Chemical loss of polar vortex ozone inferred from UARS MLS measurements of ClO during the Arctic and Antarctic late winters of 1993

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Abstract. A computationally cheap, and easily initialized photochemical model utilizing UARS MLS measurements of ClO to calculate ozone destruction rates within the polar vortices due to the ClO + ClO, ClO + BrO, and ClO + O catalytic cycles is developed. The method involves calculating local reactive chlorine concentrations from individual ClO retrievals, and then inferring the diurnal cycle of ClO from a quadratic expression using the relevant kinetic parameters. In test integrations this simple treatment is shown to give good agreement with more detailed model calculations. Analysis of the late Arctic and Antarctic winters of 1993 yields similar vortex-averaged ozone loss rates at 465 K of ~1% per day in both hemispheres, while the reactive chlorine remains enhanced. Net ozone destruction in the north is less, largely because the elevated ClO and Cl_2O_2 concentrations are less persistent. The estimated chemical destruction on isentropic surfaces in the lower stratosphere is broadly similar to the observed change in ozone distribution, implying that the change is dominated by chemical destruction.

Introduction

Following the initial observation of exceptionally low column ozone (O_3) amounts in the southern polar regions during Antarctic spring [*Farman et al.*, 1985], there have been numerous reports of similar winter/spring ozone reductions in subsequent years in both the Antarctic [e.g., *Johnson et al.*, 1994; *Hofmann et al.*, 1994], and, to a lesser degree, the Arctic [e.g., *Browell et al.*, 1993; *Manney et al.*, 1994]. These studies have revealed the major depletion to be located in the lower stratosphere, and it is now generally accepted that the principal cause is catalytic chemistry involving the chlorine monoxide radical [*WMO*, 1992]. This chemistry has become increasingly important in the last few decades as the atmospheric chlorine loading has risen owing to anthropogenic emissions. The ozone depletion occurs in polar regions during the late winter and early spring as a consequence of the low temperatures prevailing at high latitudes giving rise to the formation of polar stratospheric clouds (PSCs). Heterogeneous reactions on the surface of these clouds release chlorine from HCl and $ClONO_2$ reservoir compounds into the reactive (ozone destroying) forms, priming the polar atmosphere for chemical ozone destruction [*Solomon et al.*, 1986].

Quantifying chemical ozone loss in the polar vortices from observations of ozone alone is not straightforward because the distribution of the gas is continually being changed by atmospheric transport processes [*Solomon*, 1990]. A complementary approach is to calculate the expected destruction directly from measurements of the ozone destroying chemicals. The Microwave Limb Sounder (MLS) instrument aboard the Upper Atmosphere Research Satellite (UARS) is providing the first global data set of chlorine monoxide (ClO) measurements. It thus presents a unique opportunity to perform a global analysis of the impact of chlorine chemistry on polar ozone over extended periods during the winter and spring based on continually updated ClO amounts. In this paper a simple model for calculating chemical ozone destruction from the MLS data is described and its accuracy verified by comparison with more detailed calculations. The model is then used to estimate the rate of ozone loss inside the 1992-1993 northern and 1993 southern polar vortices. Ozone changes inferred from chemistry alone are compared with observations. See *Froidevaux et al.* [1994] for an overview of zonal mean ozone observations from the first 2 years of MLS operations, and *Manney et al.* [1995a] for the observed evolution of high-latitude ozone in relation to polar vortex dynamics for two northern and three southern winters, including the winters described here.
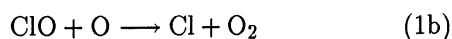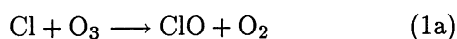
Description of Data

The MLS instrument [*Barath et al.*, 1993] sounds an area of the atmosphere, with full zonal coverage, from 34° on one side of the equator to 80° on the other, the hemisphere of high-latitude coverage alternating every ~36 days, a "UARS month". Primary retrievals are O_3, H_2O, ClO, temperature, and pressure. MLS "Version 3" ClO and O_3 data were used for this study. ClO profiles are measured between 100 and 0.46 hPa, with a vertical resolution of ~5 km, at around 1300 locations per day, distributed between the day and night sides of the orbit. Noise uncertainties for individual ClO retrievals in the lower stratosphere are around 0.4 ppbv [*Waters et al.*, 1996], which in conjunction with the pronounced diurnal variation exhibited by this species (minimum at night) implies that meaningful individual measurements of ClO can be obtained only from illuminated regions containing concentrations considerably enhanced above the usual background of around 0.1 ppbv. Such regions are found within the winter/spring polar vortices [*Waters et al.*, 1993a, b], but the requirement for daylight restricts the useful data to a maximum of one vertical profile of ClO per day at any one location. The local times of the measurements vary; however, owing to the slow precession of the satellite, on any given day, local times of daylight retrievals at a particular latitude differ by not more than ~20 min. The precision of individual O_3 retrievals in the lower stratosphere at 46 hPa is around 0.2 ppmv [*Froidevaux et al.*, 1996]. Absolute accuracies of the Version 3 ClO and ozone are estimated at 15–20%. The effect of known errors in the Version 3 ClO data [*Waters et al.*, 1996] was reduced by adjusting the 22 and 46 hPa polar vortex enhanced ClO values as follows before using them in the calculations: (1) all values were multiplied by a scaling factor varying quadratically from unity at zero ClO to 0.92 at 1.8 (and −1.8) ppbv ClO; (2) to account for bias errors occurring under the conditions of depleted gas phase HNO_3 typical of the Antarctic winter vortex, ClO values measured within this vortex were reduced by 0.2 ppbv. Subsequent to the completion of this work, an additional scaling error of 8% was discovered in the Version 3 ClO data; see *Waters et al.* [1996] for validation of the MLS ClO measurements, and detailed description of the Version 3 uncertainties and errors.

Estimation of Ozone Loss

The first catalytic cycle advanced as a possible pathway for ozone destruction was as follows:
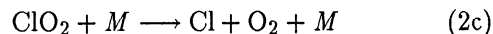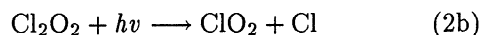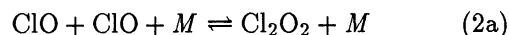
Cycle 1 [*Molina and Rowland*, 1974]

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (1a)$$

$$ClO + O \longrightarrow Cl + O_2 \qquad (1b)$$
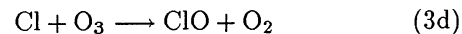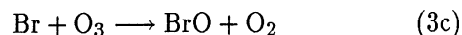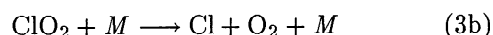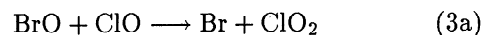
Net $\qquad\qquad O_3 + O \longrightarrow 2O_2$

However, further studies [e.g., *Anderson et al.*, 1989;

McKenna et al., 1990] have indicated that in chemically perturbed polar vortices containing enhanced reactive chlorine, the bulk of the chemical ozone loss is due to the following two cycles:
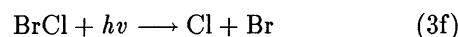
Cycle 2 [*Molina and Molina*, 1987]

$$ClO + ClO + M \rightleftharpoons Cl_2O_2 + M \qquad (2a)$$

$$Cl_2O_2 + h\nu \longrightarrow ClO_2 + Cl \qquad (2b)$$

$$ClO_2 + M \longrightarrow Cl + O_2 + M \qquad (2c)$$

$$2 \times (Cl + O_3 \longrightarrow ClO + O_2) \qquad (2d)$$

Net $\qquad\qquad 2O_3 \longrightarrow 3O_2$

Cycle 3 [*McElroy et al.*, 1986]

$$BrO + ClO \longrightarrow Br + ClO_2 \qquad (3a)$$

$$ClO_2 + M \longrightarrow Cl + O_2 + M \qquad (3b)$$

$$Br + O_3 \longrightarrow BrO + O_2 \qquad (3c)$$

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (3d)$$

Net $\qquad\qquad 2O_3 \longrightarrow 3O_2$

Cycle 3 can also be initialized by a more minor reaction channel of ClO and BrO

$$BrO + ClO \longrightarrow BrCl + O_2 \qquad (3e)$$

$$BrCl + h\nu \longrightarrow Cl + Br \qquad (3f)$$

Because the applicable data set consists of only a single measurement of ClO per day at any one point in the atmosphere, it is necessary to infer the total local ozone depletion for the day from this one observation. The methods used for the three separate catalytic cycles are now given, beginning with cycle 2.

