Geophysical Validation of SCIAMACHY: 2002-2004

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ACP - Special Issue

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Overview of SCIAMACHY validation: 2002–2004

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Abstract. SCIAMACHY, on board Envisat, has been in operation now for almost three years. This UV/visible/NIR spectrometer measures the solar irradiance, the earthshine radiance scattered at nadir and from the limb, and the attenuation of solar radiation by the atmosphere during sunrise and sunset, from 240 to 2380 nm and at moderate spectral resolution. Vertical columns and profiles of a variety of atmospheric constituents are inferred from the SCIAMACHY radiometric measurements by dedicated retrieval algorithms. With the support of ESA and several international partners, a methodical SCIAMACHY validation programme has been developed jointly by Germany, the Netherlands and Belgium (the three instrument providing countries) to face complex requirements in terms of measured species, altitude range, spatial and temporal scales, geophysical states and intended scientific applications. This summary paper describes the approach adopted to address those requirements.

Since provisional releases of limited data sets in summer 2002, operational SCIAMACHY processors established at DLR on behalf of ESA were upgraded regularly and some data products – level-1b spectra, level-2 O3, NO2, BrO and clouds data – have improved significantly. Validation results summarised in this paper and also reported in this special issue conclude that for limited periods and geographical domains they can already be used for atmospheric research. Nevertheless, current processor versions still experience known limitations that hamper scientific usability in other periods and domains. Free from the constraints of operational processing, seven scientific institutes (BIRA-IASB, IFE/IUP-Bremen, IUP-Heidelberg, KNMI, MPI, SAO and SRON) have developed their own retrieval algorithms and generated SCIAMACHY data products, together addressing nearly all targeted constituents. Most of the UV-visible data products – O3, NO2, SO2, H2O total columns; BrO, OCIO slant columns; O3, NO2, BrO profiles – already have acceptable, if not excellent, quality. Provisional near-infrared column products – CO, CH4, N2O and CO2 – have already demonstrated their potential for a variety of applications. Cloud and aerosol parameters are retrieved, suffering from calibration with the exception of cloud cover. In any case, scientific users are advised to read carefully validation reports before using the data. It is required and anticipated that SCIAMACHY validation will continue throughout instrument lifetime and beyond and will accompany regular processor upgrades.

1 Introduction

SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY) is a spectrometer on-board ESA’s Environmental Satellite Envisat launched on 1 March 2002. SCIAMACHY measures sunlight reflected or transmitted by the Earth’s atmosphere in the ultraviolet, visible, and near-infrared wavelength region (240–2380 nm) at moderate spectral resolution. SCIAMACHY observes earthshine radiance in limb and nadir viewing geometry and solar and lunar light transmitted through the atmosphere in occultation viewing geometry.

The primary objective of the SCIAMACHY mission is to improve our knowledge of the chemistry and physics of the Earth’s atmosphere (troposphere, stratosphere, and mesosphere), including anthropogenic changes or the variability of natural phenomena. SCIAMACHY’s contribution are vertical and horizontal distributions of atmospheric constituents and parameters such as trace gases, aerosols, cloud information, temperature and pressure. Specific topics for SCIAMACHY’s scientific mission are:

– stratospheric ozone chemistry, including the verification of expected effects of the Montreal Protocol and
Fig. 1. Overview of SCIAMACHY operations between March 2002 and April 2005. Green denotes periods with nominal measurements, blue are the periods where the instrument was heated to evaporate the ice layer on the detectors (the near infra-red channels cannot be used during this period for retrieval of CO, CH$_4$, N$_2$O, CO$_2$), yellow are periods where Envisat was off, red are the periods where SCIAMACHY was off. Courtesy: C. Chlebek, DLR.

Table 1. Availability of the anticipated level 2 products from SCIAMACHY. Note that some of the “recommended” products are in fact included in the operational data files, but they have no geophysical meaning yet. “NRT”: near-real time; “OL”: offline (see Sect. 5); “av”: available; “glob”: larger or global dataset; “rec”: recommended, not available; “cs”: few case study periods; “dev”: under development; “–”: not planned or development not started.

<table>
<thead>
<tr>
<th>Product</th>
<th>spectral region</th>
<th>operational</th>
<th>scientific</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$ column</td>
<td>UV/vis</td>
<td>av</td>
<td>av glob</td>
</tr>
<tr>
<td>NO$_2$ column</td>
<td>UV/vis</td>
<td>av</td>
<td>av glob</td>
</tr>
<tr>
<td>BrO column</td>
<td>UV/vis</td>
<td>av av</td>
<td>glob</td>
</tr>
<tr>
<td>SO$_2$ column</td>
<td>UV/vis</td>
<td>rec rec</td>
<td>glob</td>
</tr>
<tr>
<td>OClO column</td>
<td>UV/vis</td>
<td>rec rec</td>
<td>glob</td>
</tr>
<tr>
<td>HCHO column</td>
<td>UV/vis</td>
<td>rec rec</td>
<td>dev</td>
</tr>
<tr>
<td>H$_2$O column</td>
<td>UV/vis,NIR</td>
<td>rec rec</td>
<td>cs</td>
</tr>
<tr>
<td>N$_2$O column</td>
<td>UV/vis</td>
<td>rec rec</td>
<td>cs</td>
</tr>
<tr>
<td>CO column</td>
<td>UV/vis</td>
<td>rec rec</td>
<td>cs</td>
</tr>
<tr>
<td>CO$_2$ column</td>
<td>UV/vis</td>
<td>rec rec</td>
<td>cs</td>
</tr>
<tr>
<td>CH$_4$ column</td>
<td>UV/vis</td>
<td>rec rec</td>
<td>cs</td>
</tr>
<tr>
<td>cloud cover</td>
<td>UV/vis</td>
<td>av av</td>
<td>glob</td>
</tr>
<tr>
<td>cloud top height</td>
<td>UV/vis</td>
<td>rec rec</td>
<td>glob</td>
</tr>
<tr>
<td>AAI</td>
<td>UV/vis,NIR</td>
<td>rec rec</td>
<td>cs</td>
</tr>
<tr>
<td>AOT</td>
<td>UV/vis,NIR</td>
<td>rec rec</td>
<td>cs</td>
</tr>
<tr>
<td>O$_3$ profile</td>
<td>UV/vis</td>
<td>–</td>
<td>av glob</td>
</tr>
<tr>
<td>NO$_2$ profile</td>
<td>UV/vis</td>
<td>–</td>
<td>av glob</td>
</tr>
<tr>
<td>BrO profile</td>
<td>UV/vis</td>
<td>–</td>
<td>glob</td>
</tr>
<tr>
<td>OClO profile</td>
<td>UV/vis</td>
<td>–</td>
<td>rec glob</td>
</tr>
<tr>
<td>H$_2$O profile</td>
<td>UV/vis,NIR</td>
<td>–</td>
<td>rec dev</td>
</tr>
<tr>
<td>CO$_2$ profile</td>
<td>UV/vis</td>
<td>–</td>
<td>rec cs</td>
</tr>
<tr>
<td>CO profile</td>
<td>NIR</td>
<td>–</td>
<td>rec –</td>
</tr>
<tr>
<td>CH$_4$ profile</td>
<td>NIR</td>
<td>–</td>
<td>rec –</td>
</tr>
<tr>
<td>N$_2$O profile</td>
<td>NIR</td>
<td>–</td>
<td>rec –</td>
</tr>
<tr>
<td>CO profile</td>
<td>NIR</td>
<td>–</td>
<td>rec –</td>
</tr>
<tr>
<td>pressure profile</td>
<td>UV/vis,NIR</td>
<td>–</td>
<td>rec –</td>
</tr>
<tr>
<td>temperature profile</td>
<td>UV/vis,NIR</td>
<td>–</td>
<td>rec –</td>
</tr>
<tr>
<td>aerosol profile</td>
<td>UV/vis,NIR</td>
<td>–</td>
<td>rec –</td>
</tr>
</tbody>
</table>

Amendments on future developments of the ozone layer;
- climate research by observation of radiatively active species and transport tracers important for understanding global warming, like greenhouse gases, aerosols, and clouds;
- tropospheric pollution associated with industrial activity, urban concentration and biomass burning;
- troposphere-stratosphere exchange processes;
- monitoring and understanding of special events and hazards such as volcanic eruptions, solar proton events, and related regional and global consequences.

A complete description of SCIAMACHY and its mission can be found in Bovensmann et al. (1999) and references therein.

SCIAMACHY has been in operation for more than three years now, and is a very stable instrument with only few short periods of “off-time” as was shown by Chlebek et al. (2004), see Fig. 1. The detectors are regularly heated up (decontamination) to evaporate a small ice layer on the NIR detectors.

A number of instrumental and calibration issues are known to affect the quality of the retrieved trace gases. The issues which are currently (April 2005) believed to affect the retrievals most are (Lichtenberg et al., 2005): 1) a radiance offset and a different irradiance offset, 2) insufficient polarisation correction, 3) errors in calibration of NIR detectors (channel 7 light leak, changing “slit function”, thermal contribution to dark current).

The currently retrieved SCIAMACHY level 2 data products are listed in Table 1. The main objective of the validation is to accompany each of these products by a complete description of the systematic and random deviations from other well-established measurement systems, formulated in such a way that it is of direct use for algorithm improvement, instrument characterisation and atmospheric research.
To achieve this, we need: (1) a large amount of suitable validation measurements and (2) detailed analyses of the SCIAMACHY data with respect to the validation data set. This is more than a straightforward calculation of the average bias and scatter, as is outlined in Sect. 2, where the validation methods are described.

In Sect. 3 an overview is presented of the overall organisation of the international validation of SCIAMACHY. Section 4 describes the validation measurements performed in dedicated campaigns and by regular measurement systems, often organised in global networks. The contents, availability and expected upgrades of the SCIAMACHY products are described in Sect. 5. Preliminary validation results are summarised in Sect. 6, and the necessary future validation efforts will be discussed in Sect. 7.

2 Validation methods

Satellite validation is often understood as a simple comparison exercise concluding to a once-and-for-all assessment of the difference between the satellite data being validated and a reference data set of “validated” quality. Although such comparisons are indeed the basis for investigating the quality of the satellite data, they are by no means sufficient for assessing the usefulness of the data for its intended scientific applications. Finding an agreement within estimated error bars offers no guarantee that the retrieved values contain new information coming from the measurement itself. Therefore, beyond the calculation of differences between SCIAMACHY and correlative data sets, it is recommended to use several other validation methods, each with its own potential contribution to the overall assessment of the usefulness of the data.

It is important to investigate, both qualitatively and quantitatively, how well SCIAMACHY data represents known geophysical signals that are either observed by other measurement systems or deduced from our understanding of the atmosphere. These signals may include meridional and zonal structures, vertical structures, temporal cycles on seasonal, day-to-day and diurnal scales, special events of tropospheric pollution, etc.

Geophysical (level 2) quantities are retrieved from SCIAMACHY spectra (level 1) using auxiliary data, such as output from radiative transfer models, or climatologies. Simplifications or misinterpretations therein can result in systematic errors in the retrieved quantities that may depend on geophysical, instrumental or algorithm parameters. It is important to investigate the influence of these parameter-dependent systematic errors on the intended scientific use.

Validation also plays a diagnostic role in the improvement of retrieval algorithms. Careful investigation of comparison time-series, the use of assimilation tools, and the intercomparison of SCIAMACHY data retrieved with independent algorithms have been powerful in revealing internal inconsistencies in SCIAMACHY data.

The comparison of remotely sensed geophysical quantities with correlative data is not straightforward. A major difficulty results from the convolution of atmospheric variability with the smoothing/scanning properties inherent to the remote sensing approach. Different observation techniques and retrieval methods yield different sampling of the atmosphere in time and in space, different averaging of its 3-dimensional structure, and different sensitivity to ancillary atmospheric and instrumental parameters. As a direct consequence of those differences in the perception of the atmospheric field, atmospheric structures and variability can critically corrupt the reliability of the comparison by introducing systematic biases and additional scatter. Therefore, sophisticated methods have been developed to deal with representativeness errors in the comparisons:

- the use of radiative transfer tools to better determine the vertical and line-of-sight smoothing of both SCIAMACHY and correlative data (modelling of slant column, weighting functions, averaging kernels);
- the use of modelling and assimilation tools to deal with transport and photochemical effects (including diurnal cycles);
- the use of meteorological analyses to discriminate the effects of dynamic variability (e.g., use of backward trajectories, transformation to equivalent latitude and isentropic coordinates);
- the synergistic use of complementary correlative data sources offering different smoothing/sampling properties, sensitivity and errors budgets.

The latter point is of great importance for SCIAMACHY validation. The SCIAMACHY data products potentially support an assortment of scientific applications, spanning from regional to global scales, from the ground up to the mesosphere, from short-term to decadal timeframes. Local studies carried out at single stations constitute the preferred approach to detailed investigation. They benefit from local research and excellent understanding of local geophysical particulars; they assure full control and accurate error budgets of the instrumentation, and the availability of adequate ancillary data. Complementary studies exploiting pseudo-global sources yield access to patterns, sensitivity and space/time structures on the global scale. Satellite-satellite intercomparisons improve the statistical significance of validation results due to the large amount of possible collocations.

3 Validation organisation

SCIAMACHY is an Announcement of Opportunity (AO) instrument provided by the AO instrument Providers (AOIPs) Germany and the Netherlands with a contribution from Belgium. In principle, the AOIPs have the responsibility for the
Fig. 2. A scheme of the SCIAMACHY validation organisational structures set-up by SCIAVALIG (orange) and by ESA (blue). The validation scientists actually doing the work are supported by both organisations, if they have an approved AO proposal for SCIAMACHY validation (green).

validation of SCIAMACHY, but since ESA has the responsibility for the operational SCIAMACHY data processor, ESA includes the validation of SCIAMACHY into their Envisat validation programme as well. The two complementary organisation structures from ESA and SCIAVALIG are illustrated in Fig. 2.

3.1 ESA’s organisation

In 1997 ESA raised an Announcement of Opportunity (AO) for the use of Envisat data. The Principal Investigators of the approved AO projects dealing with the validation of SCIAMACHY, GOMOS and MIPAS were gathered in the Atmospheric Chemistry Validation Team (ACVT). The ACVT is divided in the following subgroups:

**GBMCD:** Ground-based Measurements and Campaign Database subgroup.

**ESABC:** Envisat Stratospheric Aircraft and Balloon Campaign, and

**MASI:** Models and data Assimilation, Satellite Inter-comparisons.

A subgroup of the overall Envisat Calibration and Validation team is also the:

**SCCVT:** SCIAMACHY Calibration and Verification Team.

The ESABC subgroup is more than a working group. ESA, DLR, and CNES together financed dedicated campaigns for the validation of SCIAMACHY, MIPAS and GOMOS (Sect. 4.3). These campaigns are referred to as ESABC campaigns, and are prepared and coordinated in the ESABC group. Preparation and results of other campaigns are only presented and discussed within the ESABC group.

In addition, ESA supports a dedicated validation data centre, the NILU Atmospheric Data Base for Interactive Retrieval (NADIR), which is operated by the Norwegian Institute for Air Research (NILU). This centre hosts all correlative measurements from the dedicated Envisat validation campaigns.

3.2 SCIAVALIG’s organisation

The organisation of the validation of SCIAMACHY from the AOIP’s side is delegated to the SCIAMACHY Validation and Interpretation Group (SCIAVALIG), a subgroup of the SCIAMACHY Science Advisory Group (SSAG). SCIAVALIG consists of an international scientific consortium of representatives of 12 institutes participating in the
validation. It is chaired by the Royal Netherlands Meteorological Institute (KNMI), the Belgian Institute for Space Aeronomy (BIRA-IASB), and the University of Heidelberg (IUP-Heidelberg). SCIAVALIG has established a list of validation requirements (SCIAVALIG, 1998), defined an essential “core” validation programme (SCIAVALIG, 2002), and has set up an organisational structure for the continuous monitoring of validation results throughout the lifetime of SCIAMACHY. The core validation programme is mainly funded by the AOIPs, and is embedded in the ESA AO programme via several AO projects. The “national coordinators” of SCIAVALIG (who are the authors of this paper) are responsible for the practical coordination of this programme.

To take the best benefit of every component of the complementary efforts and structures, “product coordinators” have been appointed by SCIAVALIG to collect and digest validation results from the different contributors, address apparent inconsistencies, identify unsolved needs, and foster interaction with algorithm developing teams and processor experts for an efficient translation from validation results towards algorithm changes.

4 Correlative measurements

The core validation programme was complemented by a selection of AO projects from international partners. The major component of the SCIAMACHY validation programme consists of comparison studies with correlative measurements acquired by independent instrumentations from various platforms, namely, ground-based stations and ships, aircrafts, stratospheric balloons, and satellites.

4.1 Ground-based and ship-based instruments

Ground-based instruments provide the appropriate correlative data to fulfil four main tasks of the SCIAMACHY validation programme:

- quick validation before public release of a new product or just after the release of a near-real time product;
- detailed geophysical validation from pole to pole and for a variety of geophysical states, including dependencies on measurement and atmospheric parameters like, e.g., solar zenith angle and temperature;
- after major improvement of a retrieval algorithm, verification of correctness of changes and preliminary quality assessment of the resulting data product;
- long-term validation, including detection of trends and other time-varying features.

The list of stations providing correlative measurements for SCIAMACHY validation is given in Table 2. The nationally funded core validation programme, constituting the backbone of the validation, includes complementary types of instrumentation (see list in the next paragraph), yielding all together nearly all targeted species, and operating at about forty stations distributed from the Arctic to the Antarctic and from South America to the Indian Ocean, as indicated in Table 2. Thanks to long-lasting collaborations established mainly in the framework of WMO’s Global Atmospheric Watch programme (GAW), and particularly within its affiliated ozonometric networks (see Fioletov et al., 1999, and references therein) and the Network for the Detection of Stratospheric Change (NDSC, Lambert et al., 1999, and references therein), international partners contribute through AO projects with a long list of instruments which add significantly to the geographical coverage of the ground-based instrumentation included in the core validation programme.

The ozone column amount is monitored at a variety of ground-based stations by Dobson and Brewer ultraviolet spectrophotometers and by Russian/NIS ultraviolet filter radiometers of the M-124 design. A network of about 30 DOAS instruments, all certified for the NDSC, monitor the column amount of species absorbing in the UV-visible part of the spectrum like O₃, NO₂, BrO, OCIO, HCHO, SO₂, H₂O and IO. Some of them have multi-axis observation capabilities yielding separation of the tropospheric and stratospheric columns. Seven Fourier Transform IR spectrometers (FTIR), also carrying NDSC certification, report the vertical column amount and sometimes the vertical distribution of a bunch of species including O₃, NO₂, CO, CH₄, N₂O, CO₂, HCHO, and H₂O. Six microwave (MW) radiometers measure the thermally induced rotational emission of selected species, like O₃, H₂O and ClO. Ground-based ozone differential absorption lidars (DIAL) and/or electro-chemical ozone sondes yield the vertical distribution of tropospheric and stratospheric ozone, at high and moderate vertical resolution. Aerosol and cloud properties are recorded by lidar and aerosol instruments.

In addition to the instruments operating continuously at ground-based sites, two instruments operated on board the German Research vessel Polarstern.
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Table 2. Ground-based stations contributing to the SCIAMACHY validation effort, and associated SCIAMACHY data products. In the
column “core” is indicated when a station is used within the nationally funded core validation programme. The column “netw” identifies
stations belonging to the NDSC (“N”) and/or Russian/NIS M-124 (“R”) networks. “c”: column; “p”: profile; “ccf”: cloud cover fraction;
“ctp”: cloud top pressure; “AAI”: absorbing aerosol index.
station
Ny-Ålesund
Barentsburg
Thule
Summit
Tiksi
Scoresbysund
Andoya/Alomar
Murmansk
Kiruna
Igarka
Sodankyla
SondreStromfjord
Zhigansk
Salekhard
Pechora
Markovo
Arhangelsk
Vindeln
Reykjavik
Orlandet
Yakutsk
Jokioinen
Harestua
Gardermoen
Lerwick
Saint Petersburg
Oslo
Magadan
Vitim
Norrkoping
Ekaterinburg
Krasnoyarsk
Moscow
Zvenigorod
Obninsk
Omsk
Samara
Bremen
Nikolaevsk
Petropavlovsk
Aberystwyth
Irkutsk
Legionowo
Lindenberg
De Bilt
Bilthoven
Voronezh
Cahirciveen Valentia
Uccle
Hradec Králové
Camborne
Praha
Karaganda
Hohenpeissenberg
Zugspitze
Bern
Yuzhno Sahalinsk
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Jungfraujoch
Payerne
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Bucharest
Egbert
Monte Cimone
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78.9
78.1
76.5
72.2
71.6
70.5
69.3
69.0
67.8
67.5
67.4
67.0
67.2
66.7
65.1
64.7
64.6
64.2
64.0
63.0
62.0
60.8
60.2
60.1
60.1
60.0
59.9
59.6
59.4
58.6
56.8
56.0
55.8
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53.1
53.1
53.0
52.7
52.3
52.2
52.2
52.1
52.1
51.7
51.6
50.8
50.2
50.1
50.0
49.8
47.8
47.4
47.0
46.9
46.8
46.6
46.8
44.8
44.3
44.2
44.2
43.9
43.7

11.9
13.2
−68.8
−37.8
128.9
−22.0
16.0
33.1
20.4
86.6
26.7
−50.7
123.4
66.7
57.1
170.4
40.5
19.8
−22.6
9.0
129.6
23.5
10.8
11.0
−1.2
30.3
10.8
150.8
112.6
16.1
60.6
92.9
37.6
36.8
36.2
73.4
50.4
8.9
140.7
158.8
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Fig. 4. Route of the first Polarstern cruise (ANT XIX) between November 2001 and June 2002.

German research vessel Polarstern (Fig. 3) to facilitate the validation of SCIAMACHY measurements in remote marine regions (Fig. 4): a MAX-DOAS (Multi-Axis Differential Optical Absorption Spectroscopy) and an FTIR (Fourier Transform InfraRed) instrument. The Polarstern made three cruises within this time period: the first between November 2001 and May 2002, the second between October 2002 and February 2003, the third between October 2003 and July 2004. The moveable MAX-DOAS experiment measured constantly during all three cruises and the investigation of large scale latitudinal cross-sections of atmospheric trace gases were done. The FTIR instrument was operating during the second and third campaign from Bremerhaven to Africa.
4.2 Airborne campaigns

The German aircraft validation activities were concentrated on missions with the meteorological research aircraft Falcon 20 (D-CMET) operated by the German Aerospace Center (DLR). Many features make the Falcon an excellent aircraft for the validation experiment. Three large optical windows, two in the bottom and one in the roof enable operation of large lidar experiments both for tropospheric and stratospheric research. Specially manufactured polyethylene windows allow remote sensing in the microwave spectral region. The aircraft carries a data acquisition system and an extensive instrument package capable of measuring position, altitude, static pressure and temperature.

Within the SCIA-VALUE (SCIamachy VALidation and Utilization Experiment) project two major campaigns with 28 flights were flown in September 2002 and February/March 2003, see Fig. 5. Both campaigns consisted of large-scale latitudinal cross-sections from the polar regions to the tropics as well as longitudinal cross-sections at polar latitudes. To validate SCIAMACHY, three different types of remote sensing instruments were installed on board the Falcon 20 (Fig. 6). The AMAXDOAS (Airborne Multi-Axis Differential Optical Absorption Spectrometer), which is an experiment developed jointly by the Universities of Heidelberg and Bremen, is able to measure tropospheric and stratospheric columns of key gases like O$_3$, NO$_2$, BrO and OClO absorbing in the UV-visible wavelength range. ASUR (Airborne SUbmillimeter Radiometer) operated by the University of Bremen is a passive microwave sensor. A broad range of molecular lines can be detected containing the molecules that play an important role in the catalytic destruction of ozone. The frequency band includes emission lines of O$_3$, ClO, HCl, HNO$_3$, N$_2$O, H$_2$O, HO$_2$, CH$_3$Cl, NO, HCN, and BrO. The Ozone Lidar Experiment (OLEX) developed and operated by DLR complete the scientific payload of the Falcon. In the zenith looking mode this instrument provides high resolution two-dimensional cross-sections of ozone number densities, aerosol extinction, and cirrus cloud cover information from about 2 km above aircraft flight level up to a height of 30 km (Fix et al., 2005).

The stratospheric research aircraft M55-Geophysica is also involved in Envisat validation. It performed two mid-latitude campaigns in July and October 2002 from a basis in Forli, Italy and a high latitude campaign in January and March 2003 in Kiruna. For the Envisat validation flights, the M55 was equipped with two sets of instruments. The so-called chemical flights are performed with six in-situ and one remote-sensing instrument, able to measure, among others, concentrations of H$_2$O, O$_3$, NO, NO$_2$, N$_2$O, CH$_4$, BrO, and columns of O$_3$, and NO$_2$ (Kostadinov et al., 2003; Heland...
et al., 2003). For the the so-called cloud/aerosol flights, the remote-sensing instrument was replaced by six instruments for the characterisation of aerosol and cloud properties. Although the in-situ instruments remain on-board, these flights were optimised for measuring the cloud and aerosol properties.

Within the MOZAIC program (Marenco et al., 1998) started in 1994, five long-range Airbus A340 aircrafts are equipped with in situ-instruments measuring $O_3$, $H_2O$, $CO$ and $NO_y$. They provide data from all over the world along the flight tracks at the upper troposphere, lower stratosphere altitude level from 9–12 km and down to the ground around 60 airports. These measurements are a unique dataset at the tropopause region and will be useful especially for development and validation of products distinguishing between troposphere and stratosphere.

Table 3. Balloon launches used for SCIAMACHY validation.

<table>
<thead>
<tr>
<th>Payload</th>
<th>Launch dates</th>
<th>Launch site</th>
<th>Target species</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIPAS-B</td>
<td>24 Sep 2002</td>
<td>Aire sur l’Adour, France</td>
<td>$O_3$, $NO_2$, $H_2O$, $CO$, $CO_2$, temperature, pressure</td>
</tr>
<tr>
<td>PI: Fischer</td>
<td>7 Dec 2002</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 March 2003</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 July 2003</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td>TRIPLE</td>
<td>24 Sep 2002</td>
<td>Aire sur l’Adour, France</td>
<td>$CO_2$, $CH_4$, $NO_2$, $N_2O$, $H_2O$, $BrO$</td>
</tr>
<tr>
<td>PI: Fischer</td>
<td>6 March 2004</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 June 2004</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td>LPMA-DOAS</td>
<td>18 Aug 2002</td>
<td>Kiruna, Sweden</td>
<td>$O_3$, $NO_2$, OCIO, BrO, $CH_4$, $N_2O$, $H_2O$, $CO$, temperature, pressure, irradiance</td>
</tr>
<tr>
<td>PI: Camy-Peyret</td>
<td>9 March 2003</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23 March 2003</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 Oct 2003</td>
<td>Aire sur l’Adour, France</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 March 2004</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td>SAOZ-MIR</td>
<td>23 Feb–4 March 2003</td>
<td>Bauru, Brazil</td>
<td>$O_3$, $NO_2$, 2004: $H_2O$</td>
</tr>
<tr>
<td>PI: Pommereneau</td>
<td>26 Feb–6 April 2004</td>
<td>Bauru, Brazil</td>
<td></td>
</tr>
<tr>
<td>SAOZ</td>
<td>4 Oct 2002</td>
<td>Aire sur l’Adour, France</td>
<td>$O_3$, $NO_2$,temperature,pressure</td>
</tr>
<tr>
<td>PI: Goutail</td>
<td>18 Oct 2002</td>
<td>Aire sur l’Adour, France</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 June 2004</td>
<td>Bauru, Brazil</td>
<td></td>
</tr>
<tr>
<td>SAOZ + SAOZ-BrO</td>
<td>1 Oct 2002</td>
<td>Aire sur l’Adour, France</td>
<td>$O_3$, $NO_2$,temperature,pressure, $BrO$</td>
</tr>
<tr>
<td>PI: Goutail/Pirre</td>
<td>23 Feb 2003</td>
<td>Bauru, Brazil</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16 March 2003</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 March 2003</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31 Jan 2004</td>
<td>Bauru, Brazil</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 Feb 2004</td>
<td>Bauru, Brazil</td>
<td></td>
</tr>
<tr>
<td>FIRS-2</td>
<td>20 Oct 2002</td>
<td>Ft. Sumner, NM, USA</td>
<td>$O_3$, $H_2O$, $N_2O$, $NO_2$, 2003/2004: $CO$, $CH_4$, $CO_2$, temperature</td>
</tr>
<tr>
<td>PI: Chance</td>
<td>20 Sep 2003</td>
<td>Ft. Sumner, NM, USA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23 Sep 2004</td>
<td>Ft. Sumner, NM, USA</td>
<td></td>
</tr>
<tr>
<td>MANTRA</td>
<td>3 Sep 2002</td>
<td>Vanscoy, Canada</td>
<td>$O_3$, $NO_2$, $H_2O$, $N_2O$, $CH_4$, aerosol, pressure, temperature</td>
</tr>
<tr>
<td>PI: Strong</td>
<td>25 Aug 2004</td>
<td>Vanscoy, Canada</td>
<td></td>
</tr>
<tr>
<td>SALOMON</td>
<td>19 Sep 2002</td>
<td>Aire sur l’Adour, France</td>
<td>$O_3$, $NO_2$, OCIO, aerosol</td>
</tr>
<tr>
<td>PI: Renard</td>
<td>4 March 2002</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td>SPIRALE</td>
<td>2 Oct 2002</td>
<td>Aire sur l’Adour, France</td>
<td>$O_3$, $NO_2$, $CO$, $CH_4$</td>
</tr>
<tr>
<td>PI: Pirre</td>
<td>21 Jan 2003</td>
<td>Kiruna, Sweden</td>
<td></td>
</tr>
<tr>
<td>SDLA-LAMA</td>
<td>8 Aug 2002</td>
<td>Kiruna, Sweden</td>
<td>$H_2O$, $CH_4$</td>
</tr>
<tr>
<td>PI: Pirre</td>
<td>11 March 2004</td>
<td>Kiruna, Sweden</td>
<td>$H_2O$, $CH_4$</td>
</tr>
<tr>
<td>ELHYSA</td>
<td>1 March 2003</td>
<td>Kiruna, Sweden</td>
<td>$O_3$, $NO_2$, OCIO</td>
</tr>
<tr>
<td>AMON</td>
<td>1 March 2003</td>
<td>Kiruna, Sweden</td>
<td>$O_3$, $NO_2$, OCIO</td>
</tr>
<tr>
<td>RADIBAL</td>
<td>8 March 2004</td>
<td>Kiruna, Sweden</td>
<td>aerosol</td>
</tr>
<tr>
<td>PI: Brogniez</td>
<td>6 Aug 2002</td>
<td>Kiruna, Sweden</td>
<td>$H_2O(c)$, $CO_2(c)$, $CO(c)$, $O_3(c)$, $N_2O(c)$, $CH_4(c)$</td>
</tr>
</tbody>
</table>
Table 4. Satellite instruments used in the core validation for intercomparison with SCIAMACHY.

<table>
<thead>
<tr>
<th>Instrument Name</th>
<th>Platform/Operator</th>
<th>Target Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOME</td>
<td>ERS-2/ESA</td>
<td>O$_3$(c/p), NO$_2$, BrO(c), HCHO</td>
</tr>
<tr>
<td>SUSIM</td>
<td>UARS/NASA</td>
<td>solar ultra-violet energy</td>
</tr>
<tr>
<td>HALOE</td>
<td>UARS/NASA</td>
<td>O$_3$, NO$_2$, NO, CH$_4$, N$_2$O, CO$_2$, H$_2$O(p)</td>
</tr>
<tr>
<td>SBUV/2</td>
<td>NOAA-1+14/16 / NOAA</td>
<td>O$_3$(p)</td>
</tr>
<tr>
<td>TOMS</td>
<td>Earth Probe/NASA</td>
<td>O$_3$, SO$_2$(c), AAI</td>
</tr>
<tr>
<td>OSIRIS</td>
<td>ODIN/SNSB</td>
<td>O$_3$, NO$_2$(p)</td>
</tr>
<tr>
<td>SAGE II+III</td>
<td>ERBS+METEOR-3M / NASA</td>
<td>O$_3$, NO$_2$, H$_2$O, aerosols(p)</td>
</tr>
<tr>
<td>SABER</td>
<td>TIMED/NASA</td>
<td>O$_3$, H$_2$O(p)</td>
</tr>
<tr>
<td>POAM III</td>
<td>SPOT-4 / CNES</td>
<td>O$_3$, H$_2$O, NO$_2$, aerosols(p)</td>
</tr>
<tr>
<td>SOLSTICE</td>
<td>UARS/NASA</td>
<td>solar UV spectral irradiance</td>
</tr>
<tr>
<td>AATSR</td>
<td>Envisat / ESA</td>
<td>spectral reflectance (555, 659, 865 nm), cloud cover, cloud top height</td>
</tr>
<tr>
<td>MERIS</td>
<td>Envisat / ESA</td>
<td>spectral reflectance (390–1040 nm), cloud cover, aerosol</td>
</tr>
<tr>
<td>MOPITT</td>
<td>EOS-TERRA / NASA</td>
<td>CO(c/p)</td>
</tr>
<tr>
<td>MODIS</td>
<td>EOS-TERRA / NASA</td>
<td>cloud cover, cloud top pressure, aerosol</td>
</tr>
</tbody>
</table>

4.3 Balloon campaigns

Balloon-borne measurements provide snapshot type vertical profile measurements of very high precision. The dedicated balloon campaigns for the atmospheric chemistry instruments MIPAS, GOMOS and SCIAMACHY are financed by ESA, DLR and the French space agency CNES (Centre National d’ Etudes Spatiales), the costs and responsibilities are shared according to an agreement between the three agencies. Part of this agreement is to use all balloon flights as much as possible for all three satellite instruments.

CNCES provides the facilities and staff for launching scientific payloads with large stratospheric balloons from dedicated stations. The availability of the CNES equipment is an important constraint for the implementation of campaigns. Within the ACVT sub-group ESABC, the involved scientists from the balloon teams and representatives of the agencies frequently met to organize the Envisat validation balloon campaigns. The launch sites and campaign times are selected to cover mid-latitudes, northern latitudes and the tropics during several seasons as much as possible within the available resources.

Until May 2005, SCIAMACHY validation measurements were performed during 16 balloon campaigns from launch sites in Kiruna, Sweden (August 2002, December 2002/January 2003, March 2003, July 2003, March 2004, June 2004), Aire sur l’Adour, France (September/October 2002, October 2003), Bauru, Brazil (February/March 2003, January/April 2004, June 2004), Vancosy, Canada (September 2002, August 2004), and Fort Sumner, New Mexico, USA (October 2002, September 2003, September 2004). Table 3 lists the payloads and the measured species relevant for SCIAMACHY.

Further ESABC supported campaigns are already planned in Brazil (June/July 2005), and Kiruna (January/February 2006). With these campaigns, high latitudes in summer with usual conditions and in spring with the possibility of ozone depletion are covered as well as mid-latitudes and tropical regions.

Explicitly funded for the validation of SCIAMACHY are the LPMA/DOAS (combining a Limb Profile Monitoring of the Atmosphere FTIR and a Differential Optical Absorption Spectrometer instrument), the TRIPLE (combining a resonance fluorescence ClO/BrO instrument, an in-situ Fluorescence Induced Stratospheric Hygrometer FISH, a cryogenic total air sampler (BONBON) and a tunable diode laser measuring H$_2$O and CH$_4$) and the MIPAS-B (Michelson Interferometer for Passive Atmospheric Sounding – balloon version) balloon gondolas. These constitute the German contribution to the balloon-borne validation of Envisat.

These three balloon payloads together measured atmospheric profiles of O$_3$, NO$_2$, OClO, BrO, CH$_4$, N$_2$O, H$_2$O,
Table 4 lists the satellite instruments used for the validation of SCIAMACHY products. SCIAMACHY’s precursor GOME on board ERS-2 follows Envisat with a thirty minutes delay. Since the GOME channels are almost identical to the UV-visible channels of SCIAMACHY, GOME is the first choice for validating UV-visible nadir products. Unfortunately, since June 2003 the tape recorder on board ERS-2 stopped recording data, so that GOME measurements are restricted to areas where direct downlink of data is possible (currently about 30% is retrieved). TOMS and SBUV II as nadir looking instruments provide total columns. HALOE, SAGE II/III, and POAM III are solar occultation instruments, providing trace gas profiles at sunset and sunrise. SABER observes infrared emissions in limb, retrieving ozone and water vapour profiles. OSIRIS also operates in limb mode, providing ozone profiles. SUSIM and SOLSTICE results are used for comparison with solar irradiance measurements, needed to check the radiometric calibration of SCIAMACHY.

In addition intercomparisons are performed between the three atmospheric chemistry instruments on board Envisat: MIPAS, GOMOS and SCIAMACHY.

5 SCIAMACHY data

5.1 Operational products

The raw data of the SCIAMACHY instrument are sent from Envisat to the receiving stations, reformatted there and stored as “level 0” products. Rearranged and combined with the appropriate calibration information, they are converted by the SCIAMACHY data processor to the so-called “level 1b” products. These contain the measured spectra as raw data and the calibration information needed to derive spectra in physical units.

The level 1b products are the basis to derive atmospheric parameters from the SCIAMACHY measurements. Two operational processors are implemented to derive these parameters: the Near-Real Time (NRT) and the Offline (OL) level 1b-2 processor. The NRT processor derives trace gas columns, cloud and aerosol information from SCIAMACHY nadir measurements, the OL processor additionally contains trace gas vertical profiles derived from the limb measurement.

Several software updates to the operational processors have been performed since the launch of Envisat. An overview of the software version numbers and the periods to which they apply is given in Table 5.

The first (re-)processing of the entire mission started in March 2004 with software version 5.01. A later software
Fig. 7. The fraction of level 1b orbits available in March 2005 for several software versions. Orbits, processed with more than one software version, have only been counted for the latest software version. This plot does not account for Envisat or SCIAMACHY off-time, so part of the “missing” data will actually never become available (see Fig. 1). Software versions 5.01 and 5.04 have been used for reprocessing the entire mission.

Fig. 8. The same as Fig. 7, but now for level 2 orbits.
version (5.04) was introduced in August 2004 and the re-
processing was continued with this version. Note that not
all data within the listed time ranges are processed. This
can be seen in Figs. 7 and 8, which shows the fraction actu-
ally available to the validation teams for each processor ver-
sion. For the latest level 2 NRT version (5.04, orange bars
in Fig. 8) this fraction is on average 45% between July 2002
and March 2005.

The auxiliary files and the initialisation files used in the
processors are different for different software versions. Pe-
riods with erroneous initialisation or auxiliary files are in
principle listed in ESA’s data disclaimer. The data dis-
claimers can be found on ESA’s web site http://envisat.esa.
int/dataproducts/availability/disclaimers .

SCI-AVALIG, with input from the validation community,
has defined a validation reference set: a small subset of
SCIAMACHY measurements coinciding with selected val-
idation measurements between July 2002 and April 2003.
With this reference set it should be possible to derive a first
statement of the product quality from comparison with the
validation measurements after every processor upgrade, pro-
vided that this set is processed first.

For the second workshop of Atmospheric Chemistry Val-
idation of Envisat in May 2004 (ACVE-2), the 2002 part of
the reference set was processed to level 1b and level 2 NRT
and OL products with the most recent processors (NRT: 5.01
and OL: 2.1, see Table 5). The OL products contained only
ozone and NO₂ profiles. The NRT products contained entries
for all planned nadir products, but only O₃, NO₂, BrO, and
cloud cover fraction could be used for comparison studies;
the retrieval of the other species was suffering from calibra-
tion issues or from errors in the processors.

5.2 Scientific products

Many institutes interested in the SCIAMACHY project de-
veloped their own retrieval algorithms to derive atmospheric
products from SCIAMACHY measurements as an alterna-
tive for the operational products. These non-operational
products, hereafter called “scientific products”, are more ad-
vanced than the operational ones. For many atmospheric pa-
rameters, scientific products are the only ones available at the
time of writing of this paper. The availability of the scientific
products varies. For some products, almost complete datasets
exist. This is the case for O₃, NO₂, BrO, OClO, SO₂, and
H₂O columns, and for O₃, NO₂ and BrO profiles.

The improvement of scientific products usually goes faster
than that of the operational products, because changes can be
faster implemented without the restricting needs of an op-
erational processor regarding design, stability and documen-
tation. The knowledge gained by validation and further de-
velopment of scientific products can help considerably in the
improvement of the operational products.

Table 1 gives an overview of the current availability of op-
erational and scientific products. Section 6 gives a short sum-
mary of first validation results, including information about
the institutes developing the scientific products.

6 Validation results

This section contains a summary of validation results re-
ported during the Second Workshop on the Atmospheric
Chemistry Validation of Envisat (ACVE-2; May 2004, Fras-
cati), during the SCIAMACHY Validation Workshop (De-
cember 2004, Bremen), and in the literature till October
2005. It must be noted that for all products the data sets
suitable for evaluation were too limited to cover all geophys-
ical states of interest. Qualitative and quantitative statements
hereafter are valid only for the data sets and algorithm ver-
sions available at the time of the investigation.

6.1 Level 1 products

The solar spectral irradiance measured by SCIAMACHY has
been compared with the high-resolution Kurucz solar spec-
trum (Skupin et al., 2005) and with balloon measurements
(Gurlit et al., 2005). These comparisons have revealed de-
ciciencies in the absolute radiometric calibration of the so-
lar irradiance, with offsets ranging between 6% and 15%. Com-
parisons of the spectral reflectance, i.e., the ratio of the
earth radiance at nadir and the solar irradiance with GOME,
MERIS and modelled reflectance spectra, show wavelength
dependent offsets varying between 5% and 25% (Acarreta
and Stamnes, 2005; van Soest et al., 2005). Such offsets
cannot be explained by absolute calibration errors of the so-
nar irradiance alone, suggesting also uncertainties with the
absolute calibration of the earth radiance different from solar
irradiance calibration errors. Reflectance comparisons have
also revealed the presence of residual polarisation sensitivity
structures in the spectra even after application of the polar-
sation correction (Tilstra and Stamnes, 2005).

According to recent studies, the calibration improves
greatly by recalculating calibration parameters from on-
ground measurements and extended analysis of in-flight
measurements. With these improvements, the mean solar ir-
radiance for SCIAMACHY channels 3–6 is expected to agree
with the Kurucz data to within ±2–3%, and for channels 1
and 2 within ±5–10% (Skupin et al., 2005). The reflectance
is expected to agree within ±2–7% for channels 1–6. How-
ever, these changes are not yet implemented in the opera-
tional chain at this time.

The near-infrared channels 7 and 8 are hampered by vari-
ous effects, the most important being: varying ice layer on
the cooled detectors causing transmission loss and further ef-
fects; light-leak in channel 7; non-linearity of the detector
electronics; variable dark current (Lichtenberg et al., 2005).
The current calibration of these channels is insufficient to
start the validation of reflectance data in this wavelength re-
3

http://envisat.esa.int/dataproducts/availability/disclaimers .
Table 6. Summary of the validation status per product in March 2005 for the latest software versions. Details can be found in Sect. 6, applicable subsections are listed in the second column (“sect”). “B” means average systematic deviation between SCIAMACHY and correlative measurements. If a range is given, the systematic deviation depends on the geophysical state and/or measurement parameters. If the sign of the bias is negative, SCIAMACHY is on average lower than the correlative measurement. “S” means average scatter of the deviations. Software version numbers (for operational products) and responsible institutes (for scientific products) are shown in parentheses. “BIRA”=BIRA/IASB Brussels, “Heid”=IUP-Heidelberg, “IFE”=IFE/IUP-Bremen, “KNMI”=KNMI De Bilt, “SAO”=SAO Harvard, “SRON”=SRON Utrecht.

<table>
<thead>
<tr>
<th>product</th>
<th>sect</th>
<th>average agreement</th>
<th>special features / remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>solar irradiance spectrum (NRT 5.04, SciaL1C 2.2.9)</td>
<td>6.1</td>
<td>B: +6/+13%</td>
<td></td>
</tr>
<tr>
<td>nadir earth radiance spectrum (NRT 5.04, SciaL1C 2.2.9)</td>
<td></td>
<td>n/a</td>
<td>no validation sources</td>
</tr>
<tr>
<td>limb earth radiance spectrum (NRT 5.04, SciaL1C 2.2.9)</td>
<td></td>
<td>n/a</td>
<td>no validation sources</td>
</tr>
<tr>
<td>spectral reflectance (NRT 5.04, SciaL1C 2.2.9)</td>
<td>6.1</td>
<td>B: −5/−25%</td>
<td>residual polarisation structures</td>
</tr>
<tr>
<td>earth fractional polarisation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₃ column (NRT 5.04)</td>
<td>6.2.1</td>
<td>B: −2/−10%</td>
<td>dependence on SZA, cloud cover; known errors in retrieval for Oct–Dec</td>
</tr>
<tr>
<td>O₃ column (OL 2.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂ column (NRT 5.04)</td>
<td>6.2.1</td>
<td>B: −1/−1.5%, S: 5%</td>
<td></td>
</tr>
<tr>
<td>NO₂ column (OL 2.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂ column (BIRA,Heid,IFE,KNMI)</td>
<td>6.2.2</td>
<td>B: −7·10¹⁴ / +10¹⁴ molec/cm²</td>
<td>bias depends on retrieval method and settings</td>
</tr>
<tr>
<td>BrO slant column (NRT 5.04)</td>
<td>6.2.3</td>
<td>not specified</td>
<td>Large positive bias for small SCDs</td>
</tr>
<tr>
<td>BrO slant column (OL 2.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BrO slant column (BIRA,Heid,IFE,SAO)</td>
<td>6.2.3</td>
<td>not specified</td>
<td>Consistent with GB (2 stations) and GOME</td>
</tr>
<tr>
<td>SO₂ column (BIRA,IFE)</td>
<td>6.2.4</td>
<td>unknown</td>
<td>Qualitatively ok; special events needed for validation</td>
</tr>
<tr>
<td>OCIO slant column (Heid,IFE)</td>
<td>6.2.5</td>
<td>not specified</td>
<td>consistent with GOME</td>
</tr>
<tr>
<td>HCHO column (IFE,SAO)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O column (IFE)</td>
<td>6.2.6</td>
<td>B: −0.05 g/cm²</td>
<td></td>
</tr>
<tr>
<td>N₂O column (IFE)</td>
<td>6.3</td>
<td>S: 20%</td>
<td></td>
</tr>
<tr>
<td>CO column (Heid,IFE,SRON)</td>
<td>6.3</td>
<td>S: 30%</td>
<td>validation too limited</td>
</tr>
<tr>
<td>CO₂ column (IFE)</td>
<td>6.3</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>CH₄ column (Heid,IFE,SRON)</td>
<td>6.3</td>
<td>S: 5%</td>
<td></td>
</tr>
<tr>
<td>cloud cover (NRT 5.04)</td>
<td>6.2.7</td>
<td>unknown</td>
<td>good, compared to scientific products</td>
</tr>
<tr>
<td>cloud cover (OL 2.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cloud cover (KNMI)</td>
<td>6.2.7</td>
<td>unknown</td>
<td>good, compared to NRT 5.04</td>
</tr>
<tr>
<td>cloud top pressure (KNMI)</td>
<td>6.2.7</td>
<td>B: 100 hPa</td>
<td>with respect to MODIS</td>
</tr>
<tr>
<td>Absorbing Aerosol Index (KNMI)</td>
<td>6.2.8</td>
<td>not specified</td>
<td>compares well with TOMS; sens. to lv1 errors</td>
</tr>
<tr>
<td>Aerosol Optical Thickness (IFE)</td>
<td>6.2.8</td>
<td>not specified</td>
<td>compares well with MERIS; sens. to lv1 errors</td>
</tr>
<tr>
<td>O₃ profile (OL 2.5; limb)</td>
<td>6.4.1</td>
<td>B: 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>B: −15%</td>
<td>20–24 km</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B: 100 hPa</td>
<td>25–40 km; 20% of profiles show unrealistic features</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B: −3/−6%</td>
<td>16–40 km; zigzag shaped difference profiles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S: 10%</td>
<td>20–35 km</td>
</tr>
<tr>
<td>O₃ profile (IFE 1.61; limb)</td>
<td>6.4.1</td>
<td>B: 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>B: 100 hPa</td>
<td>20–24 km</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B: 100 hPa</td>
<td>20–35 km</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>NO₂ profile (OL 2.5; limb)</td>
<td>6.4.2</td>
<td>B: −20/+5%</td>
<td>60S–70S, 19–36 km</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B: +10/+60%</td>
<td>25N–30N, 25–36 km</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B: −35/+25%</td>
<td>40N–53N, 19–36 km;</td>
</tr>
<tr>
<td>NO₂ profile (IFE,SAO; limb)</td>
<td>6.4.2</td>
<td>B: &lt;15%</td>
<td>22–33 km; compares reasonable to balloon profiles</td>
</tr>
<tr>
<td>BrO profile (IFE,SAO; limb)</td>
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<td>OCIO profile (SAO; limb)</td>
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<tr>
<td>H₂O profile (IFE; limb)</td>
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6.2 Level 2 products from nadir UV-visible

Apparent slant column amounts of O₃, NO₂, BrO, OCIO, SO₂, HCHO and H₂O are retrieved from SCIAMACHY UV-visible spectra measured at nadir. When the vertical distribution of the constituents controlling the optical path through the atmosphere is known a priori, slant columns can be converted into vertical columns using an air mass factor (AMF) calculated with a radiative transfer model. Also retrieved from nadir UV-visible data are the fractional cloud cover, cloud top pressure, absorbing aerosol index (AAI), and aerosol optical thickness (AOT).

