On the consistency of methane retrievals using TCCON and multiple spectroscopic databases.

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Abstract. The next and current generation of methane retrieving satellites are reliant on the Total Carbon Column Observing Network (TCCON) and other similar systems for validation, and understanding the biases between satellite and TCCON methane retrievals is as important as when TCCON started in 2004. In this study we highlight possible biases between different methane products by assessing the retrievals of the main methane isotopologue $^{12}CH_4$.

Using the TCCON GGG2014 retrieval environment, retrievals are performed using five separate spectroscopic databases from four separate TCCON sites (namely, Ascension Island, Ny-Ålesund, Darwin and Tsukuba). The Spectroscopic databases include the TCCON GGG2014 and GGG2020 spectroscopic databases; the HIgh-resolution TRANsmission molecular absorption database 2016 (HITRAN2016); the Gestion et Etude des Informations Spectroscopiques Atmosphériques 2020 (GEISA2020) database; and the ESA Scientific Exploitation of Operational Missions - Improved Atmospheric Spectroscopy (SEOM-IAS) database. We assess the biases in retrieving methane using the standard TCCON windows and the methane window used by the Sentinel 5-Precursor (S5P) TROPOspheric Ozone Monitoring Instrument (TROPOMI) for each of the different spectroscopic databases. We further assess the sensitivity of these biases to locally changing atmospheric conditions such as water vapour and temperature.

We find significant biases when compared to standard TCCON retrievals, in some cases up to ∼x3 the retrieval noise limit depending on the window and database. We also find strong evidence that different windows in different spectroscopic databases exhibit different levels of sensitivity to changing local conditions such as light path length and water vapour. Such that inter-comparisons between different instruments using different retrieval windows should take these sensitivities into account. Based on cross-comparison studies with the standard TCCON methane windows, retrievals using the S5P/TROPOMI spectral range show results as reliable as the operational TCCON products. We therefore recommend that this TROPOMI methane window should be considered in future TCCON methane retrievals.

1 Introduction

Methane is widely acknowledged to have a significant impact on the global climate (IPCC, 2014), but the processes via which it enters and is removed from the atmosphere are still poorly understood, with bottom up (scaled up in-situ measurements) estimations of the global methane budget not agreeing with top down estimations (models) (Kirschke et al., 2013; Saunois et al., 2019). This disconnect is one of many reasons that has led to the development of multiple satellite missions, with the aim of improving the knowledge of the global methane budget.

The launch of the S5P satellite, with the TROPOMI instrument (Veefkind et al., 2012), and the future S5 mission with its Ultra-Violet Near infrared Shortwave infrared (UVNS) instrument (Ingmann et al., 2012), represent a significant advancement in space-based Greenhouse Gas (GHG) remote sensing, building on a decade of progress from the Greenhouse Gases Observing Satellite (GOSAT) (Yoshida et al., 2013). Unlike GOSAT, TROPOMI and UVNS exploit the $4190 - 4340$ cm^{-1} spectral range, which has not been explored in detail from previous space-based instruments for methane retrievals. The Scanning Imaging Absorption spectrometer for Atmospheric CartograpHY (SCIAMACHY) (Bovensmann et al., 1999) onboard the ENVIronmental SATellite (ENVISAT) was sensitive to this spectral range, but was plagued with detector issues (ice build-up). The Measurements Of Pollution In The Troposphere (MOPITT) instrument (Drummond and Mand, 1996) is also sensitive to this spectral range, but is also affected by technical issues and has never successfully retrieved methane in this spectral window. The follow-on to GOSAT (GOSAT-2) also uses this spectral range; processing for GOSAT-2 is currently on-going. In addition, the wide spectral sensitivity of the limb viewing Canadian Atmospheric Chemistry Experiment (ACE)- Fourier Transform Spectrometer (FTS) (Bernath et al., 2005) includes this spectral window, but again the methane products of ACE-FTS do not include retrievals in this window. S5P/TROPOMI and S5/UVNS will therefore be relying on spectroscopic parameters for which only limited experience is available in their application to space-based methane retrieval instruments (Checa-Garcia et al., 2015; Galli et al., 2012). TCCON, although sensitive to this spectral range, has primarily provided its methane abundances retrieved from the 6000 cm^{-1} spectral range, allowing for direct comparisons with SCIAMACHY and GOSAT.

In this study, we make retrievals of the two main methane isotopologues using the TCCON GGG2014 (Toon, 2015) retrieval environment. Spectra are taken from four different TCCON sites in order to assess the impact of varying atmospheric conditions at different global locations. We assess the differences in abundances of the isotopologues and the quality of the fits when retrieved from standard TCCON spectral windows, and methane spectral windows in the TROPOMI/UVNS spectral range. We also quantify the variations in retrieval abundances when using five separate spectroscopic databases, and the application of non-Voigt line broadening shapes. The sensitivity of the retrievals to variations in water vapour concentration and path length are studies, allowing for the assessment of how differing windows and spectroscopic databases are sensitive to these variations.

TCCON is a global network of 27 ground based Fourier Transform Spectrometers (FTS) (Wunch et al., 2010), with the primary aim of providing reference total column (an weighted average value for a nadir viewing profile) abundances of numerous atmospheric species calibrated against aircraft profiles (Wunch et al., 2010, 2011), including methane, for validation and

cross-calibration purposes. TCCON operates in a wide spectral range (4000 – 11000 cm^{-1}) and records direct solar spectra.

55 TCCON is currently one of the key sources of reference data for the validation of satellite-based GHG retrievals, e.g. the Orbiting Carbon Observatory (OCO)-2, GOSAT and TROPOMI (Yoshida et al., 2011; Crisp et al., 2012; Lorente et al., 2021). TCCON instruments have both high spectral resolution (0.02 cm^{-1}), and high Signal to Noise Ratios (SNR) due to direct solar viewing geometry, and insensitivity to atmospheric scattering, thus making TCCON measurements higher quality than satellite measurements and excellent comparison datasets for satellite retrievals.

60 TCCON and TROPOMI/UVNS both have overlapping spectral windows in the Shortwave Infrared (SWIR) methane absorption regions, highlighted in Table 1.

Table 1. Methane SWIR windows commonality between S5P/S5 and TCCON

Methane window	S5P/TROPOMI	S5/UVNS	TCCON
5970-6289 cm^{-1}	N	Y	Y
4190-4340 cm^{-1}	Y	Y	Y

When validating methane products from TROPOMI and UVNS, retrieval products using the $4190 - 4340$ cm^{-1} window will be compared with TCCON methane products generated using the standard TCCON windows (Table 4). Therefore potential biases associated with the choice of fit windows should be quantified and understood. Indeed, if the $4190 - 4340$ cm^{-1} window

65 proves to be as accurate as the standard TCCON windows, then there is justification to integrate TCCON retrievals from this window into future TCCON retrieval products. In addition, numerous algorithms will be used to provide methane data products from TROPOMI/UVNS (Hu et al., 2016; Schneising et al., 2019), which may use differing spectroscopic databases and are therefore subject to differing biases. Building on examples of similar past studies (Checa-Garcia et al., 2015; Galli et al., 2012), the high SNR and high spectral resolution makes TCCON data an excellent resource to assess any potential

70 variations due to differences in the spectroscopic databases. By investigating the biases present in TCCON observations made at several sites over several seasons. We can infer some of the potential spectroscopic related biases in satellite retrievals, and their dependencies on local conditions such as water vapour that are relevant to ongoing TROPOMI validation, and future S5/UVNS validation.

In addition to assessing the window and spectroscopic source biases for the main methane isotopologues, the opportunity is

75 taken to calculate the δ^{13}C metric (see Eq 2). This is a metric that has been used in numerous studies globally to differentiate methane source types (Fisher et al., 2017; Nisbet et al., 2016; Rigby et al., 2017; Rella et al., 2015), e.g. fossil fuel burning or wetlands. Calculating total column values of this metric would be highly beneficial for understanding the global methane budget, but is unlikely to be achievable with TCCON with an accuracy that would be sufficient for that purpose. However, calculation of δ^{13}C with TCCON will allow for an assessment of how far current technology is from making a useful total

80 column assessment. δ^{13}C metric requires the concentration of the two main methane isotopologues ^{12}CH$_4$ and ^{13}CH$_4$, which make up roughly 99% and 1.1% of global atmospheric methane respectively. Almost all measurements of this metric are limited to in situ studies or airborne flask measurements, which although highly accurate, by their nature are spatially limited.

Some effort has gone into satellite based retrievals of this metric (Buzan et al., 2016; Weidmann et al., 2017; Malina et al., 2018, 2019), but the results of these studies show this to be a challenging task. Therefore the calculation of the $\delta^{13}C$ metric is a target of secondary importance in this study.

This paper is structured as follows, section 2 outlines the methods used in this study, including details about the TCCON sites and spectra used, as well as the retrieval method. Information about the spectroscopic databases used in this study are also given. The results of this study are shown in section 3 outlining the biases between sites and databases, including an assessment of the sensitivity of the retrievals to local condition variability. Section 4 discusses the results shown in sections 3, and conclusions are shown in section 5.

2 Methods, tools, datasets and requirements

2.1 TCCON sites used in study

We use TCCON spectra from four different sites identified in Table 2. Datasets over a single year were chosen in order to represent a wide range of seasonal conditions. The years chosen represent the years with maximum data coverage.

Table 2. TCCON sites used in this study.

TCCON Site	Lat/Lon	Date Range	Number of Spectra	Conditions
Ascension Island, Atlantic ocean	7.92°S, 14.3°E	Jan-Dec 2015	1518	Arid, little precipitation subject to some seasonal variation.
Darwin, Australia	12.5°S, 130.9°E	Jan-Dec 2020	39160	Tropical, significant water vapour background.
Ny-Ålesund, Spitsbergen	78.9°N, 11.9°E	April-Oct 2019	6315	Cold, dry, limited short-term variability.
Tsukuba, Japan	36.1°N, 140.1°E	Jan-Dec 2020	6162	Seasonal, cold dry winters, hot wet summers.

The mean background conditions for each site, as well as the variations over the dataset periods shown in Table 2 are indicated in Table 3. Significant variations in conditions and SZA are apparent between the TCCON sites, suggesting a wide

range of capture conditions. We note the distributions of the conditions shown in Table 3 may not be normally distributed, but these statistics serve as a useful baseline to show the condition variations between the sites.

Table 3. TCCON sites water vapour, temperature and SZA average and variation.

TCCON Site	Water Vapour mean $\pm\sigma$	Temp mean $\pm\sigma$	SZA mean $\pm\sigma$
Ascension Island	4510 ppmv $\pm$ 890	27.5 $°\pm$ 1	38°$\pm$ 18
Darwin, Australia	5430 ppmv $\pm$ 1740	30.9°$\pm$ 3	45°$\pm$ 18
Ny-Ålesund, Spitsbergen	1440 ppmv $\pm$ 600	1.7°$\pm$ 6	69°$\pm$ 8
Tsukuba, Japan	3200 ppmv $\pm$ 2470	22.9°$\pm$ 9	50°$\pm$ 18

2.2 GFIT Retrieval Algorithm

In this study we use the GGG2014 environment, which includes the GFIT retrieval algorithm (Wunch et al., 2010), which is summarised briefly here. GFIT employs a nonlinear least-squares fitting scheme: A forward model (radiative transfer model which simulates radiation transfer through an atmosphere or a body of gas) is used to calculate synthetic irradiance spectra based on a set of parameters known as state vector elements (typically trace gas concentrations) and model parameters (e.g. temperature and pressure profiles). These synthetic irradiance spectra are then fit to the measured irradiance spectra by adjusting the state vector elements to provide a final result, normally a trace gas abundance. In the case of GFIT the state vector can include the following.

- first target gas scaling factor (desired output).

- interfering gas scaling factor.

- continuum level of the irradiance spectrum.

