Atmospheric Chemistry and Physics

Atmospheric carbon gases retrieved from SCIAMACHY by WFM-DOAS: version 0.5 CO and CH_4 and impact of calibration improvements on CO_2 retrieval

M. Buchwitz[1], R. de Beek[1], S. Noël[1], J. P. Burrows[1], H. Bovensmann[1], O. Schneising[1], I. Khlystova[1], M. Bruns[1], H. Bremer[1], P. Bergamaschi[2], S. Körner[3], and M. Heimann[3]

[1]Institute of Environmental Physics (IUP), University of Bremen FB1, Bremen, Germany
[2]Institute for Environment and Sustainability, Joint Research Centre (EC-JRC-IES), Ispra, Italy
[3]Max Planck Institute for Biogeochemistry (MPI-BGC), Jena, Germany

Abstract. The three carbon gases carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4) are important atmospheric constituents affecting air quality and climate. The near-infrared nadir spectra measured by SCIAMACHY on ENVISAT contain information on the vertical columns of these gases which we retrieve using a modified DOAS algorithm (WFM-DOAS or WFMD). Our main data products are CO vertical columns and dry-air column averaged mixing ratios of methane (CH_4) and CO_2 (denoted XCH_4 and XCO_2). For CO and CH_4 we present new results for the year 2003 obtained with an improved version of WFM-DOAS (WFMDv0.5) retrieved from Level 1 version 4 (Lv1v4) spectra. This data set has recently been compared with a network of ground based FTIR stations. Here we describe the WFMDv0.5 algorithm, present global and regional maps, and comparisons with global reference data. We show that major problems of the previous versions (v0.4 and v0.41) related to the varying ice-layer on the SCIAMACHY channel 8 detector have been solved. Compared to MOPITT the SCIAMACHY CO columns are on average higher by about 10–20%. Regionally, however, especially over central South America, differences can be much larger. For methane we present global and regional maps which are compared to TM5 model simulations performed using standard methane emission inventories. We show that methane source regions can be clearly detected with SCIAMACHY. We also show that the methane data product can be significantly further improved using Lv1v5 spectra with improved calibration. For CO_2 we present three years of SCIAMACHY CO_2 measurements over Park Falls, Wisconsin, USA, retrieved from Lv1v5. We show that the quality of CO_2 retrieved from these spectra is significantly higher compared to WFMDv0.4 XCO_2 retrieved from Lv1v4.

1   Introduction

Carbon monoxide (CO) is a major tropospheric air pollutant and carbon dioxide (CO_2) and methane (CH_4) are the two most important anthropogenic greenhouse gases. Knowledge about the global distribution of these carbon gases is therefore important. CO plays a central role in tropospheric chemistry (see, e.g., Bergamaschi et al., 2000, and references given therein) as CO is the leading sink of the hydroxyl radical (OH) which itself largely determines the oxidizing capacity of the troposphere and, therefore, its self-cleansing efficiency and the concentration of greenhouse gases such as CH_4. CO also has large air quality impact as a pre-curser to tropospheric ozone, a secondary pollutant associated with respiratory problems and decreased crop yields. Satellite measurements of CH_4, CO_2, and CO in combination with inverse modeling have the potential to help better constrain the uncertainties of the magnitude of the surface fluxes than currently possible with the highly precise but rather sparse data from the network of surface stations (see Houweling et al., 1999, 2004; Rayner and O'Brien, 2001, and references given therein). A better understanding of the sources and sinks of CH_4 and CO_2 is important for example to accurately predict the future concentrations of these gases and associated climate change. Monitoring of the emissions of these gases is also required by the Kyoto protocol.

High quality trace gas column retrieval from the SCIAMACHY near-infrared spectra is a challenging task for many reasons, e.g., due to calibration issues mainly related to high

Correspondence to: M. Buchwitz
(michael.buchwitz@iup.physik.uni-bremen.de)

and variable dark signals and changing detector characteristics (Gloudemans et al., 2005), because it is difficult to detect the weak CO lines which are close to the noise level and superimposed by strong absorption features of water and methane, and because of the challenging accuracy and precision requirements for CO$_2$ (Rayner and O'Brien, 2001; Houweling et al., 2004) and CH$_4$ (Meirink et al., 2006).

When developing a retrieval algorithm many decisions have to be made (selection of spectral fitting window, inversion procedure including definition of fit parameters and use of a priori information, radiative transfer approximations, etc.) to process the data in an optimum way such that a good compromise is achieved between processing speed and accuracy/precision of the data products. In this context it is important to point out that other groups are also working on this important topic using different approaches (see Gloudemans et al., 2004, 2005; Frankenberg et al., 2005a,b,c, 2006; Houweling et al., 2005; Barkley et al., 2006a,b; Bösch et al., 2006).

SCIAMACHY has not been specified to measure CO$_2$ and CH$_4$ regional surface fluxes in contrast to the future near-infrared/nadir missions OCO/USA (Crisp et al., 2004) and GOSAT/Japan (http://www.jaxa.jp/missions/projects/sat/eos/gosat/index_e.html) which will have, for example, higher spectral and spatial resolution compared to SCIAMACHY to maximize spectral information and to have higher probability for cloud free ground pixels. Nevertheless, SCIAMACHY makes similar measurements as will be performed by OCO and GOSAT and therefore can be considered the predecessor of these dedicated CO$_2$ and/or CH$_4$ missions.

Initial carbon gas vertical column data products derived from SCIAMACHY nadir observations with WFM-DOAS version 0.4x (0.4 and 0.41) have been compared with global reference data in Buchwitz et al. (2005b) and ground based Fourier Transform Infra Red (FTIR) spectroscopy measurements (De Maziere et al., 2004; Sussmann and Buchwitz, 2005; Warneke et al., 2005; Dils et al., 2005; Sussmann et al., 2005). A comparison of the new version 0.5 CO and methane data products with ground-based FTIR measurements has recently been performed by Dils et al. (2006), including a comparison of WFMDv0.4 XCO$_2$ at three stations. Here we present a description of the WFMDv0.5 algorithm and a comparison with global reference data. For CO$_2$ we present an initial investigation concerning the impact of recent calibration improvements (e.g., improved dark signal calibration) on the CO$_2$ retrieval which will result in a significantly improved CO$_2$ (but also methane and potentially CO) data set in the near future.

This paper is organized as follows: In Sect. 2 the SCIAMACHY instrument is introduced followed by a description of the WFM-DOAS retrieval algorithm in Sect. 3. In Sect. 4 we present and discuss the carbon gas results. Conclusions are given in Sect. 5.

2 The SCIAMACHY instrument

SCIAMACHY (Burrows et al., 1995; Bovensmann et al., 1999) is a spectrometer that measures reflected, scattered and transmitted solar radiation in the spectral region 214–2380 nm at moderate spectral resolution (0.2–1.6 nm). On the Earth's day side SCIAMACHY mainly performs a sequence of alternating nadir and limb observations. The horizontal resolution of the nadir measurements depends on orbital position and spectral interval but is typically 60 km (e.g., for methane and CO$_2$) or 120 km (e.g., for CO) across track times 30 km along track. These measurements can be inverted to obtain a large number of (primarily) atmospheric data products (Bovensmann et al., 1999).

Overall, the in-flight optical performance of SCIAMACHY is as expected from the on-ground activities. One exception is a time dependent optical throughput variation in the SCIAMACHY near-infrared (NIR) channels 7 (the main CO$_2$ channel) and 8 (the only CO channel and main CH$_4$ channel) due to ice build-up on the detectors which adversely affects the trace gas retrieval (Buchwitz et al., 2005b; Gloudemans et al., 2005). This effect is limited by regular heating of the instrument. The WFM-DOAS version 0.5 methane and version 0.4 XCO$_2$ results presented in this paper have been derived from channel 6 which is not affected by an ice-layer. The WFM-DOAS version 0.5 CO is retrieved from channel 8 using a correction procedure for ice-layer induced errors.

3 WFM-DOAS retrieval algorithm

The retrieval of a long-lived and therefore relatively well-mixed gas such as carbon dioxide and methane is extremely challenging as only small variations on top of a large background are of relevance in order to obtain information on their surface sources and sinks. Therefore, the retrieval algorithm has to be very accurate. In addition, the algorithm also has to be very fast to process huge amounts of data. We have developed the Weighting Function Modified Differential Optical Absorption Spectroscopy (WFM-DOAS) retrieval algorithm to accomplish this task.

WFM-DOAS (Buchwitz et al., 2000b, 2004, 2005a,b; Buchwitz and Burrows, 2004) is an unconstrained linear-least squares method based on scaling (or shifting) preselected vertical profiles. The fit parameters for the trace gases are directly the desired vertical columns. The logarithm of a linearized radiative transfer model plus a low-order polynomial is fitted to the logarithm of the ratio of a measured nadir radiance and solar irradiance spectrum, i.e. the observed sun-normalized radiance. The WFM-DOAS reference spectra are the logarithm of the sun-normalized radiance and its derivatives computed with a radiative transfer model (Buchwitz et al., 2000a). In order to avoid time-consuming
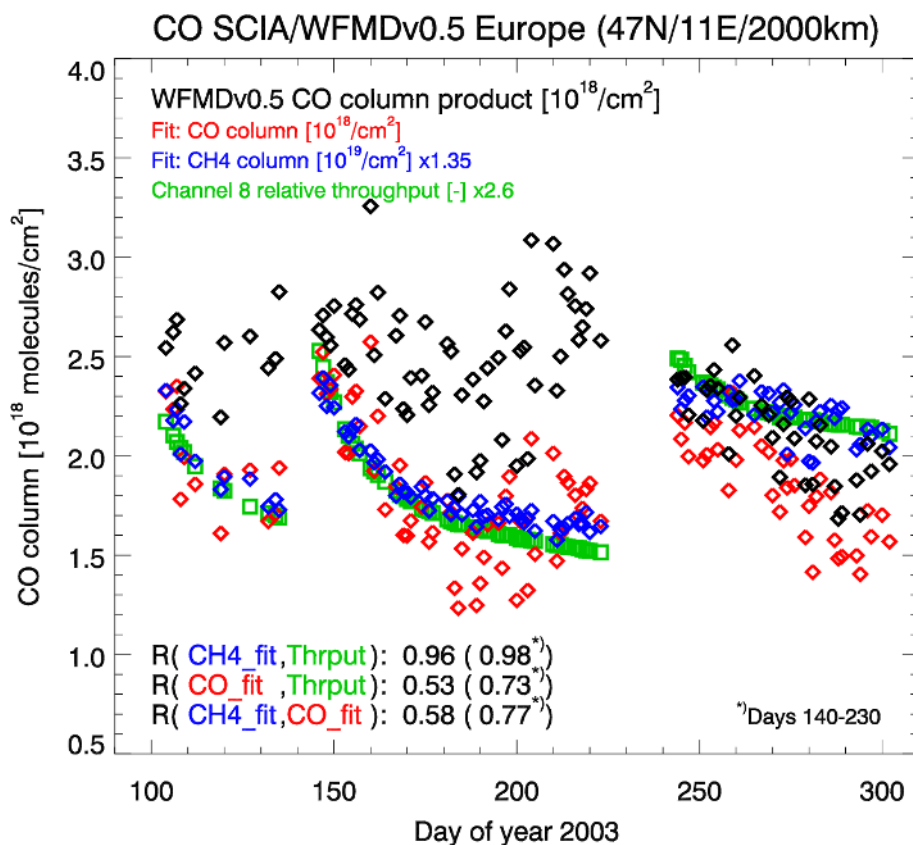
Fig. 1. The black symbols show daily averages of the SCIAMACHY WFM-DOAS v0.5 CO column data product over Europe for the year 2003. The CO product has been obtained by multiplying the CO columns from the spectral fit (red symbols) with a correction factor derived from the simultaneously fitted methane columns. The correction factor is the ratio of an a-priori methane column divided by the retrieved methane column which is shown as blue symbols. The green symbols show the average optical throughput of channel 8 determined from ratios of solar spectra. The throughput varies because of a changing ice layer on the channel 8 detector. As can be seen, the methane column is highly correlated with the throughput, indicating a time dependent bias of the retrieved methane column due to the changing ice layer (the correlation coefficient is 0.96 for the entire time period and 0.98 for the time period day 140 to day 230 of year 2003). The uncorrected CO columns (red) show significant day to day variations but a significant correlation with throughput (0.73 for the time period day 140–230) and methane (0.77 for days 140–230).

on-line radiative transfer simulations, a fast look-up table scheme has been implemented.

Due to the varying ice-layers on the channel 7 and 8 detectors (see Sect. 2) the in-orbit spectrometer slit function of SCIAMACHY is different from the one measured on-ground and changes with time (Gloudemans et al., 2005; Buchwitz et al., 2005b). The slit function currently used by WFM–DOAS has been determined by applying WFM–DOAS to the in-orbit nadir measurements. The one that resulted in best fits, i.e. the smallest fit residuum, has been selected.

Basically the same algorithm is used to retrieve CO, methane, and CO_2. There are however also trace gas specific differences which will be discussed in the following subsections.

3.1 CO specific aspects

Carbon monoxide v0.5 is retrieved from a small spectral fitting window (2324–2335 nm) located in channel 8 covering several absorption lines of CO. Compared to our initial v0.4 CO product (Buchwitz et al., 2004, 2005b) v0.5 CO has been significantly improved.

The v0.5 CO column product is retrieved from an optimized spectral fitting window and generated without the application of a scaling factor (the v0.4 product was scaled by a factor 0.5). The shift of the fitting window resulted in CO columns being significantly lower (nearly a factor of two) compared to the fitting window used for v0.4 CO thus eliminating the need for significantly downscaling the columns as was necessary for v0.4. This shows that the selection of a fitting window for SCIAMACHY CO retrieval is critical and requires careful analysis of real data especially for a weak
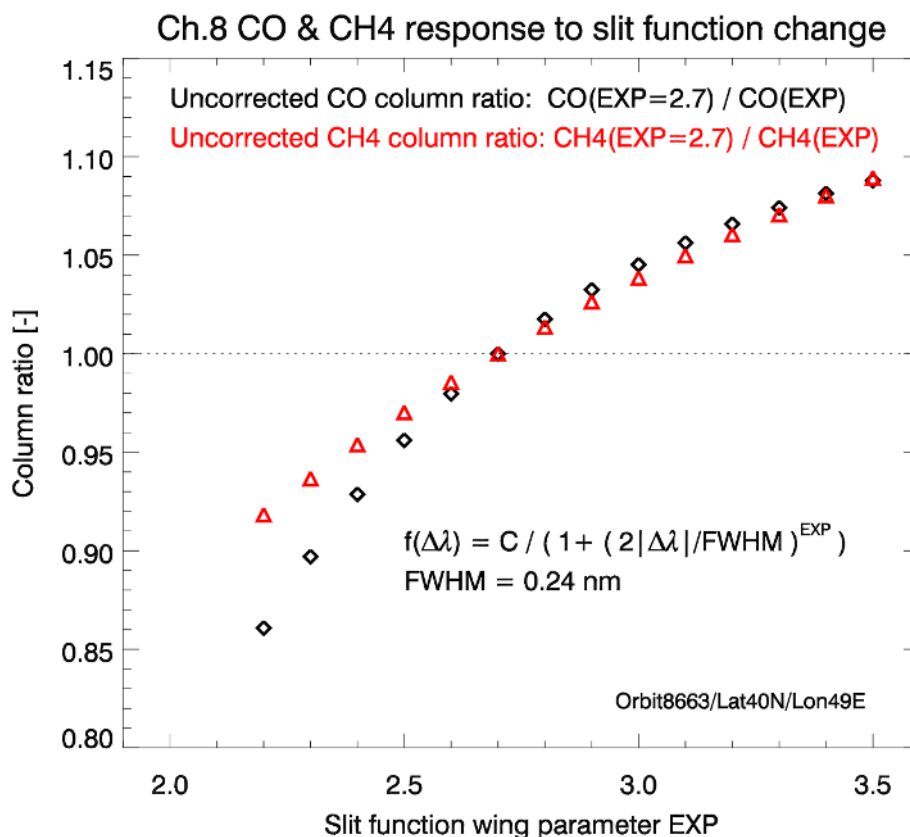
Fig. 2. Ratios of CO columns (black symbols) and methane columns (red symbols) retrieved using different spectrometer slit functions. The SCIAMACHY slit function is changing with time due to the varying ice layer on the channel 8 detector. The main effect is a broadening of the wings at (nearly) constant full width at half maximum ($FWHM$) (see Gloudemans et al., 2005, and references given therein) and may be modeled using the slit function $f(\Delta\lambda)$ given in the annotation of the figure. Here $\Delta\lambda$ is the spectral distance (in nm) from the center wavelength of a detector pixel, C is a constant selected such that (numerical) integration of f over wavelength gives unit area, $FWHM$ is the selected full width at half maximum (here: 0.24 nm), and EXP is a parameter that mainly determines the relative contributions of the wings, i.e., the shape of the slit function for $|\Delta\lambda|$ larger than $0.5 \times FWHM$. As can be seen, both the CO and methane columns change as a function of EXP in a similar but not exactly identical way.

absorbers such as CO with superimposed much stronger absorption features of other gases and potentially calibration errors on the order of the depth of the absorption lines ($\sim$1–3%). For simulated measurements such a large dependence of the retrieved column on the fitting window has not been found. The probably most important reason for the significant dependence of the retrieved CO column on the choice of the spectral fitting window is that residual calibration errors are more critical for the WFM-DOAS version 0.4 fitting window (2359–2370 nm) compared to the version 0.5 fitting window (2324–2335 nm). The version 0.4 fitting window is located at the long wavelength end of channel 8, i.e., at larger wavelength compared to the version 0.5 fitting window, where the nadir radiance is typically much smaller compared to the version 0.5 fitting window because of the decrease of the solar irradiance with increasing wavelength and because of significantly larger absorption of water vapor. Furthermore, also the sensitivity of the instrument is lower at

the end of channel 8 compared to the center of the channel (where the version 0.5 fitting window is located) because of the drop of the detector pixel quantum efficiency at longer wavelength. The retrieval of CO using the version 0.4 fitting window is also adversely affected by much stronger water absorption lines compared to the version 0.5 fitting window as water is a highly variable spectrally interfering gas and accurate fitting of the much smaller CO lines is more difficult. In addition, uncertainties in the water vapor spectroscopic line parameters result in less accurate CO columns in case of stronger interfering water lines.

