Accurate mobile remote sensing of XCO$_2$ and XCH$_4$ latitudinal transects from aboard a research vessel

F. Klappenbach$^1$, M. Bertleff$^1$, J. Kostinek$^1$, F. Hase$^1$, T. Blumenstock$^1$, A. Agusti-Panareda$^2$, M. Razinger$^2$, and A. Butz$^1$

$^1$IMK-ASF, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
$^2$The European Centre for Medium-Range Weather Forecasts (ECMWF), Shinfield Park, Reading, RG2 9AX, UK

Correspondence to: F. Klappenbach (friedrich.klappenbach@kit.edu)

Received: 2 June 2015 – Published in Atmos. Meas. Tech. Discuss.: 20 July 2015
Revised: 17 November 2015 – Accepted: 18 November 2015 – Published: 1 December 2015

Abstract. A portable Fourier transform spectrometer (FTS), model EM27/SUN, was deployed onboard the research vessel Polarstern to measure the column-average dry air mole fractions of carbon dioxide (XCO$_2$) and methane (XCH$_4$) by means of direct sunlight absorption spectrometry. We report on technical developments as well as data calibration and reduction measures required to achieve the targeted accuracy of fractions of a percent in retrieved XCO$_2$ and XCH$_4$ while operating the instrument under field conditions onboard the moving platform during a 6-week cruise on the Atlantic from Cape Town (South Africa, 34°S, 18°E; 5 March 2014) to Bremerhaven (Germany, 54°N, 19°E; 14 April 2014). We demonstrate that our solar tracker typically achieved a tracking precision of better than 0.05° toward the center of the sun throughout the ship cruise which facilitates accurate XCO$_2$ and XCH$_4$ retrievals even under harsh ambient wind conditions. We define several quality filters that screen spectra, e.g., when the field of view was partially obstructed by ship structures or when the lines-of-sight crossed the ship exhaust plume. The measurements in clean oceanic air, can be used to characterize a spurious air-mass dependency. After the campaign, deployment of the spectrometer alongside the TCCON (Total Carbon Column Observing Network) instrument at Karlsruhe, Germany, allowed for determining a calibration factor that makes the entire campaign record traceable to World Meteorological Organization (WMO) standards. Comparisons to observations of the GOSAT satellite and concentration fields modeled by the European Centre for Medium-Range Weather Forecasts (ECMWF) Copernicus Atmosphere Monitoring Service (CAMS) demonstrate that the observational setup is well suited to provide validation opportunities above the ocean and along interhemispheric transects.

1 Introduction

Carbon dioxide (CO$_2$) and methane (CH$_4$) are the most important anthropogenic greenhouse gases (Stocker et al., 2013). To understand their emission and uptake processes at the Earth’s surface, inverse modeling approaches exploit the observed variability of the atmospheric concentration fields (e.g., Peters et al., 2007; Chevallier et al., 2010; Peylin et al., 2013). Estimating surface fluxes of CO$_2$ and CH$_4$ in particular requires accurate as well as spatially and temporally dense observations of the atmospheric abundances. Such observations have been delivered for decades by ground-based in situ monitoring stations (e.g., Masarie et al., 2014), though their coverage in remote regions is sparse. Remote sensing of column-average CO$_2$ (XCO$_2$) and CH$_4$ (XCH$_4$) from satellites is an emerging technique that promises improved coverage and data density but faces challenging accuracy requirements on the order of fractions of a percent (e.g., Chevallier et al., 2007; Bergamaschi et al., 2009). Therefore, XCO$_2$ and XCH$_4$ soundings recorded by satellites such as Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY (SCIAMACHY), Greenhouse Gases Observing Satellite (GOSAT) (Burrows et al., 1995; Bovensmann et al., 1999), or the recently launched Orbiting Carbon

Published by Copernicus Publications on behalf of the European Geosciences Union.
Observatory-2 (OCO-2) require thorough validation through ground-based measurements.

To this end, the Total Carbon Column Observing Network (TCCON) has been established. Currently operating more than 20 ground-based high-resolution lab Fourier transform spectrometers (FTS) at stations worldwide (Wunch et al., 2011; TCCON-Wiki, 2015). These ground-based FTS collect solar absorption spectra in direct-sun view allowing for accurate knowledge of the light path through the atmosphere and thereby, avoiding one of the largest sources of error for satellite remote sensing of XCO$_2$ and XCH$_4$ (Rayner and O’Brien, 2001). The typical accuracy of TCCON spectrometers is reported better than 0.8 ppm (parts per million) for XCO$_2$ and 7 ppb (parts per billion) for XCH$_4$ (Wunch et al., 2010). The TCCON FTS operate at high spectral resolution and therefore, require stationary containers that can house the rather bulky and delicate instruments. Developments are underway to prove performance of smaller and more robust remote sensing instruments that can be easily deployed in remote regions, in larger numbers, and on mobile platforms (Kobayashi et al., 2010; Krings et al., 2011; Kawasaki et al., 2012; Petri et al., 2012; Gisi et al., 2012; Frey et al., 2015).

Here, we demonstrate performance of such a small and robust spectrometer for accurate observations of XCO$_2$ and XCH$_4$ on a mobile platform. We deployed a Bruker™ EM27/SUN FTS aboard the German research vessel (RV) Polarstern traveling from South Africa to Germany during a 5-week cruise in March/April 2014.

The EM27/SUN FTS is a table-top, portable instrument operating at medium spectral resolution of 0.5 cm$^{-1}$. Performance of the EM27/SUN FTS in stationary configuration has been proven for XCO$_2$ by Gisi et al. (2012) using measurements alongside the TCCON instrument at Karlsruhe, Germany. Previously, Notholt et al. (1995) and Warneke et al. (2005) have shown that RV Polarstern is an excellent carrier to investigate hemispheric gradients of a large variety of atmospheric constituents including the man-made greenhouse gases. Instrumentation, however, is challenged by harsh ambient conditions. In particular, the moving platform poses a challenge for direct solar absorption spectroscopy since the solar intensity has to be fed precisely into the spectrometer’s entrance aperture, irrespective of the movements of the platform. In the view of satellite validation, shipborne measurements are particularly interesting since currently there are only a few island observatories (e.g., Geibel et al., 2010; Schneider et al., 2012) that allow for validating XCO$_2$ and XCH$_4$ derived from glint-mode satellite operations over the oceans.