- continuum tilt

- continuum curvature

- frequency shift

- zero level offset

- solar scaling (differences in shifts of atmospheric and solar lines)

- fit channel fringes

Note that not all of the above are not routinely included in the state vector, for example the continuum curvature especially is not commonly included in the state vector. This option is designed to remove instrument features, but may also attempt to

remove other effects due to the spectroscopic database, as noted in the TCCON wiki (TCCON, 2020). GFIT assumes a fixed profile shape for each trace gas, and the sub-column amounts for each altitude/pressure level are not independently scaled. Unlike in most satellite retrieval algorithms, aerosol and albedo terms are not included in the state vector, because TCCON operates in direct solar viewing, where scattering is considered unimportant and surface terms are not necessary. The retrieved trace gas column is calculated by multiplying scaling factors from the retrieved state vector by the a priori vertical column abundances. Dry air Mole Fractions (DMF) are calculated by dividing the scaled trace gas column with the total column O_2, retrieved from a wide window in the 7885 cm^{-1} spectral range multiplied by the volume mixing ratio of O_2 0.2095. DMF gas volumes identify retrieved abundances as mole fractions, as opposed to absolute concentrations, all retrieved $^{12}CH_4$ abundances are referred to as DMF values.

Because of the high spectral resolution of the TCCON instruments (0.02 cm^{-1}), most spectral lines are resolved, radiative transfer calculations are performed on a line-by-line basis. GGG includes a spectroscopic database in its environment, which is similar to other more widely adopted databases (see below). TCCON has a standard set of spectral windows for methane retrievals, all of which are in the 6000 cm^{-1} methane absorption window range. In this study we include the TROPOMI/UVNS SWIR spectral windows (4190-4340 cm^{-1}). This window along with a description of all of the windows considered in this study are described in Table 4 below.

Table 4. Spectral windows used in study.

Window	Window spectral range (cm^{-1})	Target species	Background species	Window source
1	4190-4340	$^{12}CH_4$	CO_2, H_2O, HDO, CO, HF, N_2O, O_3	Sentinel 5 baseline
2	5880-5996	$^{12}CH_4$	CO_2, H_2O, N_2O	TCCON standard
3	5996.45-6007.55	$^{12}CH_4$	CO_2, H_2O, N_2O, HDO	TCCON standard
4	6007-6145	$^{12}CH_4$	CO_2, H_2O, N_2O, HDO	TCCON standard

Windows 2-4 are standard TCCON methane retrieval windows which in this study are used for $^{12}CH_4$, and window 1 is based on the TROPOMI spectral window (Galli et al., 2012; Hu et al., 2016), given that no standard windows exist in this spectral window for TCCON. In addition, TCCON methane products are the result of a standardised process where a weighted average of three retrieved values from windows 2, 3 and 4 described in Table 4.

For $^{13}CH_4$ retrievals, windows 1 and 4 are used.

2.3 Spectroscopic Databases

We use parameters from five separate spectroscopic databases, which are as follows: 1) The database included with GGG2014 (Toon, 2015), which currently assumes a Voigt line shape for all lines. 2) The database included with the updated GGG2020 software, referred to in this study as GGG2020, which includes numerous updates to the GGG2014 spectroscopic parameters, and some application of non-Voigt parameters. 3) HITRAN2016, which is a well-established spectroscopic database that has

been used in numerous satellite based studies previously (Galli et al., 2012). Methane has been updated in the current release HITRAN2016 (Gordon et al., 2017) from the previous release (HITRAN2012), with new lines and parameters included for

145   both of the main isotopologues. HITRAN2016 includes the additional parameters required to model non-Voigt lines shapes, however the current version does not include these parameters for methane (at the time of writing). 4) The GEISA2020 database (Delahaye et al., 2021) is another spectroscopic database, similar in design and goals to the HITRAN databases. The GEISA database does not currently include non-Voigt line shape parameters. 5) SEOM-IAS (Birk et al., 2017), specifically developed for the TROPOMI spectral window and designed around non-Voigt atmospheric line shape profiles. This database only has

150   data within the 4190-4340 cm^{-1} spectral range, and can therefore only contribute to window 1 of this study.

For clarification purposes, there are no official releases of the spectroscopic parameters used in the GGG TCCON retrievals. We refer to the databases used in this study as GGG2014 and GGG2020 in order to differentiate with them, based on the GGG retrieval environment releases, with GGG2020 due for release in the near future (Laughner et al., 2021).

Some work has been performed previously comparing spectroscopic databases e.g. (Jacquinet-Husson et al., 2016; Armante

155   et al., 2016), generally indicating that the need to resolve differences between spectroscopic databases remains. Yet none have specifically targeted the TROPOMI SWIR spectral region, therefore this study is the first case with respect to the TROPOMI spectral window with TCCON.

Further to exploring the impact of differing spectroscopic database parameters, we investigate the use of non-Voigt broadening parameters. Ngo et al. (2013) find the standard Voigt profiles used for spectral line broadening may be inadequate for trace

160   gas retrievals (based on laboratory studies), which can lead to errors larger than instrument precision requirements. In order to calculate more accurate line shapes for remote sensing purposes, numerous models have been proposed. In this paper we use the quadratic Speed Dependent Hard Collision (qSDHC) model (Ngo et al., 2013; Tran et al., 2013). This model includes additional parameters based on speed dependence of collisional broadening and velocity changes of molecules due to collisions, on top of the standard parameters of pressure-induced air broadening, and pressure induced line shift. Note that only the

165   SEOM-IAS database uses these additional parameters, the remaining spectroscopic databases do not include these parameters for methane at the time of this paper. We use the FORTRAN routines provided with Ngo et al. (2013) to implement the qSDHC model into the GFIT algorithm, modified to include first order Rosenkranz line mixing effects. Mendonca et al. (2017) report that incorporating speed dependent and line mixing has a significant effect on calculated methane columns when compared against assuming Voigt dependency. They find a 1.1% difference in total methane column abundances from 131,124 spectra.

170   The implication is that it is important to account for the additional physical parameters included in non-Voigt models, when retrieving methane.

We note the introduction of $^{13}CH_4$ into spectroscopic databases in the TROPOMI spectral region is relatively recent, and in the case of HITRAN, was only introduced in the 2012 release (Brown et al., 2013), thus suggesting that $^{13}CH_4$ spectroscopic parameters may retain high levels of uncertainty.

2.4 Analysis structure and metrics

The following section describes the assessment metrics used in this study. Firstly we assess the quality of the fit of the measured and modelled spectra for each window indicated in Table 4 for each spectroscopic database at each TCCON site. The quality of the fit is expressed through Root Mean Square Error (RMSE) of the residual between the calculated transmission spectra, and the TCCON measurement transmission spectra, and the χ^2 test, quantitatively defined as:

$$\chi^2 = \sum_i [\mathbf{y_{measured}} - \mathbf{y_{calculated}}]^2.$$

(1)

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Where $\mathbf{y_{measured}}$ refers to the measured TCCON spectrum, and $\mathbf{y_{calculated}}$ is the synthetic spectrum calculated by the forward model. Secondly we assess the variance of the calculated DMFs of $^{12}CH_4$ for each window, spectroscopic database and TCCON site w.r.t the standard methane window used in TCCON retrievals currently, which is a weighted average of windows 2, 3 and 4. This variance is described through the RMSE of the residual between the retrieved DMF of $^{12}CH_4$ for a specific window and the retrieved DMF of the standard TCCON retrieval window, normalised by dividing by the retrieval error of the standard TCCON retrieval window (NRMSE). The variance is also given by the absolute mean residual between the retrieved DMF of $^{12}CH_4$ for a specific window and the retrieved DMF of the standard TCCON retrieval window, normalised by dividing by the retrieval error of the standard TCCON retrieval window (NAmean).

Following the assessment of the retrieval variance between windows and databases, we investigate if locally changing conditions impact biases between spectroscopic databases and windows. Variations in the retrieval conditions throughout the course of a day of measurements are included in TCCON error budgets, for example artefacts can appear in TCCON retrievals at extreme SZA values (Wunch et al., 2011).

We therefore investigate if the methane retrieval biases vary with respect to the following local parameters 1) SZA, where extreme angles can cause errors in the air-mass assumptions and affect characteristics of the Instrument Lineshape function (ILS) (Wunch et al., 2011). 2) Water vapour (retrieved by TCCON) through the course of a day at a range of TCCON sites. The GFIT retrieval algorithm is a scaling retrieval algorithm for all trace gas fitting, meaning that an incorrect apriori trace gas profile shape will yield errors in the retrieval. The GFIT water vapour apriori is based on a profile taken at midday for each specific retrieval, meaning that any significant variations from this daily profile will yield errors in the retrieval, that will vary depending on the impact of water vapour on a specific spectral window. 3) Temperature, which is not included in the retrieval state vector and dependencies on temperature will not be removed in the retrieval process. Temperature errors are introduced through the spectroscopic cross sections (An et al., 2011), therefore poor knowledge of spectroscopic parameters will potentially lead to temperature based errors.

These dependencies are quantified by identifying the possible existence of a linear correlation (using Pearson correlation coefficient and linear fit gradient) between the variations of water vapour, SZA and measured temperature against the bias between the retrieved methane isotopologue DMFs for each window and spectroscopic database, against the DMFs from the standard TCCON methane retrieval window normalised by the noise from the standard TCCON methane retrieval window.

The magnitude of the metrics defined above can be put into context by comparisons with the TCCON error budget. TC-CON typically aims for precision of <0.3% on methane retrievals, and has a rough estimate of 1% systematic uncertainties (dominated by in-situ calibration which can affect sites differently (Wunch et al., 2015)). Therefore it is possible to judge the variation of $^{12}CH_4$ DMFs between windows and databases based on these biases and precision.

Finally, although the quality of the $^{13}CH_4$ fit metrics in this study are not covered in detail, we instead calculate the $\delta^{13}C$ metric in order to understand the plausibility and variation of retrieving $^{13}CH_4$ from TCCON. Fundamentally the final aim of retrieving $^{13}CH_4$ is to calculate $\delta^{13}C$. How much $\delta^{13}C$ 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‰ in $\delta^{13}C$ is required in order to determine natural annual variability at the surface. However, variability in $\delta^{13}C$ can be higher in the troposphere and stratosphere due to variability of the OH sink and the fractionation caused by OH (Röckmann et al., 2011; Buzan et al., 2016), with evidence that $\delta^{13}C$ can vary by up to 10‰ in different air parcels (Röckmann et al., 2011). Based on these factors, we assume a rough total column $\delta^{13}C$ variability of 1‰, which equates to a total uncertainty of <0.02 ppb on $^{13}CH_4$ retrievals, or roughly 0.1% of the total column. This is clearly an unrealistic target for individual retrievals, given the uncertainty requirements for $^{12}CH_4$ 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‰ $\delta^{13}C$.

$$\delta^{13}C = \left(\frac{(^{13}CH_4/^{12}CH_4)_{sample}}{(^{13}CH_4/^{12}CH_4)_{VPDB}} - 1 \right) \times 1000‰, \tag{2}$$

where VPDB refers to Vienna Pee Dee Belemnite, an international reference standard for ^{13}C assessment. Tropospheric methane typically exhibits a $\delta^{13}C$ value of roughly -47‰ (Rigby et al., 2017), and total column measurements from TCCON should not deviate from this value to a significant degree. Therefore this tropospheric $\delta^{13}C$ value acts as a useful proxy, to determine the stability and variability associated with retrievals of methane isotopologues from different spectral windows, spectroscopic databases, location and time using the tropospheric $\delta^{13}C$ value as a baseline. In terms of $^{13}CH_4$, there are no published precision and accuracy requirements or statistics with TCCON.

3 Results

3.1 Quality of spectral fitting

An example of residual transmission spectra from the Ny-Ålesund site is shown in Fig 1, with the standard deviation of a selection of retrievals within the same time period indicated by the red lines. Qualitatively we note clear differences in the quality of the fits between windows and databases, for example there are clear deviations apparent, especially in window 1 for HITRAN and GEISA.

