Comparisons between measurements and models of Antarctic ozone loss

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Abstract. We present estimates of the chemical loss of lower stratospheric polar ozone during the Antarctic late winter directly from UARS Microwave Limb Sounder (MLS) ozone measurements in 1992, 1993, and 1994. These agree to within a few percent with estimates of the chemical loss inferred from UARS MLS ClO measurements. Thus, our results support the current theories of polar O_3-depleting chemistry, and we find no evidence for significant unknown chemistry during this period.

1. Introduction

Significant stratospheric ozone loss has been observed both in the Antarctic and the Arctic polar vortices [*Farman et al.*, 1985; *Solomon*, 1999, and references therein]. Halogen-catalyzed chemistry has been proposed and is now widely accepted as the principal cause [*Dessler*, 2000, chapter 7]. Recently, however, several studies of the Northern Hemisphere have concluded that models incorporating the current halogen chemistry significantly underestimate the observed Arctic O_3 loss. *Woyke et al.* [1999], for example, compared a CH_4/O_3 correlation from a balloon flight on February 3, 1995, with a reference CH_4/O_3 correlation derived from Halogen Occultation Experiment (HALOE) data. They found that the observed cumulative ozone loss at 480-K potential temperature was a factor of 2 larger than the modeled ozone loss during this period. *Becker et al.* [1998] suggested a similar shortfall in the Arctic polar vortex in late January 1992 between 465- and 485-K potential temperature by comparing a box model calculation of O_3 loss rates with O_3 loss rates based on O_3 sonde measurements and trajectory calculations. *Hansen et al.* [1997], *Deniel et al.* [1998], and *Goutail et al.* [1999] used three-dimensional models to calculate O_3 loss. They also concluded that the modeled O_3 loss was less than the observed O_3 loss. The findings of these papers, if substantiated, suggest problems in our theories of polar O_3 chemistry.

These previous analyses have all looked at O_3 loss in the Arctic. A primary difficulty with determining O_3 loss in this region is accounting for transport of O_3. In addition, none of the previous analyses utilized direct measurements of ClO for the O_3 loss calculation. Instead, ClO had to be inferred using various methods. Thus, while disagreements between modeled and measured O_3 loss might be due to missing or incorrect chemistry, other potential explanations also exist.

In order to reduce potential alternative explanations, we explore the possibility of missing chemistry by examining O_3 loss in the Antarctic during the late winter. The dynamics of

the Antarctic polar vortex at this time are much simpler than the Arctic because both vertical transport within the vortex and horizontal transport into the vortex are negligible. In addition, we will use direct measurements of ClO. Thus a disagreement between observed and modeled ozone loss would strongly suggest problems in our understanding of the chemistry of the polar vortex.

2. Data and Methodology

Briefly, we first derive vortex-averaged polar chemical O_3 loss at 465-K potential temperature (~46 hPa, ~20 km) from UARS Microwave Limb Sounder (MLS) measurements of O_3. We will refer to this as the "observed loss" throughout this paper. Then we infer the corresponding chemical O_3 loss from simultaneous ClO measurements and a fixed BrO mixing ratio. We will refer this as the "modeled loss." A comparison between these two quantities provides a test whether the observed chemical O_3 loss is well accounted for by current halogen chemistry.

2.1. Data

We use O_3 and ClO data (version 4) interpolated to the 465-K potential temperature surface. These measurements are made by the MLS [*Barath et al.*, 1993] onboard the Upper Atmosphere Research Satellite (UARS) [*Dessler et al.*, 1998]. This instrument observes to 84°S, thus seeing ~95% of the area of the vortex (which extends to ~60°S in the Southern Hemisphere). MLS version 3 O_3 [*Froidevaux et al.*, 1996] and ClO data [*Waters et al.*, 1996] have been validated, and version 4 data have uncertainties similar to version 3 uncertainties (L. Froidevaux and J. Waters, personal communication, 2000). The precision of an individual O_3 measurement at 46 hPa is ~0.2 ppmv with absolute accuracy of 20%. The precision of an individual version 4 ClO measurement at 46 hPa is ~0.4 ppbv, and the accuracy is the combination of a 0.2-ppbv bias uncertainty and a 15% scaling uncertainty. Meteorological fields are obtained from the United Kingdom Meteorological Office (UKMO) [*Swinbank and O'Neil*, 1994].