Figure 1 illustrates the track of RV Polarstern, started out at Cape Town, South Africa (34°S, 18°E) on 5 March 2014, and entered port at Bremerhaven, Germany (54°N, 19°E) on 14 April 2014. During the cruise the EM27/SUN spectrometer operated whenever cloud conditions permitted direct-sun view on 31 out of 40 days, in total collecting 5738 spectra for which XCO$_2$ and XCH$_4$ could be derived. Beside record-
and for evaluating the hemispheric concentration gradients in a global model (Sect. 4). Section 5 concludes the study.

2 Instrumentation

The key instrumentation was an EM27/SUN FTS (Sect. 2.2) available for purchase at Bruker™ Optics together with a custom-built solar tracker (Sect. 2.1).

2.1 Custom-built solar tracking system

The solar tracker used was based on the “Cam-tracker” setup initially designed for stationary platforms by Gisi et al. (2011). Here, it was modified for mobile applications and its performance could be demonstrated through its operation on RV Polarstern: the system consists of two mirrors that rotate along an azimuth and elevation axis driven by two stepper motors, and it is able to point toward every point on the sky hemisphere above the instrument. A camera observes the solar image centered about the entrance aperture of the spectrometer. An image analysis software fits circles to the solar image and the aperture. The mismatch between the circle centers drives a PID (proportional-integral-differential) control unit which adjusts the mirrors to finally recenter the solar image. On stationary platforms, PID (proportional-integral-differential) control cycles exceeding a second are acceptable given that the solar disk moves slowly (< 0.005° s⁻¹) across the sky. Under such conditions, Gisi et al. (2011) showed that tracking errors are typically less than 0.003° which was well below the targeted tracking accuracy of 0.05° needed to keep pointing-induced XCO₂ errors below 0.1 ppm.

Adapting the solar tracking system to mobile applications posed the following two major challenges.

– At start-up or after interruptions of the tracking operations, the solar tracker needs to find the solar disk without knowledge of the observatory’s orientation. For stationary operations the attitude of the observatory is typically given at start-up (and left unchanged) and astronomical calculations provide the initial relative position of the sun.

– The PID control cycle needs to cope with the potentially fast motion of the platform in addition to the slow motion of the solar disk.

Basically, the used tracking procedure can be split into two parts that tackle the required adaptations: the coarse and the fine-tracking mode. The latter is a refinement of the concept proposed by Gisi et al. (2011). Both required additional or exchange of hardware.

The coarse-tracking mode relied on a 185° fish eye-lens (Lensation, BFM2320) that was mounted on a CMOS digital camera (VR-magic, model C-9+ PRO BW CMOS, 1288 × 1032 pixel) that observed the sky hemisphere above the instrument. The brightest spot on the camera image gave the approximate position of the solar disk. A lookup table that was generated through lamp calibration in our laboratory translated image positions into azimuth and elevation angles of the tracking mirrors. The angular resolution of the coarse tracking is approximately 0.15° pixel⁻¹ and is strongly variable within the field of view. Thus, it is not accurate enough to perform the entire tracking process with the desired accuracy of 0.05°. However, the coarse-tracking ensures that the solar disc of about 0.53° diameter can be located within the field of view (FOV) of the fine-tracking camera in the range of 10°–15°.

Once the solar image was within the FOV of the fine-tracking camera (VR-magic, model C-9+ PRO BW CMOS, 1288 × 1032 pixel, f = 50 mm), coarse tracking went idle and fine-tracking mode took over and centered the solar image on the aperture of the spectrometer through a circle fitting routine. In order to enhance the tracking velocity for a moving platform, it was essential to update the motor control parameters (position, speed, or acceleration) as frequently as possible. To minimize the time lost during communication between the fine-tracking camera and the control unit (embedded PC system, ARK-2150 by Advantech), the camera only transmitted a region of interest of approximately 200 pixel × 200 pixel out of the full camera frame of 1288 pixel × 1032 pixel via USB. Additionally each motor was connected via its own RS485 connection to the control unit to enable simultaneous send and receive to/from both motors. Based on this hardware setup, our custom-built image acquisition, processing, PID and motor control software achieved control cycle durations on the order of 20–30 ms corresponding to an update frequency of 33–50 Hz. Table 1 summarizes individual contributions.

We evaluate the onboard performance of the solar tracker by examining the deviations between the center of the solar image and the targeted center of the spectrometer aperture. The deviations were logged during the entire campaign on board RV Polarstern. While such an assessment provides an estimate of the tracking precision, it does not allow for quantifying systematic tracking errors, e.g., due to a misalignment of the actual and the assumed center of the spectrometer aperture. A misalignment of the latter kind would lead to a sys-

<table>
<thead>
<tr>
<th>Task</th>
<th>Duration ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Image acquisition</td>
<td>≈ 10</td>
</tr>
<tr>
<td>Image processing</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Motor position request</td>
<td>5–10</td>
</tr>
<tr>
<td>Update motor speed</td>
<td>5–10</td>
</tr>
<tr>
<td>Overall average</td>
<td>≈ 22</td>
</tr>
</tbody>
</table>

Table 1. Leading contributions to the duration of fine-tracking control cycles of the solar tracker (average values retrieved from housekeeping data logged during the measurement campaign aboard RV Polarstern).
tematic pointing offset, i.e., the solar tracker does not point exactly to the center of the sun but slightly to the limb. However, the fine-tracking camera and aperture were carefully aligned in the lab to avoid such systematic errors.

Figure 2 (left) shows the logarithmic occurrence count of tracking deviations in azimuth and elevation directions. The desired tracking accuracy of 0.05° is red encircled. 98.7% of the entire campaign data are within this tracking error regime. The record includes all kinds of interruptions such as shadowing by the ship’s infrastructure or cloudy conditions. The tracking accuracy of the entire data accounts for 0.0076° (1σ), which means, that 68.3% of all data points feature an accuracy of this value or better. The origin of the star-shape pattern remains unclear.

