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**CH₄, CO, and H₂O
spectroscopy for
TROPOMI**

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Abstract

The TROPospheric Monitoring Instrument (TROPOMI) will be part of ESA's Sentinel-5 Precursor (S5P) satellite platform scheduled for launch in 2015. TROPOMI will monitor methane and carbon monoxide concentrations in the Earth's atmosphere by measuring spectra of back-scattered sunlight in the short-wave infrared (SWIR).

S5P will be the first satellite mission to rely uniquely on the spectral window at $4190\text{--}4340\text{ cm}^{-1}$ ($2.3\text{ }\mu\text{m}$) to retrieve CH_4 and CO. In this study, we investigated if the absorption features of the three relevant molecules CH_4 , CO, and H_2O are adequately known. To this end, we retrieved total columns of CH_4 , CO, and H_2O from absorption spectra measured by two ground-based Fourier transform spectrometers that are part of the Total Carbon Column Observing Network (TCCON). The retrieval results from the $4190\text{--}4340\text{ cm}^{-1}$ range at the TROPOMI resolution (0.45 cm^{-1}) were then compared to the CH_4 results obtained from the 6000 cm^{-1} region, and the CO results obtained from the $4190\text{--}4340\text{ cm}^{-1}$ region at the higher TCCON resolution (0.02 cm^{-1}).

For TROPOMI-like settings, we were able to reproduce the CH_4 columns to an accuracy of 0.3% apart from a constant bias of 1%. The CO retrieval accuracy was, through interference, systematically influenced by the shortcomings of the CH_4 and H_2O spectroscopy. In contrast to CH_4 , the CO column error also varied significantly with atmospheric H_2O content. Unaddressed, this would introduce seasonal and latitudinal biases to the CO columns retrieved from TROPOMI measurements. We therefore recommend further effort from the spectroscopic community to be directed at the H_2O and CH_4 spectroscopy in the $4190\text{--}4340\text{ cm}^{-1}$ region.

1 Introduction

Methane (CH_4) and carbon monoxide (CO) have a large impact on climate variability and air quality. Accurate monitoring with high spatial and temporal coverage allows the scientific community to better model atmospheric chemistry, atmospheric transport,

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and land-atmosphere interactions (bush-fires, regional CH₄ emissions of wetlands and livestock etc.). Both ground-based observations and satellite observations are currently used to monitor CH₄ and CO.

The Total Carbon Column Observing Network (TCCON) is a global network of ground-based Fourier transform spectrometers, established in 2004 (Wunch et al., 2011a). Its goal is to remotely measure column abundances of CO₂, CO, CH₄, N₂O and other molecules that absorb in the near-infrared and short-wave infrared (SWIR). Currently, there are 18 operational observation sites affiliated with TCCON. TCCON measurements are used to validate satellite measurements (Butz et al., 2011; Morino et al., 2011; Parker et al., 2011; Wunch et al., 2011b; Reuter et al., 2011), and they also provide direct constraints on global greenhouse gas inventories (e.g., Yang et al., 2007; Fraser et al., 2011). Thanks to their high spectral resolution (0.02 cm⁻¹), the measured spectra can also be used to evaluate spectroscopic databases (e.g., Tran et al., 2010).

ESA's Sentinel-5 Precursor (S5P) satellite – due for launch early 2015 – will complement a series of satellites that monitor CH₄ and CO concentrations in the Earth's atmosphere. Its payload, the TROPOspheric Monitoring Instrument (TROPOMI) (Veefkind et al., 2012), is an imaging spectrometer that will measure back-scattered solar radiation spectra in the nadir and off-nadir directions. TROPOMI will feature a wide swath of 2600 km with a ground pixel area of 7 × 7 km² (for the sub-satellite point), which implies daily global coverage of the Earth's surface with ~ 7 × 10⁶ measured spectra. The spectrometer will measure the SWIR range at 4190–4340 cm⁻¹ with moderate spectral resolution (0.45 cm⁻¹). This range covers strong absorption lines by CH₄ and water vapour (H₂O) as well as weak absorption by CO and deuterated water (HDO).

During one decade of operations, the SCanning Imaging Absorption spectroMeter for Atmospheric Cartography (SCIAMACHY) (Bovensmann et al., 1999) has demonstrated that this type of satellite observations allows for the retrieval of total atmospheric columns of CH₄ (e.g., Frankenberg et al., 2006; Bergamaschi et al., 2009) and CO (Buchwitz et al., 2007; de Laat et al., 2010). Since February 2009, the Greenhouse gases Observing SATellite (GOSAT) (Kuze et al., 2009) is providing CO₂ and CH₄ con-

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centration measurements as well, which are currently subject to validation (Butz et al., 2011; Morino et al., 2011; Wunch et al., 2010; Parker et al., 2011). Another satellite observation set of tropospheric CO is provided by the Measurements Of Pollution In The Troposphere (MOPITT) instrument, active since the year 2000. CO total columns both from the SWIR and from the thermal-infrared near 2100 cm^{-1} are retrieved from the MOPITT data (Deeter et al., 2009). In the coming years, S5P will fill the gap between the currently orbiting satellites and later missions such as Sentinel-5. A common goal of these missions is to monitor atmospheric CH₄ concentrations with the accuracy and spatio-temporal coverage that enable inverse modelling of CH₄ sources on regional and weekly scales. S5P will also provide users with a CO product at high spatial and temporal sampling, a single measurement having an uncertainty of 10 % at most. In contrast, SCIAMACHY data have to be averaged in time (roughly one month) and space ($\sim 5^\circ \times 5^\circ$) to reach a comparable accuracy.

The absorption lines of CH₄ and CO in the SWIR can be used to infer the total atmospheric concentration with high sensitivity to the Earth's surface and lower atmosphere where sources are located. The main challenge for the inversion technique is the desired accuracy: for CH₄, residual retrieval biases as small as a few per mill could be detrimental to inverse modelling of sources and sinks (Bergamaschi et al., 2009). The scientific objective for CO – an overall accuracy of better than 15 % (Vidot et al., 2012) – seems less demanding, but the CO absorption lines are hard to detect among the strong absorption lines of CH₄ and H₂O. The retrieval accuracy depends on accurate knowledge of the light path of the back-scattered sunlight through the Earth's atmosphere. Scattering by particles such as aerosols, water and cirrus clouds can modify the light path and induce retrieval errors. The two studies published recently by Butz et al. (2012) and Vidot et al. (2012) focused on this error source and – using synthetic input spectra – concluded that the scientific goals of TROPOMI can be achieved with the predicted instrumentation. Butz et al. (2012) cautioned, however, that a few other, unrelated, error sources had not yet been assessed. One of them, which is hard to assess by means of synthetic input spectra alone, is the inaccuracy of the assumed

molecular absorption lines of CH₄, CO, and H₂O. This error source is the topic of this study.

