



Greenhouse gas emissions of Berlin – Part 1: Instrumental calibration of spectrometers

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Use of portable FTIR spectrometers for detecting greenhouse gas emissions of the megacity Berlin – Part 1: Instrumental line shape characterisation and calibration of a quintuple of spectrometers

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Abstract

Several low resolution spectrometers were used to investigate the CO₂ and CH₄ emissions of the megacity Berlin. Before and after the campaign the instruments were tested side-by-side. An excellent level of agreement and stability was found between the different spectrometers: the drifts in XCO₂ and XCH₄ are within 0.005 and 0.035 %, respectively. The instrumental line shape characteristics of all spectrometers were found to be close to nominal. Cross-calibration factors for XCH₄ and XCO₂ were established for each spectrometer. An empirical airmass correction factor has been applied. As a last calibration step, using a co-located TCCON spectrometer as a reference, a common factor has been derived for the low-resolution campaign spectrometers, which ensures that the records are compatible to the WMO in-situ scale. Finally as a first result of the Berlin campaign we show the excellent agreement of ground pressure values obtained from total column measurements and in situ records.

1 Introduction

The continuing increase of atmospheric greenhouse gas abundances is the major driver of anthropogenic global warming. Accurate measurements of the variable atmospheric concentrations are required for the quantification of sinks and sources of these gases (Olsen and Randerson, 2004). In the last years great efforts have been undertaken to measure column-averaged dry air mole fractions of greenhouse gases with global coverage. Examples are satellite-borne instruments like SCIAMACHY (Frankenberg et al., 2006), GOSAT (Morino et al., 2011) or the recently launched OCO-2 sensor (Frankenberg et al., 2015). For the validation of OCO-2, a network of ground based high resolution Fourier-transform infrared (FTIR) spectrometers of the type 125HR from Bruker has been initiated by Caltech: the Total Carbon Column Observation Network (TCCON). Currently, about 23 TCCON globally distributed stations measure the column-averaged abundances of greenhouse gases in the atmosphere, by recording

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solar absorption spectra in the near infrared (NIR) (Wunch et al., 2010). TCCON has been carefully calibrated against in situ aircraft measurements and sets the reference for remote-sensing measurements of column-averaged greenhouse gas observations. However, it is difficult to use this technical approach for the observation of sources and sinks on a regional scale, because the laboratory spectrometers applied for TCCON are not portable. Recently, KIT developed in cooperation with Bruker, Ettlingen, a portable low resolution FTIR spectrometer for the observation of greenhouse gases in the NIR and demonstrated the excellent stability of the device (Gisi et al., 2012). The spectrometer is now available from Bruker under the part name EM27/SUN. This lightweight device has low infrastructure demands so it can be operated on a campaign basis, at remote places and even on mobile platforms as ships (Klappenbach, 2015). These features not only enable the EM27/SUN to contribute to the total column measurements of the TCCON in previously underrepresented regions, in particular it can be used to gain additional information about isolated sinks and sources of greenhouse gases. Boundary layer abundances of greenhouse gases influenced by emissions from cities have been observed since long using mass spectroscopy (von der Weiden-Reinmüller et al., 2014) or cavity ring down techniques (Newman et al., 2013). The downside of this approach is the high sensitivity to local sources which overemphasizes the near vicinity and the sensitivity with respect to assumptions on vertical exchange of air masses. Here we demonstrate another approach to measure the emissions of a mega city. For this purpose, we operated five EM27/SUN spectrometer surrounding the Berlin conurbation. Over a period of three weeks, we measured the total column of CO₂, CH₄, H₂O and O₂ at the different stations. As the emission of Berlin is small compared to the atmospheric background signal, in the sub percentage order, high precision and stability of the instrument are a prerequisite. This kind of method has been applied for the quantification of individual exhausts before, however, focusing on gases which do not require a comparable level of precision and stability (Mellqvist et al., 2010). In the first part of this study, we present the comprehensive calibration procedures of the spectrometers which we applied. We performed lab-air observations

of water vapour signatures for the determination of instrumental line shape (ILS) characteristics. Moreover, we tested the participating instruments side-by-side for several days before and after the campaign, determined the level of instrumental stability and deduced calibration factors for XCH_4 and XCO_2 in order to assure that data measured by different spectrometers are compatible between each other and with TCCON measurements.

2 Instrumentation and spectrometer characteristics

2.1 EM 27 SUN spectrometer

For the acquisition of solar spectra we utilize the Bruker EM27/SUN which was developed in collaboration with the KIT. A detailed description of the spectrometer can be found in Gisi et al. (2012), in the following only a short overview including changes from the original setup is given.

