We are very grateful for the comments received from both reviewers and each point is addressed below individually:

Answers to comments from Referee #1

1) Is there some reference that supports the validity of comparing the total column amount of CO2, XCO2, with the in situ CO2 amount , as shown in Figure 6. I believe that when averaging kernels and error covariances are taken into account there is little valid overlap. See Rodgers and Connor, JGR, 108, 4116, 2003.

The CO_2 in situ time series in MLO is used here to characterize a global background atmosphere at 19N latitude. The behavior of the surface concentration can be assumed to be valid as the lifetime of CO_2 is sufficient long. The following sentence was modified in lines 168-172 in order to clarify that a direct comparison between MLO (in situ) and Altzomoni (FTIR) was not sought in this exercise: "Although both data sets show a similar behavior, the intention of using MLO in this context was to investigate the relative bias between both beamsplitter ensembles with a common reference by arranging the data into bins."

The sentence in lines 203-205 was also changed to: "For comparison, the detrended diurnal cycle of the MLO data is also shown in the figure and despite that it is at a different location and corresponds to in situ measurements, it shows a similar behavior with a smaller amplitude and a minimum which occurs 3 hours later."

2) Since one of the main objectives of the work is to compare the error contributions of KBr and CaF2 beamsplitters, which of the error sources in Table 2 might have some physical justification for being different between the two beamsplitters. In Table 3 the largest differences in error for CO2 between the splitters seems to be in the noise and solar line contributions. Is there a reason for this?

Temperature and solar lines are expected to have small contributions to the errors and these differences depend mostly on the chosen ensembles, but the only error source that is expected to differ significantly because of the beamsplitter is the noise. This is due to the fact that the SNR changes with the optical set-up as it can be inferred from Figure 1. Errors due to the solar lines in the case of CO_2 are less than 0.01%, the differences in percentage in both the Statistical and the Systematic contributions might seem big but they are rather small compared to the other sources. The following sentence was added in line 125: "The largest error difference between beamsplitters is expected to originate from the noise for a given ensemble, since the spectral windows used for the retrievals are measured with different signal/noise ratios (see Fig. 1)."

Minor points

Line 7 define XCO2
Done

Line 17 water vapor contributes more than any other gas to radiative forcing
The sentence in lines 16-17 was changed to: "... contributing more than any other anthropogenic gas to the positive total radiative forcing of the Earth ..."

Line 24 it might be good to add some numbers to describe where the near infrared is, various readers may have various ideas about what is near or far (also line 90)
The sentence in lines 24-25 was changed to: "... in the near infrared (NIR, 3,300-13,000 cm^{-1}) spectral region ..."

We also changed line 90: "... spectra in the mid-infrared (MIR, 200-3,300 cm^{-1}) region ..."

Line 55 /characterisitc/characteristic/
Done

Line 59 /begun/began/
Done

Line 62 /is part/has been part/
Done

Line 104 comment on how effective the removal of the baseline curvature is wrt the retrieval
The removal of the baseline curvature with the radiometric calibration has very low impact on the retrieval, the average change in the total columns of CO_2 and O_2 for three days of measurements (85 measurements) is +0.021 $\pm$ 0.00086 % and +0.0053 $\pm$ 0.00033 %, respectively. This might be due to the 20 baseline points used in the retrieval code, similar to what was recommended by Kiel et al., 2016.

Lines 101-104 were changed to: "The baseline curvature in the spectral region around the dip introduced by the KBr beamsplitter is removed using a simplified radiometric calibration, assuming that the tungsten lamp produces a blackbody spectrum (T=1700 K) and that there is no self-emission of the optical set-up in the spectral region above 4000 cm^{-1}. This calibration has a low impact on the columns (+0.021% for CO_2, +0.0053% for O_2) due to the simultaneous fit of the baseline in the retrieval code."

Line 115 /to assess/an assessment of/
Done

Line 117 /determine where does/determining where/
Done

Line 120 /allows to/allows one to/
Done

Line 154 /ensamble/ensemble/ also in Line 168,215
Done

Line 246 <sub>2<sub> also Line 257, 287
Done

Line 254 n/a-n/a also Line 301, 310
Done

Figure 5. The reference that we found mentioning the TCCON precision goal (0.25) is Wunch et al., 2011.
The caption in Fig. 5 was changed to: "The black lines depict the existing precision goals for CO_2 found in the literature."

Answers to comments from Referee #2 (P. O. Wennberg)

Major comments:
1. As clear from the abstract and introduction, a major motivation for this work is to enable the Mexico UNAO group to develop XCO2 capability and join TCCON. I thus suggest that the group expand the scope of this investigation to include processing of their spectra (at least the ones obtained with the CaF2 beamsplitter) using the standard TCCON processing code. Both Hase and Blumenstock run TCCON sites and are thus fully versed in the mechanics of assisting in this extension of scope. Given the

clear desire of Baylon et al to join the network, such a modest expansion of scope will thus serve additionally to provide additional knowledge transfer from the KIT group to the Mexico group.

We agree with the reviewer that a site like Altzomoni, with the available instrumentation, has the potential to join the TCCON network and contribute to global carbon cycle studies. We will look into the possibilities to develop the capability in Mexico to use the community code GFIT in the near future. However, the intention of this work is to present an assessment of the precisions of CO2, O_2 and X_{CO_2} obtained when using both beamsplitters so that we can prove the value of our measurements and use this data with confidence for reporting and analyzing X_{CO_2} variability in the region. This is relevant to the community since several NDACC instruments use a KBr beamsplitter and could easily add-on their capability by including an InGaAs detector in their measurement routines. Moreover, doing routine measurements with the CaF_2 beamsplitter and analyzing the data according to the TCCON guidelines would require extra resources in funding and manpower which at the moment we have in limited amounts.

