Implications of upper stratospheric trace constituent changes observed by HALOE for O_3 and ClO from 1992 to 1995

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Abstract. Measurements from the Halogen Occultation Experiment (HALOE) of the upper stratosphere show increases in HCl and H_2O and decreases in CH_4 and O_3 during the period 1992-1995. These changes all coincide with the decline of solar cycle 22. Using a simple photochemical model, we find that 4 major components contribute to the O_3 decrease: 1) an increase in total chlorine as indicated by increasing HCl 2) an additional increase in reactive chlorine due to repartitioning of Cly by the decreasing CH_4 3) a decrease in odd oxygen production due to decreased solar flux and 4) an increase in odd hydrogen loss due to increasing H_2O. At 2 mbar, the Cly repartitioning is the largest cause of O_3 changes. Because the Cly repartitioning coincides with decreasing solar flux, some recent observational estimates of the long-term response of upper stratospheric O_3 to solar UV irradiance variability may be too large. Compared with the HALOE O_3 data, the model O_3 exhibits a larger negative trend. This appears to be because the model O_3 is more sensitive to the increased H_2O than is the observed O_3. The 20-30% decline in CH_4 also implies a large increase in ClO which exceeds that expected from CFCs. Observations of ClO from the Microwave Limb Sounder (MLS) support this inference.

Introduction

Two components of long term variability ("trends") have been identified for upper stratospheric O_3: one caused by solar cycle UV irradiance changes and the other caused by increases in the chlorine abundance due to the release of chlorofluorocarbons (CFCs). It is generally accepted that increasing CFCs resulted in a 5-10% decrease of equatorial upper stratospheric O_3 from 1979-1991 [*World Meteorological Organization (WMO), 1995*]. But the response of upper stratospheric O_3 to long term solar UV changes is not as well quantified since 2D models underestimate observed changes [*Chandra and McPeters*, 1994].

Recently, *Nedoluha et al.* [1998a] (hereinafter, N98a) described a decrease in upper stratospheric CH_4 measured by HALOE and suggested that it is due to decreased upwelling in the tropical lower stratosphere, possibly in response to the recovery of the atmosphere from the Mt. Pinatubo eruption. In addition, *Nedoluha et al.* [1998b] (hereinafter, N98b) described long term increases in stratospheric H_2O.

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The goal of this paper is to compare the role of these source gas changes with solar and anthropogenic influences for O_3 and ClO trends.

Summary of Data and Trends

HALOE data offer a unique opportunity to examine O_3 and chlorine trends with a one dimensional photochemical model. HALOE measures all of the important long lived trace constituents (H_2O, CH_4, HCl, and NOx) and temperature that are inputs required for such a model. Multi-year trends have now been reported for most of these constituents. In addition to CH_4 and H_2O changes (N98b), *Russell et al.* [1996] reported increases in lower mesospheric HCl and HF which result from tropospheric CFC increases. N98a also discussed changes in upper stratospheric NO_2 and argued that they are consistent with the CH_4 changes. NO is the only constituent which has not been discussed in this context. While HALOE V18 NO is clearly increasing, much of this is due to an incorrect assessment of the NO gas cell amount used in the data processing. This problem will be corrected in the V19 data set, to be released later in 1998. Finally, the period we are considering (January 1, 1992 to December 31, 1995) corresponds to the declining phase of solar cycle 22. Using an irradiance variability model derived from UARS [*Lean et al.*, 1997], we estimate a decrease in the solar flux near 200 nm and thus in the O_2 photolysis rate of about 8%.

Each of the above trace constituent and solar flux trends is expected to decrease O_3 in the upper stratosphere. HCl and H_2O increases respectively lead directly to more catalytic odd chlorine and odd hydrogen O_3 loss while the solar flux decrease means less odd oxygen production. Finally the CH_4 decrease should lead to less O_3 through the repartitioning of chlorine compounds, as expressed in the following equation which gives the ratio of active to inactive chlorine

$$Cl/HCl = \frac{k_1[OH] + J_{HCl}}{k_2[CH_4] + k_3[H_2] + k_4[HO_2] + k_5[H_2CO]} \quad (1)$$

This equation shows that the reaction of Cl with CH_4 and H_2CO (which is produced from CH_4) leads to the sequestering of reactive chlorine as HCl. Our calculations indicate that the CH_4 and H_2CO terms account for over 75% of the Cl loss from 35-50 km. Thus a 20-30% decrease in CH_4 should increase reactive chlorine. In this paper we quantify this increase.

