Chapter 3

Polar Stratospheric Ozone

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EXECUTIVE SUMMARY

Springtime Antarctic ozone depletion remains very large and is essentially unchanged since the early 1990s. The minimum column abundance in 2001 was ~100 DU (Dobson unit), similar to the minimum values in the last decade. The processes are well understood.

Certain estimates of the strength of the ozone hole, *e.g.*, the area enclosed by the 220 DU contour, show interannual variability, so that it is not yet possible to say that the ozone hole has reached its maximum. Much of the variability appears to be associated with processes at the vortex collar and is consistent with the almost constant halogen loading and meteorological variability.

The degree of chemical loss of ozone for all Arctic winters during the last decade is now reasonably well documented. The accuracy of state-of-the-art approaches to quantify chemical ozone loss from ozone observations is better than 20%.

The Arctic winter/spring ozone column continues to be variable, reflecting the variable meteorology of the Northern Hemisphere stratosphere. Lower column ozone was present during the cold winter of 1999/2000 than in the warmer, more disturbed winters 1998/1999 and 2000/2001. The variability arises from natural variability and a number of forcing factors. It is not possible to isolate the importance of these factors just from observations; model studies are needed to do this. The Arctic oscillation can be used as an index to describe variability, but not causality.

There was very large local ozone depletion in the Arctic vortex in 1999/2000 reaching 70% by early April in a narrow region around 20 km. Integrated column losses were greater than 80 DU. The winter of 1999/2000 was characterized by persistent low temperatures and a strong vortex. In contrast, in the warmer more disturbed polar vortex of 1998/1999 the estimated loss is very small. These observations are consistent with our expectation that Arctic ozone losses are expected to be variable and largest in cold stratospheric winters.

Satellite and radiosonde observations show that the springtime polar lower stratospheres continue to cool. Since 1979 there has been a trend of the order of -2K/decade at 70 degrees latitude. However, due to large springtime variability, particularly in the Arctic, the magnitude of this cooling remains uncertain. There has also been a statistically significant annually-averaged lower stratospheric cooling at both poles.

Modeling studies now demonstrate that the springtime cooling in the Arctic lower stratosphere over the 1980-2000 period is, in part, due to stratospheric ozone depletion, but the degree of attribution is hindered by the large dynamical variability in this region. In Antarctica modeling studies re-affirm that ozone loss is the major cause of the springtime cooling. They also indicate that well-mixed greenhouse gas (WMGHG) and stratospheric water vapor increases are likely contributors to the annually-averaged cooling. However, due to climate variability in the models, longer integrations are needed for attribution.

Synoptic and mesoscale motions (baroclinic and gravity waves) can lead directly to, and enhance, PSC formation in both hemispheres. For the first time, operational meteorological analyses have been demonstrated to contain credible information about the gravity wave field in high latitudes.

ClOOCl, the key intermediate in chlorine-catalyzed ozone loss in the perturbed polar regions, has been measured for the first time in the Arctic winter polar vortex. These observations confirm the role of this species in ozone depletion, and the observed abundances agree well with inferred values that have appeared in previous assessments.

New studies indicate that the photochemical balance between ClO and ClOOCl is well understood during the winter, using a termolecular rate constant for ClO+ClO+M $\rightarrow$ ClOOCl +M that is up to 25% larger than is currently recommended and absorption cross sections for ClOOCl as currently recommended.

Measurements of the inorganic chlorine species and the organic source compounds demonstrate that the budget of inorganic chlorine in the polar regions is balanced to within the uncertainties of the measurements, insofar as our understanding of the photochemical balance between ClO and ClOOCl is fundamentally correct.

Modeling studies of the latitudinal, seasonal, and diurnal variations in BrO column abundances agree well with observations from eleven ground sites, indicating that the processes that govern ozone loss due to bromine in the polar regions are well understood. There are some minor discrepancies between observations of BrO and the expected photochemical behavior, suggesting that there may be a small abundance of an unknown species or a small error in a rate constant. However, this result is largely inconsequential for assessing the role of bromine in polar ozone loss.

Observations of BrO in the winter Arctic vortex by *in situ* and remote detection techniques are in broad agreement and consistent with a total bromine budget of ~20 +/- 4 parts per trillion. This result now allows for more accurate assessment of the contribution of bromine to polar ozone loss. At present, the fractional contribution of bromine to total ozone loss ranges from between 30 and 60%, depending on temperature and abundances of ClO. Considering the observed leveling off of abundances of sources of chlorine (reported in Chapter 1), the role of bromine in polar ozone loss will continue to increase relative to that of chlorine until the current upward trends of the bromine source gases reverse.

New laboratory and field studies have led to refinements in the recommendations for the rate constants of several key reactions that couple the photochemistry of HO_x and NO_x (species that are largely controlled by natural processes) and to the discovery of a new process (near-IR photolysis of HNO_4). Together with new observations of HO_x, NO_x, and ozone in late spring and summer, these studies have demonstrated that our understanding of the photochemistry of HO_x and NO_x in the lower stratosphere is fundamentally sound.

Removal of nitrogen compounds (denitrification) has been observed to occur in the Arctic lower stratosphere in several cold winters. Denitrification of up to 70% of the total reactive nitrogen was observed at some levels of the lower stratosphere in winter 1999/2000. Our understanding of what causes denitrification has improved considerably. It is now clear that sedimentation of large nitric acid hydrate particles can account for observed Arctic denitrification, although the mechanism of formation of the sedimenting particles remains uncertain. Sedimentation of ice containing dissolved nitric acid, which has been the preferred mechanism in stratospheric models, is not the dominant mechanism in the Arctic.

Observations and modeling results show that Arctic denitrification can increase lower stratospheric ozone loss by as much as 30% at a given level. Model calculations suggest that the magnitude and vertical extent of denitrification could increase considerably in a future colder Arctic stratosphere, leading to increased ozone loss over a broader altitude range. The denitrification mechanism is not well represented in current global models, which currently limits the ability of the models to reproduce the large ozone losses observed in cold Arctic winters and to reliably predict future ozone losses in the Arctic.

The chemical composition of liquid and solid polar stratospheric cloud particles has been measured directly for the first time. Measured compositions are in agreement with model calculations for liquid particles and nitric acid trihydrate, which have been used in stratospheric models for many years. These measurements give confidence in the microphysical models that are central to simulations of polar ozone loss.

Significant chemical loss of ozone (~0.5 ppmv) in the lower stratosphere during January has been observed in several cold Arctic winters. The observations indicate that the loss occurred exclusively during periods when the air masses are exposed to sunlight. These January ozone losses cannot be fully explained with our current understanding of the photochemistry. For cold Arctic winters the ozone loss during January contributes about 25% to the overall loss of ozone over the winter.

Coupled chemistry-climate simulations generally agree with past trends in total ozone, particularly over the Antarctic. Discrepancies with observations can, in some cases, be large and stem in particular from modal temperature biases and transport errors. These errors can be reduced with the use of higher spatial resolution and improved representations of sub-grid scale processes.

It is now possible to estimate the timing of the start of ozone recovery from several coupled models. For the Arctic, this could occur within the timeframe 2004-2019 and for the Antarctic 2001-2008. These dates are based on just three models and subject to large error. However, each model is consistent in showing a later start to recovery in the Arctic, which occurs several years after the peak in halogen amount in each model. This indicates that increases in well-mixed greenhouse gases have delayed the start of ozone recovery in the models. Interannual variability is also very large in the Arctic, so that unambiguous detection of ozone recovery may not occur there before 2030.

Few 3-D models have been run beyond 2050. These suggest that full Antarctic ozone recovery (to 1980 levels) may be expected by 2045-2055. In the Arctic, the model ozone changes are much smaller than in the Arctic and, once ozone recovery begins, the model results suggest that full ozone recovery may occur earlier, possibly as early as 2030. Hence, it is plausible that, by the time of unambiguous detection of the start of ozone recovery, Arctic ozone may have already fully recovered. However, some of the models do not include particle sedimentation that could delay the full recovery of Arctic ozone beyond 2030.

0 INTRODUCTION

This chapter provides an update on our understanding of changes in polar ozone, and the polar vortex, in the recent past and considers possible future developments. It builds on earlier assessments, concentrating mainly, but not exclusively, on work reported since the last assessment report (World Meteorological Organization (WMO), 1999).

The last assessment reported that the Antarctic ozone hole continued unabated, with essentially near-complete destruction of ozone in the low stratosphere, and that the factors controlling the depletion - meteorological pre-conditioning, halogen activation, ozone depletion in sunlight - were well understood. In the Arctic, substantial ozone losses were reported in several winters during the 1990s, depending on the meteorological conditions. The report highlighted the vulnerability of the Arctic to large ozone losses in a cold winter while chlorine abundances remain high during the next decade or so. Less chemical loss was to be expected in the Arctic in winters with a warm, disturbed vortex. Difficulties with the precise quantification of Arctic ozone loss were indicated. The last assessment highlighted specific uncertainty issues surrounding the understanding of the different types of polar stratospheric clouds, and the process of denitrification, which can limit our ability to model present and future polar ozone loss.

The coupling between atmospheric chemistry and climate has been recognized increasingly in recent assessments. In WMO (1999) a late winter/springtime cooling in the polar lower stratospheric temperatures of ~3-4 K/decade was noted (although with the large dynamical variability in that region the statistical significance of the trend was not high) and the role of ozone, water vapor and the well-mixed greenhouse gases was explored. 3-D coupled chemistry-climate models were used for the first time to look at the possible recovery of the ozone layer; these models all indicated a delay in recovery beyond the time of the peak in stratospheric halogen abundance.

Since the last assessment there has been considerable progress in basic research that we report below. Satellite data sets on ozone and temperature have been further extended. In addition, scientific impetus has been provided by several major field campaigns to study the Arctic stratosphere. Results from the National Aeronautics and Space Administration's Photochemistry of Ozone Loss in the Arctic Region in Summer (NASA's POLARIS), aimed at

understanding the summer polar stratosphere, the European Union's (EU's) THESEO, a polar and middle latitude campaign, and the joint NASA/EU Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment-THESEO (SOLVE-THESEO 2000) are reported here. These campaigns produced new data to address some of the uncertainties remaining after the last assessment.

Section 3.1 updates polar ozone measurements in both Antarctica and the Arctic, concentrating on the winter and spring seasons when the largest ozone depletion is observed. As well as considering the total ozone columns, updated information on various possible indicators of ozone recovery, suggested in the last assessment, are presented briefly. The updated polar temperature trends are also presented here.

Section 3.2 reviews our understanding of the relevant physical and chemical processes controlling the polar vortex and its composition. The Arctic field campaigns have provided new data on a disturbed winter with considerable exchange between polar and middle latitudes (1998/1999) and the cold polar winter of 1999/2000, which led to large local ozone depletion. Many new complementary constituent measurements provide an important constraint on chemical loss processes. Important new measurements of particles were also made in the winter polar stratosphere, leading to advances in our understanding of particle composition and denitrification. Improved understanding of the dynamics in and around the polar vortex has also been developed.

Section 3.3 looks in detail at our quantitative understanding of polar ozone loss. In earlier assessments it was recorded that models often fail to quantify correctly the observed ozone loss. A variety of methods to derive ozone loss from measurements are reviewed in this section. Estimated losses in recent Arctic and Antarctic winters are considered and compared with each other and with model estimates.

In WMO 1999, it was recognized that the future development of the ozone layer does not depend just on changes in stratospheric halogen loading but also, very importantly, on a number of other factors connecting chemistry and climate. These factors are discussed in Section 3.4. Temperature changes are particularly important since polar heterogeneous chemistry is strongly temperature dependent and, furthermore, temperature changes are related to the strength of the polar vortex, descent within the vortex, and mixing with lower latitudes. The attribution of the trends in polar stratospheric temperatures, presented in Section 3.1, is discussed and the role of

changes in well-mixed greenhouse gases, in ozone, water vapor and aerosol particles are reviewed. Future stratospheric temperature changes are discussed.

Finally, in Section 3.5, possible future states of the polar stratosphere are explored in sensitivity calculations using coupled chemistry/climate models. Results from these models were reported for the first time in an assessment in WMO 1999, and the models are still being developed. An extensive review of the present uncertainties in chemistry/climate models is presented here followed by some examples of sensitivity calculations to consider the polar stratosphere during the next 50 years.

1 OBSERVATIONS AND TRENDS OF OZONE AND TEMPERATURE IN THE POLAR STRATOSPHERE

1.1 Measurements in the Antarctic/Arctic

In this section, we update information on instruments that measure ozone and other species that are pertinent to polar ozone issues. We briefly review the status of a variety of ozone and related measurements for the Antarctic and Arctic. Total ozone observations and ozonesondes have been extensively discussed in previous reports, and are further reviewed in Chapter 4 of this assessment.

Earth Probe (EP) Total Ozone Mapping Spectrometer (TOMS): Data from the TOMS instrument have been extensively used to track Arctic and Antarctic ozone changes. The TOMS data are discussed in Chapter 4's Section 4.2.2.2. The EP/TOMS operational processing configuration has recently been changed in order to apply a correction to a cross-track bias error that has grown since 2000. While 2001 data are included herein, they are of slightly greater uncertainty (see discussion in the Earth Probes TOMS description in Section 4.2.2.2).

Microwave Limb Sounder (MLS): The MLS observations started in September 1991 with the launch of the Upper Atmosphere Research Satellite (UARS). It gives column and profile data on ozone, ClO, and HNO_3. Recently, the satellite and instrument have experienced problems and the instrument is only turned on when there are situations of particular interest. In particular, MLS was taken out of stand-by mode on 31 January 2000 and was operated during the 2-13 February and 27-29 March periods in conjunction with the SOLVE-THESEO 2000 campaign (Santee *et al.*, 2000).

Halogen Occultation Experiment (HALOE): The HALOE observations also started in September 1991 with the launch of UARS. HALOE is a solar occultation instrument that makes measurements in the IR at both sunset and sunrise. HALOE measurements are used to retrieve profiles of O_3, HF, HCl, CH_4, H_2O, NO, NO_2, and aerosol extinction. The HALOE occultation latitudes are variable over the course of the northern winter, but do not reach the high northern latitudes. During the winter of 1999-2000, the maximum latitude sampled by HALOE was approximately 63˚N in mid-March. HALOE typically has difficulty sampling the polar vortex during mid-winter, but does sample the vortex edge region in the fall (Pierce *et al.*, 2001).

GOME: The Global Ozone Monitoring Experiment (GOME) instrument was launched in 1995 aboard the second European Remote Sensing (ERS-2) satellite. It measures column ozone, NO_2, BrO and OClO, and O_3 profiles. Details on the GOME instrument can be found in Burrows *et al.* (1999). The GOME data have been subject to validation exercises (Hansen *et al.*, 1999; Hoogen *et al.*, 1999; Corlett and Monks., 2001; Ionov *et al.* ,2001; Piters *et al.* ,1999; Rathman *et al.*, 1997).

The Polar Ozone and Aerosol Measurement (POAM) is a solar occultation instrument that provides ozone, water vapor, NO_2, and aerosol extinction profiles in the polar regions. POAM II was launched in 1993 aboard the French Satellite Pour l'Observation de la Terre (SPOT)-3 satellite. These measurements were interrupted by the failure of the SPOT-3 satellite in November 1996. POAM III was subsequently launched on the French SPOT-4 satellite in March 1998 and is currently operational.

Intercomparisons between POAM III and other instruments have been published by Lucke *at al.* (1999); Lumpe *et al.* (2002); Randall *et al.* (2002). Results from POAM III include studies on dehydration (Nedoluha *et al.*, 2000); ozone loss (Randall *et al.*, 2002; Hoppel *et al.*, 2002); and PSCs (Bevilacqua *et al.*, 2002).

The Improved Limb Atmospheric Spectrometer (ILAS) is a satellite instrument that uses solar occultation technique (Sasano *et al.*, 1999; Nakajima *et al.*, 2002). ILAS was launched onboard the ADvanced Earth Observing Satellite (ADEOS) on 17 August 1996. ILAS made measurements over high latitude regions from 57˚N to 71˚N and from 64˚S to 88˚S from late October 1996 until late June 1997.

ILAS consists of an infrared spectrometer that covers the wavelength region from about 6 to 12 micron. ILAS made measurements of vertical profiles of O_3, HNO_3, NO_2, N_2O, methane

(CH_4), and H_2O from the infrared spectrometer as well as vertical profiles of aerosol extinction coefficient at 780 nm from the visible spectrometer. Ozone data are validated by correlative and coincident measurements from several instrumental techniques (Sugita *et al.*, 2002). Nitric acid, NO_2, and H_2O data have also been validated (Koike *et al.*, 2000; Kanzawa *et al.*, 2002; Irie *et al.*, 2002).

1.2 Polar Ozone and Temperature Trends

1.2.1 Polar Ozone Trends

Ozone is primarily produced in the mid-latitudes and tropics by photo dissociation of oxygen by hard UV-radiation (below 242 nm), and is transported towards the poles by the Brewer-Dobson circulation. An annual cycle in ozone results, shown by the climatological values in Figure 1.2-1. Because of the stronger Brewer-Dobson circulation in the Northern Hemisphere (NH), the Arctic is both warmer and has larger column ozone amounts than the Antarctic. In the Northern Hemisphere there is usually a maximum in the column in late winter/early spring. At South Pole, there is less annual variation (larger annual variations are expected at the vortex edge). In recent years, the annual cycle has been modified by polar ozone depletion, most obviously in the Southern Hemisphere.

Figure 1.2.1 also shows recent year-round ozone measurements from the Arctic Ny Ålesund station (78.9˚N, 11.9˚E) and the South Pole station, updating polar observations since the last assessment. The Antarctic observations in the last few years continue to show the extremely low spring ozone values that have characterized the ozone hole during the 1990s. The low Antarctic values begin with the chemical ozone losses during August and September and end upon the break-up of the vortex in November or December. During the summer, ozone is destroyed photochemically, especially at the poles during continuous sunlight conditions (Brühl *et al.*, 1998), and the climatological seasonal minimum is reached in autumn.

In the Arctic, the March-April ozone maximum is occasionally reduced below the climatology in some years (*e.g.*, in 1997, the magenta triangles) because of severe chemical ozone loss and reductions in ozone transport (Andersen and Knudsen, 2002). In these low ozone years, the column ozone rapidly increases with the break-up of the vortex (*e.g.*, early April 1997). Of the most recent winters, 1999/2000 also has somewhat lower ozone columns than the

climatology, to be discussed later. Extremely low Ny Ålesund column ozone values at the beginning of 1996 (Figure 1.2-1 gold triangles) can partially be explained by the early onset of the ozone depletion that year (see Section 3.2). The lowest 1996 values occur in an 'ozone minihole' event (Weber *et al.*, 2002) (see Section 2.1.2). A complicating factor in the upper panel in Figure 1.2-1 is that occasionally Ny Ålesund is outside the vortex, as is evident from the large variations on a broad range of spatial and temporal scales.

Extremely high Ny Ålesund column ozone values in December 1998 (Figure 1.2-1 black diamonds) and February 2001 (red circles) were caused by sudden warmings. The warmings in these years also result in high temperatures, thereby preventing the formation of polar stratospheric clouds.

The largest ozone depletion occurs in the polar vortices during springtime. Figure 1.2-2 shows the springtime ozone values in the Arctic and Antarctic (63˚ to 90˚) since 1970 (updated from Newman *et al.*, 1997). The Arctic column ozone averages were extremely low during the mid-1990s, but have been relatively high in 4 of the last 5 winters. As noted in the previous paragraph and as is apparent in Figure 1.2-1, these higher ozone values are associated with stratospheric sudden warmings. The downward secular ozone trend apparent through 1997 and its reversal over the last few years can be associated with a long-term variation of stratospheric warmings.

Figure 1.2-2 also shows that the Antarctic ozone hole continues to display the low values over the last 4 years that were apparent during the early and mid-1990s. The notably higher value in October 2000 resulted from greater dynamical activity, as is also apparent in Figure 1.2-1.

The polar column ozone averages of Figure 1.2-2 in the 63˚ to 90˚ region generally coincide with the polar vortices. However, in the NH the vortex is usually smaller and the 63˚ to 90˚ region may contain air outside the vortex. The absolute minimum in the NH occurred in 1997, when the vortex was cold, very large and pole-centered. However, the column chemical ozone loss in the vortex was probably much larger in 1995, 1996, and 2000 (see Section 3.2). However, Andersen and Knudsen (2002) have argued that about 75% of the 63˚ to 90˚N depletion from 1992-2000 relative to the 1979-1982 average is due to ozone depletion inside the vortex, so the plot does give quite a good indication of the Arctic vortex depletion.

The two previous figures have shown recent ozone observations. We now turn attention to the trends derived from these observations. Large total column ozone trends have been seen in both the Arctic and Antarctic polar vortices during the spring (Figure 1.2-3). To obtain these trends with better correlation with the polar vortices, a potential vorticity coordinate (equivalent latitude) remapping technique was applied to a trend analysis of homogenized satellite data from TOMS and GOME (Bodeker *et al.,* 2001). In this coordinate the center of the vortices are at about 90˚ and the edges at 60˚ to 75˚ (as shown). After applying a regression model including trends and variability (seasonal cycle, QBO, solar cycle, volcanic effects, ENSO) to the data from 1978 to 1998, statistically significant linear trends were obtained.

The largest Arctic negative trend (1.93 ± 0.40 %yr^{-1}) is observed in March, while the largest Antarctic negative trend (2.95 ± 0.40 %yr^{-1}) is observed in October. In the Arctic vortex the 1978-2000 trend has almost doubled compared to the 1978-1991 period (1.05 ± 0.96% yr^{-1}) due to severe vortex depletions in the 1990s (Section 3.2). In the Antarctic vortex trends have weakened due to saturation of the ozone losses, but the total depletion over the whole period has in fact increased. Figure 1.2-3 shows the trends when 1999 and 2000 data are added, which results in slightly smaller negative trends than previously in the Antarctic spring column ozone. In the Arctic adding the exceptionally warm winter of 1998/1999, when no significant ozone depletion in the vortex occurred, leads to a substantial reduction of the downward trends. Figure 1.2-3 shows steep gradients in the trends across the edge of the vortex. It also reveals statistically significant negative ozone trends in May, June, and July just inside the Antarctic vortex, which were not found in previous trend analyses, but confirms earlier findings (Roscoe *et al.,* 1997; Lee *et al.,* 2001) (see Section 3.7.2).

As the ozone loss mainly occurs in the 12- to 20-km layer, the partial column ozone from 12 to 20 km provides a good representation of the long term decrease of the stratospheric ozone in Antarctica and could be used as an indicator of ozone recovery (see WMO, 1999). Figure 1.2-4 gives monthly averaged partial column ozone in September, October, and November based on the ozone sonde observation at Syowa (1968-2001). The partial column ozone has decreased considerably from the early 1970s (~80% in September, ~85% in October, ~80% in November). The October partial column has not shown appreciable change since 1992. On the other hand, the September and November partial columns continue to show small reductions during the 1990s. The averaged partial column ozone over the three months (September to November) has

also shown decreases during the 1990s, with relatively smaller interannual variability. Because Syowa is located near the vortex edge region, these September and November ozone reductions during the 1990s may be related to cooling near the vortex collar.

Spatially averaged characteristics of the Antarctic ozone hole from 1979 to 2000 based on the total column ozone observed by satellites (TOMS series and TOVS for 1995) are shown in Figure 1.2-5. These parameters include the maximum area, the minimum total column ozone, the ozone mass deficiency, and the date of the ozone hole's disappearance. The maximum area of the ozone hole increased rapidly during the 1980s and gradually during the 1990s, with year-to-year variations, and reached the maximum in 2000. The minimum total ozone, which usually appears in late September or in early October, has been approximately 100 DU since 1993 (Figure 1.2-5) after the considerable decrease during the 1980s and the early 1990s. The ozone mass deficiency in the ozone hole (O_3 MD) is defined as the ozone mass deficiency from 300 DU in the sunlit area poleward of 60˚S averaged for 105 days (1 September – 15 December). O_3 MD varied in concert with the Antarctic ozone hole area and was at the highest level ever in 2000. The date of the disappearance of the Antarctic ozone hole (disappearance of the total ozone values below 220 DU), has generally been occurring later in the season. As a whole, observations show that the Antarctic ozone hole has been slightly larger in the last few years in comparison to the mid 1990s. These observational results could be explained by ozone decreases near the vortex edge (*e.g.*, Bodeker *et al.*, 2001, 2002; Lee *et al.*, 2001). Although the size of the Antarctic polar vortex has not increased, it has been stronger as shown in Figure 1.2-6. There has been a tendency towards a cooling of the vortex due to ozone depletion (the temperature trends are discussed immediately below) and the polar vortex has been more persistent with some interannual variability. These conditions could result in more extensive PSCs in the sunlit vortex edge, and larger chemical depletion of ozone. This would expand the area of the hole, and delay its disappearance.

1.2.2 POLAR TEMPERATURE TRENDS

There is substantial observational data on the polar stratosphere available from ~1979, including radiosonde and satellite measurements, and analyses of various types (Ramaswamy *et al.*, 2001). Figure 1.2-7 illustrates the time series of temperatures at 70˚N (March) and 70˚S (November) from National Center for Environmental Protection (NCEP) reanalyses and CPC

analyses (for descriptions, see WMO, 1999, Chapter 5). There are large interannual variations manifest in both hemispheres which generally complicates the determination of statistically significant trends.

The Microwave Sounding Unit channel-4 (MSU-4) data and the Stratospheric Sounding Unit (SSU) derived temperature trends (1979-1998) for 70˚N and 70˚S are shown in Table 4.1 (see also Figure 1.2-8). These are an update to the 1979-1994 trends presented in Ramaswamy *et al.* (2001). The 70˚ latitude is chosen for the comparisons as this is the highest latitude for which SSU trend data is available. Both MSU-4 and SSU-15X signals originate from a range in altitude in the stratosphere and do not conform to one particular height. The SSU peak signal corresponds to a pressure of roughly 50 hPa and shows a statistically significant (at the 2σ level) cooling of nearly 3K/decade at 70˚N in MAM and 70˚S in SON, and approximately 1.2K/decade for the annual average temperature change at both poles. The instrument also shows cooling significant at the 1σ level for most other seasons. The MSU-4 data (peak signal from approximately 100 hPa) also shows a significant cooling during the spring in both hemispheres (-1.8 K/decade at 70˚N and –1.1 K/decade at 70°S) and at both poles. These MSU-4 trends are roughly half the magnitude of the SSU trend. The observed satellite trends for this period are one of cooling in all seasons at both 70˚N and 70˚S.

It should be noted that the magnitude and statistical significance of the trends in both regions are dependent on the end year considered. This is more crucial for the Arctic, especially during winter/spring when the time series reveals large interannual variations in temperatures (see Figure In 1.2-8; also Labitzke and Van Loon, 1995). The trend sensitivity can be appreciated by comparing the latest (1979-1998) MSU trend at 70˚N (March, as shown in Figure 1.2-8) with the corresponding MSU trends shown in WMO (1995) (Figure 8.11 for the period 1979-1991).

Comparing the satellite 1979-2000 annual-mean trends with those obtained for the 1979-1994 period (WMO, 1999), there is now a statistically significant cooling at the 95% confidence level in the mid-to-high southern latitudes (Ramaswamy *et al.,* 2002a). The northern midlatitudes continue to exhibit a statistically significant cooling trend (see WMO, 1999) while the higher latitudes (Arctic region) now have a cooling trend significant at the 90% confidence level. As in the satellite data, the 1979-2000 sonde trends yield a annually averaged cooling trend in the northern polar region. The sonde trend is somewhat smaller than the satellite trend

(see Table 4.1), although this may be partially due to the time period for the trend analysis being longer in the sonde data (note that 3 of the last 4 years have been relatively warmer, see Figure 1.2-7). The CPC analysis at 50 hPa also shows a cooling at both poles, consistent with the satellite data and sonde data.

2 BASIC POLAR STRATOSPHERIC PROCESSES

2.1 Transport and Dynamics

This section discusses the structure and dynamics of the polar stratosphere, including trace gas transport. Section 2.1.1 gives a brief overview of the mean vortex structure, providing a context for the later assessment. Section 2.1.2 assesses recent studies of the dynamics and structure, including variability and trends. An important point is the apparent delay in polar-vortex breakdown in springtime of both hemispheres; extending the cold winter season is a critical factor in increasing the likelihood of chemical ozone loss, but even in the absence of chemical processes, the continued isolation of the polar region into the springtime leads to a 'dynamical' ozone deficit. Section 2.1.3 examines transport processes, including the mean meridional circulation and issues of transport inside, outside, and across the boundary of the polar vortex; these play a crucial role in fixing the distributions of ozone and other trace gases, which impacts both the physical processes (such as radiative heating) and chemical ozone loss.

2.1.1 THE POLAR VORTEX: MEAN STRUCTURE

The winter stratospheric circulation is dominated by the polar night jet, which is at the edge of the polar vortex. Understanding the polar vortex dynamics is central to our ability to understand recent ozone change and to predict future ozone.

The polar vortex structure is well understood: absence of solar heating in winter leads to strong radiative cooling, which is offset by the adiabatic warming caused by the descending branch of the Brewer-Dobson circulation. This circulation is caused by the damping of planetary and gravity waves in the middle atmosphere (*e.g.*, Fels, 1985). An illustration of the polar vortex (Figure 2.1-1) shows the polar night jet (peaking near 60˚N at about 45 km) and the strong descent (shown by the meridional stream function) which is proportional to the radiative cooling. Descent in the polar region leads to (diabatic) downward transport, carrying ozone and other

trace gases from the mesosphere to the lower stratosphere during winter (*e.g.*, Rosenfield and Schoeberl 2001).

