Decrease of carbon tetrachloride (CCl_4) over 2004-2013 as inferred from global occultation measurements with ACE-FTS

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INSTRUMENTATION AND OBSERVATIONAL DATABASE

The ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer) has been launched in August 2003 onboard the Canadian SCISAT satellite (Bernath et al., 2005). This intrument si still in operation to date, with no significant degradation of its performances. Since the beginning of routine operation in February 2004, it has recorded up to 15 sunrise and sunset occultations per day, with successive infrared solar spectra collected (within 2s) from 150 km altitude down to the cloud tops. The resulting vertical resolution is about 3-4 km, while the spectral resolution achieved in the broad 750-4400 cm^{-1} range is of 0.02 cm^{-1}. Signal-to-noise ratio of 200-300 are typically obtained in the spectral region of interest here.

The analysis of the ACE-FTS spectra are routinely performed at the University of Waterloo (Ontario, Canada), with an algorithm described by Boone et al. (2013). Numerous species are currently retrieved from the observations (see http://www.ace.uwaterloo.ca), among which carbon tetrachloride (CCl_4). The microwindow used to determine the vertical distributions of CCl_4 encompasses its broad unresolved strong ν_3 and weaker $\nu_1 + \nu_4$ combination bands near 12.7 µm (796 cm^{-1}). More specifically, the mixing ratio profiles of CCl_4 are retrieved in the 7 - 25 km altitude range by fitting the occultation measurements in the 787.5 - 805.5 cm^{-1} spectral range.

Here we used the more than 24000 occultations including CCl_4 measurrements and available from Version 3.5 in the 85ºS-85ºN latitude range, from February 2004 onwards (see **FIGURE 1**), updating the work of Allen et al. (2009). **TABLE 1** provides some information on the distribution of the measurements with time and space.

Latitude range	Date range	# Occultations (Days)
60-85ºN	23-Feb-2004 - 16-Mar-2013	7303 (1085)
35-60ºN	23-Apr-2004 - 21-Feb-2013	3153 (517)
35ºS-35ºN	1-Apr-2004 - 11-Jun-2013	3438 (685)
35-60ºS	30-Sep-2004 - 12-Mar-2013	3014 (512)
60-85ºS	2-Jan-2005 - 16-Mar-2013	7276 (1086)
ALL	23-Feb-2004 - 11-Jun-2013	24184 (2112)