Description of Model Calculations

We use a photochemical model described by *Siskind et al.* [1995]. It is a standard one dimensional time dependent model of the upper stratosphere and lower mesosphere that calculates the diurnal variation of O_3, OH, ClO and other
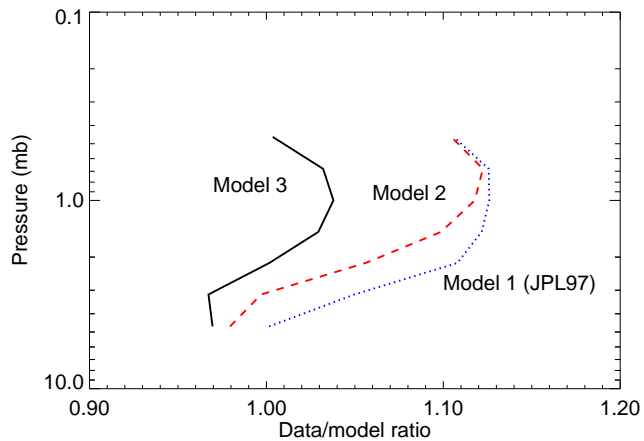
Figure 1. Ratio of HALOE O_3 to models. Each ratio is the average of 300 days of calculations (see text).. Model 1 uses reaction rate coefficients from JPL97, Model 2 uses JPL97 chemistry plus branching ratios of 5% for ClO + OH → HCl + O_2 and 2% for ClO + HO2 → HCl + O_3, Model 3 is the same as Model 2 plus a 30% reduction in the rate coefficient for O + HO_2 → OH + O_2.

short lived constituents. For the present work, we have made two changes. First we have added the chemistry of H_2CO by assuming that all losses of CH_4 lead to H_2CO. The resultant decrease in reactive chlorine (see equation (1)) leads to a model O_3 increase of about 3% between 40-45 km. Second, our new solar reference spectrum, derived from UARS data and defined as the average of the SEP86 and NOV89 spectra of [*Lean et al.*, 1997], contains 9-12% higher irradiance near 200 nm than our previous spectrum [*WMO*, 1986]. As a result, the O_2 dissociation rate is increased and our new model predicts more O_3. Compared to the *Siskind et al.* [1995] model, the combination of these two changes yields about 8% more O_3 in the upper stratosphere. Compared to the *Summers et al.* [1997] model which includes H_2CO, but uses the *WMO* [1986] solar spectrum, the present model predicts 4-5% more O_3 between 40-50 km.

We used the model to simulate the 300 days of HALOE data which occur within 30°of the equator (where the CH_4 decrease is largest and the HALOE sampling is most regular) from 1992 to 1995. Each day of data is, in turn, an average of 14-16 sunset occultations. While our approach is similar to that used by *Crutzen et al.* [1995] our results differ somewhat because we use the newer version 18 HALOE data, a much larger sample of data, and we account for solar variability. We initialized the model with the long lived reservoir species measured by HALOE. Only sunset data are used here because at sunrise a significant fraction of NOx is in the form of N_2O_5 that is not measured by HALOE. For NO which currently contains an erroneous trend, we first detrended the data using the regression fit discussed below. By completely detrending the NO, we may be introducing a small error into the model; however, by assuming the actual NO trend follows the small NO_2 trends given by N98a we estimate the effect on the model O_3 to be no more than 0.1-0.2 %/yr at 36 km (5 mbar) and near zero at higher altitudes. Finally, to obtain a daily varying estimate of the solar flux, we used the wavelength dependent solar proxy

model [*Lean et al.*, 1997, Fig. 17] to derive scaling factors for 3 wavelength bins (180-208 nm, 208-255 nm, and 255-275 nm). These are then used to scale the reference spectra.