The asymmetry of the polar vortices in the two hemispheres is a consequence of the different topographic features: the weaker wave activity propagating from the Southern Hemisphere troposphere provides less forcing and therefore a weaker Brewer-Dobson circulation than in the Northern Hemisphere (*e.g.,* Randel and Newman, 1998). The Antarctic vortex is more symmetric, stronger and colder than the Arctic, as illustrated by the 50-hPa geopotential height distributions in middle winter (Figure 2.1-2). Even in the absence of chemical ozone destruction, these dynamical differences lead to substantially more ozone in the Arctic than in the Antarctic vortex, especially in springtime.

The main impacts of these dynamical differences on Arctic (compared to Antarctic) ozone are from the stronger diabatic descent, which transports trace species downwards more rapidly, and the decreased likelihood of PSC formation. Since PSCs form at temperatures near 195 K at 50 hPa (see Section 2.2), they can form every winter in the Antarctic vortex core, but only on colder-than average days in the Arctic (*e.g.*, Pawson *et al.*, 1995; Pawson and Naujokat, 1999).

While these basic mechanisms that determine the vortex structure and tracer transport in polar regions are now well understood, there are important aspects for which the complexity is only partially described. Recent results pertaining to these uncertainties are assessed in the next section.

2.1.2 POLAR VORTEX: CAUSES OF INTERANNUAL VARIABILITY AND ITS IMPLICATIONS

Differences between the hemispheres, caused by the stronger wave driving in the Northern Hemisphere, are also evident in the year-to-year variations. Figure 1.2-8 shows what appear to be robust temperature trends in the springtime, but interpretation of such trends is complex, because of the large interannual variability of high-latitude temperature (Figure 1.2-7), which varies with time of year and is different in the two hemispheres (Figure 2.1-3: *e.g.,* Scaife *et al.*, 2000b). Southern hemispheric variability peaks in late winter and spring (*e.g.*, Kuroda and Kodera, 1998), while northern hemispheric variability is large throughout the season (*e.g.*, Labitzke, 1982). The variability of the stratosphere (defined in terms of departures from the long-term mean) is characterized by a ‘see-saw’ of temperature and mass between the polar region and mid-latitudes (*e.g.*, Labitzke, 1982): anomalously weak wave forcing leads to a strong

polar vortex and a weak Brewer-Dobson circulation (*e.g.*, Figure 2.1-1), with a cold polar region and warmer mid-latitudes (the converse is true for strong wave forcing). Newman *et al.* (2001) demonstrated the quantitative linkage between the upward-propagating wave activity through the tropopause region and the strength of the polar vortex.

The occurrence of a strong, cold polar vortex leads to anomalously low ozone in the polar region, since the transport of ozone-rich air is weak and because the potential for PSC processing, a precursor to chemical ozone loss, is enhanced. This means that in years with weak tropospheric wave forcing a stronger polar vortex will result in less ozone in the polar region. Chipperfield (1999) reported results from a 6-year simulation using the SLIMCAT chemistry and transport model (CTM), driven by UKMO analyses of the meteorology. The horizontal winds and temperatures are taken from the UKMO analyses, and the vertical motion is diagnosed using a radiation scheme. The model simulates the interannual variations in chlorine activation during northern winters, and reproduces the repeatable pattern of activation observed during southern winters. Chipperfield and Jones (1999) utilized the same model to evaluate the relative contributions of photochemical and dynamical processes to interannual variability in northern high latitude ozone, and show that dynamical variations dominate interannual variability. Hadjinicolau *et al.* (2002) find similar results using a long run of the same model, driven by ECMWF analyses.

In the Northern Hemisphere, the anomalies in polar vortex strength are a part of what is now known as the Arctic Oscillation (AO) (Thompson and Wallace, 1998). The AO and its Southern-Hemispheric counterpart are also referred to as the annular modes. The annular structure of the AO in the stratosphere can be traced to the surface, with a strong link to the North Atlantic Oscillation (NAO) in the Northern Hemisphere (Thompson and Wallace, 1998). While there is some debate about the role of the stratosphere in forcing anomalies in the tropospheric component of the AO (*e.g.*, Perlwitz and Graf, 2001; Ambaum *et al.*, 2001), that is beyond the scope of this assessment of stratospheric ozone. This discussion focuses on the stratospheric component of the AO.

A high (low) AO index corresponds to a strong (weak) vortex and low (high) polar ozone column values (Thompson and Wallace, 2000; Hartmann *et al.*, 2000). Thompson *et al.* (2000) estimated that approximately 40% of recent apparent polar ozone loss in March could be explained by the tendency of the AO to remain positive in the springtime, which describes a

strong, cold and isolated polar vortex. However, on the basis of the observations, it cannot be determined whether the signal in ozone is caused by the AO anomaly, or whether the AO anomaly is a consequence of ozone depletion, or whether both are coherently forced by some other factor.

There is strong evidence that the AO signal originates near the subtropical stratopause and propagates poleward and downward through the mechanism of wave forcing (*e.g.*, Baldwin and Dunkerton 1999; Kuroda and Kodera 1999; Kodera *et al.* 2000; and Christiansen, 2001). Kodera and Kuroda (2000) show how the interannual variability of wave forcing can cause such anomalies to take different phases in different years.

Isolating causes of variability and the factors that drive trends is not straightforward. Apart from the link between the AO strength and the upward propagation of planetary waves, other mechanisms have been related to the polar vortex. Model simulations reveal that a substantial year-to-year variability in the stratospheric vortex (and hence the AO) can exist in the absence of variations in boundary conditions or other forcing mechanisms (*e.g.*, Yoden *et al.*, 1999; Hamilton, 1999). This variability, forced by internal dynamics of the atmosphere, means that many factors often invoked as causes of interannual variability in the real atmosphere may or may not be significant. Despite this, there is some evidence of coupling between the polar vortex and other atmospheric variations: the main relationships that have been studied are the quasi-biennial oscillation (QBO) of tropical winds, the 11-year variability of solar radiation, the phase of the El Niño-Southern Oscillation (ENSO), and major volcanic eruptions. While polar vortex composites grouped according to these mechanisms show apparent signals, several factors complicate their interpretation and robustness. The most severe complications are that the observational record covers only about four decades and that some of the forcing factors vary in unison. For instance, following Labitzke and van Loon (1997) and grouping northern mid-winter polar vortex structure according to the solar cycle (high or low) and the phase of the QBO (East or West) leads to twelve winters in the low/West category, with a strong polar vortex; however, five of these twelve winters coincide with ENSO cold events or volcanic eruptions, which have the same anomalies (see Figure 2.1-4). Determining robust relationships from observations on the basis of these overlapping factors and the internal variability is thus impossible.

Models have been used to address these questions. The SKYHI General Circulation model (GCM) with an artificially forced QBO reproduces observed QBO-related interannual variability in the Arctic vortex (stronger when the tropical winds are westerly, weaker when easterly) and variations in wintertime stationary wave patterns (Hamilton, 1998). Shindell *et al.* (1999b) found that the QBO significantly modulated the strength and propagation of planetary wave energy in the troposphere in the Goddard Institute for Space Studies (GISS) model, leading to warmer (3- to 5-K) zonal-mean temperatures at high southern latitudes for late winter and early spring during the QBO easterly phase. Niwano and Takahashi (1998) studied the influence of the QBO on the Northern Hemisphere winter circulation; their model reproduced the relationship between the polar vortex strength and the QBO phase and a related North Atlantic Oscillation (NAO) pattern in the troposphere. These and earlier studies have worked on the premise that the lower stratospheric winds impact planetary wave propagation, while more recent work (Gray *et al.*, 2001) has shown that the polar vortex anomalies are more strongly related to winds near the tropical stratopause (which are indirectly affected by the QBO).

There are two important factors in isolating the impacts of solar forcing on the circulation and climate. First, stratospheric ozone changes modulate the response of the temperature to the changes in solar irradiance (Haigh, 1994). However, studies of solar impacts on ozone, mostly using two-dimensional models, have been plagued by an inability to reproduce the solar-ozone relationship detected in observations (*e.g.*, Brasseur, 1993; Hood and Zhou 1999). Second, inclusion of the correct spectral dependence of solar irradiance variations in the atmospheric heating rate calculations is essential to capture the correct vertical structure of heating rates (Haigh, 1999; Shindell *et al.*, 1999a; Larkin *et al.*, 2000). However, even incorporating these feedbacks, climate model studies generally remain inconclusive about the role of solar-induced perturbations in the variability of the Arctic polar vortex.

Volcanic aerosol loading impacts polar ozone by perturbing stratospheric chemistry and transport. Chemical perturbations from heterogeneous reactions on aerosols are discussed in Section 2.2. Here, circulation perturbations arising from anomalous radiative forcing is discussed. Increased volcanic aerosol loading of the tropical lower stratosphere leads to a warmer tropical lower stratosphere some months after a volcanic eruption (*e.g.*, Robock, 2000), which is discussed in more detail in Chapter 4. The polar response to this tropical warming has a northern polar vortex remaining anomalously cool in the winter following the eruption (*e.g.*,

Kodera, 1994), as shown in Figure 2.1-4. Figure 2.1-4 shows that the three volcanic eruptions affected winters with ENSO warm events and that they 'reverse' the ENSO anomalies, leading to anomalously strong, cold polar vortices (van Loon and Labitzke, 1987; Labitzke and van Loon, 1989), thereby increasing the likelihood of negative polar ozone anomalies. Based on only three events (and because of the factors discussed above), these results must be interpreted with caution. This relationship has also been isolated in models (Kirchner *et al.*, 1999; Ramachandran *et al.* 2000).

The importance of synoptic and mesoscale waves for PSC formation [2.1.1.3]

While temperatures low enough for PSC formation occur on the large scales (*e.g.*, Pawson and Naujokat 1997, 1999), the likelihood of their occurrence is enhanced by the temperature perturbations induced by medium-scale waves (*e.g.*, Grewe and Dameris, 1997; Sato *et al.*, 2000; Teitelbaum *et al.*, 2001), as well as by topographic and inertial gravity waves (*e.g.*, Dörnbrack *et al.*, 2001, 2002). The temperature perturbations induced by these waves can cause sufficient additional cooling for PSCs to form in locations where the large-scale flow would not support them. This is particularly important on the vortex edge, where the processed air can be irreversibly transported into the middle latitudes (in the presence of breaking waves) and where the air masses are more likely to be illuminated, enhancing the potential for ozone depletion.

Ozone mini-holes occur due to synoptic-scale, reversible advection (*e.g.*, McKenna *et al.*, 1989; Newman *et al.*, 1988), related to upper tropospheric anticyclonic structures. The high tropopause, coupled with ascending motion, leads to extremely low total ozone values with lifetimes of up to several days. Steinbrecht *et al.* (1998) show that correlations in tropopause height correlate with ozone concentration changes in the region up to 23 km, illustrating the depth of the disturbances. However, the low ozone values themselves are short-lived features that are unrelated to chemical loss. The dynamical forcing which causes ozone mini-holes also causes adiabatic cooling, which can lead to synoptic-scale temperature perturbations of sufficient magnitude to allow PSC formation (*e.g.*, McKenna *et al.*, 1989; Grewe and Dameris, 1997). The importance of baroclinic disturbances in producing PSC formation near the polar vortex edge has been discussed by Hood *et al.* (2001) and Teitelbaum *et al.* (2001). Orsolini and Limpasuvan (2001) showed how these disturbances are linked to the storm tracks, which vary in unison with

the AO. There is thus a flow-dependent nature to the likelihood of synoptic-scale PSC formation and to the likelihood that they contribute to ozone loss on the vortex edge region.

Just as baroclinic waves help PSC formation on the synoptic scales, mesoscale disturbances from gravity waves are also important. Volkert and Intes (1992) demonstrated PSC formation in wave crests over Scandinavia in their model of topographically forced gravity waves. The importance of gravity-wave PSCs was also demonstrated by Deshler *et al.* (1994) and Meilinger *et al.* (1995). High-resolution radiosonde data have recently provided much needed information on stratospheric gravity wave morphologies in and around the Antarctic (Pfenniger *et al.*, 1999; Zink and Vincent, 2001) and Arctic (Whiteway and Duck, 1999; Yoshiki and Sato, 2000). While the microphysical effects of a background spectrum of gravity waves are smaller than first thought (Bacmeister *et al.*, 1999), it is now accepted that mesoscale temperature decreases due to large-amplitude gravity waves, particularly mountain waves, can lead to temperatures low enough for PSC formation (Carslaw *et al.*, 1998b, 1999; Schulz *et al.*, 2001), and lead to structure inside larger-scale PSCs (Toon *et al.*, 2000). The detailed microphysics associated with PSCs is discussed in Section 2.2.1 of this chapter.

Important advances have been made in our ability to model lower stratospheric gravity waves and, especially, to resolve such waves in global meteorological analyses. Dörnbrack *et al.* (2001) demonstrated that the high-resolution ECMWF operational meteorological analyses capture gravity wave structures over Scandinavia. This represents an important advance for applying the analyses to our understanding of the gravity-wave morphology and its importance for PSC formation. An additional advance of some importance was made by Dörnbrack *et al.* (2002), who detected inertia-gravity waves over Scandinavia in the ECMWF analyses and *in situ* data, noting their role for PSC formation. The isolation of gravity waves in such operational analyses points to their potential utility in mountain wave forecasting and analysis, meaning that the off-line models that have been used for such studies could eventually become unnecessary.

Another important role played by gravity waves (from all sources) is that they transport momentum into the middle atmosphere; as these waves break, they deposit momentum to the mean flow, constituting an important driving mechanism for the Brewer-Dobson circulation. The importance of these waves for driving the flow and reducing biases in global models is discussed in more detail in Section 5.2.1 below.

2.1.3 POLAR TRANSPORT AND MIXING

This section discusses in detail the physical processes that lead to the redistribution of trace gases in the polar regions. Trace gas distributions are determined by the balance between the slow mean meridional circulation and the more rapid, quasi-isentropic mixing (*e.g.,* Holton 1986); the following discussion examines these components of transport in and around the polar vortex and the exchange across the vortex edge.

Manney *et al.* (2002) examines impacts of using different meteorological analyses, which impact the amount of exchange between middle latitudes and the vortex. Despite the uncertainties, the consensus is that the vortex remains quite isolated in wintertime. Vertical transport (discussed in Section 2.1.3.1) leads to descent in and around the vortices, while mixing (Section 2.1.3.2) redistributes ozone and trace gases on isentropic levels; there is some exchange across the vortex edge, associated with large-scale mixing events.

Descent in the polar vortex [2.1.3.1]

Descent inside the polar vortex builds up (or maintains) lower stratospheric ozone over the winter, making it an important process to understand. The descending branch of the Brewer-Dobson circulation is driven by wave forcing of the flow (see Section 2.1.1). Descent rates can be determined in several manners: (i) 'directly' from the vertical velocities produced in routine meteorological analysis systems, such as the UKMO (Swinbank and O'Neill, 1994) and the DAO (Rood *et al.,* 1997), (ii) based on the cross-isentropic transport determined by diabatic heating rates, and (iii) using measurements of long-lived trace gases with well-understood vertical gradients. The various estimates are in reasonably good agreement, showing stronger descent in the upper stratosphere than in the lower stratosphere and unmixed descent from the upper to the lower stratosphere. The strongest descent occurs in the Antarctic vortex, but is more variable in the Arctic, where it can occur on the vortex edge when the temperature is higher there (*e.g.*, Manney *et al.,* 1999).

Schoeberl *et al.* (1995) used HALOE CH_4 data to estimate the descent rate as 1.8 km/month inside the Antarctic vortex in February-October 1992. Descent rates over Antarctica were deduced from ISAMS CO data for April to July 1992 by Allen *et al.* (2000) and from POAM-III H_2O data by Nedoluha *et al.* (2000). Abrams *et al.* (1996) demonstrated strong

descent in the upper stratosphere (3.2 km/month at 40 km) with weak descent in the lower stratosphere (0.8 km/month at 20 km) based upon the Atmospheric Trace Molecule Spectroscopy (ATMOS) data from November 1994. Kawamoto and Shiotani (2000) also used HALOE data and United Kingdom Meteorological Office (UKMO) meteorological analyses to investigate the interannual variability of the descent rate, using the for the February-October (winter) averages in 1992-1997 HALOE CH_4 data. They find that the descent varies between 1.2-1.8 km/month using the 0.6 ppmv CH_4 contour inside the polar vortex and is consistent with the wave driving determined from the UKMO analyses To summarize, the various estimates of Antarctic descent rates give reasonably consistent results, given that they are presented for different levels, seasons and years.

The vortex core [2.1.3.2]

The degree of mixing within the vortex core has come under scrutiny because of assumptions about representing the bulk behavior of the vortex with irregular temporal and spatial sampling. If the core is well mixed, then measurements anywhere within the vortex will suffice to characterize its behavior. If the core is not well mixed, then more frequent sampling at separated locations is necessary to do this. Schoeberl *et al.* (1990) assumed that the vortex was relatively well mixed in assessing ozone loss using ER-2 data from the Airborne Arctic Stratospheric Expedition (AASE)-I mission during the Arctic winter of 1988-1989. Richard *et al.* (2001) used ER-2 data from the SOLVE-THESEO 2000 campaign to show that tracer-tracer relationships inside the vortex during the Arctic winter of 1999-2000 are distinct and compact, suggesting a rapid mixing in the Arctic. While current evidence suggests that the Arctic vortex is relatively well mixed in the absence of intrusions of air from the vortex edge, Lee *et al.* (2001) present evidence that the Antarctic vortex is separated into two regions: a strongly mixed vortex core and a weakly mixed ring of air extending to the vortex boundary. This may arise from the fundamentally different meteorology of the two hemispheres.

Transport across the vortex edge and mixing [2.1.3.3]

The balance of mass and trace gases in and around the polar vortex is determined by the downward transport and exchange across the vortex edge. Any vertical gradient in the vortex-averaged mass flux will be compensated for by flow across the vortex edge. The discussion

below will separate the transport across the vortex edge in winter from transport occurring as the polar vortex breaks down.

Planetary wave breaking can be responsible for vortex shrinking as well as sharpening of the vortex edge (*e.g.*, Thuburn and Lagneau, 1999). A number of studies have shown considerable variability in the width of the Antarctic vortex edge when it is perturbed (Teitelbaum *et al.,* 1999; Perez *et al.*, 2000), which result in non-linear irreversible transport and mixing of vortex air into mid-latitudes (Teitelbaum *et al.*, 1999). Lidar observations at Dumont d'Urville (66.4˚S, 140˚W) allow sampling at and around the moving vortex edge (Godin *et al.* 2001); observations of Pinatubo aerosols, made during October and November 1992, show the sharpness of the vortex edge and low mixing between the inner vortex and the outside air above 400 K.

The first obstacle to determining the cross-vortex flow is to unambiguously define the vortex edge. Chen (1994) defined it as the potential vorticity (PV) contour which has the smallest lengthening rate; he found a vertical dependence to the transport across the edge, with more transport out of the vortex at potential temperatures lower than 400 K than at higher levels. Tuck *et al.* (1995) reached similar conclusions using ER-2 data, showing also that the vortex edge region can be quite wide. This viewpoint of the polar vortex as a reasonably well-isolated entity is now generally accepted, but the amount of 'leakage' from the vortex (as a function of altitude) is not yet well understood. Different proposed definitions of the vortex edge include the wind maximum and the strongest gradients in PV (*e.g.,* Bowman, 1996; Nash *et al.,* 1996). The uncertainty in defining the vortex edge remains, so there is no unambiguous estimate of the vertical structure of cross-vortex transport. Mechanisms for the transport are at least qualitatively understood and are discussed here.

Recent results continue to sustain our understanding of the vortex edge impermeability (Chen, 1994) and of the polar vortex as a quasi-isolated containment vessel. Norton and Chipperfield (1995) and Jones and MacKenzie (1995) had argued that ozone-depleted air from the polar vortices makes only a small contribution to middle latitude ozone loss. High-resolution, single-level models with weak dissipation *(e.g.,* Juckes and McIntyre 1987; Mo *et al.,* 1998; Thuburn and Lagneau, 1999; Sobel and Plumb, 1999), have further confirmed that the export of air from the polar vortex is constrained. Vincent and Tranchant (1999) also found little mixing across the vortex edge at 520 K in the Antarctic. Li *et al.* (2002) used a CTM driven by analyzed

winds to show that less air is indeed exported from the Antarctic polar vortex to middle latitudes than descends into the troposphere.

Laminae and filaments could be an important mechanism in the mixing of air across the quasi-impermeable vortex edge. Such structures are common in winter and spring. As pointed out in WMO (1999) the filaments/laminae, *i.e.*, material sheets that tilt outward with increasing height (Schoeberl and Newman, 1995; Newman and Schoeberl, 1995) with initial horizontal scales of a few thousand kilometers, can lead to irreversible mixing on the timescale of 20-25 days over which they decay. Laminae have been detected in a variety of data types, including in-situ aircraft observations (Newman *et al.*, 1996); sondes and lidar (Bird *et al.*, 1997; Orsolini *et al.*, 1997; Teitelbaum *et al.*, 2000); and satellites (Appenzeller and Holton, 1997; Manney *et al.*, 1998, 2000). They have been successfully modeled (*e.g.*, Orsolini *et al.*, 1997). Waugh and Dritschel (1999) analyzed the relationship between Rossby wave breaking and vortex structure. These studies show that filamentation can lead to vortex air being peeled off and eventually mixed irreversibly into the surf zone, although some air may re-join the polar vortex. Furthermore Manney *et al.* (1998, 2001) have also shown that lamination processes within the polar vortex did not result from exchange across the vortex edge but rather from transport variations within the vortex.

Hence there is thus a need to assess the behavior of laminae and magnitude of their contribution to the total exchange between the vortex and midlatitudes. Appenzeller and Holton (1997) attempted to diagnose the production of tracer laminae using satellite data and meteorological analyses, as a first step in determining their contribution to transport. Nevertheless there arose some limitations regarding the use of such a diagnostic (Kettleborough and Holton, 1999), because (a) it does not include small vertical scales that are relevant in defining tracer lamination and (b) there can be a reversible contributions. In other words the proposed diagnostic could overestimate the transport and mixing.

A principal challenge to modeling the polar ozone in the Northern Hemisphere and the effects of polar processes on middle latitudes is to ensure that the models produce the appropriate balance among the many processes that contribute directly or indirectly to the polar lower stratospheric ozone tendency. Both transport and photochemical processes contribute. The year-to-year variability in meteorological fields is significant, and the northern vortex may be cold and strong, as the winters 1996-1997 and 1999-2000, or warmer and more disturbed, as the

winter 1997-1998 (Sinnhuber *et al.*, 2000; Guirlet *et al.*, 2000). Simulations have focused on replicating observations for ozone and other trace gases, and quantifying model sensitivity to various processes (Chipperfield and Pyle, 1998). Such studies point out the importance of developing a better understanding of the physical processes leading to denitrification, so that model parameterizations respond appropriately to changes in temperature, water vapor, or nitric acid that may result from climate change.

Millard *et al.* (2001) utilized advanced diagnostics developed by (Lee *et al.*, 2001) to quantify the importance of polar processes to ozone change at middle latitudes. Both the chemical processes that contribute to polar ozone loss and the transport process that impact mixing between high latitudes and middle latitudes vary depending on the meteorology of a particular year. CTMs have been utilized to address questions concerning specific winters. For example, Lefèvre *et al.* (1998) utilized a CTM forced by winds from ECMWF to show that both transport and photochemical processes contribute to the record low ozone observed by TOMS during northern spring 1997 (Figure 1.2-2). Like the studies of Guirlet *et al.* (2000), results are broadly consistent with observations. However, as shown by Douglass *et al.* (2001), the model results separating photochemical and transport contributions are sensitive to the vertical velocity and to the ozone vertical gradient.

The breakdown of the polar vortex, whether by a major midwinter warming or in the final warming, allows vortex air to be mixed relatively easily with that from middle latitudes. Atkinson and Plumb (1997) showed that as the Antarctic vortex breaks down, a substantial amount of ozone-depleted air is transported to middle latitudes. Once there, it can effectively mix with the ambient air masses. Effective diffusivity has been used as a diagnostic for mixing by Allen and Nakamura (2001), who show increases in mixing lengths as the polar vortices break up.

2.2 Polar Stratospheric Clouds

PSCs play two important roles in polar ozone chemistry. First, the particles support chemical reactions leading to active chlorine formation, which can catalytically destroy ozone. Second, nitric acid removal from the gas phase can increase ozone loss by perturbing the reactive chlorine and nitrogen chemical cycles in late winter and early spring.

PSCs are divided into two main categories. Type I PSC particles contain nitric acid, either in the form of liquid ternary solutions with water and sulfuric acid or as solid hydrates of nitric acid. Type II PSCs are made of ice particles. Knowledge of PSC particle sizes, number concentrations, composition, phase and evolution is central to efforts to develop prognostic models of how PSCs affect the chemistry of the polar stratosphere. *In situ* observations of PSCs from balloons or aircraft are often used to obtain detailed information on cloud particle size distribution and composition. Remote sensing platforms, such as lidar and satellites, provide complementary information on phase and large-scale time evolution of PSCs, respectively. We now briefly review recent advances in our understanding of PSC properties and their effect on denitrification and dehydration.

2.2.1 Observations of PSC Physical Properties and Their Interpretation

In situ

The last assessment (WMO, 1999) described considerable improvements in our understanding of liquid PSCs, but highlighted the outstanding uncertainties in the properties of solid particles. Solid nitric acid-containing PSC particles are important because, in contrast to the sub-micron liquid aerosol, they may be present with sufficiently low number concentrations ($< 10^{-2}$ cm^{-3}) to allow a few particles to grow to large sizes, leading to sedimentation and denitrification. Our understanding of the range of solid particle number concentrations and sizes that can form in the polar stratosphere has improved since the last assessment as a result of new *in situ* observations.

Observations in the Arctic stratosphere at altitudes from 16 to 20 km in January to March 2000 detected a population of large nitric acid particles with very low number concentrations (Fahey *et al.,* 2001; Northway *et al.,* 2002a), see Figure 2.2-1. Large particles, with similar sizes and number concentrations as those observed by Fahey *et al.* (2001), were detected by the Multiangle Aerosol Spectrometer Probe (MASP) (Carslaw *et al.,* 2002). These measurements (Fahey *et al.,* 2001; Northway *et al.,* 2002a) are very important because they provide conclusive evidence that such large particles are composed principally of nitric acid (probably present as nitric acid hydrates).

Observations of large nitric acid particles raises several questions. The most obvious question is how these particles compare with previous observations in the Arctic and Antarctic.

Balloon-borne instruments such as the Optical Particle Counter (OPC) (*e.g.*, Deshler *et al.*, 1991, 1994; Deshler and Oltmans, 1998; see also WMO, 1999 and references therein), which has flown in many previous Arctic winters, is capable of detecting particles up to 20 μm in diameter with number concentrations greater than about $6x10^{-3}$ cm^{-3}. However, this is higher than average particle concentrations (~10^{-4} cm^{-3}) measured by Fahey *et al.* (2001). Further, the forward scattering spectrometer probe (FSSP) instrument, which measured PSC size distributions during the 1989-1990 Arctic winter (Dye *et al.*, 1992), could not have detected PSCs with number concentrations below about 10^{-3} cm^{-3}. Thus, if large nitric acid particles were present in previous Arctic winters, at number concentrations near and below 10^{-4} cm^{-3}, then the available *in situ* instruments at the time would not have been able to detect them (Table 2.2.1). However, it is interesting to note that in earlier Antarctic measurements the OPC instrument, which operated at a different inlet flow rate, detected large PSC particles with number concentrations as low as 10^{-4} cm^{-3} (Table 2.2.1). Thus populations of very few (~10^{-4} cm^{-3}) large PSC particles have been observed previously, but it is only through recent measurements (Fahey *et al.*, 2001) that we have learned such large particles are indeed enriched in nitric acid.

Table 2.2.1. Observations of solid PSC particle size and number density

Number density (cm^{-3})	Average Diameter (μm)	Atmospheric References	Location
10^{-1}-1	1-2	Voigt *et al.*, 2000a, b	Arctic
10^{-3}-10^{-2}	1-4	Dye *et al.*, 1992*	Arctic
10^{-4}-10^{-2}	4-10	Hofmann and Deshler, 1991*	Antarctic
10^{-5}-10^{-3}	10-20	Fahey *et al.*, 2001# Northway *et al.*, 2002a#	Arctic

*Note that these measurements are mode diameters of a log normal distribution.

#These observations on the average show PSC number densities of about 2 x 10^{-4} cm^{-3} with a mode diameter centered near 14 μm, assuming a nitric acid trihydrate (NAT) composition.

The second question is whether these large particles present at very low number concentrations can denitrify the stratosphere. Simple calculations presented by Fahey *et al.* (2001) demonstrate that large nitric acid particles can grow to their optimal observed sizes in about 5 to 8 days, implying that they must have nucleated several kilometers above the aircraft flight altitude. Instantaneous downward flux calculations of nitric acid contained in such large particles indicate that they were capable of causing significant denitrification (Fahey *et al.*, 2001, Northway *et al.*, 2002b). 3-D model simulations of particle growth further show that the observed PSC sizes are consistent with growing NAT and/or nitric acid dihydrate (NAD) particles (Carslaw *et al.*, 2002). However, it is important to note that PSCs with size distributions different to those measured in winter 1999/2000 have been observed in previous winters in both hemispheres (see Table 2.2.1). Model simulations by Jensen *et al.* (2002) show that previously observed PSC particle size distributions (Dye *et al.*, 1992; Hofmann and Deshler, 1991), with number concentrations in the range of 10^{-2} to 10^{-3} cm^{-3}, are also capable of efficiently denitrifying the polar stratosphere.