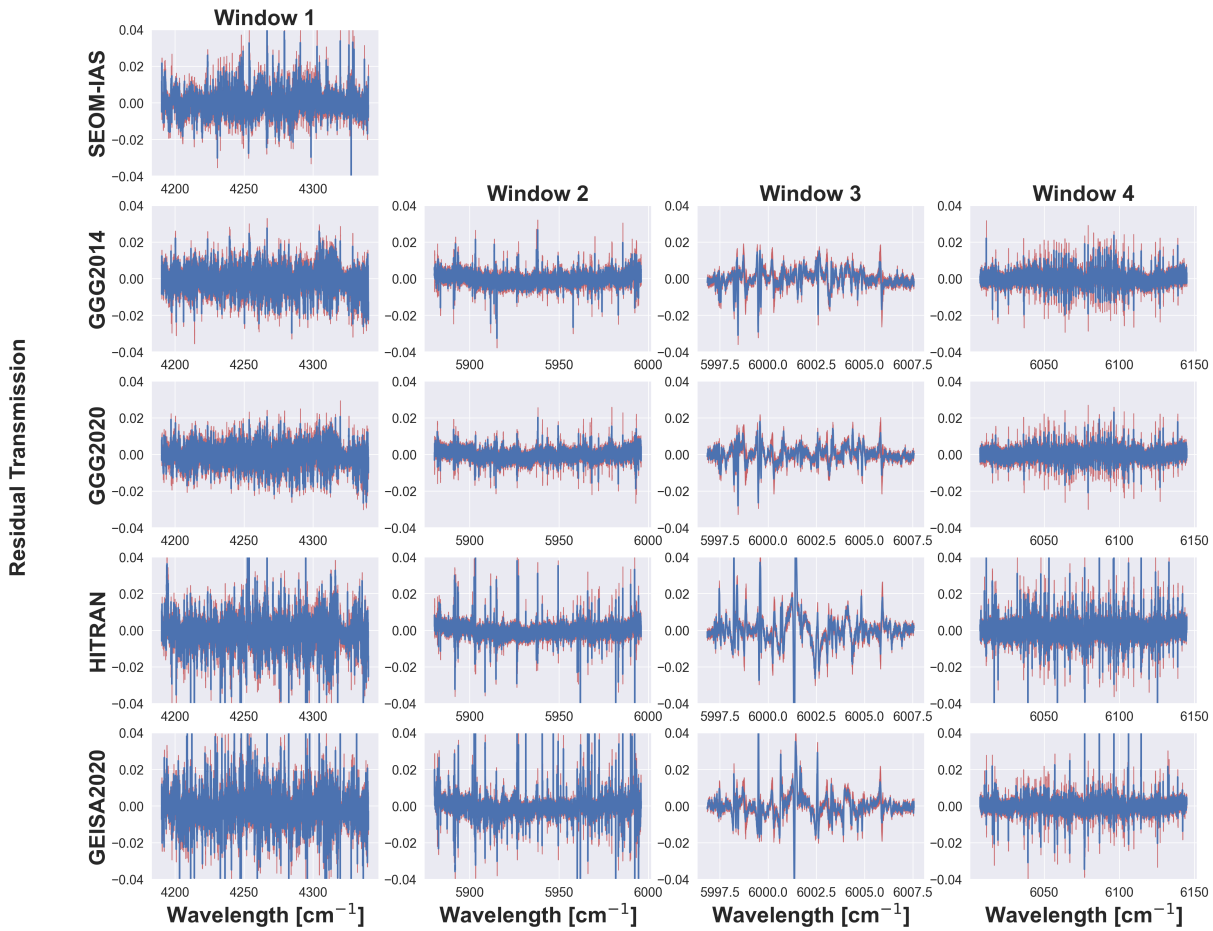



Figure 1. Example residual transmission spectra calculated from measured and fitted spectra from the Ny-Ålesund in 2019. The blue line indicates an example of the fit residual between the calculated transmission and the measured transmission. The red lines indicates the standard deviation of the residual, based on all spectra taken over the entire dataset. The columns of this figure identify the residuals of a specific window, and the rows a specific database, as identified in the axis labels.

The analysis statistics for the residual transmission spectra (as discussed in sect. 2.4) shown in Fig 1 are shown in Fig 2, as well as the associated statistics for the other TCCON sites considered in this study. What is clear from Fig 2 is the fit statistics for each spectroscopic database, irrespective of TCCON site and window generally have the same pattern in terms of quality. For window 1 SEOM-IAS usually has the best fit metrics (i.e. the lowest magnitudes), followed by GGG2020, GGG2014, HITRAN and then GEISA. In windows 2-4 where SEOM-IAS has no data, GGG2020 typically shows the highest quality fits, suggesting the latest iteration of the GGG2020 spectroscopic parameters has superior performance to the older version.

Window 1 typically shows the poorest fit metrics of all windows, possibly because it is the largest window, but also because it is more complex region in terms of absorption (Brown et al., 2013) than the other windows. Window 4 for example is also wide, but typically shows higher quality fits than any of the other windows in this study. The implication being that the

knowledge of spectroscopic parameters in window 1 is still lacking in comparison to the traditional TCCON windows. There are differences in the metrics between TCCON sites, with Ascension Island showing poorer fits than any of the other sites, similar to Darwin. This is to be expected however since these instruments are not identical, and capture spectra under differing conditions. We note that all instruments are run according to TCCON specifications but their respective configurations are not exactly the same. This is normal and necessary as different sites need local adjustments to account for different local conditions such as altitude, humidity or cloud conditions. Most of the effects caused by such individual configurations are removed by the differential CO_2 and CH_4 DMF retrievals but will affect individual spectra. For example, in the case of Tsukuba and Ascension, the configuration effects cannot be compared directly except for detector noise, which turned out to be comparable. However, the signal on the detector of the Ascension Island instrument is at least 50% lower than that of the Tsukuba instrument.

Likely reasons are: 1) The Ascension FTS runs on a higher spectral resolution (0.014 cm^{-1} vs. 0.02 cm^{-1}) and a faster scanner speed (10 kHz vs. 7.5 kHz). Both reduce integration time per spectral pixel. 2) The illumination of the InGaAs detector on Ascension is kept low on purpose to avoid saturation. This setting cannot be readjusted in between site visits and has to last for months. Other sites may use similar techniques, and may vary depending upon need. 3) The solar tracker has known issues with pointing at the centre of the sun at low SZAs but cannot be replaced easily. In addition, dust buildup on the solar tracker mirrors reduces the reflectively of the mirrors quickly. They are cleaned weekly but a signal loss in the order of 20% over a few days is not uncommon.

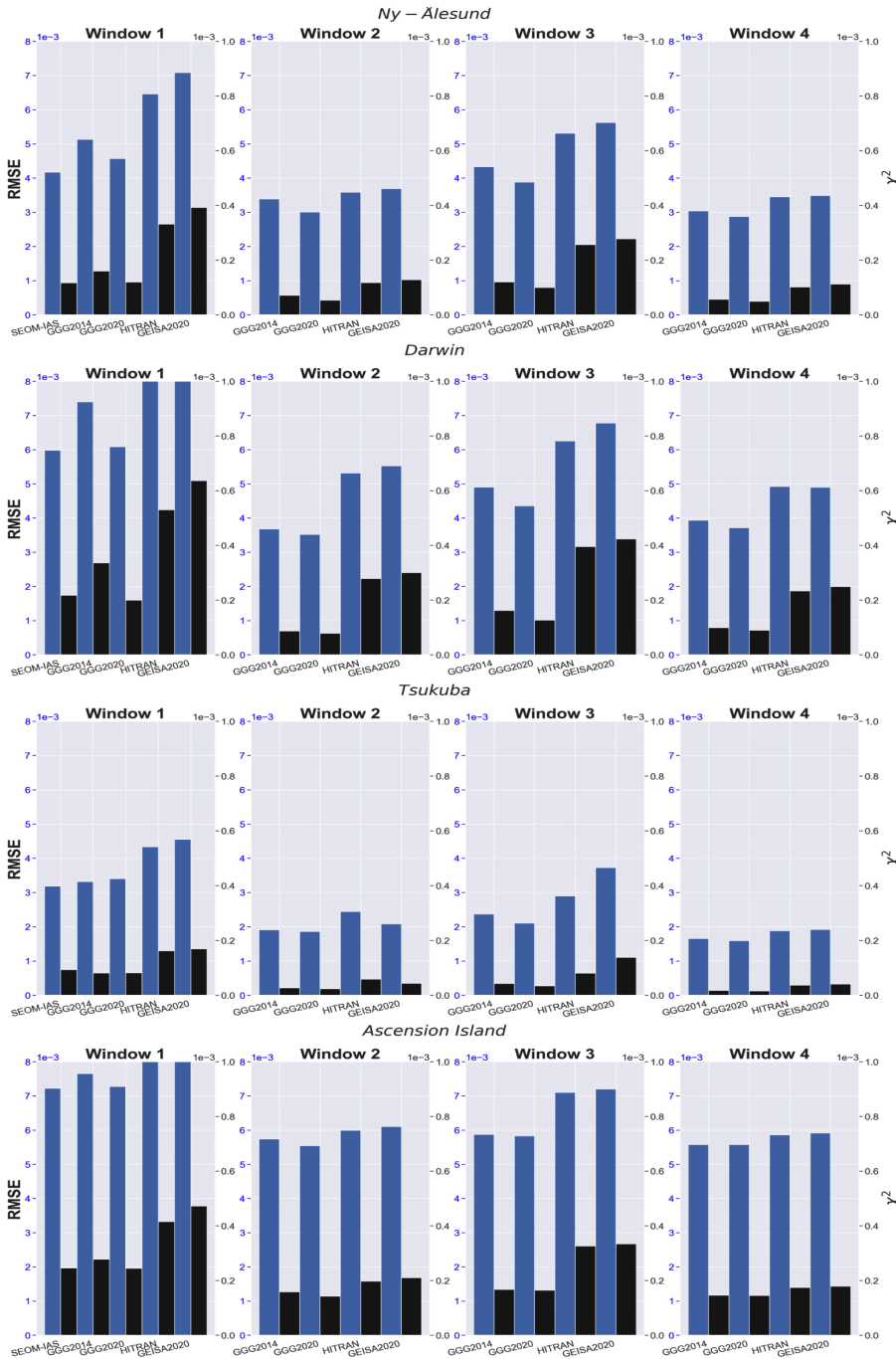



Figure 2. Bar chart indicating the fit statistics for a selection of retrievals from each of the TCCON site. Each row of the figure refers to results from each of the TCCON sites, indicated by the row title. Each column shows the results from each window, indicated by the title of each column. Each subplot shows the RMSE and χ^2 values for each spectroscopic database indicated in the x-axis, with the blue bars referring to the RMSE values, with magnitudes shown on the left-hand y-axis. The black bars refer to the χ^2 values, with the magnitudes indicated on the right-hand y-axis.

Since all trace gases are fit simultaneously in all of the windows, there no specific metrics associated with $^{13}CH_4$. $^{13}CH_4$ in this study is fit in windows 1 and 4.

265 3.2 Quantification of variance between windows and databases

The entire time series available for this study for each TCCON site are shown in Figs. 3, 4, 5 and 6. Qualitative inspection of these figures shows scatter between all windows for each database, further the HITRAN, GESIA and SEOM-IAS databases show significant positive bias w.r.t. the standard deviation of the reference TCCON retrieval, indicated by the dashed black lines. Quantitative metrics for these figures are shown in Fig 7.

