

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

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Received 11 January 2005; revised 15 March 2005; accepted 6 April 2005; published 22 June 2005.

[1] Volume mixing ratios (VMRs) of HF, HCl, CCl₂F₂, CHClF₂ (HCFC-22), and SF₆ in the lower stratosphere have been derived from solar occultation measurements recorded with spaceborne high resolution Fourier transform spectrometers. Atmospheric Chemistry Experiment (ACE) VMRs measured during 2004 have been compared with those obtained in 1985 and 1994 by the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument. Trends are estimated by referencing the measured VMRs to those of the long-lived constituent N₂O to account for variations in the dynamic history of the sampled air masses. Pressure-gridded measurements covering 10–100 hPa (~16 to 30 km altitude) were used in the analysis that includes typically 25°N–35°N latitude. The VMR changes provide further evidence of the impact of the emission restrictions imposed by the Montreal Protocol and its strengthening amendments and adjustments and are consistent with model predictions and known sources and sinks of halocarbons. Decreases in the lower stratospheric mixing ratios of CCl₃F and HCl are measured in 2004 with respect to 1994, providing important confirmation of recent ground-based solar absorption measurements of a decline in inorganic chlorine. Trends estimates are compared with other reported measurements and model predictions. **Citation:** 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.

1. Introduction

[2] The potential for recording high spectral resolution infrared solar occultation measurements from space was pioneered by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer (FTS) which flew successfully during four U.S. shuttle flights, Spacelab 3 from April 29–May 6, 1985, the Atmospheric Laboratory for Science and Applications (ATLAS) 1 mission from 24 March–3 April 1992, the ATLAS 2 mission from 8–16 April 1993, and the ATLAS 3 mission from 8–14 November 1994 [Gunson *et al.*, 1996]. Measurements at 0.01 cm⁻¹ spectral resolution) with a vertical resolution of 3–4 km were recorded in 2.2 s intervals covering altogether 600–4800 cm⁻¹.

[3] A similar set of infrared FTS measurements is now being recorded by the Atmospheric Chemistry Experiment (ACE), also known as SCISAT-1. This Canadian designed and built satellite was successfully launched on August 12, 2003 into a 74° inclined orbit at 650 km altitude [Bernath *et al.*, 2005]. The ACE FTS operates at 0.02 cm⁻¹ resolution from occultations covering 750–4400 cm⁻¹.

[4] An important geographic measurement overlap occurred near 30°N latitude during the ATMOS 1985, ATMOS 1994, and ACE 2004 missions. The purpose of this paper is to report trends of HF, HCl, CCl₂F₂, CCl₃F, CHClF₂, and SF₆ from measured volume mixing ratios (VMRs) of the target gases to those of the long-lived constituent N₂O to account for variations in the dynamic history of the sampled air masses.

2. ATMOS/ACE Trend Analysis

[5] The approach for the analysis of ATMOS and ACE observations for trends is similar to the method in an earlier

Table 1. ATMOS/ACE Lower Stratospheric VMRs and Uncertainties Near 30°N Latitude

Year	HF (ppbv)	HCl (ppbv)	CCl ₂ F ₂ (ppbv)	CCl ₃ F (ppbv)	CHClF ₂ (ppbv)	SF ₆ (pptv)
1985	0.156 ± 0.027	0.892 ± 0.060	0.222 ± 0.015	0.094 ± 0.052	0.042 ± 0.004	1.22 ± 0.113
1994	0.377 ± 0.036	1.355 ± 0.092	0.305 ± 0.019	0.166 ± 0.069	0.097 ± 0.002	2.69 ± 0.066
2004	0.462 ± 0.043	1.239 ± 0.083	0.303 ± 0.020	0.167 ± 0.052	0.160 ± 0.005	5.12 ± 0.078

1 ppbv = 10⁻⁹ per volume; 1 pptv = 10⁻¹² per volume. Uncertainties are computed by dividing the standard deviation by the square root of the number of overlapping intervals.

