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Trends in atmospheric halogen containing gases since 2004

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ABSTRACT

The changes in the atmospheric concentration of 16 halogenated gases in the atmosphere have been determined using measurements made by the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS). ACE-FTS has been used to measure the change in concentration between 2004 and 2010 of CCl₄, CF₄, CCl₃F (CFC-11), CCl₂F₂ (CFC-12), C₂Cl₃F₃ (CFC-113), CH₃Cl, ClONO₂, COF₂, COCl₂, COClF (HCFC-22), CH₃CCl₂F (HCFC-141b), CH₃CClF₂ (HCFC-142b), HCl, HF and SF₆ between 30°N and 30°S. ACE-FTS measurements were compared to surface measurements made by the AGAGE network and output from the SLIMCAT three-dimensional (3-D) chemical transport model, which is constrained by similar surface data. ACE-FTS measurements of CFCs show declining trends which agree with both AGAGE and SLIMCAT values. There are problems with the ACE-FTS retrievals of CFC-113 and HCFCs, with work currently ongoing to correct these problems. At lower altitudes the volume mixing ratio (VMR) of these species increase with altitude. This is due to problems with the retrievals at high beta angle (the angle between the orbital plane and the Earth–Sun vector). Although some of the retrievals have problems, we are confident that the trends are generally reliable. The concentrations of HCFCs appear to be increasing with ACE-FTS, SLIMCAT and AGAGE all showing positive trends. ACE-FTS measurements of the decomposition products (COFCl and COCl₂) do not show any significant trends. SLIMCAT data show a negative trend for COFCl which corresponds to the decrease in CFC-11, its assumed major source, during this time. COF₂ measurements from ACE-FTS show an increasing trend, while SLIMCAT shows a decreasing trend again linked to its assumed production from CFCs. ClONO₂ is highly photosensitive, thus the ACE-FTS occultations have been divided into local morning and evening occultations. Evening measurements of ClONO₂ show a decreasing trend in VMR, while morning measurements show an increasing trend. The reason for this difference is not understood at this time. The SLIMCAT output used in this study was not saved as local sunrise and sunset: therefore, only 24 h mean fields are available for ClONO₂. These SLIMCAT data show a decreasing trend. SLIMCAT and ACE-FTS both show an increasing trend in the VMR of HF and a decreasing trend in the VMR of HCl. These results illustrate the success of the Montreal Protocol in reducing ozone depleting substances. The reduction in anthropogenic chlorine emissions has led to a decrease in the VMR of stratospheric HCl.

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The replacement of CFCs with HCFCs has led to an increase in the VMR of HF in the stratosphere. As chlorine-containing compounds continue to be phased out and replaced by fluorine-containing molecules, it is likely that total atmospheric fluorine will continue increasing in the near future.

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1. Introduction

In 1974 Molina and Rowland [1] suggested that chlorofluorocarbons (CFCs) would lead to the destruction of stratospheric ozone. It was the dramatic discovery of the Antarctic 'ozone hole' in 1985 [2] that illustrated the destructive power of long-lived halogenated gases. At this time, CFCs were widely used for a variety of applications such as in air conditioners and as foam blowing agents. The 1987 Montreal Protocol on substances that deplete the ozone layer and its subsequent amendments and adjustments [3] have phased out the production of CFCs and halons. As a temporary measure, CFCs have been replaced by hydrochlorofluorocarbons (HCFCs) that have shorter atmospheric lifetimes because they react with the OH radical. However, HCFCs still destroy stratospheric ozone and they are in turn being phased out and replaced by hydrofluorocarbons (HFCs). Because they contain no chlorine, HFCs have no direct chemical effect on stratospheric ozone. It is the UV photolysis of halogenated source gases in the stratosphere that releases reactive F, Cl and Br atoms, but F rapidly forms the very stable HF molecule so only Cl and Br atoms lead to ozone destruction. Iodine-containing gases would also destroy stratospheric ozone, but these molecules have such a short atmospheric lifetime that they do not reach the stratosphere [4].

Although HFCs do not destroy stratospheric ozone they are very powerful greenhouse gases, as are CFCs and HCFCs. Indeed, taken as a group, halocarbons are about equal to tropospheric ozone in terms of a positive anthropogenic radiative forcing, and only CO₂ and CH₄ are more important [5]. The Montreal Protocol has been successfully implemented since 1987 with the aim of eradicating the use of substances which are damaging to the ozone layer. It has fortuitously had a larger impact on reducing greenhouse gas emissions than the first commitment period of the Kyoto Protocol [6]. However, the Montreal Protocol has also led to rapidly increasing concentrations of HFCs that have serious implications for climate change. Velders et al. [7] predict that global-warming-potential-weighted HFC emissions in 2050 could be 9–19% of global CO₂ emissions.

It is crucial to assess the performance of the Montreal Protocol in reducing the concentrations of ozone depleting substances (ODSs) and to monitor the recovery of the ozone layer. Therefore, every 4 years the World Meteorological Organisation (WMO) and the United Nations Environmental Programme (UNEP) publish a report on the "Scientific Assessment of Ozone Depletion", carried out by the Scientific Assessment Panel (SAP) of UNEP. The 2010 report was released in early January 2011 [4] and as usual relies heavily on high precision in-situ surface measurements of ODSs, with relatively modest contributions from satellite observations.

High quality in situ measurements offer accurate and precise measurements of surface concentrations of ODS from a number of sites around the globe. Remote sensing from orbit allows the concentrations of these substances to be measured as a function of altitude, generally offering extensive spatial coverage, but with reduced accuracy and precision. Both spatial and temporal averaging of satellite data improves measurement precision, but often significant biases remain due to spectroscopic errors in the retrievals. Limb sounding satellite instruments such as MIPAS [8] and solar occultation instruments such as ACE-FTS [9,10] offer extensive four-dimensional (latitude, longitude, altitude and time) coverage of the atmosphere which is only possible from orbit. In particular, these satellite instruments make routine measurements of atmospheric composition in the stratosphere, where ozone depletion occurs.

2. The Atmospheric Chemistry Experiment

The Atmospheric Chemistry Experiment (ACE) Fourier transform spectrometer (FTS) was launched on board the satellite SCISAT-1 in August 2003. The main goal of the mission is to study 'the chemical and dynamical processes that control the distribution of ozone in the stratosphere and upper troposphere' [9]. SCISAT-1 is in a circular low earth orbit with an inclination of 74° [10], giving ACE almost global coverage from the Antarctic to the Arctic.

ACE builds on the legacy of the Atmospheric Trace Molecule Spectroscopy instrument (ATMOS) which was carried onboard NASA Space Shuttles on four different occasions (1985, 1991, 1992 and 1993). The pioneering observations of many halogenated gases (HF, HCl, HOCl, ClONO₂, CH₃Cl, CF₄, CFC-12, CFC-11, CCl₄, COF₂, HCFC-22 and SF₆) from orbit were made by ATMOS [11]. ACE's primary instrument is a high-resolution (0.02 cm⁻¹) FTS which operates between 750 and 4400 cm⁻¹. ACE-FTS operates in solar occultation mode, in which atmospheric absorption spectra are measured at a series of tangent heights during sunrise and sunset. Atmospheric profiles for more than 30 molecules are currently retrieved from ACE-FTS spectra with version 3.0 (<http://www.ace.uwaterloo.ca>), and the retrieval methodology is described by Boone et al. [12]. SCISAT-1 was launched by NASA in August, 2003 and the first routine data are available starting in February 2004. The ACE-FTS is in its eighth year of operation, so we are now in a position to observe long term trends in the VMRs of atmospheric gases. Some earlier halocarbon trend analyses were carried out by Rinsland et al. [13,14] by combining ACE-FTS and ATMOS measurements.

The ACE-FTS currently (v.3.0) measures 16 halogen-containing gases, CCl₄, CF₄, CCl₂F₂ (CFC-12), CCl₃F (CFC-11), C₂Cl₃F₃ (CFC-113), CH₃Cl, ClONO₂, COF₂, COCl₂, COClF, CHF₂Cl

(HCFC-22), $\text{CH}_3\text{CCl}_2\text{F}$ (HCFC-141b), CH_3CClF_2 (HCFC-142b), HCl, HF and SF_6 with version 3.0 retrievals and 7 years of data (2004–2010). This paper presents the changes in atmospheric concentrations of these species as measured by the ACE-FTS in the tropics. The values and trends are interpreted by comparison with output from the SLIMCAT three-dimensional chemical transport model and in-situ surface measurements. The goal is to give a general overview of global trends to demonstrate the utility of ACE satellite observations rather than details on the retrievals global distributions and trends of individual molecules.

3. Measurements

The majority of halogenated source gases reach the stratosphere by upwelling through the tropical tropopause region so we focus on tropical observations. However, the ACE orbital inclination angle of 74° , chosen to optimise the study of ozone chemistry at high latitudes, results in relatively few tropical occultations [9]. The extended latitude band (tropics and sub-tropics) between 30°N and 30°S was chosen to increase the sample size. The positions of the occultations used in this survey are shown in Fig. 1.

Occultations which were made between 30°N and 30°S were separated into 7 annual groups. The number of occultations from each year used in this study is shown in Table 1. The occultations in each of these bins were then filtered using the median absolute deviation (MAD) of the data from that bin. Outliers were removed by discarding individual points which were greater than 2.5 MAD from the median of the raw data. The 2.5 MAD filter was used since this includes 95% of the ACE data ensuring that only outliers were removed. The remaining data were used to calculate a mean concentration at each altitude in the retrieval range. Thus, a mean vertical profile of each species for every year was produced.

The halogenated species retrieved in version 3 are displayed in Table 2. The microwindows used to retrieve these species can be found in the supplementary material.