A third question is how these large nitric particles form in the polar stratosphere. Both homogeneous (Tabazadeh *et al.*, 2001) and heterogeneous (Tolbert and Toon, 2001; Drdla *et al.*, 2002) freezing mechanisms have been suggested to account for the formation of large nitric acid particles. For such nucleation mechanisms to operate, the cooling caused by synoptic-scale uplift of air masses (Teitelbaum *et al.*, 2001; Spang *et al.*, 2001; Hendricks *et al.*, 2001; Saitoh *et al.*, 2002) can provide favorable conditions for solid PSCs to form. Laboratory observations show that concentrated aqueous nitric acid aerosols can homogeneously crystallize into hydrates of nitric acid (Disselkamp *et al.*, 1996; Bertram *et al.*, 1998 a, b; Prenni *et al.*, 1998; Salcedo *et al.*, 2001). The stratospheric particle system has also been studied using thin films, where gas phase HNO_3 and H_2O are absorbed by cold aqueous sulfuric acid solutions (Iraci *et al.*, 1994, 1995, 1998). The results of these thin film experiments show that HNO_3 uptake in sulfuric acid can cause freezing of nitric acid hydrates in solution. Tabazadeh *et al.* (2001) have recently extrapolated the laboratory homogeneous freezing rates of Salcedo *et al.* (2001) and obtained nucleation rates sufficient to produce large nitric acid particles in a microphysical model. Note that the nucleation rates extrapolated from Salcedo *et al.* (2001) are much higher than upper limits derived from earlier bulk freezing experiments with 1-milliliter samples, which used stratospheric temperatures and liquid phase compositions (Koop *et al.*, 1995; 1997). Modeling

studies (Drdla *et al.*, 2002) further show that heterogeneous freezing can also produce large particles if only a very small fraction (< 0.1%) of stratospheric aerosol particles contained an effective freezing nucleus, although it is not clear what the freezing nucleus should be (Biermann *et al.*, 1996). In addition to direct homogeneous and heterogeneous freezing mechanisms, the large particles may also form by a gradual sedimentation from the base of 'mother clouds' containing much higher number concentrations of small solid particles (Füglistaler *et al.*, 2001; Dhaniyala *et al.*, 2001), such as those generated by lee wave clouds (Carslaw *et al.*, 1998a).

The freezing mechanisms described above are all capable of producing low number concentrations of sedimenting nitric acid particles. However, model simulations do strongly suggest that the large nitric particles, observed during the winter of 1999-2000 winter, were unlikely to have nucleated in synoptic-scale ice clouds, which were not sufficiently prevalent in the days preceding the observations (Carslaw *et al.*, 2002, Drdla *et al.*, 2002). Further analysis of satellite data in the Antarctic also seems to suggest that large nitric acid particles formed in the winter of 1992 independent of synoptic-scale ice clouds (Tabazadeh *et al.*, 2000).

A final question is whether these large particles observed *in situ* can also be detected by lidar. Aircraft lidar observations in January to March 2000 detected regions of enhanced aerosol backscatter in regions where large nitric acid particles were detected (Flentje *et al.*, 2000). However, Flentje *et al.* (2000) inferred an approximate size for the particles based on the sedimentation speed of the particle layer, rather than directly from the lidar signal. Their derived particle sizes are in reasonable agreement with *in situ* observations (Fahey *et al.*, 2001).

Overall, the assessment of both the Arctic and Antarctic studies, on observed and inferred PSC particle sizes, indicates that large nitric acid particles cannot initially nucleate on synoptic-scale ice clouds. However, the formation mechanism of large nitric acid particles still remains uncertain. Thus more laboratory and field studies are needed the better to test which of the above mechanisms is most likely to dominate the rate of large nitric acid particle production in the polar stratosphere.

Remote

Lidar observations are useful for constraining PSC particle sizes. Depolarization measurements by lidar can also provide strong evidence for the presence of solid PSC particles. As indicated above, only large solid PSC particles can cause denitrification, and lidar

observations provide valuable information on the horizontal and vertical extents of solid PSC particle distributions in the stratosphere.

Lidar studies provide new estimates of the occurrence of solid PSC particles, which is an important parameter for constraining microphysical models. Toon *et al.* (2000) have re-analyzed lidar observations from all DC 8 flights during the 1989-1990 Arctic winter and find that large solid PSC particles are more common in the Arctic stratosphere than the smaller liquid PSC particles (type 1b). From 3 years of lidar observations from Ny Ålesund (79˚N), Biele *et al.* (2001) have shown that at least 50% of PSCs contained solid particles, with some of these clouds being of type 1b, normally attributed to pure liquid clouds. Several studies have also derived new estimates of solid particle number concentrations. Gobbi *et al.* (1998) have analyzed many Antarctic lidar vertical profiles and estimate that solid PSC particles comprised less than 1% of the available condensation nuclei (therefore, typically less than 0.1 particles cm^{-3}). Toon *et al.* (2000) derived similar values for the 1989-90 winter Arctic stratosphere. Biele *et al.* (2001) and Tsias *et al.* (1999) estimate that many depolarizing clouds must typically contain fewer than about 0.005 - 0.01 cm^{-3} solid particles and that such particles can rarely grow to their equilibrium sizes. In summary all the lidar studies discussed here suggest that large solid particles that can cause denitrification are widely distributed in both hemispheres.

Some clouds observed by lidar are consistent with high number densities of small solid nitric acid particles (typically >1 cm^{-3} and < 2 μm diameter) (Tsias *et al.,* 1999; Toon *et al.,* 2000; Hu *et al.*, 2002). These clouds are frequently associated with the outflow from mountain waves (*e.g.*, Hu *et al.*, 2002). Efficient NAT nucleation on numerous small ice particles formed in wave clouds could be an important mechanism for generating such a dense population of small solid PSC particles (Carslaw *et al.,* 1998a, 1999; Wirth *et al.,* 1999; Larsen *et al.,* 2002). Some studies suggest that small solid PSC particles generated by wave clouds may also play a central role in producing large nitric acid particles that lead to denitrification (see Section 2.2.1).

Satellite instruments are also capable of observing PSC particles. SAM II (McCormick *et al.,* 1981); CLAES (Mergenthaler *et al.,* 1997); POAM (Steele *et al.* 1999*;* Fromm *et al.,* 1999; Fromm *et al.,* 1997; Bevilacqua *et al.*, 2002) and ILAS (Kondo *et al.,* 2000, Irie *et al.,* 2001) instruments have taken many aerosol extinction vertical profiles of PSCs in the Arctic and Antarctic stratosphere over the last two decades. Several recent studies have paired up aerosol extinction measurements with water and nitric acid gas phase measurements onboard the same

(Tabazadeh *et al.*, 2000; Stone *et al.*, 2001; Nedoluha *et al.*, 2000; Dessler *et al.*, 1999) or different satellites (Santee *et al.*, 2002) to determine the scale and magnitude of denitrification and dehydration in both polar regions (see Sections 2.2.3 and 2.2.4).

2.2.2 PARTICLE COMPOSITION

Inferred particle compositions

PSCs that exist at temperatures greater than the ice frost point have long been accepted to be composed of nitric acid and water, either in the form of a nitric acid hydrate or as supercooled solution droplets of nitric acid, sulfuric acid, and water (supercooled ternary solutions, STS). Numerous attempts have been made to infer the composition of nitric acid-containing PSCs by comparing particle volumes (either measured directly or derived from satellite extinction) and/or gas phase nitric acid concentrations with equilibrium model calculations assuming various particle compositions (WMO, 1999; Hopfner *et al.*, 1998; Steele *et al.*, 1999; Santee *et al.*, 2002; Saitoh *et al.*, 2002; Strawa *et al.*, 2002). These studies have provided strong support for the existence of STS droplets, but confirmation of the presence of different nitric acid hydrates has been more difficult to establish (WMO, 1999). This difficulty may be due to the fact that nitric acid hydrate particles, which can be considerably larger than STS droplets, are often not in thermodynamic equilibrium (*e.g.*, Tsias *et al.*, 1999; Biele *et al.*, 2001).

Direct determinations of particle composition

New *in situ* observations using an aerosol mass spectrometer have measured PSC particle composition (Schreiner *et al.*, 1999, 2002; Voigt *et al.*, 2000a, b; Larsen *et al.*, 2000, 2002). The observed nitric acid to water mole ratio using an aerosol mass spectrometer in a mountain-induced gravity wave cloud over Scandinavia (Voigt *et al.*, 2000b) shows close agreement with an STS droplet composition predicted by a model. The same aerosol mass spectrometer flown in January 2000 detected NAT particles, identified by a H_2O to HNO_3 mole ratio of 3:1 and confirmed to be solid particles from collocated backscatter measurements (Voigt *et al.*, 2000a; Larsen *et al.*, 2000); see Figure 2.2-2. These direct observations of particle composition in PSCs are important because they confirm that the thermodynamic models used to predict liquid aerosol compositions (*e.g.*, Carslaw *et al.*, 1997a) are reliable, and that NAT, long predicted to exist in the stratosphere (Hanson and Mauersberger, 1988), actually does exist there.

2.2.3 DENITRIFICATION

Observations of denitrification

In situ Arctic observations from the ER-2 aircraft in January to March 2000 detected the most severe and extensive denitrification observed in the Arctic stratosphere (Popp *et al.*, 2001), see Figure 2.2-3. Average removal of as much as 60% of NO_y was observed throughout the core of the vortex near 20 km (Figure Popp). Waibel *et al.* (1999) have also analyzed balloon-borne observations of denitrification in 1995. These observations reveal an approximate 50% reduction in total reactive nitrogen (NO_y) at 20 km . Using tracer measurements to eliminate deficits due to mixing (see Section 3), Waibel *et al.* (1999) concluded that at least 82% of the observed NO_y loss at 20 km was due to denitrification. Sugita *et al.* (1998) and Hintsa *et al.* (1998) have also observed similar levels of Arctic denitrification near 20 km in 1995 and 1996 winters, respectively. Together, these observations show that some Arctic air parcels were severely denitrified (> 50%) near 20 km in several cold winters.

Figure 2.2-4 shows the time evolution of HNO_3 in both hemispheres for a number of winters on three potential temperature surfaces, based on MLS observations. Large permanent depletions (> 80%) in HNO_3 vapor amounts occur only in the Southern Hemisphere (Santee *et al.*, 1999), but much smaller irreversible depletions (~ 20%) have also been observed in cold Arctic air parcels (Dessler *et al.*, 1999; Santee *et al.*, 2000, 2002). However, large permanent depletions in HNO_3 concentrations (> 40%) have been observed in cold Arctic winters by satellite instruments with finer vertical resolution than MLS (~6 km vertical resolution), such as the ILAS instrument, which has a 1-2 km vertical resolution (Kondo *et al.*, 2000; Irie *et al.*, 2002. Thus, extensive denitrification does occur in both hemispheres based on both *in situ* and remote sensing observations. However, severe denitrification in the Arctic must be narrow in depth because if the denitrified layers were deeper than 6 km, then MLS would have been able to detect this irreversible loss in gas phase nitric acid (Tabazadeh *et al.*, 2001). Individual nitric acid vertical profiles from the ILAS instrument (Kondo *et al.*, 2000; Irie *et al.*, 2002) during the winter of 1996-1997 further show that the vertical range of denitrification in the Arctic is typically ~2- to 3-km deep (from about 18 to 21 km) with immediate nitrification occurring below this altitude range.

Tabazadeh *et al.* (2000) have shown that denitrification over a broad altitude range (> 10 km in depth) occurs rapidly in the Antarctic when the duration of an average PSC event is about 2 weeks (defined to be the time spent by an isentropic air parcel below 195 K at 450 K potential temperature). Tabazadeh *et al.* (2000) suggest that deep extensive denitrification currently occurs only in the Antarctic because average Arctic PSC events last nearly half as long as those in the Antarctic, during the mid to late June time period, when denitrification occurs rapidly in the south pole (see the MLS plot). The short persistence of PSC events in the NH limits the extent of severe denitrification to only a few kilometers, as observed in many past cold Arctic winters (Popp *et al.*, 2001; Sugita *et al.*, 1998; Hintsa, *et al.*, 1998; Kondo *et al.*, 2000; Irie *et al.*, 2001, 2002). In Section 3.3 the effect of denitrification depth on ozone loss is assessed for both hemispheres.

Model simulations of denitrification

Improvements in our understanding of PSC particle sizes and number concentrations (Section 2.2.1) now allow for more sophisticated treatments of denitrification in models. Current 3-D chemical transport models include a highly simplified representation of denitrification that is now recognized to be incorrect. These models assume that nitric acid is carried downwards on sedimenting ice particles wherever temperatures are lower than the ice frost point (Chipperfield *et al.*, 1993; Considine *et al.*, 2000). Removal of nitric acid on sedimenting ice particles is clearly not operating in the Arctic because models, using this assumption, have been unable to produce any denitrification by this mechanism (Chipperfield and Pyle; 1998; Davies *et al.*, 2002).

Drdla *et al.* (2002) have used a coupled microphysical-chemistry trajectory model to show that synoptic-scale ice clouds could not have caused the massive denitrification observed during the 1999-2000 winter. They concluded that the large nitric acid particles that caused denitrification were not nucleated on ice particles.

Jensen *et al.* (2002) have used a 1-D version of the CARMA microphysics cloud model to show that solid nitric acid solid number densities in the range of 10^{-2} to 10^{-3} cm^{-3} are the most efficient in causing rapid denitrification. The CARMA cloud model has also been used to show (see Figure 4 in Tabazadeh *et al.*, 2001) that the vertical range over which denitrification occurs is normally quite deep in the Antarctic (> 10 km) but limited in the Arctic, in general agreement

with many observations of denitrification in both hemisphere (*i.e.*, Santee *et al.*, 1999; Popp *et al.*, 2001; Sugita *et al.*, 1998; Hintsa, *et al.*, 1998; Kondo *et al.*, 2000; Irie *et al.*, 2001, 2002). The Arctic denitrified layers are shallow in depth mainly because the stratosphere, even in cold winters, is too warm below about 17 km for nitric acid hydrate particles to exist.

Waibel *et al.* (1999) simulated denitrification by assuming that ice acted as the nucleus for NAT formation. Most of the denitrification calculated in the model was caused primarily by sedimentation of NAT particles, with a fixed number concentration of $5x10^{-3}$ cm^{-3}, released upon ice evaporation. In these 3-D model simulations, in which a simplified treatment of horizontal transport was used, NAT particles were assumed to be in equilibrium with gas phase nitric acid.

Davies *et al.* (2002) have included a parameterization in a 3-D CTM of NAT particle sedimentation assuming sizes and number concentrations representative of those observed by Fahey *et al.* (2001). NAT particles were assumed to be in equilibrium with gas phase nitric acid in these simulations. The calculated denitrification magnitude was similar to that observed in winter 1999/2000. In contrast, the modeled denitrification was significantly less than observed when NAT was allowed to only nucleate on ice particles. This result is consistent with previous simulations (Carslaw *et al.*, 2002; Drdla *et al.*, 2002) showing that the observed large nitric acid particles could not have nucleated on synoptic-scale ice clouds during the winter of 1999-2000.

Mann *et al.* (2002) have developed a 3-D model of denitrification that takes into account the time-dependence of both growth and sedimentation of large NAT particles. In these simulations NAT particle growth times are on the order of several days and therefore the magnitude of denitrification strongly depends on individual particle growth cycles. In fact, the extent of modeled denitrification is strongly amplified when areas of low temperature are stable and concentric with the vortex, allowing for individual particles to persist for a longer time and to grow to larger sizes. Thus the area of cold temperatures by itself is perhaps not the best indicator for predicting the severity of denitrification in the Arctic.

In summary, new model calculations show that the long-accepted mechanism of nitric acid removal on sedimenting ice particles cannot account for observed levels of denitrification. Denitrification is most likely caused by sedimentation of large nitric acid particles. Various models are able to reproduce, in broad terms, the observed levels of denitrification by assuming sedimentation of large nitric acid particles. In addition, recent model calculations show that

Arctic denitrified layers are normally shallow in depth because the stratosphere is too warm below about 17 km to allow for large particles to carry much nitric acid beyond this altitude. The sensitivity of ozone loss to denitrification is discussed in Section 3.3.

2.2.4 DEHYDRATION

Figure 2.2-5 shows the time evolution of water vapor in the Southern Hemisphere during 1998 (Nedoluha *et al.*, 2000). Severe dehydration is observed over a 10 km altitude range. Similar results are also obtained from analysis of MLS water vapor data during the Antarctic winter of 1992 (Stone *et al.*, 2001). In the Arctic removal of ~ 1 ppm of water vapor over a 1-2 km altitude range has been observed by the ILAS instrument (Pan *et al.*, 2002). The lack of extensive and deep dehydration in the Arctic is also supported by *in situ* observations (Vömel *et al.*, 1997; Hintsa *et al.*, 1998; Herman *et al.*, 2002). Overall, the Arctic climate, even in cold years, it too to allow for formation of widespread persistent ice clouds that lead to dehydration. The sensitivity of ozone loss to dehydration is discussed in Section 3.

2.3 Polar Ozone Chemistry

The chemical loss of polar ozone during winter and spring occurs primarily by two gas phase catalytic cycles that involve halogen oxide radicals:

Cycle 1

$$ClO + ClO + M \rightarrow ClOOCl + M \quad (1a)$$
$$ClOOCl + h\nu \rightarrow 2Cl + O_2 \quad (1b)$$
$$2(Cl + O_3 \rightarrow ClO + O_2) \quad (1c)$$
$$\text{Net: } 2O_3 \rightarrow 3\,O_2$$

Cycle 2

$$BrO + ClO \rightarrow Br + Cl + O_2 \quad (2a)$$
$$\rightarrow BrCl + O_2 \quad (2a\_)$$
$$BrCl + h\nu \rightarrow Br + Cl \quad (2b)$$
$$Br + O_3 \rightarrow BrO + O_2 \quad (2c)$$
$$Cl + O_3 \rightarrow ClO + O_2 \quad (1c)$$
$$\text{Net: } 2\,O_3 \rightarrow 3\,O_2$$

Abundances of ClO in the polar vortex are greatly elevated by reactions of inactive chlorine reservoir species on various types of polar stratospheric clouds (PSCs) that form when temperatures drop below about 195 K (see Section 3.2.2). Abundances of BrO determine the removal rate by cycle (2), which contributes about 50% to the total chemical loss rate of polar ozone (Chipperfield and Pyle, 1998). In contrast to ClO, the abundance of BrO is not strongly affected by reactions involving PSCs because less than half of the available inorganic bromine budget is sequestered in reservoirs such as $BrNO_3$ and HBr prior to processing.

Since the last assessment, new studies have addressed the rates of ozone destruction by cycles (1) and (2) in an effort to reconcile apparent discrepancies between measured and modeled chemical loss rates of Arctic ozone (see Section 3.3). The chlorine and bromine cycles are discussed separately below. Model calculations reveal that, at present and for the foreseeable future, winter polar ozone loss will be dominated by reactions involving ClO and BrO (*e.g.*, Chipperfield and Pyle, 1998; Shindell *et al.*, 1998b).

2.3.1 CHLORINE

A number of modeling studies have had difficulty accounting for observed chemical loss rates of Arctic ozone, particularly during mid-winter when insolation is weakest (see Section 3.3). As a consequence, attention has focused on reducing uncertainties in key rate parameters, in particular those for formation and photolysis of the chlorine oxide dimer (ClOOCl), reactions k_{1a} and J_{1b}. These reactions determine the rate of ozone loss by cycle 1, such that uncertainties in these kinetic parameters couple directly into the uncertainties in modeled ozone loss rates. Results of these studies are summarized in Section 3.2.3.1.1.

The loss of polar ozone via cycles 1 and 2 is determined by the temporal evolution of ClO. Numerous studies have examined the seasonal variations of inorganic chlorine partitioning, including production of high abundances of reactive chlorine (ClO_x, defined as [ClO]+2[ClOOCl]) by PSCs ('activation'), maintenance of high abundances of ClO_x throughout the winter, and deactivation of ClO_x back to HCl and $ClNO_3$ ('recovery'). These results are summarized in Section 3.2.3.1.2.

Simultaneous measurements of the major inorganic and organic chlorine species have provided, for the first time, the ability to examine the overall chlorine budget for the Arctic stratosphere during a period of rapid ozone loss. These investigations can assess the possible

role of species not considered in standard models, such as higher oxides of chlorine. The results of these studies are summarized in Section 2.3.1.3.

Chlorine Photochemistry [2.3.1.1]

Our understanding of the key kinetic parameters governing ozone loss by cycle 1 (k_{1a} and J_{1b}) has improved through new laboratory studies and atmospheric observations. Bloss *et al.* (2001) found k_{1a} to be up to 25% larger than the value recommended in the Jet Propulsion Laboratory (JPL) 00-3 compendium (Sander *et al.*, 2000) at temperatures below 210 K. The impact of this increase on calculated ozone loss rates depends on the manner in which the models treat ClO. In the case of models constrained by observed abundances of ClO, the rate of ozone loss due to cycle 1 is roughly proportional to the increase in k_{1a}. For models that allow ClO and ClOOCl to re-partition within the constraint of constant active chlorine, the total loss rate is largely independent of this change in k_{1a} because ClO abundances respond in the opposite sense to the change in the rate constant (Figure 2.3-1). Thus, the maximum effect of an increase in k_{1a} based on the results of Bloss *et al.* (2001) is to increase total ozone loss rates by no more than 25% under cold polar conditions. Such an increase is insufficient to fully resolve the factor-of-two discrepancies between modeled and measured Arctic ozone loss rates found in several recent studies (*e.g.*, Woyke *et al.*, 1999; Becker *et al.*, 2000).

The recommended absorption cross section for ClOOCl has not changed since the last assessment. However, there have been several important laboratory and theoretical studies (Moore *et al.*, 1999; Kaledin and Morokuma, 2000; and Toniolo *et al.*, 2000) of the product yields from photolysis of ClOOCl at wavelengths longer than 300 nm, the spectral region that contributes most to the overall photolysis rate of ClOOCl. These new results reduce a significant uncertainty in our knowledge of ozone loss rates. Only production of ClOO+Cl (leading to $2Cl+O_2$ upon the rapid thermal decomposition of ClOO at polar temperatures) results in catalytic loss of ozone; production of ClO+ClO from ClOOCl photolysis leads to a null cycle that has no effect on ozone. Prior to this assessment, fundamental assumptions regarding the products of ClOOCl photolysis had not been examined in the laboratory at key wavelengths.

Moore *et al.* (1999) recently reported that Cl and molecular oxygen (O_2) are the primary products of photolysis of ClOOCl at 248 nm and at 308 nm. Further, they found that ClOO

products rapidly decompose due to excess vibrational energy. Thus, chlorine atoms and O_2 are the primary products of photolysis of ClOOCl under stratospheric conditions, a conclusion further supported by electronic structure calculations (Kaledin and Morokuma, 2000; Toniolo *et al.*, 2000).

Several new sets of atmospheric observations provide strong quantitative tests of our understanding of k_{1a} and J_{1b}. Recent balloon-borne *in situ* observations of the rate of decay of ClO immediately after sunset in the Arctic vortex are explained well by the larger value for k_{1a} at temperatures near 190 K (Vömel *et al.*, 2001) (Figure 2.3-2). Similar conclusions were reached in studies of *in situ* observations of ClO and ClOOCl from the ER-2 aircraft that examined the ratio k_{1a}/J_{1b} in the Arctic vortex during the same winter (Stimpfle *et al.*, 2002) and of earlier ground-based ClO observations from McMurdo Station, Antarctica (Shindell and de Zafra, 1995).

The chemical loss rate of ozone, particularly during early winter, is also quite sensitive to the dependence of J_{1b} on solar zenith angle (SZA). The first atmospheric observations of ClOOCl, together with simultaneous observations of ClO provide important constraints on this parameter (Stimpfle *et al.*, 2002). In particular, the balance between ClO and ClOOCl in daylight, which is controlled by the ratio J_{1b}/k_{1a}, closely tracks a photochemical model that employs the Bloss *et al.* (2001) value for k_{1a} and the SZA dependence for J_{1b} based on the JPL 00-3 recommended absorption cross sections for ClOOCl (Figure 2.3-3). The analysis of J_{1b} of Avallone and Toohey (2001) used JPL 00-3 recommendations for k_{1a}; a reanalysis using the Bloss *et al.* (2001) value would lead to larger absolute values for J_{1b} that would be more consistent with those found by Stimpfle *et al.* (2002). The significantly smaller value for J_{1b} based on absorption cross sections of Huder and DeMore (1995) can be ruled out by the combined results of these studies as well as Shindell and de Zafra (1995), Raffalski *et al.* (1998), Vömel *et al.* (2001), and Solomon *et al.* (2002). Furthermore, there is no evidence that supports the notion that ClOOCl may photolyze at an appreciable rate in optically thin spectral regions (*i.e.*, > 420 nm). Such a process could enhance ozone loss rates at high SZAs and account for some of the discrepancy between measured and modeled ozone loss rates in mid-winter (Rex *et al.*, 2002b and Section 3).

Finally, we note that Solomon *et al.* (2000) suggested that the ratio J_{1b}/k_{1a} is nearly 50% too low based on an analysis of ground-based measurements of ClO column over Antarctica in 1996. However, a subsequent analysis of data obtained during 5 winters (1996 to 2000) (Solomon *et al.*, 2002) found good agreement between measurements of column ClO and model calculations employing the value of this ratio from current recommendations (Sander *et al.*, 2000).

Chlorine Seasonal Evolution [2.3.1.2]

Another element critical in accounting for ozone loss is the temporal evolution of the ozone-destroying halogen radicals. Mixing ratios of ClO remain elevated (~1 to 2 parts per billion by volume (ppbv)) from May/June until September (Figure 2.2-2) for all years over Antarctica for which observations are available (WMO, 1995; WMO, 1999; Santee *et al.*, 2000; Wagner *et al.*, 2001, 2002; Solomon *et al.*, 2002), where temperatures between 14 and 24 km remain very low (below PSC thresholds) for several months (Figure 2.1-3b). In addition, the southern polar vortex remains intact well into the spring season. Under these conditions, the total amount of ozone destroyed over Antarctica is nearly complete for an 8 to 10 km thick altitude layer (*e.g.*, Figure 2-1.2.4 (*this figure might be deleted*)), a condition that is relatively insensitive to the chemical loss rate at contemporary abundances of inorganic chlorine (WMO, 1999).

Three-dimensional chemical transport models are able to simulate the seasonal evolution of ClO in the Antarctic polar vortex remarkably well (Ricaud *et al.*, 1998; Solomon *et al.*, 2000; 2002). Figure 2.3-4 compares ground based column measurements of ClO above Scott Base, Antarctica (77.8˚S) to calculations from the SLIMCAT model. Comparisons for the ClO mixing ratio at 480 K are also shown. During mid- to late-winter, the rise of ClO is determined primarily by increasing solar illumination at mid-day. The good agreement between theory and observations of column ClO during this time period suggests that the altitude range over which chlorine is activated is reproduced well by the model. During early spring, the short-term fluctuations in ClO are related to movement of the vortex over Scott Base, and the longer-term decline in ClO is the result of recovery into the reservoirs HCl (the primary sink for ClO_x in the denitrified Antarctic vortex) and $ClNO_3$ (Solomon *et al.*, 2002). As a result of widespread suppression of gas-phase HNO_3 in SLIMCAT, high abundances of ClO are sustained throughout

the early spring season (September) until ozone is nearly completely removed. In October, HCl is observed to reappear much faster than $ClNO_3$ in the core of the vortex due to the shift in partitioning of Cl/ClO and NO/NO_2 to favor Cl and NO driven by exceedingly low ozone, while ClO recovers mainly to $ClNO_3$ in the edge region of the Antarctic vortex (*e.g.*, Douglass *et al.*, 1995; Ricaud *et al.*, 1998). Because most models simulate these features reasonably well, they are able to account for Antarctic ozone loss in a quantitative manner.

The situation for the Arctic winter is quite different, as chemical ozone loss depends more critically upon the details of chlorine activation, deactivation, and the timing of the break-up of the northern polar vortex. During cold Arctic winters, high levels of ClO are observed throughout the polar vortex (Raffalski *et al.*, 1998; Stachnik *et al.*, 1999, Klein *et al.*, 2000; Santee *et al.*, 2000; Stimpfle *et al.*, 2002). Considerably more year-to-year variability is seen in Arctic measurements of ClO compared to Antarctic data, and peak values of Arctic ClO for cold winters are somewhat lower than observed in the Antarctic (Figure 2.2-2). Recent GOME measurements of OClO (Figure 2.3-5), which indicate much greater year-to-year variability in active chlorine for the Arctic as well as considerably higher levels of active chlorine for the Antarctic (Wagner *et al.*, 2001, 2002), provide a picture consistent with the MLS observations of ClO. The GOME observations of Antarctic OClO are also consistent with earlier ground based observations of OClO (Miller *et al.*, 1999).