work comparing ATMOS 1985 and 1994 VMRs [Rinsland *et al.*, 1996]. Target VMRs near 30°N latitude have been compared with those of N₂O, taking into account the latter's trend in the lower stratosphere as a function of time. We assumed a linear N₂O volume mixing ratio growth rate of 0.75 ppbv yr⁻¹ (1 ppbv = 10⁻⁹ per volume) since 1977 based on measurements from Climate Monitoring and Diagnostics Laboratory (CMDL) surface stations [Elkins *et al.*, 2004]. The corrected N₂O VMRs are noted hereafter by N₂O*. ATMOS version 2 results adopted in previously [Rinsland *et al.*, 1996] were replaced by version 3 retrievals [Irion *et al.*, 2002] because of their improved precision. ACE version 1 retrievals (C. R. Boone *et al.*, Retrievals for the Atmospheric Chemistry Experiment, submitted to *Applied Optics*, 2005) and ATMOS retrievals provide VMRs with statistical uncertainties from algorithms that retrieve profiles from fits to multiple species in microwindows over pre-specified altitude ranges.

[6] For each molecule, a plot was first generated to examine the distribution of VMR vs. N₂O*. Selection criteria were adopted to eliminate data points with limited precision based on statistical uncertainty. ACE provided the most measurements with fewer for ATLAS 3, and the fewest for Spacelab 3. VMRs binned by 5 ppbv N₂O* increments to obtain averages and standard deviations reported in Table 1. Systematic errors in the trend include differences in the spectroscopic parameters assumed in generating the two databases, algorithm differences, and uncertainty in the assumed trend for N₂O.

[7] The exponential trend model assumed in the previous study [Rinsland *et al.*, 1996] is not appropriate to characterize the evolution of the volume mixing ratio V over the two decade time period of the combined ATMOS/ACE database. Instead, we adopted an empirical polynomial expression

$$V = a_0 + a_1(t - t_0) + a_2(t - t_0)^2 \quad (1)$$

to determine the time dependence of V from fits to the 1985, 1994, and 2004 volume mixing ratios. In equation (1), t is time and t₀ is the time of the measurements from the first ATMOS mission. The coefficients a₀, a₁, and a₂ and their statistical uncertainties were determined from a

least-squares fit to each measurement set as described in the next section.

3. Results

[8] Lower stratospheric VMRs and uncertainties for each molecule and time period are presented in Table 1 based on the VMR binning procedure comparing measurements of overlapping N₂O* intervals from ~25–35°N latitude. Trends are reported in Table 2 expressed as a percentage change with respect to the best fit obtained with Equation 1 and the best-fit coefficients a₀, a₁, and a₂. The reported trend and corresponding uncertainties in Table 2 are computed by taking the derivative of V from equation 1. In Figures 1–6, N₂O* is the N₂O volume mixing ratio after correcting the measured N₂O volume mixing ratio of each time period for the temporal increase in N₂O as described in section 2.

3.1. Hydrogen Fluoride (HF)

[9] Figure 1 illustrates the ATMOS/ACE lower stratospheric HF vs. N₂O* relation derived for 1985, 1994, and 2004. Dashed lines connect average HF versus average N₂O VMRs from overlapping 5 ppbv N₂O* increments. Vertical error bars denote VMR standard deviations. Only volume mixing ratios with overlapping N₂O* increments were used in the analysis and are displayed. Sampling was limited to two occultations for Spacelab 3, 3 occultations for ATLAS 3, and 44 ACE occultations with the latitude range of the occultations reported at top.

