Interactive comment on "Diurnal cycle and multi-decadal trend of formaldehyde in the remote atmosphere near 46 N" by B. Franco et al.

Anonymous Referee #1

Received and published: 22 December 2015

We thank Referee#1 for his/her review and the constructive comments. Please find below our responses written in blue.

This paper presents a multi-decadal time series (01/1988-06/2015) of HCHO total columns retrieved from ground-based high-resolution Fourier transform infrared (FTIR) solar spectra recorded at the high-altitude station of Jungfraujoch (Swiss Alps, 46.5°N, 8.0°E, 3580 m a.s.l.). The HCHO diurnal cycle is first investigated and quantitatively characterized by fitting a parametric model to the observations. A maximum of HCHO is found around noontime and is attributed to the modulation of insolation during daytime and its impact on methane oxidation. Retrieved HCHO columns are then compared to simulations from the 3D-CTM GEOS-Chem and a trend analysis over a 27-year period is performed. All the individual FTIR measurements are scaled beforehand to a fixed local time using the parametric model in order to remove the effects of the intra-day modulation on both comparison and trend results. Sensitivity tests with GEOS-Chem suggest that the atmospheric CH4 oxidation is the main driver of the seasonal and inter-annual HCHO column variations at Jungfraujoch. The observed trend, with an increase between 1988 and 1995, followed by a decrease between 1996 and 2002, and again an increase from 2003 onwards, is seen to be related to the atmospheric CH4 fluctuations and the short-term OH variability.

This paper is well written and presents very interesting results which fit well with the scope of ACP. I recommend the final publication of the manuscript after addressing the following comments:

Specific comments:

Page 31295, lines 1-4: Ground-based FTIR retrievals with DOFS lower than 0.35 have been discarded from the study. Using a DOFS threshold value lower than 0.5 means that retrievals for which the information content comes mainly from the a priori (DOFS between 0.35 and 0.5 in the present case) and not from measurements are also selected for the study. Figure 2a shows that around local noon the DOFS is very low (<0.5), especially for the summer months. The question is therefore: how the choice of the a priori affects the amplitude of the intra-day variations derived for the different months of the year? Should we expect larger or lower amplitude when using an a priori profile having higher or lower concentration (and therefore column) values than for the a priori chosen in this study? Sensitivity tests are needed here in order to investigate this issue.

The Referee raises an interesting point. We performed sensitivity tests by alternatively adopting two realistic a priori profiles encompassing the WACCM distribution we used. These profiles, presented in the figure here below (S1), are derived from nearly 2000 ACE-FTS solar occultation measurements (version 3.5) between 36.5 and 56.5° N and from a 2005.5 – 2013.5 simulation with GEOS-Chem v9-02 (standard full chemistry simulation), respectively. The entire BRUKER time series has been refitted and for both new time series, the monthly intra-day variations of HCHO column was re-evaluated using our parametric model. We found that the amplitude of the modelled diurnal cycle is lower/higher when

adopting a lower/higher a priori profile. Consistent with the lower DOFS values around noontime, the bias to the WACCM-based diurnal cycles is higher for the summer months and reaches a maximum during the 12-14h (UTC+1) time range (see figure S2 here below): in between this time range, the maximum systematic bias is ±3.6% in January and ±10.2% in July. We propose now to discuss this issue in the manuscript as follows, and to add both figures as Figs. S1 and S2 in the Supplement to support the discussion.

Page 6, lines 527-545: "Given the lower DOFS values characterizing the retrievals performed around mid-day, especially in summer (see Fig. 2a), the a priori profile adopted for the retrievals will have an impact on the HCHO total columns obtained from such observations. The a priori profile used in Franco et al. (2015b) for the HCHO retrieval is derived from WACCM v6 (Whole Atmosphere Community Climate Model; see e.g., Chang et al., 2008) simulations above ISSJ over the 1980-2020 period. According to sensitivity tests adopting either a lower or a higher realistic a priori profile (i.e. derived from ACE-FTS occultation measurements and GEOS-Chem simulations; see Fig. S1 in the Supplement), the diurnal cycle fitted by the parametric model will show somewhat lower or larger amplitude, respectively (see Fig. S2). We gauge at ±10% the maximum systematic uncertainty that can affect the fit of the HCHO intra-day variations due to the choice of the a priori profile. Such maximum uncertainty is reached around noontime for the summer months only, and as such can be considered as highly conservative."

