Improved FTIR retrieval strategy for HCFC-22 (CHClF2), comparisons with in situ and satellite datasets with the support of models, and determination of its long-term trend above Jungfraujoch

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Authors' response to Anonymous Referee #1 (https://doi.org/10.5194/acp-2019-73-RC1)

We use blue text for referee's comments and black text for authors' response to these comments.

General Comment

This paper describes an improved HCFC-22 retrieval strategy from ground-based FTIR solar spectra at Jungfraujoch. They showed the possibility to distinguish the tropospheric and lower stratospheric partial columns from the FTIR spectra and compared their results with independent datasets (AGAGE and MIPAS) and models (BASCOE CTM and WACCM). However, there are some issues that should be clarified before this paper is published in ACP, which are described in the comments below.

> Thank you for your comments that will help to improve our manuscript. Here follows our response to your major and technical comments:

Major Comments

1) I have a concern on comparison between AGAGE (MHD and JFJ) data and FTIR mean tropospheric mixing ratio shown in Section 4.3. First of all, the way to calculate mean tropospheric mixing ratio from FTIR data is not described in detail. I think that SFIT-4 retrieval of FTIR spectra gives total column and vertical profiles with averaging kernel information. How the authors derive mean tropospheric mixing ratio from that information? Do they divide tropospheric HCFC-22 column between station altitude and 11.21 km by the amount of air molecule numbers at the same altitude range? Please explain in the text.

> We have modified the beginning of Section 4.3 (Section 4.4 in the modified manuscript) in order to precise how the tropospheric mean mixing ratio series is derived. The SFIT-4 algorithm returns, alongside total and partial columns, the vertical profile of the target species (i.e., HCFC-22) mixing ratios on the fixed 41-layer vertical grid used to model the atmosphere above our site. We then compute the mean mixing ratio for all the layers located between surface and 11.21 km altitude to get our "FTIR mean tropospheric mixing ratio".

2) Annual variations are seen in both derived total columns (Fig. 3) and tropospheric mean VMR (Fig. 4) in FTIR data, both having peaks in summer to fall. Such annual variations are not seen in AGAGE MHD nor JFJ data. However, there are no explanations nor discussion on the cause of the derived annual

variation. I wonder the derived annual variation may come from two reasons: a) The nature of FTIR measurement principle, i.e. measuring column amount above the observational station. The column amount might be affected by the height of tropopause height, which is higher in summer. b) The higher emission of HCFC-22 from the regional summertime use of air-conditioner, as is pointed out by Xiang et al. (2014). Please discuss more about the cause of the retrieved annual variation in FTIR data which are not seen it AGAGE data.

3) The scatter plot in Fig. 4 looks somewhat strange. We see many dots which are horizontally aligned. For example, there are several points for MHD value of ~145, but the next group jumps to >160. However, the actual trend of MHD values look more continuous. Please check if something wrong appeared or not to create this scatter plot.

4) In Section 4.4 (P.8, L.19), the authors claim that they do not show amplitude and phase of the seasonal cycle of tropospheric column series. However, as I mentioned in the above comment, differences in tropospheric annual variations are seen between FTIR retrieval and AGAGE data. I think they should show the figure which shows amplitude and phase of seasonal cycle of tropospheric columns as well, and discuss on the cause of such variation in more detail.

> Referee's comments 2, 3 and 4 are related and therefore addressed together in our response. The significant tropospheric annual cycle seen in our FITR time series is discussed in the original manuscript at the end of the section dealing with the lower stratospheric columns time series (Section 4.4), Page 8 Lines 18-24. Following your comment and those from reviewer #2, we realised that this discussion was not at the most appropriate place in the manuscript. Therefore, we have decided to switch Section 4.3 (troposphere) and Section 4.4 (stratosphere).

As explained in the information content Section (3.3), the main improvement resulting from this work is the determination of two independent times series from our spectra. Since the vertical limit between these two series is at 11.21 km (as indicated by the information content analysis), an altitude close to the mean tropopause height at Jungfraujoch, we assumed that the lower partial column or profile thus defined (from surface up to 11.21 km high) was mostly representative of the troposphere. Moreover, HCFC-22 seems to have no or a weak vertical gradient in the troposphere [see Figure 4 in Chirkov et al. (2016) or Figure 1 in Xiang et al. (2014)].

