Variations in the free chlorine content of the stratosphere (1991-1997): Anthropogenic, volcanic, and methane influences

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Abstract. Remote sensing of chlorine monoxide (ClO) by the Microwave Limb Sounder experiment aboard the Upper Atmosphere Research Satellite (UARS) has provided global measurements of variations in stratospheric free chlorine for 1991-1997. Linear trends were obtained from a multiple regression analysis of this data set at low latitudes and midlatitudes. ClO increases in the upper stratosphere (2 hPa) are significantly larger than expected from trends in chlorine source gases alone. Much of the upper stratospheric ClO variability can be explained by changes in CH_4, as measured by the UARS Halogen Occultation Experiment. Decreasing ClO in the lower stratosphere is consistent with a relaxation from a chemically perturbed state attributed to the 1991 Mt. Pinatubo eruption.

1. Introduction

Anthropogenic production of chlorofluorocarbons (CFCs) has been linked to the issue of ozone depletion since the early 1970s, when initial predictions of the potential for ozone loss were made [*Molina and Rowland*, 1974]. Long-term increases in the gaseous inorganic chlorine content of the upper atmosphere, where chlorine is released from these halogenated source gases via photolysis and reaction with OH and $O(^1D)$, have been expected and indeed observed, based on measurements of the main stratospheric reservoirs of chlorine, HCl [*Rinsland et al.*, 1991; *Gunson et al.*, 1994; *Russell et al.*, 1996; *Zander et al.*, 1996; *Achard et al.*, 1997; *Wallace et al.*, 1997], and $ClONO_2$ [*Reisinger et al.*, 1995; *Rinsland et al.*, 1996]. Until now, there have been no analogous measurements of long-term changes in reactive or free chlorine (made up primarily of ClO, directly involved in ozone destruction), although one would expect increases in its abundance as well. In the lower stratosphere, volcanic eruptions such as the large Mt. Pinatubo eruption in June of 1991 can indirectly increase the free chlorine content of the lower stratosphere, through chemical reactions on the surfaces of the volcanic sulfate aerosols that are produced and transported throughout the globe in the months following the eruption. Various studies have addressed the impact of such heterogeneous chemistry on the lower stratosphere and on

enhanced ozone depletion [e.g., *Hofmann and Solomon*, 1989; *Rodriguez et al.*, 1991; *Brasseur and Granier*, 1992; *Fahey et al.*, 1993; *Kinnison et al.*, 1994; *Wennberg et al.*, 1994; *Solomon et al.*, 1996]. It is now accepted that aerosol conditions, whether at "background" levels or during volcanically enhanced periods, are an essential component for an accurate understanding of ozone photochemistry in the lower stratosphere. In particular, the reaction $N_2O_5 + H_2O \rightarrow 2\ HNO_3$ on aerosol surfaces is expected to play a key role by decreasing the abundance of gaseous reactive nitrogen (NO_x), which in turn slows down the conversion of ClO (a key reactive chlorine radical involved in the depletion of ozone) to $ClONO_2$. The anticorrelation between ClO and NO_2 has been verified by in situ measurements of these species in the lower stratosphere [*Stimpfle et al.*, 1994; *Wennberg et al.*, 1994], and postvolcanic decreases in lower stratospheric NO_x have indeed been observed [*De Mazière et al.*, 1998, and references therein]. Moreover, in situ midlatitude measurements of ClO and aerosols have demonstrated that increases in aerosol surface area concentration correlate with increases in ClO [*Wilson et al.*, 1993]. At temperatures lower than 205 K (with higher water content of the aerosol solutions), additional reactions, for example, $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$, $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$, and $HCl + HOCl \rightarrow Cl_2 + H_2O$, can play a significant or dominant role in the repartitioning from reservoir (inactive) chlorine forms to free (reactive) chlorine [e.g., *Borrmann et al.*, 1997; *Webster et al.*, 1998].

A long-term global study of lower stratospheric free chlorine (or ClO) abundances has not been performed before because of the paucity of such observations on an extended temporal and spatial scale. Uncertainties remain concerning the budget of inorganic chlorine in the lower stratosphere, as well as the time variation (and aerosol surface area

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dependence) of HCl and ClO in the lower stratosphere [*Avallone et al.*, 1993; *Jaeglé et al.*, 1996; *Dessler et al.*, 1997; *Webster et al.*, 1998]. In this context, the Microwave Limb Sounder (MLS) [*Barath et al.*, 1993; *Waters et al.*, 1999] aboard the Upper Atmosphere Research Satellite (UARS) has provided a unique global "long-term" data set for ClO since late 1991. However, terms such as "long-term" or "trends" need to be understood in the context of the 6 years (1991-1997) studied here and should generally be used with caution, especially since ClO variations in the future (next decade) may well differ significantly from the results herein. In this paper, we present results from the MLS observations of global ClO variations, in conjunction with two-dimensional model simulations of atmospheric chemistry and transport over this time period, including the effects of anthropogenic and volcanic influences on free chlorine. Important global measurements of CH_4, H_2O, and HCl obtained by the UARS Halogen Occultation Experiment (HALOE) [*Russell et al.*, 1993] are also used in this analysis. *Ricaud et al.* [this issue] present a related study of MLS ClO data, focusing on the modeling of diurnal and seasonal variations at heights above 30 km.

2. Global Variations in ClO (1991-1997)

The MLS measurements are obtained from observations of thermal emission at microwave wavelengths [*Waters et al.*, 1999] as the instrument's antenna scans vertically through the Earth's atmospheric limb. The ClO data have been validated previously and compare well with other measurements [*Waters et al.*, 1996]; Version 4 data are used in this analysis. The MLS measurements are not significantly degraded by the presence of stratospheric aerosols [*Waters et al.*, 1999], which is important for the post-Pinatubo period. We discuss observations made between September 21, 1991 (shortly after the satellite launch), and June 14, 1997. After this, a different operating mode was used (with only one radiometer turned on), in order to accommodate low-battery power conditions on the satellite; temperature data from MLS were then lost, and tangent pressure information was obtained from the ozone band (at 206 GHz) rather than the oxygen band (at 63 GHz). Moreover, the amount of available MLS data (number of observing days per month) decreased significantly after June 1997. We have limited this analysis to the time period prior to July 1997, since we do not currently have enough evidence to demonstrate that the post-June 1997 measurement mode can provide consistent trend information with sufficient precision. MLS data were obtained daily or nearly so from late 1991 through 1993. Some periods of reduced observations also occurred between 1994 and mid-1997 because of a combination of instrument scanning and UARS problems. The satellite undergoes yaw maneuvers on a periodic basis of order 36 days (referred to as a "UARS month"), leading to alternating coverage of the 80°S-34°N and 80°N-34°S latitude regions.

