CFC-11, CFC-12 and HCFC-22 ground-based remote sensing FTIR measurements at Reunion Island and comparisons with MIPAS/ENVISAT data

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Abstract

Profiles of CFC-11 (CCl\textsubscript{3}F), CFC-12 (CCl\textsubscript{2}F\textsubscript{2}) and HCFC-22 (CHF\textsubscript{2}Cl) have been obtained from Fourier transform infrared (FTIR) solar absorption measurements above the Saint-Denis (St Denis) and Maïdo sites at Reunion Island (21ºS, 55ºE) with low vertical resolution. FTIR profile retrievals are performed by the SFIT4 program and the detail retrieval strategies along with the systematic/random uncertainties of CFC-11, CFC-12, and HCFC-22 are discussed in this study. The FTIR data of all three species are sensitive to the whole troposphere and the lowermost stratosphere, with the peak sensitivity between 5 and 10 km. The trends derived from the combined St Denis and Maïdo FTIR time-series are -0.86±0.12% and 2.75±0.12% for CFC-11 and HCFC-22, respectively, for the period 2004 to 2016, and -0.76±0.05% for CFC-12 for 2009 to 2016. These measurements are consistent with the trends observed by the National Oceanic and Atmospheric Administration (NOAA) Global Monitoring Division’s (GMD) Halocarbons & other Atmospheric Trace Species Group (HATS) measurements at Samoa (14.2ºS, 170.5ºW) for CFC-11 (-0.87±0.04%), but slightly weaker for HCFC-22 (3.46±0.05%) and stronger for CFC-12 (-0.60±0.02%).

The ground-based FTIR data have also been compared with the collocated Michelson Interferometer for Passive Atmospheric Sounding (MIPAS/ENVISAT) data, and found to be in good agreement: the observed mean relative biases and standard deviations of the differences between the smoothed MIPAS and FTIR partial columns (6-30 km) are (-4.3% and 4.4%), (-2.9% and 4.6%) and (-0.7% and 6.0%) for CFC-11, CFC-12, and HCFC-22, respectively, which are within the combined error budgets from both measurements.

1. Introduction

CFC-11 (CCl\textsubscript{3}F), CFC-12 (CCl\textsubscript{2}F\textsubscript{2}) and HCFC-22 (CHF\textsubscript{2}Cl) are the major sources of chlorine in the stratosphere after photolytic decomposition, and therefore play an important role in stratospheric ozone depletion (Molina and Rowland, 1974). In addition, these gases absorb thermal infrared radiation and contribute significantly to the greenhouse effect (Lashof and Ahuja, 1990). Due to the long lifetime of these gases (CFC-11: ~60 years; CFC-12: ~120 years;
HCFC-22: ~12 years (Ko et al., 2013)), they are good tracers to study transport and mixing processes in the upper troposphere and lower stratosphere region (Hoffmann and Riese, 2004).

Because of the vital importance of these gases, the Advanced Global Atmospheric Gases Experiment (AGAGE) in-situ network has been measuring CFC-11 and CFC-12 continuously since 1978 and HCFC-22 since the 1990s (Cunnold et al., 1997; Dunse et al., 2005). NOAA's Halocarbons & other Atmospheric Trace Species Group (HATS) sampling network started monitoring CFCs from flask grab samples in 1977 and via online in-situ techniques starting in 1977 (Elkins et al., 1993). HCFC-22 was added to the NOAA/HATS measurements in 1992.

Because of the use of chlorofluorocarbon (CFCs) as propellant and refrigerant in the 1980s, the in-situ measurements show the rapid rise of CFC-11 and CFC-12 at that time. To reduce substances that deplete the ozone layer, amongst others CFCs, 27 nations around the world signed a global environmental treaty, the Montreal Protocol, on September, 1987 (Murdoch and Sandler, 1997). The hydrochlorofluorocarbons (HCFCs) were applied to replace the CFCs after the Montreal Protocol, since they react with tropospheric hydroxyl (OH), resulting in a shorter lifetime compared with CFCs. As a result, accelerated increases are observed for HCFCs since 2004 in the global atmosphere (Montzka et al., 2009). The tropospheric concentrations of CFC-11 and CFC-12 reached their maximums in 1992 and 2003 respectively, and a decline has been observed since then (Elkins et al., 1993; Montzka et al., 1996; Walker et al., 2000).

Apart from the in-situ measurements, observations of CFCs and HCFCs abundances have also been made using remote sensing infrared spectroscopy techniques. Space-based observations provide the global distributions and trends of CFCs and HCFCs; examples are the measurements of CFC-11 and CFC-12 from ILAS (Improved Limb Atmospheric Spectrometer), of CFC-11, CFC-12, CFC-113, HCFC-22, HCFC-142a and HCFC-142b from ACE-FTS (Atmospheric Chemistry Experiment - Fourier Transform Spectrometer) and of CFC-11, CFC-12 and HCFC-22 from MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) (Khosrawi et al., 2004; Hoffmann et al., 2008; Mahieu et al., 2008). Also ground-based FTIR measurements are able to monitor the CFCs and HCFCs (Notholt, 1994), especially at the Swiss Jungfraujoch station (Zander et al., 2005; Mahieu et al., 2010; Mahieu et al., 2013), where comparisons with the ACE-FTS measurements show a good agreement (Mahieu et al., 2015). They can provide long time-series of CFC-11, CFC-12, HCFC-22 total columns and are therefore very good candidates for supporting the evaluation of satellite and model data and for the evaluation of trends: the Jungfraujoch CFC-11, CFC-12, and HCFC-22 time series and trends have been included in the most recent Scientific Assessment of Ozone Depletion (Carpenter et al., 2014).