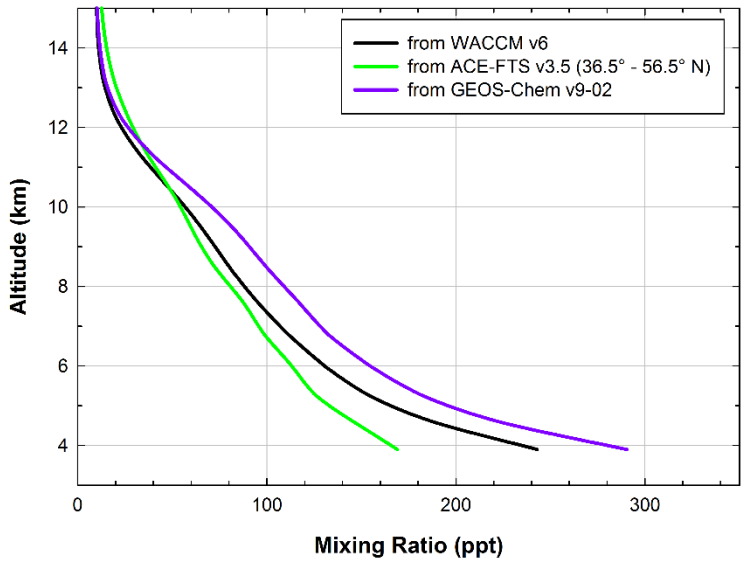


Figure S1. A priori profiles of HCHO over the ISSJ derived from 1980 – 2020 WACCM v.6 simulations (in black), from nearly 2000 ACE-FTS solar occultation measurements (version 3.5) between 36.5 and 56.5° N (in green) and from a 2005.5 – 2013.5 simulation with GEOS-Chem v9-02 (in purple). The WACCM profile is used for the standard HCHO retrievals at the ISSJ, while the ACE-FTS and GEOS-Chem profiles are used for sensitivity tests (see text).

