JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 111, D22312, doi:10.1029/2006JD007073, 2006

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A global inventory of stratospheric chlorine in 2004

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Received 12 January 2006; revised 21 July 2006; accepted 7 August 2006; published 30 November 2006.

[1] Total chlorine (Cl_{TOT}) in the stratosphere has been determined using the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) measurements of HCl, $ClONO_2$, CH_3Cl, CCl_4, CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $CHClF_2$ (HCFC-22), CCl_2FCClF_2 (CFC-113), CH_3CClF_2 (HCFC-142b), COClF, and ClO supplemented by data from several other sources, including both measurements and models. Separate chlorine inventories were carried out in five latitude zones (60°–82°N, 30°–60°N, 30°S–30°N, 30°–60°S, and 60°–82°S), averaging the period of February 2004 to January 2005 inclusive, when possible, to deal with seasonal variations. The effect of diurnal variation was avoided by only using measurements taken at local sunset. Mean stratospheric Cl_{TOT} values of 3.65 ppbv were determined for both the northern and southern midlatitudes (with an estimated 1σ accuracy of ±0.13 ppbv and a precision of ±0.09 ppbv), accompanied by a slightly lower value in the tropics and slightly higher values at high latitudes. Stratospheric Cl_{TOT} profiles in all five latitude zones are nearly linear with a slight positive slope in ppbv/km. Both the observed slopes and pattern of latitudinal variation can be interpreted as evidence of the beginning of a decline in global stratospheric chlorine, which is qualitatively consistent with the mean stratospheric circulation pattern and time lag necessary for transport.

Citation: Nassar, R., et al. (2006), A global inventory of stratospheric chlorine in 2004, *J. Geophys. Res.*, *111*, D22312, doi:10.1029/2006JD007073.

1. Introduction

[2] The decrease in stratospheric ozone since the mid-1970s is largely due to the anthropogenic emission of organic chlorine and bromine compounds. Many of the organic chlorine compounds including chlorofluorcarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons and others are chemically stable in the troposphere where they behave as greenhouse gases, contributing to global climate change. Brewer-Dobson circulation transports these compounds to the tropical stratosphere and subsequently distributes them to the middle and high latitudes. In the stratosphere, they are broken down by UV photolysis or reaction with radicals such as $O(^1D)$ and OH, ultimately resulting in the formation of active chlorine species such as chlorine monoxide (ClO). Active chlorine species participate in catalytic cycles destroying stratospheric ozone [*Molina and Rowland*, 1974; *Stolarski and Cicerone*, 1974; *Farman et al.*, 1985; *Molina and Molina*, 1987], until they undergo conversion to reservoir species such as chlorine nitrate ($ClONO_2$) or hydrogen chloride (HCl). A detailed review of these processes is given by *Solomon* [1999].

[3] Prior to the widespread use of ozone depleting gases only a few decades ago, total chlorine (Cl_{TOT}) in the stratosphere had a volume mixing ratio (VMR) equal to the natural background level of about 0.6 ppbv (parts per billion by volume), which is primarily due to CH_3Cl. Measurements indicate that mean stratospheric Cl_{TOT} reached 3.70 ± 0.20 ppbv around 1997 [*Sen et al.*, 1999] and has recently begun a slow decline [*Anderson et al.*, 2000; *Mahieu et al.*, 2004] as a result of the emission restrictions required by the Montreal Protocol and its amendments, but the exact date and the VMR of the maximum in stratospheric Cl_{TOT} are somewhat ill

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0148-0227/06/2006JD007073$09.00

defined [*Waugh et al.*, 2001]. Most modeling studies predict that global stratospheric ozone should fully recover shortly after stratospheric chlorine declines to 2.0 ppbv [*World Meteorological Organization* (*WMO*), 1999; *Prather and Watson*, 1990; *Prather et al.*, 1996], but predictions of the date that chlorine will reach this level range from 2040 to 2070 [*Engel et al.*, 2002]. Furthermore, increases in stratospheric water vapor and stratospheric cooling associated with climate change both enhance polar stratospheric cloud (PSC) formation, which makes predicting the exact date of ozone recovery even more difficult [*Austin et al.*, 1992, 2002; *Shindell et al.*, 1998; *Shindell and Grewe*, 2002].

[4] Until there is more certainty regarding the recovery of global stratospheric ozone, it will remain necessary to monitor ozone levels and make continual measurements of the species that contribute to stratospheric chlorine. There are currently a variety of different instruments that can measure chlorinated species in the atmosphere from the ground, aircraft, balloons or space-based platforms. *Zander et al.* [1992, 1996] determined mean stratospheric Cl_{TOT} values of 2.58 ± 0.10 ppbv in 1985 and 3.53 ± 0.10 ppbv in 1994 for northern midlatitudes, primarily using measurements from the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument which flew four times on the NASA Space Shuttle (1985, 1992, 1993, and 1994). Similarly, a value of 3.70 ± 0.20 ppbv was determined based on measurements by the balloon-borne MkIV interferometer during the Arctic summer of 1997 [*Sen et al.*, 1999]. Both of these instruments are high-resolution infrared Fourier transform spectrometers, which are capable of measuring a large number of chlorine-containing species. The determination of total chlorine from their measurements was made by summing the chlorine contributions from all significant individual species averaged over a range of stratospheric altitudes. During the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE) campaign, air samples were collected from a NASA ER-2 aircraft between 10 and 21 km altitude in the 2000 Arctic winter [*Schauffler et al.*, 2003]. Laboratory analysis of the air samples gave individual VMR profiles of 15 chlorine-containing species and a similar approach of summing profiles yielded a Cl_{TOT} value of about 3.6 ppbv.

[5] The Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) has produced a record of HCl at 55 km from 1991 to 2005 [*Russell et al.*, 1996b; *Anderson et al.*, 2000], but has now been retired. According to the HALOE method, the ratio of HCl to total inorganic chlorine (Cl_y) at 55 km altitude is 0.93 at the equator and 0.95 at high latitudes, so measurements of HCl at a given latitude are divided by this ratio to obtain Cl_y, which has often been used as an approximation for Cl_{TOT}. *Russell et al.* [1996b] state that HCl/Cl_{TOT} is less than 1 mostly due to $CHClF_2$ (HCFC-22), one of the few organic chlorine species known to exist in the upper stratosphere in significant amounts at that time [*Weisenstein et al.*, 1992; *Rummukainen*, 1996; *Coheur et al.*, 2003]. HALOE determined Cl_y values of 3.3 ± 0.33 ppbv in June 1995 [*Russell et al.*, 1996b] and over 3.5 ppbv in 2000 [*Anderson et al.*, 2000] which indicate that HALOE Cl_y are somewhat lower than Cl_{TOT} determined by ATMOS or MkIV at a similar time.

[6] Although ground-based measurements provide less global coverage than satellites, a large number of sites make measurements of chlorine-containing species, which together make an important contribution to assessing chlorine levels in the atmosphere and their temporal evolution. Some of the most important sets of ground-based measurements come from the Atmospheric Lifetime Experiment, the Global Atmospheric Gases Experiment and the Advanced Global Atmospheric Gases Experiment (ALE/GAGE/AGAGE) [*Prinn et al.*, 2000], the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) measurements [*Montzka et al.*, 1996, 1999] and the Network for the Detection of Stratospheric Change (NDSC) [*Rinsland et al.*, 2003], which has recently been renamed the Network for the Detection of Atmospheric Composition Change (NDACC). The in situ ALE/GAGE/AGAGE and NOAA/CMDL measurements both indicate declining levels of tropospheric chlorine, largely driven by declines in CH_3CCl_3 and CCl_4 [*Prinn et al.*, 2000]. The NDSC solar absorption measurements are used to infer total column amounts of a number of species, including HCl and $ClONO_2$. These measurements indicate that Cl_y in the lower stratosphere has been decreasing very slowly ($-0.7 \pm 0.3\%$/yr, 1σ) since it peaked in late 1996 [*Mahieu et al.*, 2004].