The MLS and GOME measurements show that elevated levels of ClO_x in the Arctic, even for cold years, decline rapidly in early spring, in contrast to the Antarctic, where high ClO_x persists well into spring (Figures 2.2-2 and 2.3-5). Consequently, the total quantity of ozone destroyed in the Arctic vortex depends strongly on the rate of chlorine deactivation, which in turn is related to the extent of denitrification (*e.g.*, Rex *et al.*, 1997; Waibel *et al.*, 1999; Tabazadeh *et al.*, 2000) and the efficiency of chlorine reactivation (*e.g.*, Solomon, 1999; Hanisco *et al.*, 2002; Drdla and Schoeberl, 2002). Abundances of ClO_x over the Arctic decrease rapidly when temperatures increase above ~200 K, due to photochemical release of NO_x from nitric acid that remains in excess of reactive chlorine throughout the winter. During this recovery period, observations have shown that $ClNO_3$ is the primary inorganic chlorine species, representing >80% of the available chlorine (Chapter 3, WMO 1995). It has long been assumed that chlorine can be readily reactivated on PSCs during this recovery period (provided temperature drops

below ~195 to 200 K), leading to significant additional ozone loss. However, a recent study based on analyses of *in situ* observations of OH and HO_2 (Hanisco *et al.*, 2002) indicates that key heterogeneous reactions that reactivate chlorine proceed more slowly than currently recommended rates. The consequences of this finding have yet to be explored in photochemical model studies of Arctic ozone loss.

New simultaneous remote measurements of the major organic and inorganic chlorine species within the Arctic polar vortex during late autumn 1999, before widespread activation, indicated that abundances of HCl exceeded $ClNO_3$ for air masses that were soon to become activated (Salawitch *et al.*, 2002c). This result differs from that of Webster *et al.* (1993) during the same season in 1991, where HCl abundances were found to be significantly less than half of the available inorganic chlorine (*e.g.*, Figure 3-1 of WMO 1995). Variations in sulfate aerosol loading, which was highly enhanced in 1991 following the eruption of Mt. Pinatubo, may account for the differences in the initial HCl vs. $ClNO_3$ partitioning (*e.g.*, Webster *et al.*, 2000). Most importantly, three dimensional chemistry and transport models (Ricaud *et al.*, 1998; Massie *et al.*, 2000; van den Broek *et al.*, 2000) as well as trajectory simulations (Woyke *et al.*, 1999; Danilin *et al.*, 2000) are able to simulate well the high levels of ClO observed in the Arctic, indicating that chlorine activation schemes used in photochemical models are relatively accurate in describing large-scale features of chlorine activation. Recent model simulations also suggest that the rate and extent of halogen activation in the polar vortex are not as sensitive to PSC composition as previously thought (Carslaw *et al.*, 1997b; Becker *et al.*, 1998; Woyke *et al.*, 1999; Danilin *et al.*, 2000). This lack of sensitivity arises because most heterogeneous halogen activation rates are much faster at low temperatures than deactivation rates of ClO_x for air parcels outside of PSCs (*e.g.*, Solomon, 1999).

While models simulate the seasonal evolution of ClO in the Arctic reasonably well for cold winters, they have some difficulty for warm winters, where minimum temperatures are close to the threshold for formation of PSCs (*e.g.*, Klein *et al.*, 2000). For the winter of 1998/1999, ground-based observations of ClO from Ny Ålesund, Spitzbergen (78.9˚N) revealed little or no enhancements above background levels, whereas the SLIMCAT model predicted ClO mixing ratios as high as 1.0 ppbv. This discrepancy has been attributed to a small cold bias (~1K) in the UKMO temperatures input to the SLIMCAT model (Klein *et al.*, 2000, Knudsen *et al.*, 2002), although it is also possible that the PSC nucleation scheme in SLIMCAT is unrealistic at

temperatures near NAT thresholds. In either case, such a problem highlights the extraordinary sensitivity of Arctic ClO to temperatures and microphysics schemes for winters where the minimum temperatures are very close to the threshold for formation of PSCs.

Chlorine Budget [2.3.1.3]

Ideally, an assessment of the chlorine budget should be based on simultaneous measurements of the primary inorganic (*e.g.*, HCl, $ClNO_3$, ClO, ClOOCl) and organic chlorine species (*e.g.*, chlorofluorocarbons and other chlorine containing halocarbons). Until recently, such a budget for the mid-winter periods of the polar stratosphere had to rely on calculated abundances of ClOOCl because there were no observations of this important reservoir of reactive chlorine. Nonetheless, a significant number of studies (all of which lack observations of ClOOCl) have indicated good agreement between the inorganic and organic chlorine budget for the lower polar stratosphere (*e.g.*, von Clarmann *et al.*, 1995; Engel *et al.*, 1997; Mickley *et al.*, 1997; Ricaud *et al.*, 1998; Michelsen *et al.*, 1999; Pierson *et al.*, 1999; Stachnik *et al.*, 1999; Salawitch *et al.*, 2002c). Analyses of observations of ClO, constrained by the rate parameters for k_{1a} and J_{1b} at values similar to those discussed in the previous section, have inferred that ClOOCl and ClO contain comparable amounts of chlorine during the period of maximum activation (Stachnik *et al.*, 1999; Avallone and Toohey, 2001). Although the rate of cycle (1) (and hence its contribution to ozone loss) can be inferred from measurements of ClO, photolysis of ClOOCl represents the true rate-determining step in this catalytic cycle. Thus, it is important to demonstrate the presence of ClOOCl at abundances necessary to explain observed ozone losses.

The most comprehensive set of measurements to date to assess the chlorine budget was obtained from the NASA ER-2 aircraft during the Arctic winter of 1999-2000. Measurements of ClO, ClOOCl, $ClNO_3$, HCl, and numerous chlorofluorocarbons (CFCs) were all obtained simultaneously on a number of flights during times of rapid chemical loss of ozone. Based on these observations, the sum of concentrations of these major inorganic chlorine species (termed Cl_y^{inorg}) falls about 10 to 25% short of the inorganic chlorine content estimated from measured organic source compounds (termed Cl_y^{org}) (Stimpfle *et al.*, 2002). However, Cl_y^{inorg} and Cl_y^{org} agree within measurement error, so it is unclear whether this discrepancy is significant.

Further insight can be gained from examination of the chlorine budget from other instruments inside the Arctic vortex. These comparisons rely on calculated concentrations of ClOOCl, termed ClOOCl*, assuming a steady state relation with measured ClO. Observations of $[HCl]+[ClNO_3]+[ClO]+2[ClOOCl^*]$ versus N_2O obtained by a balloon Fourier transform infrared (FTIR) instrument near the edge of the Arctic vortex on 15 March 2000 agree well with estimates for Cl_y^{org} (Salawitch *et al.*, 2002c). Additionally, balloon-borne microwave and whole air sampler measurements of $[HCl]+[ClO]+2[ClOOCl^*]$ versus N_2O for air in the core of the Arctic vortex on 27 January 1995 (Stachnik *et al.*, 1999), made under conditions of highly elevated ClO, also agree well with estimates of Cl_y^{org}. These observations support the good understanding of the chlorine budget noted by the other studies cited in the first paragraph of this section, given the caveat that abundances of ClOOCl are based on calculations for all of these studies. Also, these findings are consistent with reasonably good agreement (differences of about ±15%) between the disappearance of organic chlorine and the appearance of inorganic chlorine observed for the summer polar stratosphere (Section 2.4.3), a region of the atmosphere for which the contribution to Cl_y^{inorg} is dominated by HCl and $ClNO_3$.

NOTE: This material may be revised once a paper for the ER-2 measurement of ClOOCl exists. We will not refer to any paper that not has been submitted prior to the Les Diablerets meeting.

2.3.2 BROMINE

Cycle 2 (BrO + ClO) makes important contributions to polar ozone loss. As shown below in Section 2.3.2.1 there is now reasonably good agreement between measurements of BrO obtained by various techniques. This is a significant advance in our understanding because important differences had been noted in the previous assessment (WMO, 1999). This convergence of measurements allows for fairly accurate assessment of the contribution of bromine to chemical loss of polar ozone.

Profiles of inorganic bromine based on measurements of BrO have recently been compared to estimates based on the observed fall off (with increasing height) of the organic source species. These comparisons, discussed in Section 2.3.2.2, show a slight offset that may result from either direct influx of ~3 parts per trillion by volume (pptv) of inorganic bromine

across the tropical tropopause or some organic species not accounted for. Finally, long-term measurements of BrO discussed also in Section 2.3.2.2 have been used to determine trends in total bromine loading that can be compared to trends based on the organic bromine content of the lower atmosphere. (This sentence will have to be modified if the bromine trends material below is removed or greatly altered).

Bromine Monoxide (BrO) Abundances [2.3.2.1]

Harder *et al.* (1998) compared *in situ* BrO measurements from the ER-2 aircraft and a balloon flight with profiles of BrO obtained by the Differential Optical Absorption Spectroscopy (DOAS) technique (Figure 2.3-6). There is a systematic difference in these two sets of observations, where DOAS is somewhat larger than *in situ*, although this is within the combined uncertainties of the measurements. Consequently, the estimates of the inorganic bromine budget based on these sets of measurements have ranged from ~16 pptv (*in situ*) to ~20 pptv, (DOAS) (Avallone *et al.*, 1995; Pfeilsticker *et al.*, 2000). It is important to note that, because these sets of observations were obtained 5 years apart, more than half of this difference can be explained by trends in the bromine source gases, as discussed below.

Sinnhuber *et al.* (2002) compared ground-based zenith sky measurements obtained at eleven sites to simulations from the SLIMCAT model in an effort to examine the detailed processes that govern the partitioning of BrO. Comparisons for three sites are shown in Figure 2.3-7. The simulated abundances of BrO generally agree to within ~10% of the observations over a wide range of seasons, latitudes, and solar zenith angles. The results are consistent with a total stratospheric bromine loading (sum of organic and inorganic) of 20±4 pptv, in agreement with the values deduced from previous remote measurements of BrO.

The SLIMCAT model tends to overestimate BrO column abundances at high latitudes, typically when ClO abundances are elevated (Figure 2.3-7). Conversely, Friess *et al.* (1999) find a discrepancy in the opposite sense between BrO slant column measurements made at Kiruna, Sweden (67.9˚N) in winter and SLIMCAT model calculations that use JPL 97-4 kinetics (DeMore *et al.*, 1997) and a bromine loading of 20 pptv (the model underestimates midday measured BrO columns by 20 to 40%). Sinnhuber *et al.* (2002) note that the discrepancy highlighted in their study can be reduced by increasing the rate constant for reaction (2a_) to the upper limit of the uncertainty of the Sander *et al.* (2000) recommendation. Friess *et al.* (1999),

however, report that the discrepancy they found is evidence for several pptv of BrO in the free troposphere. The Friess *et al.* (1999) interpretation is consistent with interpretations based on other remote observations of BrO (*e.g.*, Harder *et al.*, 1998; Fitzenberger *et al.*, 2000).

The discrepancies outlined above have a relatively minor impact on ozone loss rates calculated directly from cycle (2) or on observed abundances of ClO and BrO in the polar vortices. However, they do raise questions about the completeness of our understanding of coupled bromine/chlorine chemistry. Similar questions have been raised based on aircraft observations of BrO at 20 km (*in situ*) and 12 km (remote) within the perturbed polar vortex. Specifically, Avallone and Toohey (2001) report that mixing ratios of BrO did not drop to near-zero as expected with increasing SZA after sunset, when reservoir species like bromine nitrate ($BrNO_3$), bromide chloride (BrCl), and hypobromous acid (HOBr) are expected to sequester nearly all available reactive bromine. Similarly, Wahner and Schiller (1992) previously reported non-zero BrO column abundances above 12 km in darkness that were difficult to explain. Avallone and Toohey (2001) suggest that thermal decomposition of a weakly bound molecule, such as BrOOCl, may be able to maintain a few pptv of BrO following sunset, but note that such a process would have little impact on ozone loss rates because of the rapid decline of ClO at sunset. The existence of adducts of bromine and chlorine oxides has been postulated in theoretical studies (Gleghorn, 1997; Bridgeman and Rothery, 1999; Gomez and Pacios, 1999; Papayannis *et al.*, 2001) and has been observed in an argon matrix (Johnsson *et al.*, 1995).

The previous assessment noted the spectroscopic detection of OBrO in the mid-latitude stratosphere, with implied mixing ratios as high as 20 pptv (Renard *et al.*, 1997). As such, OBrO would be the dominant nighttime reservoir for inorganic bromine in the mid-latitude stratosphere. The same group has since reported the presence of smaller amounts of OBrO in the nighttime, polar stratosphere (Renard *et al.*, 1998). However, abundances of even a few hundredths of a ppt of OBrO in the nighttime stratosphere are contrary to our present understanding of bromine photochemistry (Chipperfield *et al.*, 1998). Erle *et al.* (2000) recently reported measurements of upper limits for OBrO that are appreciably smaller than values observed by Renard *et al.* (1997, 1998), indicating that one of the sets of observations are in error or that abundances of OBrO are highly variable. The explanations for non-zero BrO mixing ratios in darkness and possible detection of OBrO remain a mystery.

Bromine Trends and Budget [2.3.2.2]

Will need work based on lack of accepted papers by 7/02.

During the Arctic winter of 1998/1999, vertical profiles of all known major organic bromine species were measured between 9 and 28 km (Pfeilsticker *et al.*, 2000) (Figure 2.3-8). The expected profile for inorganic bromine that was inferred from the source gases agrees well (*i.e.*, differences are within the measurement uncertainties) with a second profile that was estimated from spectroscopic observations of BrO and a photochemical model estimate of the BrO/Br_y ratio (see Figure 2.3-8) (Pfeilsticker *et al.*, 2000). This result indicates that the budget of bromine and its photochemistry in the lower stratosphere are reasonably well understood. For early 1999, the mixing ratio of total bromine estimated at 25 km in air of 5.6-year mean age was 18.4 (+1.8, -1.5) pptv based on organic precursor measurements, and 21.5 ± 3.0 pptv from BrO measurements. This slight offset allows for the possibility of a bromine influx of 3.1 (-2.9, +3.5) pptv from the troposphere to the stratosphere (Pfeilsticker *et al.*, 2000).

Remove some of the text below, unless we can refer to the EU Assessment? Also, the Toohey *et al.*, 2002 paper must be submitted in order to stay in the text below.

Attempts to quantify temporal trends in inorganic bromine in the stratosphere traditionally have been hampered by the lack of long-term observations and the relatively small quantities (~10 pptv or less) of the bromine species. Two groups have recently examined different data sets that may shed some light on this issue, which is important in the context of polar ozone loss because the source of bromine to the stratosphere is expected to have increased by nearly 30% over the past decade (Wamsley *et al.*, 1998).

Pfeilsticker *et al.* (see Figure 2.12, EUR19867, 2001) have taken the approach of examining the fall-off of total bromine with altitude, deduced from measurements of BrO. They rely on separate measurements of carbon dioxide (CO_2) or sulfur hexafluoride (SF_6) and model simulations to determine the age of air versus altitude. Their results are consistent with a rate of increase of total bromine of about 0.7 pptv/year over the period 1995-2000. Using BrO observations at 20-22 km from the Arctic polar vortex when simultaneous measurements indicate high (> 1 ppbv) mixing ratios of ClO, Toohey *et al.* (2002) report that BrO increased about 30 to 40% over the period 1989-2000, consistent with the trends in organic source gases reported by Wamsley *et al.* (1998). Assuming a budget of ~20 pptv for total bromine, these results imply a

rise rate of about 0.5 to 0.7 ppt/year, in good agreement with the results presented by Pfeilsticker *et al.* (see Section 2.3.2, EUR19867, 2001).

These results suggest that the contribution of bromine to ozone loss in the polar regions has increased faster than that of chlorine due to abundances of bromine that continue to increase at a time when those of chlorine are leveling off (see Chapter 1). Model studies indicate that catalytic cycles involving BrO account for as much as 60% (depending on abundances of ClO and temperatures) of the total chemical loss of ozone in the Arctic for cold winters (Chipperfield and Pyle, 1998). The contribution of BrO reactions to the total loss of Antarctic ozone is somewhat less than for the Arctic due to lower temperatures and widespread denitrification in the SH vortex. However, since ozone loss by the BrO cycle also depends on ClO, future major declines in Cl_y are expected to lead to reductions in chemical loss of polar ozone essentially independent of changes to Br_y (Chipperfield and Pyle, 1998).

2.4 The Polar Summer Lower Stratosphere

In both hemispheres, the annual cycle of total ozone has a strong decrease from the spring maximum to a minimum by mid-fall (*e.g.*, Dobson, 1966; Dütsch, 1974; Bowman and Krueger, 1985). Column abundance of ozone declines by ~35% at high northern latitudes during summer (Toon *et al.*, 1999; Lloyd *et al.*, 1999). The rate of chemical ozone destruction in late spring/early summer is as large as in the polar stratosphere. This large decline, and the fact that the summer circulation is weak and quite zonally symmetric, makes the summer period a good test of understanding. Models typically have been unable to capture the full magnitude of the decline. To address this issue the POLARIS experiment was flown from Fairbanks, AK, with three deployments during the early spring, summer, and early fall of 1997. This mission examined the seasonal ozone decrease using a complete payload of instruments aboard the NASA ER-2 high altitude aircraft (Newman *et al.*, 1999).

The summer lower stratosphere is mixed vigorously by waves which penetrate in the presence of the weak summer westerlies (Wagner and Bowman, 2000). Orsolini (2001), however, has shown that remnants of polar vortex air can retain their identity until well into the summer in the lower stratosphere. Rosenlof (1999) has studied the annual cycle of ozone transport in high northern latitudes. She found that the seasonal cycle in transport was an important contributor to the seasonal march of ozone at high latitudes during middle to late

summer, with the eddy contribution to ozone reduction more than offsetting the ozone increase by advection at this time. In early summer transport is weak and *in situ* photochemical destruction dominates the ozone tendency. In contrast, Pierce *et al.* (1999) using a Lagrangian model with HALOE data found that the transport term was important

In situ measurements of NO_x, HO_x, and ClO_x radical species (Fahey *et al.,* 2000) and long-lived tracers of stratospheric transport (Toon *et al.,* 1999) confirm the summertime loss of ozone is due primarily to the gas-phase catalytic cycle:

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + O &\rightarrow NO + O_2 \\ \text{Net: } O + O_3 &\rightarrow 2\,O_2 \end{aligned}$$

Fahey *et al.* (2000) calculated the ozone chemical tendency based on measurements of radicals from the major families and found that chemical processes dominate overall tendency in the mid-summer. Although this ozone loss process is generally understood (Brühl *et al.,* 1998), ozone abundances calculated using two- or three-dimensional models tend to exceed observations for high-latitude summer (*e.g.,* Chipperfield, 1999). This discrepancy has been attributed to inadequacies in model transport (*e.g.,* Fahey and Ravishankara, 1999).

New measurements of NO_x, HO_x, and ClO_x species in the summer polar stratosphere have provided quantitative tests of our understanding of processes that regulate the abundance of radicals in each family. Measurements in the summer polar stratosphere are particularly useful because heterogeneous reactions, normally the dominant loss process for NO_x, proceed at slower rates than gas phase loss reactions due to uninterrupted periods of solar illumination that restrict the build-up of N_2O_5 (*e.g.,* Gao *et al.,* 1999; Osterman *et al.,* 1999). In the sections which follow, we briefly assess recent advances in our understanding of stratospheric photochemistry based on these observations.

2.4.1 SUMMERTIME NO_x CHEMISTRY

Observations of NO, NO_2, HNO_3, and NO_y obtained in the summer polar stratosphere revealed higher levels of NO_x (relative to total NO_y) and NO_2 (relative to HNO_3) than could be accounted for by constrained photochemical box models using the JPL 97-4 set of recommended kinetic parameters (Gao *et al.,* 1999; Jucks *et al.,* 1999; Osterman *et al.,* 1999; Cohen *et al.,*

2000; Perkins *et al.*, 2001) (Figure 2.4-1). During polar summer, production and loss of NO_x are regulated primarily by the OH + NO_2 and OH + HNO_3 reactions for a broad range of altitudes (*e.g.*, Osterman *et al.*, 1999). New laboratory data for OH + NO_2 (Dransfield *et al.*, 1999; Brown *et al.*, 1999a) and OH + HNO_3 (Brown *et al.*, 1999b) led to a re-evaluation of the rate constant for both of these reactions in the JPL 00-3 compendium. Use of the JPL 00-3 kinetic parameters significantly improves the agreement between measured and modeled ratios of NO_x/NO_y and NO_2/HNO_3 (Gao *et al.*, 1999; Jucks *et al.*, 1999; Osterman *et al.*, 1999; Cohen *et al.*, 2000; Perkins *et al.*, 2001; Salawitch *et al.*, 2002b) (Figure 2.4-1).

Simultaneous measurements of NO, NO_2, O_3, ClO, and HO_2 during polar summer provide a stringent test of our understanding of the rapid photochemistry linking NO to NO_2 (Del Negro *et al.*, 1999). Photolysis rates for NO_2 (J_{NO_2}) inferred from the chemical measurements are in excellent agreement with values calculated with radiative models and those measured with a spectroradiometer (Del Negro *et al.*, 1999). Recently, this comparison has been extended to larger SZAs of 80 to 93˚ (Gao *et al.*, 2001a). Values of J_{NO_2} derived from the *in situ* chemical measurements agree well (differences < 11%) with results from a multiple scattering actinic flux model. The linearity of the correlation between these two computations of J_{NO_2} over the SZA range 80 to 93˚ demonstrates the model scattering calculation is accurate for twilight conditions (Gao *et al.*, 2001a).

Loss of ozone by NO_x chemistry in the summer polar regions may become more important in the future due to rising levels of NO_2 (Liley *et al.*, 2000; McLinden *et al.*, 2001). Nitrous oxide (N_2O), the source gas for NO_x and NO_y, is rising at about 3% per decade (*e.g.*, McLinden *et al.*, 2001). Interestingly, concentrations of NO_2 at Southern Hemisphere mid-latitudes have been observed to be increasing at a faster rate of 5% per decade (Liley *et al.*, 2000). This increase has been interpreted as being due to rising N_2O as well as declining levels of O_3, which alters the NO/NO_2 partitioning and the diurnal variation of NO_x (McLinden *et al.*, 2001).

2.4.2 SUMMERTIME HO_x CHEMISTRY

Measurements of OH and hydroperoxyl radical (HO_2) in the high latitude stratosphere during spring provide an important test of our understanding of twilight sources of HO_x because

abundances of these species are nearly in photochemical steady state under the slowly varying SZA conditions up to 93˚. Observed abundances of OH and HO_2 in the lower stratosphere significantly exceeded those from standard model calculations for SZA > 85˚ (Wennberg *et al.*, 1999); agreement is much better at lower zenith angles. The high zenith angle discrepancy is larger than can be explained by any reasonable adjustments to the rate of bromine nitrate ($BrNO_3$) hydrolysis and /or assumptions regarding Br_y (Salawitch *et al.*, 2002b). The data suggest the presence of a photolytic source of HO_x that operates more efficiently than known HO_x sources during twilight (Wennberg *et al.*, 1999). Including a photolytic pathway for photolysis of HNO_4 via excitation of purely vibration modes longward of 760 nm (the near IR) based on recent laboratory measurements (Roehl *et al.*, 2002), a process first suggested by Donaldson *et al.* (1997), leads to significant improvements in measured and modeled HO_x near twilight due to the rapid photolysis of HNO_4 (Salawitch *et al.*, 2002b). This process also reduces the efficiency of the OH+HNO_4 sink of HO_x, altering the coupling between NO_x and HO_x in stratospheric and upper tropospheric models (Salawitch *et al.*, 2002b). The global implications of this process have yet to be evaluated.

Balloon-borne observations of OH, HO_2, H_2O, and O_3 obtained over Fairbanks, Alaska suggest important gaps in our understanding of several HO_x reactions (Jucks *et al.*, 1998). Discrepancies between measured and modeled abundances of OH and HO_2 are reduced with a ~25% downward adjustment of the ratio of the rate constants for atomic oxygen (O) + HO_2 and O + OH and either a 25% reduction to the rate constant for OH + HO_2 (the primary HO_x sink) or a 25% increase in the HO_x production rate (Jucks *et al.*, 1998). These modifications are within the uncertainties of the laboratory measurements and are consistent with the results of HO_x model/measurement studies discussed in the previous assessment. The new insight provided by the simultaneous observations of OH and HO_2 is that the required modifications to the rate constants appear not to appreciably affect odd oxygen production rates in the upper stratosphere (Jucks *et al.*, 1998).

2.4.3 SUMMERTIME Cl_y CHEMISTRY

The first *in situ* observations of $ClNO_3$ were obtained in the high-latitude stratosphere during the summer of 1997 (Stimpfle *et al.*, 1999). These observations are in good agreement

with values of $ClNO_3$ determined using a photochemical steady state relation constrained by simultaneous observations of [ClO] and [NO_2] (ratio of measured to modeled $ClNO_3$ is 1.15±0.36). These results, together with a study that used balloon-borne remote measurements (Sen *et al.,* 1999), confirm the photochemical mechanism by which abundances of NO_x regulate the abundance of ClO in regions of the stratosphere that are NO_x-limited (*i.e.*, mixing ratio of NO_x > mixing ratio of ClO_x).

Simultaneous observations of $ClNO_3$ and HCl from a balloon (Sen *et al.,* 1999) and the ER-2 aircraft (Voss *et al.,* 2001) test our understanding of the kinetic processes that regulate the partitioning within the inorganic chlorine (Cl_y) family. Model calculations using JPL 00-3 recommendations agree extremely well with the balloon-borne remote observations of both $ClNO_3$ and HCl (Figure 2.4-2), whereas the aircraft *in situ* measurements of the ratio [$ClNO_3$]/[HCl] are ~55 to 60% lower than values based on a steady-state calculation (Voss *et al.,* 2001). This discrepancy has not been resolved and is the subject of ongoing investigations.

Simultaneous observations of the major inorganic and organic chlorine species in the summer polar stratosphere provide a test of the chlorine budget. The observed increase in the inorganic chlorine content (*e.g.,* HCl+$ClNO_3$+HOCl+ClO) of stratospheric air with decreasing N_2O from both the ER-2 and MkIV agrees well (differences less than ~10%) with estimates of inorganic chlorine based on the observed disappearance of organic source molecules (Sen *et al.,* 1999; Bonne *et al.,* 2000) (Figure 2.4-2). However, the ER-2 based estimate of inorganic chlorine is ~15% less than the MkIV estimate for mixing ratios of N_2O below about 175 ppbv. This offset is probably due to differences in the measurements of $ClNO_3$ noted in the previous paragraph. These results extend the conclusions of the previous assessment regarding the good quantitative link between abundances of inorganic chlorine species and their halogen sources to a new region of the atmosphere (*i.e.,* polar summer) and to a new class of observations (*i.e., in situ*). These findings are particularly relevant for the discussion of the chlorine budget for the winter polar stratosphere (Section 2.2.1.3).

3 QUANTIFICATION OF POLAR OZONE LOSS: OBSERVATIONS AND MODELS

Quantification of the degree of chemical ozone loss in the polar stratosphere is hampered by the pronounced dynamically induced variability of the ozone layer in these regions in winter/ spring. Precise quantification of the chemically induced contribution to observed changes in the ozone abundance are particularly difficult in the Arctic stratosphere, where the degree of ozone loss is smaller and the dynamic activity is more pronounced than in the Antarctic. Over the last decade a number of approaches have been developed to overcome these difficulties. Major challenges of recent years have been to (a) assess how reliable the results of these approaches are and hence how precise current estimates of the degree of Arctic ozone losses are, and (b) determine whether the degrees of ozone losses calculated by up to date chemical models agree with the observational results within the combined uncertainties of the models and the observations. The latter question is crucial to assess our current ability to make projections of future polar ozone losses in a potentially colder stratosphere.

Severe Arctic ozone loss has been reported for some recent cold Arctic winters. No significant loss was found during warmer winters. Overwhelming evidence exists that large Arctic ozone losses were the result of increased levels of radical halogen species that resulted from heterogeneous chemical processing on the surface of Polar Stratospheric Clouds (WMO 1998, c.f. also Section 2). About 80 % of the stratospheric chlorine and bromine loading are of anthropogenic origin. Since the relevant ozone destruction cycles are linear to quadratic in the concentration of active chlorine, by far the largest fraction of the ozone losses discussed in this section is anthropogenic. However, no quantitative study exists to precisely quantify the small degree of ozone loss that would be expected in a cold Arctic winter for natural levels of halogens in the stratosphere.

3.1 Approaches to Quantify Chemically Induced Ozone Loss in the Arctic

Two principal techniques are currently used to quantify chemically induced ozone losses in the Arctic:

1. Studies that take into account the effect of transport explicitly by using transport calculations based on meteorological analyses, or

2. Studies that allow for transport effects implicitly by using the relation between ozone and a long lived chemical tracer.

In the following the approaches that have been used in a consistent way for several winters are briefly assessed.

3.1.1 APPROACHES THAT USE EXPLICIT TRANSPORT CALCULATIONS

Bulk Advection [3.1.1.1]

In this section approaches are assessed that use explicit transport calculations to advect bulk quantities like vortex averages or gridded ozone fields and compare these with later measurements of ozone, a concept first published by Manney *et al.* (1994).