To assess these errors, we will retrieve CH₄ and CO columns from the spectra of ground-based Fourier transform spectrometers at two different locations, both at their native high resolution (0.02 cm⁻¹) and convolved with the TROPOMI instrument response function to produce lower-resolution spectra (0.45 cm⁻¹). The results of the retrievals in the 4190–4340 cm⁻¹ range will then be compared to the reference values obtained from 5880–6174 cm⁻¹ (for CH₄), and from 4209–4313 cm⁻¹ (for CO) at the native resolution. The paper is structured in the following way: In Sect. 2, we will characterise the measurements and the inversion method to evaluate them. The results and their implications for the spectroscopic databases of CH₄, H₂O, and CO will be presented in Sect. 3. Section 4 will conclude the paper with recommendations for the S5P mission.

2 Methodology

In this section, we present the TCCON observations and the different spectral ranges used for this study (Sect. 2.1), before explaining our forward model (Sect. 2.2) and the inversion method (Sect. 2.3). After verification of our inverse method (in Sect. 2.4) the approach to analyse the results is described in Sect. 2.5.

2.1 TCCON observations

We chose two sets of TCCON observations to cover both wet and dry atmospheric conditions: 50 spectra measured at Darwin (in the tropical northern region of Australia) between December 2005 and November 2007, and 50 spectra measured at Park Falls (inland, close to the US-Canadian border) between July 2004 and February 2006 (Deutscher et al., 2010; Washenfelder et al., 2006). Each of the 100 spectra was measured on a different day, the days being evenly distributed in time. The Park Falls

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data cover a large range of solar zenith angles (SZA) between 20 and 80 degrees. The Darwin spectra have a narrower spread in observation geometry ($35 < \text{SZA} < 45$ degrees for 48 of 50 spectra). For evaluation, we split the spectra into the ranges listed in Table 1 and, whenever TROPOMI spectra were to be simulated, convolved them with the expected TROPOMI instrument response function (Sect. 2.2).

Table 1 summarises all spectral windows referred to in this study. The windows used by the TCCON science team are: windows 1, 2, and 3 for CH₄, the windows labelled 4 for H₂O, and the windows labelled 5 for CO. Windows 6a and 6b cover the expected spectral range for TROPOMI. The original resolution corresponds to a full width half maximum (FWHM) of 0.0134 cm^{-1} (window 6a), and the TROPOMI resolution has a FWHM of 0.45 cm^{-1} (window 6b).

2.2 Forward model

In contrast to the more elaborate forward model required to invert back-scattered sunlight spectra (Hasekamp and Butz, 2008), the forward model in this study neglects scattering processes. The TCCON spectrometers measure direct sun-light, which is, to a good approximation, only affected by molecular absorption on its way through the atmosphere. The modelled signal $F(k)$ can be written as an integral over the entire height h of the atmosphere.

$$F(k) = R \otimes S_{\odot} g \exp \left(- \int_0^{\infty} dh n(h) \sigma(\rho, T, k) f(\mu_0) \right) \quad (1)$$

S_{\odot} denotes the solar radiance, for which we adopted the solar line list used by the TCCON science team (G. C. Toon, private communication, 2010). The other terms in Eq. (1) are the instrument gain g , the wavenumber of the spectrum k , the molecular cross-sections $\sigma(\rho, T, k)$, the particle density of the considered absorber molecules $n(h)$, and finally $f(\mu_0)$, the SZA dependent air-mass (Kasten and Young, 1989). After

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integrating over height and atmospheric constituents, one needs to convolve the modelled absorption spectrum with the instrument response function R before comparing it to the measurements. To reproduce the TCCON retrieval values, we assumed the instrument line shape to be a sinc function convolved with a rectangular function, with 0.02 cm^{-1} between the first zero-crossings (corresponding to $\text{FWHM} = 0.0134\text{ cm}^{-1}$) and an oversampling rate of $1.9 \times \text{FWHM}$. To simulate TROPOMI-like spectra, we convolved the TCCON spectra with a Gaussian instrument line shape with a coarser FWHM of 0.45 cm^{-1} and an oversampling rate of $2.5 \times \text{FWHM}$. Figure 1 shows the two spectral resolutions in the SWIR window between 4190 and 4340 cm^{-1} .

The HITRAN 2008 molecular spectroscopic database (HITRAN08, Rothman et al., 2009) served as our default cross-section database, with the exception of the H₂O line lists. For H₂O in windows 1 to 4, we combined the line list by Jenouvrier et al. (2007) with HITRAN08 by selecting for each absorption line the version that produced the smaller spectral fit residuals. For the TROPOMI range at 4190 – 4340 cm^{-1} , we used the line list developed by Scheepmaker et al. (2012). These line lists are not identical to the H₂O spectroscopy used by the TCCON science team. The latter improved the fit quality in spectral window 1, whereas it led to larger fit residuals in the TROPOMI range. To keep the paper short, we will only present retrievals obtained with the H₂O line lists developed for this study. The CH₄, CO, and CO₂ line lists used by the TCCON science team are the HITRAN08 line lists that were also used for this study. Figure 2 shows the relative strength of the CH₄, H₂O, and CO absorption features in the range of 4190 – 4340 cm^{-1} . The cross-sections were evaluated at $p = 1000\text{ mbar}$, $T = 296\text{ K}$ and multiplied with columns N_i representative for observations at Darwin to obtain approximate optical depths (Eq. 1).

2.3 Inverse method

We used the same inversion approach as described by Butz et al. (2012). We optimised the state vector x , subjected to the forward model F (Eq. 1), from the TCCON measurements y by minimising Eq. (2). The state vector x contained the following el-

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ements: total column number density $N_i = \sum n_i(h)$ for CO and H₂O, a profile for CH₄, three parameters to fit a wavenumber dependent instrumental gain g , and two auxiliary parameters to compensate for a spectral shift of the measured spectrum with respect to the tabulated cross-sections. By default, pressure, temperature, and the height profiles of the absorbing species were not retrieved in the state vector. We assumed a fixed a priori atmospheric profile for CH₄, H₂O, and CO, and fitted only a scalar correction factor to the initial N_i . The exception to this rule was CH₄. The spectral fit residuals decreased by 10 %, when the CH₄ column was retrieved as a 12-layer height profile. The state vector thus contained twelve instead of one entry for CH₄. They were summed up in the end to yield a total CH₄ column. As for all other species, the degrees of freedom of the inversion were insufficient to retrieve a meaningful profile.

