Trends in stratospheric HCl from the ACE satellite mission

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ABSTRACT

The Montreal Protocol has banned the production of long-lived chlorine-containing gases such as chlorofluorocarbons (CFCs) that deplete stratospheric ozone. These halogenated compounds ultimately form HCl in the upper atmosphere; the effectiveness of the Montreal Protocol can therefore be monitored by measuring stratospheric HCl. The Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) measures infrared solar occultation spectra of the Earth's atmosphere from which altitude profiles of HCl volume mixing ratios (VMRs) are determined. The upper stratospheric HCl VMR time series has a linear trend of $-4.8 \pm 0.2\%$/decade for 2004–2017, highlighting the continuing success of the Montreal Protocol.

1. Introduction

The Montreal Protocol is an international treaty that controls substances such as chlorofluorocarbons (CFCs) and halons that deplete stratospheric ozone [1]. Stratospheric ozone prevents deleterious near ultraviolet radiation (200–300 nm) from reaching the ground. Rowland and Molina [2] discovered that long-lived chlorofluorocarbons (CFCs) emitted by human activities are inert in the troposphere but are photolyzed in the stratosphere and release chlorine atoms. These chlorine atoms destroy ozone in a catalytic cycle involving the ClO free radical. Ultimately CFCs are oxidized to CO_2, HF and HCl. The success of the Montreal Protocol can therefore be monitored by measuring the amount of stratospheric HCl.

Atmospheric HCl can be measured from the ground by high resolution infrared spectroscopy using lines from the fundamental band in the 3.5 μm region and the Sun as a light source. The total column density of HCl is being measured by a network of infrared Fourier transform spectrometers as part of the NDACC (Network for the Detection of Atmospheric Composition Change; http://www.ndsc.ncep.noaa.gov/) [3].

HCl volume mixing ratio (VMR) measurements as a function of altitude can be obtained from high altitude balloons with in situ measurements [e.g., 4] or with an infrared spectrometer using the Sun as a light source [e.g., 5]. More comprehensive global observations have been made from satellite platforms starting with the HALOE (Halogen Occultation Experiment) instrument on NASA's Upper Atmosphere Research Satellite (UARS) from 1991 to 2005 [6]. More recent HCl measurements (2004-present) are being made by the Canadian Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) on SCISAT [7] and the Microwave Limb Sounder (MLS) on NASA's Aura satellite [8].

Many papers have been published on atmospheric HCl trends such as by Froidevaux et al. in 2006 [9] and in 2015 [10]. Froidevaux et al. [10] have combined HALOE, MLS and ACE-FTS data to provide a multi-instrument HCl time series for 1991 to 2012 called GOZCARDS (Global OZone Chemistry And Related trace gas Data records for the Stratosphere). Brown et al. [11] used tropical ACE-FTS data for the period 2004–2010. HCl trends are also reported every 4 years in the WMO ozone assessment [12]. In the present paper, we update global HCl trends derived from ACE-FTS data for 2004–2017.

A complicating factor in determining stratospheric HCl trends is dynamical variability. For example, recent HCl volume mixing ratios (VMRs) in the lower stratosphere in the Northern Hemisphere have increased because of dynamics [13], while the overall global stratospheric trend remains negative. The effects of dynamical variability on the HCl VMR time series can be reduced by using the correlation with a long-lived tracer such as N_2O [e.g., 14]. The HCl trend values determined by HALOE [6] were in the lower mesosphere at 55 km to avoid problems with dynamical variability in the stratosphere and because almost all the source gases are converted to HCl at high altitude.