We will focus on three time periods determined by the availability of the satellite data. These periods are August 14 through September 20, 1992; August 9 through September 16, 1993; and August 6 through September 11, 1994. They

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correspond to the last few weeks of winter and are a period when O_3 is rapidly being destroyed in the Antarctic vortex.

2.2. Observed Loss

In this section we describe the calculation of chemical O_3 loss directly from measurements of O_3, which we refer to as the observed loss. The time evolution of the abundance of O_3 in some volume of the atmosphere is described by the continuity equation:

$$\frac{\partial[O_3]}{\partial t} = P - L - \vec{V} \cdot (\nabla[O_3]) \tag{1}$$

where P is the photochemical production rate of ozone, L is the chemical loss rate of ozone, and $\vec{V} \cdot (\nabla[O_3])$ is the net transport of ozone out of the volume. Our analysis will focus on the late winter. During this period, the chemical production rate P is approximately zero, so rearranging and solving for L yields

$$L = -\left(\frac{\partial[O_3]}{\partial t} + \vec{V} \cdot (\nabla[O_3])\right). \tag{2}$$

From (2), we see that the chemical O_3 loss at a fixed point in space can be calculated as the sum of two terms: the local change of O_3 and the net transport.

The local change of O_3 can be determined from successive observations of O_3 in the volume. We will neglect transport for the following reasons. First, it is generally agreed that the Antarctic polar vortex is a horizontally well-isolated "containment vessel" and the horizontal transport of O_3 is insignificant during the late winter [Schoeberl et al., 1992]. Second, radiative heating calculations suggest that the net radiative heating rate during this time period is small, so the accompanying vertical motion is also small [Rosenfield et al., 1994]. As a result, both horizontal and vertical transports are small, and we will ignore them. We will discuss the uncertainties associated with this assumption later.
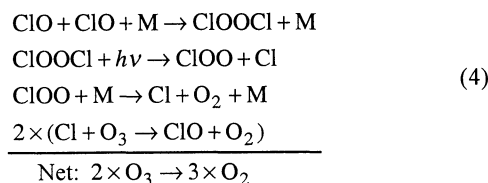
Thus, (2) reduces to

$$L = -\frac{\partial[O_3]}{\partial t}. \tag{3}$$

In this paper, the volume under examination is the Antarctic polar vortex at 465-K potential temperature. When we take the derivative of the vortex-averaged O_3 abundance, we obtain
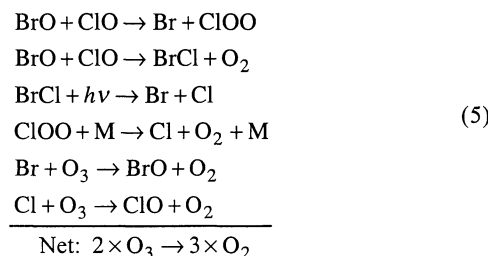
the vortex-averaged loss rate. All vortex averages in this paper are area-weighted averages, with the vortex defined using the algorithm of Nash et al. [1996] using UKMO meteorological fields. Other definitions of vortex edge [Manney et al., 1994; Jones et al., 1989] yield similar results.

2.3. Modeled Loss

In this section, we describe the calculation of O_3 loss from measurements of ClO, which we refer to as the modeled loss. The modeled loss is determined from the two generally accepted halogen-catalyzed mechanisms that have been proposed to account for the bulk of the chemical O_3 loss in the lower stratospheric polar vortices [Anderson et al., 1989; Salawitch et al., 1993; MacKenzie, et al., 1996]:

$$\begin{array}{c} ClO + ClO + M \rightarrow ClOOCl + M \\ ClOOCl + hv \rightarrow ClOO + Cl \\ ClOO + M \rightarrow Cl + O_2 + M \\ \underline{2 \times (Cl + O_3 \rightarrow ClO + O_2)} \\ \text{Net: } 2 \times O_3 \rightarrow 3 \times O_2 \end{array} \tag{4}$$

and

$$\begin{array}{c} BrO + ClO \rightarrow Br + ClOO \\ BrO + ClO \rightarrow BrCl + O_2 \\ BrCl + hv \rightarrow Br + Cl \\ ClOO + M \rightarrow Cl + O_2 + M \\ Br + O_3 \rightarrow BrO + O_2 \\ \underline{Cl + O_3 \rightarrow ClO + O_2} \\ \text{Net: } 2 \times O_3 \rightarrow 3 \times O_2 \end{array} \tag{5}$$

