

Trends in atmospheric HFC-23 (CHF₃) and HFC-134a abundances[☆]Anton M. Fernando^{a,*}, Peter F. Bernath^{a,b}, Christopher D. Boone^c^a Department of Physics, Old Dominion University, Norfolk, VA 23529, USA^b Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA^c Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

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ABSTRACT

The Montreal Protocol banned the production of major ozone depleting substances such as chlorofluorocarbons (CFCs) to protect the Earth's ozone layer. The resulting increased production and emissions of CFC-replacement hydrofluorocarbons (HFCs) has caused a dramatic increase in their atmospheric abundances. Although these HFCs do not contribute directly to the depletion of the ozone layer because they contain no chlorine, they are powerful greenhouse gases with large global warming potentials. In January 2019, the Kigali Amendment to the Montreal Protocol came into force to phase out long-lived HFCs. The two most abundant HFCs in the atmosphere, HFC-134a (CF₃CH₂F) and HFC-23 (CHF₃), are measured from orbit by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS). These measurements will be useful for monitoring the Kigali Amendment to the Montreal Protocol. Analysis of the ACE-FTS measurements provides near-global distributions and confirms the rapid increase in HFC-134a (4.9 ± 0.1 ppt per year) and HFC-23 (0.75 ± 0.02 ppt per year) volume mixing ratios (VMRs).

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1. Introduction

In 1974, Molina and Rowland discovered that chlorofluorocarbons (e.g., CFC-12 (CF₂Cl₂), CFC-11 (CCl₃F)) that were mainly used for refrigeration, air-conditioning applications and aerosol propellants cause destruction of stratospheric ozone [1]. The discovery of the Antarctic ozone hole spurred the adoption of the Montreal Protocol to control the production of CFCs and other ozone depleting substances (ODSs) [2]. The Montreal Protocol is an international treaty signed by almost all nations (currently 197) to protect the stratospheric ozone layer [3]. As a temporary substitute for CFCs, hydrochlorofluorocarbons such as HCFC-22 were introduced because they have shorter atmospheric lifetimes and hence smaller ozone depleting potentials (ODPs) than CFCs [4]. HCFCs for dispersive use are now essentially phased out in developed countries but are still produced in developing countries.

Hydrofluorocarbons (HFCs) such as CF₃CFH₂ (HFC-134a) have been introduced to replace CFCs and HCFCs because they contain no chlorine and have very small ODPs [5,6]. Although the HFCs do not directly contribute to the depletion of stratospheric ozone they are potent greenhouse gases. These HFCs have relatively long atmospheric lifetimes and are rapidly accumulating in the atmo-

sphere [7]. HFCs are projected to make a significant contribution to global warming [8].

The Montreal Protocol was amended in Kigali, Rwanda in 2016 to phase out long-lived HFCs. The goal of the Kigali amendment is to gradually decrease global HFC use by 80–85% by the late 2040s. First HFC reductions will come into effect in developed countries in 2019, and by 2024 most of the developing countries will also start to freeze HFC consumption [3,9,10].

HFC-134a is a CFC-12 replacement in domestic, commercial and automotive air conditioning applications [11,12]. HFC-134a contributes more than half of all HFC emissions associated with CFC replacements and has a Global Warming Potential (GWP) of 1430 (100-yr) [13]. The main atmospheric sink for HFC-134a is the reaction with tropospheric OH and as a result the lifetime of HFC-134a is 13.4 years [6,13]. Photolysis in the stratosphere is typically not an important sink for HFCs as their absorption cross sections are negligible in the range of stratospheric UV radiation [14]. Since 2000, HFC-134a has been the most abundant HFC in the atmosphere [15].

The HFC-23 (CHF₃) is not directly produced as a CFC replacement, but as a byproduct of HCFC-22 production, by over-fluorinating CHCl₃ (chloroform). Small amounts of HFC-23 are also used as a raw material for Halon-1301 (CBrF₃), as a low temperature refrigerant, in fire extinguishers and in the semiconductor industry [16]. The atmospheric lifetime of HFC-23 is 222 years and the GWP is 12,400 (100-yr) [13].

[☆] Fully documented templates are available in the elsarticle package on CTAN.

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Table 1
Microwindow list for CF₃CFH₂ (HFC-134a) retrievals.

Center frequency (cm ⁻¹)	Microwindow width (cm ⁻¹)	Lower altitude limit (km)	Upper altitude limit (km)
829.03 ^a	0.50	5	25
1090.40 ^b	0.40	5	25
1104.44	2.80	5	25
1950.10 ^c	0.35	6–7	20
2623.95 ^d	0.65	5	20

^a Included to improve results for interferer CHF₂Cl.

^b Included to improve results for interferer O₃ isotopologue 2 (OO¹⁸O).

^c Included to improve results for interferer H₂O.

^d Included to improve results for interferer H₂O isotopologue 4 (HDO) & CO₂ isotopologue 3 (OC¹⁸O).

Table 2
Interfering molecules for CF₃CFH₂ (HFC-134a) retrievals.