Cycle 2 Ozone Destruction

During the day, the slowest step of cycle 2 is (2a) the self reaction of ClO to form the dimer, Cl_2O_2, but this step is rate determining for the cycle as a whole only at temperatures below about 200 K, that is, when the inequality $J_{Cl_2O_2} >> k_{-2a}[M]$ is satisfied. At higher temperatures, reaction (−2a), the thermal decomposition of Cl_2O_2 back to ClO, which short-circuits the cycle and causes no ozone destruction, is sufficiently fast to compete significantly with the photodissociation reaction (2b), required to continue the cycle. However, (2c) and (2d) the reactions subsequent to the photodissociation are always very rapid relative to the preceding reactions, so, irrespective of temperature, the instantaneous rate of ozone loss due to cycle 2 can be expressed as [*Ko et al.*, 1989]

$$\frac{-d[O_3]}{dt} = 2J_{Cl_2O_2}[Cl_2O_2] \qquad (4)$$

In the daylight polar vortex the photolysis of Cl_2O_2 is sufficiently fast that Cl_2O_2 and ClO can be assumed to be in photochemical equilibrium, and the right-hand

side of equation (4) is then equal to twice the rate of reaction (2a) multiplied by the factor $(J_{Cl_2O_2})(J_{Cl_2O_2} + k_{-2a}[M])^{-1}$. *Salawitch et al.* [1993] used this latter expression to infer ozone loss due to this cycle.

The ozone loss over 1 day, $-\Delta O_{3(24hrs)}$, is given by the integral of (4), that is,

$$- \Delta O_{3(24hrs)} = 2 \int_{sunrise}^{sunset} J_{Cl_2O_2}[Cl_2O_2]\,dt \qquad (5)$$

Integration need be performed only over the daylight period because the cycle, requiring a photolysis reaction, cannot proceed at night.

Under conditions of enhanced reactive chlorine, the diurnal variations of ClO and Cl_2O_2 are due almost entirely to interchange between these two species, and in order to evaluate (5) at the location of a ClO measurement, the diurnal cycles must be inferred from this one measurement. We do this in two stages: firstly, the MLS ClO measurement is used to infer the total reactive chlorine for that day, then on the assumption that the total reactive chlorine is constant throughout the day, ClO and Cl_2O_2 amounts appropriate to different times are inferred. The details are as follows.

Since, as already remarked, the photolysis lifetime of the dimer is short during the hours of daylight, its daytime steady state concentration may be expressed as

$$[Cl_2O_2] = \frac{k_{2a}[ClO]^2[M]}{J_{Cl_2O_2} + k_{-2a}[M]} \qquad (6)$$

Now k_{2a} and k_{-2a} can be calculated at the local temperature (available from U.S. National Meteorological Center analysis [*Finger et al.*, 1993]), and $J_{Cl_2O_2}$ can be evaluated for the solar zenith angle appropriate to the time of measurement, taking into account the ozone column observed by MLS. Thus $[Cl_2O_2]$ at the measurement time can be estimated.

The total reactive chlorine, Cl^*, can now be calculated from

$$[Cl^*] = [ClO] + 2[Cl_2O_2] \qquad (7)$$

Having found Cl^*, we need to find how ClO varies through the daylight hours. Substituting (6) into (7) leads to the quadratic expression [*Rodriguez et al.*, 1989]

$$\frac{2k_{2a}[M]}{J_{Cl_2O_2} + k_{-2a}[M]}[ClO]^2 + [ClO] - [Cl^*] = 0 \qquad (8)$$

Putting values of $J_{Cl_2O_2}$ calculated at 15-min intervals through the day into (8) and assuming that Cl^* does not vary significantly over one daylight period, a series of values for [ClO] are obtained. These can be converted into $[Cl_2O_2]$ from (7), allowing the integration of (5) to give a value for the local daily ozone loss due to cycle 2. Repeating this procedure for each suitable satellite measurement of ClO allows global maps of daily ozone destruction to be produced.

Cycle 1 Ozone Destruction

Cycle 1 is rate limited by reaction (1b), so the daily ozone destruction by this cycle can be expressed as

$$- \Delta O_{3(24hrs)} = 2 \int_{sunrise}^{sunset} k_{1b}[ClO][O]\,dt \qquad (9)$$

At the winter pole, the concentration of O atoms in the stratosphere is controlled by the photolysis and recombination reactions

$$O_3 + h\nu \longrightarrow O + O_2 \qquad (10)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (11)$$
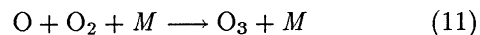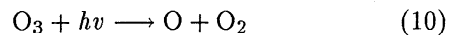
such that in the steady state

$$[O] = \frac{J_{O_3}[O_3]}{k_{11}[O_2][M]} \qquad (12)$$

Ozone is measured by MLS at the same locations as ClO, and shows little daily variation in the lower stratosphere, so the diurnal cycle of O at the points for which the ClO cycle has been inferred can be obtained from (12) simply by calculating the J_{O_3} cycle. Expression (9) can thus be evaluated.

Cycle 3 Ozone Destruction

The expression for daily ozone loss due to cycle 3 analogous to (5) and (9) is

$$- \Delta O_{3(24hrs)} = 2 \int_{sunrise}^{sunset} (k_{3a} + k_{3c})[ClO][BrO]\,dt \qquad (13)$$

While it is not possible to evaluate this expression rigorously in the absence of measurements of BrO or another bromine species simultaneous to those of ClO, an approximate solution can be obtained. In stratospheric regions of high ClO and low NO_2 concentrations, typical of the polar vortices in late winter and early spring, almost all the inorganic bromine is in the form of either BrO or BrCl, with BrO dominating during the day and BrCl at night [*Wahner and Schiller*, 1992]. The night reservoir BrCl is very readily photolyzed, so photochemical equilibrium is established soon after sunrise, with the steady state concentration of BrO given by

$$[BrO] = \frac{[BrO + BrCl]}{1 + \frac{k_{3e}[ClO]}{J_{BrCl}}} \qquad (14)$$

If the [BrO + BrCl] term in (14) is given a value consistent with the estimated total inorganic bromine in the stratosphere, then a series of J_{BrCl} values calculated through the day at the position of the ClO measurement can be used in conjunction with the estimated diurnal cycle of ClO to obtain a similar cycle for BrO. An approximate value for the daily ozone loss can thus be obtained from (13).

