

VALIDATION OF WFM-DOAS V0.6 CO AND V1.0 CH₄ SCIENTIFIC PRODUCTS USING EUROPEAN GROUND-BASED FTIR MEASUREMENTS

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ABSTRACT

New WFM-DOAS retrieval algorithm products, CO (v0.6) and CH₄ (v1.0) have recently become available. The total column amounts of these CO and CH₄ products, retrieved from SCIAMACHY nadir observations in its near-infrared channels, have been compared to data from a European harmonized FTIR network as developed during the UFTIR project (<http://www.nilu.no/uftir>). The years considered are 2003 and 2004 only (the new WFM-DOAS data is also available for the year 2005). Comparisons have been made for individual data, as well as for monthly averages. To maximize the number of reliable coincidences that satisfy the temporal and spatial collocation criteria, the SCIAMACHY data have been compared with a temporal 3rd order polynomial interpolation of the ground-based data. For comparison purposes we have also compared the old v0.5 datasets with the same FTIR measurement ensemble. The validation shows a clear improvement of the data quality with the new version products.

1. INTRODUCTION

The validation of previous version (v0.5) WFM-DOAS scientific data products [1] with FTIR measurements [2] resulted in some marked observations. The most striking of which was the need to apply a solar zenith angle correction to the CH₄ v0.5 data products. Also CO data showed some strong biases during summer. All in all, WFM-DOAS v0.5 showed clear quality improvements with respect to previous versions, but still exhibited obvious flaws in certain areas. Recently new WFM-DOAS products have been developed which could further enhance the data quality.

High quality CO and CH₄ data would be most welcome to the scientific community since the SCIAMACHY instrument [3,4] onboard ENVISAT, has the potential to make nadir observations in the near-infrared (NIR; 0.8–2.38 μm) and thus has the important advantage over TIR measurements in that they are sensitive down to the

earth's surface, where most emission sources are located. For CH₄, the lack of good data is even more acute since the MOPITT instrument (Measurements Of Pollution In The Troposphere) is delivering only CO profile data retrieved from the TIR channels; the expected CH₄ products are still unavailable due to instrument calibration problems [5].

The purpose of the current validation is to identify quantitatively to what extent the SCIAMACHY WFM-DOAS NIR products have been improved, by comparing the available SCIAMACHY data with correlative, i.e., close in space and time, independent data – in casu from a remote-sensing network of ground-based (g-b) FTIR spectrometers. For more in-depth information about the WFM-DOAS SCIAMACHY retrieval algorithms and data products, the reader is referred to papers by Buchwitz et al. [1, 6–10]

The methodology used in this validation is identical to the one used to validate the previous v0.5 dataset [2], only another FTIR g-b dataset has been used for this study.

2. THE GROUND-BASED DATA

The g-b correlative data are collected from 7 European FTIR spectrometers that are operated at various stations of the Network for the Detection of Atmospheric Composition Change (NDACC, formerly called Network for the Detection of Stratospheric Change or NDSC, <http://www.ndacc.org>). All stations collaborated in the UFTIR project (<http://www.nilu.no/uftir>) in which a common retrieval strategy was established in order to obtain an as uniform as possible dataset, thus limiting station to station biases. Table 1 identifies the locations of the contributing stations. The g-b FTIR data are obtained from daytime solar absorption measurements under clear-sky conditions only. This implies that number of FTIR and thus correlative data points are limited and the collocation criteria thus cannot be too strict in order to retain a statistically significant dataset.

For comparison purposes, all data have been converted to average volume mixing ratios (vmrs) using ECMWF pressure data, as explained in the methodology section.

Table 1. Spatial coordinates of the ground-based FTIR stations.

Station	Lat N	Lon E	Altitude(m)
NY.ALESUND	78.91	11.88	20
KIRUNA	67.84	20.41	419
HARESTUA	60.22	10.75	580
BREMEN	53.11	8.85	27
ZUGSPITZE	47.42	10.98	2964
JUNGFRAUJOCH	46.55	7.98	3580
IZANA	28.30	-16.48	2367

3. THE WFM-DOAS DATA

Briefly, WFM-DOAS (henceforth called WFMD) is one of three scientific SCIAMACHY CO and CH₄ retrieval algorithms currently under development. The other algorithms (IMLM [11] and IMAP [12]) are not discussed in this paper.

For WFMD, the final so-called dry-air normalized XCH₄ data products are the total column values of said species divided by the total column values of CO₂, scaled to be a proxy for dry air. Thus the dry air normalized product is equal to its measured total column value multiplied by the ratio of the expected vmr of the dry air proxy (a constant) over its measured total column value. For instance $XCH_4 \text{ (ppb)} = CH_4 \text{ (molec cm}^{-2}\text{)} * 370e3 \text{ (ppb)} / CO_2 \text{ (molec cm}^{-2}\text{)}$. WFMD CO, however uses CH₄ measurements (from the same fitting window) to correct the total column values but does not provide dry air normalized XCO vmrs. This normalisation should improve the data quality, given the fact that systematic retrieval errors, such as residual cloud contamination, are eliminated to a large extent from the ratio product.

To avoid cloud contamination (which takes over the role of the Earth's surface leading to significant errors), for XCH₄, WFMD filter their measurements based on a lower threshold for the height-corrected O₂ column: the column must be at least 90% of the expected total column assuming constant O₂. This method effectively filters high-altitude clouds, while the dry air normalisation should reduce the impact of remaining low altitude cloud contamination. WFMD CO uses a similar scheme using CH₄ total column data. An additional major advantage of this method is that over regions with low surface albedos (over water) where the data quality is strongly degraded, the data measured above low altitude clouds over these regions are still viable, thus largely improving the global data coverage. The WFMD data products come with a quality flag which effectively filters out any bad data due to cloud

contamination, high solar zenith angles, low signal-to-noise and other criteria.