Because individual profiles of ClO are generally noise-dominated except under conditions of enhanced chlorine during polar winter, we have averaged ClO data into broad latitude bins in order to present results with enough statistical significance. To remove small biases [*Waters et al.*, 1996] observed in nighttime data at pressures larger than 4 hPa (in a region where nighttime abundances of ClO should be very

close to zero), we have subtracted nighttime mean values over each UARS month from the corresponding daytime values for these pressures. Weighting of the individual profiles by cosine of latitude has also been applied in order to obtain "area-weighted" zonal mean abundances. A time series of these abundances for the 30°S-30°N latitude bin is shown in Figure 1. Some screening of the data was performed in order to avoid occasional spikes and poor data coverage. In addition to the standard MLS quality checks used to bypass rare cases of bad profiles [see *Waters et al.*, 1996], occasional ClO spikes (values larger than 5 ppbv or less than -3 ppbv) were omitted, and days with nonrepresentative latitudinal coverage (i.e., not covering at least a quarter of the latitude bin under consideration on both sides of the center latitude) were excluded. Furthermore, ClO monthly values with an error (standard error in the mean) more than twice the average monthly error (over the 6-year time period) were excluded, eliminating most months with only a few days of data. The robustness of the results was checked by comparing trend results from daily averages to those from the monthly averages. Also, upper stratospheric values at 1 and 2 hPa were analyzed using monthly daytime and nighttime data separately, and the results were found to be consistent; the results shown here include all data (day and night) at these pressures. Since the results of the various sensitivity studies did not differ significantly from each other (outside the one-sigma error bars), we feel that the trend results shown here are robust (within their error bars).

A multiple regression analysis is applied to the zonal mean monthly values by using the following regression model abundances $f(t)$ to fit the data (t represents the day giving the central date for each UARS month): $f(t) = C + L\,t + a_1 \cos(2\pi t/P_1) + b_1 \sin(2\pi t/P_1) + a_2 \cos(2\pi t/P_2) + b_2 \sin(2\pi t/P_2) + a_3 \cos(2\pi t/P_3) + b_3 \sin(2\pi t/P_3)$. The periods P_i represent annual, semiannual, and quasi-biennial oscillation (QBO) timescales, corresponding to 12 months, 6 months, and 27 months, respectively; the 27-month period is a first-order representation of the QBO, but our results are not significantly biased by this term or by changing that period by a few months. The slope or linear component of interest is L. We first fit the nonlinear coefficients to the data with a standard singular value decomposition routine, and then fit a slope to the "anomalies" given by the data values minus the nonlinear components of the model. The fitted linear term (plus constant) is shown as a solid line in Figure 1, for each of the six main pressure surfaces where ClO is retrieved in Version 4 data; data at lower or higher pressures are not considered reliable enough to draw significant conclusions.

Also shown in Figure 1 are model values from the Lawrence Livermore National Laboratory (LLNL) 2-D transport-chemical model of the stratosphere and troposphere, both with a simulation of the Mt. Pinatubo eruption effects based on aerosol loading of the lower stratosphere (thick dashed lines) and without such effects (thin dashed lines); these two model cases differ significantly only at pressures larger than 10 hPa (lower stratosphere). The main characteristics of this model have been described in previous work [*Kinnison et al.*, 1994]. The version used here was updated to use more recent estimates of photochemical rate constants [*DeMore et al.*, 1997] and also includes the reaction of OH with ClO to form HCl and O_2 [*Lipson et al.*, 1997]. This model includes a representation of the observed trends in
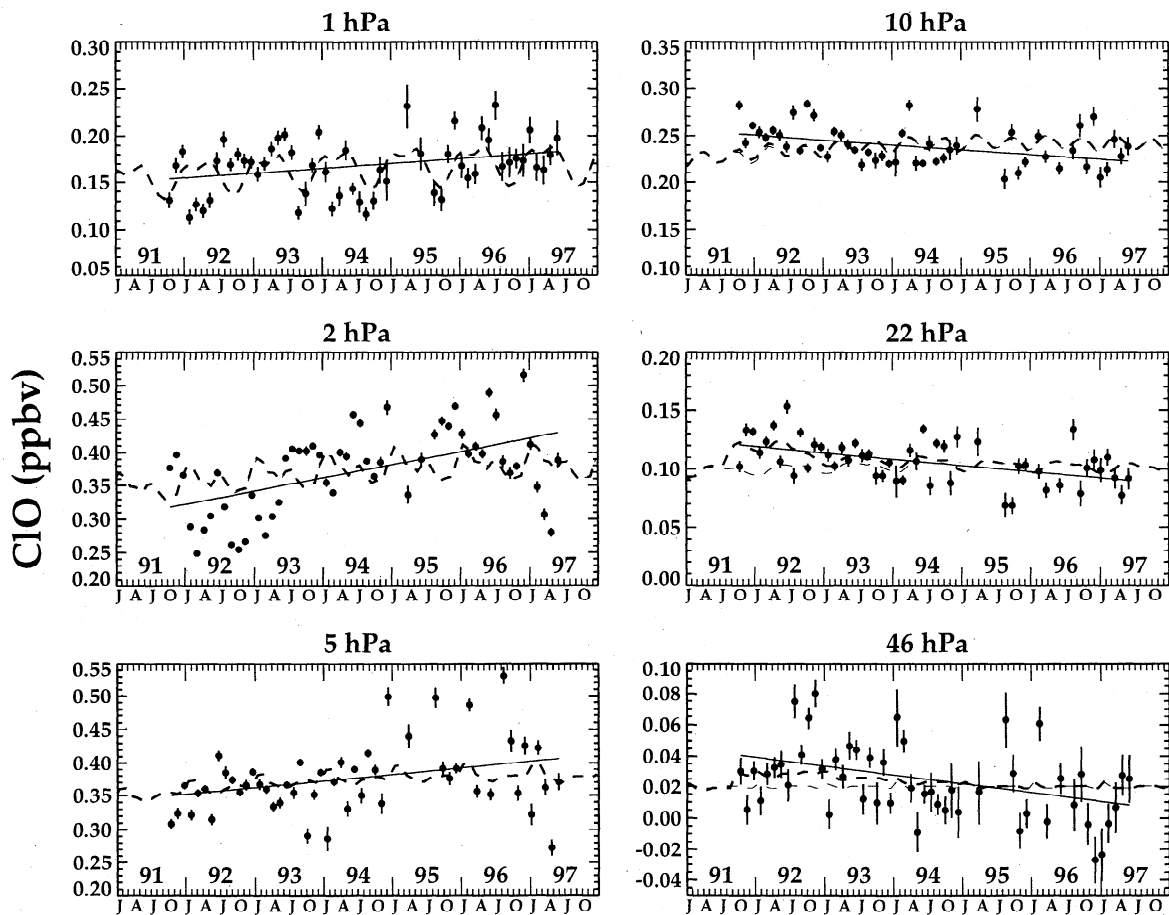
Figure 1. Zonal mean ClO abundances for latitudes of 30°S-30°N from Microwave Limb Sounder (MLS) measurements between late 1991 and mid-1997 at various pressures (2 hPa and 5 hPa are, more precisely, 2.2 hPa and 4.6 hPa). Dots represent averages over roughly 36-day time periods (see text); error bars represent the estimated precision for the mean values. Solid lines give the slopes obtained from a multiple regression fit to the data (after the nonlinear components of the model fit have been subtracted from the data). Thick dashed lines represent the expected behavior from the Lawrence Livermore National Laboratory (LLNL) 2-D chemical-transport model including anthropogenic and volcanic influences; scaling factors have been used to match the average model values to the average data values (see text). Model pressure grid points are at 0.94, 2.2, 5.0, 9.3, 21.5, and 49 hPa, very close to the pressures used in the MLS retrievals. Thin dashed lines are model values that do not include heterogeneous chemistry effects of volcanic aerosols arising from the June 1991 eruption of Mt. Pinatubo; these lines are distinguishable from the thick dashed lines mainly at 22 hPa and 46 hPa.

