

Ozone Temperature Correlations in the Upper Stratosphere as a Measure of Chlorine Content

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Abstract: We use data from the Nimbus-7 Limb Infrared Monitor of the Stratosphere (LIMS) for the 1978-1979 period together with data from the Upper Atmosphere Research Satellite Microwave Limb Sounder (UARS MLS) for the years 1993 to 1999, the Aura MLS for the years 2004 to 2011, and the Aura High Resolution Infrared Limb Sounder (HIRDLS) for the years 2005 to 2007 to examine ozone-temperature correlations in the upper stratosphere. Our model simulations indicate that the sensitivity coefficient of the ozone response to temperature ($\Delta \ln(O_3)/\Delta(1/T)$) decreases as chlorine has increased in the stratosphere and should increase in the future as chlorine decreases. The data are in agreement with our simulation of the past. We also find that the sensitivity coefficient does not change in a constant-chlorine simulation. Thus the change in the sensitivity coefficient depends on the change in chlorine, but not on the change in greenhouse gases. We suggest that these and future data can be used to track the impact of chlorine added to the stratosphere and also to track the recovery of the stratosphere as chlorine is removed under the provisions of the Montreal Protocol.

I. Introduction

The addition of anthropogenic ozone-depleting substances (ODSs) to the atmosphere has led to a global decrease in stratospheric ozone [e.g. Stolarski et al., 1992]. The Montreal Protocol, signed by all of the countries of the world, limits the production of these ODSs [Velders et al., 2007]. The result has been a peak in the stratospheric amounts of the chlorine and bromine molecules that cause ozone destruction [Newman et al., 2007]. The observed decline in ozone has slowed, and annually-averaged ozone column amounts have been nearly constant for the last decade [chapter 2 of WMO 2011]. One of the current challenges is determining if we can attribute this change in the ozone trend to the leveling off of ODSs. A complication in this attribution is the increase in ozone expected from the cooling of the stratosphere as a result of increasing greenhouse gases (GHGs). The cooling slows down the ozone loss reactions leading to an increase in ozone (see e.g. Waugh et al. [2009]; Li et al. [2009] for details).

We adopt an alternative approach to the detection and attribution of ozone recovery to ODSs that involves the use of ozone-temperature correlations in the upper stratosphere. Barnett et al. [1975] first used the ozone-temperature correlation during a stratospheric warming to test the temperature dependence of the ozone loss reactions. They found that the ozone-temperature relationship was consistent with the known temperature dependence of the photochemical reactions leading to ozone loss in the upper stratosphere. Rood and Douglass [1985] pointed out that dynamical perturbations could complicate the derivation of photochemical information from the ozone-temperature anti-correlation. Douglass and Rood [1986] applied these concepts in a study of spatial variations of ozone and temperature observed at 1 hPa by the Limb Infrared Monitor of the Stratosphere (LIMS) on the Nimbus 7 satellite, showing that valuable photochemical information could be obtained with proper correction for dynamical terms. They suggested that, because of the smaller temperature dependence of the chlorine catalytic reactions, future ozone and temperature measurements could be used to quantify the impact of chlorine chemistry on the stratosphere. Froidevaux et al. [1989] investigated ozone-temperature correlations using LIMS data from 6 hPa up to 0.2 hPa. They emphasized the importance of wave effects on the relationship, especially at the lower altitudes. They concluded that the difference between the temperature dependence of chlorine reactions and the other ozone-destroying reactions was not large enough to use the ozone-temperature sensitivity to track future changes in chlorine. We come to a different conclusion in this paper.

Chandra et al. [1995] attempted to determine the impact on ozone of increasing chlorine by examining the magnitude of the seasonal cycle of ozone in the upper stratosphere. The annual cycle of ozone in the upper stratosphere near 1-2 hPa is strongly driven by temperature variations. Addition of chlorine should reduce the sensitivity of ozone to temperature and lessen the seasonal variation of ozone. Chandra et al. [1995] also noted a decrease of 10–25% per decade in the annual amplitude of ozone at 2 hPa between 40°–60° in both hemispheres between 1979 and 1993. They concluded that this was in general agreement with the model predictions of a decrease in amplitude as chlorine increased and that this provided support that chlorine was responsible for decreases of ozone in the upper stratosphere.

