

A global inventory of stratospheric fluorine in 2004 based on Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) measurements

R. Nassar,^{1,2} P. F. Bernath,¹ C. D. Boone,¹ S. D. McLeod,¹ R. Skelton,¹ K. A. Walker,^{1,3} C. P. Rinsland,⁴ and P. Duchatelet⁵

Received 11 April 2006; revised 29 June 2006; accepted 7 August 2006; published 30 November 2006.

[1] Total fluorine (F_{TOT}) in the stratosphere has been determined using Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) measurements of HF, COF₂, COClF, CF₄, CCl₃F (CFC-11), CCl₂F₂ (CFC-12), CHClF₂ (HCFC-22), CCl₂FCClF₂ (CFC-113), CH₃CClF₂ (HCFC-142b), CH₂FCF₃ (HFC-134a), and SF₆. The retrieval of HFC-134a (CH₂FCF₃) from spaceborne measurements had not been carried out prior to this work. Measurements of these species have been supplemented by data from models to extend the altitude range of the profiles and have also been complemented by estimates of 15 minor fluorine species. Using these data, separate fluorine budgets were determined in five latitude zones (60°–82°N, 30°–60°N, 30°S–30°N, 30°–60°S, and 60°–82°S) by averaging over the period of February 2004 to January 2005 inclusive, when possible. Stratospheric F_{TOT} profiles in each latitude zone are nearly linear, with mean stratospheric F_{TOT} values ranging from 2.50 to 2.59 ppbv (with a 1σ precision of 0.04–0.07 ppbv and an estimated accuracy of 0.15 ppbv) for each zone. The highest mean F_{TOT} value occurred in the tropics, which is qualitatively consistent with increasing levels of stratospheric fluorine and the mean stratospheric circulation pattern.

Citation: Nassar, R., P. F. Bernath, C. D. Boone, S. D. McLeod, R. Skelton, K. A. Walker, C. P. Rinsland, and P. Duchatelet (2006), A global inventory of stratospheric fluorine in 2004 based on Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) measurements, *J. Geophys. Res.*, *111*, D22313, doi:10.1029/2006JD007395.

1. Introduction

[2] Halogenated gases such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and halons are very stable, with long lifetimes in the troposphere. When these gases are transported to the stratosphere, they dissociate releasing F, Cl, and Br radicals. Cl-containing radicals and the much less abundant Br-containing radicals participate in the destruction of ozone via catalytic cycles which have the greatest impact in the springtime polar vortices. In contrast, F radicals quickly react with CH₄ and H₂O producing the stable reservoir molecule HF. The formation of HF prevents fluorine from undergoing similar catalytic cycles [Stolarski and Rundel, 1975].

[3] Despite the fact that fluorine does not directly participate in ozone depletion, monitoring of atmospheric fluorine

levels is important for a number of reasons: (1) to compare with emission inventories reflecting the quantities of individual species used and emitted that often contain chlorine or bromine, (2) to check the validity of methods for the determination of total stratospheric chlorine which is the main contributor to polar ozone decline, and (3) fluorinated species in the troposphere behave as greenhouse gases, some species with global warming potentials orders of magnitude larger than CO₂ [World Meteorological Organization (WMO), 2003].

[4] HF is the dominant fluorine species in the middle and upper stratosphere. The Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument which flew four times on the NASA Space Shuttle (1985, 1992, 1993, and 1994) measured HF along with six other fluorine species. The 1985 ATMOS measurements were used to create a fluorine inventory for 30°N, including a profile of total fluorine (F_{TOT}) throughout the stratosphere [Zander *et al.*, 1992]. The Halogen Occultation Experiment (HALOE) on the NASA Upper Atmospheric Research Satellite (UARS) measured HF between 1991 and 2005. HALOE HF at 55 km in altitude has been used to calculate total inorganic fluorine (F_y) [Russell *et al.*, 1996; Anderson *et al.*, 2000], which serves as a proxy for F_{TOT} .

[5] The Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE FTS) is a high-resolution infrared Fourier transform spectrometer (FTS) on the SCISAT-1 or

¹Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

²Now at Department of Earth and Planetary Sciences and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA.

³Now at Department of Physics, University of Toronto, Toronto, Ontario, Canada.

⁴NASA Langley Research Center, Hampton, Virginia, USA.

⁵Institute of Astrophysics and Geophysics, University of Liège, Liège, Belgium.

ACE satellite, launched in August 2003 [Bernath *et al.*, 2005]. Since it is very difficult to monitor HF with microwave or infrared emission instruments, the ACE FTS is only the third spaceborne instrument capable of measuring HF, and with ATMOS and HALOE now retired, it is the only one currently making these measurements. It also measures profiles of several other important fluorine-containing molecules, some of which are also unique to the ACE FTS. The ACE FTS method for the determination of stratospheric F_{TOT} is similar to the approach employed using measurements by ATMOS [Zander *et al.*, 1992] and the MkIV balloon-borne FTS [Sen *et al.*, 1996], which were based on a summation of the abundances of relevant species, although the present work has been carried out with a much larger set of available measurements and on a global scale.

[6] Perhaps the most important reason for revisiting the fluorine budget is that the partitioning between fluorine-containing gases in the stratosphere is continually changing. As a result of the Montreal Protocol and subsequent amendments, abundances of CFCs and halons are decreasing, most HCFCs are near their predicted maxima, and hydrofluorocarbons (HFCs) are rapidly increasing [WMO, 2003]. ACE FTS measurements of several of these species have been reported in the past (based on version 1.0 data) by Rinsland *et al.* [2005, 2006a], which combined the ACE FTS measurements with ATMOS measurements to demonstrate changes in abundances of these species over time. Furthermore, it is now possible to retrieve some fluorine-containing species which could not be retrieved in the past.

[7] This paper reports the first retrievals of HFC-134a (CH_2FCF_3) from spaceborne measurements, and demonstrates the ACE FTS method for determining F_{TOT} by creating a near global ($82^\circ S-82^\circ N$) inventory of stratospheric fluorine species in 2004. With the absence of other satellite instruments measuring HF, this approach may provide the primary source of global stratospheric fluorine abundances in the coming years.