In this study, we provide the first ground-based FTIR time series of CFC-11, CFC-12 and HCFC-22 in the Southern Hemisphere, namely at two stations, both located at Reunion Island (21°S, 55°E): Saint-Denis (St Denis) and Maïdo, and we compare them to MIPAS/ ENVISAT colocated data. Section 2 describes the FTIR experiments at Reunion Island as well as the retrieval strategy for each target CFC along with the uncertainty analysis. In addition, we provide the three species’ trends derived from our FTIR time-series and compare them to the trends observed at American Samoa (SMO) from in-situ measurements for CFC-11 and CFC-12 and flask samplings for HCFC-22, which is one of NOAA's baseline observatories (14.2°S, 170.5°W, 77m a.s.l.) at a similar latitude as Reunion Island. Vertical profile and partial column comparisons of the FTIR measurements with the MIPAS data are discussed in Sect. 3. Conclusions are drawn in Sect. 4.
2. Reunion Island FTIR data

2.1 FTIR experiments at Reunion Island

As explained in Baray et al., (2013), the atmospheric observations at Reunion Island are carried out at two sites, namely St Denis (20.90° S, 55.48° E, 85 m a.s.l.), close to the coast, and the Maïdo mountain site (21.07°S, 55.38° E, 2155 m a.s.l.). At present, both sites are equipped with a Bruker 125HR FTIR instrument. These FTIR instruments contribute to two important networks: NDACC (Network for the Detection of Atmospheric Composition Change) and TCCON (Total Carbon Column Observing Network) dedicated to greenhouse gas observations. Each network requires a particular spectral coverage (mid-infrared (600-4500 cm\(^{-1}\)) in NDACC and near-infrared (4000-8000 cm\(^{-1}\)) in TCCON) and therefore a corresponding instrumental configuration (optical filters, beamsplitters and detectors) and operation mode (including spectral resolution). Since March 2013, when the FTIR spectrometer at Maïdo became operational, the Maïdo FTIR has been dedicated to NDACC and the St Denis FTIR to TCCON.

2.1.1 La Reunion - St Denis

The Royal Belgian Institute for Space Aeronomy (BIRA-IASB) started the FTIR solar absorption experiments at La Reunion in St Denis in 2002, with a Bruker 120M FTIR spectrometer, first on a campaign basis with campaigns in 2002 (October), 2004 (August to October) and 2007 (May to November), and then in continuous mode since June 2009 (Senten et al., 2008; Vigouroux et al., 2009; Duflot et al., 2010; Vigouroux et al., 2012; Baray et al., 2013). In September 2011, BIRA-IASB started the replacement of the Bruker 120M by a Bruker 125HR: the Bruker 125HR was installed next to the Bruker 120M and both instruments were set up to make collocated measurements until November 2011, when BIRA-IASB disassembled the Bruker 120M. Since then, at St Denis, BIRA-IASB operates only the Bruker 125HR. Since October 2013 the instrument is primarily dedicated to TCCON measurements and no more NDACC measurements have been made. Because the CFC retrieval windows requires a KBr beamsplitter and a MCT detector (600 to 1400 cm\(^{-1}\)), the CFC data presented in this work at Saint-Denis and requiring the NDACC observational configuration cover the August 2004 - November 2011 period.

2.1.2 La Reunion – Maïdo

BIRA-IASB started operating a second Bruker 125HR FTIR spectrometer at the Maïdo observatory in March 2013 and dedicated it primarily to NDACC measurements with MCT and InSb detectors. As such, our CFC time series at Maïdo cover the March 2013 – present time period.

2.2 FTIR retrieval

The NDACC ground-based FTIR experiment observes the absorption of the direct solar radiation with high spectral resolution (0.0035-0.0110 cm\(^{-1}\)) and uses the pressure broadening effect of absorption lines to retrieve volume mixing ratio (vmr) profiles of target gases. In this study, the FTIR retrievals are based on an optimal estimation method (Rodgers, 2000), carried out with the SFIT4 algorithm (https://wiki.ucar.edu/display/sfit4), which is an open source code, jointly developed at the NASA Langley Research Center, the National Center for Atmospheric Research (NCAR) and the National Institute of Water and Atmosphere Research (NIWA). The
National Centers for Environmental Prediction (NCEP) provide the 6-hourly pressure and temperature profiles. The difference between NCEP and the balloon sounding measurements above Reunion Island is used to create the systematic and random error covariance matrices of the water vapor and temperature profiles. HBr cell measurements performed on a daily basis to verify the alignment of the instrument and to obtain the instrument line shape (ILS) using the LINEFIT14.5 program (Hase et al., 1999); the ILS is provided as an input parameter in the forward model of SFIT4.

### 2.2.1 Retrieval strategy

CFC-11, CFC-12 and HCFC-22 have weak absorptions in the infrared spectral range, requiring careful selection of the retrieval spectral windows in order to minimize the interfering absorptions from other species. The microwindows (see Table 1) are the same as in the work of Mahieu et al. (2010), except for CFC-12: the 922.50-923.60 cm\(^{-1}\) window is however not appropriate for the humid site of Reunion Island because of the strong water vapor lines present at the edge of the window (922.13 cm\(^{-1}\)). To avoid such interferences from water vapor, we prefer to use the 1160.2-1161.4 cm\(^{-1}\) for our CFC-12 retrievals at Reunion Island. The left panels in Fig. 1 show the typical transmittances along with the absorption lines of the target and interfering species, and the fitting residuals for the CFC-11, CFC-12 and HCFC-22 retrievals at St Denis. The interfering gases are also listed in Table 1: as indicated in the Table, either a full profile retrieval is performed or only a scaling of the a a priori profile (column retrieval).

In each microwindow, the background transmittance \( \mathbf{\beta} \) describes the shape caused by the optics in the instrument (especially the bandpass filter) as a second order polynomial of the wavenumber:

\[
\mathbf{\beta} = [1 + a(w - w_0) + b(w - w_0)^2] / (1 + z_0) \quad (1).
\]

In Equation (1), \( a \) is the slope coefficient, \( b \) is the curvature coefficient, \( w_0 \) is the first wavenumber in the microwindow (cm\(^{-1}\)), \( w \) is the vector of all wavenumber in the microwindow, and \( z_0 \) is the zero level offset (zshift). The parameters \( a \), \( b \), and \( z_0 \) can be fitted in SFIT4 in addition to the target gases profiles and interfering species profiles or columns. The calculated transmittance \( y_e \) is the result of bringing the background, absorptions and zshift together:

\[
y_e = \mathbf{\beta} \cdot (\zeta(t(w)) + z_0) \quad (2),
\]

Where \( t(w) \) is the calculated transmittance (after the absorption from each species and solar lines) and \( \zeta(t(w)) \) is the transmittance after convolution with the ILS. If necessary, a beam correction can also be applied to fitting the baseline of the transmittance in each microwindow. It creates a zshift-like parameter \( z_b \) for the interferogram perturbation (IP) model:

\[
y_e = \mathbf{\beta} \cdot (\zeta(t) + z_0 + z_b) \quad (3),
\]

SFIT4 uses 4 parameters (\( A \): amplitude; \( T \): period; \( \phi \): phase and \( \tau \): slope for the amplitude) to retrieve each beam (the maximum number of beams is 20):

\[
\mathcal{g} = A(1 + \tau(w - w_0))e^{i(2\pi/T(w - \phi))} \quad (4),
\]

\[
z_b = \zeta(\mathcal{g}) \quad (5),
\]
Table 1 lists the parameters used for fitting the background in the CFC-11, CFC-12 and HCFC-22 retrievals. Since the retrieval windows of CFC-12 and HCFC-22 are narrow, linear fit is enough to characterize the spectral background \((b=0)\). However, the retrieval window of CFC-11 (830-860 cm\(^{-1}\)) is very wide and contains several saturated H\(_2\)O absorption lines, therefore zshift, slope, and curvature were retrieved together to fit the oscillating shape of the background in the CFC-11 microwindow, and for the CFC-11 retrieval at Maïdo, it turned out necessary to retrieve also one IP-type beam. Together with one IP-type beam, the retrieved CFC-11 total columns at Maïdo show better agreements with MIPAS data and the ground-based HATS SMO in-situ measurements along with a much smaller fitting residual in comparison with without-beam retrievals. Fig. 2 shows the average residual transmittance for the CFC-11 retrievals at Maïdo, with and without fitting a beam parameter. The spikes mainly result from the strong absorption lines of H\(_2\)O. The a priori values for the IP beam parameters were obtained by fitting the mean residuals of all without-beam retrievals. It is clear from Fig. 2 that adding one IP-type beam was useful to remove the background oscillation of the residuals at Maïdo. As such oscillation was not found for the St Denis CFC-11 residuals, the beam parameters retrieval was only applied for Maïdo.

We use the empirical pseudo-line-lists (PLL) created by G. Toon (details see http://mark4sun.jpl.nasa.gov/pseudo.html) for the CFC-11, CFC-12, HCFC-12 and COCl\(_2\) spectroscopy, and HITRAN 2012 (Rothman et al., 2013) for the remaining species (see Table 1). The a priori profiles of interfering gases, except H\(_2\)O and O\(_3\), are the mean of 1980-2016 monthly data from Whole Atmosphere Community Climate Model (WACCM, version 6, ftp://acdc.ucar.edu/user/jamesw/IRWG/2013/WACCM/V6/). In order to reduce the influence of O\(_3\) and H\(_2\)O uncertainties, preliminarily retrieved profiles of O\(_3\) and H\(_2\)O obtained with the settings of Vigouroux et al. (2015) are used, as input for the CFC-11, CFC-12 and HCFC-22 retrievals. The a priori profiles of target species are the mean of 2004-2016 monthly data from WACCM after scaling to the annual mean of ground-based NOAA/HATS SMO flask grab samples and in-situ measurements of 2009 for St Denis and 2014 for Maïdo. As such, the a priori profiles of CFC-11 and CFC-12 for St Denis are a little larger than the ones for Maïdo, while the a priori profile of HCFC-22 for St Denis is a little smaller than that for Maïdo (see Fig. 2). However, all the retrievals at St Denis or at Maïdo use the same a priori profiles. The profiles of the three gases decrease rapidly above 20 km and become close to zero vmr values at 30 km for CFC-11, 40 km for CFC-12 and 100 km for HCFC-22.

The a priori covariance matrix (regularization matrix) is another important input parameter in the optimal estimation method. Ideally, the diagonal values of covariance matrix represent the natural variability of the gas concentration around the a priori profile. Therefore, in our study, 2004-2016 monthly data from WACCM are used to provide the variability for the FTIR retrieval, which agrees with the a priori profile ensemble. The variabilities of CFC-11, CFC-12 and HCFC-22 are then 5%, 2% and 15%, respectively. The gas profile correlation width is set to 4 km from 0 to 100 km in the SFIT4 retrieval, and the retrieved profiles for CFC-11, CFC-12 and HCFC-22 are shown in Fig. 2.

Table 1 lists the DOFS of the total columns of CFC-11, CFC-12 and HCFC-22, along with the standard deviation \((\sigma)\); they are 1.1±0.1, 1.5±0.1, 0.9±0.1 respectively at St Denis and 1.1±0.1, 1.6±0.1, 1.1±0.1 respectively at Maïdo. The right panels of Fig. 1 shows the typical averaging kernels of the CFC-11, CFC-12 and HCFC-22 retrievals at St Denis; they represent the vertical
sensitivity of the measurement as a function of altitude. The FTIR retrievals of all three species are sensible to the whole troposphere and the lowermost stratosphere, with the peak sensitivity around 5-10 km. We have to keep in mind that the retrieved profiles of CFC-11, CFC-12 and HCFC-22 have very poor vertical resolution: the DOFS range from 0.9 to 1.6 and the full widths at half maximum of the averaging kernels are very wide (~8 km).

2.2.2 Error budget

According to the optimal estimation method (Rodgers, 2000), the final state \( \hat{x} \) satisfies

\[
\hat{x} = x_a + \hat{G}(y - F(\hat{x}, b) + \hat{K}(\hat{x} - x_a)) \quad (6),
\]

\[
\hat{G} = (S_a^{-1} + \hat{K} G^{-1} \hat{K})^{-1} \hat{K} G^{-1} \quad (7),
\]

where \( x_a \) is the a priori state vector; \( \hat{G} \) is the contribution function, indicating the sensitivity of the retrieval to the measurements; \( \hat{K} \) is the weighing function, representing the sensitivity of the measurements to the state vector; \( y \) is the observed spectrum and \( F(\hat{x}, b) \) is the forward model (with model parameters represented by \( b \)) evaluated in the final state; \( S_a \) is the a priori covariance matrix and \( S_a \) is the measurement error covariance matrix. If we consider the different uncertainty components, formula (6) can be approximated as,

\[
\hat{x} = x_a + \hat{G}(F(x_i, b) + \varepsilon_y + \varepsilon_y + K_x b - F(\hat{x}, b) + \hat{K}(\hat{x} - x_a)) \quad (8),
\]

in which, \( x_i \) is the true state of the atmosphere; \( \varepsilon_y \) is the forward model error, \( \varepsilon_y \) is the measurement noise; \( K_x \) is the sensitivity of the measurements to the forward model parameters

\[
K_x = \frac{\partial F(x_i, b)}{\partial b}. \]

It is worth noting that this equation is approximated using a Newton iterative algorithm, which is also subject to an error, but the convergence criterion guarantees that the iteration error gets smaller than the noise error on the spectrum. So it is ignored.

We can rewrite formula (8) as

\[
\hat{x} - x_i = (\hat{A} - I_{n_y}) (x_i - x_a) + \hat{G}(\varepsilon_y + \varepsilon_y + K_x b) \quad (9),
\]

where \( \hat{A} = \hat{G} \hat{K} \) is the averaging kernel.

The first term in the right side of the equation (9) is the smoothing error, the second term contains three parts: the forward model error; the measurement error and the forward model parameters error. The forward model parameters error comes from the atmospheric (temperature, a priori profiles, pressure …), spectroscopic, geometrical and instrumental parameters, which are not included in the state vector, but do have an impact on the forward model calculation. Each error contains both a systematic and a random part.

Tables 2 and 3 list the different contributions to the total average retrieval uncertainty, at St Denis and Maida, resp., including smoothing, measurement noise, retrieval parameters (slope; curvature; wavenumber shift; zero-level offset (zshift); beam parameters; solar line shift; simple phase correction), interfering species, temperature profile, solar zenith angle (SZA), spectroscopic parameters (line intensity, air-broadened half-width, temperature dependence of the air-broadened half-width). We assume that the measurement and retrieval parameters have very small systematic uncertainties (set to zero in our case) and that the spectroscopic parameters have negligible random errors. Because zshift is in the state vector for CFC-11, the zshift uncertainty included in retrieval parameters uncertainties but in the model parameters uncertainties for CFC-12 and
HCFC-22. The total average systematic/random uncertainties associated with the retrieved columns for CFC-11, CFC-12, and HCFC-22 are 7.0%/2.0%, 1.8%/1.1%, 4.4%/4.5%, respectively, at St Denis and 6.7%/1.6%, 1.8%/1.1%, 4.5%/4.1% respectively at Maïdo. The systematic uncertainties originate mainly in the uncertainties on the spectroscopic parameters, as well as in the temperature uncertainty. The random uncertainty is dominated by the smoothing error, the uncertainty on the SZA and the measurement noise; especially for HCFC-22, the measurement noise error is very significant due to the narrow and weak absorption of HCFC-22 (see the left bottom panel in Fig. 1).

2.2.3 Total column time series

Fig. 4 shows the time series of retrieved total columns of CFC-11, CFC-12 and HCFC-22 at St Denis and Maïdo, together with their uncertainties (in unit of molecules/cm²). Although the retrievals use the same database of spectra, the numbers of successful retrievals for CFC-11, CFC-12 and HCFC-22 are different. Fig. 4 indicates that the time series of CFC-12 has the largest data density, because the 1160.2-1161.4 cm⁻¹ microwindow falls in the middle of the spectrum with high signal to noise ratio (SNR), while the microwindows 830.0-860.0 cm⁻¹ and 828.75-829.4 cm⁻¹ lie in the edge of the spectrum, with lower SNR due to the optical filter shape. Fig. 4 also shows that there is an offset between the total columns of all three species at St Denis and Maïdo, since the altitude of St Denis (85 m a.s.l.) is much lower than that of Maïdo (2155 m a.s.l.).

2.2.4 Trend analysis and seasonal cycle

Because of the different altitudes of St Denis and Maïdo, it is difficult to compare the total columns of St Denis and Maïdo directly. Therefore, for the trend analysis we extract from the profiles at St Denis the partial columns (2.155-100 km) of CFC-11, CFC-12 and HCFC-22. We plot in Fig.5 these partial columns at St Denis (light coral) together with the total columns at Maïdo, and we can see that they are in good agreement. Also shown for comparison in Fig.5, are the in-situ and flask daily mean measurements at SMO. We use the Chromatograph for Atmospheric Trace Species (CATS) in-situ daily mean data for CFC-11 and CFC-12 (http://www.esrl.noaa.gov/gmd/hats/insitu/cats/) and the flask data for HCFC-22 (Montzka et al., 1993). The precision of the in-situ and flask measurements is about a few of tenths of a ppt for CFC-11, CFC-12 and HCFC-22. Our FTIR measurements could capture the main trends of these species very well, but the scatter of the FTIR retrievals are much larger than the in-situ measurements mainly due to the larger retrieval uncertainties of the FTIR measurements, and the FTIR columns is also associated with the scatter on the air column (e.g., due to tropopause shifts and P-variations).

To derive the secular trends from the FTIR and in-situ measurements daily means \( Y(t) \), with \( t \) the time in fractional year, we use a regression model that includes a Fourier series (3rd order) to describe the seasonal cycle:

\[
Y(t) = A_0 + A_1 \cdot t + \sum_{k=1}^{3} A_{3k} \cos(2k \pi t) + A_{3k-1} \sin(2k \pi t) + \epsilon(t) \quad (10),
\]

where \( A_0 \) is the intercept at \( t=0 \), \( A_1 \) is the secular (annual) trend, \( A_2 \) to \( A_7 \) are the seasonal cycle parameters, and \( \epsilon(t) \) are the residuals between the observations and the model. The auto-correlation in the residuals must be taken into account to avoid the underestimation of trend uncertainties. We follow the approach of (Santer et al., 2000), which by combining their Eqs. 3 to 6, leads us to the following corrected uncertainty \( \sigma_c \) on the regression parameters:
\[ \sigma_c = \sigma_d \cdot \frac{(n-2)}{(n_e-2)} \quad (11), \]

with \( \sigma_d \) the uncertainty directly provided by the regression model, \( n \) the number of daily means in the \( Y(t) \) time-series, and \( n_e \) the effective sampling size:

\[ n_e = \frac{n}{1+r} \quad (12), \]

with \( r \) the auto-correlation, with a time-lag of 1, in the residuals.

Table 4 gives the annual percent changes and their uncertainties of CFC-11, CFC-12 and HCF-22 (%) from both FTIR at Reunion Island and from the in-situ and flask measurements at SMO. The trends from MIPAS, ACE, and Jungfraujoch FTIR measurements in Carpenter et al. (2014) are also listed in Table 4 for comparison. The ACE-FTS (2004-2010) trends were determined by averaging the mixing ratios in molecule-dependent altitude ranges within tropical occultation (30°N-30°S), the MIPAS (2004-2010) trends were calculated by 10-15 km partial column for the 20°N-20°S, and Jungfraujoch is the total columns of FTIR measurements. The annual percent change, in this study, is defined as the ratio of the annual change to the mean of all the measurements that are used to do the trend analysis. Since the time range of Maïdo measurements only covers about 3 years, we do not perform trend analysis on Maïdo data only.

For CFC-11, the total column annual change at St Denis (2004-2011) is -0.69±0.15%, which is slightly weaker than the one derived from SMO measurements (-0.89±0.01%). It is also weaker than the trends reported by MIPAS, ACE, and Jungfraujoch FTIR measurements. However, the annual change of the combined FTIR partial columns at St Denis and total columns at Maïdo (2004-2016) is very close to the SMO measurements (-0.86±0.12% vs. -0.87±0.04%). For CFC-12, the total column annual change at St Denis (2004-2011) is -0.26±0.10%, which is also slightly weaker than the one derived from SMO measurements (-0.37±0.08%), but in agreement within the estimated uncertainties. It is also in agreement with the ACE-FTS and Jungfraujoch reported trends. Fig. 4 shows that the concentration of CFC-12 has a significant trend change around 2004 (increasing before 2004 and decreasing after), therefore, it is better to select the data after 2009 to do the trend analysis. The annual change of the combined partial columns at St Denis and total columns at Maïdo (2009-2016) is stronger than that derived from the SMO measurements (-0.76±0.05% vs. -0.60±0.02%). For HCFC-22, the annual change of St Denis partial columns (3.14±0.43%) is close to that reported from ACF-FTS data and Jungfraujoch measurements for approximately the same period, but slightly smaller than that derived from the SMO measurements (4.04±0.06%). The trend of the combined partial columns at St Denis and total columns at Maïdo (2004-2016) is also smaller than that of the SMO measurements (2.75±0.12% vs. 3.46±0.05%).

Fig. 6 shows the seasonal cycles of CFC-11, CFC-12 and HCFC-22. The red lines represent the modeled seasonal cycle obtained by Eq. 10 for the 2004-2016 St Denis - Maïdo time-series, and blue lines represent the mean of FTIR measurements for each month during the 2004-2016 period, after subtraction of the trend (removing the systematic retrieval error), together with the standard deviation \( \sigma \) on the mean (thin error bars). The standard deviation \( \sigma \) represents the random error of the FTIR retrievals, and the 2 \( \sigma \) error on the mean \( \left( \frac{2\sigma}{\sqrt{n}} ; n \text{ being the number of measurements for each month} \right) \) is also shown with thick blue lines. For CFC-11 and HCFC-22, there is no obvious seasonal variation, since the uncertainty is very large. However, there is a significant seasonal variation for CFC-12, for which the concentration is highest in March-May.
and lowest in September-November.

3. Comparison with ENVISAT/MIPAS data

3.1 MIPAS introduction

ENVISAT was successfully launched into space on March 1, 2002 carrying several sensors, including MIPAS, a cryogenic limb emission Fourier transform spectrometer (FTS) which observes many trace gases from a wide spectrum covering 865-2410 cm\(^{-1}\) (Fischer and Oelhaf, 1996). The mission ended on 08 April 2012. From July 2002 to March 2004, MIPAS was operated in full spectral resolution (FR) mode (spectral resolution: 0.05 cm\(^{-1}\)), covering the altitude range from 6 km to 68 km. Due to the failure of one of the interferometer slides, MIPAS was operated with a reduced spectral resolution (0.121 cm\(^{-1}\)), the so-called RR mode, starting January 2005. The RR mode covers the altitude range from 6 km to 70 km (Fischer et al., 2008). In this paper, we use the Institute of Meteorology and Climate Research (IMK) generated MIPAS/ENVISAT products, taken from https://www.imk-asf.kit.edu/english/308.php. The retrieval windows of MIPAS are 831.0-853.0 cm\(^{-1}\) for CFC-11; 915.0-925.0 cm\(^{-1}\) for CFC-12; 803.50-804.75 cm\(^{-1}\), 808.25-809.75 cm\(^{-1}\), 820.50-821.12 cm\(^{-1}\), and 828.75-829.50 cm\(^{-1}\) for HCFC-22. A dedicated spectroscopic database was applied for MIPAS retrieval (Fauld and Teffo, 2003). The detailed MIPAS CFCs retrieval strategies can be found in previous publications (Hoffmann et al., 2005; Kellmann et al., 2012; Chirkov et al., 2016); all the products have been validated to some degree by comparison with other space experiments, air-borne in-situ instruments, ground-based measurements, or independent ENVISAT MIPAS analyses (Hoffmann et al., 2008).

3.2 Vertical profile comparison

There is no temporal overlap between MIPAS data and Maïdo measurements, so the MIPAS footprints within ±2º latitude ±5º longitude around St Denis are selected to compare with the St Denis FTIR measurements. The overpass times of MIPAS above Reunion Island are around 6:30 and 18:30 UTC, due to the sun-synchronous orbit of ENVISAT. As the FTIR measurements are recorded only during daytime, the MIPAS data around 6:30 UTC are chosen in the following analysis.

Fig. 7 shows the comparison of averaged profiles between FTIR measurements and MIPAS data. The individual FTIR-MIPAS data pair was selected when the FTIR measurement and the MIPAS observation were collocated within ±3 hours around 6:30 UTC on the same day. If more than one MIPAS datapoint was found on a given day, the closest (in geodetic distance) MIPAS data point was taken. If more than one FTIR measurement exists on a given day, each FTIR measurement together with the closest MIPAS datapoint will be taken as one individual data pair. In total, there are 60, 86 and 42 FTIR-MIPAS data pairs for CFC-11, CFC-12 and HCFC-22, respectively. It is worth noting that, to account for the sensitivity of the retrieval to the true profiles and to take into account the low vertical resolution of the FTIR retrieved profiles, the MIPAS profile \(\hat{x}_{\text{MIPAS}}\) is smoothed by the FTIR averaging kernel (AK) \(A_{\text{FTIR}}\) (Rodgers and Connor, 2003):

\[
\hat{x}_{\text{MIPAS}} = x_{\text{FTIR}}^{\text{a priori}} + A_{\text{FTIR}}(\hat{x}_{\text{MIPAS}} - x_{\text{FTIR}}^{\text{a priori}}) \quad (13),
\]

Where \(x_{\text{FTIR}}^{\text{a priori}}\) is the FTIR a priori profile and \(\hat{x}_{\text{MIPAS}}\) is the MIPAS profile after
smoothing correction is applied. The MIPAS profile was interpolated onto the FTIR retrieval grids (keeping the total column unchanged). Fig. 7 mainly focuses on the vertical range from 6 to 30 km, because there aren’t any MIPAS measurements below 6 km (Fischer et al., 2008) and the FTIR sensitivity is very weak above 30 km along with a very small relative difference (less than 1%) between the smoothed MIPAS and FTIR ((MIPAS-FTIR)/FTIR × 100%) above 30 km for all three species (see right panels in Fig. 7). Since the FTIR retrievals have very poor vertical resolution, the “oscillation” of the profiles of the relative difference between FTIR and MIPAS could be caused by the FTIR retrievals. Anyhow, for CFC-11, the FTIR concentration is larger than the smoothed MIPAS concentration value between 6 km and 30 km: the largest difference is of order -7% around 15 km. For CFC-12, the FTIR retrieval is larger below 14 km and smaller above 14 km than the smoothed MIPAS data. The peaks are around 6 km (-8%) and 18 km (2%). For HCFC-22, the FTIR retrieval is very close to the smoothed MIPAS data: the relative difference is within ±5% between 6 and 30 km.

3.3 Partial column comparison

In this section, we compare the MIPAS and St Denis FTIR partial columns (PC) from 6 to 30 km, for the same collocated pairs as in Sect. 3.2. The DoFS of the partial columns of CFC-11, CFC-12, HCFC-22 are 0.6±0.1, 0.9±0.1, 0.6±0.1. Table 5 exhibits the statistical values of the comparison: relative bias and standard deviation of the difference between the MIPAS (raw and smoothed) and FTIR, together with the partial column uncertainties from both data sets. The largest mean relative bias is found for CFC-11 (-4.3%), showing that the FTIR partial columns are larger than the MIPAS ones, which is probably caused by the large systematic error of FTIR CFC-11 retrievals (10.5%). For CFC-12, the bias is -2.7% which is also within the uncertainty budget of combined data sets. The lowest relative bias is found for HCFC-22 (-0.7%) but the standard deviation is large (6.0%) because of the large FTIR retrieval errors (7.8%/7.1%) and MIPAS retrieval error (5.0%). Overall, the biases and standard deviations between the two data sets lie within the uncertainty budgets for the three species.

Fig. 8 shows the time series of the monthly means of partial columns of CFC-11, CFC-12 and HCFC-22 FTIR measurements at St Denis (grey) along with the raw MIPAS data (red). The smoothed MIPAS data are not shown here, because more than half of MIPAS data do not correspond with an individual FTIR measurement within one day or even one week, and the differences between partial columns of smoothed and unsmoothed data are within 1.0%. Note that the bias between the raw MIPAS and FTIR data also contains the smoothing error, but the bias already lies within the uncertainty budget even without smoothing error (see Table 5). Fig. 8 shows that the monthly means of MIPAS and FTIR data are in a good agreement.

4. Summary

CFC-11, CFC-12 and HCFC-22 mixing ratio profiles were retrieved at Reunion Island from St Denis and Maïdo ground-based solar absorption FTIR measurements between 2004 and 2016. The retrieval microwindows are carefully selected to minimize the interfering absorptions from other species. The averaging kernels of CFC-11, CFC-12 and HCFC-22 are very similar, and the retrieved information comes mainly from the troposphere and lower stratosphere with low vertical resolution. As expected as a response to the Montreal Protocol, negative trends of total columns of CFC-11 and CFC-12 and a positive trend of HCFC-22 were observed at St Denis and Maïdo,
which is in good agreement with the in-situ surface data and other remote sensing results (e.g., SMO in-situ and flask measurements and Jungfraujoch FTIR data, resp.). The observed FTIR total column trends above St Denis between 2004 and 2011 are $-0.69\pm 0.15\%/\text{yr}$ for CFC-11, $-0.26\pm 0.10\%/\text{yr}$ for CFC-12 and $3.14\pm 0.43\%/\text{yr}$ for HCFC-22. The trends of combined FTIR partial columns (2.155-100 km) at St Denis and total columns at Mayotte are $-0.86\pm 0.12\%$ for CFC-11 and $2.75\pm 0.12\%$ for HCFC-22 between 2004 and 2016, and $-0.76\pm 0.05\%$ for CFC-12 between 2009 and 2016. These trends are consistent with the ones observed at SMO for CFC-11 ($-0.87\pm 0.04\%$), but slightly smaller for HCFC-22 ($3.46\pm 0.05\%$) and larger for CFC-12 ($-0.60\pm 0.02\%$).

The FTIR measurements were also compared with collocated MIPAS/ENVISAT data around St Denis. There are 60, 86 and 42 FTIR-MIPAS collocated data pairs for CFC-11, CFC-12 and HCFC-22 within $\pm 2^\circ$ latitude, $\pm 5^\circ$ longitude and $\pm 3$ hours around 6:30 UTC. The differences between FTIR and smoothed MIPAS profiles from 6 to 30 km altitude are within $\pm 10\%$ for CFC-11 and CFC-12, and $\pm 5\%$ for HCFC-22. The relative biases and standard deviations of the differences between the partial columns (6-30 km) of smoothed MIPAS and FTIR are $-4.3\% \pm 4.4\%$, $-2.9\% \pm 4.6\%$ and $-0.7\% \pm 6.0\%$ for CFC-11, CFC-12, and HCFC-22, respectively, which lie within the error budgets from both data sets. Overall, the time series of MIPAS monthly partial columns show a good agreement with the St Denis FTIR partial column data.

**Acknowledgments**

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**References**


Mahieu, E., Bader, W., and Franco, B.: Recent results derived from regular ground-based FTIR observations at the Jungfraujoch and other NDACC stations, ACE Science Team Meeting, 2015.


Table 1. Microwindows, interfering gases, spectroscopic database, a priori profile and background

<table>
<thead>
<tr>
<th>Target gas</th>
<th>CFC-11 (CCl₃F)</th>
<th>CFC-12 (CCl₂F₂)</th>
<th>HCFC-22 (CHF₂Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwindows (cm⁻¹)</td>
<td>830.0-860.0</td>
<td>1160.2-1161.4</td>
<td>828.75-829.4</td>
</tr>
<tr>
<td>Profile retrieval</td>
<td>CFC-11, H₂O</td>
<td>CFC-12, N₂O</td>
<td>HCFC-22</td>
</tr>
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<td>Column retrieval</td>
<td>HNO₃, O₃, COCl₂, CO₂</td>
<td>O₃, CH₄, H₂O</td>
<td>CO₂, H₂O, O₃</td>
</tr>
<tr>
<td>Spectroscopy</td>
<td>PLL, HITRAN2012</td>
<td>PLL, HITRAN2012</td>
<td>PLL, HITRAN2012</td>
</tr>
<tr>
<td>A priori profile</td>
<td>WACCM</td>
<td>WACCM</td>
<td>WACCM</td>
</tr>
<tr>
<td>St Denis background</td>
<td>slope, curvature, zshift</td>
<td>slope</td>
<td>slope</td>
</tr>
<tr>
<td>DOFS (St Denis)</td>
<td>1.1±0.1</td>
<td>1.5±0.1</td>
<td>0.9±0.1</td>
</tr>
<tr>
<td>Maïdo background</td>
<td>slope, curvature, zshift, beam</td>
<td>slope</td>
<td>slope</td>
</tr>
<tr>
<td>DOFS (Maïdo)</td>
<td>1.0±0.1</td>
<td>1.6±0.1</td>
<td>1.1±0.1</td>
</tr>
</tbody>
</table>
Table 2. Systematic and random uncertainties (in %) for CFC-11, CFC-12, and HCFC-22 at St Denis. Sb represents the relative uncertainties of the non-retrieved parameters. For temperature, the systematic/random Sb matrix was created by the mean/standard deviation of the differences between NCEP and the balloon observations. For the spectroscopic parameters, 0.07, 0.01 and 0.05 are the relative uncertainties of CFC-11, CFC-12 and HCFC-22, which are according to the PLL database, respectively. When a relative uncertainty is smaller than 0.01%, it is considered negligible and represented as “-”. For zshift, the same uncertainty is adopted for the systematic and random error; zshift is included in the retrieval parameters for CFC-11, but not for CFC-12 and HCFC-22. For SZA, the systematic uncertainty is 0.001 and the random uncertainty is 0.002 (in the bracket).

<table>
<thead>
<tr>
<th>Error</th>
<th>Sb</th>
<th>Systematic</th>
<th>Random</th>
<th>Systematic</th>
<th>Random</th>
<th>Systematic</th>
<th>Random</th>
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<td>Smoothing</td>
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<td>0.79</td>
<td>0.47</td>
<td>0.51</td>
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<td>Measurement</td>
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<td>-</td>
<td>0.21</td>
<td>-</td>
<td>4.05</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>0.10</td>
<td>0.02</td>
<td>0.13</td>
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<td>Temperature</td>
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<td>0.15</td>
<td>1.00</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>SZA</td>
<td>0.001 (0.002)</td>
<td>0.21</td>
<td>0.42</td>
<td>0.36</td>
<td>0.72</td>
<td>0.63</td>
<td>1.26</td>
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<td>Line intensity</td>
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<td>1.00</td>
<td>-</td>
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</tr>
<tr>
<td>T-dependence of line width</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>0.15</td>
<td></td>
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<tr>
<td>Air-broadening of line width</td>
<td>0.07/0.01/0.05</td>
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<td>-</td>
<td>0.07</td>
<td>-</td>
<td>1.53</td>
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<tr>
<td>szshift</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>0.12</td>
<td>0.09</td>
<td>0.10</td>
<td>0.12</td>
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<tr>
<td>Total</td>
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<td>1.8</td>
<td>1.1</td>
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<td>4.5</td>
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</table>
Table 3. Same as Table 2, but for Maïdo.

<table>
<thead>
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<th>Error</th>
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<th>Random</th>
<th>Systematic</th>
<th>Random</th>
<th>Systematic</th>
<th>Random</th>
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<tr>
<td>Smoothing</td>
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<td>0.90</td>
<td>0.02</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>0.12</td>
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<tr>
<td>Interfering species</td>
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<td>0.03</td>
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<tr>
<td>Temperature</td>
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<td>0.84</td>
<td>0.16</td>
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<tr>
<td>SZA</td>
<td>0.001(0.002)</td>
<td>0.25</td>
<td>0.51</td>
<td>0.22</td>
<td>0.44</td>
<td>0.22</td>
<td>0.44</td>
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<td>-</td>
<td>0.98</td>
<td>-</td>
<td>4.22</td>
<td>-</td>
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<tr>
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<td>0.05</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Air-broadening of line width</td>
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<td>-</td>
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<td>zshift</td>
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<td>-</td>
<td>0.12</td>
<td>0.07</td>
<td>0.10</td>
<td>0.05</td>
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<tr>
<td>Total</td>
<td>6.7</td>
<td>1.6</td>
<td>1.8</td>
<td>1.1</td>
<td>4.5</td>
<td>3.6</td>
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Table 4. The annual percent changes (in %/year, relative to the mean of data used in the trend analysis) and uncertainties of FTIR total columns of CFC-11, CFC-12 and HCF-22 at St Denis (2004-2011) and of the combined partial columns (2.155-100 km) at St Denis along with the total columns at Maïdo (2004-2016 for CFC-11 and HCFC-12, and 2009-2016 for CFC-12). The trends from in-situ and flask measurements at SMO are also given for the same time periods. The trends observed by MIPAS (2004-2010), ACE-FTS (2004-2010) and by the ground-based FTIR at Jungfraujoch (2004-2010) % in %/yr relative to the 2007 annual mean are taken from Carpenter et al. (2014) as described in the text.