[7] Comparisons between measurement sets and industry-reported levels of source gas production and emission with modeling studies of chemistry and transport helps to obtain a complete understanding of the distribution and composition of chlorine species in the stratosphere, which aids in making accurate predictions about ozone recovery. In the present work, stratospheric Cl_{TOT} is calculated by taking the sum of the chlorine contribution from VMR profiles of individual chlorine-containing species measured by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS), supplemented by profiles of species measured by other instruments or, in some cases, calculated profiles. Daytime Cl_{TOT} profiles are determined separately in five latitude zones (60°–82°N, 30°–60°N, 30°S–30°N, 30°–60°S and 60°–82°S) during the period of February 2004 to January 2005 inclusive. Cl_{TOT} profiles are then averaged over a range of stratospheric altitudes to obtain a value for mean stratospheric Cl_{TOT}, as by *Zander et al.* [1992, 1996]. The results of this global inventory of stratospheric chlorine can be used for comparing with other measurements as well as reported emission inventories, for assessing the effectiveness of the Montreal Protocol and for incorporating into models to predict the eventual date of recovery of the ozone layer.

2. Definitions of Total Stratospheric Chlorine

[8] The method for determination of stratospheric Cl_{TOT} in this work is similar to the method of *Zander et al.* [1992, 1996] based on the sum of all significant chlorine-containing species in the stratosphere. In the present work, total organic chlorine CCl_y, total inorganic chlorine Cl_y, and

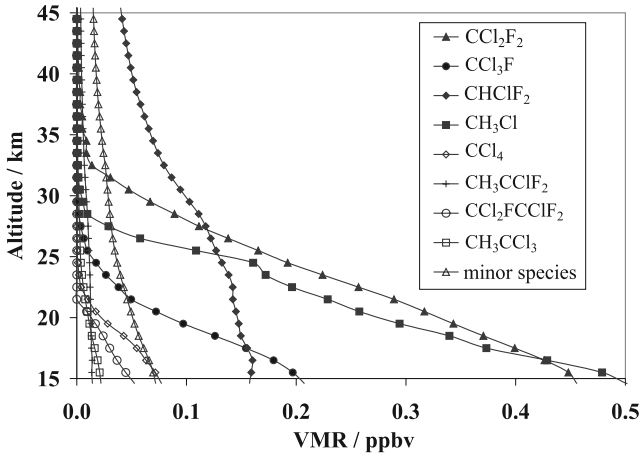

Figure 1. Average organic chlorine profiles for the southern midlatitudes (30°–60°S) in 2004.

total chlorine Cl_{TOT} as a function of altitude were determined using the following summations:

$$CCl_y = 4[CCl_4] + 3[CCl_3F] + 2[CCl_2F_2] + [CH_3Cl] + [CHClF_2] + 3[CCl_2FCClF_2] + [CH_3CClF_2] + 3[CH_3CCl_3] + \textit{minor species} \quad (1)$$

$$Cl_y = [HCl] + [ClONO_2] + [COClF] + [ClO] + 2[ClOOCl] + [HOCl] + 2[COCl_2] \quad (2)$$

$$Cl_{TOT} = CCl_y + Cl_y \quad (3)$$

CCl_y includes the source gases which comprise most of the chlorine in the troposphere and lower stratosphere. Figure 1 shows an example of the component profiles of CCl_y at southern midlatitudes. Cl_y consists of reservoir species and short-lived species, which dominate in the middle and upper stratosphere. Most major species in this inventory were measured by the ACE-FTS, although species shown above in italics are primarily based on data from other sources including both measurements and models. The detailed methods for obtaining profiles of all species are described in the following sections.

3. ACE-FTS Measurements of Chlorine-Containing Species

[9] The Atmospheric Chemistry Experiment (ACE), also known as SCISAT-1 is a Canadian satellite that was launched by NASA on 12 August 2003. The ACE instruments make solar occultation measurements during up to 15 sunrises and 15 sunsets per day from a 74° inclination circular orbit at an altitude of ~650 km. The ACE orbit was chosen to optimize occultation opportunities over midlatitude and polar regions, with the primary objective of investigating processes related to ozone depletion during the polar springtime. The primary instrument on SCISAT-1 is the ACE-FTS, a high-resolution Fourier transform spectrometer operating in the 750–4400 cm^{-1} range. During each occultation, the ACE-FTS can measure spectra at a series of tangent heights, which are subsequently inverted to give profiles of temperature, pressure, and molecular VMRs with a vertical resolution of 3–4 km. These are provided on both the measurement grid and on a 1-km grid. The inversion process first requires the retrieval of temperature and pressure by fitting measured CO_2 spectral lines to calculated ones from a forward model in multiple narrow spectral regions, referred to as microwindows. After retrieving temperature and pressure, VMR profiles for numerous molecules are determined in a similar manner, with the temperature and pressure fixed. An overview of the ACE mission is given by *Bernath et al.* [2005] and a description of ACE-FTS retrievals is given by *Boone et al.* [2005]. The altitude ranges of the microwindows used for all ACE-FTS retrieved chlorine species and the acceptable altitude range used to determine the ACE-FTS average profiles are shown in Table 1. In many cases, the spectral contribution from known interfering species including O_3, CH_4, H_2O, HDO and others were accounted for during the retrieval process. ACE-FTS retrieved VMR profiles are not constrained by the a priori; however, above the retrieval range, the a priori profile is scaled based on the values retrieved at the two highest points [*Boone et al.*, 2005]. When necessary, a more reliable method was found for extending individual mean VMR profiles above the retrieval range, as described later.

[10] Since profiles of $ClONO_2$ and ClO exhibit diurnal variation, day and night profiles should not be averaged together, especially if these species are not necessarily measured at coincident locations and times. Using the longitude (λ, ranging from −180° to +180°) and universal time (UT) in hours for the reference tangent point of each occultation, local times (LT) were determined using:

$$LT = UT + (24/360)\lambda \quad (4)$$

The above equation gives the LT relative to the stated UT calendar day, so 24 hours were added or subtracted accordingly (to values less than zero or greater than 24) to determine the standard local time (SLT) relative to the diurnal cycle. It should be noted that although all ACE occultations are labeled as sunrise or sunset as seen from orbit, outside of the tropics, this label is not necessarily indicative of whether it is a sunrise or sunset at the measurement location; however, since ACE measurements only occur at twilight, measurements before or after local noon are sunrises or sunsets, respectively. For this chlorine inventory, only measurements taken at local sunset have been used, giving the daytime composition of the stratosphere and thus facilitating direct comparison to the ATMOS chlorine budgets [*Zander et al.*, 1992, 1996].

[11] Table 2 lists the number of ACE-FTS profiles averaged for each latitude zone; however, profiles with an unphysical shape (such as noise spikes or oscillations) were discarded as outliers, so the actual number for a given species is typically lower. In addition, some profiles are also missing one or more points at the upper and/or lower end of the altitude ranges in Table 1, as a result of variation in the tangent heights of ACE-FTS measurements prior to interpolation to the standard grid [*Boone et al.*, 2005]. Approximately the first year of ACE-FTS measurements (February 2004 to January 2005 inclusive) was averaged to determine