2. ACE Method for Determining Total Stratospheric Fluorine

[8] In the present work, the volume mixing ratios (VMRs) of total inorganic fluorine F_y , total organic fluorine CF_y and total fluorine F_{TOT} at discrete stratospheric altitudes were determined using the summations below, where the square brackets indicate the VMR of a species. For the purpose of this work, F_y and CF_y are defined below, and F_{TOT} is the sum of all significant fluorine species including both F_y and CF_y .

$$F_y = [HF] + 2[COF_2] + [COCIF] + 6[SF_6]$$

$$CF_y = 4[CF_4] + [CCl_3F] + 2[CCl_2F_2] + 2[CHClF_2] \\ + 3[CCl_2FCClF_2] + 2[CH_3CClF_2] + 4[CH_2FCF_3] \\ + \text{minor species}$$

$$F_{TOT} = F_y + CF_y$$

[9] As in the ACE FTS global inventory of stratospheric chlorine [Nassar *et al.*, 2006], mean profiles for each species and F_{TOT} were determined in five latitude zones ($60^\circ-82^\circ N$, $30^\circ-60^\circ N$, $30^\circ S-30^\circ N$, $30^\circ-60^\circ S$, and $60^\circ-82^\circ S$) over the 17.5–50.5 km range; however, since no fluorine-containing species exhibit major diurnal variations, occultations at all local times could be combined in an average, unlike in the chlorine inventory. Profiles for each species in the above equations (with exception of the “minor species”) were based on ACE FTS retrieved profiles; although, various methods were used to extend the profiles when they did not span the entire stratosphere. The spectral microwindows and altitude ranges for the retrieval of each species are given in Table 1, and a detailed description of the ACE FTS retrieval approach is given by Boone *et al.* [2005]. Figure 1 shows an example of average northern midlatitude profiles for fluorinated species included in this inventory. Brief descriptions of the method for obtaining profiles of each species follow.

2.1. HF, CF_4 , CCl_3F (CFC-11), and CCl_2F_2 (CFC-12)

[10] The CCl_3F and CCl_2F_2 data utilized here are from the ACE FTS version 2.2 data set. Although HF and CF_4 , are included in version 2.2, they were retrieved to higher altitudes specifically for this work. If the retrieval range for a species was below 54.5 km, then above the retrieval range, a priori profiles were automatically scaled to produce a similarly shaped profile using the value at the second highest retrieved point. If this was insufficient, the retrieved profile was manually extrapolated to zero.

2.2. COF_2

[11] COF_2 is included in version 2.2, but ACE FTS retrievals were extended to higher altitudes specifically for this work, using a latitude-dependent altitude range which is highest in the tropics and lowest near the poles. COF_2 makes a maximum contribution to F_{TOT} in the tropics, where it contributes $\sim 24\%$ at its peak near 39.5 km. A slightly weaker peak is centered at 28.5 km at midlatitudes and at 25.5 km at northern high latitudes. At southern high latitudes, the mean profile has a primary peak at 23.5 km and a secondary peak at 36.5 km. Since COF_2 has only been retrieved up to approximately 40 km from ACE FTS spectra, the profiles were extended based on the shape of the tropical profile modeled by Kaye *et al.* [1991], shifted appropriately for the middle and high latitudes.

2.3. COCIF

[12] COCIF results from the breakdown of CCl_3F , so it has a peak in the lower to middle stratosphere. Retrievals of COCIF involving averaged ACE FTS spectra have been carried out by Rinsland *et al.* [2006b]; however, a routine operational retrieval has not been developed at the time of this writing. The tropical and midlatitude COCIF profiles in this work were based on the retrieval of Rinsland *et al.* [2006b] using ACE FTS measurements, which uses the COCIF lines from the ATMOS supplemental line list [Brown *et al.*, 1987, 1996] and also accounts for many interfering species. The dates and latitude ranges to retrieve average profiles in that work were similar to, but did not exactly match the ranges used for other species in this work. Therefore a tropical COCIF profile was included based on

Table 1. Microwindows for Fluorine Species Retrieved From ACE FTS Measurements^a

Species	Retrieved Altitude Range for Mean Profile, km	Microwindow		
		Center, cm ⁻¹	Width, cm ⁻¹	Range, km
HF	12.5–59.5	3788.33	0.40	12.5–51.5
HF	12.5–59.5	3833.71	0.40	18.5–54.5
HF	12.5–59.5	3877.75	0.35	12.5–59.5
HF	12.5–59.5	3920.39	0.30	27.5–59.5
HF	12.5–59.5	4001.03	0.30	12.5–59.5
HF	12.5–59.5	4038.37	0.45	12.5–59.5
HF	12.5–59.5	4075.30	0.35	45.5–59.5
HF	12.5–59.5	4109.94	0.35	25.5–49.5
COF ₂	12.5–37.5/41.5 ^b	1930.18	0.35	12.5–37.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1936.97	0.30	12.5–37.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1937.06	0.30	15.5–7.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1938.26	0.30	30.5–37.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1939.97	0.30	12.5–37.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1949.81	0.30	12.5–37.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1950.70	0.50	12.5–37.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1952.03	1.00	12.5–37.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1953.36	0.30	30.5–37.5/41.5 ^b
COF ₂	12.5–37.5/41.5 ^b	1954.17	0.30	20.5–37.5/41.5 ^b
COCIF ^c	17/19–30 ^d	1860.35	0.70	17/19–30 ^d
COCIF ^c	17/19–30 ^d	1862.55	1.30	17/19–30 ^d
COCIF ^c	17/19–30 ^d	1864.30	0.60	17/19–30 ^d
COCIF ^c	17/19–30 ^d	1865.45	1.10	17/19–30 ^d
COCIF ^c	17/19–30 ^d	1866.80	0.40	17/19–30 ^d
COCIF ^c	17/19–30 ^d	1868.80	0.60	17/19–30 ^d
COCIF ^c	17/19–30 ^d	1870.575	0.35	17/19–30 ^d
COCIF ^c	17/19–30 ^d	1874.95	0.90	17/19–30 ^d
CF ₄	20.5–44.5	1283.20	8.00	20.5–44.5
CCl ₃ F (CFC-11)	5.5–21.5	842.50	25.00	5.5–21.5
CCl ₂ F ₂ (CFC-12)	6.5–27.5	922.00	4.00	6.5–27.5
CCl ₂ F ₂ (CFC-12)	6.5–27.5	1161.00	1.20	12.5–24.5
CCl ₂ FCIF ₂ (CFC-113)	7.5–16.5	817.50	25.00	7.5–16.5
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
CH ₃ CClF ₂ (HCFC-142b)	8.5–18.5	1134.50	4.00	8.5–18.5
CH ₃ CClF ₂ (HCFC-142b)	8.5–18.5	1193.60	3.60	8.5–18.5
CH ₂ FCF ₃ (HFC-134a)	5.5–16.5	1190.00	20.00	5.5–16.5
SF ₆	7.5–30.5	948.50	7.00	7.5–30.5

^aThe spectral contributions from interfering species including H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, HDO, N₂O, ¹²CO₂, ¹³CO₂, O₃ and others were accounted for as required.

^bLatitude-dependent retrieval range where the retrieval went highest in the tropics and lowest for polar latitudes.

^cSpecial circumstances for the retrieval of this species are outlined in the text.

^dThe lower-altitude limit for the COCIF retrieval is 19 km for tropical occultations and 17 km for midlatitudes.

the 20°S–20°N range and both the northern and southern midlatitude profiles were based on the 30°–50°N range, using occultations spanning 2004 to 2005. The signal-to-noise ratio for COCIF is low and since the peak VMR value decreases with latitude, a high-latitude profile for COCIF was not retrieved by *Rinsland et al.* [2006b]. Therefore high-latitude profiles were based on the model results of *Kaye et al.* [1991], scaled to 2004 based on the predicted change in the stratospheric abundance of CCl₃F given in *WMO* [2003]. COCIF only makes a small contribution to F_{TOT}, with a peak in the profile of ~0.10 ppbv in the tropics, ~0.05 ppbv at midlatitudes and ~0.02 ppbv at high latitudes, but in the future it would be desirable to carry out a complete ACE FTS COCIF retrieval, as was done for the other species.