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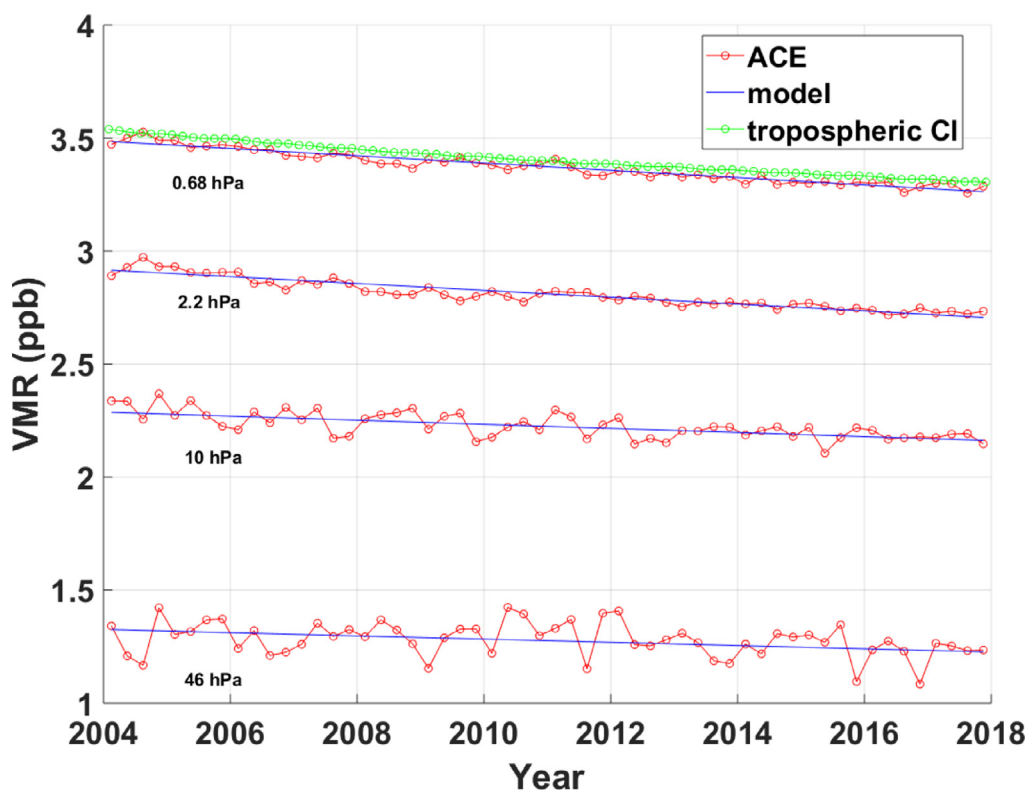*E-mail address:* pbernath@odu.edu (P. Bernath).

Fig. 1. De-seasonalized HCl VMR time series from ACE-FTS data for 60°S–60°N and the total effective tropospheric chlorine lagged by 4 years (see text). The blue lines are linear fits. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Methods and results

ACE is a Canadian satellite mission [7] that measures atmospheric absorption spectra in the limb geometry using the Sun as a light source (solar occultation). The ACE orbit (74° inclination to the equator, 650 km altitude) concentrates measurements at high latitudes but also provides coverage of mid-latitudes and tropics [Fig. 6 in ref. 7]. The ACE-FTS is a high resolution (0.02 cm^{-1}) Fourier transform spectrometer that covers the 750–4400 cm^{-1} region; the current processing version used in our analysis is 3.5/3.6 [as summarized in ref. 7]; see http://www.ace.uwaterloo.ca/ for the v.3.5/3.6 HCl and N$_2$O microwindow list [15].

The ACE-FTS HCl data product is provided on a 1 km altitude grid and has a vertical resolution of about 3 km over the 6–57 km altitude range at the poles and 7–63 km in the tropics. The VMRs for 60°S–60°N were interpolated onto a pressure grid spaced at $p_i = 1000 \times 10^{-i/6}$ (hPa) corresponding to an altitude spacing of about 2.7 km as was used by GOZCARDS [10] and in the recent trend analysis by Stolarski et al. [14]. After discarding large negative and positive values, the VMRs were filtered at each pressure level by removing all values that were outside 2.5 standard deviations from the median. Quarterly averages were then computed for Dec–Feb (DJF), Mar–May (MAM), Jun–Aug (JJA), Sep–Nov (SON) at each pressure level to make a time series for MAM 2004 to SON 2017. The time series at each pressure level was de-seasonalized by computing the quarterly average for the entire time series and subtracting this value from the corresponding quarter to obtain a time series of anomalies. These anomalies were converted back to a de-seasonalized VMR time series at each pressure level by adding the 2004–2017 average. A time series of N$_2$O VMRs was derived using the same method described above for HCl.