In addition to the optimized fitting window a correction has been applied to reduce time dependent biases caused by the ice-issue (e.g., slit function change), to improve the retrieval for partially cloud covered scenes and to make the retrieval less sensitive to aerosol and albedo variability. The correction is based on the retrieved methane column obtained from the same fitting window from which the CO is
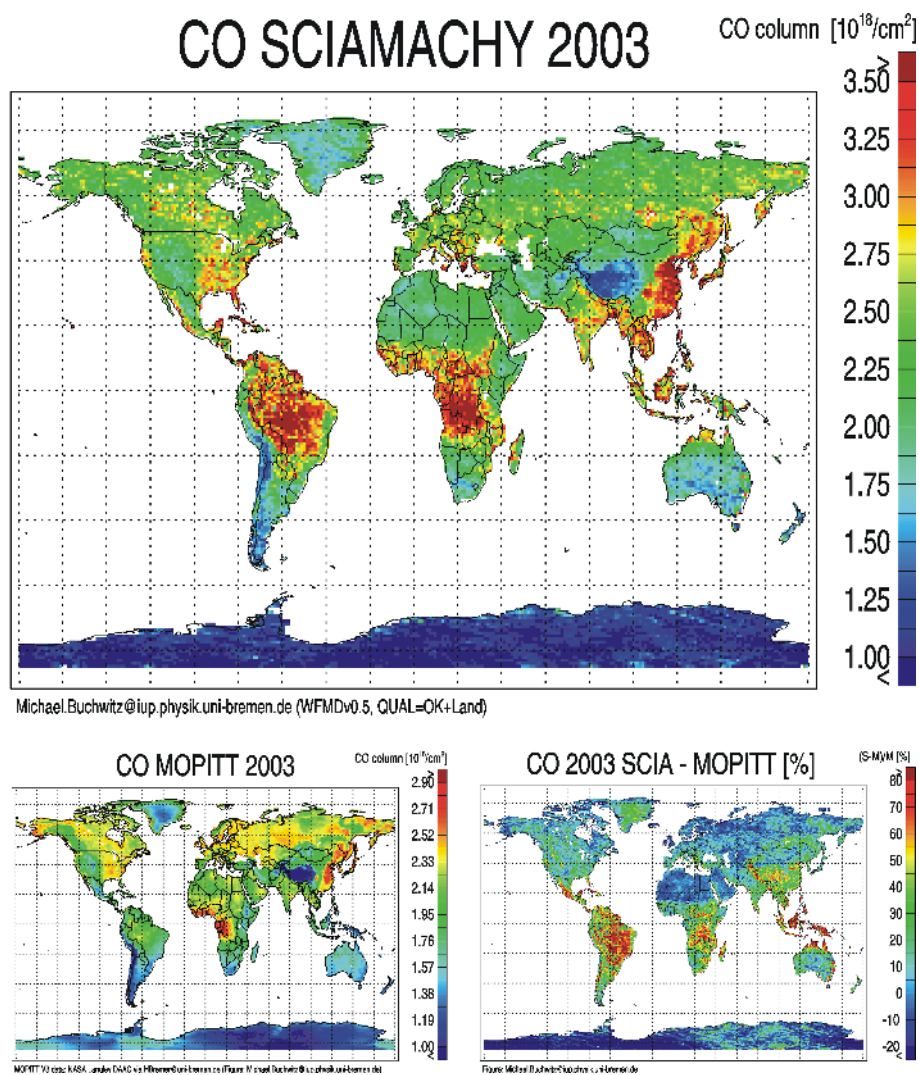
Fig. 3. Year 2003 average of SCIAMACHY/WFM-DOAS version 0.5 CO columns (top) compared to MOPITT operational CO columns (Lv2V3) over land (bottom left). Note that the scale is different because the SCIAMACHY CO columns are typically higher compared to MOPITT (on average by about 10%). The relative CO column differences (SCIAMACHY–MOPITT) are shown in the bottom right panel.

retrieved. A correction factor, defined as the ratio of an assumed (a-priori) methane column (given below) and the retrieved methane column, is applied to the retrieved CO column. The a-priori methane column is computed using a single (scene independent) methane profile taking into account the surface elevation of the corresponding ground pixel. The assumed methane column is 3.6×10^{19} molecules/cm^2 for a ground pixel with a surface elevation equal to sea level (corresponding to an assumed surface pressure of 1013 hPa). This approach makes use of the fact that the variability of the methane columns is low (few percent) compared to the variability of the CO columns.

Figure 1 illustrates this approach. It is shown that both the uncorrected CO and methane columns are correlated with the independently measured channel averaged relative optical throughput determined from ratios of solar spectra. The variation of the throughput is primarily due to the changing thickness of the ice layer on the channel 8 detector. The columns change because of the ice induced slit function changes. Figure 2 shows the typical response of the retrieved columns caused by a changing slit function. As can be seen the response is similar for both gases but not identical. The change of the weak absorber CO is typically larger than the change of the much stronger absorber methane. As a consequence our approach to correct the CO column using the retrieved methane column is not perfect. It will typically result in a correction in the right direction (i.e., towards higher CO columns) but the correction may not be large enough. This is most probably the reason why the corrected CO shown in Fig. 1 for the time period day 190 to day 310 still appears to

follows the throughput curve. We estimate the accuracy of this method to about 10–20%. In Gloudemans et al. (2005) a somewhat different approach is described to use the retrieved methane columns to correct the CO columns for ice-layer induced biases.

The WFM-DOAS v0.5 CO column data product contains for each measurement a quality flag to indicate a (potentially) successful measurement. To decide if a measurement is successful, a number of criteria have been defined based on the value of the root-mean-square of the fit residuum, the CO fit error, and the methane correction factor. The methane correction factor, for example, has to be close to 1.0 (within 20%) for a measurement to be classified as successful. Otherwise the disturbances due to clouds, aerosols, surface reflectivity, calibration issues, etc., are considered too large to be corrected for. Note that because of the correction procedure the quality flag does not depend on the cloud mask (i.e., the quality flag is independent of the pixel being classified as cloud contaminated or not). This is also a major difference to version 0.4 CO. Because of this the number of pixels being classified useful for version 0.5 is about ten times larger than for version 0.4.

3.2 Methane specific aspects

For methane we derive dry air column averaged mixing ratios XCH$_4$ by normalizing the retrieved methane column with the simultaneously observed airmass estimated by retrieving the column of a reference gas whose column is less variable than methane. Initially (for v0.4) we used oxygen (O$_2$) columns retrieved from the O$_2$ A band (760 nm) (Buchwitz et al., 2005a,b). Unfortunately, the sensitivity of the retrieved O$_2$ column with respect to, e.g. aerosol, is quite different compared to methane mainly because of the large spectral distance between the two fitting windows. For v0.41 XCH$_4$ (Buchwitz et al., 2005b) we use CO$_2$ retrieved from the 1.6 μm region (channel 6). The new v0.5 XCH$_4$ data product is derived in a similar way as the v0.41 data product, except that methane is retrieved from channel 6 (1629–1671 nm) instead of channel 8. There are two reasons why methane retrieval from channel 6 should give better results compared to channel 8: (i) channel 6 is not affected by an ice-layer, and (ii) the channel 6 methane absorption band is located close to the channel 6 CO$_2$ band thus improving the cancellation of errors when the ratio is computed. This approach has been introduced by Frankenberg et al. (2005c). For each ground pixel a quality flag is set using similar criteria as for CO (the criteria are: CH$_4$ and CO$_2$ column fit errors less than 10%; CH$_4$ and CO$_2$ columns within 20% of assumed (a-priori) column (3.6×10^{19}molecules/cm^2 for CH$_4$ and 8×10^{21}molecules/cm^2 for CO$_2$ for a ground pixel with an average surface elevation corresponding to sea level), SZA less than 88 deg, forward scan pixel (i.e., no fast back scan pixel because of four times larger ground pixel size). As for CO the quality flag is independent of the pixel being

classified as cloud contaminated or not. There is however one difference compared to CO: because of the high accuracy and precision requirements for methane and the reduced quality of measurements over water, only pixels over land are classified useful.

3.3 Carbon dioxide specific aspects

The SCIAMACHY/WFM-DOAS version 0.4 XCO$_2$ retrieval algorithm is described in detail in Buchwitz et al. (2005a) and Buchwitz et al. (2005b). The CO$_2$ columns are retrieved using a small spectral fitting window (1558–1594 nm) located in SCIAMACHY channel 6 which covers one absorption band of CO$_2$ and weak absorption features of water vapor. Similar as for methane, dry air column averaged mixing ratios XCO$_2$ are determined. The air columns used to normalize the CO$_2$ columns are obtained from the simultaneously measured oxygen (O$_2$) columns retrieved from the O$_2$ A-band (see also Houweling et al., 2005, for SCIAMACHY CO$_2$ retrieval and van Diedenhoven et al., 2005, for SCIAMACHY O$_2$ retrieval).

Because of the large spectral distance between the CO$_2$ band (1580 nm) and the O$_2$ band (760 nm) the sensitivity of the spectral nadir measurements with respect to aerosols, (partial) clouds, and surface reflectivity is quite different for CO$_2$ and O$_2$. This results in light path length related errors on the retrieved CO$_2$ and O$_2$ columns which do not perfectly cancel when the CO$_2$ to O$_2$ column ratio, i.e. XCO$_2$, is computed (Buchwitz et al., 2005a). We estimate the XCO$_2$ error to about a few percent with both random and systematic components (Buchwitz et al., 2005a,b).

Because of the high precision and accuracy requirements for XCO$_2$ the contamination by clouds needs to be minimized as much as possible. In order to identify cloud-contaminated ground pixels we currently use a threshold algorithm based on sub-pixel information provided by the SCIAMACHY Polarization Measurement Devices (PMDs) (details are given in Buchwitz et al., 2005a). In short, we use PMD1 which corresponds to the spectral region 320–380 nm located in the UV part of the spectrum. Strictly speaking, the algorithm detects enhanced backscatter in the UV. Enhanced UV backscatter mainly results from clouds but might also be due to high aerosol loading or high surface UV spectral reflectance (despite the low sensitivity of PMD1 for surface reflectivity changes compared to PMDs 2–7; note that PMD1 has been selected because of its low sensitivity to surface properties). As a result, ice or snow covered surfaces may wrongly be classified as cloud contaminated.

The main problem of WFM-DOAS version 0.4 as applied to Level 1 version 4 (Lv1v4) spectra is a systematically underestimation of the CO$_2$ columns and an overestimation of the O$_2$ columns (Buchwitz et al., 2005a,b). To compensate for this, the initially retrieved CO$_2$ and O$_2$ columns are scaled with constant factors (1.27 for CO$_2$ and 0.85 for O$_2$). The factors have been chosen such that the
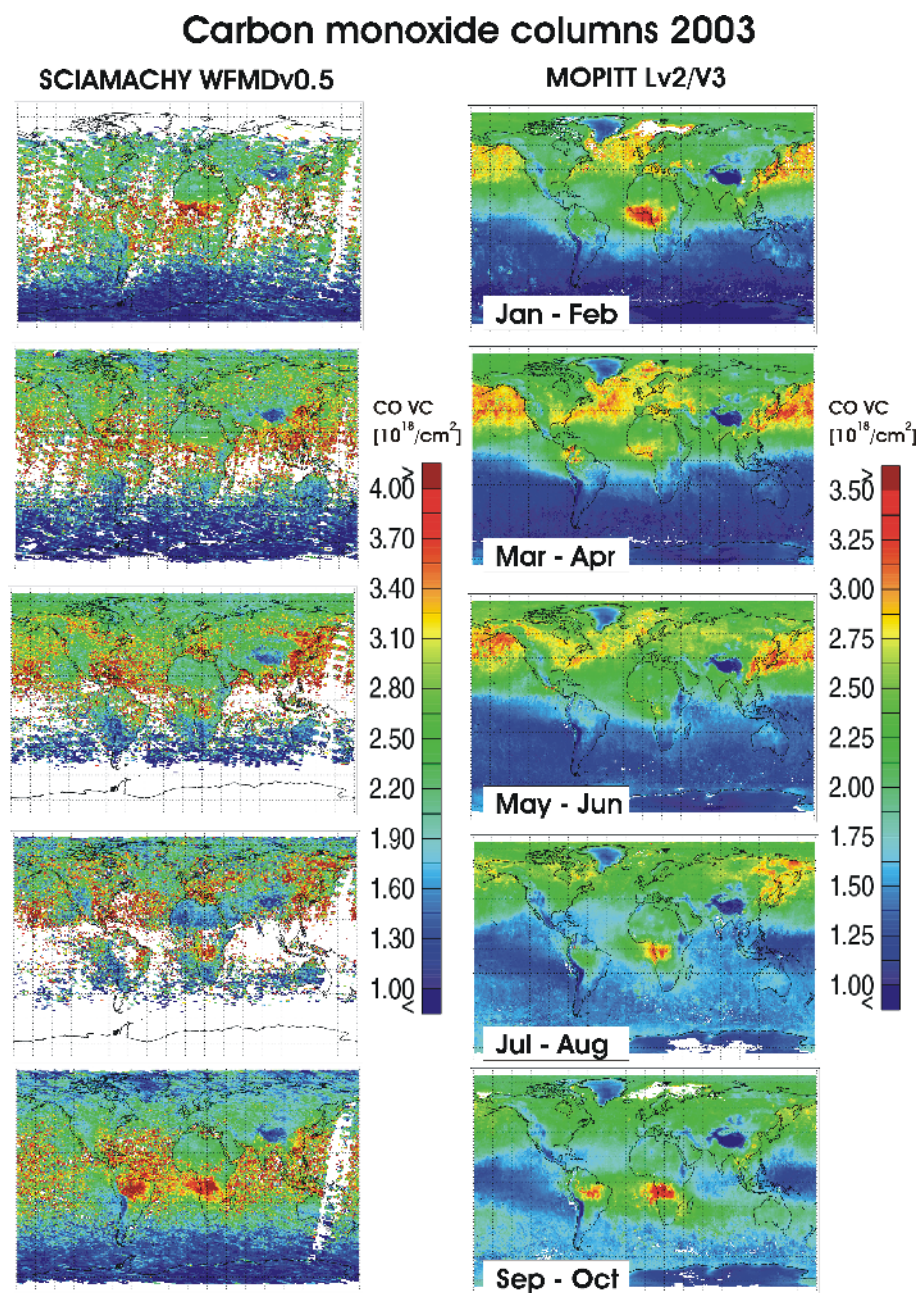
Carbon monoxide columns 2003

Fig. 4. Comparison of year 2003 bi-monthly averages of SCIAMACHY/WFM-DOAS version 0.5 CO (left) with MOPITT (right).

CO$_2$ and O$_2$ columns are close to their expected value of about 8×10^{21} molecules/cm^2 and 4.5×10^{24} molecules/cm^2, respectively, for a cloud-free scene with a surface elevation close to sea level. Despite (up)scaling of the XCO$_2$ it is shown in Dils et al. (2006) that version 0.4 XCO$_2$ is still a few percent too low compared to FTIR. Because WFMDv0.4 XCO$_2$ is scaled we focused in Buchwitz et al. (2005a) and Buchwitz et al. (2005b) on spatial and temporal XCO$_2$ variability and not on absolute values when comparing the SCIA-MACHY XCO$_2$ with reference data, e.g., by comparing XCO$_2$ anomalies.