Figure 2 (right) shows the dependency of the tracking precision on the angular acceleration for an illustrative day of the ship cruise. Because the PID parameters were changed along the entire cruise, we focus on that representative day. To simplify the evaluation, we analyze just the azimuth component. The azimuth component is physically the most inert part of the system and serves as a conservative estimate. The elevation component, however, shows very similar behavior. Generally, the larger the accelerations required to compensate ship movements, the poorer the tracking precision. The linear dependency of tracking precision on angular acceleration can be used to derive a maximum acceleration up to which our solar tracking performs within the required limits: as long as the angular acceleration did not exceed approximately 6.5° s⁻², the tracking precision complied with the 0.05° requirement.

2.2 Fourier transform spectrometer EM27/SUN

The Bruker™ EM27/SUN FTS is a table-top Fourier transform spectrometer of approximately 25 kg weight. It was designed in the framework of a cooperation between KIT and Bruker™ for stationary XCO₂ and XCH₄ measurements (Gisi et al., 2012). Here, we give a brief overview of the most important features.

The EM27/SUN is constructed as a RockSolid™ pendulum interferometer with two cube corner mirrors and a CaF₂ beam splitter. The optical path difference of 1.8 cm corresponds to a spectral resolution of 0.5 cm⁻¹. A 127 mm parabolic mirror together with the 0.6 mm aperture defines an semi-FOV of 2.36 mrad. With the solar disc as light source, this FOV corresponds to approximately 51.0% of the solar diameter. The InGaAs non-cooled detector (HAMAMATSU™ G12181-010K) with a sensitive area of approximately 0.8 mm², has a spectral response from 5000 to 11 000 cm⁻¹. Typical exposure times are approximately 58 s for 10 double sided interferograms, recorded in DC-mode. Differences to the prototype device used by Gisi et al. (2012) are a slightly different focal length of 127 mm instead of 101.6 mm and a detector with a spectral coverage of 5000 to 11 000 cm⁻¹ instead of 6000 to 9000 cm⁻¹. The latter adjustment was necessary to cover the spectral range of CH₄ absorption. Further, a bandpass filter (Thorlabs FB1650-12, center wavenumber: 6061 cm⁻¹, FWHM (full width at half maximum): 44.0 cm⁻¹) has been mounted in front of the internal calibration lamp in order to characterize the ghost-to-parent ratio as described in Dohe et al. (2013) or Messerschmidt et al. (2010).

Gisi et al. (2012) showed, that this instrument is highly stable against thermal influences in particular as demonstrated by observations in summer and winter in Karlsruhe. Furthermore moderate mechanical stress due to deployment and dismounting do not harm the accuracy of the instrument. This makes the instrument in particular suitable for campaign purposes.
F. Klappenbach et al.: Accurate mobile remote sensing of XCO$_2$ and XCH$_4$

Table 2. List of key retrieval parameters. The line lists are altered from the original HITRAN line lists where “mod” indicates a modification suggested by Lamouroux et al. (2010) to take line mixing effects into account. Likewise “TCCON” indicates a modification suggested by Wunch et al. (2011).

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>O$_2$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral window cm$^{-1}$</td>
<td>6173–6390</td>
<td>5897–6145</td>
<td>7765–8005</td>
<td>8353.4–8463.1</td>
</tr>
<tr>
<td>Line list</td>
<td>HITRAN08 (mod)</td>
<td>HITRAN08</td>
<td>HITRAN08 (TCCON)</td>
<td>HITRAN09 (TCCON)</td>
</tr>
<tr>
<td>Disturbing gas</td>
<td>H$_2$O, CH$_4$</td>
<td>H$_2$O, CO$_2$</td>
<td>H$_2$O</td>
<td>–</td>
</tr>
<tr>
<td>Continuum points</td>
<td>40</td>
<td>20</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>SZA dependency ($\Theta = 80^\circ$)</td>
<td>$\approx 0.6%$</td>
<td>$\approx 0.4%$</td>
<td>none</td>
<td>not assessed</td>
</tr>
<tr>
<td>A priori profile</td>
<td>CAMS</td>
<td>CAMS</td>
<td>static</td>
<td>CAMS</td>
</tr>
</tbody>
</table>

3 Data reduction and evaluation

The following section guides through the data evaluation process. Section 3.1 describes the spectral retrieval of absorber total columns from the recorded solar absorption spectra. Various quality filters (Sect. 3.2) and corrections (Sect. 3.3) guarantee that quality of the estimated XCO$_2$ and XCH$_4$ is consistently high throughout the ship cruise.

3.1 Spectral retrieval

We used the software package PROFFIT v.9.6 (Hase et al., 2004) for the spectral retrieval of absorber total columns. In principle, PROFFIT is capable of retrieving vertical profile information from high spectral resolution measurements of the atmospheric transmittance in direct-sun view (García et al., 2012). The medium resolution of 0.5 cm$^{-1}$ of the EM27 FTS, however, is insufficient to extract profile information from the pressure and temperature dependent absorption line shapes. Therefore, here, we chose a configuration that retrieved a scaling parameter for the a priori absorber profiles. In particular the number of degrees of freedom (DOF) was chosen to be one (DOF = 1).

The absorber total columns to be retrieved were the ones of the targeted species CO$_2$ and CH$_4$, and the ones of the ancillary species molecular oxygen (O$_2$) and water vapor (H$_2$O). The latter is an interfering species. O$_2$ was used to calculate the dry air mole fraction $X_{gas}$ of the desired target gas via

$$X_{gas} = 0.209420 \cdot \frac{C_{gas}}{C_{O2}}$$

where $C_{gas}$ is the gas total column in units molec m$^{-2}$. Referencing the targeted gas abundance to the known O$_2$ abundance is a common approach to cancel out instrument and retrieval related errors common to the retrievals of O$_2$ and the target species.

The a priori profiles of CO$_2$ and CH$_4$ are taken from the CAMS global cyclic 1-day forecasts which are based on the ECMWF Integrated Forecasting System (IFS) as documented by (Agustí-Panareda et al., 2014; Massart et al., 2014). The H$_2$O profiles are from the IFS 1-day forecasts extracted from the same model simulation as CO$_2$ and CH$_4$.

We interpolated all profiles temporally and spatially on the model grid (0.5° × 0.5° × 3 hourly) in order to avoid discontinuities. The top level of the CAMS data (0.1 hpa ≈ 65 km height) was extrapolated upon ≈ 120 km height in order to fit the layers of the meteorological profiles described below. Meteorological parameters such as pressure and temperature vertical profiles were based on the monthly latitudinal mean profiles provided by CIRA-86$^1$ (Fleming et al., 1988) that reaches up to 120 km height in 77 levels. If available, these meteorological profiles were supplemented by the daily noon-time radiosonde measurements from aboard RV Polarstern that reached altitudes up to 30 km height (König-Langlo, 2014). If no radiosonde data were available, the data from the global model reanalysis from the National Centers for Environmental Prediction (NCEP) (Kalnay et al., 1996) was used to supplement the initial profile up to approximately 30 km height. The NCEP data were downloaded via the Goddard auto mailer system (Schoeberl et al., 2014). This combined profile was interpolated on a 49 layer grid from measurement height up to 120 km.

The a priori O$_2$ profile a priori was a generic static profile, that represented a typical situation.

We used the High Resolution Transmission (HITRAN) database (Rothman et al., 2009) from 2008 to calculate the atmospheric gas absorption lines. While as we left the line list for CH$_4$ unchanged, we modified the line lists of CO$_2$ as suggested by Lamouroux et al. (2010) to take line-mixing effects into account. The line list for O$_2$ was modified according to TCCON recommendations. Finally, the H$_2$O line list was based on HITRAN updates from 2009.

Table 2 gives an overview of the most important retrieval parameters among the various spectral windows.

---

$^1$CIRA stands for “COSPAR International Reference Atmosphere”, whereas COSPAR stands for “Committee on Space Research”.

---

www.atmos-meas-tech.net/8/5023/2015/  Atmos. Meas. Tech., 8, 5023–5038, 2015
The instrumental line shape (ILS) of the instrument was determined analyzing water vapor absorption lines along a light path through ambient air in our laboratory. We collimated a 50 W light bulb and positioned at ~ 4.0 m distance to the spectrometer. A data logger (MRC, MHB-382SD) provided temperature and pressure readings and allowed to calculate the appropriate absorption line shapes. Parameters defining the ILS are retrieved together with the ambient H₂O abundance from absorption spectra in the spectral range at 7000–7400 cm⁻¹ using the LINEFIT software package version 14 (Hase et al., 1999). We found ILS parameters 0.99594 for the modulation efficiency and 2.83 × 10⁻³ for the phase error in the post campaign retrieval. As long as no instrumental changes (e.g., accidental or intentional changes in the optical alignment) are undertaken, the inferred ILS parameters were shown to be constant over month-long timescales (Gisi et al., 2012; Frey et al., 2015).

We performed the pre-processing with the Python routine “Calpy_mobile” program developed at KIT. This routine requests and downloads the meteorological profile data at the Goddard auto-mailer system and generates the input profiles with the radiosonde data. Additionally it performs the DC correction (Keppel-Aleks et al., 2007a) (see Sect. 3.3) on the interferogram, the Fourier transformation and finally exports it into a binary input format for PROFFIT.

3.2 Quality filters

We operated the spectrometer semi-automatically from morning to afternoon on deck of the RV Polarstern whenever outside weather conditions were not too harsh. Therefore, spectra were recorded also under unfavorable conditions, e.g., when the sun was partially obscured by ship structures or when lines-of-sight crossed the exhaust plume (EP) of the ship. To exclude such measurements from the scientific data set, we applied three quality filters: the DC filter screened strong intensity fluctuations. The O₂ filter gave an estimate on the retrieval quality with the ground pressure as reference. Finally the EP filter (exhaust plume) removed measurements, where the instrument’s line of sight passed the ships exhaust plume.

The DC filter was designed to sort out intensity fluctuations during the measurement. These fluctuations can for example be introduced by variable cirrus clouds or by the ship’s structures obscuring the line of sight. We operated the EM27/SUN FTS in the DC mode, i.e., the spectrometer recorded the full interferogram including its smoothly varying DC part. Strong fluctuations in the DC part are indicative for varying source brightness. Affected measurements can be corrected with the low pass filtered interferogram Iₚ (Keppel-Aleks et al., 2007b). The implementation of the low pass was a running mean on the interferogram over 61 sampling points with 5 iterations.

However, this DC correction did not remove the entire DC effect, and especially strong variations still appear to influence the retrieval result. Based on the DC correction, we defined a filter criterion DC to sort out affected measurements:

\[ DC = \frac{|I_p|_{\text{max}} - |I_p|_{\text{min}}}{|I_p|_{\text{max}}} \]  

The higher the value of the DC criterion, the stronger the effect on the retrieved trace gas. Effects of the DC filter are examined in Figs. 3 and 4 and discussed together with the next filter. Here, we choose a filter threshold DC < 0.05 that discards 23.2 % of the recorded spectra.

The O₂ filter was based on the comparison between surface pressure calculated from the retrieved O₂ column and the in situ measured surface pressure (König-Langlo, 2014) as suggested by Wunch et al. (2011). Deviations indicate a false measurement since the O₂ concentration in the atmosphere can be assumed constant. We took a scaling factor of 0.9705 into account for calibrating the spectroscopically retrieved surface pressure p_{ret} to the in situ measurements p_{in situ} (Wunch et al., 2011), the ratio

\[ R_{p_{sat}} = \frac{0.9705 \times P_{O_2,dry} + P_{H_2O}}{p_{in situ}} \]  

scatters around unity. Here, we screened spectra whenever R_{p_{sat}} deviated by more than 0.3 % from unity removing 6.3 % of the DC-filtered spectra. We determined the filter thresholds for both the DC and O₂ filters by the definition of a quality criterion Q for the retrieved XCO₂: we selected a subset of representative days from 22 to 25 March 2014. First, we removed diurnal variations from the record by fitting a 3rd order polynomial for each day and subtracted the polynomial from the retrieved XCO₂. The standard deviation of the
residual XCO₂ time series now defines our quality criterion $Q$ in units of ppm.

Figure 3 illustrates how the DC filter and the O₂ filter affects the quality criterion $Q_{XCO₂}$. In general the stricter the filter thresholds the better the precision but the fewer data passing the quality filters. Figure 4 shows the XCO₂ measurements for these 4 representative days and the effect of the DC and O₂ filters with the selected thresholds. The overlap of the two filters is very little, showing that they filter for independent effects.

Under the assumption that the 3rd order polynomial removed all geophysical variability due to local surface fluxes and advective transport, this quality criterion provides a precision estimate for the EM27/SUN amounting to $Q_{XCO₂} = 0.11$ ppm for XCO₂. Following an analogous procedure for XCH₄ yields $Q_{XCH₄} = 0.61$ ppb.

The third filter is the exhaust-plume filter (EP filter). The ship’s funnel was located at a few tens of meters distance to the spectrometer setup and rose to approximately 12 m above deck. If the line of sight passed through the exhaust plume, enhancements in the observed XCO₂ were to be expected. In order to screen such observations, we calculated the enhancement pattern in the XCO₂ time series from our line of sight (los), the prevailing wind conditions, and the ship’s exhaust.

An estimated exhaust flux $E_s$ fed a simple plume model that calculated the XCO₂ enhancement $E_{los}$ and took into account the relative wind speed and direction between the ship-based spectrometer and the plume. We relied hereby on the plume diffusion model from Bovensmann et al. (2010). Defining the $x$ coordinate as downwind direction and the $y$ coordinate as the crosswind direction, the enhancement

$$E_{los} = \int_{los} \frac{E_s}{v_{rel} \sqrt{2\pi \cdot \sigma_y(x)}} \cdot \exp\left(-\frac{y^2}{2 \sigma_y(x)^2}\right) \, dx \, dy,$$  

(4)

where $v_{rel}$ is the relative wind velocity between ship and plume, and the parameter $\sigma_y(x) = 0.104 \cdot x^{0.894}$ dilutes the plume in crosswind direction ($y$). Thereby, we assume a class C for the atmospheric stability (Bovensmann et al., 2010). Here the exhaust flux $E_s := 1$ is given in arbitrary units (AU). Relative wind velocities $v_{rel}$ and directions were taken from the records of the onboard meteorological station. The line of sight from instrument position up to 30 m was projected into the downwind ($x$) and crosswind ($y$) direction and then. $E_{los}$ was calculated by numerically integrating Eq. (4). Figure 5 shows a day where according to the label book the line of sight passed the exhaust plume as confirmed by the record of relative wind velocities and directions. Measured O₂ columns and XCH₄ were not affected by the ship’s exhaust, XCO₂, however, were found enhanced by up to 2 ppm. Our model yielded an enhancement $E_{los}$ that was similar in temporal pattern to the observed XCO₂ enhancement that confirmed the overall applicability of our approach.

The EP filter threshold was set such that whenever $E_{los}$ was larger than 0.001 the spectrum was flagged contaminated. 11.1 % of the spectra were discarded by the EP filter. Additionally, 2.8 % of the spectra were rejected due to contamination by the exhaust plume after inspection by eye.

In total, the three filters (DC, O₂, and EP) described above screened about 38.2 % of the recorded spectra.
3.3 Corrections

Two major corrections were necessary to make the XCO₂ and XCH₄ records consistently accurate along the ship cruise: a spurious dependency of the retrieved target gas abundances on solar zenith angle needed to be corrected, and an overall calibration factor needed to be found to make the spectroscopic measurements consistent with the WMO (World Meteorological Organization) calibration scale.

We could reproduce a well known (e.g., Deutscher et al., 2010; Wunch et al., 2011), spurious dependency of XCO₂ and XCH₄ retrieved from TCCON measurements on slant air-mass A, defined as \( A = 1/\cos(\theta) \) with solar zenith angle \( \theta \), with our campaign data. With increasing air mass, the XCO₂ and the XCH₄ retrievals tend to be lower. The source of this effect remains unclear, although uncertainties of spectroscopic line broadening parameters and shortcomings of the Voigt line shape model are likely candidates. Wunch et al. (2011) suggested an empirical correction based on a diurnal effect combined with a \( \theta \)-dependent term. Figure 6 shows that also our XCO₂ and XCH₄ retrievals clearly correlate with SZA. Given that the retrieved surface pressure derived from retrieved O₂ columns did not show such dependency, it must have been driven by the CO₂ and CH₄ column retrievals. To correct for this artifact, we fitted a correction polynomial \( c_{SZA,\ gas}(\theta) \) for the gases CO₂ and CH₄ according to

\[
c_{SZA,\ gas}(\theta) = a \cdot |\theta|^3 + b \cdot |\theta| + c,
\]

where \( a, b, \) and \( c \) are free fit parameters. Thereby, the correction was by definition chosen to vanish at \( \theta = 45^\circ \) as suggested by Wunch et al. (2011) with referencing the measurement to \( \theta = \pm 45^\circ \) for forenoon and afternoon separately.

The corrected XCO₂ and XCH₄ records are then calculated through

\[
X_{SZA,\ gas} = \frac{X_{\ gas}(\theta)}{c_{SZA,\ gas}(\theta)}.
\]

Figure 6 shows the retrieved correction parameters. For the extreme case of \( \theta = 80^\circ \) relative to \( \theta = 0^\circ \), the correction amounts to \( \approx 0.4 \% \) for XCO₂ and \( \approx 0.3 \% \) for XCH₄. A key assumption for this correction is that the measurements took place far away from localized sources and sinks of CO₂ and CH₄. So, no diurnal concentration cycles were to be expected that correlate with the assumed spurious air-mass dependence. Generally, this assumption appeared to be true for our ship-borne measurements above the Atlantic. Meteorological transport can cause advection of diurnal concentration variability from the larger source/sink region. Over the course of the entire measurement campaign, we assume that such transport effects have a statistical pattern such that the air-mass correction is not contaminated in a systematic way.

