

Black: referee's comments red: authors' answers

First of all, we want to thank the two referees for the detailed analysis of our paper.

For the details, please look into the paper with keeping track of changes.

Anonymous Referee #1

The manuscript "Retrieval of atmospheric CH₄ vertical information from TCCON FTIR spectra" by Zhou et al. uses FTIR spectra recorded at six different TCCON sites and applies an alternative data processing: instead of column-averaged dry air mole fractions of CH₄, altitude profiles (or rather partial columns) of tropospheric and stratospheric CH are retrieved. The results are compared to several other data sets for validation:

- standard TCCON CH₄ column data product
- stratospheric profiles from ACE-FTS
- a proxy used in TCCON to separate tropospheric and stratospheric partial columns
- tropospheric and stratospheric in-situ CH₄ profiles at one site

In my opinion, the manuscript addresses an important issue: a profile data product from TCCON spectra have been requested by several TCCON data users in the past. So, in principle, this study could be very useful to evaluate the possibilities and limitations of such a data product.

Unfortunately, the manuscript fails at this attempt. While the retrieval itself looks fine, the validation of the method is flawed. The most obvious way to validate the method would have been comparing the retrieved profiles to in-situ aircraft and balloon (aircore) profiles. Dozens of such profiles have been measured at various TCCON stations during the last 10-15 years and are available for the TCCON community. However, the authors decided to select six sites of which only one actually had in-situ profiles during the - also arbitrarily chosen - time period. Why did they not use TCCON sites that had aircraft profiles in the past and processed the spectra from those days? It would have been easy to apply the profile retrieval to other time periods. I understand that they did not want to process many more years of TCCON data. But I also do not see a need for using the same time period for all stations in the first place.

As a result, they struggle with the validation of their retrieved stratospheric profiles. They resort to using satellite CH₄ profiles from ACE-FTS where the precision and accuracy is more than an order of magnitude worse than the TCCON standards for column retrievals. Instead, they could have done an extensive comparison with data from the Sodankylä site but for an extended time period. And there are more TCCON sites that have been covered by aircore measurements than just Sodankylä. One is even part of this study: Orleans!

In the troposphere, it is even more puzzling why the bulk of available in-situ aircraft profile data was completely ignored. Even during the same time period, several TCCON sites were overflown by the NASA ATom campaign. And several of the sites that have been used in this study had aircraft profiles taken during the IMECC campaign in 2009. Why did they not process spectra from that time period for these sites instead? There is no obvious reason why they limited themselves to 2016-17. Given these issues, I cannot recommend publication without major revisions. The authors should try their profile retrieval on stations and time periods with corresponding aircraft or aircore in-situ CH₄ profiles. If they do so, the whole section 3.3 (ACE-FTS comparison) could be dropped. The section 3.4 (TCCON proxy) would still be useful to evaluate if the proxy method or a profile retrieval provides better results.

General comments:

Why were these sites selected? Among those, Sodankylä is the only one where in-situ profiles were used to validate the retrieval. Others sites do have profiles but they were ignored. To my knowledge, two sites never had any kind of in-situ profiling but were included nonetheless.

Aircraft/aircore profiles at the selected sites:

- Sodankylä: many during several campaigns (but only a limited set used here)
- Bialystok, Bremen, Orléans: aircraft profiles taken 2009 but not used here. Data published in Geibel et al.: Calibration of column-averaged CH₄ over European TCCON FTS sites with airborne in-situ measurements, Atmos. Chem. Phys., 12, 8763-8775, <https://doi.org/10.5194/acp-12-8763-2012>, 2012.
- Ny-Alesund: never
- St Denis: never

ATom visited several TCCON sites in 2016/17, the data is publicly available. Why was this data set completely ignored?

Why was the time frame 2016-17 selected? There is no special reason given and I cannot see one that requires to try the SFIT4TCCON on the same time period for all sites. It would make much more sense to use it on periods with available in situ profiles for each site. Why was St. Denis used as the prototype? It is probably the wettest site of all and not necessarily characteristic for the others.