6.2.1 O₃ column

Preliminary validations based on sporadic sets of SCIAMACHY O₃ columns processed with versions 5.01 and 5.04 of the NRT processor were overviewed by Lambert et al. (2004a). They concluded that the NRT O₃ column products offer in most cases the level of quality that could be expected from this processor based on version 2 of the GOME Data Processor (GDP). For several seasons and latitudes, the agreement to ground-based networks and satellite measurements is indeed within the 2–10% range, with a global tendency to underestimate correlative data by a few percent. Ground-based comparisons of the SCIAMACHY NRT O₃ columns confirm the expected presence of errors inherited from GDP 2, like dependences on the solar zenith angle, season and viewing angle. The apparent absence of meridional structures between SCIAMACHY NRT 5.01/5.04 and ground-based total O₃ is surprising at first glance but it can be the result of compensating errors which vary with time and latitude, e.g. errors associated with rotational Raman scattering (RRS) and with the temperature dependence of the O₃ absorption cross-section. Between October and December, unexpectedly, much larger errors appear than those reported for GOME. Those errors correlate with the cloud fraction, ghost vertical column and air mass factor, and they show up at several latitudes. This explains apparent differences between individual comparison results and vindicates the maintenance of a network-based effort instead of only a few “representative” stations. It is expected that the OL SCIAMACHY processor will be upgraded in 2005 to a GDP 4-like version, including a better treatment of RRS, of the cross-sections temperature dependence and of the air mass factor, and therefore significant improvements are anticipated. Comparisons with GOME retrievals from IFE/IUP-Bremen (WF-DOAS 1.0) confirm these results and additionally show that the dependencies of the deviations on solar zenith angle, latitude, and total ozone disappear when SCIAMACHY total ozone is retrieved with an algorithm equivalent to GOME WF-DOAS 1.0 (Bracher et al., 2005a).

SCIAMACHY O₃ column data sets have also been produced by scientific processors developed at BIRA-IASB, IUP/Bremen and KNMI. Those processors are based on recent GOME O₃ column retrieval algorithms (GDOAS, Spurr et al., 2004; TOGOMI, Valks and van Oss, 2003; WF-DOAS, Coldewey-Egbers et al., 2005) which have demonstrated to bring the SZA/season/latitude dependencies of the GOME O₃ column product down to the “1% level”, that is, to the level of accuracy that can be reached with well-maintained and calibrated ground-based sensors. Those algorithms have also proven to be stable and relatively insensitive to instrumental degradation over the entire GOME lifetime, enabling accurate O₃ trend monitoring. First validation of preliminary SCIAMACHY O₃ columns generated by the scientific algorithm developed at KNMI shows a good agreement of 1–1.5% (usually a slight underestimation) and a RMS of about 5% with most of ground-based data sets (Eskes et al., 2005).

6.2.2 NO₂ column

Validations of the SCIAMACHY NO₂ column data were reviewed by Lambert et al. (2004b) in May 2004 for NRT version 5.01 and for scientific products generated at BIRA-IASB, IFE/IUP-Bremen, IUP-Heidelberg, KNMI, and SAO. This review was updated with NRT version 5.04 in December 2004. Both NRT versions and the scientific products have demonstrated to capture major geophysical signals appropriately. For NRT 5.01 and 5.04, the two validation reviews conclude to a good agreement (of a few times \(10^{14}\) molec/cm\(^2\)) with correlative data over clean areas in the Southern winter-spring and Northern summer. Much larger deviations (systematic overestimations up to \(1.5\cdot10^{15}\) molec/cm\(^2\) over clean areas and more in polluted conditions) are observed in other cases, e.g. from October till the end of the year for several latitudes but not all, and with a clear correlation with cloud fraction, ghost vertical column and air mass factor values. It is anticipated that, in spring 2005, a GDP 4-like algorithm will be implemented in the OL SCIAMACHY processor and that the NRT NO₂ column product will improve significantly. It is important to note that, while GOME GDP 2.7 NO₂ columns were strongly affected by instrumental degradation after 2001, the new level-1 calibration implemented in 2002 solved the problem for the subsequent GDP versions, yielding stable data sets over the entire GOME lifetime.

Coordinated validations carried out on the SCIAMACHY NO₂ scientific products have shown that stratospheric NO₂ columns already have a good quality. Differences between the different products exist because of differences in retrieval settings and assumptions. The retrieval algorithm differences that have most impact concern the profile database used for air mass factor calculations, the way cross-sections temperatures are determined, and the way clouds are handled. More detailed validation is ongoing, with special attention to tropospheric NO₂ products.
6.2.3 BrO column

SCIAMACHY BrO slant columns are retrieved by the NRT processor and by scientific algorithms developed at BIRA-IASB, IFE/IUP-Bremen, IUP-Heidelberg and SAO. Due to the low signal/noise ratio and to remaining polarisation features of SCIAMACHY in the classical GOME BrO window (345–359 nm), the SCIAMACHY BrO window in NRT version 5.01 has been shifted to shorter wavelengths (335–347 nm). Thanks to this shift, at moderate and large slant column values, an acceptable agreement better than 20% is found between NRT 5.01 and all scientific SCIAMACHY data sets, and also with GOME despite the spectral window difference. This level of agreement is also observed with ground-based UV-visible measurements after due conversion to vertical columns and appropriate treatment of the diurnal cycle. Detailed investigation further confirms that SCIAMACHY and other BrO sensors capture polar spring emissions and short-term variability in a consistent way. However, in summer, for slant column values smaller than 1.5·10^{14} molcm^{-2}, version 5.01 of the NRT product reports systematically higher values than other systems by 20% to 100% (Van Roozendael et al., 2004).

6.2.4 SO$_2$ column

SCIAMACHY SO$_2$ column data are routinely retrieved by the scientific processors developed and operated at BIRA-IASB and IFE/IUP-Bremen. SCIAMACHY SO$_2$ data give a clear picture of volcanic emissions, sulphur plant fires and other pollution events. They show good agreement with SO$_2$ columns derived from GOME, despite the significant differences in spatial resolution and sampling. Quantitative validation is nevertheless hampered by the lack of independent measurements. Further details are given by Bramstedt et al. (2004).

6.2.5 OClO slant columns

SCIAMACHY OClO slant columns produced by the scientific processors at IFE/IUP-Bremen and IUP-Heidelberg have been compared with OClO slant columns from GOME and with other observations from AMAXDOAS and ground-based UV-visible spectrometers. Using a polarisation sensitivity spectrum and an empirical correction spectrum in the spectral fit, and considering diurnal cycle and atmospheric variability effects, SCIAMACHY OClO data are consistent with those from other sensors and show the expected relation to atmospheric conditions (Wagner et al., 2004; Wang et al., 2003).

6.2.6 H$_2$O columns

An overview of the validation status of the scientific SCIAMACHY H$_2$O columns (IFE/IUP-Bremen, MPI) in May 2004 was given by Timmermans et al. (2004). With the MPI algorithm (based on the GOME algorithm by Lang et al., 2003), a negative bias of 20 to 25% was reported. The IFE product (Noël et al., 2004) showed about 10% too low water vapour values when compared to ozone sondes. A more recent validation effort of an improved version of the IFE product shows a systematic bias of −0.05 g/cm$^2$, and a scatter of 0.5 g/cm$^2$ with respect to SSM/I measurements (Noël et al., 2005).

6.2.7 Clouds

An overview of the validation status of the SCIAMACHY cloud products in May 2004 was given by Fournier et al. (2004). They concluded that the operational SCIAMACHY cloud fraction correlated well with the cloud fraction retrieved with FRESCO (KNMI), and is not sensitive to errors in the radiance calibration, as FRESCO is. A viewing angle dependent error was pointed out in the operational product. Independent validation still has to be performed. The FRESCO cloud-top pressure shows a RMS difference of about 100 hPa when compared to MODIS (Fournier et al., 2005).

6.2.8 Aerosol parameters

An overview of the validation status of the SCIAMACHY aerosol products can be found in von Hoyningen-Hüne et al. (2004) and de Graaf et al. (2004). The aerosol algorithms are very sensitive to errors in the reflectance. However, after using an empirical correction factor for the reflectance, it was shown that the SCIAMACHY Absorbing Aerosol Index (KNMI) compared well to TOMS and the SCIAMACHY Aerosol Optical Thickness (IFE/IUP-Bremen) compared reasonably well to MERIS.

6.3 Level 2 products from nadir near infrared

Columns of CO, CH$_4$, N$_2$O, and/or CO$_2$ have been retrieved from SCIAMACHY near-infrared (NIR) measurements by the IMAP-DOAS (Frankenberg et al., 2005a,b), IMLM (Gloudemans et al., 2005) and WFM-DOAS (Buchwitz et al., 2005b) scientific algorithms. First order corrections for the thermal variation of the dark current signal along the orbit, dead/bad pixels, light leak in channel 7, and the build-up of ice on the detectors of channels 7 and 8 affecting signal transmission and line shape functions, have been implemented. Such corrections significantly improve the level 2 data products, however, the retrieval residuals are still larger than the expected instrument noise. Refinements of the algorithms are still progressing, e.g. using more CO lines in the retrieval is envisaged. Accurate validation methods are also under refinement, e.g., to deal properly with issues posed by clouds and by small-scale variations of the surface properties and altitude.

Correlative studies have been conducted using ground-based data from a pole-to-pole network of 12 FTIR
instruments and from the FTIR operated during two cruises of the Polarstern ship from Bremerhaven to Africa; CO column data from the EOS-Terra MOPITT satellite; CO and CH₄ data from the TM3 (KNMI) and TM5 (IMAU) models; and ancillary data like fire maps produced by ERS-2 ATSR and EOS-Aqua MODIS. The general potential of SCIAMACHY NIR products is demonstrated (Buchwitz et al., 2005a; De Mazière et al., 2004; Gloudemans et al., 2005; Warneke et al., 2004; Dils et al., 2005; Sussmann et al., 2005), in particular its capabilities to detect source/sink areas of CO, CH₄ and CO₂ and to track their transport. Provisional precision estimates for SCIAMACHY CO (30%) and CH₄ (5%) vertical columns are not far away from the nominal requirements and can already be used in a variety of applications. Even so, inverse modelling analyses seem to indicate that nominal precision requirements are a firm precondition to the potential improvement of existing emission catalogues. The current estimated precision for N₂O is 20%. It is expected that this will be improved in the near future. For CO₂, current validation is too limited to give firm conclusions.

6.4 Level 2 products retrieved from limb UV-visible

6.4.1 O₃ profile

Up to now, the availability of O₃ profile data generated from SCIAMACHY limb spectra by the OL processor has been limited to a few verification orbits not designed for geophysical validation, and to a limited data set produced with version 2.1 of the OL processor. Both versions are based on the Optimal Estimation retrieval method. They rely on limb spectra not corrected for pointing errors of the satellite platform and therefore resulting O₃ profiles are expected to exhibit a shift in altitude registration. In May 2004, a review of preliminary validations of SCIAMACHY OL O₃ profiles (Brinksma et al., 2004) concluded that version 2.1 O₃ profiles agree to within 10% to ground-based data (ozone sonde, lidar, microwave, FTIR), and to within 30% to satellite data (HALOE, SAGE-II, SAGE-III, SBUV/2). More recently, a preliminary validation of version 2.5 O₃ profiles with ground-based instruments and satellites showed that 20% of the profiles have unrealistic values. The other 80% show no systematic deviations above 24 km, but are significantly underestimated below 24 km, by 15% (Brinksma et al., 2005). It is anticipated that a new OL limb O₃ profile data product based on an alternative retrieval approach and including a correction for pointing errors should be made available to validation teams in 2005.

Synergistic use of complementary ground-based network data by De Clercq et al. (2004) allowed characterisation of an altitude shift in the ozone profiles. This shift was found to drift monotonically from 1.5 km to 3 km between two successive updates of the on-board orbit-model, performed each time Envisat flies over the Caribbean and over Australia. This drift causes fictitious meridional and zonal structures in the O₃ profile product. The implementation of a new version of the orbit propagator model on 9 December 2003 improve the altitude registration of the SCIAMACHY O₃ profile (von Savigny et al., 2005).

SCIAMACHY limb O₃ profiles have also been generated by IFE/IUP-Bremen. Validation results have been reported for three different software versions: 1.6, 1.61, and 1.62. A cross comparison with GOMOS, MIPAS and SCIAMACHY IFE 1.6 O₃ profiles showed an agreement within 15% between 21 and 40 km (Bracher et al., 2005b). This same version 1.6 agrees within 10–15% with sondes after an altitude correction of −2 km had been applied to account for Envisat pointing problems (Segers et al., 2005). The profiles generated with software version 1.61 were validated for five months spread over 2004 with ground-based and satellite data. The systematic bias of the IFE profiles, after a downward shift of 1.5 km was applied, is −3% with respect to lidars, averaged between 16 and 40 km, and −6% with respect to SAGE II over the same latitude range. The difference profile has a characteristic zigzag shape with a wavelength of approximately 8 km, the systematic bias being a few percent larger around 32 and 24 km, and a few percent smaller around 20 and 28 km (Brinksma et al., 2005). Butz et al. (2005) recently compared balloon borne measurements with SCIAMACHY IFE 1.62 O₃ profiles. In this software version the tangent height is retrieved explicitly, in order to reduce errors caused by the satellite pointing mismatch. They find an agreement within 20% between 20 and 30 km. The agreement generally becomes worse below 20 km.

6.4.2 NO₂ profiles

An overview of the validation status of the SCIAMACHY NO₂ profiles (OL vs. 2.1) in May 2004 was given by von Savigny et al. (2004). They concluded that the OL product was about 50% larger than HALOE between 25 and 40 km (Bracher et al., 2005c). About 10% of the OL profiles appear to be entirely unrealistic. The IFE/IUP-Bremen profiles were within 15% of the HALOE profiles (22–33 km). Both IFE and SAO NO₂ profiles compared reasonably to SÃOZ balloon profiles.

A more recent comparison of OL vs. 2.4 and 2.5 NO₂ profiles with collocated and photochemically corrected SAGE II (vs. 6.2) measurements yield improved OL NO₂ profiles (Bracher; personal communication, Feb. 2005). However, the quality of the retrievals strongly depend on latitude and/or solar zenith angle (SZA). For high southern latitudes (60° S–70° S) the OL NO₂ profile retrievals agree with photochemically corrected SAGE II profiles within −20% to +5% for the 19–36 km altitude range. At low northern latitudes (25° N–30° N) the OL concentrations were systematically higher by 10–60% in the 25–36 km altitude range. At northern mid-latitudes (40° N–53° N) the agreement was again better: −35% to +25% between 19 and 36 km.
Retrievals with the DLR prototype processor that will replace the current OL processor in the future are in good agreement with the IFE NO₂ profile retrievals (Doicu et al., 2006).

Comparisons between SCIAMACHY NO₂ profiles retrieved by IFE/IUP-Bremen (version 1) and HALOE (version 19) show good agreement (within 12%) between 22 and 33 km. Comparisons with SAGE II show a systematic negative bias of 10 to 35% between 20 and 38 km, where SAGE II sunset profiles are suspected to be too high (Bracher et al., 2005c). A cross comparison with GOMOS, MIPAS and SCIAMACHY IFE v1 NO₂ profiles show an agreement within 20% between 27 and 40 km (Bracher et al., 2005b). Butz et al. (2005) recently compared balloon borne measurements with SCIAMACHY NO₂ profiles retrieved by IFE/IUP-Bremen, IUP-Heidelberg, and SAO Harvard. They find an agreement within 20% between 20 and 30 km. The agreement generally becomes worse below 20 km.

6.4.3 BrO profiles

Profiles of BrO have been retrieved from SCIAMACHY limb spectra by IFE/IUP-Bremen, SAO, and IUP-Heidelberg. Preliminary validation relies on comparisons with balloon-based data acquired either by UV-visible solar occultation during ascent/descent and sunset/sunrise (three LPMA/DOAS and seven SAOZ-balloon flights) or by resonance fluorescence (three TRIPLE flights), and with simulations provided by the SLIMCAT chemical-transport model of the stratosphere. The direct comparison of photochemically uncorrected BrO profiles from balloons and from SCIAMACHY limb spectra shows promising results in the middle stratosphere but reveals possible problems below 20 km (Dorf et al., 2005; Pfeilsticker et al., 2004; Rozanov et al., 2005). Further validation is needed, that will include photochemical corrections for balloon observations along calculated air mass trajectories.

7 Validation plans

Scientific publications in which SCIAMACHY products are used need to address the quality (like accuracy, precision, features) of these products focused on the effect the quality has on the results presented in the publication. It is our goal to give a general description of the quality for all SCIAMACHY products that are well-documented and generally available, including both operational and scientific products.

A complete description of the quality of a SCIAMACHY product should be formulated in such a way that it is of direct use for scientific research. In particular the behaviour of deviations (between SCIAMACHY data and correlative data) with respect to relevant algorithm, instrument, and atmospheric parameters should be specified. Examples of such parameters are: surface albedo, scan mirror angle, solar zenith angle. Some product specific features (or obvious errors) can be observed from the analysis of the product itself, without comparison to correlative data. Also, the descriptions of these features, and where they occur (what algorithm, instrumental or geophysical parameters), should be part of the complete description.

Ideally, all SCIAMACHY products should be compared to several, i.e. more than one, independent sources of well-established correlative data. The results of these comparisons should be combined to get a consistent description of the behaviour of the product.

To achieve our long-term goal it is necessary that: 1) processors are bug free and known improvements to the algorithms are implemented, 2) a consecutive period of at least one year of data is processed with the latest software version, and enough collocations with correlative data are included within this data set, and 3) the manpower for data analysis is available.

The current operational nadir UV-visible products (NRT 5.04 and OL 2.5), i.e., vertical columns of O₃ and NO₂, and slant columns of BrO, OCIO and HCHO, are based on the algorithms used in the GOME Data Processor (GDP) version 2.4. An upgrade of these algorithms to the algorithms currently used in GOME (GDP version 4.0) is currently being implemented and reprocessed data should be available in early 2006. Validation of the current product has confirmed similar features of O₃ and NO₂ as in GOME version 2.4 (see Sects. 6.2.1 and 6.2.2), and further validation is waiting for the processor upgrade.

The current operational nadir NIR products are still unrealistic, see Sect. 6.3. Upgrades of the level 0–1 and the level 1–2 processors should improve these products; the validation can hopefully start after these upgrades have been performed. For NIR products this will not be done before 2006.

In the O₃ and NO₂ profiles, generated with the operational OL processor version 2.5, several unrealistic features have been found (see Sects. 6.4.1 and 6.4.2). Validation of these products should also continue after the next processor upgrade, planned for fall 2005.

For many of the products of SCIAMACHY enough correlative measurements are available. However, the SCIAMACHY measurements themselves are not all processed with the current operational processors (NRT 5.04/OL 2.5) and/or distributed to the validation teams, making it difficult to continue or complete the validation of the operational products. To monitor the long-term product quality of the instrument, a basic amount of correlative data over SCIAMACHY’s lifetime is required.

Most of the available funding for SCIAMACHY validation from the national space agencies of Germany, The Netherlands, and Belgium, was applied in the first two years.
of operation, since the necessary effort was expected to be largest in that period. Dedicated validation measurements have indeed been performed successfully, but the analysis of the SCIAMACHY data still has to be performed for all SCIAMACHY products after bugs have been fixed, algorithms have been improved, and the data have been reprocessed and distributed. Only very limited funding is currently available to perform these tasks.

8 Conclusions

With the support of ESA and of a list of international partners, an extensive SCIAMACHY validation programme has been developed jointly by Germany, the Netherlands and Belgium to face complex requirements in terms of measured species, altitude range, spatial and temporal scales, geophysical states and intended applications. Preparation of the validation has been successful:

- An organisational structure has been set up to coordinate this large-scale validation campaign, to monitor continuously the validation results (Sect. 3) and to foster exchanges between the different validation actors;
- Numerous independent validation measurements of all planned SCIAMACHY products have been performed (Sect. 4), with a special concentration in the first two years of operation;
- The required manpower to analyse the data was available in the first two years of operation, for a large part funded by the national space agencies in the three instrument-providing countries.

The validation itself has been however hampered, firstly by delays in the production and delivery of operational data by the Envisat ground segment, secondly by delays in the development of the data processors.

Since the first release of early SCIAMACHY data in summer 2002, the operational processors established at DLR on behalf of ESA were upgraded regularly (see Table 5) and some data products (level 1b spectra, O₃, NO₂, BrO and clouds data) have improved considerably. Validation has shown that for limited periods and geographical domains they can already be used for scientific studies. Nevertheless, the NRT level-1-to-2 processor is still affected by a series of bugs, which result in major errors preventing from scientific usability in other periods and domains, e.g., the O₃ and NO₂ columns in the last months of the year or the BrO columns at small BrO abundances. Scientific users are advised to read carefully validation reports and quality statements before using the data.

Free from the constraints of operational processing, independent research algorithms developed at scientific institutes usually are more flexible and they allow dedicated investigation of specific retrieval issues. Seven scientific institutes (BIRA-IASB, IFE/IUP-Bremen, IUP-Heidelberg, KNMI, MPI, SAO and SRON) have developed their own retrieval algorithms and generated SCIAMACHY data products, addressing all together nearly all targeted constituents. Their UV-visible data products – O₃, NO₂, SO₂, H₂O total columns; BrO, OClO slant columns; O₃, NO₂, BrO profiles – are already of acceptable, if not of excellent, quality and are available publicly, sometimes in near-real-time (see Table 1 and Sect. 6). Several near-infrared column products – CO, CH₄, N₂O and CO₂ – are still under development but they have already demonstrated their potential for a variety of applications. Most of them can be obtained on request. All scientific products will be judged first on their availability and description and after that on their usefulness for scientific research by the monitoring of the validation results.

SCIAMACHY is a remarkable stable instrument starting the fourth year of almost continuous measurements (see Fig. 1). It is required and anticipated that SCIAMACHY validation will continue throughout the instrument lifetime and beyond, anticipating algorithm updates and reprocessing of data for many years to come. The actual amount of work will obviously depend on funding and manpower considerations.

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SCIAMACHY Level 1 data: calibration concept and in-flight calibration

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Abstract. The calibration of SCIAMACHY was thoroughly checked since the instrument was launched on-board ENVISAT in February 2002. While SCIAMACHY’s functional performance is excellent since launch, a number of technical difficulties have appeared, that required adjustments to the calibration. The problems can be separated into three types: (1) Those caused by the instrument and/or platform environment. Among these are the high water content in the satellite structure and/or MLI layer. This results in the deposition of ice on the detectors in channels 7 and 8 which seriously affects the retrievals in the IR, mostly because of the continuous change of the slit function caused by scattering of the light through the ice layer. Additionally a light leak in channel 7 severely hampers any retrieval from this channel. (2) Problems due to errors in the on-ground calibration and/or data processing affecting for example the radiometric calibration. A new approach based on a mixture of on-ground and in-flight data is shortly described here. (3) Problems caused by principal limitations of the calibration concept, e.g. the possible appearance of spectral structures after the polarisation correction due to unavoidable errors in the determination of atmospheric polarisation. In this paper we give a complete overview of the calibration and problems that still have to be solved. We will also give an indication of the effect of calibration problems on retrievals where possible. Since the operational processing chain is currently being updated and no newly processed data are available at this point in time, for some calibration issues only a rough estimate of the effect on Level 2 products can be given. However, it is the intention of this paper to serve as a future reference for detailed studies into specific calibration issues.

1 Introduction

SCIAMACHY (SCanning Imaging Absorption spectrometer for Atmospheric CHartographY) is a scanning nadir and limb spectrometer covering the wavelength range from 212 nm to 2386 nm in 8 channels (see Table 1). It is a joint project of Germany, the Netherlands and Belgium and was launched in February 2002 on the ENVISAT platform. The nominal mission life time of ENVISAT is 5 years. SCIAMACHY was designed to measure column densities and vertical profiles of trace gas species in the mesosphere, in the stratosphere and in the troposphere (Bovensmann et al., 1999). It can detect O3, H2CO, SO2, BrO, OCIO, NO2, H2O, CO, CO2, CH4, N2O, O2, (O2)2 and can provide information about aerosols and clouds. In addition to the spectrally resolved measurements of the radiance reflected from the Earth’s atmosphere, the polarisation of the
incoming light is measured with 7 broadband sensors. In this paper we describe the optical layout of SCIAMACHY, its different observation modes and the on-ground and in-flight calibration concept. We also cover unexpected calibration problems encountered in-flight that require adjustments in the data processing.

During the on-ground calibration the polarisation sensitivity and the radiometric sensitivity was extensively measured for a range of scanning angles. A dedicated on-board calibration unit that contains a White Light Source (WLS) and a Spectral Line Source (SLS) allows monitoring the instrument during the whole mission. Solar measurements are additionally employed to measure light path degradation (see Noël et al., 2003).

All calibration and science data are linked down to ESA ground stations where they are further processed under responsibility of ESA. The user is provided with two types of SCIAMACHY data: (1) Level 1 data, which contain the spectrum, polarisation fractions and other information and (2) Level 2 data containing geophysical products like total columns or profiles of atmospheric trace gases. Level 1 data are generated from raw, uncorrected Level 0 data and are split up in Level 1b and Level 1c data. Level 1b data are still uncalibrated, but contain all the necessary information to do a full calibration. Level 1c data are produced by applying some (or all) calibration steps to Level 1b data. ESA provides a tool to calibrate Level 1b data, but the user can also use third party software or develop dedicated software to calibrate the data. Often in this paper we will speak of “operational” data processing as opposed to “scientific” processing. Operational data processing is done by ESA and/or is using official ESA tools, while scientific data products are products that scientists have developed themselves. An example for scientific processing is a software package developed at SRON that produces fully calibrated Level 1c data and already incorporates some of the corrections that will become available operationally only after an update of the ESA data processor. Many scientific Level 2 products have been developed by different research groups at IHE, KNMI, IUP Heidelberg, SRON and other institutes. The operational processor was mainly developed by DLR-IMF in collaboration with ESA.

The operational data processing is currently (spring 2005) being updated from the previous version (5.04) to include the latest calibration algorithms and key data. The implementation of this new calibration will be checked and – if necessary – be adjusted until end 2005. After the revision of the data processing, all data will be re-processed with the new processing chain. Excluded from the current update are important corrections for the IR detectors (see below), partly because no operational algorithm is available at this point in time and partly because other corrections were set at a higher priority. Without these corrections operational products from the IR wavelength range will be of lower quality and users must develop their own retrieval algorithm or must make use of trace gas products developed in the scientific community (e.g. Buchwitz et al., 2005; Gloudemans et al., 2005; Frankenberg et al., 2005).

The paper is organised as follows: the first section describes the different instrument modes and the layout of the instrument. Then the overall calibration concept is discussed in the second section before the individual calibration steps are explained in Sects. 3–7. Section 8 treats unexpected effects that require an adjustment of the calibration procedure such as ice in channels 7 and 8 and the light leak in channel 7. Finally, in Sect. 9, a summary of the most important open calibration issues is given.

2 The instrument

SCIAMACHY has various observation modes to obtain spectra from the Earth’s atmosphere, the sun and the moon. Two scanner modules, the so-called Elevation Scanner Module (ESM) and Azimuth Scanner Module (ASM) can be used to direct light into the instrument. Both scanner modules can be rotated a full 360° and have identical flat, uncoated mirrors mounted on one side and a diffuser mounted on the other side. The scanners enable SCIAMACHY to perform observations in the following modes (see also Noël et al., 2002):

Nadir: The instrument is looking directly down to the Earth and uses only the ESM mirror. The Instantaneous Field of View (IFOv) is approximately 25 km × 0.6 km (along × across track), the typical ground pixel size is 32 km × 60 km at a full swath width of 960 km (scanning East–West). Higher spatial resolution is possible in special operation modes.

Limb: The instrument looks into flight direction using the ASM mirror for East-West scans and the ESM mirror to sample heights from the horizon to an altitude of 93 km in 3 km steps. The IFOv is 103 km × 2.6 km (azimuth × elevation) at the tangent point around 3000 km ahead of the satellite. The typical spatial resolution is 240 km × 3 km covering 960 km in one East-West scan. The ESM scanner compensates for the curvature of the Earth to keep the same tangent height for each individual East–West scan. At the end of each Limb measurement a dark signal measurement is made at a tangent height of 250 km.

Solar Occultation: The sun is tracked, starting at sunrise over the Northern Pole and is followed through the atmosphere from 17 km to the upper edge of the atmosphere. In this observation mode the small aperture is inserted into the optical path to reduce the signal in all channels. Additionally, the Neutral Density Filter (NDF) reduces the light in channels 3–6 by a factor of about 5.

Solar Irradiance: In this observation mode a solar spectrum is measured with a mirror diffuser combination (either ASM mirror + ESM diffuser + NDF filter or ASM diffuser + ESM mirror) to obtain a solar reference spectrum.
Lunar Occultation: Similar to the solar occultation mode, the moon is tracked through the atmosphere in this mode. However, due to the orbit of ENVISAT and the revolution of the moon, lunar observations are only possible at certain times over the North or South Pole. Since in the Northern hemisphere the sun and moon rise coincide, observations are only made when ENVISAT is in the Southern hemisphere. Here the moon is visible once per month for a time period of approximately a week (depending on season). The phase of the moon varies between 0.6 and 1 during the week of observations. The NDF and the small aperture are not needed in this observation mode.

Monitoring: In this mode the sun or the moon are observed above the atmosphere in order to measure any degradation of the instrument optical path. In the sun modes the small aperture and the NDF is used. The sun can be observed with both mirrors (Limb configuration), in Limb configuration with an extra mirror in front of the Nadir mirror or in the so-called sub-solar mode using only the Nadir mirror. Sub-solar measurements are only possible when the satellite crosses the equator on the day side. The extra mirror is used to determine the degradation of the ESM mirror. It is protected when not employed and it is assumed that it will not degrade significantly during the mission.

Calibration: SCIAMACHY has a dedicated calibration unit with a 5 Watt Tungsten halogen WLS for instrument monitoring and a PtCrNe spectral line source (SLS) to perform in-flight spectral calibration. Both lamps can be observed only with the ESM (mirror or diffuser).

A simplified optical train for all possible observation modes is shown in Fig. 1. After passing the scanners a 31 mm diameter telescope mirror produces a focus on the entrance slit of the spectrometer. The entrance slit is 180 µm wide and 8 mm high, resulting in an Instantaneous Field of View (iFoV) of 0.045 degrees in the dispersion direction and 1.88 degrees in the cross-dispersion direction. After the slit the beam is collimated and is directed into the Optical Bench Module (OBM).

The OBM design is based on the double dispersing spectrometer principle. The light is first dispersed by a pre-disperser prism creating an intermediate spectrum. Small pick-off prisms and subsequent dichroic mirrors direct the light into the 8 so-called science channels. Each of these channels contains a grating for the final dispersion of the light to moderate spectral resolution. At the pre-disperser prism p-polarised light is split off to the Polarisation Measurement Devices (PMDs) through a Brewster reflection. The PMDs are broadband sensors with wavelength ranges that cover approximately the wavelengths measured in channels 2–6 and 8 (see Table 1). Additionally to the 6 PMDs A–F measuring Q the PMD 45 measures the U Stokes parameter. The PMDs are non-integrating devices that are read out at 40 Hz. The polarisation of the incoming light can be derived by combining the measurements in the science channels and the PMD measurements as will be explained in Sect. 7.

The science channels of SCIAMACHY employ two types of detectors. For the UV/VIS range (channels 1–5) standard silicon EG&G Reticon detectors with 1024 pixels are used. The pixels are sequentially read out in approximately 30 ms for the complete array. The near IR channels 6–8 employ Indium Gallium Arsenide (InGaAs) detectors manufactured by EPITAXX (now owned by JDS Uniphase). The focal plane array for these channels was designed and built by SRON (Hoogeveen et al., 2001). All 1024 pixels of the IR detectors are read out in parallel with dedicated amplifiers. In order to cover the whole wavelength range from 971 to 2386 nm, the composition of the IR detector material had to be adjusted leading to side effects important for the calibration: The InGaAs light detecting layer of the IR detectors is epitaxially grown on an InP substrate. For optimal detector performance, the lattice constant of the InGaAs layer and the InP substrate must match. Ideal lattice matching between detector and substrate material occurs for 53% Indium and 47% Gallium only. Detectors with this composition are sensitive only up to wavelengths of 1600 nm at 200 K. For sensitivity beyond this wavelength, a higher Indium and lower Gallium content is needed. The composition of the detector material in channels 6+ (pixels 794–1023 in channel 6), channel 7 and channel 8 was changed accordingly. However, this results in a larger lattice constant and thus in a mismatch with the lattice constant of the InP substrate. Therefore, these channels have a reduced performance in terms of detector dark current, noise and number of usable pixels (see Sect. 4.2).

The sequential readout of the individual pixels in channels 1–5 leads to an effect called spatial aliasing: Pixels that are read out at a different time see a different ground scene because of the movement of the satellite and the scan mirrors, introducing a wavelength dependent bias into the spectrum. The magnitude of the effect depends on the variability of the ground scene. In order to reduce spatial aliasing in the

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**Table 1.** Spectral characteristics of the science channels and the PMDs. The detector temperature values are the approximate minimum and maximum value from the year 2004 excluding periods when the detectors are heated for decontamination purposes. The PMD wavelength range is defined such that it contains 80% of the signal, the range of the science channels is the total range.

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<td>1</td>
<td>212–334</td>
<td>0.24</td>
<td>205.8–207.5</td>
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<tr>
<td>2</td>
<td>300–412</td>
<td>0.26</td>
<td>205.0–207.0</td>
<td>A</td>
<td>310–365</td>
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<tr>
<td>3</td>
<td>383–628</td>
<td>0.44</td>
<td>224.0–225.0</td>
<td>B</td>
<td>455–515</td>
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<tr>
<td>4</td>
<td>595–812</td>
<td>0.48</td>
<td>223.0–224.3</td>
<td>C</td>
<td>610–690</td>
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<tr>
<td>5</td>
<td>773–1063</td>
<td>0.54</td>
<td>221.4–222.4</td>
<td>D/45</td>
<td>800–900</td>
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<tr>
<td>6</td>
<td>971–1773</td>
<td>1.48</td>
<td>199.0–201.2</td>
<td>E</td>
<td>1500–1635</td>
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<tr>
<td>7</td>
<td>1934–2044</td>
<td>0.22</td>
<td>145.0–149.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>2259–2386</td>
<td>0.26</td>
<td>143.7–147.6</td>
<td>F</td>
<td>2280–2400</td>
</tr>
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overlap of channel 1 and channel 2 from 300–334 nm and in the overlap of channels 2 and 3 (383–412 nm) the wavelength direction in channel 2 is reversed, i.e. high pixel numbers correspond to short wavelengths. This ensures that the channel overlap between consecutive channels observe the same ground scene. Channels 6–8 pixels are – as mentioned earlier – read out in parallel and thus do not suffer from spatial aliasing.

The scanning motion of the mirrors and the readout of the detectors are synchronised by pulses with a frequency of 16 Hz (corresponding to 62.5 ms). Since the time needed for the readout of all 1024 pixels of the UV/VIS channels is 28.78 ms, the minimum exposure time of the detectors is set to 62.5 ms/2. = 31.25 ms to allow for a proper synchronisation. The IR channels 6–8 can also be read out in the so-called “hot mode” allowing much shorter integration times of down to 28 µs. However, in measurements with integration time shorter than the synchronisation time of 62.5 ms all readouts except one are discarded i.e. not sent to the ground station. For example, in a measurement with 31.25 ms integration time only every second readout is actually available in the data product. Integration times shorter than 62.5 ms are only used in calibration and monitoring modes.

In order to reduce the noise on the signal, the detectors are cooled by a dual-stage, passive radiative cooler (SCIAMACHY Radiative Cooler, SRC). The first stage provides cooling to channels 1-6 and the second stage to channels 7 and 8. Seasonal variations of the detector temperature are compensated by manual adjustment of the power to three so-called trim heaters. Channels 6+, 8 and 5 (in decreasing order of sensitivity) show a significant temperature dependence of their quantum efficiency. The responses of those detectors changes up to 2–3% per Kelvin depending on the wavelength. Table 1 shows the approximate detector temperature range for the year 2004, excluding decontamination periods. The temperature of the optical bench is actively controlled by a feed-back loop holding the temperature stable at 255.251 K ± 40 mK over one complete orbit. The remaining temperature variation over the orbit leads to a small change of the background signal in channel 8 (see Sect. 4.2).

Finally, a special feature of the readout of the detectors has to be mentioned. The total integration time in a channel is defined as the product of the Pixel Exposure Time (PET) and a co-adding factor. The detectors are always read out after the time specified in the PET parameter. The co-adding factor determines how many readouts are summed up before the data are sent to the ground station. If the co-adding factor

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**Fig. 1.** Simplified optical train of SCIAMACHY for the different observation modes. Only elements not common to all paths are shown. Note that the NDF is only in the light path of channels 3–6. Mirrors are marked blue, diffusers yellow. The optical path in the monitoring mode for the sun is marked red, the path for the moon is marked blue. “sm. AP” denotes the small aperture, “Extr. M” the extra mirror that can be put into the light path optionally.
is larger than 1, the individual readouts are not available in the data product, only the sum of the readouts is. It is possible to assign consecutive pixels to so-called clusters, each having its own co-adding factor, i.e. the integration time in each cluster can be a multiple of the PET in a given channel. Only one PET value per channel is possible. The cluster definition can be tuned such that the spatial resolution in the spectral windows containing the most important trace gases is the highest. In this way the scientific return can be optimised within the limits of the data rate that is available to SCIAMACHY for downlinking the data. A drawback of this concept is that it introduces several complications in the data processing of SCIAMACHY. The different integration times of the clusters mean that not the complete spectrum is available for every record in the data. If, for example, we have two clusters A and B in a channel and cluster A has an integration time two times larger than the integration time of cluster B, then a full spectrum containing data from both clusters is only available in every second record of the data. Generally, a full spectrum over a channel is available in the data only for the longest integration time of the channel (since only then all clusters of the channel have been read out). The same is true for the complete spectrum over the whole spectral range of SCIAMACHY, only that this is available after the longest integration time of all channels. The observation mode, the cluster definition and the integration time setting for the channels constitute what is called a “state”. SCIAMACHY has 70 pre-defined states that cover all Earth observation, monitoring and calibration modes.

3 Calibration concept

The calibration aims to convert electronic signals of the detectors (Binary Units/second) into physical units (e.g. W/m²/nm/sr). The general calibration formula is

\[ S_{\text{det}} = I(\lambda) \cdot \Gamma_{\text{inst}}(\lambda) \cdot Q E(T_{\text{det}}, \lambda) + S_{\text{stray}} + DC + S_{\text{elec}}(1) \]

where \( S_{\text{det}} \) is the signal measured on the detector in Binary Units/second, \( I \) is the incoming intensity, \( \Gamma_{\text{inst}} \) the total transmission of the instrument, \( Q E \) the quantum efficiency, \( S_{\text{stray}} \) the stray light, \( DC \) the total dark signal and \( S_{\text{elec}} \) electronic effects like non-linearity. This equation must be solved for every detector pixel. In order to obtain the spectrum as a function of wavelength \( \lambda \), the wavelength has to be determined for each pixel and the equation has to be inverted to calculate the intensity \( I \). Additionally, to get the true shape of the spectrum the instrument specific slit function has to be applied. The transmission of the instrument is dependent on the polarisation of the incoming light. The individual calibration steps to obtain the spectrum will be explained in more detail in the following sections. First the general concept behind the calibration of the SCIAMACHY instrument is discussed.

The experience of the Global Ozone Monitoring Experiment (GOME), launched on-board the ERS–2 satellite in 1995, where various air-vacuum effects led to calibration problems, showed that spectrometers should ideally be calibrated under thermal vacuum (T/V) conditions (see e.g. Aben et al., 2000). In the case of SCIAMACHY, a calibration performed completely under T/V conditions was not possible, because the range of incidence angles on the mirror(s) and mirror–diffuser combination that had to be covered could not be realised in the available vacuum tank. Therefore a combination of T/V and ambient measurements was used. The radiometric sensitivity and the polarisation sensitivity of the instrument were measured under T/V conditions for one reference angle \( \alpha_0 \) and all necessary instrument modes (limb, nadir and irradiance). In order to be able to calibrate all incidence angles on the mirrors (or diffusers), component level measurements of all possible mirror combinations and the mirror-ESM diffuser combination were made under ambient conditions. In the component level measurements only the scanner modules with the mirror and diffuser are mounted on an optical table that allows to orient the mirror (combination) at arbitrary angles w.r.t. to the calibration light source and each other. The reflectivity of the components is then measured using a dedicated detector different from the ones used in SCIAMACHY. These ambient measurements were performed for a selected set of angles (including \( \alpha_0 \)) and wavelengths. The reference angle measurement is used to transfer the results from the ambient measurement to the T/V measurement. Measurements were done for unpolarised light, s- and p-polarised light and \( \pm 45^\circ \) polarised light. The combination of T/V measurements and ambient measurements provides ideally the correct instrument response for all incidence angles at begin of life of the instrument. The implicit assumptions for the combination of the T/V and ambient measurements are that the polarisation dependence of the mirrors and diffusers are the same in air as they are in vacuum and that there is no temperature dependence. Both assumptions are reasonable for SCIAMACHY, since uncoated mirrors are used. Critical points in the transfer of ambient to T/V measurements are the geometry (incidence angles on the mirrors or diffusers), the illumination conditions and the detector used in the component measurements. Obviously, errors in the geometry lead to a wrong angle dependence of the calibration quantity to be measured. The illumination during instrument measurements and during component measurements will always be different. While the footprint of the light source on the component can be matched to the footprint during the instrument measurements, it is impossible to re-create the exact illumination conditions potentially leading to systematic errors in the calibration. Finally, care has to be taken that the detector used in the ambient measurements does not introduce artifacts. In order to minimise
possible errors in ambient measurements, only ratios of measurements were used in the ambient calibration where possible.

In addition to the on-ground calibration measurements, in-flight measurements of the dark signal are performed in every orbit. Changes of the instrument performance in-flight are tracked with internal light sources (WLS and SLS) and solar measurements. For more details on monitoring see e.g. Noël et al. (2003). Details of the calibration are described in the following sections.

4 Detector corrections

This section describes corrections related to the electronics of the detectors and the detectors themselves (\(S_{\text{elec}}\) and \(DC\) in Eq. 1). The UV/VIS channels 1–5 and the IR channels 6–8 have to be treated separately in the calibration due to the differences in detector material and readout electronics. The signal in this section is described in terms of Binary Units (BU). The Analog-to-Digital Converter (ADC) of SCIAMACHY codes the signal on the detector in 16 bit meaning that detector signals (or “fillings”) are in the range between 0 BU and 65 535 BU.

4.1 Channels 1–5 (UV/VIS)

4.1.1 Memory effect

The first correction that has to be applied is the so-called memory effect (see e.g. Lichtenberg, 2003). The memory effect was discovered in 1996 during an investigation of the linearity of channels 1–5. In a number of measurements that covered the range from low detector fillings to saturation it was found that the signal deviated from a linear response \(^2\). The deviation was not dependent on the actual signal level, but on the signal level of the previous readout (hence the name memory effect). Note that the effect depends on the signal level including the analog offset (see below) and dark current. Thus it is the first correction to be applied. In order to characterise the memory effect, WLS measurements followed by several dark measurements were done on-ground and in-flight. The difference between the first dark measurement after the WLS measurement and subsequent dark measurements gives a correction value as a function of detector filling. This value has to be subtracted from the data to correct for the memory effect. The memory effect is the same for all pixels. The total correction for a single readout is – depending on the channel – between −0.61% and 0.21% of the detector filling of the previous readout with a maximum effect at fillings around 19 000 BU–21 000 BU (see Fig. 2).

Since the memory effect introduces instrument features that depend on the previous readout, it is not easily possible to make a quantitative estimate of the effect on scientific data. Qualitatively, the memory effect leads to two different kinds of deviations from the “true” spectrum. First, the absolute value of the signal will be wrong, but for measurements that have a reasonable S/N this is not considered a major problem. The second effect, however, is more serious. Since the memory effect changes rapidly as a function of the previous signal for a large range of detector fillings, there is a risk that artificial spectral features are introduced into the measurements. Differential retrieval methods, such as Differential Optical Absorption Spectroscopy or DOAS (see e.g. Solomon et al., 1987; Platt, 1994; Burrows et al., 1999) are very sensitive to changes of the spectral shape of a line, thus the memory effect cannot be neglected. In general the effect on the data is strongest when for a certain spectral region the previous readout had detector fillings that lead to a large memory effect and the current readout has a very weak signal or when

\(^2\)Defined by doing a linear fit for all points of up to 90% of the maximum detector filling.
the spectrum shows a high variability in signal levels (e.g. partially clouded scenes on a dark background like ocean).

In three cases the memory effect cannot be calculated directly from the available data in a channel. First, if the data are co-added, the individual detector readouts are not available. In this case PMD measurements, which are read out more frequently than the science channels, are used to estimate the signal in the science channels during the individual readouts in a co-adding sequence. The estimated signals are then used to approximate the total memory effect. Second, each time the instrument changes into a different state (see Sect. 2 for the definition of a state) the mirrors move first into an idle position and then into the position required by the new state. During the movement to the new position the detectors are continuously read out, picking up an arbitrary signal from the moving mirror. Data obtained while the mirrors are still moving are dumped on-board. Thus the previous readout for the first spectrum in a state is not available. The operational processor uses some approximation to estimate the signal during mirror movement, but it is impossible to determine how accurate this approximation is. For this reason it is recommended not to use the first readout in a state or, if one does so, carefully inspect the spectrum for artifacts. The third case is the Limb observation mode: Before each observation of a new tangent height there is a so-called “reset readout” of the detectors with an integration time of 31.25 ms, which is not linked down to the ground station. The signal of the reset readout is estimated using the Limb measurements itself and then applied to the first readout at the new tangent height.

4.1.2 Dark correction

The second detector correction that has to be applied is the dark signal correction. The dark signal is measured in every orbit in the eclipse using 5 different states. In channels 1–5 two components contribute to the dark signal: the analog offset (AO) and the leakage current (LC). The analog offset is independent of integration time, it is just a fixed signal added to the measured signal to avoid negative values. The leakage current is caused by thermally created electron-hole pairs. The total dark signal for the UV/VIS channels is

\[
DC_{UV/VIS} = f_{coadd} \cdot AO + f_{coadd} \cdot t_{PET} \cdot LC
\]  

where \( f_{coadd} \) is the co-adding factor of the cluster and \( t_{PET} \) is the pixel exposure time (see Sect. 2). Note that the analog offset is multiplied with the co-adding factor since it is added to the signal for every individual detector readout. The dark signal correction is derived in-flight by a linear fit to the dark measurements with different integration times. The dark signal in the UV/VIS channels is dominated by the analog offset. The leakage current is only 0.04–0.5 BU/s (Kleipool, 2002) and did not change significantly since launch.

4.2 Channels 6–8 (IR)

4.2.1 Non-linearity

The IR channels do not suffer from the memory effect. However, there is a significant non-linearity that has to be corrected before applying other corrections. The non-linearity has been measured during the on-ground calibration campaign and a correction algorithm was defined (Kleipool, 2003). The maximum non-linearity is around 250 BU, which can be significant for weak absorbers like CO. A non-linearity correction has been derived for each of the channels 6, 6+, 7 and 8 separately. Within these channels the non-linearity differs for odd and even pixels because they are connected to different multiplexers. Additionally there is a clear difference in the non-linearity between pixels with numbers higher and lower than 511. This leads to a total of 14 correction curves, four per channel with the exception of channel 6+, which covers only pixels 794 to 1024 (see Sect. 2). Figure 2 shows the non-linearity curves derived for channel 8. The accuracy of the non-linearity correction is around 5–21 BU for detector fillings in the range from 10 000 to 40 000 BU, depending on the channel.

4.2.2 Bad and dead pixels

In addition to the non-linearity, Channels 6+, 7 and 8 contain a significant number of pixels with reduced performance due to the lattice mismatch between the light detecting InGaAs layer and the InP substrate. These pixels are called bad or dead pixels. There are various effects that make these pixels unusable: a few are disconnected, thus preventing any signal readout. Some pixels are so-called Random Telegraph (RT) pixels that spontaneously and unpredictably jump between two or more levels of dark current leading to different detected signals for the same intensity. Other effects include excessive noise or too high leakage current leading to saturation of the detector. All these effects were measured on-ground and a so-called Bad and Dead pixel Mask (BDM) was created. Pixels in the BDM have to be ignored in any retrieval. Recently it has been discovered that the BDM changes in-flight. The most likely reason is the impact of high energy protons on the detector (Kleipool et al., 2006). The effect of the changes of the BDM on CH₄ and CO is described in detail by Gloudemans et al. (2005). It is demonstrated that one bad pixel that is not included in the BDM can change the CH₄ retrieved total columns by a factor of up to 2. Clearly, the effect on individual retrievals depends on the position of the bad pixel in the retrieval window and on the used retrieval algorithm.