The EM27/SUN features a RockSolid™ pendulum interferometer with two cube corner mirrors and a CaF_2 beamsplitter. This setup achieves high stability against thermal influences and vibrations. Gimbal-mounted retroreflectors move a geometrical distance of 0.45 cm leading to an optical path difference (OPD) of 1.8 cm which corresponds to a spectral resolution of 0.5 cm^{-1} . As a minor modification of the prototype spectrometer described by Gisi et al. (2012), the production device contains an off-axis mirror with a focal length of 127 mm for centering the solar beam on the detector. Together with the field stop (0.6 mm diameter) this leads to a semi Field-of-View (FOV) of 2.36 mrad. Measurements are recorded with an InGaAs detector operated at ambient temperature. Due to an electronics update it is now possible to record double-sided interferograms (IFG) of 0.5 cm^{-1} resolution. The detector is a photodiode type G12181-010K from Hamamatsu with a size of $1\text{ mm} \times 1\text{ mm}$ and spectral coverage from 5000 to $11\,000\text{ cm}^{-1}$. In contrast to the detector used in the prototype that operated in the spectral region between 6000 and 9000 cm^{-1} , the wider spectral coverage allows the

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observation of CH₄. In addition, total columns of O₂, CO₂ and H₂O are derived from the recorded spectra. The detector signal is DC coupled and thereby supports the correction of variable atmospheric transmission (Keppel-Aleks et al., 2007).

2.2 Ghost to parent ratio

The EM 27 records spectra in the region from 100 to 15 798 cm⁻¹, so in order to satisfy the Nyquist theorem the sampling of the IFG has to be performed at every zero-crossing of the laser signal (HeNe laser, wavelength 633 nm). If the signal is not taken at exactly zero intensity, systematic sampling errors are introduced leading to artefacts in the measured spectrum, so called sampling ghosts (Messerschmidt et al., 2010; Dohe et al., 2013). Bruker recently released an effective workaround for this problem which we adopted for our measurements. A temporal linear interpolation is applied for locating the downward zero crossings. This method suppresses the ghosts below the detection limit ($< 5 \times 10^{-6}$). In addition, we tested this set up for possible line shape errors and other kinds of out-of-band artefacts, but found no detrimental effects.

2.3 Instrumental line shape

Precise knowledge of a spectrometer's instrumental line shape (ILS) is of utmost importance to gain correct information from measurements as using wrong ILS values leads to systematic errors in the gas retrieval. The ILS can be divided into two parts. One part describes the modulation loss through inherent self-apodization of the spectrometer which is present also in an ideal instrument. This contribution can easily be calculated utilizing the OPD and FOV of the spectrometer. The other component of the ILS results from misalignments and optical aberrations of the spectrometer and can be characterised by a modulation efficiency amplitude and a phase error, both functions of the OPD (Hase et al., 1999). These parameters have to be deduced from lab measurements.

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For the TCCON spectrometer, the standard procedure to derive the ILS are gas cell measurements. In contrast, we determine the ILS by measuring several meters of lab air and evaluating the water vapor lines in the spectral region between 7000 and 7400 cm^{-1} . As light source a collimated standard 50 W halogen light bulb is used.

5 With this approach no gas cell is necessary, which is advantageous for measurement campaigns. For the analysis of the measured data we use version 14 of the retrieval software LINEFIT (Hase et al., 1999). In LINEFIT one can choose between a simple and extended ILS model. As the ILS characteristics were close to nominal, we used the simple two-parameter ILS model. For the H_2O linelist we use the HITRAN 2009 linelist
10 with minor adjustments, see Sect. 4.1. Needed parameters are ground pressure, ambient temperature and the distance between spectrometer and light source. Temperature and pressure were recorded using the MHB-382SD data logger with a temperature accuracy of $\pm 0.8^\circ\text{C}$ and pressure accuracy of ± 3 hPa (above 1000 hPa) or ± 2 hPa (below 1000 hPa). A typical fit result is shown in Fig. 1. The SD of the residual is very low,
15 $1\sigma = 0.24\%$.

We measured the ILS for the different spectrometers before and after the Berlin campaign. The resulting ILS values are presented in Table 1. For the trace gas retrieval we use the mean value of the measurements before and after the campaign, the setup for these experiments was exactly the same. One can see that the values
20 show very good agreement. The correlation between modulation efficiency amplitude and X_{CO_2} was deduced from a sensitivity study and is in agreement with Gisi et al. (2012). Instrument 2 has the biggest difference in terms of ILS modulation efficiency before and after the campaign with 0.24 %, corresponding to a change of only 0.04 % for the column-averaged dry-air mole fraction (DMF) of carbon dioxide, X_{CO_2} . Note that
25 this is not self-evident since the instruments were transported from Karlsruhe to Berlin in a Transporter, thus experiencing a lot of mechanical impacts and vibrations.