To retrieve \mathbf{x} , regularisation is required because the inverse problem is ill-posed i.e. the measurements \mathbf{y} contain insufficient information to retrieve all state vector elements independently. The Phillips-Tikhonov regularisation method (Phillips, 1962; Tikhonov, 1963) finds the optimised state vector $\hat{\mathbf{x}}$ by minimising a cost function that is the sum of the least-squares cost function and a side constraint weighted by the regularisation parameter $\gamma \geq 0$ according to

$$\hat{\mathbf{x}} = \arg \min_{\mathbf{x}} (\|\mathbf{S}_y^{-1/2} \mathbf{F}(\mathbf{x}) - \mathbf{y}\|^2 + \gamma \|\mathbf{W}\mathbf{x}\|^2). \quad (2)$$

\mathbf{W} is the weighting matrix, and \mathbf{S}_y is the diagonal measurement error covariance matrix containing the noise estimate. For \mathbf{S}_y we assumed a signal-to-noise ratio of 1000 (Wunch et al., 2011a).

The set-up of the atmospheric input was not changed with respect to Butz et al. (2012): the atmosphere was divided into a grid of 72 planar atmospheric layers (equidistant steps in terms of pressure). By default, temperature, pressure, and height were kept constant. The initial values for pressure, temperature and the H₂O profile were taken from the ECMWF (European Centre for Medium-Range Weather Forecasts) ERA-Interim analysis provided 6-hourly on a $1.5^\circ \times 1.5^\circ$ latitude \times longitude grid.

We checked that the surface pressure agreed within 0.1 % to the pressure measured at the TCCON stations. For the CH₄ and CO a priori profiles, we relied on the Chemistry Transport Model (TM4) profiles (Meirink et al., 2006). The priors were obtained from a one-year average at the corresponding geolocation of the observation sites.

2.4 Reference retrievals

Throughout this paper we used the atmospheric total columns N_i (in molecules cm⁻²) obtained from the spectral ranges 5880–6174 cm⁻¹ (for CH₄) and from 4209–4319 cm⁻¹ (for CO) as reference values. These spectral ranges are also used by the TCCON science team as input for their retrieval algorithm GFIT (Wunch et al., 2011a). Dedicated effort in the past years to improve CH₄ and H₂O spectroscopy in the 5880–6174 cm⁻¹ range (Frankenberg et al., 2008; Tran et al., 2010; Jenouvrier et al., 2007) has enabled accurate retrieval of CH₄ columns from this spectral range. This has been confirmed by validation of GFIT retrievals with independent aircraft measurements. Similarly, the accuracy of retrieved CO columns from the 4209–4319 cm⁻¹ spectral range by GFIT has also been confirmed by validation with aircraft measurements.

Our inversion algorithm being not identical to GFIT, we first verified our algorithm. We checked if it reproduces the CH₄ and CO total columns derived with GFIT when the same spectral ranges and spectral resolution were used (see Table 1). A complication arose when inter-comparison of our CH₄ results from windows 1, 2, and 3 showed that the retrieval quality from window 1 (5880–5996 cm⁻¹) was unsatisfying. A closer inspection revealed that there were several strong H₂O absorption lines not well captured by our line list. We therefore decided to discard window 1 altogether and reproduce the GFIT values for CH₄ from the average of windows 2 and 3. For all observation windows, the spectrum measured at Park Falls on 21 June 2005, turned out to produce much larger spectral fit residuals than the average. The GFIT retrieval also assigns large error bars to the columns retrieved from this spectrum. This data point was therefore omitted from further analysis.

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Comparing our retrieved CH₄ values from windows 2 and 3 to the GFIT values, we found a bias between the two datasets of 0.1 % for both Parkfalls and Darwin and standard deviations of 0.26 % and 0.18 % for Park Falls and Darwin, respectively. For CO, we found biases of 1.6 % and –2.8 %, and standard deviations of 1.1 % and 1.8 % for Park Falls and Darwin, respectively. The small differences between our algorithm and GFIT may be explained by differences in averaging kernels and a priori profiles for CH₄, CO, and H₂O (smoothing and interference errors), and differences in the H₂O line list. These differences are consistent with the error bars provided by the GFIT algorithm. Therefore, we considered our retrieved columns from the 5990–6174 cm⁻¹ range (for CH₄) and from 4209–4319 cm⁻¹ range (for CO) as reference values and the standard deviations given above as the associated error σ_{ref} .

2.5 Analysis of the results

To discuss the retrieval accuracy, we used the following three diagnostic quantities throughout this study. They quantify by how much the quality of the retrieved columns decreased when CH₄, CO, and H₂O columns were retrieved from 4190–4340 cm⁻¹ at the TROPOMI resolution compared to the reference results (spectral ranges listed in Table 1). For the standard deviation and the bias, we interpreted the columns of CH₄, CO, and H₂O retrieved at Park Falls or Darwin as a time-series and compared it to the time-series of the reference values:

1. The reduced χ^2 of the fit: the sum of the residuals between the modelled spectra and the corresponding measured spectra, divided by the degrees of freedom ν (number of spectral pixels minus the degrees of freedom of the fit):

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$$\chi^2/\nu = \sum_{k=1}^K \left(\frac{y_{\text{meas},k} - y_{\text{mod},k}}{\sigma_k} \right)^2 / \nu \quad (3)$$

In the results section, we will list the average $\langle \chi^2/\nu \rangle$ over all spectra.

2. The σ_N standard deviation of the differences between the retrieved columns at TROPOMI-like settings and the reference values. This number serves as an estimate of the accuracy of our results including systematic errors. In the tables, we will always compare it to the error σ_{ref} of the reference retrievals. If σ_N is not much larger than σ_{ref} , the differences between the two retrievals are statistically insignificant.
3. The bias b of the new retrieval values with respect to the reference values, calculated from the median of the relative differences.

3 Results

In this section, we compare the inversion results (CH₄ in Sect. 3.1, CO in Sect. 3.2) for the TROPOMI spectral range to the reference retrievals. An option to improve the CO retrieval accuracy is presented in Sect. 3.3.