Here we present first results of WFM-DOAS applied to SCIAMACHY Lv1v5 spectra which have an improved calibration compared to the previous Lv1v4 spectra from which the initial v0.4 XCO$_2$ year 2003 data set has been retrieved (for details concerning the calibration concept see Lichtenberg et al. (2005)). We will show that significantly improved CO$_2$ spectral fits are obtained and that the CO$_2$ columns retrieved from Lv1v5 spectra are higher by about 20%. This eliminates the need for a (large) CO$_2$ scaling factor.
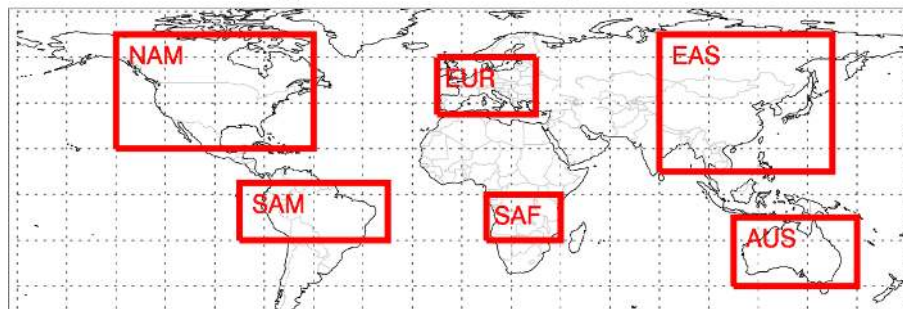
Regions for CO comparison

Fig. 5. Regions selected for a comparison of the SCIAMACHY and MOPITT CO columns: North America (NAM), Europe (EUR), Eastern Asia (EAS), South America (SAM), South Africa (SAF), and Australia (AUS).

4 Trace gas results

We have processed all available SCIAMACHY Lv1v4 spectra of the year 2003 by WFM-DOAS (details concerning the processed orbits are given in Buchwitz et al., 2005b). The WFM-DOAS version 0.5 year 2003 data set will be discussed in the following for CO (Sect. 4.1) and XCH$_4$ (Sect. 4.2). For XCO$_2$ we have additionally processed all available Lv1v5 spectra of the years 2003 to 2005 covering the area around Park Falls, Wisconsin, USA. These data will be presented in Sect. 4.3.

4.1 Carbon monoxide (CO)

To assess the quality of the new SCIAMACHY/WFM-DOAS version 0.5 CO column data product we have compared it with operational version 3 CO columns from MOPITT/EOS-Terra (Deeter et al., 2003). Figure 3 shows a comparison of year 2003 averages of both independent data sets. Figure 3 has been obtained by directly averaging the CO column data products of both sensors without considering differences in spatial and temporal sampling, horizontal resolution, and altitude sensitivity (a comparison of spatially co-located measurements is given below). The comparison is restricted to measurements over land because of the reduced quality of the SCIAMACHY near-infrared/nadir measurements over oceans caused by the low albedo of water in the near-infrared which results in low signals and low signal-to-noise ratios. Overall, both data sets agree reasonably well but there are also significant differences. On average, the SCIAMACHY data are higher compared to MO-PITT by 0.20×10^{18} molecules/cm^2 (10.5%) but regionally the differences can be much larger (up to 80%), e.g. over South America. The standard deviation of the difference is 0.48×10^{18} molecules/cm^2 (27.9%).

Figure 4 enables a comparison between the two data sets for bi-monthly averages including the SCIAMACHY measurements over water. Especially over water the differences to MOPITT are large (see above). The time dependence of CO over central and south Africa and South America

mainly originating from biomass burning (see e.g. van der Werf et al., 2004) is qualitatively in good agreement showing maximum values north of the equator in Africa in January/February and south of the equator in Africa and South America in September/October. The inter-hemispheric difference is clearly visible in the SCIAMACHY data. A comparison with MOPITT based on monthly means (not shown here) using the measurements over land and water shows that the inter-hemispheric CO difference as measured by both sensors is in good agreement (mean difference within 3%, correlation coefficient r=0.9).

For a more quantitative assessment we have performed a detailed comparison for six regions which are shown in Fig. 5. Figure 6 shows daily averages of co-located SCIAMACHY and MOPITT CO columns for each region. Typically the SCIAMACHY columns are higher than MOPITT. For the northern hemispheric regions the average difference is in the range 10% (Europe) to 20% (north America, eastern Asia). Larger differences are found over southern Africa (30%) and South America (45%). The time dependence of CO over both regions is however in good agreement (the correlation of the daily averages is 0.67 and 0.8) but there appears to be a constant offset relative to MOPITT of nearly 1.0×10^{18} molecules/cm^2.

Figure 7 shows a similar comparison as presented in Fig. 6 but restricted to cloud free SCIAMACHY pixels. Because the cloud contaminated pixels have been removed from the comparison Fig. 7 contains significantly less data (less days) for comparison. Nevertheless, the comparison with MOPITT gives nearly identical results as Fig. 6 where the cloud contaminated pixels were included. From this one may conclude that the difference between SCIAMACHY and MOPITT is not due to clouds or the way the CO is corrected for partial cloud cover using the simultaneously measured methane.

According to Figs. 6 and 7 the SCIAMACHY WFM-DOAS version 0.5 CO is typically higher compared to MOPITT. Dils et al. (2006) have performed a comparison of FTIR columnar CO at 11 ground stations with WFM-DOAS version 0.5 CO, SCIAMACHY CO retrieved using
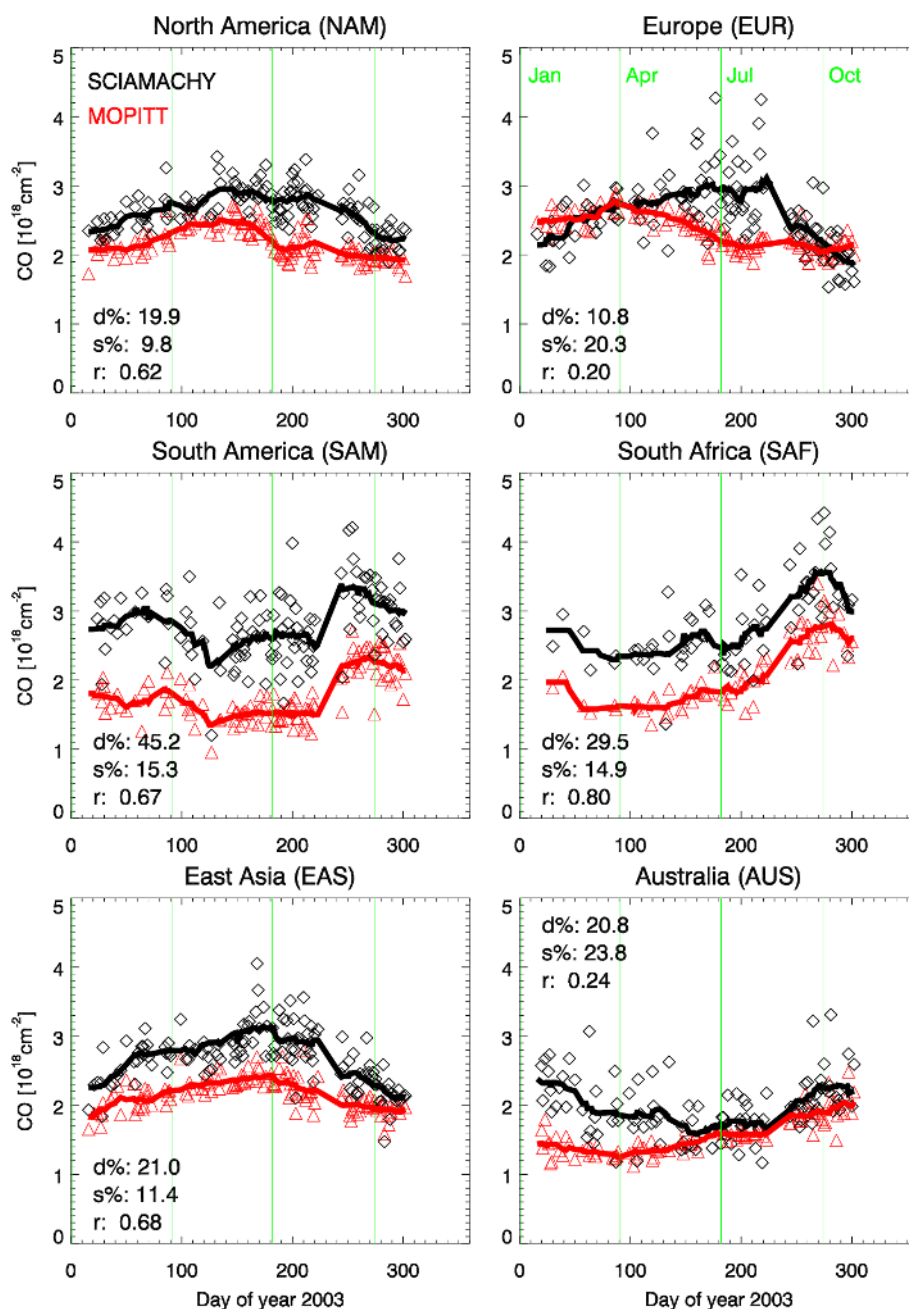
Fig. 6. Comparison of the SCIAMACHY (black) and MOPITT (red) CO columns for the six regions shown in Fig. 5. For the comparison both the daily SCIAMACHY and MOPITT columns have been gridded on a 0.5°×0.5° latitude/longitude grid. The symbols show the daily average of all coincident grid points. For SCIAMACHY all measurement have been averaged for which the WFM-DOAS v0.5 quality flag indicates a (potentially) successful measurement. The solid lines represent a 30 days running average. For each region the following numbers have been computed based on the (not smoothed) daily averages: *d%* is the mean difference SCIA–MOPITT in percent, *s%* denotes the standard deviation of the difference in percent, and *r* is the correlation coefficient.

the SRON IMLM algorithm and the University of Heidelberg IMAP-DOAS algorithm, and MOPITT. This comparison shows that depending on the location of the ground station and the time of the year SCIAMACHY WFM-DOAS version 0.5 CO may be somewhat higher or lower compared to FTIR

or MOPITT. They compared more than 20 000 WFM-DOAS version 0.5 CO column measurements co-located with FTIR and found an average deviation below 1% with a standard deviation of 25% relative to FTIR (more precisely relative to a polynomial fit through the FTIR data) and a correlation coef-
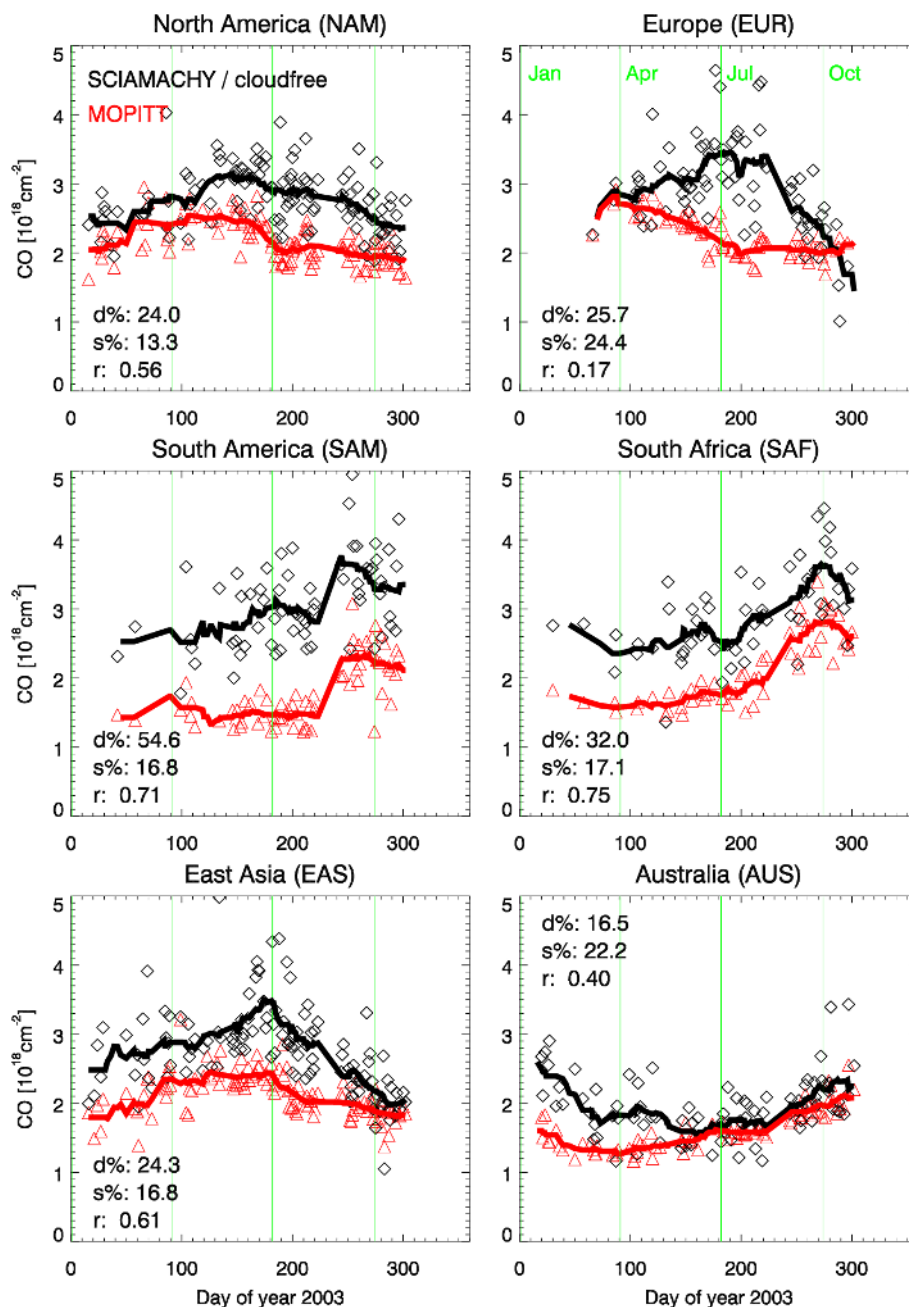
Fig. 7. As Fig. 6 but only for SCIAMACHY cloud free pixels.

ficient of 0.86 for monthly mean values. For northern hemispheric stations they found that the SCIAMACHY/WFM-DOAS CO columns are typically lower compared to FTIR by up to –8.3% (for Ny Alesund, Spitsbergen). For the southern hemispheric stations (Wollongong, Lauder, Arrival Heights) they found typically an overestimation up to 22.6% (for Lauder). Unfortunately, none of the stations is located in the major CO source regions of South America and central/southern Africa. It is also shown in Dils et al. (2006) that significant differences exist between the three independent

algorithms that have been used to retrieve CO from SCIA-MACHY.

What could be the reason for the differences between SCIAMACHY and MOPITT especially over Amazonia (SAM region) where the differences are largest? One reason might be the different vertical weighting of both sensors with SCIAMACHY having higher sensitivity for boundary layer CO. In order to address this issue it is important to also use model simulations and additional measurements (e.g., in-situ CO measurements). We have not yet
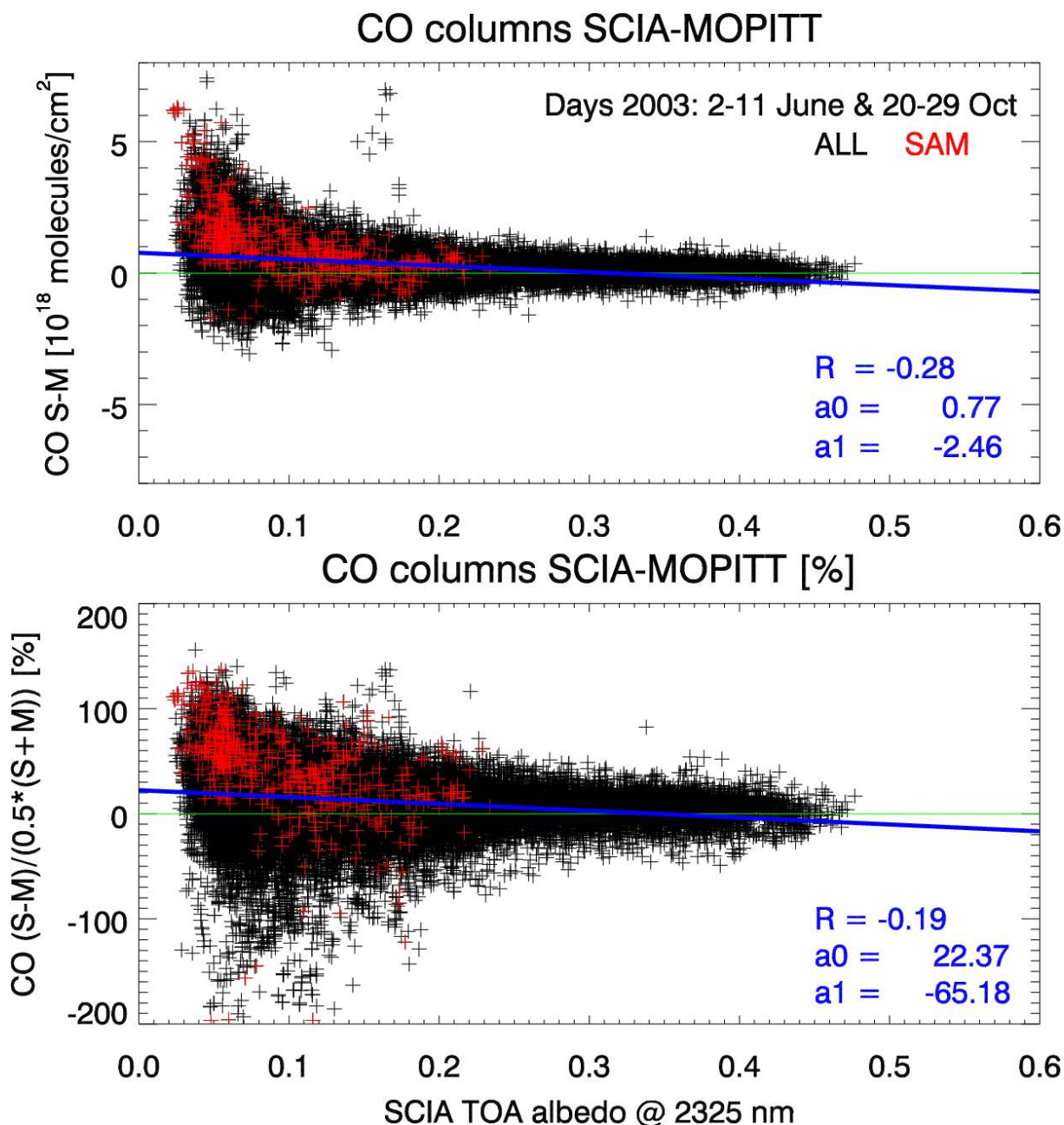
Fig. 8. Difference of CO columns of SCIAMACHY and MOPITT as a function of top-of-atmosphere (TOA) albedo at 2325 nm as measured by SCIAMACHY. The top panel shows the absolute difference of the CO columns, the bottom panel shows the percentage difference. The comparison is based on daily gridded data using only cloud free SCIAMACHY measurements over land with good quality as indicated by the WFM-DOAS CO product quality flag. The black crosses correspond to all measurements, the red crosses to the subset located in the SAM region (South America). The blue lines show the linear fit of the difference (of all measurements) as a function of TOA albedo. R is the correlation coefficient and a0 (y-axis intersection for x=0) and a1 (slope) are the two parameters of the linear fit.