One of the main concerns expressed by the referee is the reason behind the chosen time period (2016-2017) and the chosen sites. This paper is the result of work done in the EU RINGO project in which one work package was dedicated to demonstrate the feasibility of vertical profiles retrievals of CH₄ from TCCON spectra. The study is based on six TCCON sites from the RINGO partners in the project: BIRA, University of Bremen and FMI. The initial setup of the RINGO project and the practical limitations were the main reasons to limit this study to the analysis of 2 years of data at these six sites. We agree with the referee and are willing to expand this study to all TCCON sites but this will cause significant delay: firstly an agreement between BIRA and all TCCON PIs is necessary and secondly additional resources to cover IT costs need to be found (and BIRA has no perspective on this in the near future). We also believe that the six chosen sites are representative for the majority of the TCCON network covering a large latitude band. To extend the SFIT4TCCON retrievals to more TCCON stations, we need to get the spectra from the individual TCCON PIs. We would like to mention that this work was presented to the entire TCCON community at the IRWG-TCCON annual meeting in May this year at Wanaka, New Zealand. We invited the TCCON community to take part in this study, given the technical limitations we are facing. However, until now, only the spectra from these six sites are available. In this paper, we present the CH₄ profile retrieval method, and we can make the CH₄ profile retrieval easily for other time period and at other sites when the NIR spectra and extra supports are available in the future.

Concerning the in-situ comparisons: among the six sites, Bialystok, Bremen and Orleans have been validated in the past with IMECC aircraft measurements (Geibel et al., 2012) and Sodankyla has been calibrated with AirCore measurements. As the referee mentions, the Sodankyla AirCore data have been used in this study to validate the vertical profile retrieval results and we will add to the revised version a comparison against all available IMECC aircraft profiles for the Bialystok, Bremen and Orleans sites (not necessarily within the chosen time period). The AirCore measurements at Orleans are not added in the revised version, and the reason is discussed later. Unfortunately, no Atom profile (<https://acd-ext.gsfc.nasa.gov/Missions/ATom/Flights/>) is available at these six sites.

St. Denis is used as the prototype, as the site is very humid and the H₂O is very important in the CH₄ retrieval (as we can see the retrievals from Band 1 have an artificial curve): if the retrieval method works in humid conditions, then also in dry conditions.

Specific comments:

The data product is called SFIT4TCCON but - unlike the name suggests - it is not an official TCCON data product. Was the use of the name "TCCON" approved by the TCCON PIs? I am a TCCON PI myself but I am not aware of this.

Thanks for the suggestions. We agree that the SFIT4TCCON is not appropriate. So we use "SFIT4NIR" as the new name for our retrievals.

Section 2.2.1:

- p. 4, l. 11: Diurnal variations above St Denis are assumed to be small. What about the biomass burning season, would this still be true? At least there should not have been much biomass burning activity during the chosen time frame. It would have been easy to check other sites TCCON sites for these criteria. Also, I do not understand why the band with the highest correlation between CH₄ and dry air pressure is best choice.

Thanks for the suggestions.

We realize that it is not appropriate to use the correlation between the dry air column and the CH₄ column to select the retrieval window. The dry air total column and CH₄ total column are correlated if we assume that the XCH₄ is relatively constant during the day. There is no strong CH₄ emission at St Denis, especially in non-biomass burning period. However due to the vertical and horizontal transport, and the reaction with OH, the XCH₄ can be variable. According to the TCCON measurements, the daily standard deviation of XCH₄ is within 3 ppb (~0.16%), while the daily standard deviation of dry air total column is about 0.14%. As the two standard deviations are in the same order, it is very difficult to use the variation of the dry air column to select the variation of the CH₄ total column. We think this is a very interested topic but might beyond the scope of this paper. In order to avoid the confusion, in the revised version, we will remove this paragraph and the argument to select band 2 will be based on the fact that the fit in Band 2 is the best and less affected by H₂O.

- p. 6, l. 8-10: the " $Sa^{-1} = \dots$ " should be a numbered equation. The quantity "L1" is not described at all, "T" only very briefly. Provide a reference linking Tikhonov 1963 to the Sa matrix. In the cited reference, Tikhonov certainly did not refer to Rodger's original work which came years later (1976).

This will be taken into account in the revised version.

Section 2.2.4:

- How was the SFIT4 column AVK calculated?