4.2.3 Dark correction

After application of the non-linearity and the BDM, the dark signal has to be corrected. The dark signal correction in channels 7 and 8 is complicated by the presence of a
The dark signal in these channels becomes
\[
DC_{IR} = f_{coadd} \cdot AO + f_{coadd} \cdot F_{PET} \cdot LC + 
+ f_{coadd} \cdot F_{PET} \cdot \Gamma_{icel} (\lambda, t) \cdot QE (T_{det}, \lambda) \cdot BG_{1h}(\varphi)
\] (3)

where \( \Gamma_{icel} \) is the transmission coefficient of the ice layer and \( QE \) is the quantum efficiency of the detector. For channels 6+ and 8 the quantum efficiency varies with detector temperature \( T_{det} \), whereas the first part of channel 6 and channel 7 show no significant temperature dependence. The thermal background is caused by the thermal radiation emitted by the instrument and is the dominant part of the dark signal (\( \approx 4000 \) BU/s) in channel 8. The thermal background signal depends on the orbit phase \( \varphi \), because the temperature of the instrument is not completely stable, but varies over one orbit due to the changing angle of the solar irradiation. The variation of the dark signal can be up to 60 BU/s which has significant impact on the retrievals of trace gases. Gloudemans et al. (2005) showed a comparison of retrievals with and without correction of the orbital variation results in differences of up to 4% in \( \text{CH}_4 \) total columns. The orbital variation of the dark signal is measured once a month during a special calibration orbit in which only dark signal measurements are performed by looking to 250 km tangent height in Limb mode. Discussions are under way on how to best implement the orbital variation in the operational processing. The variation of the transmission makes the dark signal correction time dependent meaning that for the channels 7 and 8 a dark signal correction calculated from measurements in the same orbit has to be used.

4.2.4 Pixel-to-Pixel Gain (PPG)

The final detector related correction is the PPG correction. The pixels in the IR detectors do not show the same, uniform response to the incoming light as observed in the UV/VIS channels. Variations of a few percent can be observed from pixel to pixel. The PPG is derived by first smoothing a WLS measurement, assuming the spectrum is flat. Then the original spectrum is divided by the smoothed measurement, leaving only the high frequent variations that are caused by the different pixel gains in the result, which can then be used to correct the PPG. Preliminary investigations by SRON show that the PPG is very stable since launch (R. Jongma, private communication, 2005). It is important to realise that the PPG is an effect that is caused by combined effects of the electronics and the detector and is thus only associated with the individual pixel and not with the wavelength. One example where this becomes an issue is the calculation of the Earth reflectance by dividing it by a sun spectrum. The spectrum of the sun is slightly Doppler shifted due to the movement of the satellite relative to the sun. The PPG correction has to be applied before the Doppler shift is corrected.

5 Wavelength calibration

The spectral calibration of the SCIAMACHY data is regularly updated using in-flight data with the exception of channels 7 and 8 (see below). In order to determine the exact wavelength value for each pixel a combination of a basis wavelength calibration and an in-flight wavelength calibration is used. The basis wavelength calibration is determined from on-ground data. The in-flight calibration calculates only the difference to the basis wavelength calibration. This has the advantage that only a small correction has to be applied, because it is expected that the wavelength calibration of SCIAMACHY is relatively stable over the mission lifetime. The small correction can be modelled with a lower order polynomial function avoiding the problem of oscillations possible for higher order polynomial fits, especially at the channel edges. In the in-flight calibration the pixel position of selected lines is determined using the Falk algorithm (Falk, 1984). The pixel positions are then used together with the basis wavelength calibration and the theoretical line positions to determine the wavelength of each pixel (for details see Slijkhuis, 2000). Measurements of solar Fraunhofer lines are used as a quality check.

On-ground, the wavelength calibration was performed both with the internal SLS and an external SLS. However, for channels 7 and 8 not enough useful lines are available to calculate the wavelength calibration with a sufficient accuracy. In channel 8 this is caused by bad pixels that interfere with the determination of the line position. Channel 7 only contains two strong doublet lines preventing an accurate determination of line positions over the whole channel. In both channels data from on-ground gas cell absorption measurements are used to establish the wavelength calibration. This calibration is also used for in-flight data, i.e. the wavelength calibration is not updated regularly in-flight. In the future it might be possible to update the calibration using sun, moon or Earth (ir)radiance spectra.

As mentioned above, during the on-ground calibration the internal SLS of SCIAMACHY and an external SLS was used to check the wavelength calibration. A comparison between the external and internal spectral lamp measurements revealed a wavelength shift of up to 0.07 nm. The shift is explained by a partial blocking of the light path during internal SLS measurements. This so-called “blocking shift” was characterised and is corrected when the wavelength calibration is applied.

Checks of the spectral calibration in-flight have shown that SCIAMACHY is spectrally very stable. An analysis of on-ground and in-flight (Ahlers, 2004a) data show an absolute shift of the wavelength calibration between \(-0.04\) nm in channel 1 to \(-0.01\) nm in channel 3 and the largest shift
of 0.07 nm in channel 5. The other channels show no significant shift. The reason for the large shift in channel 5 is unknown. However, since the wavelength calibration is calculated from in-flight data and uses the on-ground data only as an initial starting point the shift will not influence trace gas retrievals. More important is the spectral stability of the instrument. Investigations done after launch by Ahlers (2004a) show that the spectral stability is better than the requirement of 0.02 pixels/orbit. Possible exceptions are spectral regions near the channel borders, here a detailed investigation still has to be performed. The blocking shift was also verified in-flight by comparing spectral lines positions from the sun-over-diffuser measurements to those of SLS measurements (Ahlers, 2004b). The difference between the wavelength calibration derived from SLS measurements (not applying the blocking shift correction) and sun measurements is up to 0.15 nm, suggesting an increase of the blocking shift. However, the sun measurements show a large spread and the fit used to determine the wavelengths has a lower accuracy. Therefore, it is not clear if the blocking shift has increased or if this is only an artifact caused by the lower quality of the fit of the sun measurements. Further investigations are needed for clarification.

6 Stray light

There are two types of stray light ($S_{\text{stray}}$ in Eq. 1), spectral stray light and spatial stray light. Spectral stray light is light of a certain wavelength that is scattered to a detector pixel ‘belonging’ to a different wavelength. It can lead to distortions of the shape of the spectrum. The reason is usually a reflection in the instrument after the dispersion of the light beam. Spectral stray light can originate from the same channel (intra-channel stray light) or it can scale with the intensity in a different channel (inter-channel stray light). Spatial stray light enters the telescope from outside the IFoV. Spatial stray light is dispersed in an identical way as the light from the observation target. Depending on the source of the stray light it can add an additional offset to the spectrum and/or can distort the spectrum if the primary source of the stray light has spectral characteristics that differ significantly from the observed target. Stray light is usually characterised as a fraction of the total measured intensity for a given pixel.

6.1 Spectral stray light

Ideally, in the spectral stray light determination the stray light contribution from each individual pixel to all other pixels would be measured separately. However, this so-called full matrix approach is not always feasible. In the case of SCIAMACHY a $8192 \times 8192$ matrix would be required making the calculation of stray light very slow. Another problem is that usually only a very small fraction of the incoming light is stray light. If the full matrix approach is used, the signal in one pixel does only produce a very weak stray light signal in the other pixels which can very well be below the measurement threshold. In order to avoid the problems related to the full matrix approach the spectral stray light for SCIAMACHY was separated into three types: (1) Uniform stray light, (2) ghost stray light and (3) channel 1 stray light. Each type of stray light was characterised on-ground using measurements employing a monochromator. A monochromator gives light in a narrow, well-defined spectral band. The central wavelength of the spectral band can be adjusted. In the derivation of the stray light fractions from monochromator measurements it is assumed that any signal in detector pixels outside this spectral band is caused by stray light. During the on-ground calibration the spectral stray light was measured by changing the central wavelength of the monochromator spectral band, covering the whole wavelength range of SCIAMACHY. The integrated light of the monochromator peak(s) is divided by the light detected outside the peak, giving the stray light fraction. The resulting data are part of the calibration data set and are used to correct the spectral stray light in flight.

The first type of spectral stray light, the uniform stray light, is caused by a diffuse reflection that adds signal to all detector pixels in a given channel. It is by definition not dependent on wavelength. The uniform stray light fraction is calculated in channels 2–8 relative to the average signal in the channel and has values between 0.07% and 0.1% depending on the channel. The relative error of the uniform stray light value from the on-ground calibration is between 15% and 40% of the calculated value, again depending on the channel. Even if the maximum error is assumed, the largest expected stray light fraction is 0.14% which is well within the requirements. It is assumed that the uniform stray light is not dependent on polarisation.

Ghost stray light is caused by a more or less focused reflection of one part of a spectrum to another part of the spectrum. It can distort the shape of the “true” spectrum, because it does not add signal to all pixels equally. The effect of the ghosts on the retrieval depend very much on the shape and dynamic range of the measured spectrum and are not easily predictable. During the on-ground measurements 15 ghost signals were detected in channels 2–8. The total sum of ghost stray light in a channel is at maximum 1% of the incoming intensity. The current correction does not consider the polarisation of the light, an investigation if the polarisation has to be taken into account is planned for the future.

For channel 1 the situation is less favourable with respect to stray light levels. The on-ground measurements showed that the spectral stray light in channel 1 can be up to 10% of the incoming signal for a typical input spectrum. It is also highly wavelength dependent. The main reason for the larger stray light fraction in channel 1 is the high dynamic range of the spectra in this channel, with the lowest signal 3 orders of magnitude smaller than the highest signal. The coarse, artificial separation in uniform and ghost stray light
is not sufficient for a correction in channel 1 and an alternative method had to be formulated. The chosen approach combines the correction of uniform and ghost stray light in a modified matrix approach. In order to avoid signal-to-noise problems during the spectral stray light measurements, 10 wavelengths bands were defined separately for s and p-polarised light leading to a total of 20 bands. For both polarisation directions 9 bands were located in channel 1 to characterise intra-channel stray light and 1 band covered the signal from channels 2 -5 to characterise inter-channel stray light.\(^3\) For each band the stray light contribution to all detector pixels was calculated leading to a \(10 \times 1024\) matrix for both, s- and p-polarised light. The correction has an accuracy of around 25% and reduces the stray light by an order of magnitude leaving at most 1% stray light in the spectrum after correction.

6.2 Spatial stray light

Spatial stray light is clearly observed in SCIAMACHY limb measurements at altitudes above 90 km and in data taken in Nadir configuration over the North pole. The latter is expected since at that position in the orbit the sun shines directly into the limb port of the instrument producing a considerable amount of stray light. In order to minimise stray light above the Pole the ASM is rotated such that the edge of the diffuser/mirror points in flight direction preventing a direct reflection into the telescope. The observed stray light in this orbit position is caused by remaining reflections of sun light from the baffles and other parts of the Limb port. The stray light in Limb measurements was not expected and was first discovered in measurements taken at 150 km tangent height, where no atmospheric light should be present. These measurements were originally intended to determine the orbital variation of the dark signal in channel 8 (see Sect. 4.2) and as an optional dark correction for the Limb measurements. Investigations (van Soest, 2005) show that the stray light is not caused by a light leak, because spectral structures like air glow emissions and atmospheric absorptions are visible in the measurements, which means that the signal is spectrally dispersed and thus goes through the optics of the instrument. Comparison with MERIS data showed that the stray light does not correlate with the intensity of the scene at the sub-satellite point, ruling out the possibility that light is entering through the Nadir port and is subsequently directed into the telescope. Measurements of the Limb scans at high altitude and Limb scans at a lower tangent altitude of 10 km show a good correlation confirming that the stray light is caused by light entering the instrument through the slit from regions outside the FOV. The stray light is highest in channel 2-4 and is very low in channels 1, 5 and 6. The effect of the stray light on the Limb retrievals will be assessed in a future investigation. The Limb scan has been adjusted to take the dark measurement at 250 km instead of 150 km on 26 May 2003 (orbit 6456). At that height the spatial stray light is reduced by an order magnitude to 5–10 BU/s making an estimation of the orbital variation of the dark signal possible. However, the dark signal correction of the data should be done with the dark signal derived from eclipse data.

7 Polarisation

7.1 Theoretical concept

SCIAMACHY is – as all grating spectrometers without a polarisation scrambler – sensitive to the polarisation of the incoming light, i.e. the response will not only depend on the intensity but also on the polarisation of the light. In the polarisation correction the instrument is represented by a so-called Mueller matrix and the light is represented by the Stokes vector (see e.g. Coulson, 1988):

\[
\begin{pmatrix}
S \\
Q \\
P \\
U
\end{pmatrix}_{\text{det}} =
\begin{pmatrix}
M_{11} & M_{12} & M_{13} & 0 \\
M_{21} & M_{22} & M_{23} & 0 \\
M_{31} & M_{32} & M_{33} & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}^{D,P}
\begin{pmatrix}
I \\
Q \\
P \\
U
\end{pmatrix}_0
\]

On the left hand side of the equation we have the light as detected by the instrument, i.e. in front of the detectors. On the right hand side we have the Mueller matrix \(M_{\text{inst}}\) describing the response of the instrument \((D)\) the science channels, \(P\) the PMD channels) to the incoming light represented by the Stokes vector. The first element of the Stokes vector, \(I\), denotes the total intensity of the light (we use \(S\) for the detected signal here). \(Q\) is a measure for the polarisation along the x or y-axis of a chosen reference frame and can be described as \(Q=I_x-I_y\). \(U\) is a measure for the polarisation along the \(\pm 45^\circ\) direction and is defined as \(U=I_{45}-I_{-45}\). Note that the total intensity can be written as \(I=I_x+I_y\) or as \(I=I_{45}+I_{-45}\). Often \(Q\) and \(U\) are normalised to the total intensity \(I\), we will denote normalised fractions with \(q\) and \(u\) in the remainder of this paper. Note that the formula above is only correct for Earth observations where the circular polarisation of the light \(V\) can be neglected. This is usually the case (see e.g. Hansen and Travis, 1974) and thus circular polarisation is not considered in the polarisation correction. All Mueller matrix elements are dependent on wavelength and on the incidence angle of the light on the scan mirror(s) or diffuser. In the calibration, ambient measurements on component level and instrument T/V measurements have to be combined meaning that the actual instrument matrix has to be calculated by a multiplication of the matrix for the scanner (combination) and the OBM. However, we will not go into detail in this paper and will just use \(M_{\text{inst}}\) as the instrument matrix describing the complete instrument. Note that each observation mode has its own matrix, e.g. the Mueller matrix for Nadir observations is not the same as the matrix

---

\(^3\)The channel 1 detector material is not sensitive for light with wavelengths above 1000 nm, so the IR channels do not have to be considered.
for Limb observations. For more information, the reader is directed to Slijkhuisk (2000) and Frerick (1999). The Stokes parameters relate in the following way to the polarisation angle $\chi$ and the degree of linear polarisation $P$:

$$\chi = \frac{1}{2} \arctan \left( \frac{U}{Q} \right)$$

(5)

$$P = \sqrt{Q^2 + U^2} / I$$

(6)

The detectors of SCIAMACHY are only sensitive to the intensity reducing Eq. (4) to

$$S_{\text{det}} = M_{11}^D \cdot I \cdot \left( 1 + M_{12}^D M_{11}^D q + M_{13}^D M_{11}^D u \right)$$

(7)

where $I$ is the intensity and $q$ and $u$ the polarisation fraction of the incoming light, and $S_{\text{det}}$ the detected intensity. $M_{11}^D$ is the radiometric response function of the science detectors (see Sect. 8) and the reciprocal of the term in brackets is in effect the desired polarisation correction factor. Note that we are leaving out here the so-called m-factors that take into account a possible degradation of the light path (see Sect. 9.3). The m-factors correct for each light path long term degradation of the instrument. For details the reader is referred to Slijkhuisk (2000).

7.2 Calculation of the polarisation correction

The calculation of the polarisation correction is the most complicated part of the calibration of SCIAMACHY data. Therefore we will first describe the general steps that have to be done and after that go into some more detail. The basic steps are

1. Definition of polarisation reference frames to be able to convert calibration data to the correct observation reference frame.
2. Determination of the polarisation sensitivity of the instrument:
   (a) Measurement of the instrument response to polarised light which is stored as calibration data
   (b) Translation of the calibration data into the Mueller matrix approach
3. Calculation of the polarisation of the incoming atmospheric light
   (a) Determination of $Q$ and $U$ for single scattering in the UV
   (b) Determination of $Q$ and $U$ from PMD D and PMD 45, these two measure the polarisation for the same wavelength range (but see also Sect. 7.3)
   (c) Determination of $U$ and $Q$ for the PMD A–C, E, F wavelengths using a theoretical $U/Q$ ratio
4. Interpolate the $Q$ and $U$ values to the full wavelength grid of SCIAMACHY

7.2.1 Polarisation reference frames

Two reference frames are used for SCIAMACHY: the calibration reference frame used for calibration measurements and the observation reference frame used in the data product. The polarisation reference frame used in the calibration is defined w.r.t. the direction of the slit: looking in the direction of the light entering the instrument after the scan mirrors, the +45° polarisation direction is obtained by a 45° clockwise rotation from the p-polarisation direction. The p-polarisation direction is aligned with the long side of the entrance slit of SCIAMACHY. The polarisation reference plane used for measurement data is the local meridian plane containing the satellite, the zenith and the centre of the FOV with the flight direction pointing into the negative y-direction and the z-direction pointing to the instrument. In this reference frame the p-polarisation ($\eta = 1$) is parallel to the plane and the 45° direction can be obtained by rotating counter-clockwise from the x-direction to the y-direction. This reference frame differs from that used in the calibration making a coordinate transformation necessary. The data processor handles all transformations from the calibration reference frame to the observation frame and v.v. internally. The calculated polarisation fractions in the Level 1 data product are those in the observation polarisation frame.

7.2.2 Determination of the instrument polarisation sensitivity

The polarisation sensitivity was measured on-ground using ratios of measurements as far as possible to minimise influences of the measurement set-up on the data. SCIAMACHY shows a different sensitivity to s- and p-polarised light and to +45° and −45° polarised light. In order to correct the measurements of the atmosphere, the following quantities have to be measured: (1) The sensitivity to s-polarised light relative to p-polarised light. This is called $\eta$ and is derived from ratios of measurements with fully s- and fully p-polarised light. (2) The sensitivity of +45° polarised light to −45° polarised light. This quantity is called $\zeta$ and is determined from ratios of measurements using +45° and −45° polarised light. (3) To be able to determine the atmospheric polarisation, also the ratio of the signals in the PMDs to the signal in the science detectors was determined for all four polarisation directions. Care was taken to ensure that the intensity in all these measurements was the same, because otherwise a difference in intensity could have been mistaken for an effect of the polarisation of the light. The Mueller matrix elements from Eq. (7) relate in the following way to $\eta$ and $\zeta$:

$$\frac{M_{12}^D}{M_{11}^D} = \frac{1 - \eta}{1 + \eta}$$

(8)

4The latter is a consequence of a rotation of the polarisation direction of the incoming light by the pre-disperser prism, due to stress induced birefringence in the prism.
\[
\frac{M_{13}^D}{M_{11}^D} = \frac{1 - \zeta}{1 + \zeta}
\] (9)

Using Eq. (7) we can define \(c_{\text{pol}}\) from
\[
I = c_{\text{pol}} \cdot \frac{S_{\text{det}}}{M_{11}^D}
\] (10)

Combining the above equation with Eqs. (8) and (9) the polarisation correction factor \(c_{\text{pol}}\) written in terms of the on-ground measurements is
\[
c_{\text{pol}} = \left[ 1 + \frac{1 - \eta}{1 + \eta} \cdot q + \frac{1 - \zeta}{1 + \zeta} \cdot u \right]^{-1}
\] (11)

with \(q\) and \(u\) being the polarisation fractions of the incoming light, which have to be determined in the following steps. Note that \(c_{\text{pol}}\) depends on wavelength, on the scan angle of the mirror(s) and the observation mode, i.e. \(c_{\text{pol}}\) is different for Nadir and Limb observations.

### 7.2.3 Calculation of the polarisation of the atmospheric light

For the determination of \(q\) and \(u\), the on-board PMDs and theoretical models are used. Only a short summary of the polarisation calculation is given here, for details the reader is referred to Slijkhuis (2000). First the polarisation is determined for a few individual points. The polarisation near 300 nm (where no PMD is measuring) is determined theoretically from the scattering geometry in a single scattering approximation. The ratio of the signal in the science detectors and the PMDs is used to determine the polarisation for the central wavelengths of the PMDs. Since the PMDs have a much wider bandwidth than the science detectors, mathematically the signal \(S_{\text{PMD}}\) in the PMDs is written as the sum over a number of “virtual pixels” that have the same characteristics as the corresponding science channel pixels. This gives the following equation for the signal \(S_{\text{PMD}}\)
\[
S_{\text{PMD}} = \sum_{i=\lambda_{\text{start}}}^{\lambda_{\text{end}}} M^{P,i}_{11} I_{0,i} \cdot \left( 1 + \frac{M^{P,i}_{12}}{M^{P,i}_{11}} \cdot q + \frac{M^{P,i}_{13}}{M^{P,i}_{11}} \cdot u \right)
\] (12)

with \(M^{P,i}_{xx}\) being the Mueller matrix elements as derived from the on-ground PMD calibration for the virtual pixel \(i\) covering a certain wavelength and \(\lambda_{\text{start,end}}\) denoting the wavelength range of the PMD. Note that the PMDs A-F show a weak sensitivity to \(u\) and that the signal of PMD 45 is weakly dependent on \(q\). Therefore, additional assumptions have to be made to determine \(q\) and \(u\) from the PMDs. First the polarisation fractions are determined iteratively from PMD D and PMD 45 (these 2 PMDs measure \(q\) and \(u\) at the same wavelengths)\(^\text{5}\). Then \(q\) and \(u\) are determined using the following assumptions for \(u/q\):

\(^\text{5}\)Note that in the current processor version 5.04 the \(u\) value is derived from a theoretical \(u/q\) using the measured \(q\) value from PMD D instead of the described approach, see Sect. 7.3.

- The value of \(u/q\) for wavelengths smaller than a predefined wavelength \(\lambda_{\text{singlesc,sc}}\) is set to the single scattering value assuming that in this wavelength range single scattering dominates.

- For wavelengths larger than a wavelength \(\lambda_{\text{Aerosol}}\) the value of \(u/q\) is set to the value determined from PMD D and PMD 45 assuming that in this spectral region aerosol scattering and clouds dominate the polarisation of the light.

- In between \(\lambda_{\text{singlesc,sc}}\) and \(\lambda_{\text{Aerosol}}\) a linear interpolation to the central wavelengths of the PMDs is used.

It is also possible to use the channel overlaps to determine the polarisation. The wavelength range of all channels except channels 6 and 7 and channel 7 and 8 overlap (see Table 1). In the overlap regions the same signal is measured, but the polarisation sensitivity is different in the two overlapping channels. One can exploit this difference to determine the polarisation. However, so far \(q\) and \(u\) values determined from the overlaps are not very realistic. This is possibly related to problems with the low signal in the science channels near the channel boundary and problems with the radiometric calibration in that region (see e.g. Tilstra and Stammes, 2004). In the current data processor version 5.04 the channel overlaps are not used to determine \(c_{\text{pol}}\).

### 7.2.4 Interpolation to full wavelength grid

The result of the calculations described above are 7 values for \(q\) and \(u\), 6 values at the central wavelengths of the PMDs and one single scattering value at 300 nm. The final step in the polarisation algorithm is an interpolation of \(Q\) and \(U\) to the full wavelength grid of the science channels. The polarisation fractions for wavelengths between the wavelengths of PMD A and PMD F are calculated by an Akima interpolation (Akima, 1970), the polarisation fractions below 300 nm are set to the single scattering value and the fraction for wavelengths beyond the PMD F wavelength are set to the PMD F value. That leaves the region between 300 and 340 nm. The polarisation degree in this region changes rapidly due to the strong decrease of O\(_3\) absorption. No PMD measurements are available here. In order to obtain the polarisation fractions in this region the so-called Generalised Distribution Function (GDF) which was originally developed for GOME (Aberle et al., 2000) is used. The connection between the wavelength regions where different methods are used is done such that the gradient of the resulting curve remains continuous.

The polarisation correction factor \(c_{\text{pol}}\) can now be calculated for the whole wavelength range using \(q\), \(u\) and \(\eta\), \(\zeta\) in Eq. (11).
7.3 Problems

Looking at Eq. (11) one limitation of the calibration approach becomes clear. The polarisation correction is dependent on the accuracy of the $q$ and $u$ determination. The polarisation sensitivity (see Fig. 3) shows spectral features especially in channels 1–3 and in the channel overlaps. Whenever there is an error in the determined polarisation fractions, these spectral features will be visible in the polarisation corrected spectra. The measurement of the polarisation in SCIAMACHY with broadband sensors inevitably introduces an – unknown – error into the polarisation fractions. The spectral features in the polarisation sensitivity will be reintroduced through the polarisation correction, scaled by the error in $q$ and $u$. A preliminary investigation showed that this is mostly an issue for channels 1–5, where the atmospheric polarisation is relatively high. Since the instrument is more sensitive to the $q$ polarisation fraction, a large error here affects the spectra the most while an error in the $u$ fraction is negligible in most cases. For retrievals large features and features that correlate with a spectral structure of trace gases are most critical, a slow variation over the channel is less critical. Channel 1 and 2 show a strong sensitivity and are most susceptible to errors in the polarisation fractions (for an example see Tilstra and Stammes, 2005). A spectral feature of $\eta$ and $\zeta$ around 480 nm in channel 3 prohibits DOAS retrievals of $O_3$ in that spectral window. Further investigations are planned.

However, not all problems are necessarily related to an error in the determination of the polarisation fraction. Experience has shown that in the past errors in the data processor, in the derivation of the polarisation sensitivities from on-ground measurements and in the conversion of the different polarisation reference frames led to an incorrect polarisation correction. The processor and the calibration data were reviewed by SRON, DLR, TPD and IfE and both were corrected where necessary. Still, there are a few remaining problems. A check of the derived polarisation fractions shows that the values derived from PMD A for limb configurations are still unphysical for some observation geometries (see Fig. 4, bottom). In addition, with the current calibration data and processor version 5.04 it is not possible to derive correct $u$ values (see Fig. 4, top). The reason is still not clear, but possible causes are stray light in PMD 45, systematic errors during the on-ground calibration or a problem with the data processor algorithm. In view of the problems, it was decided not to use the original approach as it is described in the previous section to determine $u$. Schutgens et al. (2004) show that an approach based on the single scatter value of the polarisation leads to good results for most observation geometries and ground scenes. Therefore, the current version of the data processor determines $u/q$ from a single scattering approach for the whole wavelength range to calculate a $u_{\text{singleisc}}$ until the reason for the unphysical $u$ values determined from PMD 45 and PMD D is found. Investigations for a solution are ongoing.

The polarisation correction in the IR (PMD F) suffers from the transmission loss due to ice in channels 7 and 8 (see Sect. 9.1), since the polarisation fractions are determined using the ratio between the signal in the science channels and the PMDs. A correct retrieval requires a correction of the transmission in the IR channels. This is not yet implemented in the data processor. Other – most likely minor – effects that possibly change the polarisation sensitivity in the IR channels are the detector temperature change and the ice layer itself. Here, a study still has to be performed. It is recommended not to use the polarisation correction in the IR until at least the transmission correction is implemented. Since the polarisation in that wavelength range is relatively weak, the impact of not correcting for the polarisation sensitivity of the instrument is expected to be moderate.

In Limb observations, the calculated polarisation showed an unexpected drift with increasing tangent height. This is maybe related to the spatial stray light in Limb observations (see Sect. 6.2). Therefore, a scaling factor is applied to the polarisation measured at 30 km to calculate the polarisation...
at larger tangent heights. This is allowed, because the depolarisation remains constant above this height (McLinden et al., 2002).

An additional problem in the polarisation correction algorithm is related to the cluster concept (Tilstra et al., 2005). Jumps in the reflectance spectrum can appear between clusters with different integration times after normalisation to the integration time. The polarisation correction at shorter integration times is generally not as good as for longer integration times, because information from the missing parts of the spectrum in the channel is needed for a successful correction. This information has to be approximated for short integrations, since data from clusters with a longer integration time are not available in every readout (see last paragraph of Sect. 2). This can lead to an erroneous polarisation correction causing jumps at cluster boundaries.

In the meantime, alternative polarisation correction methods for the UV have been proposed by Tilstra and Stammes (2005) and Hasekamp et al. (2002). These methods incorporate the polarisation sensitivities \( \eta \) and \( \zeta \) themselves to determine a correction for the polarisation.

8 Radiometric calibration

8.1 Concept and on-ground measurements

The final step in the calibration of the data is the radiometric calibration. The retrieval of trace gases usually uses the reflectance, the ratio of the radiance reflected from the Earth’s atmosphere and solar irradiance. The solar irradiance is measured with on-board diffusers in-flight. Using Eqs. (7) and (11) the reflectance can be written as

\[
R = \frac{\pi \cdot I_{\text{Earth}}}{\mu_0 \cdot I_{\odot}} = \frac{\pi \cdot \eta_{\text{det}} \cdot \eta \cdot \zeta_{\odot}}{\mu_0 \cdot M_{11}^{\odot} \cdot S_{\text{det}}^{\odot}} \tag{13}
\]

with \( I_{\text{Earth},\odot} \) and \( S_{\text{Earth},\odot} \) as the Earth and sun intensity and measured signal, \( \mu_0 \) the cosine of the solar zenith angle, and \( M_{11}^{\odot} \) the radiometric responses for sun-diffuser measurements. \( M_{11}^{\odot} \) is the radiometric response for nadir and has to be used for nadir measurements, while \( M_{11}^{\odot} \) has to be used for limb measurements. For a proper calibration the instrument responses have to be determined as a function of wavelength \( \lambda \) and incidence angle \( \alpha \). As already mentioned in Sect. 3 the radiometric response was measured on instrument level under T/V conditions and the mirror (combination) and the mirror diffuser combination were measured under ambient conditions. In order to transfer ambient measurements to T/V measurements the ratio of a T/V measurement to an ambient measurement at the same incidence angle, the reference angle \( \alpha_0 \) is used:

\[
C_A(\lambda, \alpha_0) = \frac{R(\lambda)}{\eta_{\text{det}}(\lambda) \cdot R_N^L(\lambda, \alpha_0) + R_P^N(\lambda, \alpha_0)} \tag{14}
\]

where \( R \) is the radiometric response measured under T/V conditions in nadir configuration, \( \eta_{\text{det}} \) is the polarisation sensitivity of the OBM without the scan mirrors and \( R_{N,P}^N \) is the reflectivity of the nadir mirror for s- and p-polarised light. Using this relation, the radiometric response for Earth observations and sun observations can be written down as

\[
M_{11}^{N,L}(\alpha) = C_A \cdot [\eta_{\text{det}} \cdot R_N^L(\alpha) + R_P^N(\alpha)] \tag{15}
\]

\[
M_{11}^{\odot}(\alpha) = C_{\text{NDF}} \cdot C_A \cdot [\eta_{\text{det}} \cdot \eta_{\text{NDF}} \cdot B_s(\alpha) + B_p(\alpha)] \tag{16}
\]

where \( \alpha \) is the incidence angle on the mirror and diffuser, \( C_{\text{NDF}} \) is a factor that corrects for the Neutral Density Filter (NDF) that is in the light path for sun measurements, \( \eta_{\text{NDF}} \) is the polarisation sensitivity of the NDF and \( B_s,p \) is the reflectivity of the combination ASM mirror + ESM diffuser. Note that all elements of the above equations are wavelength dependent. The term in brackets in the above equations constitutes the so-called scan angle correction, which is derived from ambient measurements. The reflectance in terms of calibration measurements and detector signal becomes (using the above two equations and Eq. 13)

\[
R = \pi \frac{\eta_{\text{det}} \cdot \eta \cdot \zeta_{\odot}}{\mu_0 \cdot S_{\text{det}}^{\odot}} \cdot \left[ \frac{\eta_{\text{det}} \cdot \eta_{\text{NDF}} \cdot B_s(\alpha_1) + B_p(\alpha_1)}{\eta_{\text{det}} \cdot R_N^L(\alpha_2) + R_P^N(\alpha_2)} \right] \tag{17}
\]
It was already mentioned that SCIAMACHY can measure the solar spectrum in two ways: Using the ESM diffuser (this is the originally foreseen way) and using the ASM diffuser. The ESM diffuser showed large spectral features of 1—3% in on-ground measurements. Model calculation predicted that the retrieval of many products (e.g. BrO, SO$_2$ or OCIO) with DOAS could be made impossible by the spectral features (de Beek, R., Bovensmann, H., 2000). An analysis of in-flight data was done by Ahlers et al. (2004) and confirmed the presence of spectral features. The ASM-diffuser has been installed in a later stage on the back side of the mirror, after investigations of on-ground measurements revealed the presence of the spectral features. This diffuser is manufactured differently from the ESM diffuser leading to much smaller spectral features. No absolute calibration of the ASM diffuser could be performed, because SCIAMACHY was already integrated with ENVISAT when the diffuser was installed. Preliminary investigations showed that DOAS retrievals are significantly improved by using data of the ASM diffuser for the solar reference (see e.g. Sierk, 2003). Therefore, for DOAS retrievals that have an insufficient quality using the ESM diffuser spectrum, the usage of the ASM diffuser solar reference should be considered. After the update of the data processor to version 6.0, both solar references will be available in the Level 1 product.

8.2 Problems

Shortly after launch comparisons of modelled sun spectra from Kurucz (1995) and measured sun spectra showed that the solar irradiance measured with SCIAMACHY was around 10% too high for all wavelengths (see e.g. Skupin et al., 2003; Gurlit et al., 2005). The reflectance on the other hand was around 10–20% too low as comparisons with GOME (Tilstra et al., 2003; Latter et al., 2003), MERIS (Acarreta and Stamnes, 2005) and radiative transfer models (van Soest et al., 2005) revealed. The deviations could be traced back to two causes: (1) a wrong absolute value of the reflectivity $B_{s,p}$ (see Eq. 16) and (2) a insufficient scan angle correction derived from the ambient measurements. In the daily solar irradiance measurements in-flight 30 individual spectra of the sun are taken. During these measurements the incidence angles on the diffuser change due to the movement of the satellite relative to the sun. The insufficient angle correction was identified with the help of an additional set of on-ground calibration measurements with the same incidence angles as in the first in-flight ESM diffuser sun measurement. The data were not used for the radiometric calibration, since the instrument had to be tilted in the vacuum tank for these measurements making measurements in nadir configuration impossible. The sun irradiance derived from these data came close to known standards (Ahlers, 2003). The on-ground data used for the radiometric calibration were measured with a different geometry not matching the in-flight incidence angles and was relying on the scan angle correction from ambient data.

The reason for the inadequate scan angle correction and the wrong absolute value of $B_{s,p}$ is unclear. It could be either an error in the algorithms that were used to calculate $B_{s,p}$ from the ambient measurements or not all effects of the measurements set-up were taken into account. It is conceivable that the illumination conditions during the measurements made for $B_{s,p}$ were different from those encountered in-flight or that detector effects were not fully corrected (the ambient measurements were done on component level, not using the instrument detectors). SRON will review the on-ground calibration and the used algorithms to find possible errors. However, a complete review will take some time and although DOAS type retrievals do not rely on the absolute values of the reflectance, the retrieval of the aerosol optical thickness, cloud fraction algorithms, the determination of the surface albedo and vertical ozone profiles from nadir need radiometrically accurate data. Without a proper correction to the radiometric calibration these products loose accuracy.

In order to provide useful data before the review is finished, a new radiometric calibration data set was calculated by IfE (Noël, 2005) with input from SRON and TPD. TPD provided a new scan angle correction for $B_{s,p}$ (Schrijvers, 2004) and the raw, on-ground measurement data, SRON provided the new non-linearity (Kleipool, 2003) and memory effect correction (Lichtenberg, 2003) and an in-flight derived NDF transmission. IFE calculated from these inputs new calibration data, improving the interpolation of the ambient data to the full grid, correcting an apparent error in the ambient characterisation of the limb reflectivity $R_{s,p}^L$ and incorporating a new absolute value for the reflectivity $B_{s,p}$. Two different calibration data sets were calculated in this way, using two different types of on-ground data, the “spectralon” data measured with a NIST calibrated FEL lamp and the “NASA sphere” data measured with an internally illuminated, BaSO$_4$ coated sphere already used in NASA’s SBUV and TOMS programs for absolute radiometric calibration. Both calibration data sets were tested by KNMI in September 2004 using a set of 3 reference orbits.

The result of these tests were

- both new calibration data sets improve the offset value of the reflectance, the comparison with MERIS and Doubling-Adding KNMI (DAK) radiative transfer model show a deviation of at maximum 5%.

- the new calibration data introduce spectral features, most dominant around 350 nm (not polarisation related) and 880 nm,

- the spectralon data show better results than the NASA sphere data.

On the basis of these results the new spectralon calibration data will be implemented in the data processing update. Further verification and validation will be performed to assess
Fig. 5. Comparison of SCIAMACHY calculated reflectance with model calculations, using original calibration data (left) and “spectralon” calibration data (right). It can clearly be seen that the new radiometric calibration improves the overall offset of the reflectance, but also introduces a new spectral feature around 350 nm. Note that the dip around 300 nm is probably an artifact caused by insufficient characterisation of the ozone profile in the model (figure taken from Tilstra et al., 2004).

the quality of the new calibration and to assess the impact of the spectral features that were introduced.

9 In-flight effects

9.1 Ice in channels 7 & 8

Shortly after the very first cooling of the detectors, a significant loss of transmission in channel 7 and 8 was discovered. Investigations showed that an ice layer growing on top of the cylindrical lens covering the detectors was responsible. Only channel 7 and 8 are affected because these channels are cooled down to around 145 K while the other channels have temperatures of 200 K or higher (see Table 1). A likely source of the contamination is the carbon fibre supporting structure of ENVISAT itself, since it is known that carbon fibres can accumulate a substantial amount of water. The water contained in the fibres started to gas out once the satellite was in orbit. SCIAMACHY is covered by a double layer of multilayer insulation (MLI) blankets, one from ENVISAT and one from the instrument itself to prevent strong thermal gradients while in orbit. The MLI has a number of venting holes to allow the outgassing of the instrument and prevent a contamination of surfaces, but apparently the venting volume allowed by the holes is not large enough or the holes are obstructed. Thus, the contaminant is not (or too slowly) removed from the instrument volume. Other instruments on ENVISAT have also reported problems due to contamination (see e.g. Perron, 2004; Smith, 2002).

Under the assumption that the ice layer consists purely of water ice the layer thicknesses can be calculated using an absorption coefficient from Grundy and Schmitt (1998). The ice layer thickness is up to 230 µm (600 µm) in channel 7 (channel 8) six months after a decontamination. In order to remove the ice from the detectors and to restore the transmission, regular decontaminations at high temperatures are performed. The only heater on-board having enough power to heat the detectors to sufficiently high temperatures is the decontamination heater of the SRC which was installed to

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before it can settle on the detector lens. However, this explanation is purely based on the observed transmission behaviour of channel 7 and up to now no part of the detector module could be identified as a second cold trap. The difference in the behaviour of channel 7 and 8 is puzzling, since both channels are of identical design and operate at almost the same temperature (the difference is around 1 K). Thus, one would expect a similar behaviour.

Regardless of the reason of the ice layer build-up and its behaviour over time, the calibration and the operations of SCIAMACHY have been adjusted to minimise the effect of the ice. The first adjustment were made to the decontamination frequency. Originally it was required to decontaminate the cooler at least every six months to prevent irreversible damage to the cooler. The in-flight experience has shown that the cooling power did not decrease in 3 years of operations. Therefore it was decided to only do a decontamination, when the transmission in channel 7 and 8 drops below a level where a useful retrieval of trace gases is no longer possible. This prevents a situation like in summer 2004, were the transmission in channel 7 was degraded by 60% in the first 40 days after the decontamination. After that period the transmission increased again, but stabilised around 40% only, i.e. at a much lower level than after previous decontaminations (blue triangles in Fig. 7). Apart from this adjustment in operations, the ice layers lead to the following effects that can affect trace gas retrieval (see also Gloudemans et al., 2005):

Signal-to-noise loss due to transmission loss: When a sun reference from the same day is used, the effect on the value of the reflectance is only minor since the transmission loss cancels in the ratio of Earth and solar spectrum. However, the overall signals are lower, leading to a decreased signal-to-noise-ratio.

Change of slit function: The slit function is changed significantly by the scattering effect of the ice layer on the detector. This scattering is dependent on the thickness and the structure of the ice, which is not uniform over the detector array. A correction scheme using known trace gas contents for a certain geolocation as well as the effect on the retrieval if the slit function is not corrected is presented in Gloudemans et al. (2005).

Change of the dark signal: The dominant part of the dark signal in channel 7 and 8 is the thermal background (see Sect. 4.2). The thermal background is attenuated by the ice just like any other optical signal on the detector, leading to a variation of the dark signal on the timescale of a few orbits. Thus the IR data have been corrected with a dark signal measured as close as possible to the trace gas measurements. This has been implemented in the data processing in 2004 (version 5.01). In addition, the orbital variation of the background in channel 8 will also change with the transmission. It is currently investigated if this affects retrievals in channel 8.

9.2 Light leak in channel 7

After launch it was discovered that channel 7 shows a spurious signal in Limb dark measurements that is much higher than the spatial stray light found in the other channels (see Sect. 6.2). The signal shows no spectral signature, but is a broadband feature. This excludes the possibility that it is caused by light going through the complete optical system of the instrument. Further investigations were done by SRON to characterise the light leak. In this study, limb dark measurements at 250 km from all available Level 1b data of February 2004 were used to evaluate the light leak of channel 7. In order to determine the magnitude of the light leak, the data were corrected for non-linearity, dark signal (derived from the eclipse part of the orbit) and spectral stray light. Ideally, the signal should be zero after the corrections. Figure 8 shows the result for three pixels 103 (triangles), 502 (boxes) and 835 (stars). In the upper panel the light leak signal as a function of orbit phase shows a maximum of 120 BU/s.
Fig. 7. Comparison of transmission behaviour after decontaminations. Daily updated plots are available at http://www.sron.nl/index.php?option=com_content&task=view&id=322&Itemid=795. Different symbols/colours mark different decontaminations. Shown is the transmission as a function of time since the cool down in days. The development after the decontaminations in December 2003 (crosses) and June 2004 (triangles) are marked blue. The development after the last decontamination in December 2004 is marked in red. All values are normalised to a measurement in January 2003 done shortly after a decontamination removed the ice. Left: channel 7. Right: channel 8.

Fig. 8. Light Leak signal in channel 7 for pixels 103 (triangles), 502 (boxes) and 835 (stars). On the top panel the residual signal after being corrected for nonlinearity, dark measurement and spectral stray light is shown as a function of orbit phase, with phase zero defined as entry of the satellite into eclipse; sunrise occurs around orbit phase 0.4. The high peak seen at that orbit phase is caused by sunlight shining into the limb port and was expected. The bottom panel shows the mean absolute deviation for the same pixels from one month of data.

The signal is spectrally smooth and shows a systematic behaviour with orbit phase. However, the variation of the light leak signal from one observation to another is nearly as high as the light leak signal itself (see bottom panel of Fig. 8). This indicates that it is not only dependent on orbit phase, but probably also depends on the observation geometry and the presence of regions with high albedo, possibly caused by clouds. Up to now no set of parameters could be found to fully characterise and correct the light leak with sufficient quality. While to the authors knowledge no retrieval has been attempted from channel 7 data\(^6\), it is very likely that most retrievals will be severely affected because of the magnitude of the signal caused by the light leak and its unpredictable behaviour. Clearly, further study to understand the cause of the light leak and to develop a correction is needed.

9.3 In-flight degradation monitoring

Only a short summary of the monitoring is given here. Details of the application of the monitoring to the calibration can be found in Slijkhuis (2000) and first results are described by Noël et al. (2003). Preliminary monitoring results can be found at http://www-iup.physik.uni-bremen.de/sciamachy/LTM/LTM.html. The correction of a given light path is done by comparing calibration and monitoring measurements to the same measurement at a chosen reference point in time. The results are the so-called m-factors, which will be incorporated in the Level 1 files and used in the calibration of the data. At the moment of this writing not enough Level 1 data of sufficient quality are available to do a proper monitoring, therefore a preliminary monitoring is done on the basis of Level 0 files. The results show that the UV channels 1 and 2 show an average degradation of the transmission of around 10% in the 3 years since launch. All other channels show a stable transmission with the exception of channels 7 and 8, where the ice layer leads to a gradual loss of transmission in between the decontaminations. A first investigation into the spectral dependency of the degradation seems to indicate that the channel edges and the regions with high albedo are more affected.

\(^6\)Possible products in this channel are temperature profiles, cloud fractions and CO\(_2\) total columns.
a high polarisation sensitivity degrade the fastest. Degradation at the channel boundaries is expected. It is caused by a slow outgassing of the channel–separating dichroic mirrors. Studies to further investigate the degradation are planned.

10 Conclusions

In this paper we have described the basic concepts of the calibration of the SCIAMACHY instrument on-board ENVISAT. The calibration uses a combination of on-ground T/V and ambient measurements and a number of in-flight measurements. The individual calibration steps as well as problems encountered in the SCIAMACHY calibration have been discussed. The instrument itself has shown in general an excellent performance in the last 3 years. No major hardware problems were encountered and the in-orbit performance has not changed much with respect to the on-ground calibration. Notable exceptions are the ice deposition in channels 7 and 8, which is a problem that SCIAMACHY shares with two other instruments on the ENVISAT platform, the light leak in channel 7 and the growing number of degraded pixels in channel 7 and 8. Several errors in the on-ground calibration and the data processing were found in the last years, a large number of which will be corrected in the current update of the processing chain. After the update, the level 1 data will be significantly improved. Summarising, the following points can be made:

Memory effect: This effect is only seen in channels 1–5 and is an additive correction. Its effect on the retrieval is difficult to predict, but consecutive measured spectra of a highly variable scene and spectra with a high dynamic range are most likely to be affected. An updated version of the memory effect correction will be implemented during the current update of the operational processor to version 6.0.

Non Linearity: This effect is only seen in channels 6–8 and is an additive correction. The effect on the retrieval is expected to be minor. Only the retrieval of weakly absorbing trace gases is assumed to be affected. The non linearity correction will be implemented during the current update of the operational data processor.

Bad and Dead Pixels: Bad and dead pixels have to be masked out for retrievals, because they can ruin the retrieval of trace gases. Recently it has been discovered that the number of bad and dead pixels increases in-flight. The original calibration concept did not foresee a frequent update of the bad and dead pixel mask. Discussions between SRON and ESA have started on how to best implement a regular update of the mask into the operational processing.

Dark correction: The dark correction in channels 1–6 did not show strong variation since launch. In the channels 7 and 8 the dark correction changes every orbit, because of the ice layer growth. These channels need a dark correction derived from an orbit measured as close as possible in time to the science measurement. Since March 2004 the operational processor (version 5.01) uses the closest available dark measurement in the dark correction.

Orbital variation of darks: Channel 8 shows a variation of the dark signal within one orbit caused by minute changes of the OBM temperature. The orbital variation has a significant impact on CH₄ retrievals and has to be taken into account in the retrieval. It will be implemented during the current update of the operational data processor.

Changes caused by ice: The growing ice layer in channels 7 and 8 leads to a decrease of the transmission. A lower signal-to-noise ratio in the reflectances is the result. A correction of the transmission is straight-forward, but not yet implemented in the operational processing. More detrimental to trace gas retrievals is the change of the instrument slit function caused by scattering of the incoming light by the ice layer. While SRON developed a slit function correction based on scenes with known trace gas content, it is not possible to implement this algorithm in the operational processing. An operational correction is not available at this moment. The operations of the instrument now include regular decontaminations to remove the ice.

Light leak channel 7: The spurious signal caused by the light leak can be as high as 120 BU/s. While some dependence of the signal on the orbit phase can be seen, the variation over time can be as high as the average light leak signal itself. Due to the erratic nature of the signal, no correction algorithm could be developed so far. The light leak will severely affect all retrievals in this channel.

Spectral calibration: SCIAMACHY is spectrally very stable with the possible exception of the channel overlaps, where a detailed investigation is needed.

Stray light: Apart from channel 1 the amount of spectral stray light is very low. A dedicated stray light correction for channel 1 is implemented in the processing and is able to reduce the stray light to around 1% of the incoming intensity for individual pixels. Spatial stray light was discovered in Limb observations. Investigation showed that the stray light is entering through the slit from regions outside the IFoV. The impact of the spatial stray light on retrievals and a possible correction has still to be investigated.

Polarisation correction: A conceptual limitation of the polarisation correction used in the calibration is the sensitivity to errors in the retrieved  q and u values. Spectral features in the polarisation sensitivity  q and  ζ will be introduced through the polarisation correction when the polarisation fractions are wrong. The size of the effect depends on the polarisation degree and the size of the error. Channels 1–3 are most sensitive to this kind of error. The currently implemented polarisation correction is not able to retrieve a physical value for  u from the PMD D/PMD 45 combination, therefore a value
for $\alpha$ determined from the single scattering approximation is used in the determination of the correction factor $c_{pol}$. For some cases the polarisation fraction determined with PMDA in limb are unphysical. While a systematic study is missing, results show that the polarisation correction does not always remove all polarisation effects from the data. The correction was reviewed during the last year and improvement and bug fixes are implemented during the current update of the processor. After the implementation is finished, a new verification of the polarisation correction is planned.