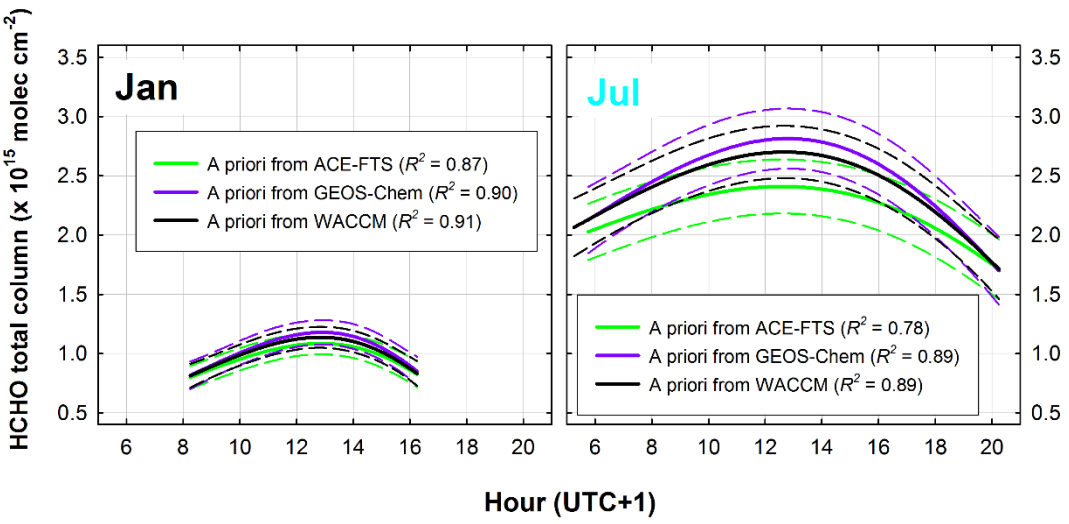


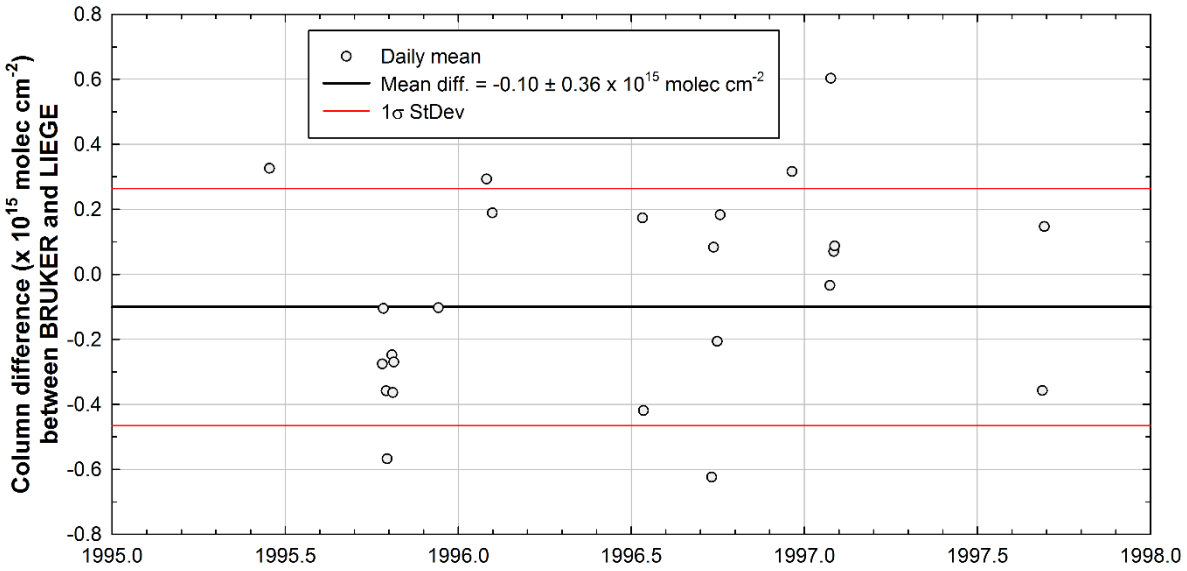
Figure S2. Same as Fig. 1, but according to sensitivity tests adopting either a lower (in green) or a higher (in purple) realistic a priori profile than WACCM (used in Franco et al., 2015b; in black) to retrieve the entire BRUKER time series of HCHO total columns. These profiles are presented in Fig. S1. For both new time series, we re-fitted the monthly intra-day variations of HCHO column using our parametric model (see Eq. 1). We found that the amplitude of the fitted diurnal cycle is lower or higher according to the adoption of a lower or higher a priori profile, respectively. Consistent with the lower DOFS values around noontime, the bias to the WACCM-based diurnal cycles is higher for the summer months and reaches a maximum during the 12-14h (UTC+1) time range: in between this time range, the maximum systematic bias is ±3.6% in January and ±10.2% in July.

Page 31305-6, Section 5.1: In addition to the correlation coefficient, the authors should also provide the slope and intercept values corresponding to the scatterplot presented in Figure 6. This Figure shows that the intercept is about 0.3E15 molec/cm2, which is quite higher than 0. Can a possible bias between the LIEGE and BRUCKER data sets be fitted by the bootstrap method? If yes, the authors should try to include it in their trend analysis and check whether the inferred bias value is indeed not significant.

We now provide the slope (0.784) and intercept (0.284 x 10^{15}) values of the linear regression in Fig. 6.