4. VALIDATION CRITERIA

Due to the inherent differences between ground-based FTIR measurements and satellite SCIAMACHY data, several issues have to be resolved before validation can commence. The most important differences are (1) differences in time/place of measurement, (2) altitude of the FTIR station versus the SCIAMACHY ground height, (3) the difference in the FTIR and SCIAMACHY airmass, and (4) differences in retrieval parameters, averaging kernels etc. We will discuss these inherent differences below

4.1. Collocation criteria

One of the prime criteria for a thorough validation is a sufficiently large inter-comparison dataset. Given the limited number of FTIR measurements, this would require very relaxed temporal and/or spatial overlap criteria. The criteria adopted for temporal and spatial 'collocation' stem from choosing the best compromise between achieving better or worse statistics and keeping more or less natural variability in the data. Spatial collocation has been defined as data being within $\pm 2.5^\circ$ latitude and $\pm 10^\circ$ longitude of the FTIR ground station (hereinafter indicated as the large collocation grid). Data that have been taken closer to each other (within $\pm 2.5^\circ$ latitude and $\pm 5^\circ$ longitude, hereinafter indicated as the small collocation grid) have been looked at in particular. The spatial collocation criteria adopted here are loose; however making those more stringent would have made the number of coincidences too small, especially at the high-latitude stations.

To achieve the maximum temporal overlap, we have decided to compare the individual WFMD datapoints, with a fitted 3rd order polynomial through the FTIR data instead of the FTIR data itself. Thus temporal coincidence has been defined as data being taken at the same time, in which the real g-b FTIR data set has been approximated by a continuous set of interpolated values. Apart from comparing the individual data, several comparisons have been made also between monthly mean FTIR and SCIAMACHY data.

4.2. Altitude correction

Because the target molecules have most of their total concentration in the lower troposphere, the total column amount is strongly dependent on the FTIR observatory's or SCIAMACHY pixel's mean altitude. To eliminate any apparent differences or variations in the data set that are due to this altitude dependence, we have normalised all total column data using ECMWF operational pressure data (P) into mean volume mixing ratios:

$$C_{\text{vmr}} = C_{\text{totcol}} / (P * 2.12118e^{11}) \quad (1)$$

Herein C_{vmr} is the mean volume mixing ratio (in ppbv), C_{totcol} the measured total column value (in molec cm^{-2}), and, for the FTIR g-b data, P the pressure at station altitude (in Pa). The factor converts pressure (Pa) into total column (molec cm^{-2}) values. The same normalisation has been applied to the overpass CO SCIAMACHY data, using the pressure corresponding to the mean altitude of the observed ground pixel. X_{CH_4} is already a normalised product and is validated as is. The use of this normalisation procedure to improve the comparisons, relies on the assumption that the volume mixing ratio of the considered species is constant as a function of altitude. This is the best assumption at hand in the absence of auxiliary information, but still relatively crude. The approximation is relatively good for CH_4 with an almost constant tropospheric vmr, but worse for CO that has a more variable vmr in the troposphere. An error assessment study using TM4 CO and CH_4 profile data, kindly provided by J.F. Meirink [13], has taught us that for the three high altitude stations (Jungfraujoch, Zugspitze and Izaña) the errors associated with this approximation can be as large as 20% for CO and 3% for CH_4 . To compensate for these relatively large errors, all CO and CH_4 SCIAMACHY vmrs are multiplied by a profile correction factor prior to any further comparison. This factor was derived by taking the ratio of the calculated TM4 vmr above the station altitude and above ground level (as determined by the model's orography) at the station's geo-location. Note that the spatial resolution of the model ($2^\circ \times 3^\circ$) does not correspond with that of a SCIAMACHY pixel and thus the correction can never be perfect. We thus opted to keep the correction as simple and clear as possible. Therefore it is not calculated at the SCIAMACHY pixel geo-location for each measurement individually. We did however calculate this correction ratio for each measurement day since for several stations a small but clear seasonal dependence of this factor was noticeable. The impact of such a correction is only significant for the three high altitude stations and it did not have any significant impact on the scatter or seasonality.

4.3. Airmass difference

An additional difference between FTIR and SCIAMACHY, for which no obvious solution is available, is the fact that the column measured by SCIAMACHY is an average column above the area covered by a SCIAMACHY pixel which extends beyond the location of the g-b station. For channel 8 products, as CO, the pixel size is $30 \times 120 \text{ km}^2$, for channel 6 products (CH_4) $30 \times 60 \text{ km}^2$. Consequently, for example for a mountainous g-b station, the SCIAMACHY column also samples to some extent the

valleys around the station that often harbour significantly higher concentrations of pollutants compared to the mountain site. This might create an apparent bias between the FTIR and SCIAMACHY measurements.

Additionally, to obtain a statistically significant dataset, the spatial collocation criteria include all SCIAMACHY pixels centred within $\pm 2.5^\circ$ latitude and $\pm 5^\circ$ or $\pm 10^\circ$ longitude of the FTIR ground-station coordinates (for the small grid and large grid collocation, respectively), thus covering an even wider area, which in turn may influence the data scatter as compared to that of the FTIR g-b measurements. Unfortunately there is no way around this inherent difference and thus when interpreting all validation results, one must always keep this point in mind. To have an indication of the impact of spatial collocation, all parameters have been calculated for both the small and large spatial collocation grid.

4.4. Averaging Kernels

Before making the comparisons, we have verified that the total column averaging kernels of both data products (g-b FTIR and SCIAMACHY) are very similar, showing a rather uniform sensitivity close to 1 from the ground to the stratosphere [14,15]. The associated smoothing errors for both datasets are negligible compared to the observed differences between them. Therefore we have compared the data products as such, without taking the averaging kernels explicitly into account.

5. METHODOLOGY

In order to quantify the data quality we have calculated the bias, scatter and correlation coefficients of the WFM-DOAS products. A more elaborate explanation on these parameters is given in [2].

5.1. Bias

To calculate the bias, time series of the relative differences between the selected SCIAMACHY individual mean vmrs (x_j^{SCIA}) and the corresponding values from the 3rd order polynomial interpolation through the normalised g-b FTIR daily network data (x_j^{PF}), i.e., $[(x_j^{\text{SCIA}} - x_j^{\text{PF}}) / x_j^{\text{PF}}]$ have been made for all the different WFM-DOAS target products. An overall weighted bias over the considered time period, b , was calculated for each target product and station, following

$$b = \text{mean}_w \left(\frac{x_j^{\text{SCIA}} - x_j^{\text{PF}}}{x_j^{\text{PF}}} \right) \quad (2)$$

in which mean_w is the weighted mean of a dataset which consists of N x_j elements. In our case the weight is equal to $1/(\text{err}_j)^2$ in which err_j is the error on the individual measurement. The thus calculated biases are listed in Tables 4 to 5. An overall average weighted bias (i.e., a mean over all stations) was calculated as well and is also listed in Tables 2-3. The weighted standard errors on the biases reported in Tables 2 to 5 are given by

$$\frac{3}{\sqrt{N}} \times \text{sd}_w \left(\frac{x_j^{\text{SCIA}} - x_j^{\text{PF}}}{x_j^{\text{PF}}} \right) \quad (3)$$

in which sd_w stands for the weighted standard deviation.