Radiometric calibration: The basis of most retrievals is the ratio of the radiance reflected from the Earth’s atmosphere to the solar irradiation. SCIAMACHY can measure the solar irradiation with two diffusers, mounted on the ESM and the ASM. Preliminary studies showed that the ASM diffuser is more suitable for DOAS type retrievals than the ESM diffuser. The ASM diffuser is not radiometrically calibrated, while the ESM diffuser is. However, the original radiometric calibration produced solar spectra that were up to 10% too high and reflectances that are good within 5% in the tested wavelength range, but they also introduce spectral features. Usually retrievals that need an accurate reflectance are not as sensitive to spectral features as DOAS type retrievals, but it has to be investigated, if this is a valid assumption for the introduced spectral features. The new radiometric calibration data are incorporated in the current update and investigations on how to improve the radiometric further are going on.

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Large-scale validation of SCIAMACHY reflectance in the ultraviolet

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Abstract. In this paper we present an extensive validation of calibrated SCIAMACHY nadir reflectance in the UV (240–400 nm) by comparison with spectra calculated with a fast radiative transfer model. We use operationally delivered near-real-time level 1 data, processed with standard calibration tools. A total of 9 months of data has been analysed. This is the first reflectance validation study incorporating such a large amount of data. It is shown that this method is a valuable tool for spotting spatial and temporal anomalies. We conclude that SCIAMACHY reflectance data in this wavelength range are stable over the investigated period. In addition, we show an example of an anomaly in the data due to an error in the processing chain that could be detected by our comparison. This validation method could be extremely useful too for validation of other satellite spectrometers, such as OMI and GOME-2.

1 Introduction

The reflectance measured by a satellite instrument is at the basis of all geophysical information derived from the observations. The quality of the retrieved data depends crucially on the quality of the reflectance and its calibration. Besides, the spectral reflectance data set of the earth in the UV-visible-NIR range that was started with GOME (Global Ozone Monitoring Experiment) (Burrows et al., 1999) may be relevant for global change research, if it can be continued over a long time period. Therefore, it is of vital importance that the reflectance is carefully characterised spectrally and radiometrically, but also temporally and spatially to accommodate for trends and other systematic anomalies. Such a characterisation of SCIAMACHY nadir reflectance is the aim of this validation study. The properties of the observed radiation as derived from the raw measurements are collectively called “level 1 data”. These include earth radiance, solar irradiance, reflectance and polarisation.

Calibrated level 1 data is produced from the unprocessed (level 0) detector signal through application of a set of calibrations and corrections, e.g. wavelength calibration, radiometric calibration, polarisation correction, dark current corrections, etc. (Slijkhuis, 2001). Anomalies in level 1 data may be caused by the instrument, by the auxiliary parameters used for calibration and correction, and by the algorithms used to apply these.

A common strategy in the validation of retrieved geophysical parameters is the comparison with a collocated observation made by a different instrument. In the validation of level 1 data, this procedure is not generally applicable, as there is usually no instrument that can perform an independent collocated measurement. SCIAMACHY is in a relatively favourable position in this respect, since SCIAMACHY reflectance can be compared with that measured by MERIS (Medium Resolution Imaging Spectrometer) on the same platform (Acarreta and Stammes, 2005) and with the reflectance measured by the GOME spectrometer on ERS-2, which is in the same orbit with 30 min time difference. A drawback of this approach is the dependence on the calibration of the other instrument, which is a concern especially for the degraded UV channel of GOME. The MERIS calibration has been shown to be accurate to within 2–3% (Santer et al., 2005), but this instrument is not equipped with a UV band. Validation of the SCIAMACHY IR channels is also not possible by comparing with these instruments.

The nadir reflectance measured by a satellite instrument can, however, also be validated by comparing it with the reflectance that is calculated with a radiative transfer model (RTM). In order for this method to work, a careful estimate has to be made of the state of the atmosphere that is being sampled, along with the sensitivity of the spectrum to all parameters. The estimated parameters are the input for the
RTM, which calculates the spectrum expected from the satellite instrument. We choose to employ this technique in this paper, and apply it to the UV part of the spectrum, for two reasons: first, it complements the validation by comparison with other satellite instruments, and second, the sensitivity of the UV spectrum to the ground albedo and clouds, which are the main uncertainties in the input parameters, is small, especially for $\lambda<350$ nm (Tilstra et al., 2005). The major error source around 300 nm is ozone, which can be estimated accurately.

SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography) is a large spectral range, medium resolution spectrometer aimed at studying the composition of the Earth’s atmosphere (Bovensmann et al., 1999). The instrument was launched onboard the ESA Envisat platform in 2002. Several different retrieval algorithms are applied to obtain information about trace gas concentrations. The different methods present specific requirements to the quality of the level 1 data. Ozone, NO$_2$ and other trace gas column densities, for example, are typically retrieved with a DOAS-type retrieval scheme (Platt, 1994), which is particularly sensitive to small scale spectral structures in the reflectance spectrum, and less so to broadband offsets. Ozone profile retrieval and retrieval of aerosol or surface properties, on the other hand, critically depend on the absolute radiometric calibration, and suffer less from spurious structures in the spectrum. Wavelength calibration is of crucial importance to all.

All systematic SCIAMACHY reflectance validation activities until present have concentrated on nadir data from specially processed verification data sets. Although these verification data have the same properties, in theory, as the operational data product, a validation of operational SCIAMACHY data may reveal characteristics of those data that would not be found otherwise. There may be accidental differences between the processing of dedicated verification data and the operational chain. More importantly, some systematic properties of the data only show up in a data set that covers a large area geographically and a long time span. Validation of a large data set may reveal certain correlations that are overlooked if single orbits are investigated. Conversely, due to considerations of computing time and data volume, investigation of a large data set is less suited for a high spectral resolution investigation of possible residual structure in the reflectance spectrum.

2 Data and method

2.1 SCIAMACHY data

We investigate SCIAMACHY data from the near-real-time delivery stream, dated from 1 September till 15 December 2003, and from 1 April till 31 August 2004. These data are commonly used as a basis for geophysical retrieval products generated by scientific institutes. Over these periods, the instrument was stable, apart from a decontamination between 18 and 30 June. Data from this period have been excluded from the study. There were no large changes in the operational level 0–1b data processor configuration. The 2003 data have processor version 4.01 or 4.03, while the 2004 data have versions 5.01 and 5.04. We found no trace of the change in minor version number in the data. Noticeable effects of the difference between the processor versions 4.0x and 5.0x will be discussed below. Some parameters in the calibration key data have also changed, but signatures of a difference cannot be found in our analysis.

The level 1b data are calibrated to level 1c using ESA’s SCialic program, v2.2.9, using all calibration options (i.e., memory effect, dark current, stray light, pixel-to-pixel gain, etalon, and polarisation corrections, and wavelength and radiometric calibrations). From the calibrated radiance $I$ and solar irradiance $E$ observations, a reflectance $R_{\text{obs}}$ is calculated which is defined as:

$$R_{\text{obs}} = \frac{\pi I}{\mu_0 E}.$$  

$\mu_0$ is the cosine of the solar zenith angle.

Each SCIAMACHY state is divided in four “substates”, labelled “East”, “East-Center”, “West-Center”, and “West”, to yield four reflectance measurements per state. The dimensions of a substate are 240 km in the scan direction and 450 km in the flight direction of the satellite. Within each substate suitable ground pixels are averaged. The substates are introduced to limit data volume and computing time, and to average the very small signal for $\lambda<290$ nm, while keeping the possibility to study a possible viewing angle dependence and to be able to handle ground albedo variation. Four substates still allow a reasonably homogeneous ground albedo to be assigned to a scene and keep the possibility of investigating an eventual scan angle dependence.

2.2 Simulation and data selection criteria

The reflectance observed by SCIAMACHY is compared to the reflectance spectrum calculated with a radiative transfer model (RTM). The RTM we use is LidortA (van Oss and Spurr, 2002). This is a fast code based on the discrete ordinates algorithm (Chandrasekhar, 1950). In retrieval applications it has the enormous advantage of calculating the derivatives of the reflectance with respect to the input parameters analytically. We used this feature for determining the sensitivity of our method to some of the input parameters in another study (Tilstra et al., 2004). LidortA is a scalar model; the error made by ignoring the polarisation in the TOA (top-of-atmosphere) reflectance is corrected using a precalculated look-up table. The RTM is run on the ECMWF pressure grid of 60 layers up to 65 km.
We calculate the relative difference $d_R$ between the reflectance derived from data measured by SCIAMACHY and the reflectance $R_{\text{sim}}$ modelled by our RTM:

$$d_R = \frac{R_{\text{obs}}}{R_{\text{sim}}} - 1.$$  \hspace{1cm} (2)

The wavelength range covered is 250–400 nm for most of the data studied, part of the comparison was only done for 270–340 nm for reasons of computational cost. We only apply this method in the UV because this spectral range can be modelled with relatively coarse guesses for the atmospheric state and ground albedo.

The sensitivity of the simulation to input parameters, as well as an end-to-end error estimate of the use of RTM simulations as a validation method, are the subjects of another paper (Tilstra et al., 2005). For a full discussion we refer to that work. Its main conclusion is that the standard deviation of the error in the simulation due to input parameters is approximately 3% over the wavelength range 250–400 nm, and up to 8% around 305 nm where the sensitivity to the ozone profile and column is largest. The sensitivity study of Tilstra et al. (2005) does not include clouds. Our cloud filtering procedure adds an offset between 0% and 2% to their error estimate for $\lambda > 310$ nm, which is largest for the longer wavelengths in the study. In general, the error in the simulation is caused almost exclusively by errors in ozone for $\lambda < 300$ nm, while for $\lambda > 330$ nm, only errors in surface and lower-atmosphere parameters, such as clouds, aerosol, and ground albedo, contribute. In the intermediate wavelength range, all input parameters add significantly to the simulation error.

The wavelength grid for the RTM run has a spacing of 1 nm. SCIAMACHY data are convolved with a Gaussian synthetic slit function of 1 nm width before interpolating to the RTM grid. The ozone absorption cross section used in the RTM calculations was also convolved with this function. Since the contribution of inelastic scattering is small, and the atmospheric scattering cross sections are essentially constant over the 1 nm wavelength bins, this is an adequate approximation.

Based on the sensitivities of the RTM reflectance to input parameters, we defined a few criteria to decide upon acceptance or rejection of a ground pixel. These are listed below:

- Clouds: We only include (nearly) cloud-free pixels. The radiance from clouded pixels depends too strongly on the assumed value of the cloud albedo to be useful in a study like this.

The cloud mask is based on cloud fractions from the cloud retrieval scheme FRESCO (Koelemeijer et al., 2001), available from the TEMIS project website\(^1\). FRESCO is a very stable, reliable cloud retrieval scheme that has been validated against several independent data sets. The main drawback is that it overestimates cloud fractions over areas with large ground albedo in the O$_2$-A band, leading to rejection of e.g. states over desert.

We require the state to have a maximum of 20% cloud coverage; if the average cloud fraction in a state is larger it is entirely rejected. From the states with a cloud fraction less than 20%, only pixels with a cloud fraction smaller than 5% are included in the average over the substate. In this paper, the term “cloud free” means that a scene fulfills this criterion.

The error introduced by treating a pixel with a 5% cloud fraction as “cloud free” can be estimated by studying the correlation between $d_R$ and cloud fraction. We find that the maximum error incurred is 5% of the reflectance for $\lambda \approx 380$ nm, assuming 5% cloud coverage of the substate. For $\lambda < 300$ nm there is no sensitivity to clouds. In the set of accepted substates, we have 2% cloud coverage on average. It gives rise to a positive error of about 0.02 in $d_R$, smaller for shorter wavelengths. The effect can be compensated in principle by adjusting the ground albedo, but our study of the albedo sensitivity of the TOA radiance (Tilstra et al., 2005) demonstrates that this is not straightforward, as for most common surface types the sensitivity is wavelength dependent.

- Ground albedo: Ground albedos for individual cloud free ground pixels are obtained from the GOME LER (Lambertian Equivalent Reflectance) database (Koelemeijer et al., 2003) by spatial and temporal interpolation. Subsequently the albedos of accepted ground pixels in each substate are averaged. For each state, only one RTM run is performed; the atmospheric and surface parameters are identical for the 4 substates. For this reason, the ground albedo of a state has to be homogeneous. Substates with a ground albedo that differs from the average albedo of the state by more than 20% are excluded from the comparison.

- Solar zenith angle: Only nadir SCIAMACHY data with small to moderate solar zenith angles are included. The cloud and ozone data, that are inputs for the RTM, often suffer from reduced accuracy for large solar zenith angles. This diminishes their value as a reference. To prevent any influence on our study, we only include data with solar zenith angles smaller than 75°, corresponding to SCIAMACHY state IDs 4–7.

- Missing input: (Sub)states for which any of the input data are missing are rejected.

Other inputs needed for the RTM run are temperature, pressure, and ozone profiles. The temperature and geopotential height profiles are taken from ECMWF operational analyses. For the ozone profiles we use either the TOMS v8

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\(^1\)Tropospheric Emission Monitoring Internet Service, http://www.temis.nl/
ozone profile climatology (McPeters et al., 2003), or profiles derived from collocated SCIAMACHY limb measurements in the Chappuis band (Rozanov et al., 2004; Brinksma et al., 2004). The TOMS climatology is parameterised in month, latitude, and ozone column. For the ozone column density we take an interpolated value from the assimilated TOSOMI data set (Eskes et al., 2004), available from the TEMIS website, and retrieved by a method that is not sensitive to absolute radiometric calibration. The ozone profiles are interpolated to ECMWF pressure levels, using ECMWF temperature and geopotential height profiles. We assume that no aerosol is present; a significant contribution to TOA radiance due to aerosol only occurs in desert areas and would give rise to an error in $dR$ smaller than 2–3% in those regions for $\lambda > 300$ nm (Tilstra et al., 2005). Desert areas are often (erroneously) flagged clouded by FRESCO and thus rejected.

The data included in the validation has a spatial coverage that is shown in Fig. 1. This figure represents all selected data from April till June 2004, using the TOMS climatology for ozone profiles. The coverage in the case of collocation with limb-retrieved ozone profiles is smaller as these are not always available.

Ideally, the relative difference between observation and simulation $dR = 0$, though in practice we expect some scatter, caused by inaccuracies of the RTM input. Biases are either caused by the calibration of the measurement, or by systematic deviations of the input data. The probability of the latter has been minimised by the selection of the spectral range of the study, where the sensitivity to most input parameters is small and by a very strict cloud mask. The only ingredient of the simulation that is difficult to filter is the ozone profile. A deviation in the ozone profile, however, gives a clear spectral signature and can thus be discriminated.

3 Results and discussion

In this section we will primarily discuss data from 1 April till 18 June 2004, using the TOMS climatology as an ozone profile source. Data from 1 July till 31 August 2004, using the TOMS climatology have also been studied, but for a smaller wavelength range. There is no difference between the two periods in 2004, before and after decontamination of the instrument.

3.1 Spectral analysis

Figure 2 shows a spectrum of histograms of relative differences between reflectances derived from measured SCIAMACHY data and calculated with the RTM. For each wavelength in the calculated spectrum, a histogram of relative differences is made. The bin size of the histograms is 0.02. In Fig. 2 all data in accepted West (top) and East (bottom) substates from 1 April till 18 June 2004 are used (orbits 10 907–12 036). Ozone profiles come from the TOMS climatology. The spectrum has been normalised to the absolute maximum count (100% in the colour scale). The analysis of means and standard deviations was performed by fitting a Gaussian curve to the histogram for each wavelength.

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A few observations can be made about Fig. 2. First, the relative difference over most of the spectral range is between $-0.15$ and $-0.20$. This confirms previous findings in studies of the radiometric calibration of SCIAMACHY, compared to MERIS (Acarreta and Stammes, 2005) and GOME (Latter et al., 2003). The result is also consistent with a study comparing SCIAMACHY solar irradiance with theoretical reference spectra (Noël, 2004). The centre of the histograms for East substates is at a $dR$-value that is 0.01 higher than for West, in the range 310–400 nm (because the analysis is done by fitting, features of the ensemble that are smaller than the bin size can be discerned). This difference is smaller than the accuracy of the simulation applied to any one scene, but the standard deviation of the mean of an ensemble of scenes is smaller by $\sqrt{N}$. Since a difference between East and West substates persists in the average over thousands of scenes, it must be a real, systematic feature.

Second, there is a remaining feature between 300–310 nm which we attribute to a systematic inaccuracy of the ozone profile. We used the TOMS v8 Ozone Profile Climatology in these calculations, which has been developed for use with the TOMS instrument. Possible limitations in other applications have not yet been studied, to our knowledge. The feature in the spectrum for East substates is at a $dR$-value that is 0.01 higher than for West, in the range 310–400 nm (because the analysis is done by fitting, features of the ensemble that are smaller than the bin size can be discerned). This difference is smaller than the accuracy of the simulation applied to any one scene, but the standard deviation of the mean of an ensemble of scenes is smaller by $\sqrt{N}$. Since a difference between East and West substates persists in the average over thousands of scenes, it must be a real, systematic feature.

Third, the spread in East substates for $\lambda>320$ nm is larger than in West substates by about 0.02. The standard deviation of $dR$ in West substates is between 0.025 and 0.05, in East substates between 0.04 and 0.07. We do not have a full explanation for this observation. The number of accepted substates is substantially smaller for East than for West. The larger rejection rate for East substates is probably due to sun glint geometries over ocean, which are detected as clouded by Fresco. A residual effect of higher radiance caused by sun glint may persist in the comparison between observed and simulated reflectance, leading to a positive bias (1% in Fig. 2) and smaller accuracy for East substates. In addition, the difference may be caused partly by shortcomings of the polarisation correction applied by the calibration utility, since East scenes are much more strongly polarised than West. However, the sensitivity of the instrument to polarisation between 320 and 340 nm is very small so there we expect no effect. Also, the polarisation sensitivity exhibits a spectral structure around 350 nm, which we do not see in Fig. 2.

Fourth, an odd–even stagger is present, particularly for $300 \text{ nm} < \lambda < 340$ nm. This is probably an effect due to the undersampling of the ratio $dR$ and differences between the wavelength calibrations of the SCIAMACHY data and the ozone absorption cross sections we used. After we became aware of possible problems due to undersampling, we investigated the error incurred on a small set of spectra and found it to be less than 1% r.m.s. The effects of undersampling are only manifest on wavelength scales close to the grid spacing, and hence do not affect our conclusions which are about larger spectral ranges. However, in future applications of this method, it is advisable to decrease the sampling interval of the simulation to 0.5 nm at most, and interpolate these data to compute $dR$.

Finally, the spread for $\lambda<290$ nm becomes larger for smaller wavelengths. This is due to the small signal in this wavelength range, and hence the extreme sensitivity to calibration accuracy.
The width of the $d_R$-histograms shown in Fig. 2 (West) agrees well with the accuracy of the comparison predicted by the sensitivity studies presented by Tilstra et al. (2005). In the same study we found that for wavelengths larger than 400 nm the ground albedo has a large impact on the TOA radiance. The increasing spread in the relative difference $d_R$ for $\lambda > 320$ nm is caused by the increasing sensitivity to ground albedo. Since the knowledge of surface albedo is limited, we do not apply this method to longer wavelengths.

We note that by this method, small scale spectral structure cannot be detected reliably. For this purpose, a careful comparison of individual spectra is a better strategy. However, it is possible to find anomalies of approximately 3–4 nm wide, provided the sensitivity to any of the input parameters does not exhibit any spectral structure at the wavelength under consideration.

One useful application of the results presented in Fig. 2 is the correction of the instrument’s radiometric calibration with a polynomial fit based on the relative difference between observed and simulated reflectance. The advantages of determining a correction based on in-flight measurements are that it is based on the actual state of the instrument in operation, and it can easily be updated in a consistent manner to compensate for degradation effects.

### 3.2 Geographical analysis

The particular value of the technique we present in this paper is the potential to study spatial or temporal anomalies, which would not be found if a single state or a single orbit were studied. To demonstrate this, we made maps of the relative difference $\overline{d_R}(\lambda_0)$, spectrally averaged in a 20 nm wide window around $\lambda_0$, given in nm. Figure 3 is a map of $d_R(280)$ (i.e. the mean $d_R$ between 270 and 290 nm), covering part of channel 1 of the instrument.

Figure 3 shows that $d_R(280)$ is very constant over the globe, with values ranging between $-0.20$ and $-0.10$, apart from the South Atlantic Anomaly (SAA), the large black spot over South America and the Southern Atlantic. There is no significant other geographical dependence. The magnitude of the increased noise in the SAA, caused by cosmic radiation, is large compared to the real detector signal, and thus appears as a large positive difference $R_{\text{obs}} - R_{\text{sim}}$. Our analysis clearly indicates the exact extent of the SAA, and provides a reliable data set that can be used to mask out the phenomenon. The current mask used in data processing is a rectangular box in (lon, lat) coordinates, extending from (120° W, −60° S) to (50° E, 10° N). It covers all of Southern America, the Southern Atlantic, Central and Southern Africa and a large part of the Eastern Pacific (Slijkhuis, 2001). The masked region is so large that nearly half of the orbits pass through the SAA. Since calibration measurements that are flagged as being affected by the SAA are not used, an oversized mask leads to a waste of calibration data.

The scenes affected by the SAA have not been masked out in the analysis of Sect. 3.1. About one in 25 substates included in the analysis is in the SAA region, and these have a large, positive $d_R$. Their contribution to Fig. 2 is a very sparse cloud of points with $\lambda < 300$ nm and positive $d_R$. Its density is so low that it can not be seen in Fig. 2. The effect of scenes in the SAA on the discussion in Sect. 3.1 is very small, because the Gaussian fits to the histograms are
hardly affected by a sparse set of points in the far wing of the distribution.

In a similar manner as described for Fig. 3, we made a map of $d_R(330)$, displayed in Fig. 4. For this wavelength range, 320–340 nm in channel 2 of SCIAMACHY, $d_R$ is again constant over the globe, with values scattered between $-0.15$ and $-0.20$. Note that the colour scales for Figs. 3 and 4 differ. Only at higher northern latitudes, notably in Canada and Siberia, and in central Africa, $d_R(330)$ appears to be higher than for the rest of the world. We do not have an explanation for this observation. A possible cause for the higher observed reflectance in Africa could be an increased aerosol load due to biomass burning in this season, which we neglect.

Case study: Effect of erroneous dark current in 2003

The analysis of the data from 1 September–15 December 2003 was done with ozone profiles derived from SCIAMACHY limb measurements, in the wavelength range 270–340 nm. This data set is more sparse because limb data are not available for all days, and because of a stricter setting (a maximum allowed difference of 10%) of the filter for ground albedo inhomogeneity. The data show the same behaviour as discussed above for the channel 2 wavelength range 320–340 nm, shown in Fig. 4. The relative difference between the reflectance observed by SCIAMACHY and that simulated by the RTM is homogeneous over the studied part of the globe, with values of $d_R(330)$ around $-0.15$. On average, the relative difference in this data set is 0.03 less negative than the analysis of the 2004 data based on TOSOMI total ozone and TOMS climatology profiles. Whether this difference is caused by annual or seasonal effects in SCIAMACHY data, or by a difference in the ozone profiles used for the input of the simulation, cannot be decided strictly on the basis of these data. Ozone profile validation results (Brinksma et al., 2004), and the absence of observed seasonal effects in SCIAMACHY, however, suggest that the limb ozone profile is the most likely cause of the observed difference.

For the wavelength range in channel 1, the conclusion is different. A map of $d_R(280)$ is shown in Fig. 5. Again, the SAA is clearly visible as a compact region of large observed radiance. However, there is another large region where the difference between SCIAMACHY and RTM reflectance is markedly higher than for the rest of the world, namely over the Central and Western Pacific, Australia, Eastern Asia, and the Indian Ocean. This area coincides with the region from which orbits are processed specifically by one of two Envisat data processing facilities, namely the ESRIN station. Four orbits daily are processed at ESRIN, the remaining ten are processed at Kiruna.

Investigation of the processor initialisation files showed that the ESRIN facility used an erroneous dark current file. The relative error in the tabulated parameter was negligible, but owing to the very small signal for wavelengths smaller than 300 nm, the resulting error in the reflectance is 40%. In other channels of SCIAMACHY, the calibrated detector signal is much larger and small errors in the dark current have a much smaller effect, that may often remain unnoticed.

As a result of a general processor reconfiguration, the faulty dark current file was replaced in March 2004. It is advised not to use SCIAMACHY channel 1 data processed by the ESRIN facility prior to this date. A difference between Kiruna and ESRIN orbits was also found in SO$_2$ retrievals from channel 2 (A. Richter, personal communication, www.atmos-chem-phys.org/acp/5/2171/ Atmos. Chem. Phys., 5, 2171–2180, 2005)
2004), probably caused by the same error. Investigation of TOSOMI ozone (retrieved from channel 2) and Observation minus Forecast data from the TOSOMI ozone assimilation showed no feature associated with the anomalies in level 1 data.

The average reflectance difference $\bar{d}_R(280)$ of orbits processed at Kiruna is scattered between $-0.10$ and $+0.10$. This higher average value compared to the 2004 data of Fig. 3 may be caused by the pointing inaccuracy of the Envisat platform, affecting the limb profiles (Brinksma et al., 2004). Pointing accuracy was improved in December 2003. The wrong altitude of the ozone maximum influences the integrated stratospheric ozone column density and hence the simulated spectrum.

### 3.3 Temporal analysis

A critical issue for long term instrument performance is degradation of optical components or sensors. Also, the calibration of the instrument may, for whatever reason, show slow drifts or season variations that cannot be discovered by investigating a single state or orbit. Our validation system is a valuable tool for monitoring changes on long time scales.

An example is given in Fig. 6. It displays the average $d_R$ over the entire wavelength range (250–400 nm), as a function of orbit number. Values $>0$ are in the SAA region and hence cannot be trusted. But the rest of the data present a clear picture. The instrument and its calibration are stable over the investigated period, except for two episodes (approx. orbits 11 220–11 280 and orbits 11 950–12 036) where the reflectance as derived from SCIAMACHY measurements is a significant 3% lower than normal. After the first episode, the spread in the data starts to increase, until the end of the investigated period. The most probable explanation of these sudden changes of instrument behaviour is an operation or data processing change, though the documentation available to the authors does not mention any exceptions.

**Case study: Decontamination in channel 1**

With time, an ice layer forms on the infrared detectors of SCIAMACHY, because they act as a cold trap. This ice causes transmission loss and scattering problems. To alleviate this situation, SCIAMACHY is periodically heated to a temperature of 280 K to remove the ice layer. This heating is called decontamination. In these periods, data from the IR channels cannot be used, while the UV-Vis channels are supposedly not affected.

We performed our study for a period which included a decontamination episode. A non-nominal decontamination took place between orbits 12 031 and 12 208. In channel 2 the effect of the heating is not significant, although the average reflectance observed by SCIAMACHY is about 1% lower than just before and after decontamination. But in channel 1 the effect of decontamination is huge, in fact, much larger than the effect of the SAA. The higher temperature increases the dark current by a relatively small amount, which is, however, about 10 times the calibrated signal for pixels in the wavelength range 270–290 nm. This change in the dark current is not adequately accounted for. An example is given in Fig. 7.
3.4 Application to other instruments

The validation of satellite-measured reflectance spectra by comparison with RTM simulations is not limited to SCIAMACHY. Other instruments for which this method may be successfully applied are OMI (Ozone Monitoring Instrument) and the GOME-2 series. In principle, it would also be suitable for GOME, but the stringent selection criteria for clouds and ground albedo homogeneity, given GOME’s large ground pixel size, will lead to a high data rejection rate.

OMI (Stammes et al., 1999; Levelt et al., 2002) is ideally suited to be tested with the validation technique described in this paper. Most of the instrument’s spectral range (270–500 nm) can be simulated reliably. The small footprint ensures that many pixels are cloud free, and provide a good possibility to group pixels with a homogeneous ground albedo. Cloud retrieval from the O$_2$–O$_2$-band at 477 nm (Acarreta et al., 2004) can provide exactly collocated information for cloud masking. The range of viewing angles of OMI is very large, 114$^\circ$, so it is important to be able to check viewing angle dependence. OMI has the advantage that it is not sensitive to polarisation. Our fast RTM provides the possibility to evaluate the large amount of data generated by the instrument.

GOME-2 is very similar to SCIAMACHY’s UV-Vis channels in nadir mode. The comparison of GOME-2 reflectance with an RTM can be conducted in exactly the same manner as described here for SCIAMACHY.

4 Summary and conclusions

In this paper, we have presented a flexible and versatile method for validation of reflectance measured by remote sensing spectrometers in the UV. It was applied to SCIAMACHY level-1 data from the operational near-real-time data stream, that is often used by research groups as a basis for scientific retrievals. We have shown an analysis of data from late 2003 and mid 2004, demonstrating the power of the method.

The findings are consistent with earlier results, but supplements them in a number of ways. The spread in our histogram analysis of Fig. 2 validates the study of the reliability of the comparison between observed and simulated reflectance for single states (Tilstra et al., 2004, 2005). The extent of the SAA was shown to be much smaller than the mask that is currently used in data processing. Figure 3 can be used as a basis for a more accurate mask. The potential of our method for discovering inhomogeneities in the data processing or instrument performance were shown by the examples of the effect of decontamination on the reflectance in channel 1 (Fig. 7), and the large consequence of a small error in the dark current parameters used by the data processor (Fig. 5).

We also found two short episodes where the reflectance (average 250–400 nm) derived from the SCIAMACHY observations is approximately 3% lower than normal.

A general conclusion that we draw from all these examples is that observations for $\lambda<300$ nm should be handled with care. The calibrated signal in this spectral range is orders of magnitude smaller than the corrections that are applied to the raw measurements. As a result, the level 1c data that are used as input for retrievals are extremely sensitive to calibration inaccuracies. The errors introduced can easily amount to 100%. If these data are to be used for retrievals, an averaging procedure should be applied, as well as quality control, e.g. by comparing with an RTM.
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SCIAMACHY Absorbing Aerosol Index – calibration issues and global results from 2002–2004

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Abstract. The validity of the Absorbing Aerosol Index (AAI) product from the SCanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) is discussed. The operational SCIAMACHY AAI product suffers from calibration errors in the reflectance as measured by SCIAMACHY and neglect of polarisation effects in the AAI computational algorithm. Therefore, the AAI product was recalculated, compensating for the errors, with reflectance data from the start of measurements of SCIAMACHY until December 2004. Appropriate correction factors were determined for the UV to correct for the radiometric error in the SCIAMACHY reflectances. The algorithm was provided with LookUp Tables in which a good representation of polarisation effects was incorporated, as opposed to the LookUp Tables of the operational product, in which polarisation effects were not accounted for. The results are presented, their validity discussed, and compared to the operational product and independent AAI data from the Total Ozone Mapping Spectrometer (TOMS). The AAI is very sensitive to calibration errors and can be used to monitor calibration errors and changes. From 2004 onwards, the new SCIAMACHY AAI is suitable to add to the continuation of the long-term AAI record. Important changes in the long-term AAI record due to instrument and algorithm changes are highlighted. Recommendations are given for improvement of the operational AAI product.

1 Introduction

The AAI is a dimensionless index indicating the presence of ultraviolet (UV)-absorbing aerosols in the Earth’s atmosphere (Herman et al., 1997; Torres et al., 1998; De Graaf et al., 2005). The AAI has been used for a long time in remote sensing to indicate UV-absorbing aerosols, like desert dust (e.g. Chiapello et al., 1999; Alpert and Ganor, 2001; Pandithurai et al., 2001; Spichtinger et al., 2001; Prospero et al., 2002; Moulin and Chiapello, 2004) and biomass burning aerosols (e.g. Hsu et al., 1996, 1999; Gleason et al., 1998; Duncan et al., 2003; Darmenova et al., 2005) over both land and oceans.

Initially developed as an error estimate in the TOMS ozone retrieval algorithm (Herman et al., 1997; Torres et al., 1998), the AAI records have become the longest records of global aerosol measurements available. Starting with Nimbus–7/TOMS in 1978, American TOMS instruments have provided daily global aerosol maps continuously for over 25 years, with a data gap only between May 1993 and June 1996. From 1995, the European ERS–2/GOME provided additional and independent AAI information, adding to the continuity of the AAI record and validity of the AAI as an aerosol detection quantity (De Graaf et al., 2005). Now, Envisat/SCIAMACHY results will be added to the AAI records.

Operational data production of SCIAMACHY started at the end of July 2002. Several improvements and changes of the data processor and key data characteristics followed in the subsequent two and a half years. In this paper, the operational AAI product of this period is presented briefly.

Improper characterisation of the instrument’s response functions (key data) results at the moment in calibration errors in the measured reflectances of SCIAMACHY of up to 20%. This yields AAI errors in the order of 4–6, which is about 100% of the signal (De Graaf and Stammes, 2002). In this paper, correction factors for the reflectances are used and their validity for the calculation of AAIs is investigated.

The operational AAI product is calculated using precalculated LookUp Tables (LUTs) of theoretical reflectances in a cloud-free and aerosol-free atmosphere. These LUTs were constructed with a radiative transfer model (Spurr and...
balanced (Balzer, 2000) which neglected polarisation effects. Here, the AAI is further improved using LUTs in which linear polarisation is accounted for. The effects of this are presented and discussed.

The result of the changes mentioned above is an off-line AAI algorithm using calibrated SCIAMACHY reflectances, off-line LUTs, and additional calibration constants, producing SCIAMACHY scientific AAI. All off-line products developed after launch of the ENVISAT spacecraft are termed scientific products, to distinguish them from the operational products owned by ESA, and can be found at http://www.sciamachy-validation.org. The scientific AAI is presented and investigated, and compared to the operational product and other independent aerosol data.

This paper continues with a brief summary of the theory behind the AAI (Sect. 2). The characteristics of SCIAMACHY are described (Sect. 3), followed by a description of the operational AAI product and its shortcomings (Sect. 3.1). Improvements for an off-line product are discussed, leading to a new algorithm for a scientific AAI (Sect. 3.2), the results of which are laid out in Sect. 4. The spatial and temporal patterns of global aerosols found in the data are discussed and compared to TOMS AAI data. Sunglint and other problems in the data, related to the specific definition of the AAI, are pointed out. Finally, the results are discussed and some recommendations for future improvements are given (Sect. 5).

2 Absorbing Aerosol Index

The Absorbing Aerosol Index (AAI) is a measure for the spectral contrast between the reflectance of the real atmosphere-surface system, that may be affected by the presence of UV-absorbing aerosols, and that of a modelled atmosphere-surface system, that does not contain UV-absorbing aerosols. The modelled atmosphere may contain scatterers (Rayleigh scattering molecules, non-absorbing aerosols and cloud particles, as well as absorbing gases) and is bounded below by a surface with a wavelength independent reflectivity. The AAI is defined as the positive part of the residue, where the residue $r$ is defined as (Herman et al., 1997)

$$r = -100 \cdot \{ \nu \log \left( \frac{R_s}{R_{\lambda_0}} \right)_{\text{meas}} - \nu \log \left( \frac{R_s}{R_{\lambda_0}} \right)_{\text{Ray}} \}.$$  

(1)

$R_s$ is the reflectance at a wavelength $\lambda$, $R_{\text{meas}}$ is the measured reflectance in the atmosphere with aerosols, as opposed to a calculated reflectance in an aerosol-free atmosphere $R_{\text{Ray}}$, with only Rayleigh scattering and absorption by molecules and surface reflection and absorption. The reflectance is defined as $R = r I / (\mu_0 E_0)$, where $I$ is the radiance at the top of the atmosphere (TOA), $E_0$ is the solar irradiance at TOA perpendicular to the direction of the incident sunlight and $\mu_0$ is the cosine of the solar zenith angle $\theta_0$.

If the surface albedo $A_s$ for the Rayleigh atmosphere calculation is chosen so that

$$R_{\lambda_0}^{\text{meas}} = R_{\lambda_0}^{\text{Ray}} (A_s),$$  

(2)

where $\lambda_0$ is a reference wavelength, Eq. (1) can be reduced to

$$r_\lambda = -100 \cdot \nu \log \left( \frac{R_{\lambda}}{R_{\lambda_0}^{\text{Ray}}} \right).$$  

(3)

where $R_{\lambda_0}^{\text{Ray}}$ is calculated for surface albedo $A_s(\lambda_0)$, so the surface albedo is assumed to be constant in the range $[\lambda, \lambda_0]$. In this paper the traditional residue wavelength pair, $\lambda = 340$ nm and $\lambda_0 = 380$ nm, is adopted.

On the assumption that the atmosphere is bounded from below by a Lambertian surface, which reflects incident radiation uniformly and unpolarised in all directions, the surface contribution to the reflectance at TOA can be separated from that of the atmosphere (Chandrasekhar, 1960):

$$R(\mu, \mu_0, \phi - \phi_0, A_s) = R_0(\mu, \mu_0, \phi - \phi_0) + \frac{A_s t(\mu)t(\mu_0) - A_s s^* }{1 - A_s s^*}.$$  

(4)

The first term, $R_0$, is the path radiance, which is the atmospheric contribution to the reflectance. The second term is the contribution of the surface with an albedo $A_s$, $t$ is the total atmospheric transmission, $s^*$ is the spherical albedo of the atmosphere for illumination from below, $\mu$ is the cosine of the viewing zenith angle $\theta$ and $\phi - \phi_0$ is the relative azimuth angle. The path radiance $R_0$ is calculated with LUTs of $t(\mu, \mu_0)$, $t(\mu)$ and $s^*$ for all wavelengths used. Then the surface albedo $A_s$ in Eq. (2) can be found from

$$A_s = \frac{R - R_0}{t(\mu)t(\mu_0) + s^*(R - R_0)},$$  

(5)

by replacing $R$ by $R_{\lambda_0}^{\text{meas}}$ in Eq. (5). Note that this equation allows negative surface albedos, which occurs for highly absorbing (aerosol) layers.

Sensitivity studies show (Torres et al., 1998; De Graaf et al., 2005) that UV-absorbing aerosols produce an effect on the spectrum that cannot be simulated with a pure Rayleigh atmosphere and an adjusted surface albedo, creating large, positive residues, even for wavelength independent aerosol refractive indices. Scattering effects are much better represented with a Rayleigh atmosphere and underlying adjusted surface albedo, yielding small, negative residues. The AAI is therefore defined as the positive part of the residue, thereby filtering clouds and scattering aerosols.

3 SCIAMACHY

SCIAMACHY is part of the payload of the European “Environment Satellite” Envisat, launched on 1 March 2002 onboard an Ariane-5 launch vehicle from the Guyana Space Centre into a polar orbit at about 800 km altitude, with an
equator crossing-time of 10:00 a.m. (local time) for the descending node, orbiting the Earth every 100 min. SCIAMACHY is a spectrometer designed to measure sunlight, transmitted, reflected and scattered by the Earth’s atmosphere or surface in the ultraviolet, visible and near-infrared wavelength regions (240–2380 nm) at a moderate spectral resolution of 0.2–1.5 nm (Bovensmann et al., 1999). The radiance is observed in two alternating modes, nadir and limb, yielding data blocks called states. The nadir state swath is approximately 960×490 km², and it is scanned from east to west in four seconds by rotation of one of the two internal mirrors. The result is a subdivision of the states into ground-pixels of approximately 60×30 km² at the optical integration time (IT) of 0.25 s. Longer integration times of 0.5 s and 1.0 s also occur, yielding groundpixels of 120×30 km² and 240×30 km². Even longer integration times occur, but they will not be considered here. The extra-terrestrial solar irradiance is measured each day, once per 14 orbits.

3.1 Operational AAI algorithm

SCIAMACHY’s operational AAI product (L2-AAI) is calculated directly after downlinking of the data in the so-called near-real time level 1 (L1) to level 2 (L2) processing step. The processing steps are described in detail in Balzer et al. (2000). A brief summary is given here, to highlight the most important differences with the scientific AAI product, described below.

The reflectance is determined in the level 0 (L0) to L1 processing step for each groundpixel from channel 2, cluster 9, which contains the spectrum from 320.14 nm to 391.76 nm. Common normal mode ITs in cluster 9 are 0.25 s, 0.5 s and 1.0 s. These are constant within states, but can vary within orbits. The AAI is computed using the reflectances at 340 nm and 380 nm. A Rayleigh reflectance is determined from a pre-calculated LUT, for each pixel, dependent on geometry and surface height. The LUT has inputs for 11 reference heights from 0 to 5 km and 8 reference albedos from 0.0 to 0.9. The solar zenith angle \( \theta_0 \) must be between 15° and 85° and the viewing zenith angle \( \theta \) lower than 35°, otherwise no AAI is calculated.

The L2-AAI suffers from two major flaws. Firstly, the original LUTs were calculated with the use of a scalar radiative transfer model, so that polarisation was not accounted for in the Rayleigh scattering computations. When the LUTs were calculated, only a scalar version of the model, LIDORT (Spurr et al., 2001), was available. The residual calculations are sensitive to errors in the reflectances, see Fig. 1a. This figure shows the residual in a modelled Rayleigh atmosphere where polarisation has not been accounted for as a function of viewing and solar zenith angles. Relative azimuth angle is zero. (b) The scientific residue compared to the operational level-2 AAI data for orbit 10969, states 5–9. The colours refer to pixels with approximately the same viewing geometry. The first four pixels of 30×60 km² in a forward swath are called East pixels, the next 4 Center–east, the next 4 Center–west and the last 4 West pixels. The dashed line is the one-to-one line.

Secondly, the reflectances as measured by SCIAMACHY are underestimated in the UV by 10–20%, as reported by several workers (e.g. Tilstra et al., 2004). This results in an offset of the AAI of about 4–6 (De Graaf et al., 2004), which is of the order of the maximum expected AAI. To correct for these errors, a scientific AAI algorithm was constructed, which uses corrected SCIAMACHY L1 data (calibrated reflectances).

3.2 Scientific AAI algorithm

The scientific AAI (SC-AAI) is calculated off-line, i.e. after L1 data have been received via satellite link at the Royal
The surface albedo is calculated directly using Eq. (5). (De Haan et al., 1987), in which polarisation is accounted for.

The Doubling-Adding KNMI (DAK) radiative transfer model detail in De Graaf et al. (2005). The LUTs were created using calibration errors and improvements. This is illustrated in Fig. 2, which shows the number of pixels available at KNMI for the SC-AAI calculation, the processor version number that processed the L1 data of a certain period, and the results.

The uppermost panel and the colour code show the L1 processor version number, which reflects the status of the calibration process. Processor version 3.51 was the default when the first data became available. The processor was steadily updated to version 5.04 in December 2004, but reprocessed data have replaced older versions frequently (the newest available data was always used). The lower panel shows the number of residues that have been determined in a day. Because a residue is computed for all pixels which have a reflectance at 340 nm and 380 nm, this is a good measure for the amount of SCIAMACHY data of a certain day available at KNMI. The centre panel of Fig. 2 shows the scientific residue, averaged daily over the globe, as the normal black line and some isolated dots. The bold black line is its 30 day running mean.

The daily global scientific residue was highly erratic in the beginning, ranging from −7 and lower to more than 0.5. This is due to the very few number of measurements available at that time and the poor status of the calibration. Often, only one orbit was available on a day and the measurements frequently gave poor results. In 2004 the results improved considerably as the spread in the measurements decreased.

The monthly mean residues, averaged over the globe, are given as black diamonds. They are not exactly the same as the 30 day running mean, mainly because the monthly means are first monthly averaged per gridbox and then averaged over the globe. In 2004 the monthly mean maps of SC-AAI show results in the expected range of −2 to −1.

4 Results

The L2 data can be obtained from the European Space Agency (ESA). The scientific data are available at http://www.temis.nl. Both gridded daily data and gridded monthly means are available as well as daily and monthly pictures. The SC-AAI was determined from all SCIAMACHY L1 data available from 22 July 2002 to 31 December 2004.

The calibration processor of SCIAMACHY has regularly been updated over the last two and half years. This is reflected in the AAI data, which is very sensitive to calibration errors. In that way the AAI can be used as a monitor for calibration errors and improvements. This is illustrated in Fig. 2, which shows the number of pixels available at KNMI for the SC-AAI calculation, the processor version number that processed the L1 data of a certain period, and the results.

The changes are illustrated in Fig. 1b. This figure shows the scientific residue compared to the L2-AAI for 5 states of orbit 10969 on 5 April 2004 over the Sahara, where a dust plume was present at that time. Note that the scientific residue is the quantity that is determined for all SCIAMACHY pixels. The SC-AAI is the quantity that signals the presence of aerosols, or other absorbing effects, by filtering of negative residues. The figure shows the offset of 4–6 of the L2-AAI compared to the scientific residue, caused by the underestimation of the reflectances. Moreover, it shows that the offset differs by about two for east and west pixels, which is caused by the neglect of polarisation in the L2-AAI. This behaviour is found throughout the data.

Netherlands Meteorological Institute (KNMI). The data are calibrated and radiances and irradiances are extracted to determine the reflectances at 340 nm and 380 nm. These reflectances are averaged over a one nm wide window. After this, the reflectances are corrected for the underestimation of the reflectance by SCIAMACHY. This correction consists of a simple multiplication of the reflectances by a constant factor. Several factors were tried and the best multiplication factors were 1.210 for \( R_{340} \) and 1.130 for \( R_{380} \) (Tilstra et al., 2004). Note that different multiplication factors will lead to a linear shift in the resulting AAI (De Graaf et al., 2004, 2005).

The corrected reflectances are used in Eqs. (2) and (3). The inversion process and the LUTs used therein are described in detail in De Graaf et al. (2005). The LUTs were created using the Doubling-Adding KNMI (DAK) radiative transfer model (De Haan et al., 1987), in which polarisation is accounted for. The surface albedo is calculated directly using Eq. (5).

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The monthly mean residues, averaged over the globe, are given as black diamonds. They are not exactly the same as the 30 day running mean, mainly because the monthly means are first monthly averaged per gridbox and then averaged over the globe. In 2004 the monthly mean maps of SC-AAI show results in the expected range of −2 to −1.
The L2-AAI, shown in purple, correlates well with the scientific residue, but note that the y-axis is shifted by +6. The correction factors used to correct the reflectances to compute the SC-AAI cause a linear shift of the residue. The differences that remain between the SC-AAI and L2-AAI are due to the neglect of the polarisation in the Rayleigh atmosphere calculations and different sensitivities to processor changes.

An example of SCIAMACHY SC-AAI measurements is given in Fig. 3, which shows the SC-AAI on 16 June 2004. The daily global coverage of SCIAMACHY is illustrated, which is only 1/6th of the globe. The black rectangles are the outlines of the nadir states. Only within these states can an AAI be derived. This resolution makes daily monitoring of aerosols difficult, but the data is provided daily to offer the best possible resolution to end-users. The irregularly spaced orbits show that not all orbits were available, which was often the case (see Fig. 2, lower panel).

On 16 June 2004 desert dust aerosols can be found over northern Africa, the Middle East region, and parts of China, which are very common in these areas in June. Over the northern Atlantic low SC-AAI values can be observed in a number of states, with clear parts in the east pixels of some states. These are desert dust plumes extending over the Atlantic, with sun glint (see below) pixels removed from the data. Also over the Mediterranean Sea and the northern Pacific some remnants of sun glint can be observed.

4.1 Sun glint

Sun glint is a problem that occurs throughout the year. Sun glint generates a high SC-AAI signal in the eastern pixels of SCIAMACHY. If the sun glint angle is defined as the angle for which sun glint would occur if an ocean was a perfect mirror, the deviation from this angle $\Delta \Omega_{\text{glint}}$ can be defined for each pixel as

$$
\cos(\Delta \Omega_{\text{glint}}) = \cos \theta_0 \cos \theta + \sin \theta_0 \sin \theta \cdot \cos(\phi - \phi_0). \tag{6}
$$

Because the roughness of the oceans spreads out the sun glint signal, pixels having a sun glint deviation angle $\Delta \Omega_{\text{glint}}$ larger than zero can also be affected by sun glint. The geometrical sun glint condition was defined as the geometry for which the sun glint deviation angle was lower than 12°. A pixel satisfied the sun glint condition when it satisfied the geometrical sun glint condition and had an ocean as underlying surface. The underlying surface was determined using the 0.25° x 0.25° GTOPO elevation database with an ocean flag. Pixels satisfying the sun glint condition were removed.

The residues of all pixels satisfying the sun glint condition of three months (October–December 2004) were compared to all land pixels satisfying the geometrical sun glint condition. The average residue of the sun glint pixels was $-0.38$ and that of the land pixels was $-1.38$. The average residue for pixels not satisfying the geometrical sun glint condition was $-1.56$ over both land and ocean. This was considered a confirmation that the high residue in ocean sun glint pixels was anomalous and caused by sun glint.