performed a comparison with model simulations. de Laat et al. (2006) discuss a comparison of regionally averaged monthly mean CO columns retrieved from SCIAMACHY using the SRON IMLM algorithm in comparison with model simulations for the time period September 2003 to August 2004 (interestingly de Laat et al. (2006) note that they se-

lected this time period because of insufficient quality of the spectra prior to September 2003, i.e., for large parts of the time period analyzed in this paper). For several regions they found good agreement with the model simulations. For South America however (roughly corresponding to the SAM region shown in Fig. 6) they found large disagreement be-
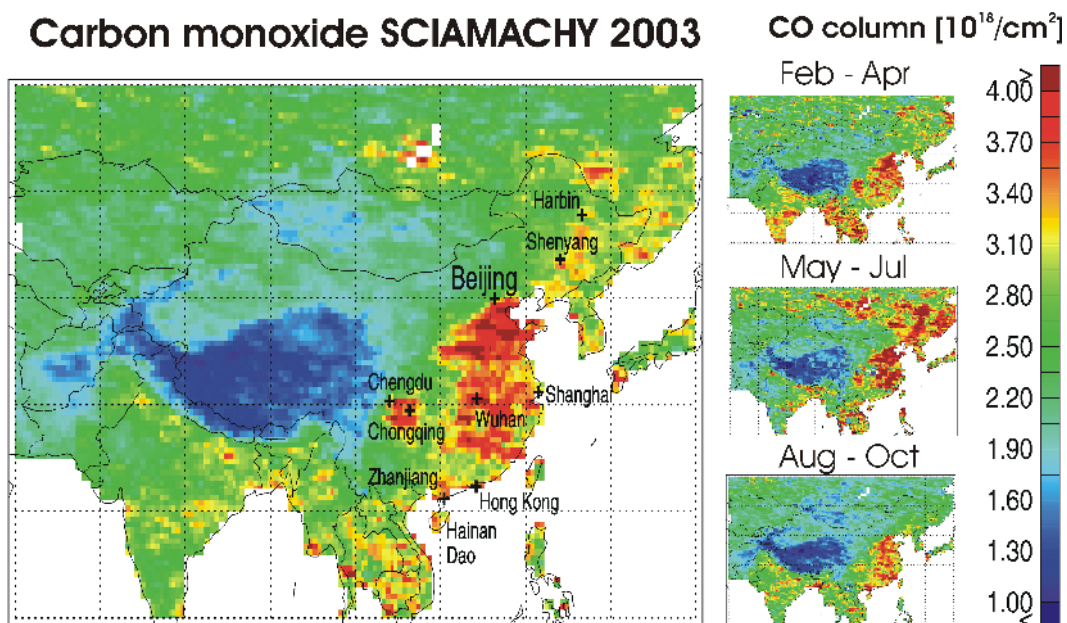
Fig. 9. Year 2003 SCIAMACHY/WFM-DOAS version 0.5 CO over China including seasonal variation (right). All CO measurements over land are shown for which the WFM-DOAS quality flag indicates a successful measurement.

tween SCIAMACHY/IMLM CO and the model simulations (large scatter of the SCIAMACHY measurements of up to or even much larger than 50%). For southern Africa (i.e., south of / southern part of SAF region shown in Fig. 6) the SCIAMACHY/IMLM CO shows also large differences (about 50% higher values of SCIAMACHY compared to the model for October 2003 and systematically higher values of SCIAMACHY (about 30–50%) for February to July 2004). They conclude that differences of the monthly means are typically below 13% except for regions with large instrument-noise errors (i.e., low albedo regions and/or regions with only a few data points due to, e.g., persistent cloud cover) such as their South America region.

Figure 4 shows that the SCIAMACHY WFM-DOAS version 0.5 CO over the oceans especially in the tropics/subtropics is higher than MOPITT suggesting a high bias of SCIAMACHY potentially related to the low albedo of water around 2.3 both random and systematic μm (~1%). Therefore, it could be that also the SCIAMACHY CO measurements over land (e.g., SAM and SAF regions shown in Fig. 6) are to a certain extent biased high due to the relatively low surface albedo of vegetation of about 0.1 (see e.g., ASTER Spectral Library, http://speclib.jpl.nans.gov). If there is an albedo dependent bias of the SCIAMACHY CO measurements over these land regions then the bias will be significantly lower than the possible bias over water because of the much higher albedo of vegetation compared to the extremely low albedo of water. In order to investigate this we have computed top of atmosphere (TOA) albedos (at 2325 nm) from a number of days of cloud free SCIAMACHY

measurements in June and October 2003. The TOA albedo is defined as $R\pi/I/\cos(SZA)$, where R is the nadir radiance, I is the solar irradiance and SZA is the solar zenith angle. Because 2325 nm is a relatively transparent wavelength for cloud free measurements, the TOA albedo is a good proxy of the surface albedo. Figure 8 shows the difference between SCIAMACHY and MOPITT CO as a function of SCIAMACHY measured TOA albedo. As can be seen, there is a slight dependence of the difference on albedo with SCIAMACHY CO on average biased high for low albedos. There is however large scatter (larger than the bias) and the correlation is low (less than 0.3). Figure 8 suggests that on average there appears to be a high bias of SCIAMACHY CO for low albedo scenes (albedo less than about 0.1) of up to about 20% or 0.8×10^{18} molecules/cm^2.

Finally we present some regional results focusing on China. Air pollution resulting from large-scale fossil fuel combustion and fossil fuel related activities has become a problem with increasing importance, especially for countries with an increasing energy demand and inherent fuel consumption such as China. The quantification of concentrations near the sources and the subsequent transport of pollutants is important, for example, for monitoring and forecasting of air pollution. The left panel of Fig. 9 shows yearly averaged vertical columns of CO over China. Clearly visible are large regions of elevated CO (shown in red) indicating CO source regions. Elevated CO is present over a large area south of Beijing, in the Red Basin around Chengdu/Chongqing, around Shenyang, and over Hainan Dao and Zhanjiang. The elevated CO detected with SCIAMACHY clearly correlates with ma-
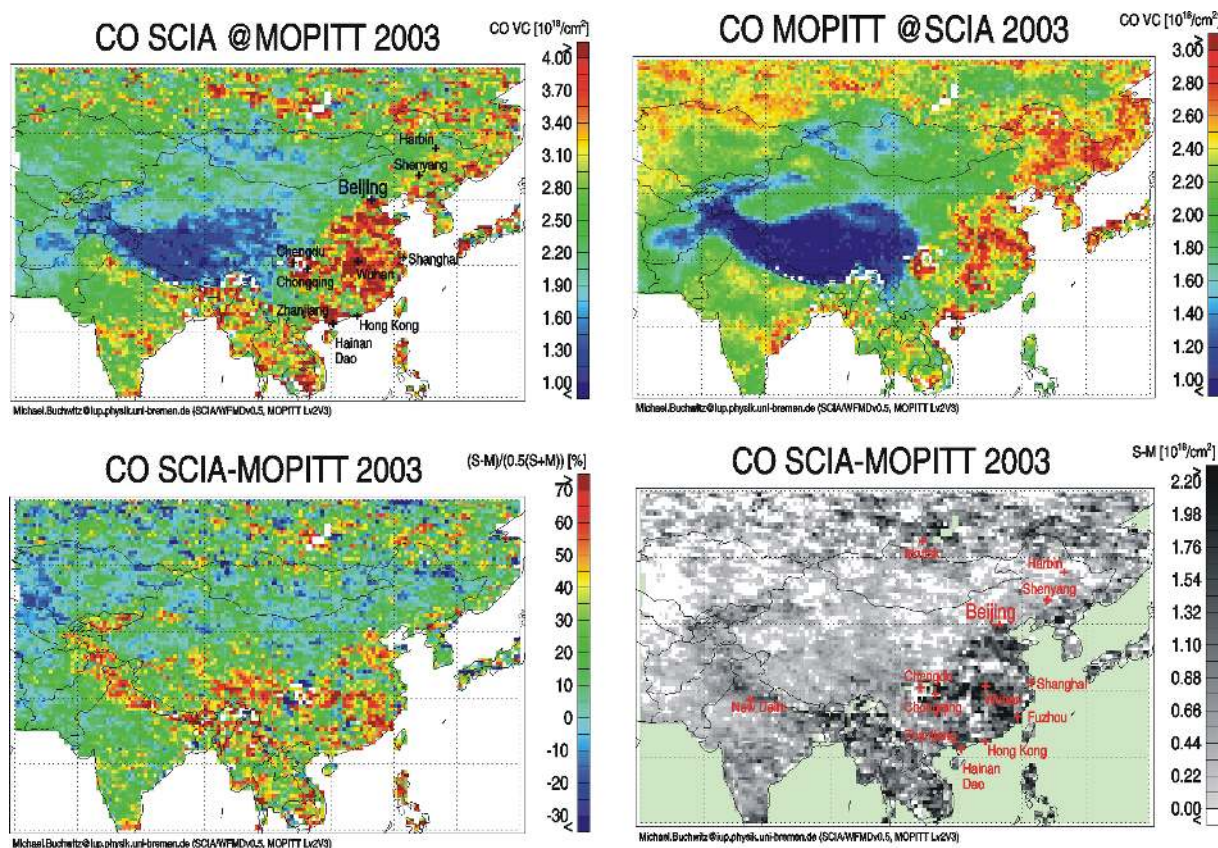
Fig. 10. Comparison of SCIAMACHY CO over China with CO from MOPITT. Top left panel: As Fig. 9 but generated by averaging only those SCIAMACHY measurements where also a coincident MOPITT measurements exists. Top right panel: Year 2003 average of all MOPITT measurements where also a coincident SCIAMACHY measurements exists. Bottom left panel: Relative difference between SCIAMACHY and MOPITT (SCIAMACHY – MOPITT, i.e., positive values indicate higher values of SCIAMACHY). Bottom right panel: Absolute difference between SCIAMACHY and MOPITT (SCIAMACHY – MOPITT).

jor cities, for example Chongqing and surroundings where more than 30 million people are living. The three panels on the right hand side of Fig. 9 show tri-monthly averaged CO columns. The largest CO columns are observed in the May to July 2003 average over large parts of eastern China and around Chongqing/Chengdu. High columns are also observed over these regions during other times of the year, especially around Beijing during February to April.

As SCIAMACHY's near-infrared measurements have higher sensitivity to boundary layer CO compared to the CO retrieved from the thermal infrared measurements of MO-PITT one would expect that the differences to MOPITT are largest near surface source areas of CO. Figure 10 shows a comparison of the CO columns retrieved from both sensors over the same area also shown in Fig. 9. For the comparison the daily data of both sensors have been gridded and only those grid boxes have been used for the comparison where measurements exist for both sensors ("coincident measurements"). Figure 10 shows yearly averages of the coincident CO columns of both sensors as well as the relative and the absolute difference. The differences are relatively

small (less than about 0.4×10^{18} molecules/cm^2) outside major source regions (e.g., Himalaya, large parts of northern China) but significantly larger over major source regions (e.g., around Beijing, Wuhan, Fuzhou, Zhanjian, around Lake Baikal (north-east of Irkutusk), the Ganges plain (e.g., around New Delhi), along the Brahmaputra river, and over large parts of south-east Asia (e.g., parts of Burma, Thailand, and southern Vietnam around Ho Chi Minh City)). Qualitatively the higher values of SCIAMACHY observed over surface source regions of CO compared to MOPITT are consistent with what one would expect from a sensor with higher sensitivity for boundary layer CO.

4.2 Methane (CH$_4$)

Figure 11 shows a comparison of the new SCIAMACHY/WFM-DOAS version 0.5 XCH$_4$ data product derived from channel 6 with independent TM5 model simulations performed at the EC Joint Research Centre (JRC), Ispra, Italy (Bergamaschi et al., 2000, 2005a). The TM5 model is a two-way nested atmospheric zoom
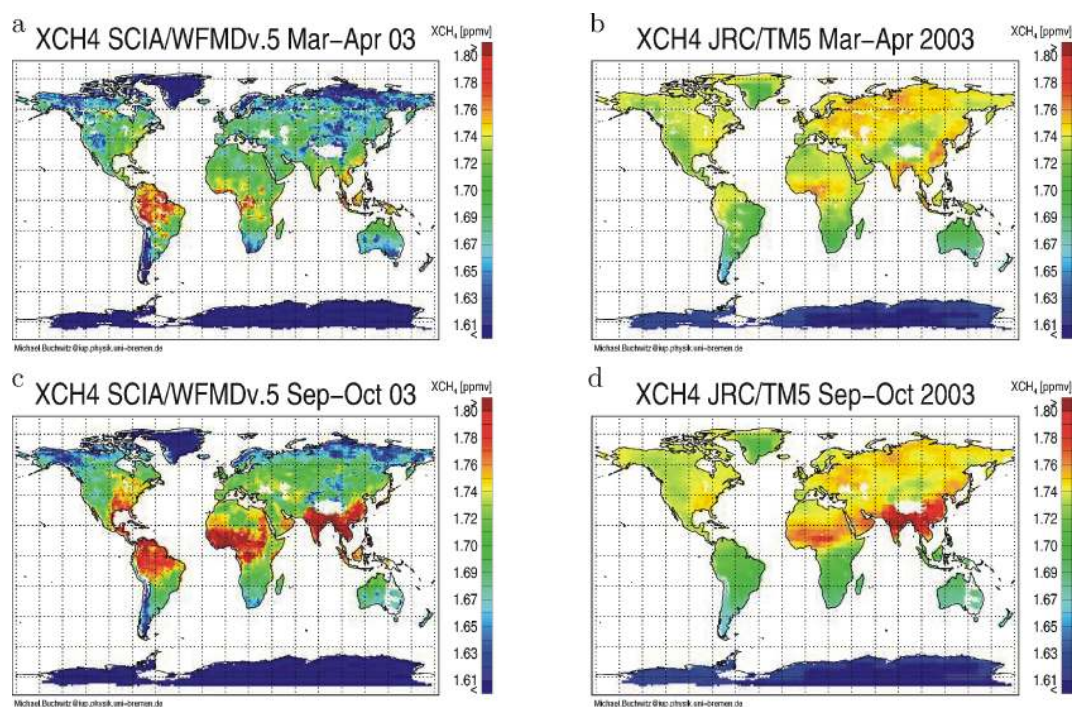
Fig. 11. Comparison of bi-monthly year 2003 averages of SCIAMACHY/WFM-DOAS version 0.5 methane (left) with TM5 model simulations (right).

model (Krol et al., 2005). It allows to define zoom regions (e.g. over Europe) which are run at higher spatial resolution (1×1 degrees), embedded into the global domain, run at a resolution of 6×4 degrees. We employ the tropospheric standard version of TM5 with 25 vertical layers. TM5 is an off-line model and uses analyzed meteorological fields from the ECMWF weather forecast model to describe advection and vertical mixing by cumulus convection and turbulent diffusion. Methane (a priori) emissions are as described by Bergamaschi et al. (2005a) and shortly summarized here: Anthropogenic emissions of domestic ruminants, fossil fuel production, waste treatment, biofuel, and minor sources are based on EDGAR 3.2 for year 1995 (Olivier and Berdowski, 2001), emissions from rice paddies are from Matthews et al. (1991) and biomass burning emissions from Houweling et al. (1999); natural emissions from wetlands are from Walter et al. (2001); emissions from wild animals and termites, as well as CH₄ uptake by soils are from the GISS data base (Fung et al., 1991), and emissions from the ocean are from Houweling et al. (1999). Chemical destruction of CH₄ by OH radicals is simulated using pre-calculated OH fields based on CBM-4 chemistry and optimized with methyl chloroform. For the stratosphere also the reaction of CH₄ with Cl and O(^{1}D) radicals are considered. The TM5 simulations are currently being refined, e.g. by implementing a multiple zoom mode (Bergamaschi et al., 2005b) and optimization versus highly accurate surface measurements Bergamaschi

et al. (2006)[1].