Figure 1 compares 3 model simulations, each an average of 300 separate daily calculations, with the similarly averaged HALOE data. Model 1 uses reaction rates from the JPL97 handbook [*DeMore et al.*, 1997] and underestimates the O_3 by 10-12% in the 40-50 km region. This is the remnant of the O_3 deficit problem whereby models have historically underestimated O_3 in the upper stratosphere. Model 2 assumes 5% of the reaction ClO + OH leads to HCl + O_2 [*Lipson et al.*, 1997] and 2% of the reaction ClO + HO_2 leads to HCl + O_3 [*Finkbeiner et al.*, 1995]. As expected, the additional pathway to divert Cly to the HCl reservoir leads to greater O_3 in the model. The remaining difference between the model and the HALOE data increases with altitude above 45 km. This is suggestive of a problem with the HOx chemistry since the HOx catalytic cycle dominates O_3 destruction at the higher altitudes. Thus Model 3 uses the chemistry of Model 2 plus a 30% reduction in the O + HO_2 reaction rate. This is on the order of, although less than, the change proposed by *Summers et al.* [1997]. The combination of lower ClO and lower OH give the best agreement to the average absolute magnitude of the HALOE O_3 data. They also improve the absolute agreement with the MLS ClO data described below. For example, at 2 mb, the 4 year average ClO is 0.54, 0.43 and 0.39 ppbv for Models 1,2, and 3 respectively; for MLS it is 0.36 ppbv.

Analysis of Trends

The predicted O_3 trend from the three simulations for 1992-1995 is compared with HALOE data in Figure 2. In all cases, the trends are estimated using a multiple regression approach which fits annual, semi-annual, quasi-biennial and linear trend terms to the data (N98a). The percentage trend is defined as the linear term divided by the mean value of the fit. The error bars are the 1 sigma values calculated from chi-square [*Press et al., 1992*, p. 658]. For both model and data, the largest errors are due to atmospheric variability not in the regression model (e.g. non-linear trends). The estimated uncertainty in HALOE O_3 measurements due
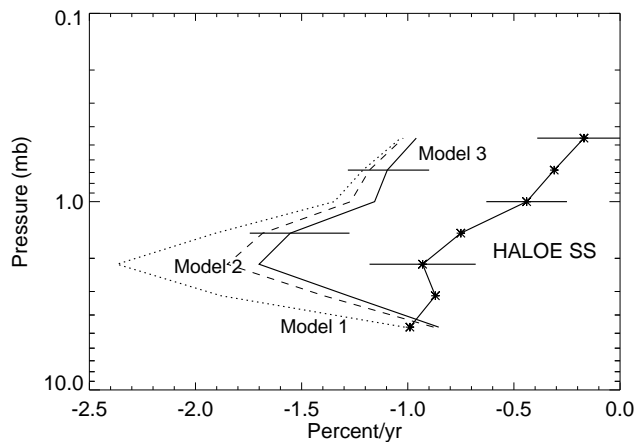

Figure 2. Calculated linear trend for the 3 O_3 models of Figure 1 and HALOE sunset data. The error bars are 1 σ values.

to instrument drift is less than 0.1%/year [*SPARC*, 1998], smaller than the errors shown in Figure 2. The figure shows that Model 1 predicts an O_3 decrease which maximizes at 2.4 %/year at 2 mb. This greatly exceeds the observed decrease which is only 1.0%/year. The other two models which both incorporate the lower ClO, give a smaller trend. That the difference between Models 2 and 3 is small indicates that inclusion of the modified HOx chemistry has little effect on the calculated O_3 trend. Between 0.5 - 3 mb, both Models 2 and 3 agree quite well in shape with the HALOE data, however, both predict larger trends than the data suggest, particularly in the lower mesosphere. While the 2 sigma errors in Figure 2 would overlap slightly, the same difference is seen above 45 km in a model initialized with sunrise data and compared with HALOE sunrise O_3 data (not shown). We therefore believe the discrepancy is significant and discuss this further below.