2.4. CHClF₂ (HCFC-22)

[13] The ATMOS and MkIV fluorine budgets [*Zander et al.*, 1992; *Sen et al.*, 1996] did not include CHClF₂ in the upper stratosphere, however, according to the modeling work of *Weissenstein et al.* [1992], CHClF₂ exists in the upper stratosphere in significant quantities. Their modeled

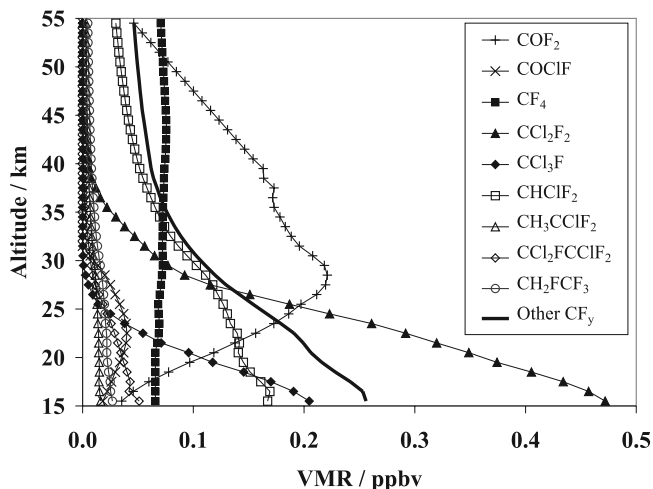


Figure 1. Northern midlatitude (30°–60°N) profiles of species included in the ACE FTS fluorine inventory. HF is not shown because its VMR is mostly above 0.5 ppbv, and SF₆ is not shown as it occurs at very low levels.

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, 45°N , 90°E is shown in Figure 2.

[14] Since the ACE FTS version 2.2 retrievals of CHClF_2 used in this work only extend as high as 24.5 km, they were extended to higher altitudes using the SCTM-1 profile scaled by a factor of 1.062 based on a comparison of the mean midlatitude measured value in 2004 and the modeled value from 2000, both at 19.5 km. The resulting profile was very similar to (yet much smoother than) ACE FTS northern and southern midlatitude profiles over the 17.5–24.5 km range. This scaled profile was grafted onto both ACE FTS midlatitude profiles beginning at 25.5 km. For northern high latitudes, the scaled 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 it down by 10 km to coincide with the ACE FTS measurements. Similarly, the tropical profile was shifted upward by 10 km to coincide with ACE FTS 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 *Weissenstein et al.* [1992], although their model results showed a more symmetrical relationship between the northern and southern hemispheres.

2.5. $\text{CCl}_2\text{FCClF}_2$ (CFC-113) and CH_3CClF_2 (HCFC-142b)

[15] $\text{CCl}_2\text{FCClF}_2$ and CH_3CClF_2 are not included in version 2.2 or any earlier data versions, but were retrieved for this work and the ACE FTS stratospheric chlorine inventory [Nassar et al., 2006]. These two species were not included in the fluorine inventory of *Zander et al.* [1992]; however, their retrieval from ACE FTS measurements was described by *Dufour et al.* [2005], which represented the first retrieval of these species from space-based measurements. The chemistry responsible for the breakdown of CFCs is similar but distinct from that of HCFCs or other classes of species. Therefore CFC-113, which has a lifetime of 85 years, was extended above 16.5 km by scaling the shape of the profile of CFC-12 which has a lifetime of 100 years, by a factor of 0.099. HCFC-142b, which has a lifetime of 17.9 years, was extended above 18.5 km by scaling the shape of the profile of HCFC-22 which has a lifetime of 12.0 years, by a factor of 0.103. Lifetimes of these species were taken from the 2002 WMO Report [WMO, 2003]. The scale factors were determined by taking the global mean values of $[\text{CCl}_2\text{FCClF}_2]/[\text{CCl}_2\text{F}_2]$ and $[\text{CH}_3\text{CClF}_2]/[\text{CHClF}_2]$ at the last point prior to the extension, i.e., the highest retrieved point. Since these species rapidly photodissociate in the stratosphere, they make a small contribution to F_{TOT} above the highest altitude point in their respective retrievals.

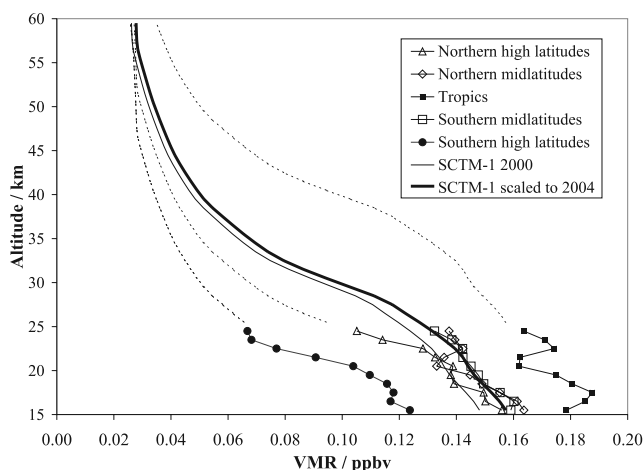


Figure 2. CHClF_2 (HCFC-22) profiles in the stratosphere: the SCTM-1 model for 45°N in 2000 (thin line), the SCTM-1 profile scaled to 2004 (thick line), and the ACE FTS measured values in each latitude zone. The scaled and shifted SCTM-1 profiles for extending the ACE FTS measurements to higher altitudes are shown as dotted lines.

2.6. CH_2FCF_3 (HFC-134a)

[16] HFC-134a is an important CFC replacement compound. Although it is not an ozone depleting substance, it is a greenhouse gas with a very high radiative efficiency and is becoming a significant contributor to the fluorine budget as its VMR is rapidly increasing. The retrieval of HFC-134a from ACE FTS spectra is the first retrieval of an HFC from space-based measurements. The ability to retrieve HFC-134a (as well as CFC-113 and HCFC-142b) from ACE FTS measurements was predicted prior to launch [Coheur et al., 2003].

[17] The ACE FTS HFC-134a retrievals employed a 20 cm^{-1} wide microwindow centered at 1190 cm^{-1} over an altitude range of 5.5 to 16.5 km. Absorption cross sections for the retrievals were from HITRAN 2004 [Rothman et al., 2005] and are based on the laboratory measurements of *Clerbaux et al.* [1993] and *Nemtchinov and Varanasi* [2004]. The cross sections, the spectral fit and the residual for the HFC-134a retrieval are shown in Figure 3 for a single measurement at a tangent height of 10.2 km. Interferences from N_2O and the first four isotopologues of H_2O were accounted for in the retrieval, including two relatively strong lines of the H_2^{16}O isotopologue in the window for which the line shapes fit poorly in the troposphere (a general problem for H_2O with ACE FTS measurements). The fitting weights were therefore set to zero in the vicinity of the two strong H_2O lines. *Clerbaux et al.* [1993] state an uncertainty of $7 \times 10^{15}\text{ cm molecule}^{-1}$ (approximately 8%) for the HFC-134a cross sections in the spectral region utilized in the ACE FTS retrieval, while *Nemtchinov and Varanasi* [2004] estimate the accuracy of their cross sections to be 2–10%, where the highest uncertainty is associated with weakly absorbing lines. The uncertainty in the cross sections makes the largest contribution to the total uncertainty in the ACE FTS HFC-134a retrieval which is estimated to be about 12%.