The effect of using a sun glint deviation angle $\Delta \Omega_{\text{glint}}$ lower than 12° is illustrated in Fig. 4. Figure 4a shows the sun glint deviation angle for SCIAMACHY pixels on 12 December 2004 over the Indian Ocean, Indonesia and Australia, and the south-west Pacific. The pixels satisfying the sun glint condition are marked in red, other ocean pixels’ sun glint deviation angles are marked according to the continuous colour scale. Figure 4b shows the SC-AAI when no sun glint mask is applied. Several bands with high SC-AAI values can be distinguished in the eastern pixels over the oceans, but not over land. Applying the 12° sun glint deviation angle mask removes most of the pixels with high signals (Fig. 4c). A more severe sun glint mask, e.g. removing all ocean pixels with sun glint deviation angles lower than 15°, improves the picture on 12 December 2004, because it is not likely that any aerosol events caused the high signals on this day in the area shown. But since the sun glint mask does not discriminate between sun glint and aerosol events, the sun glint mask will remove pixels with aerosol information for situations with aerosol plumes over the oceans. To reduce this problem the condition was set strict enough that sun glint is removed from most of the pixels, leaving only some small remnants in clear sky pixels with sun glint deviation angles close to 12°. These remnants will not easily be mistaken for artificial aerosol events. On the other hand, the condition is not so strict that it will remove all aerosol pixels from aerosol plumes over oceans. The locations of pixels satisfying the sun glint condition are easily recognised and the gaps which the sun glint mask produces are small enough so they will not greatly reduce the signal caused by aerosols.
4.2 Spatial and temporal patterns

Three-monthly means of SC-AAI in 2004 are presented in Fig. 5 to show the most persistent aerosol sources and seasonal variations. The range of the AAI data plotted in Fig. 5 is from $-0.4$ to $2.5$. Theoretically, for a well-calibrated AAI positive values should indicate absorbing aerosols. In reality some fine-tuning is needed to establish the right threshold. Figure 2 shows that the average of the scientific residue is about $-2$, lower than the global average GOME residue in the period 1995–2000 (De Graaf et al., 2005), which was $-1.2$. The correction factors for the SCIAMACHY reflectance offset are not entirely correct, causing the residue to be smaller than usual (see Sect. 4.4). Therefore, the lower plotting boundary was lowered to $-0.4$.

The first panel of Fig. 5 is the average of the monthly means of January, February and December (JFD) of 2004. Only a few persistent aerosol sources over the Sahara show up in the plot. As was shown in Fig. 2, the average AAI in the first two months of 2004 was very low, probably due to incorrect calibration. Still, the southern part of the Sahara shows some signal.

The next panel in Fig. 5 shows the boreal spring (MAM) main aerosol sources. As was found with GOME (De Graaf et al., 2005), very persistent aerosol sources are found over northern Africa and the Middle East. SCIAMACHY also detects the aerosol plumes north-west of India, which were never detected by GOME because of its data storage problem in that region.

In the summer (JJA) the typical desert dust plume over the Sahara, extending far over the northern Atlantic, is clearly present. This is one of the most prominent features of the AAI and can be observed in all summer months. Also the biomass burning aerosol plume west of Angola, that was found every summer of 1995–2000 by GOME, is present. The aerosol plumes over the northern Sahara and the Middle East are strongest and most persistent, as a result of the most northerly position of the Inter-Tropical Convergence Zone (ITCZ) at that moment.

In autumn (SON) all aerosol plumes present in the summer are weaker, but still discernible. A clear plume is visible over the north-west of Australia. This plume frequently showed up in the GOME data as well, but was difficult to distinguish from the noise, because of the large footprint of GOME ($40\times320$ km$^2$). SCIAMACHY data however clearly show a persistent aerosol source in this area. Possible sources might be desert dust from Australia or biomass burning from Indonesia and Australia or both.

4.3 Comparison with TOMS AAI

The SCIAMACHY SC-AAI was compared to the TOMS AAI. However, the TOMS AAI is different from the SCIAMACHY AAI in several ways. The definition of the TOMS AAI has changed with the introduction of version 8 data...
Fig. 5. Maps of the seasonally averaged global SC-AAI. Shown are the mean SC-AAI in January, February and December of 2004 (Winter), mean SC-AAI in March, April and May 2004 (Spring), mean SC-AAI in June, July and August 2004 (Summer) and mean SC-AAI in September, October and November 2004 (Autumn).

(2004), which has increased the sensitivity of the TOMS index, compared to that of version 7 data. This fact is not very widely known, but has quite large implications for the interpretation of the index. Also, the calibration differences of the instruments have an impact on the behaviour of the indices. Before the indices are compared, the different definitions are given and the differences in sensitivities will be highlighted.

Two wavelengths in the UV are used to calculate the AAI (Eq. 1). In the definition of the V7 TOMS AAI (also used for SCIAMACHY), the reference wavelength $\lambda_0$ is the largest of the two wavelengths (360 nm for TOMS and 380 nm for SCIAMACHY). In the definition of the V8 TOMS AAI this has changed and the reference wavelength is the shortest wavelength (331 nm for TOMS). This has increased the sensitivity of the index, see Fig. 6 where the monthly averaged TOMS V8 AAI is compared to the monthly averaged TOMS V7 AAI. The V8 AAI is about $1.5-2$ times as sensitive as the V7 AAI and correlates nonlinearly. Also the V7 AAI was valid only from 0.7 upward, to indicate the presence of absorbing aerosols, in V8 this threshold has changed to zero (P. K. Bhartia, pers. comm.). Note that the majority of the points in Fig. 6 are on the line where V7 TOMS AAI is zero.

In the V7 definition this meant that there would be no absorbing aerosols, while all V8 pixels with AAI larger than zero now do indicate absorbing aerosols.

The reason for the increased sensitivity is the larger optical thickness at the lower wavelength (about 60% larger at 331 nm compared to 360 nm). In the AAI method all atmospheric scattering and absorbing effects are modelled with an adjusted surface albedo under a Rayleigh atmosphere. At the lower wavelength the atmospheric effects are relatively larger and the retrieved surface albedo is affected more strongly. The relationship between the V7 and the V8 AAI is nonlinear, because the reflectivity at the reference wavelength is a nonlinear function of geometry and atmospheric conditions. Nonlinear relationships between AAIs with different reference wavelengths were also found by De Graaf et al. (2005).

Also note that the sensitivity of the TOMS AAI changes with the different TOMS instruments since different instruments had different channels. Currently, EP/TOMS uses channels in the UV at 331 nm and 360 nm. Before this (i.e. data from before 1996), TOMS instruments had channels in the UV at 340 nm and 380 nm. The same is true for GOME and SCIAMACHY: for GOME the wavelengths used were...
Fig. 6. Comparison of monthly averaged TOMS V7 AAI and TOMS V8 AAI, for all valid points in the period January 2002–July 2003. TOMS V7 AAI is only defined for values >0.7.

The performance of the SC-AAI was compared to TOMS data, see Fig. 7. In this figure the zonal averages of the SCIAMACHY residue (black bold solid line), the SCIAMACHY AAI (black normal solid line), the TOMS V7 residue (purple dashed line), the TOMS V7 AAI (green dashed-dotted line), and the TOMS V8 AAI (red dotted line) are plotted, for 2002, 2003, and 2004. The TOMS V7 residues are daily values, the TOMS V7 AAI are monthly averages. These V7 products are no longer available, because the data are replaced by V8 data, but the V7 residues in the figure had been saved from previous studies. The monthly averaged TOMS V7 AAI were only available from January 2002 to July 2003, the daily TOMS V7 residues were available from January 2002 to June 2004. All other other products are freely available for the periods that the various instruments produced measurements. The SCIAMACHY data is cut-off above 60° N and S. Zero values (and invalid data) are not plotted, hence the curves do not always extend to the poles.

The differences between the TOMS V7 residue (purple dashed line) and the TOMS V7 AAI (green dashed-dotted line) show the behaviour of averaging a quantity that is defined by a threshold. Since only TOMS V7 residues larger than 0.7 are defined as TOMS V7 AAIs, the averaged TOMS V7 AAI is always positive and the zonal structure of the AAI is different from the zonal structure of the residue because the number of points over which is averaged is not constant for the AAI (it is not always defined). The same holds for the SCIAMACHY AAI (black normal solid line) and the SCIAMACHY (black bold solid line) residue. Since the calibration of SCIAMACHY is different from that of TOMS the threshold from which to define the AAI is different and comparison of the AAIs is difficult. Instead we compare residues (SCIAMACHY and TOMS V7), because an error in the calibration in one or both instruments will only yield a different absolute value of the residue (assuming the sensitivity of the residue to the geometry and atmospheric conditions is the same). Of the version 8 data only AAI data are provided in the TOMS L3 datasets. The full residuals are provided on the TOMS L2 datasets but these were not investigated.

In 2002 the SCIAMACHY residue (and hence SC-AAI) results are not very satisfactory, no clear zonal pattern is discernible in Fig. 7. In 2003 a local peak is seen around 25° N, but the picture is mostly determined by the noise near the poles. In 2004 the noise level has dropped below the signal level and is confined to a region near 60° N and S. The SCIAMACHY residue correlates well to the TOMS V7 residue in 2004, although the SCIAMACHY residue is lower by about 0.2. The SCIAMACHY residue correlates also well with the TOMS V8 AAI in 2004 (but shifted by −0.4).

A clear peak in the SCIAMACHY residue can be distinguished between 5°−30° N, which is where the major Northern Hemisphere (NH) deserts are located. A smaller peak can be found on the Southern Hemisphere (SH), between 0°−30° S. The TOMS V7 AAI shows the same behaviour, although the relative differences between the NH and SH are less than in the SCIAMACHY residue. In the period 1996–2000 both TOMS and GOME found a similar behaviour, with a large difference between the NH and SH (De Graaf et al., 2005).

From the difference between the SCIAMACHY and TOMS V7 residues we might conclude that the quotient of the correction factors is not correct, producing smaller residues than expected. Therefore the threshold where absorbing effects and scattering effects are separated, and from which the AAI must be defined, is smaller than that of TOMS, probably even negative. Whether the correction factor for the smallest wavelength (\( R_{340} \)) is too large or...
the correction factor for the largest wavelength ($R_{380}$) is too small cannot be determined, because the residue only gives information about the slope of the reflectance spectrum. From the value of $-0.2$ between SCIAMACHY and TOMS V7 residues we can conclude the error in the quotient of the correction factors is about $0.5-1\%$. The TOMS V8 AAI is larger than the SCIAMACHY residue by about 0.4, but this additional value is caused 'TOMS' higher sensitivity and greater daily global coverage. When more positive values are found the (zonal) average will increase since the number of pixels over which is averaged will increase.

5 Conclusions

The scientific Absorbing Aerosol Index product (SC-AAI) of SCIAMACHY shows promising results for 2004. The underestimated reflectance of SCIAMACHY in the UV (Tilstra et al., 2004) was corrected with constant multiplication factors at the AAI wavelengths 340 nm (1.210) and 380 nm (1.130). This resulted in an AAI that is almost in the expected range of lower than zero for scattering events (clouds and scattering aerosols) and higher than zero for absorbing aerosols. However, Figs. 5 and 7 show that the correction factors are still not correct and a better calibration of the reflectances is necessary. The error in the quotient of the correction factors is about $0.5-1\%$.

The SC-AAI algorithm accounts for polarisation in the Rayleigh reflectances, thereby improving the viewing angle offset found in the operational AAI product (L2-AAI). As the L2-AAI is calculated in the level 1 to level 2 processing stage, the LUTs used by the processor can easily be updated using a radiative transfer model incorporating (linear) polarisation. This would improve the L2-AAI and make it a useful product. The only problem remaining then for the operational product would be the reflectance offset, which can be corrected using a linear shift of the AAI. This change of LUTs is highly recommended.

The SCIAMACHY SC-AAI has revealed sun glint related problems in the interpretation of the AAI. Sun glint can easily be defined geometrically, but the sun glint mask used for SCIAMACHY pixels does not distinguish between high AAI as a result from sun glint or from aerosol events. This might be improved using the absolute value of the reflectances. Absorbing aerosol events reduce the reflectances, but more so at the lower wavelength, causing a positive residue. It is anticipated that sun glint will increase the reflectances, but probably more so at the higher wavelength, also creating a positive residue.

The SC-AAI gives reasonable results after March 2004, when the processor version was updated to version 5.01. The seasonal means in 2004 show the same characteristics as were found by GOME in 1995–2000 and the same as found by TOMS. This makes SCIAMACHY suitable for the continuation of the long-term AAI record, now that GOME is failing and EP/TOMS is suffering from degradation.

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Alternative polarisation retrieval for SCIAMACHY in the ultraviolet

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Abstract. We introduce an alternative method for the retrieval of polarisation in the ultraviolet by the satellite spectrometer SCIAMACHY. Unlike the operational polarisation retrieval algorithm, this method does not use the Polarisation Measurement Devices (PMDs) onboard SCIAMACHY, but only requires the reflectance signal. This makes the algorithm more robust and less sensitive to calibration errors caused by either improper characterisation of the instrument’s response functions (key data) or degradation of the optical components.

The alternative polarisation retrieval is able to retrieve the full state of atmospheric polarisation in the wavelength range between 330 and 400 nm, which is essentially the wavelength region covered by SCIAMACHY’s PMD 1. This allows a direct comparison with the current operational product.

When we compare the alternative polarisation algorithm with the operational algorithm, we find in some cases agreement, but not in other cases. The alternative algorithm compares well with an analytical model of the polarisation of a cloud-free scene. Using the alternative algorithm the polarisation-sensitive feature in the SCIAMACHY reflectance around 350 nm is automatically corrected for.

1 Introduction

Satellite instruments for remote sensing of atmospheric composition like SCIAMACHY (Bovensmann et al., 1999), GOME (Burrows et al., 1999), and GOME-2 (Callies et al., 2000) all have a common problem. Due to a variety of optical elements, such as mirrors, gratings and prisms, the radiometric response functions of the instruments depend on the polarisation of the incoming light. A correction for this sensitivity is possible, but only in-flight because it requires knowledge of the polarisation of the light. For that reason, these instruments are equipped with Polarisation Measurement Devices (PMDs) to determine the polarisation at a given number of distinct wavelengths.

This paper will present a validation study on the SCIAMACHY polarisation product in the UV. We validate the polarisation product by introducing an alternative method to determine the polarisation. This alternative method does not use the PMD measurements, only the reflectance, and can therefore be regarded as an independent source. From comparing this source to the operational polarisation product, we conclude that there are still discrepancies found in the operational product. We attribute these remaining problems to the calibration of the instrument.

The outline of the paper is as follows. In Sect. 2 we start with a short description of the SCIAMACHY satellite instrument. Section 3 introduces the concept of atmospheric polarisation and its relevance to the radiometric calibration of SCIAMACHY. Section 4 is completely devoted to the alternative polarisation retrieval we introduce in this paper. In Sect. 5 we compare the alternative retrieval with the operational polarisation retrieval. The paper ends with conclusions.

2 Description of SCIAMACHY

SCIAMACHY is a remote sensing spectrometer designed to record sunlight before and after it has been scattered by the Earth’s atmosphere. The instrument is located onboard the Envisat satellite, which was launched on 1 March 2002. Using a series of eight spectral detectors, SCIAMACHY is able to cover virtually the entire spectrum between 240 and 2400 nm. Radiance measurements can be performed in both nadir or limb mode (Bovensmann et al., 1999). These modes generally alternate each other and the blocks of data generated from these nadir or limb modes are called states.
Figure 1 shows the footprints of two nadir states taken from orbit 2509, dated 23 August 2002. The size of a nadir state is approximately 960 × 490 km². The limb state that lies in between the two nadir states is not indicated. The smaller footprints are created when the instrument scans the Earth from east to west by rotating one of its internal mirrors. The resulting groundpixels are linked to an optical integration time (IT) of 0.25 s and their size is about 60 × 30 km². Indicated by the green and blue regions are pixels that are related to integration times of 0.5 s and 1.0 s that can also occur. These pixels cover roughly 120 × 30 km² and 240 × 30 km² of the Earth’s surface, respectively. Next, in Fig. 2 we present a typical reflectance spectrum as measured by SCIAMACHY. The reflectance $R$ is defined as

$$R = \frac{\pi I}{\mu_0 E},$$

where $I$ is the radiance reflected by the Earth atmosphere (in W m⁻² nm⁻¹ sr⁻¹), $E$ is the solar irradiance at the top of atmosphere (TOA) perpendicular to the solar beam (in W m⁻² nm⁻¹), and $\mu_0$ is the cosine of the solar zenith angle $\theta_0$. The solar irradiance is measured each day, once per 14 orbits.

The spectrum shown in Fig. 2 was taken from orbit 2509. The coloured bars on top of the graph indicate the wavelength regions that are covered by the eight spectral channels, and their overlap. Notice that the spectrum is not continuous over the full extent of the wavelength range, and that there are obvious problems in channels 7 and 8. Different parts of the spectrum are presented with different colours. This is to distinguish between wavelength regions that are read out with different integration times. For nadir observations, a spectrum generally consists of 56 of such wavelength regions, called clusters. In Fig. 2 the red, green, and blue parts of the spectrum are clusters having an integration time of 0.25 s, 0.5 s, and 1.0 s, respectively.

The relationship between the radiance $I$ and irradiance $E$ on the one hand, and the raw instrument signals $S_{\text{earth}}$ and $S_{\text{sun}}$ on the other, is

$$I = c_{\text{rad}} \cdot c_{\text{pol}} \cdot S_{\text{earth}}$$

$$E = c_{\text{irrad}} \cdot S_{\text{sun}}$$

Here $c_{\text{rad}}$ and $c_{\text{irrad}}$ are both calibration constants for unpolarised light that were determined pre-flight. The calibration
constant $c_{\text{pol}}$, subject of this paper, performs a correction on the radiance for the effects of polarisation and can only be determined in-flight, as it is scene dependent. This is explained in detail in the next section. The solar spectrum does not need to be corrected for polarisation effects because sunlight is unpolarised.

### 3 Polarisation correction

Atmospheric radiation is usually described by means of a Stokes vector $\{I, Q, U, V\}$, in which the component $I$ refers to the radiance defined in the previous section, and the components $Q$ and $U$ both characterise the linear polarisation of the light (van de Hulst, 1981). Circular polarisation, described by the Stokes parameter $V$, is negligible for atmospheric radiation (Coulson, 1988) and never taken into account. The linear polarisation parameters $Q$ and $U$ are defined with respect to a reference plane, and are usually expressed in terms of the degree of linear polarisation $P$ and the direction of polarisation $\chi$ according to

\[
\frac{Q}{I} = P \cos 2\chi \quad \text{(4)}
\]

\[
\frac{U}{I} = P \sin 2\chi \quad \text{(5)}
\]

The direction of polarisation $\chi$ is mainly determined by the geometry that defines the sun-atmosphere-satellite system. A recent study has shown that it deviates very little from its theoretical single scattering value (Schutgens et al., 2004). This means that we can use $\chi \approx \chi_{ss}$, where $\chi_{ss}$ is calculated from geometry only (e.g. Tilstra et al., 2003). The degree of polarisation $P$ does not only contain scattering geometry information, but also information about the properties of the observed scene. For wavelengths below 300 nm, where ozone absorption is so strong that single scattering is a good approximation, the degree of polarisation only depends on the scattering geometry, and is given by

\[
P_{ss} = \frac{1 - \cos^2 \Theta}{1 + \Delta + \cos^2 \Theta}, \quad \text{(6)}
\]

where $\Theta$ is the single scattering angle, and $\Delta$ is a correction factor for depolarisation due to molecular anisotropy. At 350 nm, $\Delta=0.0621$ (Bates, 1984). Equation (6) is not valid above 300 nm, but may serve as a practical upper limit, or first estimate, for polarisation validation (see e.g. Krijger et al., 2005).

Spectrometers like GOME or SCIAMACHY are unfortunately not only sensitive to the intensity of the radiation, but also to its polarisation. More specifically, the instrument’s response to atmospheric light is given by (Slijkhuis, 2001)

\[
R_{\text{pol}} = R_{\text{unpol}} / c_{\text{pol}} = \left(1 + \mu_2^D Q/I + \mu_3^D U/I\right) \cdot R_{\text{unpol}}, \quad \text{(7)}
\]

where $R_{\text{pol}}$ stands for the reflectance including polarisation effects (i.e. as it would be reported by SCIAMACHY), and $R_{\text{unpol}}$ for the true reflectance. The constants $\mu_2^D$ and $\mu_3^D$ are the optical response functions of the spectral channels to $Q$ and $U$, respectively. They both depend on wavelength, spectral channel, and the position of the scan mirror. To retrieve the true reflectance $R_{\text{unpol}}$, Eq. (7) should be inverted, but this requires knowledge of the Stokes parameters $Q$ and $U$. For that reason, SCIAMACHY is equipped with seven PMDs which measure the polarisation with broad spectral bands centred at six wavelengths. A correction for the sensitivity to polarisation can then be applied using Eq. (7) (Slijkhuis, 2001).
At the moment, however, the quality of this polarisation correction is not sufficient, as is illustrated by Fig. 3. In this figure we have plotted (in green) part of a reflectance spectrum as measured by SCIAMACHY, with the polarisation correction not applied. The observed scene was completely clouded and located over the Atlantic Ocean. As clouds tend to decrease the degree of polarisation $P$, and hence $Q/I$ and $U/I$, the spectrum does not suffer much from the neglect of not applying the polarisation correction (cf. Eq. 7). When switching on polarisation correction, however, a strong polarisation feature is introduced in the reflectance spectrum (blue curve). In this case the polarisation feature is caused by the fact that the data processor is not functioning correctly. However annoying, this polarisation feature in the original spectrum around 350 nm also has the potential to supply information about the polarisation of the detected radiation. In the next section the polarisation feature around 350 nm will be used to retrieve polarisation Stokes parameters from the reflectance spectrum measured by SCIAMACHY.

4 Alternative polarisation retrieval algorithm

Figure 4 explains the steps of the polarisation retrieval algorithm we will present in this section. In the first window, denoted by (a), we have plotted the reflectances of clusters 9 and 10, as measured by SCIAMACHY, and without any correction for polarisation effects. Both clusters are part of spectral channel 2 (cluster 9: 320–392 nm; cluster 10: 309–320 nm), and are, in this case, read out with an integration time (IT) of 0.25 s. It was already explained in Sect. 3 that the reflectance $R_{\text{pol}}$ shown in window (a) is linked to the true reflectance $R_{\text{unpol}}$ according to

$$ R_{\text{pol}} = (1 + P \beta) R_{\text{unpol}}, $$

where

$$ \beta = \mu_2^D \cos 2\chi + \mu_3^D \sin 2\chi. $$

In step (b) we take the response functions $\mu_2^D$ and $\mu_3^D$, which depend only on the position of the scan mirror, from the calibration database. Their specific shape reveals the origin of the polarisation feature at 350 nm seen in (a). Next, in step (c), we make the assumption that the direction of polarisation $\chi$ may be approximated by its single scattering value $\chi_{\text{ss}}$ (Schutgens et al., 2004). Using $\chi = \chi_{\text{ss}}$, we obtain $\beta_{\text{ss}}$. Owing to the specific shape of $\beta_{\text{ss}}$, we can determine two wavelengths $\lambda_1$ and $\lambda_2$ for which $\beta_{\text{ss}} = 0$. These are, as can be seen from Eq. (8), wavelengths for which the reflectance signal measured by SCIAMACHY is insensitive to the degree of polarisation $P$, and therefore unaffected by the polarisation sensitivity of the spectral channel. The wavelengths $\lambda_1$ and $\lambda_2$ are determined for every spectrum. Typical values are $\lambda_1 = 335 \pm 5$ nm and $\lambda_2 = 365 \pm 5$ nm.
Fig. 4. Graphical description of the steps of the polarisation retrieval algorithm. (a) Work with the reflectance not corrected for polarisation effects. (b) Determine the polarisation sensitivity elements $\mu_2$ and $\mu_3$ of the spectral channel. (c) Calculate $\beta_{ss}$, and determine the two wavelengths $\lambda_1$ and $\lambda_2$ for which the reflectance is "insensitive" to polarisation ($\beta_{ss} \approx 0$). (d) Construct a linear function between $\lambda_1$ and $\lambda_2$. (e) Apply Eq. (7) with $R_{\text{unpol}}$ substituted by the linear function to find a suitable fit to the reflectance by variation of $P$. (f) Calculate $Q/I$ and $U/I$ and correct for polarisation using Eq. (7). The polarisation feature around 350 nm is successfully removed from the reflectance.

Now, step (d) is based on the essential assumption that the shape of the Earth’s reflectance spectrum between these two wavelengths is linear. As the two wavelengths are no more than $\sim 30$ nm apart this is in fact quite a reasonable assumption which has been checked with validated GOME spectra. So we determine the linear function between $\lambda_1$ and $\lambda_2$. In step (e) we substitute $R_{\text{unpol}}$ in Eq. (8) for this linear function, and fit the resulting equation to the reflectance $R_{\text{pol}}$ shown in (a) by variation of $P$, which we assume to be constant over this small wavelength range. Step (f), finally, involves calculating the Stokes parameters $Q/I$ and $U/I$ from Eqs. (4) and (5), and finding the true reflectance $R_{\text{unpol}}$ by inversion of Eq. (8).

The six-step algorithm described above is simple and robust. The only real approximation made is the assumption that the reflectance changes linearly over the wavelength interval $(\lambda_1, \lambda_2)$. Deviations caused by this approximation should not be large and we estimate them to be of the order of a few percent for worst-case scenarios only. Secondly, we have assumed $\chi = \chi_{ss}$ (Schutgens et al., 2004). Note that the current SCIAMACHY data processor is built around the same simplification. In special situations, like exact back-scattering, this may cause noticeable deviations. Thirdly, it is assumed that the degree of polarisation is constant over the interval $(\lambda_1, \lambda_2)$. The retrieved $P$ should therefore be considered as an effective $P$ over the full “bandwidth” of the polarisation feature. The assumption that $P$ can be considered spectrally constant is implemented in the data processor as well (Slijkhuis, 2001), and here the relevant wavelength range is even much larger, 67 nm to be exact. Last but not least we have assumed that the response functions $\mu_2$ and $\mu_3$ are known correctly. The latter assumption is not trivial in the case of SCIAMACHY, which currently has calibration errors.

The main advantage of the retrieval algorithm, apart from its simple implementation, is the fact that it does not require input from the PMDs. The operational processor requires both the spectral channel and the PMD signals to calculate polarisation. So, the operational algorithm depends on much more calibration key data than the alternative algorithm. Notice that an absolute calibration of the reflectance is unimportant for the alternative polarisation retrieval, and that absolute calibration errors in $\mu_2$ and $\mu_3$ would lead to wrong $Q/I$ and $U/I$, but their combination would still result in a right polarisation correction of the reflectance, and removal of the polarisation feature at 350 nm.
At this point it should be mentioned that a similar method as the one presented in this paper, based on the same ideas and assumptions, has recently been published by McLinden et al. (2004). Here the degree of linear polarisation is derived from limb-scattered sunlight measured by the OSIRIS instrument (flown on the Odin satellite). The polarisation retrieval is again realised by making use of the instrumental sensitivity to the state of polarisation of the detected light.

In the next section we will focus on the Stokes parameters, and compare these with the ones obtained by the operational product as well as with model calculations.

5 Results

5.1 Alternative algorithm versus operational product

For a first verification we focus on the Sahara state shown in Fig. 1, which was completely cloud-free at the time of SCIAMACHY's overpass. Around these latitudes, spectral channel 2 has an integration time of only 0.25 s which results in many small pixels. In Fig. 5 we compare for all these pixels the operational product with our own polarisation retrieval algorithm. In the left window we plotted the normalised Stokes parameter \( Q/I \) as a function of the theoretical single scattering value for three cases. The first two cases are the \( Q/I \) of the operational product, for processor versions 4.02b and 5.00. These are indicated by black plusses and diamonds, respectively. The coloured circles are the \( Q/I \) obtained using our alternative polarisation retrieval algorithm.

The colours enable the reader to distinguish between different scan mirror positions. Points having the same colour relate to virtually the same scattering geometry, and therefore show almost identical values for the single scattering \( Q/I \). For cloud-free scenes the scattering geometry is the most important parameter determining the polarisation of reflected sunlight, which explains why colours are also grouped together along the vertical axis of Fig. 5. Notice that the single scattering \( Q/I \) is a valid approximation for wavelengths below 300 nm (Schutgens and Stammes, 2002, 2003) so that the left window of Fig. 5 basically compares \( Q/I \) at and below 300 nm with \( Q/I \) at 350 nm.

All three approaches in the left window roughly follow the behaviour of the theoretical single scattering result, which is promising. However, there is disagreement about the absolute magnitude of the polarisation. Software version 5.00 is in agreement with the alternative polarisation retrieval algorithm, but software version 4.02b is not. This is shown more clearly in the right window of Fig. 5. Here we have plotted \( Q/I \) of the operational product against the \( Q/I \) found by the polarisation retrieval of this paper. Plots for the Stokes parameter \( U/I \) turn out to be very similar to those in Fig. 5, which is why these are not presented.

Next, in Fig. 6, we present a similar comparison, but now for a different nadir state of orbit 2509, where SCIAMACHY observed a less homogeneous part of the Sahara desert, which was partly clouded. The left window is interesting, because it clearly illustrates the depolarising effect of clouds. More importantly for this paper, this time there is good agreement between all three algorithms (see right window of Fig. 6). Especially the sudden agreement between the two operational products is striking. For the entire orbit, software version 5.00 systematically behaves better than...
software version 4.02b. Agreement between our own algorithm and software version 5.00 of the operational product is as good as sketched in Figs. 5 and 6 at latitudes 30° S–60° N, but becomes worse near the polar regions. It should be noted that we only looked at verification orbits 2509 and 2510.

Also note that the agreement with the official SCIAMACHY polarisation product only “suggests” that our alternative polarisation retrieval is working properly. It is not a proof. Obviously, we require another verification approach.

5.2 Comparison with an analytical polarisation model

Needing a second verification tool, we make use of the model introduced by Tilstra et al. (2003). In this simple model, atmospheric polarisation is the result of a Rayleigh scattering atmosphere including only single scattering. Surface reflection is included by adding a depolarising Lambertian surface below the atmosphere. Clouds are not included in the model, so the model can only be used for cloud-free scenes. In this model, the degree of polarisation \( P_{\text{model}} \) is given by

\[
P_{\text{model}} = \frac{1 - \cos^2 \Theta}{1 + \Delta + \gamma + \cos^2 \Theta},
\]

where \( \Theta \) is the single scattering angle, and

\[
\gamma = \frac{4 \, A \, M}{\Delta'} \left[ \frac{\exp(-M \tau_R)}{1 - \exp(-M \tau_R)} \right].
\]

In these equations, \( M=1/\mu_1+1/\mu_0 \) is the geometrical air mass factor, and \( \Delta'=2\rho_0/(1-\rho_0) \) is a correction factor for depolarisation due to molecular anisotropy, as is \( \Delta=(1-\rho_0)/(1+\rho_0/2) \), where \( \rho_0 \) is the depolarisation factor of air. At 350 nm, \( \rho_0=0.0301 \), and we find \( \Delta=0.0621 \) and \( \Delta'=0.9555 \) (Bates, 1984). The other variables, \( A \) and \( \tau_R \), are the surface albedo and the Rayleigh optical thickness of the atmosphere. Surface reflection is treated by this analytical model as just another depolarisation correction factor (cf. Eq. 6). For the surface albedo \( A \) and the Rayleigh optical thickness \( \tau_R \) we use reasonable values (\( A=0.3; \tau_R=0.6 \)). However, both, and the surface albedo in particular, are not meant to reproduce the actual values, but also account for multiple scattering and other matters that are not or insufficiently treated by the model.

The result of the comparison is shown in Fig. 7. Here we have plotted the degree of polarisation \( P \), as found by our own polarisation retrieval for the same state as shown in Fig. 6, as a function of the scattering angle \( \Theta \). The mean of the colours used is the same as before. The black diamonds are the model results calculated using Eqs. (10) and (11). Here \( A \) and \( \tau_R \) were kept fixed, i.e. all the black diamonds in Fig. 7 have the same \( A \) and \( \tau_R \).

Apparently the model is capable of explaining the dependence of \( P \) on \( \Theta \). Below 145° the measured data spread out which is caused by the fact that a cloud is present in part of the state. Clouds generally lower the degree of polarisation of atmospheric radiation. The model does not take clouds into consideration, which in this case is not a real problem because below 145° some unclouded pixels are also present. For these pixels, the model data mimic the measurement data in great detail. The conclusion can be drawn that the alternative polarisation algorithm responds properly to scene characteristics as well as to scattering geometry. On the other hand, it cannot be fully excluded that an overall multiplicative error in \( P \) would exist.
Fig. 7. Degree of linear polarisation $P$ versus the single scattering angle $\Theta$ for the same state shown in Fig. 6. The coloured circles are produced by the alternative polarisation retrieval of this paper, the black diamonds arise from a single scattering model that includes surface reflection below a cloud-free atmosphere. The pixels that so nicely follow the model calculations are cloud-free, those that deviate are clouded. Thus, there is a very high correlation between the actual scene and the results of the polarisation retrieval algorithm.

5.3 Integration times

The SCIAMACHY operational product provides normalised Stokes parameters $Q/I$ and $U/I$ for all the integration times that are used in a particular state. The polarisation retrieval discussed in this paper basically only calculates the polarisation for the IT with which the measurements of cluster 9 (320–392 nm) were performed. However, polarisation values for longer ITs may be obtained by binning of the reflectances of the small pixels. For example, the IT of the two specific nadir states discussed in this paper is 0.25 s. By simply binning the reflectances of the 0.25 s pixels (cf. Fig. 1) we can build the reflectance that would have been measured had the IT been longer. This reflectance then goes into the algorithm discussed in Sect. 4 to arrive at polarisation values for 0.5 s, 1 s, 5 s, or even 10 s IT. The quality of these polarisation values is by definition just as high if not better.

6 Conclusions

In this paper we have introduced an alternative method for the retrieval of polarisation in the UV by the satellite instrument SCIAMACHY. The method does not rely on the input of the relevant Polarisation Measurement Device in the UV (PMD 1) but instead uses only the reflectance signal (not corrected for polarisation effects). This makes the alternative algorithm more robust and less susceptible to calibration errors than the operational SCIAMACHY polarisation retrieval. Furthermore, the alternative algorithm automatically corrects for the polarisation-sensitive feature in the SCIAMACHY spectra around 350 nm.

Using this alternative polarisation retrieval, we were able to validate the polarisation Stokes parameters $Q/I$ and $U/I$ of the two latest versions of the SCIAMACHY data product (at the time of writing: software versions 4.02b and 5.00). As it turns out, the overall behaviour of the newer version 5.00 of the operational product is realistic, and distinctly better than version 4.02, but still often both software versions lack the proper values of $Q/I$ and $U/I$. Without further analysis, we cannot say whether it is the calibration of the operational data processor that is insufficient or the data processor itself that is working incorrectly (including the calibration step from level-1b to level-1c by the SciaL1C tool).

To verify the alternative algorithm we use an analytical model to mimic the retrieved degree of polarisation for different viewing geometries. The model is able to follow the angular behaviour related to different scattering geometries very closely, indicating that the alternative algorithm is able to cope with the changing conditions in a proper manner. This can also be concluded from the proper response to clouds when present in an observed scene.

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Surface pressure retrieval from SCIAMACHY measurements in the 
$O_2$ A Band: validation of the measurements and sensitivity on 
aerosols

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Abstract. We perform surface pressure retrievals from cloud-free Oxygen A band measurements of SCIAMACHY. These retrievals can be well validated because surface pressure is a quantity that is, in general, accurately known from meteorological models. Therefore, surface pressure retrievals and their validation provide important insight into the quality of the instrument calibration. Furthermore, they can provide insight into retrievals which are affected by similar radiation transport processes, for example the retrieval of total columns of $H_2O$, CO, $CO_2$ and $CH_4$. In our retrieval aerosols are neglected. Using synthetic measurements, it is shown that for low to moderate surface albedos this leads to an underestimation of the retrieved surface pressures. For high surface albedos this generally leads to an overestimation of the retrieved surface pressures. The surface pressures retrieved from the SCIAMACHY measurements indeed show this dependence on surface albedo, when compared to the corresponding pressures from a meteorological database. However, an offset of about 20 hPa was found, which can not be caused by neglecting aerosols in the retrieval. The same offset was found when comparing the retrieved surface pressures to those retrieved from co-located GOME Oxygen A band measurements. This implies a calibration error in the SCIAMACHY measurements. By adding an offset of 0.86% of the continuum reflectance at 756 nm to the SCIAMACHY reflectance measurements, this systematic bias vanishes.

1 Introduction

The satellite instrument SCIAMACHY (Bovensmann et al., 1999), launched March 2002 on ENVISAT, and its precursor GOME (Burrows et al., 1999), launched in 1995 on ERS-2, measure in the Oxygen A absorption band, near 760 nm. These measurements are of great importance for the retrieval of cloud properties (Koelemeijer et al., 2001; Rozanov and Kokhanovsky, 2004) and aerosol properties (Koppers et al., 1997). These retrievals assume the surface pressure is known. Alternatively, surface pressures can be retrieved from the Oxygen A band measurements (Barton and Scott, 1986; Bréon and Bouffié, 1996; Vanbauce et al., 1998; Dubuisson et al., 2001; Ramon et al., 2004). Surface pressure retrievals can be used to scale total column retrievals of other species, e.g. $H_2O$, CO, $CO_2$, $CH_4$, in order obtain volume mixing ratios (Buchwitz et al., 2005a,b) or for light path corrections (Kuang et al., 2002). Furthermore, surface pressure retrievals can be well validated because surface pressure is a quantity that is, in general, accurately known from meteorological models. Therefore, surface pressure retrievals and their validation provide important insight into the quality of the instrument calibration (Dubuisson et al., 2001). Furthermore, they can provide insight into retrievals which are affected by similar radiation transport processes, for example the retrieval of total columns of $H_2O$, CO, $CO_2$ and $CH_4$ from SCIAMACHY measurements. The most important potential error source for surface pressure retrievals from cloud-free measurements is scattering by aerosols (Bréon and Bouffié, 1996; Dubuisson et al., 2001). As the relevant aerosol information is usually not available, surface pressures retrieved from the Oxygen A band neglecting aerosol scattering are normally referred to as apparent surface pressures.

In this paper apparent surface pressures are retrieved from SCIAMACHY Oxygen A band measurements. To interpret the retrieved apparent surface pressures, first the effect of aerosols on the retrieval of surface pressure is studied using simulated measurements. The surface pressures retrieved from SCIAMACHY measurements are validated with reference surface pressures from a meteorological model. Additionally, the retrieved surface pressures are compared with
surfaces pressures retrieved from coinciding GOME Oxygen A band measurements. Measurements of GOME overlap very well with those of SCIAMACHY with a time lag of only about 30 min, allowing a good comparison. Although SCIAMACHY has been calibrated on ground, this calibration needs to be validated in flight. Therefore, the results and validation of our retrievals are useful to identify calibration inaccuracies.

The paper is constructed as follows. First the retrieval method is presented in Sect. 2. The effect of aerosols on the surface pressure retrieval and on the Oxygen A band measurements is studied using simulated measurements in Sect. 3. Then, in Sect. 4, the surface pressures retrieved from SCIAMACHY measurements are presented and compared with the findings from the simulated measurements and with surface pressures retrieved from GOME measurements. The discussion and conclusions follow in Sect. 5.

2 The retrieval method

For the retrieval of a state vector \( x \) from a measurement vector \( y \), a forward model \( F \) is needed that describes how \( y \) depends on \( x \), i.e.

\[
y = F(x) + e,
\]

with error term \( e \). The measurement vector \( y \) contains the reflectances measured at different wavelengths and the state vector \( x \) contains the unknown parameters to be retrieved. For the surface pressure retrievals in this paper the state vector \( x \) contains at least the following parameters: (1) the surface pressure, (2) the surface albedo at 756 nm and (3) the linear spectral dependence of the surface albedo. Additionally, \( x \) may contain instrument parameters such as a wavelength shift and response function parameters.

Since SCIAMACHY and GOME are polarisation sensitive instruments, the intensity \( I_{\text{pol}} \) measured by a certain detector pixel at wavelength \( \lambda_i \) is not only affected by the intensity of the light that enters the instrument but also by its state of polarisation, viz.

\[
I_{\text{pol}}(\lambda_i) = I_{\text{TOA}}(\lambda_i) + m_{12}(\lambda_i)Q_{\text{TOA}}(\lambda_i) + m_{13}(\lambda_i)U_{\text{TOA}}(\lambda_i),
\]

where \( m_{12} \) and \( m_{13} \) are elements of the instrument’s Müller matrix normalised to its element (1,1). Furthermore, \( I_{\text{TOA}}, Q_{\text{TOA}}, \) and \( U_{\text{TOA}} \) are the elements of the intensity vector \( I_{\text{TOA}} \) defined by

\[
I_{\text{TOA}}(\lambda) = \int_0^\infty d\lambda \, S(\lambda_i, \lambda) I_{\text{TOA}}(\lambda),
\]

where \( I_{\text{TOA}}(\lambda) \) is the intensity vector of the light at the entrance of the instrument. The spectral response function \( S \) is described by

\[
S(\lambda_i, \lambda) = \frac{a_1^2}{((\lambda_i - \lambda)/\Delta_p)^4 + a_0^2},
\]

where \( \Delta_p \) is the width of the detector pixels, assumed to be 0.217 nm. The width of the response function is determined by \( a_0 \). For SCIAMACHY and GOME, the value of \( a_0 \) is approximately 1.1772 and 0.7377, respectively. The normalisation factor \( a_1 \) is determined by the requirement

\[
\int_0^\infty S(\lambda_i, \lambda)d\lambda = 1.
\]

Similarly to the earth radiances, SCIAMACHY and GOME also measure the solar irradiance \( F_o \) to obtain the polarisation sensitive reflectances \( R_{\text{pol}} \) defined by

\[
R_{\text{pol}} = \frac{I_{\text{pol}}}{F_o}.
\]

The common approach to account for the polarisation sensitivity of SCIAMACHY and GOME is to apply a polarisation correction to the radiances \( I_{\text{pol}} \) using the Polarisation Measurement Devices (PMDs). However, the broadband PMD measurements are not sufficient to correct for the polarisation sensitivity in spectral regions where the state of polarisation is varying rapidly with wavelength, as is the case for the Oxygen A band (Stam et al., 2000; Schutgens and Stamnes, 2003). Moreover, the SCIAMACHY PMD are not yet well calibrated. In our retrieval approach, these errors due to polarisation sensitivity are avoided by using the polarisation sensitive reflectances \( R_{\text{pol}} \) as the elements of the measurement vector \( y \). This means that the forward model \( F \) directly models the polarisation sensitive reflectances \( R_{\text{pol}} \). This approach was introduced by Hasekamp et al. (2002) for the retrieval of Ozone profiles from GOME.

The main part of the forward model \( F \) is an atmospheric radiative transfer model. In this study the SRON radiative transfer model (Hasekamp and Landgraf, 2002) is used, which uses a Gauss-Seidel iteration scheme to solve the plane-parallel radiative transfer equation. This model fully includes polarisation and multiple scattering. A Rayleigh scattering atmosphere is assumed with 60 km thick layers. The absorption line parameters are taken from the HITRAN 2004 spectroscopic database (Rothenberg et al., 2003, 2005) and a Voigt lineshape is assumed. The cross-section sampling and radiative transfer calculations are performed on a 0.005 nm spectral resolution. Figure 1 shows an example of the Oxygen A band at 0.005 nm resolution and at SCIAMACHY resolution. The Oxygen A band consists of 2 branches which are resolved in the SCIAMACHY resolution, i.e. the deep R branch around 761 nm and the broader P branch around 765 nm. All retrievals are performed using iterative non-linear least squares fitting. For these fits, \( \ln(R) \) is used instead of \( R \). All retrievals are performed using iterative non-linear least squares fitting. For these fits, \( \ln(R) \) is used instead of \( R \).
3 Retrieval from simulated measurements

Dubuisson et al. (2001), among others, have shown that aerosols significantly affect surface pressure retrievals from Oxygen A band measurements. Furthermore, they showed that the effects of aerosols depend on surface albedo. To study the effects of aerosols on the retrieval of surface pressure from SCIAMACHY, SCIAMACHY measurements are simulated for atmospheres with different aerosol loads and above several surface albedos. Subsequently, the apparent surface pressure from these simulated measurements are retrieved using a forward model with only Rayleigh scattering included. For these retrievals, the state vector \( \mathbf{x} \) (see Eq. 1) contains only the surface pressure and surface albedo and the linear spectral dependence of the surface albedo. The SCIAMACHY measurements are simulated for a nadir viewing geometry with a solar zenith angle of 40° and the US standard atmosphere with a surface pressure of 1000 hPa. Desert dust aerosols are included of which the characteristics are given in Table 1. The optical aerosol properties are calculated using Mie theory.

Figures 2a and 2b show the difference between the true surface pressure and the retrieved apparent surface pressure (\( \Delta P = P_{\text{true}} - P_{\text{apparent}} \)) as a function of retrieved apparent surface albedo, for different aerosol optical thicknesses and height distributions, respectively. Figures 2c and 2d show \( \Delta P \) as a function of apparent surface albedo for varying solar zenith angles and viewing geometries, respectively. Although depending on aerosol optical thickness, aerosol height distribution, aerosol type and geometry, two general effects are observed: (1) For low and moderate surface albedos the surface pressures are underestimated in the retrieval. This is due to the relatively high contribution to the measured radiances of photons that are scattered back by the aerosol layer, reducing the photon path. Furthermore, most of the light penetrating through the aerosol layer is absorbed by the surface. This effect was also identified by Dubuisson et al. (2001). (2) At large surface albedos, the surface pressures are, in general, overestimated in the retrieval. Here, most photons penetrating through the aerosol layer are reflected by the surface and travel through the aerosol layer once more. Due to (multiple) scattering in the aerosol layer the photon path is enhanced, resulting in an overestimation of the surface pressure. This effect was not previously recognised by Dubuisson et al. (2001).

Furthermore, the results show that the effects of aerosols on the surface pressure retrieval increase with increasing aerosol optical thickness, while the aerosol height distribution only significantly impacts the surface pressure retrieval above low albedos. The solar zenith angles (SZA) impact the sensitivity of surface pressure retrieval on aerosols above all surface albedos. Starting at SZA=10°, the values for \( \Delta P \) first decrease towards larger SZA, reach a minimum for SZA=40°, and then increase towards larger SZA. This behaviour is due to the fact that, on the one hand, an increase in SZA, and therewith geometrical path, causes (1) an enhanced optical path due to multiple scattering and on the other hand (2) leads to a decrease in optical path due to increased extinction. Below SZA≈40°, the former effect dominates, while the latter effect dominates for higher SZA. Also the viewing geometry significantly impacts the sensitivity of surface pressure retrieval on aerosols above all surface albedos. Maximum values of \( \Delta P \) occur at nadir geometries. The aerosol type affects the apparent surface pressure retrieval as well (not shown). Generally, a decrease in the aerosol particle size leads to an increase in multiple scattering and therewith apparent surface pressures.

To summarise, Fig. 2 shows that due to varying aerosol optical thickness and height distribution and varying geometry, the expected range in \( \Delta P \) is about 30 hPa above high surface albedos and about 300 hPa above low surface albedos. This is

### Table 1

Characteristics at 765 nm of the two modes of the desert dust aerosols used in this study, based on aerosol model DL from Torres et al. (2001). A log-normal size distribution is assumed. The relative contribution of the modes to the number concentration is represented by the fraction. The aerosols are evenly distributed over the first 2 kilometres and decrease in number as \( p^3 \) from 2 to 10 km, unless indicated otherwise. The single scattering albedo of the aerosols used is 0.97605.

<table>
<thead>
<tr>
<th>mode</th>
<th>Effective radius</th>
<th>Size variance</th>
<th>Refr. index</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.105 µm</td>
<td>0.323 µm²</td>
<td>1.53</td>
<td>0.99565</td>
</tr>
<tr>
<td>2</td>
<td>1.605 µm</td>
<td>0.418 µm²</td>
<td>1.53</td>
<td>0.00435</td>
</tr>
</tbody>
</table>

Dubuisson et al. (2001)
The difference between the true surface pressure used in the simulated measurements including aerosols and the apparent surface pressure retrieved ignoring aerosols, \( \Delta P = P_{\text{true}} - P_{\text{apparent}} \), as a function of retrieved apparent surface albedo. The true surface albedos are 0, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6. The retrieved values are indicated by plusses. A nadir viewing geometry with a solar zenith angle of 40° is used. Panel (a) shows the retrieved values for different values of the total aerosol optical thickness \( \tau \) at 765 nm. To obtain \( \tau \) at the more common wavelength of 550 nm, the values have to be multiplied by 1.11. Panel (b) shows the retrieved values for different height distributions. Here, our standard aerosol distribution (see Table 1) is modified such that the lower layer with evenly distributed aerosols is extended to higher levels, indicated by the layer top. In panel (c), the retrieved \( \Delta P \) and surface albedos are shown for varying solar zenith angles (SZA) with a nadir viewing geometry. Panel (d) shows the retrieved values for different viewing angles (VA), when a relative azimuth angle of 50° is taken. Solid and dashed lines indicate negative and positive viewing angles, respectively. In Panels (b), (c) and (d) an aerosol optical thickness of 0.4 is taken.

