Retrieval of atmospheric CO_2 with enhanced accuracy and precision from SCIAMACHY: Validation with FTS measurements and comparison with model results

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[1] The Bremen Optimal Estimation differential optical absorption spectroscopy (DOAS) (BESD) algorithm for satellite based retrievals of XCO_2 (the column-average dry-air mole fraction of atmospheric CO_2) has been applied to Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) data. It uses measurements in the O_2-A absorption band to correct for scattering of undetected clouds and aerosols. Comparisons with precise and accurate ground-based Fourier transform spectrometer (FTS) measurements at four Total Carbon Column Observing Network (TCCON) sites have been used to quantify the quality of the new SCIAMACHY XCO_2 data set. Additionally, the results have been compared to NOAA's assimilation system CarbonTracker. The comparisons show that the new retrieval meets the expectations from earlier theoretical studies. We find no statistically significant regional XCO_2 biases between SCIAMACHY and the FTS instruments. However, the standard error of the systematic differences is in the range of 0.2 ppm and 0.8 ppm. The XCO_2 single-measurement precision of 2.5 ppm is similar to theoretical estimates driven by instrumental noise. There are no significant differences found for the year-to-year increase as well as for the average seasonal amplitude between SCIAMACHY XCO_2 and the collocated FTS measurements. Comparison of the year-to-year increase and also of the seasonal amplitude of CarbonTracker exhibit significant differences with the corresponding FTS values at Darwin. Here the differences between SCIAMACHY and CarbonTracker are larger than the standard error of the SCIAMACHY values. The difference of the seasonal amplitude exceeds the significance level of 2 standard errors. Therefore, our results suggest that SCIAMACHY may provide valuable additional information about XCO_2, at least in regions with a low density of in situ measurements.

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1. Introduction

[2] Although CO_2 is the dominant anthropogenic greenhouse gas, there are still large uncertainties of its natural global sources and sinks [*Stephens et al.*, 2007]. The theoretical studies of *Rayner and O'Brien* [2001] and *Houweling et al.* [2004] showed that satellite measurements of CO_2 have the potential to significantly reduce surface flux uncertainties if a precision of about 1% for regional averages and monthly means can be achieved. However, *Miller et al.* [2007] and *Chevallier et al.* [2007] found that undetected biases of a few tenths of a part per million on regional scales can limit surface flux inverse modeling.

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[3] Presently, there are only two satellite instruments orbiting the Earth which enable the retrieval of the column-average dry-air mole fraction of atmospheric carbon dioxide (XCO_2) with significant sensitivity in the boundary layer where the largest signals of sources and sinks occur. These are SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Cartography) [*Burrows et al.*, 1995; *Bovensmann et al.*, 1999] aboard ENVISAT (Environmental Satellite), which was launched in 2002, and TANSO (Thermal and Near infrared Sensor for Carbon Observation) [*Yokota et al.*, 2004] aboard GOSAT (Greenhouse Gases Observing Satellite), which was launched in 2009. Both instruments measure near and shortwave infrared (in this paper referred to as NIR) reflected solar radiation in absorption bands at around 0.76, 1.6, and 2.0 μm. OCO (Orbiting Carbon Observatory) [*Crisp et al.*, 2004] was another satellite designed to observe atmospheric carbon dioxide in the same spectral regions as TANSO and SCIAMACHY. Unfortunately, the satellite was lost shortly after liftoff on 24 February 2009 [*Palmer and Rayner*, 2009]. The launch of OCO-2, which is a rebuild of OCO, is planned for 2013.

[4] In contrast to TANSO and OCO, SCIAMACHY was not specifically designed for the retrieval of XCO_2. As a result of SCIAMACHY's coarser spatial and spectral resolution, the achievable accuracy is expected to be lower. Nevertheless, within the years 2002 to 2009 SCIAMACHY was the only satellite instrument measuring XCO_2 with significant sensitivity in the boundary layer. Therefore, the retrieval of XCO_2 from SCIAMACHY with realistic error estimates is crucial to start a consistent long-term time series of XCO_2 observations from space.

[5] Several somewhat different XCO_2 retrieval algorithms for SCIAMACHY already exist [*Buchwitz et al.*, 2000b; *Buchwitz and Burrows*, 2004; *Buchwitz et al.*, 2005a, 2005b; *Houweling et al.*, 2005; *Barkley et al.*, 2006a, 2006c, 2006b; *Bösch et al.*, 2006; *Barkley et al.*, 2007; *Schneising et al.*, 2008]. None of these algorithms explicitly account for the scattering processes in the atmosphere; that is, they adjust no scattering related parameters. If anything, they account only indirectly for scattering via the light path proxy method which applies, for example, for the WFM-DOAS algorithm [*Buchwitz et al.*, 2000b; *Buchwitz and Burrows*, 2004; *Buchwitz et al.*, 2005a, 2005b; *Schneising et al.*, 2008]. The assumption of this method is that photon pathlength modifications are identical at 0.76 and 1.6 μm. In this approximation, scattering errors cancel out because CO_2 is divided by O_2 when calculating XCO_2. Unfortunately, both bands have a relatively large spectral separation and show also large differences of the strength of absorption. For this reason, path length modifications due to scattering by aerosols and clouds in both bands are not identical, resulting in possible XCO_2 retrieval errors.

[6] Generally, scattering related errors remain a major source of uncertainty for SCIAMACHY XCO_2 retrievals and easily exceed the precision and accuracy estimates for clear sky conditions. This is supported by the following two examples: Mineral dust aerosols may introduce retrieval errors of 10% [*Houweling et al.*, 2005]. Undetected cirrus clouds with a cloud optical thickness (COT) below 0.1 can result in retrieval errors of about 8% [*Aben et al.*, 2007; *Schneising et al.*, 2008].

[7] Unfortunately, the detection of clouds with optical thicknesses below 0.1 is challenging for nadir measurements in the visible and near infrared spectral region [e.g., *Reuter et al.*, 2009; *Rodriguez et al.*, 2007]. Satellite occultation measurements as well as lidar observations show that subvisible cirrus clouds occur quite frequently. The maximum occurrence probability of about 45% lies within the tropics and follows the seasonality of the inter tropical convergence zone (ITCZ) [*Wang et al.*, 1996; *Winker and Trepte*, 1998; *Nazaryan et al.*, 2008]. Therefore, ignoring scattering by thin clouds can result in serious retrieval biases that vary spatially and temporally. *Schneising et al.* [2008] identified subvisual cirrus clouds as the most likely cause for an unrealistic amplitude and phase of the southern hemispheric seasonal cycle of XCO_2 retrieved with WFM-DOAS.

[8] For the high spectral resolution instruments TANSO and OCO, algorithms have been developed that correct for scattering effects [*Kuang et al.*, 2002; *Bril et al.*, 2007; *Connor et al.*, 2008; *Butz et al.*, 2009]. The Bremen Optimal Estimation DOAS (BESD) algorithm aims to significantly reduce scattering related errors of SCIAMACHY retrieved XCO_2. It uses SCIAMACHY nadir data at 0.76 and 1.6 μm and explicitly considers scattering by an (optically thin) ice cloud layer and aerosols assuming a default profile. The scattering information is transferred from the O_2-A band to the CO_2 band by using a merged fit window approach to simultaneously retrieve scattering related parameters and XCO_2. BESD uses the SCIATRAN 3.1 radiative transfer code [*Rozanov et al.*, 2005] with the correlated-k approach of [*Buchwitz et al.*, 2000a]. Spectral line parameters are taken from the HITRAN 2008 database [*Rothman et al.*, 2009]. A detailed algorithm description of BESD is given by *Reuter et al.* [2010]. Their theoretical studies with simulated measurements suggest that in many cases an accuracy and precision of XCO_2 better than 1% is achievable in the presence of thin ice clouds with an optical thickness of up to 1.0. A modified version of this algorithm is described by *Bovensmann et al.* [2010].