Table 1. Microwindows for Chlorine Species Retrieved From ACE-FTS Measurements

Species	Retrieved Altitude Range for Average Profile, km	Microwindow		
		Center, cm^{-1}	Width, cm^{-1}	Range, km
HCl	8.5–56.5	2701.26	0.30	8.5–35.5
HCl	8.5–56.5	2703.03	0.30	35.5–46.5
HCl	8.5–56.5	2727.77	0.40	8.5–44.5
HCl	8.5–56.5	2751.97	0.30	47.5–54.5
HCl	8.5–56.5	2775.75	0.30	40.5–56.5
HCl	8.5–56.5	2798.95	0.35	51.5–56.5
HCl	8.5–56.5	2819.48	0.30	20.5–53.5
HCl	8.5–56.5	2821.47	0.30	18.5–56.5
HCl	8.5–56.5	2841.63	0.40	20.5–49.5
HCl	8.5–56.5	2843.67	0.30	15.5–56.5
HCl	8.5–56.5	2865.16	0.26	38.5–56.5
HCl	8.5–56.5	2906.30	0.30	45.5–56.5
HCl	8.5–56.5	2923.57	0.50	20.5–47.5
HCl	8.5–56.5	2923.73	0.30	44.5–49.5
HCl	8.5–56.5	2925.90	0.30	17.5–56.5
HCl	8.5–56.5	2942.67	0.40	15.5–53.5
HCl	8.5–56.5	2944.95	0.30	10.5–56.5
HCl	8.5–56.5	2961.00	0.40	25.5–47.5
HCl	8.5–56.5	2963.11	0.50	8.5–56.5
HCl	8.5–56.5	2981.00	0.50	40.5–56.5
HCl	8.5–56.5	2995.88	0.30	45.5–50.5
HCl	8.5–56.5	2998.14	0.30	52.5–56.5
$ClONO_2$	12.5–34.5	780.15	0.60	12.5–19.5
$ClONO_2$	12.5–34.5	1202.86	0.50	12.5–17.5
$ClONO_2$	12.5–34.5	1292.60	1.60	18.5–34.5
$ClONO_2$	12.5–34.5	1728.28	0.50	12.5–17.5
COClF[a]	17/19–30[b]	1860.35	0.70	17/19–30[b]
COClF[a]	17/19–30[b]	1862.55	1.30	17/19–30[b]
COClF[a]	17/19–30[b]	1864.30	0.60	17/19–30[b]
COClF[a]	17/19–30[b]	1865.45	1.10	17/19–30[b]
COClF[a]	17/19–30[b]	1866.80	0.40	17/19–30[b]
COClF[a]	17/19–30[b]	1868.80	0.60	17/19–30[b]
COClF[a]	17/19–30[b]	1870.575	0.35	17/19–30[b]
COClF[a]	17/19–30[b]	1874.95	0.90	17/19–30[b]
ClO[c]	12.5–24.5	823.475	5.00	11.5–29.5
ClO[c]	12.5–24.5	828.475	5.00	11.5–29.5
ClO[c]	12.5–24.5	833.475	5.00	11.5–29.5
ClO[c]	12.5–24.5	838.475	5.00	11.5–29.5
ClO[c]	12.5–24.5	843.475	5.00	11.5–29.5
CH_3Cl	9.5–24.5	2966.50	0.40	9.5–24.5
CH_3Cl	9.5–24.5	2966.90	0.40	9.5–24.5
CH_3Cl	9.5–24.5	2967.30	0.70	9.5–24.5
CCl_4	8.5–22.5	799.85	11.00	8.5–22.5
CCl_3F (CFC-11)	5.5–21.5	842.50	25.00	5.5–21.5
CCl_2F_2 (CFC-12)	6.5–27.5	922.00	4.00	6.5–27.5
CCl_2F_2 (CFC-12)	6.5–27.5	1161.00	1.20	12.5–24.5
$CHClF_2$ (HCFC-22)	5.5–24.5	809.30	1.10	5.5–14.5
$CHClF_2$ (HCFC-22)	5.5–24.5	820.85	0.70	5.5–11.5
$CHClF_2$ (HCFC-22)	5.5–24.5	829.03	0.50	5.5–24.5
CCl_2FClF_2 (CFC-113)	7.5–16.5	817.50	25.00	7.5–16.5
CH_3CClF_2 (HCFC-142b)	8.5–18.5	1134.50	4.00	8.5–18.5
CH_3CClF_2 (HCFC-142b)	8.5–18.5	1193.60	3.60	8.5–18.5

[a]Special circumstances for the retrieval of this species are outlined in the text.
[b]The lower altitude limit for COClF is 19 km for tropical occultations and 17 km for midlatitudes.
[c]The ACE-FTS ClO retrieval was only used for southern high latitudes over a reduced altitude range.

values for 2004, while attempting to account for seasonal variations; however, the limited coverage provided by the ACE orbit often results in periods of more than a month where no measurements are made for some latitude zones.

3.1. Organic Species: CH_3Cl, CCl_3F, CCl_2F_2, CCl_2FClF_2, CH_3CClF_2, CCl_4, and $CHClF_2$

[12] Profiles of methyl chloride (CH_3Cl), CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and HCFC-22 ($CHClF_2$) were retrieved using the ACE-FTS version 2.2 retrieval algorithm

Table 2. Number of Profiles Averaged in Each Latitude Zone for the Period of February 2004 to January 2005 Inclusive

	Maximum ACE-FTS Profiles	Odin SMR ClO Profiles
Northern high latitudes (60°–82°N)	63	72
Northern midlatitudes (30°–60°N)	131	58
Tropics (30°S–30°N)	170	157
Southern midlatitudes (30°–60°S)	180	22
Southern high latitudes (60°–82°S)	135	38

which is described by *Boone et al.* [2005]. CFC-113 (CCl_2FClF_2), HCFC-142b (CH_3CClF_2) and carbon tetrachloride (CCl_4) were specially retrieved for this work. The ACE-FTS retrievals of CCl_2FClF_2 and CH_3CClF_2 used in this work are the first retrievals of these two species from spaceborne measurements [*Dufour et al.*, 2005].

[13] In the troposphere and lower stratosphere CCl_y species dominate Cl_{TOT}, with the largest contributions from CH_3Cl (the only significant natural source of organic chlorine), CCl_2F_2, and CCl_3F. From the surface up to the middle stratosphere, CCl_2F_2 with two chlorine atoms, makes the largest contribution to Cl_{TOT} of all CCl_y species. $CHClF_2$ (HCFC-22) is only the fourth largest organic chlorine species in the upper troposphere, but in the middle and upper stratosphere it is long-lived and is the dominant CCl_y species.

[14] The ATMOS and MkIV chlorine budgets [*Zander et al.*, 1992, 1996; *Sen et al.*, 1999] did not include $CHClF_2$ in the upper stratosphere because its VMR was below their detection limits. However, *Weisenstein et al.* [1992] have shown that it exists in the upper stratosphere in significant quantities. Their modeled value in the upper stratosphere was based on the surface value in 1985, but in a more recent work by *Coheur et al.* [2003], a profile of $CHClF_2$ is determined with the global three dimensional chemical transport model SCTM-1 [*Rummukainen*, 1996]. The SCTM-1 model output for 1 January 2000, 00:00 UT, at 45°N, 90°E is shown in Figure 2. This profile was scaled by a factor of 1.062 based on a comparison of ACE-FTS average midlatitude measured value of $CHClF_2$ in 2004 and their modeled value from 2000 at 19.5 km. The profile was very similar to (yet much smoother than) the retrieved northern and southern midlatitude profiles over the 17.5–24.5 km range. The scaled profile was grafted onto both midlatitude profiles above the range of ACE-FTS retrievals (beginning at 25.5 km). For northern high latitudes, the scaled midlatitude profile was shifted down by 5 km before grafting it to the ACE-FTS measurements. The need for this shift results from descent in the winter Arctic vortex [*Nassar et al.*, 2005] contributing to the annual average profile for northern high latitudes. The southern high-latitude profile showed much more descent than the north, so it was necessary to shift the midlatitude profile down by 10 km to coincide with the ACE-FTS measurements. Similarly, an upward shift by 10 km was required to coincide with the ACE-FTS tropical measurements. These ACE-FTS profiles and the scaled and shifted SCTM-1 profiles are shown in Figure 2. The application of shifts to the $CHClF_2$ profiles depending on their latitude is qualitatively consistent with the latitudinal distribution of $CHClF_2$ in 1985 modeled by *Weisenstein et al.* [1992], although their model results showed a more symmetrical relationship between the Northern and Southern Hemispheres. While some of the hemispheric asymmetry in the measured high-latitude profiles is likely real, much of it can be attributed to the lack of complete seasonal coverage at high latitudes due to the ACE orbit and the exclusion of local sunrises.

3.2. Inorganic Species: HCl, $ClONO_2$, COClF, and ClO

[15] HCl exhibits a nearly constant increase with altitude throughout the stratosphere. It is the dominant chlorine species in the middle and upper stratosphere, representing about 96–98% of total chlorine at 55 km. The profile of $ClONO_2$ approximates a Gaussian distribution with a peak ranging from 23.5 km at southern high latitudes to 28.5 km in the tropics. At its peak, $ClONO_2$ typically accounts for 25% of the chlorine budget. Profiles of HCl and $ClONO_2$ were taken from ACE-FTS version 2.2 data.

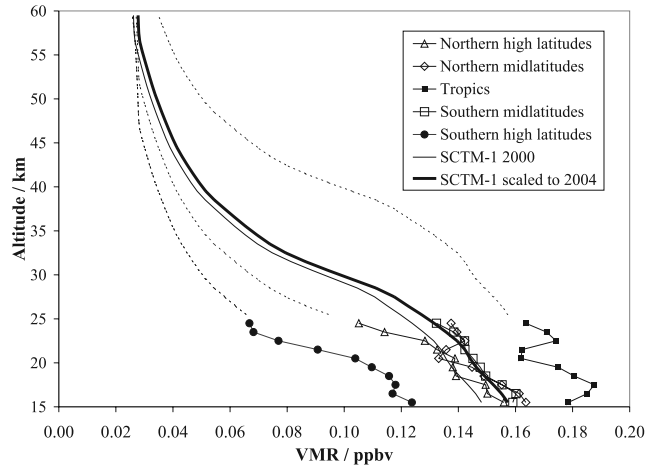

Figure 2. Profiles of $CHClF_2$ (HCFC-22) in the stratosphere: the SCTM-1 modeled profile for 45°N in 2000, the SCTM-1 profile scaled for 2004, and ACE-FTS measured values in the northern high latitudes, northern midlatitudes, tropics, southern midlatitudes, and southern high latitudes. The scaled and shifted SCTM-1 profiles for extending the ACE-FTS measurements to higher altitudes are shown as dotted lines.

