\) loss rates here reach over 2.6 DU day\(^{-1}\). Moreover, the chemical loss in 2002 extends more equatorward during this period, although there was more overall chemical loss in 2000.

5) EFFECT ON MIDLATITUDES

Figure 13 (above) indicates that the disturbed vortex of 2002 potentially resulted in a larger impact of polar processing on the midlatitudes in September. This is confirmed in Fig. 14 which shows the September-averaged LS O\(_3\) column chemical loss rate (dash-dot line). This loss rate generally increases with latitude with, in 2000, a maximum loss of 2.4 DU day\(^{-1}\) near the vortex edge. In 2002, the smaller vortex loss (∼1.8 DU day\(^{-1}\)) is accompanied by a larger loss by ∼0.2 DU day\(^{-1}\) between 55°S and 35°EL. In 2000, the chemical production rate of O\(_3\) for EL poleward of 65°S is small. However, the disturbed nature of the vortex in 2002, and the exposure of high EL air to stronger sunlight at lower geographical latitudes, resulted in a larger production rate of around 0.2 DU day\(^{-1}\) inside the vortex. This offsets some of the already smaller chemical loss in this year.

Chemical ozone loss in the polar LS stratosphere can be described by a number of catalytic cycles (see appendix A). Diagnosis of the contribution of these cycles to the total chemical change helps indicate the source of the differences in ozone loss. For the CTM experiments, we see that the relative contribution of the ClO + ClO cycle, which is an indicator of polar influence, is greater poleward of 50°S than in 2000 (not shown). This supports the conclusion that in 2002 more significant export of air occurred earlier in the season.

6) CONTRIBUTIONS OF DYNAMICS AND CHEMISTRY TO O\(_3\) CHANGE

To assess the relative importance of dynamical and chemical process, we have analyzed the different contributions to the O\(_3\) change. Figure 14 also summarizes the September-averaged ozone change and its chemical and transport (horizontal and vertical) contributions.
The chemical loss, which is largest in the polar region, has been discussed above. In 2000, the overall change in O₃ poleward of 50°S is dominated by the chemical loss, with a small increase caused by vertical transport (descent) and a larger increase caused by horizontal transport. Horizontal transport also contributes to decrease in midlatitude O₃. In 2002, average net chemical loss at high latitudes is around 1.6 DU day⁻¹ (compared with 2.4 DU day⁻¹ in 2000), and this is partly offset by an increase in the flux from vertical transport (e.g., 0.9 DU day⁻¹ at 75°S compared to 0.45 DU day⁻¹ in 2000). The disturbed nature of the vortex in 2002 has led to a very different diagnosis of the role of horizontal transport at high latitudes. In this year, the horizontal transport plays a much more significant role in causing the net increase in September O₃ poleward of 80°S, clearly related to the sudden warming and vortex elongation.

5. Discussion and conclusions

We have used a 3D offline chemical transport model to study the unusual 2002 Antarctic ozone hole and compare it with similar calculations for 2000. Based on comparisons with O₃ observations, the CTM gives a good simulation of the transport associated with the major warming of late September 2002 when forced with both ECMWF and UKMO analyses. In particular, the model successfully reproduces the split of the ozone hole on 25 September 2002. In this sense, both sets of analyses do well in capturing the unusual meteorology in this region.

The model ozone budget has been diagnosed to separate the effects of chemistry and dynamics. In general, the warmer temperatures of 2002 compared to 2000 lead to smaller average values of active chlorine (ClOₓ), which in turn leads to smaller average values of polar chemical ozone loss. However, the daily, high-latitude partial O₃ column loss rates in late September 2002, when the vortex was disturbed, were similar (−2.6 DU day⁻¹) to the largest loss rates modeled in 2000 (−3.2 DU day⁻¹ in early September). Moreover, the disturbed dynamical conditions in 2002 lead to a slightly larger export of activated air to the southern midlatitudes in September. Overall, despite the observations of a smaller-than-average Antarctic ozone hole, the CTM suggests that there was still considerable chemical depletion.

A significant difference in the model between 2002
and 2000 is associated with the winter/spring transport of ozone. In a typical year, such as 2000, the cold, stable vortex results in only modest transport (descent) of O₃, and in this sense the dynamical conditions aid the occurrence of small winter/spring ozone columns. However, in 2002, winter/spring descent, caused by the disturbed vortex, contributed to an increase in column ozone.