4. SLIMCAT 3D Chemical Transport Model

To interpret the ACE observations we compare with output from the SLIMCAT off-line three-dimensional (3-D) Chemical Transport Model (CTM). SLIMCAT contains a detailed treatment of stratospheric chemistry including

Table 1

Number of ACE v.3 vertical profiles used in this study for each year.

Year	Number of occultations		
	Morning	Evening	Total
2004	57	200	257
2005	159	293	398
2006	127	162	289
2007	99	127	226
2008	122	168	290
2009	180	174	354
2010	94	150	244

Table 2

Halogen species currently retrieved routinely by ACE and their minimum and maximum retrieval altitudes.

Species	Altitude (km) equatorial
HCFC-141b ($\text{CCl}_2\text{F}-\text{CH}_3$)	8–22
HCFC-142b ($\text{CClF}_2-\text{CH}_3$)	5–21
HCFC-22 (CHF_2Cl)	7–30
CFC-11 (CCl_3F)	6–28
CFC-12 (CCl_2F_2)	5–36
CFC-113 ($\text{C}_2\text{Cl}_3\text{F}_3$)	7–20
COClF	15–32
COCl_2	10–28.5
COF_2	12–45
SF_6	12–32
CF_4	15–55
CCl_4	7–30
HF	12–57
HCl	7–63
ClONO_2	10–36
CH_3Cl	12–40

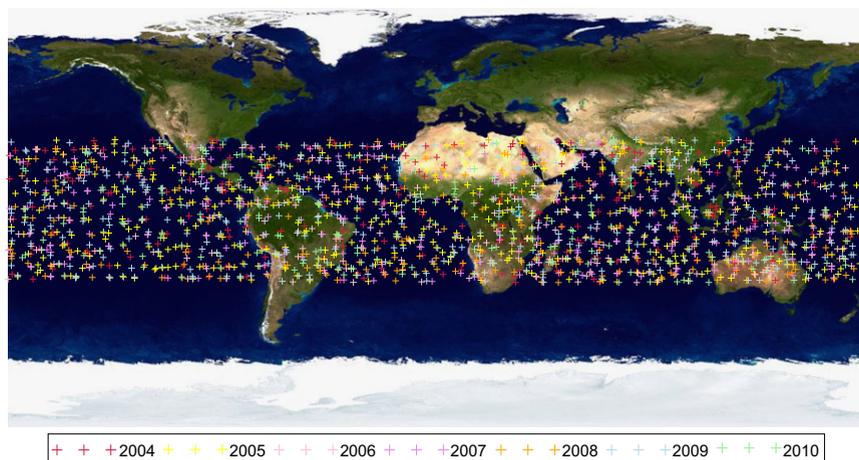


Fig. 1. The positions of the ACE occultations used in this study between the latitudes of 30°N and 30°S .

the major species in the O_x , NO_y , HO_x , Cl_y and Br_y chemical families [15,16]. The model chemistry explicitly includes all of the chemical species listed in Table 2, except CF_4 and $COCl_2$. The model uses winds from meteorological analyses to specify horizontal transport while vertical motion in the stratosphere is calculated from diagnosed heating rates. This approach gives a realistic stratospheric circulation [17,18].

For this study, SLIMCAT was integrated from 1977 to the present day at a horizontal resolution of $5.6^\circ \times 5.6^\circ$ and 32 levels from the surface to about 60 km (run 540). The model used a σ - θ vertical coordinate [17] and was forced by European Centre for Medium-Range Weather Forecasts (ECMWF) reanalyses (ERA-Interim from 1989 onwards). The volume mixing ratio of source gases at the surface level were specified using data files compiled for WMO (2010) [4], which are based on observations such as AGAGE. These global mean surface values define the long-term tropospheric source gas trends in the model, which should therefore agree well with surface observations over the same time. For comparison with ACE, the model zonal mean monthly output was averaged to create annual means between $30^\circ S$ and $30^\circ N$ on a 1 km altitude grid. For SF_6 comparisons a separate model run was performed using the same setup but with an idealised SF_6 tracer. This run models tropospheric SF_6 based on estimated emission rates.

5. Results and discussion

5.1. Carbon tetrachloride, carbon tetrafluoride, methyl chloride and sulphur hexafluoride

Carbon tetrachloride (CCl_4) was first retrieved from ACE observations for the 2004 global stratospheric chlorine budget derived by Nassar et al. [19]. Around 3% of the total stratospheric chlorine budget was made up of CCl_4 in 2004, and the concentrations are decreasing because production is banned by the Montreal Protocol. A study of the global atmospheric distribution of CCl_4 from ACE data was published in 2009 [20]. When compared with SLIMCAT it can be seen that ACE measurements have a consistently higher mixing ratio (Fig. 2). The CCl_4 profiles were averaged in the region between 5 and 17 km where the profiles are roughly constant. A linear least squares fit was fitted to the annual data. The error in the gradient which is presented here is the statistical error on the gradient. Measurements made by ACE since 2004 show a linear decrease of 1.32 ± 0.09 ppt ($1.2 \pm 0.1\%$) per year. Simulations using the SLIMCAT model show a similar decrease of 1.23 ± 0.05 ppt ($1.4 \pm 0.1\%$) per year during this time (Fig. 3). These values are in agreement with measurements made using AGAGE between 2007 and 2008 of a decrease of 1.1 ppt (1.3%) per year [4]. The boundary conditions used by SLIMCAT are based on

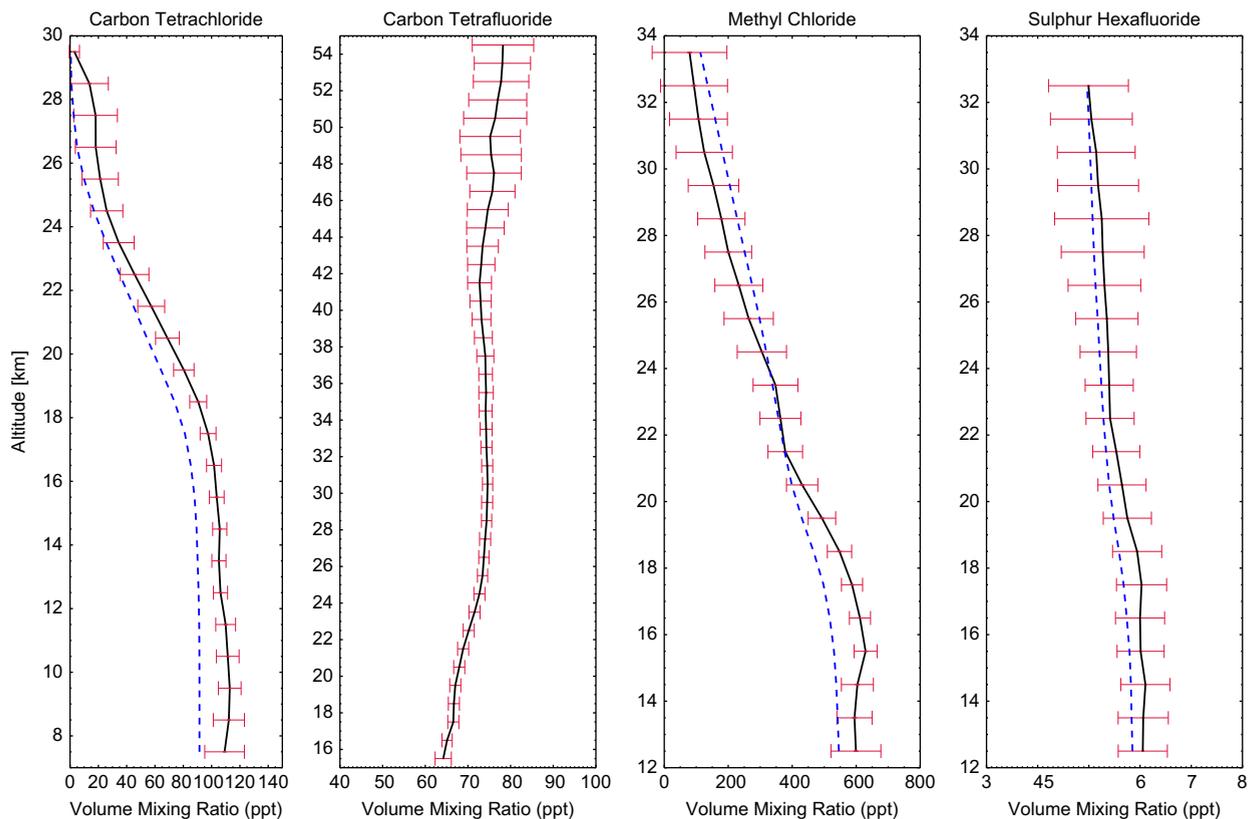


Fig. 2. Average vertical profile of carbon tetrachloride, carbon tetrafluoride, methyl chloride and sulphur hexafluoride (ppt) between $30^\circ N$ and $30^\circ S$ from 2004 to 2010 from ACE (black) and SLIMCAT (blue). The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