[16] COClF results from the breakdown of CCl_3F, so it has a peak in the lower to middle stratosphere [*Kaye et al.*, 1991]. Retrievals of COClF involving averaged ACE-FTS spectra were carried out by *Rinsland et al.* [2006]; however, a routine operational retrieval has not been developed at the time of this writing. The tropical and midlatitude COClF profiles in this work were based on the *Rinsland et al.* [2006] retrieval using ACE-FTS measurements. Their dates and latitude zones were similar but did not exactly match the zones used for other species in this work. In spite of this discrepancy, a tropical COClF profile was included based on the 20°S–20°N zone and both the northern and southern midlatitude profiles were based on the 30°–50°N zone, using occultations spanning 2004 to 2005. The signal-to-noise ratio for COClF is low and since the peak VMR value decreases with latitude, a high-latitude profile for COClF was not retrieved by Rinsland et al. (unpublished manuscript, 2006), so high-latitude profiles were based on the model results of *Kaye et al.* [1991] scaled to 2004 based on the change in stratospheric abundance of CCl_3F. COClF only makes a small contribution to Cl_{TOT}, with a peak in the profile of ~0.10 ppbv in the tropics (less than 3% of Cl_{TOT} at that altitude), ~0.05 ppbv at midlatitudes and ~0.02 ppbv at high latitudes, so its accuracy has a small impact on Cl_{TOT}, but in the future, it would be desirable to carry out a routine operational ACE-FTS COClF retrieval, as was done for other species.

[17] ClO has a single peak in the upper stratosphere for most seasons and latitudes but is enhanced in the winter

polar vortices causing a second highly variable peak in the lower stratosphere. In the upper stratosphere, it can comprise close to 20% of Cl_{TOT}. Since the signal-to-noise ratio for ClO in ACE-FTS spectra is usually very low, most of the ClO measurements used in this work are from the submillimeter receiver (SMR) [*Urban et al.*, 2005] on the Odin satellite [*Murtagh et al.*, 2002], just as *Zander et al.* [1996] used ClO measurements from the Millimeter-wave Atmospheric Sounder (MAS) [*Hartmann et al.*, 1996; *Aellig et al.*, 1996] for the ATMOS chlorine budget. Version 1.2 SMR ClO profiles were obtained for the period of February 2004 to January 2005 inclusive, to match the temporal range of the ACE-FTS measurements. From the SMR data set, only measurements with a solar zenith angle between 88° and 92° and made during local sunset were chosen. The latitudes for the SMR data were selected to match the ACE-FTS mean latitudes in the five latitude zones, 71 ± 2° for high latitudes, 45 ± 1° for midlatitudes and 15 ± 2° for the tropics (assuming symmetry about the equator). Since all ACE-FTS southern high latitude daytime measurements occurred during the Southern Hemisphere winter months, SMR ClO profiles were selected for this date range rather than using data with full seasonal coverage.

[18] The SMR profiles were interpolated to the ACE-FTS 1-km grid using a cubic spline interpolation, then averaged in each latitude zone. The number of SMR profiles included in each average is shown in Table 2. Profiles with unphysical shapes were discarded as outliers, as was done with the ACE-FTS data. In a few cases, an unphysical increase in SMR ClO profiles above 51.5 km was manually removed, but this is above the range of altitude considered in the calculation of stratospheric Cl_{TOT}. This lower mesospheric increase has recently been identified as an artifact in version 1.2 of the SMR data and has apparently been corrected in SMR version 2.0 data (D. P. Murtagh, private communication, 2006).

[19] At southern high latitudes in the 12.5–24.5 km range, strong ClO enhancement was measured by the ACE-FTS. Since lower stratospheric ClO enhancement is extremely variable, these measurements have been used so that the ClO profiles are properly matched to those of other species. The ACE-FTS ClO retrievals are somewhat noisy but averaging 119 southern high-latitude profiles produced a smooth result. Weak ClO enhancement is observed for northern high latitudes, but since the signal-to-noise ratio is still low, the SMR profiles were used rather than ACE-FTS measurements in this altitude range.

4. Chlorine-Containing Species Not Measured by the ACE-FTS

[20] Some species that contribute to stratospheric chlorine were not measured by the ACE-FTS, so they have been included in this inventory based on measurements by other instruments, model values or estimates as described in the following subsections.

4.1. Organic Species: CH_3CCl_3 and Minor CFCs, HCFCs, and Halons

[21] CH_3CCl_3 and a number of minor organic chlorine species make a small contribution to Cl_{TOT} in the stratosphere. Measurements from the SAGE III Ozone Loss and Validation Experiment (SOLVE) campaign [*Schauffler et al.*, 2003] were used to estimate profiles of CH_3CCl_3, $CClF_2CClF_2$ (CFC-114), CCl_2FCF_3 (CFC-114a), CCl_2FCF_3 (CFC-115), CH_3CCl_2F (HCFC-141b), and $CBrClF_2$ (Halon-1211). The SOLVE measurements were made from whole air samples collected during an aircraft campaign from January to March 2000, between 52° and 88°N latitude over a range of 10–21 km altitude. Empirical equations for the SOLVE VMR profiles of the chlorine contribution from these species were provided on an N_2O scale [*Schauffler et al.*, 2003]. These were converted to an altitude scale using ACE-FTS retrieved mean N_2O profiles from each of the five latitude zones then the profiles of each chlorine-containing species were multiplied by a scale factor to account for the changes in abundance which occurred between 2000 and 2004. Scaling was carried out using the ratio between the 2004 to 2000 surface values in Table 1–16 of *WMO* [2003]. The profiles should theoretically scale without significant changes to their shapes since their stratospheric VMRs were increasing or decreasing at an approximately constant rate in 2000 which was at least 4 years before (or after) the year of maximum VMR for any of these species.

[22] The SOLVE profiles are only valid over the 50–315 ppbv N_2O range [*Schauffler et al.*, 2003], where 50 ppbv corresponds to an altitude of ~23.5 km at southern high latitudes and ~39.5 km in the tropics. CFC-114a and Halon-1211 were negligible above this altitude. The HCFC-141b and CFC-115 profiles appeared satisfactory above this altitude range, each with only a small contribution in the upper stratosphere. Since CH_3CCl_3 is expected to completely break down in the stratosphere [*Weisenstein et al.*, 1992], the CH_3CCl_3 profiles were manually extrapolated to smoothly reach zero VMR above the measured altitude range.

[23] At 17.5 km in altitude, CH_3CCl_3 contributes between 0.015 ppbv chlorine at southern high latitudes and 0.08 ppbv chlorine in the tropics (0.4–2.2% respectively). The combined total chlorine contribution from the other species at 17.5 km is 0.04 ppbv at southern high latitude and 0.08 ppbv in the tropics and decreases to just over 0.01 ppbv at the top of the stratosphere, with the largest contributions from the minor species due to CFC-114 and HCFC-141b. When all of these species are combined, their contribution to Cl_{TOT} is significant, but errors of 20–30% on any individual species would make a very small change to Cl_{TOT}; therefore, although an accurate estimate of profiles for each of these minor species was sought, it is not critical to main objective of this paper.

4.2. Inorganic Species: HOCl, $COCl_2$, and ClOOCl

[24] Efforts to retrieve HOCl from ACE-FTS spectra are in progress; however, *von Clarmann et al.* [2006] have retrieved HOCl from MIPAS spectra, so these profiles are the basis for the HOCl profiles in this chorine inventory. Since their work indicates that HOCl exhibits a small diurnal variation, and the selected ACE-FTS measurements are at sunset, a day-night average of their profiles has been used which was manually extrapolated to 54 km to obtain a smooth transition to zero, since the published profiles abruptly end at 50 km. The work of *von Clarmann et al.* [2006] indicates latitudinal variation in HOCl with the

altitude of the maximum 2.2 ± 0.3 km lower for the 45°N–45°S latitude zone than for the more poleward latitudes of 45°–90° in each hemisphere. This is a 2.2 km shift for a change in mean latitude from 22.5° to 67.5°, or 0.0488 km per degree. To account for latitudinal variability in both the altitude and value of the maximum VMR, scale factors and shifts were applied to the mean (day-night) 30°N profile. The resulting HOCl profiles make a maximum contribution to Cl_{TOT} of 0.192 ppbv (5.3%) at 35.5 km for the tropics, 0.167 ppbv (4.6%) at 36.5 km for midlatitudes, and 0.098 ppbv (2.6%) at 37.5 km for high latitudes.