5.2. Scatter

We have also evaluated the scatter of the selected SCIAMACHY measurements, σ_{scat} , for each station and target species, for comparison with the corresponding ones of the FTIR data.

Since the FTIR data are daily averages, the SCIAMACHY data have been averaged as well and a daily bias (b_{day}) has been calculated (as in Eq. 1). Note that while the daily averages for the FTIR data are pure averages in time, the SCIAMACHY averages (y_i^{SCIA}) are also spatial averages over the collocation grid around the FTIR station. Thus the scatter is influenced by the natural variability within the collocation grid as well as the actual retrieval errors. The latter are strongly related to the solar zenith angle and surface albedo, thus considerable station to station differences of the scatter are not unlikely.

σ_{scat} is then obtained as the statistical 1σ weighted standard deviation of the daily averaged SCIAMACHY data (y_i^{SCIA}) with respect to the polynomial interpolation of the daily FTIR data, corrected for the daily bias (b_{day}), according to:

$$\sigma_{\text{scat}} = \text{sd}_w \left(\frac{y_i^{\text{SCIA}} - (1 + b_{\text{day}}) y_i^{\text{PF}}}{(1 + b_{\text{day}}) y_i^{\text{PF}}} \right) \quad (4)$$

Thus the scatter is not calculated with respect to the SCIAMACHY data itself but to the bias-corrected FTIR polynomial fit. The complete set of σ_{scat} values, including those from small grid collocated measurements, are listed in Tables 2 to 5.

5.3. Correlation Coefficient

To have a clearer view on the ability of SCIAMACHY to reproduce temporal variations, an important data quality requirement, we have calculated the weighted monthly averages, z_k , of both the original ground-based data (without a polynomial fitting procedure) and the

SCIAMACHY data, on the large collocation grid and satisfying all selection criteria. Time series of these SCIAMACHY monthly averages have been plotted in Figures 1 to 4, again for both target products, algorithm versions and stations. The errors depicted on these Figures represent the weighted statistical errors on these monthly averages and do not represent the measurement and retrieval errors on the individual data.

$$\frac{3}{\sqrt{N_k}} \times \text{sd}_w \left(x_{j,k}^{\text{SCIA}} \right) \quad (5)$$

in which N_k is the number of individual SCIAMACHY measurements, $x_{j,k}^{\text{SCIA}}$, for month k .

A useful marker for the ability to reproduce seasonal and latitudinal variations is the correlation coefficient (R) between the SCIAMACHY and FTIR monthly averages. Only monthly mean SCIAMACHY values which have been derived from at least 10 individual measurements have been taken into account. It turns out to be impossible to produce meaningful R values for the individual stations, given the limited temporal variation of the $g-b$ data and the limited number of data points. However, the overall correlation coefficient per retrieval method over all stations and time does provide useful information.

6. RESULTS

6.1. CO

From the previous study [2], limited to 2003 only, we saw promising results for CO v0.5. The correlation coefficients were reasonably high over an 11 station quasi-global network but the scatter remained at least twice as large as the FTIR scatter (to be fair the SCIAMACHY scatter also includes natural variability) and had not yet reached the target 10% precision for reverse modelling purposes. The only structural deviations that could be detected (although this was hampered by the still relatively large scatter) was exceedingly high summer CO over Europe. A reanalysis of the old CO v0.5 data for the year 2003 does not yield (and shouldn't yield) any significant differences. Due to the more limited FTIR network the overall correlation coefficient has decreased to 0.52 (for the large grid), which is expected.

The new CO v0.6 data has definitely improved. The correlation coefficient has increased significantly (to 0.86), the scatter has decreased to 20.5 % (although still larger than the 6.82 % FTIR scatter) and the large summer CO values seen previously in the WFMD v0.5 Zugspitze, Kiruna, and Jungfrauoch data have all disappeared (Fig. 1). Also the previous consistent underestimation of early year 2003 data is no longer apparent.

Only for the Izaña station does one observe a deviational behaviour. The new CO v0.6 data at this station look too large at the start of the year as well as in the Sept-Oct period. For 2004 (Fig. 2), the situation is improved at Izaña but even then the Sept-Oct period looks too high.

At all the stations, the WFMD 2003 data exhibit an overall significant positive bias – see also Tables 2 and 4.

The 2004 CO v0.6 data confirm all the above, with almost identical R and σ_{scat} values. However there is a very large difference in the observed overall bias. Looking at the individual station data as listed in Table 4, this 2003-2004 bias change occurs at all stations, except for Ny Alesund. What may have caused this bias shift remains currently unclear. Also less encouraging are the July-Aug CO spikes over Zugspitze and Jungfraujoch, as seen in Fig. 2. However looking closer we see large FTIR CO values at the Jungfraujoch station as well during that month, so attributing this offset to an error on behalf of the WFMD algorithm would be premature.

Table 2. Summary of the statistical results of comparisons between SCIAMACHY and FTIR g-b data for CO over all stations: Bias is the calculated weighted bias (in %, see Eq. 2), using the small grid (SG = $\pm 2.5^\circ$ LAT, $\pm 5^\circ$ LON) and large grid (LG = $\pm 2.5^\circ$ LAT, $\pm 10^\circ$ LON) spatial collocation criteria. The indicated errors represent the weighted standard errors of the ensemble of individual weighted biases (see Eq. 3). N is the number of correlative individual SCIAMACHY data. σ_{scat} is the percentage 1σ weighted standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit (see Eq. 4). R is the correlation coefficient between the monthly mean SCIAMACHY and FTIR data.