The instantaneous loss rate of O_3 due to these two mechanisms can be expressed as [e.g., MacKenzie et al., 1996]

$$\frac{d[O_3]}{dt} = -2J_{ClOOCl}[ClOOCl] - 2(k_1 + k_2)[ClO][BrO]. \tag{6}$$

Here J_{ClOOCl} is the photolysis rate of ClOOCl; k_1 and k_2 are the reaction rates for $BrO + ClO \rightarrow Br + ClOO$ and $BrO + ClO \rightarrow BrCl + O_2$, respectively. Both cycles require sunlight to proceed; thus if we know the time series of the abundances of ClOOCl, ClO, and BrO during the day, we can calculate the chemical loss of O_3 during that day as
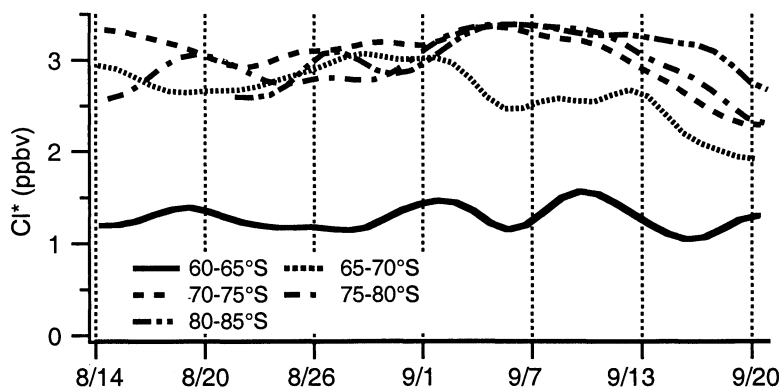

Figure 1. Total reactive chlorine (Cl*=ClO+2xClOOCl) derived from UARS MLS ClO measurements at several equivalent latitudes and at 465-K potential temperature in August and September 1992.

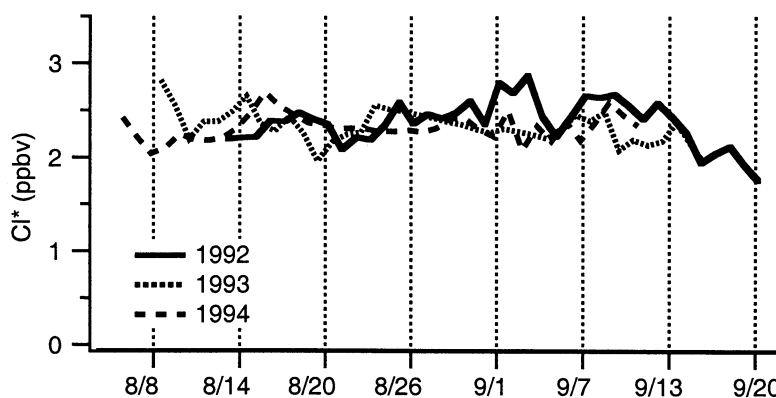**Figure 2.** Antarctic polar vortex-averaged total reactive chlorine (Cl*=ClO+2xClOOCl) derived from UARS MLS ClO measurements at 465-K potential temperature in August and September 1992, 1993, and 1994.

$$L = 2 \int\limits_{sunrise}^{sunset} \left(J_{ClOOCl}[ClOOCl] + (k_1 + k_2)[ClO][BrO] \right) dt . \quad (7)$$

