



# Trends in halogen-containing molecules measured by the Atmospheric Chemistry Experiment (ACE) satellite

Johnathan Steffen<sup>a,\*</sup>, Peter F. Bernath<sup>b,a</sup>, Chris D. Boone<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Waterloo, Waterloo, ON, N2L 3G1, Canada

<sup>b</sup> Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, 23529, USA

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## ABSTRACT

The Montreal Protocol has banned the production of long-lived halogen-containing molecules such as chlorofluorocarbons (CFCs) that are responsible for the widespread destruction of stratospheric ozone. Sixteen halogen-containing trace gases ( $\text{CCl}_4$ ,  $\text{CF}_4$ , CFC-11, CFC-12, CFC-113,  $\text{CH}_3\text{Cl}$ ,  $\text{ClONO}_2$ ,  $\text{COCl}_2$ ,  $\text{COClF}$ ,  $\text{COF}_2$ , HCFC-22, HCFC-141b, HCFC-142b,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{SF}_6$ ) are observed globally by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) which measures atmospheric spectra via solar occultation from low-Earth orbit. The ACE satellite was launched in August 2003 and continues to operate with minimal degradation to this day. ACE is uniquely able to provide global long term trends of the concentrations of many atmospheric constituents. In this work we present time series trends and altitude-latitude distributions of halogen-containing trace gases. For 12 molecules the altitude-latitude distributions are reliable, but for  $\text{CF}_4$ , CFC-113, HCFC-141b and HCFC-142b the distributions are anomalous likely because of spectroscopic interference in the retrieval. These 16 species can be categorized as source gases such as CFCs emitted at the surface and product gases such as  $\text{HCl}$ ,  $\text{HF}$  and  $\text{ClONO}_2$  that are formed by chemical reactions from the source gases. Many of these substances deplete stratospheric ozone and are potent greenhouse gases that contribute to climate change.

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## 1. Introduction

In 1974 Molina and Rowland [1] reported that chlorofluorocarbons such as CFC-11 ( $\text{CCl}_3\text{F}$ ) and CFC-12 ( $\text{CCl}_2\text{F}_2$ ) are inert in the troposphere but are photodissociated in the stratosphere to release Cl atoms that can destroy ozone in a catalytic cycle involving the ClO free radical. CFCs are used as refrigerants and blowing agents, and are released in the atmosphere as a result of human activity. Stratospheric ozone protects us from deleterious UV radiation in the 200–300 nm region. Most of the stratospheric chlorine released from the organic source gases ends up in reservoir compounds such as  $\text{HCl}$  and  $\text{ClONO}_2$  that do not react with  $\text{O}_3$ , although only after taking part in many catalytic ozone-destroying reactions. However, in 1985, Farman, Gardiner and Shanklin [2] discovered the Antarctic ozone hole in the stratosphere, caused by the conversion of inactive chlorine-containing reservoir molecules into reactive species that destroy ozone catalyzed by polar stratospheric clouds (PSCs) [3].

The loss of most of the stratospheric ozone within the polar vortex during Antarctic spring spurred the international commu-

nity to adopt the Montreal Protocol (1987) which controls and phases out the production of ozone depleting substances such as CFCs. The Montreal Protocol is a binding international treaty that has been universally ratified. Over time there have been many amendments and adjustments arising from regular meetings of the parties. Although CFC production is now banned, the temporary use of hydrochlorofluorocarbons (HCFCs) such as HCFC-22 ( $\text{CHClF}_2$ ) is still permitted in developing countries. HCFCs have shorter atmospheric lifetimes than CFCs because they react with OH, but still deplete stratospheric ozone. HCFCs are being replaced by hydrofluorocarbons (HFCs) that contain no chlorine. Ultimately HFCs will also be replaced due to their contribution to global warming.

CFCs, HCFCs and HFCs generally have large global warming potentials (GWPs) because of their long lifetimes and strong absorption in the atmospheric window region near 10  $\mu\text{m}$ . The gases associated with the Montreal Protocol are therefore contributing to climate change. Recognizing this problem, the parties to the Montreal Protocol adopted the Kigali Amendment in 2016 to phase out the production of long-lived HFCs such as HFC-134a ( $\text{CF}_3\text{CFH}_2$ ) in favor of short-lived compounds such as hydrofluoroolefins (HFOs). HFOs, e.g., HFO-1234yf ( $\text{CH}_2=\text{CF}_3$ ), do not destroy stratospheric ozone and have a negligible GWP.

\* Corresponding author.

E-mail address: [jsteffen@scisat.ca](mailto:jsteffen@scisat.ca) (J. Steffen).

To monitor compliance with the Montreal Protocol, halogen-containing gases are measured by a variety of techniques on the ground, from air-borne platforms and from orbit. For example, extensive in situ measurements are made by the AGAGE network [4] and from the analysis of samples collected by the NOAA flask network [5]. The ground-based Fourier transform spectrometers (FTSs) of the NDACC network [6] measure total atmospheric column densities of many species including organic source gases and the final HCl product gas. The balloon-borne MkIV FTS [7] and aircraft campaigns such as HIPPO [8] provide altitude-resolved abundances. Notable satellite observations have been made by MIPAS [9] and ACE [10] FTSs. These atmospheric abundances can be analyzed to make “top-down” estimates of emissions [11].

Of the 16 halogen-containing species measured by the ACE-FTS, 10 can be classified as source gases ( $\text{CCl}_4$ ,  $\text{CF}_4$ , CFC-11, CFC-12, CFC-113,  $\text{CH}_3\text{Cl}$ , HCFC-22, HCFC-141b, HCFC-142b,  $\text{SF}_6$ ) emitted from the surface and 6 are product gases ( $\text{ClONO}_2$ ,  $\text{COCl}_2$ ,  $\text{COClF}$ ,  $\text{COF}_2$ , HCl, HF) formed by chemical reactions from the source gases. The product gases and three of the source gases are not regulated by the Montreal Protocol:  $\text{CF}_4$  and  $\text{SF}_6$  contain no chlorine and therefore do not directly deplete stratospheric ozone and  $\text{CH}_3\text{Cl}$  is mainly emitted by natural sources such as plants. However,  $\text{CF}_4$  and  $\text{SF}_6$  are powerful greenhouse gases and contribute to global warming.

## 2. Atmospheric chemistry experiment

The Atmospheric Chemistry Experiment (ACE) began with the launch of SCISAT in August 2003 [10]. The primary ACE instrument is a Michelson interferometer (ACE-FTS), which employs the solar occultation measurement technique, collecting a series of atmospheric transmittance spectra over the course of a sunrise or sunset event experienced by the orbiting satellite. The ACE orbit is nearly circular, with an orbit inclination of  $73.9^\circ$  to the equator and an altitude of 650 km. SCISAT's orbit was designed for near global coverage while maximizing measurements at high latitudes. ACE orbits the Earth approximately 15 times per day, with each orbit allowing one sunset and one sunrise occultation. The number of occultations actually measured by the ACE-FTS is often limited by the available ground station down-link time.

The ACE-FTS covers the  $750\text{--}4400\text{ cm}^{-1}$  range using two detectors (HgCdTe and InSb) and has  $0.02\text{ cm}^{-1}$  spectral resolution. Complementing the ACE-FTS is the small spectrophotometer, Measurement of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation (MAESTRO). MAESTRO originally covered the  $285\text{--}1030\text{ nm}$  region in two overlapping segments. There are also two solar imagers that operate at  $0.525$  and  $1.02\text{ }\mu\text{m}$ .

The main goal of the ACE mission is to understand the chemical and dynamical processes that control the distribution of ozone in the stratosphere and upper troposphere, particularly in the Arctic, with a secondary goal to explore the relationship between atmospheric chemistry and climate change. ACE measures many atmospheric constituents regulated by the Montreal Protocol because of their large Ozone-Depleting Potentials (ODPs), such as CFC-11 and HCFC-22. As of version 3.6, the ACE mission has produced data products for 35 atmospheric molecules, with more coming in future versions.

While the original proposal outlined a two-year mission, ACE has entered its sixteenth year in orbit with only a small decline in performance. ACE's long lifetime and global coverage puts it in a unique position to produce long-term trends and distributions of atmospheric molecules of interest, providing insight into their potential impact on the stratospheric ozone layer and their contribution to climate change.

## 3. Results / discussion

### 3.1. Methods

The data used in this work are from the v3.5/3.6 Level 2 ACE data set available via signup online (<https://databace.scisat.ca/l2signup.php>). The data were first filtered using the flag guidelines outlined by Sheese et al. [12]. Next, the data were plotted by altitude in 1 km bins so obvious outliers could be easily removed. Finally, an average at each altitude was calculated and points outside 'n' median absolute deviations (MAD) were removed, with 'n' depending on the molecule in question. Values of 'n' were chosen to be as small as possible while still encompassing  $\approx 99\%$  of the data, choosing to err on retaining a questionable outlier as opposed to rejecting it.

After filtering, data were then binned into years and quarters for trend analysis, and  $5^\circ$  latitude and 1 km altitude bins for distributions. The quarters used by this work were December, January, February (DJF); March, April, May (MAM); June, July, August (JJA); and September, October, November (SON). Averages were calculated for each bin and plotted for each molecule to create trends and distributions. VMR distributions presented in this work are averaged over the entire ACE mission (2004–2018).

Trends were calculated using a linear regression least-squares model. In the cases for which two lines were used to fit the trends, the break point was chosen by plotting the graph and finding the intersection of the two lines to get the break point. Although a linear trend analysis is not always completely appropriate, it is a reasonable approximation for ACE data. Seasonal variations were filtered by fitting and subtracting sine waves with a least-squares residual approach using periods of half a year and a year. The portion of the global distribution used to create each trend value is outlined with a black box in its respective global distribution figure. Boxes were drawn to enclose the main part of the distribution where the VMRs are the largest. Adjusting the boundaries of the boxes has only a minor effect on the trends. All VMRs in the box were included in the trend analysis without weighting.

Statistical significance of trends was determined using a Student's *t*-test with a 95% confidence interval. Errors presented are the Standard Error of the slope (all reported errors are one standard deviation). The 't' in each trend line formula is defined as  $t = \text{year} - 2004.25$ . Table 1 contains a summary of the trend results from this study in ppt/year and %/year (in parentheses). The %/year trend values in Table 1 were calculated by dividing the VMR/year by the average VMR for the time period. For comparisons with data from other sources, the linear trend equations (Table 1) were used to calculate the ACE VMR values (and %/year values) for a particular year (or range of years).

The analysis reported here uses a similar methodology to that of Brown et al. [13]. Brown et al. used only  $30^\circ\text{S}\text{--}30^\circ\text{N}$  v3.0 data for 2004–2010.