Molecule	Isotopologue	Lower altitude limit (km)	Upper altitude limit (km)
CCl ₂ F ₂	CCl ₂ F ₂ ^a	5	25
CHF ₂ Cl	CHF ₂ Cl ^a	5	25
H ₂ O	H ₂ O	5	20
HCOOH	HCOOH	5	25
H ₂ O	HDO	5	20
O ₃	O ₃	5	25
O ₃	OO ¹⁸ O	5	25
O ₃	O ¹⁸ OO	5	25
CH ₄	CH ₄	5	22
CH ₄	CH ₃ D	5	22
CO ₂	OC ¹⁸ O	5	20
COF ₂	COF ₂	6–7	20

^a Using absorption cross sections.

Measuring HFC-23 and HFC-134a abundances and trends is useful for monitoring the Kigali amendment. In this work we determine the global distributions and trends of HFC-134a and HFC-23 based on ACE-FTS satellite measurements.

2. Observations and retrievals

The SCISAT satellite, also known as the Atmospheric Chemistry Experiment (ACE) was launched by NASA into low Earth circular orbit (altitude 650 km, inclination 74° to the equator) in August 2003 [17]. It continues to collect measurements of the Earth atmosphere, deriving information on altitude variations for atmospheric pressure, temperature, and numerous molecules. The primary instrument on board is a Fourier transform spectrometer (ACE-FTS) that features high resolution (0.02 cm⁻¹) and a broad spectral range in the infrared (750–4400 cm⁻¹). The mission employs the solar occultation measurement technique, collecting a series of atmospheric transmittance spectra as the Sun rises or sets from the orbiting satellite point of view. Molecular abundances are expressed as volume mixing ratios (VMRs) with statistical errors on a standard fixed 1 km retrieval grid associated with the forward model. The input aperture of the FTS is about 3 km as projected on to the limb of the atmosphere. The effective vertical resolution, however, is somewhat better than this value depending on the vertical sampling which changes with the orbit orientation relative to the Sun and refraction in the lower atmosphere [17].

The HFC-134a and HFC-23 retrievals employed here are both “research products”, generated in advance of the upcoming ACE-FTS version 4 data product with a preliminary version of the software that will be used for ACE-FTS version 4 processing. The required inputs of pressure and temperature profiles along with measurement tangent heights were taken from ACE-FTS version 3.5/3.6 processing results [17,18].

For the preliminary version 4 software, deficiencies in the calculation of the ACE-FTS instrumental line shape (ILS) yielded enhanced residuals in regions with dense O₃ lines, which impacted the retrievals for both molecules. For these research products, an

empirical local ILS was employed in each fitting microwindow, tailored to minimize the residuals from overlapping O₃ lines in the window in order to avoid introducing systematic errors in the retrieved VMR profiles for the HFCs. Subsequent improvements in the ACE-FTS ILS calculation circumvent the need for these localized (in wavenumber) adjustments to the ILS in upcoming version 4 processing [19], but these local ILS adjustments played a crucial role in reducing systematic errors when these research products were generated.

Table 1 provides the microwindow set employed in the HFC-134a retrieval using the infrared absorption cross sections of Harrison [20]. The primary microwindow near 1104 cm⁻¹ contains the HFC-134a spectral feature, while the other microwindows serve to improve the information content for weak absorbers in the primary window, which helps stabilize the retrieval. In Tables 1–4 “Lower Altitude Limit” and “Upper Altitude Limit” are the lower and upper limits of the altitude range of the microwindow. Where two numbers are provided for an altitude limit, the first number refers to the altitude limit at the poles (latitude 90°), while the second number denotes the altitude limit at the equator (latitude 0°), with an assumed variation of the square of the sine of the latitude for points in between.

Table 2 details the interferences involved in the retrieval. VMR profiles for all the interferers are retrieved simultaneously with the HFC-134a profile using a global least-squares analysis [18], including separate profiles for different isotopologues of the same molecule.

The microwindow list for HFC-23 retrievals is provided in Table 3 using the infrared absorption cross sections of Harrison [21]. This molecule has a relatively broad spectral feature. Rather than using a single broad microwindow in the analysis, a collection of microwindow slices across the spectral feature (spanning a wavenumber range of 1154–1162 cm⁻¹) are employed in the retrieval. This approach allows one to avoid regions with bad fitting residuals (such as in the vicinity of H₂O lines at low altitudes) that might introduce systematic errors in the retrievals. A common set of baseline parameters (baseline scale and baseline slope)

Table 3
Microwindow list for CHF₃ (HFC-23) retrievals.

Center frequency (cm ⁻¹)	Microwindow width (cm ⁻¹)	Lower altitude limit (km)	Upper altitude limit (km)
1154.06 ^a	0.64	5	25
1156.64 ^a	2.56	5	25
1158.98 ^a	1.08	5	25
1161.43 ^a	0.78	5	25
1950.10 ^a	0.35	6–7	25
2566.22 ^b	0.26	12	21
2723.31 ^c	0.45	8	21

^a Microwindows employ the same baseline parameters (scale and slope).