Nevertheless, the tropopause height varies throughout the year with minimum values in winter and maximum values in summer. Consequently, in winter, our mean mixing ratios should also include layers of low HCFC-22 concentration representative of the stratosphere, inducing this way a seasonal signal. Note that, for the period of comparison used in Section 4.3 (i.e., 1999-2018), the average tropopause height above Jungfraujoch is (11.10 ± 2.61) km [2σ; using the World Meteorological Organization (1957) thermal definition and the National Centers for Environmental Prediction pressure-temperature daily profiles]. We investigated the possible effect of the tropopause annual cycle by

computing tropospheric columns (below 11.21 km) from the HCFC-22 a priori profile used for the inversion (see Section 3.2) shifted up and down by about 2 km (i.e., a value representative of the spread around the mean tropopause height). This vertical shifting induces less than 2% of variation peak-to-peak on the tropospheric partial columns, i.e., less than the 7% peak-to-peak observed in our tropospheric column time series.

Another possible explanation to this tropospheric cycle is discussed by Chirkov et al. (2016). They compared mean upper tropospheric mixing ratios retrieved from MIPAS to surface in situ measurements and also noticed a significant annual cycle in their MIPAS time series, in contrast with the in situ data considered in their paper. They attributed this difference to the fact that their time series was capturing the intrusion of HCFC-22-poor stratospheric air at mid-latitudes Upper Troposphere / Lower Stratosphere (UTLS) at the time of the polar vortex breakdown (early spring).

Concerning now the higher emissions of HCFC-22 during summer from the regional summertime use of air-conditioner (Xiang et al., 2014), they should not be responsible of a strong annual cycle as depicted by our tropospheric time series. Indeed, these authors also stated that these emissions should be balanced by the increase of OH scavenging during summer. As written Page 8 Lines 18-24 of our original manuscript, the seasonal cycle in in situ series is in fact weak in amplitude, with broad maxima in winter and broad minima in summer.

Finally, the layered structure of the scatter plot of Figure 4 is actually caused by the seasonal cycle that is present in the FTIR mean tropospheric mixing ratio series, spreading the FTIR data around the in situ values (see Figure 1c hereafter).

Following the above discussion, we modified the end of the tropospheric Section (4.3) to more elaborate on the seasonal cycle retrieved in our data.

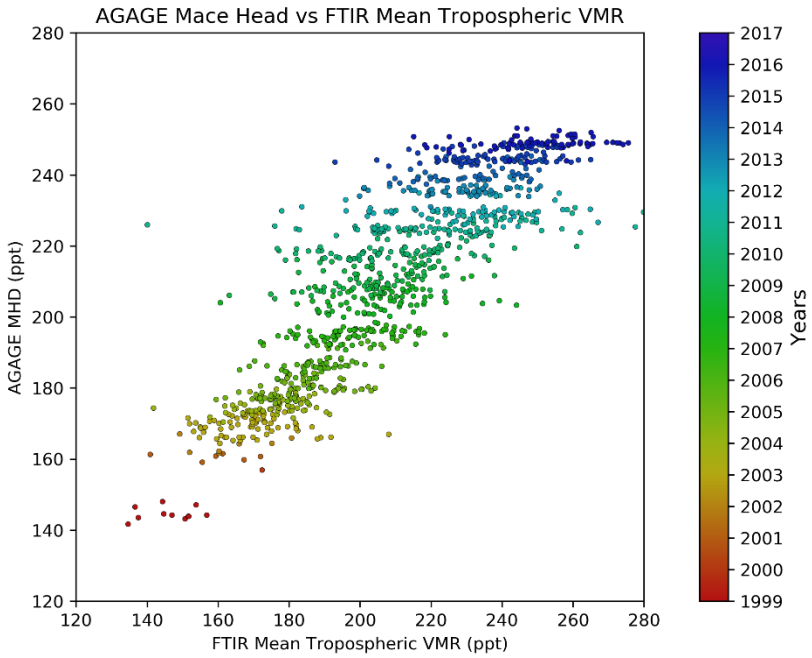

Figure 1c: Daily coincidences between AGAGE Mace Head (MHD) and Jungfraujoch FTIR mean tropospheric VMR time series. Points are coloured according to the year of measurement (see right colour bar).

Minor Comments/Typos

Figure 6: What is the value of the age of air? I think the right hand side axis to show the age of the air is missing.

> The age of air cycle is given in relative values (%). As written in Figure 6's caption, the mean age of air for the considered period is 2.96 year with a peak-to-peak amplitude range of 0.37 year.

P.1, L.33: The global warming potential of HCFC-22 should be 1810 (IPCC AR4) or 1780 (WMO O3 Assessment 2018), not 1760.

> We gave the value of AR5 (Table 8.A.1, Page 731 of IPCC, 2013)

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