### 3.2. $\text{CCl}_4$

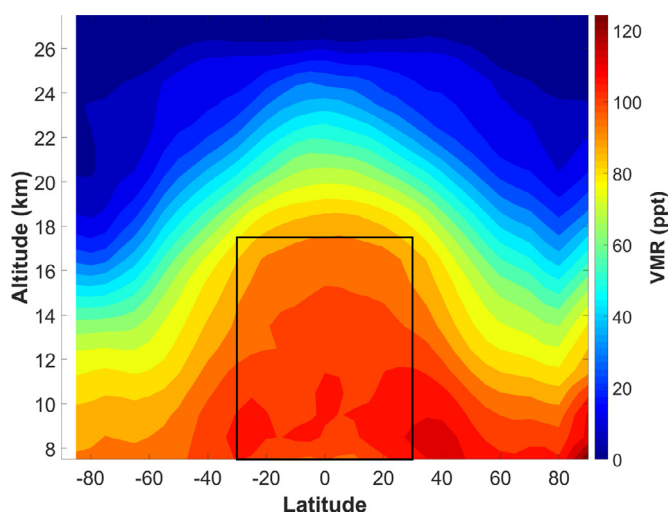
Carbon tetrachloride ( $\text{CCl}_4$ , CFC-10) is an anthropogenic chlorine-containing source gas that saw major use in the mid-20th century as a feedstock for the production of CFC-11 and CFC-12.  $\text{CCl}_4$  is both an ozone-depleting substance with an ozone-depleting potential of 0.72 as well as a potent greenhouse gas with a 100-year global warming potential of 2110 [14].  $\text{CCl}_4$  was phased out in 1996 and 2006 for developed and developing countries, respectively, under the London (1990) and Copenhagen (1992) amendments to the Montreal Protocol, except for use as a feedstock to produce HFCs [15].

However, discrepancies exist between bottom-up emissions estimates derived from reported production and feedstock usage and

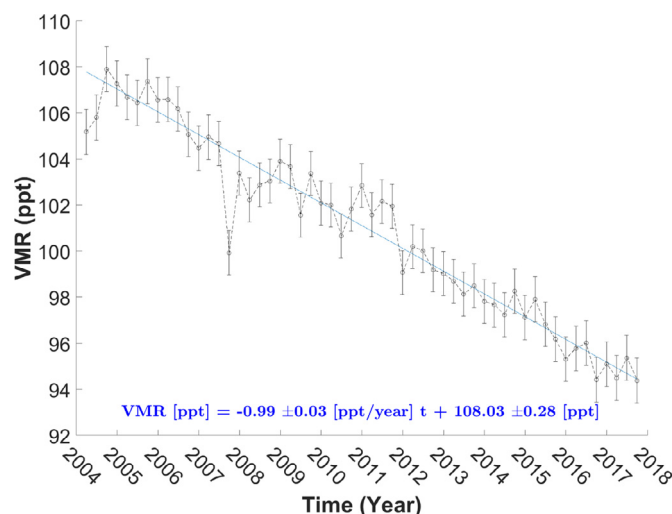
**Table 1**

Summary of each trend determined in this work, including how the data was delimited to calculate each trend. Percentage values of trends are presented in parentheses.

Molecule	'n' MADs	Trend 1 (ppt/year)	Trend 2 (ppt/year)	Break
CCl <sub>4</sub>	2.5	$-0.99 \pm 0.03$ ( $-0.98 \pm 0.03$ )	–	–
CF <sub>4</sub>	3.0	$0.53 \pm 0.01$ ( $0.66 \pm 0.02$ )	–	–
CFC-11	6.0	$-2.33 \pm 0.14$ ( $-0.96 \pm 0.06$ )	$-1.79 \pm 0.13$ ( $-0.79 \pm 0.06$ )	Pre-2012/Post-2012
CFC-12	6.0	$-2.1 \pm 0.14$ ( $-0.40 \pm 0.03$ )	$-3.83 \pm 0.13$ ( $-0.76 \pm 0.03$ )	Pre-2012/Post-2012
CFC-113	3.0	$-0.59 \pm 0.02$ ( $-1.03 \pm 0.04$ )	–	–
CH <sub>3</sub> Cl	2.5	$0.25 \pm 0.21$ ( $0.04 \pm 0.03$ )	–	–
ClONO <sub>2</sub>	2.5	$5.90 \pm 2.14$ ( $0.86 \pm 0.31$ )	$7.04 \pm 2.18$ ( $0.93 \pm 0.29$ )	Sunset/Sunrise
COCl <sub>2</sub>	3.0	$0.14 \pm 0.02$ ( $0.90 \pm 0.14$ )	$-0.19 \pm 0.06$ ( $-0.74 \pm 0.25$ )	12.5–17.5 km/19.5–28.5 km
COCIF	2.5	$0.35 \pm 0.11$ ( $-0.57 \pm 0.19$ )	–	–
COF <sub>2</sub>	2.5	$0.72 \pm 0.36$ ( $0.25 \pm 0.13$ )	–	–
HCFC-22	6.0	$7.56 \pm 0.15$ ( $3.67 \pm 0.07$ )	$4.36 \pm 0.20$ ( $1.74 \pm 0.08$ )	Pre-2012/Post-2012
HCFC-141b	2.5	$0.53 \pm 0.03$ ( $1.64 \pm 0.10$ )	–	–
HCFC-142b	6.0	$1.26 \pm 0.05$ ( $5.69 \pm 0.21$ )	$0.23 \pm 0.03$ ( $0.82 \pm 0.09$ )	Pre-2012/Post-2012
HCl	2.5	$-25.94 \pm 1.90$ ( $-0.80 \pm 0.06$ )	$-8.25 \pm 0.92$ ( $-0.26 \pm 0.03$ )	Pre-2009/Post-2009
HF	2.5	$15.12 \pm 1.29$ ( $0.81 \pm 0.07$ )	$9.27 \pm 1.47$ ( $0.48 \pm 0.08$ )	Pre-2011/Post-2011
SF <sub>6</sub>	3.0	$0.18 \pm 0.01$ ( $3.37 \pm 0.19$ )	$0.26 \pm 0.01$ ( $3.65 \pm 0.1$ )	Pre-2012/Post-2012



**Fig. 1.** CCl<sub>4</sub> VMR distribution between 85°S–90°N latitude and 7.5–27.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.



**Fig. 2.** CCl<sub>4</sub> VMR trend of  $-0.99 \pm 0.03$  ppt/year between 30°S–30°N latitude and 7.5–17.5 km altitude.

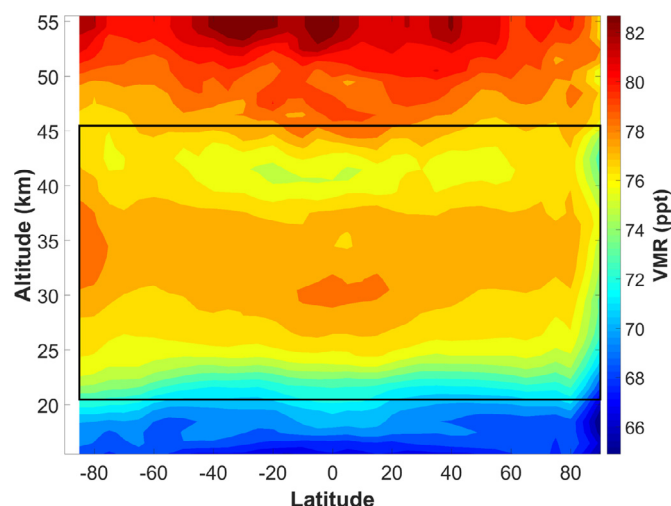
top-down emissions estimates derived from atmospheric observations [16,17]. Recent work by Park et al. suggests a large portion of this discrepancy is due to unreported emissions from China totalling approximately  $23.6 \pm 7.1$  Gg/year between 2011 and 2015 [11]. The v2.2 and v3.5/3.6 CCl<sub>4</sub> data [18] are biased high by 20–30% relative to ground-based measurements. A new preliminary ACE-FTS retrieval has been shown by Harrison et al. to resolve this bias by using new absorption cross sections and avoiding more of the spectral interference of other molecules [19], which has been incorporated into ACE v4.0.

A global mission average distribution for CCl<sub>4</sub> (Fig. 1) has been created between 7.5–27.5 km, and a trend analysis used averaged profiles between 30°S–30°N and between 7.5–17.5 km (Fig. 2). The majority of CCl<sub>4</sub> exists in the lower stratosphere and within the tropics, with a sharp decline outside these boundaries. There is a decline of  $-0.99 \pm 0.03$  ppt/year ( $-0.98 \pm 0.03\%$ /year) over the entire ACE mission. This is lower than the previously reported ACE trend by Brown et al. [13] of  $-1.32 \pm 0.09$  ppt/year which averaged profiles between 5.5–17.5 km in the tropics, as well as the value reported by Valeri et al. using MIPAS data from a similar region of  $-1.28 \pm 0.012$  ppt/year [20]. AGAGE, NOAA, and UCI report percentage trends from 2015 to 2016 of  $-1.5$ ,  $-1.2$ , and  $-0.3\%$ /year, respectively. In comparison, ACE reports a trend of  $-1.02\%$ /year during 2015–2016. The ACE-FTS VMR presented here is 96.4 ppt in 2016,

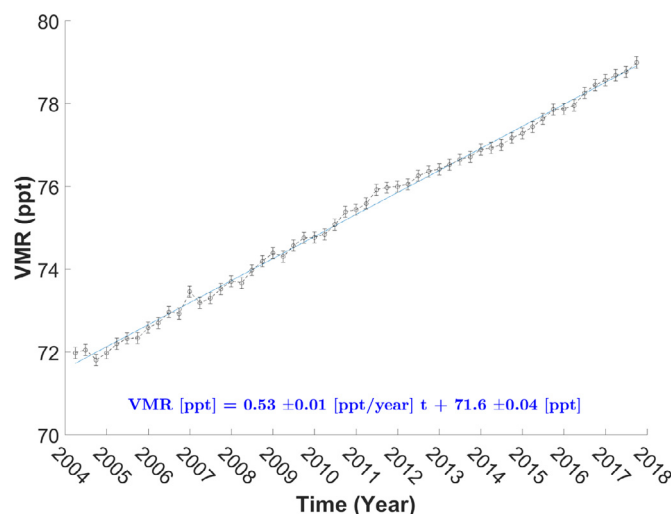
biased high compared to the 2018 WMO reported VMRs of 79.9, 81.2, 81.9 ppt [21].

### 3.3. CF<sub>4</sub>

CF<sub>4</sub> is a very potent greenhouse gas with a global warming potential of  $\approx 6630$  [22]. CF<sub>4</sub> has no significant sinks in the troposphere and stratosphere, and is remarkably long-lived, having an atmospheric lifetime greater than 50,000 years [21]. This makes CF<sub>4</sub> useful as an atmospheric tracer. The main source of CF<sub>4</sub> is fugitive gas emission from aluminum production [23]. CF<sub>4</sub> also has a natural source due to degassing from the mineral fluorite [24], but this source is estimated to be negligible compared to anthropogenic emissions. The ACE-FTS global distribution of CF<sub>4</sub> sees large unexplained enhancements above  $\approx 25$  km. Irregularities exist in the distribution (Fig. 3) between 40–45 km as VMRs briefly drop and then rise again, most likely due to artifacts in the retrieval. The source of these problems is not well understood but, as usual, there may be problems with the cross sections and particularly spectral interference from other molecules. CF<sub>4</sub> is increasing at a rate of  $0.53 \pm 0.01$  ppt/year ( $0.66 \pm 0.02\%$ /year) across all latitudes when averaged between 20.5–45.5 km over the ACE mission. Previously, Brown et al. reported a trend of  $0.54 \pm 0.03$  ppt/year in the tropics between 25–40 km during 2004–2010 [13],



**Fig. 3.** CF<sub>4</sub> VMR distribution between 85°S–90°N latitude and 15.5–55.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.