[25] Efforts to retrieve phosgene ($COCl_2$) from ACE-FTS spectra have recently begun, but no ACE-FTS $COCl_2$ product was available at the time of this writing. It is very difficult to retrieve because its spectral lines are buried in the stronger spectrum of CCl_3F. $COCl_2$ was not included in the chlorine budgets based on ATMOS [*Zander et al.*, 1992, 1996] or MkIV measurements [*Sen et al.*, 1999]; however, it has since been successfully retrieved from MkIV balloon-borne infrared solar occultation spectra by *Toon et al.* [2001]. A line of best fit was drawn through the MkIV points in the 6–30 km range measured between September 1992 and March 2000. The $COCl_2$ profile based on these points was included directly (without scaling or shifting) in each of the five latitude zones since no clear latitudinal shift can be determined from the data. Although some change to the shape of the $COCl_2$ profile would be expected due the decrease in CCl_3F emission which has occurred since about 1994 [*WMO*, 2003], this can be ignored since $COCl_2$ makes only a very minor contribution to total stratospheric chlorine (a maximum of ~0.065 ppbv Cl at 20 km).

[26] The ClO dimer (ClOOCl) only occurs in significant quantities in the polar vortices, where it exists in equilibrium with ClO. Although no known remote measurements of ClOOCl were found, *Stimpfle et al.* [2004] have made in situ measurements in the Arctic vortex from a NASA ER-2 aircraft during the SOLVE/THESEO-2000 campaign. More recently, *Von Hobe et al.* [2005] made in situ aircraft measurements during the SOLVE II/VINTERSOL-EUPLEX and ENVISAT validation campaigns using the HALOX instrument. The measurements by *Stimpfle et al.* [2004] confirm the basic mechanism for loss and production of ClOOCl (equations (5)–(7)) but indicate some uncertainty in the rate constants.

$$\mathrm{ClO} + \mathrm{ClO} + \mathrm{M} \xrightarrow{k^{prod}} \mathrm{ClOOCl} + \mathrm{M} \tag{5}$$

$$\mathrm{ClOOCl} \xrightarrow{j} \mathrm{ClO} + \mathrm{ClO} \tag{6}$$

$$\mathrm{ClOOCl} + \mathrm{M} \xrightarrow{k^{loss}} \mathrm{ClO} + \mathrm{ClO} + \mathrm{M} \tag{7}$$

Using these reactions and solving the rate law, a relationship for the expected ClOOCl profile can be determined from the profile of ClO and the appropriate values of the rate constants for ClOOCl production (k^{prod}), loss by thermal decomposition (k^{loss}) and loss by photolytic decomposition (j).

$$\frac{d[\mathrm{ClOOCl}]}{dt} = k^{prod}[\mathrm{ClO}]^2[\mathrm{M}] - j[\mathrm{ClOOCl}] - k^{loss}[\mathrm{M}][\mathrm{ClOOCl}] = 0 \tag{8}$$

$$k^{prod}[\mathrm{ClO}]^2[\mathrm{M}] = \left(j + k^{loss}[\mathrm{M}]\right)[\mathrm{ClOOCl}] \tag{9}$$

$$K_{eq} = \frac{[\mathrm{ClOOCl}]}{[\mathrm{ClO}]^2} = \frac{k^{prod}[\mathrm{M}]}{j + k^{loss}[\mathrm{M}]} \tag{10}$$

Stimpfle et al. [2004] recommend combinations of the above three rate constants that give results consistent with their observations. The value of the photolysis rate constant (j) used here, is the value determined by *Stimpfle et al.* [2004] based on cross sections determined by *Burkholder et al.* [1990] shown by *Stimpfle et al.* [2004] as a function of solar zenith angle (SZA). Since all ACE-FTS measurements occur at a SZA of 90°, a value of $j = 4.4 \times 10^{-4}\ s^{-1}$ at a SZA = 90° was used in this work. k^{loss} is determined from the empirical equation $k^{loss}(T) = 9.81 \times 10^{-7} \exp(-7980/T)$ molecules^{-1} cm^3 s^{-1} from *Nickolaisen et al.* [1994] and $k^{prod}(T) = 1.49 \times 10^{-32}\ (T/300)^{-4.50}$ molecules^{-2} cm^6 s^{-1} from *Bloss et al.* [2001]. (The uncertainties for both rate constants have been ignored in this approximation of the ClOOCl concentration.)

[27] Using the above rate constants, the ratio $k^{prod}[M]/(j + k^{loss}[M])$ was then calculated using ACE-FTS retrieved values of temperature and density for each high-latitude profile. Since ACE-FTS individual ClO profiles tend to be noisy, the ratio of constants for each profile was applied to the averaged ClO profile to calculate ClOOCl profiles. From the individual ClOOCl profiles, an average profile is calculated over the altitude range of 12.5–26.5 km where ClO enhancement is observed at high latitudes in each hemisphere.

5. Results

[28] Mean profiles for each latitude zone of all chlorine containing species in section 4 are available as auxiliary material.[1] The chlorine contribution based on species measured by the ACE-FTS varies with altitude, although for the northern midlatitudes at 17.5 km where CCl_y dominates, 87% of the chlorine comes from species measured by ACE. The percentage gradually decreases to 80% between 37.5 and 40.5 km, then gradually increases up to almost 98% above 54.5 km, where nearly all chlorine is contained in HCl. Figure 3 shows profiles of CCl_y, HCl, $ClONO_2$, ClO, and a combined profile for the chlorine contribution from HOCl, $COCl_2$, COClF and ClOOCl, between 15 and 55 km altitude. It indicates that total chlorine is nearly constant throughout this altitude range. *Zander et al.* [1996] determined mean Cl_{TOT} by averaging all points in the 16.4–50.2 km altitude range which was intended to span the

[1]Auxiliary materials are available at ftp://ftp.agu.org/apend/jd/2006jd007073.