Finally, we calibrated the entire campaign records to those of the TCCON station at Karlsruhe, Germany (Hase et al., 2015), which in turn is calibrated to WMO standards according to TCCON requirements. TCCON XCO₂ and XCH₄ were retrieved with the GGG2014 software package (Wunch et al., 2011, 2015). We operated the campaign instrument alongside the Karlsruhe TCCON instrument during 4 consecutive days in May 2014 after the ship campaign. Retrievals from the EM27/SUN measurements followed the approach outlined in Sect. 3 including the quality filters described in Sect. 3.2 and the aforementioned correction terms. Hourly means \( \langle X \rangle_h \) of the XCO₂ and XCH₄ were calculated and used to determine the calibration factor \( \gamma_{gas} \) according to

\[
\gamma_{gas} = \left\langle \frac{X_{\ EM27}}{X_{\ wmo}} \right\rangle_h,
\]
where brackets indicate averaging over the entire data set. We then referenced the entire EM27/SUN data set to the WMO calibrated TCCON reference with the global scaling factor \( \gamma_{\text{gas}} \):

\[
X_{\text{gas, wmo}} = \frac{X_{\text{gas}}}{\gamma_{\text{gas}}}. \tag{8}
\]

Figure 7 shows the post campaign reference measurements.

We found calibration factors \( \gamma_{\text{XCO}} = (0.99568 \pm 0.00049) \) and \( \gamma_{\text{XCH}} = (0.98162 \pm 0.00073) \) where the error estimate refers to the standard deviation among the calibration data set. Note that the calibration factor for \( O_2 \) (see Sect. 3.2) was still present in the un-referenced data and is included in the calibration factor \( \gamma_{\text{gas}} \). Note further, that this calibration was obtained with the reprocessed TCCON-Karlsruhe data set. This improvement was found to be necessary because the station Karlsruhe differs in the optical setup from other TCCON stations (M. Kiel, personal communication, 2015). The difference can be scaled by using \( \gamma_{\text{XCO}, \text{old}} / \gamma_{\text{XCO}, \text{new}} = 1.00219487 \) and \( \text{XCH} \) by 1.00103463.

### 4 XCO\(_2\) and XCH\(_4\) over the Atlantic

Figure 8 shows the final XCO\(_2\) and XCH\(_4\) records measured above the Atlantic in March/April 2014 from aboard RV Polarstern. All corrections (see Sect. 3.3) and quality filters (see Sect. 3.2) were applied. In order to motivate the usefulness of such ship deployments for satellite and model validation, Fig. 8 additionally shows satellite soundings from the Greenhouse Gas Observing Satellite (GOSAT) and XCO\(_2\) and XCH\(_4\) modeled by the CAMS (Copernicus Atmosphere Monitoring Service) data assimilation and forecasting system (Agusti-Panareda et al., 2014; Massart et al., 2014). Satellite soundings were correlated to RV Polarstern records with a 5° latitudinal/longitudinal radius in addition with a 4 h temporal coincidence radius (see Fig. 1). Model data were temporally and spatially interpolated to the RV Polarstern measurements in order to avoid discontinuities.

The lower panel shows the differences of the various greenhouse gas products to the campaign record. Here averages of all EM27/SUN soundings within the coincidence criteria were subtracted from the individual satellite soundings.

For GOSAT, we discuss three different GOSAT retrieval methods, the RemoTeC-full-physics (FP) and RemoTeC-proxy (Butz et al., 2011; Guerlet et al., 2013; Schepers et al., 2012) retrieval as well as the Atmospheric CO\(_2\) Observations from Space (ACOS) approach (O’Dell et al., 2012; Crisp et al., 2012). Even though the in-orbit operations of GOSAT have been adapted to maximize the number of ocean-glint soundings during the campaign period, the number of coincident and quality-assured retrievals amounts to a few tens of samples, that largely varied among the retrieval approaches. The main difference between the RemoTeC-FP and the RemoTeC-proxy algorithm is the way the light path through the atmosphere is estimated. While RemoTeC-FP retrieves aerosol parameters simultaneously with XCO\(_2\) and XCH\(_4\) and takes multiple scattering effects into account, the RemoTeC-proxy approach is restricted to XCH\(_4\) only and uses the retrieved CO\(_2\) column together with CarbonTracker-modeled CO\(_2\) as a light path proxy. ACOS is, as well as RemoTeC-FP, a full-physics approach, i.e., simultaneously retrieving XCO\(_2\) and atmospheric scattering properties. Differences between RemoTeC-FP and ACOS relate to details how aerosol and cloud scattering parameters are implemented and how the inverse problem is solved. Most importantly here, ACOS delivers many more data than RemoTeC-FP for ocean-glint soundings since RemoTeC-FP resorts to a conservative cloud and aerosol filtering scheme using the “upper edge” method (Butz et al., 2013). ACOS does not deliver XCH\(_4\). For the comparison with all the GOSAT products the smoothing effect of the averaging kernel matrix is neglected. Compared to systematic errors introduced by temporal and spatial distance, we consider these effects to be negligible.

CAMS provides global operational analysis and forecast of CO\(_2\) and CH\(_4\) in near real time. Here we have used a forecast without any data assimilation with a horizontal resolution of around 80 km and 60 vertical levels from surface to 0.1 hPa. The atmospheric CO\(_2\) and CH\(_4\) mixing ratio fields modeled by CAMS rely on the ECMWF IFS model\(^2\). The IFS has a simple carbon module (Boussetta et al., 2013) to model the CO\(_2\) uptake and release from vegetation. The CO\(_2\) biogenic fluxes from vegetation are adjusted to correct for large-scale biases by using a climatology of optimized CO\(_2\) fluxes (Agusti-Panareda et al., 2015; ECMWF Tech Memo 2015). The CH\(_4\) fluxes and other CO\(_2\) fluxes are prescribed by inventories and seasonally varying climatologies, including the chemical sinks for CH\(_4\) in the troposphere and stratosphere. A more detailed description of the CO\(_2\) and CH\(_4\) forecast configuration can be found in Agustí-Panareda et al. (2014) for CO\(_2\) and in Massart et al. (2014) for CH\(_4\). The plotted data stem from the model simulation, where the meteorology is re-initialized daily using ECMWF meteorological analyses but CO\(_2\) and CH\(_4\) are free running, i.e., no assimilation of CO\(_2\) and CH\(_4\) observations is performed.