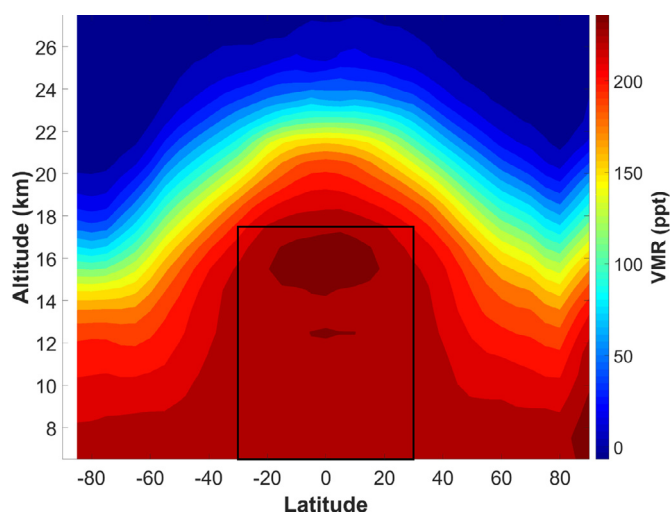


**Fig. 4.** CF<sub>4</sub> VMR trend of  $0.53 \pm 0.01$  ppt/year between 85°S–90°N latitude and 20.5–45.5 km altitude.

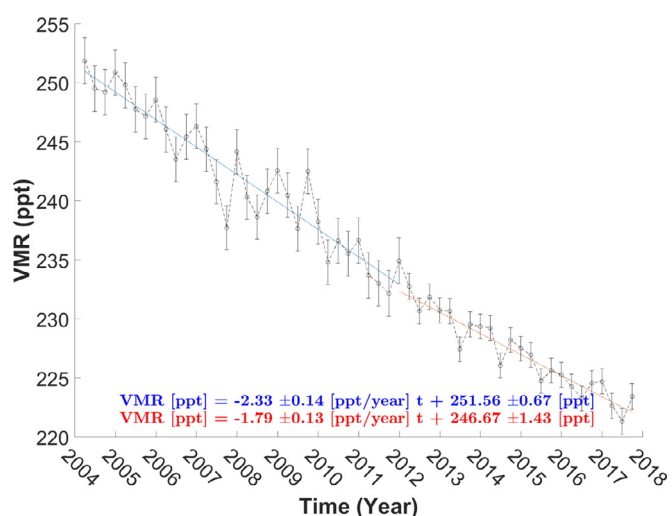
Mühle et al. report AGAGE tropospheric trends of  $0.686 \pm 0.002$  and  $0.702 \pm 0.001$  between 1993–2008 and 1994–2008 in the Northern Hemisphere and Southern Hemisphere, respectively [23]. AGAGE reports a VMR of 82.7 ppt and trend of 1.0%/year [21] between 2015 and 2016. ACE reports a trend during the same time-frame of 0.68%/year and 2016 VMR of 77.8 ppt, which are each biased low. (Fig. 4)

### 3.4. CFC-11

CFC-11 is a major anthropogenic chlorine source gas and is the second most abundant CFC in the atmosphere. Production of CFC-11 is currently banned under the Montreal Protocol. CFC-11 is long-lived (52 years) and does not have a sink in the troposphere, but undergoes photolytic dissociation in the stratosphere. Despite being banned under the Montreal Protocol, there are observations suggesting illegal emissions in East Asia [25]. Enhancement of CFC-11 is seen in the troposphere and the lower tropical stratosphere (Fig. 5), with VMRs of CFC-11 dropping off quickly outside of these bounds. Averaging profiles in the tropics between 6.5 and 17.5 km CFC-11 yields a rate of  $-2.33 \pm 0.14$  ppt/year ( $-0.96 \pm 0.06\%$ /year) before 2012 and  $-1.79 \pm 0.13$  ppt/year ( $-0.79 \pm 0.06\%$ /year) af-



**Fig. 5.** CFC-11 VMR distribution between 85°S to 90°N latitude and 6.5–27.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.



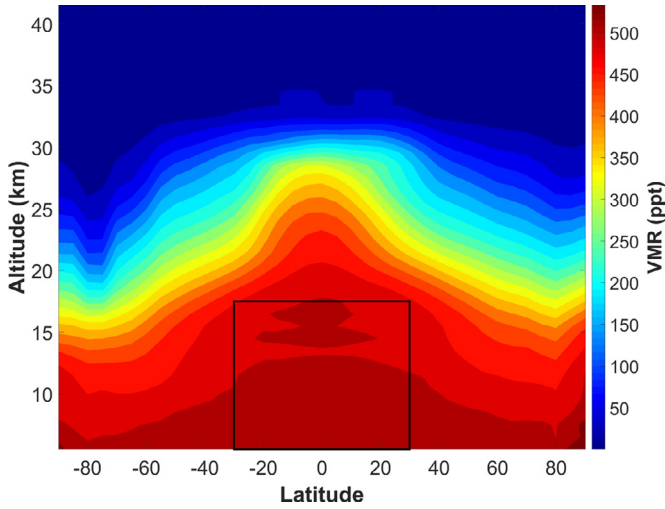
**Fig. 6.** CFC-11 VMR trend of  $-2.33 \pm 0.14$  ppt/year pre-2012 and  $-1.79 \pm 0.13$  ppt/year post-2012 between 30°S–30°N latitude and 6.5–17.5 km altitude.

ter (Fig. 6). Brown et al. report a trend in the tropics between 7–16 km during 2004–2010 of  $-2.21 \pm 0.07$  ppt/year [13]. AGAGE, NOAA, and UCI report VMRs of 229.6, 229.8, and 227.4 ppt for 2016 [21]. The 2016 ACE VMR of 225.6 ppt compares well with these values. The changes for 2015–2016 for AGAGE, NOAA and UCI are  $-0.6$ ,  $-0.6$  and  $-0.8\%$ /year, respectively, in agreement with the ACE trend of  $-0.79\%$ /year for 2015–2016.

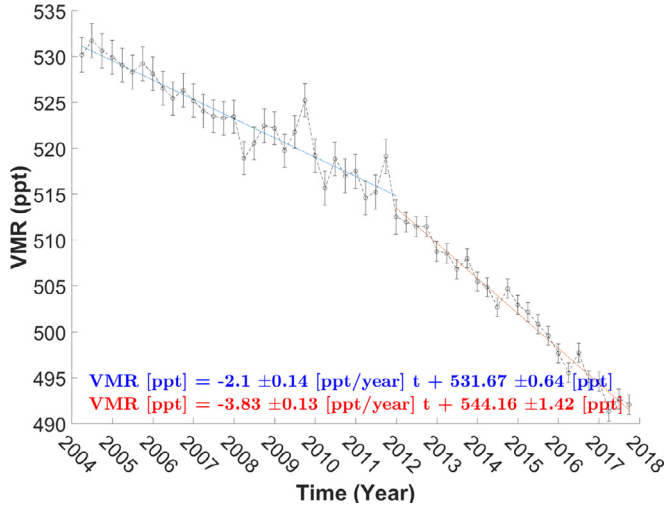
### 3.5. CFC-12

CFC-12 is an anthropogenic chlorine source gas and is the most abundant CFC in the atmosphere. It was originally produced as an aerosol propellant and refrigerant before being phased out by the Montreal Protocol due to its role in stratospheric ozone depletion. CFC-12 undergoes photolytic dissociation in the stratosphere, releasing a chlorine atom which goes on to destroy ozone [1]. As an anthropogenic chlorine source gas which gets removed in the stratosphere, the majority of the CFC-12 distribution is in the troposphere and lower tropical stratosphere (Fig. 7). There is a break in the trend reported here (Fig. 8) between 2011 and 2012, which shows a decline of  $-2.10 \pm 0.14$  ppt/year ( $-0.40 \pm 0.03\%$ /year) and  $-3.83 \pm 0.13$  ppt/year ( $-0.76 \pm 0.03\%$ /year) before and after





**Fig. 7.** CFC-12 VMR distribution between 90°S–90°N latitude and 5.5–41.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.



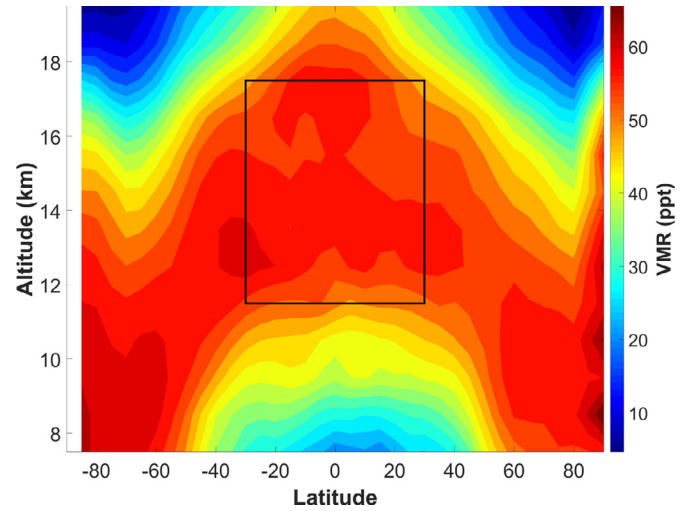
**Fig. 8.** CFC-12 VMR trend of  $-2.10 \pm 0.14$  ppt/year pre-2012 and  $-3.83 \pm 0.13$  ppt/year post-2012 between 30°S–30°N latitude and 5.5–17.5 km altitude.

the break, respectively. Brown et al. report an ACE-FTS trend of  $-1.90 \pm 0.12$  ppt/year in the tropics between 5 and 17 km during 2004 to 2010 [13]. AGAGE, NOAA, and UCI report 2016 VMRs and trend values of 516.1, 512.2, 515.6 ppt and  $-0.7$ ,  $-0.6$ , and  $-0.8\%/year$  [21]. The current ACE-FTS VMR of 499.2 ppt in 2016 is biased slightly low, while the ACE-FTS trend during 2015–2016 of  $-0.76\%/year$  is consistent with values from the 2018 WMO report.