The SFIT4 implementation uses optimal estimation and the methane VMR profile is in the state vector in relative units (relative to the CH₄ apriori). The column averaging kernel (CAVK) can be calculated from this 2D state vector averaging kernel (calculated analytically) using standard methods.

Section 2.2.5:

- 5% uncertainty might be fine for St Denis sources but may underestimate the variability closer to CH₄ sources. Check available aircraft profiles (e.g. from ATom, HIPPO etc.) as well as aircore to get a better grip on the expected variability. The model data might be too smooth.

Thanks for the recommendation. Unfortunately, there are no CH₄ in situ profiles (aircraft or AirCore) available at St Denis, and even at Sodankyla, we only have a few AirCore measurements. Therefore, in this study, the random a priori covariance matrix is estimated from the covariance matrix of the WACCM 492 monthly means (41 years). For the systematic uncertainty, we have chosen a value of 5% (about 90 ppb in the troposphere), based on the difference between the SFIT4TCCON a priori CH₄ mole fraction near the surface and the local in situ measurements (Zhou et al., 2018). As CH₄ is relatively stable in the atmosphere with a life time of 9-10 years, it is assumed that 5% systematic uncertainty is acceptable for all altitudes. This is also only relevant for the smoothing uncertainty which is cancelled in the comparison with the in situ profiles since we apply the smoothing equation.

Eq. 7: Why did you use pressure and not the O₂ column for the calculation dry air column? There are good reasons why TCCON abandoned surface pressure as a proxy for airmass years ago.

By using the ratio between the target species and O₂ can reduce the uncertainties common to both gases (Yang et al., 2002), e.g. the surface pressure and solar tracker pointing. However, there is a systematic uncertainty in the spectroscopy of O₂, as the Xair of TCCON data is close to 0.98. In addition, the retrieved O₂ is also affected by the airmass, so that the TCCON retrievals are corrected with an airmass dependent factor. For the CH₄ profile retrieval, the O₂ retrieval is not simultaneously performed, and we do not apply the airmass dependent and independent correction for our retrieval. The uncertainty of the surface pressure at these TCCON sites is within 0.1 hPa, which means that the uncertainty of the dry air total column derived from the surface pressure is within 0.1%. By comparing the XCH₄ between the TCCON standard retrievals and SFIT4NIR retrievals, the bias of the SFIT4NIR retrievals are within the TCCON reported uncertainty.

Section 3.2

- It is doubtful that surface in-situ measurements from 20 km away are representative for St Denis. If you think otherwise, you should provide some reasonable arguments.

We think comparing the tropospheric XCH₄ at St Denis and in situ measurement at Maido is reasonable. Some arguments are added in the revised version.

CH₄ is well-mixed in the lower atmosphere with a life time of 8–10 years (Kirschke et al., 2013). Maido is located in the high mountain (2155 m), which is less affected by the surface. In addition, there is no strong methane emission nearby.

Section 3.3

- I understand the need to find something to compare the stratospheric profiles with. However, given the very limited precision and accuracy listed here for the 10-year old ACE-FTS data (25%), I wonder how useful this comparison can be. One might be better off comparing to zonal means with better statistics. That might also provide profiles for the stations where reasonable co-locations could not be found.

In the revised version: “The older version v2.2 data of the ACE-FTS CH₄ data have been compared to space-based satellite, balloon-borne and ground-based FTIR data (De Maziere et al., 2008). The accuracy of the version 2.2 data is within 10% in the upper troposphere - lower stratosphere (UTLS), and within 25% in the middle and higher stratosphere up to the lower mesosphere. The uncertainty of the new version of the ACE-FTS data has a reduction of about 10% near 35-40 km and a slight reduction at 23 km (Waymark et al., 2014). ”.