In a given day, UARS MLS provides ClO measurements in the vortex only at a small range of local times. To infer the diurnal cycles of ClOOCl and ClO from these ClO measurements, we assume that the ClO and ClOOCl are in photochemical equilibrium at the time of the ClO measurement was taken and derive the total reactive chlorine from each daytime ClO measurement. Total reactive chlorine, often referred to as Cl*, is the sum of the abundance of ClO and 2 times the abundance of ClOOCl. When the derived Cl* for a measurement of ClO exceeds 3.4 ppbv, we set it to 3.4 ppbv to keep consistent with a realistic upper limit of Cl* in the lower stratosphere for the time period being considered [*Gunson et al.*, 1994]. This method does not work just after sunrise and before sunset since J_{ClOOCl} is changing rapidly and the system is not in steady state. We use the method of *MacKenzie et al.* [1996] to reject those measurements. Namely, we calculate the J_{ClOOCl} values for the time and place a daytime measurement of ClO was taken and for a time of 5 min earlier. If they differ by more than 10%, then we discard that measurement. The derived values of Cl* are then binned by their equivalent latitudes and averaged to determine a distribution of Cl* versus equivalent latitude in the vortex for each day.

To calculate O_3 loss during a day, we cover the vortex by a 2.5° longitude by 3.75° latitude grid. For each grid point, we assign a value of Cl* corresponding to the point's equivalent latitude using the relation derived from MLS measurements. Assuming that the Cl* is constant through the day, we calculate the time series of ClO and ClOOCl throughout the day at each grid point assuming photochemical steady state. This allows us to obtain the O_3 loss using (7). The rate constants and cross sections are taken from the Jet Propulsion Laboratory 1997 assessment [*DeMore et al.*, 1997]. J_{ClOOCl} is calculated from the Goddard three-dimensional chemical transport model [*Kawa et al.*, 1995]. Values of temperature and pressure used in the calculation are from the UKMO meteorological fields.

We assume a fixed BrO mixing ratio of 12 pptv throughout the vortex at 465 K in our calculations, which is a typical BrO mixing ratio measured at high latitudes and is consistent with model results [*Harder et al.*, 1998, and reference therein].

3. Results

Figure 1 shows Cl* between 60°S and 85°S during the 1992 Southern Hemisphere late winter. At 70°S and poleward, Cl* is 3 ppbv or higher, suggesting that most of the Cl_y in this region has been converted to reactive, O_3-destroying forms. At 65-70°S, Cl* starts out around 3 ppbv but begins decreasing to around 2 ppbv by the end of winter. At 60-65°S, Cl* is between 1.0 and 1.5 ppbv throughout the time period.

Figure 2 shows the vortex-average Cl* for the 1992, 1993, and 1994 Antarctic late winter. Averaged over the vortex, Cl* is 2-2.5 ppbv, suggesting that ~70% of the total chlorine in the vortex has been converted into reactive form. Chlorine stays highly activated throughout this period and shows little interannual variability. Note that each year the satellite starts and ends its view of the high southern latitudes a few days earlier than the previous year.

In Figure 3 we plot the vortex-averaged observed and modeled loss. We present the integrated loss in Figure 3 because the observed loss rate, obtained from the derivative of the ozone time series, contains large random fluctuations due to precision uncertainty in the data. By integrating the daily loss rate, however, the effects of the random fluctuations are greatly reduced. The observed O_3 losses are 1.68, 1.63, and 1.41 ppmv in 1992, 1993, and 1994, respectively. Given initial abundances of O_3 of 2.75, 2.90, and 2.82 ppmv in 1992, 1993, and 1994, this corresponds to losses of 61%, 56%, and 50% during the late winter in these years. It should also be noted that rapid loss of O_3 continues for several weeks into the spring, leading to the destruction of the vast majority of O_3 at this altitude.