[9] The publication at hand focuses on the results from the first application of BESD to measured SCIAMACHY data, its validation with Fourier transform spectrometer (FTS) measurements and a comparison with NOAA's (National Oceanic and Atmospheric Administration) assimilation system CarbonTracker. In the following, the analyzed data sets and the details of the validation strategy are described and explained. Subsequently, the results are discussed and conclusions drawn.

2. Data Sets

[10] The analyzed validation period ranges from January 2006 to December 2009. For large parts of this period, FTS measurements as well as CarbonTracker data are available at four of the TCCON (Total Carbon Column Observing Network) sites: Park Falls (USA), Bremen (Germany), Darwin (Australia), and Lauder (New Zealand). For each of these sites, we have generated three XCO_2 time series comprising SCIAMACHY, FTS, and CarbonTracker data. These time series are the basis for our validation and intercomparison study.

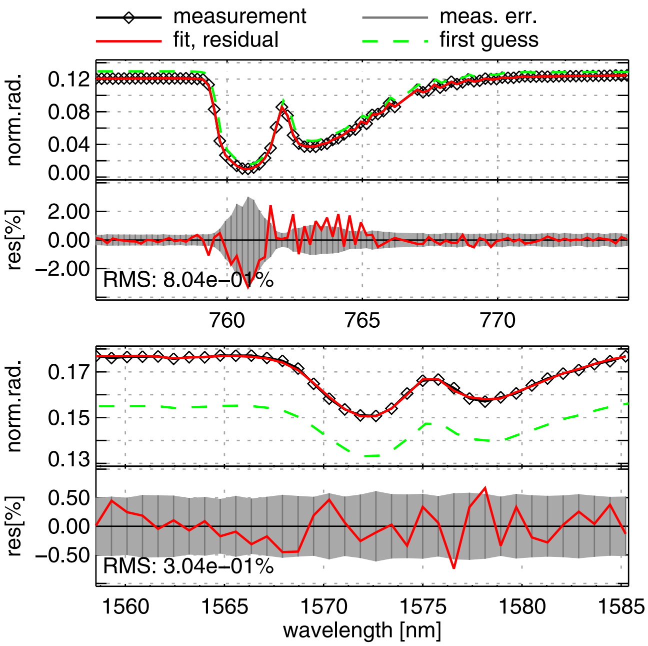

Figure 1. O_2 and CO_2 fit windows with SCIAMACHY measurements, first guess, fitted Sun-normalized radiation, residual, and measurement error for an exemplary SCIAMACHY pixel over Park Falls taken at 20 April 2007.

2.1. SCIAMACHY

[11] SCIAMACHY nadir and corresponding Sun spectra are used as input for the XCO_2 retrieval algorithm BESD, described by *Reuter et al.* [2010]. We use spectra from version 6.03 (January 2006 to September 2009) and version 6.05 (October 2009 to December 2009) and apply all calibration procedures implemented in ESA's SciaL1C calibration and extraction tool for SCIAMACHY level 1b data. This includes also the usage of M-factors, which correct for instrumental degradation.

[12] Other inputs for BESD are ECMWF (European Centre for Medium-Range Weather Forecasts) reanalysis profiles of temperature, pressure and humidity. A digital elevation model is used to calculate the first guess of the surface pressure considering subpixel variations of the surface height. All other inputs are constant in space and time. This applies especially to the a priori CO_2 profile.

[13] The XCO_2 retrieval algorithm of *Reuter et al.* [2010] is used without any conceptual modifications. However, we had to adjust the measurement errors provided in the SCIAMACHY level 1b data to obtain optimal convergence behavior.

[14] *Bösch et al.* [2006] found residuals with a root mean square (RMS) difference of about 0.5% between fitted and measured SCIAMACHY radiances. Within the development phase of BESD, experiments with unweighted least squares fits produced comparable values. These are also similar to the filter criteria used by *Schneising et al.* [2008], who reject retrievals with RMS values exceeding 0.25% in the CO_2 or 2% in the O_2 fit window.

[15] The SCIAMACHY level 1b measurement errors agree well in terms of their magnitude with values of the instrument noise simulator which have been used for the theoretical studies of *Reuter et al.* [2010] and *Buchwitz and Burrows* [2004]. However, they are considerably smaller than the residuals mentioned above. *Bösch et al.* [2006] discussed several physical phenomena but also instrumental effects which may contribute to this discrepancy. Therefore, we scale the original errors of the SCIAMACHY data making them conform with the expected residuals. This affects the retrieval's sensitivity to almost all retrieved parameters. In particular, the surface pressure retrieval becomes more imprecise, the degrees of freedom for XCO_2 are reduced, and the estimated errors of the retrieved XCO_2 are enhanced.

[16] We compensate these effects by the following: (1) The a priori uncertainty of the surface pressure is reduced to 0.3%, which strongly constrains the surface pressure retrieval. This values seems to be realistic; *King* [2003] and *Lammert et al.* [2008] validated the sea surface pressure of ECMWF model analyses and found much smaller standard deviations of about 1 hPa and 0.5 hPa, respectively. (2) The a priori uncertainty of the CO_2 profile is enhanced by a scaling factor so that the effective a priori uncertainty of XCO_2 amounts to 47 ppm. This enables the retrieval to put more weight on the measurement and less weight on the a priori information. In this way, the resulting degrees of freedom for XCO_2 lie within an interval between 0.9 and 1.1 in about 80% of all analyzed cases. (3) Statistical analysis of the residuals shows that most residuals have a similar shape and that the stochastic fluctuations are relatively small compared to the average residual. This directly translates to retrieval errors with a relatively large systematic component and a minor stochastic component. Therefore, one can expect that the estimated errors are much larger than the actual scatter of the retrieval results. For this reason, we multiply the estimated XCO_2 errors by 0.22. In this way, the individual XCO_2 error bars still vary realistically relative to each other, for example, with albedo but their average corresponds to 2.5 ppm, which is the standard deviation of all collocated differences between SCIAMACHY and FTS retrieval results.

[17] Other minor changes to the retrieval algorithm are: the maximum number of iterations is reduced to seven, a Levenberg-Marquardt method replaces Newton's method to minimize the cost function, and the a priori uncertainty of the aerosol profile scaling (APS) is set to 0.5 instead of 1.0. Additionally, a narrower CO_2 fit window is used so that all channel 6+ spectral pixels are excluded. A typical fit result is shown in Figure 1.