3 Measurement sites and data acquisition

In order to measure during the campaign small differences upstream and downstream of a source, a instrument to instrument consistency is of utmost importance for this setup. For this purpose, calibration measurements were carried out.

3.1 Calibration measurements at KIT Campus North

The calibration measurements were performed before the Berlin campaign on three sunny days between 6 June and 16 June and after the campaign on three consecutive days 16–18 July on top of our office building north of Karlsruhe, with an altitude of 133 m a.s.l., coordinates are 49.094° N and 8.434° E. The spectrometers were moved from the lab on the fourth floor to the roof terrace on the seventh floor thus being exposed to mechanical stress. Then they were coarsely oriented north, without effort for levelling. If further orientation was needed, we manually moved the spectrometer so that the solar beam was centered onto the entrance window. The CamTracker program was then able to track the sun. As we operated the EM27/SUN in summer, it was heated up to temperatures above 40 °C. In order to protect the electronics from the heat, we built a sun cover for the EM27/SUN, which considerably reduced the temperatures inside the spectrometer. We recorded double-sided interferograms with 0.5 cm⁻¹ resolution. With 10 scans and a scanner velocity of 10 kHz, one measurement takes about 58 s.

For precise time recording, we used a GPS Receiver. Additionally on-site pressure and temperature profiles are available from tall tower meteorological measurements.

3.2 Berlin campaign measurements

We decided to target Berlin for several reasons. Firstly, Berlin is a megacity, so we expect to measure detectable enhancements. Secondly, the city is relatively isolated,

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so that CO₂ emissions really can be attributed to Berlin. Thirdly, the flat topography is favorable, which supports the interpretation of the recorded data.

During the campaign period 23 June–11 July measurements were performed at five different stations around Berlin, four of them roughly located on a circle with a radius of 12 km around the city centre of Berlin. One instrument was positioned inside the Berlin motorway ring in Charlottenburg, closer to the city centre than the other instruments. A map with the different sites is shown in Fig. 2. The coordinates and altitudes of the different stations are displayed in Table 2. At the sites, temperature and pressure profiles were recorded using the MHB-382SD data logger. To obtain comparable data, we measured a long time series in Karlsruhe to determine calibration factors between the different loggers. The data was used to calculate the exact altitude of the stations. The records of ground pressure were also used in the creation of the model atmosphere. The measurement procedures (scan speed, resolution, numerical apodisation, etc.) applied during the campaign were identical to those applied for the calibration measurements.

4 Data analysis

4.1 Data processing

In a first step, the recorded interferograms are Fourier transformed using the Norton-Beer-Medium apodisation function. This apodisation is useful for reducing sidelobes around the spectral lines, an undesired feature in unapodised low resolution spectra, which would complicate the further analysis. Furthermore, a DC-correction is performed. Together with a quality filter, which discards IFGs with intensity fluctuations above 10 % and intensities below 10 % of the maximal modulation amplitude, this is implemented in a Python tool. In this work, we analyzed spectra utilizing the PROFFIT Version 9.6. This code is in wide use and has been thoroughly tested in the past, e.g. (Schneider and Hase, 2009; Schneider et al., 2010; Sepúlveda et al., 2012). Due to

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the low resolution of the EM27/SUN, we fitted the atmospheric spectra by scaling of a-priori trace gas profiles. As source of the a-priori profiles, we utilized the WACCM ver. 6 climatology (<http://www2.cesm.ucar.edu/working-groups/wawg>).

For the retrieval we need accurate temperature and pressure profiles. In case of the Karlsruhe calibration experiments we use on-site data together with MERRA model data, which provides temperature and pressure data on a $1.25^\circ \times 1.25^\circ$ grid from 1000 to 0.1 hPa 8 times a day. For the Berlin campaign we utilize local meteorological radiosonde data and the NCEP model to set up the temperature profiles. We take the NCEP data as the starting values and apply a linear ascent during the day, which is the temperature difference between the 12 a.m. and 6 p.m. sonde data, for the first height levels (until an altitude of approximately 4 km). For the height levels above 4 km we take the unaltered NCEP data, as the change during the day is negligible. For the pressure profiles we use the time series of the logger data, scale the values to 30 m.a.s.l. and take the smoothed mean of the different stations pressure data. We calculate the pressure of the different altitude levels from the barometric height formula using a scaling height of 8.7 km.

Every retrieval is dependent on proper spectroscopic parameters for the solar lines and atmospheric gases absorption lines. We use the HITRAN 2008 line list in its original form for CH_4 , the HITRAN 2008 linelist with a line-mixing parameterisation for CO_2 adopted from a code provided by Hartmann (Lamouroux et al., 2010) and the linelist used by TCCON for O_2 . For the H_2O linelist we use the HITRAN 2009 linelist with changes used by (Wunch et al., 2010) and additional ad hoc adjustments where it seemed appropriate.