atmospheric CFCs, CH_4, and N_2O through specification of surface concentrations. Vertical and horizontal eddy coefficients are specified in the troposphere, and the tropospheric chemistry of CH_4 and hydrochlorofluorocarbons is included. The model was run for 28 years from 1970, starting from a calculated steady state 1970 atmosphere, using observed halocarbon surface mole fractions as time-dependent lower boundary conditions for the Cl and Br source species. From 1979, the surface area density of sulfate aerosol in the model stratosphere is interpolated from a data set inferred from the Stratospheric Aerosol and Gas Experiment (SAGE) observations, SAGE II being most relevant for the MLS time period, with some aerosol data coming from the SAGE I and Stratospheric Aerosol Measurement (SAM) observations; in the volcano-free case, aerosol surface area is fixed at 1995 values. The circulation in the model is annually periodic based on a steady state representation of 1995 source gas

abundances and decadal scale climatological temperature and fixed throughout the run. This model will not represent any interannual variations in stratospheric dynamics driven by volcanic emissions or any other source. Systematic errors in the model include unrepresented processes (wave-forcing processes, solar cycle variability in ultraviolet irradiance, QBO), errors in photochemistry affecting radical family partitioning, and, probably of greater importance, errors in the mean circulation, which can impact the calculated age of air. In Figure 1, all model values have been scaled by the ratio of average ClO from the data to average model ClO, with scaling factors of 1.31, 1.14, 1.11, 1.03, 0.96, and 1.36, respectively, from lowest to highest pressure. We are focusing more on the expected trends than on the absolute values of ClO; however, there is generally good agreement in the absolute values, based on the above scaling factors and given the typical 15% level of accuracy (systematic error) for
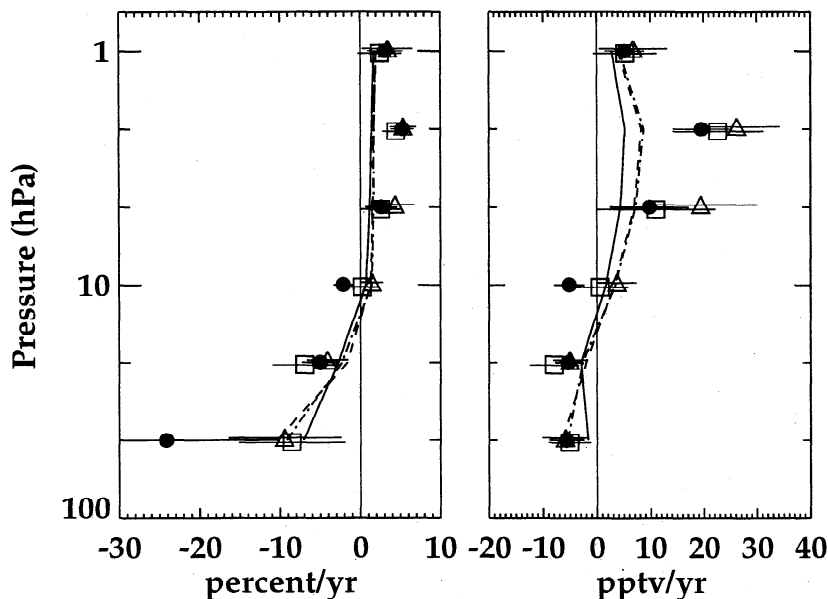
Figure 2. Summary of fitted trends in ClO for three latitude bins at various pressures. MLS data yield values summarized as dots (30°S-30°N), triangles (30°N-50°N), and squares (30°S-50°S). LLNL model trends from linear fits to deseasonalized monthly model values are also shown (solid curve for 30°S-30°N, dashed curve for 30°N-50°N, and dash-dot curve for 30°S-50°S). Units are in %/yr and pptv/yr. Error bars represent twice the root mean square uncertainty estimate (or a 95% confidence limit).

MLS ClO data and possible systematic errors in the model. The main message from Figure 1 is that global values of ClO have increased in this time period in the upper stratosphere, but they have decreased in the lower stratosphere (at pressures of about 20-50 hPa). The volcano-free model case in Figure 1 leads to slight increases in lower stratospheric ClO as opposed to a decreasing trend.