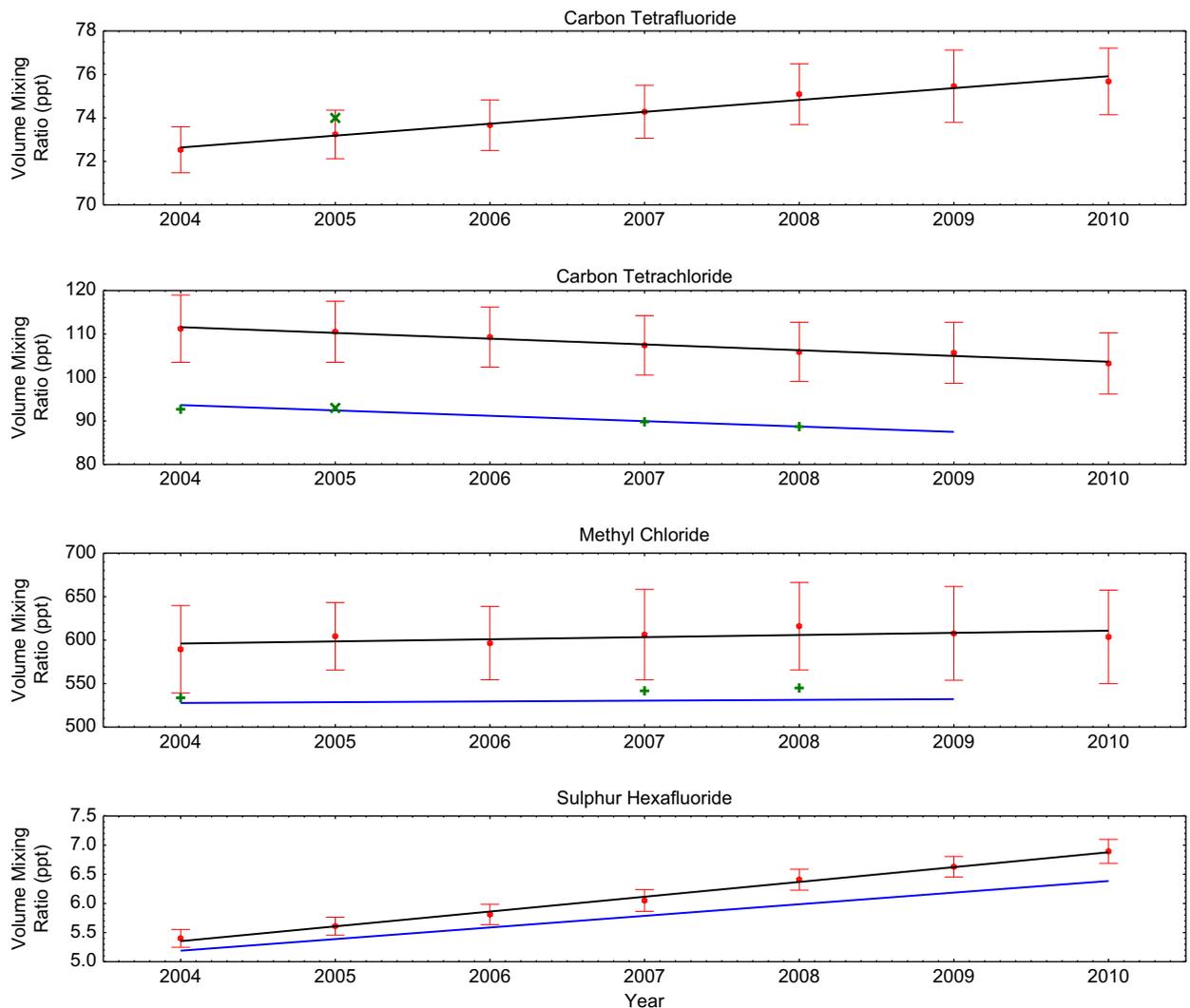


Fig. 3. Volume mixing ratio of carbon tetrachloride, carbon tetrafluoride, methyl chloride and sulphur hexafluoride averaged between 30°N and 30°S for 2004 to 2010 from ACE (black line) and the SLIMCAT model (blue line). Also shown are surface mixing ratios from WMO (2010—plus), IPCC (2007—cross). The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

AGAGE measurements. Thus, SLIMCAT values should agree with AGAGE measurements. SLIMCAT values at the surface are those of AGAGE and the differences at higher altitude thus show the impact of atmospheric loss between the surface and the tropopause.

Carbon tetrafluoride (CF_4) is an important anthropogenic atmospheric tracer that is produced primarily as a by product during electrolytic aluminium production. The average vertical profile of CF_4 from ACE data can be seen in Fig. 2. CF_4 was used in the 2004 global stratospheric fluorine budget [21]. Work by Rinsland et al. [14] found that CF_4 was increasing at a rate of 1.034 ppt per year between 1994 and 2004. Measurements made by Muhle et al. [22] showed an average increase of 0.69 ppt per year between 1994 and 2008. The CF_4 profiles were averaged in the region between 25 and 40 km where the profiles are roughly constant. Measurements of the VMR of CF_4

made by ACE-FTS between 2004 and 2010 showed an increase of 0.54 ± 0.03 ppt ($0.74 \pm 0.04\%$) per year (Fig. 3).

The main sources of CH_3Cl are emissions from the ocean and biomass burning. Measurements made by ACE-FTS of CH_3Cl biomass plumes have been studied by Rinsland et al. [23]. CH_3Cl is the main source of natural chlorine in the atmosphere and was included in the 2004 global stratospheric chlorine budget [19]. Below 21 km ACE measurements of CH_3Cl are higher than those from SLIMCAT (Fig. 2). Above 24 km ACE measurements are lower than those from SLIMCAT. The CH_3Cl profiles were averaged in the region between 12 and 17 km where the profiles are roughly constant. There has been a small increase in the concentrations of CH_3Cl during this time. ACE-FTS measures an annual increase of 2.46 ± 1.37 ppt ($0.4 \pm 0.2\%$) per year (Fig. 3). SLIMCAT data shows an increase of 0.88 ± 0.1 ppt ($0.17 \pm 0.1\%$) per year.

Data from the 2010 WMO report showed an increase of 2.5 ± 1.2 ppt ($0.45 \pm 0.2\%$) per year between 2004 and 2008. The small SLIMCAT trend is a reflection of the constant surface VMR in the boundary condition files prepared for WMO (2010). The recent data (including ACE) might point to a small positive trend, which is not reflected in the assumptions in the model.

SF₆ has a global warming potential of 16,300 over a 20-year timeframe, and its emissions are regulated under the Kyoto Protocol. The long lifetime of 3200 years and strong infrared absorption cross sections, in an atmospheric window region near 950 cm^{-1} , are responsible for making this molecule a potent greenhouse gas. There are no natural sources of SF₆ and it is used near electrical equipment to suppress discharges. SF₆ was measured by ATMOS during its operational lifetime. These observations have been compared to observations made by ACE-FTS by Rinsland et al. [13]. The vertical profile of SF₆ as measured by ACE-FTS is shown in Fig. 2. The SF₆ profiles were averaged in the region between 12 and 17 km where the profiles are roughly constant. ACE-FTS measurements show the concentration of SF₆ has increased between 2004 and 2010 at a rate of 0.25 ± 0.01 ppt ($4.2 \pm 0.1\%$) per year (Fig. 3). SLIMCAT data show an increase of 0.20 ± 0.01 ppt ($3.5 \pm 1.2\%$) per year.

5.2. CFC-11, CFC-12 and CFC-113

CFC-11 is the second most abundant CFC in the atmosphere. Comparisons between measurements made in 1985, 1994 (ATMOS) and 2004 (ACE) showed a levelling off of emissions between 1994 and 2004 [13]. Validation of ACE-FTS version 2.2 (V.2.2) measurements of CFC-11

was made by comparison with balloon-borne FTS measurements [24]. Comparisons with the FIRS-2 instrument showed agreement within 10% below 16 km. ACE-FTS measurements were also compared to the Mk-IV instrument, with agreement to 10% above 12 km and 20% below 12 km. CFC-11 was used in both the global stratospheric fluorine and chlorine budgets [19,21]. The vertical profile of CFC-11 from both ACE-FTS and SLIMCAT can be seen in Fig. 4. There is good agreement between ACE and SLIMCAT profiles especially at lower altitudes. In the middle stratosphere, SLIMCAT underestimates ACE which could be due to a slightly too slow stratospheric circulation, i.e. too slow tropical upwelling in the Brewer-Dobson circulation. The CFC-11 profiles were averaged in the region between 7 and 16 km where the profiles are roughly constant. There has been a decrease in the concentrations of CFC-11 in the troposphere between 2004 and 2010. ACE-FTS measurements show an annual decrease of 2.21 ± 0.07 ppt ($0.9 \pm 0.1\%$) per year. SLIMCAT data show a decrease of 3.03 ± 0.13 ppt ($1.2 \pm 0.6\%$) per year (Fig. 5). There is good agreement between ACE and AGAGE measurements which show a decrease of 2.0 ppt (0.8%) per year between 2007 and 2008 [4].