The HCl time series are displayed (Fig. 1) for the pressure levels 0.68, 2.2, 10 and 46 hPa at the approximate altitudes of 51, 42, 31

and 21 km, respectively, using the US standard atmosphere [16] to estimate altitudes (these approximate altitudes are only provided for the convenience of the reader and are not used in the analysis). The linear trend lines are also plotted and for 0.68 hPa two lines are used (see discussion below). Also included in Fig. 1 is the total effective tropospheric chlorine [17] lagged by 4 years.

Linear trend values are derived from the de-seasonalized HCl time series for 13 pressure levels from 68 hPa to 0.68 hPa (about 19–51 km) for 60°S–60°N and are plotted with one standard deviation error bars in Fig. 2. Linear regression was used with a constant, a linear term and a term for the N$_2$O VMR [as in ref. 14] (i.e., VMR$_{HCl}$(t) = $a + bt + c$VMR$_{N2O}$(t) with constants a, b and c). The term with the N$_2$O VMR accounts for some of the HCl variability due to dynamics and improves the determination of the linear trend value, b. The de-seasonalized N$_2$O time series was first corrected for a steady N$_2$O VMR increase of +0.28%/year [14]. The trend error bars were estimated using the procedure of Weatherhead et al. [14,18] and include the effects of first order autocorrelation in the time series. The standard error in the trend estimate b is given by $\sigma_N n^{-3/2}[(1+\varphi)/(1-\varphi)]^{1/2}$, in which σ_N is the standard deviation of the residuals (i.e., the difference between observed and modeled HCl VMRs), φ is the autocorrelation of the residuals and n is the number of years of data [18]. The 13 VMR time series for HCl and N$_2$O, and HCl trend values with errors are provided as supplementary data.

In order to assess the effect of atmospheric dynamics on the trend values, the same analysis was carried out for 3 additional latitude bins (30–60°N, 30°S–30°N, 30–60°S) and these trend values are also provided in the supplementary data. All the values for the highest 3 pressure levels in the upper stratosphere (0.68, 1, 1.5 hPa) are within 0.5% of the 60°S–60°N bin but, as expected, there were substantial differences in trends in the lower stratosphere [15] even when N$_2$O was included in the trend analysis.
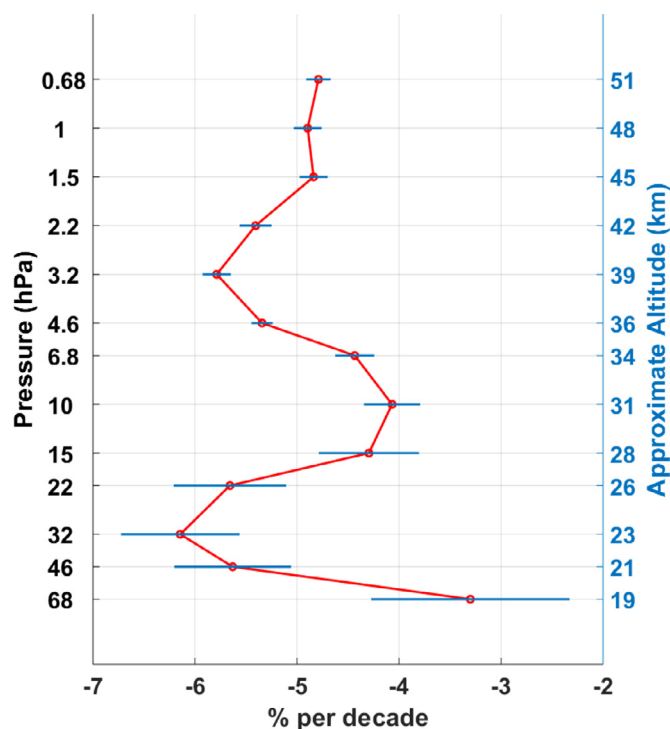
Fig. 2. Linear HCl trends as a function of pressure (approximate altitudes are on the right) for 2004 to 2017 for 60°S–60°N with one standard deviation error bars (see text).