Therefore, the uncertainty of the stratospheric XCH₄ of each individual ACE-FTS measurement should be around or within 10%. As we select the ACE-FTS measurements

within the $\pm 3 \times 30$ (latitude x longitude) co-located box around each site, normally there are more than 1 ACE-FTS measurements. At Orleans and Bialystok, the mean co-located number of ACE-FTS measurements for each FTIR measurement day is about 4.0. At St Denis, the mean co-located number of ACE-FTS measurements for each FTIR measurement day is about 3.2. The mean of the co-located ACE-FTS measurements is applied to compare with the FTIR measurement. By doing the average, the uncertainty of the ACE-FTS measurement is reduced to about 5% (assuming all random uncertainty, then $\sqrt{N} \approx 2$). Figure 8 in the revised version shows that the seasonal cycles of the stratospheric XCH₄ from the ACE-FTS and SFIT4NIR measurements are close to each other. The amplitude of the seasonal cycle of the stratospheric XCH₄ is about 15%, which is larger than the uncertainty of the ACE-FTS measurements.

- If you decide to make the major revisions that I recommend, this whole section could be dropped.

We prefer to leave this section because it can show the seasonal cycle of the stratospheric XCH₄.

Section 3.4

- Due to the H₂O interference in the HF microwindow, I would trust the N₂O method more for a tropical site like St. Denis.

Yes. The HF absorption line at a humid site is strongly affected by the H₂O line.

- p. 14, l. 10 to p. 15, l. 4: it should not be too difficult to find out which of the raised possibilities 1) to 3) are true. The source code for the TCCON retrieval as well as the handling of the a priori profiles is available.

The possible reasons are mainly from the proxy method, which are from its assumption.

Further investigation should be carried out to figure out which one is the dominated reason.

Section 3.5

- I believe that the Aircore measurements are the most trustworthy validation source for the tropospheric and stratospheric profiles. There are other TCCON sites which had simultaneous aircore profiles taken. Why were these not used? This would also improve the statistics in Fig. 11, which suffers from the fact that a very limited range of XCH₄ was compared.

Thanks for the suggestion. We add the comparison between the IMECC aircraft measurements and SFIT4NIR retrievals in the revised version (Section 3.6). The SFIT4NIR retrievals are carried out on these aircraft overflight days. Since the aircraft profile only covers the vertical range from ~300 to 13000 m, we only compare their tropospheric parts. The aircraft measurements confirm that there is an about 1.0% overestimation in the SFIT4NIR tropospheric XCH₄, which is consistent with the result from the comparison between the AirCore measurements and SFIT4NIR retrievals.

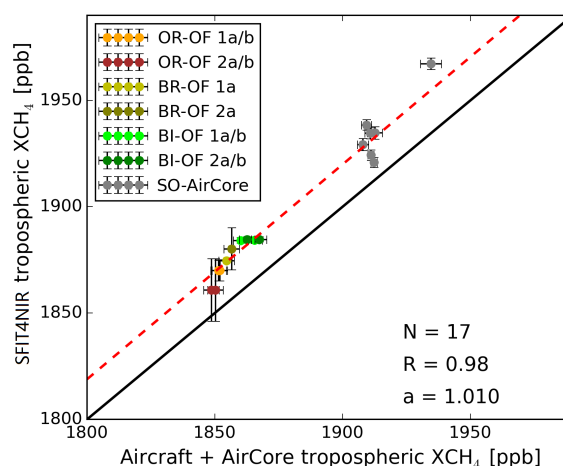


Figure 1. The scatter plots of XCH₄ between the SFIT4NIR and the IMECC aircraft measurements together with the AirCore measurements for the tropospheric components. The black line is the one-to-one line and the dashed red line is the regression line with the intercept to zero ($y = a \cdot x$). N is the co-located measurement number, R is the correlation coefficient, and a is the slope.

The AirCore measurements at Orleans are not used in the paper, because there is an underestimation of 0.5% in the AirCore XCH₄ measurements. Figure 2 shows that the AirCore XCH₄ is $0.5 \pm 0.2\%$ lower than the SFIT4NIR retrievals, and the AirCore XCH₄ is $0.5 \pm 0.2\%$ lower than the TCCON retrievals. Note that, the AirCore data has been smoothed with SFIT4NIR/TCCON AVK, when comparing with SFIT4NIR/TCCON retrievals. The SFIT4NIR retrieved XCH₄ is close to the standard TCCON retrieval, which is consistent with the results in Section 3.1. As an example, the time series of the XCH₄ from the AirCore, TCCON and SFIT4NIR measurements on 17 February 2017, together with their profiles and differences are shown in Figure 3.