^b Included to improve results for interferer H₂O.

^c Included to improve results for interferer N₂O isotopologue N¹⁵NO.

^d Included to improve results for interferer H₂O isotopologue HDO.

Table 4
Interfering molecule(s) for CHF₃ (HFC-23) retrievals.

Molecule	Isotopologue	Lower altitude limit (km)	Upper altitude limit (km)
CH ₃ CCl ₂ F	CH ₃ CCl ₂ F ^a	5	20
H ₂ O	H ₂ O	5	20
CCl ₂ F ₂	CCl ₂ F ₂ ^a	5	25
H ₂ O	HDO	5	21
O ₃	O ₃	5	25
PAN ^a	PAN ^{a,b}	5	20
N ₂ O	N ₂ O	5	25
N ₂ O	N ¹⁵ NO	5	21
N ₂ O	¹⁵ NNO	5	20
N ₂ O	N ₂ ¹⁸ O	5	21
CH ₄	CH ₄	5	25
CH ₄	CH ₃ D	5	25
COF ₂	COF ₂	6–7	20

^a Using absorption cross sections.

^b Peroxyacetyl nitrate.

is used for all of the microwindow slices. Once again, a set of microwindows containing information on interferers but no contribution from HFC-23 are included to promote stable convergence in the least-squares analysis. Details on the interferers in the HFC-23 retrievals are provided in Table 4.

The new ACE HFC-23 and HFC-134a retrievals improve on the original research versions [15,22] by using the improved cross sections of Harrison [20, 21] and optimized microwindows. Note that ACE-FTS reports VMR values, not dry air mole fractions as is customary for surface measurements. The corrections for water vapor in the upper troposphere are negligible compared to the statistical and systematic errors of the ACE-FTS HFC VMR values.

3. Results and discussion

The ACE-FTS altitude profiles of HFC-134a and HFC-23 VMRs were filtered to remove outliers. All negative and large positive values were removed from the data for each altitude and values that were more than 2 standard deviations away from the mission averages were also discarded. This filtering removed 4% of the HFC-134a data and 1% of the CHF₃ data.

Figs. 1 and 2 represent the annual mission average altitude profiles covering all the latitudes of CHF₃ and HFC-134a VMRs from 2004 to 2018 (only January and February data are available for 2018). Fig. 1 shows that CHF₃ VMR altitude profiles increase steadily at 1–2 ppt per year, except between 2005–2006 and 2016–2017. Fig. 2 shows that HFC-134a annual altitude profiles increase by 3–4 ppt per year, approximately at a steady rate. The HFC-134a annual altitude profiles (Fig. 2) display an unexplained glitch at 9.5 km. It is unphysical for the VMR to be consistently low at a constant altitude of 9.5 km so there is problem in the retrieval. Fig. 3 represents the ACE-FTS average altitude profiles of HFC-134a and CHF₃ VMRs for 2017. The percentage standard error of the annual altitude profiles of CHF₃ averages are around 30–40% and

for HFC-134a are around 50–60% (similar to Fig. 3). There are two years (2007 and 2011) for which anomalous increases are noted in the HFC-134a annual altitude profiles. This anomalous change lies within the uncertainties of the annual VMR averages and may not be real.

The Advanced Global Atmospheric Gases Experiment with Gas Chromatography with Mass Spectrometry (AGAGE GC-MS) system is used to measure concentrations of atmospheric species such as HCFCs and HFCs that are important for the Montreal Protocol. These gases are analyzed at AGAGE remote sites with a gas chromatograph-mass spectrometer (GC-MS) to obtain VMRs and are used to estimate global monthly VMR averages [23–25].

Fig. 4 represents the overall mission annual average time series of CHF₃ for 60°S–60°N along with AGAGE 12-box model values obtained from Simmonds et al. [23] (Simmonds et al. [23] provide data only up to 2016.) The 12-box model determines annual VMR values for CHF₃ assuming that the atmosphere consists of four zonal regions (90°S–30°S N, 30°S–0°S N, 0°S–30°S and 30°S–90°S) and at vertical heights of 500 and 200 hPa. These modeled VMRs were adjusted by comparison with the atmospheric observations of Simmonds et al. [23]. The Scientific Assessment of Ozone Depletion: 2018 provides annual mole fractions for 2012, 2015 and 2016 with a change of the mole fractions per year of CHF₃. For CHF₃ global mole fraction values (calculated from AGAGE in situ global measurements) were 24.9 ppt for 2012, 28.1 ppt for 2015 and 28.9 ppt for 2016 and, the annual mole fraction change is reported as 0.8 ppt yr⁻¹ (2.9% yr⁻¹) for the period 2015–2016 [26]. These reported values are reasonably consistent with the calculated ACE-FTS values of 23.2 ± 0.3 ppt for 2012, 25.4 ± 0.3 ppt for 2015, 26.3 ± 0.5 ppt for 2016 and the ACE trend of 0.9 ppt (3.2%) yr⁻¹ for the period 2015–2016.