Figures 2 and 3 show a clear dependence of both \( \Delta P \) and the spectral fitting residual on the aerosol height distribution and optical thickness. This implies that, when the true surface pressure and the aerosol type are known, information about the aerosol optical thickness and height distribution can be retrieved from the Oxygen A band measurements. This was previously demonstrated by Koppers et al. (1997).

In addition to aerosols, Rayleigh scattering also has a large effect on the surface pressure retrievals, although the Rayleigh scattering optical thickness at these wavelengths is relatively low (≈0.025). This effect is illustrated in Fig. 4, which shows \( \Delta P \) retrieved while neglecting all scattering from simulated SCIAMACHY measurements for atmospheres including aerosols and, additionally, for a clear-sky atmosphere.
Fig. 3. Residuals between the simulated reflectance measurements $R_{meas}$ for an atmosphere including aerosols and the fitted reflectances $R_{mod}$ ignoring aerosols. The residuals are defined as $(R_{mod} - R_{meas}) / R_{meas} \times 100\%$. A surface albedo of 0.1 is used. The residuals are shown for different values of the aerosol optical thickness (a) and different height distributions (b), similar to Fig. 2a and Fig. 2b respectively.

atmosphere including only Rayleigh scattering. In the clear-sky case, neglecting Rayleigh scattering in the retrieval leads to an underestimation of the surface pressure above all surface albedos. For aerosol loaded atmospheres, a comparison of Fig. 4 with Fig. 2 shows that, at low albedos and for a low aerosol optical thickness, the effect of neglecting Rayleigh scattering dominates the effect of neglecting aerosols. Furthermore, at large albedos the effect of neglecting Rayleigh scattering can partly compensate for the effect of neglecting aerosols. The large effect of Rayleigh scattering can be explained by the fact that the Oxygen A band contains a large number of optically thick absorption lines (see Fig. 1) for which only few photons penetrate through the atmosphere to high pressure levels. At low pressure levels, aerosol optical depths are generally low and thus the reflectance at the wavelengths of these optically thick absorption lines is mainly determined by Rayleigh scattering. Therefore, neglecting Rayleigh scattering in the forward model leads to an increase in the depth of these absorption lines which leads to an underestimation of the surface pressure.

The simulations in this section show that aerosols significantly affect the Oxygen A band measurements. When retrieving surface pressure neglecting aerosol scattering, characteristic residuals as shown in Fig. 3 are expected. Furthermore, surface pressures retrieved using the Oxygen A band are expected to underestimate the actual surface pressure at low and moderate albedos and overestimate them at high albedos.

Fig. 4. Similar to Fig. 2a, but when $\Delta P$ and the apparent surface albedo are retrieved while neglecting all scattering. The solid black line shows results of retrievals from simulated measurements for a clear-sky case including only Rayleigh scattering.

4 Retrieval from SCIAMACHY measurements

4.1 Data

For this study, the reflectances in the Oxygen A band measured by SCIAMACHY and GOME are analysed. The characteristics of the Oxygen A band measurements for both instruments are summarised in Table 2.

The SCIAMACHY reflectances (level 1b data) used in this study are improved by replacing calibration data using
For both instruments all calibration options are applied, with the exception of the polarisation sensitivity correction, which is not needed because the polarisation sensitive measurement is modelled directly (see Sect. 2). Furthermore, on the reflectances measured by SCIAMACHY a multiplicative correction factor of 1.2 is applied. This correction factor was found by Acarreta et al. (2004) and Acarreta and Stammes (2005) by comparing the measured reflectances with those measured by MERIS, also on ENVISAT.

Cloudy pixels are excluded from the data. To identify clouds in SCIAMACHY measurements, we use the SPICI method developed by Krijger et al. (2005) using the PMD measurements. For GOME, an adapted version is used.

As reference surface pressures for validation, the pressure profile data from the UKMO Stratospheric Assimilated dataset are combined with the TerrainBase surface elevation database. The UKMO dataset has a spatial resolution of $2.5 \times 3.75^\circ$ and the grid-box containing the centre of the instrument footprint is taken. The TerrainBase data has a resolution of $5 \times 5$ arc-minutes and is averaged over the instrument footprint. To calculate the absorption cross-sections, the temperature profiles are taken from the UKMO dataset.

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1Available at http://www.sron.nl/~hees/SciaDC.
Table 3. Mean and standard deviation of the retrieved wavelength shifts $\Delta \lambda$ and response function parameters $a_0$.

<table>
<thead>
<tr>
<th>$\Delta \lambda$</th>
<th>mean</th>
<th>standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-0.0772$ nm</td>
<td>$0.00115$ nm</td>
</tr>
<tr>
<td>$a_0$</td>
<td>1.09573</td>
<td>0.0356539</td>
</tr>
</tbody>
</table>

4.2 Retrieval results

First, SCIAMACHY and GOME measurements above southern Europe and northern Africa on 23 January 2003 are analysed. False colour images of the data used are shown in Fig. 5. In SCIAMACHY, Nadir and Limb measurements are alternated. Since for this study only Nadir measurements are used, the SCIAMACHY orbits are broken up into several blocks, generally referred to as states. The solar zenith angles and relative azimuth angles for these data range from about 40–60° and 30–60°, respectively.

To retrieve apparent surface pressures from SCIAMACHY measurements, the state vector $x$ (Eq. 1) contains (1) the surface pressure, (2) the surface albedo at 756 nm, (3) the linear spectral dependence of the surface albedo, (4) a wavelength shift $\Delta \lambda$ and (5) the response function parameter $a_0$ (see Eq. 4). The instrument parameters (4 and 5) did not significantly interfere with the other retrieved parameters and are very similar for each retrieval. The mean and standard deviation of the instrument parameters retrieved are given in Table 3.

Figure 6 shows the absolute differences between retrieved apparent surface pressures and the reference surface pressures ($\Delta P = P_{\text{reference}} - P_{\text{apparent}}$). Figure 7 shows $\Delta P$ as a function of the retrieved surface albedo. Much variation is seen, ranging from $\Delta P = -60$ to 300 hPa. Clearly, systematic differences are seen between retrievals above land and sea, i.e. high and low surface albedos. In general, $\Delta P$ is positive for albedos lower than 0.1 and negative for higher surface albedos. The few low surface pressures retrieved above high surface albedos are probably due to clouds not flagged by the cloud filter used.

Also shown in Fig. 7 are results from the simulated measurements as presented in Fig. 2, for an aerosol optical thickness of 0.1 and 0.3, respectively. The retrieved values match the results from the simulated measurements well for low albedos (<0.1). However, for higher albedos, the retrieved values for $\Delta P$ are systematically about 20 hPa lower. Several other aerosol types and height distributions were tried, none of which match these retrievals.

For comparison, surface pressures retrieved from the GOME measurements are shown in Fig. 8. Similar variations as in the SCIAMACHY retrievals of Figs. 6 and 7 are seen. However, the values of $\Delta P$ are systematically about 20 hPa higher than those retrieved from SCIAMACHY and are in line with the simulations presented in Sect. 3.

To verify the observed systematic difference in $\Delta P$ retrieved by SCIAMACHY and GOME for other data, e.g. for other geometries and geolocations, values of $\Delta P$ are retrieved from an extended dataset. This dataset includes all cloud-free measurements in two orbits from 23 August 2002 and two orbits from 23 January 2003, all over Europe, Africa and the South Atlantic Ocean (i.e. orbits 2509, 2510, 4699 and 4700). The solar zenith angles and relative azimuth angles in this dataset range from about 20–80° and 0–60°, respectively. Table 4 shows the mean values and standard deviations of $\Delta P$ retrieved from SCIAMACHY and GOME data, within several apparent surface albedo bins. Above low albedos (<0.2), the standard deviations become large, as expected from the conclusions made in Sect. 3. Therefore, the comparison between $\Delta P$ retrieved by SCIAMACHY and GOME is very sensitive to varying atmospheric conditions and geometries. Above moderate and high albedos, on the other hand, values of $\Delta P$ retrieved by GOME are systematically about 20 hPa higher, confirming the conclusions made above. Thus, it seems likely that the surface pressures retrieved from SCIAMACHY data suffer from a systematic error(s), probably due to a calibration error(s) in the measurements.

The effect of several SCIAMACHY calibration errors on the retrieved surface pressures is investigated. First, it is found that changing the multiplicative factor applied on the measured reflectances (Acarreta et al., 2004, see Sect. 4.1) only minimally affects the retrieved surface pressure. The reason for this is that the relative depth of the Oxygen A band contains the surface pressure information. On the other hand, the retrieved surface pressures are affected when an offset is added to the measured reflectances. To determine a suitable calibration correction for SCIAMACHY, apparent surface pressures are retrieved from the SCIAMACHY measurements on which several offsets are applied. The offsets are defined as a percentage of the continuum reflectance around 756 nm, after multiplication by 1.2. Figure 9 compares, for

<table>
<thead>
<tr>
<th>Apparent Surface albedo</th>
<th>$\Delta P$ SCIAMACHY [hPa]</th>
<th>$\Delta P$ GOME [hPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–0.05</td>
<td>133 (69.1)</td>
<td>133 (79.4)</td>
</tr>
<tr>
<td>0.05–0.1</td>
<td>98.3 (106)</td>
<td>140.2 (129)</td>
</tr>
<tr>
<td>0.1–0.2</td>
<td>20.7 (70.3)</td>
<td>66.7 (106)</td>
</tr>
<tr>
<td>0.2–0.3</td>
<td>−12.5 (20.5)</td>
<td>11.3 (16.3)</td>
</tr>
<tr>
<td>0.3–0.4</td>
<td>−14.3 (22.5)</td>
<td>2.25 (13.4)</td>
</tr>
<tr>
<td>0.4–0.5</td>
<td>−25.7 (12.6)</td>
<td>−2.05 (16.7)</td>
</tr>
<tr>
<td>0.5–0.6</td>
<td>−22.6 (28.2)</td>
<td>−0.257 (27.0)</td>
</tr>
</tbody>
</table>
Fig. 7. $\Delta P$ as a function of apparent surface albedo for SCIAMACHY orbits 4700 (left) and 4699 (right). Results from the 5 individual SCIAMACHY states per orbit, as seen in Fig. 6, are colour-coded in black, blue, green, yellow and red going from north to south. Two results from simulated measurements for atmospheres with aerosol optical thicknesses of 0.1 and 0.3, as presented in Fig. 2, are plotted with dashed lines.

Fig. 8. $\Delta P$ retrieved by the GOME instrument, as a map-projection (a) and as function of apparent surface albedo (b), similar to Figs. 6 and 7, respectively.

Each applied offset, the mean surface pressure retrieved from SCIAMACHY with the corresponding mean surface pressure retrieved from GOME. For this, the extended dataset described above is used. GOME ground pixels are larger than those of SCIAMACHY and do not overlap perfectly. Therefore, surface pressures and apparent surface albedos retrieved from SCIAMACHY ground pixels with their centre within a GOME ground pixel are averaged. Furthermore, SCIAMACHY and GOME observations with apparent surface albedos differing more than 2% are rejected. Because the $\Delta P$ retrieved by SCIAMACHY and GOME above low albedos is very sensitive to varying atmospheric conditions and sampling effects (see Sect. 3), only observations with apparent surface albedos above 0.1 are used in this analysis. From Fig. 9 it follows that the difference in retrieved apparent surface pressure between SCIAMACHY and GOME depends linearly on the applied offset. An offset of 0.86% of the continuum reflectance around 756 nm needs to be added to the SCIAMACHY Oxygen A band reflectance measurements, so that the retrieved surface pressures agree with those retrieved from the GOME data. Figure 10 shows $\Delta P$ as a function of surface albedo when this correction is applied. With this correction, the retrievals behave as expected from the study presented in Sect. 3 and compare well with the
GOME retrievals shown in Fig. 8b. The offset found is probably related to the inaccuracies in the reflectance calibration (Acarreta et al., 2004; Noël, 2004; Lichtenberg et al., 2005).

The different colours in Fig. 10 correspond to different SCIAMACHY states, i.e. different geolocations (see Figs. 6 and 7). Significant differences in the retrieved values of $\Delta P$ between states are seen. Because all states have approximately similar geometries, it is likely that these differences are due to the varying aerosol optical thickness, as follows from Fig. 2. In particular, the retrievals from data from the most northern state of orbit 4700 (in black) match well with results from simulated measurements corresponding to an aerosol optical thickness of 0.05–0.2, while the most southern state of orbit 4700 (in red) matches better with results from simulated measurements for an aerosol optical thickness of 0.2–0.6. This increase in aerosol optical thickness at the location of the most southern state is confirmed by the aerosol optical thickness retrieved by the MISR instrument on EOS Terra (Diner et al., 2001) on the same day, as shown in Fig. 11. However, the absolute values of the MISR optical thicknesses do not match those derived from Fig. 10. As is illustrated in Fig. 2b, this can be due to an incorrect assumption about the aerosol height distribution in our forward model. Also, the true aerosol type can be different than the one assumed. Furthermore, the MISR optical thicknesses are given at a wavelength of 558 nm, while we use a wavelength of 765 nm. However, our results are in qualitative agreement with the aerosol optical thickness retrievals from MISR.

4.3 Spectral fitting residuals

A closer inspection of the spectral fitting residuals yields valuable information. Figure 12 shows residuals from a SCIAMACHY and a GOME measurement above approximately the same location with an apparent surface albedo of $\sim0.16$. The residuals are very much alike. Also shown is a residual from a simulated measurement similar to those shown in Fig. 3. The residual from the simulated measurement is very similar to those from the real SCIAMACHY and GOME measurements. This confirms that the spectral fitting residuals are for a large part caused by neglecting aerosols in our retrieval.

However, also some high frequency scatter of about 2–5% is seen in the residuals from the SCIAMACHY and GOME measurements, which are not observed in the simulations and can thus not be caused by neglecting aerosols in the retrieval. Again these features are very common in all our spectral fitting residuals. They might be due to errors in the spectroscopy data (Chance, 1997; Rothman et al., 2003, 2005) or the instrument response functions. Furthermore, solar Fraunhofer lines (e.g. at 766.5 nm) could appear in the reflectances due to calibration errors.

5 Conclusions and discussion

In this paper we have presented surface pressure retrievals from cloud-free SCIAMACHY Oxygen A band measurements. The retrievals have been performed using a radiative transfer model that fully includes multiple Rayleigh scattering and polarisation but does not include the effect of aerosols. Using synthetic measurements, the effects of neglecting aerosols on the retrieved surface pressures have been investigated. It was found that for low and moderate surface albedos, aerosols lead to an underestimation of the retrieved surface pressures due to a reduction of the light path. For high surface albedos, scattering by aerosols leads to an enhancement of the light path and thus to an overestimation of the surface pressure. The magnitude of these effects depends on aerosol optical thickness, the aerosol height distribution and the geometry. Variations in these parameters result in expected ranges in retrieved surface pressures of about 30 hPa above high surface albedos and about 300 hPa above low surface albedos. It has also been observed that aerosols cause a characteristic spectral feature in the fitting residuals, of which the amplitude depends on the aerosol optical thickness and height distribution as well.

The apparent surface pressures retrieved from SCIAMACHY have been validated with reference surface pressures from the UKMO meteorological dataset. The difference between the SCIAMACHY apparent surface pressures and the reference surface pressures shows a dependence on surface albedo that can be explained by the fact that aerosols are neglected in the retrieval. However, also a systematic

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Fig. 9. The mean of the difference in apparent surface pressures retrieved from co-located SCIAMACHY and GOME observations as a function of the correction applied to the SCIAMACHY data. The error bars represent the standard deviation of the mean. Surface pressures and surface albedos retrieved from SCIAMACHY pixels with their centre within a GOME ground pixel are averaged. SCIAMACHY and GOME observations with apparent surface albedos below 0.1 or differing more than 2% are rejected. In total, 100 observations are compared.
Fig. 10. Same as Fig. 7, but when the SCIAMACHY reflectances are corrected by adding an offset of 0.86% of the continuum reflectance to the reflectances.

Fig. 11. Aerosol optical thicknesses at 558 nm retrieved using the MISR instrument on EOS Terra on 23 January 2003. Data from MISR orbits 16486 (west) and 16485 (east) are shown. These data were obtained from the NASA Langley Research Centre Atmospheric Sciences Data Centre. The contours of the SCIAMACHY states are indicated in red.

Fig. 12. Residuals of spectral fits of a SCIAMACHY (black) and a GOME (red) Oxygen A band measurement with a nadir viewing geometry and a solar zenith angle of approximately 40°. Both measurements are taken at approximately 13° latitude and −10° longitude and have an apparent surface albedo of ∼0.16. Note that on the SCIAMACHY measurements the correction suggested in Sect. 4.2 is applied. In blue, a residual from a simulated SCIAMACHY measurement, similar to those in Fig. 3, is shown. For this, an atmosphere including aerosols with an optical depth of 0.45 and a layer top of 8 km (see Fig. 2) is taken. The true surface pressure and apparent surface albedo are similar to those in the SCIAMACHY and GOME measurements.
The clear dependence of both the retrieved surface pressure and the spectral fitting residuals on the aerosol optical thickness and height distribution, as shown in this paper, indicates that both parameters may be retrieved from Oxygen A band measurements, when one assumes the surface pressure as known. This was previously demonstrated by Koppers et al. (1997).

For similar retrievals of total columns of other species than O$_2$, e.g. H$_2$O, CO, CO$_2$ and CH$_4$, similar effects due to aerosols as discussed in this paper, i.e. under- or over-estimation of the total column, can be expected (Dubuisson et al., 2004; Houweling et al., 2005). The retrieved total column of these species are often scaled to oxygen to correct for the light path (Noël et al., 1999; O’Brien and Rayner, 2002; Kuang et al., 2002; Dufour et al., 2004) or to obtain volume mixing ratios of the species (Buchwitz et al., 2005a,b). As pointed out by O’Brien and Rayner (2002), the light paths are affected by the height distribution and optical thickness of the absorption lines of individual species, which needs to be considered when applying such a scaling. Indeed, comparing the results shown in Fig. 2 with those presented by Houweling et al. (2005, Fig. 4a), it is apparent that aerosols impact the retrieval of CO$_2$ and O$_2$ differently. Furthermore, results shown in this paper imply that care must be taken when using the Oxygen A band for scaling of retrievals at other wavelengths, because the effects of aerosols are shown to depend significantly on surface albedo, which is spectral dependent. Additionally, the optical thickness of Rayleigh scattering and therewith its relative contribution to the total scattering varies with wavelength as well. These problems can be avoided by retrieving aerosol properties simultaneously with the total column of the trace gas, the surface albedos and the surface pressure (Kuang et al., 2002).

To conclude, this paper shows that surface pressure retrievals can be used to validate the calibration of the Oxygen A band measurements. This approach could also be used to validate the calibration of the SCIAMACHY measurements of other oxygen bands, i.e. O$_2$ B and γ and O$_4$ bands.

Acknowledgements. SCIAMACHY and GOME data were provided by ESA. The SCIAMACHY data were processed using SCIA_PATCH_NL1, available at http://www.sron.nl/~hees/SciaDC. The MISR data were obtained from the NASA Langley Research Center Atmospheric Sciences Data Center. Part of this work was supported by the Dutch User Support Programme 2001–2005 (USP) under project number EO-069.

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References


Improving cloud information over deserts from SCIAMACHY Oxygen A-band measurements

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Abstract. The retrieval of column densities and concentration profiles of atmospheric trace gas species from satellites is sensitive to light scattered by clouds. The SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) instrument on the Envisat satellite, principally designed to retrieve trace gases in the atmosphere, is also capable of detecting clouds. FRESCO (Fast Retrieval Scheme for Clouds from the Oxygen A-band) is a fast and robust algorithm providing cloud information from the O₂ A-band for cloud correction of ozone. FRESCO provides a consistent set of cloud products by retrieving simultaneously effective cloud fraction and cloud top pressure. The FRESCO retrieved values are compared with the SCIAMACHY Level 2 operational cloud fraction of OCRA (Optical Cloud Recognition Algorithm) but, also, with cloud information from HICRU (Heidelberg Iterative Cloud Retrieval Utilities), SACURA (SemiAnalytical CloUd Retrieval Algorithm) and the MODIS (Moderate Resolution Imaging Spectroradiometer) instrument. The results correlate well, but FRESCO overestimates cloud fraction over deserts. Thus, to improve retrievals at these locations, the FRESCO surface albedo databases are decontaminated from the presence of desert dust aerosols. This is achieved by using the GOME Absorbing Aerosol Index. It is shown that this approach succeeds well in producing more accurate cloud information over the Sahara.

1 Introduction

SCIAMACHY (SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY) is a space-borne spectrometer that flies on Envisat since March 2002. SCIAMACHY measures the solar radiation reflected from the atmosphere in the wavelength range between 240 and 2380 nm. This is recorded at relatively high resolution (0.2 to 1.5 nm) over the range 240 to 1750 nm, and in selected regions between 1900 and 2400 nm. SCIAMACHY is extended as compared to its precursor GOME (Global Ozone Monitoring Experiment; (Burrows et al., 1999)) with a wavelength range in the near Infrared region and able to operate with new viewing geometries namely limb and sun and moon occultations. The primary scientific objective of SCIAMACHY is the measurement of various trace gases on a global scale (Bovensmann et al., 1999).

The trace gases that SCIAMACHY detects, like O₃, NO₂, BrO, SO₂, CO and CH₄, occur not only in the stratosphere but also in the troposphere, where clouds reside. To detect these trace gases accurately, the presence and properties of clouds have to be known, in order to correct for the effect of clouds. The three cloud parameters that most strongly influence trace gas measurements are: cloud fraction, cloud albedo or cloud optical thickness, and cloud top pressure. Microphysical cloud parameters, like particle size and shape, are of minor importance (Koelemeijer and Stammes, 1999).

Clouds affect the path of photons through the atmosphere and therefore change the interpretation of the depth of an absorption band. Taking ozone as an example, the effect of clouds on ozone retrieval can be regarded as due to two main effects (Koelemeijer and Stammes, 1999): (1) albedo effect:
Clouds act as a reflecting boundary below the ozone layer and enhance the depth of the ozone absorption bands, and (2) ghost column effect: clouds shield tropospheric ozone from observation. A third, smaller effect exists, which is the enhancement of the photon path inside clouds, causing an enhancement of the absorption band depth inside clouds (Newchurch et al., 2001).

In order to correct for the albedo effect of clouds, it is necessary to retrieve the cloud fraction and cloud albedo (or cloud optical thickness) or, equivalently, the product of cloud fraction and cloud albedo, which we call the effective cloud fraction. In order to correct for the ghost column effect of clouds, it is necessary to retrieve both the effective cloud fraction and the cloud top pressure.

The above cloud effects not only occur for O$_3$ but also for other gases. Especially for NO$_2$, much of which is residing in the troposphere in polluted circumstances, the ghost column effect is very important (Boersma et al., 2004). Therefore, a cloud detection algorithm suitable for trace gas retrievals for SCIAMACHY should be able to detect at least effective cloud fraction and cloud top pressure. If the cloud top pressure is available, then the tropospheric ozone column can be determined by comparing cloudy and clear pixels, using the convective-cloud-differential technique (Valks et al., 2003b).

This paper is devoted to cloud detection from SCIAMACHY using the retrieval cloud algorithm FRESCO (Koelemeijer et al., 2001). Firstly, in Sect. 2, the FRESCO algorithm is described as well as the other cloud retrieval techniques used for SCIAMACHY. In Sect. 3, FRESCO retrievals are compared with the SCIAMACHY Level 2 operational cloud fraction of OCRA and cloud information from the algorithms HICRU and SACURA as well as from the MODIS instrument on EOS/Terra. Section 4 deals with the improvement of FRESCO retrievals over deserts. Finally, our conclusions are stated in Sect. 5.

2 Cloud retrieval techniques for SCIAMACHY

For reasons of timeliness and co-location, for operational processing it is most practical to retrieve cloud parameters from the SCIAMACHY data itself. To this aim various SCIAMACHY channels and atmospheric absorption bands can be chosen. In the case of GOME, the Polarisation Measurement Devices (PMDs) had been used by several groups to estimate the cloud fraction. The advantage of the PMDs is that they have a better spatial resolution than the spectral channels. Von Borgen et al. (2000) have developed various cloud algorithms for GOME, among which the Optical Cloud Recognition Algorithm (OCRA) technique described in Sect. 2.2. This technique uses the color of PMD images to select cloud free scenes for a global database of cloud free reflectances. The difference between the measured PMD reflectances and those from this cloud free database is used to retrieve cloud fractions. To detect cloud pressure, however, the PMDs cannot be used because they have insufficient spectral resolution to detect absorption lines of well-mixed absorbers like oxygen. In the SCIAMACHY range there are several oxygen or oxygen-oxygen absorption bands. The strongest band is the O$_2$ A-band at 760 nm. Figure 1 shows the absorption lines of oxygen in this region.

In cloud retrievals from a satellite, it is very important to have a good estimate of the surface albedo. The reason is that the cloud detection is usually performed by comparing the measured reflectance with the expected reflectance from a cloud-free scene. Recently, a new spectral surface albedo database based on 5.5 years of GOME data has been prepared (Koelemeijer et al., 2003). This database is used in FRESCO and is improved in this study, as described in Sect. 4.

2.1 FRESCO

FRESCO has been developed as a simple, fast, and robust algorithm to provide cloud information for cloud correction of ozone concentration measurements (Koelemeijer et al., 2001). FRESCO uses the reflectance in three 1-nm wide windows of the O$_2$ A-band: 758–759 nm, 760–761 nm, and 765–766 nm. The measured reflectance is compared to a modeled reflectance, as computed for a simple cloud model. In this model the cloud is assumed to be a Lambertian reflector with albedo 0.8 below a clear spherical atmosphere, in which only O$_2$ absorption is taken into account. To simulate the spectrum of a partly cloudy pixel, a simple atmospheric transmission model is used, in which the atmosphere above the ground surface (for the clear part of the pixel) or cloud (for the cloudy part of the pixel) is treated as a purely absorbing non-scattering medium. Surface albedo is required a priori for FRESCO retrievals. The surface albedo databases were deduced from a global surface Lambert-equivalent reflectance (LER) database that was generated from GOME data of June 1995–December 2000 (Koelemeijer et al., 2003). The surface albedo was found by taking the

Fig. 1. The Oxygen molecular absorption optical thickness in the oxygen A band of the Mid-Latitude Summer atmosphere.
The algorithm uses the semi-analytical asymptotical theory applied for a cloudy medium of large optical thickness (Kokhanovsky and Rozanov, 2004). The technique considers single scattering above clouds and the cloud bi-directional reflection distribution function (BRDF) instead of assuming a Lambertian surface. This makes it particularly accurate although only completely cloudy pixels can be considered. Therefore, for broken clouds extra information on the cloud fraction is required which can be obtained using the operational SCIAMACHY cloud fraction product (OCRA). The extension of SACURA to broken cloud conditions is given by Kokhanovsky et al. (2004).

2.4 HICRU

Grzegorski (2003) developed an advanced PMD technique for cloud fraction retrieval, called HICRU (Heidelberg Iterative Cloud Retrieval Utilities). The SCIAMACHY algorithm uses the intensities of PMD 3 (617–705 nm). The algorithm makes use of the threshold method with lower thresholds representing cloud-free pixels while upper ones are the intensity of cloudy pixels. The lower value is produced from image sequence analysis and the upper value is calculated iteratively depending on solar zenith angle and line of sight. Cloud fraction is obtained through linear interpolation between both thresholds (Grzegorski et al., 2004).

3 Results

3.1 SCIAMACHY data

FRESCO makes use of the SCIAMACHY measurements between 758 and 766 nm. The spectral resolution of SCIAMACHY is determined by the slit function. At these wavelengths, the full width at half maximum is 0.44 nm while it has a value of 0.36 nm and 0.57 nm for GOME and GOME-2, respectively. The higher spectral resolution of GOME allowed the instrument to capture more structures at the expense of undersampling. Figure 2 shows reflectivities, normalised to unity at 758 nm, measured by SCIAMACHY for a cloud-free and a cloudy scene over the Sahara with comparable viewing and illumination angles. Clearly, the Oxygen A-band is less deep for the cloudy scene providing information on cloud-top pressure, whereas the reflectivity in the continuum allows to derive the effective cloud fraction.

3.2 MODIS data

The SCIAMACHY operational cloud-top pressure product is derived from the ISCCP monthly mean cloud top height database, which is a climatology based on measurements of clouds from satellites (MeteoSat, GMS, GOES and NOAA). Thus, instead of using this product, MODIS (Moderate Resolution Imaging Spectroradiometer) Level 2 granules overlapping the SCIAMACHY orbit are employed to assess the accuracy of FRESCO retrievals. The co-located cloud top pressure of MODIS, onboard the Terra Platform, are produced by the infrared retrieval methods both day and night at 5-km resolution(Platnick et al., 2003). Moreover, clouds detected via
3.3 FRESCO retrievals

The absolute calibration of SCIAMACHY solar irradiance and earth radiance is not correct (Lichtenberg et al., 2005). Thus, as it affects directly the retrieval of aerosols and cloud products, a calibration correction factor of 1.20 is applied here always on FRESCO on SCIAMACHY reflectances following Acarreta et al. (2004); Acarreta and Stammes (2005). Indeed, Acarreta and Stammes (2005) showed that SCIAMACHY underestimates the reflectance by 13% at 442 nm reaching up to 21% at 885 nm as compared to MERIS.

Firstly, Fig. 3 shows FRESCO retrievals of effective cloud fraction when applying this calibration correction factor of 1.20 on SCIAMACHY radiances in the O$_2$ A-band. This concerns the orbit 12472 (19 July 2004) containing ocean, land and desert areas.

Secondly, Fig. 4 shows the retrieved values of cloud top pressure (hPa) for the reference orbit 2510 (23 August 2002). The SCIAMACHY operational product does not correlate well with both FRESCO and MODIS values. This is due to the fact that the operational product uses the monthly mean cloud-top height from the ISCCP climatology. The correlation between MODIS and FRESCO is much better but still exhibits differences for low cloud top pressures as already observed by Koelemeijer et al. (2001). These can be explained by the different methods used to derive the cloud top pressure (Oxygen A-band versus Infra-Red). There is also a systematic time difference of 1 to 2 h between the co-located measurements of MODIS and SCIAMACHY.

4 FRESCO retrievals over deserts

4.1 Effect of aerosols on surface albedo

Although Fig. 3 shows a good agreement between OCRA and FRESCO, FRESCO is sensitive to the type of landcover through the use of its surface albedo database. Indeed, the derived cloud fraction is particularly affected by cases with high surface albedo. In such cases, the retrieved cloud top pressure is also sensitive to the surface albedo, especially for low values of cloud fraction. It has been already underlined by Grzegorski (2003) and Tuinder et al. (2004) that while FRESCO retrievals, especially cloud fraction, correlate well with other cloud retrieval algorithms over land and oceans, FRESCO overestimates the effective cloud fraction over desert areas.

Figure 5 illustrates this point by considering the orbit 12472 (19 July 2004), as previously in Fig. 3, but focusing over the Sahara. The red and blue points represent the comparison of FRESCO with HICRU and OCRA, respectively. On one hand, Fig. 5 underlines an overestimation of FRESCO cloud fraction over the Sahara when compared with both OCRA and HICRU. On the other hand, OCRA and HICRU results match better what can be seen from a
Fig. 4. Comparison of the retrieved cloud top pressure (hPa) from the old version of FRESCO and the SCIAMACHY Level 2 operational product (from ISCCP climatology) with MODIS co-located values for orbit 2510 (23 August 2002). The dotted line is the one-to-one agreement.

The co-located MODIS image (Fig. 6) showing a low cloud cover at a similar time over SCIAMACHY states 14 and 15 over north-west Libya and north Niger, respectively.

Figure 7 corroborates this behaviour of FRESCO compared to OCRA when studying another cloud-free SCIAMACHY orbit over the Sahara (Orbit 11326; 30 April 2004).

This overestimation of the effective cloud fractions is caused by the surface albedo considered in FRESCO. The surface albedo is too low for deserts. This is due to uplifting of large amounts of dust, which lower the reflectance. Then FRESCO fills the missing cloud-free reflectances with clouds. For bright surfaces like deserts, with albedos of 30% or even higher (at 760 nm), aerosols may decrease the reflectance at the top of the atmosphere. Then the minimum LER from GOME, used by Koelemeijer et al. (2003) to create the surface albedo databases, does not yield the aerosol-free albedo but the aerosol-contaminated albedo.

4.2 Decontamination of the surface albedo

The monthly surface albedo databases used in FRESCO, namely at 758 and 772 nm, have been de-contaminated for the presence of desert dust aerosols. This has been achieved in two steps: (1) detection of the desert areas with the monthly LER surface albedo databases at 670 nm; (2) detection of dust aerosols using the GOME Absorbing Aerosol Index (AAI). The AAI from GOME uses the reflectances at two UV wavelengths, 335 and 380 nm. The color of the scene at these two wavelengths is compared to the color of a purely Rayleigh scattering atmosphere. The color difference, expressed as the AAI, indicates the presence of absorbing aerosols like desert dust (De Graaf et al., 2005). Figure 8 shows an example (July) of the surface albedo database at 670 nm. In this study, monthly averaged values of the AAI...
Fig. 7. Comparison of the retrieved effective cloud fraction from the old version of FRESCO and OCRA for orbit 11326 (30 April 2004). The results are shown for locations over the Sahara. The dotted line is the one-to-one agreement.

Fig. 8. Global map of surface albedo at 670 nm for July at 1-degree resolution (Koelemeijer et al., 2003).

Fig. 9. Global map of the 1995–2000 July mean GOME AAI from De Graaf et al. (2005).

Fig. 10. Difference between the old and new FRESCO retrievals of effective cloud fraction for July 2004. The new version of FRESCO incorporates the updated surface albedo databases.

were created over the 6-years of available AAI (1995–2000; http://www.temis.nl). Figure 9 gives the AAI 6-years average for July but monthly values are available from 1995 to 2000 (De Graaf et al., 2005).

Firstly, deserts have been characterised as surfaces with an albedo at 670 nm above 0.20 (Koelemeijer et al., 2003). This does not hold for high latitudes at which locations, anyway, no AAI values were retrieved as it can be seen in Fig. 9. Secondly, high values of AAI indicate the presence of absorbing aerosol layers. Thus, an AAI threshold value of 1.0 has been chosen to correct the monthly surface albedo databases over deserts.

The correction on the surface albedo when the two previous conditions (desert location and AAI larger than 1.0) are full-filled is +20%. This value has been chosen following a series of sensitivity tests in the range 1–40%. A series of twelve cloud-free and five cloudy scenes over the Sahara have been chosen using MODIS images. The surface albedo correction was changed (+1 to +40%) to evaluate the value for which FRESCO succeeds to retrieve the appropriate effective cloud fraction. An increase of the surface albedo of +20% was appropriate to improve the retrieved cloud fraction for these cloud-free scenes over the Sahara. The effect on FRESCO cloud fraction can be seen in Fig. 10. The map
The accuracy of the new version of FRESCO in retrieving the appropriate cloud information over desert is corroborated in Fig. 17. This compares the retrieved cloud top pressure values (hPa) from FRESCO with the results of MODIS and the SACURA cloud algorithm of Kokhanovsky et al. (2003)
and Rozanov and Kokhanovsky (2004) for SCIAMACHY orbit 7591 (13 August 2003; state 13) over south-east Algeria (Fig. 18). The approaches correlate reasonably well showing that FRESCO retrieves now more accurately the effective cloud fraction over deserts as well as still reasonable cloud top pressures when there are some clouds at these locations. For the same comparison, the previous version of FRESCO produced slopes of 0.85 ($R^2=0.9$) and 1.06 ($R^2=0.78$) compared to SACURA and MODIS, respectively. This shows that the improvement in effective cloud fraction leads to slightly higher FRESCO cloud top pressures but does not alter significantly the correlation with other cloud products.

5 Conclusions

In this study, the FRESCO cloud product over deserts for SCIAMACHY has been improved. The surface albedo used a priori in the cloud algorithm did not take into account the effect of dust aerosols over desert areas. Therefore, the monthly surface albedo databases at 758 and 772 nm have been decontaminated from this effect by using the GOME Absorbing Aerosol Index. The study shows that this
approach succeeds well in improving FRESCO retrievals of effective cloud fraction and cloud top pressure over the Sahara for both cloud-free and cloudy scenes. A better agreement is obtained in qualitative comparisons with images from the MODIS instrument and also in quantitative comparisons with other SCIAMACHY cloud algorithms such as OCRA, HICRU and SACURA.

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Distinction between clouds and ice/snow covered surfaces in the identification of cloud-free observations using SCIAMACHY PMDs

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Abstract. SCIAMACHY on ENVISAT allows measurement of different trace gases including those most abundant in the troposphere (e.g. CO₂, NO₂, CH₄, BrO, SO₂). However, clouds in the observed scenes can severely hinder the observation of tropospheric gases. Several cloud detection algorithms have been developed for GOME on ERS-2 which can be applied to SCIAMACHY. The GOME cloud algorithms, however, suffer from the inadequacy of not being able to distinguish between clouds and ice/snow covered surfaces because GOME only covers the UV, VIS and part of the NIR wavelength range (240–790 nm). As a result these areas are always flagged as clouded, and therefore often not used. Here a method is presented which uses the SCIAMACHY measurements in the wavelength range between 450 nm and 1.6 μm to make a distinction between clouds and ice/snow covered surfaces. The algorithm is developed using collocated MODIS observations. The algorithm presented here is specifically developed to identify cloud-free SCIAMACHY observations. The SCIAMACHY Polarisation Measurement Devices (PMDs) are used for this purpose because they provide higher spatial resolution compared to the main spectrometer measurements.

1 Introduction

Satellite-based passive remote sensing is commonly used to derive global information about the composition of the Earth’s atmosphere. Information about the total column or even vertical profiles of different gases in the Earth atmosphere can be obtained by measuring the radiance (intensity) spectrum of sunlight reflected by the Earth’s atmosphere, since these spectra contain absorption bands of gases present in the atmosphere, such as ozone. In the ultra-violet (UV), visible (VIS) and near infra-red (NIR) wavelength range the presence of clouds can strongly affect the observation of constituents in the troposphere, because clouds effectively screen the lower part of the atmosphere. When clouds are not properly accounted for, and especially when a significant part of the airmass of interest is below the cloud, (large) errors are introduced. Therefore, cloud detection algorithms are of crucial importance in satellite remote sensing.

The SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) is a joint German/Dutch/Belgian instrument on board the ESA ENVISAT satellite, which was launched on March 1st 2002 and is expected to operate for at least five years. SCIAMACHY is a grating spectrometer measuring the radiance of reflected and back-scattered sunlight between 240–2380 nm at 0.2–1.5 nm spectral resolution. In order to account for the instrument polarisation sensitivity, SCIAMACHY measures the polarisation of reflected sunlight using seven broadband detectors, referred to as the Polarisation Measurement Devices (PMDs).

The predecessor of SCIAMACHY, the Global Ozone Monitoring Experiment (GOME), was launched on 21 April 1995 on-board ESA’s second European Remote Sensing satellite (ERS-2). GOME is a de-scoped version of SCIAMACHY and only covers the ultraviolet, visible and near-infrared wavelength range from 240 to 790 nm with 0.2–0.4 nm spectral resolution (Burrows et al., 1999). GOME is also equipped with three broadband PMDs, measuring polarised light across its full wavelength range.

Several cloud detection algorithms were developed for use in GOME, like ICFA (Kuze and Chance, 1994), OCRA (Loyola, 1998), CRAG (von Bargen et al., 2000), CRUSA (Wenig, 2001), FRESCO (Koelemeijer et al., 2001), GOME-CAT (Kurosu et al., 1998), HICRU (Grzegorski et al., 2004) and SACURA (Rozanov and Kokhanovsky, 2004). These methods either use the high spectral resolution measurements from the main spectrometer, or the broadband PMD measurements, or a combination of both. Some of these
algorithms have been modified for use with SCIAMACHY measurements, but since GOME does not measure in the infra-red region none of these methods uses information in the infra-red wavelengths beyond 800 nm as measured by SCIAMACHY. Because both clouds and ice/snow covered surfaces are highly reflective and white in the GOME wavelength range, none of these algorithms distinguish between clouds or ice/snow covered surfaces in the observation. While in principle cloud detection methods using the O$_2$A band, like FRESCO and SACURA, can detect the pressure of the clouds or the surface and thus discriminate white clouds from a white surface, this is not part of the current versions of these algorithms. Without the ability to distinguish between cloudy and ice/snow covered surfaces, all observations over ice/snow covered surfaces are flagged as cloudy and therefore often not used. A method to distinguish between clouds and ice/snow covered surfaces is thus of crucial importance to be able to identify cloud-free observations.

Here the SCIAMACHY PMD Identification of Clouds and Ice/snow method (SPICI) is presented which is a variation on previous cloud-detection algorithms. It uses, a.o. the SCIAMACHY PMD measurements in the wavelength range around 1.6 $\mu$m where the reflectivity of ice/snow covered surfaces is significantly reduced while the reflectivity of clouds is still high. Using this clear spectral difference in reflectivities a distinction between clouds and ice/snow covered surfaces in the SCIAMACHY observations can be made. The algorithm consists of two steps. In the first step the algorithm only uses PMD 2, 3 and 4 to determine the presence of a white surface in the visible wavelength range. Because at these wavelengths one can not separate clouds from ice/snow covered surfaces, a second step is needed to finally detect cloud-free observations also over ice/snow covered surfaces. Because the SCIAMACHY PMDs are not radiometrically calibrated, the SPICI algorithm is developed using collocated high spatial resolution observations from MODIS on Eos-Terra.

The structure of this paper is as follows. In Sect. 2 we describe the Polarisation Measurement Devices on-board SCIAMACHY and present some illustrations of their use in colour images of the Earth which illustrates the basic concept for the cloud and ice/snow algorithm SPICI presented in Sects. 3 and 4. Section 3 starts with the definition of the cloud algorithm which represents the first step in the SPICI algorithm. Section 4 deals with the actual distinction between clouds and ice/snow covered surfaces. Validation of the SPICI algorithm is presented in Sect. 5. We finish with a summary in Sect. 6.

2 SCIAMACHY Polarisation Measurements Devices

2.1 SCIAMACHY

SCIAMACHY’s primary mission objective is to perform global measurements of trace gases in the troposphere and stratosphere (Bovensmann et al., 1999). The instrument provides column and/or vertical profile information on O$_3$, H$_2$CO, SO$_2$, BrO, OCIO, NO$_2$, H$_2$O, CO, CO$_2$, CH$_4$, N$_2$O, O$_2$, (O$_2$)$_2$, and on clouds and aerosols as well. SCIAMACHY thereto measures the radiance of reflected and back-scattered sunlight in 8 channels, covering the 240–1750 nm wavelength (channels 1–6) and two IR bands 1940–2040 nm and 2265–2380 nm (channels 7 and 8, respectively) at 0.2–1.5 nm spectral resolution. SCIAMACHY alternates between nadir and limb viewing modes for most part of the orbit. The swath of the instrument in nadir mode is 960 km, and the individual main channel measurements have a footprint on Earth ranging from 60 km $\times$ 30 km to 240 km $\times$ 30 km (across $\times$ along track), thereby providing global coverage in a period of six days (Bovensmann et al., 1999).

2.2 SCIAMACHY PMD measurements

SCIAMACHY is a highly polarisation-sensitive instrument due to the instrument’s gratings and mirrors. Neglect of such an instrument’s polarisation sensitivity can lead to errors in the radiances of several tens of percents at wavelengths where the instrument polarisation sensitivity is highest. In order to correct for this polarisation sensitivity, SCIAMACHY measures the polarisation of reflected sunlight using seven broadband detectors, referred to as Polarisation Measurement Devices (PMDs, see Table 1), which roughly cover the spectral range of the main spectrometer. Because the PMDs are mainly sensitive to parallel (to the instrument slit) polarised light, while the main channel spectrometer is sensitive to both polarisation components, information on the polarisation of the incoming light is obtained by combining the two measurements (Slijkhuys, 2000). The PMDs are read out at 40 Hz, but are down-sampled to 32 Hz for processing. This still gives a much better spatial resolution ($\approx$ 7 km $\times$ 30 km) than the main spectral channels where the fastest read-out occurs at 8 Hz, and more commonly at 1 Hz. This high PMD spatial resolution allows us to study clouds and ice/snow in more spatial detail which is the reason why we use the PMDs

<table>
<thead>
<tr>
<th>PMD</th>
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<tr>
<td>1</td>
<td>310–365</td>
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<tr>
<td>2</td>
<td>455–515</td>
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<tr>
<td>3</td>
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<td>5</td>
<td>1500–1635</td>
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<td>6</td>
<td>2280–2400</td>
</tr>
<tr>
<td>7</td>
<td>800–900    (U-sensitive)</td>
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</table>
2.3 PMD global images

Figure 1 displays the Earth surface as observed by SCIAMACHY under cloud-free conditions by combining the simultaneous PMD 2, 3, and 4 measurements. The Earth surface was gridded to 0.25° × 0.25° cells. Each PMD measurement, divided by the cosine of solar zenith angle, was inserted into the grid-cell closest to the central footprint of that measurement between November 2002 and October 2003. The measurement with lowest PMD 2 intensity was stored in each grid-cell, as clouds would show bright in the SPICI algorithm and not the main spectrometer measurements. In this paper we focus on four PMDs (PMD 2 to 5) that cover the visible and near-infrared wavelength range from 450 nm to 1700 nm.

The measured signal for each PMD can be written as:

$$S_{PMD} = \int_{\lambda_{\text{start}}}^{\lambda_{\text{end}}} M_1(\lambda) I(\lambda)(1 + \mu_2^P(\lambda)q(\lambda) + \mu_3^P(\lambda)u(\lambda))d\lambda,$$

(1)

where $S_{PMD}$ is the PMD read-out signal, and where $M_1(\lambda)$, $\mu_2^P(\lambda)$ and $\mu_3^P(\lambda)$, indicate per wavelength $\lambda$ the PMD sensitivity to the different Stokes Parameters, $I(\lambda)$, $q(\lambda)=Q(\lambda)/I(\lambda)$, $u(\lambda)=U(\lambda)/I(\lambda)$, respectively, summed over the wavelength range for which the PMD is sensitive ($\lambda_{\text{start}}$ and $\lambda_{\text{end}}$, respectively). As $\mu_3^P$ is very small for all PMDs (except PMD 7), the PMDs are mostly sensitive to $I$ and $q$. Moreover, the effect of polarisation on the intensity measured by the PMD is relatively small and even more so because we focus only on the ratio between different PMD measurements. As such any effect from polarisation is due the difference in polarisation-sensitivity or degree of polarisation. For all PMDs, except PMD 1 and 7, these differences are small.

3 Cloud recognition

3.1 SCIAMACHY PMD calibration

Clouds can easily be spotted in any visual Earth image from space, because in the visible wavelengths, clouds are bright and white whereas the background on which they appear is usually not. Obviously, this is not the case when there is snow or ice in the background, but these cases will be addressed in the next section. Clouds are white in the visible wavelengths as they reflect all wavelengths equally yet absorb little, because the water or ice particles of the cloud are

Fig. 1. Earth surface as seen by SCIAMACHY PMD 2, 3, and 4. The Earth surface was gridded to 0.25° × 0.25° cells, with each grid-cell filled with the darkest PMD 2 intensity between November 2002 and October 2003. The colors Red, Green and Blue were derived by taking the natural log of: Red: 1.0 × PMD 3 + 0.1 × PMD 4, Green: 0.5 × PMD 2 + 0.5 × PMD 3 + 0.1 × PMD 4, Blue: 1.0 × PMD 2, with a minimum value of 8.5 and a maximum of 11.0

Fig. 2. Similar to Fig. 1, showing the Earth surface as seen by SCIAMACHY PMD 4, 5, and 6, as fake blue, green and red, respectively, during the months February and March 2003. The ice-caps and snowy northern latitudes show up in purple, while clouds appear green-grey.
much larger than the wavelengths of the visual photons. This degree of “whiteness” can be used to detect the presence of clouds.

As SCIAMACHY PMDs are not absolutely calibrated, each SCIAMACHY PMD 2, 3 and 4 readout is first weighted or semi-calibrated. While each cloud will have a different reflectance (due to cloud fraction, type, altitude), the intensities in all three PMDs for each individual cloud should be similar, as clouds have a wavelength independent spectrum in the visible wavelength range (Bowker et al., 1985). The weighting factors were derived by selecting clouded scenes and normalising the readout distribution of PMD 2 and 4 to PMD 3 for these scenes. As mentioned before, PMD 1 is not used because of its strong polarisation sensitivity. The PMD signals are weighted as follows:

\[
W_4 = S_{\text{PMD}4}/A_r, \\
W_3 = S_{\text{PMD}3}/A_g, \\
W_2 = S_{\text{PMD}2}/A_b, \\
\]

where \(A_r, A_g, A_b\) are the weighting factors, 0.795, 1.000, and 0.750, respectively, and \(W\) the weighted PMD readout. These weighting factors have been derived for SCIAMACHY processor version 5.04, but can be used on earlier versions, as the changes between versions, so far, in non-calibrated PMD measurements are less than a percent for the PMDs used by SPICI.