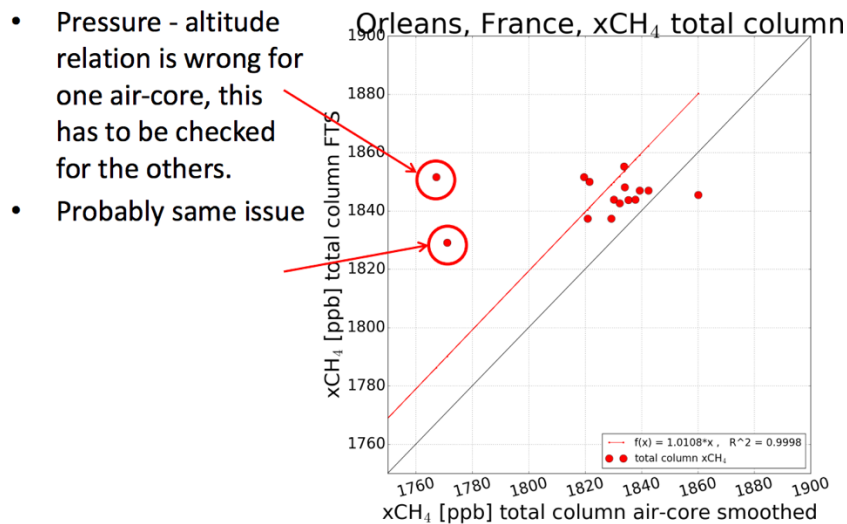
If we use the AirCore measurements at Orleans to validate the SFIT4NIR tropospheric and stratospheric XCH₄, there is an overestimation of $1.0 \pm 0.5\%$ in the SFIT4NIR tropospheric XCH₄, and an underestimation of $1.7 \pm 0.7\%$ in the SFIT4NIR stratospheric XCH₄. Since the result in the troposphere is in good agreement with the results from the AirCore at Sodankylä and IMECC aircraft measurements at Orleans, Bremen and Bialystok, it is probably that the stratospheric part of the AirCore measurement at Orleans is underestimated. There is one study from the Bremen group, they also found that the AirCore CH₄ measurements at Orleans is about 0.5% larger than the TCCON measurements (after removing the two outliers) https://tcccon-wiki.caltech.edu/@api/deki/files/3129/=TCCON_2019_Petri.pdf (Page 8; please use your TCCON wiki account to login).

It is not clear to us why there is an underestimation in the AirCore data, partially in the stratosphere. The AirCore measurements (LSCE/LMD) in 2016 and 2017 at Orleans used here have not been compared with other in situ profiles. In June 2019, there is an AirCore inter-comparison campaign within the RINGO project of 12 AirCore systems from 7 research team (LSCE/LMD, NOAA/ESRL, University of Groningen, Goethe University Frankfurt, University of Bern, Finnish Meteorological Institute, and Forschungszentrum Jülich) and of 1 sampling balloon system (<https://www.icos-ri.eu/ringo/news-and-events>). Within this campaign, we have the opportunity to understand better the uncertainty of the AirCore measurements. Note that the AirCore measurements (RUG) in 2016 and 2017 at Sodankylä has already been

compared with NOAA and GUF ones, so that we understand the uncertainty of the Sodankyla AirCore measurements better.

In conclusion, we do not include the AirCore measurements at Orleans in this paper, and further investigation is required before using the AirCore CH₄ measurements at Orleans.

Total column CH₄ comparison



(Page 8 in Petri et al., 2019, TCCON annual meeting)

In case that the reader does not have the access to the TCCON wiki, we attach the slide 8 here.