2. Likely not unrelated to 1), the observed diurnal dependence of XCO2 (Fig 10) is almost certainly a result of airmass dependent bias in the retrievals. TCCON processing includes an attempt to account for such bias. Thus, I expect that the TCCON retrievals will substantially reduce the airmass dependence shown in Fig. 10 and additionally alter the seasonal structures (modestly).

This is a very valid point. At the moment we cannot provide precise evidence that an airmass dependence is not contributing to the diurnal variability which we observe (presented as an average curve in Figure 10). As shown in Dohe, 2013 and Kiel et al., 2016 when using PROFFIT as the processing code, a refined treatment of the background continuum level and, for the case of O_2 retrievals, using a detailed model of the O_2 CIA band can reduce the airmass dependence of CO_2 and O_2 retrievals. We followed this recommendations for the analysis of our data set so we believe that an airmass dependent bias might not be responsible for all the diurnal variability of X_{CO_2} observed at Altzomoni.

The TCCON strategy fits a set of time and zenith angle dependent functions which would assume a symmetrical dependence, a correction which would not fully remove the observed daily dependence at Altzomoni (see Fig.1). This tropical mountain site is surrounded by forests covering large areas and can also be influenced by polluted air which reaches the site in the afternoon (Ochoa et al., 2012), favoring the argument that carbon capture and transport processes are dominating the diurnal variability. This is also supported by what is observed from collocated in situ CO_2 measurements.

Thus, following the reviewers comment, we have removed the sentence in line 200 which stated that CO_2 was lowered in average 1.5 ppm only through photosynthesis. The following sentence was added in its place: "Although a treatment of the airmass dependence for X_{CO_2} has been considered following Dohe, 2013 and Kiel et al., 2016, this may still not be fully corrected in the reported X_{CO_2}. However, a qualitative analysis correlating these observations with in situ measurements indicate that carbon capture and transport processes are responsible for most of the diurnal variability observed over the Altzomoni site."

Both topics focusing on the reprocessing with the community code GFIT and the development of an airmass correction at Altzomoni will be addressed in future studies.

Minor comment:

1. Ln 17. Changes in H2O vapor is likely close to changes in CO2 in net change in radiative feedback over past decades.

The sentence in lines 16-17 was changed to: "... contributing more than any other anthropogenic gas to the positive total radiative forcing of the Earth ..."

2. Ln 99. When the KBr UNAO spectra are processed with TCCON software, suggest using same continuum model described by Kiel et al.

Yes, we followed the recommendation of Kiel et al., 2016. See answers above.

3. Ln 185-187 Please explain more fully how the bias (DeltaCO2 = -0.030+- 0.070%) is translated into the scaling factor (0.9986).

The scaling factor for XCO_2 (0.9986) comes from the fact that the bias obtained was of $+0.14 \pm 0.064$ % for KBr-CaF_2 differences.

4. Ln 200. This is (at best) a hypothesis. Given the (relatively) low biomass in the area, Im exceedingly doubtful. (see above major comment 2).

An answer to this point is given above.

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Background CO_2 levels and error analysis from ground-based solar absorption IR measurements in central Mexico

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Abstract. In this investigation we analyze two common optical configurations to retrieve CO_2 total column amounts from solar absorption infrared spectra. The noise errors using either a KBr or a CaF_2 beamsplitter, a main component of a Fourier transform infrared (FTIR) spectrometer, are quantified in order to assess the relative precisions of the measurements. The configuration using a CaF_2 beamsplitter, as deployed by the instruments which contribute to the Total Carbon Column Observing Network (TCCON), shows a slightly better precision. However, we show that the precisions in X_{CO_2} $(= 0.2095 \cdot \frac{\text{Total Column CO}_2}{\text{Total Column O}_2})$ retrieved from >96% of the spectra measured with a KBr beamsplitter, fall well below 0.2%. A small bias in X_{CO_2} (KBr - CaF_2) of +0.56 ± 0.25 ppm was found when using an independent data set as reference. This value, which corresponds to +0.14 ± 0.064 %, is slightly larger than the mean precisions obtained and could be taken into account when homogenizing or comparing data from both beamsplitters. A 3-year X_{CO_2} time series from FTIR measurements at the high-altitude site of Altzomoni in central Mexico presents clear annual and diurnal cycles and a trend of +2.2 ppm/yr could be determined.

1 Introduction

During the last decades, carbon dioxide (CO_2) has exceeded the pre-industrial levels by about 40% mainly due to fossil fuel combustion and land use change (Hartmann et al., 2013), contributing more than any other anthropogenic gas to the positive total radiative forcing of the Earth and becoming the most important anthropogenic greenhouse gas (Myhre et al., 2013). The quantification of the spatial distribution and temporal variation of CO_2 sources and sinks can help to understand the anthropogenic contributions of CO_2 to the carbon cycle. This task can be achieved by monitoring the atmosphere using ground-based and satellite observations. Ground-based networks like the Global Atmospheric Watch WMO (2014) or the Total Column Carbon Observing Network (TCCON) provide data sets of CO_2 concentrations around the world. TCCON is a network of Fourier transform infrared spectrometers that record solar absorption spectra in the near infrared (NIR, 3,300-13,000 cm^{-1}) spectral region in order to retrieve column-averaged dry-air mole fractions of CO_2 (X_{CO_2}) and other molecules that absorb in the NIR (Wunch et al., 2011). TCCON aims to provide reliable, long-term validation data sets for satellite measurements and to improve current knowledge of the carbon cycle. Measurements of CO_2 from space have been done by many satellite missions like ACE (Foucher et al., 2011), AIRS (Chahine et al., 2008), IASI (Crevoisier et al., 2009), TES (Kulawik et al., 2010), SCIAMACHY (Reuter et al., 2011), GOSAT (Kuze et al., 2009) and OCO-2 (Wunch et al., 2016) with the last three missions relying on TCCON data for validation.

Studies done to estimate the CO_2 concentrations in Mexico City and central Mexico have been scarce, the first one was conducted during 1981 and 1982 in which the diurnal and seasonal variation was estimated taking air samples in different parts of the city (Báez et al., 1988). In two different campaigns (MCMA-2003 and MILAGRO) the CO_2 fluxes and concentrations during typical days in the Mexico City Metropolitan Area (MCMA) were estimated using the eddy covariance technique (Velasco et al., 2005, 2009). The first study using a FTS was done during September 2001 in the south of the MCMA using a Nicolet Nexus interferometer with a resolution of 0.125 cm^{-1} and retrieving CO_2 in the 723-766 cm^{-1} spectral region (Grutter, 2003). From this study the variability and average diurnal cycle of CO_2 was recorded with high temporal resolution.

The Altzomoni site is located to the southeast of the MCMA at a height of almost 4,000 m above the sea level. Measurements of NIR and MIR spectra have been conducted since 2012 using a Bruker IFS 120/5 HR. The site is part of the NDACC network since 2015 and has been reporting vertical columns of O_3, CO, N_2O and CH_4 among other gases. As part of the NDACC instrumental configuration, a KBr beamsplitter has been used for most of the measurements but for a limited number of days, a CaF_2 beamsplitter was also used in order to meet the TCCON instrumental requirements and compare the effect of each configuration in the retrievals of CO_2, O_2 as well as in the estimation of X_{CO_2}.

This paper presents X_{CO_2} retrieved from NIR spectra measured from December 2012 to December 2015 in the Altzomoni site and an intercomparision of how the use of KBr and CaF_2 beamsplitters affect the errors and precision of CO_2, O_2 columns and X_{CO_2} mole fractions. Section 2 describes the configuration used in the measurement of the NIR spectra and how these spectra were analyzed for producing the time series of X_{CO_2}. An evaluation of how the used beamsplitter influence the total column retrievals and the calculation of X_{CO_2} by means of an estimation of noise errors, precision and bias of each configuration is presented in Sect. 3. The ~~characterisite~~ characteristic seasonal and diurnal cycles, as well as the observed trend for this sub-tropical site in central Mexico, are presented in Sect. 4.

2 FTIR instrument, measurement site and spectral analysis

A high resolution Fourier Transform InfraRed (FTIR) spectrometer, Bruker model HR 120/5, was deployed to measure solar absorption spectra under clear sky conditions. The instrument ~~begun~~ began operations at a high-altitude location in central Mexico in 2012 as part of a collaboration between the National Autonomous University of Mexico (UNAM) and the Karlsruhe Institute of Technology (KIT) and since 2015, Altzomoni ~~is~~ has been part of the Network for the Detection of Atmospheric Composition Change (NDACC). Routine and remotely-operated measurements are performed with a spectral resolution of 0.005 cm^{-1} using a KBr beamsplitter, a set of band-pass filters and liquid-nitrogen cooled MCT and InSb detectors, according to NDACC specifications. The solar tracking is based on the Camtracker system (Gisi et al., 2011) used in other NDACC and TCCON sites and is housed in a dome which can be operated remotely.

Alternatively, an InGaAs detector is used to record near-infrared (NIR) spectra within each measurement sequence with a resolution of 0.02 cm^{-1}. These NIR spectra, used in this study to retrieve CO_2 and O_2, were recorded as the average of 2 scans taking approximately 38 seconds with a scanner speed of 40 kHz. In each measurement sequence, a set of six NIR measurements are recorded, taking around 5 minutes. This small change in solar angles allow the consideration that all measurements belong to the same airmass. A CaF_2 beamsplitter is also available and was used for a small number of days for the purpose of estimating the noise levels in each optical configuration and how this affects the retrievals.

The FTIR instrument is located at the Altzomoni high-altitude station (19.1187°N, 98.6552°W) located in central Mexico within the Izta-Popo National Park, 60 km southeast of Mexico City, at an altitude of 3,985 m a.s.l. This station is part of the University Network of Atmospheric Observatories (www.ruoa.unam.mx) and comprises a complete set of in situ and meteorological instrumentation.

The measured spectra were analyzed with the retrieval code PROFFIT which uses the radiative transfer code PROFFWD (Hase et al., 2004). For the calculation of the dry-air column-average mole fractions of carbon dioxide X_{CO_2}, CO_2 and O_2 were retrieved separately using a profile scaling procedure and with the microwindows and interfering species listed in Table 1. Pressure and temperature profiles from the National Center for Environment Prediction (NCEP) were used and the a priori profiles were obtained from the Whole Atmosphere Community Climate Model (WACCM). A single a priori profile of each retrieved species was used for the entire set of measurements.

3 Effect of the beamsplitter on the retrieval

The TCCON instrumental requirements state that the network's necessary precision is best achieved using a CaF_2 beamsplitter (TCCON-Wiki), but in the case of the Altzomoni site, this would mean sacrificing routine measurements of spectra in the mid-infrared (MIR, 200-3,300 cm^{-1}) region since the beamsplitter change needs to be performed manually. Given the location of the site and aside from complying with a long term commitment with NDACC, it is of great interest to perform measurements of gases which absorb in the MIR region in order to characterize pollution transport events in the region and study the composition of the gases emitted by the active Popocatépetl volcano. For these reasons, a KBr beamsplitter has been part of the configuration used in the site and the use of the CaF_2 beamsplitter has been limited. Figure 1 shows two tungsten NIR lamp spectra, one measured with KBr (red) and another one with CaF_2 (blue) to illustrate the features of each measurement in the NIR region. The KBr spectra shows a slightly lower intensity and a dip on the 5000-6000 cm^{-1} spectral region. Kiel et al. (2016) showed that a small curvature might affect the retrieval results if no baseline is adjusted. The settings used for the retrievals of this study adjusted a smoothed baseline with 20 parameters for each microwindow used. It's worth mentioning that the effects from the The baseline curvature in the spectral region around the dip introduced by the KBr beamsplitter are is removed using a simplified radiometric calibration, assuming that the tungsten lamp produces a blackbody spectrum (T=1700 K) and that there is no self-emission of the optical set-up in the spectral region above 4000 cm^{-1}. This calibration has a low impact on the columns (+0.021% CO_2, +0.0053% for O_2) due to the simultaneous fit of the baseline in the retrieval code.

In order to compare the impact of the KBr and CaF_2 beamsplitters on the retrievals and since far more measurements are available with the KBr beamsplitter (27,148) than with CaF_2 (2,093), an ensemble of KBr measurements was formed reproducing the size and solar zenith angle (SZA) distribution of the CaF_2 measurements. A condition imposed was to only consider sets of consecutive measurements done within a five minute lapse so that the precision of each retrieval product and SZA could be calculated. As shown in Fig. 2, the KBr ensemble consisted in measurements from 101 days between July 30, 2013 and December 30, 2015 while the CaF_2 ensemble had measurement from 43 days from February 15, 2014 to June 23, 2015.

For the case of CO_2 column measurements, two references of precision exist: Rayner and O'Brien (2001) showed that a 0.25% network precision would improve the current knowledge of the carbon cycle while Olsen and Randerson (2004) suggested that a 0.1% precision would allow to assess an assessment of the strength of the carbon sink in the Northern Hemisphere. The following subsections are dedicated to determine where does determining where the Altzomoni data fall, using routinely a KBr beamsplitter, in terms of these two benchmarks.

3.1 Retrieved CO_2 and O_2 error budgets

The error calculation implemented in PROFFIT allows one to estimate the errors associated with a total column retrieval (Barthlott et al., 2015). These include channelling and offset, instrumental line shape (ILS), temperature profile, line-of-sight (LOS), solar lines, spectroscopy and noise errors. The errors were calculated for each of the measurements that comprise the KBr and CaF_2 ensembles. The magnitude of the uncertainties and the statistical and systematic contributions for each source are listed in Table 2. The largest error difference between beamsplitters is expected to originate from the noise for a given ensemble, since the spectral windows used for the retrievals are measured with a different signal/noise ratios (see Fig. 1). The purpose of obtaining the errors from the PROFFIT software was to determine the value of noise present in each measurement and how it depends on the beamsplitter used. The noise calculation from PROFFIT takes into account the derivatives of the retrieval with respect of the measurement and the difference between the measurement and a simulated spectra from the forward model. Figures 3 and 4 show how the mean noise error from the CO_2 and the O_2 total columns depend on the beamsplitter and the SZA, while Tables 3 and 4 show the mean values of each error source for two SZA values (20 and 70°). The noise error of the CO_2 column shows good agreement between beamsplitters for SZA's above 30°, but is lower in KBr measurements at smaller angles. For the O_2 column, the errors have similar behavior for angles below 30°, but the noise errors for angles above this value remain more or less constant and are 30 - 40 % larger for KBr than for CaF_2. Overall, the total statistical and systematic errors for both beamsplitters estimated with this technique are quite similar.

3.2 Statistical precision from consecutive measurements

For a statistical estimation of the precision, we consider that the standard deviation of the consecutive measurements done within a 5-minute lapse (typically 6 spectra) represents the overall precision of the measurements. This method is based on the assumption that the actual gas columns undergo smaller changes in the short time considered than the measurement error. With the three products derived from a NIR measurement (CO_2 and O_2 columns and X_{CO_2}), three different precisions were calculated and used for estimating which part of the random error is independent from the CO_2 and O_2 columns and which part is correlated and thus cancels out when the X_{CO_2} ratio is calculated.

Assuming that the precisions of CO_2 and O_2 (σ_{CO_2} and σ_{O_2}) are due to both the noise and the correlated errors (see Eq. 1&2), and the precision of X_{CO_2} depends only in the noise from both columns (Eq. 3), a system of equations was formed and solved using the mean precisions of the three products to obtain the mean correlated and noise errors of CO_2 and O_2 for each beamsplitter.

$$(\sigma_{CO_2})^2 = (\sigma^{Correlated})^2 + (\sigma^{Noise}_{CO_2})^2 \quad (1)$$

$$(\sigma_{O_2})^2 = (\sigma^{Correlated})^2 + (\sigma^{Noise}_{O_2})^2 \quad (2)$$

$$(\sigma_{X_{CO_2}})^2 = (\sigma^{Noise}_{CO_2})^2 + (\sigma^{Noise}_{O_2})^2 \quad (3)$$

As can be seen in the results from this exercise presented in Table 5, the mean noise errors from the columns are within the range of the values obtained using PROFFIT and in the case of X_{CO_2}, the mean value from all the KBr measurements in the ~~ensamble~~ ensemble was 25% higher than with CaF_2. The contribution appears to be dominated by the noise in the O_2 retrieval. This is in accordance to the result in Sect. 3.1. However as Figure 5 shows, the mean X_{CO_2} precisions obtained from both beamsplitters were below 0.1% and those of >96% of all the spectra in the ensemble measured with a KBr beamsplitter, fall below the 0.2% value.

3.3 Bias estimation

The systematic difference between beamsplitters was estimated for the three products obtained. Since there are no temporal coincidences between the measurements with both beamsplitters, an independent set of measurements was used to calculate the bias. The ensembles were sorted in bins, so that the mean values of the data in each bin could be compared even if the measurements on the ensembles weren't coincident in time.

For X_{CO_2}, the continuous data set of CO_2 in situ measurements from the Mauna Loa Observatory (MLO; 19.5362°N, 155.5763°W, 3,397 m.a.s.l) was chosen, given the fact that both sites share a similar latitude and altitude. An in situ measurement in Altzomoni is now available but the data does not cover the entire period of the FTIR ~~ensamble. The MLO (in situ) and Altzomoni (FTIR) data sets are in good agreement, as shown in Fig 6, and both present similar seasonal cycles dominating the observed variability. However, the amplitude in the MLO time series is approximately 5 ppm larger, possibly due to the different location and that Altzomoni is measuring total columns and not surface concentrations~~ensemble. Although both data sets show a similar behavior, the intention of using MLO in this context was to investigate the relative bias between both beamsplitters ensembles with a common reference by arranging the data into bins. There were 189 coincidences for the KBr and 174 for CaF_2 data sets. The bias was obtained from the mean of the KBr$-$$CaF_2$ differences of these coincidences, sorted in 13 bins generated using the measurements in MLO. From the correlation plot for each beamsplitter and a Bland-Altman plot (Bland and Altman, 1986) for their differences shown in Figure 7, a bias of $+0.14 \pm 0.064$ % is obtained for X_{CO_2}.

In the case of O_2 total columns, a bias was calculated by estimating the dry pressure column from surface pressure measurements at Altzomoni and the H_2O total columns retrieved in the NIR spectral region, which in turn was multiplied by the factor 0.2095 to convert to O_2 column. The number of coincidences obtained between the data sets was 100 for KBr and 110 for CaF_2. Figure 8 shows the plots and KBr$-$$CaF_2$ differences resulting in a bias of -0.17 ± 0.029 %.

The bias for CO_2 column was calculated from the biases obtained above (ΔX_{CO_2} and O_2 ΔO_2) using Eq. 4:

$$\Delta X_{CO_2} = \frac{\partial X_{CO_2}}{\partial CO_2} \cdot \Delta CO_2 + \frac{\partial X_{CO_2}}{\partial O_2} \cdot \Delta O_2, \quad (4)$$

from which a value of $\Delta CO_2 = -0.030 \pm 0.070$ % is obtained. The biases and the mean values for each beamsplitter are summarized in Table 6. For the homogenization of a data set, the relative X_{CO_2} bias between beamsplitters can be corrected by multiplying the KBr data by the factor 0.9986.

4 Observed time series

Figure 9 shows the daily means of the X_{CO_2} in black, derived from 29,241 measurements done in Altzomoni during 510 days between December 28, 2012 and December 30, 2015. A function was adjusted to the data using Eq. 5, taken from Wunch et al. (2013), where x is the decimal year and the obtained fitting parameters were as follows: α = 2.19 ppm yr^{-1}, a_0 = -0.0040 ppm, a_1 = -0.93 ppm, a_2 = 0.95 ppm, b_1 = 1.60 ppm, b_2 = -0.54 ppm. The linear term determines the trend of the series which has the value of 2.2 ppm/year. The same function fitted over the MLO data set shows also a 2.2 ppm/year trend.

$$f(x) = \alpha x + \sum_{k=0}^{2} a_k cos(2\pi kx) + b_k sin(2\pi kx). \quad (5)$$

The daily average mixing ratio from all the FTIR data is presented in Figure 10. These hourly data were detrended using the fitted curve obtained for the annual cycle and the local time was converted to true solar time in order to observe the distinct effect of vegetation. ~~The concentration of CO_2 is lowered on average during the day up to 1.5 ppm through photosynthesis~~Although a treatment of the airmass dependence for X_{CO_2} has been considered following Dohe (2013) and Kiel et al. (2016), this may still not be fully corrected in the reported X_{CO_2}. However, a qualitative analysis correlating these observations with in situ measurements indicate that carbon capture and transport processes are responsible for most of the diurnal variability observed over the Altzomoni site. The weekday averages were also calculated and no distinct weekly pattern was detected from these data which indicates that the measurements are representative for the free atmosphere and the influence of the nearby cities are minimal with respect to the total column. For comparison, the detrended diurnal cycle of the MLO data is also shown in the figure ~~, showing~~ and despite that it is at a different location and corresponds to in situ measurements, it shows a similar behavior ~~but~~ with a smaller amplitude and a minimum which occurs 3 hours later.

5 Conclusions

Solar absorption FTIR measurements done with KBr and CaF_2 beamsplitters were compared using equivalent ensembles containing more than 2 thousand spectra. The two methods used for evaluating the statistical errors gave similar results. In the case of CO_2 columns, the noise levels from the KBr measurements are on average 20% lower than from CaF_2 measurements when solar zenith angles are below 30°. Measurements with larger SZA's have similar errors with both beamsplitters. Larger error differences are encountered from the O_2 column retrievals. For angles below 30°the noise in KBr measurements is around 29% lower but increases with the angle and remaines constant above the CaF_2 levels, approximately 38% higher.

Thus, in this study an estimation of the precision of each ~~ensamble~~ ensemble shows that the largest statistical error contribution in X_{CO_2} comes from the O_2 column retrieval. This outcome has the implication that column averaged mixing ratios retrieved using KBr beamsplktters have noise-related errors which are on average about 25% larger than with CaF_2. However, mean X_{CO_2}

precisions was found to be below 0.1% and >96% of the measurements made with both optical configurations fall well below the 0.2% precision.

These results provide enough evidence that measurements performed with a KBr beamsplitters are reliable and useful for carbon cycle studies. This includes all FTIR instruments which are committed to comply with NDACC requirements and have an additional InGaAs detector available for NIR spectral measurements. A larger number of sites producing confident X_{CO_2} data sets would allow to increase our current knowledge of the variability of this important greenhouse gas.

