Appendix A, Calculating tropospheric column-averaged CH_4 mole fractions from total column-averaged CH_4 mole fractions using HF total column amounts as tropopause altitude proxy:

Similar to Washenfelder et al. (2003) we calculate the tropospheric column-averaged CH_4 mole fractions ($troXCH4_{post}$) from the CH_4 total column after correcting the variation in both surface pressure and stratospheric contribution (equation A1).

$$troXCH4_{post} = \frac{CH4_{col} - b \cdot HF_{col}}{DPC} \qquad \text{(A1)}$$

being,

$troXCH4_{post}$: The a posteriori corrected tropospheric CH_4 column-averaged.

$CH4_{col}$: The CH_4 total column-averaged volume mixing ratio (VMR) retrieved from the FTIR.

b: The stratospheric slope equilibrium relationship between the CH_4 and HF columns.

HF_{col}: The HF total column-averaged VMR from the FTIR.

DPC: The dry pressure column.

Due to industrial activities HF increases continuously. This anthropogenic increase has to be removed when applying Eq. (A1). Therefore, we fit the following function to the HF time series:

$$f(t) = a_1 + a_2 t + \sum_{j=1}^{2} \left[d_j \cos(k_j t) + e_j \sin(k_j t) \right] \qquad \text{(A2)}$$

Where t is the time in days; a_1 is a constant value, a_2 is the parameter of the linear trend (d_j and e_j are the parameters that account for the annual cycle; $k_j=2\pi j/T$; T=365.25 days).

Subtracting a_2t from the HF time series yields the de-trended HF time series. Dividing the HF time series by the term (a_1+a_2t) yields the normalised HF time series. Both the de-trended and normalised HF time series keep the variability caused by changes of the tropopause altitude (as long as there is no linear trend in the tropopause altitude), but are not affected by the anthropogenic HF increase.

The CH_4-HF slope equilibrium (b-value) is calculated applying three different approaches: a) as Washenfelder et al. (2003) from the stratospheric CH_4 and HF VMR, b) from the CH_4 and HF total columns and c) fitting Eq. (A1) but substituting the $troXCH4_{post}$ for $CH4_{GAW}$. For approaches a) and b) we determine the b-value applying different datasets. We use model data (a CH4 climatology for the 2004-2006 period from WACCM, and an HF climatology for the mid 2000s from KASIMA) as well as experimental data (a 2004-2008 climatology of CH4 and HF profiles and for the latitude 25N – 35N from the ACE-FTS satellite experiment; A. Jones et al., 2011). The three approaches give different b-values. The scatter between the different b-values can be used as the b-values uncertainty.

a) The b-value is determined by calculating the regression line between the stratospheric CH_4 and HF VMR profiles obtained from the ACE-FTS measurements between the 10 and 100 hPa. We also determine a b-value from the modelled VMR profiles. The CH4-HF correlation plots are depicted in Fig. A1. We calculate the correlations for the 10 to 100 hPa levels in agreement to Washenfelder et al. (2003), but in difference to Washenfelder et al. (2003) we only determine one single b-value. Actually the b-value changes with the increase of HF amounts by about 1% per year. Consequently, using a single b-value representative for the 2004-2006/08 time period for the whole time series (2001-2010) means an uncertainty of the b-value of up to 5%. We obtain values of -679 and -743 for models and ACE-FTS profiles, respectively. For comparison Washenfelder et al., (2003) estimated a b-value for 1992 of about -950, which is in reasonable agreement with our b-values obtained for the mid 2000s.

In addition we calculate a b-value from a normalized HF-profile. The normalization means that the VMR values have been divided by the HF total column amounts. This b-value can then be applied in Eq. (A1) together with the normalized HF time series. The normalization allows using a b-value that is constant over time. We get values of -7.741e21/(molec/m^2) and -7.036e21/(molec/m^2) for models and ACE-FTS, respectively.

b) As can be seen in Fig. A1 between 10 and 100 hPa the correlation is not perfectly linear. In particular for the models profiles assuming a linear correlation might cause an erroneous b-value. Therefore, we test an additional approach that determines the b-value from correlating CH_4 and HF total column amounts. The column amounts are calculated from profiles that are shifted vertically (between -30 hPa and +30 hPa; see Fig. A2). Figures A3 and A4 plot the correlations using models profiles and ACE-FTS profiles, respectively. We get b-values of -901 and -689 for models and ACE-FTS, respectively. For normalized profiles we get -1.027e22/(molec/m^2) and -6.529e21/(molec/m^2) for models and ACE-FTS, respectively.