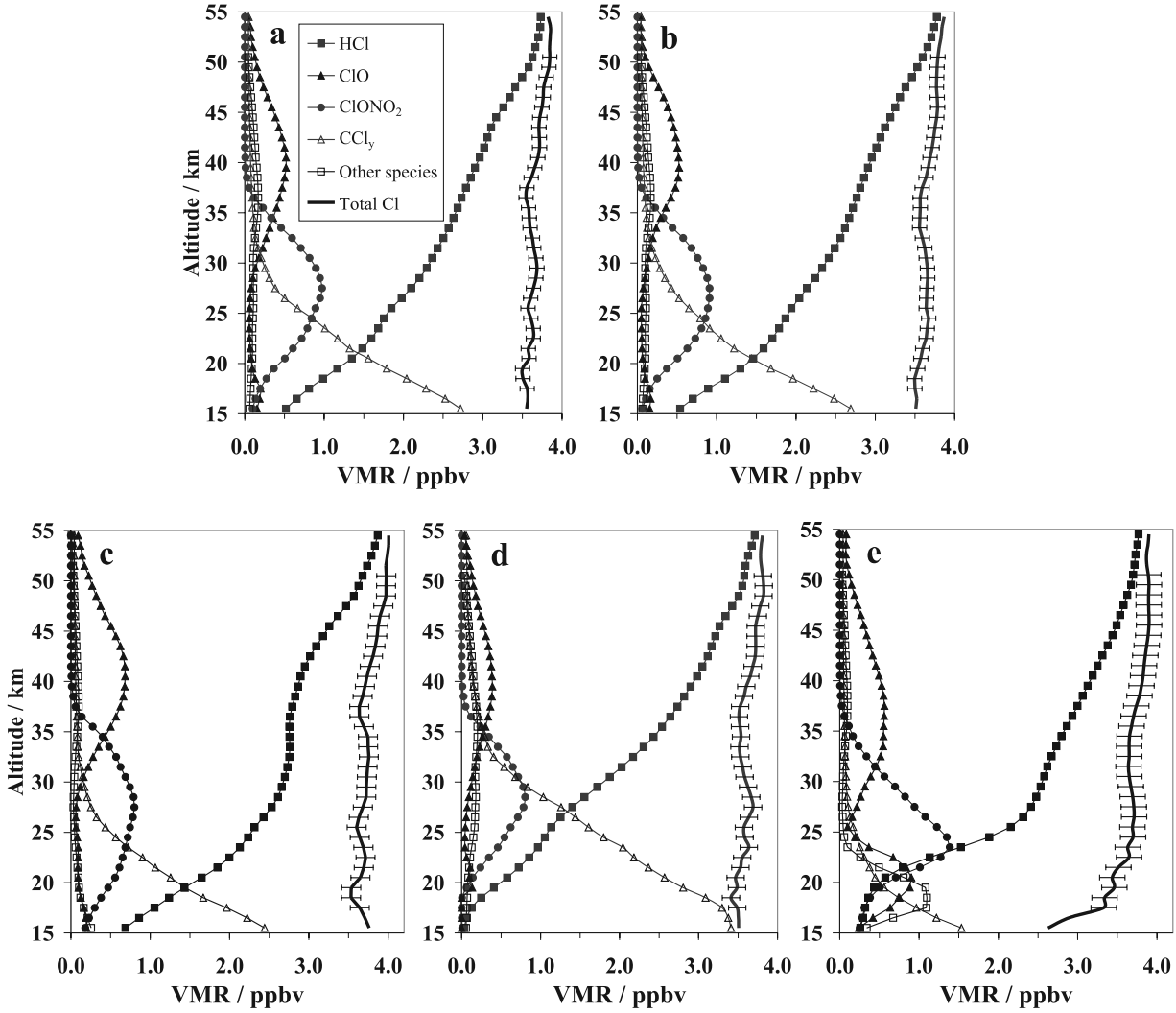

Figure 3. Stratospheric chlorine inventory for 2004 for (a) northern midlatitudes (30°–60°N), (b) southern midlatitudes (30°–60°S), (c) northern high latitudes (60°–82°N), (d) tropics (30°S–30°N), and (e) southern high latitudes (60°–82°S). Each plot shows the VMR profiles for HCl (solid squares), ClO (solid triangles), $ClONO_2$ (circles), the combined chlorine contribution from CCl_y (open triangles), the combined chlorine contribution from "other species" composed of HOCl, COClF, $COCl_2$, and ClOOCl (open squares), and Cl_{TOT} (thick line). Error bars indicating the 1σ precision are included on the total chlorine profiles for the 17.5–50.5 km range.

stratosphere for the northern midlatitudes or subtropics in November. The positions of the tropopause and stratopause exhibit large seasonal and latitudinal variations such that the lapse rate definition of the tropopause recommended by the WMO often places the tropopause as low as ~6–8 km during winter near the poles. In this work, mean stratospheric Cl_{TOT} for each latitude zone was based on points between 17.5 km and 50.5 km altitude, which are close to the positions of the local minima and maxima in mean ACE-FTS temperature profiles. One can argue that this altitude range is too high and therefore not the best representation of the stratosphere for high latitudes, but it was chosen in part to avoid the large deviation from linearity seen in the Cl_{TOT} profile at southern high latitudes, which will be discussed later.

[29] Stratospheric Cl_{TOT} values for 2004 are shown in Table 3 and the mean Cl_{TOT} values are shown in Table 4. The method of error determination used by *Zander et al.* [1996] based on the standard deviation of points over a given altitude range was adopted here and should give a reasonable estimate of the precision of mean Cl_{TOT}. Propagating the uncertainty on each species to obtain the uncertainty on total chlorine would largely overestimate the overall uncertainty because the variability in any given species is mostly a result of conversion to another species. Furthermore, it is difficult to make accurate estimates of the uncertainty for the modeled data. Perhaps the best simple estimate of the absolute uncertainty on Cl_{TOT} can be made based on the uncertainty of HCl at high altitudes, where it is the dominant contributor to Cl_{TOT}. The retrieval of HCl utilized spectroscopic parameters from the HITRAN 2004 database [*Rothman et al.*, 2005]. The HCl line intensities in HITRAN that lie in the microwindows shown in Table 1, have uncertainties in the 1–2% range, which translates to a

Table 3. Cl_{TOT} as a Function of Altitude From 17.5 to 50.5 km in Five Latitude Zones for the Period of February 2004 to January 2005 Inclusive

Altitude, km	Total Chlorine, ppbv				
	60°–82°N	30°–60°N	30°S–30°N	30°–60°S	60°–82°S
17.5	3.64	3.56	3.49	3.50	3.33
18.5	3.53	3.51	3.41	3.50	3.34
19.5	3.53	3.50	3.49	3.53	3.46
20.5	3.65	3.58	3.47	3.57	3.44
21.5	3.69	3.57	3.53	3.60	3.51
22.5	3.71	3.64	3.55	3.64	3.65
23.5	3.69	3.63	3.64	3.65	3.63
24.5	3.64	3.61	3.58	3.67	3.70
25.5	3.60	3.57	3.57	3.64	3.69
26.5	3.63	3.60	3.64	3.65	3.71
27.5	3.68	3.64	3.69	3.65	3.71
28.5	3.72	3.67	3.67	3.66	3.69
29.5	3.72	3.68	3.63	3.66	3.67
30.5	3.73	3.67	3.58	3.64	3.65
31.5	3.74	3.64	3.56	3.62	3.64
32.5	3.76	3.63	3.53	3.59	3.65
33.5	3.75	3.60	3.52	3.56	3.65
34.5	3.74	3.59	3.54	3.56	3.65
35.5	3.69	3.58	3.53	3.57	3.68
36.5	3.64	3.55	3.51	3.56	3.70
37.5	3.63	3.56	3.53	3.59	3.74
38.5	3.68	3.61	3.57	3.64	3.78
39.5	3.71	3.65	3.60	3.67	3.80
40.5	3.73	3.69	3.65	3.69	3.82
41.5	3.77	3.72	3.68	3.72	3.84
42.5	3.81	3.71	3.72	3.74	3.85
43.5	3.84	3.71	3.72	3.75	3.87
44.5	3.86	3.72	3.72	3.77	3.89
45.5	3.87	3.75	3.72	3.78	3.90
46.5	3.90	3.76	3.75	3.78	3.90
47.5	3.94	3.77	3.78	3.77	3.89
48.5	3.97	3.80	3.82	3.77	3.89
49.5	3.97	3.83	3.82	3.78	3.90
50.5	3.98	3.84	3.81	3.79	3.89

maximum of 0.08 ppbv. The uncertainty contribution to the VMR of HCl from the retrieval of pressure and temperature is also estimated to be about 2% or about 0.08 ppbv. An additional source of uncertainty for the HCl retrieval comes from the precision of the fit, which reaches a maximum at high altitudes, although this random error is reduced by averaging multiple profiles. The 1σ error contribution from the precision of the fit for the southern midlatitude mean profile, which had the highest number of profiles used to determine its mean, is only 0.003 ppbv at 18 km, and increases to 0.04 ppbv (or 1.1%) at 50 km, while for the northern high-latitude mean profile, which used the fewest profiles, the precision is 0.06 ppbv (or 1.7%) at 50 km. Combining these three sources of error gives an accuracy of 0.12–0.13 ppbv for HCl at 50 km, which includes both a systematic and random component. This value can be used to estimate the accuracy of the Cl_{TOT} values. Since HCl comprises 93% of Cl_{TOT} at 50 km (at midlatitudes), scaling the error would give an accuracy of 0.13–0.14 ppbv for Cl_{TOT}, which is equivalent to less than 4% of mean Cl_{TOT}. This uncertainty is smaller than the estimated precision from random variability in the HCl mean values at 50 km, but slightly greater than the variability of 0.09 ppbv in the midlatitude Cl_{TOT} profile over the 17.5–50.5 km range. Although the variability in the Cl_{TOT} profiles in some other latitude zones was larger than at midlatitudes, the accuracy should be comparable.