The corresponding modeled O_3 losses from halogen chemistry are 1.69, 1.51, and 1.28 ppmv. On average, ~90% of the observed losses are accounted for by the two catalytic cycles (equations (4) and (5)), with the ClO-dimer cycle accounting for about two thirds and the ClO+BrO one third for these three periods. The ClO+O cycle, which we have not considered here, accounts for ~5-10% of the loss [*MacKenzie et al.*, 1996]; including this cycle would bring theory and observation into close agreement. Therefore we do not see evidence to suggest the existence of important missing ozone-depleting chemistry during the August/September period.
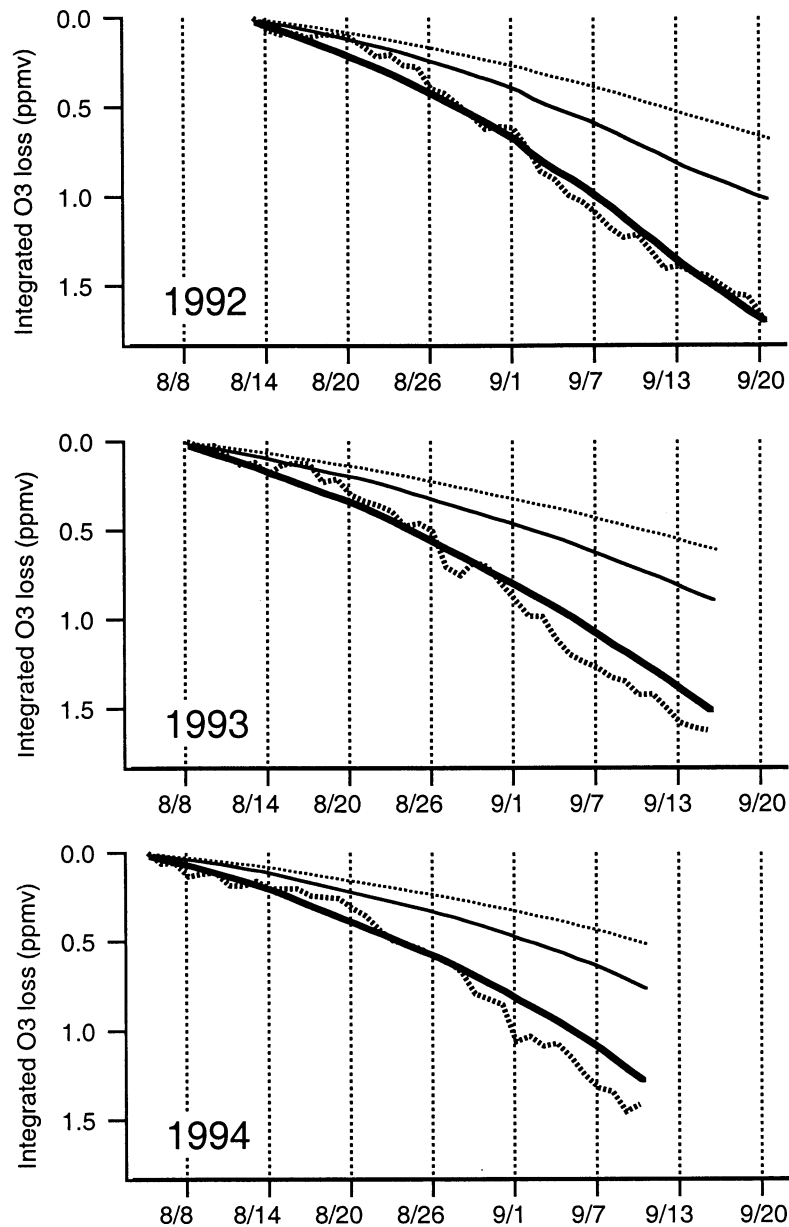
Figure 3. Antarctic vortex-averaged integrated chemical loss of O_3 in August and September 1992, 1993, and 1994 at 465 K. Heavy solid line is total modeled loss, heavy dotted line is total observed loss, light solid line is the modeled loss through the ClO+ClO cycle (equation (4)), and light dotted line is modeled loss through the ClO+BrO cycle (equation (5)).

Figure 4 shows the daily loss rate of O_3, derived from our model calculation. The O_3 loss rate increases throughout August and September, consistent with the increasing length of day throughout this period [Dessler, 2000, chapter 7]. This also explains why loss in 1992 is greater than 1993, and loss in 1993 is greater than 1994: the time period covered by the satellite observations moves earlier each year. Thus, every year the satellite observes a time period with less sunlight than the previous year, and there is consequently less integrated loss than the previous year.

