

Dear reviewer,

Thank you for reviewing our paper, and for the many helpful suggestions. In order to respond we have kept your original comments in black, our responses are in blue, and any proposed changes are in underlined blue.

The paper by Malina et al. reports on the consistency and quality of four spectroscopic databases for methane (CH₄) absorption parameters in the shortwave infrared spectral range. The evaluation tool is measurements of atmospheric absorption spectra collected in direct-sun geometry at high spectral resolution across a range of atmospheric path lengths and meteorological conditions. Topic-wise, the study is of interest to the readers of AMT since the respective spectroscopic parameters are relevant for ground-based as well as current and future satellite remote sensing experiments which aim at CH₄ column concentrations with sub-percent accuracy.

The study is based on state-of-the-art, high quality data. But, the paper is not written well. As I already indicated in my technical review for the discussion phase, the paper provides too much specific information without guidance which piece is important and, on the other hand, the paper is too superficial in some of the important aspects. If to be published, the paper needs to be made more concise and to-the-point having in mind the interests of the atmospheric sciences community.

Thank you for your comments here, please see our responses to the remainder of your comments which show how we have shortened the paper, while keeping the detail in the appendix.

In that regard, I recommend dropping the entire 13CH₄ discussion since it is essentially impossible (for the thinkable future) to perform a remote sensing experiment that yields errors low enough to make it useful for scientific purposes.

Thank you for your comment here. Reviewer 1 suggested reducing the importance of 13CH₄ retrievals in the paper. We have therefore removed most of the work relating to 13CH₄ retrievals, but have included some of the results and some of the discussion related to the challenges of retrieving 13CH₄. Despite these results showing the extreme challenge of retrieving usable values of 13CH₄ at this time, we feel it is important to document these efforts. This will help any future studies investigating 13CH₄ retrievals, allowing comparison between their efforts, and the capabilities at this time.

But I highly recommend discussing in more depth the following aspects. The key challenge of methane remote sensing is avoiding retrieval biases that correlate with geophysical conditions in a way that the errors mimic source (or sink) patterns. Reported and notorious candidates for such spurious errors are correlations between CH₄ and H₂O absorption (e.g. inducing tropical biases), correlations between CH₄ and the lengths of the lightpath (e.g. inducing seasonal

or high-latitude biases), and wrong CH₄ profile shapes in the stratosphere. TCCON is known for requiring an empirical lightpath correction for low sun observations which, presumably, originates from deficient spectroscopic parameters. A meaningful evaluation of spectroscopic databases and retrieval windows requires addressing and quantifying these dependencies. The study here does not really include these aspects although it uses a range of spectra from two TCCON sites which could serve the purpose (e.g. plotting retrieval differences against H₂O content or against path length). The study resorts to a sensitivity assessment with perturbed a priori and meteorological parameters which is not indicative for real atmospheric performance in particular since the perturbations are mere educated guesses. The most important sensitivity, the one to the stratospheric profile shape, is deliberately left out.

Thank you for these important points, based on your (and reviewer 1's) recommendations we have restructured the section on the sensitivity analysis. The sensitivity analysis is split into two sections:

1. Firstly we have included the points you recommended above, namely the sensitivity of retrieved biases with respect to changing lightpath (solar zenith angle) and water vapour conditions over the course of a series of measurements at the Tsukuba and Ascension island TCCON sites. This analysis is performed by correlating water vapour and SZA changes with changes in retrieved 12CH₄ biases, these results are included in the main text (section 3.5.1).
2. Secondly the majority of the original sensitivity analysis has been placed into Appendix C, the results of which have been summarised in the main text (section 3.5.2). We think that including the results of the sensitivity analysis is still important, these types of analyses are crucial in understanding the accuracy of retrieved values from satellites or ground instruments and are usually included in error budgets (Hu et al., 2016; Wunch et al., 2011). The point we make in this study, is that the error budgets calculated for sensitivity studies vary depending on the spectral window and the spectroscopic database, which is not normally considered in such studies and should be. We have modified the original sensitivity study, the aspect relating to instrument errors has been removed, and we have included a section relating to methane profile shape errors (as you suggested). For the profile shape errors, we used methane profiles from different seasons to induce errors due to stratospheric profiles and tropopause heights.