CFC-12 is the most abundant CFC in the atmosphere. Comparisons between measurements made in 1985, 1994 (ATMOS) and 2004 (ACE) showed a slowing rate of increase between 1985 and 2004 [13]. Validation of ACE-FTS V.2.2 measurements of CFC-12 also were made by comparisons with balloon-borne FTS measurements [24] and the agreement is similar to the CFC-11 case. CFC-12 was used in both the global stratospheric fluorine budget and the global stratospheric chlorine budget [19,21]. When the profile of CFC-12 from SLIMCAT is

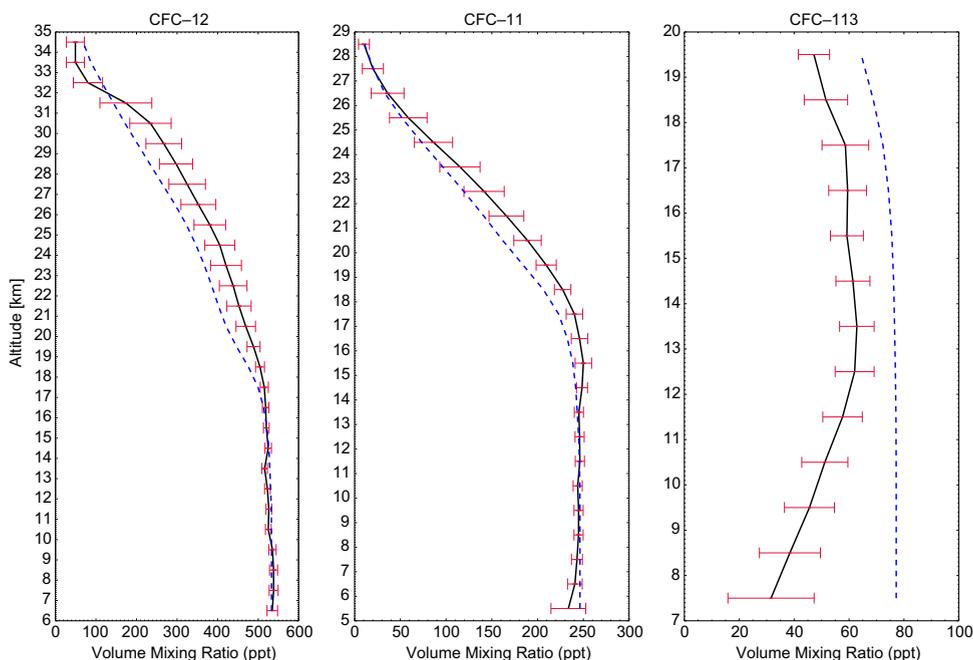


Fig. 4. Average vertical profile of CFC-11, CFC-12 and CFC-113 (ppt) between 30°N and 30°S from 2004 to 2010 from ACE (black) and SLIMCAT (blue). The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

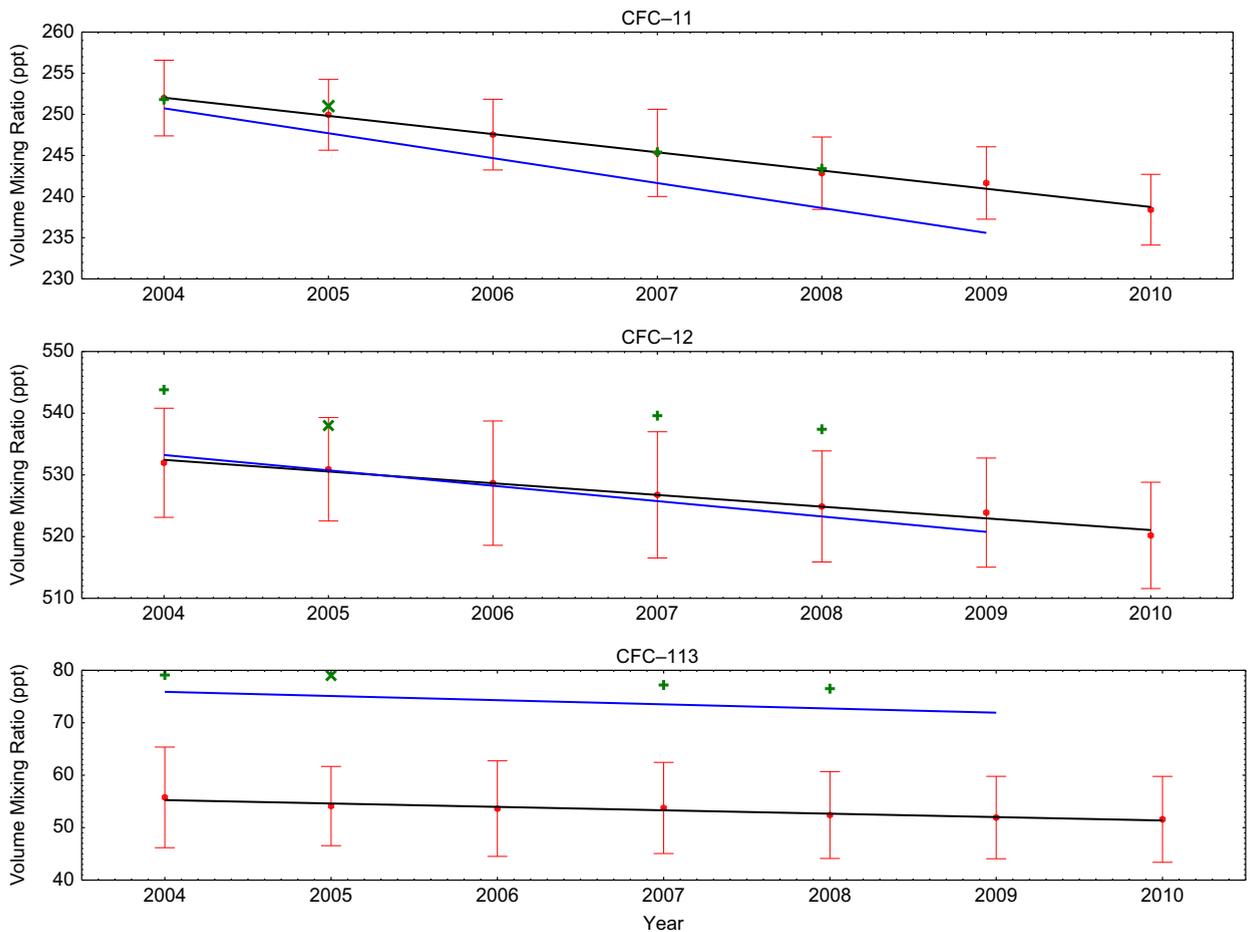


Fig. 5. Volume mixing ratio of CFC-11, CFC-12 and CFC-113 averaged between 30°S for 2004 to 2010 from ACE (black line) and the SLIMCAT model (blue line). Also shown are surface mixing ratios from WMO (2010—plus) and IPCC (2007—cross). The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

compared to that from ACE it is clear that there is good agreement at lower altitudes, but this agreement breaks down somewhat with increasing altitude (Fig. 4), again possibly due to a slow model circulation. The CFC-12 profiles were averaged in the region between 5 and 17 km where the profiles are roughly constant. There has been a decrease in the concentrations of CFC-12 in the troposphere between 2004 and 2010. ACE-FTS shows an annual decrease of 1.90 ± 0.12 ppt ($0.4 \pm 0.1\%$) per year, similarly SLIMCAT data show a decrease of 2.49 ± 0.2 ppt ($0.5 \pm 0.1\%$) per year. These measurements suggest an increased rate of decrease in VMR when compared to measurements made by AGAGE between 2007 and 2008 of 2.2 ppt (0.4%) per year between 2007 and 2008 [4].

CFC-113 was widely used in the late 1980s and early 1990s and is the third most abundant CFC in the atmosphere. The retrieval method for this molecule was outlined by Dufour et al. [25]. This was the first retrieval of CFC-113 from a space-based instrument and was within 15% of mixing ratios measured by AGAGE. CFC-113 was used in both Nassar et al.'s 2004 stratospheric fluorine and chlorine budgets [19,21]. Below 12.5 km tropical measurements of CFC-113 using ACE-FTS show an unexpected increasing VMR

with altitude (Fig. 4). This is likely due to problems in the retrieval when the satellite is at a high beta angle (the angle between the orbital plane and the Earth-Sun vector). Many of the tropical observations are at high-beta angles, which correspond to long occultations with a sunrise/sunset that is not perpendicular to the horizon as seen from the satellite. Work is ongoing to produce an improved research product. ACE measurements of CFC-113 VMR are generally lower than those from SLIMCAT. The CFC-113 profiles were averaged in the region between 6 and 17 km where the SLIMCAT profiles are roughly constant. ACE-FTS measures a decrease of 0.65 ± 0.08 ppt ($1.2 \pm 0.1\%$) per year in the VMR of CFC-113 since 2004. SLIMCAT simulations show a decrease of 0.79 ± 0.05 ppt ($1.1 \pm 0.1\%$) per year. The 2010 WMO report indicated an average decrease of 0.6 ppt (0.8%) per year [4].

5.3. HCFC-22, HCFC-141B and HCFC-142B

HCFCs are transitional replacement compounds for CFCs under the Montreal Protocol, and will in turn be phased out because they also deplete stratospheric ozone. HCFC-22 is the most abundant HCFC in the atmosphere as it has been widely used since the 1950s. Measurements

taken by ATMOS on two flights in 1985 and 1994 have been compared to measurements made by ACE-FTS in 2004 [13]. These measurements showed that the concentration of HCFC-22 in the lower stratosphere increased throughout this time. HCFC-22 was included in both the 2004 global stratospheric fluorine and chlorine budgets [19,21]. Tropical tropospheric measurements of HCFC-22 show an increasing VMR with altitude below the tropopause due to errors in the retrievals at high beta angle (Fig. 6). The version 3.0 retrievals for HCFC-22 employ two spectral regions, near 820 and 1115 cm^{-1} . Investigation of the retrievals has found that retrievals using only the region near 820 cm^{-1} do not exhibit this increasing VMR. Since there is no structure in the HCFC-22 spectral feature near 1115 cm^{-1} it is thought that retrievals in this region are more susceptible to errors from other atmospheric constituents such as aerosols. Work on a new research version of this molecule is currently underway which will rectify this problem. Despite these problems there seems to be some agreement between the ACE and SLIMCAT VMR. The HCFC-22 profiles were averaged in the region between 8 and 17 km where the SLIMCAT profiles are roughly constant. Measurements made since 2004 show that the concentration of HCFC-22 in the troposphere have risen annually. ACE-FTS measurements show an increase of 6.56 ± 0.20 ppt ($3.7 \pm 0.1\%$) per year which compares well to SLIMCAT data which show an increase of 6.24 ± 0.11 ppt ($3.6 \pm 0.1\%$) per year (Fig. 7). AGAGE measured an increase of 8.6 ppt (4.6%) per year between 2007 and 2008 [4].