[18] In the following, we describe the data filtering procedure to preselect those SCIAMACHY pixels to be analyzed. All SCIAMACHY pixels falling within a radius of 350 km around each FTS station are potential candidates for the validation time series. On average these are about 70,000 per FTS site. About 50,000 of them have a solar zenith angle smaller than 70°; higher solar zenith angles are excluded. Filtering for land only measurements reduces this to 14000 potential pixels. Even though BESD is designed to minimize errors as a result of scattering in the light path, undetected clouds are still an important possible source of error. Therefore, strict cloud filtering is still necessary. In this context, we use the MERIS (Medium Resolution Imaging Spectrometer) cloud detection algorithm that is part of ESA's Basic ENVISAT

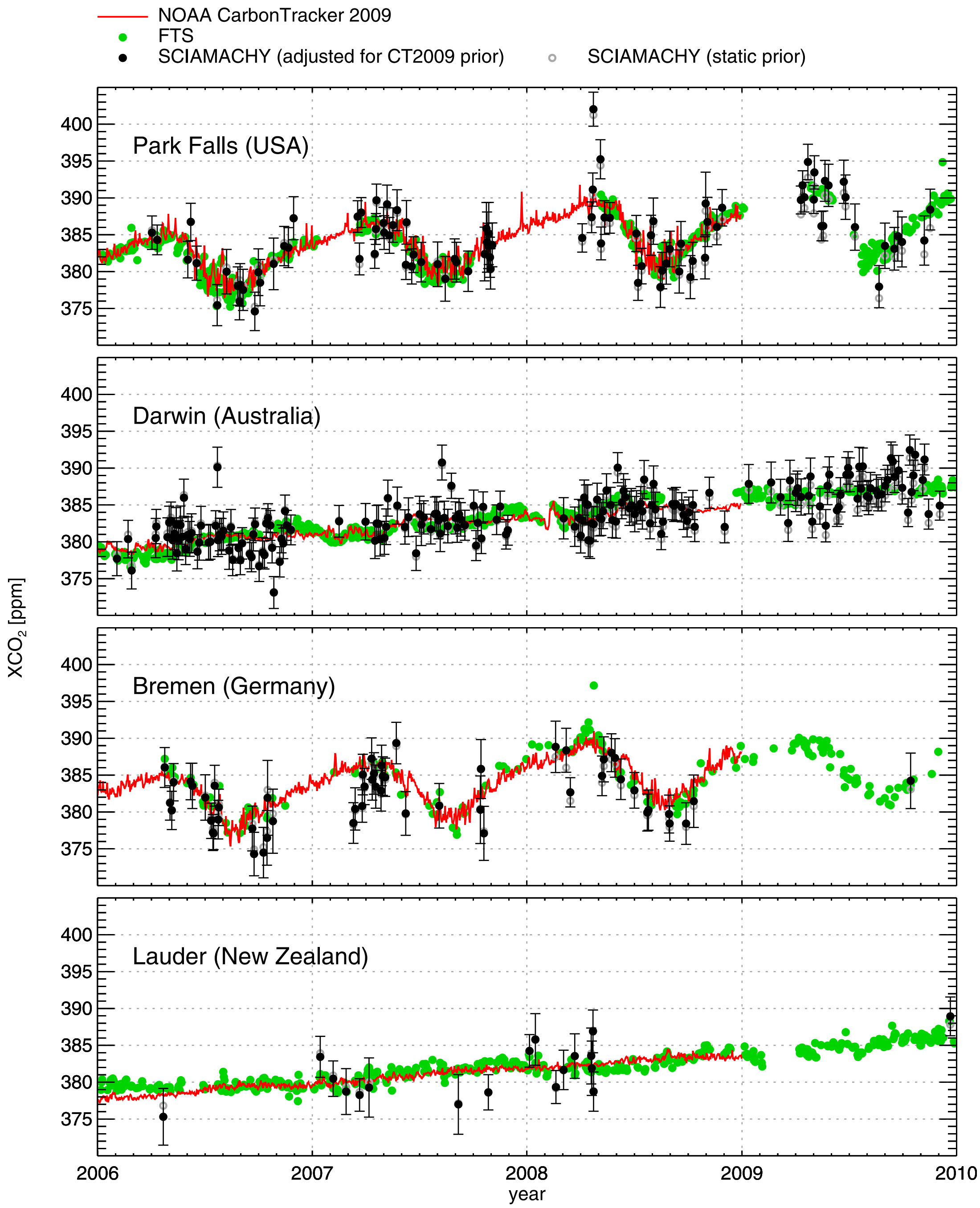

Figure 2. XCO_2 time series of individual measurements at the TCCON sites Park Falls, Darwin, Bremen, and Lauder. The corresponding statistical quantities which measure the agreement between the time series are given in Table 1.

Toolbox for AATSR and MERIS (BEAM, http://www.brockmann-consult.de/beam). The MERIS cloud mask with approximately 1 × 1 km^2 resolution gives us information about SCIAMACHY's subpixel cloud coverage. Only those SCIAMACHY pixels which are 100% cloud free within the pixel and within a surrounding of 40 km are further considered. After this filter, a 4 year time series consists of about 1400 measurements per FTS site on average.

[19] Additionally, we use only that SCIAMACHY pixel per overpass with the largest distance to the next cloud contaminated MERIS pixel. This prevents overweighting of individual overpasses and meteorological situations where several pixels fulfill the cloud filter criteria. The resulting time series of SCIAMACHY measurements which are analyzed with BESD are illustrated in Figure 2. They consists of 109 measurements at Park Falls, 63 at Bremen, 219 at Darwin, and 20 at Lauder. The data gaps around December and January result from too large solar zenith angles (Park Falls and Bremen), snow cover which is often erroneous classified as cloud (Park Falls and Bremen), and

from persistent cloud coverage (Darwin). Note, because of mountains (with frequent snow cover) nearby to Lauder and because of the narrow shape of New Zealand, we had to weaken the 40 km criterion to 20 km in order to obtain data points over Lauder.

2.2. FTS

[20] TCCON is a network of ground-based Fourier transform spectrometers recording direct solar radiation in the near-infrared with high spectral resolution [*Wunch et al.*, 2010b]. From the recorded spectra, accurate and precise column-averaged abundances of atmospheric constituents such as CO_2 are retrieved. The TCCON sites at Park Falls, Darwin, and Bremen operate a Bruker 125HR spectrometer. A similar spectrometer, a Bruker 120HR operated in Lauder over the period of this study. In order to assure comparability, all TCCON sites use the same retrieval algorithm, which is described by *Washenfelder et al.* [2006] and *Wunch et al.* [2010b]. This retrieval algorithm derives XCO_2 by using a least squares fit to scale an a priori CO_2 profile. The a priori profile is derived by an empirical model based on fits to NOAA's GLOBALVIEW CO_2 data for the troposphere and follows the decrease in the stratosphere based on the age of air [*Andrews et al.*, 2001].

[21] Accuracy and precision of the FTS measurements have been determined in many calibration and validation campaigns with airborne in situ instruments. The single-measurement precision and accuracy of the FTS instruments is better than 0.25% [*Wunch et al.*, 2010b]. The standard deviation of all cloud free measurements within 1 h amounts typically to 0.1% [*Washenfelder et al.*, 2006; *Messerschmidt et al.*, 2010; *Deutscher et al.*, 2010]. However, the precision of the FTS measurements depends on many factors, like the solar zenith angle and scatterers in the atmosphere. Precision estimates for the individual FTS measurements are given in the FTS data files. The median precision, of the entire analyzed FTS data set amounts to 0.6 ppm.

[22] *Wunch et al.* [2010a] calibrated XCO_2 of several TCCON sites against WMO-scale instrumentation aboard aircraft and found that all stations can be described by a single regression line and hence single calibration factor, with variations around the regression line. This means they found no significant systematic offsets in calibration factors between the analyzed TCCON sites. *Messerschmidt et al.* [2010] compared collocated identical TCCON FTS instruments and found that systematic offsets are indeed small (0.07%) as long as laser missamplings are eliminated.

[23] SCIAMACHY flies on a Sun-synchronous orbit with an equator crossing local time (LT) of 1000 LT. Due to the diurnal cycle of the atmospheric CO_2 concentration, we accept only FTS measurements with a maximum time difference of less than 2 h. In order to further minimize the noise, we average all FTS measurements fulfilling this criterion. The expected precision of the averaged FTS measurements can be neglected compared with the single-measurement precision which is expected from the SCIAMACHY retrievals. Additionally, only those measurements are used which are flagged as "good." In total, after filtering, the FTS time series consist of 540 measurements at Park Falls, 794 at Darwin, 180 at Bremen, and 459 at Lauder.