The required changes to the manuscript are at the edge of what seems possible under a major revision.

Specific comments:

P1 L18: What are "pressure cross sections"? Do you refer to the pressure dependence of molecular absorption cross sections?

Yes, pressure dependence was meant, however, we have re-written the abstract and pressure cross sections are no longer referred to.

P3 L72: “an average of three retrieved values from three TCCON fit windows”
Why is CH₄ separately retrieved from different windows and averaged a posteriori? If this is a simple arithmetic averaging, it tends to compromise the entire idea of using a maximum likelihood or an optimal estimation technique.

We missed a section of the documentation, which elaborates slightly. It is in-fact a weighted average, depending on the uncertainty of retrievals from each individual band. This sentence now reads:

...where a weighted average of three retrieved values from three TCCON fits windows....

This is described in the Caltech TCCON wiki (<https://tccon-wiki.caltech.edu/>).

P3 L76: The discussion of the 13CH₄ retrievals lacks the point that atmospheric gradients will be even smaller in column-average concentrations than in in-situ observations.

Thank you for this point, we have included discussion on the complexities of estimating 13CH₄ column averaged gradients in section 2.3 the ‘Analysis Criteria’, we felt this was a more appropriate place for this discussion. The text in introduction is more for briefly introducing retrievals of 13CH₄.

P4 L107: “least-squares optimal estimation” To the best of my knowledge, it is either least-squares (cost function without side-constraint, maximum likelihood principle) or optimal estimation (a priori departure as side-constraint, Bayesian statistics principle), not both together. From the list of retrieval parameters, it looks like the inversion problem is well suited for a pure least-squares technique. Optimal estimation would be required if the problem was ill-posed e.g. when retrieving concentration vertical profiles instead of column scaling factors.

Yes thank you, we have now described GFIT as:

...non-linear least squares fitting scheme....

P5 Table 2. Windows 1 and 5, 4 and 6 are only different because of technical details of the particular software used (apparently there can only be one target molecule per window). This is not of interest to the general reader and the discussion could be simplified.

We agree, this discussion has been simplified.

Please see updated discussion of Table 2.

P7 L175: The metrics should include the definition of the column-average mole fraction and its “X” notation. Later (section 3.3), the X-notation comes as a surprise.

Thank you for this point, we have decided to remove all X-notation from the paper. In this paper update, when we refer to retrieved trace concentrations we will refer to them as DMFs, for example “when we retrieved $^{12}\text{CH}_4$ DMFs we found”.

P8 L210: Using CO absorption as a proxy for $^{13}\text{CH}_4$ is inadequate, since precision and accuracy requirements for $^{13}\text{CH}_4$ are factors higher.

We agree, the references to CO have been removed, and this discussion had been re-written as follows:

In terms of $^{13}\text{CH}_4$ there are no published precision and accuracy requirements or statistics with TCCON. Fundamentally the final aim of retrieving $^{13}\text{CH}_4$ is to calculate d13C. d13C has been used to differentiate between methane source types (Fisher et al. 2017, Nisbet et al. 2016, Rigby et al. 2017, Rella et al. 2015), and variations of this value has been linked with variations in the global methane budget (Rigby et al. 2017, McNorton et al. 2016). How much d13C varies in the total varies in the total column is a complex issue (Weidmann et al. 2017, Malina et al. 2018, 2019), in-situ studies (Nisbet et al. 2016, Rigby et al. 2017, Fisher et al. 2017) all show that an uncertainty of $<1\text{‰}$ in d13C is required in order to determine natural annual variability at the surface. However, variability in d13C can be higher in the troposphere and stratosphere due to variability of the OH sink and the fractionation caused by OH (Rockmann et al. 2011, Buzan et al. 2016), with evidence that d13C can vary by up to 10‰ in different air parcels (Rockmann et al. 2011). Based on these factor, we assume a rough total column d13C variability of 1‰ , which equates to a total uncertainty of <0.02 ppb on $^{13}\text{CH}_4$ retrievals, or roughly 0.1% of the total column. This is clearly an unrealistic target for individual retrievals, given the uncertainty requirements for $^{12}\text{CH}_4$ described above. Nevertheless precision errors will be low due to the nature of TCCON, and through the fact that TCCON sites are situated in a fixed position, allowing for long term averaging to reach a required precision target. Therefore one of the minor aims of this study is to identify how far away TCCON uncertainty (including systematic errors) is from the desired uncertainty of $<1\text{‰}$ d13C.