HCFC-141b is a new species available in the version 3.0 ACE-FTS data. There is again an unexpected slope to the

VMR profile in the troposphere, suggesting that there may be problems with the retrievals at low altitudes. At low altitudes additional molecules which are not part of the forward model, such as CFC-114, HFC-23 and PAN, contribute to the spectrum in the same region as HCFC-141b. Since these molecules are not included in the calculation of the VMR, errors are introduced into this calculation. The contribution of these molecules to the spectrum decreases with altitude allowing for better retrievals at higher altitudes. There is a large and varying difference between ACE and SLIMCAT profiles up to 15 km (Fig. 6). Above 15 km ACE VMRs are considerably higher than those from SLIMCAT. The HCFC-141b profiles were averaged in the region between 8 and 17 km where the SLIMCAT profiles are constant. ACE measurements show an annual increase of 0.17 ± 0.12 ppt ($0.74 \pm 0.5\%$) per year. SLIMCAT data show an increase of 0.55 ± 0.01 ppt ($3.1 \pm 0.1\%$) per year (Fig. 7). Both of these trends are smaller than measurements made by AGAGE between 2007 and 2008, which showed an increase of 0.7 ppt (3.6%) per year [4]. After this paper was accepted for publication an update to the HITRAN database was released for HCFC-141b. The concentrations in figures 6 and 7 should be divided by a factor of 1.75 (www.cfa.harvard.edu/HITRAN/).

The use of HCFC-142b by industry has greatly increased since the early 1990s because of the implementation of the Montreal Protocol [26]. The retrieval method used by ACE was described by Dufour et al. [25], who found that there was agreement to 15% between ground based AGAGE and ACE measurements. Below 13 km SLIMCAT VMRs are generally within one MAD of the ACE measurements. Above 13 km the VMR from SLIMCAT

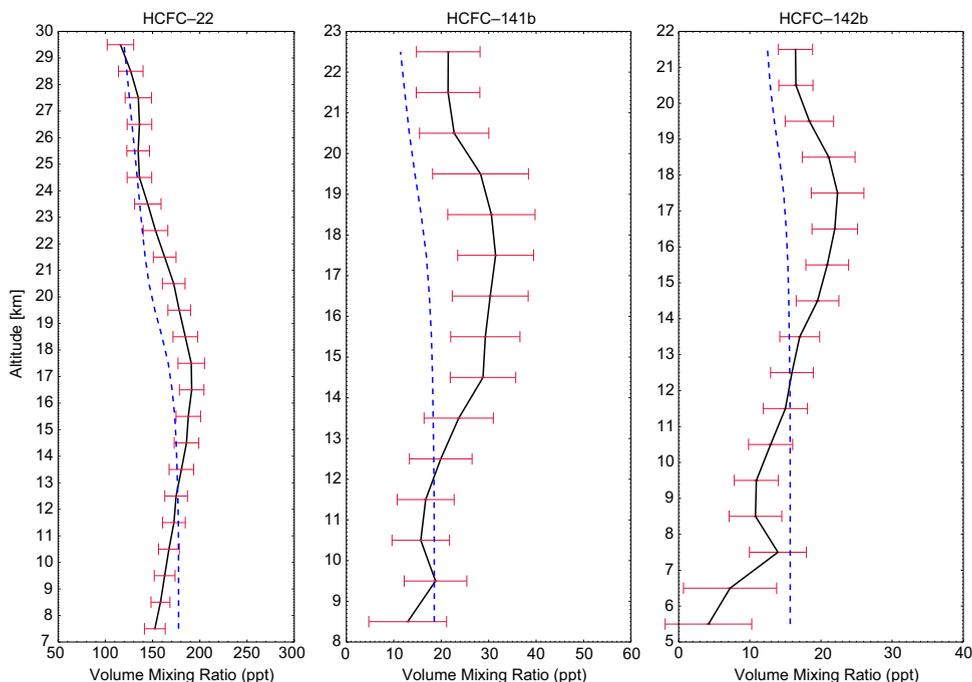


Fig. 6. Average vertical profile of HCFC-22, HCFC-141b and HCFC-142b (ppt) between 30°N and 30°S from 2004 to 2010 from ACE (black) and SLIMCAT (blue). The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

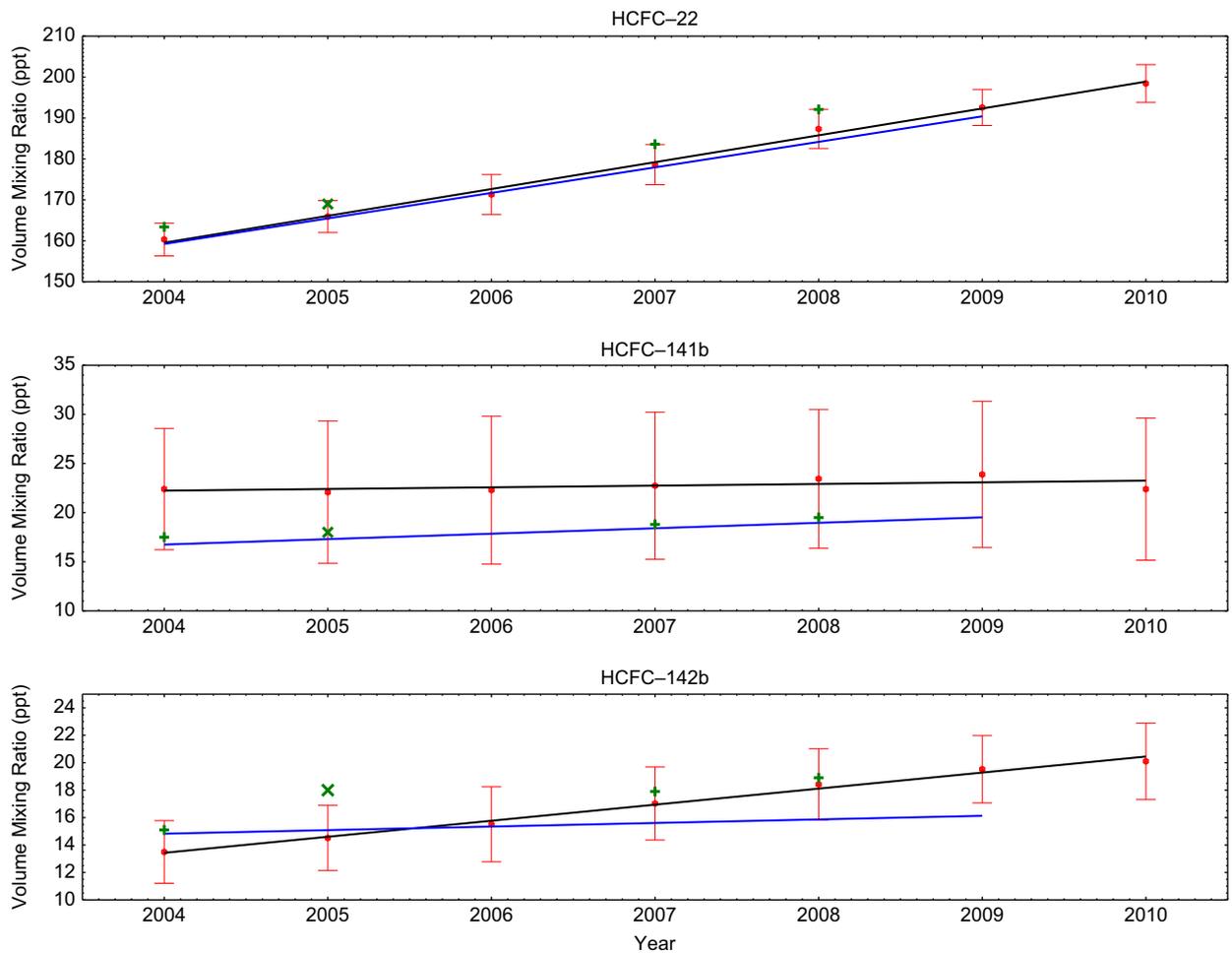


Fig. 7. Volume mixing ratio of HCFC-22, HCFC-141b and HCFC-142b averaged between 30°N and 30°S for 2004 to 2010 from ACE (black line) and the SLIMCAT model (blue line). Also shown are surface mixing ratios from WMO (2010—plus) and IPCC (2007—cross). The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

are slightly lower than ACE measurements but are always within two MAD of the ACE measurements (Fig. 6). Below 17.5 km ACE-FTS tropical measurements of HCFC-142b exhibit an unexpected increasing VMR with altitude similar to that for the CFC-113 profile. This is likely due to problems in the retrievals and work is ongoing to produce an improved research product. The HCFC-142b profiles were averaged in the region between 7 and 17 km where the SLIMCAT profiles are constant. Measurements taken since 2004 show that there has been an increase of 1.17 ± 0.05 ppt ($7 \pm 0.4\%$) per year. SLIMCAT data show a smaller increase of 0.26 ± 0.02 ppt ($1.7 \pm 0.1\%$) per year (Fig. 7). ACE-FTS measurements are in good agreement with the rate of 1.1 ppt (5.9%) per year measured by AGAGE between 2007 and 2008 [4]. Evidently, the surface data file prepared for WMO (2010) which is used in the model underestimates the observed trend.