A summary of the trends in ClO for the 1991-1997 time period discussed above is presented in Figure 2, where in addition to results from Figure 1, we have added results from midlatitude data (30°S-50°S and 30°N-50°N latitude bins). The midlatitude trends generally have larger error bars because of the smaller number of measurements. The general picture of an increase in chlorine in the upper stratosphere and a decrease in the lower stratosphere is apparent from Figure 2. Given the error bars (95% confidence level or "2 sigma" errors used here), the data show no evidence of a latitude dependence in the derived trends. This strengthens the statistical significance of these results in terms of a global assessment of chlorine trends (global results would basically be an average of the values at each pressure, with an error smaller by square root of 3 than the errors shown). Model results obtained by fitting a linear function to the deseasonalized model monthly mean values of ClO over the same time period as the data are also shown in Figure 2. While there is qualitative agreement between model and data in the main trends and their variation as a function of height, there is a clear model underestimate of the observed upper stratospheric increases, most notably at 2 hPa (where the data-derived trend is 5.2 ± 1.4 %/yr, versus a model trend of only 1.4 %/yr). We note also that the low-latitude 10 hPa trend in the observations appears to be somewhat different than at midlatitudes, since it shows a small decrease as opposed to the slight increase or flat behavior at midlatitudes. There is

only a hint of this difference in behavior in the model results but at slightly higher pressures.

Besides the sensitivity studies mentioned earlier which give us confidence in the robustness of the results, we note that the ClO measurements are obtained from the same radiometer system as the long-term MLS ozone data (the ClO line is at 204.35 GHz, while the O_3 line is at 206.13 GHz). The MLS ozone abundances have been shown to track very closely the ozone variations and trends from other well-calibrated observations [*Froidevaux et al.*, 1996; *World Meteorological Organization (WMO)*, 1998; *Cunnold et al.*, 2000]. In particular, it has been established [*WMO*, 1998] that MLS, HALOE, and SAGE II ozone abundances do not drift relative to each other by more than 0.5%/yr, typically, based on data obtained between late 1991 and the end of 1996 (essentially the same time period as we use here). We estimate that the stability of the MLS measurements is better than 0.2%/yr, based on a consideration of error sources and the lack of evidence for significant sources of instrument degradation; an error in the temperature trend is potentially the largest contributor to the MLS ozone or ClO trend estimates (note that the expected errors are, at most, a few tenths of a %/yr compared to the several %/yr variations obtained here for ClO). MLS radiances at the highest altitudes have shown excellent stability, with an implied change of less than 0.01% in the antenna system reflectivity over a 6-year period. Finally, evidence from correlative studies [*Waters et al.*, 1996, see Figures 32-34] shows that (averaged) ClO values from MLS can match and track other data sets in the lower stratosphere to better than ~0.03 ppbv; stability of average nighttime data also leads to a relative confidence level of this order. These limits on relative stability apply conservatively in the upper stratosphere, where the emission line is narrower and less subject to contamination from other effects

(interfering species and/or continuum emission). ClO variability above ~0.03 ppbv is considered to be atmospheric, and the random errors on monthly averaged ClO values are most often negligible compared to this. Hence, the error bars on the chlorine "trends" derived here (about 1.5-2%/yr for two-sigma values) are justified, given the above discussion.

3. Discussion of Chlorine Trends

3.1. Upper Stratosphere

Measurements of the tropospheric source gases show the onset of a decrease in many of the halocarbon surface abundances during the last few years [*Montzka et al.*, 1996; *Cunnold et al.*, 1997]; total tropospheric chlorine grew by 1.6% in 1992, compared to 2.9% in 1989 [*WMO*, 1995]. These changes confirm the expected reduction in halocarbon emissions as a result of the Montreal Protocol and its Amendments. UARS HALOE measurements of stratospheric HCl during 1991-1996 give trends of about 3.5%/yr [*Russell et al.*, 1996]. Other HCl data sets from sparser observations (in space and time) and with more weighting toward pre-1992 data lead to HCl trends typically within 3-5%/yr [*Rinsland et al.*, 1991; *Gunson et al.*, 1994; *Zander et al.*, 1996; *Achard et al.*, 1997; *Wallace et al.*, 1997]. Measurements of $ClONO_2$, the other temporary reservoir of chlorine in the middle stratosphere, produce similar trends, albeit with larger error bars [*Reisinger et al.*, 1995; *Rinsland et al.*, 1996]. These results are consistent with the rate of increase from the source gases at the ground. The LLNL model takes into account the rates of increase for the halocarbons, along with the time lag associated with transporting the source gases up to the stratosphere where they are decomposed into reactive chlorine; this leads to a linear component of the model ClO trend in the upper stratosphere of order 1.5-2%/yr (see Figure 2). However, stratospheric air in the LLNL model is generally too young (based on previous studies), so that changes in surface chlorine source gas abundances will be reflected too quickly at high altitude. This implies that actual rates of increase for upper stratospheric Cl could be larger than implied here by the model (although only slightly, since ground-based changes are an upper limit).

There is evidence of a significant decrease (by a few %/yr) in upper stratospheric methane from 1991 to 1997, based on HALOE observations [*Nedoluha et al.*, 1998; *Randel et al.*, 1999]. The reasons for the decrease have not yet been quantified, but they may be tied to changes in transport following the Mt. Pinatubo eruption [*Nedoluha et al.*, 1998] or to variability in the meridional transport on a decadal timescale, possibly linked to the Arctic oscillation [*Thompson et al.*, 2000]. Implications for upper stratospheric ClO and O_3 abundances have been recently discussed elsewhere [*Siskind et al.*, 1998]. Since the relationship between ClO number density ([ClO]) and the abundance of other gases in the upper stratosphere can be approximated by the following proportionality, [ClO] $\propto$ [HCl] [OH] / [CH_4], it is evident that a decrease in methane would lead to a rise in ClO [see also *Siskind et al.*, 1998]. *Siskind et al.* [1998] conclude that expected rates of increase for low-latitude upper stratospheric ClO in the 1991-1995 time period are of order 8%/yr and that the MLS trend results for that time period (calculated as discussed here) are broadly consistent with the idea that methane decreases have played a significant role in accelerating the reactive chlorine trend in the past few years. We demonstrate in Figure 3 that the variations in CH_4 (HALOE Version 18 data), averaged over 30°S-30°N at 2 hPa for the same "monthly" time periods as the MLS ClO data, are indeed highly anticorrelated with the ClO variations, for both long-term and shorter-term changes. The CH_4 abundances appear to decrease between 1992 and 1996, with a recovery taking place in the 1996-1997 timeframe. The ClO abundances increase while methane is decreasing but appear to trend downward in the last year shown, in a manner opposite to the methane behavior; the correlation coefficient between the two time series is –0.81. Similar anti-correlated behavior is observed at midlatitudes (not shown here). Figure 3 (bottom) displays the temporal variations of ratio $Q = f_{ClO} f_{CH4} / (f_{HCl} \sqrt{f_{H2O}})$, where f_X represents the abundance of species X (and where we have used the retrieved monthly mean mixing ratios from MLS for ClO and from HALOE for CH_4, HCl, and H_2O). This ratio should be essentially constant, since it represents first-order equilibrium conditions for the balance of ClO and HCl (see the earlier mention of proportionality); OH should vary roughly as $\sqrt{H_2O}$, given the expected photochemical balance for HO_x, with production proportional to H_2O and loss quadratic in OH, via the OH+HO_2 main loss mechanism. The remaining temperature dependence in this ratio should be negligible. Figure 3 shows that this ratio (normalized to its average value over the time period) does indeed remain nearly constant (the slope for Q is essentially flat, whereas this is not true for ClO or CH_4).