[10] Although fluorine does not catalytically destroy ozone, HF in combination with COF₂ provides a measure of the changes in total inorganic fluorine VMR with the total fluorine VMR given approximately by the HF VMR plus two times the COF₂ VMR [World Meteorological Organization (WMO), 2002, section 1.2.6]. The HF average VMRs in 1994 and 2004 are (2.417 ± 0.478) and (2.962 ± 0.582) times those measured in 1985. A slowdown in the HF increase rate with time in percent occurred during the 1990s compared with the 1970s consistent both with ground-based trend measurements [Rinsland *et al.*, 2002] and model predictions [Gunson *et al.*, 1996, Figure 3].

3.2. Hydrogen Chloride (HCl)

[11] Figure 2 presents the ATMOS/ACE lower stratospheric HCl VMRs vs. N₂O* for the 3 time periods in the same format as Figure 1. Our analysis relies on 3 Spacelab

Table 2. Rates of Change and Uncertainties (percent yr⁻¹) From the ATMOS/ACE Lower Stratospheric VMRs Near 30°N Latitude Assuming Equation 1

Year	HF Trend (% yr ⁻¹)	HCl Trend (% yr ⁻¹)	CCl ₂ F ₂ Trend (% yr ⁻¹)	CCl ₃ F Trend (% yr ⁻¹)	CHClF ₂ Trend (% yr ⁻¹)	SF ₆ Trend (% yr ⁻¹)
1985	20.52 ± 7.88	9.13 ± 2.73	6.14 ± 2.34	12.61 ± 4.24	14.57 ± 4.10	10.28 ± 2.28
1994	4.49 ± 4.26	1.59 ± 2.37	1.56 ± 2.27	2.58 ± 3.11	6.35 ± 2.24	7.48 ± 1.33
2004	0.02 ± 5.48	-3.62 ± 4.08	-1.67 ± 3.60	-2.42 ± 4.80	3.92 ± 2.08	5.57 ± 1.07

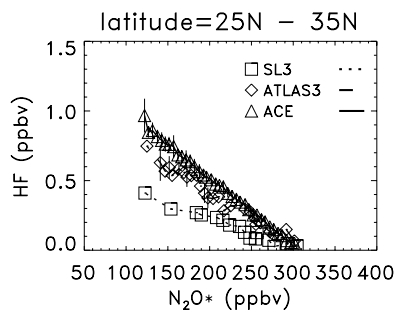


Figure 1. ATMOS 1985 (open triangles), ATMOS 1994 (ATLAS 3), and ACE 2004 lower stratospheric HF volume mixing ratios vs. N_2O^* . Open squares, open diamonds and open triangles display averages in overlapping 5 ppbv N_2O^* intervals with vertical lines indicating corresponding standard deviations.

3, 7 ATLAS 3, and 46 ACE occultations. The highest lower stratospheric HCl volume mixing ratio was measured in 1994, with a lower values measured in 2004 with respect to 1994. Average lower stratospheric VMRs for 1994 and 2004 are (1.519 ± 0.145) and (1.389 ± 0.132) relative to the 1985 value. The observation of a peak in lower stratospheric HCl is consistent with an observed stabilization [Rinsland et al., 2003a] followed by a measured $(-0.7 \pm 0.3\% \text{ yr}^{-1}$, 1 sigma) decrease in the inorganic chlorine loading since the late 1996 maximum inferred from Jungfraujoch measurements and two dimensional model predictions for HCl+ClONO₂ total columns above the site at 46.5°N latitude [Mahieu et al., 2004]. The sum of the two reservoir species accounts for more than 95% of the inorganic chlorine in the northern mid-latitude stratosphere [Zander et al., 1996]. The fit to the 3 calculated ATMOS+ACE data points with Equation 1 indicates a broad HCl maximum and evidence for the onset of a decline, consistent with the inorganic chlorine maximum above the Jungfraujoch and the related model calculations reported in that study, providing evidence that the Montreal Protocol and its strengthening amendments and adjustments have been successful in slowing and then reversing the trend in lower stratospheric chlorine.