The EM27/SUN XCO\(_2\) measurements from aboard RV Polarstern, Fig. 8 (left), show a north–south (N–S) gradient of up to 6.8 ppm between ~45° N and ~30° S at the end of the Northern Hemisphere dormant season. This is largely expected from previous assessments (e.g., Denning et al., 1995). Beside the N–S gradient, diurnal and day-to-day variations on the order of 1 ppm are found most likely originating from transport of far-away source/sink signals. Note that the

---

\(^2\)https://software.ecmwf.int/wiki/display/IFS/Official+IFS+Documentation
Figure 8. Latitudinal transects of XCO$_2$ (left) and XCH$_4$ (right) for the ship-borne EM27/SUN measurements (daily averages: black dots; all data: gray dots) and various correlative data sets (top) as well as differences of the latter to our ship records (bottom). For XCO$_2$, correlative data sets are the RemoTeC-FP retrievals from GOSAT (ocean glint: blue; land nadir: red), the ACOS retrievals from GOSAT (ocean glint: light blue; land nadir: orange), and XCO$_2$ modeled by the CAMS model (purple). For XCH$_4$, correlative data sets are the RemoTeC-FP retrievals from GOSAT (ocean glint: blue; land nadir: red), the RemoTeC-proxy retrievals from GOSAT (ocean glint: light blue; land nadir: orange), and XCH$_4$ modeled by the CAMS model (purple). For GOSAT, soundings are coincident whenever they are conducted within 5° latitude/longitude of the ship track and within a ±4h time frame. XCO$_2$ and XCH$_4$ differences shown in the lower panels are calculated according to $\Delta = X - \langle X_{EM27} \rangle_{4h}$ where the brackets indicate averaging over 4h.
exhaust of RV Polarstern itself were excluded from the data via the EP filter (see Sect. 3.2).

For XCH₄, Fig. 8 (right), the EM27/SUN soundings find a N–S gradient of roughly 0.06 ppm between ~ 45° N and ~ 30° S. Diurnal and day-to-day variability on the order of 0.01 to 0.02 ppm can be observed around 30° S 35° N. Tentatively, latitudinal variability in XCH₄ and XCO₂ follows similar patterns. For example, one might speculate whether XCO₂ and XCH₄ increasing towards the northern tropics (~ 10° N) are related to emissions of both gases from biomass burning. Though, the inner tropics lack data to confirm that hypothesis.

Both GOSAT XCO₂ retrievals, RemoTeC-FP and ACOS, generally match the EM27/SUN observations within 2 ppm. Due to sparse data coverage, RemoTeC-FP does not allow for assessing the N–S gradient. The ACOS retrievals tentatively show a weaker N–S gradient due to XCO₂ land-nadir soundings north of 23° being somewhat lower than the ship records. Scatter of the data, however, hinders robust conclusions.

The GOSAT RemoTeC-FP and RemoTeC-Proxy XCH₄ retrievals, both agree with the ship-borne records to mostly within 0.02 ppm. As for XCO₂, the yield from RemoTeC-FP is too low to infer robust conclusions but overall RemoTeC-FP delivers XCH₄ offset by 0.01 to 0.02 ppm compared to RemoTeC-Proxy retrievals. The latter fit the validation data particularly well for the tropical ocean-glint soundings. The land-nadir soundings north of 23° N show greater differences of 0.03 to 0.04 ppm, i.e., both RemoTeC-Proxy XCH₄ and ACOS XCO₂, reveal larger differences for the northern mid-latitude land-nadir observations than for the low-latitude ocean-glint soundings. Given that both algorithms and both species are affected, the most likely explanation is that our coincidence criterion is too loose to assume homogeneous concentration fields in the mid-latitudes.

The XCO₂ modeled by CAMS shows an overall excellent agreement to our ship-borne records. In the northern extratropics an offset of 1 to 2 ppm is consistent with an independent evaluation done by Agusti-Panareda et al. (2015; ECMWF Tech. Memo) using TCCON data at several sites in the Northern Hemisphere extratropics. This model bias is linked to errors in the modeled CO₂ fluxes which will be addressed by the CO₂ flux adjustment scheme under development in the CAMS forecasting system. Despite this model bias, the small variations introduced by transport processes can be resolved by both model and measurements. Differences are larger in the tropics where the model overestimates XCO₂. It is clear that the model is not able to represent accurately the CO₂ emissions from West Africa characterized by widespread biomass burning. Due to persistent cloud cover, the ship records lack data in the inner tropics; this hinders further investigation of this source related error. Smaller discrepancies of less than 1 ppm are found in the Southern Hemisphere background air. The smoothing effects introduced by the averaging kernel matrix are directly taken into account due to the use of the model a priories for the spectral retrieval. These effects are larger in the northern extratropics and tropics, but are found to be negligible in the southern extratropics. For XCH₄, model-measurement deviations are below 0.02 ppm for most of the cases. The discrepancies are also larger in the Northern Hemisphere where XCH₄ fluxes are strongest, but the relative differences are much smaller than for XCO₂.

Overall, the deployment of the EM27/SUN spectrometer on RV Polarstern demonstrated that the inferred latitudinal transects of XCO₂ and XCH₄ were of adequate quality to validate soundings from satellites such as GOSAT and to evaluate modeled concentration fields such as provided by the CAMS model. The observations collected during our ~ 5 week campaign are too sparse too allow for a statistically robust ensemble of coincidences with GOSAT, but demonstrated the potential for providing satellite validation over the oceans where other validation opportunities are sparse. Already a few ship cruises, similar to the one discussed here, conducted each year would make a great asset to XCO₂ and XCH₄ remote sensing from satellites in particular for satellites such as OCO-2 providing much denser data coverage than GOSAT. Despite the snapshot-like nature of our observations, the comparison of the ship records to the CAMS model provided hints at model errors in the CO₂ and CH₄ surface fluxes and model deficiencies in the representation of the chemical sink for XCH₄ in tropical regions. Simultaneously comparing measured and modeled XCO₂ and XCH₄ delivers additional confidence in the conclusions since transport related errors are correlated among the two species, thus helping in the model flux/transport error source attribution.