[30] In the lower to middle stratosphere, where HCl only comprises approximately half of Cl_{TOT}, an alternative method of estimating the uncertainty on Cl_{TOT} can be carried out using $ClONO_2$ in addition to HCl. At 27.5 km, $ClONO_2$ peaks at northern midlatidudes with a value of about 1.0 ppbv. The contribution to the uncertainty on $ClONO_2$ from the absorption cross sections in the microwindows used in the retrieval (Table 1) is about 5% or 0.05 ppbv, the pressure and temperature contribution is 2% or 0.02 ppbv and the contribution due to the precision of the fit at this altitude is 0.005 ppbv. These sources give a combined uncertainty of 0.054 ppbv. Using the same approach, HCl has a value of about 2.0 ppbv and a very similar uncertainty of 0.057 ppbv at this altitude. Combining the uncertainties from HCl and $ClONO_2$ gives 0.08 ppbv at an altitude where these species contribute approximately 80% of the chlorine in Cl_{TOT}, thus scaling the uncertainty would give a value of 0.10 ppbv for Cl_{TOT}. The lower-middle stratosphere uncertainty estimate is about 30–40% lower than the uncertainty estimate for 50 km, which is qualitatively consistent with the fact that the signal-to-noise ratio is better in the lower-middle stratosphere than above, but the larger estimate can be applied to the entire altitude range to provide a more conservative uncertainty estimate.

[31] If the points in the 17.5–50.5 km altitude range are fit to a straight line, in all cases, they yield a slight positive slope in ppbv/km. These slopes and the associated 1σ precision on each slope, as a result of the fit, are also shown in Table 4 and discussed in the next section. No estimate of the absolute accuracy on the slopes has been made.

6. Discussion

[32] A principal improvement of the present chlorine inventory with respect to most earlier studies is that the ACE-FTS measures a large number of species relative to other satellite instruments but also provides better global coverage than aircraft, balloon or ground-based measurements. The altitude coverage and vertical resolution of the ACE-FTS measurements are also better than those of ground-based measurements; however, the small number of measurements per day is a significant disadvantage of solar occultation relative to other observation techniques. ACE is often lacking measurements in a particular latitude zone for periods of one month or more. In this work, roughly 50% of measurements were also neglected in order to avoid averaging over diurnal variability. The seasonal

Table 4. Mean Total Chlorine With 1σ Precision and the Slope With 1σ Standard Precision for the Points From 17.5 to 50.5 km Altitude in Five Latitude Zones

	Mean Cl_{TOT}, ppbv	Slope, ppbv/km
Northern high latitudes	3.74 ± 0.12	0.010 ± 0.001
Northern midlatitudes	3.65 ± 0.09	0.007 ± 0.001
Tropics	3.62 ± 0.11	0.009 ± 0.001
Southern midlatitudes	3.65 ± 0.09	0.007 ± 0.001
Southern high latitudes	3.71 ± 0.16	0.014 ± 0.001

distribution of ACE profiles used at some latitudes means that ACE and SMR coincidences do not occur frequently enough to properly match profile by profile and annually averaged ACE-FTS profiles have simply been matched with those of SMR (which obtains better seasonal and global coverage), except at southern high latitudes, where only profiles from the same time period were used so that ClO and other species would be properly anticorrelated with respect to seasonal variability.

[33] The missing chlorine indicated by the deviation from linearity in the southern high-latitude Cl_{TOT} profile from ~15 to 21 km may be the result of some chlorine dissolved or frozen in PSCs, since this inventory only deals with measurements of species in the gas phase, but this explanation has not been verified quantitatively. Additionally, the possibility that the discrepancy may relate to measurement error resulting from the extremely cold conditions or the presence of PSCs in the Antarctic vortex cannot be completely ruled out. It is likely that some portion of the low-altitude deviation, also results from the calculated value of ClOOCl, either due to the amplification of errors in ClO affecting the ClOOCl value, errors in the rate constants, or other assumptions or approximations in the calculation. Although the values of the rate constants used were those suggested by *Stimpfle et al.* [2004], which give ClOOCl values that compare well with in situ measurements, *Von Hobe et al.* [2005], *Berthet et al.* [2005], and *Boakes et al.* [2005] all show that the correct values for these rate constants and the resulting equilibrium constant are still the subject of debate. The revised value of K_{eq} suggested by *Boakes et al.* [2005] indicates that ClOOCl may be more abundant than prior studies suggest, which would reduce the deviation from linearity in the Southern Hemisphere high-latitude Cl_{TOT} profile. Smaller deviations from a straight line in total chlorine profiles for all latitude zones may be related to very short lived (VSL) species such as CH_2Cl_2, $CHCl_3$, and C_2Cl_4; or transient species such as Cl, Cl_2, and OClO which have not been included in this inventory, but may also make a small contribution. For example, daytime OClO can contribute approximately 0.010 ppbv [*Canty et al.*, 2005] to Cl_{TOT} at certain altitudes near the poles.

[34] The slopes in Table 4 can primarily be attributed to changes in chlorine VMR which occurred during the lag time necessary for transport, with a higher value of total chlorine in older air at higher altitudes indicating that the stratospheric peak in total chlorine has already past. This result is qualitatively consistent with the lowest total chlorine values occurring in the tropics and the highest at high latitudes due to the Brewer-Dobson circulation. Although the direction of these slopes is reasonable, the absolute accuracy of the slopes is likely low and a proper quantitative check of their validity would require modeling of stratospheric transport.

[35] This chlorine inventory has shown that near the stratopause, HCl accounts for the majority of Cl_{TOT}. The Earth Observing System Microwave Limb Sounder (EOS-MLS) is a second generation MLS instrument on the NASA Aura satellite that was launched in July 2004 and measures a variety of atmospheric species including HCl. Comparisons have been made between the EOS-MLS (version 1.5) and ACE-FTS HCl data (version 2.1) by *Froidevaux et al.* [2006a]. On the basis of 623 near-coincident profiles, the

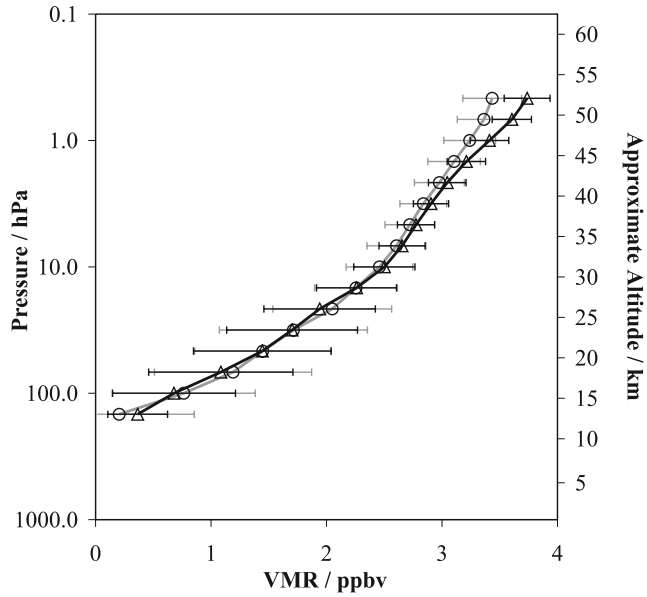

Figure 4. Comparison showing average HCl profiles based on MLS (circles, gray line) and ACE-FTS (triangles, black line) coincidences. One thousand nineteen coincidences from the period of August 2004 to 31 January 2005 were used, although at the upper and lower ends of the altitude range, fewer profiles are included in the average. The criteria for coincidences are measurements within 1° latitude, 8° longitude, and 12 hours. This comparison includes both ACE-FTS sunrise and sunset occultations, with all ACE-FTS data interpolated to the MLS vertical pressure grid. The error bars indicate the 1σ variability for each set of data.

agreement between the two instruments was typically much better than 5% from 100 hPa to about 1 hPa, above which point ACE-FTS values appear about 5–8% higher. More recent comparisons between MLS and ACE-FTS version 2.2 data using 1019 coincident profiles, give a similar result (Figure 4), indicating perhaps even better agreement in the middle and lower stratosphere. Possible causes for a slightly larger difference at high altitudes are currently under investigation.

[36] *McHugh et al.* [2005] found that ACE-FTS HCl (version 1.0) abundances are 10 to 20% larger than those from HALOE, based on a more limited sampling of 32 coincident profiles, mostly in July 2004. MLS HCl values are also high relative to HALOE by about 0.2 to 0.4 ppbv (~10 to 15%) for roughly the same time period and latitudes used in the ACE-FTS and MLS comparisons [*Froidevaux et al.*, 2006a]. The absolute accuracy of HALOE HCl reported by *Russell et al.* [1996b] is 12–24% depending on altitude, so given this wide margin of error, ACE-FTS and MLS results can be considered consistent with those of HALOE. The exact cause of the systematic difference with HALOE is not yet known, but there were early indications that HALOE HCl measurements were low relative to other observations [*Russell et al.*, 1996a, 1996b], as well as evidence from more recent comparisons [*Barret et al.*, 2005]. It is possible that both the ACE-FTS and MLS HCl measurements are slightly

high, but it is unlikely that they are the sole cause of the large difference with respect to HALOE.