P9 L256: I think the term “a priori errors” is misleading since not all parameters that are perturbed are retrieval parameters (for which an a priori exists). The assumed perturbations for the parameters are not based on actual real-world problems reported previously. For example, simply assuming a 2% bias in the methane total column will not yield any significant error sensitivity because the retrieval of the total column is unconstrained. The a priori assumption that causes problems for the CH_4 retrieval is the shape of the a priori profile e.g.

assuming a mid-latitude stratospheric profile where there is in reality a polar vortex profile. Likewise a perturbation of the water vapor column by 10% cannot assess the actual real-world problem that spectroscopic interferences between CH₄ and H₂O might induce spurious gradients between the mid-latitudes and the tropics since the H₂O content differs by factors, not just 10%. I would recommend replacing the entire perturbation study by a correlation analysis how CH₄ retrievals from TCCON spectra (from Tsukuba, Ascension Island, and possibly other stations to increase the parameter range) correlate with H₂O content, CH₄ stratospheric profile conditions, and path length dependencies and how these correlations are better or worse for the various spectroscopic databases.

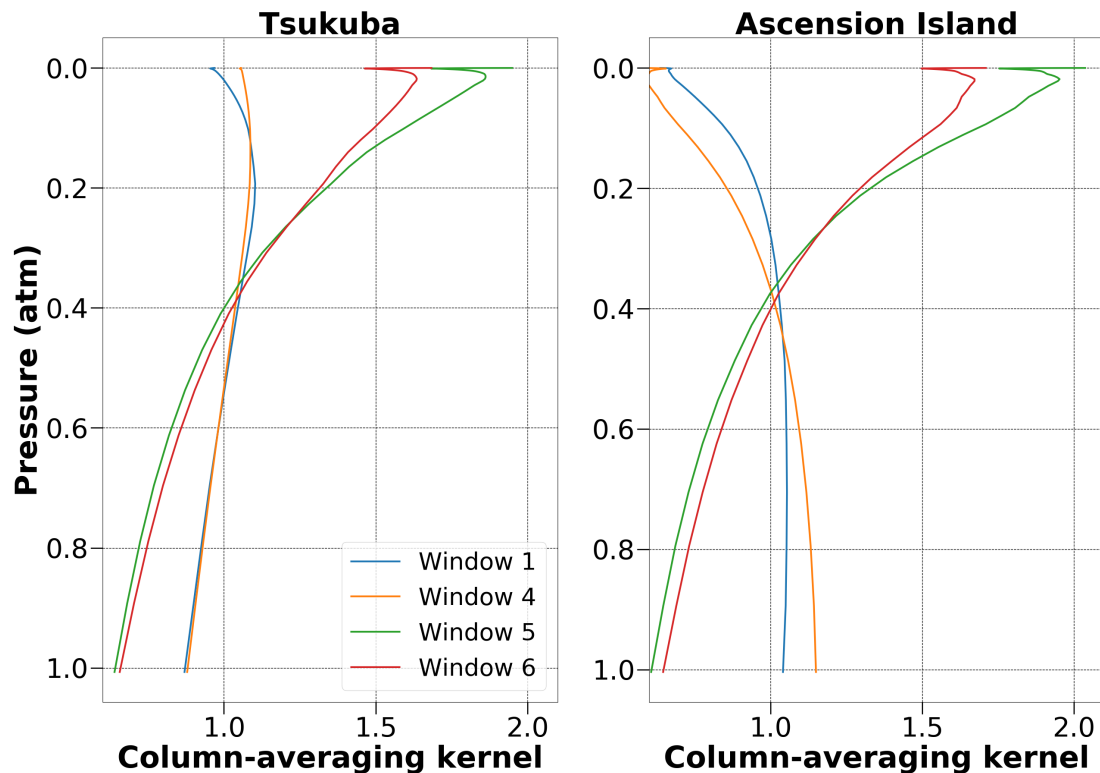
Based on your recommendation here we have undertaken the following actions:

1. We now refer to “a priori errors” as “a priori and parameter errors”, in order to distinguish between errors induced into the a priori profiles of methane and water vapour, and errors introduced into the profiles of temperature and pressure.
2. We have now included a correlation analysis on how 12CH₄ retrieval biases from Tsukuba and Ascension island correlate with local water vapour and solar zenith angle conditions, see section 3.5.1. This analysis shows that certain retrieval bands are sensitive to bias changes at high solar zenith angles. It also shows some sensitivities to water vapour variability, but only at high solar zenith angles.
3. We have decided to keep the section on perturbation errors, we disagree with your statement that this is not based on real-world problems, indeed errors present in a priori and parameter profiles are included in the TCCON error budgets (Wunch et al., 2011). So it is possible that TCCON retrievals will have to deal with errors in the a priori profile of water vapour, and sensitivity to variability over the course of a series of measurements. We base our error magnitudes on what is expected for Sentinel 5P/TROPOMI retrievals (Hu et al., 2016). We have also included additional sensitivity analysis on incorporating incorrect methane atmospheric profiles into the retrievals, in order to understand the effect.

P11 Fig.1: What is the spurious error (as a function of path length, season, latitude) that the difference of 12CH₄ and 13CH₄ averaging kernels could imply for delta-13CH₄?

Below we show the averaging kernels for a separate set of retrievals from Tsukuba and Ascension island, captured under different solar zenith angles and conditions. We note that the Tsukuba averaging kernels are very similar to those of Figure 1, this suggests that retrievals from Tsukuba show similar sensitivities with different retrieval types. The Ascension island averaging kernels suggest little change to 13CH₄, but some changes in sensitivity in the lower troposphere for 12CH₄. This implies that no additional spurious errors are caused by the differences in the 12CH₄ and 13CH₄ averaging kernels due to changing path lengths and seasons changing sensitivities, except those that already exist. Since the sensitivity of 12CH₄ in the lower troposphere is very high in both cases, and the sensitivity of 13CH₄ does not change.

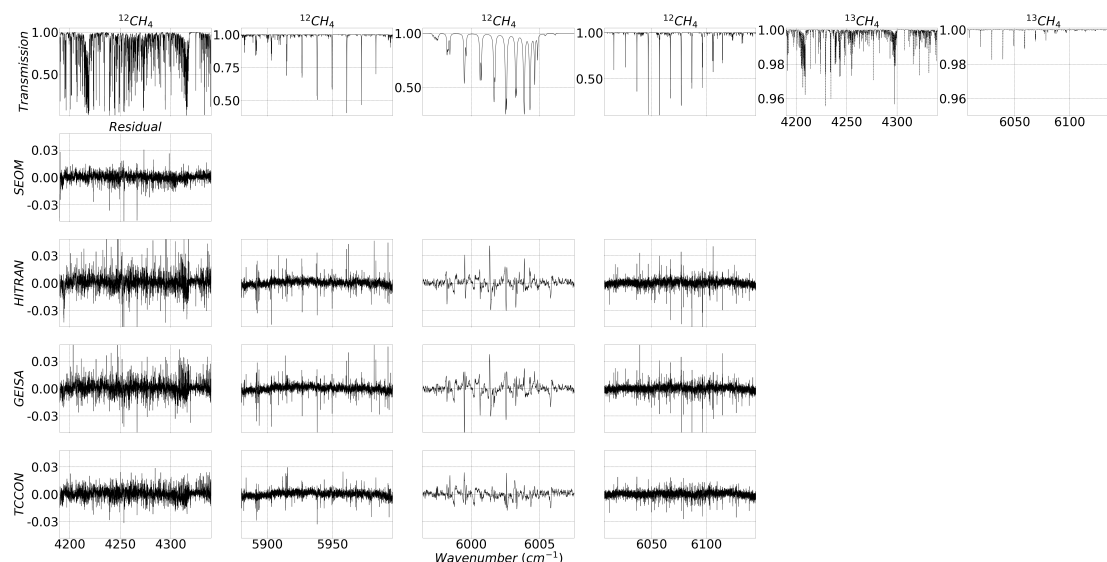
Given that differences between the 12CH₄ and 13CH₄ averaging kernels do exist, this means that any changes in methane concentration in the lower troposphere will not be fully represented in the 13CH₄ retrieval, thus causing bias. The averaging kernels for 13CH₄ windows show slightly more difference in Ascension island than Tsukuba, meaning lower tropospheric changes will be represented slightly better in window 6 than in window 5 in Ascension island.