The 'vortex average' technique involves analysis of the temporal evolution of the mean profile of ozone within the polar vortex on surfaces of potential temperature. Ozone measurements by ozone sondes (*e.g.,* Knudsen *et al.,* 1998; Rex *et al.,* 1998; Lucic *et al.,* 1999) or a remote sensing instrument, *e.g.,* the POAM II satellite instrument (Bevilacqua *et al.,* 1997) have been analyzed with this approach. The boundary of the polar vortex is usually defined by isolines of potential vorticity. Potential temperature and potential vorticity are conserved quantities in the polar stratosphere over time scales of a couple of weeks, so this coordinate system largely eliminates variability due to rapid and reversible dynamics. The slow irreversible descent of air across surfaces of potential temperature is usually accounted for by a diabatic correction calculated from descent rates using a radiative transfer model that is based on temperatures from a meteorological assimilation system. In the absence of mixing across the vortex edge, changes in ozone can be attributed to chemical loss. The largest uncertainties connected with this approach are (a) possible mixing across the vortex edge, that may impact the average ozone abundance inside the polar vortex, (b) any bias in sampling of the vortex that changes with time may lead to changes in the derived vortex average, since ozone is not uniform within the vortex, and (c) uncertainties in the calculated diabatic corrections. Knudsen *et al.* (1998) used an approach based on domain filling trajectory calculations to estimate the effect of mixing across the vortex edge for the Arctic winter 1996/1997. For this winter at the altitude of the maximum loss they found an insignificant impact of mixing on the ozone loss derived from the vortex average technique.

In the 'transport model' approach a 3-D Chemical Transport Model (3-D-CTM) is initialized with ozone observations during the early winter period. The model advects ozone passively, *i.e.*, without chemical conversion, throughout the winter, using analyzed winds and, depending on the vertical transport scheme in the model, also temperatures. Ozone measurements throughout the winter are compared with the passively advected ozone. Evolving deficits between observed ozone and the model passive ozone indicate chemical loss. This approach has been used with the REPROBUS model using data from the POAM satellite instruments and from the ground based network of Système d'Analyse par Observation Zénithale (SAOZ) instruments (*e.g.,* Lefèvre *et al.* 1998; Goutail *et al.* 1999; Deniel *et al.* 2000). Hansen *et al.* (1997); Guirlet *et al.* (2000); and Sinnhuber *et al.* (2000) have used this approach with the SLIMCAT model, using ozone lidar data, SAOZ data and ozone sonde data respectively. This approach relies on the assumption that the model transport scheme realistically represents the transport of air over a time period of several months. But when the derived ozone loss is averaged over the polar vortex as is the case in many studies, the approach only depends on a correct representation of average transport properties like *e.g.,* vortex averaged vertical subsidence and average rates of exchange of air across the vortex edge. Possible systematic errors in these average properties are the largest source of uncertainty in the transport model approach. Another source of concern is the initialization of the model ozone with data from a different type of instrument (usually measurements of the HALOE or MLS satellite instruments) than is used for the ozone observations later on. Systematic discrepancies between the different instruments make altitude dependent correction factors necessary, that are often in the order of 5% which is a substantial fraction of the ozone changes observed over the course of warmer Arctic winters. The method is sensitive to the vertical variation of the correction, because early winter measurements from one instrument at higher altitude are compared with late winter measurements from another instrument at lower altitude.

Manney *et al.* (*e.g.*, 1995a, b, 1996a, b, 1997) used a similar approach based on 'trajectory ensemble' calculations to analyze ozone data of the Microwave Limb Sounder (MLS) on the UARS satellite. Trajectory calculations are started at all points on the gridded MLS data and are run forward in time for a few weeks. Succeeding MLS measurements are interpolated to the locations of the trajectories. Differences in ozone are attributed to chemistry. The results are stated as vortex averaged ozone loss or are analyzed versus equivalent latitude, PV, etc. During

one north looking yaw cycle continuous time-series of ozone loss can be derived, accumulated losses are stated for the south looking yaw cycles, when measurements in the Arctic are not available. Schoeberl *et al.*, (2002) used trajectory ensemble calculations to advect early winter ozone observations throughout the winter and comparing it to succeeding ozone observations. Again the advected and the observed ozone fields are averaged over the polar vortex before they are compared, thus reducing the sensitivity of the approach to transport features of individual air masses. The trajectory ensemble approach uses 3-D trajectory calculations that are several months long for the advection. By using trajectories instead of a grid point advection scheme, any potential bias due to numerical diffusion of the advection scheme is eliminated. The largest uncertainty of the trajectory ensemble method comes from possible systematic biases in the long term trajectory calculations, *e.g.*, due to possible uncertainties in the vertical transport, that is based on calculated diabatic descent rates.

Lagrangian Ozone Measurements (Match) [3.1.1.2]

'Match' is a Lagrangian technique to determine the rate of chemical ozone loss. In active Match campaigns ozonesonde launches from a large network of about 35 ground stations are coordinated in real time to probe individual air masses twice over an interval of a few days (so called 'match events,' *e.g.*, von der Gathen *et al.*, 1995; Rex *et al.*, 1997, 1998, 1999b, 2002a). The coordination is based on calculations of air parcel trajectories that allow for diabatic descent. Several hundreds to more than a thousand ozonesondes are launched in a Match campaign, typically producing several match events per sonde, each at a different altitude and with different soundings as respective first measurement of the air mass. The coordination results in hundreds to thousands match events per winter. Chemical ozone loss rates are derived from a statistical analysis of subsets of match events from a certain time period (typically 14 days long) and altitude region (typically 20 K broad) by calculating linear regressions of the difference in ozone between both measurements and the sunlit time that the air mass encountered. The overall ozone loss during the winter is calculated by accumulating the measured loss rates. A similar approach has been used by Sasano *et al.* (2000) and Terao *et al.* (2002) to analyze the ozone measurements from the ILAS satellite instrument.

The largest uncertainties in this method are possible systematic errors in the trajectory calculations including the calculated diabatic subsidence rates. Individual Match events depend

on a correct representation of the motion of individual air masses by the trajectories. Therefore the length of the trajectory calculations used in Match is limited to 10 days and the majority of the Match events relies on ~5-7 days trajectories. But ozone loss rates are calculated in a statistical process from subsets of several tens of Match events, so that the derived average ozone loss rates are only sensitive to systematic trajectory errors, *e.g.*, possible systematic biases in the calculated diabatic descent rates. A statistical analysis of the data shows that observed ozone losses occur exclusively during sunlit periods along the trajectories. This suggests that any systematic biases in the trajectory calculations, if present, are so small that they do not significantly affect the derived ozone loss rates (*e.g.*, Rex *et al.*, 1998, 1999b, 2002b).

3.1.2 Approaches that Use the Relation of Ozone to an Inert Tracer

In mid-winter ozone abundances inside the polar vortex show a relatively compact relation to abundances of many long-lived tracer species such as N_2O or CH_4. In the absence of mixing any reduction of ozone versus an inert tracer indicates chemical loss of ozone. This approach has first been used by Proffitt *et al.* (1990). More recently early winter and late winter measurements of ozone, N_2O, CH_4 and HF by the HALOE satellite instrument have been used to identify chemical loss of ozone during various winters (*e.g.*, Müller *et al.* 1996, 1997). The evolution of the ozone versus N_2O relation through the winter 1999/2000 was studied using data from in-situ instruments on board of two balloon borne platforms and the high altitude aircraft ER-2 (Salawitch *et al.*, 2002a; Richard *et al.*, 2001).

Two fundamental issues have been brought up regarding the validity of the tracer relation approach. First, the existence of a compact universal relation between ozone and inert tracers has been questioned, and second the impact of mixing on results from ozone versus tracer relation studies has been discussed. Here we assess the current status of the discussion on these two points.

During polar summer the chemical lifetime of ozone in the middle and upper stratosphere is comparable or shorter than transport timescales, so the ozone-tracer relationship in the Arctic stratosphere in fall is not expected to be compact and universal (Plumb and Ko, 1992). But in fall the lifetime of ozone in the middle and lower stratosphere gets sufficiently long and it can be expected that mixing within the early polar vortex leads to compacting of the ozone-tracer relations inside the vortex. These slowly evolving more compact relations inside the vortex are

quite different from the extra vortex relations, with less ozone at a given tracer level than outside. The degree of compactness and the definition of this inner vortex 'early winter relation' is critical for the validity of the tracer relation approach. Richard *et al.* (2001) and Salawitch *et al.* (2002a) used initial O_3 versus N_2O reference relations measured well inside the polar vortex in mid-winter (December/early January). They showed that these relations were sufficiently compact and representative of initial conditions inside the polar vortex, an essential condition for the validity of the approach. But observations of the O_3 versus CH_4 relation measured well inside the Arctic vortex in mid-winter for 1999/2000 were significantly lower (differences of O_3 of ~1.5 parts per million by volume (ppmv) for values of $CH_4 \approx 0.5$ ppmv) than the suite of initial HALOE based reference relations (Müller *et al.*, 1999 and references therein) measured in the vortex edge region in October for earlier Arctic winters (Salawitch *et al.*, 2002a). The validity of these early winter HALOE reference relations is currently the subject of numerous on-going investigations. Generally results from the tracer relation approach are more reliable when the initial reference relation is measured late (*i.e.*, December / early January) and deep inside the vortex.

The second issue brought up regarding the validity of tracer relation studies is related to mixing. These considerations apply also for studies that assess the degree of denitrification based on changes in the otherwise very compact relation between NO_y and N_2O. If the relation between two tracers is curved, as is the case for both these relations, the results of the tracer relation approach can be compromised by mixing between air masses that are widely separated in tracer space (*e.g.*, Waugh *et al.* 1997, Michelsen *et al.*, 1998; Rex *et al.*, 1999a; Plumb *et al.*, 2000; Ray *et al.*, 2002). Isentropic mixing across the edge of the polar vortex or mixing of air masses inside the vortex that underwent different descent during the winter are examples for such long range mixing in tracer space. Furthermore the ozone / tracer relations inside the vortex are different from the relation outside of the polar vortex. After substantial ozone loss these differences can be very pronounced (several ppmv). Hence, any mixing across the vortex edge directly impacts the ozone / tracer relation inside of the vortex and could represent a potential source of uncertainty for the tracer relation approach.

One can attempt to distinguish mixing and chemical ozone loss (or denitrification) by using simultaneous measurements of two long-lived tracers (*e.g.*, CH_4 and N_2O) to estimate the impact of mixing (Rex *et al.*, 1999a). However, this method is dependent on the assumption that there

had been a single mixing event after the bulk of the descent and is not applicable if there is intermittent mixing at descent (Plumb *et al.* 2000). A more general approach is the use of a linear combination of several long-lived tracers to form an artificial tracer that has a compact and linear relationship with O_3 (or NO_y) (Esler and Waugh 2002). Due to its linearity this artificial relation is unaffected by mixing within the vortex, so deviations from this relationship can be more directly attributed to chemical ozone loss (denitrification). But mixing across the edge of the vortex edge is still a source of uncertainty, because the outside vortex relations are often different from the inside relations (for ozone versus N_2O this is always the case, for NO_y versus N_2O this is the case after denitrification inside of the vortex). These attempts to correct for the impact of mixing in tracer relation studies were mainly focused on studies that used the relation of NO_y versus N_2O to assess denitrification.

Salawitch *et al.* (2002a) noted that considerations that are valid for the NO_y versus N_2O relation (*e.g.*, the relation χ_2 versus χ_1 in Plumb *et al.* (2000) resembles NO_y versus N_2O) should not be applied to the interpretation of the ozone versus N_2O relation in the vortex, because ozone mixing ratios, unlike NO_y, do not approach zero at the top of the vortex due to the influence of photochemistry at 40 km. Hence the curvature of the ozone versus N_2O relation for low N_2O (*i.e.*, N_2O between 10 and 40 ppbv) is much less pronounced than that of NO_y versus N_2O and mixing can not lead to the observed changes in the ozone tracer relations that have been observed *e.g.*, by HALOE. More quantitatively simultaneous measurement of multiple long-lived tracers have been used to argue that the impact of mixing on estimates of chemical ozone loss by the tracer relation approach for the Arctic winter of 1999/2000 was negligible. Based on the temporal evolution of CO_2, CFC-11, N_2O, and O_3 within the vortex Richard *et al.* (2001) and Salawitch *et al.* (2002a) demonstrated that the vast majority of the observed changes in the O_3/N_2O relations were due to chemistry and could not have been caused by dynamics. The isolation of the Arctic vortex for this winter was also noted by a multivariate analysis of the time evolution of nearly a dozen tracers with varying lifetimes (Ray *et al.*, 2002). Rex *et al.* (2002a) showed that during January to March 2002 any mixing across the vortex edge would have led to an underestimation of the ozone loss by tracer relation studies, so that the results of tracer relation studies that rely on initial relations from early January can be regarded as conservative estimates of the loss. These results from the Arctic winter of 1999/2000 support the validity of

the tracer relation approach, provided the reference relation is defined in mid-winter, but it is currently not clear whether these results can be applied to other, more dynamically active winters (*e.g.*, Salawitch *et al.* 2002a).

3.2 Arctic Ozone Loss during the Last Decade

Since WMO (1998) a number of approaches to quantify the degree of chemical ozone loss in the Arctic have been used in a consistent way for several winters during the 1990s. Due to these long-term efforts the extent and the variability of Arctic ozone losses is now well characterized for the last ten years. Several techniques have revealed a large interannual variability of chemical ozone losses in the Arctic.

3.2.1 Ozone Loss Rates near the Maximum of the Ozone Concentration

The Match approach was used consistently over the last decade to study the evolution of chemical ozone loss at about 475 K potential temperature (~19 km altitude). At polar latitudes this level is close to the maximum concentration of ozone in the ozone layer. Figure 3-1 shows the measured ozone loss rates for the winters 1991/1992 to 2000/2001 (compilation of Match results based on Rex *et al.*, 1997, 1998, 1999b, 2002a; Schulz *et al.*, 2000, 2001). Little or no significant ozone loss was observed in 1997/1998 and 1998/1999. The accumulated ozone loss during the winter was particularly large in 1995/1996 and 1999/2000, when relatively large loss rates have been sustained for extended periods of time. The chemical ozone loss rate in the Arctic stratosphere is clearly controlled by temperature. Blue shaded areas in Figure 3-1 indicate the geographical areas (A_{PSC}) where temperatures have been below T_{PSC} (the NAT equilibrium temperature based on 5 ppmv water vapor and an average HNO_3 profile based on measurements; T_{PSC} is a convenient threshold that roughly indicates the onset of rapid heterogeneous chemistry in the stratosphere, independent of the actual composition of the PSCs). All periods of rapid chemical ozone loss in Figure 3-1 are associated with preceding large values of A_{PSC}. No significant chemical loss of ozone has been observed in warm winters, when T_{PSC} was not or only barely reached.

3.2.2 VERTICAL PROFILES OF OZONE LOSS

The determination of vertical profiles of ozone loss requires ozone losses quantifications in a broad altitude range. Ozone loss observations are typically most reliable at levels around 475 K. Below 400 K or above 550 K the uncertainty of observational studies is typically significantly larger. The problems at lower levels are (a) a strong vertical gradient in the average ozone mixing ratio profile largely amplifies the uncertainty introduced by diabatic descent, and (b) larger small scale dynamical activity (the presence of higher wave numbers) makes explicit transport calculations less reliable and leads to larger degrees of mixing, which is problematic for all approaches. Above 550 K average poleward motion and influx into the polar vortex, followed by mixing, is the main problem. The strong diabatic descent at higher altitudes causes additional uncertainty only in winters when the vertical gradient in the average ozone mixing ratio profile is significant at these levels, which is not always the case (*e.g.*, compare 1998/1999 with 1997/1998 in Figure 3-2).

Figure 3-2 shows ozone losses derived from the vortex average approach in the vertical region between Θ=360 and 570 K (update from Rex *et al.* (2002a) for various winters). Results at the lowest and highest levels shown are less reliable. It is based on several hundred ozonesonde measurements per winter inside the vortex from a network of about 35 sounding stations. The vortex-averaged ozone profiles have been plotted against the 'spring-equivalent potential temperature,' eΘ, which is the potential temperature that a given air mass reached at the end of March due to diabatic subsidence. By using eΘ, which is a conserved quantity, diabatic effects are accounted for. In the absence of mixing across the vortex edge, any change in the vortex-averaged ozone versus eΘ profile indicates chemical loss of ozone. In Figure 3-2 the large interannual variability of the ozone loss stands out. During winter 1998/1999 no significant loss of ozone was found at any part of the profile. In contrast, the loss of ozone in 1999/2000 exceeded 70% in a ~1 km thick region centered around 460 K. This local loss is slightly more than in any previous Arctic winter, with 64% local loss in winter 1995/1996 as the previous record. However, in 1995/1996 ozone loss occurred over a broader vertical region (*e.g.*, ozone loss of more than 1 ppmv occurred between ~390-530K in 1995/1996, compared to ~420-510 K in 1999/2000), so that the vertically integrated losses in both years are comparable.

The average value of APSC ($\overline{A}_{PSC}$), averaged from mid-December to end of March between 400 and 550 K potential temperature is given in Figure 3-2. Figure 3-3 shows the relation between $\overline{A}_{PSC}$ and the average accumulated ozone loss between 400 and 550 K eΘ. A surprisingly close quantitative relation between both quantities suggests that the chemical loss of ozone in the Arctic stratosphere in a given winter correlates strongly with the parameter $\overline{A}_{PSC}$. The compactness of the relation shown in Figure 3-3 is currently not fully understood. To reproduce this empirical relation is a major challenge for global chemistry transport models. The ability of models to reproduce the slope of the relation shown in Figure 3-3 is crucial, when models are to be used to predict the impact of climate changes on future ozone losses.

3.2.3 EFFECT OF OZONE LOSS ON THE TOTAL OZONE COLUMN

Estimating the total column loss of ozone also requires a good quantification of ozone losses in a broad vertical region. The region above 550 K is of less concern for ozone column loss estimates because it contributes little to the total column amount of ozone, due to the small ozone concentrations at these altitudes. But uncertainties in the ozone loss estimates at altitudes below 400 K make ozone column loss estimates generally less reliable than estimates of local ozone losses near 19-20 km. The ozone column loss has been estimated for all winters since 1993/1994 with the transport model approach. Figure 3-4 shows the difference between ozone columns as measured by the SAOZ UV-visible network in the Arctic (Ny Ålesund, Thule, Scoresbysund, Sodankylä, Salekhard, Zhigansk, and Harestua) and the column of passive ozone in REPROBUS (again, initialized with POAM measurements in early winter) above these stations. In many winters, large deficits of observed ozone compared with passively advected ozone have been observed. These deficits are attributed to chemical loss of ozone. Associated with persistently low temperatures in the winters of 1994/1995, 1995/1996, 1996/1997, and 1999/2000 large chemically induced ozone reductions of 22-31% have been observed inside the vortex. The ozone loss during the warmer winter 1998/1999 has been smaller and is hardly significant. In the relatively warm winter 1997/1998 ozone column losses derived from the transport model approach were still significant (20%). In this winter temperatures dropped below the PSC threshold only in very limited geographical regions inside the vortex and only during short periods (see Figure 3-1). From the vortex average approach (Figure 3-2) some limited ozone loss in 1997/1998 is also visible, but only below 450 K. During that year Match

results at 475 K indicate no significant loss, but results for 450 K and below are not available from Match of that year.

3.2.4 CHEMICAL OZONE LOSS IN THE ARCTIC WINTER 1999/2000

The winter of 1999-2000 had the largest potential for PSC formation for at least the last 20 years. Due to the extensive SOLVE-THESEO 2000 campaign during the winter 1999/2000 all basic approaches outlined in Section 3.1 were used to study the ozone loss throughout the winter, resulting in a better characterization of the ozone losses in 1999/2000 than in any previous winter and providing a unique opportunity to compare results from the different techniques.

All approaches identified extensive chemical loss of ozone. Figure 3-5(a) shows the evolution of the vortex averaged ozone loss in a vertical section as determined with the Match approach. Ozone loss started at altitudes above 500 K in mid January. The largest loss rates of 61+/-4 ppbv per day (vortex average) were observed at 450 K in early March. Rex *et al.* (2002a) showed that the vertical structure and the time evolution of the observed ozone loss agrees well with the vertical structure and the time evolution of observations of high levels of active chlorine. During the winter 1999/2000 only approaches that are based on ozonesonde measurements, like Match and the vortex average approach, were able to capture the full extent of the ozone loss, *i.e.*, cover the full altitude range of the loss and the time period from early January to late March in vertical resolution. Comparisons of the results with other approaches are possible for a slightly shorter period and focus on the region close to 450 K. Here the results of all approaches agree very well (see Section 3.3).

Figure 3-6 shows the impact of the cumulative ozone loss through the winter on the vortex averaged vertical ozone profile at the end of March. In a layer of air around 18 km altitude the degree of chemical ozone destruction reached 70%.

Table 3.1 gives an overview over various estimates for the deficit in the total column amount of ozone due to chemical loss of ozone. The numbers given are the difference between the actually observed column amount of ozone and the column amount of ozone that would have been present at a given day in the absence of chemical ozone loss, dynamics being equal. For comparable time periods the agreement between results from all approaches is within the error bars. The results from the SAOZ/transport model study are generally somewhat higher than the other approaches and have larger uncertainties. The results of the other approaches agree to

better than 20%. Figure 3.5c shows the evolution of the total column loss through January to March, as determined by Match. By the end of March the chemically induced ozone deficit amounted to 90 to 100 DU. This is roughly the amount of total ozone that has been supplied to the polar vortex by dynamic effects during the same time, so that the total ozone column remained relatively constant during January to March (Rex *et al.*, 2002a), which is in contrast to the natural, climatological increase of the Arctic ozone column during this season.

Table 3-1. Comparisons of chemical loss of column ozone, column [O_3*-O_3] (see Rex *et al.*, 2002a), inside the Arctic vortex for the winter of 1999/2000 as of the indicated date. N/A indicates that data for that date is not available.

Data Source:	OMS Balloon	POAM III Satellite	SAOZ Network	Ozonesondes
Method:	Tracer-Tracer (O_3 vs. N_2O)	Vortex Averaged Descent	Transport model	Match
Reference:	Salawitch *et al.* (2002a)	Hoppel *et al.* (2002)	Goutail *et al.* (2002)	Rex *et al.* (2002a)
5 March 2000	61 ± 14 DU	51 ± 11 DU	85 ± 24 DU	53 ± 11 DU
15 March 2000	N/A	67 ± 11 DU	98 ± 25 DU	71 ± 12 DU
28 March 2000	N/A	N/A	101 ± 30 DU	88 ± 13 DU

3.3 Consistency between the Different Observational Techniques

Comparisons of the different approaches used to infer Arctic ozone loss are often hampered by the fact that the altitude range, horizontal extent (vortex definition) and time periods used in the various published works are different. These differences are partly unavoidable due to the constraints of the data sets used. But often the data sets can be reanalyzed for certain time periods and regions where they overlap, so that the results can be directly compared.

For the winter 1999/2000 basically all approaches can be used to calculate the amount of ozone loss that occurred inside the polar vortex between 20 January and 12 March in the layer of

air that subsided from about 475 to 450 K during this time. This subsiding layer of air is indicated in Figure 3-5(a) by the solid black lines. Figure 3-7 summarizes the accumulated ozone losses as determined for this layer of air with the various techniques. The average of the various estimates is 1.65 ppmv of ozone loss for this specific time period and vertical region. The results from all techniques are within +/-20% of this value, all but two are within +/-10% of the average.

The winter 1999/2000 was characterized by relatively weak dynamic activity and perhaps less than average exchange of air across the vortex edge (see Section 2.1). It is reasonable to assume that for the winter 1999/2000 the agreement between different techniques to estimate the degree of chemical ozone loss from ozone observations may be better than for dynamically more active winters. However, to investigate this Harris *et al.* (2002) reanalyzed data from past winters during the 90s, using different techniques and data sets, focusing on time periods where the data sets overlap. Based on results from many winters they found an agreement of generally better than 20% between techniques that use explicit transport calculations. Results from tracer relation studies showed slightly larger discrepancies compared with these results, when the initial tracer relation was measured early in fall. This agreement is 25% or better, when the initial tracer relation is measured in mid-winter, *e.g.*, in December.

Based on these studies, the results from current estimates of the degree of chemically induced Arctic ozone losses appear to have an accuracy of about 20%.

3.4 The Effect of Denitrification on Ozone Loss in the Arctic

The effect of denitrification on ozone loss has been quantified (to some extent) in both hemispheres. In the Antarctic (complete) denitrification is shown to cause a 10% increase in the column ozone loss (Brasseur *et al.*, 1997; Portmann *et al.*, 1996).

Evidence for a much more significant impact of denitrification (see Section 2.3) on Arctic ozone losses in recent cold winters has increased. Observational results indicate that the degree of ozone loss in the Arctic was significantly amplified by denitrification during the winters of 1994/1995, 1995/1996 and 1999/2000. Using model studies Rex *et al.* (1997) concluded that in winter 1995/1996 observed ongoing chemical ozone loss in certain air masses more than one month after the last exposure to PSCs can only be explained by approximately 80% denitrification in about half of the air masses inside the polar vortex. In this winter the heavily

denitrified layer of air was limited to a very narrow vertical region of less than 1 km thickness at about 20 km altitude.

Waibel *et al.* (1999) presented measurements of denitrification in the Arctic winter 1994/1995, based on the NO_y versus N_2O relation, and used a chemical model to conclude that in the denitrified air masses the degree of ozone loss was enhanced by at least 30% compared to what would have occurred without denitrification. They show, that the model results can come close to the observed ozone loss only when the observed denitrification is taken into account.

Gao *et al.* (2001b) present measurements of varying degrees of denitrification (also based on the NO_y versus N_2O relation) in different areas of the polar vortex, as characterized by fixed ranges of N_2O and potential temperature. Succeeding observations of the rate of ozone loss based on analyzing sets of photochemically intercomparable air masses indicate largest loss rates at the N_2O levels that were most severely denitrified (about 30% larger losses than in less denitrified air). Gao *et al.* (2001b) show that these differences in the ozone loss rate can not be explained by differences in solar exposure or initial chlorine activation and hence are most likely a result of the denitrification.

These observational studies have shown that denitrification in cold Arctic winters can cause up to 30% increase in ozone loss at a given altitude, a result that is confirmed by model studies (Chipperfield and Pyle, 1998; Tabazadeh *et al.*, 2000; Drdla and Schoeberl, 2002). The more pronounced effect of denitrification on ozone loss in the Arctic, compared to the Antarctic is the result of higher temperatures in the Arctic. In the Antarctic reactivation of chlorine out of the reforming $ClNO_3$ reservoir via reactions on cold liquid aerosol particles (*e.g.*, $ClNO_3 + H_2O$) can sustain a high level of active chlorine in spring (Portmann *et al.*, 1996) This is much less effective in the Arctic, since the heterogeneous reaction of $ClNO_3 + H_2O$ is much slower at the higher temperatures typical for the Arctic spring and hence the lifetime of active chlorine is strongly dependent on the rate of formation of $ClNO_3$ and hence the abundance of HNO_3. The overall effect of denitrification on Arctic column ozone loss depends on the vertical range of severe denitrification. Currently, the effect of denitrification on Arctic ozone is limited to the altitude range of ~18 to 21 km, where most parcels are shown to be severely denitrified in cold winters (Hintsa *et al.*, 1998; Kondo *et al.*, 2000; Fahey *et al.*, 2001). Microphysical sensitivity studies have shown that a cooling of the lower stratosphere could significantly extend the vertical range of severe denitrification in the Arctic (Waibel *et al.*, 1999; Tabazadeh *et al.*, 2001).

It is important to note that current denitrification schemes that are used *e.g.*, in 3-D-CTMs have severe difficulties to correctly represent the degree of denitrification in cold Arctic winters (*e.g.*, Davies *et al.*, 2002, see also Section 2.2). In the light of the recent results that extensive denitrification (up to 80%) occurred in cold Arctic winters and that it had significant impact on the degree of ozone loss in these years, the correct representation of denitrification remains one of the major challenges for 3-D-CTMs, when they are used to study the variability of chemical ozone loss in the Arctic (*e.g.*, Chipperfield and Jones, 1999) or to predict future ozone losses in a potentially changing climate.

Dehydration, unlike denitrification, can moderate ozone loss for two reasons (Portmann *et al.*, 1996, Chipperfield and Pyle, 1998). First, in a drier atmosphere it is harder for PSCs to form. Second, heterogeneous reaction rates that lead to active chlorine production drop exponentially with decrease in relative humidity. Sensitivity studies show that dehydration (to the level of ice saturation) in the Antarctic can decrease column ozone loss by about 20% (Portmann *et al.*, 1996; Brasseur *et al.*, 1997). No large-scale model calculations have yet been performed to evaluate the role that dehydration may play in Arctic ozone loss and recovery in the future. However, it is unlikely that climate change in the near future could cause extensive dehydration in the Arctic region. Some air mass trajectory statistical analyses indicate that even a substantial cooling of lower stratospheric temperatures (by 3 to 4 K) is still insufficient to trigger the occurrence of severe dehydration in the Arctic vortex (Tabazadeh *et al.*, 2000).

3.5 Model Studies of Arctic Ozone Loss

Model investigation of polar ozone loss was the subject of intense research in recent years. Most studies concentrated on the Arctic region due to the high interannual variability of the Arctic ozone loss in relation with the year-to-year meteorological conditions. 3-D CTMs, which proved to be particularly well fitted to the non zonal character of the Arctic polar vortex, have been used to estimate the overall degree of polar ozone loss for several winters. For more specific studies or highly constrained comparisons between models and ozone loss observations photochemical box models were used.