MacKenzie et al. [1996] also calculated O_3 loss rates for the 1993 Antarctic vortex using a method similar to ours. While they also see agreement between the observed and modeled O_3 loss, important quantitative differences between their analysis and ours exist. In particular, MacKenzie et al. [1996, Fig-

ure 3d] estimate far less vortex-averaged Cl* than we calculate, 1.0-1.5 ppbv there compared to ~2.4 ppbv in this paper. Consistent with this, MacKenzie et al. [1996, Figure 4d] also calculate much lower O_3 loss rates. They calculate the O_3 loss to be about 30 ppbv d^{-1} throughout the viewing period, while we see it start out around 20 ppbv d^{-1} and increase to 60 ppbv d^{-1} by the end of the viewing period.

The uncertainty in this analysis arises from several sources: uncertainty in the O_3 and ClO data, uncertainty in the rate constants and photolysis rates, uncertainty in the meteorological fields, and uncertainty in our assumptions about the Antarctic vortex. It should be noted that because our analysis averages large numbers of measurements, the uncertainty of our calculations tends to be dominated by systematic errors.
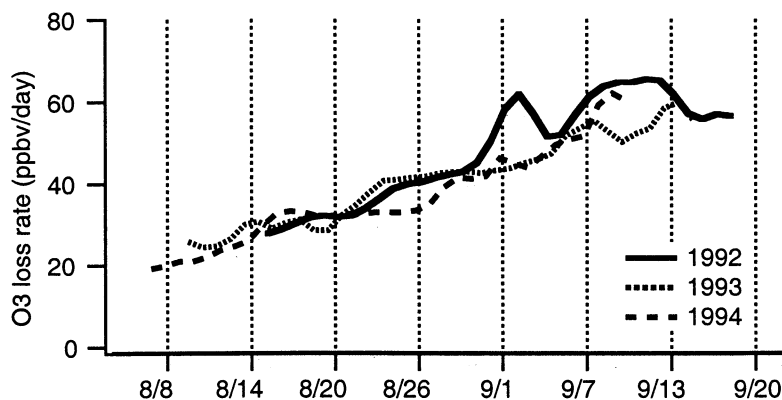
Figure 4. Antarctic vortex-averaged modeled chemical loss rate of O_3 in August and September 1992, 1993, and 1994 at 465 K calculated from the ClO+ClO and ClO+BrO cycles, and increased by 5% to account for ClO+O and other minor cycles.

The observed O_3 loss is determined directly from measurements of O_3. As a result, the accuracy of the observed O_3 loss is equal to the systematic error in the O_3 measurement, which is 20%.

The uncertainty of the modeled chemical O_3 loss arises from systematic errors in the ClO and BrO mixing ratios, the rate constants, photolysis rate of ClOOCl (J_{ClOOCl}), and the temperature field. The accuracy of the ClO measurement is 15% [*Waters et al.*, 1996]. We estimate the uncertainty of the fixed BrO abundance used to be ±2 pptv. The accuracy of both $k_{ClO+ClO}$ and $k_{ClO+BrO}$ rate constants is 25% [*DeMore et al.* 1997]. There is a warm bias in the UKMO temperature of ~1 K [*Manney et al.*, 1995]. The uncertainty in J_{ClOOCl} has a negligible effect on our calculations because the photochemical steady state [ClOOCl] adjusts in the opposite direction when J_{ClOOCl} changes, so their product shows little variations. Propagating these uncertainties into our calculations, we obtain a total uncertainty of around 50% for the calculated chemical O_3 loss in our analyses.