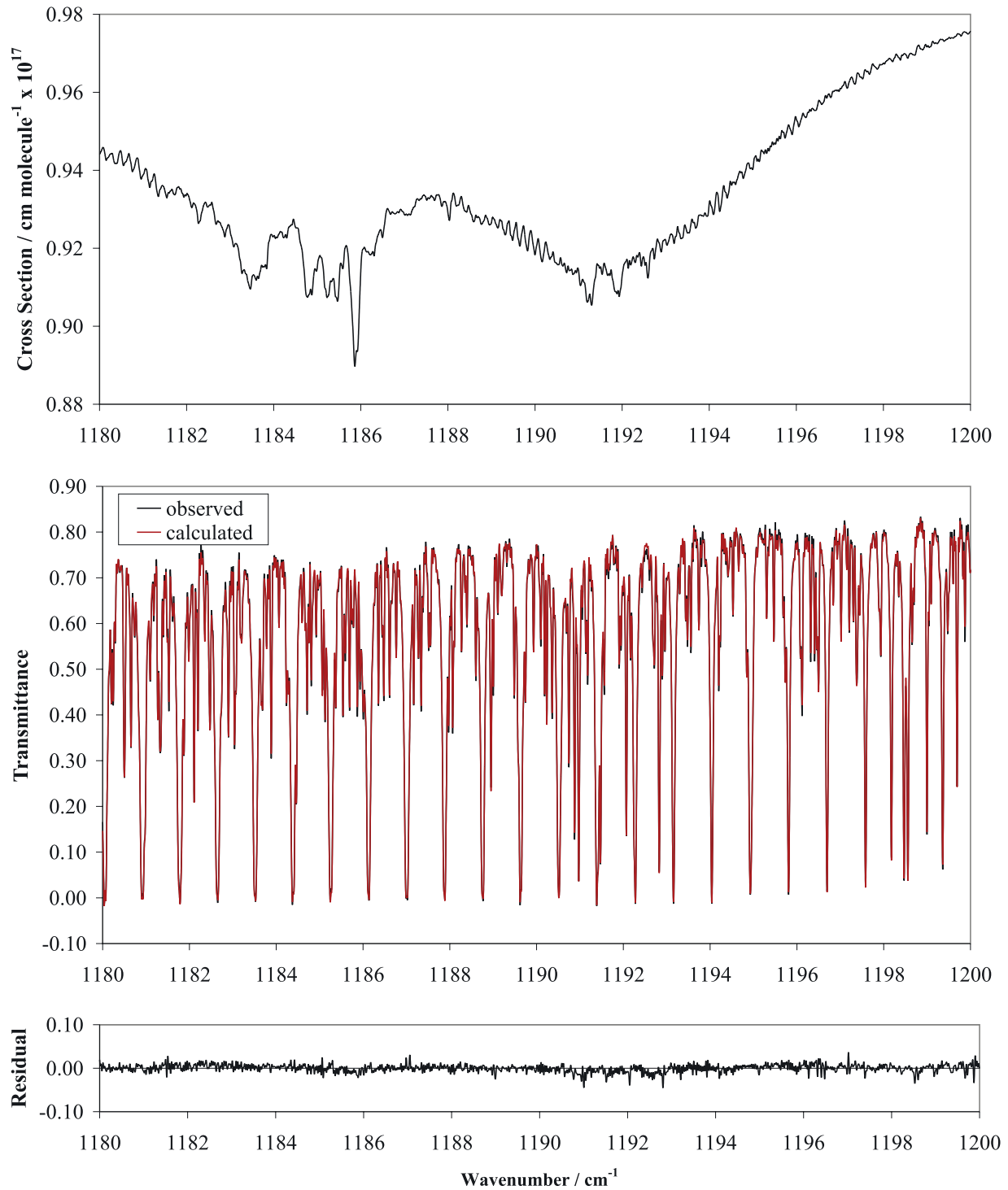


Figure 3. (top) CH₂FCF₃ (HFC-134a) absorption cross sections, (middle) the observed and calculated spectra, and (bottom) the residual spanning the 20 cm⁻¹ wide microwindow for a single measurement at an altitude of 10.2 km.

[18] The retrieved global mean value of HFC-134a at the top of the retrieval range (16.5 km) was 25.0 pptv which is slightly below the predicted surface value of ~ 27.6 pptv for 2004, which one obtains from the 2000 VMR and growth rates [WMO, 2003, Table 1–12]. Since no stratospheric profiles of any HFCs were available, the profile was

extended to higher altitudes by grafting on an extension with the same shape as the scaled and shifted HCFC-22 profiles. HFC-134a is a relatively long-lived HFC with a lifetime of 14.0 years, which is comparable to the 12.0 year lifetime of HCFC-22 [WMO, 2003]. A scale factor of 0.155

Table 2. Minor Organic Fluorine Species Included in the Fluorine Budget Based on Their Predicted Surface Values in Table 1–12 of the 2002 *WMO*, [2003] Report^a

Chemical Formula	Industrial Name	VMR	VMR Contribution to F _{TOT}
CF ₃ CF ₃	PFC-116	3.32	19.9
C ₃ F ₈	PFC-218	0.3	2.4
<i>c</i> -C ₄ F ₈	PFC-318	1.1	8.8
Total minor PFC contribution			31.1
CClF ₃	CFC-13	3.5	10.5
CClF ₂ CClF ₂	CFC-114	16.4	65.6
CCl ₂ FCF ₃	CFC-114a	1.8	7.2
CClF ₂ CF ₃	CFC-115	9.2	46
CBrClF ₂	Halon-1211	4.16	8.32
CBrF ₃	Halon-1301	3.11	9.33
CBrF ₂ CBrF ₂	Halon-2402	0.38	1.52
Total minor CFC and halon contribution			148.47
CHClFCF ₃	HCFC-124	2.7	10.8
CH ₃ CCl ₂ F	HCFC-141b	20.9	20.9
CHF ₃	HFC-23	19.1	57.3
CHF ₂ CF ₃	HFC-125	2.6	13
CH ₃ CHF ₂	HFC-152a	2.5	5.0
Total minor HCFC and HFC contribution			107.0

^aVMRs are given in parts per trillion by volume (pptv).

was applied to the HCFC-22 profiles based the ratio of the values at 16.5 km.