Fig. 5 represents overall mission average annual time series of HFC-134a for 60°S–60°N along with the HFC-134a annual time series obtained from the monthly global mean of baseline HFC-134a

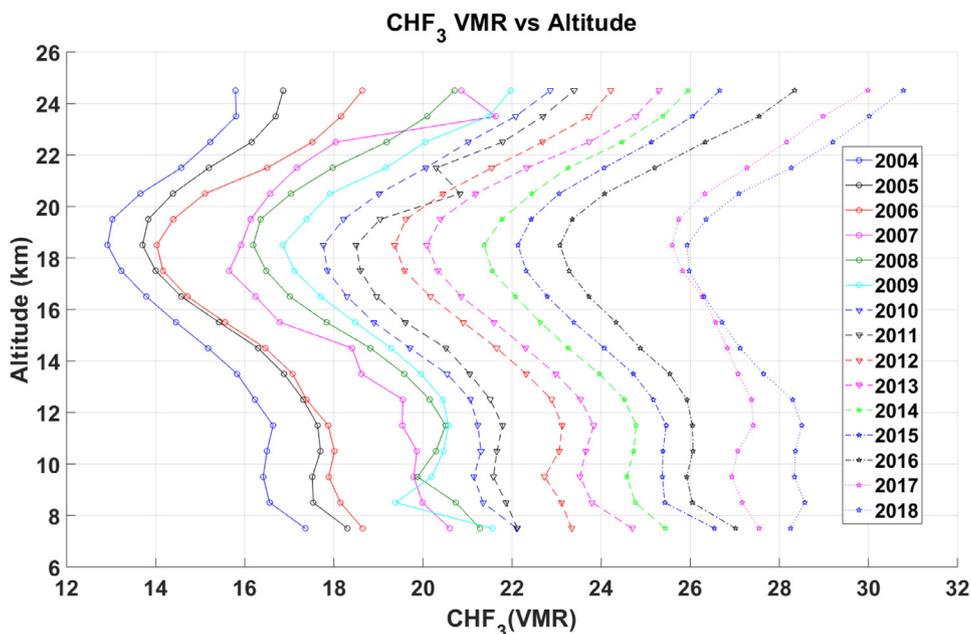


Fig. 1. ACE-FTS CHF_3 annual altitude profiles.

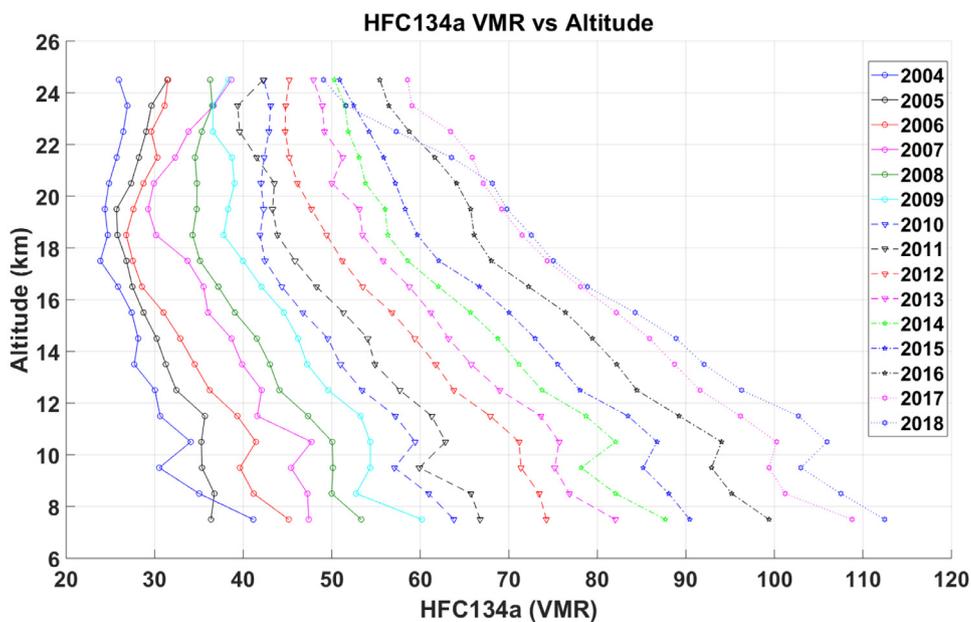


Fig. 2. ACE-FTS HFC-134a annual altitude profiles.

AGAGE GCMS-Medusa data available at the [AGAGE website](#) from 2004 to 2016 [27]. Montzka et al. [28] have also published global mean VMRs for HFC-134a based on NOAA sampling data and they are plotted in Fig. 5.

