Using Satellite Measurements of $N_2O$ to remove dynamical variability from HCl measurements

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Abstract:

Column HCl measurements show deviations from the expected slow decline following the regulation of chlorine-containing compounds by the Montreal Protocol. We use the simultaneous measurements of $N_2O$ and HCl by the MLS instrument on the Aura satellite to examine this problem. We find that the use of $N_2O$ measurements at a specific altitude to represent the impact of dynamical variability on HCl results in a derived linear trend in HCl that is negative (ranging from -2.5%/decade to 5.3%/decade) at all altitudes between 68 hPa and 10 hPa. These trends are at or near 2σ statistically significance at all pressure levels between 68 hPa and 10 hPa.

I. Introduction

HCl is the primary constituent of inorganic chlorine in the stratosphere, comprising 75-80% of the inorganic chlorine in the altitude range from 68 hPa to 10 hPa [Zander et al., 1992; Nassar, et al. 2006]. As such it provides a convenient marker for the total amount of inorganic stratospheric chlorine that can be measured from the ground and from satellites. The column amount of HCl is expected to follow the behavior of the concentration of the organic sources of chlorine as measured at the surface (e.g. CFCs) with a time delay of a few years for the CFCs to reach the stratosphere where they are converted to inorganic chlorine compounds.

Rinsland et al. [2003] showed from ground-based measurements that the amount of inorganic chlorine ($HCl + ClONO_2$) in the stratosphere leveled out using data through 2002. The next step would be to observe the expected decrease in inorganic chlorine. Recently Mahieu et al. [2014] have shown that, in fact, the measured HCl column over Jungfraujoch decreased more rapidly than expected from ground-based measurements of source gases during the early 2000’s followed by an increase from about 2007 to 2010. We show that the Microwave Limb Sounder (MLS) measurements of the lower stratospheric column of HCl also decrease and increase in concert with the Jungfraujoch data, followed by a decrease from 2011 to mid 2013 and a subsequent increase from that time to the present (see Figure 1).
Figure 1: Total column measurements of HCl above Jungfraujoch smoothed with a 3-year running mean as shown by Mahieu et al. [2014] (red curve). Also shown are the 3-year running mean smoothed zonal mean of measurements of the lower stratospheric column of HCl (100-10 hPa) from the MLS instrument on Aura for the latitude band from 45 to 50N (black curve). The MLS measurements are of partial column and have been scaled upward to match the Jungfraujoch FTIR measurements for better visual comparison.

Mahieu et al. [2014] use results from model simulations with SLIMCAT driven by ERA-Interim meteorological fields from the European Centre for Medium-Range Weather Forecasts (ECMWF) to suggest that variability in the stratospheric circulation causes the accelerated decrease and the unexpected increase in HCl column. We will explore this explanation using measurements of N$_2$O from MLS as a measure of this variability in circulation.

2. MLS Data: HCl and N$_2$O

We will use the MLS HCl data to test whether chlorine is decreasing in the stratosphere as expected from adherence to the provisions of the Montreal Protocol. MLS was launched on the Aura Satellite in late 2004 [Waters et al., 2006] and continues to operate in 2017. The record is now more than 13 years in length with altitude profiles of HCl, HNO$_3$, N$_2$O and many other species measured globally on a daily basis.

For HCl we use the version 4.2 product that has little change since the previous version 3 products. According to the MLS data quality document [Livesey et al, 2017] the useful range for HCl measurements is from 100 to 0.32 hPa. However, the useful data for trends is limited to pressures greater than 10 hPa due to the insufficient reliability of the band 14 retrievals in the upper stratosphere.

For N$_2$O we use the version 4.2 redefined standard product that uses signals from the band 3 (190-GHz channel); the standard product was redefined because the product from band 12 (640 GHz channel) deteriorated and the band was shut off in
August 2013. In the next section we will compare this redefined standard to the measurements from the 640-GHz channel and correct for the drift observed between these two channels during the time that both were yielding N₂O measurements. The 190-GHz N₂O data are stated to be useful in the 68-0.46 hPa range. We will thus restrict our analyses to pressure levels between 68 and 10 hPa in this paper where both the HCl and N₂O measurements are useful.