When doing direct comparisons across a network or using single retrievals for intercomparing timed observations, however, one needs to be cautious and consider a possible bias. We have estimated a bias of 0.14% for X_{CO_2} between beamsplitters using data from the Mauna Loa Observatory.

A rich data set of X_{CO_2} was put together from more than 3 years of measurements in central Mexico. A very distinct annual cycle was identified with an amplitude of ~6 ppm and a positive trend of 2.2 ppm/year, while the mean diurnal pattern reflects a decrease of up to ~1.5 ppm during sunlit hours. This data set confirms a small influence of anthropogenic emissions especially during the afternoon, when the regional boundary layer reaches the height of the station.

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Table 1. Microwindows and interfering species used for CO_2 and O_2 retrievals.

	Microwindows (cm^{-1})	Interfering species
CO_2	6180.0 – 6260.0, 6310.0 – 6380.0	H_2O, CH_4
O_2	7765.0 – 8005.0	H_2O, CO_2

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Table 2. Error sources used in the error estimation, the second column gives the uncertainty used and the third the statistical (Stat) and systematic (Sys) contributions of each source in percentage.

Error Source	Uncertainty	Stat / Sys [%]
Baseline (offset / channelling)	0.1% / 0.2%	50 / 50
ILS (mod. eff. / phase error)	2% / 0.01 rad	50 / 50
Line of sight	0.001 rad	90 / 10
Solar lines (intensity / scale)	1% / $1e10^{-6}$	80 / 20
Temperature	1, 2 & 5 K	70 / 30
Spectroscopic parameters (S / γ)	2% / 5%	0 / 100
Measurement noise	-	100 / 0

Table 3. Mean ensemble values of the statistical (Stat) and systematic (Sys) errors for 20° and 70° SZA (given in %), in CO_2 columns due to the assumed error sources of Table 2.

	SZA = 20°				SZA = 70°			
CO_2	KBr		CaF_2		KBr		CaF_2	
	Stat	Sys	Stat	Sys	Stat	Sys	Stat	Sys
Baseline	0.082	0.082	0.081	0.081	0.085	0.085	0.085	0.085
ILS	0.073	0.073	0.076	0.076	0.043	0.043	0.043	0.043
LOS	0.031	0.0035	0.031	0.0034	0.24	0.026	0.24	0.026
Solar lines	0.0071	0.0018	0.0092	0.0023	0.0065	0.0016	0.0082	0.0020
Temperature	0.019	0.0081	0.012	0.0053	0.031	0.013	0.032	0.014
Spectroscopy	—	2.13	—	2.16	—	2.13	—	2.13
Noise	0.039	—	0.047	—	0.037	—	0.035	—
TOTAL	0.12	2.14	0.13	2.16	0.26	2.13	0.26	2.13

Table 4. Mean ensemble values of the statistical (Stat) and systematic (Sys) errors for 20° and 70° (given in %), in O_2 columns due to the assumed error sources of Table 2.

	SZA = 20°				SZA = 70°			
O_2	KBr		CaF_2		KBr		CaF_2	
	Stat	Sys	Stat	Sys	Stat	Sys	Stat	Sys
Baseline	0.090	0.090	0.087	0.087	0.089	0.089	0.090	0.090
ILS	0.060	0.060	0.059	0.059	0.032	0.032	0.032	0.032
LOS	0.031	0.0034	0.030	0.0033	0.22	0.025	0.22	0.024
Solar lines	0.0077	0.0019	0.0077	0.0019	0.0044	0.0011	0.0047	0.0012
Temperature	0.029	0.012	0.033	0.014	0.031	0.013	0.032	0.014
Spectroscopy	—	2.12	—	2.10	—	2.89	—	2.90
Noise	0.046	—	0.063	—	0.074	—	0.053	—
TOTAL	0.13	2.12	0.13	2.10	0.25	2.89	0.25	2.90

Table 5. Mean precision, noise and correlation errors (given in %) for both ensembles, of 2,093 measurements each, using KBr and CaF_2 beamsplitters. The X_{CO_2} precision is the root-sum-square of the noise errors of CO_2 and O_2.

	σ_{CO_2}	σ_{O_2}	$\sigma^{Correlated}$	$\sigma_{CO_2}^{Noise}$	$\sigma_{O_2}^{Noise}$	σ_{XCO_2}
KBr	0.072 ± 0.0041	0.098 ± 0.0042	0.055 ± 0.0055	0.047 ± 0.0065	0.082 ± 0.0037	0.094 ± 0.0033
CaF_2	0.078 ± 0.0046	0.090 ± 0.0037	0.065 ± 0.0031	0.043 ± 0.0048	0.062 ± 0.0033	0.075 ± 0.0022

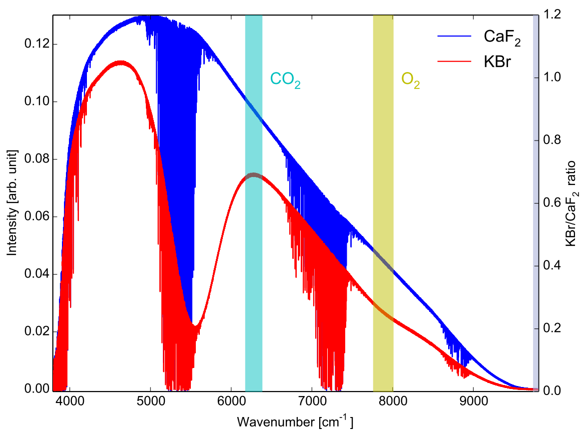

Figure 1. Spectra of a near infrared (NIR) lamp measured with KBr (red) and CaF_2 (blue) beamsplitters, the spectral regions where the CO_2 and O_2 target gases are retrieved are shown in cyan and yellow, respectively. The KBr/CaF_2 lamp intensity ratio, as shown in grey, is smooth at the target regions and is lower for O_2 (the gas which presents larger error differences among beamsplitters).