CO	v0.5 yr 2003	v0.6 yr 2003	v0.6 yr 2004
LG Bias	-2.42 \pm 0.85	9.17 \pm 0.58	0.49 \pm 0.67
LG σ_{scat}	22.3	20.5	21.0
LG R	0.52	0.86	0.83
LG N	19293	29553	20132
SG Bias	-2.72 \pm 1.27	7.94 \pm 0.88	0.24 \pm 1.01
SG σ_{scat}	27.9	22.9	23.5
SG R	0.43	0.83	0.76
SG N	9166	13639	9141

6.2. CH₄

Version 0.5 Methane showed a substantial solar zenith angle dependence for which it had to be corrected. The results shown here for the v0.5 data regard the corrected

data product. As one can see in Table 3 both R and σ_{scat} have improved significantly with the new v1.0 data, the latter coming ever closer to the 1% target precision (as well as the 0.90 % FTIR scatter). The rather substantial negative bias however still remains unchanged. This bias makes it hard to assess any structural deviations in the monthly time series (Figs. 3 and 4). All in all, the seasonality is captured rather well although for Jungfraujoch (and less apparent for Harestua and Bremen) WFMD seems to significantly overestimate this seasonality.

Table 3. Summary of the statistical results of comparisons between SCIAMACHY and FTIR g-b data for XCH₄ over all stations Bias is the calculated weighted bias (in %, see Eq. 2), using the small grid (SG = $\pm 2.5^\circ$ LAT, $\pm 5^\circ$ LON) and large grid (LG = $\pm 2.5^\circ$ LAT, $\pm 10^\circ$ LON) spatial collocation criteria. The indicated errors represent the weighted standard errors of the ensemble of individual weighted biases (see Eq. 3). N is the number of correlative individual SCIAMACHY data. σ_{scat} is the percentage 1σ weighted standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit (see Eq. 4). R is the correlation coefficient between the monthly mean SCIAMACHY and FTIR data.

CH ₄	v0.5 yr 2003	v1.0 yr 2003	v1.0 yr 2004
LG Bias	-3.45 \pm 0.05	-2.70 \pm 0.04	-3.50 \pm 0.05
LG σ_{scat}	1.75	1.40	1.40
LG R	0.55	0.65	0.66
LG N	33958	21331	10651
SG Bias	-3.52 \pm 0.07	-2.45 \pm 0.06	-3.23 \pm 0.09
SG σ_{scat}	1.85	1.49	1.50
SG R	0.64	0.70	0.68
SG N	16041	9020	4108

7. CONCLUSIONS

We have presented the new validation results for the WFM-DOAS retrieval algorithm products, CO (v0.6) and CH₄ (v1.0) using data from a European harmonized FTIR network. For algorithm intercomparison purposes we have also compared the old v0.5 datasets with the same FTIR dataset. The results, while still in a preliminary phase, clearly show that, while the ideal target precisions are not yet reached, the data has become more robust, and several issues in the old dataset (such as the CH₄ solar zenith angle dependence) have been solved.

Table 4. Statistical results of comparisons between SCIAMACHY and FTIR g-b data for CO for the individual stations. Bias is the calculated weighted bias (in %, see Eq. 2) of the SCIAMACHY data relative to the 3rd order polynomial fit through the ground based FTIR data for CO, using the small grid (SG = $\pm 2.5^\circ$ LAT, $\pm 5^\circ$ LON) and large grid (LG = $\pm 2.5^\circ$ LAT, $\pm 10^\circ$ LON) spatial collocation criteria. The indicated errors represent the weighted standard errors of the ensemble of individual weighted biases (see Eq. 3). N is the number of correlative individual SCIAMACHY data. σ_{scat} is the percentage 1σ weighted standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit (see Eq. 4).

		CO v0.5 2003 SG	CO v0.5 2003 LG	CO v0.6 2003 SG	CO v0.6 2003 LG	CO v0.6 2004 SG	CO v0.6 2004 LG
Ny Alesund	Bias	-8.20 ± 3.15	-8.50 ± 2.22	1.14 ± 2.55	1.04 ± 1.73	3.75 ± 3.58	3.29 ± 2.39
	N	1035	2131	1329	2715	864	1876
	σ_{scat}	21.6	16.7	20.4	16.1	25.1	23.9
Kiruna	Bias	-7.69 ± 3.78	-8.26 ± 2.55	2.88 ± 3.10	3.34 ± 2.08	-1.44 ± 3.58	-0.29 ± 2.60
	N	994	1956	1144	2352	830	1555
	σ_{scat}	30.4	21.9	25.5	21.8	26.3	21.3
Harestua	Bias	-2.64 ± 3.53	-4.83 ± 2.62	9.17 ± 2.51	8.25 ± 1.86	3.96 ± 2.72	4.88 ± 2.07
	N	1035	1847	1334	2449	1206	2055
	σ_{scat}	29.2	26.1	23.5	22.4	19.8	19.9
Bremen	Bias	-3.89 ± 2.78	-4.71 ± 1.99	4.91 ± 1.91	5.96 ± 1.39	-1.32 ± 2.31	-1.36 ± 1.61
	N	1512	2983	2349	4561	1508	3213
	σ_{scat}	26.23	20.4	23.4	21.3	25.4	23.6
Zugspitze	Bias	-3.50 ± 3.37	-1.03 ± 2.27	12.8 ± 2.28	13.4 ± 1.53	0.53 ± 2.97	0.70 ± 2.06
	N	1457	3265	2393	5160	1273	2588
	σ_{scat}	27.7	20.9	23.0	20.8	26.9	23.9
Jungfraujoch	Bias	-2.29 ± 3.28	-1.43 ± 2.28	8.50 ± 2.28	8.59 ± 1.60	-3.91 ± 2.31	-3.67 ± 1.50
	N	1584	3354	2419	4924	1756	3841
	σ_{scat}	26.1	23.3	24.1	21.6	23.8	20.3
Izaña	Bias	7.94 ± 3.53	5.23 ± 1.88	10.6 ± 1.90	13.2 ± 1.07	0.90 ± 2.11	1.30 ± 1.22
	N	1493	3757	2671	7392	1684	4974
	σ_{scat}	32.4	24.5	19.7	18.1	17.5	16.0