In this paper, we revisit the ozone-temperature relationship in the upper stratosphere and the response of that relationship to changes in chlorine. We combine ozone-temperature correlations

and analysis of the seasonal cycle to show that the variations observed over the last 30 years are consistent with predictions based on photochemical theory and the time variation of chlorine compounds in the stratosphere. The next section will examine the behavior of both ozone and temperature near 1 hPa using measurements from several satellite instruments. Section III will examine some model simulations showing the expectation for the ozone-temperature correlation over the past 5 decades and into the future. Section IV will show the ozone-temperature correlation for measurements compared to the model simulations. Finally, section 5 will summarize and discuss the implications of our results for detection and attribution of ozone recovery in the upper stratosphere.

II. Observed seasonal cycles in ozone and temperature at 1 hPa

The seasonal cycle of temperature in the upper stratosphere is driven by the seasonal progression of the solar zenith angle with highest temperatures in summer and lowest temperatures in winter. Ozone responds to the change in temperature because its chemical loss reactions have temperature dependent rate coefficients. Thus, the ozone concentration maximizes in winter when temperature is the lowest and is minimum in summer when temperature is the highest. Ozone also responds to seasonal changes in the photolysis rates of O_2 and O_3 . This presents an obstacle to obtaining absolute values of the chemical response of ozone to temperature. We will show that the change in the seasonal variation of upper-stratospheric ozone is dominated by the chemical response of ozone to temperature and that this change is dominated by the change in the amount of chlorine in the upper stratosphere over the past several decades.

High-vertical resolution, simultaneous observations are needed for ozone and temperature because the ozone relationship to temperature changes with altitude. Several instruments provide such data. The Limb Infrared Monitor of the Stratosphere (LIMS) instrument on the Nimbus 7 satellite operated from October 1978 through May of 1979 [Gille and Russell, 1984; Remsberg et al., 2004; 2007]. The Microwave Limb Sounder (MLS) on the Upper Atmosphere Research Satellite operated from late 1991 through 1999 [Froidevaux et al., 1996], with best coverage during the first 3 years. Aura, launched July 15, 2004, carries two instruments with the required resolution and coverage, MLS [Froidevaux et al., 2008; Livesey et al., 2008] and HIRDLS (High Resolution Dynamics Limb Sounder [Nardi et al., 2008; Gille et al., 2008]. Aura MLS continues to make measurements in 2011. HIRDLS data are available from mid-January 2005 until 2008.

Figure 1 illustrates the seasonal variation of ozone and temperature at 1 hPa in the latitude band between 45° and 50° in each hemisphere as measured by Aura MLS. The data reveal a seasonal cycle in ozone that approximately follows the solar zenith angle over much of the year, and anti-correlation of ozone with temperature. In the winter, planetary wave disturbances add noise to this picture, but an anti-correlation of ozone with temperature is still seen. The chemical lifetime of ozone at $50^\circ S$ and 1 hPa ranges from a few hours in mid summer to about 2 days in mid winter.