The limited range of available measurements of bromine species in the stratosphere indicates a total bromine level of about 10 to 20 pptv [*Traub et al.*, 1992], and for this work a value of 12 pptv for [BrO + BrCl] was adopted. Daylight BrO concentrations calculated for regions of enhanced reactive chlorine from (14) using this figure are in agreement with the 8 ± 2 pptv mea-
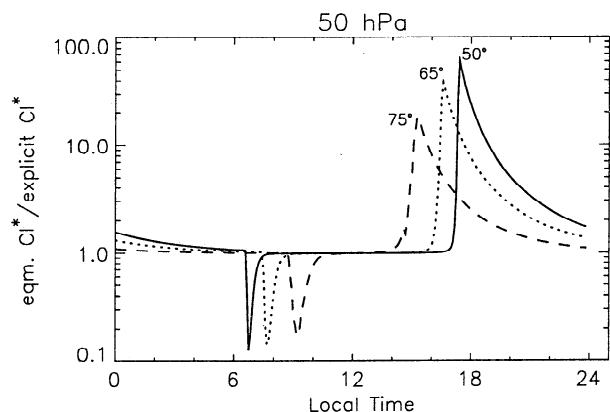
Figure 1. Ratio of the actual ($\sim$3 ppbv) Cl* (ClO + $2Cl_2O_2$) within a one-dimensional model incorporating full chemistry and calculating Cl_2O_2 individually (explicit Cl*), and the Cl* obtained at each 5-min model time step by adding the model ClO concentration to twice the steady state concentration of Cl_2O_2 inferred from this ClO concentration (eqm. Cl*). Results are shown for 50°, 65° and 75° degrees latitude, 55 days after winter solstice. Temperature equals 190 K; pressure equals 50 hPa.

sured by *Toohey et al.* [1990] at 470 K in the chemically perturbed Arctic vortex.

Validation of Method

The above procedures rely inter alia on obtaining an accurate value of the total reactive chlorine at the place of measurement from the retrieved ClO concentration, which in turn depends on the validity of the assumption that Cl_2O_2 is in equilibrium with the ClO at the measurement time. To investigate the conditions under which this approximation is reasonable, some runs of a one-dimensional photochemical model with fairly complete chemistry in which the Cl_2O_2 concentration is calculated individually without any equilibrium assumption have been carried out, and the actual concentration of Cl_2O_2 within this model at each 5-min time step compared with the steady state amount implied by (6) from the model ClO concentration (Figure 1). The one-dimensional model used is an updated version of that described by *Fabian et al.* [1982]; it contains 60 gas phase chemical reactions and 20 photodissociation reactions including all those known to be of most importance in stratospheric ozone chemistry. Expressions for chemical rate of change are integrated by an accurate variable order, variable step method, implementing the backward differentiation formulae [*Hall and Watt*, 1976]. All rate constants and photolysis cross sections used were taken from *DeMore et al.* [1992], with the exception of the BrCl cross sections which were provided by R. A. Cox (personal communication, 1988). Cl_2O_2 cross sections for wavelengths greater than 360 nm were taken from *Burkholder et al* [1990]. It can be seen from Figure 1 that just after sunrise and just before sunset

when the $J_{Cl_2O_2}$ value is changing rapidly, the reactive chlorine calculated from (6) by assuming equilibrium is a gross under- and over-estimate, respectively, of the time dependent value, but for the remainder of the day when the rate of change of $J_{Cl_2O_2}$ is slower, the steady state approximation holds well and an accurate value for total reactive chlorine is obtained. The duration of the periods when the steady state treatment can be applied decreases as one moves poleward. Depending on the time of year, it may be that at very high latitudes there is no time interval when the assumption holds, but when this is the case, the day length at these latitudes is so short that little ozone destruction will be taking place. After examining a number of model runs, it was established empirically that at the high latitudes likely to lie within the vortex, the horizontal region of the graph centered around noon, correlated well with the period in which $J_{Cl_2O_2}$ was changing by less than 10% between the 5-min time steps. On the basis of this finding, a method was devised for determining whether an acceptable Cl* estimate is possible from a given MLS ClO measurement: $J_{Cl_2O_2}$ is calculated at the time and place of the measurement and for a time, 5 min earlier; if the two values differ by more than 10%, then the measurement is discarded on the grounds that no realistic value of $[Cl_2O_2]$ can be obtained from it. In effect, this means discarding all measurements poleward or equatorward of a particular latitude, but on most days almost all MLS retrievals within the polar vortex are retained.

Having established that a correct value for the total reactive chlorine can be obtained (within the constraints of the accuracy of the ClO measurement and kinetic parameters), it is necessary to know how accurately the diurnal cycles of ClO and Cl_2O_2 can be reproduced by solving the quadratic expression. To examine this, the one-dimensional model was initialized with a representative amount of reactive chlorine, and the diurnal cycle of ClO within the model compared with that obtained simply by solving the quadratic at 15-min intervals using the noon value of ($[ClO] + 2[Cl_2O_2]$) from the model. (The diurnal cycles of Cl_2O_2 bear a simple complementary relationship to those obtained for ClO.) Figure 2 shows the results obtained at two different latitudes and heights. The variation estimated by the quadratic method is symmetrical about noon, reflecting the fact that the inferred time series of [ClO] is dependent only on the variation of $J_{Cl_2O_2}$ through the day. This simplification is not inherent in the model, but the agreement is generally very good for the daylight period. The small separations of the two plots around dawn and dusk correspond to the times when the $J_{Cl_2O_2}$ value is changing faster than the system can come to equilibrium, so the equilibrium value implied by the quadratic differs from the explicit value calculated by the model. The discrepancy is larger at dusk because at this time the reaction moving the system toward equilibrium is the self reaction of ClO, which is relatively slow and becomes increasingly so as the ClO concentration falls. These discrepancies are relatively
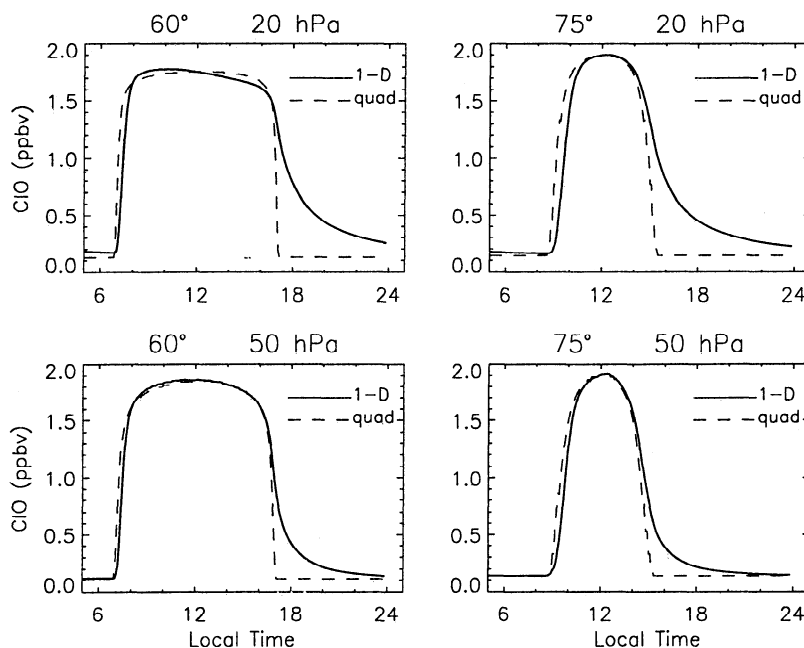
Figure 2. Comparison of diurnal plots of ClO obtained from the full one-dimensional model (unbroken line) at 60° and 75° latitude, 20 and 50 hPa, with those obtained by solving the quadratic expression at 15-min intervals using the noon value of Cl* from the model (dashed line). Results are shown for 55 days after winter solstice; temperature equals 190 K.

unimportant to the daily loss obtained by integrating (5), (9), and (13) because the bulk of the O_3 loss is occurring in the middle of the day when [ClO] is highest and the agreement is excellent. In a number of model trials at different latitudes, heights, and reactive chlorine concentrations, the difference in the daily integrals of [ClO] and [Cl_2O_2] obtained by the two methods did not exceed 10%, and was much less than this at altitudes below 40 hPa where the ozone loss tends to be greatest.