2.7. Minor Organic Fluorine Species

[19] Fifteen other organic fluorine species, listed in Table 2, including perfluorocarbons (PFCs), CFCs, HCFCs, HFCs, and halons were also included in the calculation of F_{TOT}. These species have low individual VMRs but when combined their contribution is not negligible. Profiles for the different classes of species were estimated as follows. PFCs are long-lived species with lifetimes of thousands of years; therefore their profiles are expected to be nearly vertical, resembling the profile of the simplest PFC, CF₄. The PFCs CF₃CF₃, C₃F₈ and *c*-C₄F₈ (a cyclic compound) had a combined surface VMR equivalent to 0.0311 ppbv fluorine; therefore a profile for their fluorine contribution was simulated by scaling the retrieved CF₄ profile by a factor of 0.41 (0.0311 ppbv divided by the maximum retrieved VMR of CF₄ averaged over the five latitude ranges). Profiles of the minor CFCs in Table 2 are expected to resemble the shape of the other CFC profiles. Since we have not measured any halons, these were grouped with the CFCs, resulting in a surface contribution equivalent to 0.148 ppbv fluorine, so a profile for the fluorine contribution from the minor CFCs and halons was simulated by scaling the profile of CFC-12 by a factor of 0.28. Profiles of HCFCs and HFCs are assumed to resemble the shape of the HCFC-22 profiles. The minor HCFCs and HFCs had a combined VMR equivalent to 0.107 ppbv fluorine; therefore profiles for their fluorine contribution were simulated by scaling the HCFC-22 profiles by a factor of 0.58.

[20] The procedure for estimating profiles described above is expected to introduce more error than direct measurements, although it should not be very large since the fluorine contribution from the combination of these species reaches a maximum of approximately 0.25 ppbv at the bottom of the stratosphere and decreases with altitude. It may be possible to develop a technique for the retrieval of some of these species, since averaging ACE FTS spectra of similar air masses results in spectra with further improvements to the

signal-to-noise ratio. However, the present approach should be sufficient for the purpose of calculating F_{TOT}.

2.8. SF₆

[21] ACE FTS version 2.2 SF₆ had a problem at the high-altitude end of the retrieval relating to the a priori profile that was used for the atmospheric layers above the highest retrieved altitude. After correcting the problem by using a more realistic a priori (as described below), SF₆ was re-retrieved for this work for the 7.5–30.5 km altitude range. Although the maximum mean VMR of SF₆ from ACE FTS measurements was only 0.00661 ppbv at 7.5 km in the tropics, with six fluorine atoms, this is equivalent to 0.04 ppbv fluorine. *Sen et al.* [1996], *Patra et al.* [1997], and *Burgess et al.* [2004] all report stratospheric SF₆ profiles, while *Zander et al.* [1992] reported that SF₆ decreased to zero near 20 km. According to *Ravishankara et al.* [1993] and *Morris et al.* [1995], SF₆ has a long lifetime in the stratosphere and is decomposed by UV absorption and electron reactions in the mesosphere. The *Patra et al.* [1997] results are the most consistent with a long stratospheric lifetime and decomposition beginning at the stratopause but the slope of the *Burgess et al.* [2004] profile most resembles the ACE FTS results in the lower stratosphere. A more recent paper by *Burgess et al.* [2006] shows SF₆ profiles with a shape similar to their earlier work. Therefore the new ACE FTS SF₆ a priori profiles, and extensions to the retrieval were based on a combination of the *Patra et al.* [1997] and *Burgess et al.* [2004] profiles, beginning near 30.5 km altitude and smoothly decreasing to zero at 49.5 km for the midlatitudes. In the tropics and high latitudes, a vertical shift was applied to the midlatitude extrapolation so that it coincided with the measured portion of the profile.

3. Results and Discussion

[22] Profiles of species listed above in the five latitude zones are available as auxiliary material.¹ Figure 4 shows

¹Auxiliary materials are available at <ftp://ftp.agu.org/apend/jd/2006jd007395>.