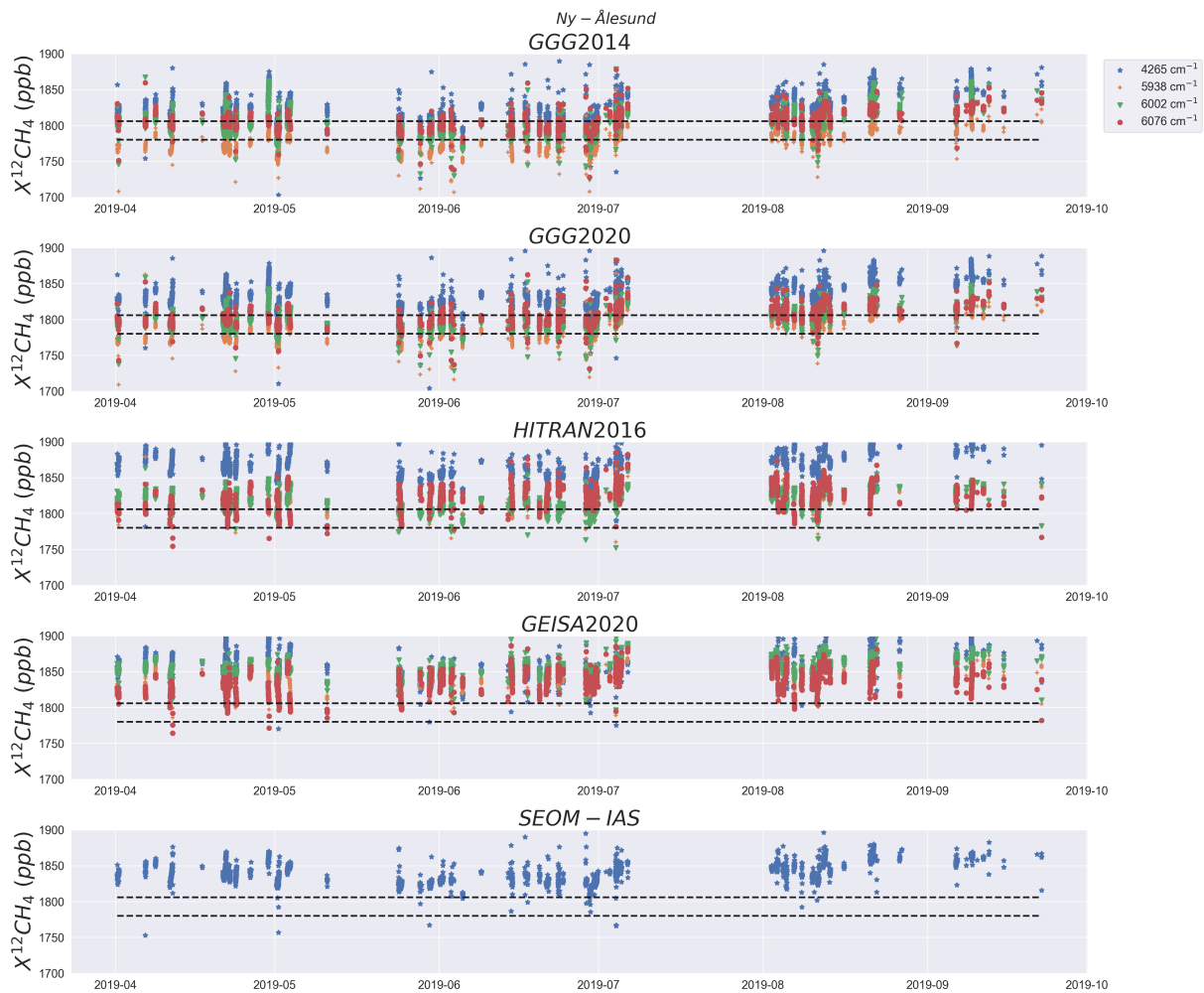



Figure 3. Retrieval time series for $^{12}CH_4$ DMFs from the Ny-Ålesund site. Each panel indicates retrievals from each spectral window (indicated in the legend) from a specific spectroscopic database, indicated in the panel title. Blue stars show retrievals from band 1, yellow pluses are band 2, green triangles are band 3 and red circles are band 4. The standard deviation about the reference TCCON retrievals are indicated by the horizontal dashed lines.

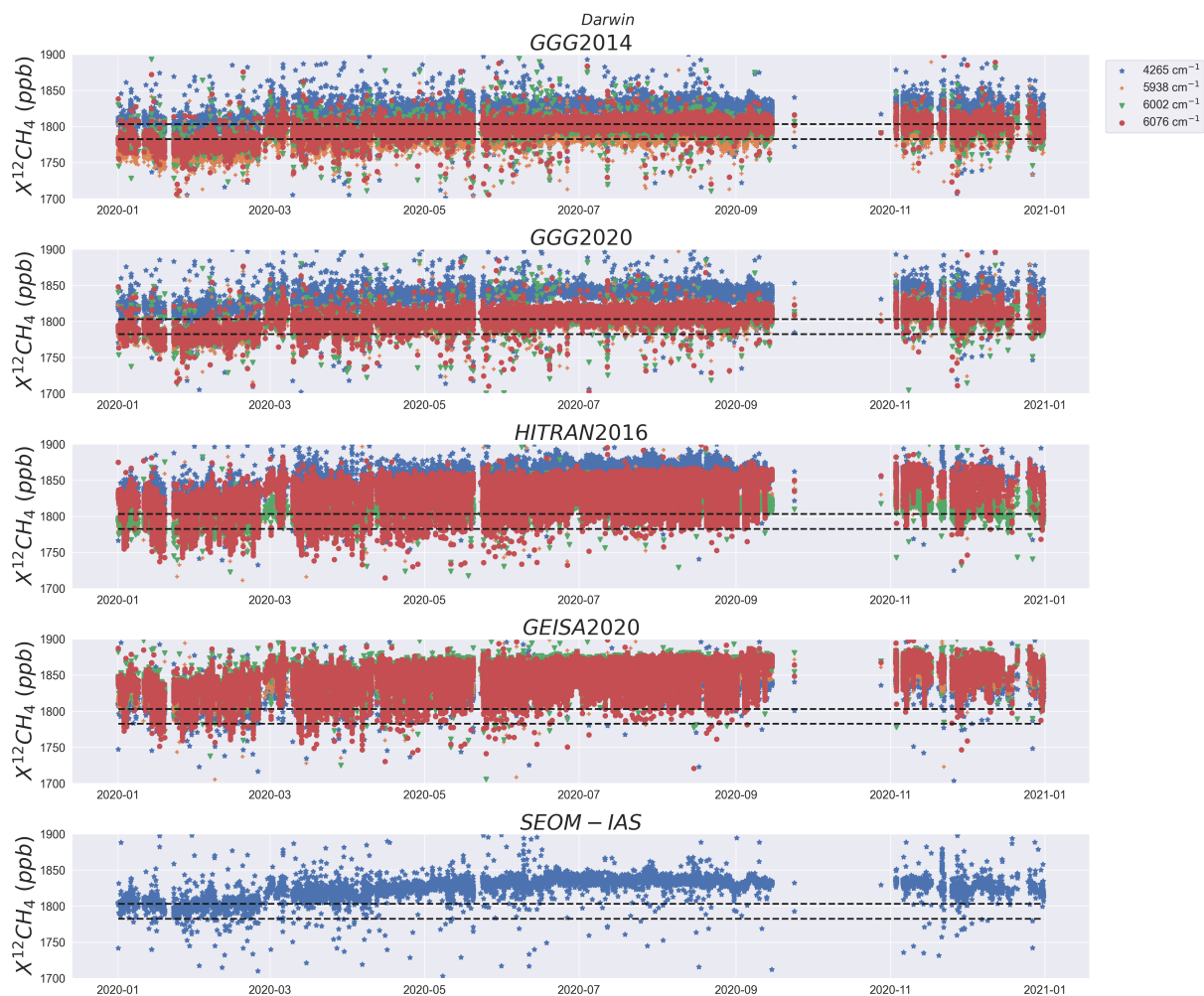



Figure 4. As Fig. 3, but for retrievals from the Darwin TCCON.

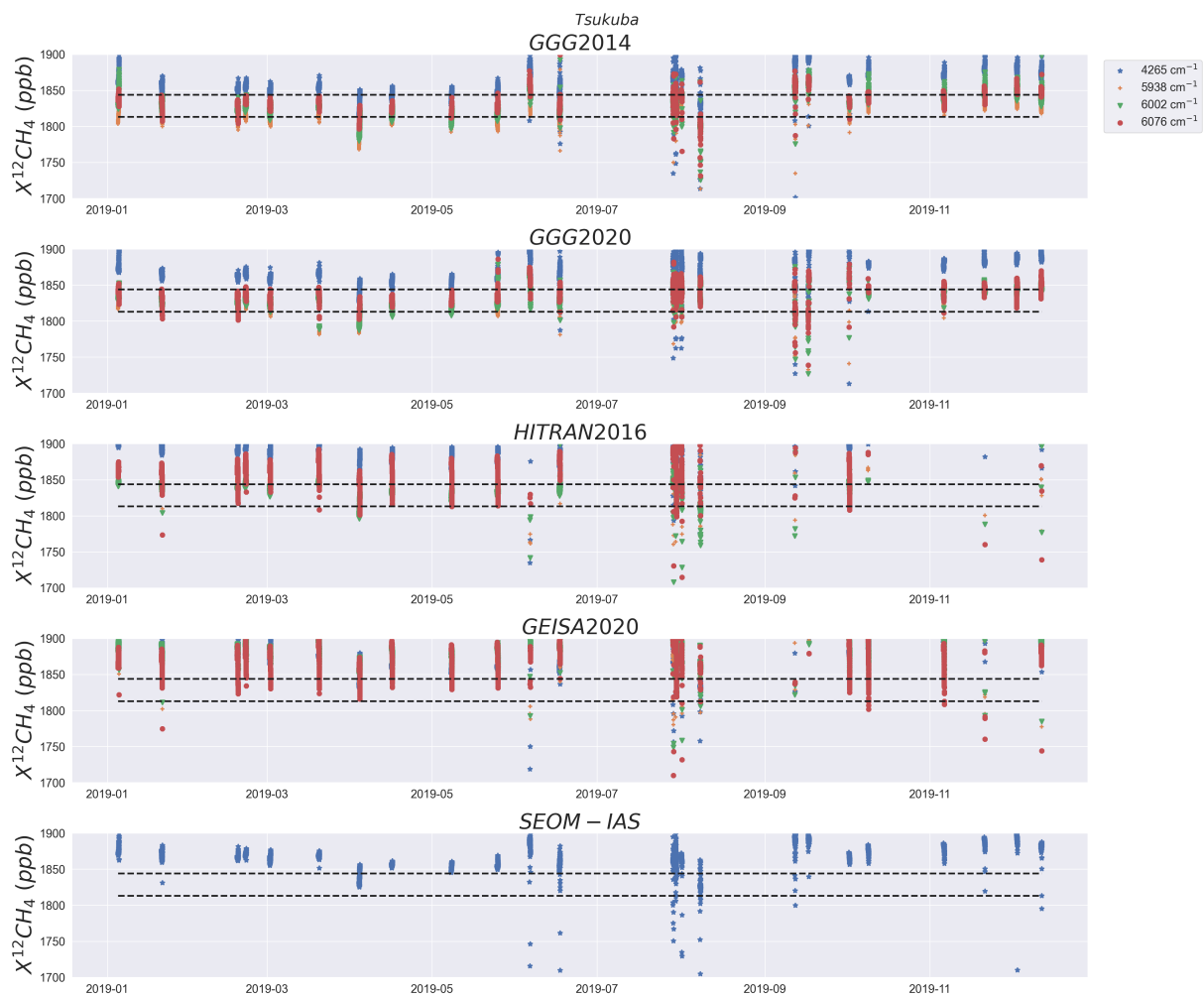



Figure 5. As Fig. 3, but for retrievals from the Tsukuba TCCON.

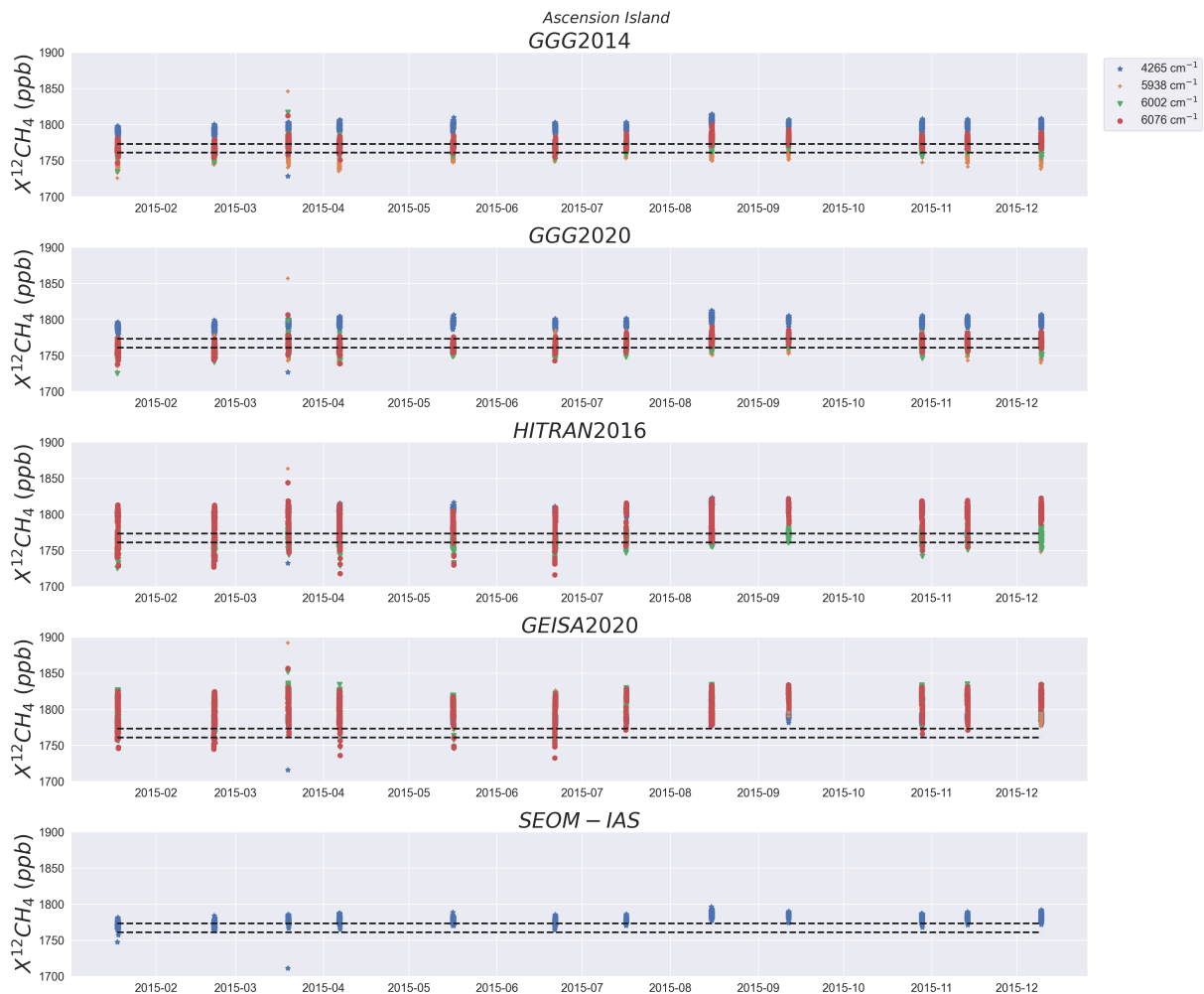



Figure 6. As Fig. 3, but for retrievals from the Ascension Island TCCON.