5.4. Decomposition products

(Phosgene, carbonyl chlorofluoride, carbonyl fluoride and chlorine nitrate)

Phosgene (COCl_2) is created in the atmosphere by the decomposition of chlorocarbons such as tetrachloroethene, methyl chloroform and carbon tetrachloride. Phosgene is rained out in the troposphere so the concentration increases with altitude within the troposphere. In the stratosphere the main source of phosgene is the photolysis of carbon tetrachloride. The main sink for stratospheric phosgene is photolysis that results in HCl formation, and ozone depletion. The first analysis of phosgene from ACE-FTS was made by Fu et al. [27], where they found a reduction in phosgene concentration in the stratosphere between the 1980s and 1990s. They attributed this decrease to the decrease in the concentrations of methyl chloroform and carbon tetrachloride because of the phase-out mandated by the Montreal Protocol. Retrieval of phosgene is difficult since its spectral feature near 844 cm^{-1} is buried under a strongly absorbing band of CFC-11. The ACE vertical profile of phosgene can be seen in Fig. 8. The phosgene profiles were averaged in the region between 22 and 24 km where the peak in the profile occurs. There appears to have been a very slight (but not statistically significant) decrease in the

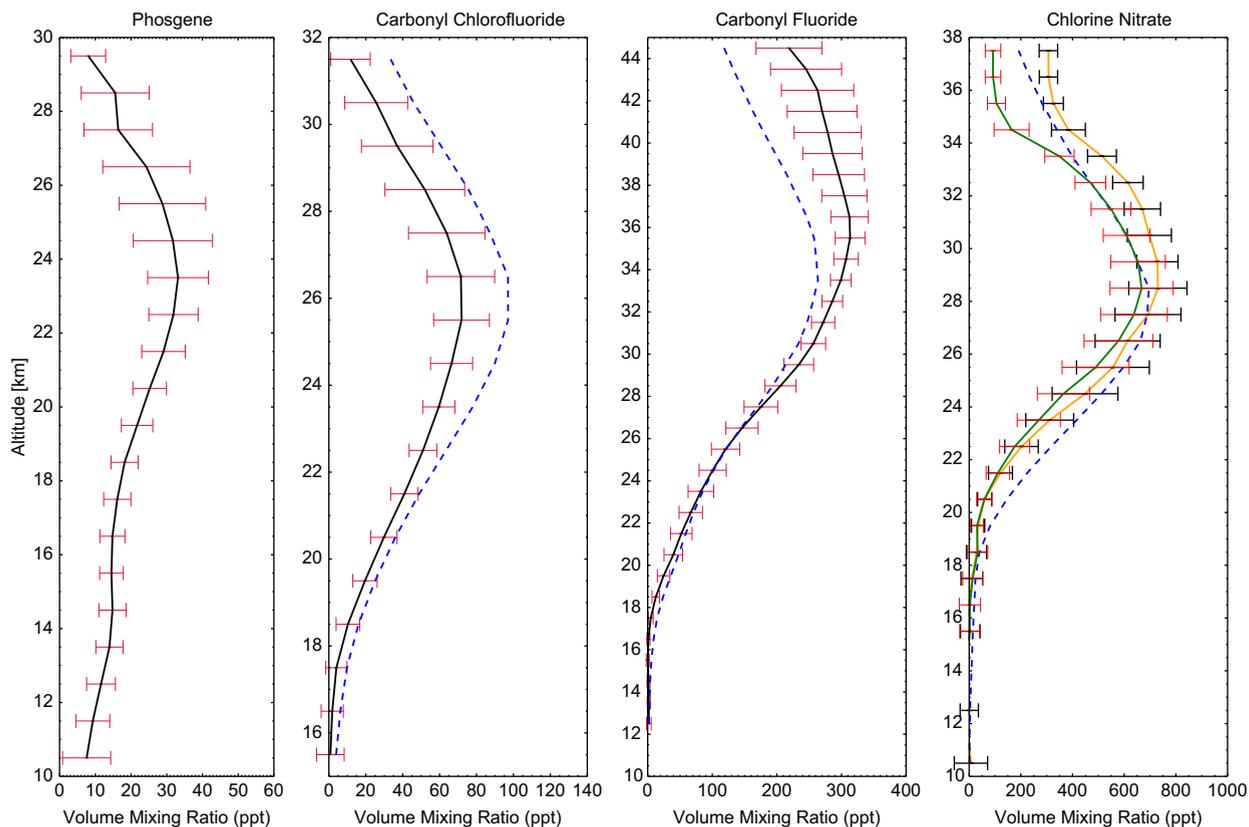


Fig. 8. Average vertical profile of phosgene from ACE and carbonyl chlorofluoride, carbonyl fluoride and chlorine nitrate (ppt) between 30°N and 30°S from 2004 to 2010 from ACE (black) and SLIMCAT (blue). Measurements made in the morning of ClONO₂ by ACE are shown in orange. Measurements made in the evening are shown in green. The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

concentration of stratospheric phosgene of 0.28 ± 0.24 ppt ($0.9 \pm 0.8\%$) per year since 2004 (Fig. 9).

Carbonyl chlorofluoride (COClF) is a significant reservoir species for both atmospheric chlorine and fluorine. COClF is produced from the decomposition of CFC-11 and thus the mixing ratio of atmospheric COClF is a good indicator for the emissions of anthropogenic chlorine. The first study of the global distribution of atmospheric COClF was undertaken by Fu et al. [28] and preliminary retrievals were made by Rinsland et al. [29]. Due to its importance COClF was included in both the global stratospheric fluorine and chlorine budgets [19,21]. Both SLIMCAT and ACE data show a peak in concentration between 24 and 28 km. SLIMCAT assumes COClF is produced from the decomposition of CFC-11 and CFC-113 and its VMRs are higher than those from ACE (Fig. 8). The COClF profiles were averaged in the region between 23 and 28 km where the peak in the profile occurs. Measurements made between 2004 and 2010 suggest that the VMR of COClF has decreased slightly during this time. ACE-FTS measurements show a statistically insignificant decrease of 0.56 ± 0.57 ppt ($0.9 \pm 0.9\%$) per year. SLIMCAT data show a more significant decrease of 1.98 ± 0.44 ppt ($2.3 \pm 0.5\%$) per year which is in line with the decrease in CFC-11 (and CFC-113) during this time (Fig. 9). The observed trend in COClF indicates that the model may be overestimating the decline in the CFCs.

Atmospheric carbonyl fluoride (COF₂) is a stratospheric decomposition product produced mainly by the decomposition of CFC-12. Additional COF₂ formation is believed to come from the decomposition of HCFC-22 and HFC-32, -125, -134a and -152a. The vertical profile has a maximum in the mid-stratosphere (Fig. 8). COF₂ was retrieved for the 2004 global stratospheric fluorine budget [21]. At its peak COF₂ accounts for 32% of the total 'inorganic' stratospheric fluorine budget [21]. There is good agreement between SLIMCAT and ACE profiles below 27 km. Above 28 km SLIMCAT, which assumes that COF₂ is produced from CFC-12, CFC-113 and HCFC-22 underestimates the ACE profile. HFC decomposition in this run of SLIMCAT is assumed to lead directly to HF (discussed later). The COF₂ profiles were averaged in the region between 30 and 40 km where the peak in the profile occurs. There has been a gradual increase of 2.32 ± 1.05 ppt ($0.8 \pm 0.4\%$) per year in the VMR of COF₂ between 2004 and 2010. SLIMCAT data, however, seem to contradict the observations made by ACE-FTS and show a decrease of 2.98 ± 0.98 ppt ($1.3 \pm 0.4\%$) per year (Fig. 9). This discrepancy is likely due to the modelling of the sources of COF₂. SLIMCAT assumes mainly CFC sources and these are declining. It does not include the HFC sources (HFC-32, -125, -134a and -152a) which are still increasing. The decrease in concentration during this