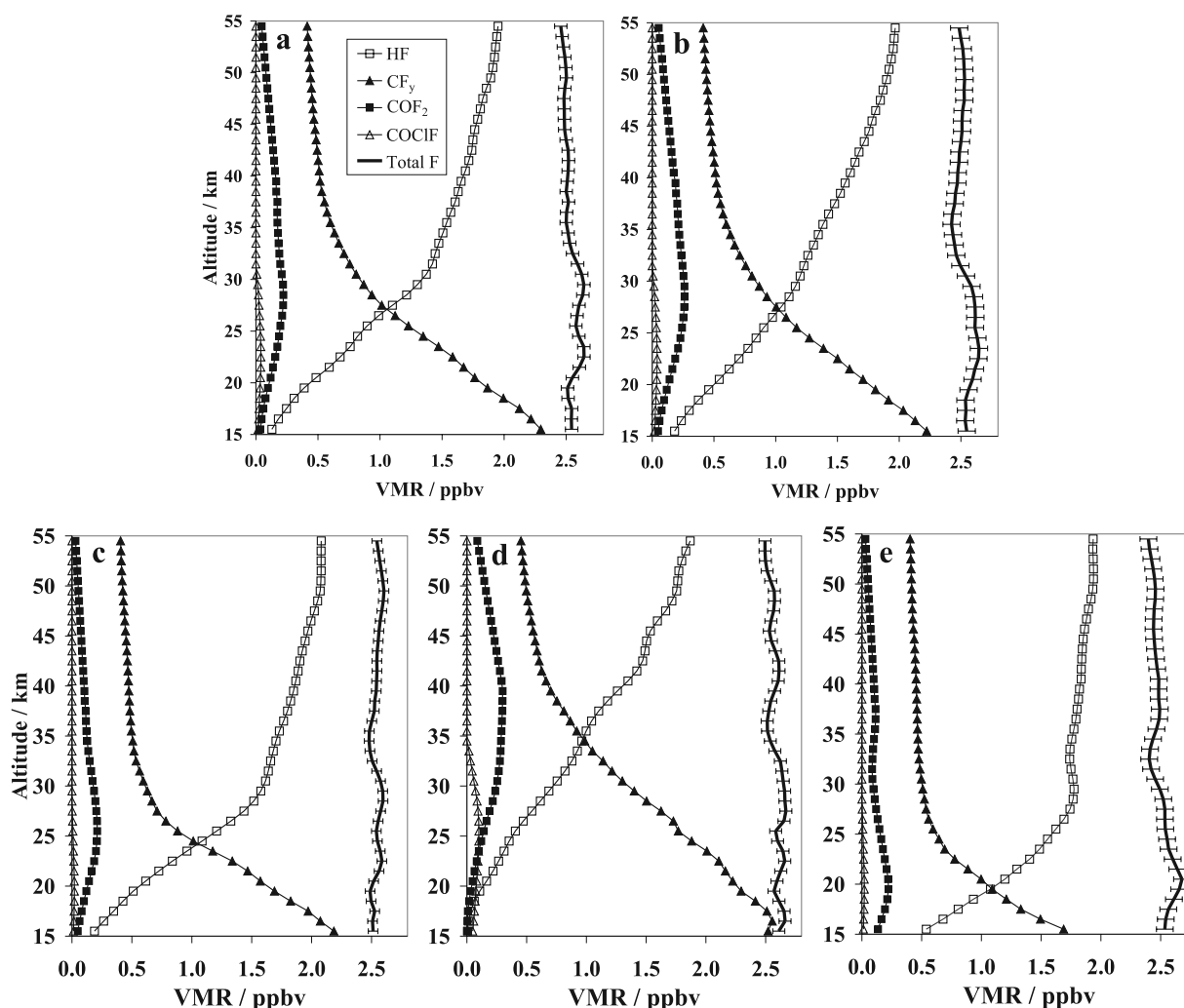


Figure 4. Stratospheric fluorine inventory for 2004: (a) northern midlatitudes (30° – 60° N), (b) southern midlatitudes (30° – 60° S), (c) northern high latitudes (60° – 82° N), (d) tropics (30° S– 30° N), and (e) southern high latitudes (60° – 82° S). SF_6 is not shown, but its contribution is included in the F_{TOT} profiles. Error bars on the F_{TOT} profiles indicate the 1σ variability.

HF, COF_2 , COClF, CF_y and F_{TOT} profiles in each latitude zone, indicating that CF_y dominates in the lower stratosphere while HF dominates in the upper stratosphere. Using retrieved temperature profiles, the altitudes of the tropopause and stratopause were determined, and by extension an appropriate altitude range (17.5–50.5 km) for determination of mean stratospheric F_{TOT} . The temperature minimum was used to define the tropopause, rather than the lapse rate as recommended by the WMO, to avoid placing the tropopause at very low altitudes during the polar winters. F_{TOT} as a function of altitude in each latitude zone is given in Table 3. Mean values of F_{TOT} in each zone ranging from 2.50 to 2.59 ppbv are given in Table 4. Aside from the highest value occurring in the tropics, there is no clear latitudinal dependence.

[23] In all latitude zones, stratospheric F_{TOT} nearly forms a straight line, where slight deviations from a line may result from atmospheric variability, error in the data or possibly missing fluorine species that make a small contribution. The very short lived species COHF and CF_3OH , which result from the dissociation of organic fluorine species [Tuazon and Atkinson, 1993], have not been included in this inventory and

may account for some missing fluorine in the midstratosphere. If F_{TOT} is fit to a straight line, it is essentially vertical with a very slight negative slope in ppbv/km (Table 4), in four of five latitude zones, the exception being the northern high latitudes. Negative slopes are qualitatively consistent with increasing fluorine over time since older air at high altitudes has a lower VMR than younger air at low altitudes; however, the slopes determined here are only marginally significant relative to their 1σ uncertainty. These very slight slopes are also highly dependent on the extrapolated profiles as well as the estimates of species not measured by the ACE FTS. Additional evidence for the continual increase in fluorine arises from the highest mean value of F_{TOT} occurring in the tropics which contains the youngest air if mean stratospheric circulation is considered. The lack of a clear pattern of latitudinal variation in the middle and high latitudes is consistent with the modeling work of Neu and Plumb [1999], which found greater mixing in the middle- and high-latitude stratosphere relative to the tropics. The reason for higher HF and F_{TOT} values in the northern hemisphere (especially at high latitudes) is not clear and could indicate a

Table 3. F_{TOT} as a Function of Altitude From 17.5 to 50.5 km in Five Latitude Zones

Altitude, km	Total Fluorine, ppbv				
	60°–82°N	30°–60°N	30°S–30°N	30°–60°S	60°–82°S
17.5	2.53	2.54	2.65	2.54	2.56
18.5	2.50	2.52	2.61	2.54	2.61
19.5	2.49	2.51	2.57	2.56	2.66
20.5	2.52	2.55	2.59	2.59	2.68
21.5	2.56	2.61	2.63	2.61	2.64
22.5	2.59	2.64	2.66	2.64	2.60
23.5	2.57	2.64	2.64	2.65	2.57
24.5	2.55	2.60	2.60	2.63	2.55
25.5	2.54	2.58	2.58	2.61	2.54
26.5	2.56	2.59	2.65	2.62	2.54
27.5	2.58	2.60	2.67	2.61	2.54
28.5	2.60	2.63	2.66	2.61	2.52
29.5	2.59	2.64	2.66	2.59	2.49
30.5	2.57	2.63	2.65	2.54	2.45
31.5	2.54	2.59	2.64	2.50	2.42
32.5	2.51	2.55	2.62	2.46	2.40
33.5	2.49	2.53	2.58	2.45	2.41
34.5	2.48	2.52	2.54	2.44	2.44
35.5	2.48	2.50	2.51	2.42	2.46
36.5	2.50	2.50	2.51	2.43	2.49
37.5	2.52	2.52	2.53	2.45	2.49
38.5	2.53	2.50	2.54	2.46	2.48
39.5	2.54	2.51	2.57	2.47	2.48
40.5	2.54	2.52	2.60	2.47	2.48
41.5	2.55	2.52	2.61	2.48	2.47
42.5	2.54	2.52	2.61	2.49	2.46
43.5	2.55	2.50	2.58	2.50	2.45
44.5	2.56	2.49	2.55	2.51	2.44
45.5	2.56	2.49	2.53	2.51	2.44
46.5	2.57	2.48	2.54	2.51	2.44
47.5	2.59	2.48	2.57	2.53	2.45
48.5	2.60	2.49	2.57	2.52	2.45
49.5	2.60	2.50	2.57	2.53	2.46
50.5	2.59	2.50	2.54	2.53	2.45

problem with the HF retrieval at high altitudes, or may be real atmospheric variability resulting from greater fluorine emissions in the northern hemisphere.

[24] The general decrease in signal-to-noise ratios with altitude for most species in ACE FTS spectra, made it necessary for us to extrapolate certain profiles. This makes little difference for F_{TOT} when species occur at low levels like SF_6 or CFC-113, but the COF_2 extrapolation which began at about 40 km has a large impact on high-altitude F_{TOT} . To ensure the validity of our mean stratospheric F_{TOT} values and slopes, the values were compared to equivalent values based on the 17.5–39.5 km range, which involved much less extrapolation. It indicated that the low-altitude range F_{TOT} values were within ± 0.02 ppbv from the values spanning the entire stratosphere.

[25] The 1σ precision of mean F_{TOT} is 0.04–0.07 ppbv, obtained using the method of error determination from Zander *et al.* [1996] for total stratospheric chlorine. It is

based on the standard deviation of points over a given altitude range and was adopted here as a reasonable estimate of the precision, but the absolute accuracy, which would include systematic errors from all sources for F_{TOT} is more difficult to determine. Propagating the uncertainty on each species to obtain the F_{TOT} uncertainty 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 accurately estimate the uncertainty for the modeled and extrapolated data.