TABLE 1

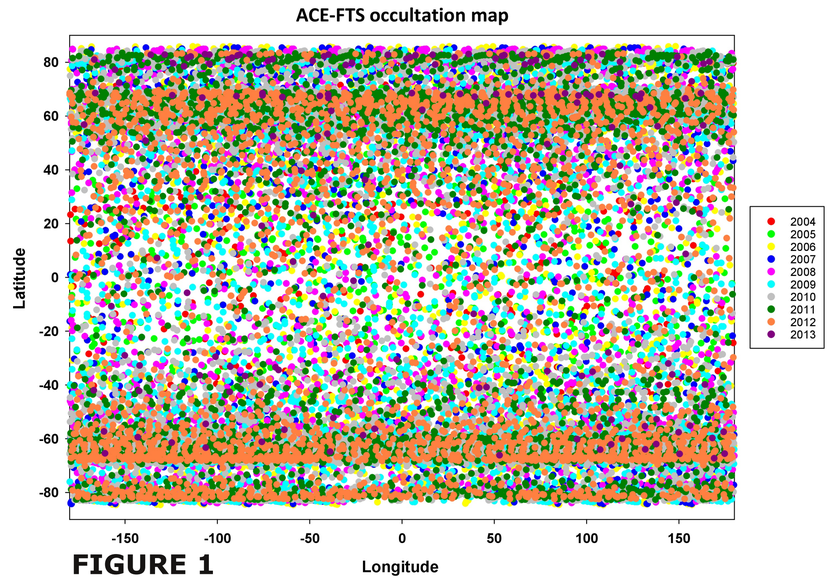

FIGURE 1

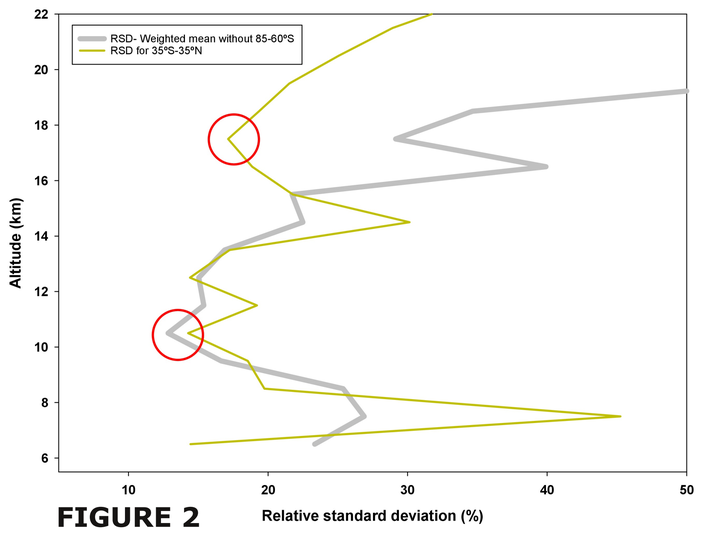

FIGURE 2

DATA SELECTION AND TREND DETERMINATION

In order to select the most appropriate atmospheric region minimizing the scatter on the CCl_4 mixing ratio, we inspected the relative standard deviations (i.e. the ratio between the standard deviation on the arithmetic mean over 2004-2013 and the mean itself) with respect to the tangent height. **FIGURE 2** shows the curves obtained for all latitude bins combined in grey (except the one for 60-85ºS which is more noisy and will require further investigations) and the one for the tropical regions in light green. It appears that minimum RSD are obtained near 10 km in both cases as well as near 17 km for the tropical occulations (see red circles). Therefore, the mixing ratios available in the 9-11 and 16-18 km altitude ranges have used for the trend determinations depicted below. These altitudes likely correspond to the best compromise between enough absorption by CCl_4 and good observational statistics.

FIGURE 3 shows the tropical daily mean mixing ratio time series near 10 and 17 km. Using the bootstrap resampling tool developed by Gardiner et al (2008) involving a linear component as well as a 3-term Fourier series to account for seasonal modulations, we derived decreasing trends significant and consistent at the 95% level of uncertainy, of -0.95±0.5 and -1.28±0.3 ppt/yr, respectively. When using the 2004.0 mixing ratios as reference, we compute relative rates of decrease of -0.79±0.40 and -1.35±0.34 %/yr, respectively. Given the good vertical mixing in the tropical belt, the ACE-FTS mixing ratios recorded near 10 km are close to surface concentrations. The global in situ surface concentrations as available from the successive editions of the WMO assessments on ozone depletion from the AGAGE and NOAA/ESRL networks are reproduced as red and dark blue squares, respectively. Although these data sets nicely evolve in parallel, mean systematic differences close to 26 or 23.5% are observed between ACE-FTS and AGAGE or NOAA/ESRL, respectively.