We compared the BRUKER and LIEGE data sets on the basis of solar spectra recorded on the same days, in terms of difference between the total column daily means considering individual measurements separated by maximum 1 hour (see the figure hereafter). The BRUKER and LIEGE data sets do not show a significant systematic bias. We added the following sentence in the manuscript:

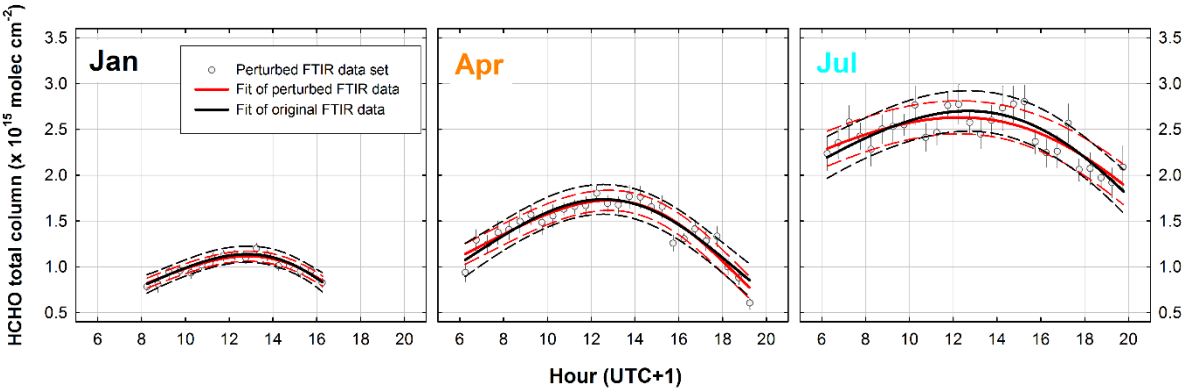
Page 8, lines 733-734: *"…(corresponding globally to measurements performed during winter and summer). Moreover, the mean difference between the BRUKER and LIEGE daily means is -0.10 ± 0.36 x 10^{15} molec cm^{-2}. Given the good consistency and absence of significant bias…"*



Page 31311, last paragraph of the conclusions: the parametric model developed in this study could be potentially used in satellite validation efforts for the conversion of the FTIR HCHO columns to the satellite overpass times. What would be the uncertainties related to this scaling? I think this should be discussed in the paper.

We agree with the Referee. Nevertheless, such uncertainties are difficult to estimate. We performed preliminary investigations to evaluate the uncertainties related to the scaling itself, using a perturbation approach. First we introduced a random perturbation to our BRUKER data sets, i.e. using the monthly diurnal cycles fitted by the parametric model, we re-scaled all the individual measurements onto hours randomly generated (inside the actual time range of measurements). Then we re-fitted the perturbed intra-day variations of HCHO with the parametric model and eventually calculated for each month the difference between the new and the original fits of the HCHO diurnal cycles. Three examples are presented below for January, April and July: the averaged absolute differences are 1.1, 1.7 and 2.2%, respectively. As these first estimates are far below the random error associated with the retrieval of the HCHO total columns (21%; see Franco et al., 2015) and since we will need more time to refine the evaluation of this uncertainty, we propose to add the following sentence in the Conclusion section.

Page 10, lines 968-973: "*…at mid-latitude of the Northern Hemisphere. In the future, it will be useful to evaluate the uncertainty associated with the scaling of the FTIR columns via the parametric model. However, we anticipate that it will be far below the random error inherent to the retrieval of individual HCHO total columns (21%; see Franco et al., 2015). The parameters of the fitting model are made available…*"



Comparisons for January, April and July between the fits of the HCHO intra-day variations from the original BRUKER data set (in black) and from a perturbed data set (in red). This latter has been produced by re-scaling all the individual measurements from the original BRUKER data set onto new hours randomly generated inside the actual time range of observations, using the monthly diurnal cycles fitted in this study by the parametric model. Based in the perturbed data set, new fits of the HCHO intra-day variations have been performed. The averaged absolute differences between the perturbed and original monthly fits are 1.1% (January), 1.7% (April) and 2.2% (July).