Figure 2: Deseasonalized monthly-mean MLS measurements of HCl concentration at 32 hPa. Measurements are area-weighted between 45°N and 50°N. The heavy dashed line is a linear least squares fit to the data and the shaded area indicates the 2σ uncertainty in that fit including consideration of auto-correlation in the time series.

To better understand the variations in HCl column amounts at 47°N observed by Mahieu et al. [2014] we begin with consideration of the MLS measurements of the HCl profile at specific pressure levels in the stratosphere. For example, Figure 2 shows the anomalies in the MLS monthly-mean measurements of HCl averaged between 45°N and 50°N latitude at the 32 hPa pressure level. The data are shown in percentage deviation from the seasonal mean of the entire data set. The data clearly show deviations of as much as ±10% with significant auto-correlation.

One way to look at the HCl anomalies shown in Figure 2 is to attempt to “explain” the variance by fitting to various measures of dynamical variability such as the Quasi-Biennial Oscillation (QBO) or El-Niño/Southern Oscillation (ENSO). This method may remove much of the dynamical variance but has at least two potential problems: 1) the fitting parameters may only remove part of the dynamical variability because of incomplete representation of that variability and 2) they may over-represent the variability because of correlation between parameters. Either of
these problems could lead to difficulties in separating real trends from apparent
trends in the residual over short time scales such as the 12 years of data since 2004.
For example, the impact of the QBO on southern mid-latitude composition depends
on the QBO phase during early (southern) winter [Strahan et al. 2015]. The
resulting dynamical variability is not easily represented by fitting a QBO plus a
seasonal term in a statistical model, because the actual variability depends on an
interaction between the two effects.

We use a different method to remove dynamical variability in the HCl data set,
taking advantage of simultaneous measurements of another species made by the
MLS instrument on the Aura satellite. The observed anomalies are the result of
dynamical variability acting on mixing ratio gradients. These gradients may be
vertical, horizontal, or a combination of both. If two constituents have gradients in
the same or opposite directions, the impact of dynamic variability will be to cause
deviations, or anomalies, that are either correlated or anti-correlated depending on
the sign of the gradients. An example is shown in Figure 3 where we plot the
deseasonalized HCl mixing ratios at 32 hPa for the latitude band 45-50N as in Figure
2 and the deseasonalized N2O mixing ratios on a reverse scale from MLS
measurements for the same latitude band and pressure level. The correlation
coefficient is -0.87 between these two anomaly time series. A similar correlation is
found between HCl and HNO3 data from MLS.

Figure 3: Deseasonalized time series of HCl (black curve, same as Figure 2) and
deseasonalized time series of N2O plotted with reverse scale on right side of figure(red
curve) for the latitude band 45-50N at 32 hPa pressure level from MLS measurements of
each constituent.

3. Time Series Analysis: Using N2O Anomalies as a Fitting Parameter
The trend that we are trying to isolate and confirm for the HCl time series is determined by the change in abundance of chlorine-containing halocarbons driven by the provisions of the Montreal Protocol on ozone-depleting substances. The chlorine-containing source gases are expected to have decreased since 2000 in response to the decreases in the chlorine-containing source gases. \( \text{N}_2\text{O} \), on the other hand, is known to be increasing at a rate of about 2.8%/decade [NOAA GMDL data updated from Elkins and Dutton [2009] available at ftp://ftp.cmdl.noaa.gov/hats/n2o/combined/HATS_global_N2O.txt]. Our approach is to use the \( \text{N}_2\text{O} \) time series at each altitude, such as that shown in Figure 3, as an explanatory variable in a time-series regression to remove the dynamical variability from the HCl time series. Trends calculated for HCl in this time-series regression are then corrected for the underlying trend in \( \text{N}_2\text{O} \).

The result of using \( \text{N}_2\text{O} \) as a fitting parameter for the 32 hPa MLS time series for HCl is shown in Figure 4. The solid red line in the figure is the residual time series after fitting, which takes advantage of the substantial covariance and shows significantly reduced variability. The resulting trend is shown by the red dashed line that has a slope of \(-4.4 \pm 2.7\) (2\( \sigma \)) %/decade. The HCl trend at this pressure level is now negative and statistically significant at more than the 3\( \sigma \) level. The same procedure has been carried out at each of the pressure levels for MLS retrievals. The result is shown in the third column of Table 1.