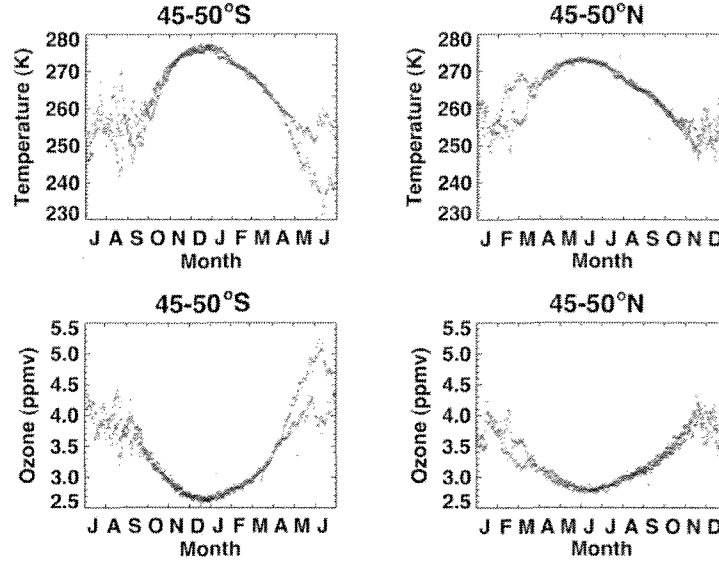


Figure 1: Four panels show Aura MLS measurements of ozone and temperature at 1 hPa for southern and northern mid latitudes. Data are shown for four years from 2004 to 2007. Note that the time scale on the x-axis has been shifted by 6 months for the southern hemisphere relative to the northern hemisphere.

One method of describing the relationship of ozone to temperature is the exponential format (Barnett et al., 1975):

$$O_3 = O_{30} \exp (B/T) \quad (1)$$

where B is the slope (in K) of the relationship between $1/T$ and the logarithm of the ozone density. Equation (1) uses the same form of temperature dependence as many of the key reaction rate coefficients involved in ozone loss processes. We will apply this method to the entire seasonal range of ozone and temperature measurements such as those shown in Figure 1. Solving for B in equation (1) we obtain

$$B = (\Delta \ln(O_3) / \Delta (1/T)) \quad (2)$$

Figure 2 shows daily ozone measurements at 1 hPa averaged between 45° and 50° south as a function of temperature measurements averaged over the same region. Four years of Aura MLS data (2005-2008) are shown along with 7 months of LIMS data (1978-1979). The data from Aura MLS show an upper stratosphere that is cooler with less ozone than that shown by LIMS. The right panel of Figure 2 shows the same data plotted as logarithm of ozone density as a function of $1/T$ with the LIMS data shifted to agree with Aura MLS at the highest temperatures (lowest ozone density). The slope of the straight line fit to these data determines the coefficient B in equation (1). We can see from Figure 2b that the slope in the early 2000s (Aura MLS) is different from the slope for the late 1970s (LIMS).

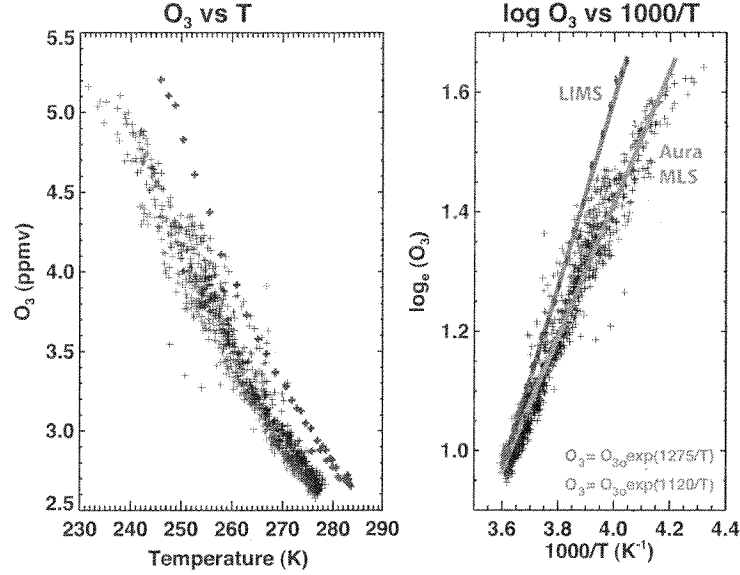


Figure 2: Left panel shows the ozone mixing ratio vs temperature at 1 hPa, 50°S using data from Aura MLS (black crosses) and using data from LIMS (blue crosses). Right panel shows data re-plotted as the logarithm of O_3 vs $1/T$ with the temperature scale for LIMS shifted to match that for Aura MLS at the highest temperatures observed by Aura MLS. Straight lines in right panel show best fit for B-coefficient of equation (1) for each data set.