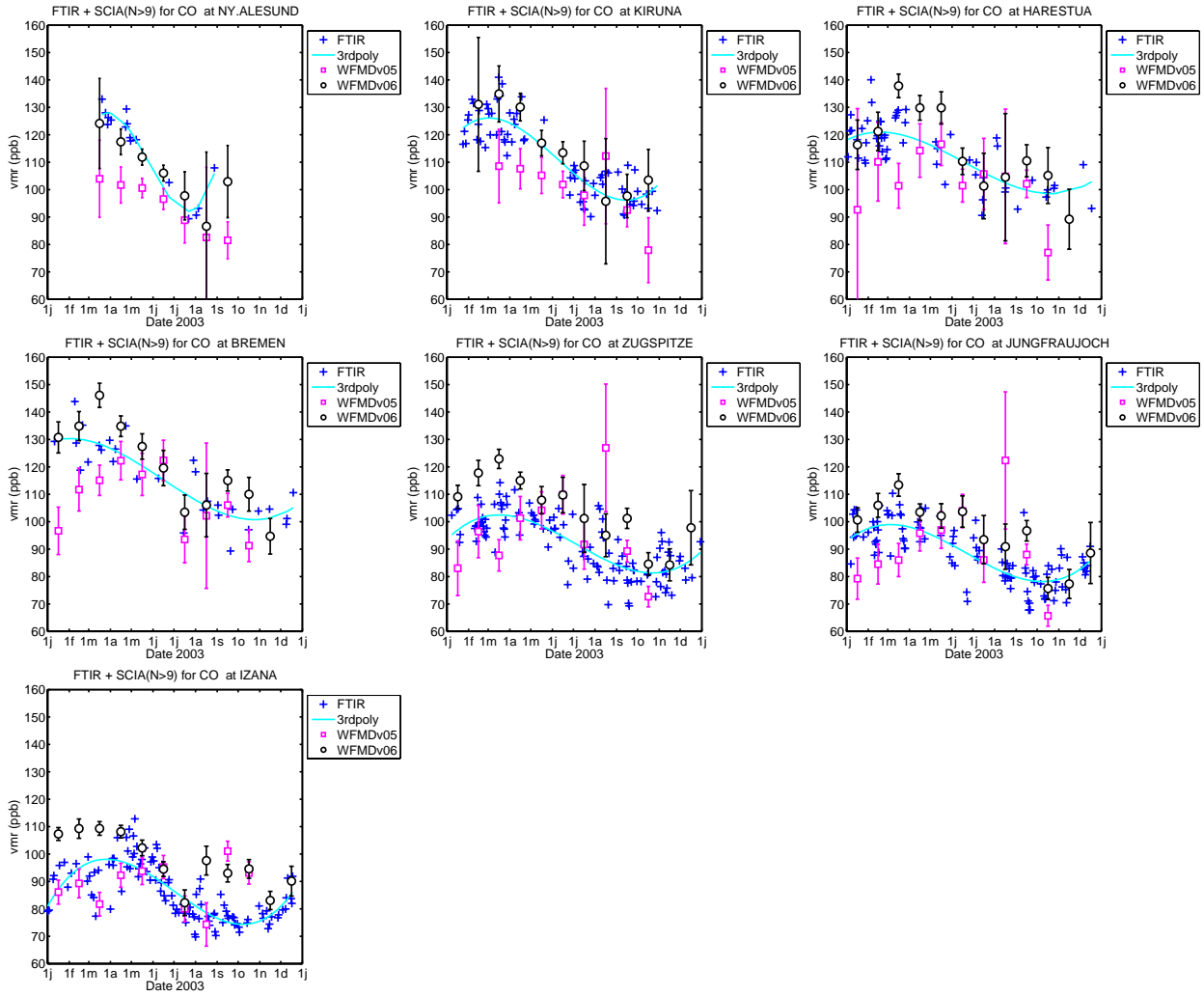


Figure 1. Weighted monthly mean vmrs for CO at all 7 stations as a function of time for the year 2003, for the WFM-DOAS v0.5 and v0.6 algorithms together with the daily averaged FTIR measurements and corresponding 3rd order polynomial fit. The large grid was chosen for the spatial collocation criteria. The error bars on the monthly mean values represent the standard error, see Eq. 5. No monthly mean data is shown for months which contained fewer than 10 SCIAMACHY measurements.