For this study we used the same TM5 data set as used for comparison with our previous methane v0.4x products (Buchwitz et al., 2005b).

Figure 11 shows a comparison of bi-monthly averages. The SCIAMACHY measurements are somewhat lower than TM5 XCH₄, especially at high latitudes. For the tropical region Fig. 11 is consistent with the findings of Frankenberg et al. (2005c) who also analyzed differences of SCIAMACHY data and model simulations (but for the time period August to November 2003) and found significantly higher methane values compared to model simulations over large parts of the tropics suggesting significantly greater tropical emissions than currently in the emission inventories. What exactly causes these high methane values still needs to be assessed (see, e.g., Bergamaschi et al., 2006[1]) but it has to be pointed out that the magnitude of the large tropical methane source is consistent with the recent discovery of methane emissions from plants (Keppler et al., 2006), with large emissions mainly in the tropical region. Frankenberg et al. (2005c) used a different retrieval algorithm (IMAP-DOAS) and compared

---

[1]Bergamaschi, P., Frankenberg, C., Meirink, J. F., Krol, M., Dentener, F., Wagner, T., Platt, U., Kaplan, J. O., Körner, S., Heimann, M., Dlugokencky, E. J., and Goede, A.: Satellite chartography of atmospheric methane from SCIAMACHY onboard EN-VISAT: (II) Evaluation based on inverse model simulations, J. Geophys. Res., submitted, 2006.
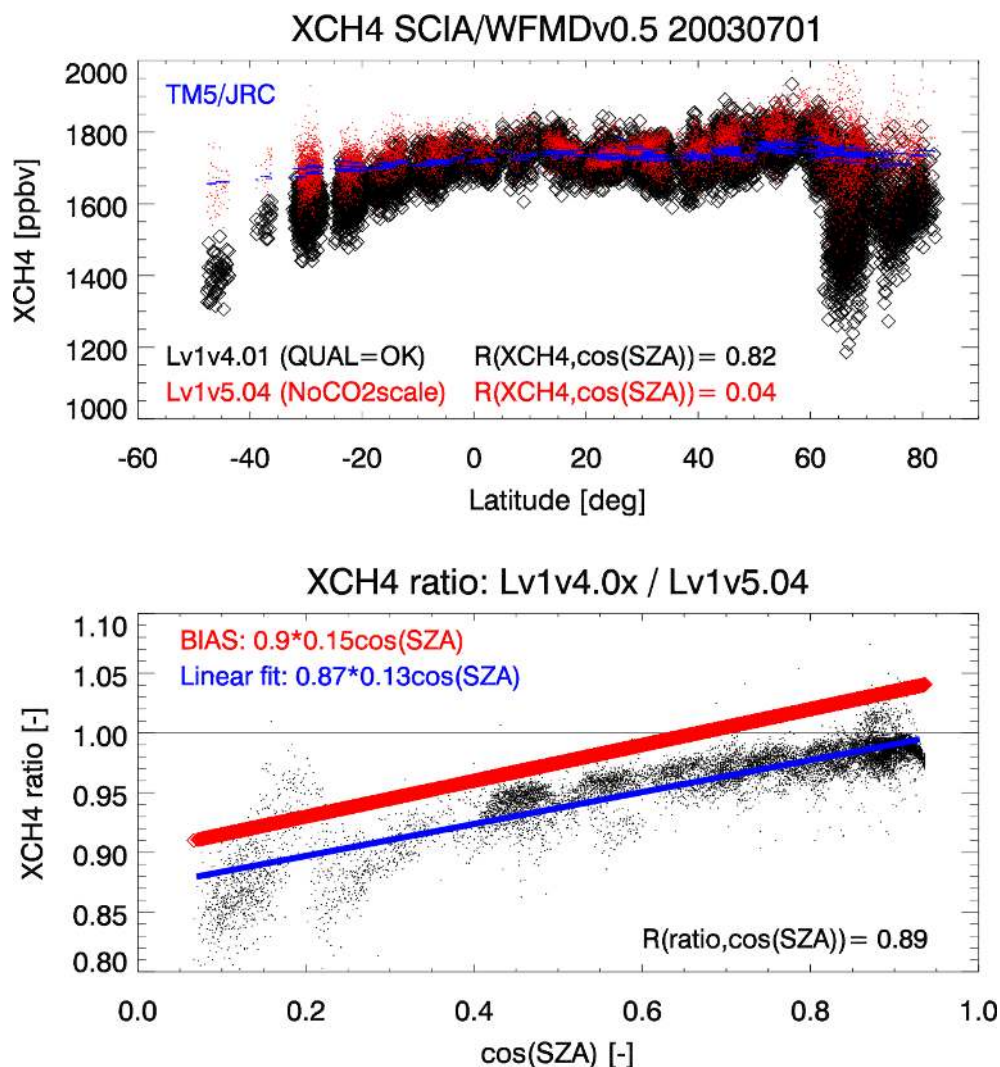
Fig. 12. Comparison of SCIAMACHY methane with TM5 model simulations for 1 July 2003. The top panel shows WFM-DOAS v0.5 methane (black symbols) for all ground pixels, including measurements over water. The corresponding TM5 model values are shown in blue. The WFM-DOAS v0.5 methane is based on SCIAMACHY Lv1v4 spectra. As can be seen, the SCIAMACHY v0.5 methane differs from the TM5 model simulations especially at high latitudes where the solar zenith angle is large. The red points show (preliminary) SCIAMACHY methane retrieved from Lv1v5 spectra which does not show low values at high latitudes. The bottom panel shows the ratio the SCIAMACHY methane derived from version 4 and 5 spectra as a function of the cosine of the solar zenith angle. BIAS is the solar zenith angle dependent bias of the SCIAMACHY v0.5 methane obtained from a comparison with ground based FTIR measurements at various stations as a function of time during 2003 (Dils et al., 2006). The slope of the red BIAS line is in good agreement with the linear fit of the ratio of the methane column versus cosine of solar zenith angle (blue line) indicating that the v0.5 methane bias is due to a calibration problem of the Lv1v4 spectra which has been solved for Lv1v5.

with a different model (TM3 model of KNMI). Figure 11 confirms these important findings and shows that they neither depend on the details of the retrieval method nor on the model used for comparison (the TM3/KNMI model used by Frankenberg et al. (2005c) is however very similar to the TM5/JRC model used here).

Figure 11 shows that especially at high latitudes the observed XCH$_4$ is significantly lower than the model XCH$_4$. When comparing time series of the SCIAMACHY mea-

surements with the ground based FTIR measurements at several stations (Dils et al., 2006) it has been found that the difference to FTIR is clearly correlated with the solar zenith angle (SZA) at the time of the measurement. We found that the SZA dependent bias is approximately given by BIAS=0.9+0.15cos(SZA), i.e., dividing the retrieved methane columns by BIAS provides a good first order correction. Figure 12 shows a comparison of one day of SCIAMACHY methane measurements compared to TM5.
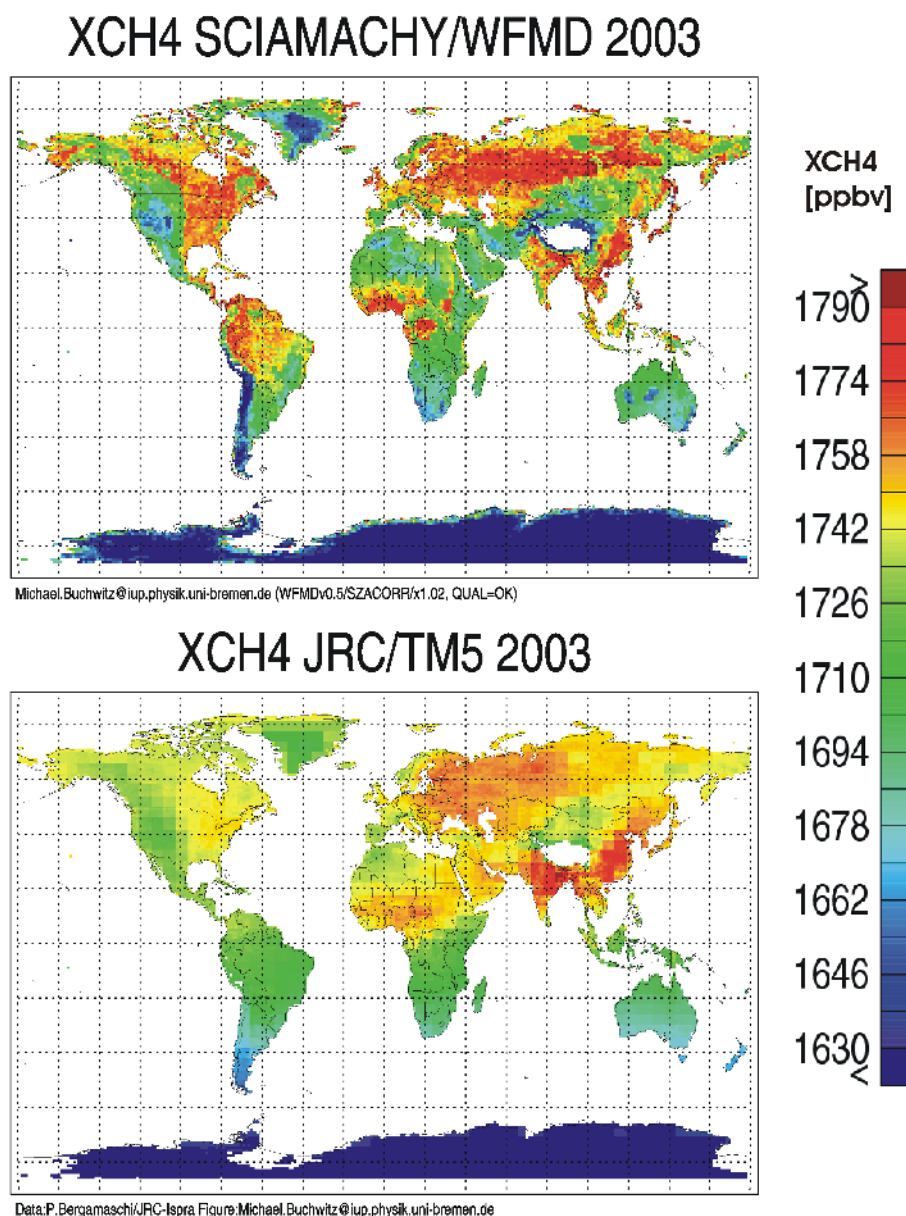
XCH4 SCIAMACHY/WFMD 2003

Michael.Buchwitz@iup.physik.uni-bremen.de (WFMDv0.5/SZACORR/x1.02, QUAL=OK)

XCH4 JRC/TM5 2003

Data:P.Bergamaschi/JRC-Ispra Figure:Michael.Buchwitz@iup.physik.uni-bremen.de

XCH4 [ppbv]

1790
1774
1758
1742
1726
1710
1694
1678
1662
1646
1630

Fig. 13. Comparison of SCIAMACHY/WFM-DOAS version 0.5 methane (top) with TM5 model simulations (bottom) for the year 2003. The SCIAMACHY map has been generated by averaging all measurements for which the WFM-DOAS quality flag indicates a successful measurement. The SCIAMACHY measurements are SZA bias corrected and scaled with 1.02.

For this day methane has been retrieved from two different versions of the SCIAMACHY spectra, namely Lv1v4 which has been used to generate the year 2003 data set discussed here, and Lv1v5 with improved calibration (e.g., much better dark signal calibration). Figure 12 shows that the solar zenith angle dependent bias is due to a calibration problem of the Lv1v4 spectra that has been solved for Lv1v5. We have not yet reprocessed all data using the improved calibration. The WFMDv0.5 methane data set we present here has been derived from Lv1v4 spectra. We use the SZA bias correction as described above. This data set is the one that has been compared with ground based FTIR measurements (Dils et al., 2006) with and without SZA bias correction and also with two other SCIAMACHY methane data products from two other groups retrieved using somewhat different approaches (Frankenberg et al., 2005c; Gloudemans et al., 2005). For the comparison between SCIAMACHY and TM5 shown in this paper the SCIAMACHY averaging kernels (which are close to but not exactly equal to 1.0) have not been considered and the SCIAMACHY methane is not corrected for CO$_2$ variability using, e.g., model simulations.
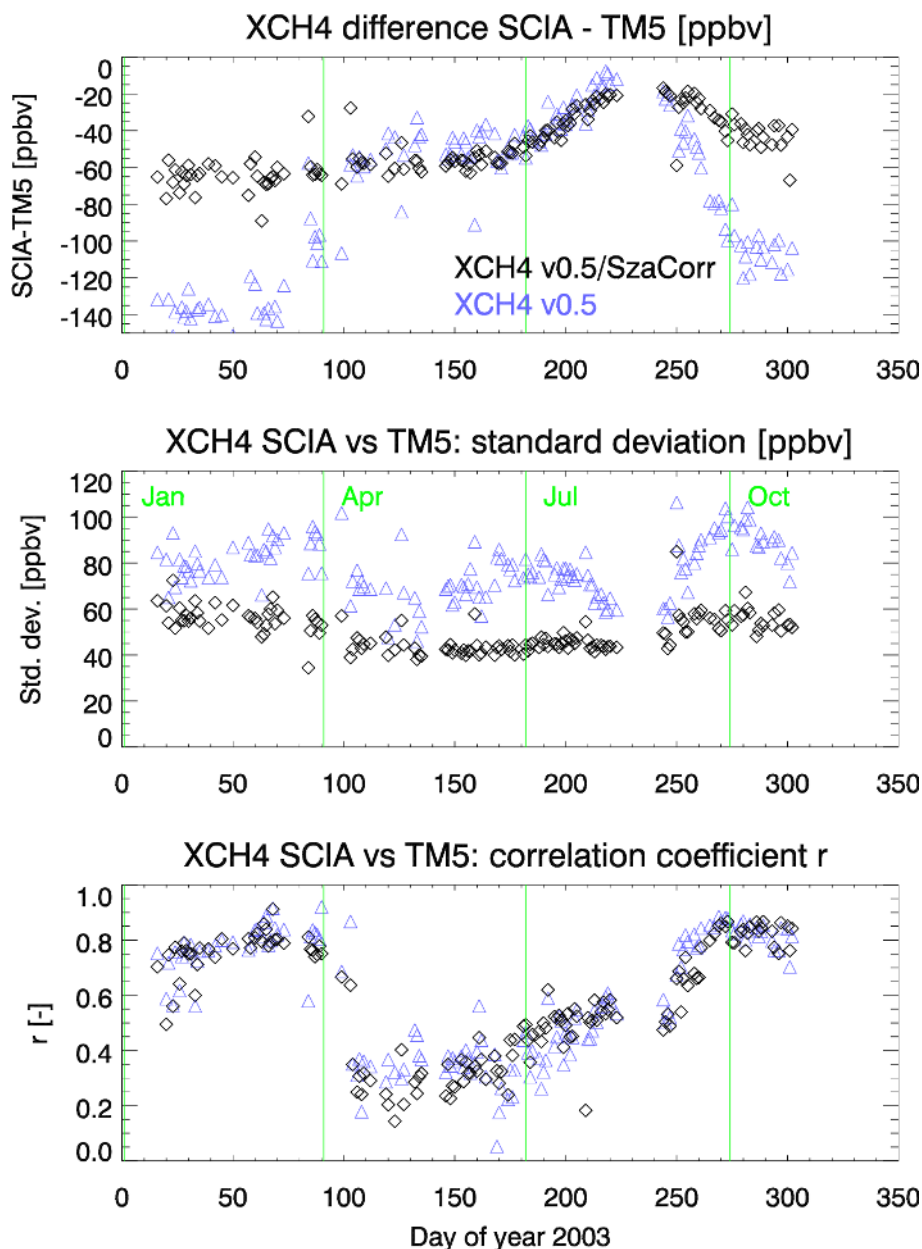
Fig. 14. Comparison of SCIAMACHY WFM-DOAS v0.5 methane with TM5 model simulations. The top panel shows the difference SCIA–TM5 (in ppbv) of the daily data during 2003. The black symbols correspond to the SZA corrected SCIAMACHY data and the blue symbols to the uncorrected data. The middle panel shows the standard deviation of the difference, and the bottom panel the linear correlation coefficient. The correlation is lower during the mid of the year not because of a change of the quality of the retrieval but due to the reduced number of measurements in the southern hemisphere (large solar zenith angles / polar night in Antarctica).

Figure 13 shows a comparison of SZA bias corrected SCIAMACHY methane with TM5. The SCIAMACHY methane has been scaled with 1.02 to enable a comparison with TM5 on the same ppbv scale. The approximately 2% low bias of version 0.5 methane (prior to scaling with 1.02) is consistent with the findings of the FTIR comparison (Dils et al., 2006).

Figure 14 shows a quantitative comparison of SCIA-MACHY methane with TM5. It is shown that the SZA bias correction results in typically much better agreement with TM5 compared to the uncorrected methane. The standard deviation of the difference of the daily data is typically 50 ppbv (∼3%) for the SZA bias corrected data.

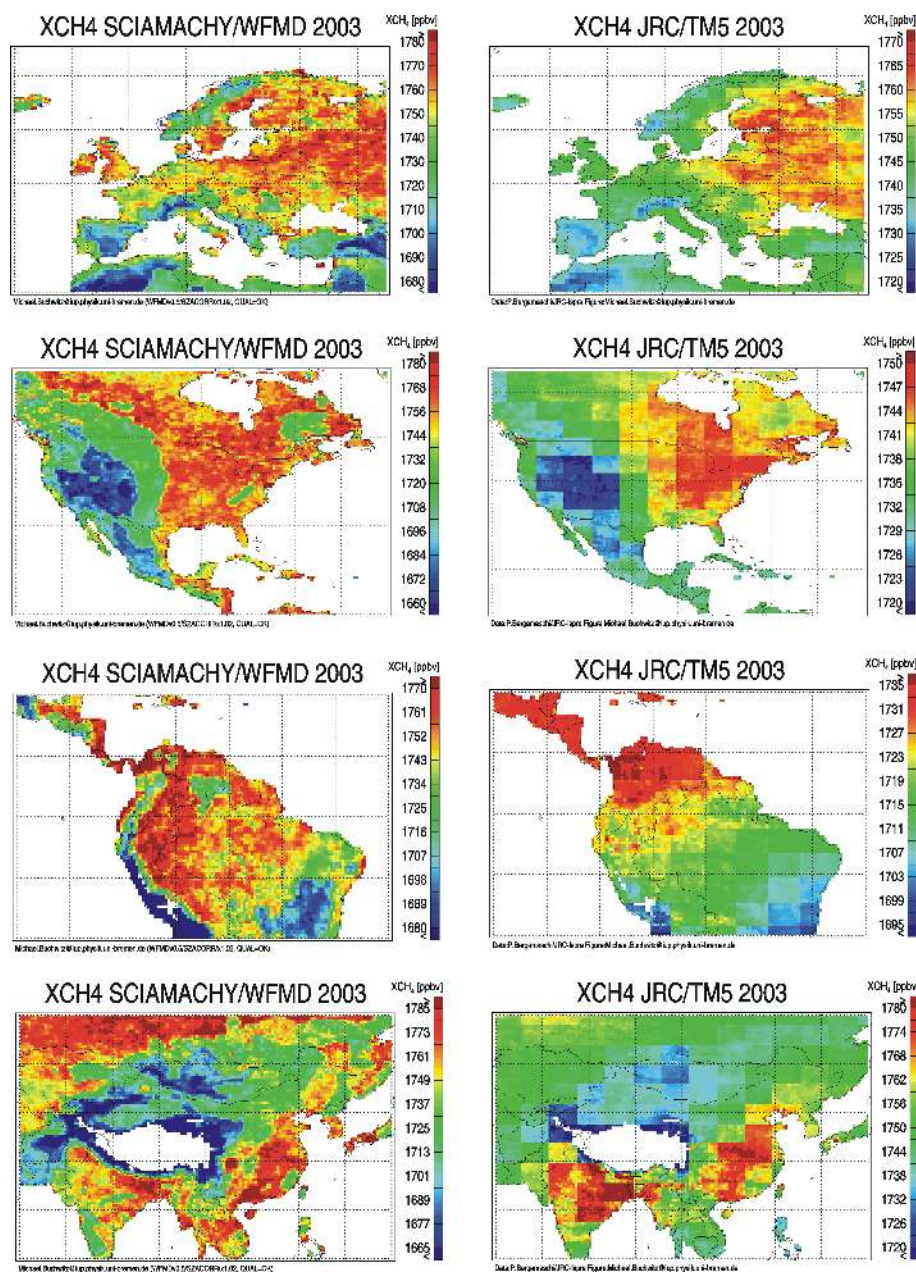Higher values of methane in the tropics compared to the model simulations are clearly visible in the uncorrected

Fig. 15. Comparison of SCIAMACHY/WFM-DOAS version 0.5 XCH$_4$ (left) with TM5 model simulations (right) for four regions using the TM5 high resolution zoom mode over Europe and low resolution mode outside Europe. The ppbv scale has been selected differently for each figure to better highlight the regional methane spatial pattern. The block-like pattern of the TM5 methane (e.g. over the US) reflects the TM5 model resolution for the TM5 low resolution mode. For each SCIAMACHY overpass there are typically several SCIAMACHY measurements within a given TM5 grid box because the SCIAMACHY resolution is higher compared to TM5 in low resolution mode. The TM5 data have been directly sampled without spatial interpolation yielding for each overpass a single TM5 value for all SCIAMACHY measurements in a given TM5 grid box. The SCIAMACHY data are SZA bias corrected and scaled with 1.02.

measurements (Fig. 11) and in the corrected measurements (Fig. 13). The SZA bias (and its correction) is small in the tropics as the solar zenith angle is relatively low and does not vary very much over the year. Both figures indicate (in agreement with Frankenberg et al. (2005c)) that a methane source is missing (or a known source is underestimated) in the trop-

ics. The results shown here give no indications that the missing methane source can be attributed to a (solar zenith angle dependent) measurement error. In order to determine the precise size of the missing methane source, however, even small measurement errors matter. We think that for such an application the SZA bias correction used here is probably not ac-
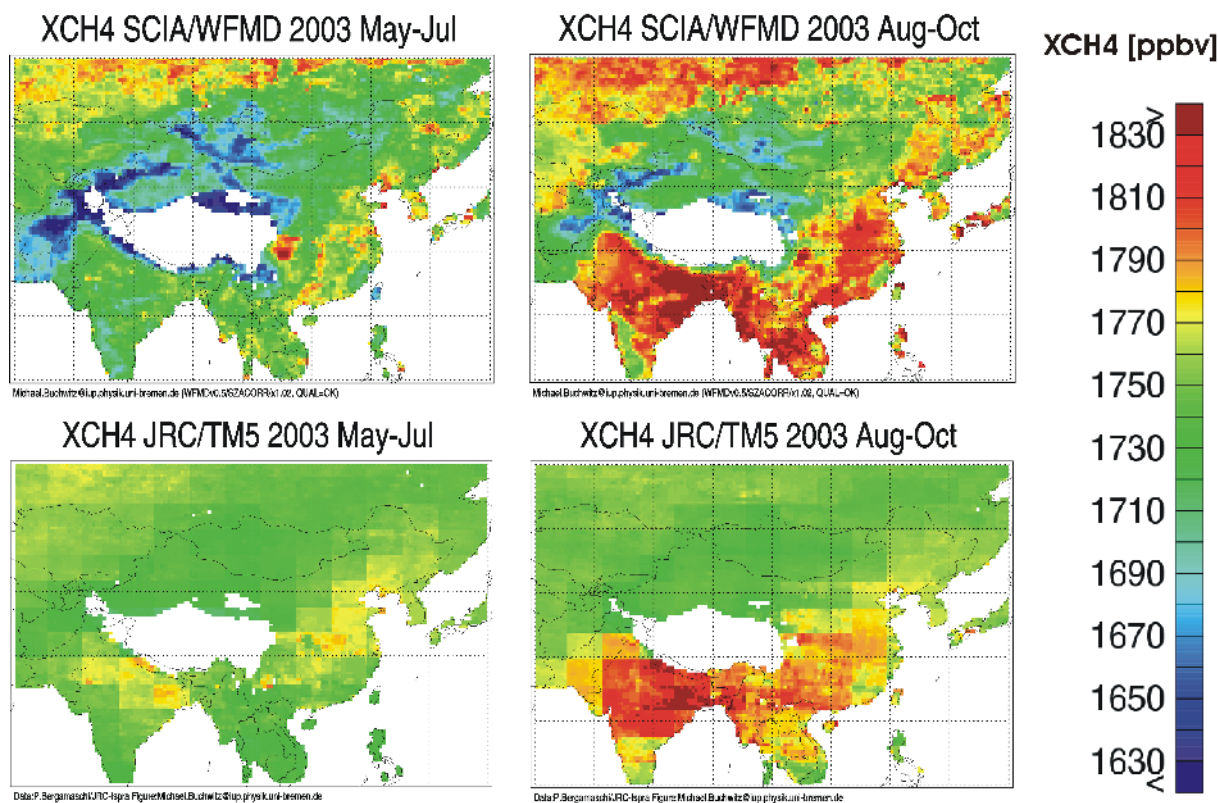
Fig. 16. Comparison of SCIAMACHY/WFM-DOAS version 0.5 XCH$_4$ (top) with TM5 model simulations (bottom) over India and China. The SCIAMACHY data are SZA bias corrected and scaled with 1.02.

curate enough and that reprocessing using version 5 spectra is needed for this application (this is currently under preparation).

Figure 15 shows detailed results for four regions, namely Europe, northern America, southern America, and south-east Asia, including a comparison with TM5. In TM5 regionally elevated methane columns (shown in red) are due to methane emissions from various sources such as fossil fuel related activities, wetlands, waste handling, ruminants, and rice cultivation. The good qualitative agreement of the SCIAMACHY methane measurements with TM5 shows that SCIAMACHY can clearly detect major source regions of methane for the various regions. The comparison with TM5 XCH$_4$ shows in general good agreement but there are also significant regional differences which are, at least partially, due to shortcomings of current methane emission data bases Bergamaschi et al. (2006)[1]. A similar comparison with TM5 as shown here for SCIAMACHY methane derived using WFM-DOAS is shown in Frankenberg et al. (2006) for methane retrieved using the University of Heidelberg IMAP-DOAS algorithm. Qualitatively the methane products derived using the two different algorithms are in good agreement, quantitatively however there are differences, e.g., due to different versions of the SCIAMACHY spectra and due to differences of the retrieval algorithms. Frankenberg et al. (2006) have investi-

gated the error due to normalization the methane column by the simultaneously retrieved CO$_2$ column used to convert the methane column into a column averaged mixing ratio. Using model simulations they found that the variations in the CO$_2$ column abundances are far smaller than those in methane. Nevertheless, some error remains (especially at higher northern latitudes) and they therefore correct the retrieved methane mixing ratios using CO$_2$ columns obtained from model simulations whereas in this paper the CO$_2$ mixing ratio is assumed constant. For our future methane data product we will also consider an improved CO$_2$ correction using, e.g., a first order correction of the CO$_2$ seasonal cycle.

India and China emit significant amounts of methane, e.g., due rice cultivation, ruminants, and wetlands. Figure 16 shows a comparison of tri-monthly averages of SCIAMACHY methane over India and China with TM5. Shown in Fig. 16 are only those measurements for which the quality flag determined by the retrieval algorithm indicates a (potentially) successful measurement. Using this approach the measurements over the Himalaya region are filtered out (the WFM-DOAS reference spectra are only strictly valid for the altitude range 0–3 km; note that for CO the quality criteria are less strict compared to methane - therefore the Himalaya region is shown in Fig. 9). Clearly visible are large regions of elevated methane (shown in red). During August to Octo-
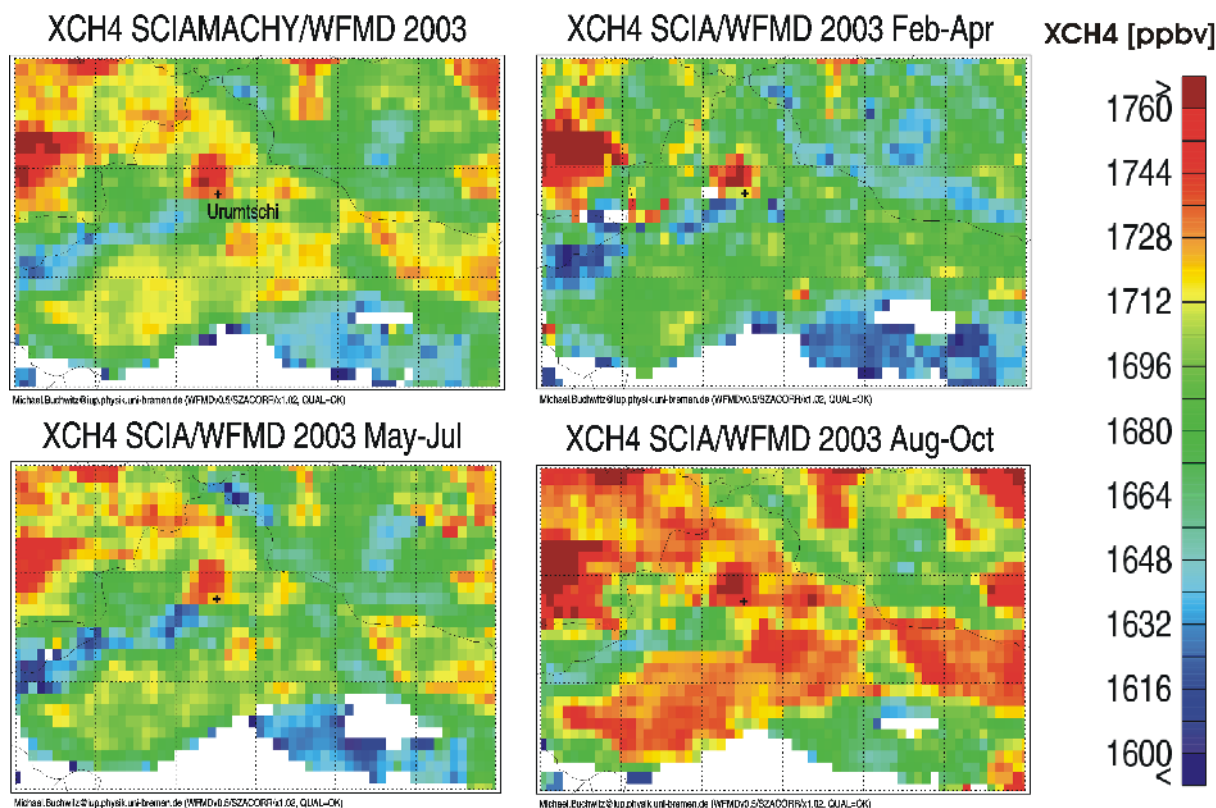
Fig. 17. Elevated methane as observed by SCIAMACHY/WFM-DOAS version 0.5 XCH$_4$ near Urumqi (or Urumtschi, indicated by a black cross) in north-west China. The year 2003 average is shown in the top-left panel. The three other panels show tri-monthly averaged methane. The SCIAMACHY data are SZA bias corrected and scaled with 1.02.

ber the methane concentrations are significantly higher compared to May to July in qualitative agreement with the model simulations. In China elevated concentrations are present in the Red Basin around Chongqing/Chengdu (see annotation of Fig. 9, left panel) even during May to July. Apart from the Red Basin Fig. 9 shows regionally elevated methane as measured by SCIAMACHY over several other areas, for example in north-west China. Figure 17 shows that methane is persistently elevated near the city of Urumqi. Urumqi lies in a region with many coal fields and coal field fires (see, e.g. http://www.coalfire.caf.dlr.de). Figure 17 suggests that significant amounts of methane are emitted in this region and accumulate in the valley located to the north-west of Urumqi (Liu Huang Gou, "Sulphur Valley").

4.3 Carbon dioxide (CO$_2$)

Global maps and time series of the SCIAMACHY/WFM-DOAS version 0.4 XCO$_2$ data product have been presented in Buchwitz et al. (2005b) including a comparison with global model simulations using TM3 (Heimann and Körner, 2003). Comparison with TM3 showed reasonable agreement especially after temporal and spatial averaging of the SCIAMACHY data. We found however also significant dif-

ferences, most notably that the measured XCO$_2$ variability is typically larger compared to the model by about a factor of 2–5. Recently Dils et al. (2006) have compared v0.4 XCO$_2$ with ground based FTIR measurements at three stations. They found a low bias of about 7% of SCIAMACHY XCO$_2$ relative to FTIR, a standard deviation of the difference of 3–4% and a quite low correlation of about $r = 0.4$. Apart from the systematic low bias it was however not possible to draw other strong conclusions from this comparison because none of the three stations (Jungfraujoch in Switzerland, Ny Alesund in Spitsbergen, and Egbert in Canada near Toronto) is ideal for a comparison with SCIAMACHY tropospheric CO$_2$: Jungfraujoch is a high altitude station not sensitive to boundary layer CO$_2$, Ny Alesund is a high latitude station (no CO$_2$ measurements during polar night and difficult measurement conditions for SCIAMACHY because of low signal due to large solar zenith angles and low snow/ice albedo in the near-infrared), and Egbert CO$_2$ shows significant scatter due to strong influence of local sources.