The second column of Table 1 shows the raw trend obtained from the MLS HCl measurements. We can see that the raw trend is essentially the same as the \( \text{N}_2\text{O} \)-fitted trend at the two highest levels (10 and 15 hPa) where dynamical variability is
relatively small. The trend at the lower levels is substantially different when using
\( N_2O \) as a fitting parameter. Using \( N_2O \) as a fitting parameter changes the lower level
trends from positive to negative with a substantial reduction in the uncertainty.

A further problem alluded to earlier in this section is that MLS now uses the 190-
GHz band for its standard \( N_2O \) product because the 640-GHz band is no longer
usable. The problem arises because the 190-GHz band displays a drift in \( N_2O \)
measurements with respect to the 640-GHz band [N. Livesey, pers. commun.]. Since
the 640-GHz band was found to be stable during its operational period, we use the
drift rate of the 190-GHz band with respect to the 640-GHz band calculated by the
MLS team for the time period in which they both were operational (2004-2012).
The results are shown in the fourth column of Table 1 with estimated uncertainties
in the fit.

<table>
<thead>
<tr>
<th>Pressure Level (hPa)</th>
<th>Raw HCl Trend (%/dec)</th>
<th>Trend with ( N_2O ) fit (%/dec)</th>
<th>( N_2O ) 190/640 drift (%/dec)</th>
<th>Surf ( N_2O ) Trend (%/dec)</th>
<th>Final HCl Trend (%/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-3.7±2.0</td>
<td>-3.0±2.0</td>
<td>-5.1±3.7</td>
<td>+2.8±0.05</td>
<td>-5.3±4.2</td>
</tr>
<tr>
<td>15</td>
<td>-3.8±3.1</td>
<td>-3.5±1.9</td>
<td>-2.9±2.2</td>
<td>+2.8±0.05</td>
<td>-3.6±2.9</td>
</tr>
<tr>
<td>22</td>
<td>-1.3±4.2</td>
<td>-3.8±2.3</td>
<td>-1.5±1.3</td>
<td>+2.8±0.05</td>
<td>-2.5±2.6</td>
</tr>
<tr>
<td>32</td>
<td>+2.4±8.8</td>
<td>-4.4±2.7</td>
<td>-2.2±1.4</td>
<td>+2.8±0.05</td>
<td>-3.8±3.0</td>
</tr>
<tr>
<td>46</td>
<td>+3.8±7.2</td>
<td>-2.3±2.3</td>
<td>-5.2±1.8</td>
<td>+2.8±0.05</td>
<td>-4.7±2.9</td>
</tr>
<tr>
<td>68</td>
<td>+3.9±4.0</td>
<td>-1.3±2.7</td>
<td>-5.0±1.6</td>
<td>+2.8±0.05</td>
<td>-3.5±3.1</td>
</tr>
</tbody>
</table>

Table 1. HCl trends derived from MLS data at 6 pressure levels. Column 1 gives the
pressure level. Column 2 gives the raw trend derived directly from the MLS HCl
measurements in %/decade with 2σ uncertainties. Column 3 gives the HCl trend derived
using MLS \( N_2O \) measurements as an explanatory variable. Column 4 gives the derived trend
in the 190-GHz channel of MLS \( N_2O \) measurements relative to the 640-GHz channel during
the time of their overlap. Column 5 gives the slope of the NOAA global surface
measurements of \( N_2O \) over the period from 2001 to 2012. Column 6 gives the overall
resulting trend obtained by combining the information in columns 3 to 5.

Finally, we note that the surface levels of \( N_2O \) increased by about 2.8%/decade. We
used the “global” nitrous oxide data reported at the NOAA ESRL Global Monitoring
Division web site (https://www.esrl.noaa.gov/gmd/hats/combined/N2O.html). We
fit a trend to the data between 2001 and 2012 to represent the ground values that
should be seen in the stratosphere about 3 years later in the MLS data. The time
delay represents the approximate mean age of air in the lower stratosphere.