We now further investigate these ClO variations at 2 hPa, in relation to our multiple regression fit as well as a simpler fit using HALOE methane observations. Figure 4 shows the multiple regression fit and the various components (for 30°S-30°N, 2 hPa), with the effect of these components (constant and linear, annual, semiannual, and QBO terms) added in succession. The full model fits best and yields a correlation coefficient of 0.86. Similar fits are obtained at the other latitudes (not shown here), but the annual term plays a more dominant role there (although its amplitude is not much different from that shown in Figure 4). Next, we explore a fit based on methane variations using the independent HALOE CH_4 data and show that this can produce essentially as good a fit, with the implication that methane variations are indeed related to ClO variations, as expected from the chemical relationship between these species. If one considers the HCl linear dependence (following the proportionality between ClO and HCl mentioned above) as an underlying driver for the (linear) time dependence, as well as the inverse relationship with methane, one arrives at a plausible functional regression model of the form $(\alpha+\beta t)/f_{CH4}$. Using this regression function (and solving for the coefficients α and β), we obtain the fits shown in Figure 5. The correlation coefficients at the various latitudes (from north to south) are 0.79, 0.82, and 0.79, nearly as high as for the multiple regression function used above. However, some of the fitted variations are amplified, compared to the observations. This is plausible, since the ClO dependence on methane is not quite as strong as an inverse relationship (there are other terms in the chemical loss mechanism for Cl, see, e.g., *Siskind et al.* [1998], which will dampen the methane effect). Using a slightly different regression model of the form $(\alpha+\beta t)/(f_{CH4})^m$, where the exponent m is less than unity (we used various values from
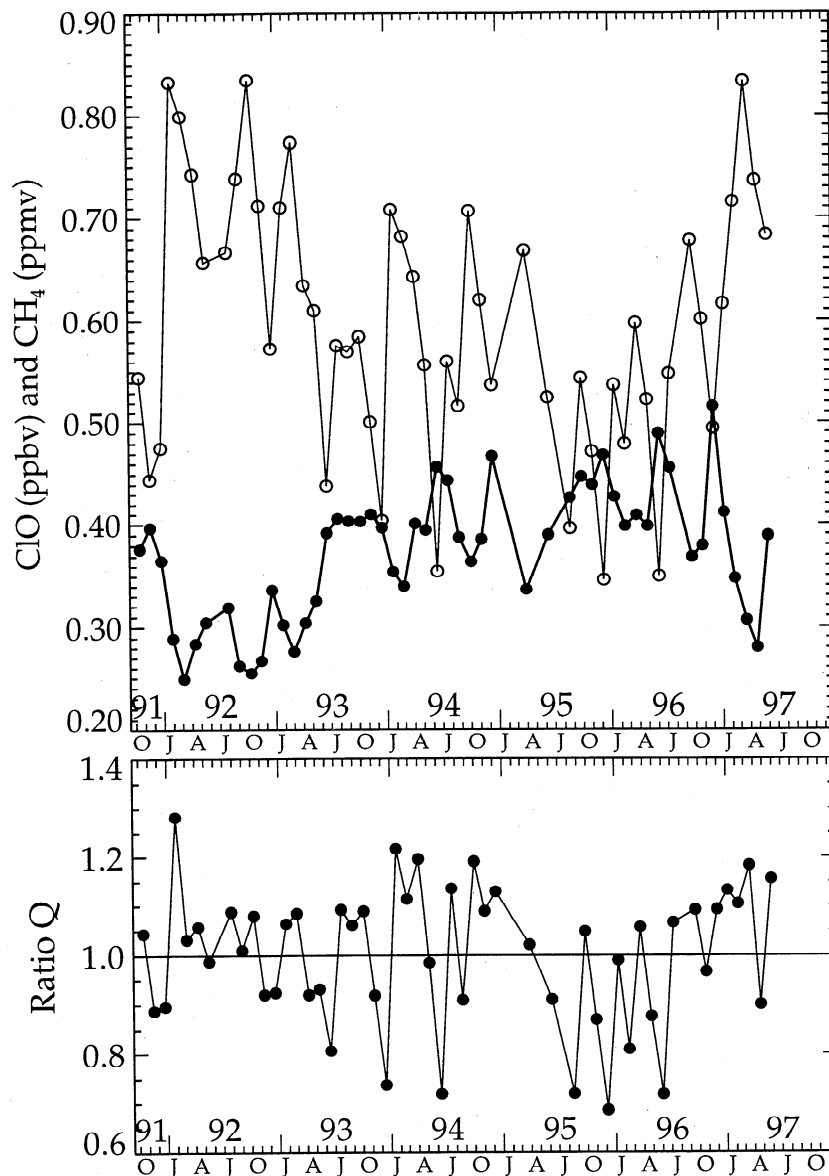
Figure 3. (top) Time series of zonal mean abundances of ClO from MLS data (filled circles) and CH$_4$ from HALOE data (open circles) for 2 hPa and 30°S-30°N. (bottom) Time series of normalized ratio Q (see text), representing first-order photochemical balance between ClO and HCl.

0.2 to 0.8), we have determined that a value of 0.5 for m optimizes both the rms residual (between fitted function and data) and the correlation coefficient (see the dashed line fits in Figure 5). This inverse square root dependence on methane is interesting and somewhat weaker than expected; we find that the monthly 2 hPa abundances of ClO and CH$_4$ over the annual cycle of the LLNL 2-D model follow a relationship with a power dependence between 0.5 and 1. Studies suggesting a correlation between methane variations and ClO variability were initially presented in the early 1980s [*Solomon and Garcia*, 1984], and the data shown here support this connection on a global scale. The 2-D model results shown in Figures 1 and 2 for expected ClO trends did not include possible variations (especially not a decrease) in methane as part of the simulation, but the observed CH$_4$ variations seem to explain why lower-than-observed ClO

"trends" are predicted [see also *Siskind et al.*, 1998]. *Randel et al.* [1999] have also examined the trends in MLS ClO data and state that there is overall general agreement between the ClO trends and the HALOE HCl trends in the upper stratosphere (increases of about 2-3%/yr), for the time period from 1993 to mid-1997. However, our analyses (not shown in detail here) of the ClO data for various 4-year periods show that the time period chosen significantly affects the "trends"; at 2 hPa for 30°S-30°N, we obtain a "trend" of more than 9%/yr (±2%/yr) for the first 4 years (late 1991 to late 1995), whereas for the last 4 years (mid-1993 to mid-1997), the result is about 2.5%/yr (±2.5%/yr). Our analyses indicate that upper stratospheric free chlorine (unlike HCl) can be subject to effects (mainly in relation to methane) that produce significantly different variations than those of the source gases for chlorine. This might be especially true for some
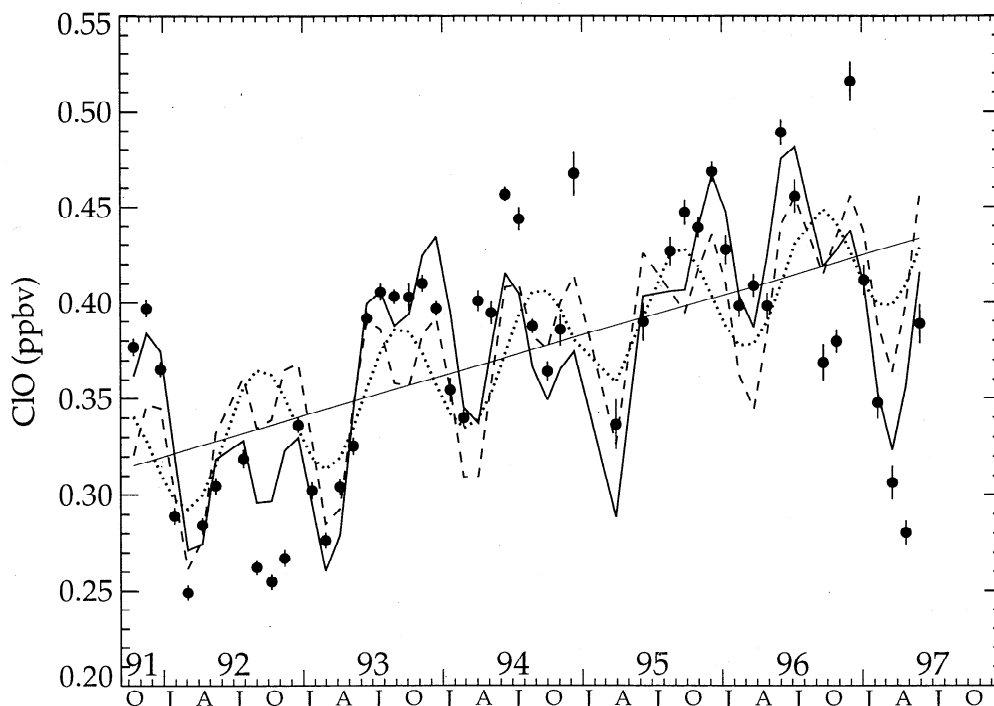
Figure 4. Various components of the multiple regression fit for ClO zonal mean values in the 30°S-30°N latitude bin at 2 hPa. Components of the fit are added in succession, from the straight line (constant and linear terms) to the dotted curve (adds the annual components), dashed curve (adds the semiannual components), and the solid curve (full fit, adds the QBO-like components).

time (several years) after a large volcanic eruption and subsequent transport-related effects on methane. The fairly smooth and monotonic rise in HCl abundances (based on HALOE observations not shown here) cannot play a significant role in the observed ClO variability; however, the large recent variability in CH_4 needs to be better understood and is a plausible cause for (or at least is related to) much of the upper stratospheric ClO variability shown here.

3.2. Lower Stratosphere

While free chlorine would also be expected to show a small increasing trend in the lower stratosphere based on CFC emissions, it is evident from the ClO data shown in Figures 1 and 2 that an opposite type of behavior occurs in this region (for this time period at least). The most obvious explanation lies in the chemical perturbations that have occurred indirectly because of the Mt. Pinatubo eruption; we emphasize that this is an indirect effect as opposed to a relaxation following direct volcanic injection of chlorine into the stratosphere (a negligible effect, see *WMO* [1995]). Under nonpolar atmospheric temperature conditions, the main heterogeneous reaction is believed to be the hydrolysis of N_2O_5, whereby water vapor and N_2O_5 react to produce HNO_3. This in turn shifts the nitrogen balance from NO_x (NO and NO_2) and N_2O_5 to HNO_3. Observations of increases in HNO_3 and decreases in NO_x after the Mt. Pinatubo eruption have confirmed this general idea [*WMO*, 1995]; HNO_3 data from MLS (not shown here; see also *Randel et al.* [1999]) and from the UARS Cryogenic Limb Array Emission Spectrometer [*Kumer et al.*, 1996] also support the idea of a post-Pinatubo recovery period

(with decreases in HNO_3 since 1992). We focus here on the effects regarding chlorine species.

The indirect effect of a decrease in NO_x is to slow the rate of conversion of active chlorine radicals (Cl, ClO) to the temporary reservoir of chlorine nitrate ($ClONO_2$). Therefore the abundance of ClO is expected to increase after the eruption and slowly relax toward nonperturbed conditions in subsequent years. Figures 6 and 7 give LLNL model results for the effects of heterogeneous chemistry after Mt. Pinatubo on the lower stratospheric ClO abundances, shown for the 30°N-50°N and 30°S-50°S latitude bins, respectively. Both model and data at 10 hPa display similar maxima in the summer and minima in the winter, whereas the seasonal maximum shifts to the wintertime at 46 hPa. In the volcanically unperturbed lower stratosphere, an annual winter maximum in aerosol surface area density suppresses NO_x through conversion to reservoirs (HNO_3 and N_2O_5), as lower solar illumination further suppresses NO relative to NO_2. This seasonal minimum in NO_x reduces $ClONO_2$ production and favors ClO over Cl, while also slowing down the loss of active chlorine resulting from reaction with CH_4. Figures 6 and 7 also show a volcano-free model case, wherein a slow ClO increase (1.2%/yr) is expected at 22 and 46 hPa, in contrast to the observations. The model differences in ClO trends between the lower and upper stratosphere (for the volcano-free case) are a reflection of trends in the different source gases that contribute to free chlorine in the two regions. In the lower stratosphere, Cl is produced mainly from source gases that photolyze readily such as CH_3CCl_3 and CCl_4, while CF_2Cl_2 contributes proportionately more in the
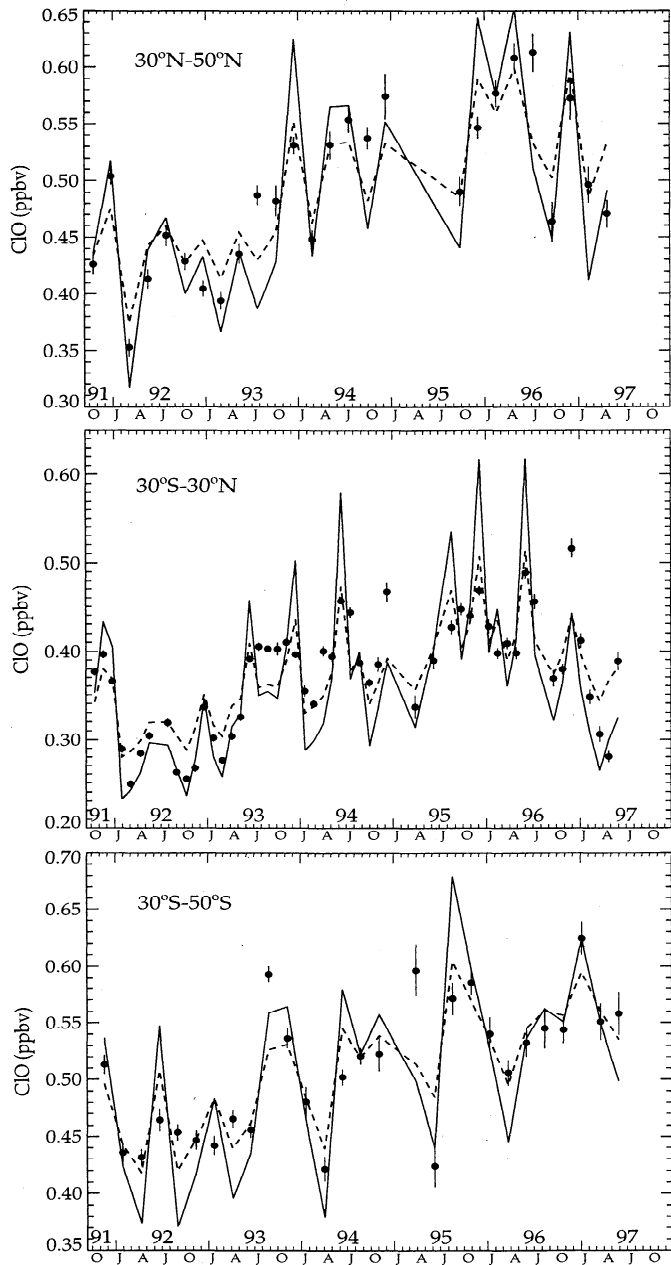
Figure 5. Regression model fits for ClO zonal mean values in three latitude bins (as indicated in the figure), using a regression model of the form $(\alpha + \beta t) / f_{CH4}$ (solid line) and $(\alpha + \beta t) / \sqrt{f_{CH4}}$ (dashed line), where the methane abundances are obtained from the HALOE data. The (empirical) square root inverse dependence on methane gives the better fit and correlation coefficient for all latitudes; the rms residual for the dashed line drops to 6-9% (depending on latitude) from 10-15% for the solid line, and the correlation coefficient increases to 0.84-0.87 from 0.79-0.82.

However, the decreasing ClO trends are the clearest first-order indication of a Pinatubo-related effect in the lower stratosphere, where, regardless of the exact amplitude and nonlinearity of the expected effects of heterogeneous chemistry, the model without such an aerosol-related impact would lead one to expect a (small) increase in ClO. The interpretation is limited, in terms of constraining details of the heterogeneous chemistry that can lead to ClO enhancements, or the relaxation timescale or latitude dependence thereof, given the error bars in both data and model. The model predicts that most of the decrease in ClO should occur prior to 1995. On the basis of fitted rates of ClO change as a function of time for different years (various 4-year time periods, not shown in detail here), there are indications of a reduction in the rate of observed ClO decrease with time at 22 hPa for southern midlatitudes, and some evidence for northern midlatitudes, with essentially no such evidence in the tropics. It is more difficult to confirm or deny this behavior at 46 hPa, where the error bars are also larger.

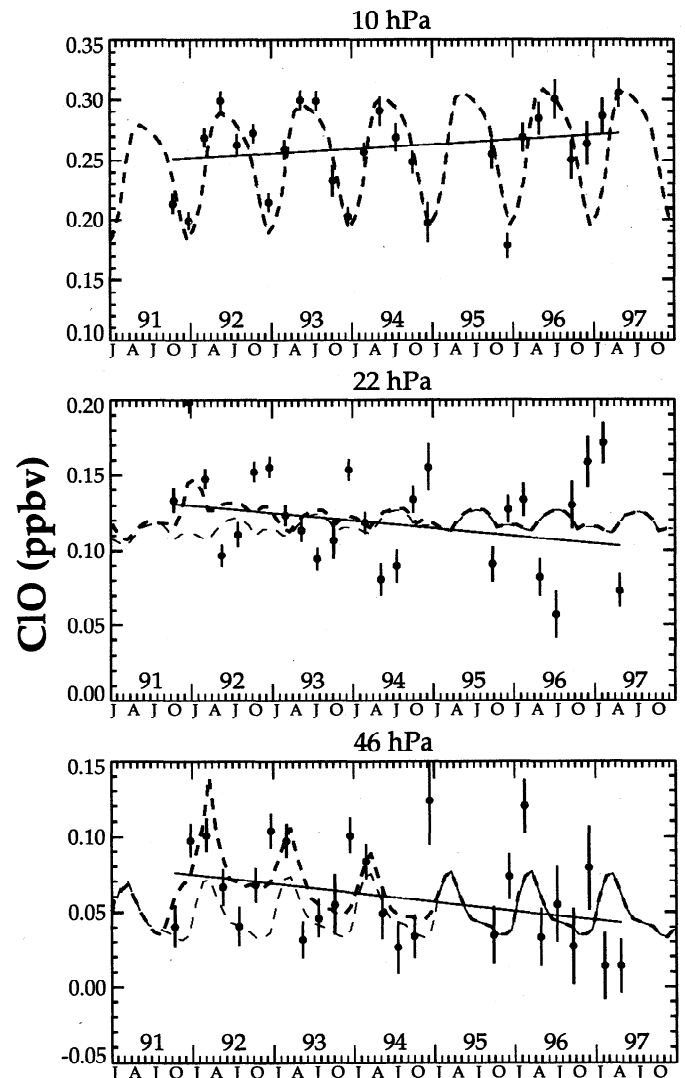Results from in situ measurements of ClO in the stratosphere have indicated that there was indeed an increase