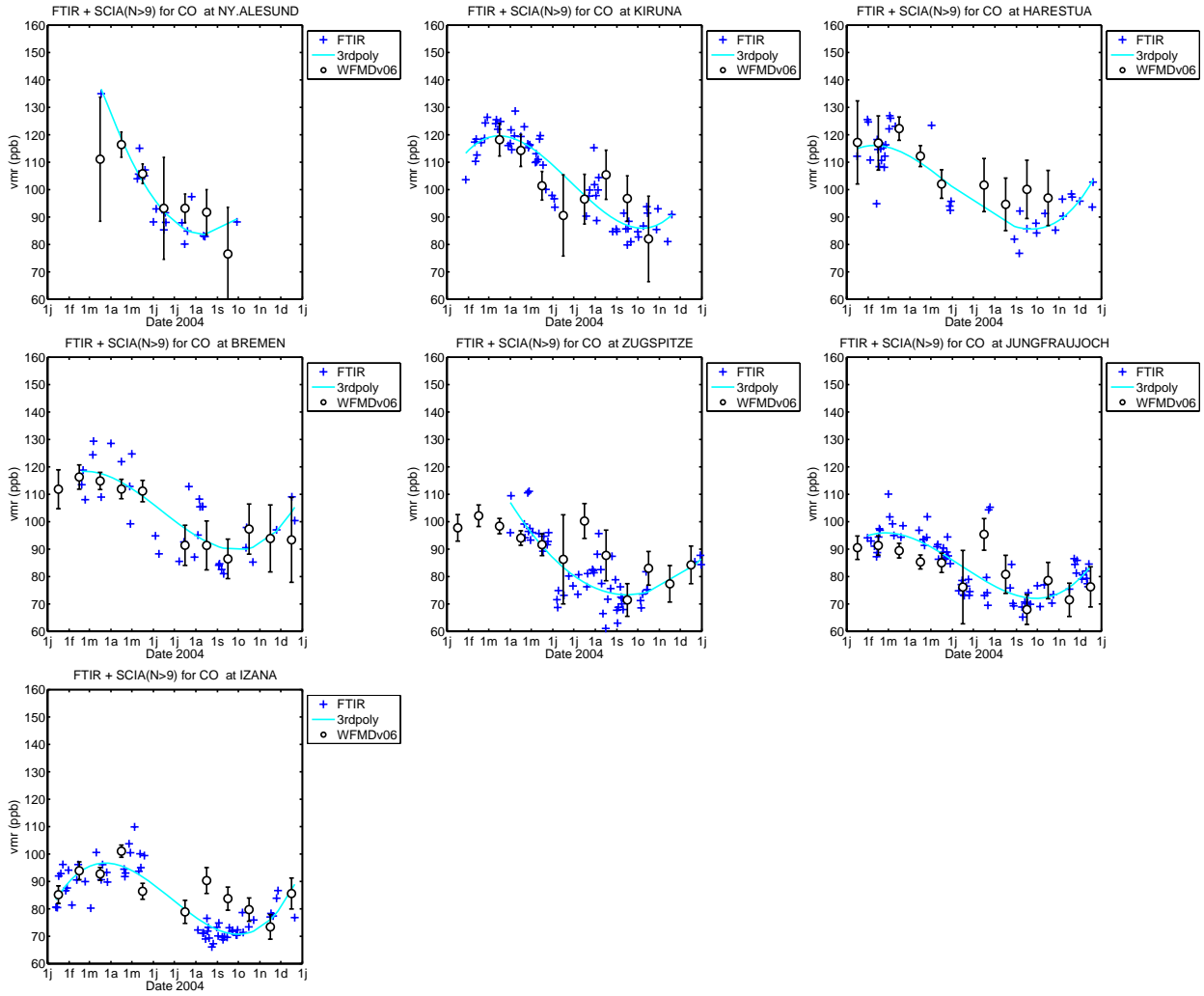


Figure 2. Weighted monthly mean vmrs for CO at all 7 stations as a function of time for the year 2004, for the WFM-DOAS v0.6 algorithm together with the daily averaged FTIR measurements and corresponding 3rd order polynomial fit. The large grid was chosen for the spatial collocation criteria. The error bars on the monthly mean values represent the standard error, see Eq. 5. No monthly mean data is shown for months which contained fewer than 10 SCIAMACHY measurements.

Table 5. Statistical results of comparisons between SCIAMACHY and FTIR g-b data for XCH₄ for the individual stations. Bias is the calculated weighted bias (in %, see Eq. 2) of the SCIAMACHY data relative to the 3rd order polynomial fit through the ground based FTIR data for CO, using the small grid (SG = ± 2.5° LAT, ± 5° LON) and large grid (LG = ± 2.5° LAT, ± 10° LON) spatial collocation criteria. The indicated errors represent the weighted standard errors of the ensemble of individual weighted biases (see Eq. 3). N is the number of correlative individual SCIAMACHY data. σ_{scat} is the percentage 1 σ weighted standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit (see Eq. 4).

		CH ₄ v0.5 2003 SG	CH ₄ v0.5 2003 LG	CH ₄ v1.0 2003 SG	CH ₄ v1.0 2003 LG	CH ₄ v1.0 2004 SG	CH ₄ v1.0 2004 LG
Ny Alesund	Bias	0.23 ± 1.68	-1.14 ± 1.17	-1.36 ± 1.29	-1.49 ± 1.34	/	/
	N	39	90	9	13	0	0
	σ_{scat}	1.77	2.59	0.62	0.53	/	/
Kiruna	Bias	-2.49 ± 0.23	-2.07 ± 0.17	-1.34 ± 0.39	-1.20 ± 0.28	-2.00 ± 0.82	-1.68 ± 0.75
	N	2600	4486	296	557	79	101
	σ_{scat}	2.38	2.20	1.77	1.68	2.00	1.81
Harestua	Bias	-2.50 ± 0.27	-2.33 ± 0.25	-1.17 ± 0.34	-0.84 ± 0.28	-2.49 ± 0.47	-2.53 ± 0.43
	N	1848	2186	390	580	245	284
	σ_{scat}	2.43	2.34	2.12	1.96	1.76	1.80
Bremen	Bias	-3.05 ± 0.13	-2.87 ± 0.10	-2.21 ± 0.20	-2.09 ± 0.16	-3.51 ± 0.38	-3.21 ± 0.23
	N	2576	4961	769	1287	273	631
	σ_{scat}	1.52	1.48	1.60	1.79	1.98	1.77
Zugspitze	Bias	-5.08 ± 0.13	-4.51 ± 0.07	-3.39 ± 0.12	-3.21 ± 0.07	-3.36 ± 0.19	-3.16 ± 0.13
	N	3879	9313	2162	5016	784	1789
	σ_{scat}	1.52	1.07	1.36	1.16	1.05	0.99
Jungfraujoch	Bias	-3.60 ± 0.12	-3.07 ± 0.08	-1.60 ± 0.10	-1.40 ± 0.08	-2.64 ± 0.19	-2.44 ± 0.13
	N	4247	8525	2830	5199	1092	2156
	σ_{scat}	1.29	1.33	1.48	1.33	1.70	1.53
Izaña	Bias	-4.45 ± 0.12	-5.19 ± 0.08	-2.93 ± 0.08	-3.35 ± 0.04	-3.64 ± 0.10	-4.02 ± 0.05
	N	852	4397	2564	8679	1635	5690
	σ_{scat}	1.18	1.33	1.16	0.10	1.20	1.16

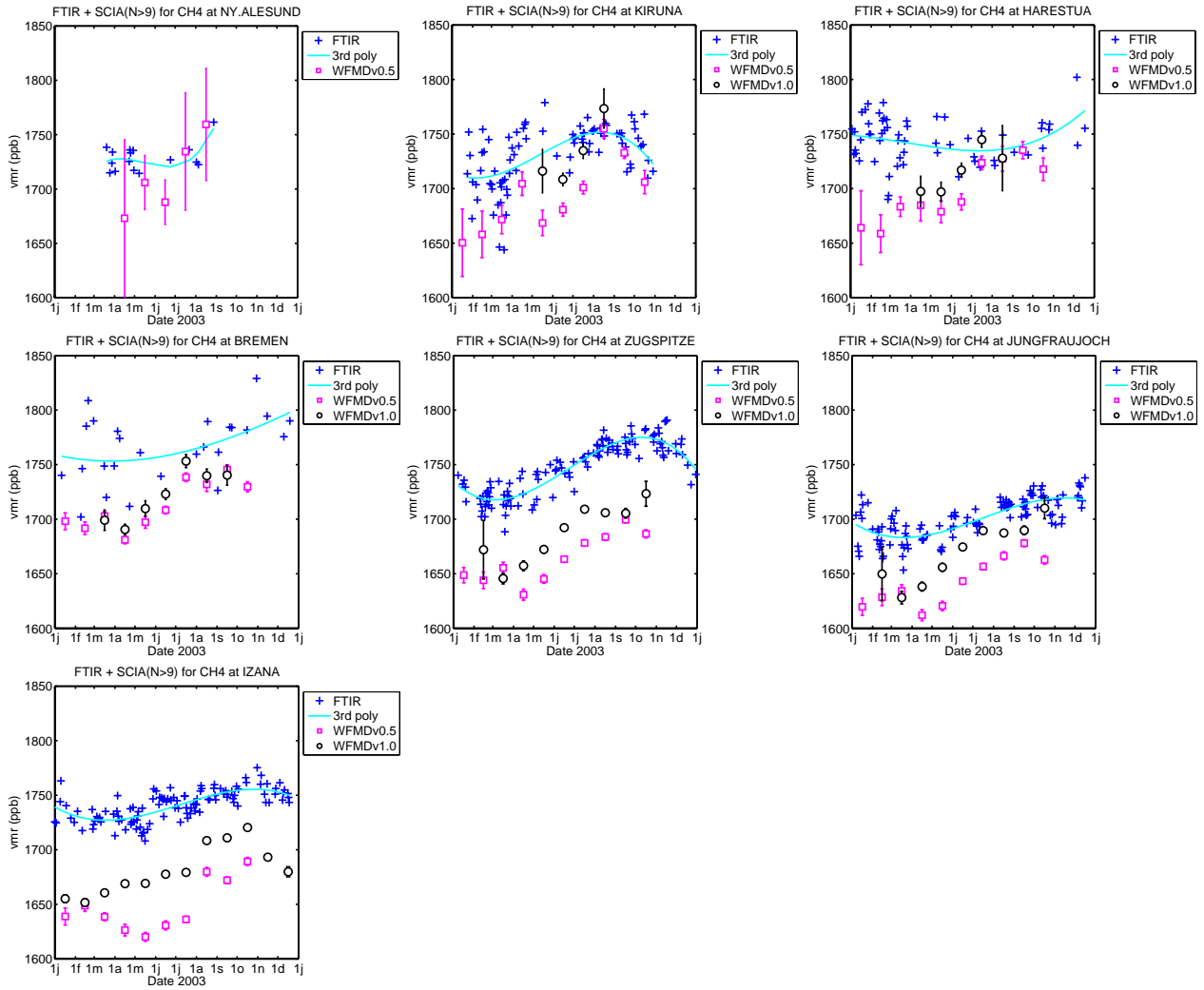


Figure 3. Weighted monthly mean vmrs for CH₄ at all 7 stations as a function of time for the year 2003, for the WFM-DOAS v0.5 and v1.0 algorithms together with the daily averaged FTIR measurements and corresponding 3rd order polynomial fit. The large grid was chosen for the spatial collocation criteria. The error bars on the monthly mean values represent the standard error, see Eq. 5. No monthly mean data is shown for months which contained fewer than 10 SCIAMACHY measurements.