3.1 CH₄ retrieval accuracy

Figure 3 shows the time-series of CH₄ columns (upper panel) and the differences (lower panel) between the results from the TROPOMI range and the 5996–6147 cm⁻¹ range. The Darwin observations are coloured red, the Park Falls observations are shown in blue. In the lower panel, solid lines belong to retrievals at TROPOMI resolution (window 6b in Table 1), dotted lines denote results from the original resolution (window 6a). The dashed lines illustrate the biases for window 6b. Table 2 lists the fit

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diagnostics. Those are, from left to right: average spectral fit residuals ($\langle \chi^2/\nu \rangle$), standard deviation of the differences in columns (σ_N) versus the reference error σ_{ref} (see Sect. 2.4), and the bias b . Table 2 shows that the CH₄ columns were well reproduced for TROPOMI-like settings. The average scatter of retrieved columns increased only from 0.18 to 0.24 % at Darwin, and from 0.26 to 0.28 % at Park Falls. These numbers did not change significantly when the original spectral resolution was assumed. The difference between the values derived from TROPOMI-like settings and the reference values from spectral windows 2 and 3 was not significant except for the two outliers in summer 2005 at Park Falls (Fig. 3). The error bars assigned to these values by the GFIT algorithm are also three times larger than the average value. The positive bias of roughly 1 % at both sites thus is the only evidence for spectroscopy-related errors affecting the CH₄ columns. This bias increased for the lower spectral resolution, which is consistent with interference errors due to inaccurate CH₄ or H₂O spectroscopy. The spectral fit residuals increased from ~ 30 at the 6000 cm⁻¹ range to ~ 100 , but they cannot be directly related to a column error.

To see if H₂O interference errors could account for the 1 % bias, we investigated the dependence of the CH₄ retrieval errors on the H₂O abundance. Figure 7, upper panel, shows CH₄ retrieval errors against H₂O Dry air Mole Fraction (DMF) at Darwin. The dashed line is the linear regression, the dotted lines show the 1- σ uncertainty level of the slope. The air-mass was between 1.2 and 1.4 for all observations. The slope is not significantly larger than zero at a 2- σ level and it increases only from 0.9 to 1.1 % for the range of observed H₂O DMF. This may be enough to account for the increase of the bias for the lower spectral resolution, but both effects are on the order of the reference retrieval accuracy.

Since there are no plans to retrieve O₂ from TROPOMI spectra, pressure was treated as a fixed parameter in the inversion method up to this point. The TCCON spectra cover several strong O₂ absorption regions and can thus also be used to derive total O₂ columns and – if one assumes a constant atmospheric oxygen ratio – a total pressure. To study the pressure-dependence of the spectroscopic line lists, we chose a different

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approach to avoid an assessment of O₂ spectroscopy. Instead of retrieving pressure and trace gas species separately, our inversion algorithm also allows for a simultaneous retrieval. For such a retrieval, the observation windows need not include O₂ absorption lines, since the line shape of any absorber depends on pressure. At each iteration step, then, the total dry air column is optimised with respect to the cross-sections of all retrieved molecules.

When we retrieved the pressure from the CH₄ and H₂O absorption features in the 5996–6145 cm⁻¹ range, the pressure retrieval yielded dry air columns that agreed with the in-situ measurements within 2%. The same approach resulted in errors larger than 10% when we chose the 4190–4340 cm⁻¹ range. The difference in retrieved CH₄ columns were smaller (0.3 to 0.8%), but still significant. Figure 4 shows the relative differences of retrieved dry air columns versus the value measured at the Park Falls site. Results from windows 2 and 3 (circles) are compared to the column errors from the TROPOMI spectral range (crosses). The dry air columns derived from the ECMWF pressure profile, which serve as our default, agree with the measured dry air columns within 0.1% standard deviation (black curve in Fig. 4).

The failure to retrieve the pressure from the SWIR band was probably caused by inaccurate pressure-broadening parameters of the CH₄ and H₂O line lists. As long as the pressure was kept fixed, these shortcomings manifested themselves primarily in the spectral fit residuals (see Fig. 8). If, however, the pressure was treated as a free parameter, the inversion routine optimised for a pressure which compensated for inaccurately predicted absorption line shapes. This resulted in pressure values as far as 10% away from the true pressure (see Fig. 4). CH₄ and H₂O were found to yield a comparable pressure over-estimation when only one of them was retrieved. The only region exempt from these problems was the 4318–4328 cm⁻¹ region where strong CH₄ and H₂O absorption bands are absent (see Fig. 1). For the CH₄ absorption bands in the 5996–6145 cm⁻¹, the pressure retrieval yielded accurate results. The CH₄ HITRAN08 database relies for this range on the line list published by Frankenberg et al. (2008) who focused on pressure-broadening effects.

We also inverted 45 spectra from one single observation day at Park Falls to check for air-mass dependent errors. Up to SZA \approx 65 degrees, no systematic influence of air-mass was found for CH₄, nor for CO columns. For larger SZA, the discrepancies caused by different averaging kernels increased to the extent at which they masked any potential spectroscopy-related errors.

3.2 CO retrieval accuracy

In contrast to CH₄ and H₂O, the CO absorption maxima are relatively sharp and well separated from each other. Nonetheless, inversion of CO in the SWIR is non-trivial because the CO signature has to be separated from the much stronger background of CH₄ and H₂O absorption. If possible, we would like to retrieve all three species at the same time, using the entire spectral range of 4190–4340 cm⁻¹. This approach worked reasonably well for CH₄.

Figure 5 shows the time-series of retrieved CO (upper panel) and the relative differences of CO columns retrieved at the TROPOMI resolution compared to window 5 at the original resolution (lower panel). The two biases were added as dashed lines in the lower panel. Table 3 lists the corresponding fit diagnostics. The CO retrieval accuracy obviously deteriorated for TROPOMI-like settings. First, the bias b increased from a few to roughly ten percent. Second, the standard deviation of the retrieved CO column error, σ_N , increased by a factor of two to three compared to the reference uncertainty. The increase of bias and standard deviation was more pronounced at Darwin than at Park Falls. An explanation might be that the average H₂O abundance at Darwin was two times higher. We will examine this conjecture in the following. The impact of CH₄ spectroscopic errors on CO are hard to identify because the atmospheric CH₄ abundance varies little compared to H₂O.

We fitted H₂O and HDO as interfering absorbers while retrieving the CH₄ and CO columns. Figure 6 compares the H₂O columns retrieved from the TROPOMI range to the columns retrieved from window 4 (around 6200 cm⁻¹). The upper panel shows the

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time-series; the lower panel shows the relative differences to the reference results from window 4 (same format as Fig. 3 for CH₄). Table 4 lists the corresponding fit diagnostics of H₂O, including results from the original (TCCON) and the lower (TROPOMI) resolution. As for CH₄, the H₂O retrieval accuracy did not deteriorate when the input spectrum was degraded to the TROPOMI resolution; σ_N in Table 4 remained almost identical. The bias of 6 or 8 % at Darwin was the only obvious difference between the H₂O derived from the TROPOMI range and from window 4. To prove that the CO retrieval errors, in particular at Darwin, were dominated by H₂O interference errors, we needed more evidence.