Calculation Uncertainties

When applying the quadratic method to the MLS data, the 0.4 ppbv random instrument noise in the ClO measurements engenders a potentially large error in the calculations for individual ClO retrievals. This is particularly true for the calculation of equilibrium [Cl_2O_2] and the ozone loss due to cycle 2, as they both have a quadratic dependence on the ClO concentration. These random errors can, however, be reduced by taking averages of results for separate retrievals. The noise uncertainty is expected to fall in proportion to $1/N^{0.5}$, where N is the number of values averaged. On a typical UARS day the calculation is performed for in excess of 100 measurements within the vortex on each pressure level, so random ClO errors can be neglected in the calculation of uncertainties in the average loss rate. The noise can lead to negative values of retrieved ClO which we have allowed for by propagating the sign of the retrieved ClO values through the ozone loss calculations. Ignoring the negative values would bias averages resulting from the calculations toward too great a loss.

The equilibrium [Cl_2O_2], and hence the Cl*, implied by a given ClO measurement are also strongly dependent on the kinetic parameters used in the calculation. In this respect a significant uncertainty lies in $J_{Cl_2O_2}$, with the equilibrium [Cl_2O_2] being almost directly proportional to the $J_{Cl_2O_2}$ value calculated for the time and location of the MLS measurement. Photolysis rates from the one-dimensional model scheme used here, are calculated without multiple scattering and with an assumed surface albedo of zero. They are consequently underestimated by up to about 40%, depending on solar zenith angle, compared to a more detailed calculation including multiple scattering and albedo effects. A recent study [*Huder and DeMore*, 1995] has obtained Cl_2O_2 cross sections which give $J_{Cl_2O_2}$ values in the polar vortex around 40–50% smaller than those obtained from the *DeMore et al.* [1992] plus *Burkholder et al.* [1990] cross sections used in this work. The $J_{Cl_2O_2}$ values we have used generally lie somewhere between the values given by more rigorous calculations using these latter cross sections and those from *Huder and DeMore* [1995]. However, when thermal dissociation of the dimer is unimportant, as it usually is wherever Cl* is significantly enhanced (because the temperature is relatively low), the calculated ozone loss due to cycle 2 is almost insensitive to the Cl_2O_2 absorption cross sections used. This is because although the calculated $J_{Cl_2O_2}$ changes, the steady state [Cl_2O_2] adjusts to keep the product $J_{Cl_2O_2}$[Cl_2O_2] the same.

The cycle 2 ozone loss is approximately proportional to k_{2a}[ClO]$_r^2$, where [ClO]$_r$ is the retrieved ClO amount. Given the corrected ClO values used in this work, which remove a portion of the systematic uncertainties, we es-

timate that the remaining uncertainty in ClO, denoted below as f_{ClO}, is of order 10% (not including the known +8% scaling error). The estimated uncertainty in k_{2a}, $f_{k_{2a}}$, is around 25%. Taking the root-sum-square of $f_{k_{2a}}$ and $(2 \times f_{ClO})$ (the latter term arising from the $[ClO]_r^2$ contribution) leads to ~30% uncertainty in the ozone loss rate. *Nickolaisen et al.* [1994] have derived an expression for k_{2a} which at polar vortex temperatures gives values about 20% lower than those of *DeMore et al.* [1992]; this result has led to an updated recommendation by *DeMore et al.* [1994]. Use of these lower values would reduce the cycle 2 ozone loss (and the $[Cl_2O_2]$ at the measurement time) here calculated by around 20%; also, the ozone loss rate uncertainty would then be about 25%.

The uncertainty in the cycle 3 ozone loss rate is determined by the accuracy with which [BrO], [ClO] and $(k_{3a} + k_{3e})$ are known. Tests with the one-dimensional model have shown that varying the total bromine amount within the accepted limits has a negligible effect on the daytime concentrations of ClO and Cl_2O_2. This confirms the assumption inherent in the simplified model that the BrO concentration implied by (4), and hence the estimated ozone loss from cycle 3, vary linearly with the assumed [BrO + BrCl] amount, while the loss from cycles 1 and 2 is independent of this quantity. Assuming a possible range of 10–18 pptv for [BrO + BrCl], then the uncertainty in [BrO] obtained from (4) using [BrO + BrCl] equal to 12 pptv is of order +50%/−25%. The uncertainties in k_{3a} and k_{3e} are around 15%, so the overall root-sum-square uncertainty in the $(k_{3a} + k_{3e})$[ClO][BrO] term for cycle 3 ozone loss is approximately +55%/−30%.

For cycle 1, based on the accuracies of the MLS O_3 measurements and the kinetic parameters used in evaluating equation (12), we estimate an uncertainty of 25% in [O], which along with the ~10% uncertainties in both [ClO] and k_{1b} leads to an uncertainty of ~30% in the ozone loss rate due to this cycle.

As stated previously, an additional error of +8% was discovered in ClO data used in this study, correction for this error would reduce the calculated ozone loss due to cycle 2 by ~15% and the cycles 1 and 3 loss by ~8%. The uncertainty in the estimated total ozone destruction due to cycles 1, 2, and 3 combined is close to the uncertainty in the cycle 2 calculation because this cycle accounts for the bulk of the loss.

Results

We now apply the above methods to MLS observations of the polar vortices. The times analyzed are the north-viewing period of the MLS instrument from February 10 to March 19, 1993, and the south-viewing period for the similar seasonal dates August 11 to September 16, 1993. Local Cl* amounts and daily ozone losses were calculated for each suitable measurement of ClO in the lower stratosphere poleward of 40°, and the results interpolated onto isentropic surfaces, that is,

surfaces of constant potential temperature, θ. On most days the latitudinal band containing the suitable ClO measurements extended from 40° to near 80°, giving approximately 200 calculations at each pressure level. But on a few consecutive days around the middle of each viewing period (see caption to Figure 3) the local times of the measurements allowed the calculation to be performed only in a very narrow latitude range, so the results for these days were found by interpolation from the adjoining days.

Maps of daytime ClO at $\theta = 465$ K (~19 km) for the initial days of the two periods can be seen in Plate 1 along with the inferred Cl*. Temperatures below the PSC formation threshold of ~195 K had been present within the two vortices for some weeks prior to these dates (although in only a small region of the Arctic vortex) [*NOAA*, 1993a; *Manney et al.*, 1994], and the extensive heterogeneous processing which has taken place is reflected in the high mixing ratios of ClO present. These imply Cl* in excess of 3 ppbv over extensive areas, suggesting that within these regions almost all the stratospheric chlorine (abundance 3.44 ±0.30 ppbv [*Gunson et al.* 1994]) is in reactive form. The occurrence and implications of such large MLS ClO retrievals in the polar vortices are discussed in more detail by *Waters et al.* [1996]. Overlain on the maps in Plate 1 is the 2.5×10^{-5} K m^2 kg^{-1} s^{-1} Rossby-Ertel potential vorticity (PV) contour (calculated from United Kingdom Meteorological Office winds and temperatures [*Swinbank and O'Neill*, 1994]), which lies within the region of strong PV gradients. This strong gradient acts as a barrier to material transport inhibiting mixing of intra- and extra-vortex air [*Hoskins et al.*, 1985]. In both hemispheres, the enhanced reactive chlorine is well constrained to the vortex area with a sharp gradient near the edge and the maximum values occurring well inside the vortex.