III. Chemistry Climate Model: What do we expect for ozone-temperature correlations?

The data show a change in slope of the ozone-temperature relationship in the direction suggested by some of the early studies i.e., the slope decreases as ozone loss due to chlorine increases. In this section, we use our chemistry climate model, GEOSCCM, to examine the expected relationship of ozone and temperature in a changing atmosphere. GEOSCCM has been described in Pawson et al. [2008] and its first two versions have been compared with data and other models through the CCMVal model inter-comparison exercises described in Eyring et al. [2006; 2007]. GEOSCCM was one of the better-rated models in photochemistry, photolysis, and transport (see Waugh and Eyring, [2008]).

For this study we use two simulations of the GEOSCCM assuming mixing ratios for greenhouse gases (GHGs) from the A1b scenario of the Intergovernmental Panel on Climate Change (IPCC) [Nakicenovic and Swart, 2000]. One used mixing ratios for ozone depleting substances (ODSs) from the Ab scenario of WMO/UNEP [WMO, 2003]. In the other simulation methyl chloride (CH_3Cl) was set to 0.6 ppbv at the lower boundary and all other chlorine source gases were set to zero. These values were kept constant throughout the time-dependent integration resulting in simulated chlorine levels that were constant and appropriate for 1960 before the anthropogenic contribution to atmospheric chlorine became significant.

We contrast the contributions to ozone loss by the various catalytic loss processes in these simulations. We choose 1 hPa for this analysis for several reasons: 1) chemical loss is fast enough that the ozone is close to a photochemical steady state, 2) loss processes are dominated by HO_x and O_x when chlorine concentrations are low such as in 1960, and 3) chlorine-catalyzed

ozone loss becomes important at a few ppbv of chlorine such as in the 1990s and 2000s. We also choose to do the analysis in the latitude zone between 45° and 50° south in order to maximize the temperature extremes over the seasonal cycle, which is not as pronounced near the equator as it is in the mid latitudes in the upper stratosphere. The southern hemisphere provides a cleaner record with a larger temperature variation for the eight months of LIMS observations than in the northern hemisphere.

Our analysis of the chemical loss terms for ozone uses the concept of rate-determining steps as described in Johnston [1975]. As an example the loss rate in molecules/cm³/sec for pure oxygen reactions is

$$\text{Loss}(\text{O}_x) = k_{\text{O},\text{O}_3}(T) [\text{O}][\text{O}_3] \quad (3)$$

where $k_{\text{O},\text{O}_3}(T)$ is the temperature-dependent reaction rate coefficient for the reaction of O atoms with O₃ molecules given by $k_{\text{O},\text{O}_3}(T) = 8.0 \times 10^{-12} e^{(-2060/T)} \text{ cm}^3/\text{molecule}/\text{sec}$ [Sander et al. 2011], [O] is the number density of oxygen atoms, and [O₃] is the number density of ozone molecules. The loss rate given above is a product of the loss frequency, $k_{\text{O},\text{O}_3}(T) [\text{O}]$ in 1/sec and the ozone concentration in molecules/cm³. The loss frequency is the inverse of the local chemical loss lifetime.

Figure 3 shows the loss terms for ozone as a function of time calculated from the constant chlorine simulation. These are given in molecules/cm³/sec in the left panel. The right panel shows the loss terms as a percentage of the total loss. The constant chlorine simulation is dominated by changes in the GHGs that cool the stratosphere. This cooling leads to a decrease in the ozone loss frequency and an increase in ozone. The total loss rate shown in Figure 3 is the product of the loss frequency and the ozone concentration. Note that the total loss rate increases between 1960 and 2055 in this simulation. The total loss rate is in photochemical steady state with the total production rate given by $\text{Prod} = J_{\text{O}_2} [\text{O}_2]$ where J_{O_2} is the photolysis rate of O₂ in molecules/sec. As the stratosphere cools, the density of O₂ at a constant pressure of 1 hPa increases and the production increases.