2.3. CarbonTracker

[24] NOAA's CarbonTracker assimilation system predicts global 3D fields of the atmospheric CO_2 mole fraction. For this purpose, it assimilates measurements of air sampling networks and tall towers. The transport of CO_2 is simulated with the TM5 model driven by ECMWF meteorological fields. A detailed description of CarbonTracker is provided by *Peters et al.* [2007]. For our work, we use CO_2 fields of the most recent CarbonTracker version (CT2009). This version provides global data with $3° \times 2°$ spatial and 3 h temporal resolution spanning the time period from January 2000 to December 2008.

[25] From the CT2009 fields, we generate two time series from January 2006 until December 2008. One consists of spatiotemporal collocations with the SCIAMACHY retrievals. The other consists of daily CarbonTracker values being collocated with the FTS station and temporally closest to SCIAMACHY's nadir overpassing local time. The first time series is used for all comparisons of SCIAMACHY with CarbonTracker while the second is used for comparisons between the FTS and CarbonTracker. Due to CarbonTracker's relatively coarse temporal and spatial resolution, both methods often refer to the same CarbonTracker grid box. As the resulting differences between both methods are marginal, only the second data set with daily values at the FTS stations is shown in Figures 2 and 3.

3. Validation Strategy

[26] TCCON provides an essential validation resource for the Orbiting Carbon Observatory (OCO), SCIAMACHY, and GOSAT. Due to their precision and accuracy, we use TCCON FTS measurements as ground truth for our analyses. However, CarbonTracker has been shown in evaluation studies to be close to reality [*Peters et al.*, 2007]. Therefore, we additionally present comparisons between FTS and CT2009 as well as SCIAMACHY and CT2009.

[27] The comparison of two column measurements and one model is not trivial as a result of the different averaging kernels. According to *Rodgers* [2000], a suitable way of tackling this issue is to adjust the measurements for a common a priori profile. This ensures that the differences between the analyzed data sets are not attributed to the a priori information. Here we use CT2009 which facilitates the comparison between all three data sets SCIAMACHY, FTS, and CT2009.

$$\vec{x}_{adj} = \hat{\vec{x}} + (\mathbf{I} - \mathbf{A})(\vec{x}_{CT2009} - \vec{x}_a). \quad (1)$$

In this equation, $\hat{\vec{x}}$ represents the retrieved profile of CO_2 concentrations (FTS or SCIAMACHY), $\vec{x}_a$ the corresponding a priori profile, $\vec{x}_{CT2009}$ the new (common) a priori profile, and $\mathbf{A}$ the column averaging kernel matrix. $\mathbf{A}$ is diagonal and is defined by the profile of the retrieval's sensitivity to CO_2, i.e., the column averaging kernel (vector).

[28] When this analysis was performed, FTS averaging kernels as well as the a priori profiles of the FTS retrieval were available for the Park Falls site. However, the FTS CO_2 averaging kernels are often close to unity. Additionally, the (FTS) a priori XCO_2 does not differ much from corresponding CarbonTracker values. For these reasons, adjusting the FTS measurements as described above results only

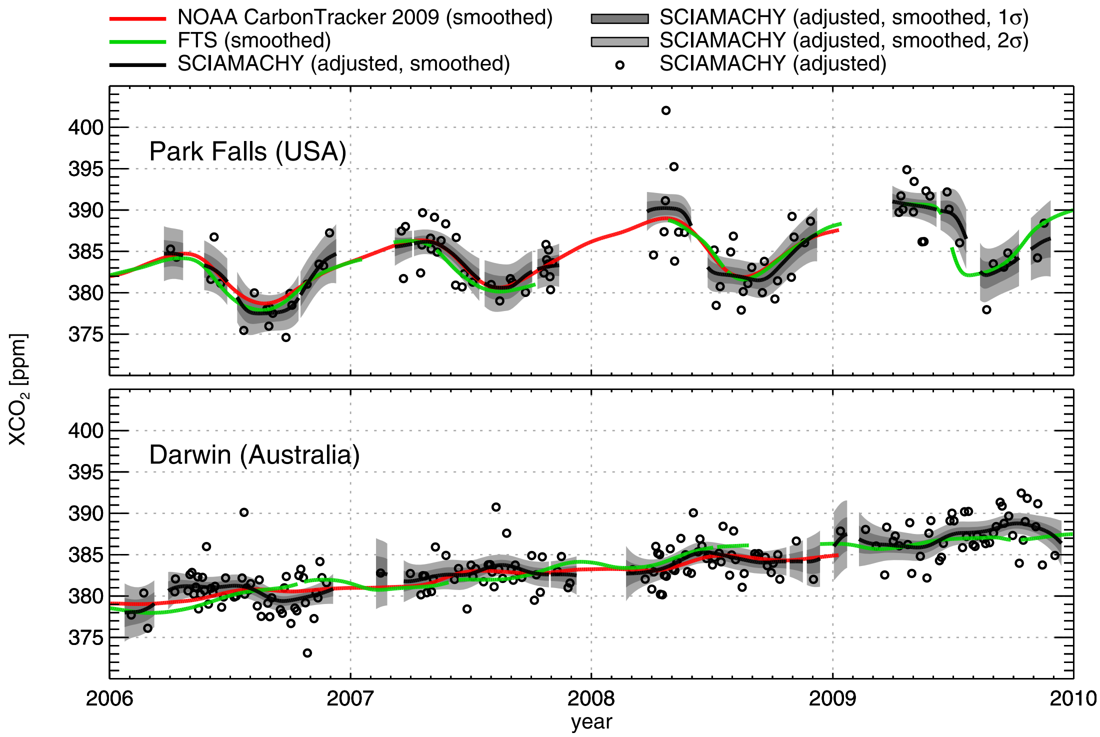

Figure 3. Smoothed representations of the time series measured at Park Falls and Darwin. The smoothing is performed by convolving the time series of Figure 2 with a Hann function with an effective width of 2 months (4 months in total). The gray shaded areas represent the standard error (1σ and 2σ).

in small modifications of about 0.1 ppm in agreement with the findings of *Washenfelder et al.* [2006]. This is small compared to SCIAMACHY's precision and as a result the adjustment of the FTS values is omitted for the three other TCCON sites.

[29] As shown by *Reuter et al.* [2010], the averaging kernels of BESD are in most scenarios close to unity, especially in the lower atmosphere. Values significantly lower than 0.9 are generally only found above (at pressures lower than) 500 hPa. This means that the results are dominated by the measurements and less by the a priori knowledge. However, it also means that there is some remaining influence from the a priori information. For this reason, a static a priori CO_2 profile is used which does not depend on time or location. This ensures that any variation of the retrieval results can be attributed to variations of the measurements and not to variations in the a priori information. These (nonadjusted) results will tend to slightly underestimate the magnitude of the XCO_2 variations (e.g., seasonal cycle and year-to-year increase). The differences between the original results with static a priori and those adjusted to CT2009 as common a priori profiles can be seen in Figure 2.

[30] Within section 4, we use the adjusted values to derive statistical quantities such as the regional relative accuracy, single-measurement precision, correlation coefficient, the year-to-year increase and the amplitude of the seasonal cycle. Many of these quantities are more valuable if they are provided together with an appropriate error estimate. For this purpose, we use a bootstrapping method [*Efron*, 1979] with a set of 100 bootstrap samples to calculate the standard error of the estimated statistical quantities. Significance is assumed for differences larger than twice the standard error.