Figure 6. Time series of ClO from the MLS observations and model, as in Figure 1, but for 30°N-50°N at the three highest pressures only.

upper stratosphere. The easily photolyzed sources also have a shorter lifetime and respond faster to emission changes at the surface. For example, CH_3CCl_3 has begun to decline, while CF_2Cl_2 has not. While there are some variations in the data that are not readily explained, the model has some limitations which do not allow for optimum simulation of year-to-year variations or coupling of dynamics, radiation, and chemistry.
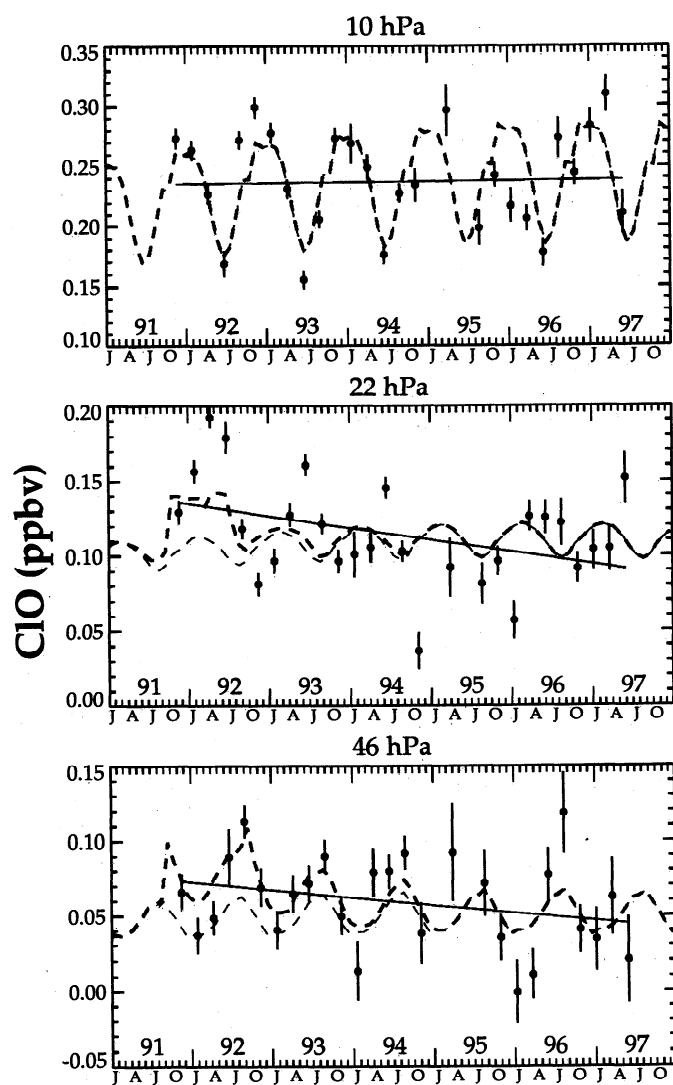
Figure 7. Time series of ClO from the MLS observations and model, as in Figure 1, but for 30°S-50°S at the three highest pressures only.

in the ClO abundances between pre- and post-Pinatubo eruption measurements [*Fahey et al.*, 1993; *Wilson et al.*, 1993; *Avallone et al.*, 1993]. Although those data sets were much more limited in space and time than the satellite observations reported here, they do seem to generally agree with our results, in terms of a Pinatubo-related increase in ClO of order a factor of two or more. The MLS ClO data at 46 hPa yield a total decay in ClO of about a factor of 4 between 1992 and 1997 for 30°S-30°N averages and about a factor of 2 for both the 30°N-50°N and 30°S-50°S latitude bins. As might be expected from lower aerosol surface area at low pressure, the observed decay at 22 hPa (decrease of ~25%) is less than at 46 hPa.

4. Conclusions

Satellite-based microwave emission measurements of ClO from UARS MLS from late 1991 to mid-1997 provide the first direct evidence of a "long-term" global rise in stratospheric free chlorine. The observed rate of ClO increase

significantly exceeds the linear trend of 2%/yr that is consistent with the rate of increase from source gases (mostly CFCs) at the ground and the similar trend in high-altitude HCl (the main reservoir for chlorine in the upper stratosphere). The connection with recent methane decreases in the upper stratosphere suggested by *Siskind et al.* [1998] seems to be the most likely explanation for these rapid changes in free chlorine. The CH_4 and ClO short- and long-term variations are strongly anticorrelated on a global scale, with some indication of a reversal in the "trends" toward less perturbed conditions in 1996-1997. Regression fits using a model of upper stratospheric (2 hPa) ClO mixing ratio varying as a combination of a linear temporal increase and an inverse dependence on methane mixing ratio, a functional form expressed as $(\alpha+\beta t)/f_{CH4}$, clearly support this ClO-CH$_4$ connection as a plausible explanation for much of the observed ClO changes. The fits for the three latitude bins considered in this work are optimized if the methane abundance in the above expression is raised to a power of 0.5. While this is a semi-empirical expression, it is based on theoretical expectations for the dependence of ClO on CH_4. We note that the methane variations are obtained from HALOE data, which are completely independent of the MLS ClO data. While the reasons for the underlying methane decrease are still not completely understood, this decrease appears to have greatly accelerated the increase in upper stratospheric ClO.

In the lower stratosphere, MLS observations indicate that ClO generally decreases during this time period. Observed decreases of about 5 pptv/yr or 5-10%/yr can be explained as post-Pinatubo eruption effects, whereby volcanic aerosol production and transport in the lower stratosphere through 1992 led indirectly to a relatively rapid increase in free chlorine, followed by a relaxation to nonenhanced conditions in subsequent years. This behavior is predicted by the LLNL 2-D model, even if the details of the relaxation rate are not easily tested, given the seasonal and interannual variability in the ClO data (and the measurement precision).

This paper contrasts the global impact of CFCs and methane on free chlorine variations in the upper stratosphere (during 1991-1997) with the indirect impact of the Mt. Pinatubo volcanic eruption on free chlorine in the lower stratosphere. As the role of halocarbons diminishes in the coming decades, the stratospheric chlorine abundances are expected to diminish (the tropospheric abundances of several of these source gases themselves have recently begun to decrease), so that future long-term decreases in stratospheric ClO are expected.

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