The main problem of the v0.4 XCO$_2$ data product is that the CO$_2$ columns measured by SCIAMACHY had to be scaled with 1.27 to compensate for a systematic underestimation of the CO$_2$ columns. The (scaled) v0.4 XCO$_2$ year 2003 data set has been retrieved from Lv1v4 spectra. The
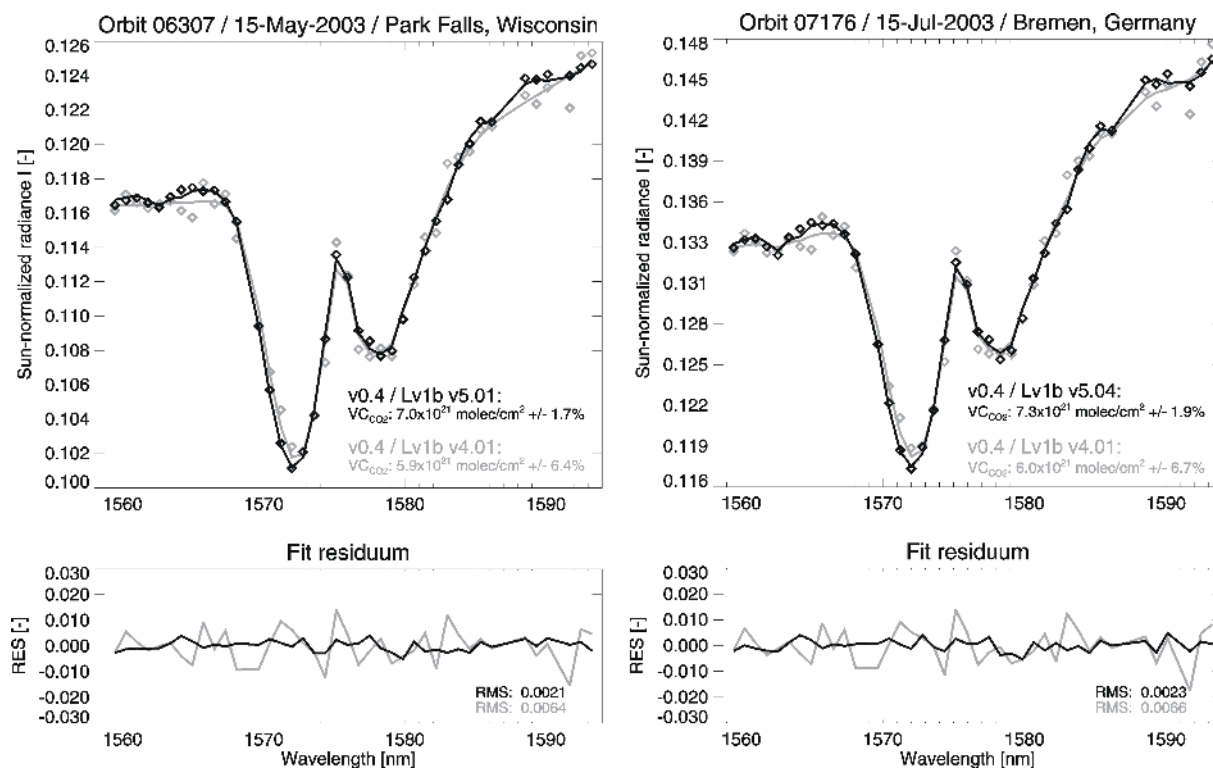
Fig. 18. Typical WFM-DOAS v0.4 CO$_2$ spectral fits for measurements over Park Falls, Wisconsin, USA (left) and Bremen, Germany (right). The top panels show the measured sun-normalized radiance as symbols (grey for Level 1 version 4 spectra and black for version 5 spectra). The solid lines correspond to the WFM-DOAS model after the fit. The retrieved (unscaled) CO$_2$ columns are given in the annotation. As can be seen, the CO$_2$ derived from the version 5 spectra compared to version 4 spectra are about 19% higher over Park Falls (column ratio: 7.0/5.9) and about 22% higher over Bremen (column ratio: 7.3/6.0). The CO$_2$ fit error improves by about a factor of four. The bottom panels show the fit residuals, i.e., the difference between measurement and WFM-DOAS model after the fit. The root-mean-square (RMS) of the fit residuals (see annotation) is about 0.2% for the Level 1 v5 spectra and about three times worse for Level 1 v4 spectra.

latest version of the spectra is Lv1v5 which has a significantly improved calibration compared to Lv1v4. Especially the quality of the near-infrared channel was very preliminary for Lv1v4. In order to use Lv1v4 near-infrared spectra it was necessary to improve the calibration by replacing ("patching") the dark signals in the binary Level 1 data files by improved ones (Buchwitz et al., 2005a,b). For the Lv1v5 spectra we found that the quality of the calibration is good enough so that the nominal calibration can be used. The results shown here for Lv1v5 have been obtained using the nominal calibration (activating all calibration steps except polarization correction).

Figure 18 shows a typical comparison of WFM-DOAS CO$_2$ spectral fits using (dark signal patched) Lv1v4 and (nominally calibrated) Lv1v5 spectra. As can be seen, the CO$_2$ columns retrieved from Lv1v5 spectra are higher by about 20% compared to the unscaled CO$_2$ columns retrieved from Lv1v4 spectra. Figure 18 also shows that the quality of the spectral fit is about a factor of three better for Lv1v5. As a consequence, the CO$_2$ fit error is improved by typically a factor 3–4: for Lv1v5 it is typically less than 2% instead of being larger than 6% for Lv1v4.

The entire year 2003 data set has not yet been reprocessed using the improved spectra because for our next version CO$_2$ product we plan to implement a number of algorithm changes to further improve the quality of the retrieved CO$_2$ (e.g., reduction of albedo sensitivity, update of spectroscopic parameters). We have however processed all available year 2003–2005 orbits over Park Falls, Wisconsin, USA. Park Falls is one of the few sites where ground based XCO$_2$ FTIR measurements are being performed. The Park Falls FTIR is part of the new Total Carbon Column Observing Network (TCCON) currently built up especially for the validation of satellite CO$_2$ measurements (Washenfelder et al., 2005). Figure 19 shows monthly averaged year 2003–2005 XCO$_2$ over Park Falls as measured by SCIAMACHY. For 2003 the (scaled) v0.4 XCO$_2$ data product retrieved from Lv1v4 spectra ("old CO$_2$") is compared to unscaled XCO$_2$ retrieved using the same algorithm applied to Lv1v5 spectra ("new CO$_2$"). In contrast to our version 0.5 CO and methane data products we have not yet implemented an automatic computation of a standard quality flag for the XCO$_2$ data product. For the computation of the monthly means we have used only cloud free measurements over land for which
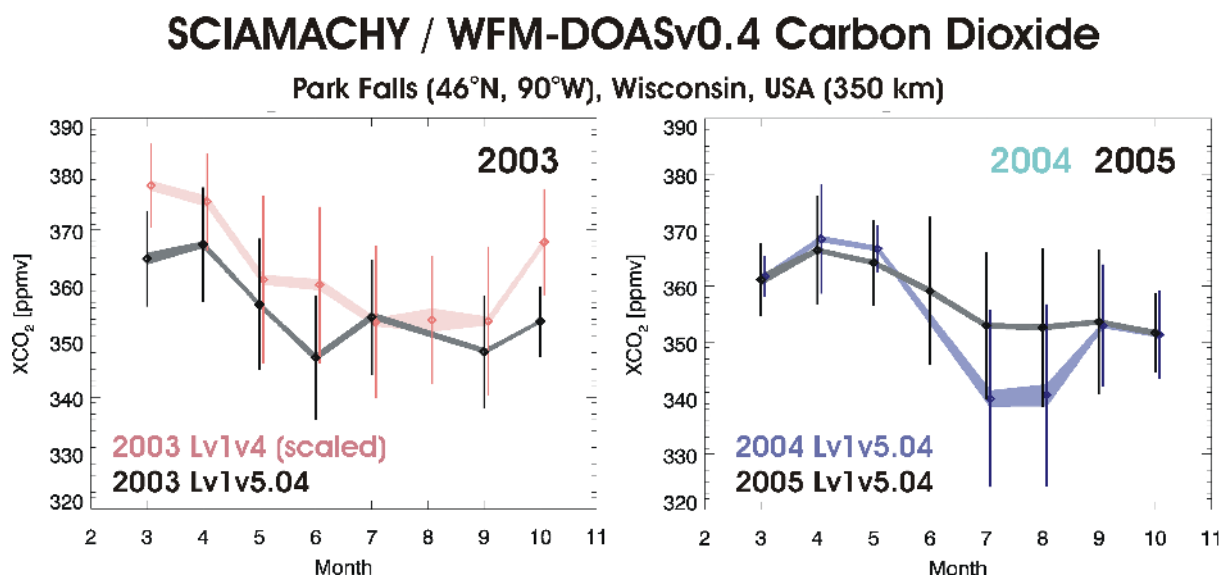
Fig. 19. Monthly mean dry air column averaged CO$_2$ mixing ratios as measured by SCIAMACHY over Park Falls, Wisconsin, USA. The left panel shows in red the WFM-DOAS version 0.4 XCO$_2$ data product for 2003 (which is scaled) retrieved from Lv1v4 spectra. The monthly mean values are shown as symbols, the standard deviations of the individual measurements for a given month as vertical lines. The thickness of the connecting line corresponds to the standard deviation (shown as vertical red lines) divided by the square root of the number of measurements used to compute the monthly means. In black the XCO$_2$ derived from Lv1v5 spectra is shown which has been generated without scaling the CO$_2$ columns. The right panel shows the measurements for 2004 (blue) and 2005 (black) retrieved from Lv1v5 (CO$_2$ not scaled).

the root-mean-square (RMS) of the CO$_2$ fit residuum is better than 0.3% for the new CO$_2$ and better than 0.8% for the old CO$_2$ reflecting the differences in the quality of the spectral fits using the old and the new calibration. In addition, only pixels have been selected whose center coordinates have a distance of less than 350 km from Park Falls. For both data sets not all orbits are currently available and due to instrument decontamination time periods there are additional large data gaps (especially in August 2003). Therefore, we were not (yet) able to compute a monthly mean value for August 2003. As can be seen, the new unscaled CO$_2$ is on average a few percent lower compared to the scaled old CO$_2$ (the unscaled old CO$_2$ would be around 285 ppmv) but the time dependence is similar although not identical, especially in June 2003. From this one can conclude that the preliminary new CO$_2$ still has a low bias of a few percent. For the years 2004 and 2005 the new XCO$_2$ is similar during spring and autumn, but different during July and August where CO$_2$ is lower in 2004 compared to 2005.

A detailed comparison with the Park Falls FTIR measurements will be performed after official release of the FTIR data and after the WFM-DOAS algorithm improvements as indicated above have been implemented. Currently only a first preliminary comparison is possible. A comparison of Fig. 19 with preliminary FTIR measurements as presented in Washenfelder et al. (2005) shows reasonable agreement with respect to the time dependence and the amplitude of

the CO$_2$ over Park Falls. For 2005 the XCO$_2$ difference between April and August as measured by SCIAMACHY is about 13 ppmv (=366−353) and about 9 ppmv for FTIR (=382−373). The SCIAMACHY averaging kernels for CO$_2$ are about 1.5 near the surface and about 1.0 around 5 km (500 hPa) (Buchwitz et al., 2005a). From this one can conclude that SCIAMACHY would overestimate CO$_2$ variability by about 25% (e.g., 11.25 ppmv instead of 9 ppmv) if the variability is mainly confined to the lowest few kilometers of the atmosphere (this is a value that has also been found by applying SCIAMACHY averaging kernels to TM3 model simulations). For a quantitative comparison of the CO$_2$ the averaging kernels of both instruments need to be considered. The FTIR CO$_2$ averaging kernels are typically closer to 1.0 in the lower troposphere (within about 0.8–1.2, depending on altitude, solar zenith angle, etc.; see Bösch et al., 2006) than the WFM-DOAS v0.4 CO$_2$ averaging kernels but they also differ from 1.0. For 2004 SCIAMACHY observes significantly lower CO$_2$ around July/August compared to 2005 in qualitative agreement with the FTIR measurements. SCIAMACHY however appears to overestimate the spring/summer CO$_2$ difference.

5   Conclusions

We have presented an improved algorithm (WFM-DOAS version 0.5) for the retrieval of vertical columns of carbon

monoxide (CO) and dry-air column averaged mixing ratios of methane (XCH$_4$) from the spectral near-infrared nadir observations of the SCIAMACHY instrument onboard the European environmental satellite ENVISAT. A comparison with global reference data (MOPITT satellite data for CO and TM5 model simulations for XCH$_4$) shows that the CO and methane v0.5 data products are significantly improved compared to earlier versions (0.4, 0.41). The results of the comparison with the global reference data are broadly consistent with the comparison of ground based FTIR measurements at 11 ground stations (Dils et al., 2006). For CO we found reasonable agreement with MOPITT with SCIAMACHY CO being typically higher compared to MOPITT. The SCIAMACHY – MOPITT comparison has been conducted by directly comparing the CO vertical column data products of both sensor not taking into account the different averaging kernels which indicate much higher sensitivity to the lower troposphere for SCIAMACHY compared to MOPITT which has his sensitivity maximum in the middle and upper troposphere. For methane we have found that the data product can be further improved using Level 1 version 5 (Lv1v5) spectra which have an improved calibration compared to Lv1v4 spectra used to generate the WFM-DOAS version 0.5 year 2003 methane data set presented here. Despite future improvements we have shown that the quality of the current data set is high enough to detect major source regions of methane (e.g., eastern US, large parts of Europe and Russia, South America, central Africa, India, China) and CO (e.g., eastern China, central and southern Africa, South America). For carbon dioxide we have presented first results obtained by applying the WFM-DOAS v0.4 retrieval algorithm to the improved Lv1v5 nadir spectra. Compared to earlier results obtained with Lv1v4 spectra we find a significant improvement with respect to the quality of the spectral fits and the retrieved CO$_2$ columns. A first qualitative comparison with preliminary FTIR measurements at Park Falls, Wisconsin, USA, indicates reasonable agreement. A detailed quantitative comparison will be performed after release of the FTIR data and after implementation of a number of further improvements of our WFM-DOAS retrieval algorithm. The results presented here demonstrate significant progress to reach our main goal which is the generation of data products with a quality good enough to provide qualitative and as much as possible quantitative information on the surface sources and sinks of these major carbon gases using e.g. inverse modeling.

References

Barkley, M. P., Frieß, U., and Monks, P. S.: Measuring atmospheric CO2 from space using Full Spectral Initiation (FSI) WFM-DOAS, Atmos. Chem. Phys. Discuss., 6, 2765–2807, 2006a.

Barkley, M. P., Monks, P. S., Frieß, U., Mittermeier, R. L., Fast, H., Körner, S., and Heimann, M.: Comparison between SCIAMACHY atmospheric CO2 retrieved using (FSI) WFM-DOAS to ground based FTIR data and the TM3 chemistry transport model, Atmos. Chem. Phys. Discuss., 6, 5387–5425, 2006b.

Bergamaschi, P., Krol, M., Dentener, F., Vermeulen, A., Meinhardt, F., Graul, R., Peters, W., and Dlugokencky, E. J.: Inverse modelling of national and European CH4 emissions using the atmospheric zoom model TM5, Atmos. Chem. Phys., 5, 2431–2460, http://www.direct.sref.org/1680-7324/acp/2005-5-2431, 2005a.

Bergamaschi, P., Frankenberg, C., Meirink, J. F., Krol, M., Dententer, F., van Weele, M., Wagner, T., Platt, U., Körner, S., and Heimann, M.: CH4 total columns from SCIAMACHY – Comparison with atmospheric models (extended abstract: https://www.icdc7.com/article41.html), Seventh International Carbon Dioxide Conference, Boulder, CO, USA, 25–30 September, 2005b.

Bergamaschi, P., Hein, R., Heimann, M., and Crutzen, P. J.: Inverse modeling of the global CO cycle, 1. Inversion of CO mixing ratios, J. Geophys. Res., 105, 1909–1927, 2000.

Bovensmann, H., Buchwitz, M., Frerick, J., Hoogeveen, R., Kleipool, Q., Lichtenberg, G., Noël, S., Richter, A., Rozanov, A., Rozanov, V. V., Skupin, J., von Savigny, C., Wuttke, M., and Burrows, J. P.: SCIAMACHY on ENVISAT: In-flight optical performance and first results, in: Remote Sensing of Clouds and the Atmosphere VIII, edited by: Schäfer, K. P., Comèron, A., Carleer, M. R., and Picard, R. H. (PDF file available from WFM-DOAS web site http://www.iup.physik.uni-bremen.de/sciamachy/NIR_NADIR_WFM_DOAS/index.html), Proceedings of SPIE, 5235, 160–173, 2004.

Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noël, S., Rozanov, V. V., Chance, K. V., and Goede, A.: SCIAMACHY – Mission Objectives and Measurement Modes, J. Atmos. Sci., 56, 127–150, 1999.