Page 31331, Figure 5d: The monthly total carbon emissions are given for a large domain over Europe (between 38-86°N and -15-55°E). Does this domain representative of the Jungfraujoch region? Do emission data exist for a smaller domain closer to Jungfraujoch and to the resolution of the GEOS-Chem model (2°x2.5°)? If yes, are the evolutions of the anthropogenic, biogenic, and pyrogenic carbon emissions similar to the ones presented in Figure 5d?

Due to the very large suite of VOC precursors of HCHO with relatively long lifetime (e.g., ethane with 2 months of lifetime), we do not think relevant to narrow the domain of emissions closer to Jungfraujoch. Indeed, Dils et al. (2011) showed with backward trajectory simulations that the typical source regions of emissions impacting the Jungfraujoch encompass Central and Western Europe and extend over North America in between 30° and 60° N. Therefore we propose here to base the emission domain considered in Fig. 5d on the findings reported by Dils et al. (2011). Please find hereafter the new Fig. 5d. In the framework of this study, the conclusions from this analysis are the same as previously. We now justify the use of this domain as follows:

Pages 7-8, lines 699-707: "*However, the wintertime total carbon emissions of anthropogenic origin as implemented into GEOS-Chem from the inventories, are approximately constant throughout the entire July 2005 - May 2013 time range (~5 Tg C month^{-1}; Fig. 5d) when integrated over the source regions of emissions impacting the ISSJ. According to Dils et al. (2011), this domain encompasses Central and Western Europe, as well as North American mid-latitudes (i.e. between 30 – 60° N and -130 – 35° E). Hence this suggests…*"

Technical corrections:

Page 31290, lines 21-22: Since MAXDOAS HCHO retrievals are also presented in Vigouroux et al. (2009), I would include this paper in the list here.

Page 2, lines 111-112: Done.

Page 31300, lines 3-5: A reference for the Weibull probability distribution should be provided here.

Page 5, line 486: Done.

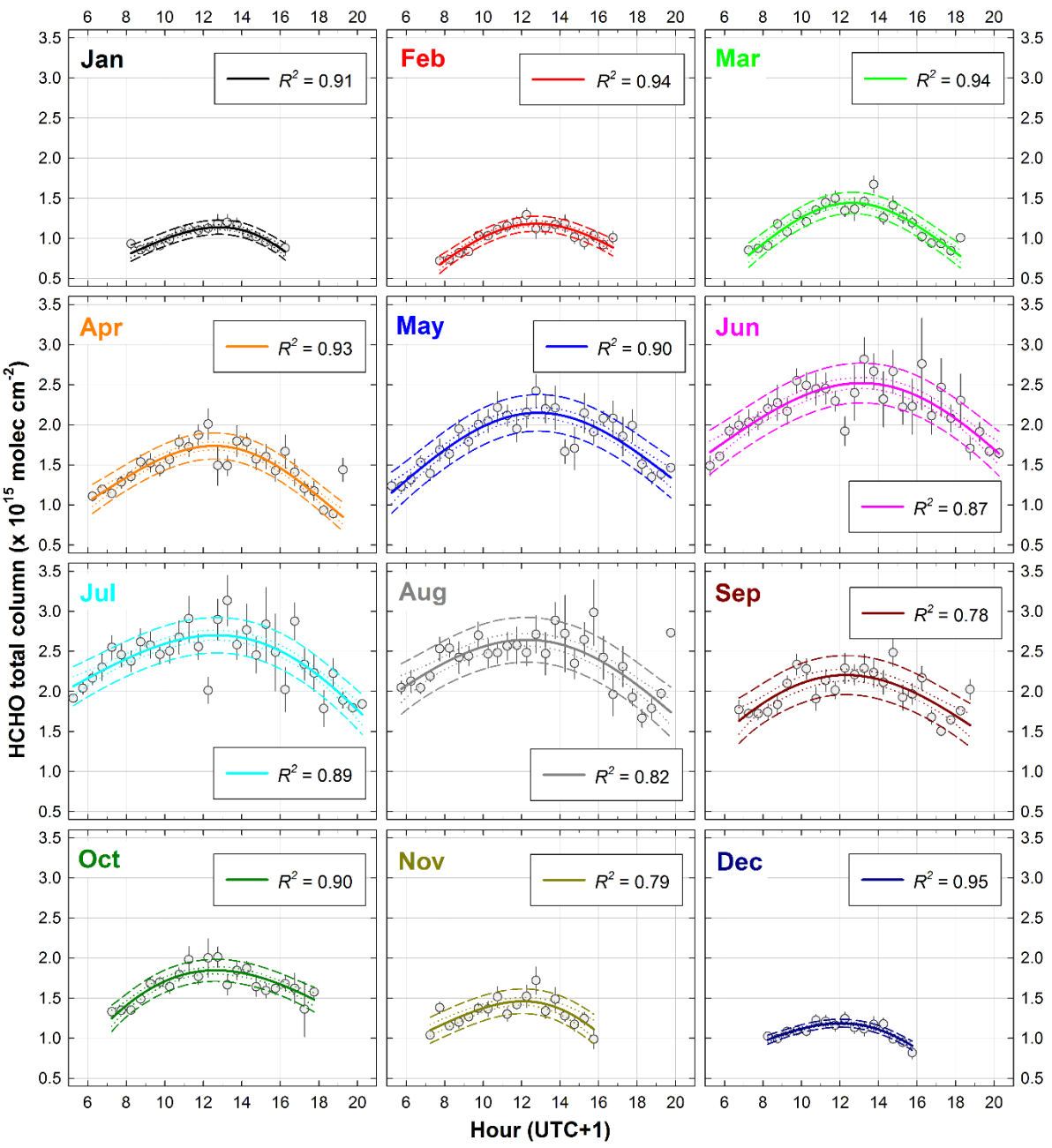
Weibull, W.: A statistical distribution function of wide applicability, J. Appl. Mech.-Trans. ASME, 18(3), 293-297, 1951.