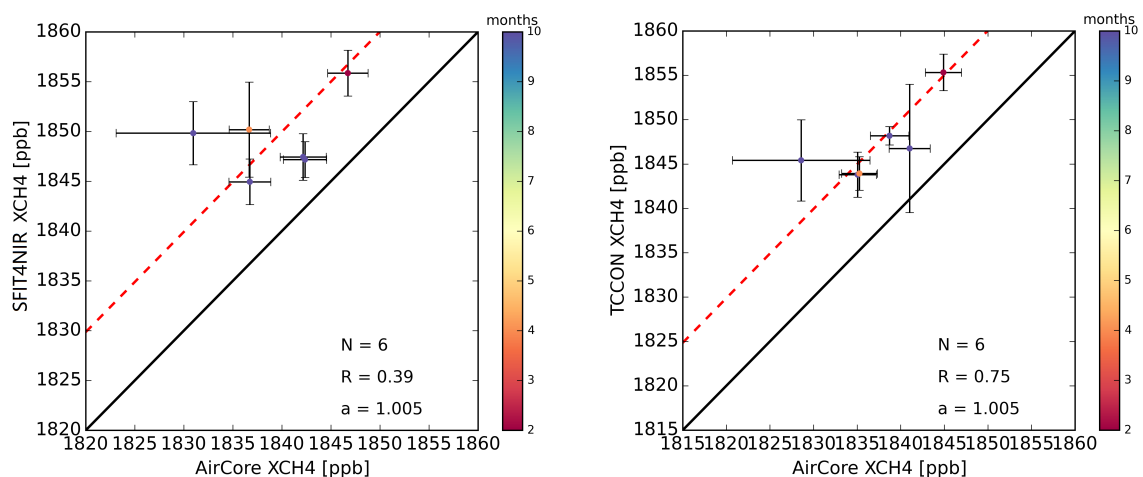


Figure 2. Left panel: the scatter plot between the smoothed AirCore and SFIT4NIR XCH₄ daily means. Right panel: the scatter plot between the smoothed AirCore and TCCON XCH₄.