4.2 Spectral windows

For the evaluation of the O_2 gas column we use the $7765\text{--}8005\text{ cm}^{-1}$ spectral region, which is also applied in the TCCON analysis (Wunch et al., 2010). For CO_2 we subsume the spectral windows used by TCCON to one larger window ranging from 6173

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to 6390 cm^{-1} . CH_4 is evaluated in the $5897\text{--}6145\text{ cm}^{-1}$ spectral domain. For H_2O the $8353\text{ to }8463\text{ cm}^{-1}$ region is used.

An example fit for the different spectral windows is shown in Fig. 3. The residuum of the spectral fit for the water column retrieval is much bigger than for the other gases.

Due to the large variability of water vapor in the atmosphere, larger linelist errors are expected. Overall the fit quality is very good with $\sigma = 0.2\%$ for CO_2 and CH_4 , $\sigma = 0.1\%$ for O_2 and $\sigma = 0.5\%$ for H_2O .

5 Results calibration measurements

In this section we present results of the calibration measurements performed before and after the Berlin campaign. First we show the uncalibrated total columns followed by column-averaged DMF X_{Gas} of carbon dioxide and methane, where X_{Gas} is defined as

$$X_{\text{Gas}} = \frac{\text{Gas}_{\text{Column}}}{\text{O}_2_{\text{Column}}} \cdot 0.2095 \quad (1)$$

To make the measurements comparable to WMO scale, in TCCON the standard procedure is to divide the calculated DMFs by a calibration factor (Wunch et al., 2010). We also apply this post processing in our work. For X_{CO_2} the factor is 0.9898 whereas it is 0.9765 for X_{CH_4} .

5.1 Total column amounts

In Fig. 4 are depicted the column values of the measured species of the different instruments. From first glance, it is clear that the shape of all the spectrometers is nearly identical. Data gaps appearing for all instruments were caused by passing clouds. In addition Instrument 4 suffered from a hardware problem on the thirteenth of June as

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the chosen reference altitude of 30 ma.s.l. and h_S the scaling height. For the sake of comparison, all pressure values derived from the spectra are transformed to this common reference altitude. We observe a systematic offset between these records and the actual ground pressure of 3.0 %. This discrepancy can mainly be attributed to oxygen line intensity errors (Washenfelder et al., 2006). In Fig. 9 we scaled the pressure values obtained from the total columns to the in situ data for better comparability. The variability of the slope of the in situ measurements is nicely reproduced by the column data.

7 Conclusions

We developed a calibration procedure for mobile FTIR spectrometers which we applied to 5 spectrometers used for observing greenhouse gas emissions from Berlin during a field campaign during June and July 2014. We were successful in demonstrating the high degree of consistency. Between the instruments we established cross-calibration factors which were found valid before and after the field campaign. Drifts were below 0.005 % for X_{CO_2} and 0.035 % for X_{CH_4} . In addition a method for deriving ILS parameters from open path measurements is described and was used for showing that the ILS is close to nominal for all instruments. Changes in the ILS before and after the campaign were very small, within 0.24 % modulation efficiency amplitude at maximum optical path difference. Furthermore an empirical air mass correction was applied to compensate for a spurious SZA dependency of the data. As a last calibration step the in situ calibration factor derived by a comparison with a co-located TCCON instrument was applied. The same empirical calibration factor of 0.9951 ± 0.0001 was found valid for both X_{CO_2} and X_{CH_4} in order to make results comparable to WMO scale.

Finally we displayed ground pressures calculated from oxygen and water vapor columns at all sites during the Berlin campaign. The excellent station-to-station consistency and the excellent agreement with ground pressure records is a further proof of the instrumental stability.

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In conclusion, we are highly confident that these portable spectrometers are very useful instruments for observing local sinks and sources of carbon dioxide and methane. In part two of this work (Hase et al., 2015), we will present the greenhouse gas observations themselves and compare these data with predictions of a simple dispersion model.

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**Table 1.** Compilation of ILS modulation efficiencies before and after the measurement campaign.

Instr.	3 Jun	15 Jul
1	0.9979	0.9996
2	0.9914	0.9938
3	0.9971	0.9997
4	1.0010	1.0020
5	0.9959	0.9963

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**Table 2.** Coordinates and altitude of the Berlin measurement stations.