3.2 Saturation

The saturation or the “whiteness” for each observed scene can then be derived from these values as follows:

\[
\text{Saturation} = \frac{\text{max}(W_4, W_3, W_2) - \text{min}(W_4, W_3, W_2)}{\text{max}(W_4, W_3, W_2)},
\]

where \(\text{max}(W_4, W_3, W_2)\) and \(\text{min}(W_4, W_3, W_2)\) are, respectively, the highest and lowest value of \(W_4, W_3,\) and \(W_2\) for each simultaneous measurement. Saturation can vary between 0–1 and will be low when all three PMDs are equally bright (= “white”) and high when the three PMD readouts differ much. For more details on the use of saturation in colour applications see Foley et al. (1990). Scenes with low saturation have thus a high “whiteness” which indicates a clouded scene (or snow covered surface). A threshold can then be determined for which all scenes with a saturation-value below this threshold are apparently clouded. A large advantage of using a saturation threshold instead of individual PMD thresholds is that saturation is determined from a ratio between PMDs. In a ratio between PMDs the geometry component is eliminated (Loyola, 1998) and as such no correction for solar zenith angle or viewing angle is needed.

3.3 MODIS

In order to derive the required saturation threshold SCIAMACHY observations are compared to MODIS (MODer-
SCIAMACHY observation corresponding to a cloud-fraction of maximal 0.02.

3.4 Threshold determination

These average MODIS cloud values over a SCIAMACHY PMD observation can be compared to the saturation-value $S$ for each individual PMD observation. For this, collocated observations (lat. 14°–55° N, long. 7° W–18° E) of SCIAMACHY (∼10:15 UT) and MODIS (∼10:50 UT) on 16 June 2004 over Europe and Africa were compared. The selected region avoids ice/snow covered areas. Figure 3 shows the number of SCIAMACHY PMD observations with a particular saturation or “whiteness” for “clouded”, “clear” and all remaining (mixed) scenes according to the MODIS data. The “clouded” and “clear” curves show two clearly distinct distributions in saturation-value, indicating that this parameter can be used to differentiate between clouded and clear scenes. Observations which are partly clouded show more variation in saturation-value, because an average of the “clouded” and “clear” scenes is found. As we want to keep the number of mistakenly flagged cloud-free observations to a minimum, we use a threshold saturation-value of 0.35 in the remainder of the study. However for studies focusing on clouds (instead of clear scenes) or where an occasional cloud is not a problem a threshold of 0.25 can be used, increasing the number of detected “clear” scenes.

3.5 Spatial comparison MODIS–SPICI

Figure 4 shows the spatial comparison between the used SCIAMACHY (∼10:15 UT) and MODIS (∼10:50 UT) observations on 16 June 2004. All SCIAMACHY PMD observations with a saturation below 0.35 are indicated as clouded, those with a higher saturation-value as clear. The colours indicate where the methods agree (blue, green) or disagree (orange, yellow). The agreement is very good, only in a few cases there is a disagreement. The most troubling disagreements are when MODIS indicates a (maybe) cloud, while SCIAMACHY PMD saturation-value indicates a clear scene. These cases only occur at the edge of clouds, likely due to movement (or formation) of clouds in the 35 min between the observations. For example, around 5° longitude and 32° latitude a cloud apparently moved to the east, as SCIAMACHY indicates clear scenes on the east of the cloud while MODIS (35 min later) indicates these scenes as clouded. On the west side of the cloud the reverse happens, confirming that the cloud moved to the east. Also the cloud cover over northern Europe for this morning is extremely patchy, resulting in some disagreements between MODIS and SCIAMACHY cloud identification. It is noted that all mixed scenes from Fig. 3 coincide with these cloud edges.

The above cloud detection scheme is based upon the “whiteness” – in the visible wavelength range – of the scene, and therefore does not distinguish between clouds and ice/snow covered surfaces. This is a problem for many cloud detection algorithms, but SCIAMACHY’s infra-red PMDs allow for differentiating between clouds and ice/snow covered surfaces as shown in the next section.
4 Ice recognition

4.1 Physical background

All existing cloud detection algorithms using PMDs are derived from GOME algorithms, which are unable to distinguish between white ice/snow and white clouds because the GOME wavelength range is limited to 800 nm. However, SCIAMACHY infra-red PMDs allow for differentiation between clouds and ice/snow covered surfaces.

Several kinds of clouds exist: water clouds, ice clouds and mixed-phase clouds. In the infra-red region around 1.6 µm, which corresponds to the wavelength range covered by PMD 5, water and ice have a distinctly different refractive index (Kokhanovsky, 2004). The imaginary part of the refractive index, which determines the absorption, is much larger for ice than water. In addition, it is noted that water and ice show very different spectral absorption features around 1.6 µm which can be used for cloud phase discrimination as was shown by Knap et al. (2002) and Acarreta et al. (2004) using SCIAMACHY measurements.

Ice/snow covered surfaces are dark compared to water clouds (Bowker et al., 1985), due to the larger imaginary refractive index around 1.6 µm and the larger effective particle radius of an ice/snow covered surface (Wiscombe and Warren, 1980; Warren, 1982). This is also observed in SCIAMACHY spectra (Fig. 5) measured with the main spectrometer where a clear difference is visible between a water cloud and ice/snow covered surface.

Clouds, however, can also consist of ice particles with a refractive index comparable to ice on the Earth’s surface, which might limit the possibility to distinguish between ice clouds and ice/snow covered surfaces. However, ice clouds have an effective particle radius still much smaller compared to ice/snow (e.g., around 15 µm compared to possibly 200 µm), therefore ice clouds show less absorption compared to ice/snow covered surfaces (Wiscombe and Warren, 1980; Warren, 1982). This is illustrated in Fig. 5 (ice cloud) where the MODIS identification of ice clouds (Platnick et al., 2003) is used to select the corresponding SCIAMACHY ice cloud spectrum. Figure 5 further shows that ice cloud spectra can be considered an intermediate case between the bright water cloud spectra and dark ice/snow surface spectra. The difference in reflectance between ice clouds and ice/snow covered surface around 1.6 µm is large enough to distinguish these in most cases (Crane and Anderson, 1984).

While changing the optical thickness of the cloud, compacting the ice/snow or changing the amount of dirt mixed with the ice/snow does change the reflectance, the large difference in reflectance around 1.6 µm between (ice and water) clouds and ice/snow remains (Kokhanovsky, 2004; Greuell and Oerlemans, 2004). This difference in absorption at 1.6 µm, and measured with PMD 5, is used in the SPICI algorithm to distinguish between (water and ice) clouds and ice/snow covered surfaces.

In order to further improve the differentiation between (ice and water) clouds and ice/snow covered surfaces, the PMD 5 measurements around 1.6 µm are normalised with the PMD 4 measurements around 850 nm. The reflectance around 850 nm is larger for ice/snow covered surfaces than (water or ice) clouds contrary to what is observed at 1.6 µm enhancing the relative difference (Bowker et al., 1985). In addition, by taking the ratio of PMDs no correction for solar zenith angle or viewing angle is needed (Loyola, 1998). Taking the ratio of PMD 5 with PMD 4 thus improves the differentiation between (ice and water) clouds and ice. While it should also be possible to use PMD 6 for this purpose, PMD 6 suffers from a very low signal-to-noise ratio, making it unsuitable for use in SPICI.

4.2 Threshold determination

The preferred approach would be to compare the expected ratio for PMD 5 and PMD 4 from theory with the measured ratio between PMD 5 and PMD 4. However, the required absolute calibration of SCIAMACHY PMDs is lacking. Therefore the threshold for the PMD 5 to 4 ratio to differentiate
between clouds and ice/snow surfaces is empirically determined using collocated MODIS observations.

Collocated MODIS and SCIAMACHY observations are used, this time observed over Antarctica on 24 January 2003 between 08:30–09:10 UT by SCIAMACHY and at 08:50 UT by MODIS. As in the previous section all MODIS observations within a single PMD observation are averaged for comparison. Figure 6 shows the number of SCIAMACHY PMD observations with a particular ratio between PMD 5 and PMD 4 for “clouded” and “clear” scenes according to averaged collocated MODIS data. As the observations are over Antarctica all “clear” scenes are observing snow or ice surfaces. The “clouded” and “clear” curves show two clearly distinct distributions, indicating that the ratio between PMD 5 and PMD 4 can be used to differentiate between clouds and ice/snow covered surfaces. Most PMD observations with a ratio $S_{\text{PMD 5}}/S_{\text{PMD 4}}$ below 0.4 appear to be ice/snow covered surfaces. In general, however, most SCIAMACHY observations occur over more diverse scenes than only ice/snow covered surfaces and clouds as here over Antarctica. The ratios of other scenes can vary and must therefore be verified, as care must be taken not to mistakenly identify clouds as ice/snow covered surfaces.

Figure 7 shows the number of SCIAMACHY PMD observations as a function of the ratio between PMD 5 and PMD 4 for “clouded” and “clear” scenes according to averaged collocated MODIS data for the scene over Europe and Africa in the previous section. Most “clear” scenes (observing sea, desert and vegetation) have a high $S_{\text{PMD 5}}/S_{\text{PMD 4}}$ ratio around 1.8, but we see a different distribution for the “clouded” scenes, varying mostly between 0.2 and 1.2. However, in these particular observations we expect to find little ice/snow covered surfaces as the observations were made in mid-summer June. If here a threshold of 0.4 was used several clouds would have been -mistakenly- identified as ice/snow covered surfaces. Therefore, a lower limit than 0.4 for the ratio $S_{\text{PMD 5}}/S_{\text{PMD 4}}$ must be used. Figure 7 suggests a value of 0.2, but studying ratios over several other SCIAMACHY orbits in the summer, shows that the lower limit for cloudy observations in the ratio is around 0.16, as illustrated in Fig. 8, which shows the SCIAMACHY data for 2 orbits on 23 August 2002, over western Europe and the Atlantic ocean, containing no ice/snow covered surfaces. No comparison with MODIS was made for this data, so no distinction is made between “clouded” and “clear” scenes, but when comparing to the ratios from 16 June 2004 (Fig. 7), the similarity in the distributions is clear. In order to avoid mistakenly identifying clouds as ice/snow, we choose a ratio between PMD 5 and PMD 4 of 0.16 to distinguish between cloud-free ice/snow covered surfaces and clouds, knowingly overestimating the amount of clouds compared to cloud-free ice/snow scenes. For observations over Antarctica or studies less sensitive to clouds a larger ratio up to 0.4 can be chosen.
4.3 Spatial comparison MODIS-SPICI

Figure 9 allows a spatial comparison between the used SCIAMACHY (08:30–09:10 UT) and MODIS (08:50 UT) observations on 24 January 2003 over Antarctica. All SCIAMACHY PMD observations with a saturation-value below 0.35 are indicated clouded, and those with a higher saturation as clear. In the next step, all indicated clouded scenes with a ratio between PMD 5 and PMD 4 below 0.16 are re-assigned as ice/snow covered surfaces. The legend indicates where the methods agree or disagree. The only notable disagreement is when a SCIAMACHY PMD observation is identified as clouded whereas MODIS assigned clear (yellow). In the east part the number of clouds is thus overestimated by SCIAMACHY compared to MODIS, but this is to be expected due to the low ratio (0.16 instead of 0.4) used for differentiating between ice/snow and clouds. For our purpose the most troubling disagreements would be where MODIS indicates a cloud, while SCIAMACHY PMD saturation-value indicates a clear ice/snow scene (red). Only in a few single cases this happens at the (western) edges of the central cloud complex, likely due to movement of the clouds in the time in-between the observations. Also SCIAMACHY indicates a few single scenes as being clear (green), while over the Antarctica all clear scenes should show ice/snow. However for the purpose of removing clouded scenes this is not relevant.

5 Method validation

In order to validate the SPICI method a final comparison was made between SCIAMACHY (13:48–14:12 UT) and collocated MODIS (14:40 UT) data observed on 30 June 2002. These observations are partly over Greenland, the Atlantic Ocean and eastern Canada, combining clouded, clear and ice/snow scenes within the same orbit. This allows a direct validation of the SPICI method as presented in the previous sections. Again all MODIS observations within a single PMD observation are averaged. Figure 10 shows the spatial comparison. Again the agreement is very good. Over Greenland ice/snow scenes are indicated where the sky is clear according to MODIS (light blue), while over the ocean the SPICI method indicated normally clear (green) or clouded (dark blue) skies at the exact same locations as MODIS. Only a few single/individual disagreements (red, orange) show-up, all occurring at the edge of large cloud complexes or over patchy cloud regions. Again most likely this is due the movement of the clouds in the time between the SCIAMACHY and MODIS observations.

A more quantitative comparison between SPICI and MODIS is summarised in Table 2 where the number of observations for the different (dis)agreements are shown. As such a total of 7552 SPICI observations with collocated MODIS observations were used. Of these 48% (3615) were confidently clouded (“clouded”), 14% (1060) were confidently
Table 2. Number of PMD observations for different agreements between MODIS and SPICI for 30 June 2002.

<table>
<thead>
<tr>
<th>SPICI</th>
<th>MODIS</th>
<th>counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>All</td>
<td>7552</td>
</tr>
<tr>
<td>Cloud</td>
<td>Cloud</td>
<td>3479</td>
</tr>
<tr>
<td>Cloud</td>
<td>Clear</td>
<td>143</td>
</tr>
<tr>
<td>Cloud Mixed*</td>
<td>1781</td>
<td></td>
</tr>
<tr>
<td>Clear</td>
<td>Clear</td>
<td>136</td>
</tr>
<tr>
<td>Clear</td>
<td>Mixed</td>
<td>917</td>
</tr>
<tr>
<td>Clear Mixed*</td>
<td>1096</td>
<td></td>
</tr>
</tbody>
</table>

*Mixed refers to neither confidently clear, nor confidently clouded.

clear (“clear”), and 38% (2877) were neither confidently clear nor confidently clouded (“mixed”). We focus on the “clouded” and “clear” observations. As SPICI has been tuned such that cloudy observations are rarely flagged cloud-free, the most important comparison is with the observations that are ‘clouded’ according to MODIS. When including ice/snow covered surfaces according to SPICI as clear, SPICI identifies 96% of the MODIS “clouded” observations as clouded and only 4% is mistakenly identified as clear. The next important comparison is the observations that are “clear” according to MODIS while SPICI mistakenly labels them clouded. These observations will often not be used and as such should preferably be kept to a minimum. As such, SPICI identifies 87% of the MODIS “clear” as clear and only 13% of the MODIS “clear” observations as clouded. By choosing different thresholds these percentages can vary, but it can be concluded that current thresholds minimise cloud-contamination in the SPICI clear observations, with an acceptable amount of cloud-free observations mislabelled as clouded. All this combined shows the very good agreement between MODIS and SPICI.

6 Summary

For the accurate detection of well-mixed tropospheric gasses, such as CH₄ and CO₂, the use of cloud-free observations is extremely important. The slightest cloud-contamination affects the quality of these data products which could make them useless. In this paper the SPICI method is presented which allows for fast and simple identification of cloud-free SCIAMACHY PMD observations. The NIR SCIAMACHY PMD measurements allow to distinguish between clouds and ice/snow covered surfaces, which in the visible wavelengths is more complicated. The method employs the ratios of different SCIAMACHY PMD measurements which makes the approach very robust with respect to e.g. calibration uncertainties. The threshold values are defined using collocated observations with the well known and validated high-spatial resolution MODIS data. The threshold values are tuned such that cloudy observations are rarely flagged cloud-free, as such some cloud-free observations are mistakenly flagged cloudy. Clearly, one can use the SPICI algorithm and adjust the criteria depending on the use of the data.

The SPICI method is very easily implemented, requiring only a few numbers. For those studies that require cloud-free scenes these are summarised as follows:

\[
\begin{align*}
W_4 & = \frac{S_{PMD4}}{0.795} \\
W_3 & = \frac{S_{PMD3}}{1.000} \\
W_2 & = \frac{S_{PMD2}}{0.750} \\
\text{Sat(uration)} & = \frac{\max(W_4, W_5, W_6) - \min(W_4, W_5, W_6)}{\max(W_4, W_5, W_2)} \\
\text{Cloud-free} & : \text{Sat} \geq 0.35 \\
\text{Ice/Snow clear} & : \text{Sat} < 0.35 \& \frac{S_{PMD5}}{S_{PMD4}} \leq 0.16 \\
\text{Cloud} & : \text{Sat} < 0.35 \& \frac{S_{PMD5}}{S_{PMD4}} \geq 0.16
\end{align*}
\]

The thresholds can be somewhat relaxed in cases where some cloud-contamination is acceptable.

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Global satellite validation of SCIAMACHY O₃ columns with GOME WFDOAS


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Abstract. Global stratospheric ozone columns derived from UV nadir spectra measured by SCIAMACHY (Scanning Imaging Spectrometer for Atmospheric Chartography; data ESA Versions 5.01 and 5.04) aboard the recently launched Environmental Satellite (ENVISAT) from January to June 2003 were compared to collocated total ozone data from GOME (Global Ozone Monitoring Experiment on ERS-2) retrieved using the weighting function DOAS algorithm (WFDOAS; Version 1.0) in order to assess the level-2 data (trace gas data) retrieval accuracy from SCIAMACHY. In addition, SCIAMACHY ozone columns retrieved with WFDOAS V1.0 were compared to GOME WFDOAS for some selected days in 2003 in order to separate data quality issues that either come from the optical performance of the instrument or algorithm implementation. Large numbers of collocated total ozone data from the two instruments, which are flying in the same orbit about 30 min apart, were spatially binned into regular 2.5° times 2.5° grids and then compared. Results of these satellite comparisons show that SCIAMACHY O₃ vertical columns (ESA Version 5.01/5.04) are on average 1% (±2%) lower than GOME WFDOAS and scatter increases at solar zenith angles above 85° and at very low total ozone values. Results show dependencies on the solar zenith angle, latitudes, and total ozone amounts which are explained by the implementation of an outdated GOME algorithm based on GOME Data Processor (GDP) version 2.4 algorithms for the SCIAMACHY operational product. The reprocessing with an algorithm equivalent to GOME WFDOAS V1.0 shows that the offset and dependencies on solar zenith angle, latitude, and total ozone disappear and that SCIAMACHY WFDOAS data are within 1% of GOME WFDOAS. Since GOME lost its global coverage in July 2003 due to data rate limitation, continuation of the total ozone time series with SCIAMACHY is of highest importance for long-term trend monitoring. Since the beginning of its operation in March 2002 the SCIAMACHY instrument has performed stable. With the application of proper algorithms to retrieve total ozone, SCIAMACHY will be able to contribute to the global long term satellite total ozone record and it has the potential to achieve the high accuracy of GOME total ozone.

1 Introduction

The stratospheric ozone layer protects the biosphere from harmful ultraviolet radiation. The discovery of the Antarctic ozone hole in the early 1980s (Farman et al., 1985), but also changes in the Arctic and lower latitudes, established the need for global measurements of ozone and other atmospheric trace gases (World Meteorological Organization, 1999). To assess current and future changes long-term observations of ozone are urgently needed. Ground-based instruments can provide long and stable records for specified location, but satellite instruments are the most effective way to achieve a global view of the atmosphere. Since 1979 the Total Ozone Mapping Spectrometer (TOMS) instruments (e.g. Bhartia and Wellemeyer, 2004) and the Solar Backscatter UltraViolet (SBUV) instruments (Bhartia et al., 1996) have made a major contribution in monitoring the ozone distribution from day to day and in particular the changes in the polar regions (World Meteorological Organization, 2003). In June 2004 a new version, version 8, of the TOMS algorithm was released which shows in comparison to worldwide groundbased measurements very good agreement (Labow et al., 2004). Currently there are three European satellite instruments successfully measuring ozone columns along with other atmospheric constituents in nadir viewing mode and successfully contributing to the long-term ozone data record: the Global Ozone Monitoring Experiment (GOME) on ERS-2 (Burrows et al., 1999a) operating since April 1995, the
Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) as part of the atmospheric chemistry payload of the third ESA Earth observation satellite platform called ENVISAT which was launched in March 2002 (Bovensmann et al., 1999) and the Ozone Monitoring Instrument (OMI) onboard EOS-AURA (Veefkind and de Haan, 2002) operating since July 2004. As satellite instruments age and unfortunately stop to measure, it is necessary to compare ozone measurements from older with those from newer instruments in order to ensure that long-term behaviour derived from a combination of ozone sensors will be useful (e.g. Cunnold et al., 1996). Furthermore, satellite instruments have to be validated during the complete lifetime to ensure ongoing quality of the measured data and to avoid long-term drifts due to instrumental aging.

GOME delivers global ozone and NO$_2$ columns as official data products from ESA. In addition, retrieval of ozone profiles and other trace gases (BrO, SO$_2$, OCLO, HCHO, water vapour) from GOME has been demonstrated (more details e.g. in Burrows et al., 1999a). The GOME total ozone retrieval algorithm using the weighting function DOAS approach (GOME WFDOAS) showed in an extensive global validation with ground-based data an agreement on average within 1% and very little seasonal variation in the differences to ground data (Coldewey-Egbers et al., 2005; Weber et al., 2005). The GOME WFDOAS algorithm was developed in competition with two other algorithms at the University of Bremen in response to an ESA Invitation to Tender. In parallel, the TOGOMI algorithm by KMNI (Valks and van Oss, 2003) and the GDOAS algorithm by BIRA-IASB were developed. The latter has been adopted with some minor modifications for the new ESA GOME algorithm GDP Version 4.0 (Lambert et al., 2004a). All three algorithms (WFDOAS, TOGOMI, and GDOAS) were shown to improve significantly upon ESA GOME total ozone (GDP) Version 3.0 (GDP V3 VALREPORT, 2002).

SCIAMACHY is the successor of GOME and the currently available ESA operational data product version 5.01/5.04 was based upon the outdated GOME version GDP 2.4. A validation reference data set of SCIAMACHY data version 5.01 has been compared to ground-based (Lambert et al., 2004b) and satellite measurements (Bracher et al., 2004; Hilsenrath et al., 2004), models, and assimilation data (Eskes and Dethof 2004) to verify the improvement upon the previous SCIAMACHY versions 3.5x and assess the geophysical consistency of the latest operational SCIAMACHY data version. These validations concluded that SCIAMACHY V5.01 improved upon previous versions, but known errors, e.g. dependence on solar elevation and on ozone column, inherited from GOME GDP 2.4 remained. An overall agreement of about 1% of SCIAMACHY V5.01 to assimilated GOME TOGOMI (Eskes and Dethof, 2004), a negative bias around 1% to ground stations (Lambert et al., 2004b) and GOME GDP 3.0 (Bracher et al., 2004), and up to 3% to SBUV/2 V7 (Hilsenrath et al., 2004) were found. However, the result has to be considered with some suspicion since ground-based validation showed a solar zenith angle dependence of 8 to 10% at high latitudes, an overestimation of low ozone columns recorded during springtime ozone depletion events, and a fractional cloud cover dependence at about one third of the stations. The poor space/time sampling (the data were only sparsely available from the second half of 2002 and the majority were measured above Europe and the south polar region) might have biased these results. In order to derive firm conclusions on the data quality of SCIAMACHY a global validation of a consolidated long term SCIAMACHY data set versions 5.01/5.04 (differences are negligible between both versions with regard to total ozone) with GOME WFDOAS V1.0 ozone columns from the first half a year of 2003 was performed. Only for this time period a large set of collocations can be found where ozone columns derived from both instruments are globally available in the latest versions. After June 2003 GOME has a reduced coverage because of a tape recorder failure. Due to the known problems with the GDP Version 2.4 algorithm (see Lambert et al. 2000) on which SCIAMACHY Version 5.01/5.04 is based, the GOME WFDOAS algorithm was applied to SCIAMACHY level-1 data for selected days and compared. These additional comparisons show that most of the problems found with SCIAMACHY Versions 5.01/5.04 are due to algorithm issues rather than due to the optical performance of the SCIAMACHY spectrometer.

2 Satellite O$_3$ data sets

SCIAMACHY is a passive remote sensing instrument, which measures the back scattered and reflected electromagnetic radiation from the atmosphere. ENVISAT flies in a sun synchronous near polar orbit at a mean altitude of 795 km with the equator crossing time in descending node at 10:00 a.m. local time. One orbits takes about 100 min, which results in about 14.3 orbits per day. SCIAMACHY comprises eight spectral channels between 240 and 2380 nm with a channel dependent spectral resolution between 0.2 and 1.5 nm. The total ozone retrieval occurs between 325 and 335 nm at a spectral resolution of about 0.2 nm. SCIAMACHY is the first satellite instrument, that makes spectroscopic observations alternating between nadir and limb viewing geometries, and, in addition, provides solar and lunar occultation modes. For this study only data from SCIAMACHY nadir observations have been used. The nadir mirror scans along the satellite track and each full scan covers a ground area of approximately 30 km along track by 960 km across track. The effective spatial resolution for ozone total columns from SCIAMACHY varies between 30 km along track and between 30 to 240 km across track as discussed in Bovensmann et al. (1999).

The nadir-viewing instrument GOME on board of ERS-2 is a combined prism and grating spectrometer that operates
in a similar way as SCIAMACHY. ERS-2 follows ENVISAT in the same orbit with a time difference of 30 min. Global coverage is achieved after 42 orbits or approximately three days, while for SCIAMACHY it takes six days because of the additional limb measurements. At latitudes higher than 65° complete coverage is provided daily except for the polar night region. Measurements cover the entire spectrum from 240 nm to 790 nm with a spectral resolution varying between 0.2 to 0.3 nm and are recorded in four separate spectral channels. The measurement sequence of an across scan lasts 6 s, three radiance measurements are taken each in 1.5 s in forward direction covering together a maximum surface area of 40 km by 960 km each and the final back scan (Burrows et al., 1999a). In June 2003, the tape recorder for intermediate data storage failed. Since that time only data are transmitted to the ground when ERS-2 is in direct contact with ground stations and this limits the coverage to an extended area in the North Atlantic sector.

Vertical column densities of ozone are retrieved from SCIAMACHY and GOME UV-VIS nadir measurements by using the Differential Optical Absorption Spectroscopy (DOAS, Platt, 1994) in the 325–335 nm (UV) spectral window. SCIAMACHY also retrieves ozone slant columns in the 425–450 nm (VIS) spectral window, but in this study only the UV results were compared. The SCIAMACHY VIS ozone product still shows major errors (e.g. Bracher et al., 2002). After generation of four versions of SCIAMACHY operational data products from the near real time processor (SCI\_NL) during commissioning phase, the SCI\_NL processor was upgraded to the newly operational version 5.01 in March 2004. Compared to previous versions, the main changes are an updated radiometric calibration of radiances (level-1 data) and the use of ozone cross-sections measured with the SCIAMACHY flight model (FM) by Bogumil et al. (2000). In August 2004 one part of the SCIAMACHY 2003 level-2 data set was processed with version 5.04, which improves mainly the (re)processing capabilities. Except for the time period from 1 January 2003 to 21 March 2003 where version 5.01 had been affected by an incorrect handling of a season index, the level-2 product of versions 5.01 and 5.04 are equal. All versions of the SCIAMACHY operational ozone column product are an adaptation of Version 2.4 of the GOME Data Processor that are three versions behind the current GOME GDP V4.0.

The new algorithm WFDOAS developed at the Institute of Environmental Physics at the University of Bremen (IUP) is used to retrieve total ozone columns from GOME in the UV spectral window 326–335 nm. WFDOAS fits vertically integrated ozone weighting functions rather than ozone cross-section to the sun-normalised radiances that enables a direct retrieval of vertical column amounts (Coldewey-Egbers et al., 2005). The WFDOAS algorithm also takes into account the slant column path length modulation as a function of wavelength that is usually neglected in standard DOAS when using single air mass factors to convert observed slant column into vertical column densities. Several auxiliary quantities directly derived from the GOME spectral range such as cloud-top-height and cloud fraction (O2-A band) and effective albedo using the Lambertian Equivalent Reflectivity (LER) near 377 nm are used in combination as input to the ozone retrieval. The most significant improvement over GOME V3.0 is the explicit treatment of the ozone dependent contribution in the Raman correction in scattered light known as Ring effect (Coldewey-Egbers et al., 2005). The precision of the total ozone retrieval is estimated to be better than 3% for solar zenith angles below 80°. A detailed validation study by Weber et al. (2005) showed that GOME WFDOAS total ozone agrees on average within 1% with selected ground-based measurements from the WOUDC (World Ozone and UV Radiation Data Centre), and only shows a negligible seasonal dependency to within 0.5% at mid latitudes and to within 1% at high latitudes, with maximum in winter and minimum in summer. At high solar zenith angles in polar regions a positive bias between 2% to 8% was found (Weber et al., 2005).

The WFDOAS algorithm by Coldewey et al. (2005) was adapted to process total ozone columns from SCIAMACHY spectral data for selected days of the first half of 2003. The SCIAMACHY weighting function DOAS algorithm (SCIA WFDOAS) combines a reading module for SCIAMACHY level-1 data with the GOME WFDOAS modules. To obtain cloud fraction and cloud-top pressure estimates the FRESCO algorithm by Koelemeijer et al. (2001) was used including the recommended correction factor of 1.25 applied to the sun-normalised radiances (Eskes et al., 2005). We used the solar spectra given in the SCIAMACHY level-1 data, which is the sun reference, measured with the SCIAMACHY ESM diffuser from the same day of nadir measurements. Due to the smaller SCIAMACHY ground pixel size (60 km×30 km) compared to GOME (320 km×40 km) we used a different topography database (20×20 km²) that was derived from the 2-min gridded global relief data set ETOP02 from the World Data Center for Marine Geology & Geophysics (http://www.ngdc.noaa.gov/mgg/fliers/01mgg04.html). Topographical data are used to determine the effective scene height in combination with the retrieved cloud top height and cloud fractions (Coldewey-Egbers et al., 2005). In SCIAMACHY WFDOAS the GOME Flight Model (FM) cross sections (Burrows et al., 1999b) were used. The use of SCIAMACHY FM cross-sections (Bogumil et al., 2000) leads to a bias of about 5% with respect to the GOME WFDOAS results. This is in agreement with Eskes et al. (2005). Apart from these changes the SCIAMACHY WFDOAS algorithm includes radiative transfer calculation based upon SCIA-TRAN V2.0 (Rozanov et al., 2002) in the iterative procedure rather than look-up tables as in the GOME WFDOAS algorithm. This new algorithm is, therefore, slower than the look-up version and for this reason only selected days have been analysed using SCIAMACHY data. The SCIAMACHY WFDOAS data presented here are still preliminary and further...
refinements of the algorithms for SCIAMACHY are planned. Only few days in 2003 have been analysed.

### 3 Comparison method

Complete data sets with near global coverage from both instruments were available for the first half of 2003. For all data sets (SCIAMACHY 5.01/5.04 and WFDOS V1.0), and GOME (WFDOS V1.0) measurements taken at solar zenith angles below 88° were included in the comparisons because at solar zenith angles above 88° the signal to noise ratio is too low. Since GOME/ERS-2 and SCIAMACHY/ENVISAT are flying in the same orbit only 30 min apart, numerous collocated measurements can be found (up to 10 000 a day). In order to quickly compare collocations of a day up to a month period, and to overcome the difference in ground pixel sizes of SCIAMACHY and GOME, the following method was applied. Daily total ozone column data were binned into 2.5°×2.5° wide cells and then compared. The centre coordinate of the satellite footprint was used to locate the bin. We tested the binning with several grid resolutions and compared the results of the comparisons to the direct comparisons where the mean value of all SCIAMACHY total ozone measurements within a GOME pixel was compared. Using 2.5° by 2.5° bins provided similar results compared to the direct comparison as will be shown later. This grid resolution seems also to roughly approximate the GOME ground pixel size in across-track direction.

When both instruments had measurements in the same grid, the mean of each instrument was compared to the mean of the other instrument as follows:

\[
100 \times \frac{(tO_3 \text{ of SCIAMACHY} - tO_3 \text{ of GOME})}{tO_3 \text{ of GOME}} \tag{1}
\]

The daily comparisons were analysed in five zonal bands (90° S to 60° S, 60° S to 23° S, 23° S to 23° N, 23° N to 60° N, 60° N to 90° N) and as a function of solar zenith angle and total ozone. In addition to that, means and root mean square (RMS) values of the mean relative deviations as a function of solar zenith angle and total ozone combining all days were determined.

### 4 Results

GOME and SCIAMACHY retrieval results and the differences between them are shown in Figs. 1, 2, 4 and 5 for 12 May 2003. This illustrates the typical results that similarly were found for other days for which total ozone data from SCIAMACHY 5.01/5.04, GOME WFDOS and SCIAMACHY WFDOS were available. In addition, Fig. 3 and parts in Figs. 4 and 5 show results from the overall comparisons of SCIAMACHY V5.01/5.04 total ozone columns to GOME WFDOS including all days from January to June 2003.

Figure 1 shows the binned SCIAMACHY V5.04, SCIAMACHY WFDOS V1.0 and GOME WFDOS V1.0 global total ozone data from 12 May 2003. As pointed out in Sect. 3, the binned data sets do not reflect exactly the location of the GOME and SCIAMACHY footprints as indicated by unevenly sized gaps in the upper and middle panel of Fig. 1, where SCIAMACHY limb measurements have been made. Although global coverage is reached for GOME above 65° N, there are small white gaps in between (Fig. 1 lower panel) that are due to the small area of each bin at high latitudes in relation to the large GOME pixel size such that the centre coordinate cannot fall into each bin. The data coverage of SCIAMACHY total ozone differs between the two
products because until now still the operational processing by ESA of SCIAMACHY level-1 and level-2 data is incomplete and done inhomogenously. Overall, total ozone values from both instruments and the two algorithms are in good agreement, but SCIAMACHY V5.04 shows lower values in the tropics and higher values in the Arctic (>70° N) than the SCIAMACHY WFDOAS and GOME WFDOAS ozone columns.

The relative deviations between the binned data sets of both SCIAMACHY retrievals (V5.04 and WFDOAS) to GOME WFDOAS, respectively, as well as between V5.04 and SCIAMACHY WFDOAS from 12 May 2003 are shown as global maps (Fig. 2, left panel) and as a function of latitude (Fig. 2 right panel). As an example, results of direct comparisons of SCIAMACHY V5.04 to GOME are added to the top right panel in Fig. 2. Here, we compared the mean
Fig. 3. Mean relative deviation (black solid line), root mean square of daily mean relative deviation (black dotted line) and number of data bins (red stars) of all comparisons between binned SCIAMACHY V5.01/V5.04 (SCIA) and GOME WFDOAS V1.0 total O$_3$ during the first half of 2003 in various zonal bands: Antarctic latitudes (upper left panel), mid southern latitudes (upper right panel), tropics (middle left panel), mid northern latitudes (middle right panel), Arctic latitudes (lower left panel), and globally (lower right panel).

of the total ozone columns V5.04 of all SCIAMACHY pixels which were measured 30 min. before GOME within the same ground scene of one (always larger) GOME pixel to the corresponding GOME WFDOAS value. Both comparison methods agree to within 0.5% for relative deviations and within 0.08% for the mean and 0.2% for the RMS for the relative deviations. Both, SCIAMACHY V5.04 compared to GOME WFDOAS V1.0 and to SCIAMACHY WFDOAS V1.0 (Fig. 2 top and bottom panels) show a clear latitudinal dependence. From 63° S to 30° S (except for 40° S) SCIAMACHY V5.04 has a bias of between $-3.5\%$ and 0% ($\pm 1-3\%$) to both GOME and SCIAMACHY WFDOAS V1.0 and from 30° N to 80° N between $-0.5\%$ and $+2\%$ ($\pm 1-3\%$) to GOME WFDOAS and between $-0.5\%$ and $+5\%$ ($\pm 1-3\%$) with respect to SCIAMACHY WFDOAS. At higher latitudes ($>50°$ S and $>65°$ N) with higher solar zenith angles ($>75°$) the relative deviations are larger and show more scattering. The global comparison of total ozone columns from SCIAMACHY and GOME retrieved by using the WFDOAS V1.0 algorithm shows except for the high latitudes (above 55° S and 75° N) no latitudinal dependence: between 55° S and 75° N SCIAMACHY WFDOAS is within 1% of GOME.
WFDOAS. The overall negative bias of SCIAMACHY to GOME WFDOAS is for SCIAMACHY WFDOAS much lower with a mean relative deviation of 0.2%, while for SCIAMACHY V5.04 (operational product) a negative bias of 0.7% (or 0.6% for direct comparisons) was found. Comparing both SCIAMACHY retrievals directly a negative bias of 0.5% between V5.04 and WFDOAS was found. It is obvious that differences between retrieval type (V5.04 and WFDOAS) are larger than differences between instruments when using the same retrieval (here WFDOAS).

Figure 3 is summarising the results from all daily comparisons of SCIAMACHY V5.01/5.04 to GOME WFDOAS between January and June 2003 based upon the binning method. The results have been grouped into various zonal bands and the number of data bins within each zonal band is also shown. If all data of one day have been available from both instruments around 3200 data bins were available for comparisons. At mid latitudes and in the tropics (Fig. 3, upper right, middle left, and middle right panels) number of bins vary between 20 and 700 per day. No significant differences in mean deviations and RMS can be observed in relation to the number of available bins. Similar conclusions can be drawn from the global comparison (90°S to 90°N, Fig. 3 lower right panel). Here, the number of bins varies between 200 and 3200. In the polar regions, the number of binned data decreases from 1200 to 0 by changing from summer to winter (Fig. 3, upper left panel) and increases from 0 to 1200 from winter to summer (Fig. 3, lower left panel). For both polar regions, a significant increase in scatter of mean relative deviations and a significant increase of RMS is observed when number of data within each bins falls below 300 (in winter season) and also for both regions the negative bias of SCIAMACHY 5.01/5.04 to GOME WFDOAS becomes significantly larger than in other seasons. During Antarctic summer (Fig. 3, upper left panel) the mean relative deviation and RMS are very stable between −1.5 and 0%, and 2%, respectively. From March until May, when the number of binned data falls below 300, both mean relative deviation and RMS are increasing to between −4.5 and −0.5% and between 2 and 4%, respectively. A similar picture is observed in the Arctic (Fig. 3, lower left panel): During winter mean relative deviation and RMS are high with −6 to 0% and 3 to 5%, respectively; in spring and early summer (March to June) the mean deviation gets smaller with a mean relative deviation of between −1 and +4.5% and a RMS of 3%. At mid latitudes a very weak seasonal signal in the differences can be observed: in the northern hemisphere (Fig. 3 middle right panel) SCIAMACHY is within 1.5% of GOME, but it seems that in summer SCIAMACHY tends generally to be lower than GOME and the RMS decreases slightly from values of 2 to 3% in winter to 1.5 to 2% in spring and summer. At southern mid latitudes (Fig. 3 upper right panel) SCIAMACHY has a mean relative deviation of −2 to 0% with RMS of 1 to 2% compared to GOME for the whole investigated time period in 2003 with no seasonal effect, but the RMS increases slightly from 1 to 1.5% in summer to 2 to 3% in winter. In the tropics, SCIAMACHY V5.01/5.04 total ozone compared to GOME WFDOAS shows very little variation throughout the half year time period. A negative bias of 0.5% to 2.5% with RMS of 1% is observed between SCIAMACHY and GOME. Similar conclusions are drawn from results containing all data (90°S to 90°N), where SCIAMACHY total ozone compared to GOME shows very little variation throughout the investigated time period with a mean relative deviation of between −2 and +0.5% and a RMS on the order of 2%.

In summary, there is generally an underestimation around 1% (RMS around 2%) of SCIAMACHY V5.01/5.04 total ozone with respect to GOME WFDOAS except for the northern mid and polar latitudes where larger variations in the differences are observed. As seen in the single day comparison (Fig. 2), SCIAMACHY V5.01/5.04 shows a clear negative bias as compared to GOME WFDOAS in the southern latitudes and tropics, while in the northern latitudes SCIAMACHY V5.01/5.04 total ozone columns shows on average a positive bias to GOME WFDOAS (polar region) or the bias disappears (mid latitudes). This is in agreement with earlier validation results of GOME V2.7 (about the same as V2.4 regarding ozone) by Bramstedt et al. (2003) where a negative bias during summer/fall (as is here the case for southern latitudes) and a reduced bias during spring/winter (as is here the case for northern latitudes) were observed. Although the time period of half a year is rather short, we can conclude that a seasonal bias is clearly observed in both polar regions, while in the mid latitudes this signal is weaker and comparisons of a longer time period need to be looked at.

In order to evaluate the results so far obtained, the validation results are investigated as a function of solar zenith angle and total ozone. Figure 4 shows the results of the comparison between SCIAMACHY V5.04 (upper left panel) and WFDOAS (upper right panel) to GOME WFDOAS and of SCIAMACHY V5.04 to SCIAMACHY WFDOAS (lower left panel) as a function of the mean SCIAMACHY solar zenith angle (SZA) within each data bin. For all three comparisons the results are shown for one day, 12 May 2003 and for the SCIAMACHY V5.01/5.04 validation with GOME WFDOAS the results including all days are plotted (Fig. 4, lower right panel). All three panels show that the operational SCIAMACHY V5.04 shows a SZA dependency in the differences to GOME and SCIAMACHY WFDOAS retrievals. Looking at the results from all SCIAMACHY V5.01/5.04 measurements (Fig. 4 lower right panel), the bias of the mean relative deviation to GOME becomes more positive (from −1.5% to 1%) between 20° and 65° SZA and more negative at higher SZA (down to −2.5%), and increases again above 85° SZA (around −0.5%). Above 85° SZA the RMS becomes significantly larger in all analyses as compared to lower SZAs. SCIAMACHY WFDOAS and GOME WFDOAS mean total ozone agree to within 1%. (RMS±1 to 2.5%). Above 80° the scatter of the results becomes
somewhat larger (RMS of 2–3%). In this case the number of bins is with 50 significantly lower than for other comparisons (between 140 to 340 bins).

Figure 5 shows now the difference as a function of SCIAMACHY total ozone. Looking at the results for all comparisons for one day (Fig. 5, upper panels and lower left panel) no correlation between the number of data bins and the mean or RMS is detected, but the plot summarising all days (Fig. 5, lower right panel) shows that RMS is becoming larger when number of data bins is decreasing. The mean relative deviations between V5.04 and GOME WFDOAS becomes more positive with increasing total ozone from 12 May, 2003 (left panels) from a mean value around −2% at 235 DU up to +3% on 12 May 2003 (upper left panel). Looking at all data for the half-year period the bias increases more slowly to about +1% at 400 DU and then decreases again (lower right panel). For the comparison of SCIAMACHY WFDOAS to GOME WFDOAS, deviation between the two total ozone retrievals are on average within 1%, except at around 365 DU with a mean value of −1.5% and around 440 DU of +1.5% for the relative deviations. We observe a jump at 365 DU which is unexpected when subtracting the results of the SCIAMACHY 5.04/SCIAMACHY WFDOAS from the SCIAMACHY 5.04/GOME WFDOAS comparisons for this day. Probably this jump can be attributed to the different data sets used for the different plots. In addition the number of bins is pretty low (<80) between 335 and 365 DU which causes that larger differences between comparisons become more pronounced.

5 Discussion and Conclusions

In this study a large global validation between operational ESA SCIAMACHY V5.01/5.04 and GOME WFDOAS V1 total ozone columns from the first half of 2003 was performed. In addition to that, for several days during this time period total ozone columns from SCIAMACHY V5.01/5.04 were compared to WFDOAS retrievals applied to SCIAMACHY (SCIAMACHY WFDOAS V1) as well as the WFDOAS retrievals for both instruments were compared. The validation was mainly done with binned data in bins of 2.5° by 2.5°, which permitted fast comparisons. It was shown that this binning method produces similar results when doing
comparisons of SCIAMACHY data that were averaged over the larger footprint of the GOME ground pixel.

The results of our study show that differences between total ozone columns retrieved from measurements from 12 May 2003 of the two instruments are low and within 2%. But, the comparison with the SCIAMACHY WFDOAS data shows that the difference between GOME and SCIAMACHY can be reduced at low and mid latitudes to within 1% and that the latitudinal dependence with SCIAMACHY WFDOAS disappears. Since the validation of GOME WFDOAS showed very good validation results with ground-based measurements, the quality of the SCIAMACHY WFDOAS ozone columns seems to be of similar quality. The same should be expected from an operational data version that is equivalent to GOME operational data version GDP V4.0 that is the third update from V2.4 on which the SCIAMACHY V5.01/5.04 is based upon. The larger differences observed between V5.01/5.04 and WFDOAS are clearly algorithm related and to a lesser extent due to instrument issues, although from both instruments shortcomings are known. Since late 1999 the degradation of the GOME UV-part in the spectra has become scan mirror angle dependent which means that the solar and the earthshine spectra observed in different scan angle directions degrade at different rates (Snel, 2001; Tanzi et al., 2001). For SCIAMACHY, the currently available processor version of level 1 spectral data has errors in the polarisation correction and radiometric correction (Tilstra and Stammes, 2005). Generally, the DOAS method, at least for ozone retrievals has been proven to be relatively insensitive to radiometric calibration errors because of the polynomial subtraction in the DOAS approach (see e.g. Bramstedt et al., 2003).

The similar behaviour of differences between SCIAMACHY V5.01/5.04 and both WFDOAS retrievals as a function of SZA and total ozone is not a real surprise since the total ozone is also somewhat dependent on the solar zenith angle during the SCIAMACHY (and GOME) measurement, with higher total ozone observed at mid latitudes at an intermediate SZA. The much larger negative bias between SCIAMACHY V5.01 and GOME WFDOAS during polar winters compared to other regions and seasons might be explained that generally at high SZA and in polar regions satellite and ground based UV-VIS measurements have larger errors due to lower signal to noise ratio at low light conditions. Because the two instruments are flying in the same orbit 30 min. apart from each other the SCIAMACHY measurements at
high northern latitudes during sunrise are taken at higher solar zenith angles than GOME measurements and therefore may probably show a larger error than collocated GOME data. The situation is reversed at high solar zenith angle in the southern latitudes. This also explains why the scatter increases at high latitudes (this is also true for SCIAMACHY WFDOAS to GOME WFDOAS comparisons). This effect seemed to be more pronounced in the Arctic region than in the Antarctic, because Antarctic winter season observations were not covered in our study.

Overall, the extensive validation of SCIAMACHY operational total ozone data version 5.01/5.04 shows on average an underestimation of GOME WFDOAS total ozone: the mean relative deviation of SCIAMACHY 5.01/5.04 varies between –2% and +0.5% with an RMS of 2 to 3% below 88° SZA. Bearing in mind, that GOME WFDOAS total ozone values are within 1% of global ground-based values (Weber et al., 2005), the results are in accordance with the comparison of SCIAMACHY data version 5.01 to NDSC ground-based measurements where an underestimation of 1% of SCIAMACHY was detected (Lambert et al., 2004b). In addition, the study also elucidated on dependencies of SCIAMACHY V5.01/5.04 differences to GOME and SCIAMACHY WFDOAS retrievals on latitudes, total ozone, and solar zenith angle. Dependencies on total ozone amount, solar zenith angle and latitudes have already been observed in the mid and high latitudes from July 1996 to June 1998 data of the operational products of GOME GDP 2.4 validated with ground-based sensors (see Fig. 4 in Lambert et al., 2000). As said before, SCIAMACHY V5.01/5.04 is based on GDP 2.4 data processor version. The shortcomings of the GDP Version 2.4 have been attributed to the following: lack of temperature correction in the ozone cross sections, air mass factors (AMF) calculations which use a ozone climatology based on an outdated two-dimensional coupled climate model, a lack of iterations to match total ozone of climatological ozone profiles used in the AMF calculations to the retrieved total ozone, the limited treatment of the atmospheric profile shape effect, and the partial unsuitability of the particular spectral analysis when the atmosphere becomes optically thick (Lambert et al., 2000). In addition, ozone filling-in as part of the overall Ring effect is not included as it is in the new generations of total ozone algorithms like the GOME WFDOAS algorithm (Coldewey-Egbers et al., 2005), TOSOMI (Eskes et al., 2005), and GDP V4.0 (Lambert et al., 2004a). Seasonal dependencies have also been observed in the comparisons of the operational products of GOME GDP 2.4 validated with ground-based sensors by Lambert et al. (2000) (see Fig. 4 therein) and in a global validation of GOME GDP 2.7 (which for the ozone retrieval does not differ from GDP 2.4) to the Dobson net work from 1997 to 2000 (Fig. 2 in Bramstedt et al., 2003). But for both GOME GDP 2.4 and 2.7 this dependence was within 4% as compared to within 2% for SCIAMACHY 5.01/5.04. Additional comparisons of SCIAMACHY 5.01/5.04, SCIAMACHY WFDOAS and GOME WFDOAS from a whole year time period will be able to clarify that issue (seasons, latitudes). In summary, the current operational SCIAMACHY total ozone data Version 5.01/5.04 shows a dependence on latitudes, solar zenith angle and total ozone that reduces the data quality to an overall negative bias around 1% with an RMS of 2 to 3%. We were able to show that a reprocessing of SCIAMACHY total ozone data with an equivalent of GOME WFDOAS improves the accuracy within to 1%. A similar improved data quality we expect from SCIAMACHY total ozone reprocessed with equivalents to GOME V4.0 (Lambert et al., 2004a) or TOSOMI (Eskes et al., 2005).