Since HFC-134a VMRs start to decrease significantly above 15.5 km, HFC-134a VMRs were considered only up to 15.5 km and the lower limit of the altitude range was chosen to be 6.5 km. The trend values were based on the unweighted annual average of all VMR bins between 6.5 and 15.5 km. The linear trend of the ACE-FTS HFC-134a time series is 4.9 ± 0.1 ppt per year. For AGAGE GCMS HFC-134a monthly data, annual means were calculated for both VMRs and their errors and then a weighted linear trend was calculated. The calculated linear trend for the AGAGE HFC-134a time series is 4.87 ± 0.05 ppt per year. The calculated linear trend for HFC-134a NOAA global flask data from Montzka

et al. [28] is 4.74 ± 0.05 ppt per year. The Scientific Assessment of Ozone Depletion: 2018 also provides annual mole fractions of HFC-134a. AGAGE in situ measurements show 6.0 ppt yr^{-1} (7.2% per yr^{-1}), NOAA flask measurements show 6.1 ppt yr^{-1} (7.4% per yr^{-1}) and UCL, flask measurements show 7.2 ppt yr^{-1} (8.5% per yr^{-1}) for 2015 - 2016. The annual mole fractions of AGAGE in situ measurements report 67.7 ppt in 2012, 83.3 ppt in 2015 and 89.3 ppt in 2016 [26]. Similarly, NOAA flask measurements report 67.5 ppt in 2012, 83.4 ppt in 2015 and 89.6 ppt in 2016 and UCL, flask measurements report 68.9 ppt in 2012, 84.9 ppt in 2015 and 92.1 ppt in 2016 [26]. These reported values are consistent with the ACE-FTS values in this study and the AGAGE values used to compare with ACE-FTS data.

ACE-FTS CHF_3 data were considered only between the altitudes 6.5 km and 12.5 km for the trend analysis. The linear trend of

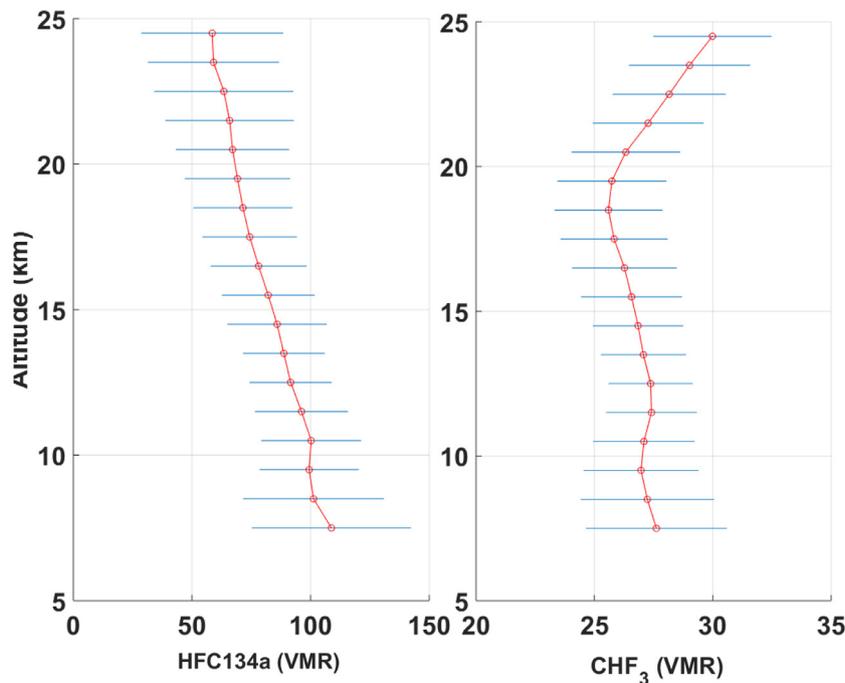


Fig. 3. ACE-FTS HFC-134a and CHF₃ average altitude profiles for 2017.