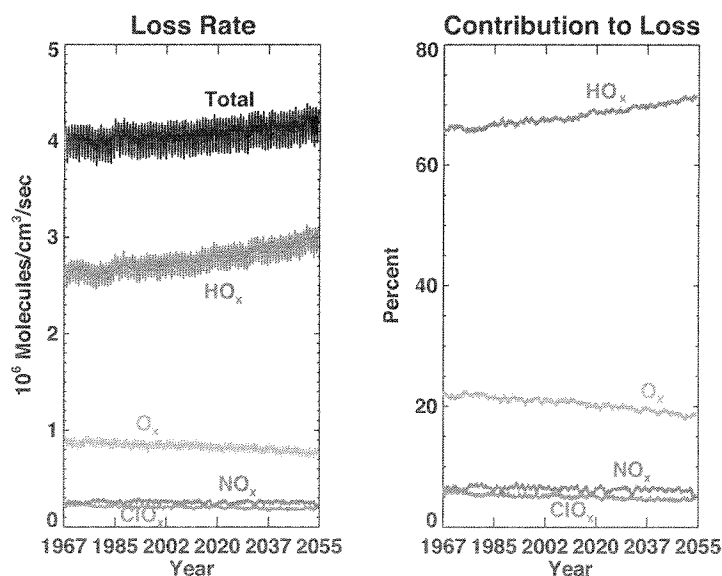


Figure 3: Left panel shows the total ozone loss rate at 1 hPa (averaged between 45° and 50°S) as a function of time in GEOSCCM simulation with chlorine constant at 1960 values and its breakdown into catalytic cycles. Rapid oscillations in loss rate are seasonal cycles. Right panel shows the fractional contribution of each catalytic cycle to ozone loss as a function of time.

The loss rate due to HO_x reactions increases because of the increase in OH and HO_2 concentrations resulting from the imposed increase of CH_4 in the GHG scenario and because the source term increases with the increase in $\text{O}(^1\text{D})$ that results from the O_3 increase. Because total loss in this region is equal to total production (photochemical steady state) the loss due to O_x reactions adjusts in the model and must decrease.

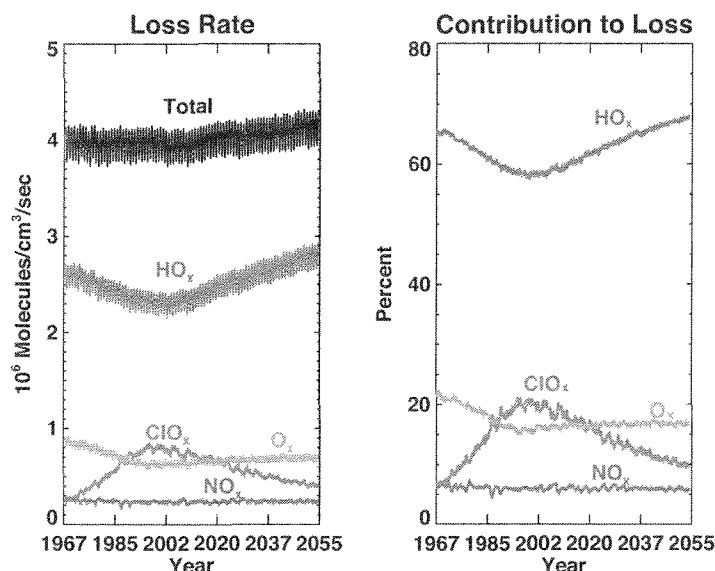


Figure 4: Left panel shows the total ozone loss rate at 1 hPa (averaged between 45° and 50°S) as a function of time in GEOSCCM simulation with time-dependent ODSs determined from the UNEP/WMO Ab scenario and its breakdown into catalytic cycles. Right panel shows the fractional contribution of each catalytic cycle to ozone loss as a function of time.

Figure 4 shows the loss rates and their fractional contributions for the standard ODS and GHG scenario described above. The primary feature of the loss rates in this scenario is the rise of the importance of the ClO_x catalytic cycle as chlorine increases due to the rise in the chlorofluorocarbon source gases. Figure 4 also shows that this rise in chlorine catalysis coincides with a decrease in the catalysis due to HO_x and O_x .

The importance of these variations in the relative contributions of the catalytic cycles is that the chlorine cycle is less temperature dependent than either the HO_x or O_x cycle. Increasing chlorine's contribution to total loss results in a decrease in the slope of the observed ozone temperature relation (Figure 2).