Site	Long. (° E)	Lat. (° N)	Altit. (m.a.s.l.)
Mahlsdorf	13.589	52.486	39.0
Charlottenburg	13.302	52.505	47.7
Heiligensee	13.228	52.622	34.5
Lindenberg	13.519	52.601	63.3
Lichtenrade	13.392	52.391	44.8

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Table 3. Calibration factors for O₂ column before and after the campaign for the different instruments. Instrument 1 has been scaled to one, which is an arbitrary choice.

Instr.	O ₂ col. before	O ₂ col. after
1	1.00000	1.00000
2	1.00010	0.99970
3	1.00037	1.00015
4	1.00236	1.00196
5	1.00120	1.00110

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Table 4. Calibration factor for $X\text{CO}_2$ and $X\text{CH}_4$ for the different instruments before and after the campaign.

Instr.	$X\text{CO}_2$ bef.	$X\text{CO}_2$ aft.	$X\text{CH}_4$ bef.	$X\text{CH}_4$ aft.
1	1.00000	1.00000	1.00000	1.00000
2	0.99924	0.99921	0.99927	0.99940
3	1.00015	1.00016	0.99971	0.99962
4	0.99987	0.99987	0.99856	0.99882
5	0.99960	0.99962	0.99892	0.99905

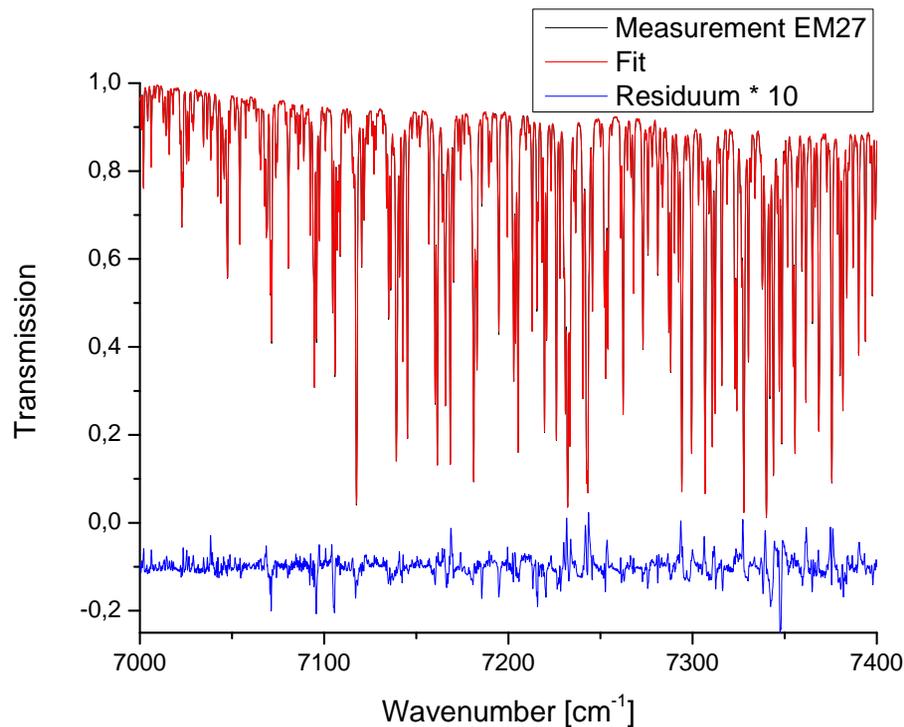


Figure 1. Transmission spectrum of 4 m lab air (black curve) in the 7000 to 7400 cm^{-1} region. Overlying is the LINEFIT calculation (red curve), the residuum multiplied by a factor of ten is shown in blue. For clarity reasons, an offset of -0.1 was added to the residuum.