270   The metrics used in Fig 7 indicate the the bias for $^{12}CH_4$ retrievals each database and window w.r.t the reference retrieval (Norm Abs Mean), and the presence of any large deviations (RMSE). These metrics are normalised by the retrieval uncertainty of the reference retrievals a weighted average of windows 2, 3 and 4 from GGG2014, thus we assume any biases with values greater than 1 cannot be attributed to uncertainty and are therefore real.

Firstly the results from Ny-Ålesund, which due to the constant nature of the atmospheric conditions can be considered as a
275   baseline. For window 1, both the NRMSE and Norm Abs Mean values for all of the databases indicate values greater than 1, thus suggesting there are still significant variations in the treatment of spectroscopic parameters in window 1. The HITRAN and GEISA databases show bias deviations twice that of GGG2014, however these values do not indicate any one database is more accurate than the other, but either large differences in spectroscopic parameters or differences in sensitivity to local conditions. Windows 2 & 3 do not show any notable biases apart from the GEISA database which generally shows the largest

280 deviations across all of the windows (except window 1). In window 4, both HITRAN and GEISA show notable deviation from the reference retrievals, which is a surprising result given this window is popular in satellite retrievals of methane (Yoshida et al., 2013). We note the NRMSE and Norm Abs Mean values are similar in the majority of cases, indicating that there is an underlying bias between the database retrievals as opposed to large spikes of differences. Considering the bias deviations across the windows, GEISA is the only example to exceed values of 1 across all windows, with window 3 showing the largest

285 deviation from the reference value.

Secondly considering the dataset from Darwin, the magnitude of the NRMSE and Norm Abs Mean values are typically lower than the equivalents in the Ny-Ålesund dataset. The relative differences between the NRMSE and Norm Abs Mean values between the databases are the same as those shown in the Ny-Ålesund dataset, i.e. GGG2014 shows the lowest differences and GEISA shows the largest, apart from in window 1 in which case it is HITRAN. Investigating each window in turn, only

290 HITRAN shows a notable deviation from the standard in window 1 with GGG2020 and GEISA not indicating a significant deviation above the standard noise level (only 0.02 and 0.07 above 1 respectively). For windows 2 & 3, only the GEISA database shows a significant bias with respect to the standard, as with Ny-Ålesund site. Again in window 4 only the HITRAN and GEISA databases show notable deviation from the standard, again suggesting the spectroscopic parameters in window 4 still have significant uncertainty w.r.t windows 2 & 3. The implication of the Darwin results w.r.t those from Ny-Ålesund are

295 that either or both the differences in the instrument setup and the local conditions impact inter-window/spectroscopic database biases.

The results for the Tsukuba retrievals are very similar to those shown for Ny-Ålesund, with GGG2014 not showing any significant differences except in window 1, as with the other sites HITRAN shows deviation in windows 1 and 4, and GEISA showing the largest differences apart from in window 1. However, the main difference is with the GGG2020 database, as with

300 the other TCCON sites the normalised absolute mean shows deviation in windows 1 and 4, however the NRMSE indicates significant differences in all windows, suggesting there are a small number of retrieval cases that have large biases w.r.t the standard values. This behaviour is not replicated in the other TCCON sites.

Finally, all results from the Ascension Island measurements indicate no deviations of any significance, contrasting with the results from all other sides. We note the standard deviation about the reference TCCON retrievals in Fig 6 is smaller than any

305 of the other TCCON sites. This suggests constant retrievals in methane over the course of the year at Ascension Island, and therefore limited opportunity for biases to form.

The results in Fig 7 clearly indicate that in the cases where deviations exist, they are reflected in all of the TCCON sites (when significant), implying that despite the fit differences shown in Fig 2 these biases cannot (purely) be attributed to errors in the TCCON instruments, but given the consistency of the deviations we can attribute these differences to spectroscopic parameters.

310 Figure 7 indicates that there are significant differences between SEOM-IAS, GEISA and HITRAN databases w.r.t. the GGG databases, which show less deviation. This is not surprising since the reference values are based on GGG2014, and GGG2020 is built upon GGG2014, however this is not the case in window 1 where larger deviations are observed. This suggests that knowledge of spectroscopic parameters in window 1 is still not as settled as the other windows which have been routinely used in TCCON. It is difficult to assess all of the differences between the databases, due to the range of parameters used; there are

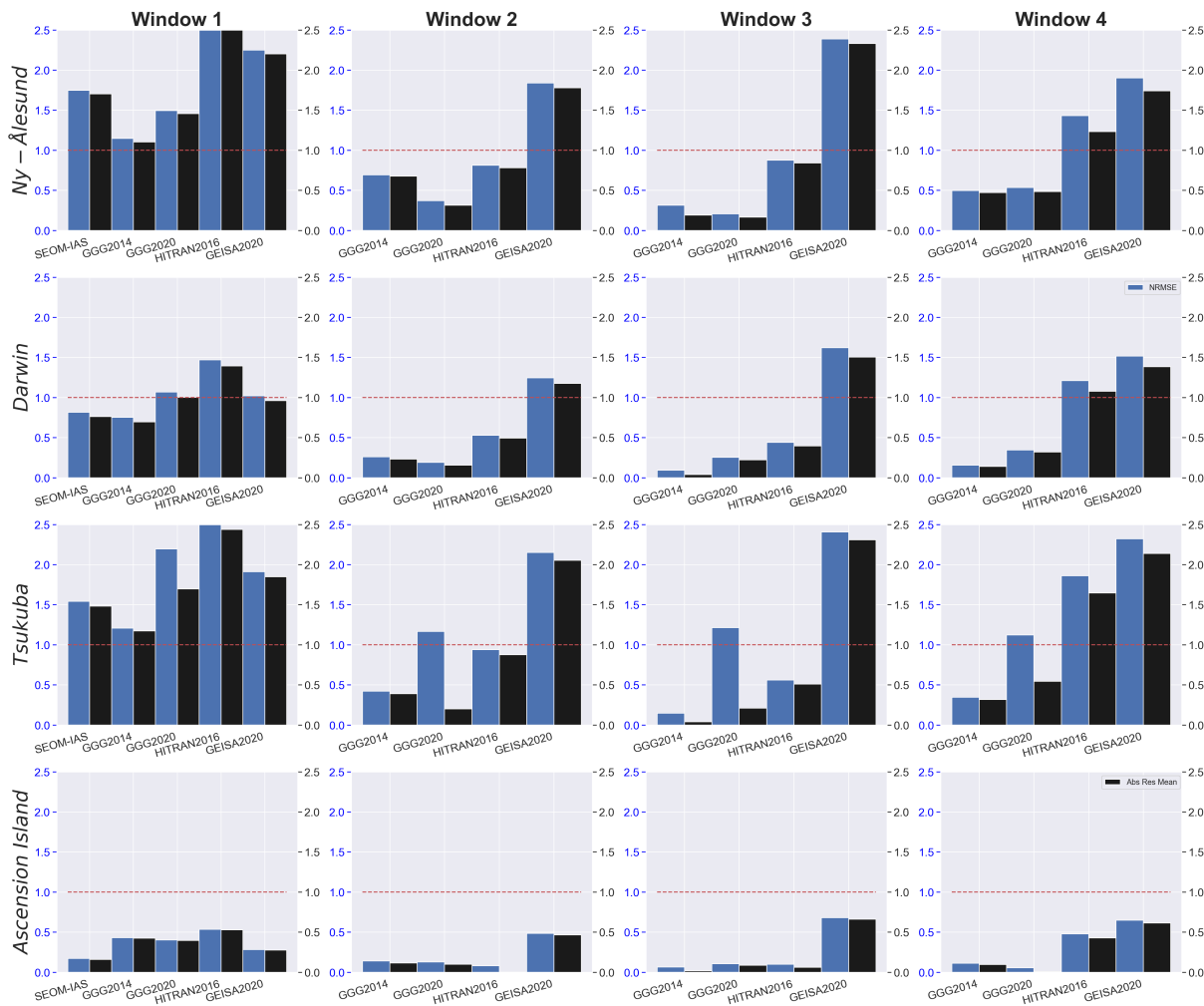
some papers which describe the sources of the spectral lines for each of the databases (Brown et al., 2013; Jacquinet-Husson et al., 2016), but specifics are limited due to the size of the databases. Complexity is added by the fact that several of these databases state that data is drawn from the same sources (Albert et al., 2009; Nikitin et al., 2015, 2017), however these papers go on to say that not all of the lines from these studies are implemented based on in house assessments of fit quality. The implication being that it is challenging to specifically identify where spectroscopic parameter differences occur between the

databases.

Figure 7. Bar plot indicating NRMSE and Normalised Absolute mean residual difference values for $^{12}CH_4$ retrievals from each TCCON site, each window and each spectroscopic database under consideration in this study with respect to the original TCCON methane retrieval window. Each row shows data from each TCCON site, as indicated by the y-axis titles, and each column shows results from each window, as indicated by the column title. Each subplot shows the NRMSE (the blue bars, magnitude shown by the left-hand y-axis) and Abs Res Mean (the black bars, indicated by the right-hand y-axis) values for each spectroscopic database as indicated by the x-axis. The horizontal red-dashed lines indicated the magnitude of 1, the value where we assume the bias values to be significant.

For $^{13}CH_4$ DMFs there is no obvious reference value available, since $^{13}CH_4$ is not typically retrieved from TCCON. We therefore chose to use GGG2014 window 1 as a reference in order to investigate window deviations. We found that apart from SEOM-IAS window 1 which showed deviation below the noise level from every TCCON site, every other case showed notable levels of deviation ranging from 1.5-5. Here we cannot attribute these disagreements purely to spectroscopic differences since $^{13}CH_4$ retrievals will be subject to high noise levels.

3.3 Impact of local condition changes on variance between windows and databases

The TCCON sites used in this study were picked to have a wide range of conditions, with Ny-Ålesund capturing spectra in largely unvarying conditions with high SZA and low water vapour, while Ascension Island is similar in unvarying conditions although with higher background water vapour conditions and lower SZAs. This is contrasted by Darwin and Tsukuba which capture spectra under a wide range of SZAs and highly variable water vapour conditions (see Table 3). It has been shown (Wunch et al., 2011) that the variability of local conditions can have an impact on the accuracy of TCCON retrievals (through the apriori data). We therefore investigate in this section if varying local conditions (specifically, water vapour, SZA and temperature) affect each window in each spectroscopic database differently.