Finally, an additional uncertainty arises from our neglect of the transport term in (2). Radiative heating calculations suggest that the net radiative heating rate during this time period is small, so we expect vertical motion to be small [*Rosenfield et al.*, 1994]. To verify this, we have calculated the magnitude of the integral of the vertical transport term of the continuity equation:

$$\int \frac{\partial[O_3]}{\partial\theta}\frac{d\theta}{dt}dt \qquad (8)$$

Using UKMO heating rates and the vertical gradient of O_3 measured by MLS, we estimate this integral to be ~0.03 ppmv at 465-K potential temperature during the time periods investigated here. This is much smaller than the integral of the local change term of (2) (~1.5 ppmv), so we conclude that the neglect of vertical transport introduces negligible error into the calculation. The magnitude of the horizontal transport of midlatitude air into the vortex is difficult to estimate, and it remains an unquantified uncertainty. However, it is generally believed that the Antarctic polar vortex is a horizontally well-isolated containment vessel and the horizontal transport of O_3 is small during the late winter [*Schoeberl et al.*, 1992]. As a result, we will assume that the uncertainty from neglect of horizontal transport is small.

4. Discussion

We show in this paper that the observed and modeled O_3 loss in the Antarctic agree to within a few percent. Based on this and assuming that the same catalytic cycles that destroy O_3 in the Antarctic are responsible for O_3 loss in the Arctic, it appears that our understanding of the catalytic destruction of polar O_3 is good. Note that because our analysis uses measurements of ClO, we make no statement about our understanding of the processes that convert chlorine from its reservoirs to Cl*.

Previous analyses [e. g., *Goutail et al.*, 1999; *Deniel, et al.*, 1998; *Woyke et al.*, 1999; *Becker et al.*, 1998] have found that O_3 loss predictions are only about one half to two thirds as big as measured loss, much worse agreement than seen in this analysis. Owing to the uncertainties in our calculations, our analysis cannot exclude such large disagreements. On the other hand, our work does not provide any support for these analyses.

We believe that there are reasons that our analysis is superior to previous analyses. As we mentioned previously, in the Arctic the transport term is bigger and the chemical loss term is smaller than in the Antarctic. In fact, they are of comparable magnitude in the Arctic. Thus, when calculating O_3 loss from O_3 observations, errors specifying the transport will result in errors in the inferred O_3 loss. By analyzing the Antarctic, our analysis is much less sensitive to errors in the transport.

Several of the previous papers have used a "conservative coordinate" approach to derive O_3 loss rates directly from O_3 measurements [*Woyke et al.*, 1999; *Proffitt et al.*, 1993; *Bregman et al.*, 1997; *Müller et al.*, 1996, 1997a, 1997b]. This approach relies on measuring ozone changes relative to a quantity that is considered conserved, such as N_2O or CH_4 abundance. It must be assumed that the correlation between O_3 and the conserved coordinate remains fixed in the absence of chemical loss and that changes in the correlation result only from chemical loss. However, as pointed out by *Plumb and Ko* [1992] and *Plumb et al.* [2000], simple invariant correlations are not necessarily expected in the polar vortex. For example, mixing in of air from midlatitudes can lead to changes in the correlations, as seen by *Strahan et al.* [1996]. Also, data used in the previous studies to derive the O_3/tracer relationship cover only a limited portion of the polar vortices. Our analysis does not suffer from the uncertainties of this

method. Clearly, validation of this approach is needed before conclusions of missing chemistry based on this method can be considered certain.

Finally, loss rates derived using the "Match" technique [von der Gathen et al., 1995; Rex et al., 1998] have also underestimated ozone loss by standard chemistry during late January in the Arctic [Becker et al., 1998]. There are no UARS MLS measurements available in the late January for applying our method to make direct comparison with the results from the Match technique. However, it should be noted that Becker et al. [1998] only found a significant underestimate during a 2-week period at the end of January. At other time periods, there was good agreement between modeled and observed O_3 loss rates. More work will be needed to address these questions.

5. Conclusions

In order to test our theories polar ozone loss, we compare the observed loss of O_3 in the Antarctic with loss calculated using a simple model. The Antarctic is a relatively simple system compared to the Arctic due to the simpler dynamics. We find agreement between the observed and modeled loss to within a few percent, suggesting that our theories of halogen-catalyzed O_3 loss are good. While the uncertainty of our analysis is large enough that we cannot rule out the larger disagreements seen in recent analyses of the Arctic, our analysis provides no support for the existence of such large disagreements.

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