3.5.1 CHEMICAL TRANSPORT MODELS

Studies using the transport model approach to estimate ozone loss from ozone measurements typically include a comparison with the ozone loss calculated by the chemistry module of the model. Chemical ozone loss inferred from the POAM II and III measurements was compared with that obtained from the REPROBUS model (Deniel *et al.*, 1998; 2000). In the same way, total ozone measurements by the SAOZ network were compared with REPROBUS and SLIMCAT simulations for various Arctic winters from 1993/1994 (Figure 3.4; Goutail *et al.*, 1999; 2002). The agreement between the observed ozone loss and the model result varies from winter to winter. Overall a couple of points can be seen in Figure 3.4. (a) The overall interannual variability of the Arctic ozone loss is reasonably well represented by the models. A large fraction (between about 60 and 100%) of the overall Arctic ozone loss is reproduced by the models. (b) In winters when substantial ozone loss was observed during January (1994/1995, 1995/1996, and 1999/2000), the models fall short of reproducing this January loss. Typically, by the end of January, only about 50% of the observed loss is accounted for by the models. The loss in January is part of the reason, why the overall loss at the end of the winter is sometimes underestimated (*e.g.*, 1994/1995). In other winters the January loss contributes only a minor fraction to the overall loss (*e.g.*, 1999/2000) or the model overestimates the loss rate later during the winter so that the overall loss at the end of the winter is better reproduced than the time evolution of the loss (*e.g.*, 1995/1996). Also, in 1995/1996 the simulated vertical distribution of the ozone loss at the end of March differs from that estimated from POAM II measurements with the model resulting in larger losses at lower altitudes and smaller losses at higher altitudes compared to the observations (Deniel *et al.*, 2000). It appears that a good agreement between observations and modeled total ozone loss at the end of the winter alone may be fortuitous and does not necessarily prove that the ozone loss mechanisms in the model are well-reproduced.

Extensive modeling studies were performed as part of SOLVE/THESEO 2000 in order to estimate the ozone loss in the winter 1999/2000. Sinnhuber *et al.* (2000) compared the chemical ozone loss estimated with SLIMCAT with that derived from the model ozone passive tracer and ozonesondes observations at Ny Ålesund (Figure 3-8). They found good agreement between the modeled ozone and observations, both indicating more than 2.5 ppmv ozone destruction by late March, corresponding to 70% ozone loss at the 450 K isentropic level, the largest ozone loss ever

produced by SLIMCAT. The reason for the large loss of ozone in the model was extensive formation of large denitrifying ice particles by the model's microphysical scheme. But the large scale formation of ice clouds in the model was merely the result of a cold bias in the UKMO temperature fields used in SLIMCAT and is not consistent with observations during SOLVE/THESEO 2000. Coincidentally the extensive denitrification produced by the erroneous representation of ice clouds in the model is in agreement with observations of denitrification. The mechanism how the observed denitrification occurred in the atmosphere is still under investigation (see Section 2.2.3) and is not included in the model used by Sinnhuber *et al.* (2000). Using a correct temperature field SLIMCAT would have significantly underestimated the ozone loss during winter 1999/2000, as in many earlier cold Arctic winters (*e.g.*, Hansen *et al.*, 1997).

The KASIMA (Karlsruhe SImulation model of the Middle Atmosphere) CTM driven by ECMWF analyses was compared with ozone measurements by a FTIR spectrometer and a millimeter wave radiometer in Kiruna for the winter 1999/2000. The modeled total ozone loss underestimates the observations by 30% and 20% respectively (Kopp *et al.*, 2002).

The Langley Research Center (LaRC) Lagrangian chemical transport model (LCTM) was used in conjunction with HALOE and POAM III satellite observations to simulate the large-scale photochemical evolution of the Arctic vortex in 1999/2000 from vortex ensemble of air mass trajectories using UKMO analyses (Pierce *et al.*, 2001). The model shows significant denitrification within the vortex in late December and early January. A significant overprediction of the level of chlorine activation is found in early March but the predicted peak ozone loss rate is in good agreement with that inferred from the Match campaign during the same period. Conversely it can be concluded that for a realistic level of active chlorine the model would have significantly underestimated the observed ozone loss rate during this period.

Grooss *et al.*, (2002) report simulations with the Chemical Lagrangian Model of the Stratosphere (CLaMS). This model simulates the dynamics and chemistry of multiple air parcels along their trajectories which are determined from ECMWF winds. The model includes mixing between neighboring air parcels. In this model study, the degree of denitrification was described from observations by using observed relations between NO_y and N_2O and the temperature history based on ER-2 measurements. The simulation was initialized on 10 February, and the

ozone loss during the mid-February to mid-March period (up to 60% at 425-450 K) agrees roughly with estimates from observations.

The various 3-D model studies focusing on the winter 1999/2000 reveal a consistent picture. The ozone loss after mid-February is well reproduced if the degree of denitrification in the model is correct, be it by coincidence like in Sinnhuber *et al.* (2000) or because it was specified from observations like in Grooss *et al.* (2002). Currently 3-D CTMs are not able to reliably reproduce the degree of denitrification within the model. This deficit limits the current ability to reliably reproduce the degree of ozone loss in cold Arctic winters.

3.5.2 SPECIFIC MODEL STUDIES

Several modeling studies using box models were conducted to compare specific ozone loss observations with model results and test our understanding of the chemical processes involved in the loss. These calculations are performed specifically for the air masses in which the ozone losses have been observed. Hence the temperature and solar zenith angle history in these studies are much more constrained than in comparisons of vortex averaged ozone losses. Becker *et al.* (1998; 2000) performed box model simulations along each trajectories of the Match data set for 1991/1992 and 1994/1995. They concluded that the model underestimated the ozone losses observed by Match in late January 1992 and 1995 by up to a factor of two above 475 K. During the other months the observed losses were also underestimated by the model but within the large uncertainties of the model mainly linked to the extent of denitrification.

Match ozone loss rates were also compared to SLIMCAT simulations for the winters 1994/1995 and 1995/1996 (Kilbane-Dawe *et al.*, 2001). The study suggests that Match may have overestimated the ozone loss rates above 525 K in January 1995 due to deficiencies in the ECMWF wind fields close to the top level of the ECMWF assimilation model (the top level was shifted to higher levels since then). In January 1995 at levels below 525 K and in January 1995/1996 SLIMCAT generally underestimated Match ozone loss rates by about 30 to 50%. It was found that the SLIMCAT photochemistry was the least able to reproduce observed ozone losses when low temperatures coincide with high solar zenith angles.

Woyke *et al.* (1999) used the tracer relation approach to quantify ozone loss in air masses that have been probed by a balloon payload providing observations of ClO, BrO, O_3, and long-lived tracers, on 3 February 1995. They used box model runs constrained by ClO and BrO

concentrations observed by the balloon, to calculate the ozone loss throughout January along the back trajectories of the air masses. Using this highly constrained approach they could explain only half of the observed ozone loss.

These results confirm that ozone losses observed during cold Arctic Januarys are currently not understood.

3.6 Quantifying Antarctic Ozone Loss

As emphasized in Section 1, the Antarctic ozone depletion is monitored by ground-based and satellite measurements since the mid-eighties. However, relatively few studies have recently concentrated on a detailed quantification of Antarctic ozone loss rates with state-of-the-art approaches to separate chemical loss from dynamical impacts. Hence our quantitative knowledge of Antarctic ozone loss rates is not as good as in the Arctic. The quantification of the accumulated overall ozone loss in the Antarctic is not challenging since by the end of the winter ozone is basically completely lost in a broad vertical region.

Hofmann *et al.*, 1997 quantified Antarctic ozone loss from the analysis of ten years of ozonesonde measurements at the south pole and made recommendations for the detection of the recovery of the Antarctic ozone. Indicators for recovery include an end to springtime ozone depletion at 22-24 km and a 12-20 km ozone column value of more than 70 DU on 15 September. Bevilacqua *et al.* (1997) used POAM II ozone observations above Antarctica to derive vortex average ozone loss rates in August and September from 1994 to 1996 in the 450-800 K potential temperature range. Over the three years significant loss of ozone is found over the whole period, except in 1994, when ozone loss was not observed in August, due to the sampling of the POAM instrument. The largest loss rates are found in September 1996 where they reach 0.1 ppmv/d below 500 K. From the analysis of the temporal evolution of total ozone at the Faraday station together with model calculations, Roscoe *et al.* (1997) showed that the ozone chemical depletion starts in June at the sunlit vortex edge, and Waters *et al.* (1999) show that enhanced abundances of ClO are observed on the sunlit edge of the Antarctic vortex by late May or early June. Ozone loss rates were evaluated above the Antarctic station of Dumont d'Urville (66.4˚S, 140˚E) from ozonesonde and lidar measurements on an interannual basis (Godin *et al.*, 2001). Interpretation of the data required careful analysis of PV-equivalent latitude to determine whether each observation was inside, in the edge or outside the vortex at

different isentropic levels. Measurements inside the vortex showed complete ozone destruction from 400 to 500 K with ozone loss rates reaching 0.06 ppmv/d in the late August-September period.

3.7 Model Studies of Antarctic Ozone Loss

The few recent model studies of the Antarctic ozone loss generally point to an agreement between models and observations. The SLIMCAT model was used to study the austral stratosphere in winter and spring 1996 together with ozonesonde measurements from various Antarctic stations (Lee *et al.,* 2000). The model shows very good agreement with measured ozone values and both the model and observations show that chemical ozone depletion follows the edge of polar night with little mixing poleward until the terminator reaches 80˚S. In a follow up study, Lee *et al.,* (2001) analyze the isentropic transport processes within the Antarctic polar vortex. Their calculations indicate two distinct regions within the vortex: a strongly mixed vortex core and a broad ring of weakly mixed air that remains isolated from the core between late winter and mid-spring and where the ozone loss is not complete. This result has an implication for the recovery of Antarctic ozone since a cooling of the stratosphere could enhance the ozone loss in the edge region and delay the ozone recovery. In another study of Antarctic ozone loss, Wu and Dessler, (2001) test the current understanding of polar ozone chemistry with version 4 MLS measurements of O_3 and ClO. By comparing the observed ozone loss estimated from the MLS ozone evolution at 465 K with a modeled ozone loss inferred from the simultaneous ClO measurements and a fixed BrO mixing ratio, they find a good agreement between both methods. However, MLS version 5 data, that has a better vertical definition of the ClO profile, resulted in a significantly reduction of the ClO concentrations at 465K compared to version 4 data that has been used in Wu and Dessler (2001). This reduction would lead to a reduction in the modeled ozone loss rate in Wu and Dessler (2001). A slight change in the ozone profile in MLS version 5 data compared to version 4 data would also reduce the ozone loss rate deduced from observations. A quantitative study would be required to assess how the conclusions of Wu and Dessler (2001) would change if MLS version 5 data had been used.

3.8 Conclusion

Arctic chemical ozone losses during the last decade have been determined by a variety of approaches and ozone loss rates are now better quantified in the Arctic than in the Antarctic. The uncertainty of state-of-the-art approaches to quantify Arctic ozone losses from ozone observations is below 20% for local losses between 400 and 550 K potential temperature and perhaps somewhat larger for total column loss estimates. Large interannual variability of the Arctic ozone loss, ranging from 0-70% loss at about 20 km for individual winters during the past decade, is driven by the variable extent of temperatures low enough for PSC formation in a given winter. Global chemical transport models reproduce a large fraction (60-100%, depending on the winter) of the observed ozone loss in the Arctic and its variability. The largest uncertainties are due to the current unrealistic representation of denitrification processes in 3-d CTMs and unexplained ozone losses during cold Arctic Januarys. These uncertainties currently prevent reliable predictions of future Arctic ozone losses in a potentially changing climate.

4 CAUSES OF POLAR STRATOSPHERIC TEMPERATURE TRENDS

4.1 Introduction

In WMO 1999, it was recognized that the future development of the ozone layer does not depend just on changes in stratospheric halogen loading but also, very importantly, on a number of other factors connecting chemistry and climate. While the observations of temperatures are discussed in Section 1.2.2, the causes of trends in polar stratospheric temperatures are discussed here: the role of changes in well-mixed greenhouse gases (WMGHGs), in ozone, water vapor and aerosol particles are reviewed. Solar effects are also noted. The onset of cold temperatures during the polar winter/ spring, its duration, interannual variations and the statistical significance of trends over the past two decades are issues that impact upon our knowledge of the chemistry-climate interactions and the detection and attribution of climate change in the polar stratosphere due to ozone and other greenhouse gases.

Observations, from radiosondes and satellites have shown a general cooling of the polar lower-stratosphere over the last few decades (WMO, 1999; Ramaswamy *et al.,* 2001). For a number of reasons detection and attribution of temperature change in the lower-stratosphere may

be easier than at the surface (IPCC, 1996). Firstly, the observed temperature change in the stratosphere is large and the response time of the stratosphere is shorter, compared to the surface. There are relatively good satellite observations of both temperature and the important atmospheric constituents over the last few decades, corresponding to the timing of polar ozone depletion. There are also potentially fewer relatively uncertain mechanisms involved in stratospheric temperature change; many of the large and uncertain surface radiative forcings, such as the anthropogenic sulfate aerosol forcing, are expected to have a minimal effect on stratospheric temperatures. Further, the magnitude of the response in the stratosphere to a given mechanism has been shown to be reasonably well approximated by purely radiative processes, and therefore may be better quantifiable than the surface temperature response (Ramaswamy *et al.*, 2001). However, the WMO (1999) ozone assessment acknowledged that the large variability of temperatures, particularly in the Arctic winter and spring, and a possible stratosphere-wide trend in stratospheric water vapor complicate the attribution issue. It is now recognized that ozone and WMGHG changes can not be considered in isolation and there is an increasing acknowledgement that it is important to attempt to quantify the feedbacks between temperature change, chemistry and stratospheric dynamics, to better understand the stratospheric temperature response.

Since the last assessment there has been improved quantification of atmospheric constituent changes and development of more sophisticated stratospheric models, especially coupled chemistry general circulation models. These have provided important insights into our understanding of polar temperature changes in the lower-stratosphere.

This section uses the updated temperature lower-stratospheric high latitude temperature trends (discussed in Section 1.2.2) and discusses the recent modeling efforts that have attempted to understand them. It concentrates on the analysis and understanding of past decadal-timescale trends in the polar lower- stratosphere; the upper stratospheric response is often more independent of latitude and is discussed in the global ozone chapter (Chapter 4). Possible future temperature-change scenarios are discussed more fully in the next section (Section 5).

4.2 Modeling Techniques

Several different types of model have been adopted for the study of stratospheric temperature change. Two types of commonly used models are briefly assessed here. Table 4.1 presents recent model results.

4.2.1 Fixed Dynamical Heating (FDH) Models

Fixed Dynamical Heating (FDH) models and Seasonally Evolving Fixed Dynamical Heating models (SEFDH) (WMO, 1999; IPCC, 2001) employ a method of calculating temperature changes using only a radiative transfer model. They have been shown to agree well with calculations using GCMs (Rosier and Shine, 2000; Ramaswamy *et al.,* 2001) and, compared to these, they are generally faster and allow the use of more sophisticated radiative transfer schemes. In contrast to the FDH technique, SEFDH techniques include a calculation for the time evolution of temperature and have been shown to improve the temperature response in the high latitude polar stratosphere, compared to GCM integrations (Forster *et al.*, 1997; Rosier and Shine, 2000). This was a region where the equilibrium temperature response calculated with FDH models overestimated the cooling resulting from short-term polar ozone depletion. Both FDH and SEFDH techniques are unable to model the response of atmospheric dynamics.

4.2.2 General Circulation Models (GCMs)

An assessment of the performance of current middle atmosphere GCMs is currently being performed by the 'GCM-Reality Intercomparison Project for SPARC' (GRIPS) (Pawson *et al.,* 2000). Preliminary analysis of their results suggest that all models have a cold-bias, at most levels in the troposphere and stratosphere, which may be indicative of errors in the radiative transfer, or input data (Pawson *et al.,* 2000). This is particularly pronounced at the poles (see Section 5.1.1); one of the largest uncertainties remains the parameterization of small-scale gravity waves (see Section 2.1.2 and Section 5.1.1). The upper boundary and vertical resolution may also be important for an accurate simulation (see Section 5.1.3). Due to large inter-annual variability particularly in the Arctic temperatures (see Section 5.1.4 and Section 2.1.2), either many transient integrations (indicated by the suffix 'T' in the model column of Table 4.1) or many years of equilibrium experiments need to be performed for statistically significant trend

calculations. It must be noted, however, that the real atmosphere has evolved through only one specific realization and that the global observational record only spans ~20 years. Experiments have been performed with both prescribed changes in atmospheric constituents (referred to as GCM in the model column of Table 4.1) and coupled chemistry GCMs (discussed in more detail in Section 5 and referred to as GCM-CHEM in Table 4.1). Whilst coupled chemistry GCMs allow interaction between radiation, chemistry and dynamics (one coupled model does not include stratospheric water vapor feedback), they have two main drawbacks when attempting to attribute stratospheric temperature change to a particular cause. Firstly their complexity makes them computationally expensive; it is therefore difficult to run them for long enough to produce statistically significant trends. Secondly, their simulation of the ozone change is imperfect; this is to be contrasted with GCMs that employ the ozone trends inferred from observations to determine the temperature response.

4.3 Causes of Stratospheric Temperature Trends

This sub-section assesses the role of different mechanisms on polar lower-stratospheric temperature trends. A variety of recent model results are compared to the satellite-derived temperature trends (discussed in Section 1.2.2). Table 4-1 and Figure 4-1 summarize the findings for the lower stratospheric temperature response at 70°N and 70°S to: a) stratospheric ozone changes, b) Well mixed greenhouse gas (WMGHG) changes, c) combined changes in WMGHGs and stratospheric ozone changes, and d) stratospheric water vapor changes. Annual and Seasonal temperature trends are shown at pressures of 50 hPa and 100 hPa. There are several factors that affect the interpretation of the comparisons of the observations and model simulations presented in this section.

(a) The satellite measurements comprise radiances from a range of altitudes. This introduces some uncertainty when model results at 50 and 100 hPa are compared with the satellite observations.

(b) This section examines a single latitude belt in the polar regions where there is a large dynamical variability.

(c) The polar trends, especially for the winter/spring season, are influenced by the end-year considered for the analysis.

4.3.1 OZONE

The stratospheric cooling over Antarctica has previously been shown to be very well correlated with ozone losses (WMO, 1999; Randel and Wu, 1999a). Shine (1986) was the first to show that such a stratospheric cooling could be due to the direct radiative response of the ozone loss. GCM and radiative model studies since then have largely confirmed this early work (Mahlman *et al.*, 1994; Ramaswamy *et al.*, 1996; WMO, 1999). In the Northern Hemisphere studies have also found a correlation between springtime Arctic temperatures and ozone (WMO, 1999; Randel and Wu, 1999a). However, the correlations are not as strong and the cooling observed during the Arctic winter is not expected from a simple radiative response to the ozone loss (Randel and Wu, 1999a). In addition, reductions of planetary wave driving reduce the strength of the residual circulation, leading to a cooling trend. This also weakens the transport of ozone rich air to the polar lower stratosphere, and could give larger heterogeneous loss rates. Hence, a correlation of temperature and ozone does not necessarily imply a causal linkage of ozone loss with temperature.

Since the last assessment several studies have employed the monthly averaged vertical trend data, based on ozone observations over the 1979-1997 period (SPARC, 1998), with most studies employing the combined trend dataset of Randel and Wu (1999b). The results of these prescribed ozone change studies are shown in the 'STRAT OZONE' section of Table 4.1. The calculations presented in the table had the benefit of more detailed ozone-trend vertical resolution compared to previous work. The ozone dataset employs stratospheric-only trends derived from the Syowa (69°S) and Resolute (75°N) ozonesondes as representative of the polar regions. The Rosier and Shine (2000) results shown in the table are slightly updated versions of the GCM runs described in their paper.

Figure 4.2 shows an illustration of the annual cycle of model-derived 100 hPa trends from the Berlin model and compares them to trends derived from reanalysis data. It is noted that trends from re-analyses data (Figure 4.2 panel c) must be interpreted with caution (WMO, 1999, Chapter 5). The Antarctic and Arctic response are discussed separately below.

Antarctic [4.3.1.1]

All studies report an ozone-induced cooling at 70°S for most seasons, with the largest cooling in all models occurring in SON and DJF. Langematz *et al.* (2002) and Ramaswamy and

Schwarzkopf (2002) find that the largest cooling at 100 hPa occurs in DJF not SON (see Section 4.4). There is a dynamically induced heating in the middle atmosphere, which adds to the radiative heating owing to more upwelling longwave initiated by the depletion of ozone in the lower stratosphere. This effect is simulated by several models (Kiehl *et al.*, 1988; Mahlman *et al.*, 1994; Ramaswamy *et al.*, 1996; Rosier and Shine, 2000), and is consistent with observations (Ramaswamy *et al.*, 2001), but is not statistically significant, in either models or observations.

Compared to the observed trends the Langematz *et al.* (2002) response underestimates the SON cooling at 50 hPa but gives a better fit with the MSU-4 observations which are representative of 100 hPa. The other models tend to overestimate the observed spring and summer cooling at 100 hPa, particularly during DJF (see Section 4.4). Caution needs to be applied to this satellite-model comparison as there are uncertainties with regards to the representation of the altitude profile of ozone loss in the models over the winter/spring period, and with regards to the interpretation of seasonal trends at 50 and 100 hPa from satellite data.

Two versions of the same model (Rosier and Shine, 2000 (updated); and Smith, 2001) produce significantly different trends in SON (Table 4.1). Both models are versions of the Reading Intermediate GCM performing 20- year equilibrium experiments. Differences between the simulations are also found in the Arctic (see below), which may imply a difference between the way the ozone trends are implemented and/or differences in the variability of the model.

Arctic [4.3.1.2]

All four models in Table 4-1 find an annually averaged cooling in the Arctic. Three of the four models find the largest cooling in MAM – which agrees qualitatively well with the satellite data. However, this modeled cooling is only about half the size of the cooling trend in the satellite data. Smith (2001), in contrast, finds a maximum cooling in DJF and smaller cooling in MAM, although differences again may be due to the large variability in the Arctic winter and are of limited significance. When comparing trends Graf *et al.*, (1998); Waugh *et al.* (1999); Langematz *et al.* (2002) and Ramaswamy and Schwarzkopf (2002) make the important point that the large natural variability in the Arctic may mean that the modeled and observed trends are not easily compared.

4.3.2 WELL-MIXED GREENHOUSE GASES (WMGHG)

In general, considering their radiative effects only, WMGHG increases are expected to have a much smaller effect on lower stratospheric temperatures than they do on temperatures above 30 hPa (Forster and Shine, 1997; WMO, 1999; Chapter 4; Ramaswamy and Schwarzkopf, 2002). This is borne out by the results presented in Table 4.1. The Langematz *et al.* (2002) trend was derived for CO_2 changes only and has been estimated by taking the difference between the results of their STRAT-OZONE and WMGHG experiment and those of their OZONE experiment. The same method has been adopted in connection with the Ramaswamy-Schwarzkopf results. This is in contrast to the updated Rosier and Shine study where WMGHG effects were studied directly. Few of the modeling studies show significant temperature trends. Some models are seen to cool their annual-mean lower stratospheres in response to WMGHG increases. The magnitude of cooling (~0.3 K/decade) agrees with earlier FDH calculations (*e.g.*, Ramaswamy *et al.*, 2001). For further discussion on the role of WMGHGs in annual-mean trends see Chapter 4.

4.3.3 COMBINED CHANGES IN WMGHGS AND STRATOSPHERIC OZONE

Since WMO (1999) several experiments with coupled chemistry-climate models have been performed for different time periods to simulate the combined effect of changes in ozone and WMGHGs. These experiments are discussed in more detail in Section 5. Here we only examine how the coupled chemistry modeling studies influence the attribution of high latitude temperature trends. Results from five of coupled chemistry experiments are presented in Table 4.1 Temperature trends are also shown for 2 different prescribed WMGHG and ozone experiments and the updated Rosier and Shine (2000) result, where individual ozone and WMGHG trends have been added.

Antarctic [4.3.3.1]

The agreement between the different models in Table 4.1 is encouraging considering: a) the range of different models employed; b) the differences between the responses, for models employing the same ozone trend dataset (Section 4.4.1.1); and c) the large uncertainty in trends derived from transient integrations. As the overall effect of WMGHG changes on lower

stratospheric temperatures is minimal (annual-mean results in Section 4.4.2), there is little difference with respect to the annual-mean temperature trends from the stratospheric ozone experiments. Therefore, for all seasons the observed cooling can be explained by either combined WMGHG and stratospheric ozone changes or stratospheric ozone changes alone (see Figure 4.1). Most of the coupled chemistry models and Ramaswamy and Schwarzkopf (2002) tend to overestimate the observed 100 hPa cooling in SON, although most results are still within the observational uncertainty range. In contrast, at 50 hPa, these models are closer to observations while some of the other models underestimate the cooling. The differences seen amongst the models at 50 and 100 hPa suggest the height profile of the applied ozone loss as a possible cause of the dipole-like behavior in the biases. Schnadt *et al.* (2002) and the study of Austin (2002) find an SON cooling whose position is too high compared to observations. These discrepancies were found to be consistent with model ozone-biases (Austin, 2002). Most models simulate the annual-mean change at 50 hPa well while all overestimate the 100 hPa trend.

Generally, the Antarctic springtime cooling is captured by the models but further improvements are needed to simulate the magnitude of the cooling and its vertical extent.

Arctic [4.3.3.2]

As for Antarctica the models are generally consistent with the observed trends, and inter-model differences are generally smaller than the 2σ uncertainty in the observations (Figure 4.1). At 50 hPa all models underestimate the MAM cooling. At 100 hPa all models (bar one) underestimate this cooling, which could indicate: 1) an underestimate of the ozone-related cooling; 2) a contribution of a missing effect, such as increases in stratospheric water vapor; 3) an underestimate of the role of natural variability. Some models yield a warming in DJF which is in contrast to the observations. In the annual-mean, only one of the models (a coupled model) is close to the observations, the rest underestimate the observed cooling.

4.3.4 STRATOSPHERIC WATER VAPOR

Since the last assessment a major development has been the burgeoning interest in the role of stratospheric water vapor. Increases in stratospheric water vapor have now been measured by satellite and ground based observing systems which are roughly twice the expected increase from

methane oxidation (see Chapter 4, Rosenlof *et al.*, 2001, SPARC, 2000). Several recent papers have examined the consequences of this increase for stratospheric temperatures.

The study of Forster and Shine (1999) used an over-simplified representation of the water vapor change, both in the perturbation and background stratospheric water values (Forster and Shine, 2002) and, perhaps, its radiative transfer scheme (Oinas *et al.*, 2001). In general, inadequacies of broadband radiative transfer codes are readily accounted for (see Forster *et al.*, 2001; Forster and Shine, 2002). Since this study, Smith (2001) (see also, Smith *et al.*, 2001), used trends derived from HALOE data over the 1992-1999 period to better represent the water vapor change. Likewise, Forster and Shine (2002) used an improved representation of the background water vapor a simulated +1 ppmv water vapor increase, derived from SPARC (2000) data. Shindell (2001) also modeled the effect on increases in stratospheric water vapor, from methane oxidation, using a coupled chemistry GCM. Although large uncertainties in the water vapor trend remain, these studies indicate a possible cooling of up to 0.5 K/decade in both hemispheres, comparable to that due to ozone. Given the present level of uncertainty in the observational trend analysis and notwithstanding the contribution of WMGHGs and stratospheric ozone to the cooling, one cannot rule out a significant effect due to stratospheric water vapor. There is an indication that a water vapor contribution is required for a quantitative accounting of the observed polar cooling (also see the discussion in Chapter 4).

4.3.5 SOLAR CHANGES

Following on from work discussed in the reviews of WMO (1999) and Ramaswamy *et al.* (2001), Van Loon and Labitzke (2000) correlate the solar cycle with stratospheric temperatures and find that the 'response' of the Arctic stratosphere depends on the phase of the QBO. During solar maximum easterly phases of the QBO coincide with a cooler Arctic stratosphere, whereas westerly phases of the QBO give a warmer stratosphere. A model simulation (Cubasch and Voss, 2000) is unable to simulate this response, although their model did not include a modulation of ozone with ultraviolet radiation. Inclusion of this feedback affects the Arctic temperature response (Haigh, 1999; Larkin *et al.*, 2000). Both these modeling studies found a warmer wintertime Arctic stratosphere during solar maximum. Recent studies with coupled chemistry models (Williams *et al.*, 2001; Labitzke *et al.*, 2002) find increased sensitivity of lower stratospheric ozone to the solar cycle, compared to earlier modeling experiments, giving

greater consistency with observations (see also EUR, 2001). Generally the latest modeling studies indicate a possible influence of the solar cycle on high latitude temperatures. However, any effect is still too uncertain to quantify and remains somewhat speculative.