Plate 1 also shows the estimated ozone loss rate due to the three cycles. It is evident that cycle 2 is dominant with a minor contribution from cycle 3. Cycle 1 is insignificant at 465 K on these dates because the concentration of oxygen atoms is very low. For all three cycles the daily loss within the vortex is highly correlated with the Cl* amount, the sensitivity to this parameter overriding other latitudinal dependencies such as day length and photolysis rates. Local daily O_3 losses of up to ~80 ppbv (2.5%) in the north and ~90 ppbv (3.0%) in the south are calculated on these days, but the maximum loss rates are confined to a small fraction of the vortex area. The small patches of ozone loss outside the vortex are associated with isolated measurements of relatively high ClO which are probably noise artifacts (see arguments by *Schoeberl et al.* [1993]). They cannot, therefore, be taken as evidence of middle latitude ozone destruction.

The estimated chemical loss in the lower stratosphere for the two periods under consideration has been averaged on isentropic surfaces, with density weighting to allow for changes in the gradient of θ with respect to pressure, over the entire vortex region (defined to lie
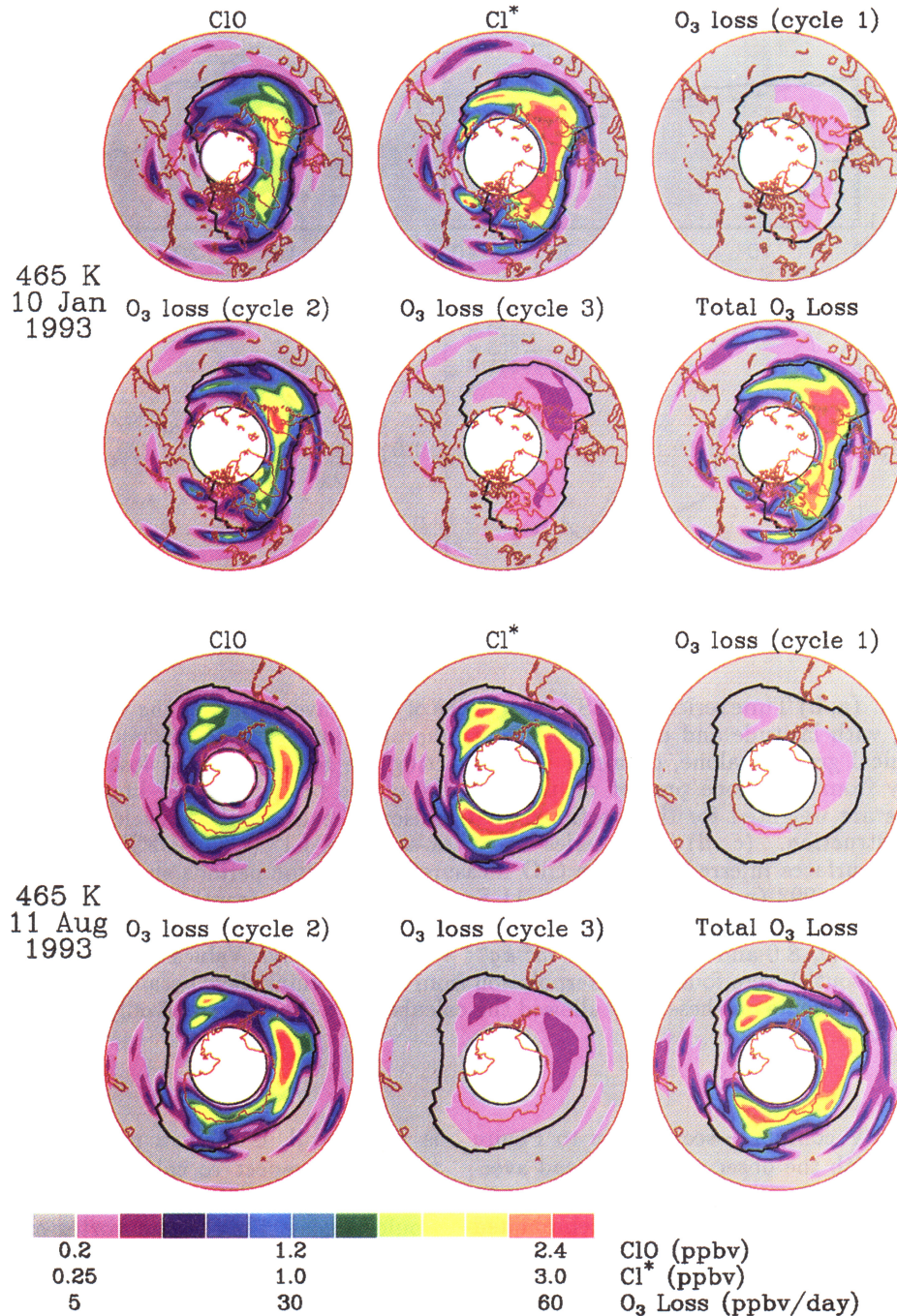
Plate 1. Polar stereographic maps of daytime ClO measured by MLS on February 10, 1993 (northern hemisphere), and August 11, 1993 (southern hemisphere), along with the inferred Cl* $(ClO + 2Cl_2O_2)$ and ozone loss rates due to cycles 1, 2, and 3, interpolated to the 465 K isentropic surface. Also shown is the sum of the ozone loss rates calculated for the individual cycles. The plot area is from the pole to 40°. The solid line represents the approximate boundary of the vortex defined by the PV contour of (negative in south) $2.5 \times 10^{-5} \ K \ m^2 \ kg^{-1} \ s^{-1}$. *Waters et al.* [1995] gives MLS maps of ClO for several additional days in the 1992-1993 northern winter.
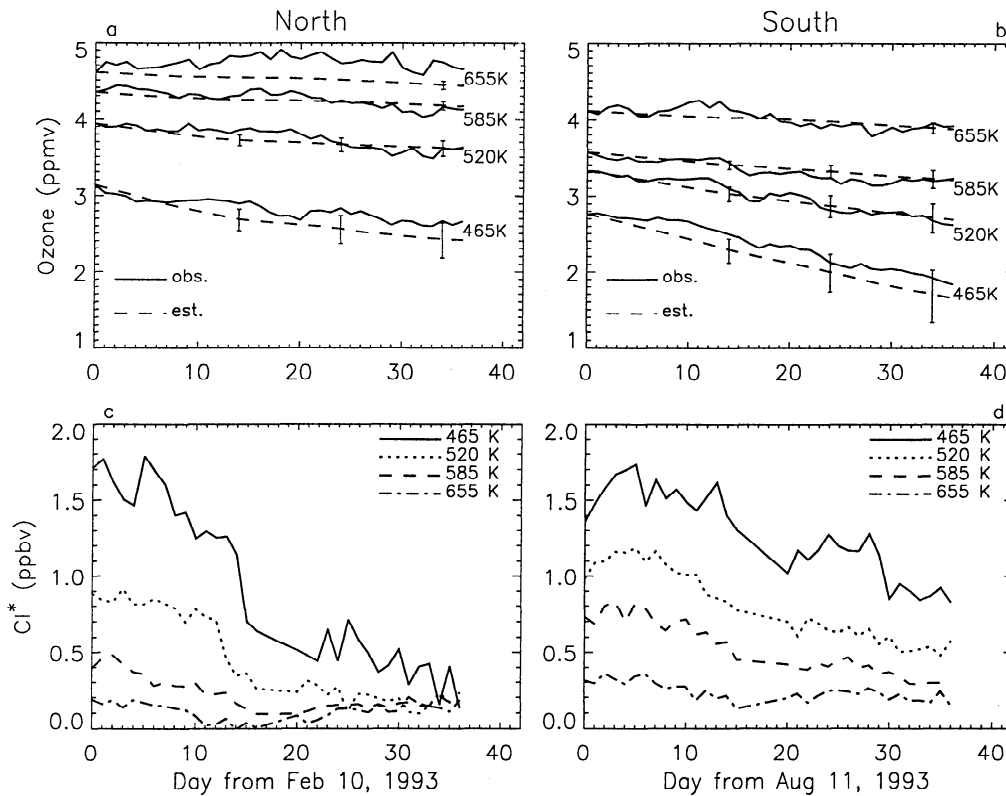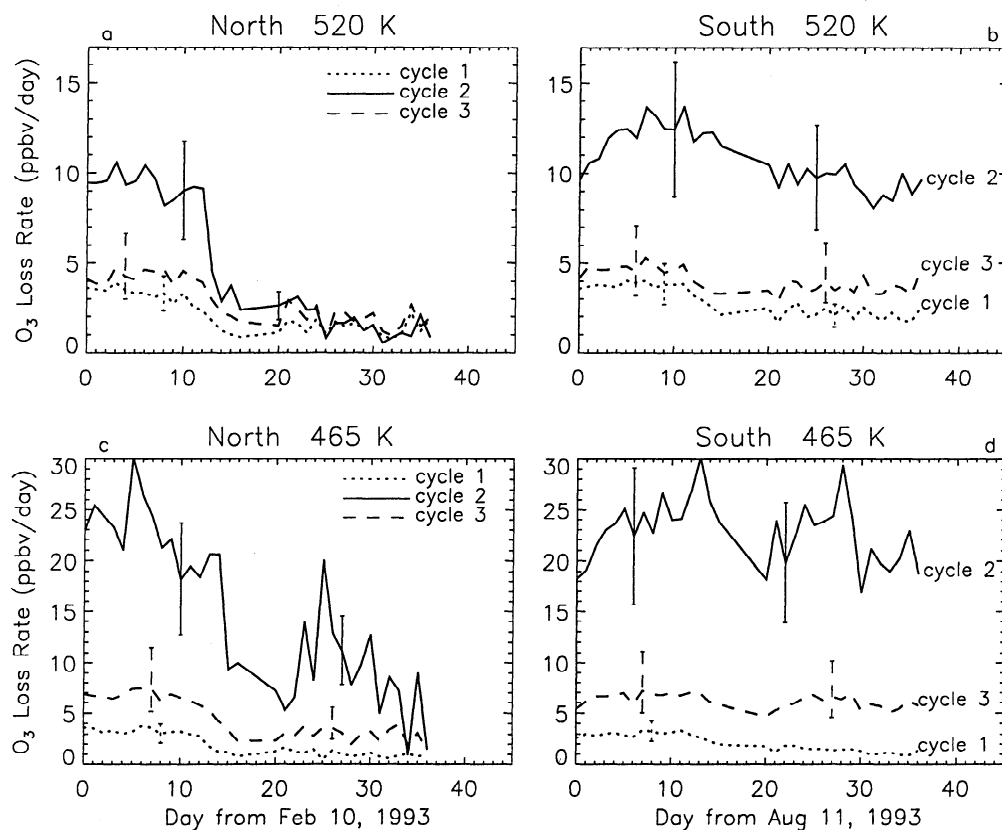
Figure 3. (a, b) Time series of MLS observations of ozone averaged over the vortex on isentropic surfaces, with latitude and density weighting (unbroken line), and the ozone change estimated on chemical grounds alone, obtained by subtracting the total estimated loss integrated up to each day from the ozone present on the first day of the period (dashed line). Error bars on the plots are weighted for the fractional contribution of each catalytic cycle to the estimated ozone destruction. (c, d) Time series of vortex-averaged Cl^* ($ClO + 2Cl_2O_2$) on the same isentropic surfaces inferred from the ClO measurements. Time periods shown are February 10 to March 18, 1993 (north), and August 11 September 16, 1993 (south). The vortex boundary at potential temperatures 465, 520, 585, 655 K was defined by the PV contours of (negative in south) 2.5, 4.0, 8.0 and $11 \times 10^{-5}\ K\ m^2\ kg^{-1}\ s^{-1}$, respectively. Values on days 17-19 (north) and 16-19 (south) were found by interpolation from the adjoining days because the local times of MLS measurements on these days allowed the calculation to be performed only in a very narrow latitude band.