4. Results

[31] Globally uniform biases produce no artificial unrealistic XCO_2 gradients. Therefore, they are unproblematic and can simply be subtracted from the retrieved XCO_2 before further analysis. Here, for convenience, we choose CT2009 as the baseline for the global offsets of SCIAMACHY and FTS XCO_2. Then, the average difference of all SCIAMACHY/CT2009 and FTS/CT2009 collocations is calculated. As a result, we add a global offset of 6.25 ppm to the SCIAMACHY data set and 1.35 ppm to the FTS data set. The entire bias corrected XCO_2 time series of SCIAMACHY, FTS, and CT2009 at all four stations are shown in Figure 2.

[32] All results, which are related to the agreement of individual collocated measurements of two data sets, i.e., their regional bias Δ, precision σ, and correlation ρ, are summarized in Table 1. Table 2 summarizes all results which are related to the seasonal cycle and the year-to-year increase.

4.1. Regional Biases

[33] As mentioned earlier, undetected biases on regional scales negatively impact surface flux inverse modeling [*Miller et al.*, 2007; *Chevallier et al.*, 2007]. Systematic differences between the four FTS sites may imply such regional-scale biases. For this reason, we calculate the systematic offsets between all three data sets separately for

Table 1. Regional Biases Δ, Precision on Single Measurement Basis σ, and Correlation ρ of All Collocated Measurements Shown in Figure 2

Location	SCIAMACHY Versus FTS			SCIAMACHY Versus CT2009			CT2009 Versus FTS		
	Δ (ppm)	σ (ppm)	ρ	Δ (ppm)	σ (ppm)	ρ	Δ (ppm)	σ (ppm)	ρ
Park Falls (USA)	−0.2 ± 0.4	2.5	0.83	−0.2 ± 0.3	3.0	0.77	0.1 ± 0.1	0.8	0.97
Darwin (Australia)	0.3 ± 0.2	2.4	0.69	0.4 ± 0.2	2.3	0.74	0.0 ± 0.1	0.9	0.93
Bremen (Germany)	−1.2 ± 0.6	2.6	0.61	−1.1 ± 0.6	2.5	0.73	0.1 ± 0.2	1.3	0.95
Lauder (New Zealand)	0.5 ± 0.8	2.5	0.47	0.5 ± 0.8	2.9	0.64	0.0 ± 0.4	0.9	0.86
Global[a]	0.0 ± 0.2	2.5	0.72	0.0 ± 0.2	2.7	0.74	0.0 ± 0.1	0.9	0.94

[a]This row corresponds to a merged data set enclosing the data of all four sites. As described at the beginning of section 4, a global offset correction is applied. Therefore, all biases are zero by definition in this case.

each station. Compared to the FTS, SCIAMACHY shows systematic differences between −1.2 ± 0.6 ppm and 0.5 ± 0.8 ppm. At all stations, the bias is smaller than (or equal) twice its standard error and smaller than its standard error at two stations. The comparison between CT2009 and FTS shows insignificant systematic differences in the range of 0.0 ± 0.4 ppm and 0.1 ± 0.2 ppm. These biases are always less than or equal their error.

4.2. Single-Measurement Precision

[34] Another important characteristic of the data set is the single-measurement precision, which we define as the standard deviation of the difference between two collocated data sets. With respect to the FTS, the SCIAMACHY XCO_2 single-measurement precision varies between 2.4 ppm and 2.6 ppm between the four stations. Using all collocations of all stations, the global single-measurement precision amounts to 2.5 ppm. This is slightly better than the 2.7 ppm obtained when comparing SCIAMACHY with CT2009. Even though the difference is not statistically significant, it indicates that SCIAMACHY may agree better with the FTS than with CT2009 even though the FTS measurements have measurement noise. Note that the three compared data sets have different spatial resolutions. Additionally, the distance between a SCIAMACHY pixel and a collocated FTS measurement can amount up to 350 km. As a result, the calculated single-measurement precisions are upper bounds because they include a representation error that can exceed 0.5 ppm [*Tolk et al.*, 2008].

4.3. Correlation

[35] The correlation is a measure of the linear dependence between two data sets. Comparing SCIAMACHY with FTS, the correlation coefficient amounts globally to 0.72 and varies from station to station between 0.47 and 0.83. The correlation coefficient does depend on the range of XCO_2 sampled (seasonal cycle, year-to-year increase, and number of samples). It is therefore not surprising that the highest correlation is found at Park Falls (large seasonal cycle, large number of coincident SCIAMACHY retrievals) and the lowest at Lauder (small seasonal cycle, only a few coincident SCIAMACHY retrievals), eventhough the single-measurement precisions are similar.

4.4. Year-to-Year Increase

[36] In order to derive the average year-to-year increase of XCO_2, we fit a linear trend model to the deseasonalized time series of SCIAMACHY, FTS, and CT2009. This analysis is based on the full time series instead of collocations only. More precisely, each of the 4 years is divided into 25 intervals. The intervals are assumed to be short enough to contain no significant seasonal component. If more than one (of the four) ith interval contains data, we calculate the linear trend for the time series of the ith intervals. This means we calculate up to 25 linear trends of subsampled time series with no seasonal component. The year-to-year increase is then calculated from the average trend.

[37] As a result of the low amount of SCIAMACHY data in the Bremen and Lauder time series, this analysis is restricted to Park Falls and Darwin. At Park Falls, we find no significant difference between the year-to-year increase of SCIAMACHY (1.88 ± 0.44 ppm/yr), FTS (2.01 ± 0.05 ppm/yr), and CT2009 (1.96 ± 0.03 ppm/yr). At Darwin, the FTS has a larger year-to-year increase of 2.30 ± 0.03 ppm/yr, which agrees with the SCIAMACHY retrieved value of 2.27 ± 0.20 ppm/yr. Compared to this, the year-to-year increase of CT2009, which amounts to 1.99 ± 0.01 ppm/yr, is significantly smaller. However, the difference between CT2009 and FTS has a similar magnitude to SCIAMACHY's noise.

4.5. Seasonal Cycle

[38] We calculate smoothed representations of the XCO_2 time series (Figure 3). This is achieved by convolving the original time series with a Hann function $h(x) = \sin^2(2\pi x/w)$

Table 2. Year-to-Year Increase as Well as Average Peak-to-Peak Amplitude of the Seasonal Cycle Calculated From the Smoothed SCIAMACHY, FTS, and CT2009 Time Series Shown in Figure 3

Location	Year-to-Year Increase (ppm/yr)			Peak-to-Peak Amplitude (ppm)		
	SCIAMACHY	FTS	CT2009	SCIAMACHY	FTS	CT2009
Park Falls (USA)	1.88 ± 0.44	2.01 ± 0.05	1.96 ± 0.03	7.92 ± 0.95	7.41 ± 0.13	6.94 ± 0.08
Darwin (Australia)	2.27 ± 0.20	2.30 ± 0.03	1.99 ± 0.01	2.48 ± 0.42	1.91 ± 0.05	1.18 ± 0.02

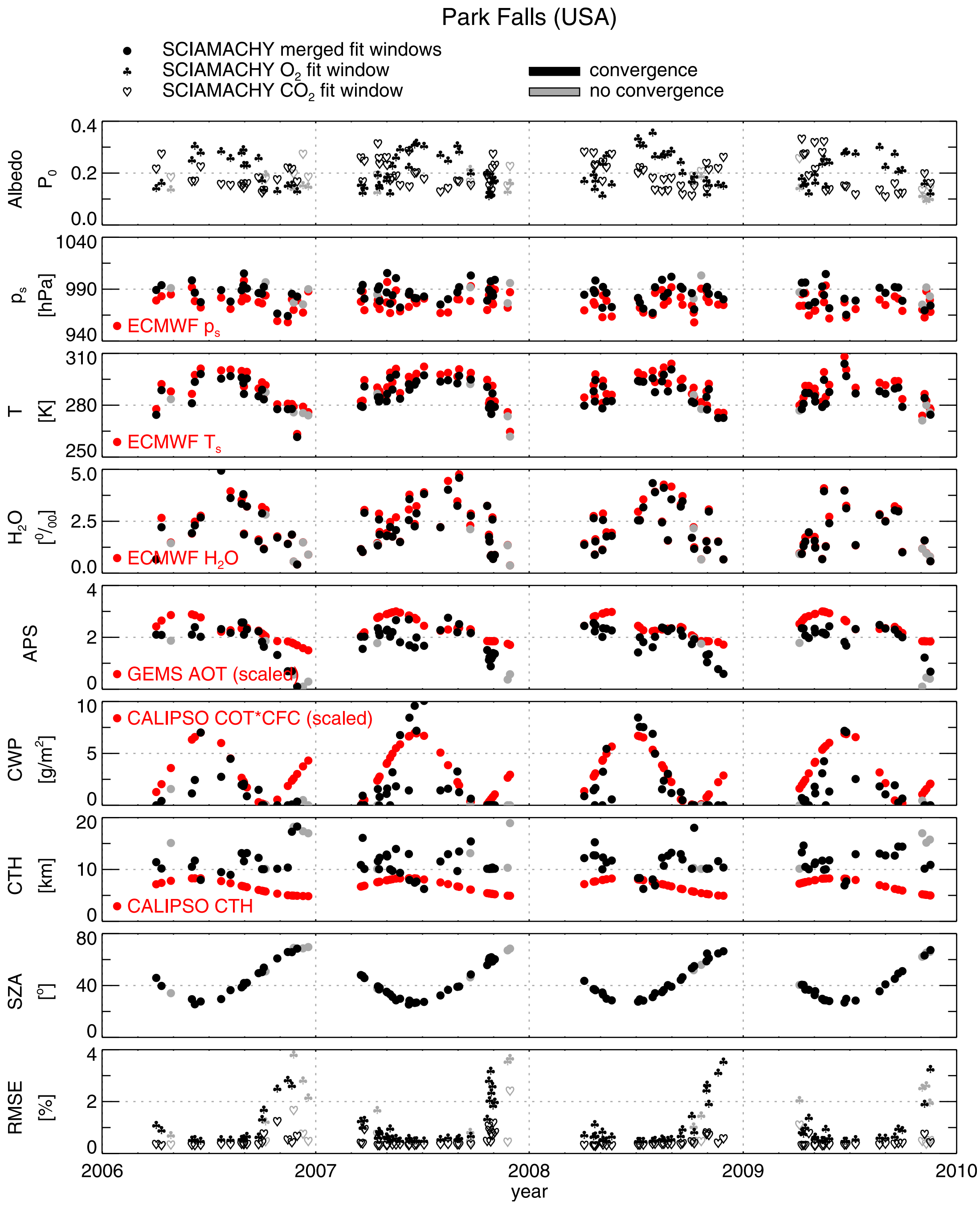

Figure 4. Park Falls time series of selected important state vector elements which are byproducts of the SCIAMACHY XCO_2 retrieval. (top to bottom) Albedo in both fit windows represented by the zeroth-order polynomial, surface pressure, 2 m temperature, column-average mole fraction of water vapor, scaling factor for a default aerosol profile (APS), cloud water/ice content (CWP), cloud top height (CTP), solar zenith angle (SZA), and root mean square error of the fit residual in both fit windows. Corresponding values of ECMWF, CALIPSO (2007), and GEMS (2005) are also shown.

with a total width *w* of 4 months which corresponds to an effective width of 2 months. The laws of error propagation are consistently applied to derive the standard error of the smoothed SCIAMACHY time series. For the same reasons as mentioned in section 4.4, we restrict this analysis to the Park Falls and Darwin time series.

[39] As shown in Figure 3, the smoothed SCIAMACHY data agree most times within 1 standard error and nearly all the time within 2 standard errors with CT2009 and the FTS. In periods with frequent measurements, the standard error is considerably reduced due to the smoothing.

[40] After subtracting the linear trend, i.e., the year-to-year increase, we calculate the average peak-to-peak

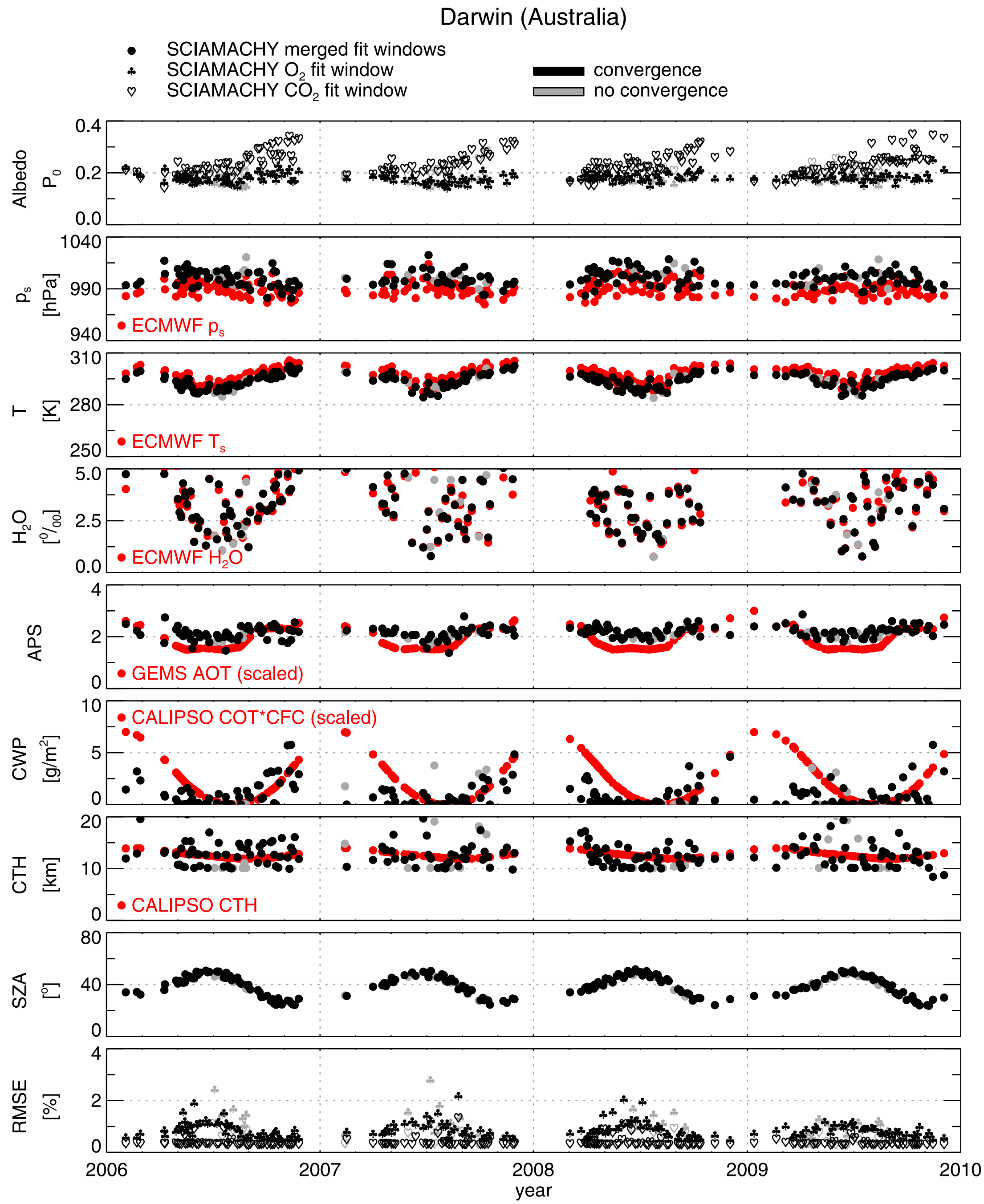

Figure 5. Darwin time series of selected important state vector elements which are byproducts of the SCIAMACHY XCO_2 retrieval. (top to bottom) Albedo in both fit windows represented by the zeroth-order polynomial, surface pressure, 2 m temperature, column-average mole fraction of water vapor, scaling factor for a default aerosol profile (APS), cloud water/ice content (CWP), cloud top height (CTP), solar zenith angle (SZA), and root mean square error of the fit residual in both fit windows. Corresponding values of ECMWF, CALIPSO (2007), and GEMS (2005) are also shown.