Bösch, H., Toon, G. C., Sen, B., Washenfelder, R. A., Wennberg, P. O., Buchwitz, M., de Beek, R., Burrows, J. P., Crisp, D., Christi, M., Connor, B. J., Natraj, V., and Yung, Y. L.: Space-based Near-infrared CO2 Measurements: Testing the OCO Retrieval Algorithm and Validation Concept Using SCIAMACHY Observations over Park Falls, Wisconsin, J. Geophys. Res., in press, 2006.

Buchwitz, M., de Beek, R., Burrows, J. P., Bovensmann, H., Warneke, T., Notholt, J., Meirink, J. F., Goede, A. P. H., Bergamaschi, P., Körner, S., Heimann, M., and Schulz, A.: Atmospheric methane and carbon dioxide from SCIAMACHY satellite data:

Initial comparison with chemistry and transport models, Atmos. Chem. Phys., 5, 941–962, 2005a.

Buchwitz, M., de Beek, R., Noël, S., Burrows, J. P., Bovensmann, H., Bremer, H., Bergamaschi, P., Körner, S., and Heimann, M.: Carbon monoxide, methane, and carbon dioxide retrieved from SCIAMACHY by WFM-DOAS: year 2003 initial data set, Atmos. Chem. Phys., 5, 3313–3329, 2005b.

Buchwitz, M. and Burrows, J. P.: Retrieval of CH$_4$, CO, and CO$_2$ total column amounts from SCIAMACHY near-infrared nadir spectra: Retrieval algorithm and first results, in: Remote Sensing of Clouds and the Atmosphere VIII, edited by: Schäfer, K. P., Comèron, A., Carleer, M. R., and Picard, R. H. (PDF file available from WFM-DOAS web site http://www.iup.physik.uni-bremen.de/sciamachy/NIR_NADIR_WFM_DOAS/index.html), Proceedings of SPIE, 5235, 375–388, 2004.

Buchwitz, M., de Beek, R., Bramstedt, K., Noël, S., Bovensmann, H., and Burrows, J. P.: Global carbon monoxide as retrieved from SCIAMACHY by WFM-DOAS, Atmos. Chem. Phys., 4, 1945–1960, 2004,
http://www.atmos-chem-phys.net/4/1945/2004/.

Buchwitz, M., Rozanov, V. V., and Burrows, J. P.: A correlated-k distribution scheme for overlapping gases suitable for retrieval of atmospheric constituents from moderate resolution radiance measurements in the visible/near-infrared spectral region, J. Geophys. Res., 105, 15 247–15 262, 2000a.

Buchwitz, M., Rozanov, V. V., and Burrows, J. P.: A near infrared optimized DOAS method for the fast global retrieval of atmospheric CH$_4$, CO, CO$_2$, H$_2$O, and N$_2$O total column amounts from SCIAMACHY/ENVISAT-1 nadir radiances, J. Geophys. Res., 105, 15 231–15 246, 2000b.

Burrows, J. P., Hölzle, E., Goede, A. P. H., Visser H., and Fricke, W., SCIAMACHY – Scanning Imaging Absorption Spectrometer for Atmospheric Chartography, Acta Astronautica, 35(7), 445–451, 1995.

Crisp, D., Atlas, R. M., Breon, F.-M., Brown, L. R., Burrows, J. P., Ciais, P., Connor, B. J., Doney, S. C., Fung, I. Y., Jacob, D. J., Miller, C. E., O'Brian, D., Pawson, S., Randerson, J. T., Rayner, P., Salawitch, R. S., Sander, S. P., Sen, B., Stephens, G. L., Tans, P. P., Toon, G. C., Wennberg, P. O., Wofsy, S. C., Yung, Y. L., Kuang, Z., Chudasama, B., Sprague, G., Weiss, P., Pollock, R., Kenyon, D., and Schroll, S.: The Orbiting Carbon Observatory (OCO) mission, Adv. Space Res., 34, 700–709, 2004.

Deeter, M. N., Emmons, L. K., Francis, G. L., Edwards, D. P., Gille, J. C., Warner, J. X., Khattatov, B., Ziskin, D., Lamarque, J.-F., Ho, S.-P., Yuding, V., Attie, J.-L., Packman, D., Chen, J., Mao, D., and Drummond, J. R.: Operational carbon monoxide retrieval algorithm and selected results for the MOPITT instrument, J. Geophys. Res., 108, 4399–4409, 2003.

de Laat, A. T. J., Gloudemans, A. M. S., Schrijver, H., van den Broek, M. M. P., Meirink, J. F., Aben, I. and Krol M.: Quantitative analysis of SCIAMACHY carbon monoxide total column measurements, Geophys. Res. Lett., Vol. 33, L07807, 10.1029/2005GL025530, 2006.

De Mazière, M., Barret, B., Blumenstock, T., Buchwitz, M., de Beek, R., Demoulin, P., Fast, H., Gloudemans, A., Griesfeller, A., Griffith, D., Ionov, D., Janssens, K., Jones, N., Mahieu, E., Mellqvist, J., Mittermeier, R. L., Notholt, J., Rinsland, C., Schrijver, H., Schultz, A., Smale, D., Strandberg, A., Strong,

K., Sussmann, R., Warneke, T., and Wood, S.: Comparison between SCIAMACHY scientific products and ground-based FTIR data for total columns of CO, CH$_4$, and N$_2$O, in Proceedings of the Second Workshop on the Atmospheric Chemistry Validation of ENVISAT (ACVE-2), ESA/ESRIN, Frascati, Italy, 3–7 May 2004, ESA SP-562 (on CD), 2004.

Dils, B., De Mazière, M., Blumenstock, T., Buchwitz, M., de Beek, R., Demoulin, P., Duchatelet, P., Fast, H., Frankenberg, C., Gloudemans, A., Griffith, D., Jones, N., Kerzenmacher, T., Mahieu, E., Mellqvist, J., Mikuteit, S., Mittermeier, R. L., Notholt, J., Schrijver, H., Smale, D., Strandberg, A., Stremme, W., Strong, K., Sussmann, R., Taylor, J., van den Broek, M., Warneke, T., Wiacek, A., and Wood, S.: Comparison between SCIAMACHY and ground-based FTIR data for total columns of CO, CH$_4$, CO$_2$ and N$_2$O, Atmos. Chem. Phys. Discuss., 5, 2677–2717, 2005,
http://www.atmos-chem-phys-discuss.net/5/2677/2005/.

Dils, B., De Mazière, M., Müller, J. F., Blumenstock, T., Buchwitz, M., de Beek, R., Demoulin, P., Duchatelet, P., Fast, H., Frankenberg, C., Gloudemans, A., Griffith, D., Jones, N., Kerzenmacher, T., Mahieu, E., Mellqvist, J., Mikuteit, S., Mittermeier, R. L., Notholt, J., Schrijver, H., Smale, D., Strandberg, A., Stremme, W., Strong, K., Sussmann, R., Taylor, J., van den Broek, M., Warneke, T., Wiacek, A., and Wood, S.: Comparison between SCIAMACHY and ground-based FTIR data for total columns of CO, CH$_4$, CO$_2$ and N$_2$O, Atmos. Chem. Phys. (submitted revised version of Dils et al. (2005), 2006.

Emmons, L. K., Deeter, M. N., Gille, J. C., Edwards, D. P., Attiè, J.-L., Warner, J., Ziskin, D., Francis, G., Khattatov, B., Yudin, V., Lamarque, J.-F., Ho, S.-P., Mao, D., Chen, J. S., Drummond, J., Novelli, P., Sachse, G., Coffey, M. T., Hannigan, J. W., Gerbig, C., Kawakami, S., Kondo, Y., Takegawa, N., Schlager, H., Baehr, J., and Ziereis, H.: Validation of Measurements of Pollution in the Troposphere (MOPITT) CO retrievals with aircraft in situ profiles, J. Geophys. Res., 109, D03309, doi:10.1029/2003JD004101, 2004.

Frankenberg, C., Platt, U., and Wagner, T.: Iterative maximum a posteriori (IMAP-)DOAS for retrieval of strongly absorbing trace gases: Model studies for CH$_4$ and CO$_2$ retrieval from near-infrared spectra of SCIAMACHY onboard ENVISAT, Atmos. Chem. Phys., 5, 9–22, 2005a.

Frankenberg, C., Platt, U., and Wagner, T.: Retrieval of CO from SCIAMACHY onboard ENVISAT: Detection of strongly polluted areas and seasonal patterns in global CO abundances, Atmos. Chem. Phys., 5, 1639–1644, 2005b.

Fung, I., John, J., Lerner, J., Matthews, E., Prather, M., Steele, L. P., and Fraser, P. J., Three-dimensional model synthesis of the global methane cycle, J. Atmos. Res., 96, 13 033–13 065, 1991.

Frankenberg, C., Meirink, J. F., van Weele, M., Platt, U., and Wagner, T.: Assessing methane emissions from global spaceborne observations, Science, 308, 1010–1014, 2005c.

Frankenberg, C., Meirink, J. F., Bergamaschi, P., Goede, A. P. H., Heimann, M., Körner, S., Platt, U., van Weele, M., and Wagner, T.: Satellite chartography of atmospheric methane from SCIAMACHY onboard ENVISAT: Analysis of the years 2003 and 2004, J. Geophys. Res., 111, 1–18, D07303, doi:10.1029/2005JD006235, 2006.

Gloudemans, A. M. S., Schrijver, H., Straume, A. G., Aben, I., Maurellis, A. N., Buchwitz, M., de Beek, R., Frankenberg, C.,

Wagner, T., and Meirink, J. F.: CH$_4$ and CO total columns from SCIAMACHY: Comparisons with TM3 and MOPITT, in Proceedings of Second Workshop on the Atmospheric Chemistry Validation of ENVISAT (ACVE-2), ESA/ESRIN, Frascati, Italy, 3–7 May 2004, ESA SP-562 (on CD), 2004.

Gloudemans, A. M. S., Schrijver, H., Kleipool, Q., van den Broek, M. M. P., Straume, A. G., Lichtenberg, G., van Hess, R. M., Aben, I., and Meirink, J. F.: The impact of SCIAMACHY near-infrared instrument calibration on CH$_4$ and CO total columns, Atmos. Chem. Phys., 5, 2369–2383, 2005, http://www.atmos-chem-phys.net/5/2369/2005/.

Heimann, M. and Körner, S.: The Global Atmospheric Tracer Model TM3. Model Description and Users Manual Release 3.8a, No. 5, Max Planck Institute for Biogeochemistry (MPI-BGC), Jena, Germany, 2003.

Houweling, S., Kaminski, T., Dentener, F., Lelieveld, J., and Heimann, M.: Inverse modeling of methane sources and sinks using the adjoint of a global transport model, J. Geophys. Res., 105(D21), 26 137–26 160, 1999.

Houweling, S., Breon, F.-M., Aben, I., Rödenbeck, C., Gloor, M., Heimann, M., and Ciais, P.: Inverse modeling of CO$_2$ sources and sinks using satellite data: A synthetic inter-comparison of measurement techniques and their performance as a function of space and time, Atmos. Chem. Phys., 4, 523–538, 2004, http://www.atmos-chem-phys.net/4/523/2004/.

Houweling, S., Hartmann, W., Aben, I., Schrijver, H., Skidmore, J., Roelofs, G.-J., and Breon, F.-M.: Evidence of systematic errors in SCIAMACHY-observed CO$_2$ due to aerosols, Atmos. Chem. Phys., 5, 3003–3013, 2005, http://www.atmos-chem-phys.net/5/3003/2005/.

Keppler, F., Hamilton, J. T. G., Braß, M., Röckmann, T., Methane emissions from terrestrial plants under aerobic conditions, Nature, 439, 187–191, 2006.

Krol, M. C., Houweling, S., Bregman, B., van den Broek, M., Segers, A., van Velthoven, P., Peters, W., Dentener, F., and Bergamaschi, P.: The two-way nested global chemistry-transport zoom model TM5: Algorithm and applications, Atmos. Chem. Phys., 5, 417–432, 2005, http://www.atmos-chem-phys.net/5/417/2005/.

Lichtenberg, G., Kleipool, Q., Krijger, J. M., van Soest, G., van Hees, R., Tilstra, L. G., Acarreta, J. R., Aben, I., Ahlers, B., Bovensmann, H., Chance, K., Gloudemans, A. M. S., Hoogeveen, R. W. M., Jongma, R., Noël, S., Piters, A., Schrjiver, H., Schrijvers, C., Sioris, C. E., Skupin, J., Slijkhuis, S., Stammes, P., and Wuttke, M.: SCIAMACHY Level1 data: Calibration concept and in-flight calibration, Atmos. Chem. Phys. Discuss, 5, 8925–8977, 2005.

Matthews, E., Fung, I., and Lerner, J., Methane emissions from rice cultivation: Geographic and seasonal distribution of cultivated areas and emissions, Global Biogeochem. Cycles., 1, 61–86, 1991.

Meirink, J.-F., Eskes, H. J., and Goede, A. P. H.: Sensitivity analysis of methane emissions derived from SCIAMACHY observations through inverse modelling, Atmos. Chem. Phys., 6, 1275–1292, 2006, http://www.atmos-chem-phys.net/6/1275/2006/.

Olivier, J. G. J. and Berdowski, J. J. M.: Global emissions sources and sinks, in: The Climate System, edited by: Berdowski, J. J. M., Guicherit, R. and Heij, B. J., A. A. Balkema Publishers/Swets & Zeitlinger Publishers, Lisse, The Netherlands, 2001.

Rayner, P. J. and O'Brien, D. M.: The utility of remotely sensed CO$_2$ concentration data in surface inversions, Geophys. Res. Lett., 28, 175–178, 2001.

Rothman, L. S., Barbe, A., Benner, D. C., Brown, L. R., Camy-Peyret, C., Carleer, M. R., Chance, K., Clerbaux, C., Dana, V., Devi, V. M., Fayt, A., Flaud, J. M., Gamache, R. R., Goldman, A., Jacquemart, D., Jucks, K. W., Lafferty, W. J., Mandin, J. Y., Massie, S. T., Nemtchinov, V., Newnham, D. A., Perrin, A., Rinsland, C. P., Schroeder, J., Smith, K. M., Smith, M. A. H., Tang, K., Toth, R. A., Vander Auwera, J., Varanasi, P., and Yoshino, K.: The HITRAN molecular spectroscopic database: edition of 2000 including updates through 2001, J. Quant. Spectrosc. Radiat. Transfer, 82, 5–44, 2003.

Sussmann, R. and Buchwitz, M.: Initial validation of ENVISAT/SCIAMACHY columnar CO by FTIR profile retrievals at the ground truthing station Zugspitze, Atmos. Chem. Phys., 5, 1497–1503, 2005, http://www.atmos-chem-phys.net/5/1497/2005/.

Sussmann, R., Stremme, W., Buchwitz, M., and de Beek, R.: Validation of ENVISAT/SCIAMACHY columnar methane by solar FTIR spectrometry at the ground-truthing station Zugspitze, Atmos. Chem. Phys., 5, 2419–2429, 2005, http://www.atmos-chem-phys.net/5/2419/2005/.

Takahashi, T., Sutherland, S. C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, Feely, R. A., Sabine, C., Olafsson, J., and Nojiri, Y.: Global sea-air CO$_2$ flux based on climatological surface ocean pCO$_2$, and seasonal biological and temperature effects, Deep-Sea Res., 49, 1601–1622, 2002.

Thornton, P. E., Law, B. E., Gholz, H. L., Clark, K. L., Falge, E., Ellsworth, D. E., Goldstein, A. H., Monson, R. H., Hollinger, D. Y., Falk, M., and Falk, J. P.: Modeling and measuring the effects of disturbance history and climate on carbon and water budgets in evergreen needleleaf forests, Agr. Forest Meteorol. , 113, 185–222, 2002.

van Diedenhoven, B., Hasekamp, O. P., and Aben, I.: Surface pressure retrieval from SCIAMACHY measurements in the O$_2$ A band: validation of the measurements and sensitivity on aerosols, Atmos. Chem. Phys., 5, 2109–2120, 2005, http://www.atmos-chem-phys.net/5/2109/2005/.

van der Werf, G. R., Randerson, J. T., Collatz, G. J., Giglio, L., Kasibhatla, P. S., Arrellano Jr., A. F., Olsen, S. C., and Kasischke, E. S.: Continental-scale partitioning of fire emissions during 1997 to 2001 El Nino / La Nina period, Science, 303, 73–76, 2004.

Walter, B., Heimann, M., and Matthews, E.: Modeling modern methane emissions from natural wetlands 1. model description and results, J. Geophys. Res., 105(D24), 34 189–34 206, 2001.

Warneke, T., de Beek, R., Buchwitz, M., Notholt, J., Schulz, A., Velazco, V., and Schrems, O.: Shipborne solar absorption measurements of CO$_2$, CH$_4$, N$_2$O, and CO and comparison with SCIAMACHY WFM-DOAS retrievals, Atmos. Chem. Phys., 5, 2029–2034, 2005, http://www.atmos-chem-phys.net/5/2029/2005/.

Washenfelder, R. A., Sherlok, V., Connor, B. J., Toon, G. C., and Wennberg, P. O.: Initial results from the total carbon column observing network, Seventh International Carbon Dioxide Conference (extended abstract: https://www.icdc7.com/article43.html), Boulder, CO, USA, 25–30 September, 2005.