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Atmospheric Measurement Techniques Discussions

Interactive comment on "Derivation of tropospheric methane from TCCON CH₄ and HF total column observations" *by* K. M. Saad et al.

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We thank Anonymous Referee #1 for his/her comments.

Specific Comments

1) Abstract: Add in the abstract the precision (in %) of the derived tropospheric CH4 columns.

Because the precision of the tropospheric CH_4 DMFs can vary from site to site, it is not possible to summarize in a single number the precision in the abstract. (Mean and median precisions vary from 0.04-1% and 0.002-0.03%, respectively, at each site.) However, we have added a section in which the uncertainty is explained more explicitly, and the mean and median precisions across sites (0.4% and 0.01%, respectively) are stated in that section.

2) Introduction: the TCCON and NDACC strengths/weakness are discussed here. It would be interesting to add the NDACC precision on tropospheric CH4 (if the authors could find any reference(s)), to be compared with the one achieved with their methodology.

The estimated precision of 0.5% and systematic error of 2.5% for daily mean values of tropospheric CH_4 that Sepúlveda et al. (2014) derive from NDACC measurements has been included in the introduction.

p. 3476, l. 7-9: The sentence "Several TCCON stations are near in situ sites,..." would be better in the Introduction part where the description of the paper should be given. (the validation is made in Sect. 3 not 2.)

This sentence was moved to the introduction.

p. 3478, l.3-7: A qualitative description of the tropospheric error is given. The precision achieved with the methodology described by the authors is an important result, therefore I would give more details here: values (or range of values) of errors propagating in Eq. 6 (total column errors, summary of β error values – even if these one are given in details later,...). The authors include "only those measurements with final errors of less than 1%". This does not give the information of the mean (or median and/or range) error achieved. Which proportion of the measurements have to be removed because

they have an error more than 1%,...

An additional section was added to explain the calculation of uncertainties in the data (Section 2.1). Uncertainties vary from site to site due to differences in tropopause height, water interference and characterization of β for a given year and latitude. About 98% of the data over all sites and years fall within a 1% error (about 950,000 out of 970,000 individual measurements included in this analysis). The number of measurements above this threshold varies across sites, only about 0.2% of the tropospheric CH_4 DMFs had an uncertainty of 100 ppb or higher. (The mean and median tropospheric CH_4 precisions are 0.4% and 0.01%, respectively, across all sites and years, and these values have been included in the added section.)

The figures include daily medians for days with more than 10 measurements that have uncertainties of less than 1% in order to illustrate how the total and tropospheric DMF standard deviations compare over time; however, individual measurements with errors higher than 1% will be included in the final dataset. Because the figure caption clearly states how this filter was applied, the sentence on p. 3478, line 7 has been removed to avoid confusion.

Sorry, I might have missed something, but I do not see the difference in the so-called β in Fig.1 and in Table 1, except that for Fig. 1 the period is 2004-2012, while Table 1 (and inset of Fig.2) shows annual values of β. Therefore I do not understand why the values of β in Fig.1 are larger than the means of annual values given in Table 1. This difference should be clarify. Maybe a different "label β" should be given in both cases.

The slopes in Figure 1 are derived from linear regressions of the ACE-FTS measurements and are included to illustrate the CH_4-HF relationship in the stratosphere. The annual, zonal values of β in Table 1 are the actual values used in the derivation of the tropospheric dry-air mole fractions (DMFs). To be consistent with the pressure-weighted column-averaged TCCON measurements, the values of β used for the tropo-

spheric CH_4 derivation are determined using a pressure-weighted regression so that upper stratosphere data points do not dominate the determination of β. The parenthetical β has been removed from Figure 1, and a sentence has been added noting the altitude-dependence of the CH_4-HF relationship.

Any idea about what happened in 2011 in the Southern Hemisphere (inset of Fig.2)?

The CH_4-HF slopes in February 2011 is anomalously steep compared to the same month in other years. HF daily median DMFs at Southern mid-latitude TCCON sites decrease in January and February 2011, and HF levels over the whole year are somewhat lower than previous and subsequent years. We do not have an explanation for this behavior. While there is a data gap in the ACE-FTS measurements October-December of 2011, those months tend to have steeper β values in the SH during those months, so we do not believe that has contributed to the anomaly.

p. 3479, l.26-27: provide the minimum retrieval altitude (mean, median or range) of ACE-FTS profiles, please.

Minimum and median minimum retrieval altitudes (5.5 km and 9.5 km, respectively) for the method validation are now included. Additionally, occultations for which the lowest HF values are more than 10 km above the tropopause are no longer included in the method validation, as these profiles contained mostly interpolated values and therefore were less indicative of actual stratospheric conditions.

p. 3480, l.14-17: "The underestimation... in NH.. is a result of the lack of secular trend in the TCCON a priori HF profiles". I'm not sure I understand well the justification. Would this lack of trend in the HF a priori not impact the slope (calculated vs integrated) rather than the offset ? Could you clarify your statement, please ? Also, maybe these offsets (Fig. 3) could be quantified, in order to help for the discussion of the validation

results (p. 3482, l. 22-25).