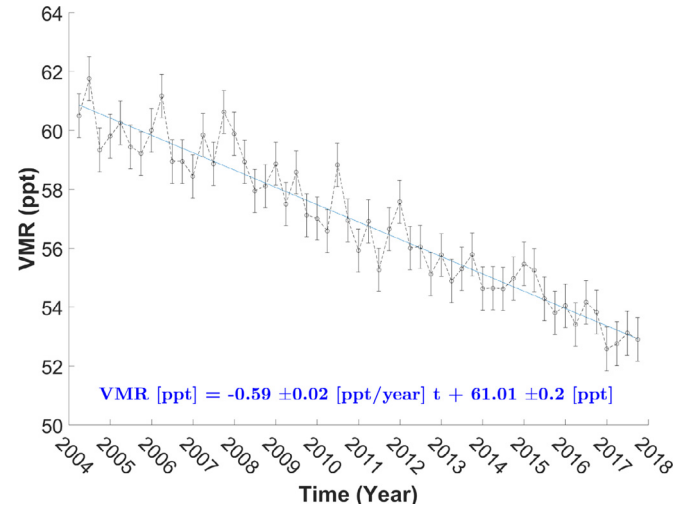
At first sight, the ACE trends look different from the NOAA trends in the VMR plots for 1978 to the present [26] but in fact they are similar when adjusted for the different observation periods. The NOAA values peak at about 2002 and show a slow non-linear decline until about 2012 and then are relatively linear from 2012 to the present. This curvature is also present in the ACE data for 2004 to 2012 (Fig. 8), but we have used a line to represent the data. The linear NOAA trend for 2004.25 to 2012 is  $-2.38 \pm 0.04$  ppt/year, compared to the ACE value of  $-2.10 \pm 0.14$  ppt/year, and is  $-3.09 \pm 0.02$  ppt/year for 2012–2018 compared to the ACE value of  $-3.83 \pm 0.13$  ppt/year.

### 3.6. CFC-113

CFC-113 is the third most abundant CFC in the atmosphere. It was produced primarily as a degreasing solvent for electronic

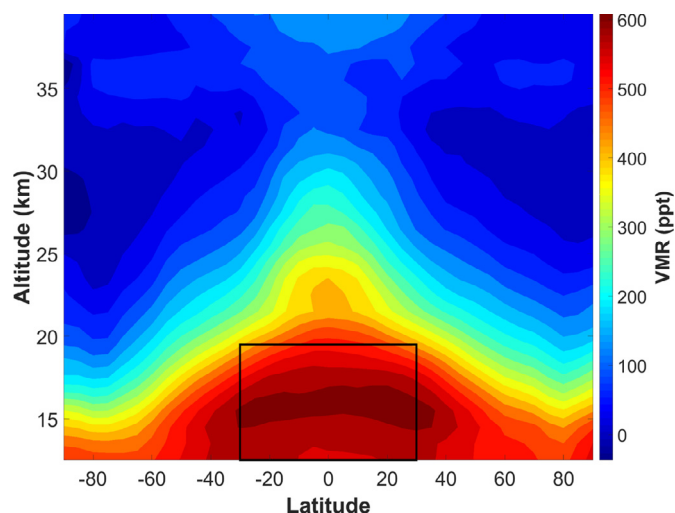


**Fig. 9.** CFC-113 VMR distribution between 85°S–90°N latitude and 7.5–19.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.

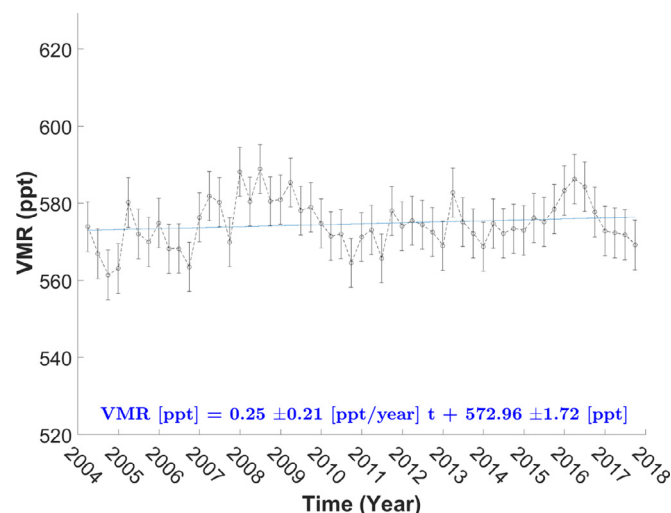


**Fig. 10.** CFC-113 VMR trend of  $-0.59 \pm 0.02$  ppt/year between 30°S–30°N latitude and 11.5–17.5 km altitude.

components and for the dry-cleaning/foam-blowing industries. Like CFC-11 and CFC-12, CFC-113 has a long atmospheric lifetime (93 years) and its primary removal is due to photolytic dissociation in the stratosphere. The distribution presented here (Fig. 9) has apparent artifacts in the lower tropical troposphere that are unexpected for a substance whose emissions are primarily anthropogenic. Clearly there is spectral interference from another tropospheric molecule which masks CFC-113 and causes a low bias which increases towards the surface. CFC-113 is currently decreasing (Fig. 10) at  $-0.59 \pm 0.02$  ppt/year ( $-1.03 \pm 0.04\%/year$ ) in the tropics between 11.5–17.5 km over the entire ACE mission. When averaged between 6–17 km in the tropics during 2004 and 2010, Brown et al. report a decrease of  $-0.65 \pm 0.08$  ppt/year [13], and trends reported by the 2018 WMO ozone report are  $-0.9$ ,  $-0.8$ , and  $-1.0\%/year$  for NOAA, AGAGE, and UCI, respectively for 2015–2016. For 2015–2016, ACE reports a trend of  $-1.09\%/year$ . AGAGE, NOAA, and UCI report 2016 VMRs of 71.4, 71.5, and 71.1 ppt [21]. ACE's 2016 CFC-113 VMR of 54.1 ppt is biased low in comparison, while the trend value is biased high.



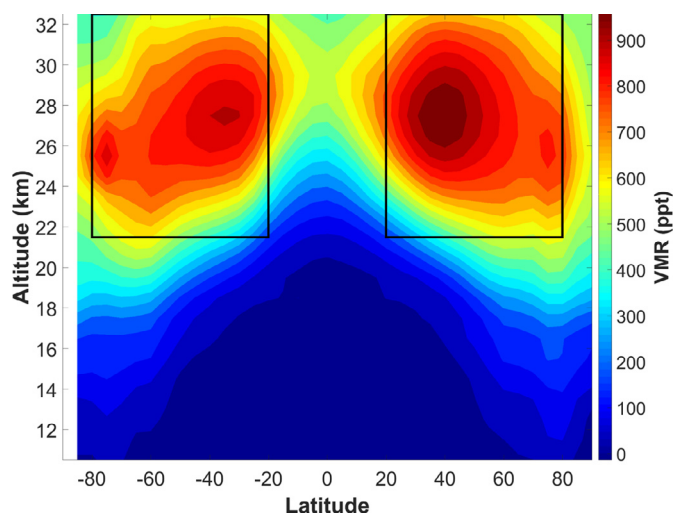
**Fig. 11.** Methyl chloride VMR distribution between 90°S–90°N latitude and 13.5–39.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.



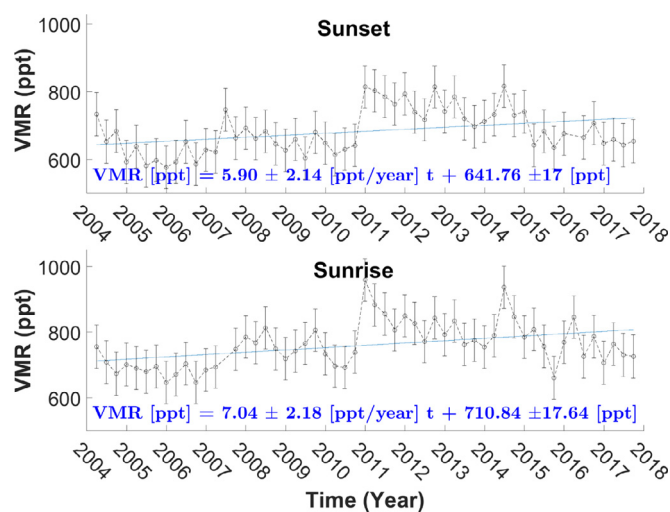
**Fig. 12.** Methyl chloride VMR trend of  $0.25 \pm 0.21$  ppt/year between 30°S–30°N latitude and 12.5–19.5 km altitude. The trend presented here is statistically insignificant.

### 3.7. $\text{CH}_3\text{Cl}$

$\text{CH}_3\text{Cl}$  (methyl chloride) is the largest source of natural atmospheric chlorine, accounting for  $\approx 16\%$  of tropospheric chlorine in 2012. The main sources of  $\text{CH}_3\text{Cl}$  are from tropical plants and oceans as well as biomass burning, with the majority of loss being due to oxidation by OH or ocean degradation [21]. The global distribution presented here (Fig. 11) shows the majority of atmospheric  $\text{CH}_3\text{Cl}$  exists in the troposphere and lower stratosphere in the tropics. The current trend (Fig. 12) gives a statistically insignificant increase of  $0.25 \pm 0.21$  ppt/year ( $0.04 \pm 0.03\%$ /year) in the tropics between 12.5 km and 19.5 km. Brown et al. report a trend between 2004 and 2010 in the tropics of  $2.46 \pm 1.37$  ppt/year [13]. AGAGE and NOAA report VMRs and trends of 552.7, 559.1 ppt and 1.5, 1.7%/year for 2016 [21]. Between 2015 and 2016, ACE reports a value of 0.04%/year. 2016 ACE VMR values of 570.0 ppt are biased slightly high, and the ACE-FTS trends over a similar time period do not agree with those presented in the 2018 WMO report.



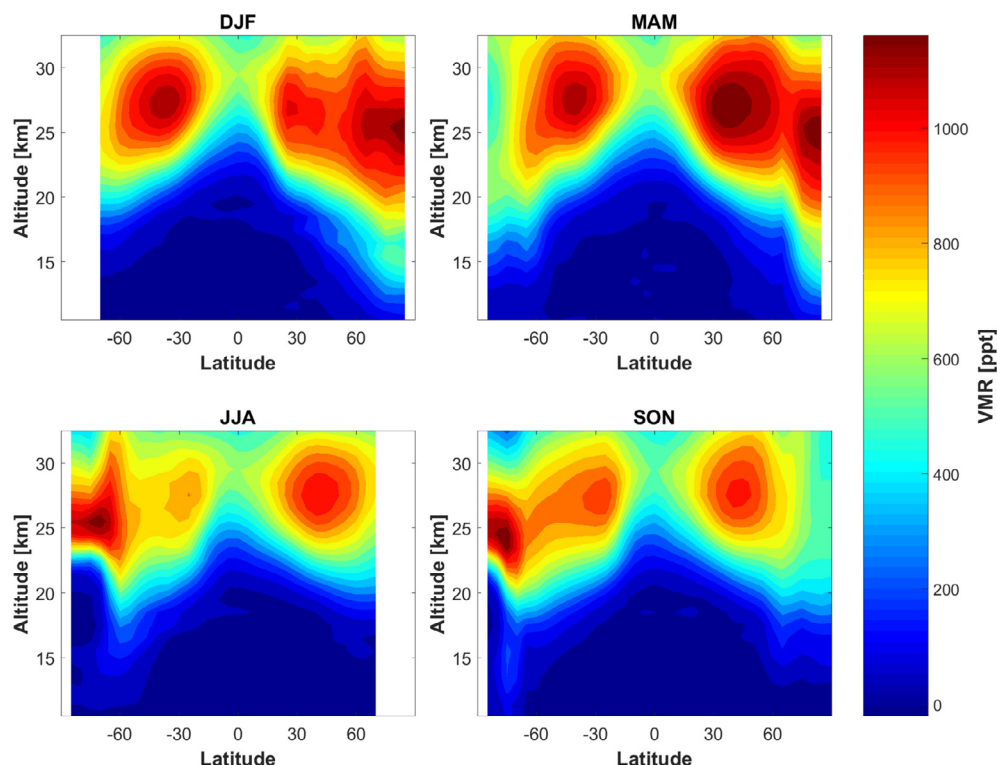
**Fig. 13.**  $\text{ClONO}_2$  VMR distribution between 85°S–90°N latitude and 10.5–32.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.