4.3.6 VOLCANOES

In the last 20 years the two large volcanic eruptions of Mt. Pinatubo and El Chichón created significant amounts of aerosol in the low-latitude stratosphere. Whilst several simulations show a low-latitude stratospheric warming the response at high latitudes is less certain (WMO, 1999). Ramachandran *et al.* (2000) simulated the Mt Pinatubo eruption in a GCM and found that the dynamical response to the aerosol forcing led to an annually averaged cooling at high latitudes up to 2 K for the two years following the eruption. Ramaswamy *et al.* (2002b) find that the high-latitude simulations of Pinatubo aerosol effects are affected substantially by the initial conditions in the model ensemble integrations. Timmreck *et al.*, (1999) also found that volcanic aerosol caused a stronger Arctic vortex. While both model and observations in the Pinatubo case indicate that polar effects were not statistically significant, the suggestion remains that volcanic eruptions may have contributed to the observed high latitude stratospheric cooling. Following a volcanic eruption, enhanced ozone loss is expected from heterogeneous chemical reactions on the volcanic aerosol (see WMO, 1999). This ozone loss would cool the stratosphere. Pawson *et al.* (1999) postulate a stepwise decrease in stratospheric temperatures following volcanic eruptions that may be connected with changes in heterogeneous ozone chemistry (Solomon *et al.*, 1998).

4.4 Timing of the Springtime Cooling Trend

Observational evidence shows that the maximum springtime stratospheric cooling trend occurs at roughly the same time as a maximum ozone loss (March in the NH and October-November in the SH (*e.g.*, Randel and Wu, 1999a, see Figure 4.2, panel c). However, most modeling studies of ozone loss and simple radiative arguments would suggest that the maximum cooling lags the ozone loss in the lower stratosphere by a month or more (*see* Figure 4.2, panels a) and b), and also: Forster *et al.*, 1997; Ramaswamy *et al.*, 2001; Langematz, 2000; Rosier and Shine, 2000; Graf *et al.*, 1998, Langematz *et al.*, 2002). For example, in Antarctica a number of the models show approximately similar cooling trends in SON and DJF for their stratospheric

ozone experiments (Table 4.1). This is especially true of the 100 hPa where radiative relaxation times are longer. The NCEP reanalyses also hints at this feature (Figure 4.2, panel c). This feature is not observed in the satellite record. Graf *et al.*, 1998 investigated whether WMGHG increases could compensate for this lag and found it could not, at least in their model. Ramaswamy and Schwarzkopf (2002) find that the effects due to ozone and WMGHG over the 1980-2000 period in the northern polar region are swamped by the dynamical variability seen in both model and observations. The finding is probably true of the other models (see Table 4.1 and especially Figure 4.2). Graf *et al.*, 1998 further suggested that the discrepancy could be due to an incorrect modeling of the dynamical response and concluded that until reasons for this are adequately resolved it represents a problem in the attribution, of particularly the Arctic cooling, to an anthropogenic cause.

4.5 Summary and Conclusions

Generally, modeling studies now demonstrate that the springtime cooling in the Arctic lower stratosphere over the 1980-2000 period is, in part, due to stratospheric ozone depletion, but the degree of attribution is hindered by the large dynamical variability in this region. In Antarctica, modeling studies re-affirm that ozone loss is the major cause of the springtime cooling. They also indicate that WMGHG and stratospheric water vapor increases are likely contributors to the annually-averaged cooling.

For combined changes in stratospheric ozone and WMGHGs there is generally a reasonable agreement between the various modeling studies; inter-model differences are generally smaller than the uncertainty in observations. However, this good agreement is probably somewhat fortuitous, as the models which used *the same* prescribed ozone change still differed in the sign of their temperature response, especially in the Arctic. Furthermore, some of the ozone-change modeling studies were equilibrium experiments and as such were less prone to differences caused by the high variability of the Arctic vortex.

In summary the cooling of the springtime high latitude stratosphere is likely influenced to a substantial extent by various mechanisms (WMGHG increases, ozone loss, stratospheric water vapor increases, volcanic eruptions and natural variability). Attribution of polar temperatures is hampered by the large variability in the polar vortices (see Figure 1.2.1). This variability not only increases the uncertainty of observational trend analyses it also means that either many

years of equilibrium studies or many ensemble integrations are needed for reliable statistics. Further, it implies that model studies performed under equilibrium conditions may be inadequate for examination of polar trends, especially in the Arctic, over a time-period of two decades. At present 20 years of an equilibrium GCM run are barely sufficient to resolve temperature changes in the Arctic winter. This would imply that 20+ member ensembles would also be needed for transient integrations. Comparison between observations and models, or between different models, is also complicated by uncertainty in the vertical profile of ozone loss, which leads to uncertainty in the temperature response. In models which simulate the chemistry this uncertainty could be larger than in those models which prescribe the ozone loss from observations. These coupled-chemistry models are discussed next.

Study	Model	Period	Notes	50 hPa (K/decade) 70N DJF	MAM	JJA	SON	Annual	70 S DJF	MAM	JJA	SON	Annual
Satellite observations													
SSU		1979-1998		-0.93	-2.99	-0.49	-0.27	**-1.17**	-0.74	-1.01	-0.66	-2.90	**-1.33**
Berlin sondes		1979-2000						**-0.61**					
UKRAOB sondes		1979-2000						**-0.90**					
Russia sondes		1979-2000						**-0.70**					
CPC analysis		1979-2000						**-0.52**					**-0.64**
STRAT OZONE													
Schwarzkopf & Ramaswamy, 2002	GCM	1979-1997		-0.34	-0.80	-0.42	0.23	**-0.33**	-1.61	-0.41	-0.13	-2.42	**-1.08**
Rosier and Shine, 2000(updated)	GCM	1979-1997		-0.17	-1.02	-0.30	-0.30	**-0.45**	-1.04	-0.27	0.41	-1.99	**-0.72**
Langematz, 2000	GCM	1979-1996		-0.64	-0.96	-0.26	-0.25	**-0.53**	-0.36	-0.13	0.00	-0.04	**-0.11**
Smith, 2001	GCM	1979-1997		-1.58	-0.25	-0.71	-0.76	**-0.83**	-1.75	-0.47	-0.91	-3.66	**-1.70**
WMGHG													
Schwarzkopf & Ramaswamy, 2002	GCM	1979-1997		1.12	-0.19	-0.25	-0.33	**0.10**	0.03	-0.24	0.10	2.16	**-0.13**
Rosier and Shine, 2000(updated)	GCM	1979-1997		-0.11	0.09	0.07	-0.07	**0.00**	-0.23	-0.32	-0.80	0.51	**-0.21**
Langematz et al., 2002	GCM	1979-1996	co2, diff.	-0.31	0.20	-0.06	-0.32	**-0.12**	0.19	-0.04	-0.14	-0.12	**-0.05**
Butchart et al, 2001	GCM-T	1991-2001	2 run avg.	2.02	-0.74	-0.02	-0.01	**0.28**	0.29	-1.35	-1.99	-1.06	**-1.04**
Shindell, 2001	GCM-T	1980-2000		-1.90	-1.20	-0.50	-0.60	**-0.90**	-0.80	-0.70	-0.60	-0.80	**-0.70**
STRAT OZONE + WMGHG													
Schwarzkopf & Ramaswamy, 2002	GCM	1979-1997		0.78	-0.99	-0.67	-0.10	**-0.23**	-1.58	-0.65	-0.03	-0.26	**-1.21**
Rosier and Shine, 2000(updated)	GCM	1979-1997	summed	-0.28	-0.94	-0.22	-0.37	**-0.46**	-1.27	-0.58	-0.39	-1.48	**-0.92**
Langematz et al, 2002	GCM	1979-1996	co2 only	-0.95	-0.76	-0.32	-0.57	**-0.65**	-0.17	-0.17	-0.14	-0.16	**-0.16**
Austin, 2002	GCM-CHEM-T	1979-1999	wat-feed	1.06	-0.75	-0.31	-0.34	**0.09**	-0.56	-0.15	-0.02	-2.85	**-0.89**
Shindell, 2001	GCM-CHEM-T	1980-2000		-1.60	-1.80	-0.50	-0.40	**-1.00**	-0.50	-0.70	-0.40	-2.80	**-0.70**
Shindell, 2001	GCM-CHEM-T	1980-2000	wat-feed	-1.70	-1.90	-0.60	-0.70	**-1.20**	-1.00	-1.00	-0.80	-2.80	**-1.40**
Schnadt et al., 2002	GCM-CHEM	1980-1990	wat-feed	-0.20	-0.72	-0.37	-0.43	**-0.37**	-1.23	0.44	-0.26	-4.02	**-1.31**
STRAT WATER VAPOUR													
Forster and Shine, 2002	FDH	1980-2000	+1 ppmv	-0.58	-0.47	-0.44	-0.56	**-0.51**	-0.49	-0.60	-0.70	-0.65	**-0.61**
Shindell, 2001	GCM-CHEM-T	1980-2000		-0.20	-0.50	-0.20	-0.10	**-0.30**	-0.10	-0.20	-0.20	-0.40	**-0.30**
Smith, 2001	GCM	1992-1999	HALOE	0.03	0.28	-0.01	-0.21	**0.02**	-0.09	-0.20	-1.00	-1.12	**-0.60**
Smith, 2001	2Dmodel	1992-1999	HALOE	0.11	0.10	0.11	0.08	**0.10**	-0.33	-0.31	-0.25	-0.23	**-0.28**

Study	Model	Period	Notes	100 hPa (K/decade) 70N DJF	MAM	JJA	SON	Annual	70 S DJF	MAM	JJA	SON	Annual
Satellite observations													
MSU-4		1979-1998		-0.72	-1.78	-0.18	-0.53	**-0.80**	-0.49	-0.47	-0.19	-1.06	**-0.55**
Berlin sondes		1979-2000						**-0.65**					
UKRAOB sondes		1979-2000						**-0.59**					
Russia sondes		1979-2000						**-0.56**					
STRAT OZONE													
Schwarzkopf & Ramaswamy, 2002	GCM	1979-1997		-0.28	-1.04	-0.62	0.09	**-0.46**	-3.32	-0.41	-0.17	-2.39	**-1.57**
Rosier and Shine, 2000(updated)	GCM	1979-1997		-0.13	-1.13	-0.57	-0.32	**-0.54**	-1.75	-0.55	0.19	-2.27	**-1.09**
Langematz, 2000	GCM	1979-1996		-0.40	-1.08	-0.27	-0.13	**-0.47**	-1.64	-0.42	-0.20	-1.38	**-0.91**
Smith, 2001	GCM	1979-1997		-1.60	-0.73	-0.72	-0.80	**-0.96**	-2.64	-0.72	-0.75	-4.08	**-2.05**
WMGHG													
Schwarzkopf & Ramaswamy, 2002	GCM	1979-1997		0.73	0.14	-0.20	-0.13	**0.14**	0.30	-0.18	-0.05	-0.10	**-0.01**
Rosier and Shine, 2000(updated)	GCM	1979-1997		0.01	0.26	0.27	-0.07	**0.12**	0.06	-0.21	-0.54	0.61	**-0.02**
Langematz et al., 2002	GCM	1979-1996	co2, diff.	-0.09	0.16	0.05	-0.14	**-0.01**	0.31	0.06	-0.12	-0.18	**0.02**
Butchart et al, 2001	GCM-T	1991-2001	2 run avg.	1.67	0.87	0.33	0.07	**0.70**	-0.14	-1.22	-1.56	-0.86	**-0.95**
Shindell, 2001	GCM-T	1980-2000		-2.30	-1.00	-0.40	-0.40	**-0.80**	-0.40	-0.40	-0.30	-0.60	**-0.50**
STRAT OZONE + WMGHG													
Schwarzkopf & Ramaswamy, 2002	GCM	1979-1997		0.45	-0.90	-0.83	-0.04	**-0.33**	-3.03	-0.59	-0.22	-2.49	**-1.58**
Rosier and Shine, 2000(updated)	GCM	1979-1997	summed	-0.12	-0.86	-0.31	-0.40	**-0.43**	-1.69	-0.76	-0.35	-1.66	**-1.11**
Langematz et al, 2002	GCM	1979-1996	co2 only	-0.49	-0.92	-0.22	-0.27	**-0.48**	-1.33	-0.36	-0.32	-1.56	**-0.89**
Austin, 2002	GCM-CHEM-T	1979-1999	wat-feed	1.31	-0.11	-0.20	-0.40	**-0.15**	-2.10	-0.21	0.13	-2.26	**-1.11**
Shindell, 2001	GCM-CHEM-T	1980-2000		-1.90	-2.00	-0.30	-0.20	**-1.00**	-0.30	-0.30	-0.30	-3.00	**-0.80**
Shindell, 2001	GCM-CHEM-T	1980-2000	wat-feed	-1.90	-1.80	-0.50	-0.70	**-1.20**	-0.50	-0.50	-0.60	-3.00	**-1.10**
Schnadt et al., 2002	GCM-CHEM	1980-1990	wat-feed	-0.16	-0.56	-0.22	-0.48	**-0.31**	-1.91	-0.01	-0.08	-1.81	**-0.96**
STRAT WATER VAPOUR													
Forster and Shine, 2002	FDH	1980-2000	+1 ppmv	-0.72	-0.58	-0.51	-0.70	**-0.63**	-0.71	-0.83	-0.86	-0.95	**-0.84**
Shindell, 2001	GCM-CHEM-T	1980-2000		-0.20	-0.40	-0.10	0.00	**-0.20**	-0.10	-0.10	-0.10	-0.30	**-0.10**
Smith, 2001	GCM	1992-1999	HALOE	-0.42	0.06	-0.30	-0.55	**-0.30**	-0.25	-0.04	-0.68	-1.26	**-0.56**
Smith, 2001	2Dmodel	1992-1999	HALOE	-0.51	-0.53	-0.61	-0.58	**-0.56**	-0.21	-0.27	-0.22	-0.01	**-0.18**

Table 4.1: Observed and modeled 70°N and 70°S seasonal lower stratospheric temperature trends over the last two decades. Trends are shown in units of K/decade for altitudes at 50 hPa and 100 hPa, for: December, January and February (DJF), March, April, and May (MAM); June,

July and August (JJA); September, October, and November (SON), and the annual-averaged trend. Dark (light) shading represents significant trends at the 2s (1s) level. Observations are described in Section 1.2.2 and models in Section 4.2

5 CHEMISTRY-CLIMATE MODELING OF THE POLAR STRATOSPHERE

5.1 Introduction

Despite considerable research, the extent to which stratospheric change can influence climate is only beginning to be understood. Before the discovery of the Antarctic ozone hole (Farman *et al.*, 1985) it was thought that increases in WMGHGs would cool the stratosphere and increase ozone (*e.g.*, Groves and Tuck, 1980). However, it is now recognized that an increase in WMGHGs may increase PSCs and decrease ozone. Possibly one of the most extreme examples of chemistry-climate coupling is the effect of increasing WMGHGs on Arctic ozone. Using a mechanistic model with reasonably comprehensive chemistry Austin *et al.* (1992) showed that a doubling of CO_2 concentrations, expected towards the end of the 21st century, could lead to severe Arctic ozone loss if large halogen abundances persisted until that time. On the other hand, the calculations of Pitari *et al.* (1992) showed only a slight reduction in Arctic ozone due to a CO_2 doubling, while again keeping chlorine amounts fixed.

Since the early 1990s, the amendments to the Montreal protocol have resulted in a considerable constraint on the evolution of halogen amounts and more recent calculations have been able to take this into consideration. For example, in a coupled chemistry-climate simulation, Shindell *et al.* (1998a) specified currently projected concentrations of halogens and WMGHGs and calculated increased ozone depletion over the next decade or so, with severe ozone loss in the Arctic in years with lower than normal temperatures. Many of the conclusions of the last report (WMO, 1999, Chapter 12), were based on the Shindell *et al.* (1998a) study. Since then a number of coupled chemistry-climate models have been developed and run. One of the main reasons for using coupled models to investigate future ozone changes is that the changes in temperatures and transport occur in a way that is consistent with the underlying physics. For example reductions in ozone can cool the stratosphere via radiative processes and this results in further changes in ozone and transport. Simulations with, for example, a CTM require the specification of temperature and winds from another source such as a different model.

This would necessarily introduce some differences between the model results, which may be significant, particularly if severe ozone loss is predicted.

Traditionally, climate models have been run with fixed WMGHGs for both present and doubled CO_2 with the investigation of the subsequent 'equilibrium climate.' Several coupled chemistry-climate runs have followed this route with multi-year 'timeslice' simulations applicable to greenhouse gases (GHG) concentrations for specific years (*e.g.*, Rozanov *et al.*, 2001; Schnadt *et al.*, 2002; Pitari *et al.* 2002b; Steil *et al.*, 2001). Other climate simulations have involved transient changes in the WMGHGs, and several coupled chemistry-climate simulations have followed this pattern (*e.g.*, Shindell *et al.*, 1998a; Austin 2002; Nagashima *et al.*, 2002). The advantage of transient experiments is that the detailed evolution of ozone can be determined in the same way that it is likely to occur (in principle) in the atmosphere, albeit with some statistical error. Comparisons with observations are direct since both atmosphere and model cover the period when WMGHGs and halogens are changing. Timeslice simulations need sufficient duration (at least 10 and preferably 20 years) to allow the interannual variability to be determined but in principle, 20 years evaluations of the same conditions may have less variability than the atmosphere in which halogens may be changing rapidly. Timeslice runs also have the advantage that several realizations of the same year are available, from which future predictions can be assessed. However, in practice this may be of less value than examining the behavior of different models, since a given model will tend to have systematic errors.

In this section, results are brought together only from 3-D models, as 2-D models are much less able to capture the dynamical processes of the polar regions. Also, because 2-D models do not treat the planetary wave dynamics in a fully realistic manner they are less able to capture the processes which give rise to trends in transport and temperature which are essential to the future predictions of ozone recovery. 2-D models are therefore better suited to process studies investigating the impacts of chemical changes, as indicated in Chapter 4. For the GCMs used in this section, both transient simulations and timeslice simulations are used, with results from both sets of simulations collected together specifically for this report, with the purpose of illustrating how the polar stratosphere might evolve during the next 50 years. A more complete model intercomparison is included in Austin *et al.* (2002).

Table 1. Models used in the comparisons. The resolution is given in degrees latitude x degrees longitude (grid point models) and T32 etc. are the resolutions in spectral models corresponding to triangular truncation of the wave space with 32 wave numbers. IS92a, refers to scenario IS92a of IPCC (1992) and WMO refers to the halogen scenario indicate in WMO (1999), Chapter 12.

Model	Horizontal Resolution	# Levels/ Upper Boundary	GHG/ Halogen Scenarios	Reference
UMETRAC	2.5x3.75	64/0.01 hPa	IS92a/WMO	Austin (2002) (Rayleigh Friction version)
CMAM	T32	65/0.0006 hPa	Observations	deGrandpre *et al.* (2000)
MAECHAM / CHEM	T30	39/0.01 hPa	IS92a/WMO	Steil *et al.* (2001) Manzini *et al.* (2002)
ECHAM4.L39 (DLR)/ CHEM	T30	39/10 hPa	IS92a/WMO	Schnadt *et al.* (2002)
UIUC	4x5	25/1 hPa	Observations	Rozanov *et al.* (2001)
CCSR/NIES	T21	30/0.06 hPa	IS92a/WMO	Takigawa *et al.* (1999), Nagashima *et al.* (2002)
GISS	8x10	23/0.002 hPa	IS92a/WMO	Shindell *et al.* (1998b)
ULAQ	10x20	18/1 hPa	IS92a/WMO	Pitari *et al.* (2002a)

The models used in the comparisons are indicated in Table 1, in order of decreasing horizontal resolution. ULAQ is the only model with a substantial aerosol package and has reasonably detailed chemistry, albeit diurnally averaged. This model has been run in timeslice mode. Of the other models run in this mode, the Canadian Middle Atmosphere Model (CMAM) and the Middle Atmosphere European Centre Hamburg model (ECHAM) with chemistry (MAECHAM/CHEM) have reasonably detailed chemistry and a high upper boundary (0.01 hPa and above), while the University of Illinois at Urbana-Champaign (UIUC) model and the ECHAM model with chemistry run at DLR (ECHAM4.L39(DLR)/CHEM) have a much lower upper boundary (1 hPa and below). The Unified Model with Eulerian Transport and Chemistry

(UMETRAC), CCSR/NIES, and GISS have been run in transient mode and the first two models have reasonably detailed chemistry while the GISS model has parameterized chemistry.

5.2 The Uncertainties in Chemistry-Climate Models

5.2.1 TEMPERATURE BIASES

As noted in Section 4.3.2, many climate models without chemistry but with a fully resolved stratosphere have a cold bias of the order of 5-10 K over Antarctica in the lower stratosphere. This suggests that their residual circulations are too weak (Pawson *et al.,* 2000), *i.e.*, there is too little downwelling in high latitudes and too little upwelling in low latitudes. This cold temperature bias would significantly impact model heterogeneous chemistry, and enhance ozone destruction. The 'cold pole problem' extends to higher stratospheric levels causing a polar night jet that is too strong and too vertically oriented, whereas the observed polar night jet slopes with height towards the equator in the upper stratosphere. The weaker jet and vertical slope allows waves to propagate into higher latitudes and maintain higher polar temperatures. A potentially important component of climate change is whether these waves will be stronger in the future, since this will likely affect the evolution of ozone: see Section 5.2.4. A practical solution to those models with a cold bias is to increase the temperatures in the heterogeneous chemistry routines (*e.g.*, Austin *et al.,* 2000) by a fixed amount (*e.g.*, 5K). The strong polar night jet is also associated with a polar vortex that breaks down later in the spring, particularly in the Southern Hemisphere. In a chemistry-climate model this can lead to ozone depletion that continues for longer than observed.

Gravity waves generated by processes other than orography (*e.g.*, clouds) are thought to play an important role in the momentum balance of the stratosphere. Nonorographic gravity-wave drag (gwd) schemes have now been developed for climate models (*e.g.,* Medvedev and Klaassen, 1995; Hines, 1997; Warner and McIntyre, 1999) and their use has resulted in a significant reduction in the cold pole problem relative to simulations that rely on Rayleigh friction to decelerate the polar night jet (*e.g.*, Manzini and McFarlane, 1998). Two of these schemes have also been shown to produce a QBO when run in a climate model (Scaife *et al.,* 2000a). The latest versions of several coupled chemistry-climate models now employ such schemes: CMAM uses the Medvedev-Klaassen scheme (Medvedev *et al.* 1998) or the Hines scheme (McLandress, 1998); UMETRAC uses the Warner and McIntyre scheme; and

MAECHAM/CHEM uses the Hines scheme (Steil *et al.*, 2001). The GISS GCM has used a non-orographic gravity wave drag scheme for many years (Rind *et al.*, 1988a, b), which is able to reproduce high latitude temperatures reasonably well (Shindell *et al.*, 1998b) but does not simulate a QBO in the tropics.

Figure 5.1 shows model temperature biases as a function of height for 80˚N and 80˚S, which are representative of the polar regions, for the winter and spring seasons. To determine the biases, a 10-year temperature climatology determined from UKMO data assimilation fields (Swinbank and O'Neill, 1994) was subtracted from the mean model temperature profiles applicable to the 1990s. The UKMO temperatures are considered to be about 2K too high at low temperatures (*e.g.*, Pullen and Jones, 1997; Manney *et al.*, 2002; Pommereau *et al.*, 2002; Knudsen *et al.*, 2002) but this is somewhat smaller than typical model biases. The upper stratospheric cold pole problem is particularly noticeable in the south in the UMETRAC (with Rayleigh friction), CCSR/NIES (which also uses Rayleigh friction) and MAECHAM/CHEM results. In the results of the UIUC and ULAQ models a warm bias is present. For the ULAQ model this is likely to be due to the inclusion of vertical diffusion (in addition to Rayleigh friction). As seen in the UMETRAC results, the winter and spring polar temperature bias can be dramatically reduced by the use of non-orographic gwd. Both UMETRAC and CMAM have very similar biases, within a few K of each other in the seasons investigated. The MAECHAM/CHEM model, which uses the Hines non-orographic gwd scheme, is only a slight improvement on the Rayleigh friction results of UMETRAC and CCSR/NIES. ECHAM4.L39(DLR)/CHEM is very similar to the MAECHAM/CHEM model, and gives similar results below 30 hPa, but does not have a non-orographic gwd scheme. At 80˚N temperature biases are somewhat smaller than at 80˚S and are sometimes positive. The northern lower stratospheric temperature biases would generally lead to insufficient heterogeneous ozone depletion in early winter but excessive ozone depletion in the more important spring period. In the Southern Hemisphere, spring cold biases could lead to more extensive PSCs than observed and delayed recovery in Antarctic ozone.

Some indication of the source of the model temperature biases in the lower stratosphere is given by Figure 5.2, which shows the heat flux [v'T'] at 100 hPa averaged over the domain 40-80˚N for January and February plotted against temperature averaged over the domain 60-90 ˚N at 50 hPa for February and March. As argued by Newman *et al.* (2001), the heat flux at 100 hPa is

indicative of the wave forcing from the troposphere and this is highly correlated with lower stratospheric temperature slightly later in the year. Newman *et al.* (2001) chose a 1-15 March temperature average, but here we choose a longer period for the temperature average to smooth model and atmospheric transients. The model results (Figures 5.2 and 5.3) are in general agreement with observations and in Table 2 results of the linear regression between the two variables are shown (see table caption for explanation of the terms T_0 and β). The results indicate that horizontal resolution may have affected the model results: in general the model regression lines were less steep (smaller β in Table 2) as the model resolution decreased, particularly in the Northern Hemisphere. This could be because low-resolution models capture the low-amplitude wave, small heat flux case, but have difficulty capturing the large heat flux case with its significant potential enstrophy cascade to larger wavenumbers. The performance of the models might also depend on the dissipation that the models have at short spatial scales, although this is more difficult to compare. The values of β are generally much smaller in the Southern Hemisphere, except for the CCSR/NIES and CMAM models. The implication of these results therefore is that models need higher resolution and non-orographic gwd schemes to improve the relationship between heat flux and temperature in order to reduce their polar temperature biases.

5.2.2 THE SIMULATION OF POLAR STRATOSPHERIC CLOUDS

PSCs have a significant impact on stratospheric ozone depletion in polar regions and recent developments in their understanding are discussed in detail in Carslaw *et al.* (2001) and Section 2.3. Coupled chemistry-climate models have a variety of PSC schemes with and without sedimentation, but such models have in some cases large climatological temperature biases in the polar regions, as indicated in Section 5.2.1. If the models are to be effective, the temperature field must give realistic distributions near the PSC temperature thresholds.

The areal coverage of PSCs provides a model comparison diagnostic. We use the temperature at 50 hPa as an indicator of likely PSC amounts, and ignore the effect of HNO_3 and sulfate concentrations on the determination of PSC surface areas (following Pawson and Naujokat, 1997; and Pawson *et al.,* 1999). Figure 5.4 shows for the models and observations the time integral throughout the winter of the PSC area at 50 hPa. A_τ is here measured in terms of the fraction of the hemisphere covered in % times their duration in days. For the ice amount, A_τ

varies dramatically in the Arctic, between zero (ULAQ and CMAM models, not shown) and 70% of the hemisphere times days. The models have large interannual variability. Arctic NAT also covers a large range, both for different models and in the interannual variability for each simulation. In accordance with their temperature biases, several models have larger areas of NAT than are typically derived from observations. The ULAQ PSCs are in good agreement with observations, despite a slight positive temperature bias, while UMETRAC and CMAM have lower PSCs than are derived from observations. In the Antarctic each model has much lower fractional interannual variation, but again the results for separate models cover an exceedingly large range for the ice amount. Clearly, the differences between different models will have a profound impact on the amount of chemical ozone depletion calculated and will be discussed further in Section 5.3.

Table 2. Statistical analysis of the linear regression between the area averaged temperature (K) at 50 hPa poleward of 60˚N for Feb and March, and the heat flux (Km/s) at 100 hPa between 40 and 80˚N for Jan. and Feb (Northern Hemisphere). The Southern Hemisphere results are for the months Aug. and Sept. and July and Aug. respectively. R is the correlation coefficient between the variables, T_0 is the intercept of the line at zero heat flux, and β is the gradient of the line.