[37] The most important implication of a difference in upper stratospheric HCl values obtained by the various instruments is the effect that it will have on Cl_{TOT}. *Froidevaux et al.* [2006b] have derived a value of 3.65 ppbv for near global (82°S–82°N) Cl_{TOT} for August 2004 based on MLS measurements of HCl from 0.7 to 0.1 hPa. Their value compares extremely well with both ACE-FTS midlatitude values of 3.65 ppbv in 2004, further reinforcing the good agreement between these two instruments. Since the discrepancy between MLS and ACE appears limited to altitudes above 1 hPa or approximately 45 km at midlatitudes (~48 km in the tropics or ~42 km for the polar winter), high biased ACE-FTS values of HCl would cause a small error in the determination of tropical mean Cl_{TOT}, but a more significant error at higher latitudes, all of which are based on the 17.5–50.5 km range. By determining mean Cl_{TOT} using a reduced altitude range of 20.5–39.5 km, values of 3.69 ± 0.05, 3.61 ± 0.04, 3.57 ± 0.06, 3.62 ± 0.04, and 3.67 ± 0.08 ppbv are obtained for northern high latitudes, northern midlatitudes, tropics, southern midlatitudes, and southern high latitudes, respectively (where the uncertainty is the 1σ precision from 20.5 to 39.5 km altitude). These values are all slightly lower than those determined using the wider altitude range.

[38] Previous chlorine inventories often neglected CCl_y in the upper stratosphere [*Zander et al.*, 1992, 1996; *Sen et al.*, 1999], thus assuming Cl_{TOT} was equal to Cl_y at high altitudes. Dividing the HALOE 2004 globally averaged HCl value of 3.13 ppbv at 55 km (J. Anderson, private communication, 2006) by the HCl/Cl_y ratios (0.93–0.95) results in Cl_y estimates of 3.29–3.37 ppbv. The difference between ACE-FTS mean Cl_{TOT} values and HALOE Cl_y values is larger than the contribution from CCl_y at 55 km, which is expected to be less than 0.06 ppbv. From this work, on the basis of the work by *Weisenstein et al.* [1992] and *Coheur et al.* [2003] and additional knowledge of source gas trends and lifetimes [*WMO*, 2003], one can estimate a value of HCl/Cl_{TOT} near 55 km altitude, since HCFC-22 accounts for about 1% (0.027–0.040 ppbv) of Cl_{TOT} and a contribution of only about 0.5% (0.019–0.023 ppbv) is due to other organic chlorine gases mainly CFC-114, CFC-115, HCFC-142b. Inorganic chlorine species that may contribute to Cl_{TOT} at this altitude include ClO, HOCl and Cl. It is difficult to determine accurate values of the contributions from these species, although a reasonable estimate would attribute the largest contribution (~0.07 pbbv at high latitudes) to ClO. Unfortunately, the version of SMR ClO measurements used here, did not appear reliable at this altitude. These estimates imply that HCl may comprise as much as ~98–99% of Cl_y or ~96–98% of Cl_{TOT} at 55 km, in contrast to the above values used by others.

[39] When using HCl at 55 km to determine stratospheric Cl_y, it is rarely emphasized that 55 km is typically in the lower mesosphere, not the stratosphere. Thus relating the Cl_y value at 55 km to Cl_{TOT} in the stratosphere is complicated both by assumptions about the value of CCl_y at that altitude and by the presence of slightly sloped stratospheric Cl_{TOT} profiles as determined in this work. Small changes in Cl_{TOT} associated with the slope, coupled with differences attributable to CCl_y, should all be considered in very accurate comparisons of HALOE Cl_y values with ATMOS, MkIV, SOLVE and ACE-FTS Cl_{TOT} values. While there is a good theoretical foundation for slightly sloped stratospheric Cl_{TOT} profiles, the present uncertainty in many parameters prevents a quantitative treatment of the slope or its use in a meaningful quantitative comparison such as the one mentioned above. However, it does imply that prior to the peak in upper stratospheric chlorine, Cl_{TOT} at 55 km should be slightly less than a true stratospheric value (below ~50 km), and after the peak it should be slightly more, which adds to the discrepancy between ACE-FTS and HALOE values.

[40] Ideally, a technique or combination of techniques that could accurately measure all relevant chlorine species over a large altitude range, would provide the most reliable approach to determining stratospheric Cl_{TOT} or Cl_y. While eleven important chlorine species have been retrieved from ACE-FTS measurements in this work, some key species are still missing, thus ACE-FTS data can only provide a partial solution at the current time, but the results obtained here are significant since they indicate that stratospheric Cl_{TOT} in 2004 may have been higher than expected from estimates derived using other techniques.

7. Summary and Conclusions

[41] A global inventory of stratospheric chlorine has been created which includes all significant inorganic and organic chlorine species in five latitude zones during the period of February 2004 to January 2005 inclusive, based on measurements by the ACE-FTS supplemented by measurements by other instruments and model results. The sum of all significant chlorine species at each altitude nearly makes a straight line, with a slight positive slope (ppbv/km). The average of these points in the 17.5–50.5 km altitude range is used to determine mean stratospheric Cl_{TOT} for each latitude zone yielding values of 3.62 ± 0.11 ppbv for the tropics, 3.65 ± 0.09 ppbv for both the northern and southern midlatitudes, 3.74 ± 0.12 ppbv for the northern high latitudes, and 3.71 ± 0.16 ppbv for the southern high latitudes (where the uncertainty given is the 1σ precision for points between 17.5 and 50.5 km and the estimated accuracy is 0.13–0.14 ppbv). Both the latitudinal variation and the slopes can be interpreted as evidence that stratospheric Cl_{TOT} is now declining, but the accuracy of the slopes does not permit quantitative conclusions.

[42] HCl is the principal component of high altitude Cl_{TOT}, and ACE-FTS and MLS HCl measurements agree very well up to 1 hPa (or ~45 km altitude). Because of the possibility that ACE-FTS HCl values above this range are biased high, an alternate set of mean Cl_{TOT} values based only on the 20.5–39.5 km altitude range were determined for the five latitude zones. These values are 0.03–0.06 ppbv lower than those based on the wider altitude range. ACE-FTS or MLS measurements and historical ATMOS or MkIV measurements, all yield higher HCl values than HALOE, which translate to larger inferred stratospheric Cl_{TOT} (or Cl_y) than obtained using HALOE data. The cause of this discrepancy cannot be determined at present. In spite of the higher stratospheric chlorine values determined in this work, the latitudinal variation in mean Cl_{TOT} and the Cl_{TOT} slopes obtained here, as well as a comparison of mean Cl_{TOT} values to past ATMOS and MkIV measurements, all

indicate that stratospheric Cl_{TOT} is now decreasing, which reinforces previous work that has shown the success of the Montreal Protocol and its amendments at controlling and reducing chlorine levels.

[43] **Acknowledgments.** We would like to thank the Canadian Space Agency (CSA) for providing the primary funding for the SCISAT-1/ACE mission and the Natural Sciences and Engineering Research Council of Canada (NSERC) for their funding contribution. Support at Waterloo was also provided by the NSERC-Bomem-CSA-MSC Research Chair in Fourier Transform Spectroscopy. R. Nassar would like to acknowledge direct funding from NSERC and the CSA. Work at the Jet Propulsion Laboratory, California Institute of Technology, was done under contract to NASA. Contributions from the University of Liège were supported by the Belgian Federal Science Policy Office, Brussels. P.F. Coheur was funded by the Fonds National de la Recherche Scientifique (FNRS, Belgium), the Belgian Science Policy, and the European Space Agency (ESA-Prodex arrangement C90-219). Financial support by the "Actions de Recherche Concertées" (Communauté Française de Belgique) is also acknowledged. Furthermore, we thank the numerous other organizations which we have not explicitly mentioned that also contributed funding to the ACE mission. We would also like to thank Jianjun Jin and Andreas Jonsson for their assistance with the Odin SMR data and John Anderson for providing HALOE HCl values. Finally, we thank the anonymous reviewers for their helpful comments and suggestions.

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