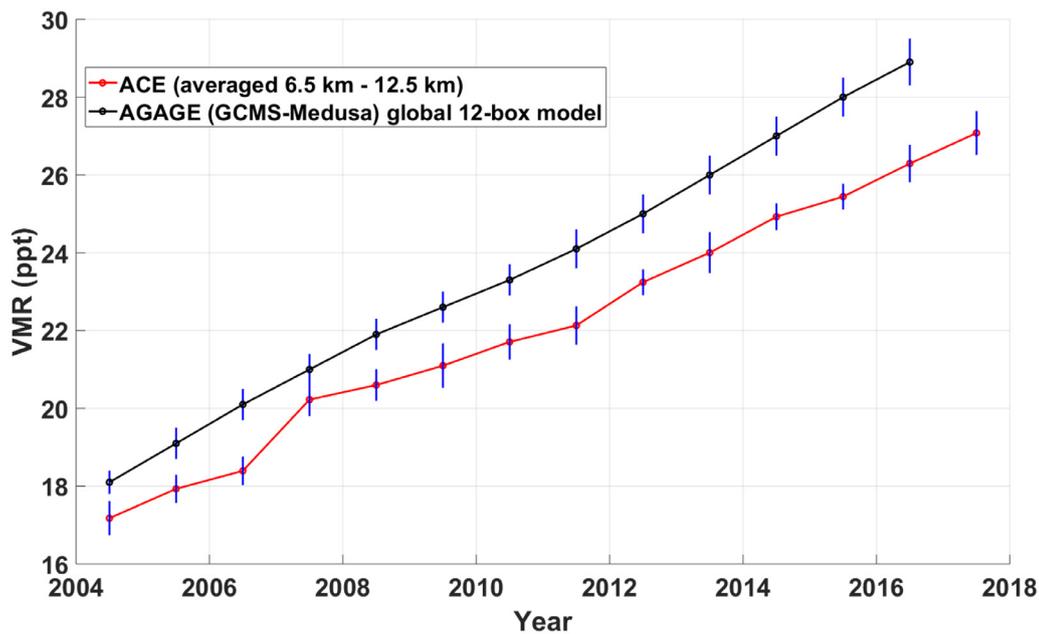


Fig. 4. ACE-FTS CHF₃ annual time series (60°S–60°N) comparison with AGAGE 12 box model data from Simmonds et al. [23] and AGAGE global mean baseline GCMS-Medusa data from the [AGAGE website](#).

the ACE-FTS CHF₃ time series is 0.75 ± 0.02 ppt per year. ACE-FTS CHF₃ data (Fig. 6) show an average 5% difference compared to AGAGE 12-box model values. (ACE-FTS CHF₃ time series were also calculated for the latitude bins 50°S–50°N and 40°S–40°S and they show no significant difference from the original 60°S–60°N ACE-FTS times series.) The reason for this discrepancy is not understood. The linear trend of the AGAGE 12-box model time series is 0.88 ± 0.01 ppt per year. ACE-FTS HFC-134a and CHF₃ trend values show excellent agreement with the AGAGE trends. The trends and the VMRs of HFC-134a NOAA global flask data also show excellent agreement with the ACE-FTS HFC-134a VMR and trend values (Fig. 5). The increasing atmospheric VMRs of HFC-134a have

been used to derive global emissions by Fortems–Cheiney et al. [29]. These HFC-134a global data show that HFC-134a global emissions are increasing [28,29] rapidly.

The ACE altitude ranges (6.5–12.5 km for CHF₃ and 6.5–15.5 km for HFC-134a) we have selected for comparisons with surface data are in the upper troposphere and lower extratropical stratosphere. Given the long lifetimes of CHF₃ (222 years) and HFC-134a (13.4 years), the gases should be well-mixed in the troposphere and lower stratosphere. Therefore, ACE-FTS VMRs and trends in Fig. 4 and Fig. 5 should be similar to the surface values.

The standard errors on the trends used in this paper are one standard deviation from a linear least squares analysis. The preci-

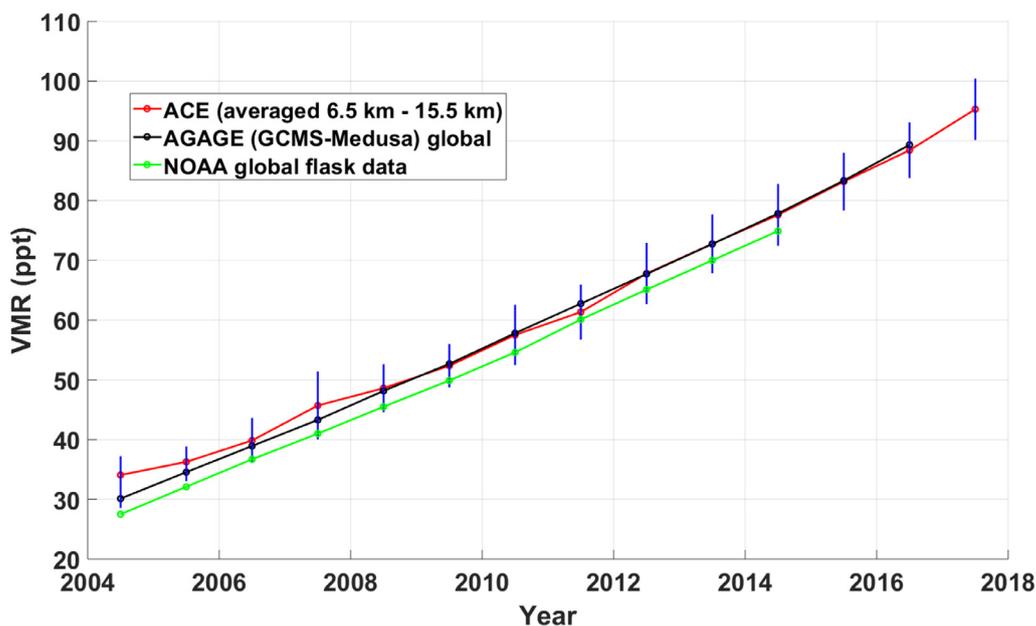


Fig. 5. ACE-FTS HFC-134a annual time series (60°S–60°N) comparison with AGAGE global mean baseline GCMS-Medusa data from the [AGAGE website](#) and NOAA global flask data from Montzka et al. [28].