We first replaced our default line list for H₂O with the HITRAN08 line list to test how sensitively the CO retrieval results reacted to the H₂O spectroscopy. The spectral fit residuals increased by a factor of 2.2 and the H₂O columns were equally biased, whereas the bias of the CO columns changed from 14.8 to 6.7 % at Darwin, and from 4.6 to 1.1 % at Park Falls. On the other hand, the standard deviation of column errors did not decrease significantly.

The CO bias would be of little consequence for the S5P mission if it were constant for all observation sites and atmospheric conditions. A further examination revealed, however, that it strongly depended on the H₂O vapour content. The correlation strength did not change when the default H₂O line list was replaced by the HITRAN08 list. This dependence would introduce undesired seasonal and latitudinal biases for the S5P mission. Figure 7 demonstrates for the Darwin observations the extent to which the CO and CH₄ retrieval errors increased with H₂O abundance. In the lower panel, the CO retrieval errors for the nominal TROPOMI range and for an optimised sub-window (see Sect. 3.3 for further explanation) are plotted against H₂O DMF. The dashed lines show the linear fits. Judging from the linear fit, the H₂O-dependence introduced a CO-bias of 15 % between the driest and the most humid day. In contrast to the weak correlation for CH₄, CO error increase with H₂O is much larger than the reference accuracy.

In this study, spectroscopic errors are primarily characterised by their impact on retrieved columns. Spectral fit residuals allow us to track down inaccurate absorption

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lines but do not directly relate to a column inversion error. We correlated the spectral fit residuals to the molecular absorption spectra by calculating Spearman's rank-order correlation coefficient (Press et al., 1986). The correlation with the H₂O absorption spectrum was significant (significance > 10 σ) for all measurements. The actual correlation strength increased with atmospheric H₂O abundance. For dry atmospheric conditions (H₂O DMF < 0.1 %), the correlation with the CH₄ absorption lines dominated over the H₂O correlation, whereas it became non-significant for wet atmospheric conditions. Figure 8, upper panel, shows a part of the fit residuals for an observation at Darwin with H₂O DMF = 1 %. The cross-sections of H₂O and CH₄, evaluated at $p = 1000$ mbar and $T = 296$ K, are shown as blue and black lines. The residuals peak to the immediate left and right of the absorption maxima of H₂O, whereas the line centres seem to be correct. Inadequate pressure broadening parameters of the strong H₂O absorption lines are an obvious interpretation for this deficiency (see the results on pressure retrievals in Sect. 3.1), but other effects, such as line mixing, probably also contributed to the residuals. There were also fit residuals peaking around CH₄ absorption lines (the lower panel in Fig. 8 shows a Park Falls spectrum for a dry Winter day) but these fit residuals were much more variable in shape and size than their H₂O counterparts.

For the CO retrievals, the 15 % threshold accuracy (Vidot et al., 2012) was met for all 100 examined spectra, but this would be the full error budget for the S5P mission. Moreover, the retrieval errors varied systematically with H₂O and additional errors due to scattering processes of aerosols and clouds are to be expected for a TROPOMI observation geometry. An improvement of the CO retrieval accuracy is therefore necessary.

3.3 Measures to improve on CO retrieval accuracy

The performance of the CO inversion at TROPOMI resolution is limited by the strong overlapping of the CO with neighbouring CH₄ and H₂O lines, both of which have systematic errors (Fig. 8). Sussmann and Borsdorff (2007) reported that the H₂O interference errors on CO in the 2050–2160 cm⁻¹ range were reduced when they retrieved an

H₂O profile instead of a scalar value. We experimented with a similar approach for the TROPOMI range, but we did not achieve a notable decrease in CO column error. One reason might be that we relied on an H₂O prior profile already close to the optimum profile.

Another means to reduce interference errors is to restrict the retrieval to a sub-window where the CO absorption lines are more pronounced relative to the CH₄ and H₂O lines. The main drawback of this approach is the loss of information, making the inversion potentially more vulnerable to instrumental effects. For the inversion of back-scattered sunlight, we also have to keep in mind that those parts of the spectrum without CO absorption lines may be needed to retrieve information on scattering particles (Vidot et al., 2012). We defined an overlapping function ω in terms of the spectral sensitivity ∂_F/∂_N as

$$\omega = \frac{\left| \frac{\partial_F}{\partial N_{\text{H}_2\text{O}}} \right| + \left| \frac{\partial_F}{\partial N_{\text{CH}_4}} \right|}{\left| \frac{\partial_F}{\partial N_{\text{CO}}} \right|}. \quad (4)$$

From Eq. (4) we optimised the CO sub-window by choosing wavenumber limits k_0, k_1 such that $\sum_{k=k_0}^{k_1} \frac{k_1-k_0}{\omega(k)}$ became maximal. This criterion led to an optimised range of 4231.3–4302.6 cm⁻¹ if one contiguous spectral range was to be used. Replacing the nominal TROPOMI range by this sub-window reduced the dependency of the CO retrieval errors with humidity. This is illustrated in Fig. 7, where the retrieval results from the CO sub-window (circles) are compared to the nominal retrieval results (crosses). The bias of the CO columns decreased by 3 to 5 % for both observation sites, and σ_N decreased from 4.8 % to 3.9 % at Darwin and from 3.3 % to 2.7 % at Park Falls.

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The current H₂O spectroscopy affected, due to interference errors, the CO retrieval accuracy at 4190–4340 cm⁻¹ when the TROPOMI resolution was assumed. For wet conditions, the retrieved CO columns deviated by almost 15% from the result at high spectral resolution. This error correlated with H₂O content in the atmosphere. Because the atmospheric H₂O abundance is highly variable, this would lead to seasonal and latitudinal biases of CO columns for the S5P mission. The CO bias reacted also very sensitively to a different H₂O line list. No shortcomings of the CO spectroscopy itself were detected. The impact of inaccurate CH₄ spectroscopy on CO retrieval errors could not be quantified because of the small variations of atmospheric CH₄. We presented a way to mitigate the impact of interference errors from H₂O and CH₄ by reducing the retrieval window, but a further improvement on H₂O and CH₄ spectroscopy is required for the S5P mission. The loss of information due to a reduced spectral range may pose a problem to the inversion of back-scattered sunlight, for which also scattering properties of the atmosphere need to be retrieved.

For CH₄ column errors, no strong correlation with H₂O abundance was found. The combined H₂O and CH₄ spectroscopy errors caused CH₄ retrieval errors consisting of a constant bias of about 1% and a standard deviation of about 0.3%. This is better than the threshold accuracy requirement of 1% for the S5P mission. Spectroscopy-related errors also manifested themselves in an increase of spectral fit residuals when we compared the TROPOMI spectral range to the 6000 cm⁻¹. This can be caused both by H₂O and by CH₄ spectroscopy. We caution that the intrinsic retrieval accuracy of CH₄ from TCCON spectra is a few tenths of a percent. This means we can only identify spectroscopic deficiencies that result in column errors with the same order of magnitude as the intended accuracy for the S5P mission. For CO, the reference accuracy is an order of magnitude better than the S5P requirement.