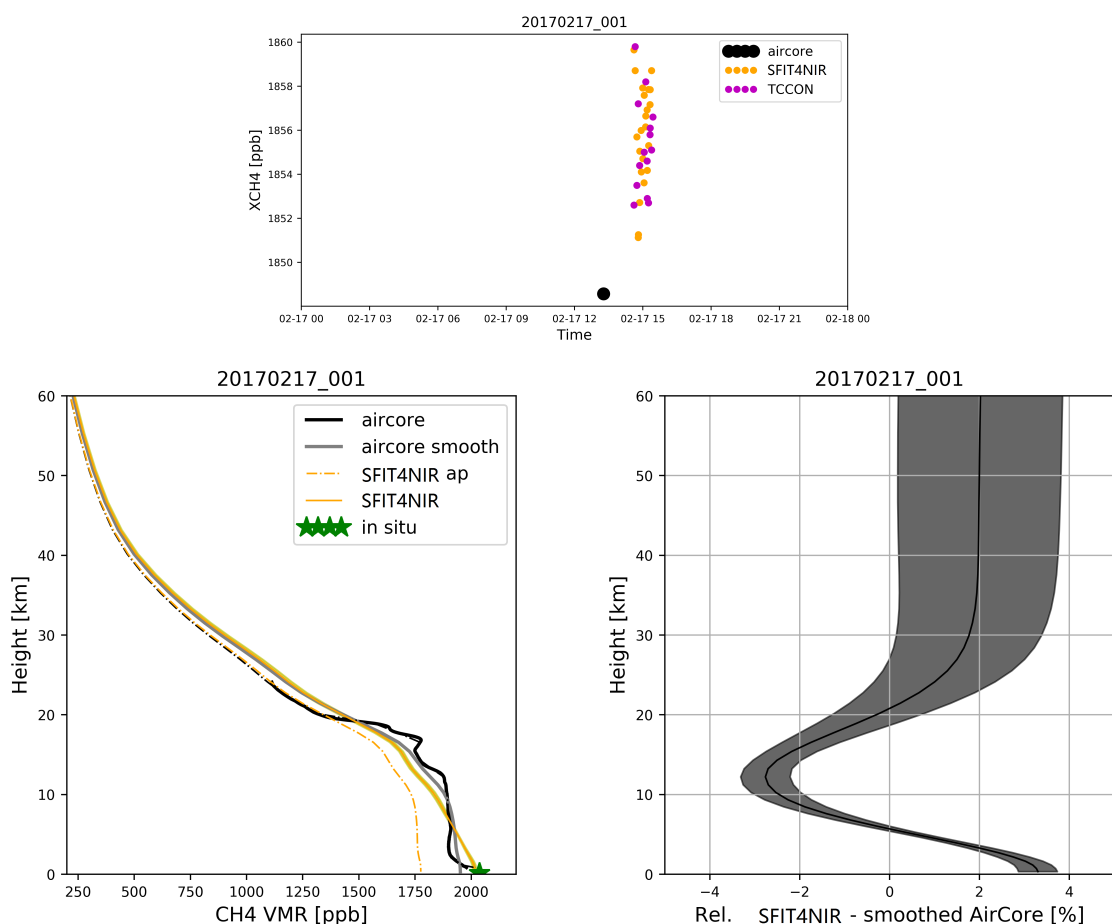


Figure 3. Upper panel: the time series of the XCH₄ from the AirCore, TCCON and SFIT4NIR measurements on 17 February 2017. Lower panels: the CH₄ profiles from AirCore and SFIT4NIR measurements (left) with their differences (right).

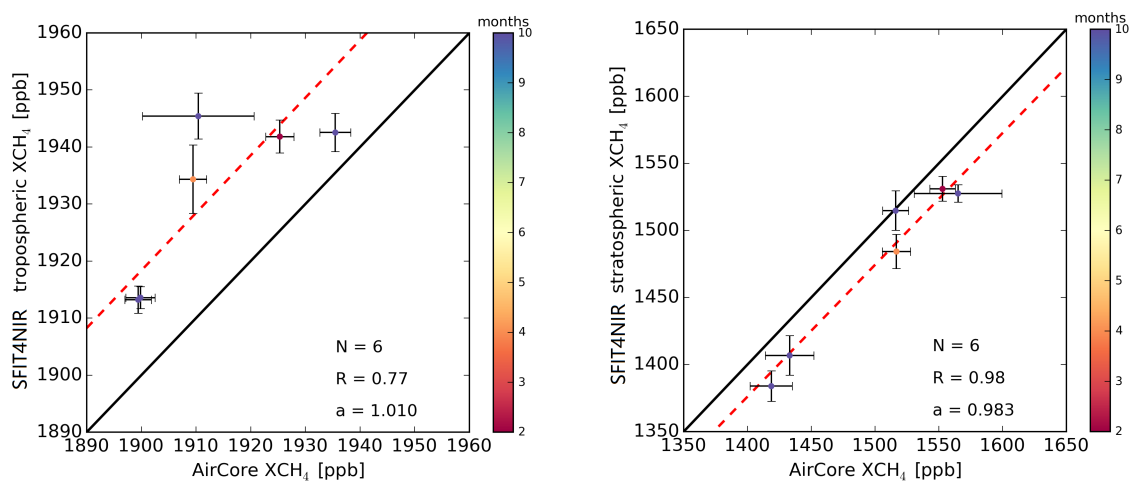


Figure 4. Left panel: the scatter plot between the smoothed AirCore and SFIT4NIR tropospheric XCH₄ daily means at Orleans. Right panel: the scatter plot between the smoothed AirCore and SFIT4NIR stratospheric XCH₄ daily means at Orleans.

References:

- All the TCCON dataset citations are wrong: they still refer to Oak Ridge National Laboratory from which the TCCON data archive moved away already in October 2017! Strange how this can happen when several TCCON PIs are listed as coauthors.

Corrected

- Acknowledgments: the authors should check if the acknowledgments are in line with what is required by the TCCON Data Use Policy.

Checked

Minor comments:

- p. 3, l. 15: I would not call that "noise".
- p. 3, l. 21: Please explain the ATM acronym at least once.
- Fig. 2: poor color choice for dry air pressure as green is already used for band 3.
- p. 6, l. 5: should be "constrain" instead of "constraint"
- p. 7, l. 5: should be "panel" instead of "penal"
- p. 8, l. 17: "The other retrieved parameters have do not contribute ..."
- p. 8, l. 28: "retrieved CH 4 total column are 3.2 and 0.5%" units missing
- Table 5: Why not just write "

Corrected

Reference:

Geibel et al.: Calibration of column-averaged CH₄ over European TCCON FTS sites with airborne in-situ measurements, *Atmos. Chem. Phys.*, 12, 8763–8775, <https://doi.org/10.5194/acp-12-8763-2012>, 2012.

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