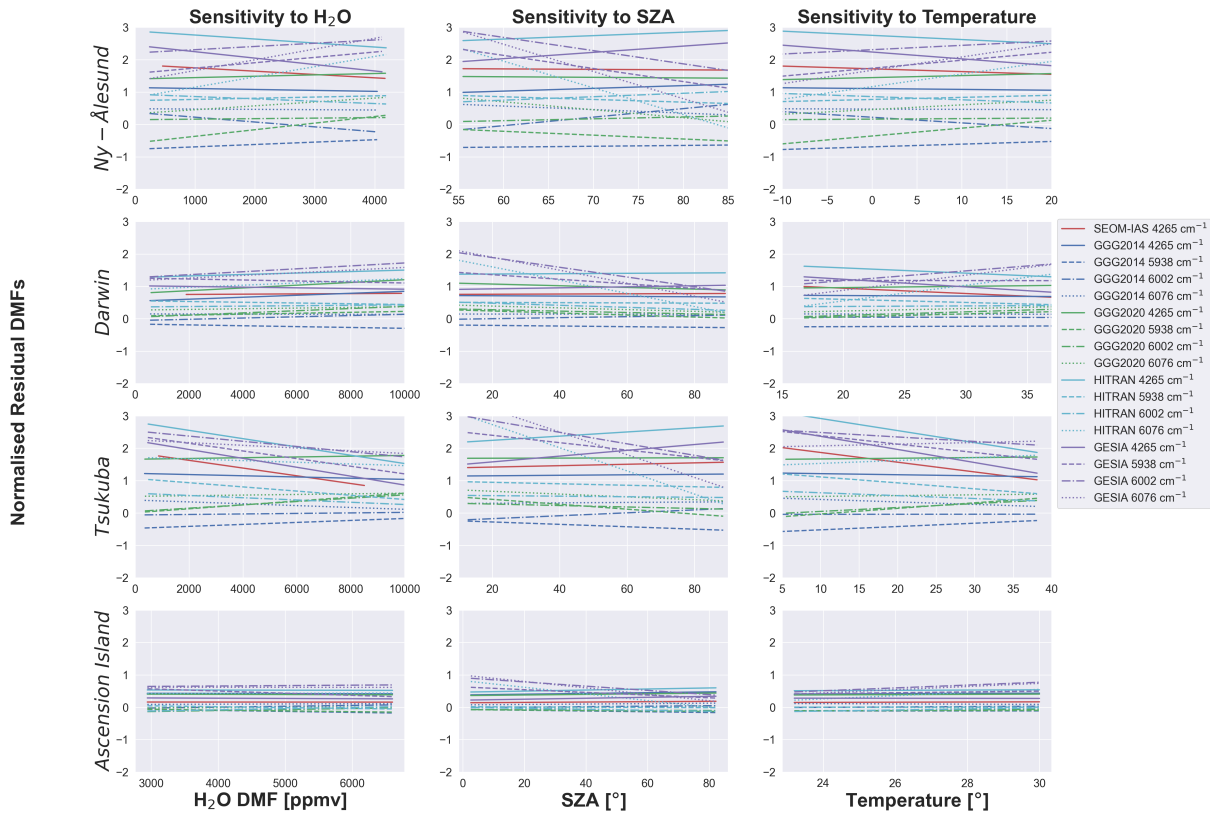



Figure 8. The sensitivity of water vapour, SZA and temperature variations on retrieved $^{12}CH_4$ DMFs from each TCCON site, spectroscopic database and windows. Each subplot shows the linear fit of the normalised residual between the retrieved window/spectroscopic database DMFs and the TCCON reference DMFs, with the fit window and spectroscopic database indicated by the legend. Each row of the figure shows data from each TCCON site as indicated in the y-axis, and each column shows the sensitivity to a specific condition as shown in the title.

The qualitative distributions indicated in Fig. 8 are explored quantitatively in more detail in Figs 9, 10, and 11. First considering the impact of SZA variations in window 1 across all sites, there is no clear pattern in the correlations. For example, GGG2014 at Ny-Ålesund and Ascension Island shows a weak correlation of ∼0.25, yet no correlation at either Darwin and Tsukuba. This pattern is repeated for all databases except GEISA2020, which shows a weak correlation across all TCCON sites. For window 2 we see weak to strong correlation in all databases across all sites, except for a few cases (e.g. HITRAN at Darwin and Ascension Island). Window 3 shows high levels of correlation to SZA variations w.r.t. all sites, with Ny-Ålesund and Ascension Island showing particularly notable correlations, especially in the GGG2014 and GEISA2020 databases. Window 4 shows large correlations for all databases in the Ny-Ålesund retrievals especially, but large negative correlations across all sites with the HITRAN and GEISA databases. Overall the results in Fig 9 indicate the retrieval biases w.r.t the reference TCCON retrievals are sensitive to SZA variations. The Ny-Ålesund site shows the largest sensitivity of all of the sites considered in this study. This could be explained by the fact that Ny-Ålesund operates at higher SZA angles than any of the other TCCON sites,

345 meaning the retrieval path length will be longer, potentially allowing for more errors to creep into the retrievals. However, the results from Ascension Island, which operates at lower SZAs than any of the other TCCON sites considered in this study also indicates large correlations, suggesting further complexity.

The sensitivity of each window to water vapour variation is explored in Fig 10. For window 1, there is weak sensitivity to water vapour variations at the Ny-Ålesund and the Darwin sites, with opposite databases showing greater sensitivity. The
350 Tsukuba site shows large negative correlations for the HITRAN, GEISA and SEOM-IAS databases, while Ascension Island shows very little correlation across all databases. Window 2 shows large correlation magnitudes, with the Ny-Ålesund and Tsukuba both showing correlations >0.5 in several cases. In general, all databases in window 2 shows correlation values >0.25 except for a small number of cases, most notably at the Darwin site. Different patterns are observed with windows 3, where Ny-Ålesund shows some significant negative correlations, while Ascension Island indicates sensitivity across all databases
355 (except GEISA). Darwin and Tsukuba show opposite behaviours with large positive correlations at GGG2014 and GGG2020 at Darwin, but large negative biases with the HITRAN and GEISA databases at Tsukuba. For window 4, notable correlations are observed for GGG2020, HITRAN and GEISA at Ny-Ålesund, but in general there are no other correlations of note across the other TCCON sites (except for GGG2014 at Tsukuba). These results are curious, we know Darwin, Tsukuba and Ascension Island have much higher background water vapour levels and variability ~x3 than Ny-Ålesund. Yet, Ny-Ålesund shows larger
360 correlation in some cases than any of the other sites with high water vapour concentrations. Tsukuba has a background water vapour content less than that of Darwin, but exhibits variability ~x2 that of Darwin, and for Tsukuba there is much greater indication of bias sensitivity to water vapour. Thus suggesting that the variability of water vapour in the atmosphere is more significant for retrieval biases, as opposed to high background levels.

The results for retrieval bias sensitivity to variations in temperature are shown in Fig 11. Comparisons of Figs 10 and 11
365 show similar results in both cases, for example, window 1 at the Ny-Ålesund site shows almost identical results. This suggests for the Ny-Ålesund site, water vapour and temperature variability occur on similar time scales, this result is expected as the atmosphere can hold more water with rising temperatures. Similar patterns are apparent at the Tsukuba site with some notable exceptions, although these exceptions occur in cases with low bias sensitivity (e.g. GGG2014 window 3), meaning these are unimportant. However, this similarity is not as apparent at the Darwin site, with window 3 showing higher retrieval
370 bias sensitivity to water vapour than to temperature variation. Indeed, Darwin does not indicate any cases with retrieval bias correlation >0.25, (unlike any of the other sites). The key exception to this pattern are the results from Ascension Island, where the values for water vapour and temperature sensitivity are significantly different. We note in this case that the temperature variation at Ascension Island (Table 3) is very small, which could explain these differences.

In general, there is no clear case of one window, database or TCCON site showing clear sensitivity over and above than
375 any of the others in all cases, meaning one site or database is not especially sensitive than the others. However there are clear indications of sensitivity to variations in the local conditions which vary between window, database and TCCON site, in some cases very strong correlations. In general, the pattern is that variability in the local conditions causes window and database biases, rather than extreme conditions by themselves. For example, Ascension Island has the least varying conditions of all of the sites, and also shows the most constant sensitivity to varying conditions. While Tsukuba has some of the most variable

380 conditions and also indicates some of the most variability when assessing water vapour variability. This assessment is not perfect, since Ny-Ålesund also shows significant dependence on local conditions, while having less variability than Darwin or Tsukuba. However, Ny-Ålesund spectra are captured at high SZA meaning lower SNR and more susceptibility to interfering elements.

We also note when calculating the Pearson's correlation coefficent for GGG2020 values for window 1 at the Tsukuba site, 385 large 'p' values were found, indicating these results are not statistically significant.

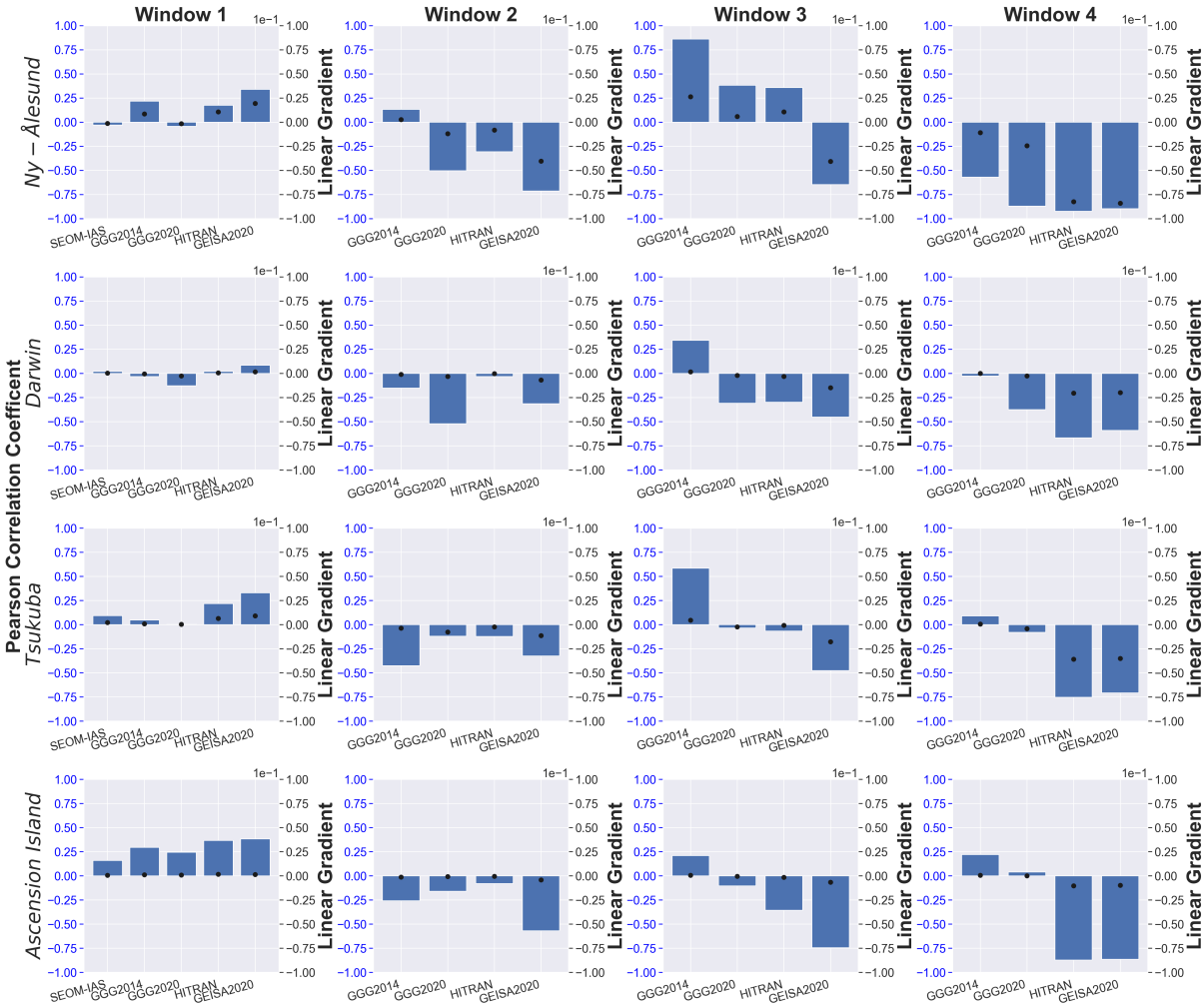



Figure 9. Bar chart indicating the statistics behind the sensitivities to SZA variations shown in Fig 8. Each row indicates the results from a TCCON site, as indicated by the y-axis label, each column shows the results from a particular window as shown by the column title. The blue bar plot show the Pearson correlation coefficent, with the left-hand blue y-axis values the appropriate scale. The black dots showing the linear gradient of the linear fits from Fig 8, with the right-hand black y-axis values as the scale.