3.3. Chlorofluorocarbon 12 (CCl_2F_2)

[12] The measurements displayed in Figure 3 are derived from 6 Spacelab 3 occultations, 9 ATLAS 3 occultations, and 45 ACE occultations. The results show a significant slowing in the rate of CCl_2F_2 increase between 1985 and

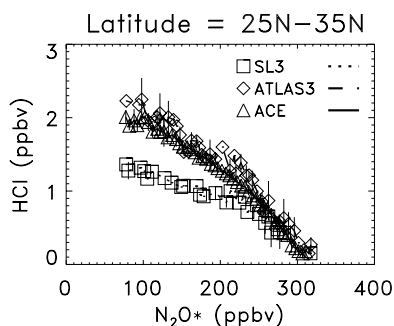


Figure 2. Same as Figure 1 except for HCl.

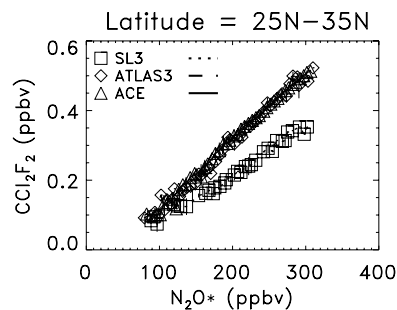


Figure 3. Same as Figure 1 except for CCl_2F_2 .

2004, consistent with infrared solar absorption measurements from the Jungfraujoch through 2000 [Zander et al., 2002] and Kitt Peak through October 2003 [Rinsland et al., 2005a]. We infer mean VMRs for 1994 and 2004 that are (1.374 ± 0.126) and (1.365 ± 0.129) times the value measured 1985 value. The trend is also consistent with the slowing of the rate of increase measured in situ at surface sites [WMO, 2002, Table 1-1]. As a consequence of its long atmospheric lifetime (~ 100 years), model scenarios predict significant atmospheric CCl_2F_2 levels will persist for decades, with a slow decline at the surface after ~ 2003 [WMO, 2002, Table 1.16 and Figure 1.22] despite emission restrictions imposed emission restrictions.

3.4. Chlorofluorocarbon 11 (CCl_3F)

[13] As displayed in Figure 4, ATMOS and ACE measurements provide evidence that the lower stratospheric loading of CCl_3F leveled off after 1994. Our analysis is based on 3 Spacelab 3 occultations, 8 ATLAS 3 occultations, and 44 ACE occultations. VMRs for 1994 and 2004 are (1.766 ± 1.222) and (1.777 ± 1.128) times the 1994 value. A slow decline in the lower stratospheric CCl_3F VMR is consistent with a decrease in the surface CCl_3F loading [WMO, 2002, Table 1.1] and the time lag for transport of surface air to the lower stratosphere.

3.5. Hydrochlorofluorocarbon 22 ($CHClF_2$)

[14] Figure 5 displays the combined ATMOS and ACE time CHF_2Cl series of 1985, 1994, and 2004 measurements vs. N_2O^* . Our analysis uses a single occultation for Spacelab 3, 8 occultations for ATLAS 3, and 45 ACE occultations. The 3 sets of measurements show a continued rise in the lower stratospheric $CHClF_2$, consistent with surface measurements and ground-based solar absorption measurements [Zander et al., 2002; WMO, 2002, Figure 1-2;

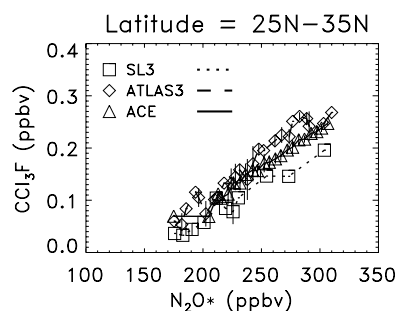


Figure 4. Same as Figure 1 except for CCl_3F .