Both H₂O and CH₄ showed an incorrect pressure-dependence at 4190–4340 cm⁻¹. This implies that not only the H₂O but also the CH₄ line list is less accurate at the

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TROPOMI range than around 6000 cm^{-1} . For atmospheric inversion this shortcoming would become important if the surface pressure was to be retrieved from the spectra. Currently, we do not intend such a pressure retrieval for TROPOMI spectra. To improve on the general accuracy of spectroscopic databases, we recommend a similar effort to be directed at the pressure broadening and pressure shift of absorption lines as done by Frankenberg et al. (2008) for CH_4 at $5860\text{--}6185\text{ cm}^{-1}$.

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**Table 1.** Overview of spectral ranges used for inversion.

window number	wavenumber range (cm ⁻¹)	target species	other absorbers
1	5880–5996	CH ₄	CO ₂ , H ₂ O
2	5996.45–6007.55	CH ₄	CO ₂ , H ₂ O
3	6007–6145	CH ₄	CO ₂ , H ₂ O
4	6073.05–6080.75, 6098.4–6100.3, 6124.4–6127.3, 6176.47–6178.13, 6252.35–6259.55, 6293.45–6309.25, 6389.35–6395.55, 6400.0–6402.3, 6466.1–6473.1	H ₂ O	CH ₄ , CO ₂
5	4208.7–4257.3, 4262–4318.8	CO	H ₂ O, HDO, CH ₄
6a	4190–4340 TCCON resolution	CH ₄ , CO	H ₂ O, HDO
6b	4190–4340 TROPOMI resolution	CH ₄ , CO	H ₂ O, HDO

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Table 2. Fit diagnostics of the CH₄ column retrievals in the 4190–4340 cm⁻¹ range, for the original (TCCON) and for the TROPOMI resolution.

	$\langle \chi^2 / \nu \rangle$	σ_N	σ_{ref}	b
Darwin TROPOMI	43	0.24 %	0.18 %	0.010
Park Falls TROPOMI	32	0.28 %	0.26 %	0.009
Darwin TCCON	106	0.28 %	0.18 %	0.008
Park Falls TCCON	83	0.29 %	0.26 %	0.004

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**Table 3.** Fit diagnostics of the CO column retrievals for the TROPOMI resolution.

	$\langle \chi^2 / \nu \rangle$	σ_N	σ_{ref}	b
Darwin	43	4.8 %	1.8 %	0.148
Park Falls	32	3.3 %	1.1 %	0.046

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Table 4. Fit diagnostics of the H₂O column retrievals at the 4190–4340 cm⁻¹ range, for the original (TCCON) and for the TROPOMI resolution.

	$\langle \chi^2/\nu \rangle$	σ_N	σ_{ref}	b
Darwin TROPOMI	43	2.6 %	1.9 %	0.082
Park Falls TROPOMI	32	4.6 %	2.4 %	0.006
Darwin TCCON	106	2.2 %	1.9 %	0.061
Park Falls TCCON	83	4.1 %	2.4 %	-0.004

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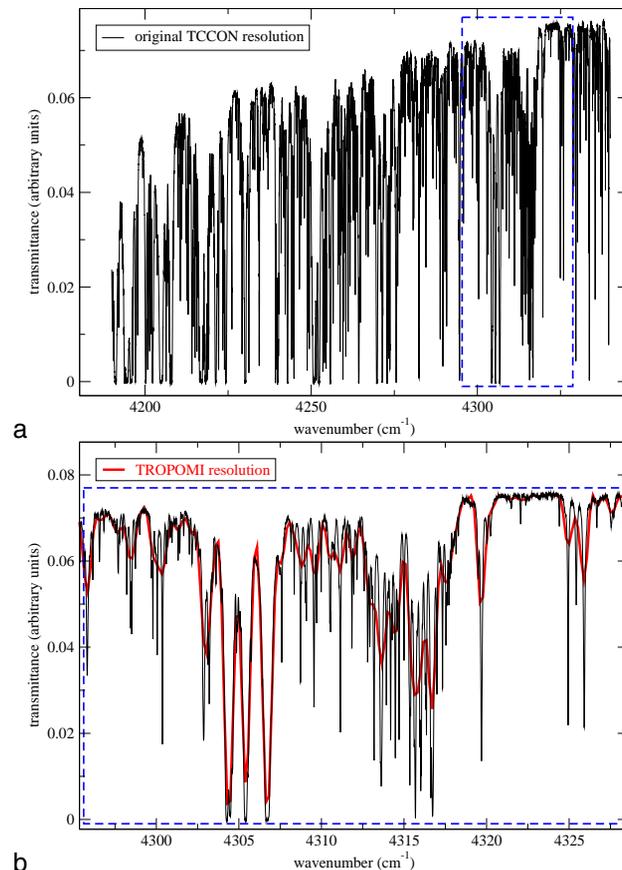


Fig. 1. (a) Original TCCON spectrum of the TROPOMI wavenumber range 4190–4340 cm⁻¹, measured at Darwin. (b) Magnification of the 4300–4325 cm⁻¹ range (blue dashed box) with both the original spectrum (black) and the same spectrum, convolved with the TROPOMI instrument response function (red).

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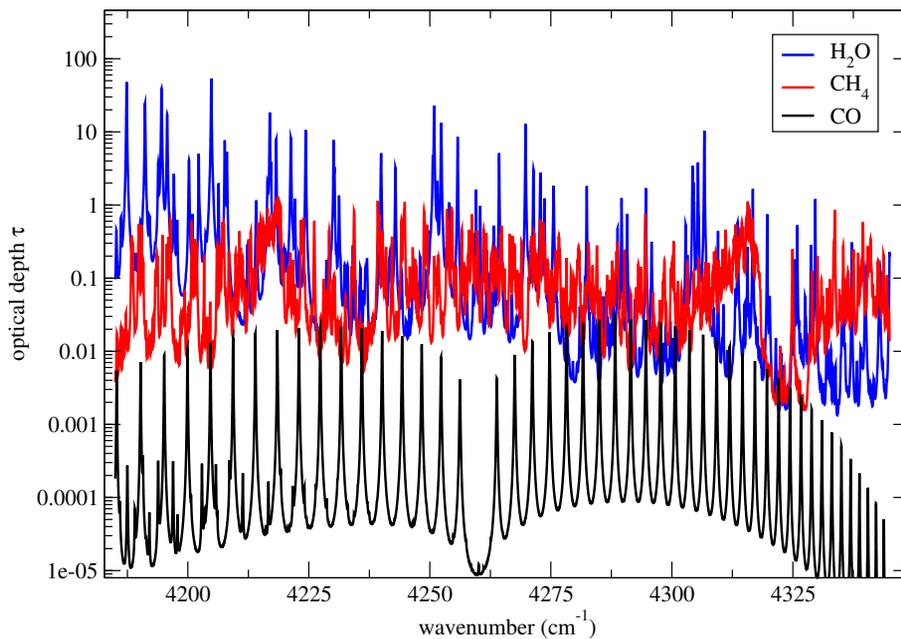


Fig. 2. Approximate optical depth versus wave numbers, attributed to the three species considered for the spectral range 4190–4340 cm^{-1} : CH₄ (red), H₂O (blue), and CO (black).