c) Finally, we calculate an empirical b-value determined by fitting all the high quality data that are available at the Izaña Observatory: the FTIR CH_4 total column amounts determined from the profiling retrieval, the FTIR HF total column amounts, and the $CH4_{GAW}$ data.

$$CH4_{col}(t) = k \cdot \left(DPC(t) \cdot CH4_{GAW}(t)\right) + b \cdot HF_{col}(t) \quad \text{(A3)}$$

The parameters b and k are obtained by least squares fit. The so-obtained b-value is the "best possible b-value". Applying this b-value in Eq. (A1) produces a $troXCH4_{post}$ with the best possible correlation to $CH4_{GAW}$. This empirical value represents the best correction that is possible with the "HF-procedure". We get a b-value of -1368 (-1.522e22/(molec/m^2) for normalized HF).

According to Eq. (A1) we calculate $troXCH4_{post}$ for the different b-values, considering the de-trended and normalized HF time series, and for CH_4 total columns obtained from the scaling retrieval. Tables A1 and A2 document the agreement between $troXCH4_{post}$ and $CH4_{GAW}$. We want to remark that the agreement between the $troXCH4_{post}$ and $CH4_{GAW}$ does only slightly depend on the applied b-value. The correlation factor (R) and the standard deviation (STD) is roughly the same for the different b-values. Even for our empirical ("best possible b-value") we get an agreement which is significantly poorer that the agreement between the directly retrieved tropospheric column-averaged CH_4 and $CH4_{GAW}$.

On the other hand the agreement strongly depends on the quality of the applied CH_4 total column data. This is documented by Tables A3 and A4, which show the same as Tables A1 and A2 but using the CH_4 total column amounts obtained from the profile retrieval. These total column amounts are of higher quality than the CH_4 total column amounts obtained from the scaling retrieval (see error estimation section of the manuscript). We conclude that in the middle infrared, the leading error source of the "HF-procedure" is the uncertainty of the applied $CH4_{col}$ and not the uncertainty of the b-value.

Reference:

Jones A., Walker K. A., Jin J. J., Taylor J. R., Boone C. D., Bernath P. F., Brohede S., Manney G. L., McLeod S., Hughes R., and Daffer W. H.: Technical Note: A trace gas climatology derived from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer dataset, Atmos. Chem. Phys. Discuss., 11, 29845–29882, 2011.

Table A1: $troCH4_{post}$ calculated from $CH4_{col}$ of the scaling retrieval.

		$troXCH4_{post}$ vs $CH4_{GAW}$			
applied method to calculated b	b-value	R	MRD (%)	STD (%)	SF
correlation of modelled VMRs (10 to 100 hPa)	-679	0.203	-2.24	1.26	0.9776
correlation of modelled columns (shifts: -30 to +30 hPa)	-901	0.247	-1.45	1.21	0.9855
correlation of ACE VMRs (10 to 100 hPa)	-743	0.216	-2.01	1.24	0.9799
correlation of ACE columns (shifts: -30 to +30 hPa)	-689	0.205	-2.21	1.25	0.9780
fit: $CH4_{GAW}$, $CH4_{FTIR}$, HF_{FTIR}	-1368	0.344	0.21	1.12	1.0021

Table A2: Same as Table A1 but for normalized HF time series.

		troXCH4$_{post}$ vs CH4$_{GAW}$			
applied method to calculated b	b-value [(molec./m^2)$^{-1}$]	R	MRD (%)	STD (%)	SF
correlation of modelled VMRs (10 to 100 hPa)	-7.741E21	0.205	-2.04	1.25	0.9796
correlation of modelled columns (shifts: -30 to +30 hPa)	-1.027E22	0.249	-1.19	1.21	0.9881
correlation of ACE VMRs (10 to 100 hPa)	-7.036E21	0.193	-2.28	1.27	0.9772
correlation of ACE columns (shifts: -30 to +30 hPa)	-6.529E21	0.185	-2.45	1.28	0.9755
fit: CH4$_{GAW}$, CH4$_{FTIR}$, HF$_{FTIRnorm}$	-1.522E22	0.341	0.48	1.13	1.0048

Table A3: Same as Table A1 but for $CH4_{col}$ from profiling retrieval.