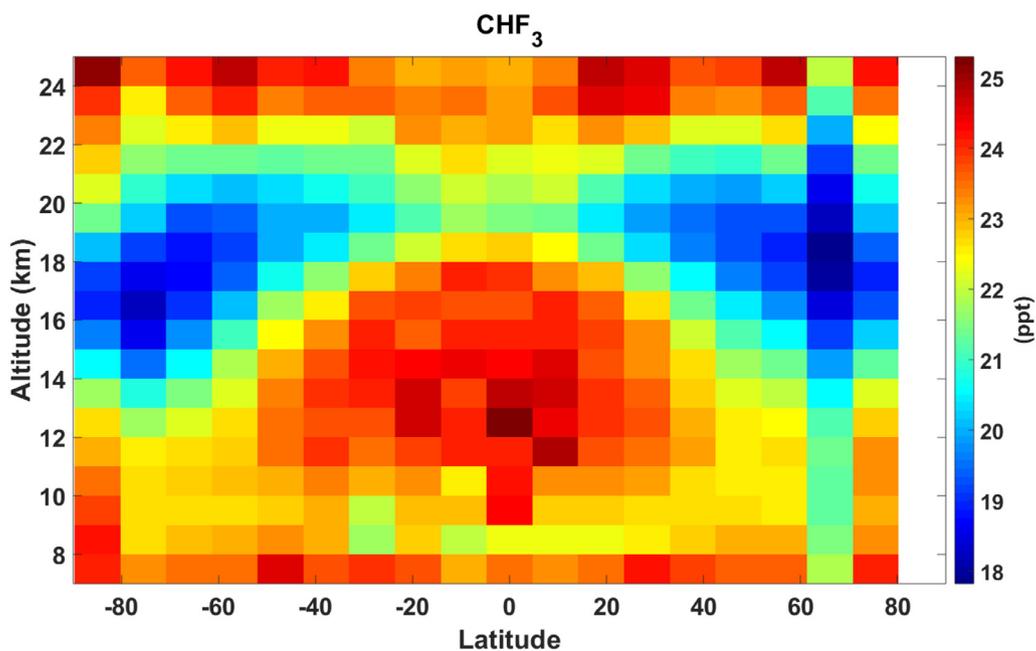


Fig. 6. CHF₃ latitudinal distribution.

sion of individual VMR data points on the 1 km altitude grid for a particular occultation for CHF₃ is roughly 20–30% and around 100% for HFC-134a based on statistical error estimates in the retrievals. Since more than 2000 data points (n) are used for the annual averages in the ACE-FTS trend analysis, the precision of these average values is smaller (for uncorrelated data the precision would be $\sqrt{n} = 45$ times smaller). The errors are therefore due to geophysical variability and systematic errors in the annual averages are not included in our analysis. For example, Harrison [20], [21] estimates the errors in the cross sections to be 3%. The systematic errors in the ACE-FTS retrievals can best be estimated by comparing with independent measurements as shown in Figs. 4 and 5.

Figs. 6 and 7 show the mission average latitudinal distributions of HFC-134a and CHF₃. The entire data set was averaged in 10°

latitude bins for each altitude. Values more than 2 standard deviations away from each bin average were excluded. Data in the 80°N–90°N bin of HFC-134a are not available as they were removed during the initial 2 standard deviation data filtering process. Both ACE-FTS HFC-134a and CHF₃ data are presented for the altitudes from 6.5 to 24.5 km. The standard deviation of the VMRs in each latitude–altitude bin of HFC-134a are 40–60% and of CHF₃ are about 20–30% for (Fig. 8). These error estimates are therefore a combination of geophysical variability and fitting errors in the least-squares analysis in the retrievals. Notice the expanded color scale in Fig. 6 for CHF₃ and the relatively large errors for HFC-134a. Most of the unusual patterns (e.g., 70°N for HFC-134a) lie within the error bars and are likely retrieval artifacts.