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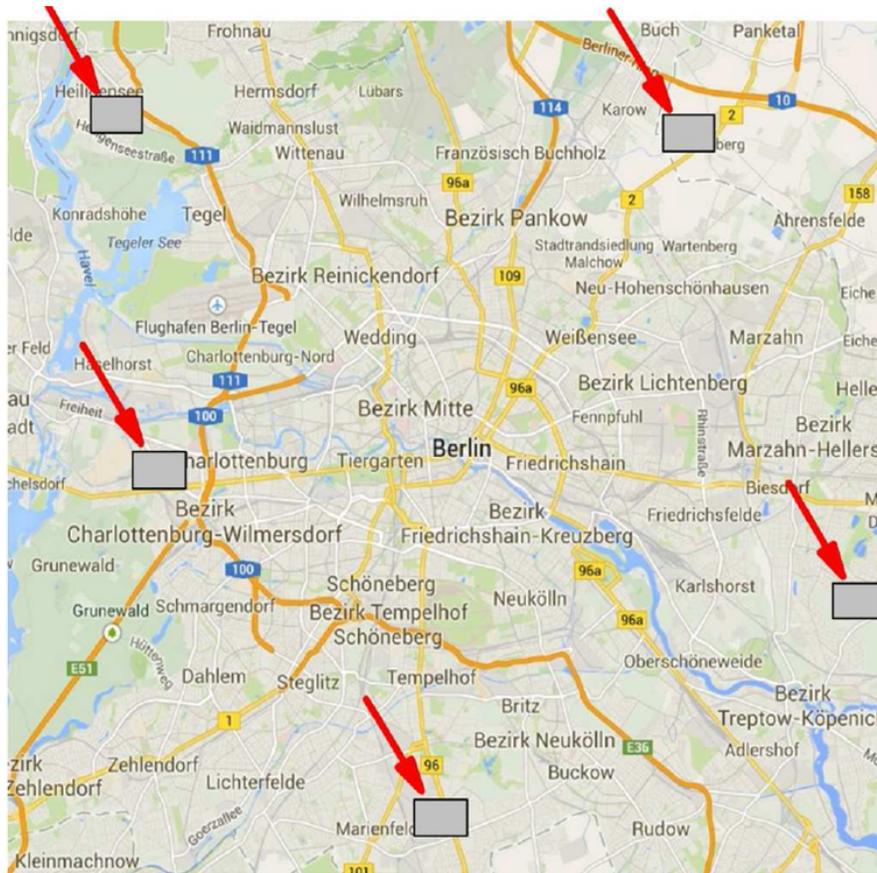


Figure 2. Map with the Berlin measurement stations.

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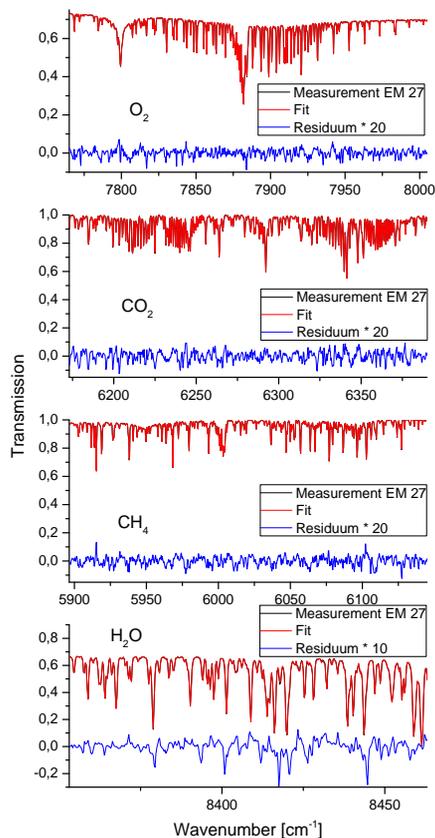


Figure 3. Spectral windows used during the retrieval for the different species. The fit is in accordance with the measurement, the residuum, which has been multiplied with a factor of 10 for H₂O and 20 for the other species, is small.

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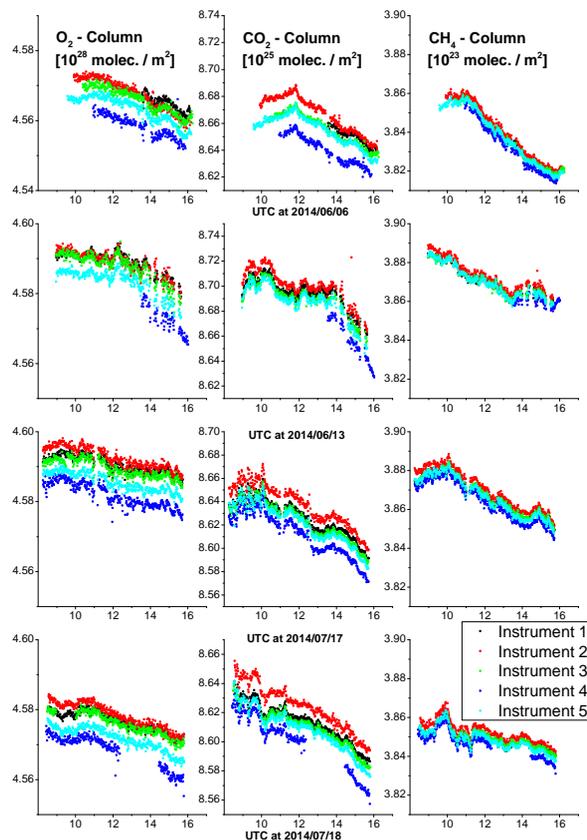


Figure 4. Total columns of O_2 , CO_2 and CH_4 for the different spectrometers on four days of the calibration measurements in Karlsruhe. The first two days are before the Berlin campaign, the other days after the campaign. One data point consists of 10 interferograms, the measurement time being 58 s each.