5 Conclusions

We used a portable EM27/SUN FTS to record direct sunlight spectra on board the German research vessel Polarstern. The solar tracking device was adapted in hardware and software such that we could record direct-sun absorption spectra regardless of the ship’s movements and achieved a tracking precision better than the required 0.05° for 98.7 % of the onboard measurements. This implies that our tracking system can handle angular accelerations up to 6.5° s⁻². To guarantee adequate accuracy of the retrieved XCO₂ and XCH₄ abundances, we defined several quality filters and correction steps. The data were filtered for intensity fluctuations during recording of the interferogram (DC filter), spurious variations in the retrieved O₂ reference (O₂ filter), and XCO₂ retrievals that were contaminated by the ship’s local exhaust plume (EP filter). After quality filtering, we corrected for a spurious SZA dependency of the retrieved concentration records, and determined an overall scaling factor with respect to the WMO calibration scale. Thus, the final XCO₂ and XCH₄ concentrations are traceable to WMO standards and show an overall precision of 0.11 ppm for XCO₂ and 0.59 ppb for XCH₄, respectively, as estimated from the scat-
ter of retrieved concentrations after subtracting a polynomial background.

The campaign record of XCO\textsubscript{2} and XCH\textsubscript{4} showed the expected north to south gradient that was overlayed by regional meteorological transport effects. The quality of our ship-based records allowed for comparisons to XCO\textsubscript{2} and XCH\textsubscript{4} retrieved from GOSAT or modeled concentration fields. Although the number of satellite coincidences was low, both the ACOS/GOSAT XCO\textsubscript{2} and RemoTeC-proxy/GOSAT XCH\textsubscript{4} tended to underestimate the interhemispheric gradient due to low retrieved concentrations in the northern extra-tropics. The comparison between the CAMS model and the ship records showed excellent agreement for XCH\textsubscript{4} and a systematic high bias for XCO\textsubscript{2} in the Northern Hemisphere associated with CO\textsubscript{2} surface fluxes.

These comparisons recommend our setup, based on the EM27/SUN FTS and a fast solar tracker, to be used for validating models and satellites, e.g., through future deployments on moving platforms such as research vessels, other ships, or land-based vehicles.

The data collected during the RV Polarstern cruise is publicly available on the PANGEA archive (PANGEA, 2014) as Supplement to this document or upon request.
Appendix A

Remote sensing instruments are usually not uniformly sensitive to all layers in the atmosphere. The averaging kernel matrix weights the contribution of individual layers to the final retrieved column. The averaging kernel matrix depends on the ILS, solar zenith angle and other parameters. In order to compare the retrieval with other products, one has to include the averaging kernel matrix in the comparison as suggested by (Rodgers et al., 2003) and can be written as follows:

\[ c_i = h^T x_i = h^T A x_{\text{true}} + h^T (I - A) x_{\text{apr}} + \epsilon_i. \] (A1)

Here the retrieved total column \( c_i \) from the instrument \( i \) is being calculated using the total column operator \( h \) and the averaging kernel matrix \( A \) on the state vector \( x_i \). \( x_{\text{true}} \) is the true, usually unknown value, \( \epsilon_i \) any kind of errors and \( I \) represents the unity matrix. A comparison to a high resolution profile (e.g., aircraft profile or model) can be calculated assuming the state vector \( x_{\text{true}} \) being the high resolution profile.

In case of \( x_{\text{true}} = x_{\text{apr}} \), the smoothing effect of the averaging kernel cancels out, and both profiles can be compared directly just by applying the total column operator.

Applying the total column operator \( h \) on the averaging kernel matrix \( A \) one gets the total column sensitivity. This can be pictured as the retrieval response to a delta function perturbation in a distinct retrieval layer. Figure A1 shows the retrieval total column sensitivity for the target species \( \text{CO}_2 \) and \( \text{CH}_4 \) in dependence on layer pressure (height) and solar zenith angle. Deviations from the ideal value of one can only be found in very high layers or shallow solar zenith angles.

Figure A1. Retrieval total column sensitivity of the target species in dependence of the layer pressure and solar zenith angle (SZA). The data are averaged over three consecutive campaign days (24 March, 31 March and 8 April). The figures can be interpreted as the factor that the total column product will be enhanced, if one additional molecule would be added to a distinct pressure layer.
The Supplement related to this article is available online at doi:10.5194/amt-8-5023-2015-supplement.

Acknowledgements. Friedrich Klappenbach, Marco Bertleff, Julian Kostinek, and André Butz are supported by the Emmy-Noether program of the Deutsche Forschungsgemeinschaft (DFG) through grant BU2599/1-1 (RemoteC). This work is supported by the Copernicus Programme funded by the European Union. We gratefully thank the crew of the RV Polarstern for their forthcoming and expert support. We thank Alfred Wegener Institute (AWI), Helmholtz Centre for Polar and Marine Research, for operating RV Polarstern and granting access to its infrastructures. We thank Otto Hasekamp and the RemoTeC team at the Netherlands Institute for Space Research (SRON) for co-developing the RemoTeC algorithm and providing RemoTeC/GOSAT retrievals. We thank Christopher O’Dell and the ACOS team at Colorado State University (CSU) and the NASA Jet Propulsion Laboratory for providing ACOS GOSAT retrievals. We thank Matthias Kiel and Matthias Frey for suggesting the DC quality criteria. Thanks again to Matthias Kiel for providing the initial version of “Calpy”.

The article processing charges for this open-access publication were covered by a Research Centre of the Helmholtz Association.

Edited by: D. Feist

References