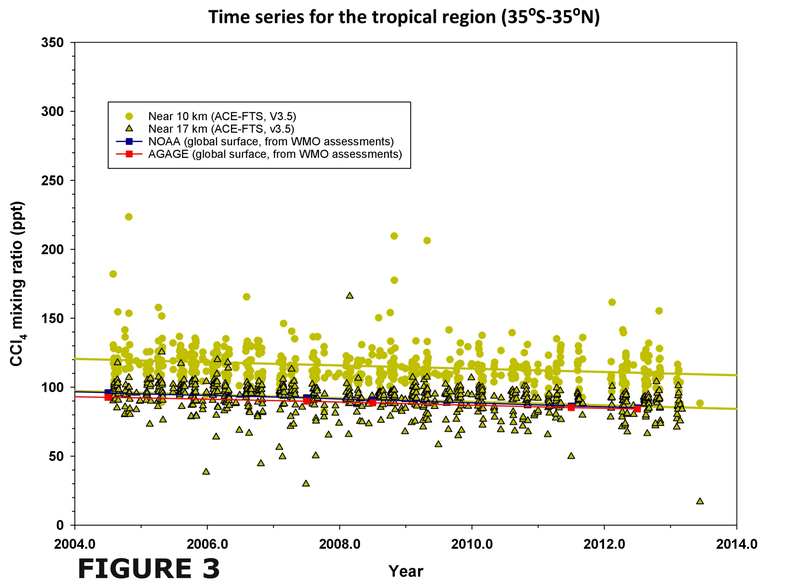

FIGURE 3

FIGURE 4 shows the tropical daily mean mixing ratio time series near 10 and 17 km. Using the bootstrap resampling tool developed by Gardiner et al (2008) involving a linear component as well as a 3-term Fourier series to account for seasonal modulations, we derived decreasing trends significant and consistent at the 95% level of uncertainy, of -0.95±0.5 and -1.28±0.3 ppt/yr, respectively. When using the 2004.0 mixing ratios as reference, we compute relative rates of decrease of -0.79±0.40 and -1.35±0.34 %/yr, respectively. Given the good vertical mixing in the tropical belt, the ACE-FTS mixing ratios recorded near 10 km are close to surface concentrations. The global in situ surface concentrations as available from the successive editions of the WMO assessments on ozone depletion from the AGAGE and NOAA/ESRL networks are reproduced as red and dark blue squares, respectively. Although these data sets nicely evolve in parallel, mean systematic differences close to 26 or 23.5% are observed between ACE-FTS and AGAGE or NOAA/ESRL, respectively.

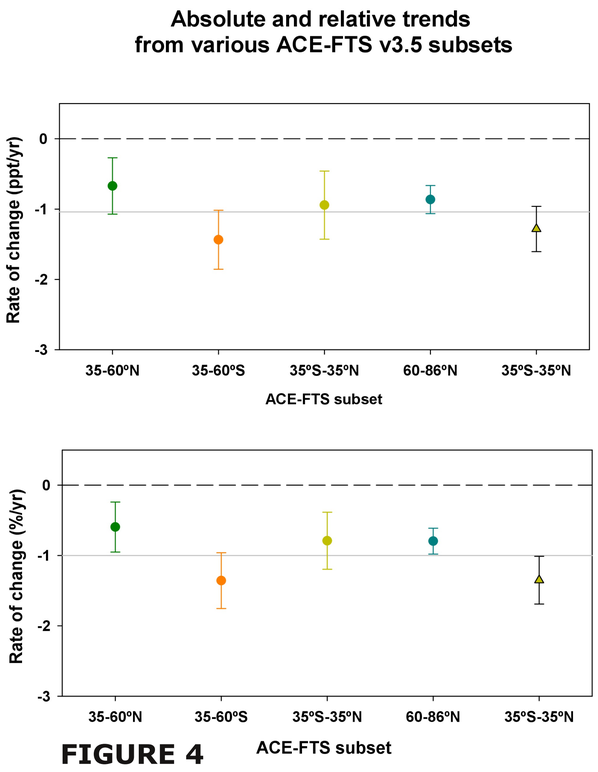

FIGURE 4

FIGURE 4 shows the absolute (ppt/yr) and relative (%/yr) trends derived for various ACE-FTS subsets as well as their associated uncertainties (95% level). There is no statistical difference among them and they all agree with a decrease close to 1 ppt/yr or 1 %/yr.

These trends are also in statistical agreement with those quoted in **FIGURE 5** (update of Rinsland et al., 2012) derived from ground-based FTIR measurements performed at the Jungfraujoch station (Swiss Alps, 3.58 km a.s.l.), using the same spectrosopic parameters for the target gas, but accounting for line-mixing affecting the nearby CO_2 Q-branch.