We calculate the time dependence of the slope, B , defined in equation (1) using the seasonal variation of O_3 and T , as in Figure 2. The solid lines in Figure 5 show the 5-year running mean of the time dependence of B from the variable ODSs and constant chlorine simulations. The value of B derived from the constant chlorine simulation is nearly constant over the time period

shown (1975 to 2040). Although the loss processes shift towards more HO_x loss and less O_x loss, B remains approximately constant as both of these cycles have similar temperature dependence [see e.g. Stolarski and Douglass, 1985] at this pressure.

It is important to note that the seasonal cycle method of this paper does not isolate the chemical contribution to the absolute value of the ozone-temperature correlation slope mainly because the photolysis rates, J_{O_2} and J_{O_3} , vary with season independent of any temperature changes. Thus, the B-coefficient represents the combination of the ozone response to temperature changes and the ozone response to changes in photolysis that are correlated with temperature changes.

Because the analysis is in an optically thin region, the annual average of the photolysis rates J_{O_2} and J_{O_3} are not changing from year to year. They thus cancel out in a time-dependent simulation, and we can use the method to observe changes in slope caused by changes in the fraction of loss that is due to chlorine chemistry.

Results from the changing ODS scenario shows that B depends on the amount of chlorine. The coefficient decreases as chlorine increases and increases as chlorine begins to decrease as specified by the time-dependent boundary conditions. The difference between model-derived B in 1960 and 2000 is about 200K compared to 120-150K between the LIMS measurements 1978-9 and the Aura measurements in the early 2000s.

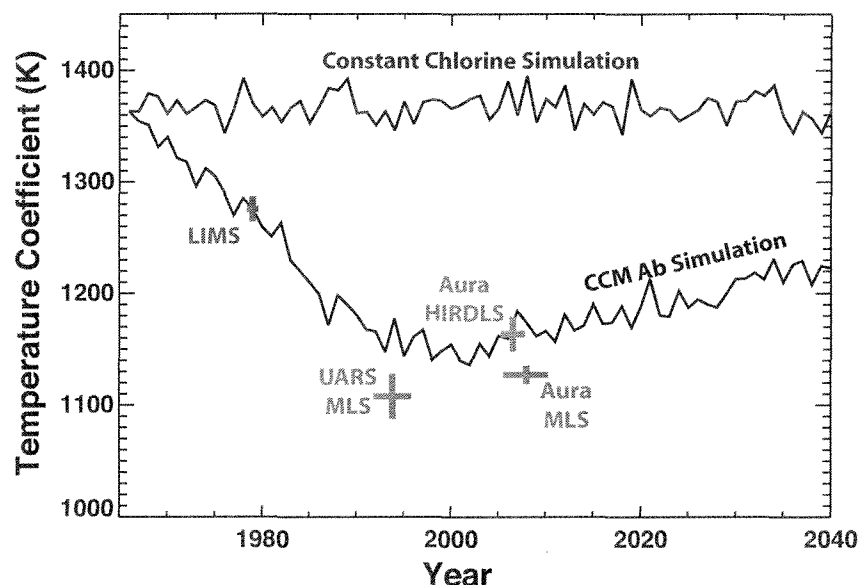


Figure 5: Temperature coefficient, B, vs time for two GEOSCCM simulations, one using the UNEP scenario Ab, the other holding chlorine fixed at 1960 values is shown. Results are for a pressure level of 1 hPa averaged between 45°S and 50°S. Deductions from data are shown for 4 satellite instruments by thick crosses. The vertical extent of crosses indicates 2σ uncertainties from fit to equation (1). The horizontal extent of crosses indicates the time period of measurements that are used for the estimates of B from measurements.