		troXCH4$_{post}$ vs CH4$_{GAW}$			
applied method to calculated b	b-value	R	MRD (%)	STD (%)	SF
correlation of modelled VMRs (10 to 100 hPa)	-679	0.509	-1.45	0.98	0.9855
correlation of modelled columns (shifts: -30 to +30 hPa)	-901	0.541	-0.67	0.96	0.9933
correlation of ACE VMRs (10 to 100 hPa)	-743	0.519	-1.23	0.97	0.9877
correlation of ACE columns (shifts: -30 to +30 hPa)	-689	0.510	-1.42	0.98	0.9858
fit: CH4$_{GAW}$, CH4$_{FTIR}$, HF$_{FTIR}$	-1368	0.582	0.99	0.94	1.0099

Table A4: Same as Table A3 but for normalized HF time series.

applied method to calculated b	b-value [(molec./m^2)$^{-1}$]	troXCH4$_{post}$ vs CH4$_{GAW}$ R	MRD (%)	STD (%)	SF
correlation of modelled VMRs (10 to 100 hPa)	-7.741E21	0.510	-1.26	0.98	0.9874
correlation of modelled columns (shifts: -30 to +30 hPa)	-1.027E22	0.542	-0.41	0.96	0.9960
correlation of ACE VMRs (10 to 100 hPa)	-7.036E21	0.499	-1.50	0.99	0.9851
correlation of ACE columns (shifts: -30 to +30 hPa)	-6.529E21	0.492	-1.67	0.99	0.9833
fit: CH4$_{GAW}$, CH4$_{FTIR}$, HF$_{FTIRnorm}$	-1.522E22	0.580	1.27	0.94	1.0130

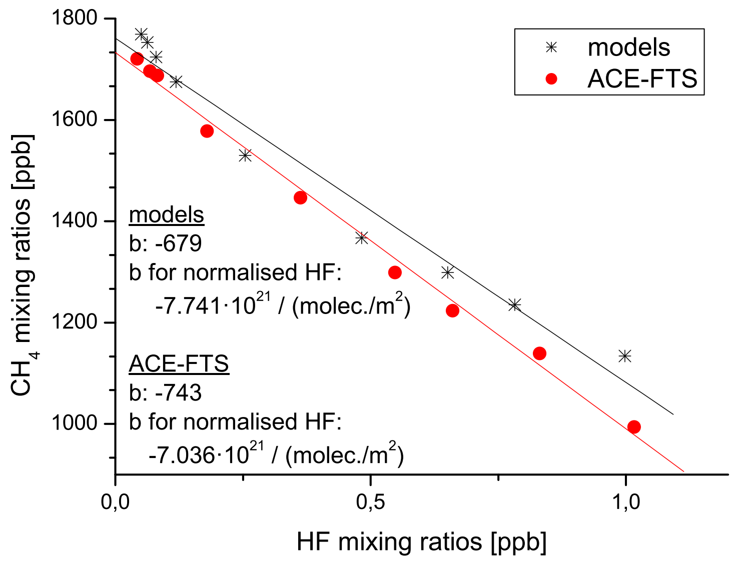

Figure A1: HF volume mixing ratio versus CH_4 volume mixing ratio between the levels 10 and 100 hPa. The solid lines represent the regression line for models (black line) and ACE-FTS (red line). The b-values are also shown for the normalized HF profiles.