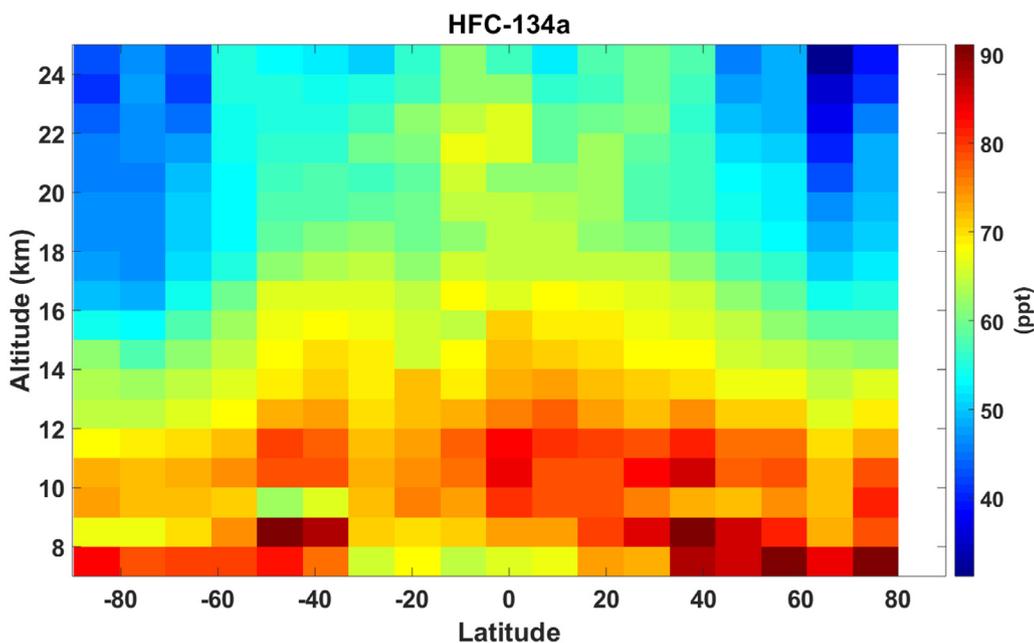
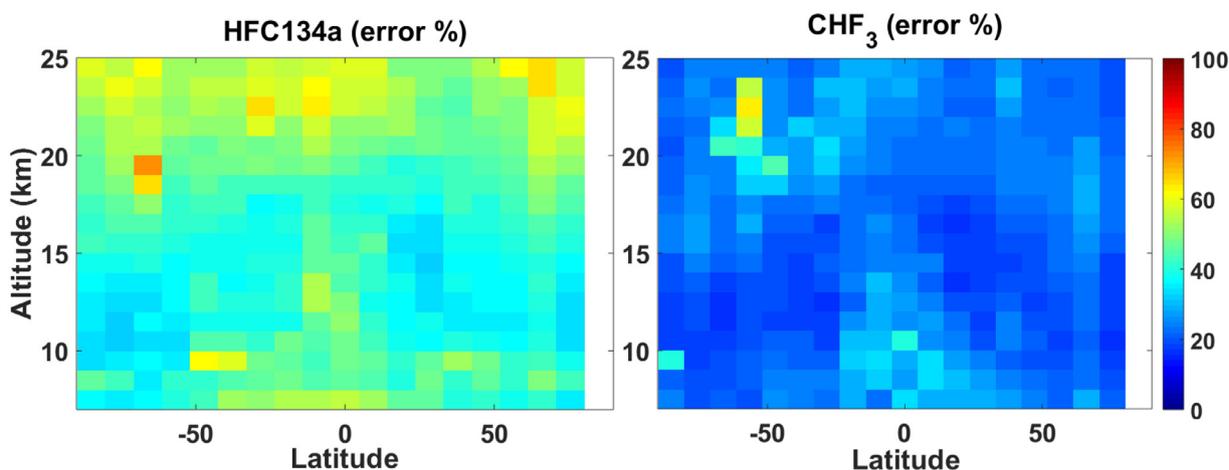


Fig. 7. HFC-134a latitudinal distribution.

Fig. 8. Percentage error in HFC-134a and CHF₃ altitude-latitude distributions.

The CHF₃ latitudinal distribution shows high VMRs (23–25 ppt) in the tropics in the upper troposphere relative to the poles. In the upper stratosphere (13.5–19.5 km) of the polar regions the volume mixing ratios of CHF₃ show low values between 18–22 ppt, and above 19.5 km the VMR values start to increase back to 23–25 ppt. There is also a band of high values from 22.5 km to 24.5 km at the top of the retrieval range. This unusual pattern may be a retrieval artifact because such VMR increases would imply a source. While such a source is conceivable from photolysis of other fluorine-containing molecules, a more likely explanation is a retrieval artifact.

In the troposphere the VMRs of the ACE-FTS HFC-134a range between 65 and 85 ppt. Compared to the CHF₃, the HFC-134a global distribution shows the expected decline with altitude. The peak HFC-134a cross section at 1104.5 cm⁻¹ is about 5 times weaker than the peak HFC-23 cross section at 1156.1 cm⁻¹ resulting in better precision for CHF₃ (Fig. 8). Both molecules suffer from severe interference from ozone. Notice however that accuracy of CHF₃ (Fig. 4) is worse than HFC-134a (Fig. 5) probably because CHF₃ has a broader feature and suffers from more interference.

4. Conclusion

The global linear trend of the ACE-FTS HFC-134a time series is 4.9 ± 0.1 ppt per year and is 4.87 ± 0.05 ppt per year for the AGAGE time series. The global linear trend of the ACE-FTS CHF₃ time series is 0.75 ± 0.02 ppt per year and the AGAGE 12-box model trend is 0.88 ± 0.01 ppt per year. ACE-FTS trend values for HFC-134a and CHF₃ are in excellent agreement with the AGAGE linear trend values. The atmospheric abundances of HFC-134a and CHF₃ are increasing rapidly.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jqsrt.2019.06.019](https://doi.org/10.1016/j.jqsrt.2019.06.019).

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