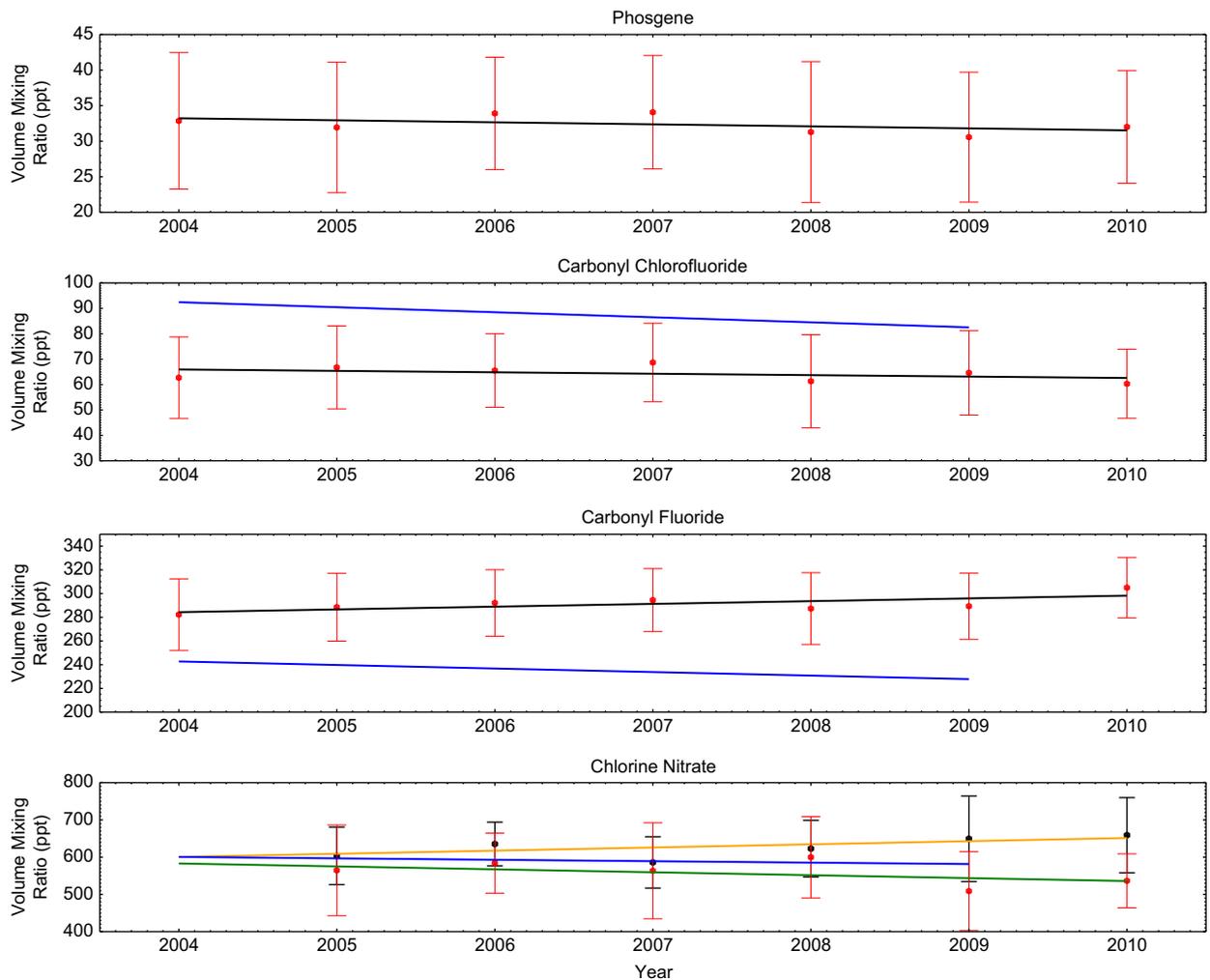


Fig. 9. Volume mixing ratio of phosgene, carbonyl chlorofluoride, carbonyl fluoride and chlorine nitrate averaged between 30°N and 30°S for 2004 to 2010 from ACE (black line) and the SLIMCAT model (blue line). ACE ClONO₂ measurements made in the morning are shown in orange. Measurements made in the evening are shown in green. The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

time is likely caused by the decreasing concentration of CFC-12 in the model.

Chlorine nitrate (ClONO₂) is a chlorine reservoir species produced by the reaction of ClO and NO₂. ClONO₂ is photolysed during the day so its concentration drops. During the night the concentration of stratospheric ClONO₂ again rises as it reforms (Fig. 8). This diurnal cycle must be accounted for when analysing data because ACE measures at only sunrise and sunset. ACE-FTS measurements of ClONO₂ have been compared to those made by MIPAS with a mean difference at the VMR profile peak between ACE and MIPAS measurements of 0.03 ppbv [30]. Further comparisons have been made between ACE total column and ground based FTS measurements. It was found that the largest difference between these measurements was 21% which was within the uncertainty of the retrievals from both the ground instrument and ACE [31]. Due to its importance in the atmosphere, ClONO₂ was included in the 2004 stratospheric chlorine budget [19].

The ClONO₂ profiles were averaged in the region between 25 and 33 km where the peak in the profile occurs. For evening measurements, the VMR of ClONO₂ has decreased between 2004 and 2010 at a rate of 9.4 ± 7.4 ppt ($1.2 \pm 0.9\%$) per year in contrast to an increase of 10.2 ± 5.4 ppt ($1.7 \pm 0.9\%$) per year for morning data (Fig. 9). Although only marginally significant, the reason for this difference is not known at this time. SLIMCAT currently does not output diurnal data for ClONO₂. Although SLIMCAT simulates the full diurnally varying chemistry, in this study output was not saved at local sunrise and sunset. Therefore, only 24 h mean fields are available for ClONO₂. These SLIMCAT data show a decrease of 3.83 ± 2.73 ($-0.6 \pm 0.4\%$) per year.

5.5. Hydrogen chloride and hydrogen fluoride

Hydrogen chloride (HCl) is the main chlorine reservoir in the stratosphere. The concentration of stratospheric HCl

from ACE data has been studied in both the Arctic and Antarctic by Dufour et al., Mahieu et al. and Santee et al. [31–33]. ACE-FTS measurements were used to validate atmospheric profiles of HCl from the Microwave Limb Sounder (MLS) onboard the Aura satellite [34]. MLS HCl profiles were within 5% of the ACE profiles. Further comparisons between ACE and MLS were also carried out by Lary and Aulov [35]. ACE-FTS measurements of HCl have also been compared to balloon-borne measurements and difference from the Mk-IV FTS was 7%. Rinsland et al. sought to build on the legacy of the ATMOS instrument by calculating the trend in stratospheric HCl between 1985 and 2004 [15]. This work found that between 1994 and 2004 there was a marked decrease in the mixing ratio of HCl. These results helped illustrate the success of the Montreal Protocol in reducing the concentration of stratospheric chlorine. There is good agreement between ACE VMRs and those from SLIMCAT in middle altitudes. In the lower and upper atmosphere the agreement is less good (Fig. 10). At altitudes between 17 and 32 km SLIMCAT underestimates the concentrations of the major CFCs (CFC-11 and CFC-12) possibly due to a slightly too slow circulation. This results in more conversion of the source gases to HCl, the main inorganic chlorine reservoir. Above about

45 km the model profile is constant, implying that all of the source gases which release Cl in the model have done so. The ACE observations continue to increase which suggest that there are long-lived sources of chlorine which are contributing to HCl production at these high altitudes. The HCl profiles were averaged in the region between 50 and 54 km where the profile peaks. Hydrogen chloride appears to have decreased between 2004 and 2010 by 26.2 ± 2.3 ppt ($0.7 \pm 0.1\%$) per year in the stratosphere (Fig. 11). This is larger than the decrease of 18.9 ± 0.9 ppt ($0.6 \pm 0.1\%$) per year shown in the SLIMCAT data. Froidevaux et al. find a decrease of 27 ± 3 ppt ($0.78 \pm 0.08\%$) per year for MLS from measurements made between August 2004 and July 2006 and 0.9% for ACE-FTS for the period between January 2004 and September 2009 [4,36].

Hydrogen fluoride (HF) is the main fluorine reservoir in the stratosphere. When fluorine-containing species undergo photolysis in the stratosphere the resulting intermediates (which include COF_2 and COFCl) go on to form HF. Rinsland et al. [13] compared measurements of HF made by ATMOS in 1985 and 1994 with those made by ACE in 2004. These results showed a slowing down in the increase of HF in the atmosphere over this time. Balloon-borne measurements by the Mk-IV FTS show reasonable

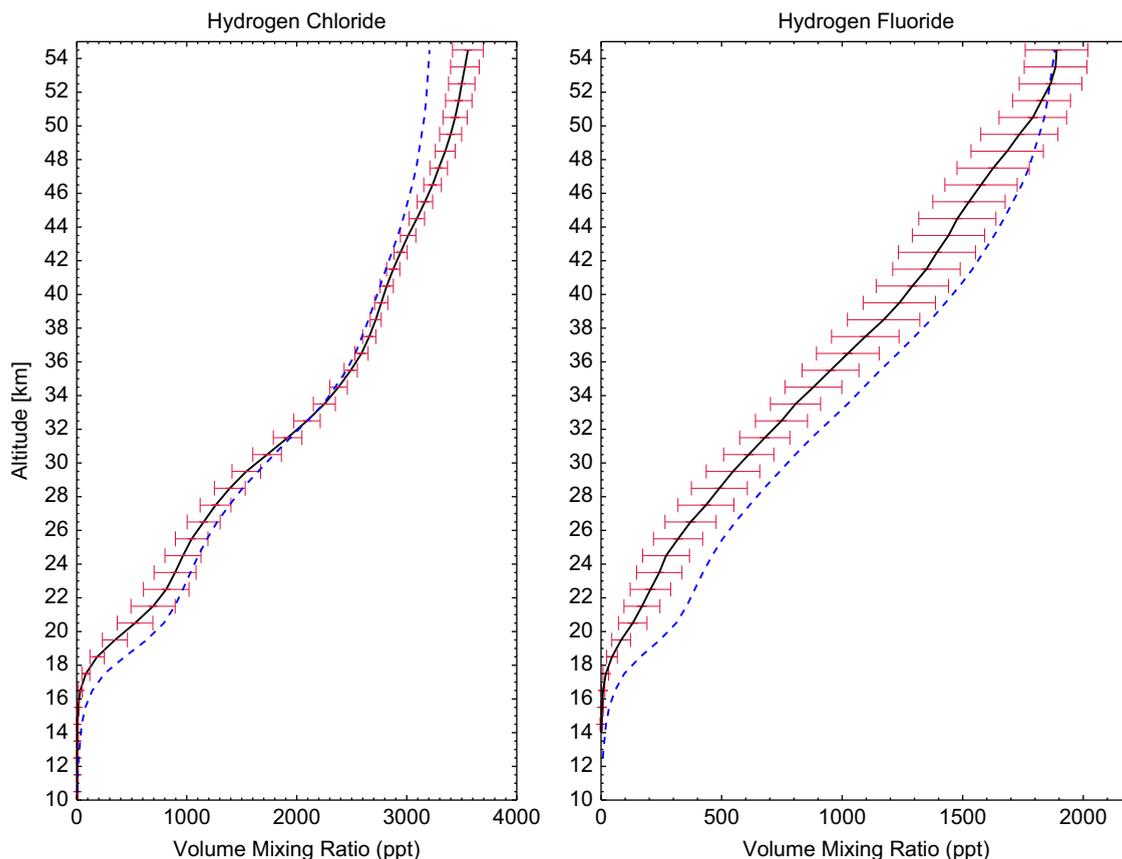


Fig. 10. Average vertical profile of hydrogen fluoride and hydrogen chloride (ppt) between 30°N and 30°S from 2004 to 2010 from ACE (black) and SLIMCAT (blue). The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