[26] Perhaps the best simple estimate of the absolute uncertainty on F_{TOT} can be made based on the uncertainty of HF, which is the dominant contributor to F_{TOT} at high altitudes. The retrieval of HF utilized spectroscopic parameters from the HITRAN 2004 database [Rothman *et al.*, 2005]. The HF line intensities in HITRAN that lie in the microwindows shown in Table 1, have uncertainties in the 2–5% range, which translates to a maximum of 0.10 ppbv HF. The uncertainty contribution to the VMR of HF from the retrieval of pressure and temperature is estimated to be about 2% or about 0.04 ppbv for each quantity. An additional source of uncertainty for the HF retrieval comes from the precision of the fit, which reaches a maximum at high altitudes, but can be reduced by averaging multiple profiles. The error contribution from the precision of the fit for the northern midlatitude mean profile is 0.001 ppbv at 18 km, 0.004 ppbv at 30 km, and increases to 0.012 ppbv (or 0.5%) at 50 km. With the line intensities as the dominant source of error, combining the upper limit of all of these sources gives an accuracy of 0.10 ppbv for HF at 50 km, which includes both a systematic and random component. This value can be used to estimate the accuracy of the F_{TOT} values. On average, HF comprises 76% of F_{TOT} at 50 km (72–82% over the five latitude zones), so scaling the error would give an accuracy of 0.15 ppbv for F_{TOT} , which is equivalent to 6% of mean F_{TOT} . Although the fluorine contribution to F_{TOT} from HF differs with each latitude zone, it is reasonable to estimate that the accuracies should be comparable. This uncertainty is smaller than the estimated precision from random variability in the HF mean values at 50 km, but greater than the precision in F_{TOT} profiles over the 17.5–50.5 km range.

[27] As mentioned earlier, HALOE on UARS measured HF from 1991 to 2005 which has been used to determine stratospheric inorganic fluorine (F_y) [Russell *et al.*, 1996; Anderson *et al.*, 2000]. F_y is calculated from HALOE HF measured at 55 km altitude by dividing HF by a latitude-dependent HF/ F_y ratio. HF and F_y in the HALOE record continue to increase [Anderson and Russell, 2004], with 2004 global mean HF and F_y values of 1.75 ppbv and 1.97 ppbv respectively (J. Anderson, private communication, 2006). By latitudinally weighting the ACE FTS HF

Table 4. Number of Profiles (Prior to Removing Outliers for Each Species), Mean Total Fluorine and F_{TOT} Slope (With 1σ Precision) for Points From 17.5 to 50.5 km Altitude in Five Latitude Zones^a

Latitude	Profiles Used	Mean F_{TOT} , ppbv	Slope, ppbv/km	HF at 55 km, ppbv	F_y at 55 km, ppbv
60°–82°N	250	2.55 ± 0.04	+0.0011 ± 0.0006	2.08	2.11
30°–60°N	287	2.54 ± 0.05	−0.0036 ± 0.0007	1.96	1.99
30°S–30°N	273	2.59 ± 0.05	−0.0027 ± 0.0007	1.87	1.95
30°–60°S	238	2.53 ± 0.07	−0.0037 ± 0.0010	1.97	2.02
60°–82°S	171	2.50 ± 0.07	−0.0056 ± 0.0008	1.94	1.97

^aACE FTS HF and F_y at 55 km are also given.

values in Table 4, a global mean value of 1.95 ppbv for HF at 55 km was determined. This is 11% higher than the HALOE HF value, similar to earlier ACE and HALOE HF comparisons [McHugh *et al.*, 2005]. In contrast, the ACE FTS global mean F_y of 2.00 ppbv is much closer to the HALOE value since our F_y at 55 km only consists of HF and COF₂ resulting in higher HF/ F_y ratios. It is not clear which species in addition to HF and COF₂ contribute to F_y at 55 km, but organic species such as CHClF₂, CF₄, CF₃CF₃, C₃F₈ and *c*-C₄F₈ account for 0.38–0.46 ppbv of F_{TOT} at 55 km.

4. Conclusions

[28] This work describes an inventory of global stratospheric fluorine including organic and inorganic species in five latitude zones during the period of February 2004 to January 2005 inclusive, based on measurements by the ACE FTS, supplemented by altitude extensions based on modeling work, and some calculated profiles for minor species. This fluorine inventory includes several species that have not been included in past fluorine inventories due to the changing composition of trace gases in the atmosphere as well as the unique ability of the ACE FTS to retrieve these species. HFC-134a is one species included in this fluorine inventory for which retrieved profiles from space-based measurements are presented for the first time. The sum of all significant fluorine-containing species at each altitude from 17.5 to 50.5 km, nearly makes a straight line, typically with a slight negative slope. Averaging these points gives mean stratospheric F_{TOT} values for each latitude zone ranging from 2.50 to 2.59 ppbv, with a 1σ variability of 0.04–0.07 ppbv and an estimated absolute accuracy of 0.15 ppbv. The highest mean F_{TOT} is found in the tropics, and most F_{TOT} slopes are negative, both of which are qualitatively consistent with increasing levels of stratospheric fluorine and the mean global stratospheric circulation pattern.

[29] **Acknowledgments.** We would like to thank the Canadian Space Agency (CSA) for funding the ACE mission and the Natural Sciences and Engineering Research Council (NSERC) of Canada for their funding contribution. Support at UW was provided by the NSERC-Bomem-CSA-MSR Research Chair in Fourier transform spectroscopy. R.N. acknowledges direct support from NSERC and the CSA. University of Liege work was supported by the Belgian Federal Science Policy Office. We also thank J. Anderson for providing HALOE HF values.