within a selected PV contour – see caption to Figure 3), and compared with the observed ozone trend averaged in the same way. Any change in the ozone field due to vertical adiabatic transport will be eliminated by this averaging process because air undergoing such motion remains on the same θ surface. The results are shown in Figures 3a and 3b. As already discussed, these ozone loss calculations used an expression for k_{2a} taken from *DeMore et al.* [1992]; use of the k_{2a} expression from *DeMore et al.* [1994] would give results toward the low ozone-loss end of the error bars on the figures.

Notwithstanding the day-to-day fluctuation in the ozone amount, the observed ozone trends and the trends calculated on chemical grounds alone are generally similar. The displacement of the observations and estimates at 465 K in both hemispheres is due to disparities occurring in only the first few days plotted, after these days both lines show a similar downward slope. Only at 655 K in the north, where the calculated destruction

is very small, is there a persistent trend of observations with respect to calculations, with the measured ozone increasing slightly over the UARS month. This would suggest that in the vortex-averaged sense, the ozone change in the lower stratosphere during the period examined is dominated by chemical processes, with dynamical effects being relatively unimportant. At 465 and 520 K the average calculated daily ozone losses are 0.7% and 0.3%, respectively, in the north and 1.3% and 0.6% in the south. These results are broadly in agreement with those of *Manney et al.*, [1995b] who inferred chemical ozone loss by comparing observations with dynamical calculations. In the 1992-1993 Arctic vortex, over a 30-day subperiod of that studied here, *Manney et al.* [1995b] find 0.5%/day chemical destruction at 465 K and 0.4%/day at 520 K, only 25-30% of which is masked by dynamical enrichment. These destruction rates are not directly comparable with those obtained from this present study because of differences

North   520 K

cycle 1
cycle 2
cycle 3

O₃ Loss Rate (ppbv/day)

South   520 K

cycle 2
cycle 3
cycle 1

North   465 K

cycle 1
cycle 2
cycle 3

O₃ Loss Rate (ppbv/day)

South   465 K

cycle 2
cycle 3
cycle 1

Day from Feb 10, 1993

Day from Aug 11, 1993

Figure 4. Time series from February 10 to March 18, 1993 (north), and August 11 to September 16, 1993 (south), of vortex-averaged daily ozone destruction rates by cycles 1, 2, and 3 at (a, b) 520 K and (c, d) 465 K. Error bars reflect the uncertainty estimates described in the text. Values for days 17-19 (north) and 16-19 (south) were found by interpolation as described in caption to Figure 3.

in the algorithms used to calculate the vortex averages (*Manney et al.* [1995b] used a different criterion for the vortex boundary, and did not include density weighting), but when averaged over the same 30-day period the estimated rates are more similar. The ozone loss rate at 465 K is greater when averaged over the whole UARS month because the shorter period does not include the first few days of the month when Cl* was highest and the estimated loss rate greatest. In the late winter Antarctic vortex of 1992, *Manney et al.* [1995b] deduce 1.5%/day destruction at 465 K and 1.0%/day at 520 K, with no significant dynamical effect. They do find ozone enrichment via diabatic (that is, cross isentropic) descent masking half of the Antarctic chemical depletion at 585 K and nearly all of it at 655 K. The close agreement at these upper levels obtained here for the Antarctic 1993 vortex between calculated ozone loss from chemistry and observed changes may argue against a significant role for dynamical enrichment. Differences could exist versus 1992 simply because of the different year being considered, although such large differences in transport effects may be unexpected. More detailed studies of the uncertainties both in models and data, for the different calculations (those done here and the type performed by *Manney et al.* [1995b]) would be required

to fully understand the significance of these differences in estimates of chemical destruction of ozone. The large ozone destruction calculated at the lower θ levels in the north between mid-February and mid-March 1993 supports the conclusions drawn by *Manney et al.* [1994] from observations of long-lived tracers that the ozone decrease measured during this time cannot be explained by transport effects and must be evidence of chemical ozone depletion.