TCCON priors were recently updated, and the new priors are used for the method validation. This change did not alter the inter-hemispheric offset, so we no longer believe this explains the offset. We do not think that inter-hemispheric biases in β determined from ACE-FTS is the reason for the observed bias, as the low sensitivity of the tropospheric CH_4 calculation to changes in β requires the bias in β to be very large in order to explain the offset. Further analysis indicates that the underestimation of tropospheric CH_4 in the Northern Hemisphere and overestimation in the Southern Hemisphere is likely a result of several assumptions that are necessary because coincident TCCON measurements do not exist for all zonal regions over the time series. TCCON averaging kernels are highly dependent on the solar zenith angle and surface pressure at the time of measurement; however, the solar zenith angles (SZA) at the ground during ACE-FTS occultations are close to 90, and the surface pressure is unknown. To address the latter, we assume that the pressure at the lowest point in the ACE-FTS profile is the surface pressure. In Fig. 3, we use the SZA calculated at the latitude, longitude and time of the occultation, which, while accurate, does not test one of the main advantages of this methodology, which is to adjust the tropospheric CH_4 calculation for seasonality and latitude (which changes the SZA). The CH_4 averaging kernel is less than 1 lower than about 500 hPa for SZAs less than 60and greater than 1 for large SZAs, and this relationship reverses in the stratosphere. The CH_4 averaging kernel is applied primarily in the troposphere for the integrated column (x-axis in Fig. 3), and the calculated tropospheric CH_4 column (y-axis in Fig. 3) applies the CH_4 averaging kernel to the a priori and "true" HF profiles, which are zero in the troposphere. Thus, the method validation is limited by the fact that we must either assume a constant SZA for all profiles, or estimate the SZA for the location and day at the same local time for each occultation. The latter approach reduces the zonal bias but depends heavily on the time of day chosen, so we use the SZA at the time of the occultation.

The other assumption that the method validation requires is $\gamma_{CH_4} = 1$ in Equations 1

and 5. However, a bias in the a priori profiles between the Northern and Southern Hemispheres would lead to offsets in retrieved vertical scale factors (γ_{CH_4}). While γ_{CH_4} is generally within 1% of 1, the values of γ_{CH_4} tend to decrease for TCCON measurements as you move northward. The impact of the interhemispheric bias varies zonally and is also impacted by the aforementioned dependence on SZA, due to the term that is a function of both the averaging kernel and vertical scale factor ($-\beta\gamma_{CH_4}\vec{a}_{CH_4}\vec{x}_{HF}$). A difference of 0.01 between hemispheres can shift the residuals from the one-to-one line by up to 4 ppb, or about one quarter of the offset in the mid-latitudes. Because this bias does not impact the TCCON retrievals, we do not include an estimate for this difference and instead report the sensitivity to this bias in the paper.

p. 3481, l.1-3: "...except in the case of Izaña". I do not see why the effects of the stratospheric variability would not be removed at Izaña. And, it seems to me (Fig.4a) that, indeed, the variability is reduced at Izaña (i.e. in 2011). Could you clarify ?

The original phrasing was vague and has been updated. As opposed to the other sites, where the tropospheric CH_4 cycle is smoother, Izaña exhibits a less pronounced and more variable seasonal cycle of tropospheric CH_4 compared to the total column, although the seasonal cycle of tropospheric CH_4 at Izaña is partially obscured by gaps in the time series. To illustrate impacts of the correction on the CH_4 seasonal cycles, plots with detrended seasonal cycles for all sites have been added.

p. 3481, l.8-11: "The variances of the tropospheric DMFs over a given day are generally equivalent to those of the corresponding total column DMFs, although...": what do you mean by "variances" ? If you mean "individual uncertainties", then why the tropospheric uncertainties are equivalent to the total columns uncertainties (we would expect larger values due to propagation of errors in Eq. 6) ? Also, the fact that the tropospheric standard deviations are larger than the total columns ones seems to reflect indeed

larger individual uncertainties of tropospheric columns, so this would mean that your "variances" are underestimated. But, if I misunderstood this text and if "variances" means something else, could you clarify what are these "variances" ?

The variances referred to are the square of the standard deviations of individual points from the daily mean DMF. Individual uncertainties are larger for tropospheric CH_4 DMFs compared to total columns, although, because the calculation has a relatively low sensitivity to β, uncertainties associated with the latter tend not to inflate the error significantly. The 1% error threshold for the figures is applied to mitigate the impact of outliers and provide more useful comparisons between the median tropospheric and total columns, as well as the intraday variability. This line has been changed to "The intraday variability of the tropospheric DMFs are generally equivalent" to avoid this confusion.