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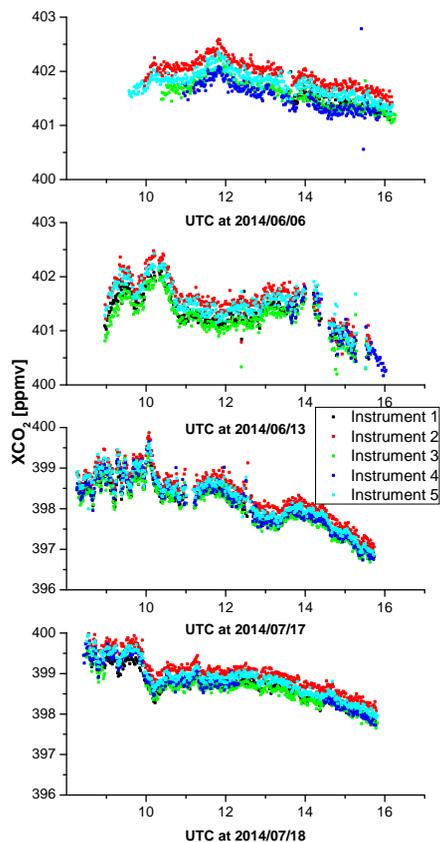


Figure 5. Uncalibrated XCO_2 values for all instruments. Experiments and measurement days are the same as for O_2 .

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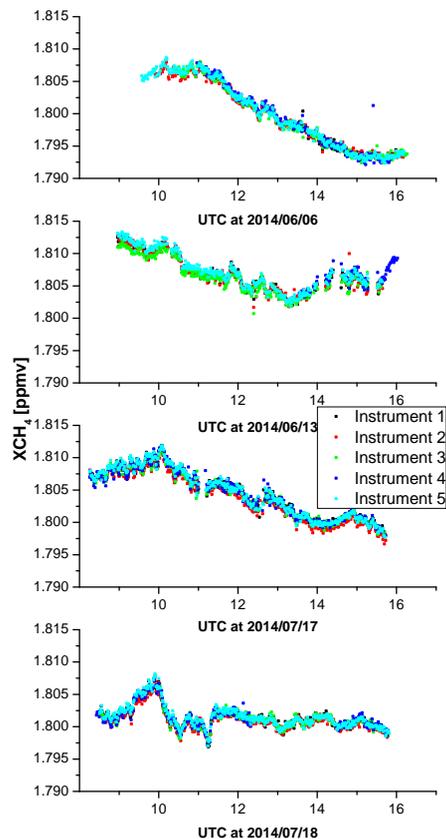


Figure 6. Calibrated XCH_4 values for all instruments. Experiments and measurement days are the same as for O_2 .

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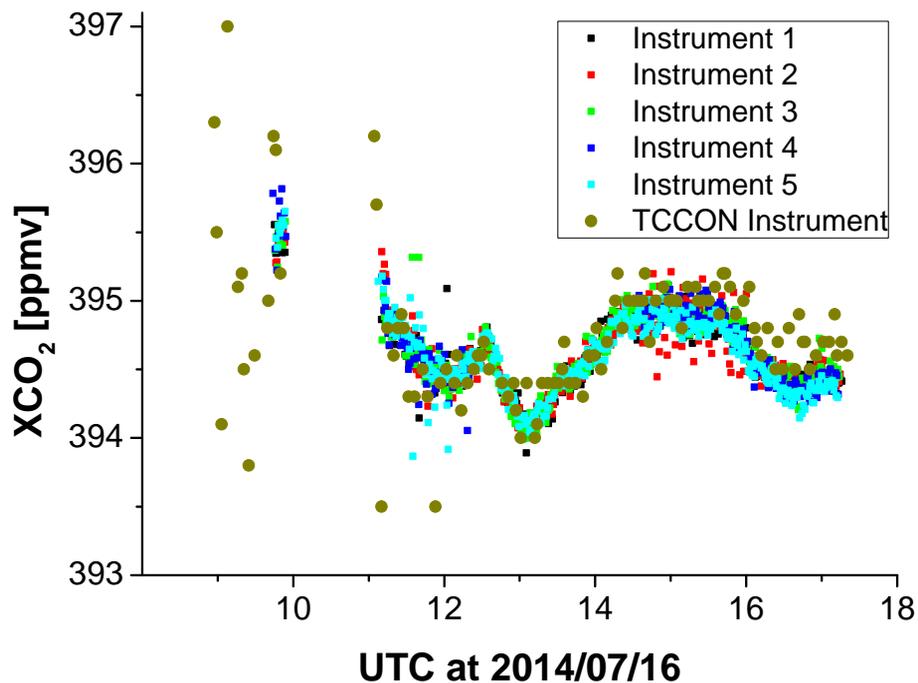


Figure 7. Calibrated and SZA corrected XCO₂ values for all EM27/SUN spectrometers on 16 July. Golden dots show XCO₂ data from a co-located TCCON instrument.