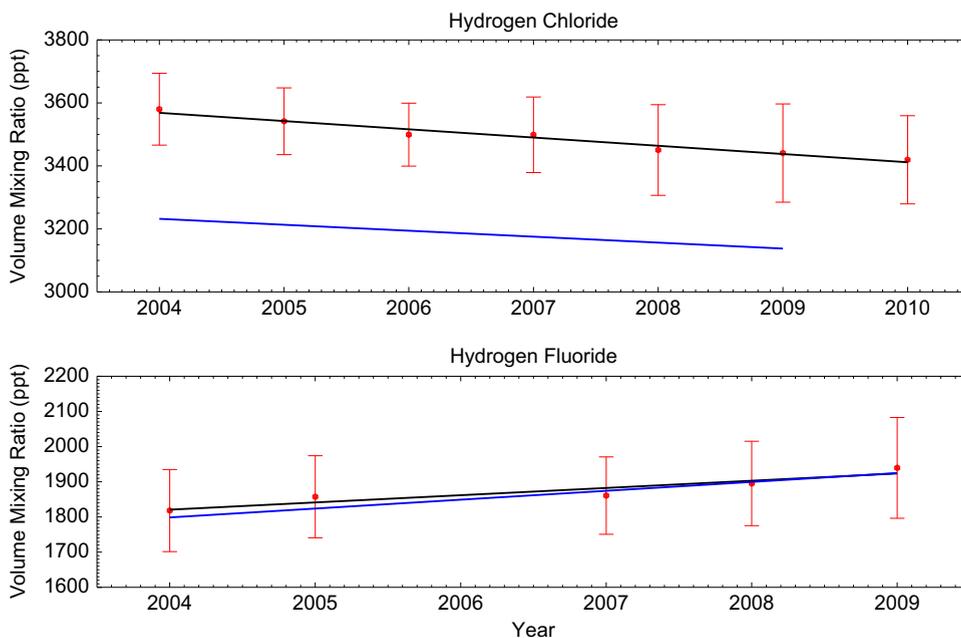


Fig. 11. Volume mixing ratio of hydrogen fluoride and hydrogen chloride averaged between 30°N and 30°S for 2004 to 2010 from ACE from ACE (black line) and the SLIMCAT model (blue line). The error bars represent one MAD of the ACE data. Note different y-axis ranges. (For interpretation of the reference to color in this figure legend the reader is referred to the web version of this article.)

agreement with ACE-FTS V.2.2 to within 10% [24]. There is good agreement between SLIMCAT and ACE VMR. Generally, the SLIMCAT VMRs are higher than ACE VMRs but are within one and a half MAD (Fig. 10). Again, as for HCl, the model underestimates the major CFC sources of this species in the mid-stratosphere and therefore overestimates the decomposition product. The assumption that HFC decomposition leads only to HF, and not COF₂, will also contribute to the overestimate of HF in the region where COF₂ is underestimated (30 km and above). Hydrogen fluoride is increasing rapidly at a rate of 20.6 ± 4.5 ppt ($0.74 \pm 0.2\%$) per year. This is consistent with an increase in other fluorinated species. SLIMCAT data shows an increase of 25.2 ± 6.0 ppt ($1.4 \pm 0.3\%$) per year (Fig. 11).

6. Conclusions

Measurements were made by ACE-FTS of 16 halogen-containing species: CCl₄, CF₄, CFC-11, CFC-12, CFC-113, CH₃Cl, ClONO₂, COF₂, COCl₂, COCIF, HCFC-22, HCFC-141b, HCFC-142b, HCl, HF and SF₆. Tropical data for these molecules from 2004 to 2010 were analysed for trends. These data were filtered so that values larger than two and a half median absolute deviations were removed. An annual mean was calculated allowing the annual variation of each species to be calculated. These results were compared to those from the SLIMCAT 3D chemical transport model and surface measurements made by the AGAGE network. The annual trends for each of the studied halogen-containing species are summarised in Table 3.

Measurements of the trends made by ACE in the upper troposphere and lower stratosphere are generally in

agreement with those made from ground-based stations. Only 3 species (CH₃Cl, HCFC-22 and HCFC-141b) have a difference of greater than 14% from ground-based measurements. The overall agreement is worse between ACE and SLIMCAT. Five species differed by more than 35% from ACE measurements at the sampled altitudes (COCIF, HCFC-141b, HCFC-142b, HCl and CH₃Cl). The VMR of the three CFCs measured in this study have decreased over time as has the VMR of CCl₄. The HCFCs in this study by contrast have increased during this time. The VMR of CF₄ has also decreased during this time. These results illustrate the success of the Montreal Protocol in reducing ozone depleting substances. The reduction in anthropogenic chlorine emissions has led to a decrease in the VMR of stratospheric HCl. The replacement of CFCs with HCFCs has led to an increase in the VMR of HF in the stratosphere. As chlorine-containing compounds are phased out and replaced by fluorine-containing molecules, it is unlikely that total atmospheric fluorine will decrease in the near future.

The retrieved ACE-FTS profiles of HCFC-22, HCFC-141b, HCFC-142b and CFC-113 exhibit an unexpected (and unphysical) increasing VMR with increasing altitude in the troposphere mainly because of spectral interferences in the retrieval. Work is ongoing to improve the retrievals for these molecules. A research version of HCFC-22 has already been produced whilst work is continuing on the other species. Nevertheless, ACE HCFC-22, HCFC-141b, HCFC-142b and CFC-113 observations still show clear trends because of the systematic nature of the effect. The sloped portion of the VMR profile will introduce small offsets in the annual averages, and the resulting offsets in the trend slopes will be much smaller than the statistical

Table 3
Results of trend analysis on ACE-FTS data of halogen containing molecules.

Species	Annual trend (ppt (%) per year)		
	ACE	Ground based	SLIMCAT
CCl ₄	-1.32 ± 0.09 (-1.2 ± 0.1)	-1.1 (-1.3)	-1.23 ± 0.05 (-1.4 ± 0.1)
CF ₄	0.54 ± 0.03 (0.74 ± 0.04)	0.69 ^a	–
CFC-11	-2.21 ± 0.07 (-0.9 ± 0.1)	-2.0 (-0.8)	-3.03 ± 0.13 (-1.2 ± 0.6)
CFC-12	-1.90 ± 0.12 (-0.4 ± 0.1)	-2.2 (-0.4)	-2.49 ± 0.20 (-0.5 ± 0.1)
CFC-113	-0.65 ± 0.08 (-1.2 ± 0.1)	-0.6 (-0.8)	-0.79 ± 0.05 (-1.1 ± 0.1)
CH ₃ Cl	2.46 ± 1.37 (0.4 ± 0.2)	2.5 ± 1.2 (0.45 ± 0.20)	0.88 ± 0.1 (0.17 ± 0.1)
COCl ₂	-0.28 ± 0.24 (-0.9 ± 0.8)	–	–
COClF	-0.56 ± 0.57 (-0.9 ± 0.9)	–	-1.98 ± 0.44 (-2.3 ± 0.5)
COF ₂	2.32 ± 1.05 (0.8 ± 0.4)	–	-2.98 ± 0.98 (-1.3 ± 0.4)
HCFC-141b	0.17 ± 0.12 (0.74 ± 0.5)	0.7 (3.6)	0.55 ± 0.01 (3.1 ± 0.1)
HCFC-142b	1.17 ± 0.05 (7 ± 0.4)	1.1 (5.9)	0.26 ± 0.02 (1.7 ± 0.1)
HCFC-22	6.56 ± 0.20 (3.7 ± 0.1)	8.6 (4.6)	6.24 ± 0.11 (3.6 ± 0.1)
HCl	-26.2 ± 2.3 (-0.7 ± 0.1)	–	-18.9 ± 0.9 (-0.6 ± 0.1)
HF	20.6 ± 4.5 (0.74 ± 0.2)	–	25.2 ± 6.0 (1.4 ± 0.3)
SF ₆	0.25 ± 0.01 (4.2 ± 0.1)	–	0.20 ± 0.01 (3.5 ± 0.1)
ClONO ₂ (evening)	-9.4 ± 7.4 (-1.2 ± 0.9)	–	–
ClONO ₂ (morning)	10.2 ± 5.4 (1.7 ± 0.9)	–	–
ClONO ₂ (24 h)	–	–	-3.83 ± 2.73 (-0.6 ± 0.4)

^a average of northern and southern hemispheres [22].

regression errors. There is a noticeable difference between the morning and evening ACE trends of chlorine nitrate that is not understood at this time.

ACE measurements are useful in deriving global trends in atmospheric composition. In general, a single ACE measurement lacks the accuracy and precision of a careful, well-calibrated ground-based measurement. ACE measurements, however, offer extensive spatial coverage that is difficult to obtain in any other way. Converting ground-based measurements into the globally averaged values needed by policy makers using an atmospheric model is not a trivial task and it is difficult to give reliable error estimates for the results. ACE also measures halocarbon abundances in the stratosphere where ozone depletion actually occurs, rather than on the ground where halocarbons are released. Averaging ACE measurements improves their precision although biases often remain because of systematic errors in the spectroscopy and in the retrievals. The sparse coverage of ACE data in the tropics requires larger latitude bands so as to increase the number of measurements which may be averaged. The ACE results reported here are only a preliminary report on more extensive analyses of individual species, and the determination of complete atmospheric fluorine and chlorine budgets.

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Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jqsrt.2011.07.005.

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