References

- Anderson, J., and J. M. Russell III (2004), Long term changes of HCl and HF as observed by HALOE, in *Ozone*, vol. II, *Proceedings of the XX Quadrennial Ozone Symposium, Kos, Greece, 1–8 June 2004*, edited by C. S. Zerefos, pp. 223–224, Univ. of Athens, Athens.
- Anderson, J., J. M. Russell III, S. Solomon, and L. E. Deaver (2000), Halogen Occultation Experiment confirmation of stratospheric chlorine decreases in accordance with the Montreal Protocol, *J. Geophys. Res.*, *105*, 4483–4490.
- Bernath, P. F., et al. (2005), Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, *32*, L15S01, doi:10.1029/2005GL022386.
- Boone, C. D., R. Nassar, K. A. Walker, Y. Rochon, S. D. McLeod, C. P. Rinsland, and P. F. Bernath (2005), Retrievals for the Atmospheric Chemistry Experiment Fourier transform spectrometer, *Appl. Opt.*, *44*, 7218–7231.
- Brown, L. R., et al. (1987), Molecular line parameters for the atmospheric trace molecule spectroscopy experiment, *Appl. Opt.*, *26*, 5154–5182.
- Brown, L. R., et al. (1996), The 1995 Atmospheric Trace Molecule Spectroscopy (ATMOS) linelist, *Appl. Opt.*, *35*, 2828–2848.
- Burgess, A. B., R. G. Grainger, A. Dudhia, V. H. Payne, and V. L. Jay (2004), MIPAS measurement of sulfur hexafluoride (SF₆), *Geophys. Res. Lett.*, *31*, L05112, doi:10.1029/2003GL019143.
- Burgess, A. B., R. G. Grainger, and A. Dudhia (2006), Zonal mean atmospheric distribution of sulfur hexafluoride (SF₆), *Geophys. Res. Lett.*, *33*, L07809, doi:10.1029/2005GL025410.
- Clerbaux, C., R. Colin, P. C. Simon, and C. Granier (1993), Infrared cross sections and global warming potentials of 10 alternative hydrohalocarbons, *J. Geophys. Res.*, *98*(D6), 10,491–10,497.
- Coeur, P. F., C. Clerbaux, and R. Colin (2003), Spectroscopic measurements of halocarbons and hydrohalocarbons by satellite-borne remote sensors, *J. Geophys. Res.*, *108*(D4), 4130, doi:10.1029/2002JD002649.
- Dufour, G., C. D. Boone, and P. F. Bernath (2005), First measurements of CFC-113 and HCFC-142b from space using ACE-FTS infrared spectra, *Geophys. Res. Lett.*, *32*, L15S09, doi:10.1029/2005GL022422.
- Kaye, J. A., A. R. Douglass, C. H. Jackman, R. S. Stolarski, R. Zander, and G. Roland (1991), Two-dimensional model calculation of fluorine-containing reservoir species in the stratosphere, *J. Geophys. Res.*, *96*, 12,865–12,881.
- McHugh, M., B. Magill, K. A. Walker, C. D. Boone, P. F. Bernath, and J. M. Russell III (2005), Comparison of atmospheric retrievals from ACE and HALOE, *Geophys. Res. Lett.*, *32*, L15S10, doi:10.1029/2005GL022403.
- Morris, R. A., et al. (1995), Effects of electron and ion reactions on atmospheric lifetimes of fully fluorinated compounds, *J. Geophys. Res.*, *100*(D1), 1287–1294.
- Nassar, R., P. F. Bernath, C. D. Boone, G. L. Manney, S. D. McLeod, C. P. Rinsland, R. Skelton, and K. A. Walker (2005), ACE-FTS measurements across the edge of the winter 2004 Arctic vortex, *Geophys. Res. Lett.*, *32*, L15S05, doi:10.1029/2005GL022671.
- Nassar, R., et al. (2006), A global inventory of stratospheric chlorine in 2004, *J. Geophys. Res.*, doi:10.1029/2006JD007073, in press.
- Nemchinov, V., and P. Varanasi (2004), Absorption cross-sections of HFC-134a in the spectral region between 7 and 12 μm , *J. Quant. Spectrosc. Radiat. Transfer*, *83*, 285–294, doi:10.1016/S0022-4073(02)00356-4.
- Neu, J. L., and R. A. Plumb (1999), Age of air in a “leaky pipe” model of stratospheric transport, *J. Geophys. Res.*, *104*, 19,243–19,255.
- Patra, K. P., S. Lal, B. H. Subbaraya, C. H. Jackman, and P. Rajaratnam (1997), Observed vertical profile of sulphur hexafluoride (SF₆) and its atmospheric applications, *J. Geophys. Res.*, *102*, 8855–8859.
- Ravishankara, A. R., S. Solomon, A. A. Turnipseed, and R. F. Warren (1993), Atmospheric lifetimes of long-lived halogenated species, *Science*, *259*, 194–199.
- Rinsland, C. P., C. Boone, R. Nassar, K. Walker, P. Bernath, E. Mahieu, R. Zander, J. C. McConnell, and L. Chiou (2005), Trends of HF, HCl, CCl₂F₂, CCl₃F, CHClF₂ (HCFC-22), and SF₆ in the lower stratosphere from Atmospheric Chemistry Experiment (ACE) and Atmospheric Trace Molecule Spectroscopy (ATMOS) measurements near 30°N latitude, *Geophys. Res. Lett.*, *32*, L16S03, doi:10.1029/2005GL022415.
- Rinsland, C. P., E. Mahieu, R. Zander, R. Nassar, P. Bernath, C. Boone, and L. S. Chiou (2006a), Long-term stratospheric carbon tetrafluoride (CF₄) increase inferred from 1985–2004 infrared space-based solar occultation measurements, *Geophys. Res. Lett.*, *33*, L02808, doi:10.1029/2005GL024709.
- Rinsland, C. P., et al. (2006b), Spectroscopic detection of COClF in the tropical and mid-latitude lower stratosphere, *J. Quant. Spectrosc. Radiat. Transfer*, in press.
- Rothman, L. S., et al. (2005), The HITRAN 2004 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer*, *96*, 139–204.
- Rummukainen, M. (1996), Modeling stratospheric chemistry in a global three-dimensional chemical transport model, SCTM-1: Model development, *Finn. Meteorol. Inst. Contrib.*, *19*, 206 pp.
- Russell, J. M., III, et al. (1996), Validation of hydrogen fluoride measurements made by the Halogen Occultation Experiment from the UARS platform, *J. Geophys. Res.*, *101*, 10,163–10,174.
- Sen, B., G. C. Toon, J.-F. Blavier, E. L. Fleming, and C. H. Jackman (1996), Balloon-borne observations of midlatitude fluorine abundance, *J. Geophys. Res.*, *101*, 9045–9054.
- Stolarski, R. S., and R. D. Rundel (1975), Fluorine photochemistry in the stratosphere, *Geophys. Res. Lett.*, *22*, 385–388.
- Tuazon, E. C., and R. Atkinson (1993), Tropospheric transformation products of a series of hydrofluorocarbons and hydrochlorofluorocarbons, *J. Atmos. Chem.*, *17*, 179–199.
- Weisenstein, D. K., M. K. W. Ko, and N.-D. Sze (1992), The chlorine budget of the present-day atmosphere: A modeling study, *J. Geophys. Res.*, *97*, 2547–2559.
- World Meteorological Organization (2003), Scientific assessment of ozone depletion: 2002, *Global Ozone Res. Monitor. Proj. Rep.* *47*, Geneva, Switzerland.
- Zander, R., M. R. Gunson, C. B. Farmer, C. P. Rinsland, F. W. Irion, and E. Mahieu (1992), The 1985 chlorine and fluorine inventories in the stratosphere based on ATMOS observations at 30° north latitude, *J. Atmos. Chem.*, *15*, 171–186.

Zander, R., et al. (1996), The 1994 northern mid-latitude budget of stratospheric chlorine derived from ATMOS/ATLAS-3 observations, *Geophys. Res. Lett.*, 23, 2357–2360.

P. F. Bernath, C. D. Boone, S. D. McLeod, and R. Skelton, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada N2L 3G1.

P. Duchatelet, Institute of Astrophysics and Geophysics, University of Liege, Allée du 6 Aout, 17, B-4000 Liege, Belgium.

R. Nassar, Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA. (ray@io.as.harvard.edu)

C. P. Rinsland, NASA Langley Research Center, Mail Stop 401A, 21 Langley Boulevard, Hampton, VA 23681, USA.

K. A. Walker, Department of Physics, University of Toronto, Toronto, ON, Canada M5S 3J3.