IV. Measurements: What do they show about ozone-temperature correlations?

Figure 5 also shows values of B obtained from the measurements by four separate satellite instruments by fitting the data records from each instrument over its entire period of measurement in the manner shown in Figure 2. Although ozone and temperature are more strongly anti-correlated during summer (Figure 1), it is not possible to obtain better results by restricting ourselves to the summer. The summer high temperatures favor the strongly temperature dependent O_x and HO_x cycles, and chlorine-catalyzed loss is less important. We find that the best solution is to include the winter data because chlorine is a more important factor when the temperatures are colder. Both the model and measurements show the time dependence of the B coefficient more clearly when B is derived using summer and winter data. For LIMS, we only have 8 months of data that extend into the early winter of the southern hemisphere. Although this limits our sampling of cold temperatures, the error introduced is small because chlorine provides only a small fraction of the total ozone loss in 1978-9.

Although values of B derived from observations are not in perfect agreement with values derived from the simulation, both show the same long-term variation (see Figure 5). That is, the LIMS data show a stronger dependence of ozone on temperature at 1 hPa than do the UARS MLS or the Aura MLS and HIRDLS data. Taken together this analysis indicates consistency between the observed and simulated dependence of the seasonal cycle of ozone loss in the upper stratosphere on changing chlorine concentrations. This result is not strongly dependent on the absolute calibration for either temperature or ozone. For the time period from mid 2005 through the end of 2007 we obtained values of B using each of 5 ozone data sets (HIRDLS, MLS version 2.2, MLS version 3.3, NOAA 17 SBUV and NOAA 18 SBUV) and 4 temperature data sets (HIRDLS, MLS version 2.2, MLS version 3.3 and NCEP reanalysis) in all combinations. The coefficient for a given ozone data set was the same whether using the MLS version 3.3 temperature data or the HIRDLS temperature data despite a 2K offset between MLS version 3.3 and HIRDLS measurements.

The result is, however, dependent on the altitude resolution of both the ozone and temperature measurements. The calculated B coefficient was smaller for lower resolution ozone measurements and larger for lower resolution temperature measurements. The requirement for high vertical resolution measurements comes from the strong altitude dependence of the B coefficient. This altitude dependence arises because of the change in the mixture of loss reactions with altitude.

V. Discussion and Conclusions

We have shown that the available data from the Nimbus 7, UARS, and Aura satellites confirms the predicted dependence of the ozone-temperature correlation slope on chlorine amount. This predicted dependence is a result of the temperature dependence of the ozone loss due to chlorine oxides being less than that due to either pure oxygen reactions or hydrogen oxide catalysis. We have shown that the ozone-temperature relationship in the upper stratosphere from our simulations changes with the addition of chlorine oxides that catalyze ozone destruction in a manner consistent with changes in the observed relationship.

The original idea in Barnett et al. [1975] was that we could use the relationship to confirm the absolute value of the temperature dependence in the upper stratosphere and relate it to the mixture of chemicals thought to be determining the overall ozone loss rate. The early attempts by these and the other authors cited in the introduction used small spatial or temporal perturbations to measure the ozone-temperature relationship with all other variable held approximately constant. That quest proved difficult for several reasons. One is that short-term perturbations are not necessarily in photochemical steady state. Time lags will distort the relationship.

In this work, we chose to use the seasonal cycle. This gave us the maximum range of temperatures over which to determine the relationship between ozone and temperature. The goal of this approach is to detect the change of the relationship as chlorine in the stratosphere has changed. An important result of this study is that in our constant chlorine simulation the B coefficient is independent of time, despite increases in greenhouse gases that cooled the stratosphere and increased the upper stratospheric ozone amount. The scenario had increasing CH₄ that led to increased ozone loss due to HO_x reactions. Because the HO_x and O_x loss cycles have nearly the same temperature dependence at the chosen altitude of 1 hPa, the overall temperature dependence for ozone loss did not change. When changes in chlorine were added to the scenario, the temperature dependence of ozone loss decreased.

Ozone increases in the coming decades are expected from a combination of the decrease of chlorine in the stratosphere and the cooling due to the increase of GHGs in the stratosphere (see e.g. Li, et al. [2009]). One of the problems of attributing ozone recovery is separating these effects from one another. The results shown here indicate that the B coefficient of the ozone temperature relationship in the upper stratosphere depends on the recovery of chlorine, but not on the GHG cooling of the stratosphere. Thus deduction of this slope from future measurements should be a direct determination of the recovery of ozone in the upper stratosphere from chlorine catalysis.

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