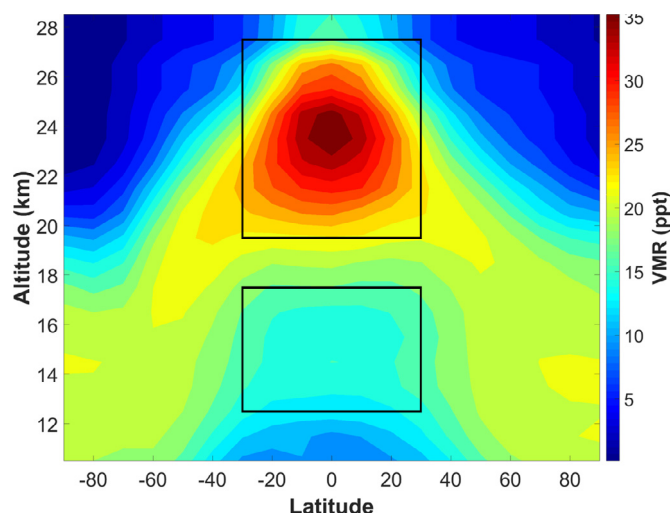
**Fig. 14.**  $\text{ClONO}_2$  VMR trends for sunset and sunrise of  $5.90 \pm 2.14$  ppt/year and  $7.04 \pm 2.18$  ppt/year respectively between 80°S–20°S & 20°N–80°N latitude and 28.5–32.5 km altitude.

### 3.8. $\text{ClONO}_2$

$\text{ClONO}_2$  is an atmospheric reservoir of chlorine with significant diurnal variation. The molecule forms via the three-body recombination reaction of  $\text{ClO} + \text{NO}_2$  [27]. Sinks of  $\text{ClONO}_2$  include photolytic dissociation, gas phase reactions with Cl, O, and OH, and reactions on polar stratospheric clouds (PSCs) [28]. The diurnal effects occur as the molecule dissociates during the day and reforms during the night. The global distribution of  $\text{ClONO}_2$  has enhancements outside of the tropics between approximately 22.5–32.5 km (Fig. 13). When binned into seasons (Fig. 15),  $\text{ClONO}_2$  shows enhancements in the Arctic and Antarctic associated with the formation of polar vortices. The trend presented here averages profiles between 20–80° latitude and 24.5–31.5 km over the entire ACE mission. Trends were calculated for both sunrise and sunset due to  $\text{ClONO}_2$ 's diurnal variations (Fig. 14).  $\text{ClONO}_2$  is increasing at a rate of  $5.90 \pm 2.14$  ppt/year ( $0.86 \pm 0.31\%$ /year) in the morning and  $7.04 \pm 2.18$  ppt/year ( $0.93 \pm 0.29\%$ /year) in the evening. Brown et al. present a previous ACE-FTS trend in the tropics between 25 and 33 km during 2004–2010 of  $-9.4 \pm 7.4$  ppt/year for sunsets and  $10.2 \pm 5.4$  ppt/year for sunrises [13]. While statistically signif-



**Fig. 15.** CIONO<sub>2</sub> seasonal VMR distributions between 85°S–90°N latitude and 10.5–32.5 km altitude. (DJF = December, January February; MAM = March, April, May; JJA = June, July, August; SON = September, October, November).

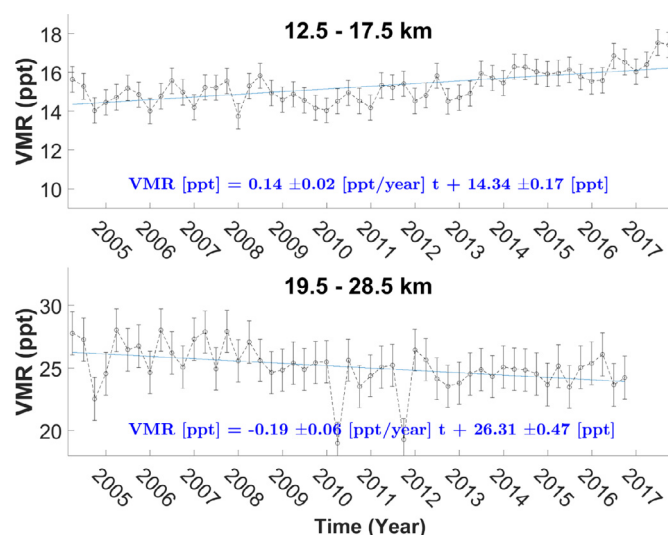


**Fig. 16.** COCl<sub>2</sub> VMR distribution between 90°S–90°N latitude and 10.5–28.5 km altitude. The two black boxes indicate the portion of the distribution used to calculate separate tropospheric and stratospheric VMR trends.

icant, the trends presented here have large errors and a more detailed analysis of the trends as a function of latitude and altitude shows inconsistent results.

### 3.9. COCl<sub>2</sub>

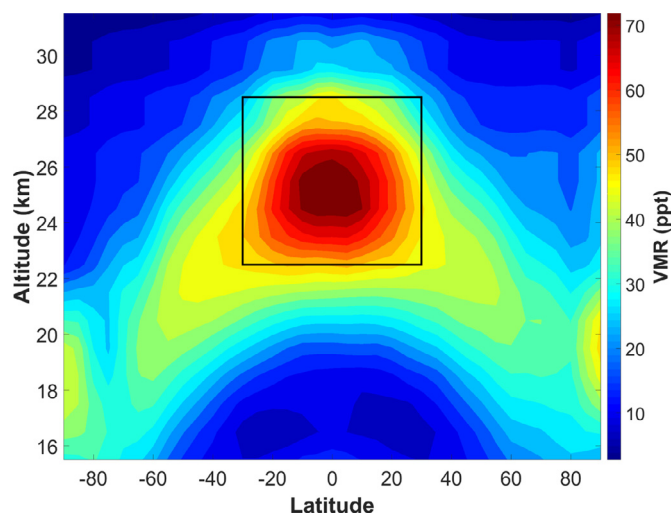
COCl<sub>2</sub> (phosgene) is used in the synthesis of many chemicals, including pharmaceuticals, insecticides, and herbicides. In the stratosphere, phosgene is produced primarily through the photolysis of CCl<sub>4</sub> [29]. In the troposphere, chlorinated hydrocarbons such as CH<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>Cl<sub>4</sub>, or CH<sub>3</sub>CCl<sub>3</sub> undergo oxidation via an OH radical to produce phosgene [30]. The first global distribution of phosgene was produced by Fu et al. and shows a



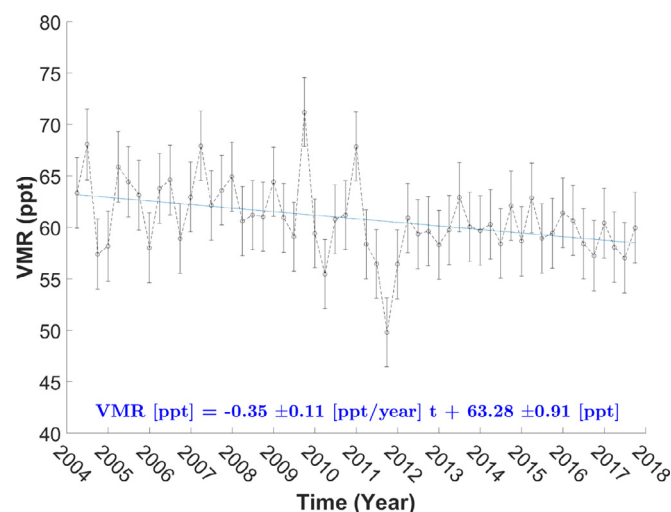
**Fig. 17.** COCl<sub>2</sub> VMR trends between 30°S–30°N latitude of  $0.14 \pm 0.02$  ppt/year and  $-0.19 \pm 0.06$  ppt/year between 12.5–17.5 km and 19.5–28.5 km, respectively.

similar distribution to the current work (Fig. 16); a large plume in the stratosphere within the tropics [31]. Two separate trends (Fig. 17) have been calculated by averaging profiles between 12.5–17.5 km in the troposphere and 19.5–28.5 km in the stratosphere. Phosgene is found to be increasing at a rate of  $0.14 \pm 0.02$  ppt/year ( $0.90 \pm 0.14\%$ /year) in the troposphere but decreasing at  $-0.19 \pm 0.06$  ppt/year ( $-0.74 \pm 0.25\%$ /year) in the stratosphere. Brown et al. report values of  $-0.28 \pm 0.24$  ppt/year between 22 km and 24 km in the tropics during 2004 to 2010 [13]. Harrison et al. show that stratospheric and tropospheric phosgene is changing at a rate of  $-0.15$  –  $-0.30$  ppt/year and  $0.00$ – $0.40$  ppt/year, respectively, between 2004 to 2016 [32]. The slightly positive trend in





**Fig. 18.** COCIF VMR distribution between 90°S to 90°N latitude and 15.5 km to 31.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.