amplitude of the seasonal cycles. At Park Falls the shape of the seasonal cycle in all data sets agrees well. The average peak-to-peak amplitudes amount to 7.92 ± 0.95 ppm for SCIAMACHY, 7.41 ± 0.13 ppm for the FTS, and 6.94 ± 0.08 ppm for CT2009. Due to SCIAMACHY's relatively large standard error, no significant difference between SCIAMACHY and both other data sets can be observed. However, CarbonTracker's underestimation of 0.47 ppm (compared to the FTS) lies above the level of significance.

[41] At Darwin the seasonal cycle is less pronounced and differences are more apparent. The agreement between the shape and amplitude of the three time series varies from year to year. Relatively good agreement of all three data sets is found in the years 2007 and 2008, whereas differences are

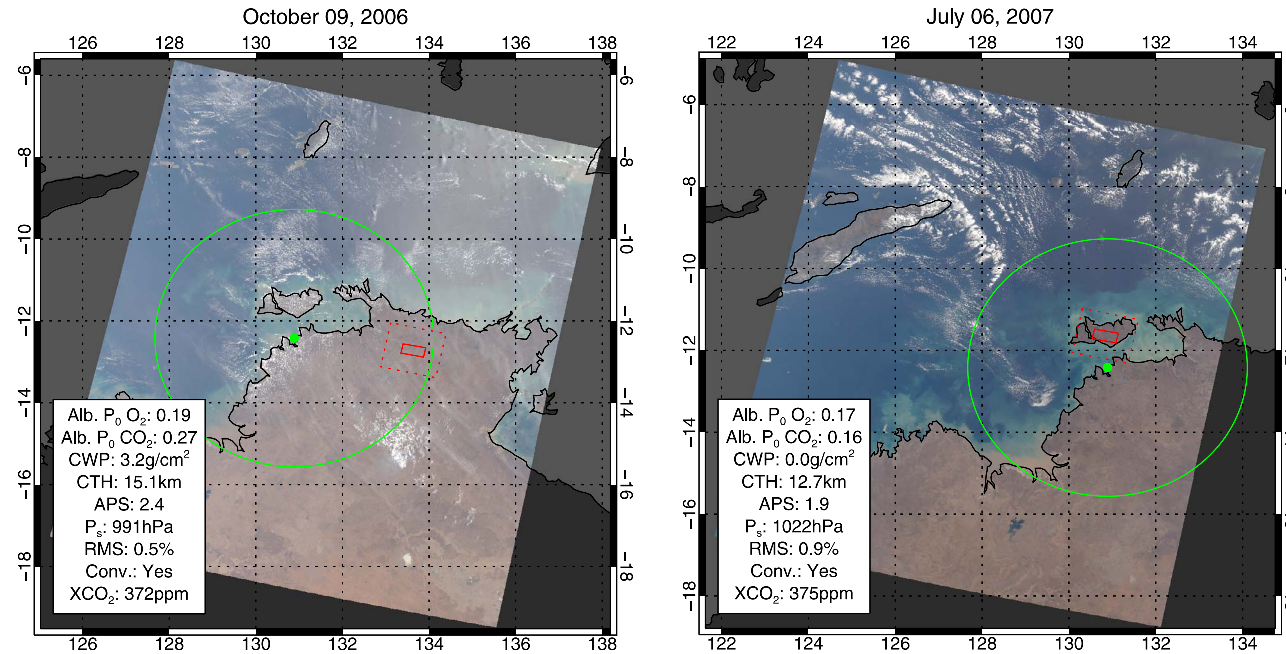

Figure 6. Meteorological situation of two exemplary SCIAMACHY measurements (red) falling in a 350 km surrounding of Darwin (green) as seen from MERIS. The SCIAMACHY pixels are encased by a 40 km cloud screening safety margin (red dotted box). (left) A typical cloud free situation. (right) In contrast to this, a situation with (undetected) cirrus clouds.

pronounced in 2006. Bearing this in mind, we characterize the peak-to-peak amplitudes. These are 2.48 ± 0.42 ppm for SCIAMACHY, 1.91 ± 0.05 ppm for the FTS, and 1.18 ± 0.02 ppm for CT2009. In this case, the differences of CT2009 to the FTS but also to SCIAMACHY are significant. No significant difference is found between SCIAMACHY and the FTS. Even though, the difference between SCIAMACHY and the FTS (0.57 ppm) is smaller than between CT2009 and the FTS (0.73 ppm), one should keep in mind that its magnitude is still quite large and the standard errors are much higher here.

4.6. Other State Vector Elements and RMS

[42] In order to ensure that the results of other important state vector elements are also reasonable, Figures 4 and 5 show time series of these parameters.

4.6.1. Albedo

[43] The retrieved albedo has a reasonable seasonal cycle and is typically within the range of 0.1 and 0.3. The O_2-A band is located directly behind the red edge; that is, green vegetation has a large albedo in this spectral region. For this reason, the growing season is readily observed in the albedo within the O_2-A band at Park Falls.

4.6.2. Surface Pressure

[44] As described above, the surface pressure is strongly constrained by the a priori knowledge, i.e., ECMWF reanalysis. As a result of the relatively strict constraint, it is not surprising that the retrieved values follow the corresponding ECMWF values very well. However, we observe a systematic offset of about 9.5 hPa, which is similar to the findings of *Bösch et al.* [2006], who attributed systematic offsets in the retrieved surface pressure to potential inadequacies of the spectroscopy.

4.6.3. Temperature and Humidity

[45] ECMWF reanalyses are the first guess and the a priori knowledge for temperature and humidity. Even though these constraints are weak, we find good agreement between the retrieved and the modeled values. The seasonal cycle agrees with the expected behavior with largest values being in summer time. The observed systematic temperature offset amounts to about −3.6 K.

4.6.4. Scattering

[46] BESD describes scattering by aerosol profile scaling (APS), the cloud ice/water path (CWP), and the cloud top height (CTH). All other scattering related parameters such as the cloud and aerosol micro physics or the aerosol profile shape are kept at default values. We use a LOWTRAN summer aerosol profile with moderate rural aerosol load, and Henyey-Greenstein phase function. The first guess (APS = 1) aerosol optical thickness (AOT) is 0.136 at 750 nm and 0.038 at 1550 nm. The cloud layer has a geometrical thickness of 500 m and consists of fractal ice crystals with an effective radius of 50 μm. The first guess values of CTH and CWP are 10 km and 10 g/m^2. This corresponds to a COT of about 0.33 at 500 nm. See also the publication of *Reuter et al.* [2010].

[47] APS and CWP show a pronounced seasonal cycle with maximum values in the summer months. Qualitatively, the seasonal cycle of APS is similar to that of the GEMS AOT. GEMS stands for “Global and regional Earth-system Monitoring using Satellite and in-situ data” and the GEMS AOT product is based on the assimilation of MODIS AOT retrievals at the ECMWF.