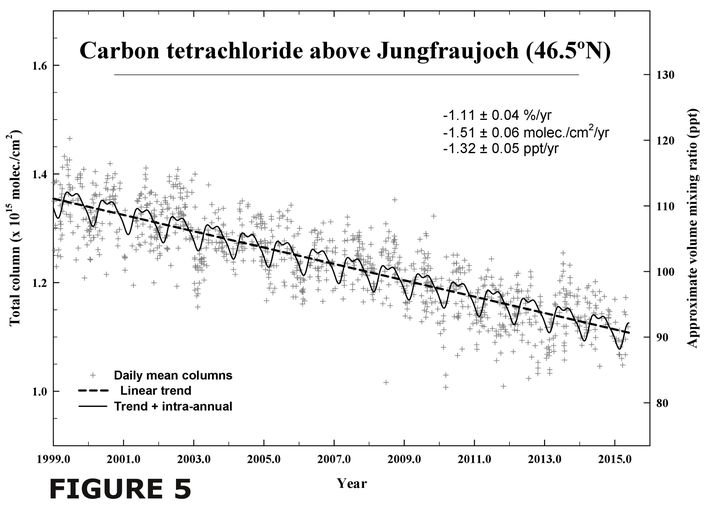

FIGURE 5

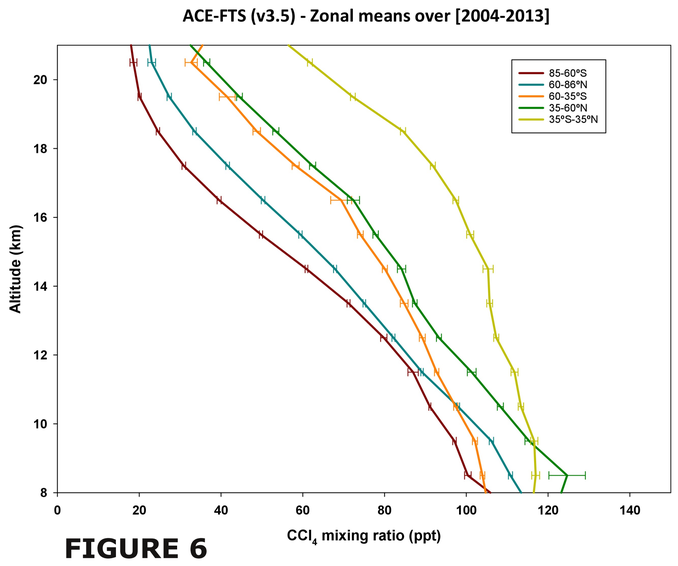

FIGURE 6

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INTERHEMISPHERIC CONTRAST

FIGURE 6 above shows the mean vertical distributions derived from the 2004-2013 ACE-FTS occultation measurements performed in the Northern (35-60 and 60-85ºN) and Southern hemisphere (35-60 and 60-85ºS). The standard errors (i.e.the standard deviations divided by the square root of the number of available measurements) are shown as horizontal thin bars. When performing pairwize comparisons, it apears clearly that the NH vertical distributions are systematically and significantly larger than their SH counterparts by about 7 ppt. This is unexpected for a species with negligible emissions and suggest either that significant emissions are still ongoing in the NH and/or that an important (e.g. oceanic) sink is at play in the SH.

SUMMARY AND OUTLOOK

ACE-FTS provides global CCl_4 measurements, currently spanning the 2004-2013 time period and, typically, the 9-25 km altitude range.

The ACE-FTS mixing ratios are sytematically biased high with respect to in situ surface measurements by AGAGE and NOAA by about 23-25%, essentially because line-mixing is not accounted for in the retrievals (while they prooved to bias high the results by 10-15% as quoted by Stiller et al. (2004) and Rinsland et al. (2012); but also because of spectroscopic parameters still affected by a large systematic uncertainty (≈10%). Hence, correction of these two error sources could allow closing the gap between the in situ and ACE-FTS remote-sensing techniques. This should be available in the next Version 4.

In the meantime, the ACE-FTS measurements (trends, interhemispheric contrast, information on the spatial distribution...) are valuable and will be used to extend the investigations presented here.

RELATED PRESENTATIONS

James Hannigan, Mathias Palm, Stephanie Conway, Emmanuel Mahieu, Dan Smale, Eric Nussbaumer, Kim Strong, and Justus Notholt, Current trend in carbon tetrachloride from several NDACC FTIR stations, talk on Monday afternoon, this meeting.

Jeremy J. Harrison, Chris D. Boone, and Peter F. Bernath, Towards improving the ACE-FTS retrieval of carbon tetrachloride, poster presentation, this meeting.

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Poster presented at the "*Solving the mystery of carbon tetrachloride*" workshop, 4-6 October 2015, Empa Akademie, Duebendorf, Switzerland