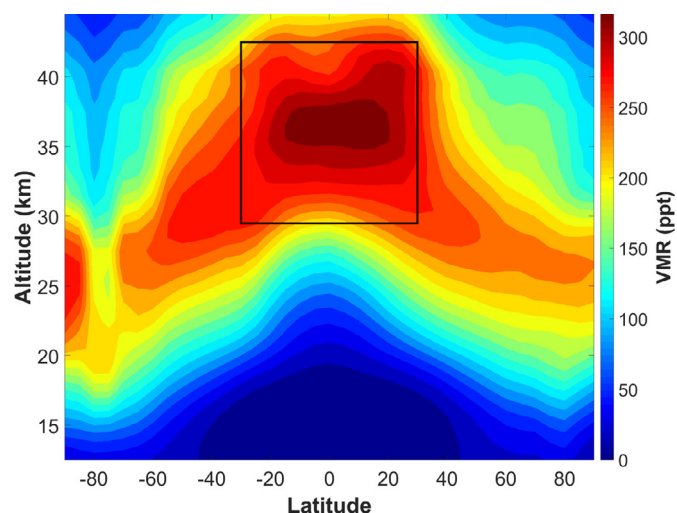


**Fig. 19.** COCIF VMR trend of  $-0.35 \pm 0.11$  ppt/year between 30°S–30°N latitude and 22.5–28.5 km altitude.

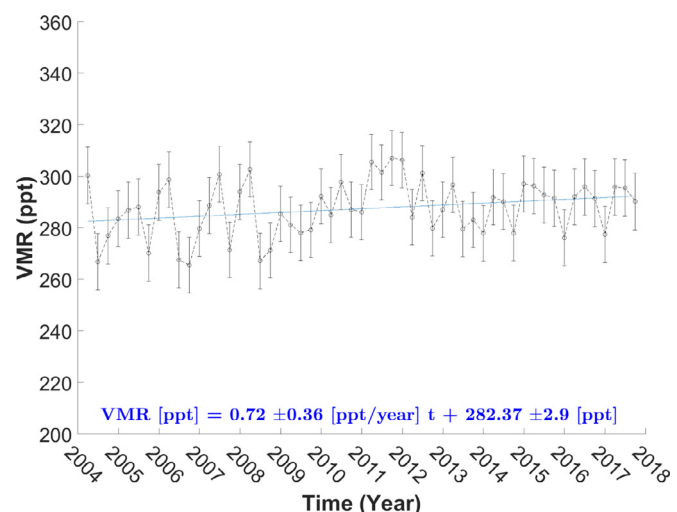
the tropical upper troposphere is suggested by Harrison et al. to be due to increases in VSLs (very short-lived substances) with lifetimes less than 6 months such as  $\text{CH}_2\text{Cl}_2$ . This decrease in the stratosphere and increase in the troposphere determined by Harrison et al. is supported by our work.

### 3.10. COCIF

COCIF is an atmospheric reservoir of both chlorine and fluorine. The main source of COCIF is breakdown of CFC-11, making it a good indicator of the presence of CFC-11 in the atmosphere [33]. Preliminary retrievals by Rinsland et al. of COCIF using ACE data were reported using tropical and mid-latitude occultation spectra from 2004–2005 [34], and COCIF became a regular ACE data product in v3.0. ACE measurements (Fig. 18) in the tropics between 22.5–28.5 km during 2004–2018 show a decreasing trend of  $-0.35 \pm 0.11$  ppt/year ( $-0.57 \pm 0.19\%$ /year) (Fig. 19), with the major area of enhancement occurring over the tropics between 24–28 km. The first global distribution of COCIF was shown by Fu et al. using ACE data between 2004–2007, finding enhancement in the tropics near 27 km [33]. Brown et al. reported a statistically insignificant trend of  $-0.56 \pm 0.57$  ppt/year [13].



**Fig. 20.** COF<sub>2</sub> VMR distribution between 90°S–90°N latitude and 13.5 km to 44.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.

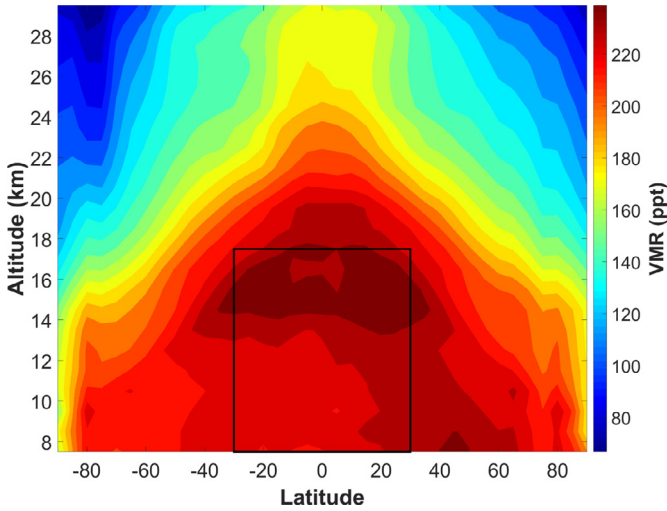


**Fig. 21.** COF<sub>2</sub> VMR trend of  $0.72 \pm 0.36$  ppt/year between 30°S–30°N latitude and 29.5 km to 42.5 km altitude.

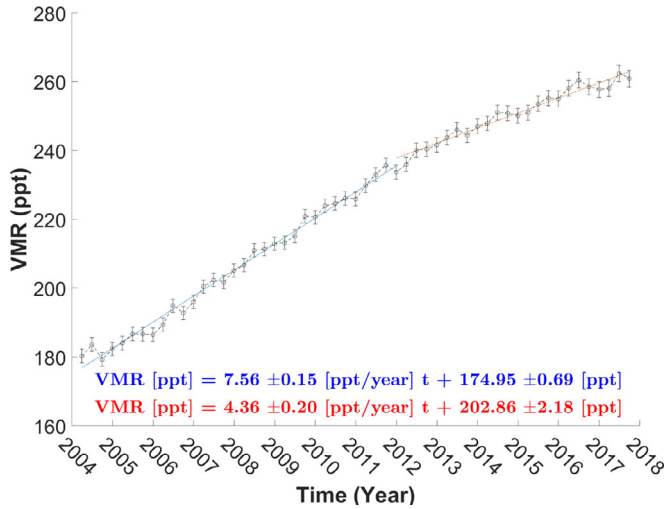
### 3.11. COF<sub>2</sub>

COF<sub>2</sub> is an atmospheric fluorine reservoir, second in atmospheric abundance to HF [35]. It is produced mainly from the atmospheric decomposition of CFC-12, CFC-113, and HCFC-22. The first retrieval of COF<sub>2</sub> from orbit was performed by Rinsland et al. using the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument [36]; COF<sub>2</sub> was detected in the stratosphere between 17 and 40 km. While CFCs are currently banned under the Montreal Protocol and are generally decreasing, HCFCs are still increasing. HCFCs are banned in developed countries as of 2020 and will be phased out in developing countries by 2030 [15]. COF<sub>2</sub> is concentrated in the middle stratosphere (Fig. 20) with a peak VMR in the tropics. Over the ACE mission, COF<sub>2</sub> has a small trend upwards at a rate of  $0.72 \pm 0.36$  ppt/year ( $0.25 \pm 0.12\%$ /year) in the tropics between 29.5–42.5 km (Fig. 21). Brown et al. report a trend of  $0.8 \pm 0.4\%$ /year in the tropics between 30–40 km during 2004–2010 [13]. Duchatelet et al. report a change of  $0.4 \pm 0.2\%$ /year for the total atmospheric column from the Jungfraujoch station between 2000–2008 [37]. Harrison et al. report ACE and MIPAS global trends of  $0.30 \pm 0.44\%$ /year and  $0.85 \pm 0.34\%$ /year between 2004 and 2010, respectively [38]. Between 2004 and 2010, ACE reports





**Fig. 22.** HCFC-22 VMR distribution between 90°S–90°N latitude and 7.5–29.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.

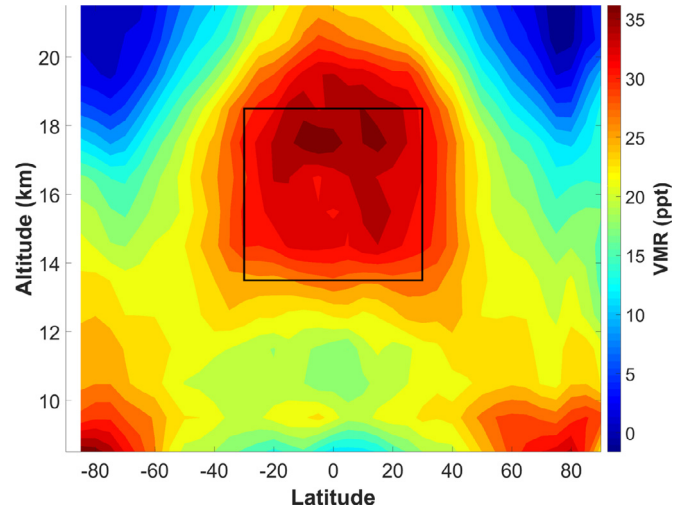


**Fig. 23.** HCFC-22 VMR trend of  $7.56 \pm 0.15$  ppt/year pre-2012 and  $4.36 \pm 0.20$  ppt/year post-2012 between 30°S–30°N latitude and 7.5–17.5 km altitude.

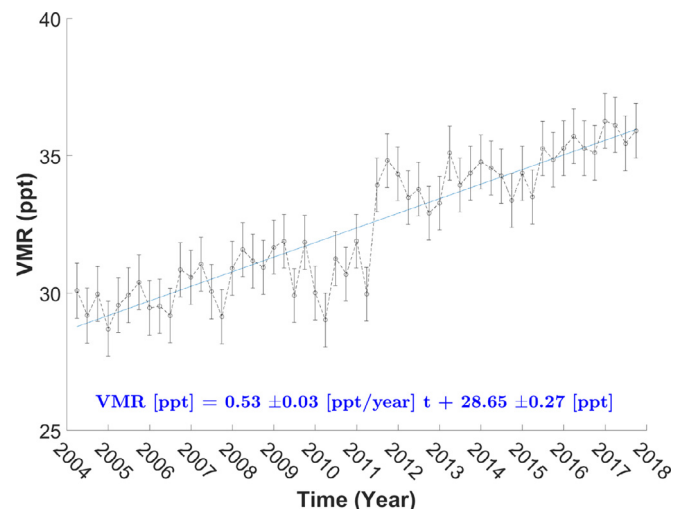
a trend of 0.25%/year, biased low in comparison with values from Duchatelet and MIPAS.

### 3.12. HCFC-22

HCFC-22 ( $\text{CHF}_2\text{Cl}$ ) is an anthropogenic chlorine source gas introduced as a transitional substance to replace CFCs phased out by the Montreal Protocol, in turn to be phased out due to its role in ozone depletion [15]. Removal in the atmosphere occurs primarily due to reaction with the OH radical in the troposphere with a small fraction of removal due to photolysis [39]. The distribution of HCFC-22 (Fig. 22) sees high values at all latitudes in the troposphere with decreases as altitude increases in the stratosphere. HCFC-22 was averaged in the tropics between 7.5–17.5 km, and in this region HCFC-22 is increasing in the atmosphere (Fig. 23) at a rate of  $7.56 \pm 0.15$  ppt/year ( $3.67 \pm 0.07\%$ /year) before 2012 and  $4.36 \pm 0.20$  ppt/year ( $1.74 \pm 0.08\%$ /year) after 2012. Brown et al. report an ACE-FTS trend of  $6.56 \pm 0.20$  ppt/year in the tropics between 8–17 km [13]. VMRs for 2016 are presented in the 2018 WMO report for HCFC-22 of 237.4, 237.5, and 242.3 ppt and trends of 1.6, 1.9, 1.8%/year for AGAGE, NOAA, and UCI, respectively in 2016 [21]. In comparison, the ACE-FTS value of 254.1 ppt in 2016



**Fig. 24.** HCFC-141b VMR distribution between 85°S–90°N latitude and 8.5–21.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.