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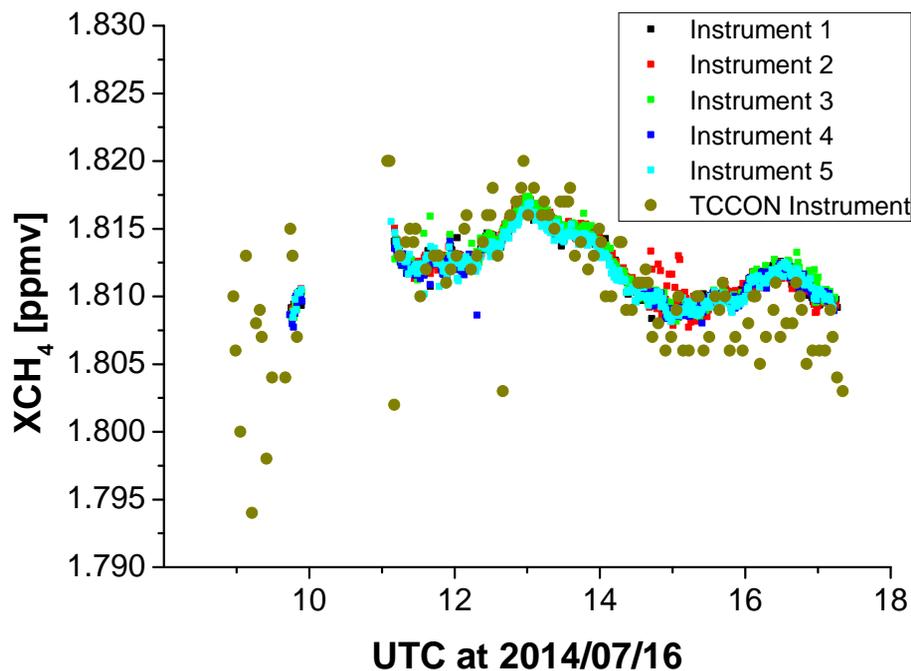


Figure 8. Calibrated and SZA corrected XCH_4 values for all EM27/SUN spectrometers on 16 July. Golden dots show XCH_4 data from a co-located TCCON instrument.

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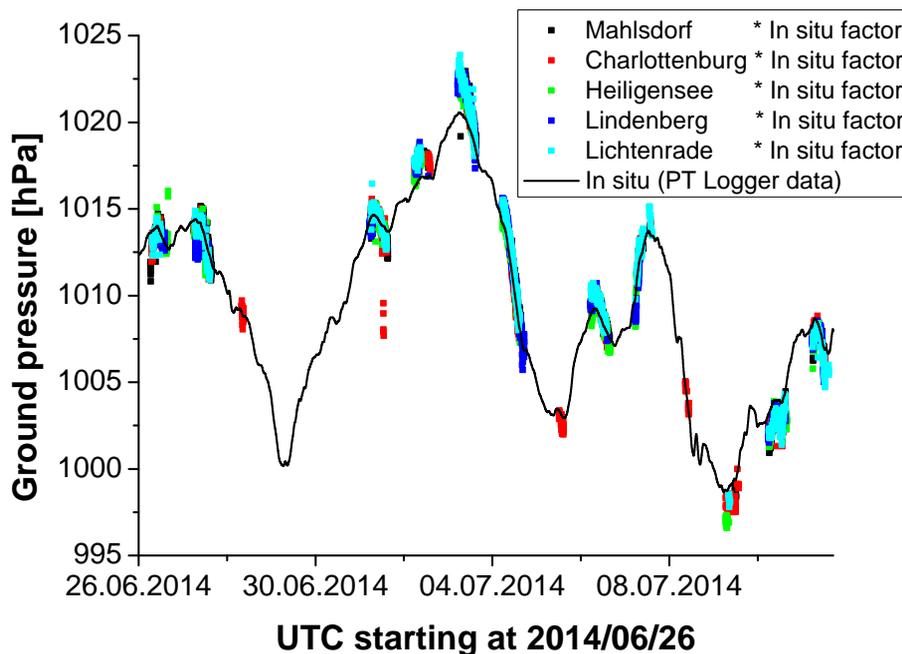


Figure 9. In situ pressure data together with pressure data calculated from total column amounts of O_2 and H_2O . The column data is scaled with an in situ factor for better comparability.

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