The final result is obtained by summing the trends in columns 3 to 5 of Table 1 and
is shown in column 6 of the table. The uncertainties were obtained by using the root
sum of squares (RSS) of the uncertainties in columns 3 to 5. This final result is also
shown in Figure 5. The blue solid line indicates the trend result obtained from a
linear fit to the deseasonalized residuals with no attempt to account for dynamical
variability (column 2 of Table 1). The red solid curve is the result when the \( N_2O \)
time series is used as a dynamical surrogate, with corrections for drift and surface
trends, in the fitting procedure (column 6 of Table 1). The shaded areas represent
$2\sigma$ uncertainties in the linear trends.

Note in Figure 5 that the use of N$_2$O as a surrogate for dynamical variability reduces
the uncertainty in the calculated trend for all of the pressure levels between 15 hPa
and 68 hPa where the MLS data for both HCl and N$_2$O are considered to be good for
trend analysis. Figure 5 also shows that the calculated linear trend in HCl using the
N$_2$O surrogate with corrections is negative at all pressure levels and is significantly
negative ($2\sigma$) at all levels from 68 hPa to 10 hPa with the exception of 22 hPa where
it has nearly $2\sigma$ significance.

4. Conclusion

In their paper, Mahieu et al. [2014] showed that total column HCl measured at
Jungfraujoch showed significant variation from the expected simple linear trend.
We have attempted to quantitatively evaluate the effect of dynamical variability on
the concentrations of HCl in the stratosphere by using N$_2$O measurements since late
2004 made by the Aura MLS instrument. Since both HCl and N$_2$O have
collection gradients (horizontal and vertical) that are acted upon by dynamical
processes to create inter-annual variability, we have used the variability of N$_2$O
concentrations determined from MLS observations as a measure of the dynamical
variability that should be expected in HCl concentrations. We suggest that this
method more reliably removes the real atmospheric variability than does the use of
other proxies.

We have shown that using an N$_2$O surrogate in trend analysis of the MLS HCl time
series results in a trend that is negative at all measured levels from 68 hPa upward
to 10 hPa and that these negative trends are statistically significant or nearly so.
The N$_2$O surrogate had little effect at the upper two levels of 10 and 15 hPa where
the dynamical variability is less significant. The surrogate had significant impact on
the derived trends lower in the stratosphere where most of the HCl column resides.

Previous data-based estimates of HCl decrease in the stratosphere include
Froidevaux et al. [2006], Jones et al. [2011], Brown et al. [2011], and Kohlhepp et al.
[2012]. All of these studies had to consider the issues we have discussed in this
paper, namely the contribution of dynamic variability to the apparent trend. In each
case, the shortness of the data record was a significant limitation to the
interpretation of potential trends due to the decrease in tropospheric organic
chlorine sources.

The results from these authors are summarized in the 2014 Ozone Assessment
Report [Carpenter and Reimann, 2015]. Specifically Froidevaux et al. [2006]
derived a trend for the 50-65 km altitude range of -8%/decade from MLS data for
the years 2004-2006. Jones et al. [2011] derived a trend of -5%/decade using
HALOE and ACE FTS data between 35 and 45 km from 1997 to 2008 at midlatitudes.
Brown et al. [2011] deduced a trend of -7%/decade for the 50 to 54 kkm range from
ACE FTS data from 2004 to 2010. Finally, Kohlhepp et al. [2012] analyzed the total
column HCl data from 17 NDACC FTIR stations for the years 2000 to 2009, obtaining
trends that ranged from -4 to -16%/decade depending on station.

The best comparison for evaluating our results is considering the change in the
organic chlorine sources at the surface. The 2014 ozone assessment, Chapter 1,
[Carpenter and Reimann, 2015] estimates changes in the tropospheric available
organic chlorine of -6%/decade from 2000-2004 followed by -4.6%/decade from
2004-2008 and -4%/decade from 2008-2012. Assuming a 3-5 year delay between
changes in the tropospheric source gases for the stratospheric chlorine implies an
average change from 2004 to 2016 of about -4.9%/decade, in agreement with our
estimate from MLS data within the uncertainty bounds.
References:


