

Black: referee's comments red: authors' answers

First, we want to thank the referee for the detailed analysis of our paper.

General Comments

This paper presents for the first time the time series of three important gases on the atmospheric chemistry, CFC-11, CFC-12 and HCFC-22, at two stations in Reunion Island. The strategic location of the ground-based station and the methodology proposed, using high-resolution Fourier Transform infrared (FTIR) solar absorption spectra and the well-established retrieval strategies, provide high confidence to the results obtained. This is also documented with a comprehensive comparison with other measurement techniques and previous studies. The paper is well-written and concise. However, the presentation of the results and their discussion is a bit confusing and it is not well structured. For example, the authors first carry out a trend analysis comparing with other techniques, such as those from MIPAS sensor, and in the following section, a validation with coincident MIPAS is presented on a measurement-to-measurement basis, but the corresponding trends are not compared to coincident MIPAS database. Moreover, the overall treatment of the theoretical errors is imprecise, so the authors should improve its description, and discussion. Detailed explanations of the sections to be corrected are mentioned in the Specific Comments. I suggest this paper maybe suitable for publication after addressing these issues and the specific ones listed below.

Specific Comments

Section 2.2.

Line 129: One of the key issues addressed by the paper is the presentation of the linear trends for CFC-11, CFC-12 and HCFC-22 as observed by ground-based FTIRs. To do so, it is very important to document/show that the spectrometers do not show any temporal drift that could affect the trend estimation. This could be done and discussed, for example, by including a Figure with the time series of Instrumental Line Shape (ILS) in Section 2.2 or of the retrieved DOFs in section 2.2.1 (line 204) or of the measurement noise.

Thanks for your suggestion. Figure a shows the time series of the modulation efficiency (ME) of ILS at St. Denis and Maito FTIR sites. Figure b shows the time series of DOFS of CFC-12 at St Denis and Maito. The time series of DOFS of CFC-11 and HCFC-22 are very similar to that of CFC-12 (not shown here). Except the mirror issue during May to November 2015 at Maito, the ME of ILS at St Denis and Maito are very stable. We added the ILS error estimations in Table 2 and 3. The ILS is not so important for CFC-11, CFC-12 and HCFC-22 retrievals, because the absorption lines of these species are not sharp and the AVKs for the 3 species show that the information is coming mainly from the troposphere (see Figure 1 in the paper). For the time series of the DOFs or SNR, they are both very flat, and no temporal shift is found. Therefore, we prefer to add one sentence in the section 2.2.1 to state that the FTIR instrument at St Denis and Maito were operated in good condition instead of adding a Figure in the paper.

“There is no significant trend in the time series of DOFS for three species at both St Denis and Maito, which allows us to do the seasonal cycle and trend analysis in sect. 3 ”

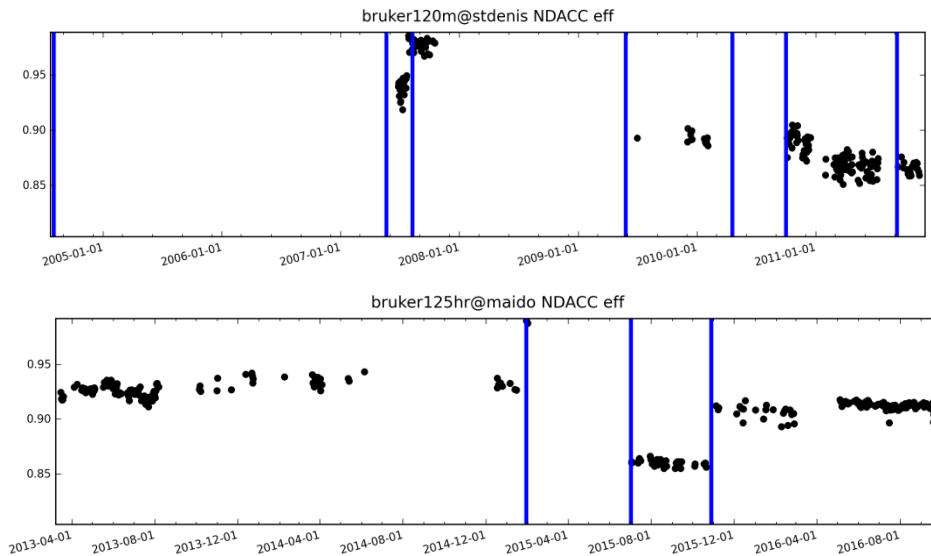


Figure a. Time series of the modulation efficiency of ILS at St. Denis (upper) and Maito (bottom) FTIR sites. Blue lines: instrument alignments.

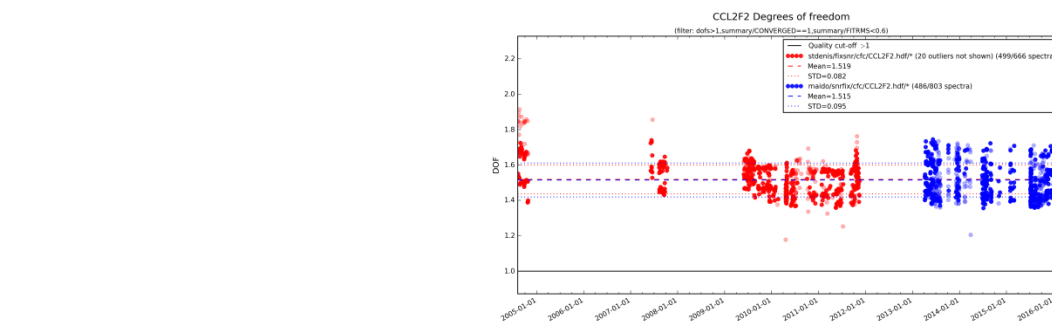


Figure b. Time series of the DOFS of CFC-12 at St. Denis (red) and Maito (blue) FTIR sites.

Section 2.2.1.

Line 192: The retrieved HCFC-22 vertical profiles at St. Denis show a stronger variability in the troposphere/lower stratosphere than in Maito (see Figure 2). It would be nice if the authors include some explanation for this observed variability?

Indeed, the retrieved HCFC-22 vertical profiles at St. Denis show a stronger variability in the troposphere/lower stratosphere than at Maito. One reason is that St. Denis data cover a much wider time range (8 years) than Maito (4 years), so that part of the variability simply comes from the trend in HCFC-22 amounts. The Figure 3 has been improved by plotting the retrieved profiles with different color for each year, to show which part of the variability comes from the trend.

However the variability within one year is still stronger at St Denis compared to Maito: this can not come from larger natural variability since this species is well mixed in the whole troposphere. The larger scatter at St Denis within one year comes from the larger random error budget at this station (see Tables 1 and 2), due to lower signal to noise ratio (so larger measurement error).

These explanations were added in the text.

Line 196: As it is stated by the authors, the a priori covariance matrix is crucial in the optimal estimation method as well as to estimate the FTIR smoothing error. Thereby, authors need to justify the use of WACCM model outputs to estimate the covariance matrices for the considered trace gases. It would be

recommendable to state how well the WACCM simulations represent the real atmospheric states or provide references on works that show ability of the WACCM model to reasonably simulate vertical distribution of the target gases.

Unfortunately, there is no reference available to confirm the performance of WACCM model for these three species. WACCM data is applied in our study, since WACCM is recommended to be used within the NDACC-IRWG community (J. Hannigan, co-chair of IRWG, personal communication), and previous research at Jungfraujoch site also used WACCM model data (Emmanuel Mahieu; personal communication). In addition, the variability of CFC-11, CFC-12 and HCFC-22 from WACCM model is very close to that from MIPAS data and ACE-FTS data at Reunion Island.

Line 204: Are the FTIR retrievals filtered according to some specific quality filter or SNR? Please, clarify, because in Section 2.2.3 the authors mention that “although the retrievals use the same database of spectra, the numbers of successful retrievals for CFC-11, CFC-12 and HCFC-22 are different”.

Thanks for your suggestion. The following sentence is added in the text: The FTIR retrievals are filtered according to the root mean square (RMS) of the residuals: only retrievals with a RMS smaller than 1.0 (St Denis) and 0.6 (Maïdo) are kept in the analysis.

Section 2.2.2.

The basis for the theoretical error estimation is presented well, but the discussion of the error budget is a bit confusing and imprecise, and it must be clarified and completed. A detailed error discussion would be very useful because it indicates where a special effort should be paid to improve the precision of the CFC-11, CFC-12 and HCFC-22 FTIR products in the future. 1) St. Denis and Maido are two humid sites. To avoid the H₂O interference, the authors follow the recommendable retrieval strategy of performing a pre-fit of H₂O previous to the target gas retrievals. Nevertheless, the effect of humidity (cross-interference of H₂O) should be included in the error estimation to analyse its remaining impact and support the two-steps strategy. 2) Other important error source that is not included in the error budget is the Instrumental Line Shape (ILS). According to Figure 1 (averaging kernels), the retrieved FTIR profiles of the target gases still show sensitivity in the lower/middle stratosphere, where the ILS' impact is not negligible. Please, consider including it into the error estimation.

1) The H₂O interference uncertainty has already been included in the interfering species error in Tables 2 and 3. The systematic/random uncertainty contribution from H₂O is 0.04%/0.35% for CFC-11, <0.01%/0.01% for CFC-12 and <0.01%/0.03% for HCFC-22 respectively at St Denis and 0.02%/0.08% for CFC-11, <0.01%/<0.01% for CFC-12 and <0.01%/0.01% for HCFC-22 respectively at Maido. The random uncertainty of H₂O is derived from the difference between sound measurements and NCEP (same as the temperature; details see 3)). The systematic uncertainty is set as 5% of the mean values.

In the revised version, we also added the systematic errors from H₂O spectroscopy uncertainty in Tables 2 and 3. The uncertainties of the H₂O spectroscopy parameters (0.10) are according to the HITRAN2012 database.

2) ILS uncertainties to the total column retrievals are also added here (see Tables 2 and 3). Since the SFIT4 algorithm has no Jacobian output when the LINEFIT parameters are directly used in the SFIT4 forward model, we can not obtain the error raised from ILS. The number given here come from a test on a 3-order polynomial fit, and the relative uncertainties of the fitting parameters are set as 5%.

3) Some details of the error estimation calculation are missed or imprecise. For example: a. How the error covariance S_b is exactly calculated (diagonal, inter-layer correlation)? b. How is the error of the interfering species estimated? c. For temperature, the S_b matrix is computed from the difference between NCEP database and balloon observations, but please state the assumed error values for reference. d. For the smoothing error, how are the systematic and random contributions computed? e. In the text the authors mention that for the retrieval parameters the systematic contribution is set to zero, but in the Table 2 the authors assume that the zshift parameter has the same systematic and random uncertainty and the corresponding results are shown. Please clarify. Also, just to homogenise the format, considering

including the systematic and random error values in Table 2 in the same way. For example, for SZA the systematic and random errors are given (I guess because they are different), but not for zshift. Please include even if they are equal. f. I guess that the error budget presented in Table 2 and 3 corresponds to the whole FTIR spectra database. Please state. g. Please specify the references for the assumed uncertainty, for example, for the spectroscopic parameters, the solar zenith angle, etc.

An extra paragraph is added in the text.

We assume that 5% of the a priori profile as the diagonal values S_a^{sys} of systematic covariance matrix and off-diagonal values are $S_a^{sys} S_a^{sys}$ (von Clarmann, 2014). The a priori profile originates from WACCM and the random uncertainty matrix S_a^{ran} is based on the covariance estimated from 2004-2016 monthly data in the following way: to remove unreal correlations between distant layers, the WACCM covariance is multiplied with an function exponentially decaying with the interlayer distance. S_a^{sys} and S_a^{ran} are propagated to the retrieved state (using (A-I)) to obtain the systematic and random smoothing errors.

In the SFIT4 software, we prefer to use S_a^{ran} as the regularization matrix in the OE algorithm, since it is close to a realistic uncertainty matrix. However, if the retrieval is not 'good' (i.e. oscillating profiles, wild AVK's (i.e. high negative components, strange rows that peak at bad altitudes, ...), We tune the realistic S_a to get a good retrieval. Therefore, the S_a in the SFIT4 is not always the same as the S_a^{ran} . In this paper, the variabilities of CFC-11 (5%), CFC-12 (2%) and HCFC-22 (15%) are keep constant for the whole vertical range, which is very close to the diagonal values in S_a^{ran} and the correlation between layer and layer is also determined by an exponential decaying function with the width set as 4 km from 0 to 100 km.

Sb in Tables 2 and 3 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 at St Denis. The random component is from 2K to 4K in the vertical range from 0 to 30 km and about 5K above 30 km, and the systematic component is about 2K for the whole vertical range. For the target spectroscopic parameters, 7%, 1% and 5% are the relative uncertainties of CFC-11, CFC-12 and HCFC-22 respectively, according to the PLL database. For the H₂O spectroscopy parameters, the relative uncertainty (10%) is taken from HITRAN 2012 dataset (Rothman et al., 2013). We assume that the random uncertainty is negligible for all the spectroscopy parameters. For zshift, 1% is adopted for both the systematic and random uncertainty according to Schneider et al., (2008). Note that zshift is included in the retrieval parameters for CFC-11, but not for CFC-12 and HCFC-22. Therefore, the zshift error is included in the retrieved parameters error for CFC-11 and the zshift uncertainty in Table 2 and 3 is only applied for CFC-11 and HCFC-22 error budget estimations. We assume 5% for ILS parameters (apodization and phase) relative systematic and random uncertainties. For SZA, the systematic uncertainty is 0.1% and the random uncertainty is 0.2%, according to the uncertainty estimation from the pysolar python software package (<http://pysolar.org/>).

Section 2.2.3, 2.2.4 and 3.

The presentation and discussion of the results are mixed through the three subsections. For example, the inter-comparison with MIPAS database is a validation study that experimentally quantifies the uncertainties of the new FTIR products. But, this is shown as the last section of the paper, when it should be the first part of the results section. Also, only a measurement-to-measurement comparison is carried out, without neither comparing annual cycles nor linear trends, when this analysis is presented and

discussed in the previous section with other database (among them MIPAS observations from literature) for linear trend, but no references are given for seasonal patterns. Specific comments are listed below:

1) Consider re-organising these three sections by merging them into a unique one. This section could include a subsection describing the “comparison/validation” dataset (MIPAS and SMO), and three subsections for the comparison at the different time scales: measurement-to-measurement, annual cycles and linear trends versus coincident MIPAS database (I would also suggest to include a more detailed comparison with SMO data). This implies that authors should carry out the comparison between the MIPAS and FTIR annual cycles and linear trends, not included until now in the paper. Regarding to SMO data the authors have different options to perform this comparison (total column-averaged dry air mole fractions of the different target gases or simply averaged tropospheric VMR values) and there are multiple references in literature. In the trend analysis subsection, the authors could include the comparison with results from literature (FTIR at Junfraujoch, ACE-FTS and MIPAS) as already shown in section 2.2.4.

Thanks for your suggestions. We regroup the section 3 as: Comparison with MIPAS data, including profile comparison, partial column comparison, trend analysis and seasonal cycle analysis.

We move the comparison with SMO time series in Section 2. The quantitative comparison between SMO and FTIR retrievals was made in section 2.3 (In-situ vs Xgas). The column averaged dry-air mole fraction of CFC-11, CFC-12 and HCFC-22 are calculated to compare with the SMO in-situ and flask measurements. We do not add a more detailed comparison between in situ SMO and FTIR data because SMO is not located in the Reunion Island, so a strict comparison would not be very meaningful as it is the case for studies at super-sites (Jungfraujoch, Izaña) where several instruments are measuring simultaneously. Therefore, our intention was not to validate FTIR individual data with in situ data, but with MIPAS data. The use of the SMO data is concentrated on the comparison of the trends, because MIPAS stopped measurements in 2012 and it was helpful to have a data set that goes up until 2016. Furthermore, it helped us in determining the useful period of the trend (e.g. only 2009-2016 for CFC-12 due to the turnaround in the trend observed with in-situ measurements). However, we give here the in situ seasonal cycles (Fig.c), but we do not include these plots in the manuscript.

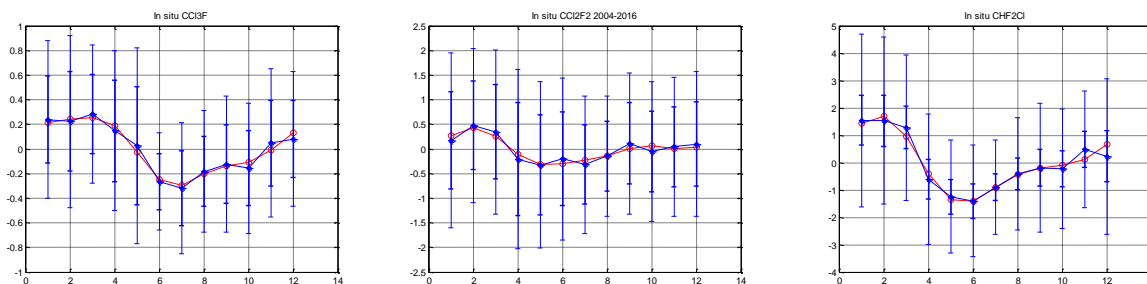


Figure c: Seasonal cycles of CFC-11, CFC-12 and HCFC-22. The modelled seasonal cycle obtained by Eq. 11 for the 2004-2016 SMO time-series is shown in red. In blue, the mean of SMO measurements for each month during the 2004-2016 period, after subtraction of the trend, is shown, together with the standard deviation σ of the mean (thin error bars). The 2σ error on the mean ($2\sigma / \sqrt{n}$; n being the number of measurements for each month) is also shown with thick blue lines.

We follow the referee’s suggestion to add more MIPAS comparisons: the MIPAS seasonal cycles are shown in addition to the FTIR ones in Fig.8 of the new manuscript. And we added the trend analysis from MIPAS data above Reunion Island, and some discussions (see Table 4 and Sect. 3).

2) Unify the FTIR products. The paper presents and discusses four different products for the target gases: total column, partial columns between 2.155-100 km, vertical profiles and partial columns between 6 and 30 km, when the FTIR is only sensitive to one wide layer (typical DOFS about 1 for CFC-11 and HCFC-22, and 1.5 for CFC-12). So, the products will show systematic differences due to the different integration ranges, but the variability observed by them will be the same or very similar.

It is hard to unify the FTIR products in this study. Total columns from St. Denis and Maito show the original FTIR retrievals. The partial column (2.155-100km) extracted from St. Denis FTIR retrievals is applied to combine with Maito data to get a longer term coverage in time series. Since MIPAS data only cover the vertical range above 6km and FTIR retrieval have a little sensitivity above 30 km, partial column (6-30km) is applied to do comparison between FTIR measurements and MIPAS data. Because of the small DOFs when the 6-30 km partial columns are used (about 0.7 for CFC-11 and HCFC-22, and 0.9 for CFC-12), we prefer to keep in addition the combination from St. Denis partial column (2.155-100km) and Maito total column to do the trend analysis so that the most information is used from our measurements.

3) Section 2.2.3. This section only addresses the presentation of the total column time series and no significant results are discussed. Thereby, consider removing it and moving part of the text to other sections. For example, the explanation of the data density could be shown in the section 2.2 (FTIR retrieval), because a quality filter is applied in the spectra or retrievals (I guess the SNR is set in the SFIT retrievals). The authors suggest that this could be due to the fact that the microwindows used for the CFC-11 and HCFC-22 estimation lie in the edge of the spectrum with lower SNR. Have the authors checked if the number of successful retrievals improve for example by reducing the broad microwindows used for CFC-11 (only taking the part with higher SNR) or have they investigated other lines?

We moved the time series part to section 2.

Figure d below shows one typical opus file used for CFC-11 retrieval ($830\text{-}860\text{ cm}^{-1}$). The interferogram indicates that this is a good case. The retrieval window is located at the edge of the spectrum. Since the CFC-11 absorption line is very broad and almost covers the whole retrieval window (see Fig.2 in the paper), it is necessary to keep the wide window ($830\text{-}860\text{ cm}^{-1}$) instead of reducing the broad window. For CFC-11 retrieval window, we follow previous researches, and have not tested other lines yet. However, very few windows are available this specie according to the Meier et al., (2004) and pseudo-line list (<http://mark4sun.jpl.nasa.gov/pseudo.html>).

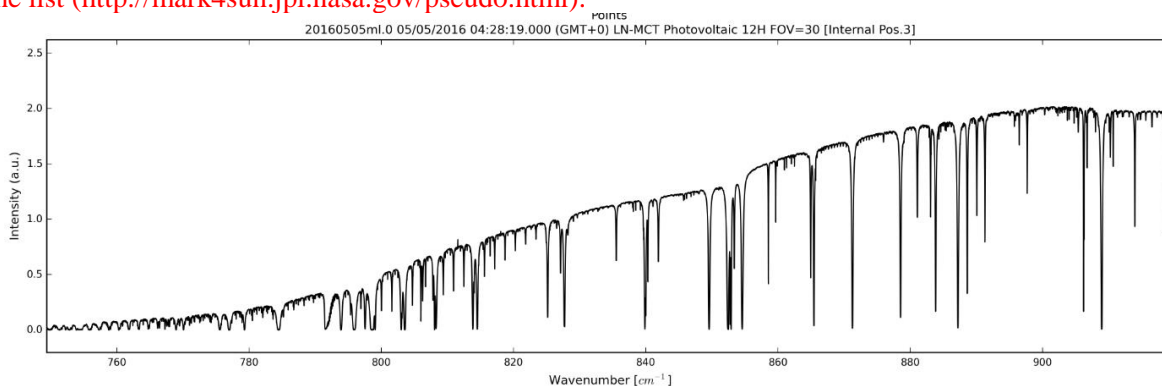


Figure d: One opus file (transmittance).

4) Section 2.2.4: a. Please consider including a more detailed comparison with SMO in-situ and flask data. b. Line 312: For CFC-12 a significant trend change is detected in 2004. Have the authors some idea of reasons of this change? It is natural or an instrumental artefact? According to the Figure 5, this trend change is also observed in the in-situ data, thereby it is likely due to natural variability of CFC-12. To take into account non-linear terms in the trend analysis, a Fourier term could be included in equation 10 to account for inter-annual trend variation (for example, refer to Gomez-Pelaez et al., 2006 and 2010). So,

the trend analysis could be done with the whole time series. c. Line 322: Have the annual cycles for CFC-12 evaluated considering the whole FTIR time series because the linear trend is only estimated from 2009 onwards? Please state. d. Line 330: A significant seasonal variation is only observed for CFC-12, which has a typical DOFS value of 1.5. Thereby, its annual cycle could be capturing the tropopause shift or part of the lower stratosphere information? As mentioned before, it would be interesting to include the annual cycles observed by MIPAS and SMO data to improve the discussion. Also, it would be nice to compare the seasonal patterns of the target gases with some references from literature.

a) A short quantitative comparison has been added. Reason for not including more details in comparisons with in situ data is given above.

b) This trend change is confirmed by in-situ measurements and satellite data (For CFC-11: increasing before 1994 and decreasing after 1994; For CFC-12: increasing before 2004 and decreasing after 2004). It is caused by reducing the CFC emissions after Montreal Protocol. We only have 1 and 4 months of data during 2004 and 2007 campaigns, respectively. We believe that using such limited data to do the non-linear fitting would not provide more reliable results for the post-turnaround trend.

c) The annual cycles for CFC-12 is estimated based on the whole time series, (using Eq. 11 applied to 2004-2016 data for FTIR; 2004-2011 for MIPAS) to enhance the precision on the annual cycle by using all available data. We added this sentence in the text.

d) MIPAS seasonal cycle analysis has been added in the text.

The seasonal cycles of CFC-11, CFC-12 and HCFC-22 at Jungfraujoch also show similar pattern: high concentrations in summer and low in winter (Mahieu et al., 2015).