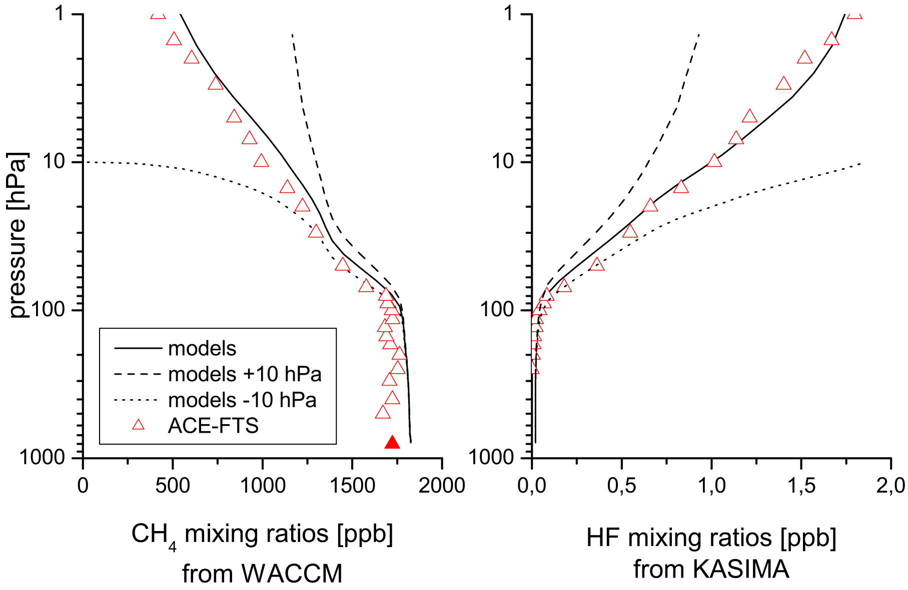

Figure A2: Solid lines correspond to the modelled profiles for CH_4 (left panel) and HF (right panel). Dotted and dashed lines show the models mixing ratios for -10 hPa and +10 hPa vertical profile shifts, respectively. Red open triangles show the ACE-FTS mixing ratios (the red filled triangle is the CH_4 concentration that we use for the lower troposphere, where ACE-FTS is not sensitive anymore).

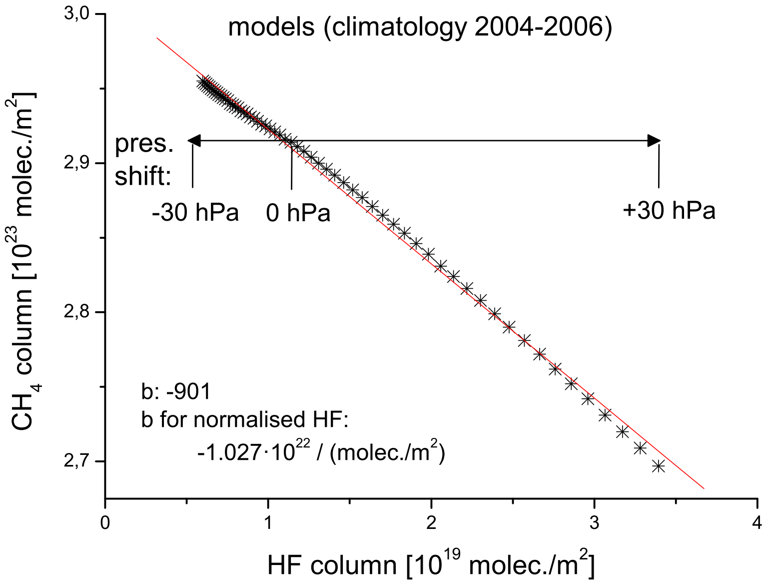

Figure A3: Correlation plot between the CH_4 and HF total column amounts obtained for different vertical shifts of the CH_4 and HF models profiles.

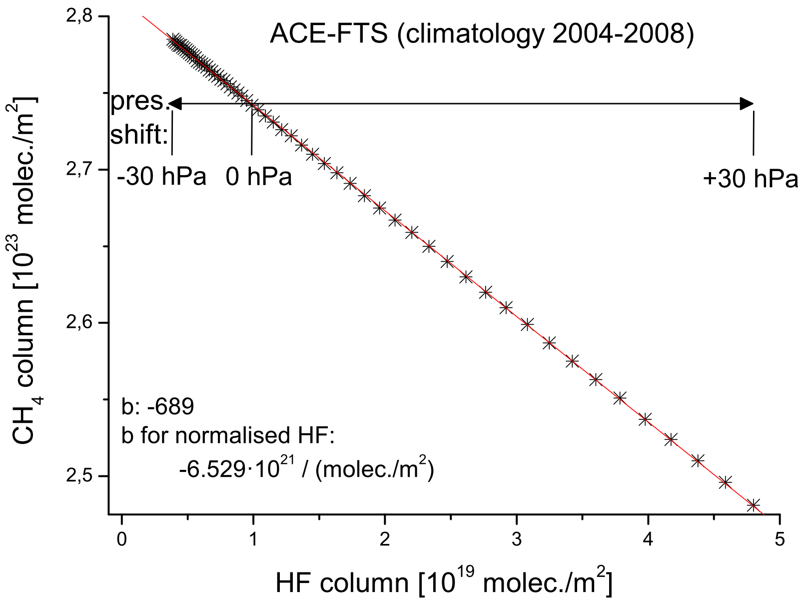

Figure A4: Same as Fig. A3 but for ACE-FTS profiles.