<table>
<thead>
<tr>
<th>Dataset</th>
<th>Time range</th>
<th>CFC-11</th>
<th>CFC-12</th>
<th>HCFC-22</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>St Denis (TC)</td>
<td>2004-2011</td>
<td>-0.69±0.15</td>
<td>-0.26±0.10</td>
<td>3.14±0.43</td>
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<tr>
<td>SMO</td>
<td>2004-2011</td>
<td>-0.89±0.01</td>
<td>-0.37±0.08</td>
<td>4.04±0.06</td>
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<tr>
<td>MIPAS</td>
<td>2004-2010</td>
<td>-1.03±0.09</td>
<td>-0.51±0.09</td>
<td>-</td>
<td>Kellmann et al., 2012</td>
</tr>
<tr>
<td>ACE-FTS</td>
<td>2004-2010</td>
<td>-0.9±0.1</td>
<td>-0.4±0.1</td>
<td>3.7±0.1</td>
<td>Brown et al., 2011</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>2004-2010</td>
<td>-0.99±0.10</td>
<td>-0.38±0.07</td>
<td>3.52±0.08</td>
<td>Zander et al., 2008</td>
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<tr>
<td>St Denis(PC) + Maïdo(TC)</td>
<td>2004-2016</td>
<td>-0.86±0.12</td>
<td>-</td>
<td>2.75±0.12</td>
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</tr>
<tr>
<td></td>
<td>2009-2016</td>
<td>-</td>
<td>-0.76±0.05</td>
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<td></td>
<td>2004-2016</td>
<td>-0.87±0.04</td>
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<td>3.46±0.05</td>
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<tr>
<td>SMO</td>
<td>2009-2016</td>
<td>-</td>
<td>-0.60±0.02</td>
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</table>
Table 5. The number of collocated MIPAS-FTIR pairs, bias and standard deviation (std) of the relative differences \(\frac{(\text{MIPAS-FTIR})}{\text{FTIR} \times 100}\%\) between the partial columns (6-30 km) of MIPAS (both the raw and smoothed data) and FTIR, together with the mean random and systematic uncertainties of the FTIR partial columns and the retrieval error of the MIPAS data (in %).

<table>
<thead>
<tr>
<th></th>
<th>CFC-11</th>
<th>CFC-12</th>
<th>HCFC-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of data pairs</td>
<td>60</td>
<td>86</td>
<td>42</td>
</tr>
<tr>
<td>Bias(_{\text{raw}})</td>
<td>-4.4</td>
<td>-3.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Std(_{\text{raw}})</td>
<td>4.7</td>
<td>4.5</td>
<td>6.3</td>
</tr>
<tr>
<td>Bias(_{\text{smoothed}})</td>
<td>-4.3</td>
<td>-2.9</td>
<td>-0.7</td>
</tr>
<tr>
<td>Std(_{\text{smoothed}})</td>
<td>4.4</td>
<td>4.6</td>
<td>6.0</td>
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<tr>
<td>FTIR PC random error</td>
<td>4.2</td>
<td>3.5</td>
<td>7.8</td>
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<td>FTIR PC systematic error</td>
<td>10.5</td>
<td>2.6</td>
<td>7.1</td>
</tr>
<tr>
<td>MIPAS PC retrieval error</td>
<td>4.1</td>
<td>4.3</td>
<td>5.0</td>
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</tbody>
</table>
Figure 1. The typical spectrum and averaging kernels of CFC-11 (upper), CFC-12 (middle) and HCFC-22 (bottom) at St Denis. The left panels show the transmission and residual (observed – calculated spectrum) for the three retrieval microwindows, along with the absorption contribution from each specie. Right panels show the averaging kernels for the target gases (no sensitivity above 50 km). The solid lines represent the sensitivities at specific altitudes. The red dashed line is the sum of the row of averaging kernel scaled with 0.1, indicating the vertical sensitivity.
Figure 2. The a priori (red line), retrieved profiles (grey lines) and the mean retrieved profile (blue line) of CFC-11, CFC-12 and HCFC-22 at St Denis (upper panels) and Maï do (bottom panels).
Figure 3. The mean residual transmittance (observed – calculated) of the CFC-11 retrievals with and without beam parameters at Maïdo. The IP beam fit line is used as a priori IP beam parameters.
Figure 4. The time series of the total columns and total uncertainties of CFC-11, CFC-12 and HCFC-22 at St Denis (black) and Maïdo (grey). The error bar contains both systematic and random uncertainties from SFIT4 retrieval ($\sqrt{\varepsilon_s^2 + \varepsilon_r^2}$).
Figure 5. In-situ daily mean (CFC-11 and CFC-12) and flask pair measurements (HCFC-22) at SMO site (blue) and individual FTIR partial column at St Denis (2.155-100 km; light coral) and total column at Maï do (2.155-100 km; grey). Upper: CFC-11; middle: CFC-12; bottom: HCFC-22.
Figure 6: Seasonal cycles of CFC-11, CFC-12 and HCFC-22. The modelled seasonal cycle obtained by Eq. 10 for the 2004-2016 St Denis -Maïdo time-series is shown in red. In blue, the mean of FTIR measurements for each month during the 2004-2016 period, after subtraction of the trend, is shown, together with the standard deviation $\sigma$ of the mean (thin error bars). The $2\sigma$ error on the mean ($2\sigma/\sqrt{n}$; n being the number of measurements for each month) is also shown with thick blue lines.
Figure 7. Left panel, for each target species (from top to bottom: CFC-11, CFC-12 and HCFC-22): averaged target species mixing ratio profile, random uncertainty (error bar) and the standard deviation of all the co-existing data pairs (shade area) for FTIR (in black) and for MIPAS (in red: raw data; in sky blue: after smoothing with the corresponding FTIR averaging kernel). The profiles (from 0 to 100 km) are also manifested in the left panels. Right panel, for each target species, averaged relative difference between MIPAS and FTIR ((MIPAS – FTIR)/FTIR × 100%) (solid lines), along with the standard deviation (dash lines).
Figure 8. The time series of the monthly means of partial columns (6 to 30 km) of CFC-11, CFC-12 and HCFC-22 from St Denis FTIR measurements (grey) and raw MIPAS data (red). Error bars represent the standard deviations of the monthly means.