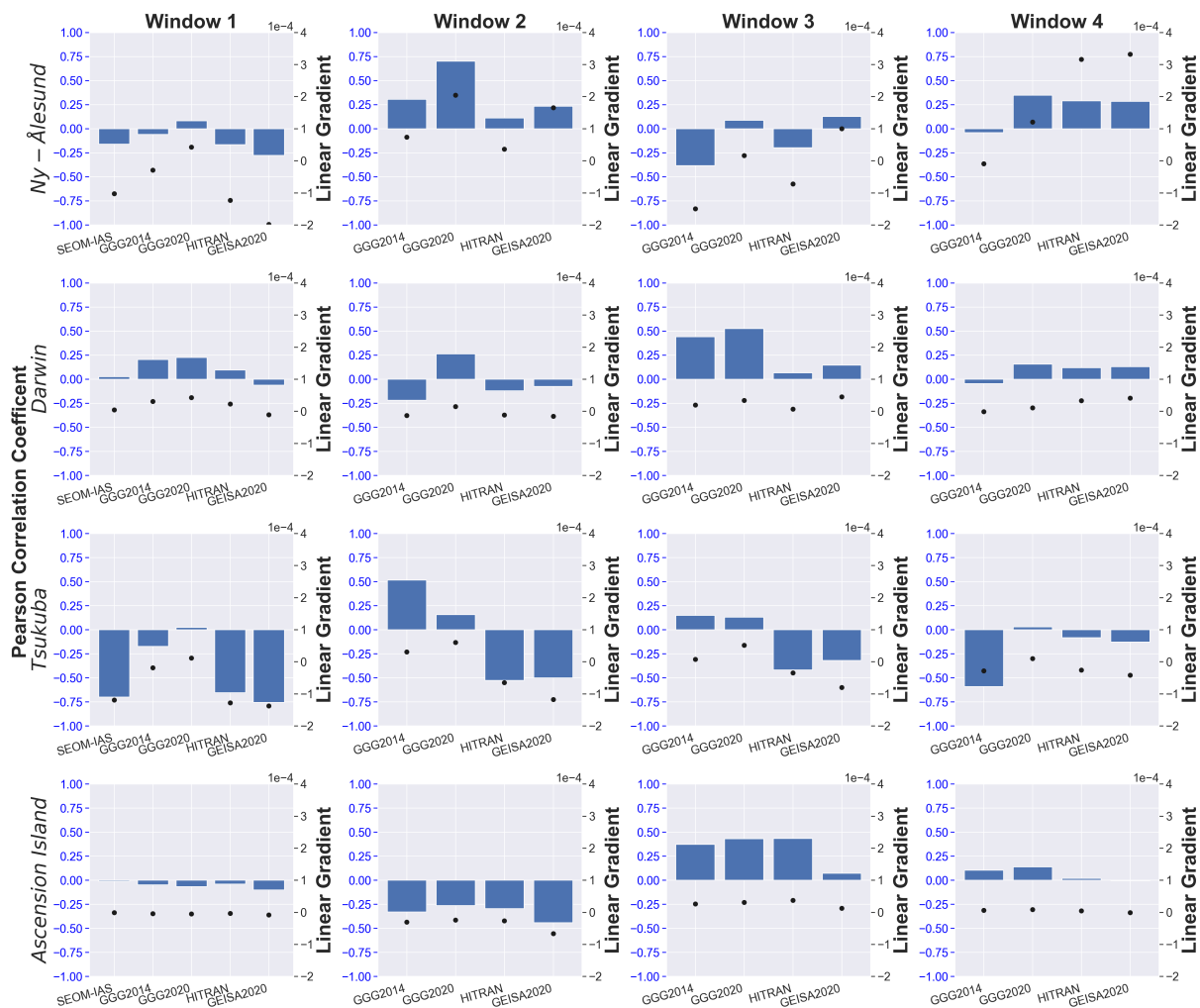



Figure 10. As Fig 9, but showing the sensitivities to water vapour variations.

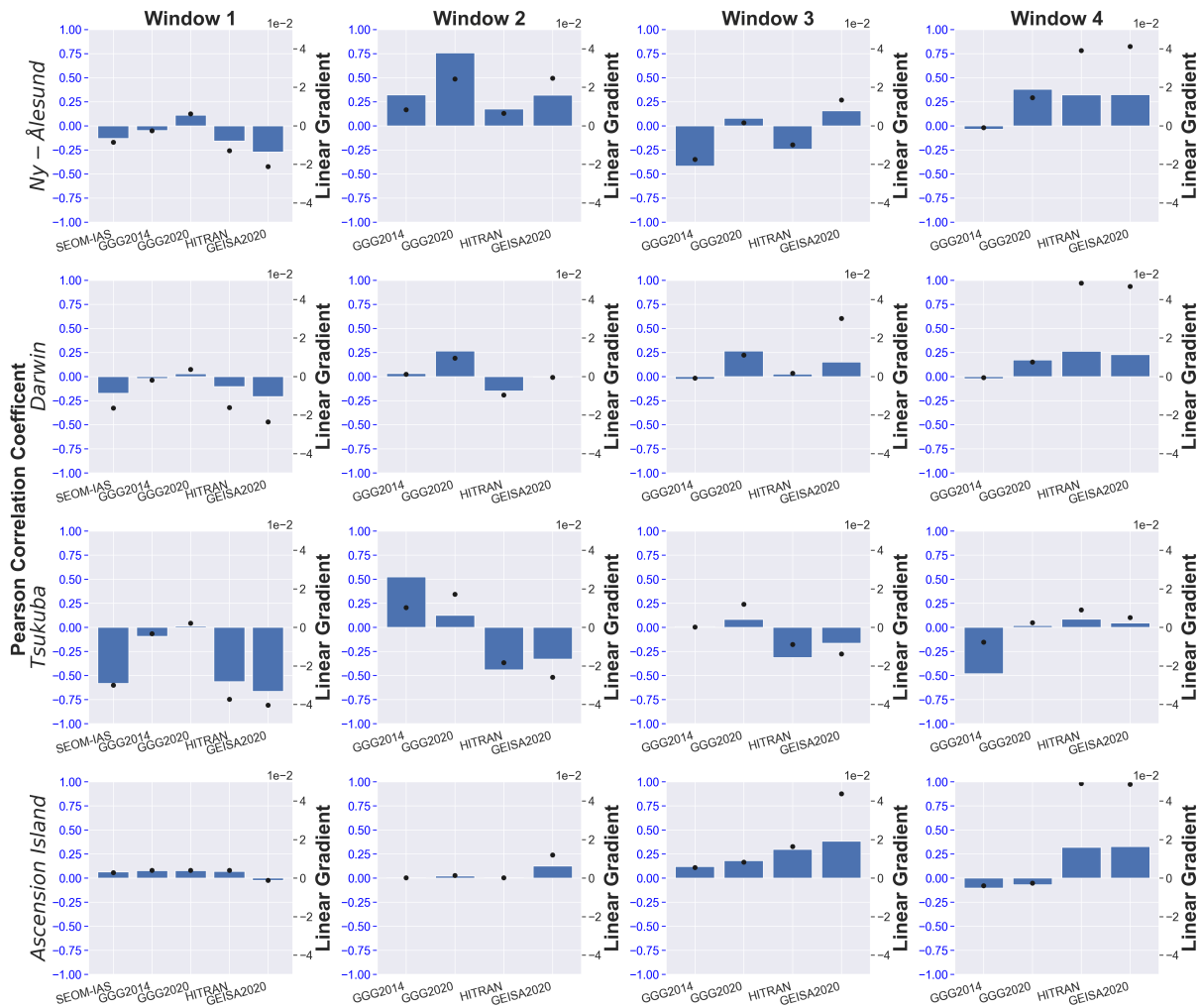



Figure 11. As Fig 9, but showing the sensitivities to temperature variations.

A similar analysis for retrieval bias sensitivities for $^{13}CH_4$ indicated high levels of sensitivity to SZA variation, especially those retrievals from Ny-Ålesund where SZAs are high. There are some windows that indicate no correlation, but the majority had values greater than 0.3. W.r.t water vapour and temperature variation, these results are mixed with different windows and databases at different sites indicating different results. However there is a general trend of sensitivity to water vapour and temperature variations, with only a small number of cases indicating no correlation. These results suggest $^{13}CH_4$ retrievals are more sensitive to changing conditions than $^{12}CH_4$, which is the expected result.

3.4 Calculation of $\delta^{13}C$ values

The calculation of the $\delta^{13}C$ values (Eq 2), can give some insight into the accuracy of $^{13}CH_4$ retrievals from TCCON, as well as the impact of local condition variations on these retrievals. $\delta^{13}C$ is calculated for all TCCON sites using all combinations of

windows from all databases in Table 5, using averaged $^{12}CH_4$ and $^{13}CH_4$ for the whole time series available for each TCCON site. There are two factors to look for in the calculation of $\delta^{13}C$, firstly the bias w.r.t. the accepted atmospheric average of -47‰ and the consistency of the calculated values across databases and windows.

Table 5. Averaged values of $\delta^{13}C$ from all TCCON sites for all possible $^{12}CH_4$ and $^{13}CH_4$ window combinations for each spectral database.

Windows $^{12}CH_4$ & $^{13}CH_4$	Windows 1 & 1	Windows 2 & 1	Windows 3 & 1	Windows 4 & 1
Ny-Ålesund	GGG2014: -102‰ GGG2020: -90.6‰ HITRAN: 8.98‰ GEISA: -66.4‰ SEOM: -91.3‰	GGG2014: -77.3‰ GGG2020: -66.1‰ HITRAN: 38.4 GEISA: -60.1‰	GGG2014: -89.5‰ GGG2020: -73.0‰ HITRAN: 37.3‰ GEISA: -67.6‰	GGG2014: -93.0‰ GGG2020: -77.1‰ HITRAN: 37.3‰ GEISA: -59.2‰
Darwin	GGG2014: -126‰ GGG2020: -78.1‰ HITRAN: -60.1‰ GEISA: -72.1‰ SEOM: -88.3‰	GGG2014: -107‰ GGG2020: -59.4‰ HITRAN: -39.9‰ GEISA:-76.5‰	GGG2014: -113‰ GGG2020: -60.8‰ HITRAN: -37.4‰ GEISA: -82.8‰	GGG2014: -63.0‰ GGG2020: -77.1‰ HITRAN: -52.1‰ GEISA: -80.2‰
Tsukuba	GGG2014: -125‰ GGG2020: -101‰ HITRAN: -52.7‰ GEISA: -71.1‰ SEOM: -77.3‰	GGG2014: -105‰ GGG2020: -81.8‰ HITRAN: -31.3‰ GEISA: -73.4‰	GGG2014: -109‰ GGG2020: -81.8‰ HITRAN: -26.3‰ GEISA: -76.7‰	GGG2014: -114‰ GGG2020: -86.1‰ HITRAN: -41.2‰ GEISA: -74.2‰
Ascension Island	GGG2014: -130‰ GGG2020: -89.3‰ HITRAN: -94.2‰ GEISA: -70.6‰ SEOM: -104‰	GGG2014: -113‰ GGG2020: -72.0‰ HITRAN: -76.1‰ GEISA: -77.1‰	GGG2014: -117‰ GGG2020: -72.6‰ HITRAN: -73.9‰ GEISA: -83.8‰	GGG2014: -120‰ GGG2020: -75.3‰ HITRAN: -90.5‰ GEISA: -82.1‰
Windows $^{12}CH_4$ & $^{13}CH_4$	Windows 1 & 4	Windows 2 & 4	Windows 3 & 4	Windows 4 & 4
Ny-Ålesund	GGG2014: 2.46‰ GGG2020: 9.08‰ HITRAN: -49.1‰ GEISA: -26.6‰	GGG2014: 29.7‰ GGG2020: 36.3‰ HITRAN: -21.3‰ GEISA: -20.0‰	GGG2014: 16.1‰ GGG2020: 28.6‰ HITRAN: -22.4‰ GEISA: -27.9‰	GGG2014: 12.2‰ GGG2020: 24.1‰ HITRAN: -27.2‰ GEISA: -19.1‰
Darwin	GGG2014: -117‰ GGG2020: -131‰ HITRAN: 65.3‰ GEISA: 134‰	GGG2014: -97.4‰ GGG2020: -114‰ HITRAN: 88.1‰ GEISA: 129‰	GGG2014: -103‰ GGG2020: -115‰ HITRAN: 91.0‰ GEISA: 121‰	GGG2014: -105‰ GGG2020: -117‰ HITRAN: 74.3‰ GEISA: 124‰
Tsukuba	GGG2014: -21.8‰ GGG2020: -26.7‰ HITRAN: 14.5‰ GEISA: 56.4‰	GGG2014: 0.953‰ GGG2020: -5.62‰ HITRAN: 37.5‰ GEISA: 53.8‰	GGG2014: -4.12‰ GGG2020: -5.66‰ HITRAN: 42.9‰ GEISA: 50.1‰	GGG2014: -9.03‰ GGG2020: -10.3‰ HITRAN: 26.9‰ GEISA:52.9‰
Ascension Island	GGG2014: -125‰ GGG2020: -140‰ HITRAN: 11.5‰ GEISA: 87.4‰	GGG2014: -107‰ GGG2020: -124‰ HITRAN: 31.8‰ GEISA: 79.9‰	GGG2014: -112‰ GGG2020: -124‰ HITRAN: 34.3‰ GEISA: 72.0‰	GGG2014: -115‰ GGG2020: -127‰ HITRAN: 15.6‰ GEISA: 74.0‰