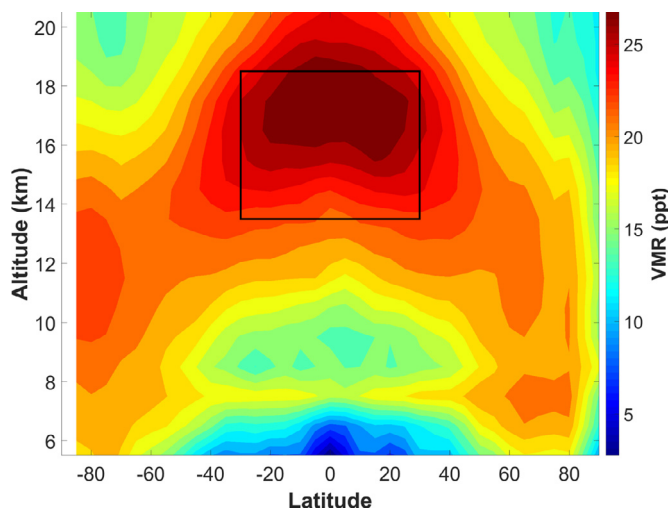


**Fig. 25.** HCFC-141b VMR trend of  $0.53 \pm 0.03$  ppt/year between 30°S–30°N latitude and 13.5–18.5 km altitude.

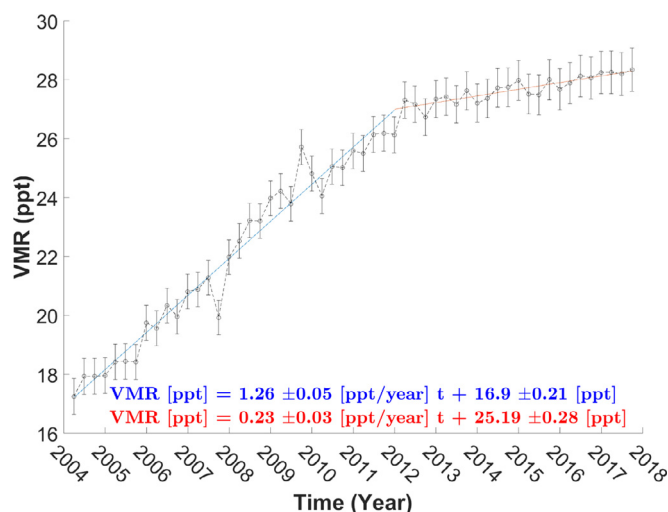
is biased slightly high, while the ACE-FTS trend between 2015 and 2016 of 1.73%/year tracks well with the 2018 WMO report.

### 3.13. HCFC-141b

HCFC-141b is a transitional substance regulated by the Montreal Protocol used as a replacement for CFC-11 as a foam blowing insulation agent [40]. While the ODP of HCFC-141b is lower than CFC-11 (0.11 and 1.0, respectively), HCFC-141b is set to be phased out by 2020 in developed countries and 2030 in developing countries due to its role in stratospheric ozone depletion [15]. Artifacts in the global distribution at low altitudes (Fig. 24) can likely be attributed to interfering molecules that bias the retrieval low [13]. Despite these interferers, the calculated trend appears to be consistent over the ACE mission. We report an increase of HCFC-141b of  $0.53 \pm 0.03$  ppt/year ( $1.64 \pm 0.10\%$ /year) in the tropics between 13.5–18.5 km during the ACE mission (Fig. 25). The 2018 WMO report lists VMRs of 24.47, 24.53, and 24.59 ppt and trends of 1.0, 1.3, 0.4%/year for AGAGE, NOAA, and UCI, respectively in 2016 [21]. The ACE 2016 VMR of 34.9 ppt and trend between 2015–2016 of 1.53%/year are biased high.



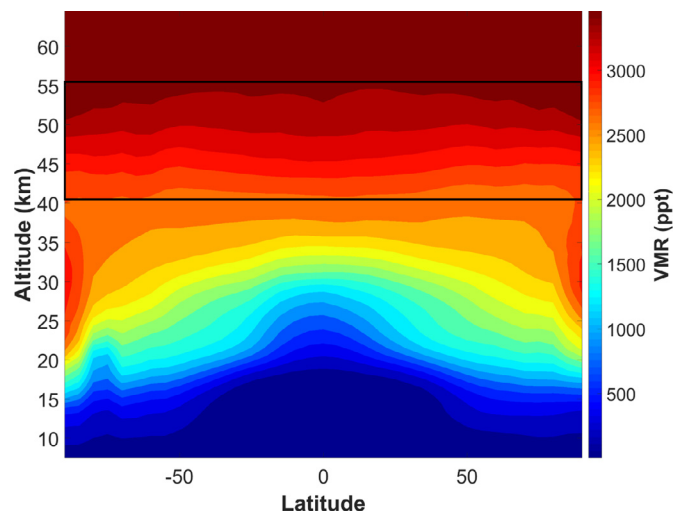
**Fig. 26.** HCFC-142b VMR distribution between  $-85^{\circ}$  to  $90^{\circ}$  latitude and 7.5 km to 29.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.



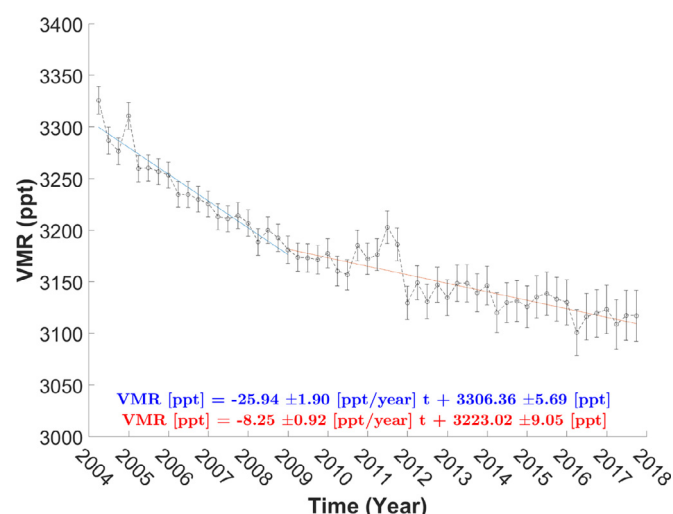
**Fig. 27.** HCFC-142b VMR trend of  $1.26 \pm 0.05$  ppt/year pre-2012 and  $0.23 \pm 0.03$  ppt/year post-2012 between  $30^{\circ}\text{S}$ – $30^{\circ}\text{N}$  latitude and 13.5–18.5 km altitude.

### 3.14. HCFC-142b

HCFC-142b was developed as a replacement for CFC-12 as a refrigerant and foam-blowing agent due to the phase out of CFCs under the Montreal Protocol [40]. HCFC-142b also contributes to stratospheric ozone removal and is a greenhouse gas [21], and will be phased out in developed countries by 2020 and developing countries in 2030. There are unphysical artifacts present in the global distribution (Fig. 26) that are unexpected for an anthropogenic source gas, such as the tropical fluctuation in the VMR between 8 and 10 km. Much like HCFC-141b, this is most likely due to spectral interference from a tropospheric molecule during the retrieval. Brown et al. report an ACE-FTS trend in the tropics between 7–17 km between 2004 and 2010 of  $1.17 \pm 0.05$  ppt/year [13], while NOAA observations reported by Montzka et al. between 2010–2012 of 0.62 and 0.67 ppt/year [41]. The trend presented here (Fig. 27) has a break in 2012, with pre-break values of  $1.26 \pm 0.05$  ppt/year ( $5.69 \pm 0.21\%$ /year) and a post-break value of  $0.23 \pm 0.03$  ppt/year ( $0.82 \pm 0.09\%$ /year), indicating significant decreases in the emissions of HCFC-142b over time. AGAGE, NOAA, and UCI list VMRs of 22.56, 22.01, and 23.16 ppt in 2016 with trends of 0.2, 0.8, and  $-0.4\%$ /year, respectively [21]. During 2015–2016, ACE reports



**Fig. 28.** HCl VMR distribution between  $90^{\circ}\text{S}$ – $90^{\circ}\text{N}$  latitude and 7.5–64.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.

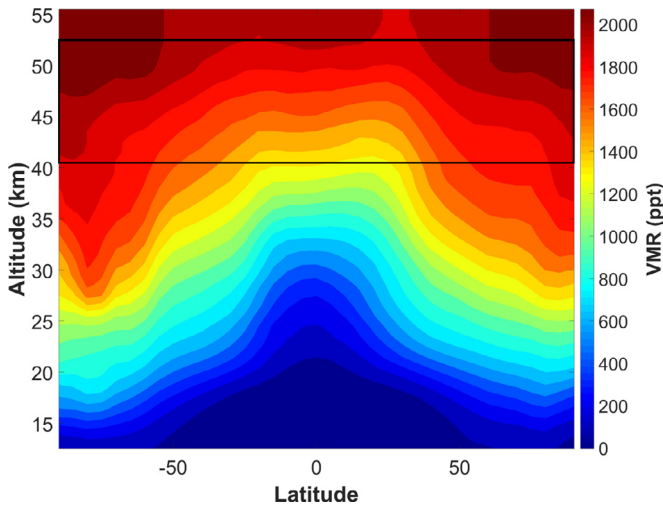


**Fig. 29.** HCl VMR trend of  $-25.94 \pm 1.90$  ppt/year pre-2009 and  $-8.25 \pm 0.92$  ppt/year post-2009 between  $90^{\circ}\text{S}$ – $90^{\circ}\text{N}$  latitude and 40.5–55.5 km altitude.

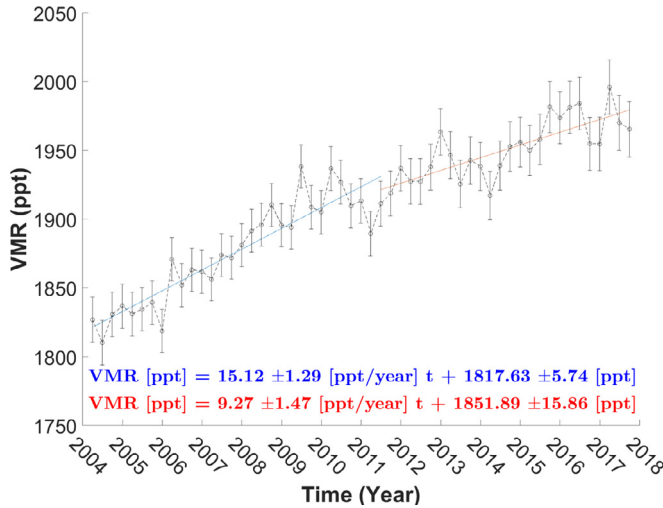
a trend value of  $0.83\%$ /year. The ACE VMR of 27.9 ppt in 2016 and the trend presented here are biased high in comparison.