To better understand the comparison of model with data, we decompose the model trend by selectively detrending the various inputs to the model. Figure 3 shows the results of 5 such calculations, all using the same reaction rates as Model 3, but with various detrended inputs. By "detrended inputs" we mean that we fit each of various HALOE inputs (e.g. CH_4, HCl, H_2O etc.) with a multiple regression function and then subtract the linear term. For example, in the case of CH_4, our new detrended input to the model is related to the original HALOE data according to

$$(CH_4)_{model} = (CH_4)_{HALOE} - a*(t - 731.5)/365. \quad (2)$$

where a is the slope in ppbv/year (N98a). The $(t - 731.5)/365$ term normalizes the data to the mid-point of the time series (January 1, 1994). The calculated O_3 trend in Figure 3 using the detrended CH_4 (Model 3a) is significantly smaller (about 0.8%/yr at 2-3 mb) than the complete model. Also the trend profile no longer has the minimum at 2-5 mb seen in the data. This suggests that the decrease in CH_4 and associated repartitioning of Cly according to (1) play an important role in the overall O_3 trend profile in the upper stratosphere.
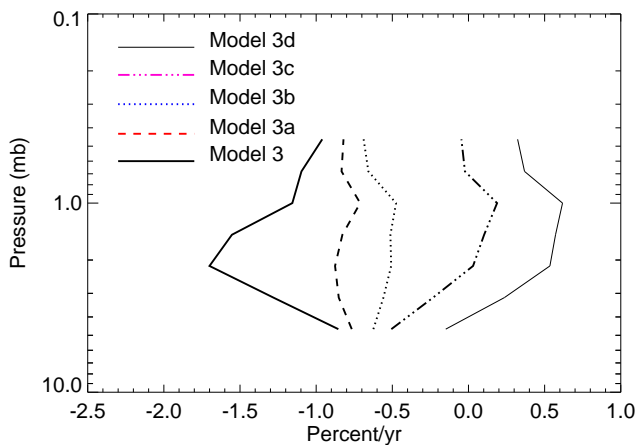

Figure 3. Decomposition of the O_3 trends in Model 3 of Figure 2. Model 3a is Model 3 but with detrended CH_4 (see text). Model 3b uses both detrended CH_4 and HCl. Model 3c uses detrended CH_4, HCl, and H_2O. The difference between Models 3b and 3c shows the dominance of the trend in H_2O in the lower mesosphere. Model 3d is the same as 3c but with fixed solar flux.
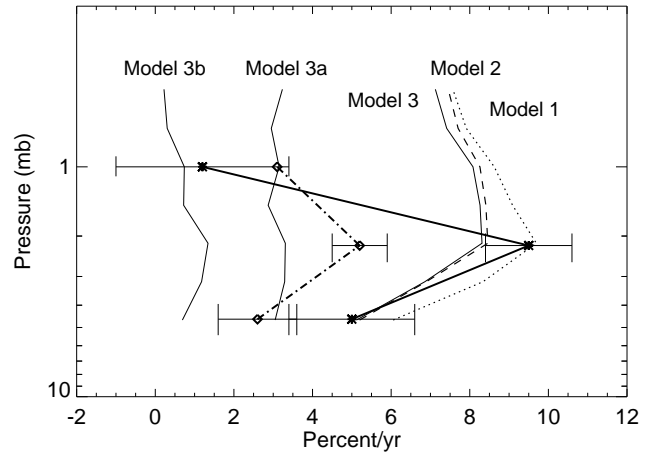

Figure 4. Estimated ClO trend from MLS data for 1992-1995 (heavy solid line) and 1991-1997 (dot dashed line) and calculated ClO trend (1992-1995 only) for Models 1, 2, 3, 3a and 3b (see Figures 2 and 3). The dominant component of the ClO trend is shown by the difference between Model 3 and 3a and is due to the CH_4 trend in the HALOE data.

The difference between each curve in Figure 3 is a direct measure of the model O_3 trend caused by detrending one more additional input. Thus the difference between Model 3a and 3b, about 0.4 %/yr, is the O_3 trend solely associated with increasing HCl. The difference between curve b and c is the change in trend due to the H_2O increase. The H_2O component of the O_3 trend increases with altitude and is dominant in the lower mesosphere. This reflects the importance of HOx chemistry above 45 km and implies that the observed 2-3% annual increase in H_2O should directly translate into a 0.7%/yr decrease in O_3 even before other effects (e.g. solar cycle) are accounted for. Since this decrease in the lower mesosphere is not seen, and since the overall model/data trend discrepancy has the same altitude dependence as the H_2O component, we suggest that the problem in the model lies with the H_2O or HOx chemistry. The solar cycle effect on the O_3 trend is the difference between Model 3c, which uses a daily varying flux, and 3d, where the solar flux is invariant. The resulting trend, about 0.4%/yr, compared with a change in the 200-205 nm solar flux of 8% over 4 years, yields a flux sensitivity factor of 0.2(= 1.6/8). This sensitivity is smaller than estimated by *Chandra et al.* [1996]; however, their analysis did not separate the O_3 trend due to Cly repartitioning or H_2O increases. The residual trend in the model O_3 (Model 3d) after the CH_4, HCl, H_2O and solar flux inputs have been detrended is due to the decrease in temperature we deduce in the HALOE data (0.3-0.4 K/yr, most likely solar cycle related [*Huang and Brasseur*, 1993]) which leads to a 0.4-0.6%/yr increase in the model O_3. There is also a small increase in NO_2 (N98a) which leads to a small negative trend in the model O_3 at 5 mb.