Table 5 indicates a wide range of results, which is unsurprising given that we calculate the mean uncertainty on a $^{13}CH_4$ retrieval over all datasets at between 18-25%. However, given that the values indicated in Table 5 are averages, this uncertainty should reduce significantly (by $\sim$ x200 in the case of Darwin), meaning that the precision should be comparable to that of an individual $^{12}CH_4$ retrieval. Firstly considering the retrievals that use $^{13}CH_4$ from window 1, these combinations yield

surprisingly consistent results site to site and window to window, except for the HITRAN results which show significant bias at the Ny-Ålesund site, although this is contrasted by the HITRAN results at Darwin and Tsukuba which indicates values very close to what might be expected. Indeed, the results from HITRAN at Ny-Ålesund show results significantly different from those at any of the other sites, which can be explained by $^{13}CH_4$ retrievals showing significantly larger biases (at least x2 any other database), and a very high Pearson's correlation (0.7). The results from GEISA are the most consistent across the window combinations for all sites, showing a maximum of ~13‰ variation across all window combination which is a remarkable result. For comparison purposes, HITRAN shows ~25‰ variation, GGG2020 ~18‰ variation and GGG2014 ~25-60‰ variation. The variations between databases in the same window combinations are larger than those in-between windows, suggesting variable dependence on local conditions, and thus differences in spectroscopic parameters. Except for HITRAN, all of the databases and windows seem to underestimate the accepted $\delta^{13}C$ values.

The results for the $^{13}CH_4$ window 4 combination are highly varied, more so than those shown for the window 1 combinations. For Ny-Ålesund both the GGG2014 and 2020 results show high levels of bias and significant variation, while the HITRAN and GEISA results show much lower bias levels and generally consistent results, with the HITRAN window 1 4 combination showing a realistic result. This is contrasted by the results from Darwin, where large biases are observed from all of the databases, but similar levels of consistency between the window combinations. Tsukuba again shows large bias levels between databases and windows, with GEISA showing high levels of consistency but large bias. Ascension Island shows similar results to Darwin (except for the HITRAN calculations), indicating similar sensitivity to background conditions. Pearson correlation coefficients for window 4 generally indicate lower levels of sensitivity to variations of local conditions than window 1, suggesting the spectroscopic parameters for $^{13}CH_4$ in window 4 have significant uncertainty. Further to this, we found that the retrieval errors generated from $^{13}CH_4$ in window 4 were at least double those from $^{13}CH_4$ in window 1. This lower uncertainty is key in explaining the lower variation in $\delta^{13}C$ metric calculated using window 1.

Overall the results in Table 5 suggest using GEISA2020 $^{13}CH_4$ retrievals from window 1 to calculate $\delta^{13}C$ values, showing high levels of consistency across all windows and sites, and relatively low bias levels. This consistency is surprising and is worth further investigation, however, Window 4 for all spectroscopic databases yield far less accurate results, suggesting more work must be done for spectroscopic parameters in this window for $^{13}CH_4$.

4 Discussion

We have shown the presence of correlations between variations in specific local conditions and retrieval biases in this paper, however it should be noted that other local conditions do vary in parallel with those indicated in Sect, 3.3. It is therefore likely that each window and spectroscopic database show bias variability due to the variation of a number of conditions simultaneously, which is why each TCCON site shows different results. The key message remains true however, that different windows in different spectroscopic databases are sensitive to varying degrees to local changing conditions. Further analysis in this topic should be assessed, for example the impact of the air-mass factor changes or variations in the O_2 retrievals may be important. We note Cygan et al. (2012); Ngo et al. (2013) identify Voigt broadening parameters for O_2 as insufficient. The

release of the GGG2020 environment may allow for the testing of the impact of non-Voigt parameters on O_2 retrievals. We have also not considered errors in the instruments themselves, for example variations in the instrument line shape function between different TCCON instruments could cause additional biases.

We note that advancements are currently being tested on retrievals of methane from TCCON spectra, for example with the "SFIT4" algorithm (Zhou et al., 2019), which allows for profile retrievals and would therefore be less subject to the methane profile errors that can occur in GGG retrievals (Wunch et al., 2011). In addition to profile retrievals, this study used the GGG2014 retrieval software, while the more recent version of this software GGG2020 has also recently been released. This update includes an improved spectroscopic database (this database was used in this study, wrapped in the GGG2014 software) and the ability to use non-Voigt line shapes for methane. Therefore further analysis using the GGG2020 software and the use of other algorithms in this study could yield improved or different results. However, it is likely that the bias problems identified in this study may remain to some degree.

In addition to understanding the biases associated with retrieving $^{12}CH_4$ DMFs from TCCON spectra with differing spectroscopic databases, this study touches a question that is of some interest to the community, "can we calculate realistic and constant $\delta^{13}C$ values from TCCON". The results shown in Table 5 suggest not this is not yet possible, since they are often significantly different from the tropospheric average $\delta^{13}C$ value which is assumed to be -47‰ (Sherwood et al., 2016), and variable between databases and windows. There are some interesting cases where results close to the expected $\delta^{13}C$ value are calculated (e.g. windows 1 & 1 for HITRAN at Tsukuba), however given the same database in the same windows yields a completely inaccurate result at another TCCON site, it is challenging to draw any conclusions without further analysis. What is clear however, is that the $\delta^{13}C$ values calculate using $^{13}CH_4$ retrievals from window 1 tend to have less biases than those calculated using window 4, and show less variation between windows and TCCON sites, as well as more consistent results between the spectroscopic databases. The implication of these results are that window 1 is superior to window 4 for retrieving $^{13}CH_4$ DMF, however whether this is due to superior information content, or more accurate knowledge of spectroscopic parameters requires further research.

However, given that TCCON retrieves total column estimates, and not in-situ samples as assumed by Sherwood et al. (2016), this assumption of -47‰ is a little unfair, since this is an assumption based on lower tropospheric averages, and does not take into account sink processes that occur further up into the atmosphere. For example Rigby et al. (2017) assume a -2.6‰ fractionation due to the chlorine sink in the stratosphere, and significant fractionation does occur in the troposphere with the OH sink (Röckmann et al., 2011). However, it can be argued here that the priority in calculating an accurate value of $\delta^{13}C$ from TCCON is a full assessment of all of the systematic biases present in the retrievals, most notably the spectroscopic biases, before discussion of the true $\delta^{13}C$ value of the total column.

5 Conclusions

In this study, using the GGG2014 retrieval environment we retrieve $^{12}CH_4$ DMFs from four TCCON sites over the course of a year in each case, with the aim of understanding the biases associated with retrieving methane in the TROPOMI spectral region

as opposed to standard TCCON methane windows. Four different windows covering the spectral range of the future S5/UVNS instrument and the current S5P/TROPOMI instrument are used. Three of the windows are routinely used in TCCON products, but the TROPOMI/UVNS window in the 4190-4340 cm^{-1} range is not. We use five sources of spectroscopic parameters, the HITRAN2016, GEISA2020, SEOM-IAS and internal TCCON databases (GGG2014 and GGG2020) in order to assess the impact of spectroscopic database uncertainties.

Firstly we analysied the quality of fit of each of the windows for each of the spectroscopic databases, for each window we find the GGG2020 spectroscopic database shows the best fit metrics, except in window 1, where the SEOM-IAS database has the best quality of fit. We note that while each TCCON site shows different fit statistics for each window, the order of the spectroscopic databases in terms of quality of fit remains the same in all cases, with GGG2020 showing the best, followed by GGG2014, HITRAN2016 and GEISA2020. Window 1 shows the poorest quality fit of all of the windows, indicating room to improve the spectroscopic parameters for window 1.

Using metrics based on bias w.r.t the standard TCCON methane retrieval window (a weighted average of three windows), we found that each of the TCCON sites, the GGG2014 and GGG2020 databases exhibited normalised biases <1 in the standard TCCON windows, meaning that these biases were below the retrieval noise limit and were therefore not significant. However in window 1, both GGG2014 and GGG2020 indicated biases >1 for most of the TCCON sites, suggesting TCCON retrievals in window 1 have a significant bias to the standard TCCON window. Similarly the HITRAN and GEISA databases showed significant biases (in some cases >2) w.r.t the standard in windows 1 and 4, indicating significant disagreement between the standard TCCON retrievals and the HITRAN and GEISA databases in these windows. Only the GEISA database showed significant disagreement with the standard in windows 2 & 3, which, based on the other results shown in this paper, suggest the GEISA database as having the largest differences of all of the databases considered in this study.

The sensitivity of the retrieved $^{12}CH_4$ DMFs to locally changing conditions such as water vapour, SZA and temperature is investigated. We find significant levels of dependence on these variations that are not necessarily mirrored across all of the TCCON sites. We conclude that some retrieval windows and spectroscopic databases are more sensitive to variable conditions than others. This sensitivity is exacerbated at TCCON locations with highly variable and challenging local conditions.

The $\delta^{13}C$ metric calculated in this study show significant bias w.r.t the expected total column value of -47‰. However, the use of the 4265 cm^{-1} window shows significant benefit over the 6076 cm^{-1} window, and more consistent results across spectroscopic databases.

The analysis in this study led to two key conclusions, firstly we recommend including the TROPOMI SWIR spectral region (in this study, window 1) into future TCCON methane retrievals. This is based on comparable fit statistics with the original TCCON methane windows, and the significant bias w.r.t the standard TCCON retrieval product. Secondly, the different spectral windows used to generate the TCCON methane products are affected by local condition variability to varying degrees. Suggesting the weighted average normally used to generate TCCON methane products should be a unique formation depending on TCCON site and season.

Code and data availability. The GGG2014 retrieval environment is available at https://tccon-wiki.caltech.edu, and TCCON L1b spectra are available upon discussion with the relevant site PI

Author contributions. MB provided and processed the Ny-Ålesund data, ND provided and processed the Darwin data, DGF provided and processed the Ascension Island TCCON data and IM provided and processed the Tsukuba TCCON data. EM devised and performed the
505 study, analysed the data and wrote the paper. BV consulted on the interpretation of the results. All authors reviewed the paper.

Competing interests. BV is an associate editor for the joint (AMT/ACP) special issue "TROPOMI on Sentinel-5 Precursor: first year in operation". DGF is an associate editor for AMT.

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510 at https://tccon-wiki.caltech.edu. Thanks to Geoff Toon at Caltech for providing advice on the use of GGG2014. HITRAN2016 is available at https://hitran.org/, GEISA2020 is available from http://ara.abct.lmd.polytechnique.fr/index.php?page=geisa-2. The SEOM-IAS database is available at https://www.wdc.dlr.de/seom-ias/. The TCCON line lists are described in the GGG documentation. The Ascension Island TCCON station has been supported by ESA under grant 3-14737 and by the German Bundesministerium für Wirtschaft und Energie (BMWi) under grants 50EE1711C and 50EE1711E. We thankfully acknowledge funding from the University of Bremen and the German Research
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