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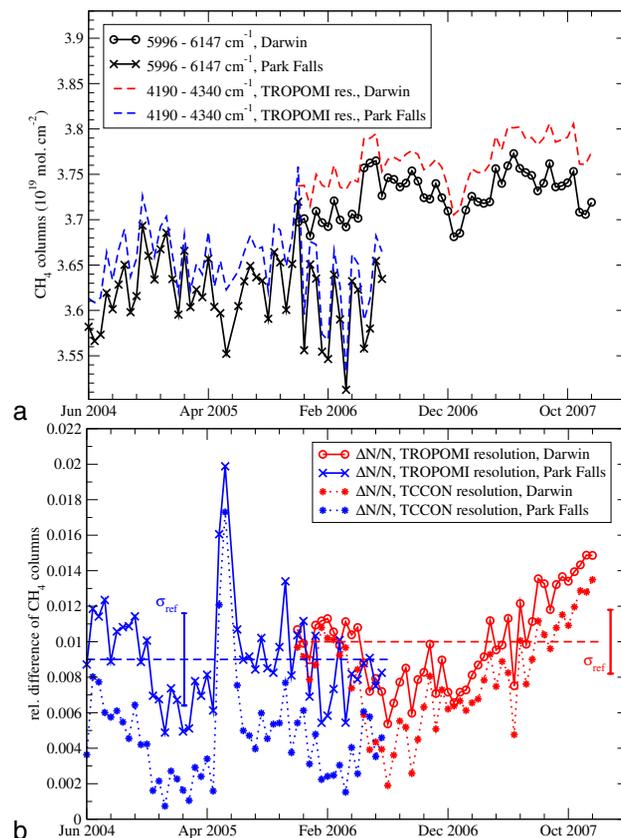


Fig. 3. CH₄ retrieval accuracy for the 4190–4340 cm⁻¹ range. **(a)** shows the time-series of CH₄ columns at Park Falls (crosses) and at Darwin (circles). **(b)** shows the relative differences between columns retrieved at original (dotted lines) and at TROPOMI resolution (solid lines) with respect to reference values from 5996–6145 cm⁻¹.

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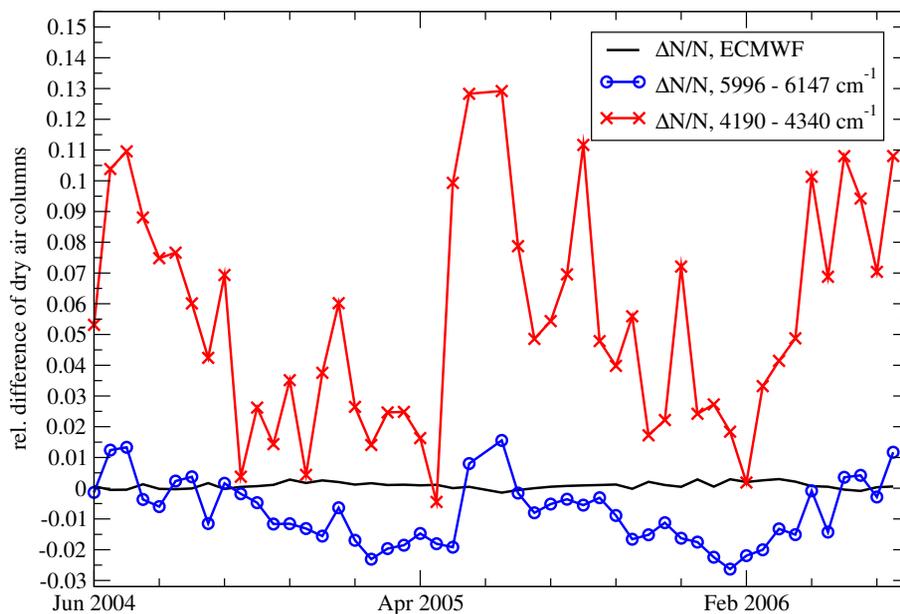


Fig. 4. Impact of spectroscopic line lists on derived pressure at Park Falls. Black: Total dry air column for fixed ECMWF pressure profile, plotted as relative difference to in-situ measurement. Circles: dry air column derived from 5996–6145 cm^{-1} , crosses: dry air column derived from 4190–4340 cm^{-1} .

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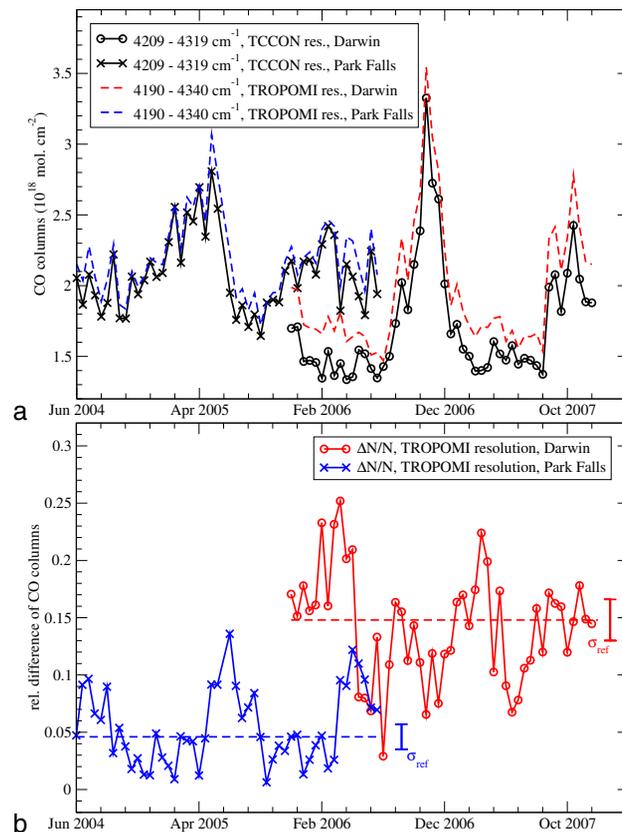


Fig. 5. CO retrieval accuracy at 4190–4340 cm^{-1} for Darwin (circles) and Park Falls (crosses). **(a)** shows the time-series, **(b)** shows the relative differences between columns retrieved at TROPOMI resolution and columns retrieved from window 5 (original high resolution).