P12 Fig.2: The figure is much too small and contains unnecessary information such as the CO and HDO transmittances. The four spectroscopic databases are indistinguishable. I would recommend dropping all panels except for the residuals – if a residual is clearly correlated with a molecular absorber you can put a symbol on the residual peak.

Reviewer 1 also requested substantial changes to this figure, the following changes have been made to this figure.

All background absorber panels have been removed, only the transmissions of 12CH₄ and 13CH₄ have been kept, in order to indicate the differences between the spectral windows. Only the transmissions calculated from the TCCON spectroscopic database are included in order to reduce clutter. From this point only residual transmissions are shown, each row shows the residuals from a specific spectroscopic database.



P16 Table 4: The table is tough to understand. It would be helpful if the table indicated which window is $^{12}\text{CH}_4$ and which one is $^{13}\text{CH}_4$ since the definitions are far away. I recommend adding an extensive caption.

We agree, we have therefore identified which window is which, and expanded the caption for the tables.

P21 Fig.7 and 8: Together with a very short and superficial discussion on page 22 the figures are largely useless (too small, point clouds masking each other). Drop for the sake of conciseness.

We have removed this figure from the paper.

P23 Why is the section called “a priori” error (similar question as for section title 2.4.2)? The section reports on the perturbation of the imposed temperature profile. Since temperature is not a retrieval parameter but a forward model parameter, there is no corresponding a priori. Probably, the title should rather be “parameter error”.

Section 3.5. has been renamed as “Sensitivity Analysis” which has been split into two parts. The first part section 3.5.1. named “Local condition variation” deals with the impact of varying solar zenith angles and water vapour on biases. The second part, section 3.5.2. has now been named “A priori and parameter errors” in order to indicate that we are perturbing the a priori and parameter profiles.

P23 Fig 9: Units missing. Wouldn’t it be the purpose of the sensitivity study to distinguish between the performance of the four databases with respect to temperature errors propagating into the retrieved CH_4 columns? From Fig.9 I cannot find any conclusive hint in that regard. Fig. 10 is more useful.

We have placed units in the titles of Figure 9, which is now in Appendix C. In order to address your comment about distinguishing between the performance of the perturbed and non-perturbed we have now included tables indicated the

biases between spectroscopic databases as well as the biases between windows. These results are compared against those identified in sect 3.3 in order to comment on the direct impact of implementing these a priori/parameter errors. These results are discussed in sect 3.5.2.

P24 Fig 10: “perturbed pressure column retrievals” Isn’t it temperature perturbation?

Thank you yes, this has been corrected. This figure has also been moved to Appendix C.

I do not comment on many editorial issues: acronyms need to be defined at first usage, jargon of the spectroscopic or TCCON community should be avoided, inconsistent use of parentheses when referencing, extensive use of the empty word “value”

We have carefully re-read the paper to address your comments.

References

- Hu, H., Hasekamp, O., Butz, A., Galli, A., Landgraf, J., Aan De Brugh, J., Borsdorff, T., Scheepmaker, R. and Aben, I.: The operational methane retrieval algorithm for TROPOMI, *Atmos. Meas. Tech*, 9, 5423–5440, doi:10.5194/amt-9-5423-2016, 2016.
- Wunch, D., Toon, G. C., Blavier, J.-F. L., Washenfelder, R. A., Notholt, J., Connor, B. J., Griffith, D. W. T., Sherlock, V. and Wennberg, P. O.: The Total Carbon Column Observing Network, *Phil. Trans. R. Soc. A*, 369, 2087–2112, doi:10.1098/rsta.2010.0240, 2011.