### 3.15. HCl

HCl is the main chlorine reservoir in the atmosphere and is mainly produced from the decomposition of chlorine-containing source gases, such as CFC-11 and CFC-12. HCl can react with OH to re-release chlorine atoms into the atmosphere which restarts the chain reactions that lead to stratospheric ozone removal [1]. The global distribution of HCl (Fig. 28) sees large increases above 30 km, with VMRs dropping off quickly below that altitude. HCl averaged at all latitudes between 40.5–55.5 km over the ACE mission is decreasing at a rate of  $-25.94 \pm 1.90$  ppt/year ( $-0.80 \pm 0.06\%$ /year) before 2009 and  $-8.25 \pm 0.92$  ppt/year ( $-0.26 \pm 0.03\%$ /year) after 2009 (Fig. 29). Brown et al. report a trend in the tropics between 50–54 km of  $-26.2 \pm 2.3$  ppt/year between 2004–2010 [13]. Bernath and Fernando present an averaged trend of  $-0.48 \pm 0.02\%$ /year between 2004–2017 and at 0.68 hPa ( $\approx 51$  km), with evidence of a break occurring around 2010 [42]. Stratospheric HCl and total tropospheric chlorine are compared and shown to have high correlation. Averaged rates of change of to-



**Fig. 30.** HF VMR distribution between  $-90^{\circ}$ – $90^{\circ}$  latitude and 12.5–55.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.

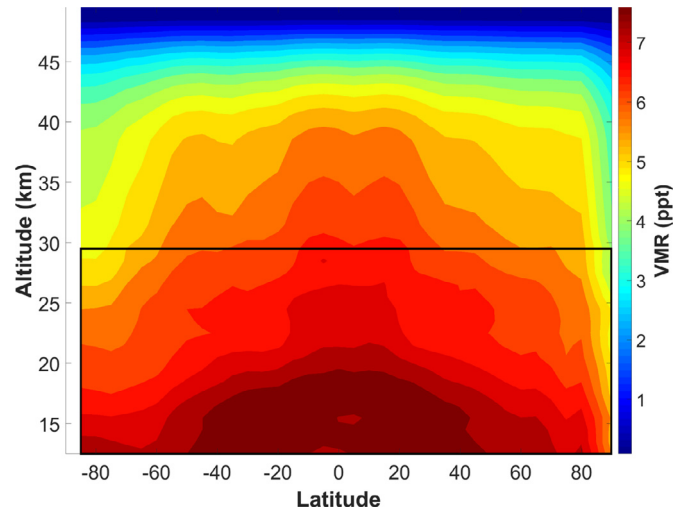


**Fig. 31.** HF VMR trend of  $15.12 \pm 1.29$  ppt/year before 2011 and  $9.27 \pm 1.47$  ppt/year post 2011 between  $90^{\circ}$ S– $90^{\circ}$ N latitude and 40.5–52.5 km altitude.

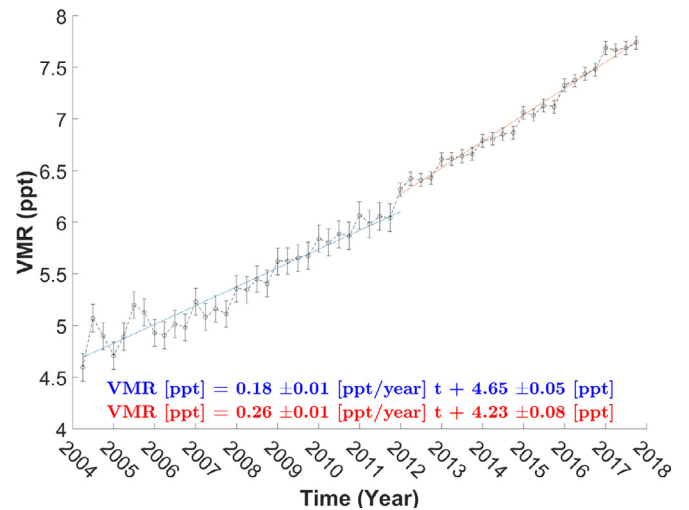
tal tropospheric Cl from the 2018 WMO report are  $-10.0 \pm 6.7$  ppt/year between 2004–2008,  $-11.8 \pm 6.9$  ppt/year between 2008–2012, and  $-4.4 \pm 4.1$  ppt/year between 2012–2016. Averaged between 2009 and 2018, the ACE-FTS HCl trend of  $-8.25 \pm 0.92$  ppt/year tracks well with the total tropospheric chlorine trends between 2004–2008 and 2008–2012, but does not show the flattening trend shown between 2012–2016. The transport time of about 4 years between the troposphere and upper stratosphere may account for this difference.

### 3.16. HF

HF is the main reservoir of fluorine in the stratosphere, produced from anthropogenic fluorine source gases such as CFCs and HCFCs. Many of these sources are banned or regulated under the Montreal Protocol [15]. Sinks of HF include photolytic dissociation in the mesosphere or transport to the troposphere where it is rained out [43]. HF is relatively stable and does not undergo the same stratospheric ozone removal reactions that HCl does [44]. The global distribution of HF (Fig. 30) sees increases in VMR with altitude in the entire stratosphere. HF is found to be increasing (Fig. 31) at a rate of  $15.12 \pm 1.29$  ppt/year ( $0.83 \pm 0.07\%$ /year) before 2011 and  $9.27 \pm 1.47$  ppt/year ( $0.50 \pm 0.08\%$ /year) in the



**Fig. 32.**  $\text{SF}_6$  VMR distribution between  $85^{\circ}$ S– $90^{\circ}$ N latitude and 12.5–49.5 km altitude. The box indicates the portion of the distribution used to calculate the VMR trend.



**Fig. 33.**  $\text{SF}_6$  VMR trend of  $0.18 \pm 0.01$  ppt/year pre-2012 and  $0.26 \pm 0.01$  ppt/year post-2012 between  $90^{\circ}$ S– $90^{\circ}$ N latitude and 12.5–29.5 km altitude.

stratosphere between 40.5–52.5 km at all latitude bands over the entire ACE mission. Harrison et al. report a trend for 2004–2012 above 40 km of  $0.52 \pm 0.03\%$ /year [44], biased low in comparison to our ACE values from 2004 to 2011.

### 3.17. $\text{SF}_6$

$\text{SF}_6$  is a long-lived gas with an atmospheric lifetime of 3200 years [21] and is a very potent greenhouse gas with a 100 year GWP of 23,500 [22].  $\text{SF}_6$  does not have any sinks in the troposphere or stratosphere, but in the mesosphere  $\text{SF}_6$  can undergo photolysis [45] and react with electrons [46]. The main sources of  $\text{SF}_6$  are fugitive emissions from its use in electrical equipment to prevent arcing as well as release during maintenance [47]. The global distribution (Fig. 32) shows  $\text{SF}_6$  abundances between  $\approx 4$ –8 ppt at all latitudes below 45 km, with the highest concentration of  $\text{SF}_6$  existing in the tropics in the troposphere. MIPAS has measured an  $\text{SF}_6$  altitude-latitude distribution and Fig. 32 shows a similar pattern [48].

A global trend (Fig. 33) was calculated at all latitudes between 12.5–29.5 km with a break between 2012–2013 of  $0.18 \pm 0.01$  ppt/year ( $3.37 \pm 0.19\%$ /year) and  $0.26 \pm 0.01$  ppt/year



( $3.64 \pm 0.10\%$ /year) for pre-break and post-break, respectively. Brown et al. report an ACE-FTS trend of  $0.25 \pm 0.01$  ppt/year in the tropics between 12–17 km [13]. AGAGE and NOAA both report VMRs of 8.9 ppt with trends of 3.8 and 3.9%/year, respectively in 2016. From 2015–2016, ACE reports a trend of 3.58%/year and VMR of 7.4 ppt, which compare well with values from the 2018 WMO report.

#### 4. Discussion and conclusions

Global distributions and trends have been calculated for sixteen halogen-containing trace gases ( $\text{CCl}_4$ ,  $\text{CF}_4$ , CFC-11, CFC-12, CFC-113,  $\text{CH}_3\text{Cl}$ ,  $\text{ClONO}_2$ ,  $\text{COCl}_2$ ,  $\text{COClF}$ ,  $\text{COF}_2$ , HCFC-22, HCFC-141b, HCFC-142b,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{SF}_6$ ). Of these sixteen, four molecules,  $\text{CF}_4$ , CFC-113, HCFC-141b and HCFC-142b, have anomalous altitude-latitude distributions likely because of spectroscopic interferences in the retrieval as is evident from the residuals (observed minus calculated spectra). In particular, CFC-113, HCFC-141b and HCFC-142b are overlapped by strong ozone absorption for which the spectroscopic data are still not satisfactory. In the case of  $\text{CF}_4$ , there seems to be a problem with the absorption cross sections used for v.3.5/3.6; new cross sections have just become available and will be used in the future.

As a result of the success of the Montreal Protocol, the VMRs of the organic source gases,  $\text{CCl}_4$ , CFC-11, CFC-12 and CFC-113 are decreasing. Starting about 2012, the rate of decrease of CFC-11 abundance has slowed, which has been attributed to illegal production in Asia [25]. The regions of the atmosphere chosen to calculate these ACE trends are almost entirely in the well-mixed troposphere. As expected, the ACE trends are therefore similar to the surface trends. The  $\text{HCl}$  product gas is also decreasing as expected [14,42], but the decrease has slowed after about 2009 because many of the shorter-lived chlorine-containing gases such as methyl chloroform have nearly disappeared from the atmosphere.

HCFC-22, HCFC-141b and HCFC-142b that have temporarily replaced CFCs are still increasing although HCFC-22 and HCFC-142b are increasing much more slowly since about 2012. The emissions of the main natural source of atmospheric chlorine  $\text{CH}_3\text{Cl}$  have remained nearly constant.

The chlorine reservoir molecule  $\text{ClONO}_2$  has a small but statistically significant increase in abundance for both sunrise and sunset occultations. These two trend values are different and are likely artifacts related to the ACE-sampling of this diurnally-varying molecule. The stratospheric abundances of  $\text{COCl}_2$  and  $\text{COClF}$  intermediates are decreasing as expected since their main sources, the CFCs, are declining. However, tropospheric  $\text{COCl}_2$  is increasing, suggested by Harrison et al. [32] to be due to increasing emissions of VSLs such as  $\text{CH}_2\text{Cl}_2$ .

$\text{CF}_4$ ,  $\text{COF}_2$  and  $\text{HF}$  are increasing as HFC abundances increase. ACE has research retrievals for the two most abundant HFCs [49], HFC-134a and HFC-23, that show rapid increases and they contribute to increasing HF abundances. The HF increases have slowed after about 2011 as the Montreal Protocol has successfully decreased CFC abundances. Presumably the  $\text{CF}_4$  increases are related to increases in aluminum production.  $\text{SF}_6$  increases are likely due to an increase in use and releases from electrical equipment.

Notice that although the ACE-FTS retrievals sometimes have biases and the global VMR distributions can have artifacts, the derived VMR trend values generally agree with independent values. The nature of these biases is not completely understood, but in general they come from errors in the absorption cross sections and from spectral interferences in the retrieval. Errors in the cross sections cause multiplicative biases, but biases from spectral interferences are often additive. Most of the biases in ACE-FTS retrievals come from spectral interference from molecules that are not completely accounted for in the forward model. Hence, the ACE trends

in ppt/year often match those of independent measurements in spite of biases in the ACE VMR values.

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