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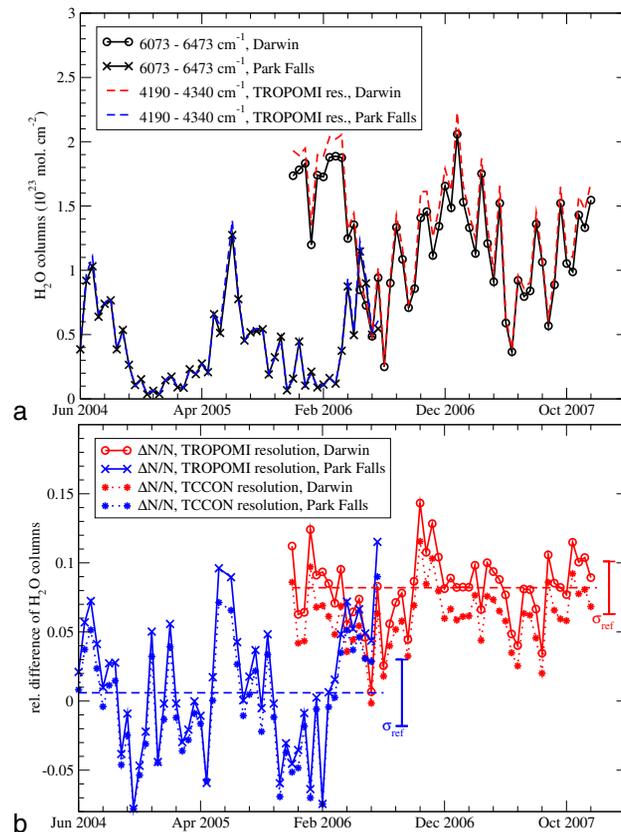


Fig. 6. H₂O retrieval accuracy at 4190–4340 cm⁻¹ for Darwin (circles) and Park Falls (crosses). **(a)** shows the time-series, **(b)** shows the relative differences between columns retrieved at 4190–4340 cm⁻¹ (for TROPOMI and original high resolution) and columns retrieved from window 4.

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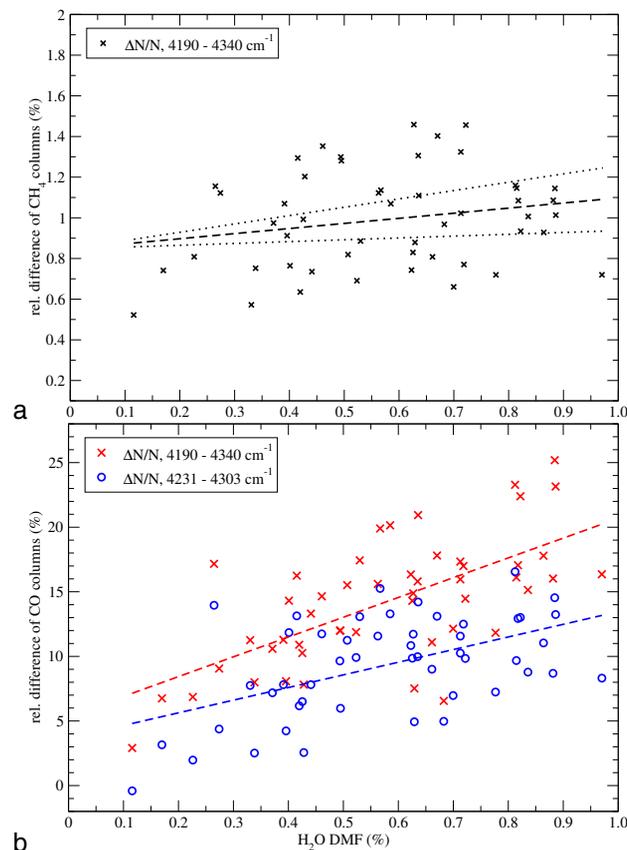


Fig. 7. Correlation of retrieval errors with humidity at Darwin. Deviations of CH_4 (a) and CO columns (b) with respect to the reference values are plotted against H_2O DMF. Red crosses indicate nominal CO retrievals, blue circles show results for an optimised CO sub-window. Dashed lines denote linear fits.

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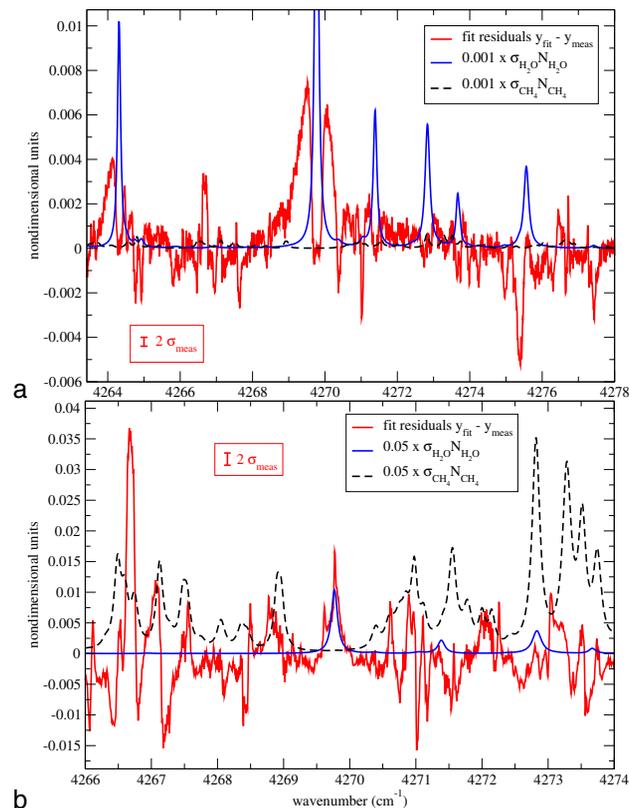


Fig. 8. Spectral fit residuals for wet atmospheric conditions at Darwin (**a**) and for dry atmospheric conditions at Park Falls (**b**). Fit residuals (red line) are over-plotted with optical depth of H₂O (blue line) and CH₄ (black dashed line), average measurement uncertainty indicated by error bars in boxes.

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