Model/Observations	**Northern Hemisphere**			**Southern Hemisphere**		
	R	T_0	β	R	T_0	β
NCEP (Observations)	**0.77**	**195.1**	**1.49**	**0.78**	**189.4**	**0.89**
UMETRAC Non-orographic gwd	0.74	196.9	1.21	0.66	188.5	0.98
Rayleigh Friction	0.67	196.2	1.21	0.51	187.7	0.67
CMAM 2000	0.54	204.6	0.76	0.48	191.2	0.86
MAECHAM/CHEM 1990	0.79	196.3	1.10	0.70	190.0	0.50
ECHAM4.L39(DLR) CHEM	0.62	198.3	0.93	0.86	186.3	0.56
CCSR/NIES	0.74	199.4	0.80	0.74	186.6	1.17
ULAQ	0.58	203.0	0.48	----	----	----

5.2.3 THE POSITION OF THE UPPER BOUNDARY OF THE GCM

There is strong evidence from a number of modeling studies (Garcia and Boville, 1994; Shepherd *et al.,* 1996; Lawrence, 1997; Austin *et al.,* 1997; Rind *et al.,* 1998; Beagley *et al.,* 2000) that the position of the model upper boundary can play a significant role in influencing transport and stratospheric dynamics due to the 'downward control principle' (Haynes *et al.,* 1991). The sensitivity of the dynamical fields to the position of the upper boundary may be larger when using non-orographic gwd schemes than when Rayleigh friction is used, although if all the non-orographic gwd that is produced above the model boundary is placed instead in the top model layer, assuming that the upward propagating waves are not simply absorbed in the top layer, this sensitivity reduces (Lawrence, 1997). Model simulations with an upper boundary as low as 10 hPa have been completed (*e.g.,* Schnadt *et al.,* 2002; Hein *et al.,* 2001; Dameris *et al.,* 1998). Schnadt *et al.* (2002) show the meridional circulation of the DLR model and this gives the expected upward motion from the summer hemisphere and downward motion over the winter hemisphere, although modeled meridional circulations are known to extend into the mesosphere (*e.g.,* Butchart and Austin, 1998). Schnadt *et al.* (2002) argue is that it is less important to have a high upper boundary, but more important to have high resolution in the vicinity of the tropopause. At present the evidence appears ambiguous: for example in the total ozone presented by Hein *et al.* (2001), insufficient ozone is transported to the North Pole, but there is excessive subtropical ozone transport. This could be related to the cold pole problem, rather than the position of the upper boundary. While the transport effect on ozone is direct, other considerations are the transport of long-lived tracers such as NO_y and water vapor that have a photochemical impact on ozone. Consequently, it is generally recognized that the upper boundary should be placed at least as high as 1 hPa (*e.g.,* Rozanov *et al.,* 2001; Pitari *et al.,* 2002b) with many models now placing their boundary at about 0.01 hPa (*e.g.,* Shindell *et al.,* 1998b; Austin *et al.,* 2001; Steil *et al.,* 2001; Nagashima *et al.,* 2002). In comparison, CMAM (de Grandpre *et al.,* 2000) has an upper boundary somewhat higher (c. 0.0006 hPa) to allow a more complete representation of gwd to reduce the cold-pole problem (Section 5.1.1) and to simulate upper atmosphere phenomena.

5.2.4 PREDICTIONS OF PLANETARY WAVES

In some GCMs, there is a significant trend in planetary wave propagation with time. In the GISS GCM, planetary waves are refracted equatorward as greenhouse gases increase (Shindell *et al.*, 2001) while in the ULAQ model a marked reduction in the propagation of planetary waves 1 and 2 to high northern latitudes is found in the doubled CO_2 climate simulated by Pitari *et al.* (2002b). In the GISS model the impact of changed planetary wave drag is largest during winter when the enhanced polar night jet strengthens the polar vortex over the Arctic (Shindell *et al.*, 1998a; Rind *et al.*, 1998). Planetary wave refraction is governed by wind shear, among other factors, so that enhanced wave refraction occurs as the waves coming up from the surface approach the area of increased wind. They are refracted by the increased vertical shear below the altitude of the maximum wind increase. Equatorward refraction of planetary waves at the lower edge of the wind anomaly leads to wave divergence and hence an acceleration of the zonal wind in that region. Over time, the wind anomaly itself propagates downward within through the stratosphere (*e.g.*, Baldwin and Dunkerton, 2001), and subsequently, from the tropopause to the surface in the GISS model.

The direct radiative cooling by greenhouse gases at high latitudes in the lower stratosphere causes an increase in the strength of the polar vortex. Planetary wave changes may be a feedback that strengthens this effect. One proposed planetary wave feedback mechanism (Shindell, 2001) works as follows: tropical and subtropical sea surface temperatures increase, leading to a warmer tropical and subtropical upper troposphere via moist convective processes. This results in an increased latitudinal temperature gradient at around 100-200 hPa leading to enhanced lower stratospheric westerly winds, which refract upward propagating tropospheric planetary waves equatorward. This results in a strengthened polar vortex.

However, climate experiments containing different physics with higher spatial resolution models (*e.g.*, Schnadt *et al.*, 2002) do not show a future trend towards reduced high latitude wave propagation. Without chemical feedback, the Unified Model (UM) predicts a future increase in overall generation of planetary waves, which leads to a greater wave flux to the Arctic stratosphere, and is even able to overcome the radiatively induced increase in the westerly zonal wind so that the overall trend is to more easterly flow. This also occurs in the Deutschen Zentrum für Luft- und Raumfahrt (DLR) model with chemical feedback (Schnadt *et al.*, 2002)

whereas in the UM with chemical feedback (UMETRAC) the trend in the heat flux during the period 1975-2020 is downwards but is not statistically significant. The Center for Climate System Research/National Institute for Environmental Studies (CCSR/NIES) model, of lower resolution than UMETRAC, has systematically lower heat fluxes but does show a downward trend during the period 1986-2050 which is marginally statistically significant. In general, the strengthening of the polar vortex appears to be critically dependent upon the relative importance of changes in wave generation versus wave propagation. These changes are likely to be highly model and resolution dependent, resulting from the particular wave forcing and drag schemes employed in each climate model. To some degree this sensitivity of the changes in planetary waves to the model simulation reflects similar uncertainties in the atmosphere: for example in the observations of the last five northern winters, four have been warm with a weaker polar vortex (see Section 1.2.2). As a result the strengthening of the vortex over the last twenty years noted by some authors (Tanaka *et al.*, 1996; Zurek *et al.*, 1996; Waugh *et al.*, 1999; Hood *et al.*, 1999). will have been modified by recent measurements.

5.2.5 Uncertainties in the Rate of Water Vapor Increase

Observations of atmospheric water vapor concentrations have revealed significant increases over the period 1964-2000 (Oltmans and Hofmann, 1995; Oltmans *et al.*, 2000). These observations and their possible implications and causes are discussed in Sections 2.2, 3, 4 and Chapter 4. In general, the increases are uncertain in magnitude and their causes have not been established.

Increased water vapor directly affects ozone chemistry, and also alters local temperatures by radiative cooling, slowing down the reaction rates of ozone depletion chemistry, which indirectly leads to more ozone. The effects on homogeneous chemistry have been studied by Evans *et al.* (1998); Dvortsov and Solomon (2001); and Shindell (2001). The models all show that increases in water vapor reduce ozone in the upper and lower stratosphere, and increase ozone in the middle stratosphere. The model results differ most in the lower stratosphere where the largest impact on total ozone column occurs. In the model of Evans *et al.* (1998), lower stratospheric ozone is reduced only in the tropics when water vapor increases, while in the other models, ozone reductions extend to mid-latitudes or to the poles. Thus, the models of Dvortsov and Solomon (2001) and Shindell (2001) show a slower ozone recovery by about 10-20 years,

and a 1-2% reduction during the next 50 years due to water vapor increase, assuming that the water vapor increase continues at the current rate. The Evans *et al.* (1998) model disagrees with these results, presumably due to differences in the model's temperature response to increasing water, which seems to dominate over its chemical impacts.

Water vapor increases also affect heterogeneous chemistry, enhancing the formation of PSCs. Kirk-Davidoff *et al.* (1999) calculated a significant enhancement to Arctic ozone loss in a more humid atmosphere. Much of this effect was based on a very large estimate of 6 to 9 K per ppmv radiative cooling induced by increased water vapor. This value has been superseded by newer results showing that this value is almost certainly much smaller, about 1.5 to 2.5 K cooling per ppmv of water (Section 4.3.3). This would in turn imply a reduced role for water vapor in enhancing PSC formation. Tabazadeh *et al.* (2000) showed that the enhancement of PSC formation due to the addition of 1 ppmv of water vapor is approximately the same as the PSC enhancement due to cooling of about 1 K. This suggests that the radiative impact of water vapor is larger than its effects on chemistry or microphysics but that all these processes should be considered in numerical models. Given the potential for denitrification in the Arctic, and the large ozone losses that could result from a slight cooling there (Tabazadeh *et al.*, 2000), it is important both to understand trends in stratospheric water vapor, and to resolve model differences in the radiative impact of those trends.

Model simulations of past water vapor trends do not agree well with observations. In UMETRAC (Austin, 2002), water vapor increases by only about 1% per decade in the stratosphere, despite the inclusion of a methane oxidation scheme. In UMETRAC the tropical tropopause temperature decreases slightly, counteracting the methane impact. In ECHAM4.L39(DLR)/CHEM (Schnadt *et al.*, 2002), water vapor increases in the lower stratosphere are significantly larger (about 3% per decade) but are still about a factor of 2-3 lower than observed. Similar results are also obtained in the GISS model. In general the modeled water vapor trend tends to be driven by methane oxidation and trends in tropopause temperature, suggesting the need to investigate the microphysics of dehydration and how this is represented in models. See EUR (2001), Section 4.3.3.

5.3 Model Assessments

In the Arctic the processes leading to stratospheric ozone depletion may undergo too much natural variability to provide a definite answer of how ozone will actually evolve. Each model may be considered as supplying a single simulation (or range of simulations in the case of the timeslice experiments) of a larger ensemble. While the mean of the ensemble can be readily computed, the atmosphere may in practice evolve in a manner anywhere within, or even outside, the envelope of the model simulations. In the Antarctic, the dominant processes are less dependent on interannual variability and hence the ozone evolution is in principle more predictable.

One of the emphases here has been on spring ozone recovery. In view of the range of results obtained, it is important to define this term carefully and it is here used in two senses: (i) the start of ozone recovery, defined as the date of the minimum spring column ozone as a function of year in the decadally averaged results, (ii) full ozone recovery defined as the date of the return of the decadally averaged spring column ozone to the value obtained in 1980.

5.3.1 THE 1960 - 2000 TIME FRAME: OZONE DEPLETION

As is well established from observations (Section 1), polar ozone has been decreasing over the last few decades. Figure 5.5 (top panel) shows the minimum daily ozone throughout the range 60-90N for the range of models of Table 1 together with TOMS data. Each model has a large interannual variability, similar to that of the observations, and hence detecting a signal is difficult. The continuous lines indicate the 10-year running means of the individual datasets for the transient model runs, which help to identify the timing of the minima. All the models indicate a slight high bias relative to observations. In the Arctic, the trends in the minimum are consistent with the observations for most of the models, although only the observed trend is statistically significant. See Table 3.

In the Antarctic (Figure 5.5, lower panel), the model runs all agree reasonably well with observations for the past and show the steady development of the ozone hole during the period. The calculated trends depend on the period chosen but even when this is taken into account both GISS and CMAM under predict the trend over the period 1980 – 2000. While the interannual variability in most of the models is similar to that observed, both CMAM and UMETRAC have a

large interannual variability. In the case of UMETRAC, this may to some extent be a product of the non-orographic gwd scheme. In CMAM the ozone minima are slightly high for the current atmosphere, but too low for 1980, giving a much-reduced trend.

Table 3. Past trends (1979-2000) in minimum ozone (DU/decade) with 2 sigma error bars for participating models and TOMS. The results for the CCSR/NIES model covers the period 1986-2000, the ECHAM.L39(DLR)/CHEM results cover the period 1960 to 1990 (Arctic) and 1980 to 1990 (Antarctic). The MAECHAM/CHEM results cover the period 1960-2000 (Arctic) and 1960-1990 (Antarctic).

Model/Observations	**Northern Hemisphere trend**	**Southern Hemisphere trend**
TOMS	-21+/- 16	-59 +/- 12
UMETRAC	-6 +/- 22	-80 +/- 31
CMAM	-8 +/- 17	-14 +/- 17
MAECHAM/CHEM	-14+/- 17	-46 +/- 5
ECHAM.L39(DLR)/CHEM	-16 +/- 14	-64 +/- 7
CCSR/NIES	-33 +/- 38	-41 +/- 21
GISS	-21 +/- 34	-34 +/- 12

The maximum size of the Antarctic ozone hole during each spring, as given by the area within the 220-DU, total-ozone contour, is shown in Figure 5.6. The results for GISS, ECHAM.L39(DLR)/CHEM and CCSR/NIES are in good agreement with observations, but may indicate a slight under prediction. A much smaller ozone hole is simulated by UMETRAC, but recent model runs, with an NO_y distribution consistent with observations show an ozone hole about 50% larger for 1995, which is in close agreement with observations. The small ozone hole area for CMAM reflects the bias and large interannual variability noted in Figure 5.5. Errors in the modeling of the size of the ozone hole can have important implications. Firstly, comparisons between models and observations for ozone amounts near 60˚S will give poor agreement if the ozone hole area is too small, even though the underlying physics of the model may be correct. Secondly, a model with a smaller ozone hole may evolve differently from that of the atmosphere due to transport and chemistry effects relating to radiative effects.

5.3.2 THE 2000 - 2020 TIME FRAME: START OF OZONE RECOVERY

The first signs of ozone recovery are expected within the next two decades (Shindell *et al.*, 1998a; Austin *et al.*, 2000; Schnadt *et al.* 2002; Rosenfield *et al.*, 2002; Nagashima *et al.*, 2002). Two-dimensional (2-D) model simulations (*e.g.*, Rosenfield *et al.*, 2002) indicate a slight delay in Arctic and Antarctic spring ozone recovery following the maximum values in halogen loading. The GISS model has a larger response than the other models with the simulation indicating a minimum in the smoothed results of about 175 DU compared with almost 100 DU higher in the other transient runs. The date of minimum Arctic ozone, again as indicated by the minimum of the smoothed curves, varies from 2004 for the CCSR/NIES model to 2019 for the GISS model. UMETRAC indicates a minimum at about the year 2015, but the simulation ends shortly afterwards and the smoothed curve is virtually flat in the final decade. All three transient runs indicate some delay in the onset of ozone recovery, due to increases in GHGs, although such a result is subject to considerable uncertainty because of the large interannual variability. Although the timeslice experiments do not have the temporal resolution to give a precise indication of the timing of future ozone recovery, the ECHAM4.L39(DLR)/CHEM model results (Schnadt *et al.*, 2002) may go against the transient model results by suggesting that increases in planetary waves occur in the Arctic speeding up ozone recovery. This may be considered the 'dynamical effect on chemistry': Increases in planetary waves transport more ozone as well as raise temperatures and decrease heterogeneous chemistry. Therefore, the net effect on ozone is that of the two potentially competing processes of dynamics and radiation. If planetary waves increase, the 'dynamical' effect increases ozone and the 'radiative' effect decreases ozone, giving a relatively small response. If planetary waves decrease, both the 'dynamical' and 'radiative' effects are negative, leading to enhanced ozone depletion. To resolve whether increases in GHGs are delaying the onset of ozone recovery, from the timeslice simulations would require more results for the period 1990 to 2015.

In the Antarctic, the runs are all in fairly good agreement. Of the transient runs, as in the Arctic, the CCSR/NIES model indicates the earliest start of ozone recovery (2001) followed by UMETRAC (2005) and GISS (2008). The minima in the smoothed curves are all comparable (109, 86, and 98 DU respectively). On the basis of the decadally averaged model results this would appear to indicate that ozone recovery would begin earlier in the Antarctic than in the

Arctic. Such an earlier start to recovery would also be detectable earlier in observations in Antarctica, because of the smaller interannual variability.

Observations of the size of the ozone hole (Figure 5.6, see also Section 1.2.1) do not indicate any clear recovery by October 2001, with interannual variability now dominating over the current trends. Indeed, the smoothed curve for the GISS results has its maximum size in 2011. For UMETRAC the maximum ozone hole area is in 2019, although the curve is virtually flat from 1995 onwards. In contrast the decadally smoothed results for the CCSR/NIES model indicate a clear peak as early as the year 2002.

5.3.3 THE 2020 - 2060 TIME FRAME: COMPLETE OZONE RECOVERY

Those models that have run beyond the year 2020 indicate some recovery in ozone. Of particular importance is the return to '1980-like conditions,' when the effects of anthropogenic halogen concentrations were negligible. As noted in WMO (1999), Chapter 12, this recovery would be to a different vertical distribution of ozone, with higher middle and upper stratospheric ozone due to the change in vertical temperature profile (see Chapter 4). Using a 2-D model, Rosenfield *et al.* (2002), determined the date for the recovery of total ozone to 1980 levels as a function of day of year and latitude. In the Arctic, this recovery was latest at the end of spring (after 2050) and earliest in autumn (before 2035). Further, the impact of CO_2 increases was shown to accelerate the recovery from that due to chemical changes alone by increasing the downwelling. In contrast, if methane amounts do not increase at the current rate, ozone recovery could be slowed down in the future by the increased importance of NO_x chemistry (Randeniya *et al.*, 2002). Over Antarctica, downwelling is less important in speeding up the ozone recovery.

The results of Figure 5.5 show similar results for the spring for 3-D models. However, in the Arctic, most models do not show substantial Arctic ozone change throughout the period 2020 to 2050, while the low values of the GISS model for the decade 2010 to 2020, are no longer present after 2030. In the Antarctic, the recovery of spring ozone, already underway by 2020, continues in the simulations completed (Figure 5-6). Recovery to 1980-like conditions occurs in the CCSR/NIES and GISS models by about 2045, and perhaps a decade later in the UMETRAC snapshot and CMAM results. The CCSR/NIES and GISS transient model results suggest a near monotonic recovery of ozone, but the UMETRAC snapshot results suggest that ozone could undergo further loss over the period 2025 to 2045. This was identified as due to increases in ice

PSCs as the lower stratospheric climate cools (Austin *et al.*, 2001), but would need to be confirmed by model simulations with more detailed PSC schemes. Of the timeslice experiments, the MAECHAM/CHEM results indicate a significant (but not `full') recovery in the Antarctic by 2030, consistent with the transient experiments. The MAECHAM/CHEM model also simulates full or near full recovery in the Arctic by 2030.

5.3.4 ATTRIBUTION OF MODEL OZONE CHANGES

In a coupled chemistry-climate model the attribution of ozone changes to dynamical and chemical processes may be ambiguous since the dynamical changes themselves may have been caused by chemical changes to the ozone amounts. This is discussed further in Chapter 4. Figure 5.4, illustrating the approximate amounts of PSCs in the model simulations, should in principle reflect the amount of chemical ozone depletion (cf. Figure 3.4). This would suggest, for example that UMETRAC has slightly less Arctic ozone depletion relative to observations and this is reflected in the Arctic ozone trend (Figure 5.5, Table 3) that is smaller than observed, although the difference is not statistically significant. Also, both MAECHAM/CHEM and ECHAM4.L39(DLR)/CHEM results for PSCs in Figure 5.4 suggest that their chemical ozone depletion is larger than observed in the Arctic although the net ozone trend is similar to observations. The implication is that transport into the polar regions is enhanced to compensate. However, this does not appear to be consistent with earlier results, *e.g.*, Hein *et al.* (2001) which if anything indicates reduced transport into the polar regions.

Similar results apply in the Antarctic. Here many of the models have similar ozone depletion rates (Figure 5.5, Table 3), similar amounts of PSCs and similar ozone trends, when allowance is made for the different periods under consideration. The main exceptions are the GISS model for which PSC diagnostics are not available, and CMAM, which has larger ozone depletion than observed in 1980. These inconsistencies in both hemispheres suggest the need for further investigation of the sizes of the transport versus chemical depletion terms in all the models included herein.

5.4 Summary

The main uncertainties of 3-D coupled chemistry-climate models stem from the performance of the underlying dynamical models. Temperature biases lead to errors in the

spatial extent of PSCs and the degree of chemical ozone depletion. The model results also suggest significant differences in the transport of ozone to high latitudes, although this is in need of further clarification. At the current stage of model performance, uncertainties in the details of PSC formation and sedimentation are probably less important in simulating ozone amounts than the model temperature biases. Nonetheless, the accurate representation of PSC processes will prove to be increasingly important as temperature biases become smaller, by for example, the inclusion of non-orographic gravity wave parameterizations. Another uncertainty is the amount of aerosol present due to future unpredictable volcanic eruptions. For a large eruption such as that of Mt. Pinatubo, sufficient aerosol would be present to provide additional sites for heterogeneous chemistry and possible severe ozone loss for a period of a few years, although this perturbation would not affect the long-term ozone trend. The impact of volcanic eruptions on coupled chemistry-climate model results has not been discussed in this Section, but further details may be found in Chapter 4.

For the transient model simulations the start of ozone recovery, as defined in Section 5.3, occurs in the Antarctic in the range 2001 to 2008, depending on the model and in the Arctic occurs in the range 2004 to 2019. In the Antarctic, however, model results suggest that the vertical and horizontal extent of the ozone hole may increase slightly further over the next few years. Thus, the results here suggest that the start of ozone recovery will occur slightly later in the Arctic than in the Antarctic. Further, since the halogen amounts are thought to have maximized in 2002 (see Chapter 1), the start of ozone recovery in the Arctic in the models is delayed by 3-18 years by greenhouse gas increases. Most of the models come to similar conclusions on this issue, but one of the coupled chemistry-climate model experiments (Schnadt *et al.*, 2002) suggests that greenhouse gas increases would tend to speed up rather than slow down ozone recovery in the Arctic. It should also be recognized that interannual variability on the sub-decadal timescale may still lead to ozone extremes. In the worst-case scenario, therefore, it may take until at least the end of the 2020s before we can be certain that ozone recovery has started in the Arctic. To put this into perspective, most models predict relatively modest changes in future spring Arctic column ozone (under 10%). The one model that does predict a major Arctic ozone change in the near future (described in Shindell *et al.*, 1998), has lower spatial resolution, simplified ozone transport, and parameterized ozone chemistry. In comparison, the other models have more accurate treatments of these processes.

On the longer timescale, to the middle of the 21st century, model predictions appear to be more uncertain. Hence, although recovery of Antarctic ozone to 1980-like conditions (‘full ozone recovery’) is to be expected by about 2050, models will need to have a better representation of the water vapor increase than has hitherto been possible, as well as an accurate specification of methane changes, for full confidence in their predictions. Although the results for the Arctic are less certain, since most models indicate relatively modest change in ozone, it is possible that `full recovery’ may occur somewhat earlier there.

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CHAPTER 3 ACRONYMS AND ABBREVIATIONS

2-D	two-dimensional
3-D	three-dimensional
AASE	Airborne Arctic Stratospheric Expedition
ADEOS	ADvanced Earth Observing Satellite
AES	Atmospheric Environment Service (Canada)
AM	annular mode
AO	Arctic Oscillation
ATMOS	Atmospheric Trace Molecule Spectroscopy
AWI	Alfred Wegener Institute (Germany)
BAS	British Antarctic Survey (United Kingdom)
BISA	Belgian Institute for Space Aeronomy (Belgisch Instituut voor Ruimte-Aëronomie, Institut d'Aéronomie Spatiale de Belgique)
CCSR	Center for Climate System Research (University of Tokyo) (verify)
CFC	chlorofluorocarbon
ClaMS	Chemical Lagrangian Model of the Stratosphere
CMAM	Canadian Middle Atmosphere Model
CNES	Centre National d'Études Spatiales (France)
CNRS	Centre National de la Recherche Scientifique (France)
CPC	
CRISTA	Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere
CTM	Chemical Transport Model
DAO	Data Assimilation Office (NASA Goddard, USA)
DJF	December, January, and February
DLR	Deutschen Zentrum für Luft- und Raumfahrt (German Aerospace Research Establishment)?
DMI	Danish Meteorological Institute
DOAS	Differential Optical Absorption Spectroscopy
DU	Dobson unit
ECHAM4.L39(DLR)/CHEM	European Centre Hamburg Model with Chemistry (Germany)
ECMWF	European Centre for Medium-Range Weather Forecasts (Reading, United Kingdom)
ENEA	Ente Nazionale Energie Alternative (Italy)
ENSO	El Niño-Southern Oscillation
EP	Earth Probe
ERS-2	second European Remote Sensing satellite
ESA	European Space Agency
EU	European Union

FDH	Fixed Dynamical Heating
FSSP	forward scattering spectrometer probe
FTIR	Fourier transform infrared
GCM	General circulation model
GHG	greenhouse gases
GISS	Goddard Institute for Space Studies (NASA, United States)
GOME	Global Ozone Monitoring Experiment
GRIPS	GCM-Reality Intercomparison Project for SPARC
gwd	gravity wave drag
HALOE	Halogen Occultation Experiment
IFOV	instantaneous field of view
IGY	International Geophysical Year
ILAS	Improved Limb Atmospheric Spectrometer
IMK	Institut für Meteorologie und Klimaforschung (Institute of Meteorology and Climate Research, Karlsruhe, Germany)
IRF	Institut für Rumdfysik (Institute of Space Physics, Sweden)
IROE	Instituto di Ricerca Sulle Onde Elettromagnetiche (Italy)
ISAMS	Improved Stratospheric and Mesospheric Sounder
ISTS	Institute for Space and Terrestrial Science (Canadian Space Agency, Canada)
IVL	Institutet för Vatten- och Luftvårdsforskning) (Swedish Environmental Research Institute, Sweden)
JJA	June, July, and August
JPL	Jet Propulsion Laboratory (California Institute of Technology, United States)
KASIMA	Karlsruhe SImulation model of the Middle atmosphere
LaRC	Langley Research Center (NASA, United States)
LCTM	Lagrangian chemical transport model
MAECHAM/CHEM	Middle Atmosphere ECHAM with chemistry
MAM	March, April, and May
MASP	Multiangle Aerosol Spectrometer Probe
MIPAS	Michelson Interferometric Passive Atmosphere Sounder
MLM	Modified Lagrangian Mean
MLS	Microwave Limb Sounder
MOS	metal oxide semiconductor
MRI	Meteorological Research Institute (Japan)
MSU	Microwave Sounding Unit
NAD	nitric acid dihydrate
NAO	North Atlantic oscillation
NASA	National Aeronautics and Space Administration

NAT	nitric acid trihydrate
NCAR	National Center for Atmospheric Research (United States)
NCEP	National Center for Environmental Protection
NDSC	Network for the Detection of Stratospheric Change
NH	Northern Hemisphere
NIES	National Institute for Environmental Studies (Japan)
NILU	Norwegian Institute for Air Research (Norway)
NMC	National Meteorological Center
NIWA	National Institute of Water and Atmosphere (New Zealand)
NOAA	National Oceanic and Atmospheric Administration
OPC	Optical Particle Counter (OPC)
PMD	polarization monitoring devices
PNJ	polar night jet
POAM	Polar Ozone and Aerosol Measurement
POLARIS	Photochemistry of Ozone Loss in the Arctic Region in Summer
ppbv	parts per billion by volume
ppmv	parts per million by volume
ppt	parts per trillion
PSC	Polar Stratospheric Cloud
PV	potential vorticity
QBO	quasi-biennial oscillation
SAGE	Stratospheric Aerosol and Gas Experiment
SAOD	stratospheric aerosol optical depth
SAOZ	Système d'Analyse par Observation Zénithale
SBUV	Solar Backscatter Ultraviolet spectrometer
SCD	slant column density
SEFDH	Seasonally Evolving Fixed Dynamical Heating models
SH	Southern Hemisphere
SOLVE	SAGE III Ozone Loss and Validation Experiment
SON	September, October, and November
SPADE	Stratospheric Photochemistry, Aerosols, and Dynamics Expedition
SPARC	Stratospheric Processes and their Role in Climate (WCRP)
SPOT	Satellite Pour l'Observation de la Terre
SSU	Stratospheric Sounding Unit
STEL	Solar Terrestrial Environment Laboratory (Japan)
STS	supercooled ternary solutions
STTA	Stratospheric Temperature Trend Analysis
SUNY	State University of New York (United States)
SZA	solar zenith angle
TEM	transformed Eulerian mean
TOMS	Total Ozone Mapping Spectrometer

TOVS	Televison and InfraRed Observational Satellite (TIROS) Operational Vertical Sounder
UARS	Upper Atmosphere Research Satellite
UIUC	University of Illinois at Urbana-Champaign (United States)
UKMO	United Kingdom Meteorological Office
ULAQ	Università degli Studi dell'Aquila (Italy)
UM	Unified Model
UMETRAC	Unified Model with Eulerian Transport and Chemistry
UV	ultraviolet
UV-C	UV-radiation (approximately 200-280 nm)
WMGHG	well-mixed greenhouse gas
WMO	World Meteorological Organization

CHAPTER 3 CHEMICAL FORMULAE AND NOMENCLATURE

Br	atomic bromine
Br_y^{org}	organic bromine profile
Br_y^{inorg}	inorganic bromine profile
BrCl	bromide chloride
BrO	bromine monoxide
$BrONO_2$	bromine nitrate
BrOOCl	bromo chloro peroxide (verify)
CH_4	methane
Cl	atomic chlorine
ClO	chlorine monoxide
ClOO	chloro peroxy radical (verify)
ClO_x	chlorine radicals
$ClONO_2$,	chlorine nitrate
ClOOCl	chlorine monoxide dimer
Cl_y^{inorg}	inorganic chlorine species
Cl_y^{org}	organic source compounds
Cl_y	total inorganic chlorine
CO	carbon monoxide
CO_2	carbon dioxide
H_2O	water
HBr	hydrogen bromide
HCl	hydrogen chloride (hydrochloric acid)
HF	hydrogen fluoride (hydrofluoric acid)
HNO_3	nitric acid
HNO_4	peroxynitric acid
HO_2	hydroperoxyl radical
HOBr	hypobromous acid
HO_x	odd hydrogen (H, OH, HO_2, H_2O_2)
IO	iodine monoxide
J_{1b}	photolysis rate
k_{1a}	first-order reaction-rate constant
NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides (NO + NO_2)

NO_y	odd nitrogen (usually includes NO, NO_2, NO_3, N_2O_5, $ClONO_2$, HNO_4, HNO_3)
N_2O	nitrous oxide
N_2O_5	dinitrogen pentoxide
O	atomic oxygen
OBrO	bromine dioxide
OClO	chlorine dioxide
O_2	molecular oxygen
O_3	ozone
O_3 MD	ozone mass deficiency
SF_6	sulfur hexafluoride
SO_2	sulfur dioxide