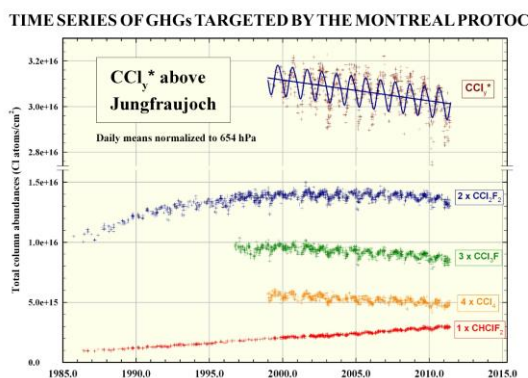


Figure e. Time series of CFC-11, CFC-12, HCFC-22 and CCl4 at Jungfraujoch, extracted from Mahieu et al., (2015)

5) Section 3: a. Line 348: Adding a brief explanation of the MIPAS products (for example, vertical resolution and sensitivity) and the expected uncertainty values will be useful for the comparison section. b. Line 365: As mentioned before, it will be interesting to have information about the vertical sensitivity of the MIPAS profiles, since smoothing the MIPAS profiles does not much sense if FTIR and MIPAS vertical sensitivity are comparable and even it could produce unrealistic results. c. Line 397: Please state if the comparison of the monthly means is for the coincident MIPAS and FTIR database or considering the respective original time series (I guess it is the last option).

a) A brief explanation of MIPAS is added in the text.

b) DOFs of MIPAS data is added in the text.

c) The comparison of the individual collocated MIPAS-FTIR data pairs is applied to evaluate the difference between two data sets (see Table 4 in the paper). The monthly means are calculated from the respective original time series, and the time series of two data sets indicate that they are in a good agreement. The explanation has been added.

Technical Comments

Line 91: State the specific goals of the NDACC network similar to TCCON network.
Added in the text.

Line 173: Figure 2 and Figure 3 are in wrong order.
Corrected.

Line 239: Replace “resp.” by respectively.
Corrected.

Line 245: Replace “uncertaintyis” by “uncertainty is”. Line 246: Do the authors mean “but not in the model parameters uncertainties for CFC-12”?
Yes, corrected.

Line 257: Remove the full stop before “together”.
Corrected.

Line 264: Replace “,” by “.”.
Corrected.

Line 275: Include reference for the in-situ and flask uncertainty.
Included in the text.

Line 287: Correct the reference of Santer et al., (2000).
Corrected.

Line 300, 305, 310: Although the period at which the trends are evaluated are included in Table 4, please include in the text for a better comparison for FTIR measurements at Junfraujoch, and SMO.
Added in the text.

Table 2 Line 589: Consider moving the sentence “When a relative” to the end of the paragraph.
Accepted.

Line 591: Replace “zshiftis” by “zshift is”.
Corrected.

Figure 1: To homogenise the figure formats, please, set the limit of the abscissa axis for CFC-11 to -0.02.
Corrected.

References Gomez-Pelaez, A.J., Ramos, R., Perez-delaPuerta, J., "Methane and carbon dioxide continuous measurements at Izana GAW station (Spain)" in GAW Report (No.168) of the "13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (Boulder, Colorado, USA, 19-22 September 2005)", edited by J.B. Miller, World Meteorological Organization (TD No.1359), 180-184, 2006.
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Gomez-Pelaez, A.J., R. Ramos, E. Cuevas, V. Gomez-Trueba, 25 years of continuous CO₂ and CH₄ measurements at Izaña Global GAW mountain station: annual cycles and interannual trends; Proceedings of the “Symposium on Atmospheric Chemistry and Physics at Mountain Sites (ACP Symposium 2010,

June 8-10, 2010, Interlaken, Switzerland)", 157-159, 2010 http://izana.aemet.es/publications/Abstract_25-year_CO2_and_CH4_Izana.pdf

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Meier, A., Toon, G. C., Rinsland, C. P., Goldman, A., and Hase, F.: Spectroscopic Atlas of Atmospheric Microwindows in the middle Infra-Red, IRF Technical Report 048, ISSN 0284-1738 (Institutet for Rymdfysik, Kiruna, Sweden), Appendix E, 2004