[48] The seasonal cycle of CWP and CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation) effective COT are also in good qualitative agreement. The

effective COT being defined as cloud fractional coverage (CFC) of thin clouds, which can probably not be detected with MERIS, multiplied by COT of these clouds. The retrieved CTH shows no clear recurring seasonal cycle. However, similarities with the corresponding CALIPSO data, which shows higher values in the Tropics (Darwin) than in Park Falls, are observed.

[49] With respect to the GEMS and CALIPSO data, used in the study, the following is to be noted.

[50] 1. CWP, CTH and APS are "effective" values and a quantitative one-to-one agreement with corresponding GEMS or CALIPSO values cannot be expected [*Reuter et al.*, 2010]. Therefore, GEMS AOT and CALIPSO CWP are scaled to nicely fit into the corresponding *y* axes of Figures 4 and 5.

[51] 2. The plotted GEMS data repeatedly show the year 2005 while the CALIPSO data shown are based on repetitions of the year 2007 only.

[52] 3. We use operational NASA level 2 CALIPSO data of version 2.01. The data is filter for COT values below 0.1 and measurements at night time, only. Additionally, the data is smoothed by convolution with a Gaussian kernel with a full width half maximum (FWHM) of 8° × 8° × 3 months. This dampens out short-term and small-scale variations so that only the seasonal changes remain.

[53] Figure 6 (right) shows a SCIAMACHY pixel near Darwin taken at 6 July 2007 underlaid with a MERIS true color composite. It is an example for a typical clear sky situation. Correspondingly, a CWP of 0.0 g/m^2 and a relatively low APS value of 1.9 are retrieved. Figure 6 (left) shows the meteorological situation around Darwin on 9 October 2006 and is an example for a situation with undetected thin cirrus clouds, which are visible in the MERIS true color composite. In this case, the retrieved values of CWP and APS are elevated and amount to 3.2 g/cm^2 and 2.4, respectively.

4.6.5. RMS

[54] The median of the relative root mean square difference between fit and measurement amounts to 0.7% in both fit windows together. With a median of 0.3% compared to 0.8%, the fit residuals are generally smaller in the CO_2 than in the O_2 fit window. Especially the latter shows a pronounced RMS seasonality. There are two reasons for this: because the fit quality depends on the solar zenith angle (e.g., due to the plane parallel assumption) and because vegetated surfaces have a low albedo in the O_2 fit window out of the growing season. The latter applies presumably not for Darwin because the seasonality of vegetation is expected to be low here.

5. Discussion and Conclusions

[55] BESD uses measurements in the O_2-A absorption band to retrieve scattering information of clouds and aerosols. This information is transferred to the CO_2 absorption band at 1580 nm by simultaneously fitting the spectra measured in both spectral regions. The explicit consideration of scattering by this approach reduces potential systematic biases due to clouds or aerosols. We show that this novel retrieval algorithm meets the expectations and predictions from the theoretical studies of *Reuter et al.* [2010] when applied to SCIAMACHY data.

[56] The XCO_2 single-measurement precision compared to FTS measurements is 2.5 ppm and similar to theoretical estimates driven by instrumental noise [*Reuter et al.*, 2010]. This can be compared with earlier studies.

[57] 1. *Schneising et al.* [2008] determined the daily standard deviations of WFM-DOAS retrieval results at several locations. They interpreted the average of the standard deviations as single-measurement precision, which amounted to about 1–2%. They also calculated the intermonthly scatter of their results and found it was about 9 ppm (2.3%).

[58] 2. *Bösch et al.* [2006] applied a modified version of an algorithm which was originally designed for OCO to SCIAMACHY data. By comparing against collocated FTS (Fourier transform spectrometer) measurements at Park Falls, they found a XCO_2 single-measurement precision of 1–2% for clear sky conditions.

[59] 3. For the high spectral resolution instruments TANSO and OCO, *Kuang et al.* [2002] estimated that a precision of 0.3 to 2.5 ppm is achievable for aerosol optical thicknesses (AOT) of up to 0.3. This is similar to the findings of *Connor et al.* [2008], who estimated that a single-measurement precision of 0.7–0.8 ppm under high Sun conditions and 1.5–2.5 ppm under low Sun conditions is realistic. However, these values are based on simulations and have not yet been confirmed with measured TANSO data.

[60] The inferred regional XCO_2 biases between SCIAMACHY and the FTS instruments are in the range of −1.2 ppm (Bremen) and 0.5 ppm (Lauder). All regional biases are smaller than twice their standard error and at two of the four sites they are smaller than their standard error. This means that we find no statistically significant regional XCO_2 biases. For comparison, *Schneising et al.* [2008] analyzed the systematic biases of WFM-DOAS relative to FTS measurements and found differences of about 4 ppm between Park Falls and Bremen. However, *Schneising et al.* [2008] used a different data set which, for example, had not been screened for clouds in the same way.

[61] We also find no statistically significant regional biases between CT2009 and the FTS measurements but the standard errors are smaller here, being in the range of 0.1 ppm to 0.4 ppm. The standard deviation of the difference between CT2009 and the FTS measurements is also smaller, being 0.9 ppm. The good agreement between CT2009 and FTS may not be overinterpreted because CarbonTracker assimilates in situ measurements in the near surroundings of some of the FTS stations. This applies especially to the Park Falls site where tall tower measurements are assimilated. This aspect has already been discussed by *Peters et al.* [2007]. An extrapolation to sites where the assimilated data product is at significant distance is, therefore, not possible.

[62] *Schneising et al.* [2008] found that WFM-DOAS produces an unrealistic seasonal cycle with a much too large amplitude in the southern hemisphere. They attributed this to undetected subvisible cirrus clouds. Using BESD, we find no significant differences in the year-to-year increase, nor any significant systematic differences in the observed seasonal amplitude when comparing SCIAMACHY XCO_2 with FTS measurements at Park Falls and Darwin. The year-to-year increase and also the seasonal amplitude of CT2009 signifi-

cantly differ from corresponding FTS values at Darwin. The differences of these quantities between SCIAMACHY and CT2009 are larger than the standard errors of the SCIAMACHY values and the differences of the seasonal amplitude exceed the significance level. The density of assimilated in situ measurements is low in the southern hemisphere, compared to the northern hemisphere, and Darwin is approximately 2000 km away from the next regularly assimilated flask measurement site. It therefore might be expected that the quality of CT2009 data may be degraded in such regions. However, it shall be noted that due to the large amount of FTS and CT2009 data and due to their low noise level, it is much easier to detect significant differences between these data sets. Compared to this, systematic differences between SCIAMACHY and FTS are more likely to remain hidden in the SCIAMACHY noise.

[63] It will be important to understand the remaining differences between FTS and SCIAMACHY retrievals. Nonetheless, the results obtained with the BESD algorithm to date suggest SCIAMACHY may provide valuable additional information about XCO_2, at least in regions where the density of assimilated in situ data is low and/or where rapid convective mixing leads to weak flux signatures in the CO_2 concentrations measured by in situ trace gas analyzers deployed at the Earth's surface. Therefore, SCIAMACHY retrieved XCO_2 may enhance our knowledge on CO_2 surface fluxes and long-range transport. Instruments with higher spectral and spatial resolution such as GOSAT or OCO-2 (in the future) have the potential to further reduce the remaining uncertainties. Therefore, our findings are especially important for the time period 2002–2009 when SCIAMACHY was the only satellite instrument with the capability of measuring the most important greenhouse gas with sufficient sensitivity near the surface.

[64] In the frame of ESA's climate change initiative (CCI), it is planned to generate the essential climate variable (ECV) XCO_2 from SCIAMACHY using the presented retrieval scheme.

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