Section 3.1: to me it is not clear enough from Fig. 8 that the new method is an improvement of the Washenfelder et al. (2003) method. I suggest a more quantitative assessment (e.g. provide the mean standard deviations in both cases, and check if the comparisons with in situ measurements are improving using the new method compared to Washenfelder).

A single site was chosen as a representative of the improvements in seasonality of the updated method, due to including the CH_4 averaging kernels. To quantify differences across sites, we have included a figure showing box plots illustrating the distribution of the differences between daily tropospheric CH_4 standard deviations using the Washenfelder et al. (2003) and updated methods. The daily standard deviations tend to decrease modestly with the updated methodology, although intraday variability is reduced by up to 40 ppb.

p. 3482, l.12-14: "...individual errors of less than 10%...": the criteria is less strict for

Fig. 8 comparisons than for the rest of the paper (Figs 4, 5, 6 and 9). Is it to increase the number of coincidences ? What is the main driver of a factor of at least 10 between the individual measurement uncertainties ?

Prior to the updates to the data, a more strict filter limited the number of coincident measurements and thus the benefit of comparing the aircraft profiles. With the updated precisions and errors, this issue no longer applies, and the error threshold is now 1%.

For Fig. 9, 10, and 11, some quantitative comparisons should be made with the Washenfelder method (e.g. correlation coefficient, and/or slope, and/or standard deviation of the differences,...) to prove that the new method is an improvement.

Box plots illustrating the distribution of the differences between daily tropospheric CH_4 standard deviations using the Washenfelder et al. (2003) and updated methods for all sites in this analysis have been included. The biggest impact of the updated method is the inclusion of the CH_4 averaging kernel, which adjusts the airmass-dependence, and thus the seasonality, of the tropospheric CH_4 calculation. This improvement is now stated more explicitly in the comparison.

Section Conclusions, l.4-7: "The methodology described here refines earlier tracer proxy methods for estimating stratospheric methane". Give a quantitative proof of this statement.

Improvements in precision and intraday variability are now quantified, and the reason for the improvement in the characterization of seasonality is now stated more clearly.

A paper in Discussion in AMTD (Wang et al., AMTD, 2014) is treating a similar subject, and by testing the two approaches of using HF and N2O (also available in TCCON measurements), reaches the conclusion that the N2O choice is improving the precision

of the derived tropospheric CH4. Did you also test this N2O approach ? Do you see some arguments in favour of HF vs N2O ?

We cite Wang et al. (2014) in this paper, but we did not replicate the tropospheric CH_4 derivation using N_2O because, unlike HF, N_2O exists in the troposphere and has a nonlinear relationship with CH_4 in the stratosphere. As Wang et al. (2014) note, however, HF retrievals suffer from interference with H_2O, and N_2O may show to be more suitable for high water vapor conditions. The Wang et al. (2014) approach using HF is sufficiently different from the one proposed in this paper that drawing conclusions on the superiority of either trace gas as a proxy would require significant intercomparisons of the methodology.

Technical Comments

Fig. 2 should appear as being "Fig. 1" since it is made reference to Fig. 2 before Fig. 1 in the text. (or introduce Fig. 1 before in the text).

Figure 1 is now introduced earlier in the text.

Fig. 1: add in the legend that data cover 2004-2012 period

The caption now states that ACE-FTS measurements are from 2004-2012.

I would plot Fig 4, 5, 6 in a single figure 4a) to 4h). Also I would add a grid on these plots, to help visualizing the shift in seasonality from total columns to tropospheric columns

Figures 4, 5 and 6 were combined, and x- and y-grids were added to the plots.

Figs. 8, 10, 11: I would remove the total columns in blue. They are not used anymore in the text, and this would enlarge visibility for tropospheric columns. (only suggestion)

We removed the total column measurements in Figure 8. Figures 10 and 11 include the total columns to illustrate the improvement of the tropospheric columns in reference to the in situ measurements, and were thus kept. To improve visibility, however, we moved the legends elsewhere in the chart and truncated the y-axis to the data range.

Additional Changes

The TCCON data was updated as follows:
- The errors for CH_4 DMFs included measurement precisions that were underestimated. In the new section on tropospheric CH_4 errors, the updated precisions are explained. Because of this update, fewer measurements are filtered out by the 1% threshold, and figures now show daily medians for days in which at least 10 tropospheric CH_4 measurements exist.
- Laser sampling errors for Darwin, Wollongong, Sodankylä and Izaña are now better characterized, and the CH_4 DMFs have now been corrected.
- A small number of points in the Park Falls dataset were not processed consistently, and these points have been corrected.

Minor grammatical errors and wording choices were changed.

The color schemes for several of the figures were changed to make the plots more clear.

References

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