The trends in HALOE CH_4 and HCl imply large increases in the ClO abundance, as shown in Figure 4. The predicted peak ClO increase from Model 1 is about 9.5%/yr at 2 mb. This decreases to 8%/yr with Model 2. Note that changing the HOx chemistry (Model 3) had no apparent effect on the calculated ClO trend. The largest component of the ClO trend is due to the decreasing CH_4. This is seen from

Model 3a (which uses detrended CH$_4$) which predicts a ClO trend of only 2-2.5%/yr. By additionally detrending the HCl input to the model, the ClO shows a near zero trend. Since most of the predicted ClO changes are due to repartitioning of Cly, ClO can be a poor proxy for anthropogenic chlorine increases if other terms in equation (1) also vary.

Figure 4 also shows ClO trends obtained from MLS Version 4 data at 1.0, 2.2 and 4.6 mb and estimated by first binning the data into approximate monthly averages (about 36 days, following the UARS yaw cycle) and then fitting a multi-component regression curve (as discussed in "Long-term variations in the free chlorine content of the stratosphere: Anthropogenic and volcanic influences", Froidevaux et al., manuscript in preparation, 1998). At 4.6 mb, to remove small biases [*Waters et al.*, 1996], the trend is estimated from daytime minus nighttime data. At 2.2 and 1.0 mb, only daytime data are used since nighttime ClO is not as close to zero. The largest uncertainty in our trend estimates appears to be due to the specific time period over which the estimate was made. Thus Figure 4 shows the trend estimated from the entire dataset (1991-1997) as well as the 1992-1995 period used for the model calculations. These trends appear to be different, even when considering the relatively large error bars, and real atmospheric variability may be a cause of this. We will investigate the question of changes in the ClO trend and the small observed trend at 1.0 mb in future work. Despite these caveats, the large ClO trends at 4.6 and 2.2 mb, clearly support our suggestion of a ClO trend enhanced over that expected from HCl (compare with Model 3a)

Discussion

We have used HALOE data and a photochemical model to estimate the relative causes of trends in O$_3$ and ClO during the declining phase of solar cycle 22 (1992-1995). Over this period, the model suggests an O$_3$ decrease greater than that seen by HALOE. The altitude dependence of this discrepancy suggests a problem with HOx chemistry even though the model is "tuned" to give good overall agreement with HALOE O$_3$. It may suggest that some other process is missing from the model rather than simply adjusting the O + HO$_2$ rate. This is consistent with an analysis of diurnal data which found that reducing the O + HO$_2$ alone worsened the agreement with ground-based microwave O$_3$ measurements [*Siskind et al.*, 1995]. We have tried other modifications to the HOx chemistry (i.e. Model B of *Summers et al.* [1997]) with no success. At present we have no explanation for this discrepancy.

Despite this uncertainty, the HALOE data nonetheless imply the existence of a new component of interannual O$_3$ change, that due to the repartitioning of Cly by decreasing CH$_4$. During the decline of solar cycle 22, the trend due to this repartitioning exceeds that from expected changes in total atmospheric chlorine or from solar flux changes. In the case of ClO, the repartitioning effect exceeds the effect of increasing CFC by more than a factor of 2. Because the CH$_4$ decrease coincides with the decline in solar activity, some observational estimates [*Chandra et al*, 1996] of the solar UV O$_3$ response may have inadvertently included the trend due to Cly repartitioning and thus overestimated the sensitivity of O$_3$ to solar UV changes. This may shed light on why models appear to underestimate the 11 year solar/O$_3$ response [*Chandra et al*, 1996].

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