Over the UARS month, the estimated ozone destruction at 465 K is ∼0.7 ppmv (24%) in the north and ∼1.1 ppmv (47%) in the south. Calculations based on aircraft measurements by *Salawitch et al.* [1993], *Proffitt et al.* [1993], and *Browell et al.* [1993] lead to a chemical loss of vortex ozone of 15-20% at this θ level over the whole of the Arctic winter/spring of 1991-1992; however, the duration of sub-PSC temperatures during that season was shorter than in 1992-1993 [*Manney et al.*, 1994], and although highly enhanced reactive chlorine was present, it declined rapidly after the beginning of February. Depleted gas phase HNO₃, suggestive of the presence of PSCs, was observed in the northern vortex in late February 1993 [*Santee et al.*, 1995], and, as can be seen from Figure 3c, vortex-averaged Cl* at 465 K remained above 1 ppbv until near the end of
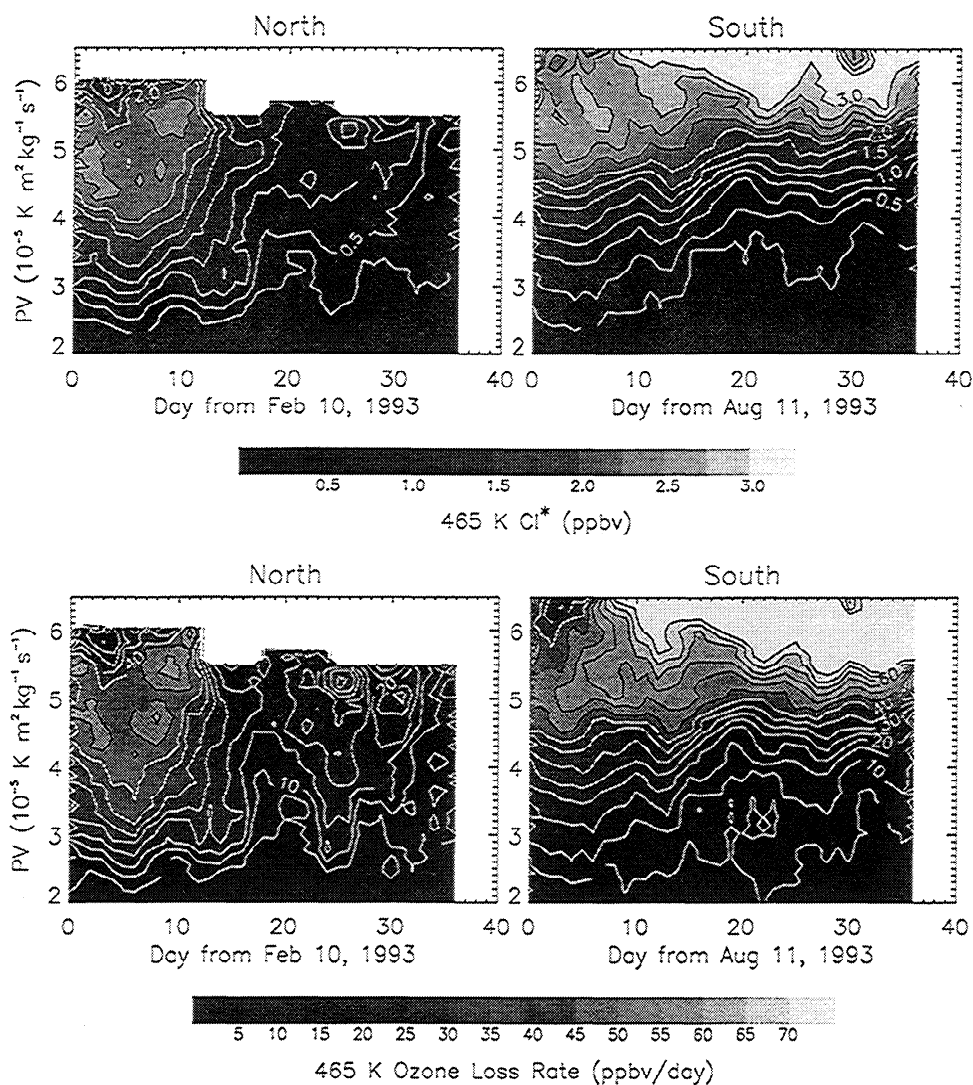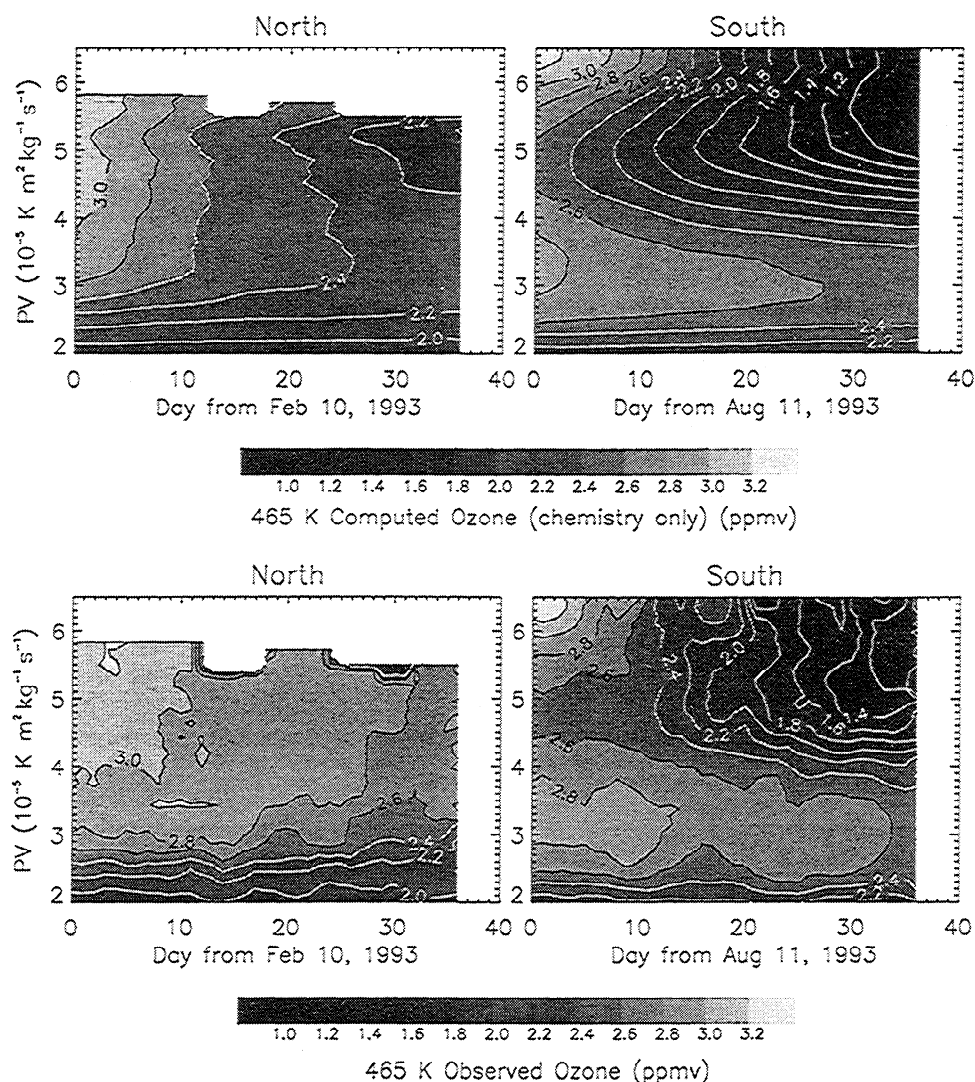
Figure 5. (top) PV versus time cross sections of Cl* mixing ratios and (bottom) inferred ozone destruction rates averaged around PV contours on the 465 K potential temperature surface. The time periods shown are February 10 to March 18, 1993 (north), and August 11 to September 16, 1993 (south). For the southern hemisphere the y axis is $-$PV.

the month. Consequently, ozone destruction was more prolonged in this year than in 1992. Also, the longer day length later in the year increases the daily ozone destruction, enhancing the additional loss. Thus the persistence of PSCs and enhanced reactive chlorine for ~4 weeks longer in 1992-1993 compared with 1991-1992 may have more than doubled the net chemical ozone loss, emphasizing the sensitivity to natural variability in the meteorological conditions.