Table 6. Mean values of X_{CO_2}, CO_2 and O_2 and the bias obtained for each of them using the beamsplitters ensembles. For X_{CO_2}, the Mauna Loa Observatory (MLO) was used and for O_2 the dry pressure column was calculated and multiplied by 0.2095. The bias of CO_2 was obtained from Eq. 4.

	KBr	CaF_2
	X_{CO_2}	
Coincidences	189	174
Mean Value FTIR [ppm]	396.07 ± 0.12	396.68 ± 0.14
Mean Value MLO [ppm]	399.82 ± 0.14	402.04 ± 0.20
Mean Difference [ppm]	-3.75 ± 0.077	-5.36 ± 0.11
Bias (KBr-CaF_2) [ppm]	+0.56 ± 0.25 (+0.14 ± 0.064 %)	
	O_2	
Coincidences	100	110
Mean Value FTIR [10^{24} molec cm^{-2}]	2.90 ± 0.00089	2.90 ± 0.00077
Mean Value dry pressure column [10^{24} molec cm^{-2}]	2.82 ± 0.00055	2.82 ± 0.00046
Mean Difference [10^{24} molec cm^{-2}]	0.078 ± 0.00050	0.081 ± 0.00051
Bias (KBr-CaF_2) [10^{24} molec cm^{-2}]	-0.0050 ± 0.00083 (-0.17 ± 0.029 %)	
	CO_2	
Mean Value FTIR [10^{24} molec cm^{-2}]	5.49 ± 0.00034	5.50 ± 0.00031
Bias [10^{24} molec cm^{-2}]	-0.0016 ± 0.0039 (-0.030 ± 0.070 %)	

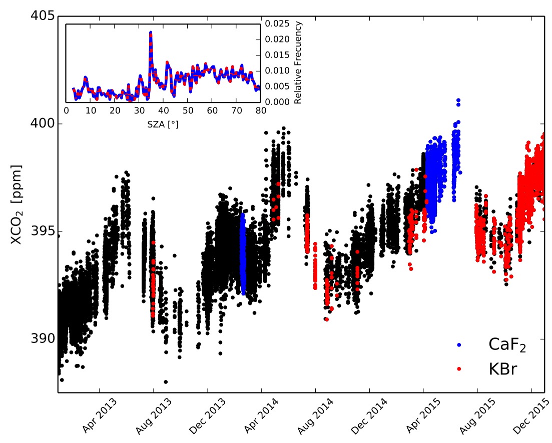

Figure 2. Time series of the X_{CO_2} data set from Altzomoni site (black points) with the elements of the KBr (red points) and the CaF_2 (blue points) ensembles. The inset plot show the SZA distribution of both ensembles.

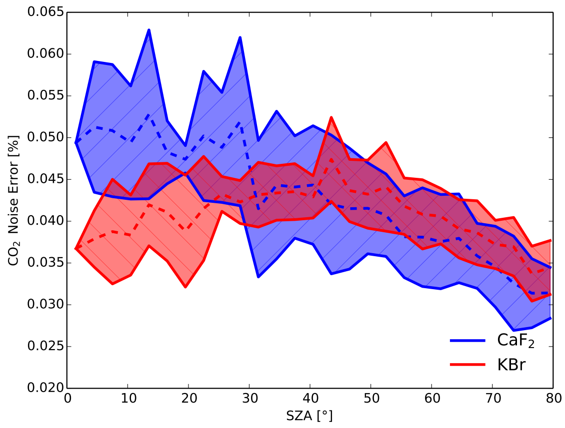

Figure 3. Mean noise error from PROFFIT for CO_2 total column in function of SZA.

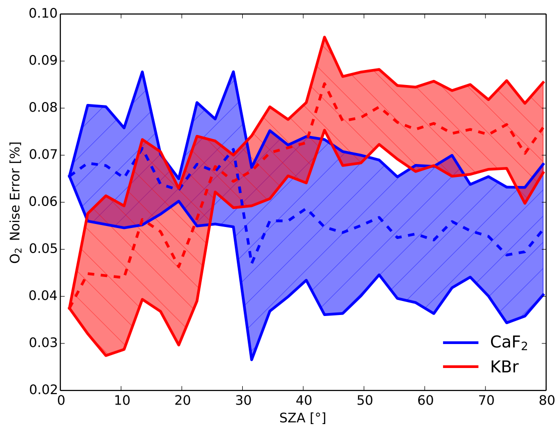

Figure 4. Mean noise error from PROFFIT for O_2 total column in function of SZA.

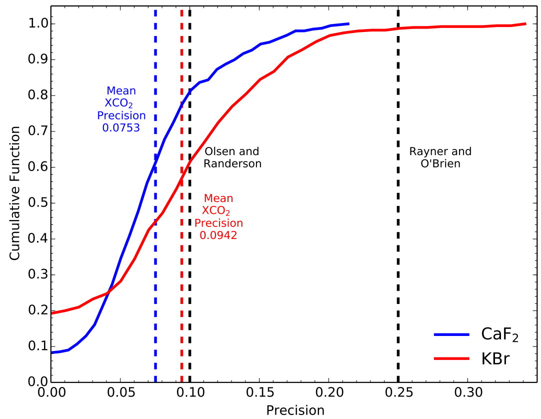

Figure 5. Cumulative function of X_{CO_2} precision for both beamsplitters with the blue and red dashed lines denoting the precision values from Table 5 obtained from the top-down approach. The black ~~line depicts~~ lines depict the ~~precision goal from TCCON~~existing precisin goals for CO_2 found in the literature.