As also found by Stolarski et al. [14], inclusion of N_2O in the model is successful in reducing the effect of dynamics [13] in the lower stratosphere in the Northern Hemisphere (30–60°N in our case). The inclusion of N_2O also decreased the error bars on the trend values, but the trend values still change substantially with altitude except in the upper stratosphere. The average upper stratospheric trend is $-4.8 \pm 0.2\%$/decade obtained by averaging the 3 values in the upper stratosphere from 1.5 hPa to 0.68 hPa; one standard deviation obtained by error propagation (i.e., square root of the sum of the squares of the original errors) is used as the error bar. Averaging the trend values over all 13 stratospheric pressure levels gives $-5.0 \pm 0.8\%$/decade, in which the error estimate is the standard deviation the trend values. Percentage trends were calculated by dividing the linear trends from the de-seasonalized time series by the mission average of the original time series.

3. Discussion and conclusion

The stratospheric trend value reported in the 2014 WMO ozone report [12] for 1997–2013 was $-5.9 \pm 1.5\%$/decade based on merged HALOE and ACE-FTS data. For 2004–2010, Brown et al. [11] reported a trend value of $-7 \pm 1\%$/decade from ACE-FTS and $-6 \pm 1\%$/decade from the SLIMCAT model. GOZCARDS [10] shows similar trend values but reports that recent values are decreasing in magnitude. Using N_2O in the model gives comparable ACE-FTS (30–60°N) HCl trend values in the lower stratosphere as the values derived by Stolarski et al. [14] for 45–50°N, e.g., at 15 hPa the MLS value is $-3.6 \pm 1.5\%$/decade compared to the ACE-FTS value of $-5.0 \pm 0.4\%$/decade.

There is also strong evidence in ACE data (Fig. 1) for a change in slope since about 2010. For example, at 0.68 hPa the 2004–2010 linear trend is $-5.9 \pm 0.5\%$/decade and from 2011 to 2017 the value is $-4.1 \pm 0.4\%$/decade, with an overall 2004–2017 linear trend of $-4.8 \pm 0.2\%$/decade. Also plotted in Fig. 1 is the total effective tropospheric chlorine [18] lagged by 4 years to account for the trans-

port time to the upper stratosphere. There is an excellent correlation ($r = 0.86$) between the two curves. The trend values for total tropospheric chlorine in Fig. 1 are $-5.8 \pm 0.1\%$/decade for 2004–2010 and $-4.0 \pm 0.1\%$/decade for 2010–2017 in excellent agreement with ACE values. The change in slope at 2010 is due to the rapid initial decline of species with shorter atmospheric lifetimes such as methyl chloroform (https://www.esrl.noaa.gov/gmd/odgi/).

The total column density trend values for 2000–2009 from 16 NDACC sites show considerable variability, but the simple average over all sites is -8%/decade [3]. A more recent NDACC value for the total Cl_y column trend (dominated by HCl) for 1997–2016 is reported as $-5.0 \pm 1.5\%$/decade [19], in agreement with the ACE trend. ACE HCl stratospheric trend values are therefore in agreement with other measurements and are correlated with tropospheric total chlorine abundances.

The conclusion from the updated ACE HCl trends is that the Montreal Protocol has been and continues to be successful. Upper stratospheric HCl VMR profile values are declining at an average rate of $-4.8 \pm 0.2\%$/decade for 2004–2017.

Acknowledgements

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2018.05.027.

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