Temperatures during the southern winter of 1993 were fairly typical of previous years [*NOAA*, 1993a], with vortex temperatures below 195 K, and hence enhanced Cl*, being present throughout the satellite viewing period ending in mid-September (Figure 3d). The rate of ozone destruction on the 465 K surface at the beginning of this period was similar to that occurring on the same seasonal dates in the north, but, unlike in the north, the rate did not decline toward the end of the period, and, consequently, the total ozone destruc-

tion was greater by ~0.4 ppmv. Expected continuing loss in the south after September 16 when the satellite switches to north viewing will further increase the excess ozone depletion over that which has occurred in the north. The estimated vortex-averaged loss rates at 465 K of ~1% per day for the Antarctic vortex are in general agreement with calculations for previous years constrained by more limited ClO observations from aircraft [*Solomon*, 1990; *Anderson et al.*, 1991].

While the peak Cl* amount at 465 K is similar in the two hemispheres, at 520 and 585 K there is a greater enhancement in the south, and a greater ozone destruction rate is estimated at these heights in this hemisphere. In both vortices the greatest ozone loss in terms of mixing ratio is calculated at 465 K, and the next most at 520 K, with the destruction at the upper two θ levels being somewhat less. Therefore, since the conversion of mixing ratios into concentration is proportional to pressure, the total number of ozone molecules lost and

Figure 6. (top) PV versus time cross sections of ozone computed from chemistry alone, and (bottom) the MLS ozone observations averaged around PV contours at 465 K. The chemically computed ozone on a given day was obtained by integrating the PV-averaged ozone destruction (shown in Figure 5) from day zero up to that day, and subtracting the result from the observed ozone on day zero averaged around the same PV contour. The time periods shown are February 10 to March 18, 1993 (north), and August 11 to September 16, 1993 (south). For the southern hemisphere the y axis is $-$PV.

the impact on the ozone column is dominated by what is occurring at the lower levels. Figure 4 shows the estimated ozone loss rate due to the three catalytic cycles separately at 465 and 520 K, and reveals the dominance of cycle 2 whenever significant ozone destruction is occurring; the rate of this cycle only falling below that of the other two at 520 K in the north after the Cl* has considerably declined from its peak mixing ratio. The rate of cycle 2 relative to that of 1 and 3 increases with decreasing height because the rapidity of the three-body reaction forming the dimer is very sensitive to pressure. At 465 K, while the Cl* remains enhanced, cycle 2 accounts for ~70% of the total loss with cycle 3 contributing ~20%, and cycle 1 contributing ~10%. The relative contribution of the dimer cycle falls with decreasing Cl* because of its quadratic dependence on the ClO concen-

tration. Cycle 1 is the least significant at these heights although at 520 K, where the oxygen atom concentration is greater, its importance is almost equal to that of cycle 3.

Time series of the Cl* amount and estimated total daily ozone destruction at 465 K averaged around PV contours are shown in Figure 5. Because PV would be conserved under frictionless adiabatic transport, it acts as a quasi-Lagrangian coordinate helping to isolate chemical effects on tracer distributions. In both the Arctic and Antarctic, the area of high Cl* values shrinks back toward the pole during the UARS month, but the effect is more pronounced in the north, where, even at the highest latitudes (highest PV values), Cl* shows a sharp decline beginning around the middle of the viewing period. The gradient of ozone loss rate with

respect to PV is slightly less than that of Cl* because the longer day length at the lower latitudes increases the destruction for a given Cl* amount. Similarly, it can be seen in the south that in the PV region where the reactive chlorine diminishes with time, the ozone loss declines less rapidly owing to the increasing illumination.

Figure 6 shows similar PV-averaged time series for the observed ozone at 465 K and the ozone values expected if the estimated chemical loss were the only factor impacting them. In the Antarctic, the chemical calculation reproduces the observations very closely, with the same ozone reduction pattern of maximum depletion near the pole decreasing toward the vortex edge apparent in both plots. Over the whole PV range, the observed ozone decrease is slightly less than that calculated to arise from chemistry alone. The loss observed in the Arctic shows less variation with PV than in the Antarctic, as does the calculated loss, but here there is a greater discrepancy between the computed and observed loss. The difference at the higher PV values is outside the estimated uncertainty of the calculation, and the overall structure of the estimated chemical loss is not so clearly discernible in the observations. This is probably a consequence of a greater motion across isentropes in the Arctic, where diabatic effects are expected to be more important [*Schoeberl et al.*, 1992], though it is also possible that there is greater horizontal mixing on scales not resolved by the MLS measurements inside the more dynamically active northern vortex. Further work would be required to to fully characterize the cause of the different agreement between computed and observed ozone loss in the two hemispheres.

Conclusions

The procedure described for calculating O_3 loss from ClO measurements gives good agreement with more rigorous model calculations, but is computationally cheap and so is well suited for dealing with the large quantities of data generated by satellite instruments. A further advantage is the ease with which the ClO measurements can be assimilated, and the calculation performed, without the problems of initializing a full photochemical model. Application of the method to ClO fields generated by MLS allows an analysis of the chemical destruction of ozone within the polar vortex to be performed for time periods in excess of a month, with the important chemical parameters being continually updated in accordance with the observational data. Thus vortexwide trends in the chemical destruction of ozone in the lower stratosphere can be estimated without the need to assume relationships between chemical species and dynamical parameters which may be necessary to extend the temporal and spatial extent of chemical data collected from aircraft.

Comparison of the ozone destruction rates estimated from MLS ClO measurements with the colocated O_3 retrievals provides a stringent test of the chemistry inherent in the calculation. At 465 K in the south, where transport effects might be expected to have a small impact relative to the chemistry, good agreement is found between observations and chemically based estimates of both the vortex-averaged ozone loss and its spatial distribution. This suggests the utility of the method and that the transport effects are indeed small. It therefore lends confidence to the results of the chemical calculations for the north where dynamics clearly play a larger relative role in the observed ozone change. In fact, the results for the Arctic do appear qualitatively consistent with the expected transport processes. The calculations show that toward the bottom of the Arctic vortex, despite there being only small regions cold enough for PSC formation, chlorine can be sufficiently activated to give daily vortex-averaged ozone loss rates similar to those in the Antarctic where PSCs are much more widespread. While the reactive chlorine remained enhanced, the estimated loss on the 465 K surface was ~1% per day in both the northern and southern winter/spring vortices of 1993, the greater time-integrated loss in the south being due mainly to the longer persistence of low temperatures and enhanced Cl* in this hemisphere.

Although the 1992-1993 northern winter was relatively cold, it was not unprecedentedly so, and in previous years sub-PSC temperatures have been known to remain as late as mid-March [*NOAA*, 1993b], that is, about 3 weeks longer than 1992-1993. The reoccurrence of such a cold winter would likely result at some θ levels in a net ozone destruction comparable with that regularly seen in the south. A narrower vertical range of intense loss in the north, such as was seen here, might, however, limit the impact on the ozone column.

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