Observations show that the evolution of ozone during the Antarctic winter and spring of 2002 was unusual, and the larger O₃ columns in themselves may indicate less halogen-related chemical loss. However,
this is clearly not caused by any “recovery” of the stratospheric chlorine loading; the expected decrease in this because of the Montreal Protocol (and amendments) will occur on a long (decadal) time scale. Rather, the simulations presented here indicate that the unusually small O$_3$ hole in 2002 was caused by the atypical meteorology. When this meteorology is imposed in an offline CTM, the model can reproduce the ozone variations (as it can during Arctic winters with different meteorology). An important question, which cannot be addressed with our model, is the cause of the unusual meteorology. Both coupled dynamical models, and continued observations will be necessary to determine if 2002 is an extreme event or indicative of a trend in polar meteorology.

In the past, the springtime Antarctic lower stratosphere has been cited as perhaps the simplest region to study in order to observe recovery, that is, the decreasing influence of halogens on O$_3$. The meteorology in 2002 has now shown that the stable vortex conditions cannot be assumed and halogen-induced chemical loss cannot necessarily be easily inferred from O$_3$ observations alone. As in the Arctic, correction may need to be made for the varying meteorological factors and seasonal transport. Overall this will complicate the search for the signs of recovery if such events were to recur.

Overall, the O$_3$ budget of the 2002 SH high-latitude lower stratosphere can be summarized by significant net polar chemical loss, but it was less than in normal
years, partially offset by a greater transport increase than normal, and mixed more efficiently to the midlatitudes.

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APPENDIX A

Catalytic O₃ Loss Cycles

The principal catalytic cycles for polar O₃ loss are as follows:

\[
\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \quad \text{(Cycle 1)}
\]

\[
\text{Cl}_2\text{O}_2 + \text{hv} \rightarrow \text{Cl} + \text{ClOO}
\]

\[
\text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M}
\]

\[
2 \times (\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2) \quad \text{net: } 2\text{O}_3 \rightarrow 3\text{O}_2
\]

\[
\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2 \quad \text{(Cycle 2)}
\]

\[
(\text{or BrO} + \text{ClO} \rightarrow \text{BrCl} + \text{O}_2)
\]

\[
\text{BrCl} + \text{hv} \rightarrow \text{Br} + \text{Cl}
\]

\[
\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2
\]

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\]

\[
\text{net: } 2\text{O}_3 \rightarrow 3\text{O}_2
\]

This cycle can be initiated by either reaction (2a) or reaction (2b).

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \quad \text{(Cycle 3)}
\]

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2
\]

\[
\text{net: } 2\text{O}_3 \rightarrow 3\text{O}_2
\]

\[
\text{ClO} + \text{HO}_2 \rightarrow \text{HClO} + \text{O}_2 \quad \text{(Cycle 4)}
\]

\[
\text{HClO} + \text{hv} \rightarrow \text{OH} + \text{Cl}
\]

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\]

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2
\]

\[
\text{net: } 2\text{O}_3 \rightarrow 3\text{O}_2
\]

The other cycles that play a minor role in Antarctic ozone depletion are not described here.

APPENDIX B

MIPAS Retrievals

This section gives details of the IMK retrievals of ozone from MIPAS. Ozone profiles in the altitude range 10–50 km were retrieved with a vertical resolution of 3–4 km and a total error (including measurement noise as well as all relevant further error sources) of up to 13%. The dominating error source below 17 km and above 25 km altitude is the uncertainty of spectroscopic data and, thus, is systematic. Between 17 and 25 km, the random error caused by measurement noise and uncertainties caused by other unknown parameters of random nature contribute equally to the total error budget. The dataset covers the polar region completely with a horizontal spacing of ~500 km along orbit and provides daytime (around 10:00 local time) and nighttime (around 22:00 local time) observations. Preliminary validation of the dataset was performed by comparison to collocated Upper Atmosphere Research Satellite/Halogen Occultation Experiment (UARS/HALOE) as well as Odin/SMR data (D.-Y. Wang et al. 2003, personal communication). Wang et al. found that, despite significant mismatches in time caused by the different observation geometries, MIPAS and HALOE agreed on global average within 0.4 ppmv in the altitude range from 10 to 50 km, with rms deviations of less than 1 ppmv. MIPAS and Odin/sub-millimeter radiometer (SMR) ozone data produced by the Odin processor at Chalmers University of Technology from the signature at 501 GHz compare equally well with global mean differences of less than 0.3 ppmv below 30-km altitude and less than 0.5 ppmv for the altitude range 10–70 km.

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