Page 31327, Figure 1: Is there a geophysical reason behind the choice of the different months in the four plots (e.g., Jun/Apr/Dec in plot 1a, Feb/Aug/Oct in plot 1b, etc) or is it only for the sake of clarity? Maybe plotting separately each month in a different plot, i.e. having Figure 1 composed of 4 x 3 plots (first line: plots for Jan, Feb, Mar; second line: plots for Apr, May, Jun;… fourth line: plots for Oct, Nov, Dec), would be preferable since the seasonal variation would then appear more clearly and Figure S1 would not be necessary. I would like also to mention the fact that Figure S1 is not easy to read since the attribution of the different curves to the different months is not easy and straightforward due to the 3D perspective.

We agree with the Referee. We now provide Fig. 1 as a 12-frame figure (4 x 3 plots), plotting each month separately for clarity purpose (please find this new figure here below). We also removed Fig. S1 from the Supplement as it is not needed anymore.

References:

Vigouroux, C., F. Hendrick, T. Stavrakou, B. Dils, I. De Smedt, C. Hermans, A. Merlaud, F. Scolas, C. Senten, G. Vanhaelewyn, S. Fally, M. Carleer, J.-M. Metzger, J.-F. Müller, M. Van Roozendael, and M. De Mazière, Ground-based FTIR and MAX-DOAS observations of formaldehyde at Réunion Island and comparisons with satellite and model data, Atmospheric Chemistry and Physics, 9, 9523-9544, 2009.


Jan
R^2 = 0.91
Feb
R^2 = 0.94
Mar
R^2 = 0.94
Apr
R^2 = 0.93
May
R^2 = 0.90
Jun
R^2 = 0.87
Jul
R^2 = 0.89
Aug
R^2 = 0.82
Sep
R^2 = 0.78
Oct
R^2 = 0.90
Nov
R^2 = 0.79
Dec
R^2 = 0.95
HCHO total column (x 10^{15} molec cm^{-2})
Hour (UTC+1)