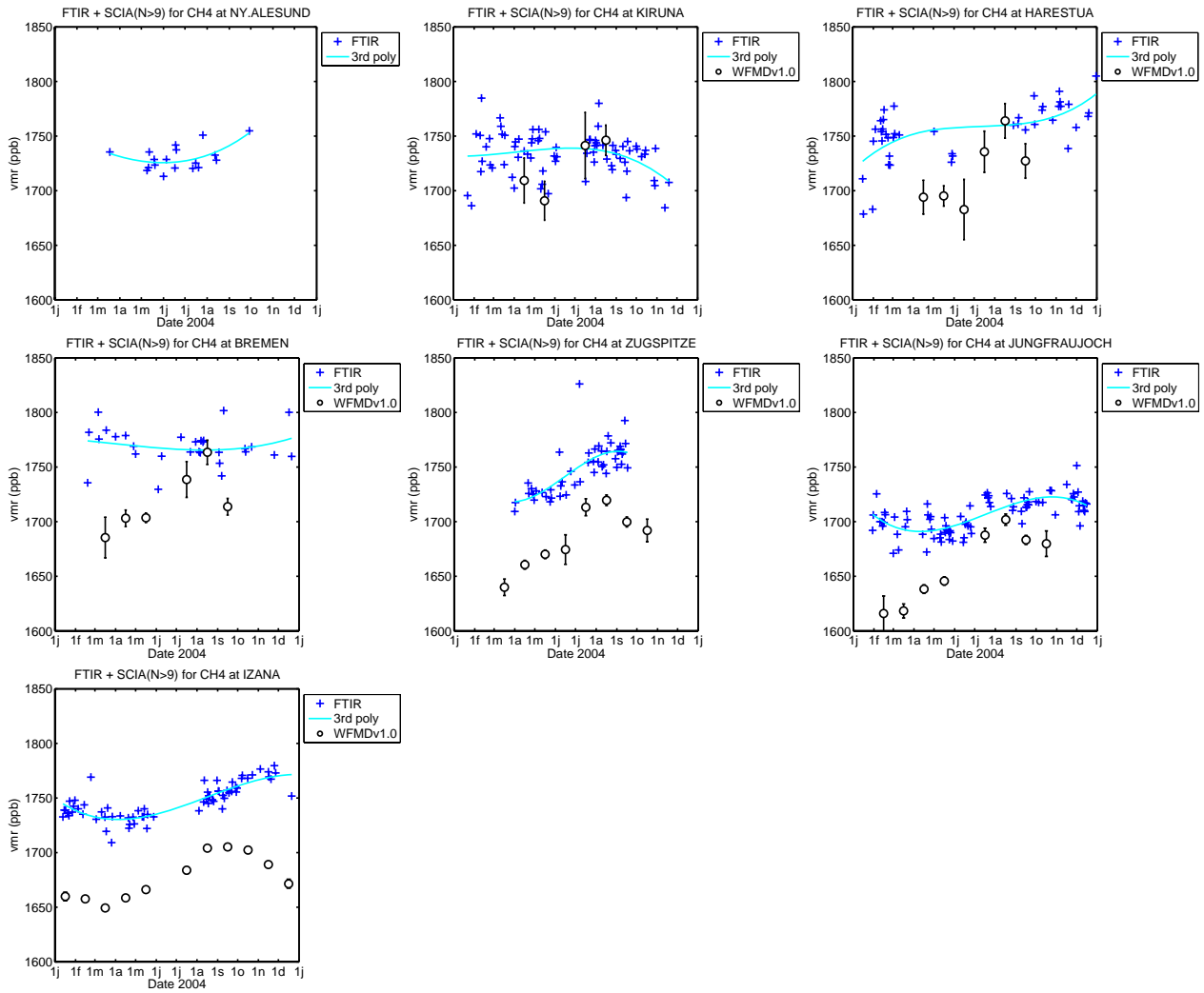


Figure 4. Weighted monthly mean vmrs for CH_4 at all 7 stations as a function of time for the year 2004, for the WFM-DOAS v1.0 algorithm together with the daily averaged FTIR measurements and corresponding 3rd order polynomial fit. The large grid was chosen for the spatial collocation criteria. The error bars on the monthly mean values represent the standard error, see Eq. 5. No monthly mean data is shown for months containing fewer than 10 SCIAMACHY measurements.

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REFERENCES

1. Buchwitz, M., R. de Beek, S. Noël, J. P. Burrows, H. Bovensmann, O. Schneising, I. Khlystova, M. Bruns, H. Bremer, P. Bergamaschi, S. Körner, and M. Heimann, Atmospheric carbon gases retrieved from SCIAMACHY by WFM-DOAS: version 0.5 CO and CH₄ and impact of calibration improvements on CO₂ retrieval, *Atmos. Chem. Phys.*, 6, 2727-2751, 2006.
2. Dils, B., M. De Mazière, J. F. Müller, T. Blumenstock, M. Buchwitz, R. de Beek, P. Demoulin, P. Duchatelet, H. Fast, C. Frankenberg, A. Gloudemans, D. Griffith, N. Jones, T. Kerzenmacher, E. Mahieu, J. Mellqvist, S. Mikuteit, R. L. Mittermeier, J. Notholt, H. Schrijver, D. Smale, A. Strandberg, W. Stremme, K. Strong, R. Sussmann, J. Taylor, M. van den Broek, T. Warneke, A. Wiacek, S. Wood., Comparisons between SCIAMACHY and groundbased FTIR data for total columns of CO, CH₄, CO₂ and N₂O, *Atmos. Chem. Phys.*, 6, 1953-1967, 2006.
3. Burrows, J. P., Hölzle, E., Goede, A. P. H., Visser H., and Fricke, W.: SCIAMACHY – Scanning Imaging Absorption Spectrometer for Atmospheric Cartography, *Acta Astronautica*, 35(7), 445–451, 1995.
4. Bovensmann, H., J. P. Burrows, M. Buchwitz, J. Frerick, S. Noël, V. V. Rozanov, K. V. Chance, and A. H. P. Goede, SCIAMACHY – Mission objectives and measurement modes, *J. Atmos. Sci.*, 56, (2), 127-150, 1999.
5. Drummond, J.R., and Mand, .G. S.: The Measurements of Pollution in the Troposphere (MOPITT) instrument: Overall performance and calibration requirements, *J. Atmos. Ocean. Tech.*, 13, 314-320, 1996
6. Buchwitz, M., V.V. Rozanov, and J.P. Burrows, A near-infrared optimized DOAS method for the fast global retrieval of atmospheric CH₄, CO, CO₂, H₂O, and N₂O total column amounts from SCIAMACHY Envisat-1 nadir radiances, *J. Geophys. Res.* 105, 15,231-15,245, 2000.
7. Buchwitz, M., R. de Beek, K. Bramstedt, S. Noël, H. Bovensmann, and J. P. Burrows, Global carbon monoxide as retrieved from SCIAMACHY by WFM-DOAS, *Atmos. Chem. Phys.*, 4, 1945-1960, 2004.
8. Buchwitz, M., R. de Beek, J. P. Burrows, H. Bovensmann, T. Warneke, J. Notholt, J. F. Meirink, A. P. H. Goede, P. Bergamaschi, S. Körner, M. Heimann, and A. Schulz, Atmospheric methane and carbon dioxide from SCIAMACHY satellite data: initial comparison with chemistry and transport models, *Atmos. Chem. Phys.*, 5, 941- 962, 2005.
9. Buchwitz, M., R. de Beek, S. Noël, J. P. Burrows, H. Bovensmann, H. Bremer, P. Bergamaschi, S. Körner, and M. Heimann, Carbon monoxide, methane and carbon dioxide columns retrieved from SCIAMACHY by WFM-DOAS: year 2003 initial data set, *Atmos. Chem. Phys.*, 5, 3313-3329, 2005.
10. Buchwitz, M., Khlystova, I., Schneising, O., Bovensmann, H. and Burrows, J.P., SCIAMACHY/WFM-DOAS Tropospheric CO, CH₄, and CO₂ scientific data products: Validation and recent developments, this issue (Third Workshop on the Atmospheric Chemistry Validation of ENVISAT (ACVE-3), 4-7 Dec. 2006, ESA/ESRIN, Frascati, Italy, to appear as ESA Publications Division Special Publication SP-642 (CD)), 2006.
11. Gloudemans, A. M. S., Schrijver, H., Kleipool, Q., van den Broek, M. M. P., Straume, A. G., Lichtenberg, G., van Hees, R. M., Aben, I., and Meirink, J. F.: The impact of SCIAMACHY near-infrared instrument calibration on CH₄ and CO total columns, *Atmos. Chem. Phys.*, 5, 2369-2383, 2005
12. Frankenberg, C., J. F. Meirink, M. van Weele, U. Platt, T. Wagner, Assessing methane emissions from global spaceborne observations, *Science*, 308, 1010-8438, 2005.
13. Meirink, J.F., Eskens, H.J. and Goede, A.P.H.: Sensitivity analysis of methane emissions derived from SCIAMACHY observations through inverse modelling, *Atmos. Chem. Phys. Discuss.*, 5, 9405-9445, 2005
14. 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.
15. 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.