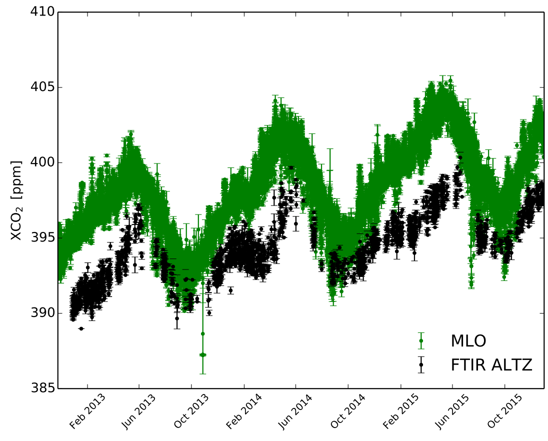

Figure 6. Hourly means of Altzomoni X_{CO_2}(FTIR ALTZ, black points) and Mauna Loa Observatory in situ CO_2 (MLO, green points)

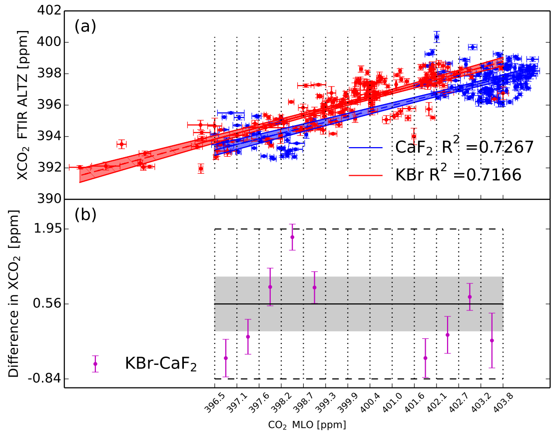

Figure 7. Upper panel (a) shows the coincidences between the hourly means of the X_{CO_2} from the KBr (red) and CaF_2 (blue) ensembles and the CO_2 from the Mauna Loa Observatory (MLO) data set with a linear regression of the two sets with the shaded area representing a 95% confidence interval. Lower panel (b) shows the difference of means of KBr and CaF_2 (purple points) for each bin (vertical lines) in a Bland-Altman plot, with the black dashed lines showing the standard deviation of all points. The black solid line represents the bias and the shaded area the standard error of the bias, both reported in Table 6.

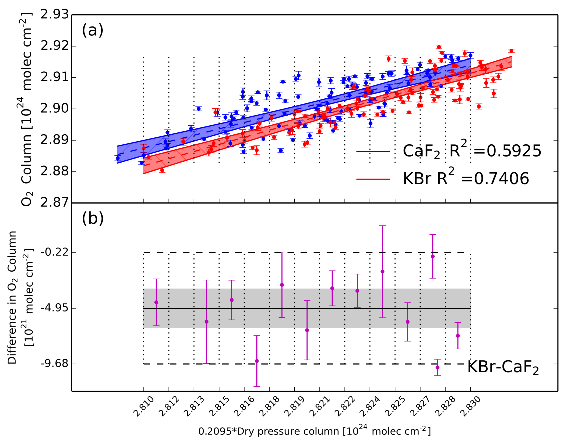

Figure 8. Upper panel (a) shows the coincidences between the hourly means of the O_2 from the KBr (red) and CaF_2 (blue) ensembles and the O_2 column obtained from the dry pressure column with a linear regression of the two sets with the shaded area representing a 95% confidence interval. Lower panel (b) shows the difference of means of KBr and CaF_2 (purple points) for each bin (vertical lines) in a Bland-Altman plot, with the black dashed lines showing the standard deviation of all points. The black solid line represents the bias and the shaded area the standard error of the bias, both reported in Table 6.

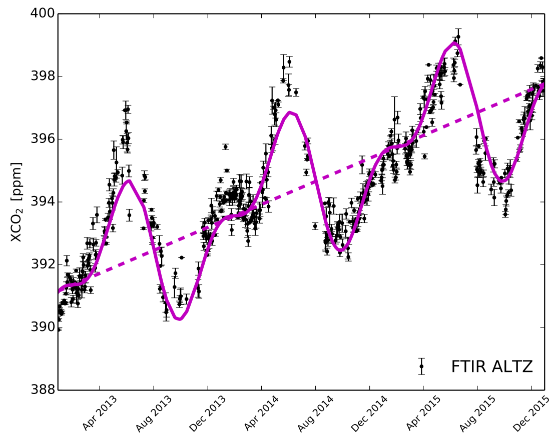

Figure 9. Daily means of the X_{CO_2} data set from the Altzomoni site (black points). The purple solid line is a curve adjusted to the series (see text) with a linear term, represented by the dashed line, of 2.2 ppm/year which is the trend for this 3-year period.

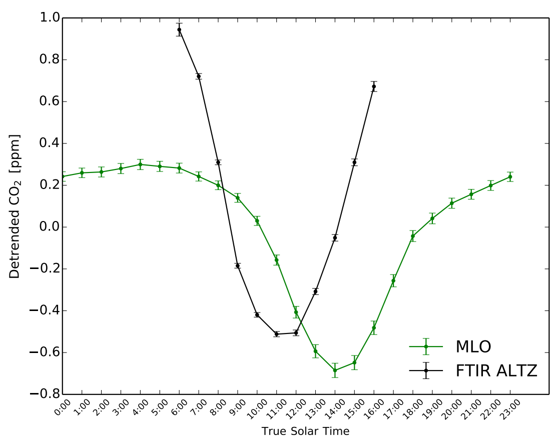

Figure 10. Detrended diurnal cycle of the X_{CO_2} data set from Altzomoni site (black line) with detrended diurnal cycle of MLO (green line). The time of each measurement was converted to true solar time. Each bin represents the average of the hour marked containing data from 0 to 59 minutes.