Rinsland *et al.*, 2005b] with a model-projected continued rise, but with a significant uncertainty in the future long-term trend resulting from large lifetime ranges and uncertainties in model parameters and in industrial emission estimates [WMO, 2002, Figure 1–13]. The VMRs (Table 1) from 1994 and 2004 correspond to (2.310 ± 0.225) and (3.810 ± 0.382) times the value from 1985, a decline in the rate increase as a percentage of the best-fit VMR (Table 2).

3.6. Sulfur Hexafluoride (SF₆)

[15] Figure 6 presents the SF₆ vs. N₂O* measurements from the two ATMOS missions and ACE. The analysis is based on measurements from a single Spacelab 3 occultation, 7 occultations from ATLAS 3, and 15 ACE occultations. The measurements (Table 1) indicate a continuous rapid rise in SF₆ lower stratospheric accumulation with VMRs from 1994 and 2004 relative to 1985 equal to (2.205 ± 0.211) and (4.197 ± 0.394) , respectively. Our measurement of a continued rise in the lower stratosphere is consistent with surface measurements [WMO, 2002, Table 1.12] and ground-based solar measurements [Zander *et al.*, 2002; Rinsland *et al.*, 2003b] and is of concern because of its long lifetime (~3200 years), its strong infrared absorption cross section, and large global warming potential [WMO, 2002, Figure 1–21].

4. Summary and Conclusions

[16] Lower stratospheric VMRs of HF, HCl, CCl₂F₂, CCl₃F, CHClF₂, and SF₆ have been inferred by comparing measured values from ATMOS 1985, ATMOS 1994, and ACE 2004 measurements near 30°N latitude with corresponding values for N₂O, taking into account the increase of N₂O as a function of time. Continued increases for HF, CCl₂F₂, CHClF₂, and SF₆ and decreases are observed for CCl₃F and HCl between 1994 and 2004, consistent with other recently reported measurements and model predictions. Although the present results have limited spatial and temporal sampling, the lower stratospheric trends provide evidence for consistency with respect to model predictions and other long-term trend studies. They are also in line with expectations resulting from the implementation of the Montreal Protocol and its strengthening amendments and adjustments and recent international assessments [e.g., WMO, 2002]. Additional measurements are needed to confirm the trends inferred from these limited, though precise measurements. There also remains a need to continue monitoring the upper atmosphere to verify compliance

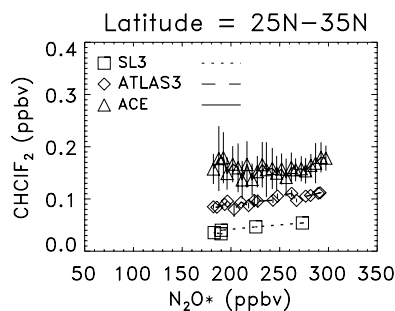


Figure 5. Same as Figure 1 except for CHClF₂.

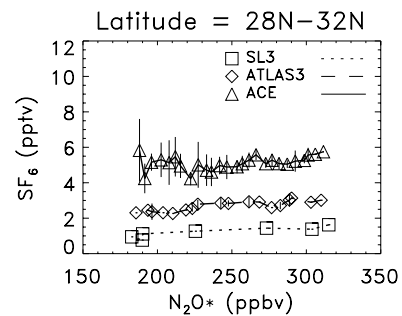


Figure 6. Same as Figure 1 except for SF₆.

with these protocols and quantify the impact of climate change on the chemistry and dynamics of the stratosphere.

[17] **Acknowledgments.** NASA Langley Research Center was supported by NASA's Upper Atmosphere Research Program, the Atmospheric Chemistry, Modeling, and Analysis Program (ACMAP), and the Tropospheric Emission Spectrometer (TES). The University of Liège was primarily supported by the Belgian Federal Science Policy Office and the EC-Directorate General, both in Brussels. Funding for ACE is provided by the Canadian Space Agency and the Natural Sciences and Engineering Research (NSERC) of Canada. Support at Waterloo was also provided by the NSERC-Bomem-CSA-MSC Industrial Research Chair in Fourier Transform Spectroscopy.

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