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Stratospheric and tropospheric NO$_2$ variability on the diurnal and annual scale: a combined retrieval from ENVISAT/SCIAMACHY and solar FTIR at the Permanent Ground-Truthing Facility Zugspitze/Garmisch

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Abstract. Columnar NO$_2$ retrievals from solar FTIR measurements at the Zugspitze (47.42°N, 10.98°E, 2964 m a.s.l.), Germany were investigated synergistically with columnar NO$_2$ retrieved from SCIAMACHY data by the University of Bremen scientific algorithm UB1.5 for the time span July 2002–October 2004. A new concept to match FTIR data to the time of satellite overpass makes use of the NO$_2$ daytime increasing rate retrieved from the FTIR data set itself [+1.02(6) E+14 cm$^{-2}$/h]. This measured increasing rate shows no significant seasonal variation. SCIAMACHY data within a 200-km radius around Zugspitze were considered, and a pollution-clearing scheme was developed to select only pixels corresponding to clean background (free) tropospheric conditions, and exclude local pollution hot spots. The resulting difference between SCIAMACHY and FTIR columns (without correcting for the different sensitivities of the instruments) varies between 0.60–1.24 E+15 cm$^{-2}$ with an average of 0.83 E+15 cm$^{-2}$. A day-to-day scatter of daily means of ≈7–10% could be retrieved in mutual agreement from FTIR and SCIAMACHY. Both data sets are showing sufficient precisions to make this assessment. Analysis of the averaging kernels gives proof that at high-mountain-site FTIR is a highly accurate measure for the pure stratospheric column, while SCIAMACHY shows significant tropospheric sensitivity. Based on this finding, we set up a combined a posteriori FTIR-SCIAMACHY retrieval for tropospheric NO$_2$, based upon the averaging kernels. It yields an annual cycle of the clean background (free) tropospheric column (<10 km) with variations between 0.75–1.54 E+15 cm$^{-2}$, an average of 1.09 E+15 cm$^{-2}$, and an intermediate phase between that of the well known boundary layer and stratospheric annual cycles. The outcome is a concept for an integrated global observing system for tropospheric NO$_2$ that comprises DOAS nadir satellite measurements and a set of latitudinally distributed mountain-site or clean-air FTIR stations.

1 Introduction

The importance of NO$_2$ in atmospheric chemistry had been described in the literature more than 25 years ago (Crutzen, 1979). Long-term research has been performed since then aiming at a better understanding of its differing role in the determination of the earth’s ozone distribution in the stratosphere (catalytic ozone destruction), and the troposphere (ozone formation via photochemical smog). While the main sources and source regions of NO$_2$ are known, large uncertainties remain on the individual source strengths and their latitudinal and seasonal variations (IPCC, 2001).

Interest in the climatic role of tropospheric NO$_2$, however, has shown up only recently, when it has been found that a significant radiative forcing (exceeding that of CO$_2$) can build up during periods with extremely elevated NO$_2$ levels in the troposphere (Solomon et al., 1999). Such pollution events might be underestimated in duration and horizontal extension due to the short lifetime of NO$_2$ in the boundary layer: However, it was shown only recently that NO$_2$-rich pollution hot spots can spread over large areas for several days (Leue et al., 2001), and that NO$_2$ transport over large distances is possible (Stohl et al., 2003; Schaub et al., 2005).

Tropospheric NO$_2$ hot spots and source strengths and their quantification in time and space can be investigated using modern nadir-looking satellite instruments like GOME,
SCIAMACHY, or OMI (Borell et al., 2004; Leveit et al., 2000). Satellite based retrievals of tropospheric NO\textsubscript{2} have to account for the stratospheric contribution which has been done by different approaches. The reference sector method makes use of unpolluted columns above the ocean as a reference (e.g., Richter and Burrows, 2002) and thus assumes negligible tropospheric NO\textsubscript{2} over the Pacific between 180\degree and 190\degree longitude, as well as longitudinal homogeneity of the stratospheric NO\textsubscript{2} layer. However, close to the Polar Vortex or during major changes in stratospheric dynamics, this approximation is introducing some artifacts at high latitudes in winter and spring. Further approaches like image processing techniques (e.g., Leue et al., 2001), or assimilation into a chemistry transport model (Boersma et al., 2004) have been applied. Another method would be to use independent data such as the SCIAMACHY limb measurements (Bovensmann et al., 1999) or, as explored in this paper, simultaneous ground-based measurements.

First comparisons of satellite derived tropospheric NO\textsubscript{2} with air borne profile and column measurements (Heland et al., 2002; Martin et al., 2004; Heue et al., 2005) showed good agreement for homogeneous situations, but in the presence of spatial gradients, differences with respect to ground-based measurements can be large (Petritoli et al., 2004). Error estimates for the satellite data are about 50\% for polluted regions and larger in clean regions (Richter and Burrows, 2002; Boersma et al., 2004). Obviously, the current satellite retrievals of tropospheric NO\textsubscript{2} are still of limited accuracy. Therefore intensive further joint investigations together with ground-based measurements are required targeting at both validation and synergistic use, i.e., an improved error assessment as well as an improvement of the satellite measurements themselves, by synergistically combining them with the complementary information attainable from ground-based measurements.

For this purpose in general terms (dealing with a variety of further trace species, satellite missions, and ground-based instrumentation), a Permanent Ground-Truthing Facility has been built up at the NDSC (Network for the Detection of Stratospheric Change) Primary Station Zugspitze/Garmisch, Germany according to the requirements of the World Meteorological Organization (WMO, 2000). It is equipped with a variety of ground-based remote sounding instrumentations, and aims at performing operational satellite validation and promoting the synergistic use of satellite and ground-based measurements (Sussmann, 2004).

Subject of this paper is validation and synergistic use of ground-based solar FTIR measurements of NO\textsubscript{2} performed at the Zugspitze together with ENVISAT/SCIAMACHY measurements (Bovensmann et al., 1999). There are three issues which have to be properly taken into account before a direct comparison is possible: i) The stratospheric NO\textsubscript{2} diurnal cycle hinders a direct comparison with FTIR measurements, which are recorded not exactly at the time of satellite overpass, ii) the high horizontal variability of boundary layer NO\textsubscript{2} makes it difficult to compare ground-based data taken at one location to satellite data within a certain selection radius around that site, and, iii) the different sensitivity of SCIAMACHY versus FTIR to tropospheric NO\textsubscript{2} has to be taken into account.

While these issues have been discussed qualitatively in many validation studies (Lambert et al., 1999; 2004; Richter et al., 2004; Sussmann et al., 2004a, b) this paper gives a quantitative treatment for validation by FTIR for the first time. This is done by i) applying a new concept for deriving virtual coincidences from the individual daily FTIR measurements to the time of ENVISAT overpass (Sect. 2), and ii) using all SCIAMACHY data within a selection radius of 200-km around the Zugspitze and applying a new pollution-clearing scheme for exclusion of local pollution hot spots (Sect. 3).

The quantitative treatment of the different sensitivities of SCIAMACHY versus FTIR to tropospheric NO\textsubscript{2} leads us to two limiting cases: i) Observed differences (satellite to ground) are only due to inherent errors in either of the two remote sounding data sets under the simplifying assumption that the two measurement systems have identical sampling characteristics or, ii) the observed differences can be attributed only to the different sampling characteristics of the two instruments under the assumption that they are both working in principle without intrinsic errors. Reality will be in between these limiting cases, and, therefore, we investigated both of them in parallel. Consequently, first a classical direct intercomparison of the times series of SCIAMACHY and FTIR NO\textsubscript{2} columns is given (Sect. 4).

The crucial part of this paper is then presented in Sect. 5. Here we make use of the differing averaging kernels (different sensitivities) of FTIR and SCIAMACHY and iterate (free) tropospheric NO\textsubscript{2} levels in order to match FTIR and SCIAMACHY data together. This results in the first (a posteriori) retrieval of tropospheric NO\textsubscript{2} from the combined use of FTIR and satellite data. The result will be discussed in terms of geophysical relevance. Section 6 gives the conclusions with an outlook on how to improve satellite based retrievals of tropospheric NO\textsubscript{2} by an integrated global observing system based on nadir-looking satellite instruments and mountain-site or clean-air FTIR stations.

2 The FTIR NO\textsubscript{2} columns data set

2.1 FTIR measurements

Ground-based data are being recorded by the NDSC-Primary Status solar FTIR instrument at the Zugspitze (47.42°N, 10.98°E, 2964 m a.s.l.) continuously since 1995. The Zugspitze-FTIR instrument and retrieval set-up has been described in detail elsewhere (Sussmann et al., 1997; Sussmann, 1999). Briefly, a high-resolution Bruker IFS 120 HR Fourier Transform Spectrometer is operated with an actively
controlled solar tracker, and liquid-nitrogen cooled MCT (HgCdTe) and InSb detectors. The FTIR data set used for this study covers the time span from 23 July 2002 to 21 September 2004 and comprises 914 InSb spectra (after elimination of bad spectra by quality control) recorded on 200 measurement days, i.e., 4.6 spectra per measurement day on average. Each spectrum resulted from averaging 5 scans with a maximum optical path difference of 175 cm (integrated within 10 min).

2.2 FTIR column retrieval

The Zugspitze NO$_2$ retrieval utilizes the prominent absorption peak at 2914.65 cm$^{-1}$ initially suggested by Camy-Peyret et al. (1983), which is a multiplet of several closely spaced and not spectrally resolved transitions. The wide micro-window used (2914.51–2914.86 cm$^{-1}$) intentionally includes the wing of the strong CH$_4$ line at 2914.50 cm$^{-1}$ which is retrieved simultaneously to avoid cross correlations. Columns are retrieved using the non-linear least squares spectral fitting software SFIT2 (version 3.90) initially developed at NASA Langley Research Center and NIWA (Pougatchev et al., 1995). We did not perform a profile retrieval, because the weak NO$_2$ absorption feature does not allow to infer altitude-resolved information. In other words, the number of degrees of freedom of signal (dofs) of the retrieval, i.e., the trace of the averaging kernel matrix (Rodgers, 1998) will always be in the order of 1 setting up the a priori covariance matrix (or its inverse) in various reasonable forms. Therefore we applied a simple (Tikhonov-regularization type) hard smoothness constraint, leading to dofs = 1, i.e., a volume mixing ratio (VMR) profile scaling. The resulting total column averaging kernels are presented in Sect. 5.1 below. As a priori the 1976 US Standard NO$_2$ VMR profile (Anderson et al., 1986) was used with the tropospheric part up to 10 km altitude set to zero. This profile will be referred to thereafter as “reduced US Standard profile”. The reason for this choice is detailed below. Daily p-T-profiles from the Munich radio sonde station (located 80 km to the north of the Zugspitze) have been utilized and the HITRAN-2004 molecular line parameters compilation was used; see Rothmann et al. (2003) for a description of the previous version.

Error estimates for the NO$_2$ column retrievals from the 2914.65 cm$^{-1}$ feature by FTIR have already been presented by Camy-Peyret et al. (1983), Flaud et al. (1983, 1988), and Rinsland et al. (1988). Individual measurement precisions of $\approx 10\%$ have been reported as well as accuracies of $\approx 10\%$ been given. Rinsland et al. (2003) have pointed to a possible significant a priori contribution to the retrievals. In extension to these previous error assessments we will thereafter investigate quantitatively in full detail the impact of differing HITRAN versions, differing a priori VMR profiles, as well as the influence of the averaging kernels on the FTIR column retrievals of NO$_2$.

![Fig. 1. NO$_2$ FTIR (profile scaling) retrieval results from one arbitrarily chosen measured Zugspitze FTIR spectrum with SZA=61° using two different NO$_2$ a priori VMR profiles, i.e., the 1976 US Standard atmosphere (blue) versus the retrieval based upon the standard profile by “Kerr et al.” (Rinsland, personal communication, 1999), distributed with the “refmod99” data set (magenta).](image)

2.3 Impact of line parameter errors on FTIR retrievals

In order to add up-to-date information on the impact of line parameter errors on the absolute accuracy of the NO$_2$ columns, we retrieved the whole FTIR data set of this study with the three most recent HITRAN versions, i.e., HITRAN 2000, HITRAN 2000 with update V11.0 9/2001, as well as HITRAN 2004, which is used throughout this study. Using HITRAN 2004 as a reference, we found the following relative changes for overall averages of the columns: HITRAN2004/HITRAN 2000=1.0003 and HITRAN2004/HITRAN 2000(9/2001 update)=1.0385. We conclude that the uncertainty of the line parameters could introduce a bias on the retrieved FTIR columns that is probably on the few per cent ($\approx 5\%$) level.

www.atmos-chem-phys.org/acp/5/2657/ Atmos. Chem. Phys., 5, 2657–2677, 2005
2.4 Impact of a priori VMR profiles on FTIR retrievals

Figure 1 shows two different FTIR retrieval results from the same arbitrarily chosen spectrum (solar zenith angle (SZA)=61°) using two different a priori profiles, i.e., the NO\textsubscript{2} profile of the 1976 US Standard atmosphere (US) versus the standard profile by “Kerr et al.” (Rinsland, personal communication, 1999), distributed with the “refmod99” data set (Kerr).

The latter yields a significantly higher (54\%) total column retrieved from the same spectrum (see Table 1). Table 1 also shows that the stratospheric columns are nearly the same for both retrievals and the difference is mainly in the tropospheric columns. This result can be understood by the different relative shape of these a priori profiles, i.e., the much higher tropospheric contribution of the “Kerr et al.” profile with its tropospheric column being a considerable fraction of the total column, together with a reduced tropospheric sensitivity of the FTIR retrieval compared to the stratospheric sensitivity: Obviously, any real perturbation in the stratosphere relative to the a priori will lead to analogous scaling of the tropospheric part of the a priori profile, independently from whether there is a real perturbation or not. This effect is described in a quantitative way using the total column averaging kernels in Sect. 5.2.

So we find the choice of the magnitude of the tropospheric part of the a priori VMR profile to be the potentially dominant biasing contribution, if the corresponding tropospheric column makes up a considerable fraction of the total column.

As a consequence for validation and synergistic use within this study we adopted the same a priori profile for the FTIR retrievals as are used for the satellite retrievals, i.e., the reduced US Standard NO\textsubscript{2} profile.

2.5 FTIR individual columns time series

The FTIR NO\textsubscript{2} columns data set used for this study is plotted in Fig. 2. Plotted are columns retrieved from individual measurements. As we will infer from our sensitivity study in Sect. 5.2, the FTIR columns are a good measure for the stratospheric column and are only weakly (if at all) influenced by tropospheric pollution events. As a consequence, Fig. 2 displays a clear annual cycle which is due to the seasonal changes in day length and thus photolysis and to a lesser degree also temperature. The daily scatter of the individual column measurements is dominated by the diurnal cycle as investigated in the next section.

Table 1. FTIR NO\textsubscript{2} column retrieval results from one arbitrarily chosen measured spectrum with SZA=61° using two different a priori profiles, i.e., the NO\textsubscript{2} profile of the 1976 US Standard atmosphere (US) versus the standard profile by “Kerr et al.” (Rinsland, personal communication, 1999), distributed with the “refmod99” data set (Kerr).

<table>
<thead>
<tr>
<th></th>
<th>US</th>
<th>Kerr</th>
<th>Kerr – US</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Column (Ground–100 km)</td>
<td>3.04E+15</td>
<td>4.67E+15</td>
<td>1.63E+15</td>
</tr>
<tr>
<td>Partial Column (10–100 km)</td>
<td>2.92E+15</td>
<td>3.02E+15</td>
<td>0.10E+15</td>
</tr>
<tr>
<td>Partial Column (Ground–10 km)</td>
<td>0.12E+15</td>
<td>1.65E+15</td>
<td>1.53E+15</td>
</tr>
</tbody>
</table>
Fig. 3. (a) The Zugspitze FTIR NO$_2$-vertical column data set as shown in Fig. 2, but plotted as a function of the time of the day. Data were classified into 12 months and linear fits to the diurnal increase performed on the monthly data sets. (b) The 12 different diurnal increasing rates obtained from the fits performed to the monthly FTIR data sets in (a). The plotted slope error bars (2 sigma) are obtained from the linear fits in (a), and the red line gives the average increasing rate, i.e., $1.02(6) \times 10^{14}$ cm$^{-2}$/h.

2.6 The stratospheric NO$_2$ daytime increasing rate as a function of season inferred from FTIR

Stratospheric total NO$_2$ has a well defined diurnal cycle with a daytime increasing rate that has been described experimentally only by a few individual days of FTIR measurements up to now (Flaud et al., 1983, 1988; Rinsland et al., 1988). The daytime increasing rate has been discussed with respect to the consequences for satellite validation with ground-based zenith-sky DOAS instruments by Lambert et al. (1999, 2004).

We reinvestigated the NO$_2$ daytime increasing rate using the full FTIR data set of this study. Figure 3a shows all individual FTIR columns of the data set, but now plotted as function of the hour of the day, and separated for the 12 different months by colors. For each month a linear fit is performed to all the individual columns of this month.

Fig. 3b gives evidence, that there is no significant seasonal change of the daytime increasing rate of stratospheric NO$_2$ within the FTIR error bars. This result is obtained for the Zugspitze located at 47° N and should be representative for mid latitudes. It is of some interest since it had been argued
from experiments with a stratospheric photochemical model that the daytime variation should be a function of the season since the build up of N$_2$O$_5$ depends on the length of the night and because its rate of photo dissociation varies with solar elevation (Flaud et al., 1983).

Since there is no significant seasonal dependence of the daytime increasing rate we infer from the 12 individual monthly rates of Fig. 3b one annual average rate. The resulting daytime NO$_2$ increasing rate is 1.02(6) E+14 cm$^{-2}$/h.

2.7 The concept of virtual-coincidence columns for FTIR data

Individual FTIR measurements are recorded sequentially and are distributed in time over the whole day. Thus, the individual FTIR columns of each day vary according to the diurnal increase. On the other hand, the individual SCIAMACHY measurements for one day (all pixels within a 200-km selection radius around Zugspitze) are all recorded nearly at the same time, i.e., the time of overpass, which is roughly at 10:00 UT.
### Table 2. Statistics of NO$_2$ data scatter for FTIR and SCIAMACHY UB1.5 measurements. SCIAMACHY data were taken within a 200-km pixel-selection radius around the Zugspitze for each day, and both cloud clearing and a pollution clearing has been applied to the data as described in the text. The index for the number of measurement days is $i$. First column: $AV_i(n_i)$, i.e., average of the numbers $n_i$ of individual measurements during each measurement day. Second column: $AV_i(\sigma_i)$, i.e., average of the “single-value standard deviations” calculated from the individual measurements for the different days. For FTIR each standard deviation is calculated relative to the daily fit (vertical offset as fit parameter) to the daytime increase with constant slope of 1.02(6) E+14 cm$^{-2}$h$^{-1}$. 3rd column: $AV_i(\sigma_i/\sqrt{n_i})$, i.e., average of the “standard deviations of the daily mean values” calculated from the individual measurements for the different days. (Again for FTIR each value is calculated relative to the daily fitted line describing the diurnal increase.) 4th column: Standard deviations of daily means calculated from the daily-means data sets as shown in Fig. 5, i.e., relative to the analytic function fitted to the annual cycle (functional fit described in Appendix A).

<table>
<thead>
<tr>
<th></th>
<th>$AV_i(n_i)$</th>
<th>$AV_i(\sigma_i)$</th>
<th>$AV_i(\sigma_i/\sqrt{n_i})$</th>
<th>$\sigma$ of daily means corrected for ann. cycle and pollution (Fig. 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zugspitze FTIR</td>
<td>4.6</td>
<td>8.8%</td>
<td>4.3%</td>
<td>9.2%</td>
</tr>
<tr>
<td>SCIAMACHY</td>
<td>22</td>
<td>6.8%</td>
<td>1.9%</td>
<td>6.5%</td>
</tr>
</tbody>
</table>

Therefore, we have to match the individual measurement times of FTIR to the time of ENVISAT overpass. Our concept to achieve this is presented in Fig. 4. For each measurement day we fitted a line with a constant slope (i.e., the daytime increasing rate of 1.02 E+14 cm$^{-2}$h$^{-1}$) to the retrieved FTIR columns, and only the vertical offset was used as a fitting parameter. Subsequently, the column was read out from this fitted line at the exact time of the daily overpass. This is what we will refer to as “virtual-coincidence column” thereafter, since it is constructed for the time of overpass which usually does not coincide with the time of a real FTIR measurement.

We give a conservative estimate of the propagation of the error of the daytime increasing rate (0.06 E+14 cm$^{-2}$h$^{-1}$, see above) into the virtual coincidence column as follows. Assuming that there is only one late-evening FTIR measurement at 19:00 UT, i.e., 9 h after the 10:00 UT satellite overpass, the error of the daytime increasing rate would then result in an error of the virtual coincidence column of $9 \times 0.06 E+14$ cm$^{-2}$h$^{-1}$=0.54 E+14 cm$^{-2}$, which would be $\approx$1% for a typical summer column level of 4.5 E+15 cm$^{-2}$. In analogy, we estimate for a winter-evening FTIR measurement at 15:00 UT a $5 \times 0.06 E+14$ cm$^{-2}$h$^{-1}$=0.3 E+14 cm$^{-2}$ error which would be $\approx$1.5% for a typical winter column level of 2 E+15 cm$^{-2}$.

### 2.8 Functional fit to daily FTIR data

The FTIR daily virtual-coincidence columns are plotted in Fig. 5. The figure also shows a fit to these data using the analytic function described in Appendix A.

This functional fit was performed for two reasons as described in our previous work (Sussmann and Buchwitz, 2005; Sussmann et al., 2005): i) In order to be able to compare FTIR to SCIAMACHY results even in case of alternating data gaps, and ii) to be able to calculate a standard deviation of the daily virtual-coincidence columns around the functional fit (describing the annual cycle), for a characterization of the day-to-day scatter.

### 2.9 Characterization of the daily scatter of FTIR NO$_2$ columns

First we want to characterize the precision of individual FTIR column measurements. For this purpose we have to derive statistical quantities with the scattering effect due to the stratospheric NO$_2$ daytime increase eliminated. This is performed using the concept of Fig. 4. For each day with index $i$ and $n_i$ measurements, the standard deviation $\sigma_i$ and the standard deviation of the mean value $\sigma_i/\sqrt{n_i}$ were calculated relative to the line fitted to the daytime increase, and subsequently the average ($AV$) of these quantities over all days was derived. The resulting $AV(\sigma_i)$=8.8% is a measure for the precision of individual FTIR column measurements. $AV(\sigma_i/\sqrt{n_i})$=4.3% is a measure for the precision of the virtual-coincidence column (Table 2).

Finally, we calculate a standard deviation of the daily virtual-coincidence columns around the function fitted to the annual cycle. This leads to a standard deviation of $\sigma$=9.2%, see Table 2. This value comprises both the precision of a daily virtual-coincidence column as well as the day-to-day scatter, and is significantly higher than the precision of a daily virtual-coincidence column alone (4.3%). Therefore the day-to-day scatter can be detected by FTIR significantly and is probably in the order of 10%. This day to day scatter should be a measure of the true stratospheric variability of NO$_2$. Although this is dominated by photolysis, there is also a dependence on the origin of the probed airmass, e.g., spring-time variability can be caused by the change in circulation.
3 The SCIAMACHY UB1.5 columns data set

3.1 SCIAMACHY measurements

The SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) was launched on ENVISAT into a sun-synchronous orbit with a 10:00 LT equator crossing time on 1 March 2002. SCIAMACHY is an 8 channel UV/visible/NIR grating spectrometer covering the wavelength region of 220 to 2400 nm with 0.2–1.5 nm spectral resolution depending on wavelength (Bovensmann et al., 1999). Along one orbit, the instrument performs alternating nadir and limb measurements, facilitating profile retrievals from the Mesosphere to the UT/LS region and also column measurements. In addition, solar and lunar occultation measurements are performed under certain conditions, as well as a solar irradiance measurement once per day. The UV/vis nadir measurements of SCIAMACHY are performed with a high horizontal resolution of up to 30×30 km$^2$. Global coverage at the equator is achieved in 6 days and more frequently at higher latitudes. Nadir data used for the total column NO$_2$ retrievals are available since August 2002.

3.2 SCIAMACHY UB1.5 column retrieval

In previous work we validated the ESA operational near-real-time NO$_2$ total column data product, versions 5.01 and 5.02 (Sussmann et al., 2004a, b). We found a significant problem of this processor in reproducing the annual cycle, i.e., the fall decrease of the columns was strongly underestimated, which is probably due to reading out (too high) climatological tropospheric columns into the retrieval data set in case of cloudy pixels. In comparison we found that the scientific algorithm of the University of Bremen (UB1.5) was able to reproduce the annual cycle properly (Sussmann et al., 2004b). Therefore, we are dealing thereafter with the University of Bremen algorithm only.

The UB1.5 algorithm is an adaptation of the GOME retrieval (Richter and Burrows, 2002). Details of this adaptation have been described by Richter et al. (2004). Briefly, the wavelength window 425–450 nm in channel 3 was chosen for the fit, and a constant correction of 1.0 E+15 cm$^{-2}$ was added to the slant columns as an empirical correction inferred from early validation, which translates to a vertical column offset of 0.05–0.5 E+15 cm$^{-2}$. The background spectrum used in the slant column fitting is the azimuth scan mirror diffuser spectrum recorded on 15 December 2002. The results of the DOAS retrievals are slant column densities (SCD) that correspond to the column of molecules integrated along the effective light path through the atmosphere. To convert these into a vertical column density (VCD), an airmass factor (AMF) is applied that corrects for the light path enhancement. (Note that due to the infrared spectral domain for the FTIR retrievals the AMF is solely determined by the air density and the geometrical cosine-correction including refraction.) The UV-DOAS AMF are a function of solar zenith angle, the instrument line of sight, the relative azimuth between viewing direction and the sun, but also depends on the vertical profile of NO$_2$ and parameters such as surface albedo, aerosol loading or clouds.

3.3 The a priori profile for SCIAMACHY UB1.5 retrievals

We have shown for the FTIR retrievals that the accurate determination of the total NO$_2$ column depends heavily on a priori assumptions on the vertical VMR profile that is not available from the measurements and therefore introduces significant biases (Table 1). The same is true in a related manner for the SCIAMACHY UB1.5 retrievals. Therefore, as an alternative approach, for the SCIAMACHY UB1.5 retrievals, a purely stratospheric AMF is calculated based on the US Standard atmosphere after removing the tropospheric part and assuming a surface albedo of 5%, and only stratospheric background aerosols (Richter et al., 2004). The columns retrieved with this AMF are expected to give a good measure for the true stratospheric column for clean regions but will significantly exceed the true stratospheric column in polluted regions. At the same time, the retrieved column will slightly underestimate the true total column in clean regions, and significantly underestimate the true total column in polluted regions. A quantitative analysis of these effects by using the concept of averaging kernels will be presented in Sect. 5.2.

3.4 Scientific SCIAMACHY UB1.5 columns: full data set and cloud clearing

The SCIAMACHY NO$_2$ columns data set retrieved by the UB1.5 algorithm at the University of Bremen for a 200-km radius around the Zugspitze is shown in Fig. 6. Plotted are columns retrieved from all individual measurements (grey), as well as a reduced data set (orange) which resulted from application of a cloud clearing scheme. We applied a simple intensity threshold which leads to an effective clearing of both cloud and snow covered pixels. This data set will be exclusively utilized throughout this paper thereafter.

The figure displays a clear annual cycle for the daily minimum values whereas the daily maxima are spiking to very high values frequently. Note from Fig. 6 that by the cloud clearing the highest spikes of the full data set have been eliminated. This can be understood in terms of the strongly enhanced sensitivity to tropospheric pollution above snow or clouds.

Obviously, quite often strong regional boundary layer pollution events occur within the 200-km selection radius around Zugspitze. The retrieved SCIAMACHY columns are a reasonable measure of both the stratospheric and total column for clean conditions, and are significantly impacted by boundary layer pollution events, although they strongly underestimate boundary pollution enhancements in
quantitative terms. This behavior will be characterized in more detail in the sensitivity study given in Sect. 5.2.

3.5 Pollution clearing for SCIAMACHY data

We saw from Fig. 6, that within the 200-km selection radius around the Zugspitze for a considerable fraction of days regional pollution “hot spots” are included resulting in occasionally high spikes in our data set. The question arises how to detect such regionally polluted pixels in order to obtain a reduced SCIAMACHY data set that is a good measure for the clean background (free) troposphere. Such a “pollution clearing” is a prerequisite for the comparison with Zugspitze FTIR measurements which are essentially not impacted by pollution due to the high altitude location and the properties of the FTIR averaging kernels (see Sect. 5.2).

As shown in Richter et al. (2004) selecting satellite data for the lowest value observed around a station on each day can improve the agreement between satellite and ground-based measurements in polluted situations. However, such a selection will always introduce a low bias. Furthermore, this would lead to a significant reduction of available data, and, thus to worse comparison statistics. Therefore, we apply a refined pollution-clearing approach that intends to compensate for the low bias introduced by a simple minimum selection. It is based on the assumption that the individual minimum column values, that are representative for a clean background (free) troposphere, are impacted by scatter due to the statistical errors of the satellite measurement. Therefore we try to include also higher “minimum values” that are within this scatter bandwidth. The resulting pollution-clearing scheme is performed in 3 steps as follows.

**Step 1.** A fit to the daily minimum values is performed (Fig. 7a). See Appendix A, for the analytic function used. This fit is restricted to days with >6 column measurements within the 200-km selection radius around the Zugspitze, in order to avoid including polluted data to the series of minimum values. Using only days with several measurements increases the probability that the smallest of these measurements is not affected by boundary layer pollution. The threshold minimum number of 6 pixels available per day was retrieved from a statistical (elbow type) distribution plot of the difference between the average column and minimum column for each day against the number of measurements available for that day. For high numbers the difference shows a small scatter around a stable value of \( \approx 1 \times 10^{15} \text{ cm}^{-2} \), while for smaller numbers it is collapsing towards zero. The minimum number of 6 used for our subsequent analysis was read out via eye from the elbow corner of this scatter plot.

**Step 2.** In order to eliminate the annual cycle we subtract the fit function result from step 1, see orange points in Fig. 7b for the result. Then we remove all columns that exceed a value of 2 times the average columns value. The result is shown by marine points in Fig. 7b. One iteration is performed (bright blue points), i.e., a cut off at 2 times the average of the marine points (red line in Fig. 7b). Using 2 times the average as a cut off criterium is an ad hoc approach to achieve our goal of eliminating few but extremely spiking maximum values from an ensemble with rather uniform minimum values.
**Fig. 7.** Orange points: the SCIAMACHY NO$_2$ vertical column data set analyzed with the UB1.5 DOAS algorithm developed at the University of Bremen. Plotted are columns retrieved from individual measurements within a 200-km selection radius around the Zugspitze. The 3 steps of the pollution clearing for SCIAMACHY data in a 200-km radius around Zugspitze are: (a) Fit (blue line) to minimum values (marine). (b) Subtraction of the fit function result (orange); data cut off at 2 times the average columns value of orange points (marine); one iteration (bright blue) based on average value of marine points (red line). (c) Adding of the fit function result from (a) yields final pollution corrected data (bright blue).

**Step 3.** Adding of the fit function (result from step 1) yields final pollution-cleared data including the annual cycle again (bright blue points in Fig. 7c).

Calculating daily averages of the pollution-cleared data leads to the SCIAMACHY time series shown in Fig. 5 (orange points). A functional fit (orange line) was then performed as described in Appendix A.

Finally, we note that our 3-step approach is just a simple attempt to select data that are representative for clean background conditions in the troposphere, i.e., for days where the
tropospheric VMR could be assumed to be constant throughout the (free) troposphere. We will present an indirect validation of our pollution-clearing approach in the following section.

3.6 Characterization of the daily scatter of SCIAMACHY NO$_2$ columns

Here we want to give statistical numbers on the NO$_2$ columns scatter for individual and daily-mean data from our pollution-cleared SCIAMACHY data set (Table 2). Although the statistical quantities are identical to our treatment of FTIR before, we point to the fact that the physical origin of the scatter on the daily scale is dominated by different processes, i.e., the diurnal cycle for FTIR and the inclusion of polluted pixels in the 200-km SCIAMACHY selection radius. Although we performed corrections for both effects, the statistical numbers retrieved from the corrected data sets are probably still residually impacted by these effects.

First we want to characterize the scatter of individual SCIAMACHY column measurements within one day. We derive statistical quantities from the pollution corrected data. For each day (overpass) with index $i$ and $n_i$ measurements within the 200-km selection radius around Zugspitze, the standard deviation $\sigma_i$ and the standard deviation of the mean value $\sigma_i/\sqrt{n_i}$ were calculated, and subsequently the average of theses quantities over all days derived. The resulting average $AV_i(\sigma_i)=6.8\%$ is a measure for the scatter of the individual pollution-cleared column measurements.

This result of 6.8% for the precision of an “individual pixel” SCIAMACHY column measurement from investigating pollution corrected data is in agreement with results from a completely independent approach given by Richter et al. (2004): The precision of the column measurements has been assessed to be between 5–10% by analyzing the variability of data over the clean Pacific region which is assumed to be unpolluted in the troposphere. This good agreement shows the validity of our pollution-clearing approach. In other words, the columns that passed our pollution-clearing scheme are obviously a good measure for clean background tropospheric situations, which might by approximated by a constant (free) tropospheric VMR.

$AV_i(\sigma_i/\sqrt{n_i})=1.9\%$ is a measure for the precision of the daily mean column of SCIAMACHY at the time of overpass within our 200-km selection radius.

Finally, we calculate a standard deviation of the daily columns around the function fitted to the annual cycle (Fig. 5). This leads to a standard deviation of $\sigma=6.5\%$, see Table 2. This value comprises both the precision of a daily overpass column as well as the day-to-day scatter. It is significantly higher than the precision of a daily overpass average column, which we estimated from $AV_i(\sigma_i/\sqrt{n_i})=1.9\%$. Thereby we learn that the true day-to-day scatter for our pollution-clearing criteria and a 200-km radius around Zugspitze is 6.5%.

4 Intercomparison of SCIAMACHY versus FTIR column retrievals

4.1 Intercomparison of scatter

We obtained in Sect. 3.6 a day to-day scatter of 6.5% from SCIAMACHY data with our pollution-clearing criteria applied to a 200-km selection radius around Zugspitze and all resulting data averaged for each day. This agrees well to the FTIR result of 9.2% for the day-to-day scatter. Both data sets are showing sufficient precisions (Table 2) to make the assessment of this $\approx10\%$ effect. Note that a perfect agreement could not be expected due to the differing averaging kernels (see Sect. 5.1) and different sampling geometries (Zugspitze point measurement versus SCIAMACHY 200-km selection radius). But this agreement gives again some evidence for the validity of our pollution-clearing scheme.

4.2 Intercomparison of absolute column levels

The difference of the time series of SCIAMACHY and FTIR is displayed in Fig. 5 (red curve). Clearly, the SCIAMACHY columns show significantly higher values throughout the full validation period. The difference ($col_{SCIA}-col_{FTIR}$) is 0.83 E+15 cm$^{-2}$ on average, with a minimum of 0.60 E+15 cm$^{-2}$ and a maximum of 1.24 E+15 cm$^{-2}$.

This kind of intercomparison of the direct-output NO$_2$ column levels from two different remote sounding systems (satellite versus ground) has been performed in many previous papers, and the differences been interpreted in terms of errors of the satellite instrument. However, we would like to point out that this approach is only the first possibility out of two limiting (theoretical) cases: i) The observed differences are due to intrinsic errors in either of the two remote sounding data sets under the simplifying assumption that the two measurement systems have identical sampling characteristics or, ii) the observed difference can be attributed to the different sampling characteristics of the two instruments (differing averaging kernels) under the assumption that they are both working in principle without intrinsic errors. Reality will be in between these limiting cases. A theoretical framework to deal with this problem for the purpose of satellite validation has been given by Rodgers and Connor (2003).

We decided to therefor follow the assumption ii) as a basis for our subsequent synergistic use of SCIAMACHY and FTIR data aiming at the retrieval of tropospheric NO$_2$. I.e., we assume the difference shown in Fig. 5 is dominated by the differing sensitivities of SCIAMACHY versus FTIR and not by intrinsic errors of SCIAMACHY (or FTIR) measurements. Clearly, this is a simplifying assumption for the purpose of this study, and future validation studies have to be performed in order to explore to which degree this assumption holds. Our concepts of “virtual coincidence” and “pollution clearing” can contribute to the required refined validation studies.
Fig. 8. Total column averaging kernels for Zugspitze FTIR (blue to green lines) and SCIAMACHY UB1.5 NO\textsubscript{2} retrievals (pink to orange lines) calculated for solar zenith angles (SZA) between 20° and 80°. Both FTIR and satellite retrievals are based upon the US 1976 Standard NO\textsubscript{2} VMR a priori profile with the tropospheric part set to zero up to 10 km altitude.

5 Combined FTIR and SCIAMACHY retrieval

In the following we make the simplifying assumption that both FTIR and SCIAMACHY are operating without intrinsic errors and show how additional independent (tropospheric) information can be gained from a combined FTIR plus SCIAMACHY retrieval.

5.1 Total column averaging kernels for the stand-alone FTIR and SCIAMACHY retrievals

Total column averaging kernels are vectors of the dimension of the number of layers or levels of the model atmosphere used, and are thereafter referred to as \( a_{\text{FTIR}} \) and \( a_{\text{SCIA}} \), respectively. Each vector component stands for a certain altitude and describes to what extent a perturbation of the true VMR profile at a certain altitude relative to the a priori profile used will be reflected in the retrieved total columns, or be underestimated, or overestimated, respectively by the retrieval. An ideal remote sounding system is described by \( a_{\text{ideal}}(111...1) \), numbers smaller than one would quantify underestimations of true perturbations, numbers above one overestimations. A mathematical description and practical details for total column kernel computations were given for FTIR previously, and can be found, e.g., in Sussmann (1999), and have been given for DOAS only recently for the first time by Eskes and Boersma (2003).

Figure 8 shows the total column averaging kernels for both the Zugspitze FTIR and the SCIAMACHY UB1.5 NO\textsubscript{2} column retrievals. The kernels indicate that both FTIR and SCIAMACHY retrievals perform with a significant underestimation of the tropospheric column, but are able to properly monitor changes in the stratospheric part. Figure 8 shows also differences, namely, i) the underestimation of the...
tropospheric column is much more pronounced for the FTIR retrieval compared to the satellite retrieval, and ii) there is a significant zenith-angle dependence of the tropospheric sensitivity in case of the satellite retrieval, but not for the FTIR retrieval.

5.2 Smoothing of tropospheric pollution

In this section, the smoothing effect of the averaging kernels of FTIR and SCIAMACHY (i.e., the under-/overestimation of the true column by the retrievals) is illustrated by a sensitivity study. We assume 3 different scenarios for the true vertical profiles $x_{\text{true}}$ (profile vectors are referred to as $x$, with units either in VMR or partial columns) which all differ in a characteristic manner from the a priori profile $x_a$ (i.e., the reduced US Standard NO$_2$ profile). The profiles for the 3 scenarios are shown in Fig. 9. Scenario 1 is for $x_{\text{true}}=x_{\text{US}}$, i.e., the US Standard NO$_2$ profile; scenario 2 uses $x_{\text{true}}=x_{\text{US}/2}$, i.e., the US Standard NO$_2$ profile with all VMR values scaled by a factor of 1/2; scenario 3) $x_{\text{true}}=x_{\text{poll}}$, i.e., $x_{\text{US}}$ but with a constant enhanced VMR value of 20 ppbv up to 4 km altitude. For the columns-ground altitude we used 1.077 km a.s.l., which is the average ground altitude within a 200-km radius around the Zugspitze. Examples are given for the Zugspitze FTIR (at 2.964 km a.s.l.) as well as theoretical numbers calculated for a FTIR at 1.077 km a.s.l.

Table 3. Results for the ratio of retrieved columns $col_{\text{ret}}$ to the true columns $col_{\text{true}}$ computed by Eq. (1), using the averaging kernels shown in Fig. 8 for SZA=60°, and the same a priori profile $x_a$, namely the US Standard NO$_2$ profile with the tropospheric part up to 10 km set to zero. Three different scenarios are given for the assumed true NO$_2$ profile $x_{\text{true}}$ as shown in Fig. 9. Scenario 1) $x_{\text{true}}=x_{\text{US}}$, i.e., the US Standard NO$_2$ profile; scenario 2) $x_{\text{true}}=x_{\text{US}/2}$, i.e., the US Standard NO$_2$ profile with all VMR values scaled by a factor of 1/2; scenario 3) $x_{\text{true}}=x_{\text{poll}}$, i.e., $x_{\text{US}}$ but with a constant enhanced VMR value of 20 ppbv up to 4 km altitude. For the columns-ground altitude we used 1.077 km a.s.l., which is the average ground altitude within a 200-km radius around the Zugspitze. Examples are given for the Zugspitze FTIR (at 2.964 km a.s.l.) as well as theoretical numbers calculated for a FTIR at 1.077 km a.s.l.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Zugspitze FTIR @ 2.964 km a.s.l.</th>
<th>FTIR @ 1.077 km a.s.l.</th>
<th>SCIAMACHY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_{\text{true}}$ ($1.077-10$ km)</td>
<td>$x_{\text{US}}$</td>
<td>$x_{\text{US}/2}$</td>
</tr>
<tr>
<td>$col_{\text{true}}$ ($1.077-10$ km)</td>
<td>0.053</td>
<td>0.053</td>
<td>0.955</td>
</tr>
<tr>
<td>$col_{\text{true}}$ ($1.077-100$ km)</td>
<td>0.950</td>
<td>0.949</td>
<td>0.058</td>
</tr>
<tr>
<td>$col_{\text{true}}$ ($10-100$ km)</td>
<td>1.003</td>
<td>1.002</td>
<td>1.239</td>
</tr>
</tbody>
</table>

We have listed in Table 3 for FTIR and SCIAMACHY for all 3 scenarios numbers for the ratio of the retrieved column $col_{\text{ret}}$ to the true column $col_{\text{true}}$, which can be calculated directly from the averaging kernels, the assumed true profile, and the a priori profile:

$$\frac{col_{\text{ret}}}{col_{\text{true}}} = a^T (x_{\text{true}} - x_a) + a^T a_{\text{ideal}} x_a$$

with

$$col_{\text{true}} = (111\ldots1) x_{\text{true}} = a_{\text{ideal}}^T x_{\text{true}}. \quad (1)$$

Table 3 contains also the analogous columns ratio with respect to the true stratospheric part above 10 km. Note that for the column-ground altitudes we used 1.077 km a.s.l., which was retrieved as an average altitude for the 200-km radius around the Zugspitze from a global 1 km×1 km elevation data set (Hastings and Dunbar, 1999). The results of Table 3 are discussed as follows.

**Scenario 1.** This scenario ($x_{\text{true}}=x_{\text{US}}$) describes a clean atmosphere, i.e., the tropospheric column $(<10$ km) is small compared to the total column (columns ratio 0.053). In this case the column retrieved by Zugspitze FTIR is slightly underestimating the true total column above 1.077 km a.s.l. (factor 0.950) and very weakly overestimating the true stratospheric column (factor 1.003). The underestimation of the true total column is even smaller for SCIAMACHY (factor 0.984). The fact that these under-/overestimations are small can be understood by the fact that $x_{\text{true}}$ is identical to $x_a$ in the stratospheric part, and close to $x_a$ within the tropospheric part $(<10$ km), where the components of $x_a$ are zero, and VMR values of $x_{\text{US}}$ are very small.

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Scenario 2. This scenario ($x_{\text{true}}=x_{\text{US}/2}$) is to test whether a significant scaling factor with respect to $x_a$ is properly reflected by the retrievals for a clean atmosphere. The answer is yes, the numbers are nearly identical to scenario 1. This can be directly understood for the FTIR retrieval, because a profile scaling retrieval is in principle always able to perfectly reflect true atmospheric changes relative to the a priori which can be modeled by one simple scaling factor. (This is only approximately correct in our case because the a priori profile is the reduced US Standard profile, and this leads to the slight deviations of the ratios from unity as in Scenario 1). This also holds for the DOAS retrieval of the a priori which can be modeled by one simple scaling factor. To perfectly reflect true atmospheric changes relative to the a priori, the corrected FTIR and SCIAMACHY columns will always underestimate the true column since the true atmosphere will always contain a larger tropospheric column than given by the a priori. The corresponding underestimation by SCIAMACHY will be less pronounced since its averaging kernels are closer to unity in the troposphere (Fig. 8). Together with the fact that both FTIR and SCIAMACHY are sampling the stratosphere properly (kernels close to unity, see Fig. 8) the following behavior can be expected for applying the appropriate averaging-kernel based corrections for the tropospheric underestimations to both FTIR and SCIAMACHY: For an iteratively increased assumed true tropospheric column (stratospheric column fixed to a realistic value), there will be a distinct level reached, where the corrected FTIR and SCIAMACHY columns will match together. This is because the correction is always larger for FTIR which starts at lower columns. In other words, the different tropospheric sensitivities of the SCIAMACHY versus FTIR kernels allow for the retrieval of tropospheric NO$_2$ by combining the two sounding systems. Our approach thereafter is to actually perform such a combined FTIR-SCIAMACHY retrieval of tropospheric NO$_2$. If the result for tropospheric NO$_2$ compares reasonably well with our a priori knowledge of background clean air levels of tropospheric NO$_2$, then we have no reason to assume that there is an intrinsic error in either of the sounding systems. Before we give a theoretical formulation of the described procedure we want to note, that this is a sensitivity study in a sense that we do not investigate other possible biasing contributions like the impact of albedo, clouds or aerosols on the SCIAMACHY retrievals.

From our discussion of the differing averaging kernels (Fig. 8) we assume for the combined retrieval by FTIR and SCIAMACHY that we can roughly obtain two independent pieces of information, i.e., stratospheric and tropospheric information. The definition of the corresponding two retrieval parameters are illustrated in Fig. 10, namely, a factor $\lambda_i$ for scaling of our (stratospheric) a priori profile ($\text{VMR}_i$), and an iterative change of the tropospheric volume mixing ratio $\text{VMR}_{\text{trop}}$ which is assumed to be constant with altitude. The interconnection of these (stratospheric and tropospheric) parts of the profile is done at their actual crossing point which is, consequently, variable in VMR and altitude.

We write the following two relations for the differences between the column inferred from the combined retrieval $\text{col}_{\text{combi}}$, the column retrieved by FTIR $\text{col}_{\text{FTIR}}$, and the column retrieved by SCIAMACHY $\text{col}_{\text{SCIAMACHY}}$ (all plotted in Fig. 11a)

\[
\text{col}_{\text{combi}} = \text{col}_{\text{FTIR}} - \text{col}_{\text{combi}}
\]

\[
\text{col}_{\text{combi}} = a^T_{\text{FTIR}} \cdot (x_{\text{combi}} - x_a) + a^T_{\text{ideal}} \cdot x_a - a^T_{\text{ideal}} \cdot x_{\text{combi}},
\]

and

\[
\text{col}_{\text{SCIAMACHY}} = \text{col}_{\text{combi}}
\]
where the vectors \( x \) stand for partial columns profiles.

Our a posteriori retrieval constraint is set up as follows

\[
x_{\text{combi}} = \lambda_1 \cdot x_a + x_{\text{trop}}
\]

with

\[
x_{\text{trop}} = \begin{pmatrix} V M R_{29} \cdot AM F_{29} \\ V M R_{1} \cdot AM F_{1} \end{pmatrix}
\]

with

\[
V M R_i = \begin{cases} 
0 & \text{if } V M R_{\text{trop}} < \lambda_1( V M R_a) \\
 V M R_{\text{trop}} - \lambda_1( V M R_a) & \text{if } V M R_{\text{trop}} \geq \lambda_1( V M R_a)
\end{cases}
\]

This describes our retrieval with the two parameters \( \lambda_1 \) and \( V M R_{\text{trop}} \) (Fig. 10). \( AM F_i \) are the infrared airmass factors (i.e., the partial air columns of the different layers) which – multiplied by \( V M R \) – give the partial columns profile \( x \).

Our retrieval constraint is set up from two parameters, i.e., it allows for retrieval of two independent degrees of freedom, because this is what can be expected from using two complementary input parameters, namely \( c o l_{\text{FTIR}} \) and \( c o l_{\text{SCIAMACHY}} \). The constraint for the stratospheric part is a simple scaling of the US standard profile as used also for the FTIR retrieval.

For the lower part we use a scaling of a \( V M R \) profile that is constant with altitude. This is because only one degree of freedom is left for this lower part, and it is the zero-order approach in our case where no better a priori information on the vertical distribution of free tropospheric background NO\(_2\) is available. Our approach of linking the two parts of the profile together just at the point where the tropospheric \( V M R \) matches the US standard profile is the simplest solution that avoids (unphysical) negative \( V M R \) gradients at the transition between the lower and upper part of the profile.

We derive a starting value for \( \lambda_1 \) by using

\[
\lambda_1 = \frac{c o l_{\text{FTIR}} - c o l_{\text{combi}}}{(10–100 \text{km})=0},
\]

because FTIR is a good measure for the true pure stratospheric column. This assumption has been tested in Sect. 5.2 and turned out to hold to a very good approximation.

From Eqs. (2), (4) and (6) it follows

\[
\lambda_1 = \frac{c o l_{\text{FTIR}}}{a_{\text{ideal}} \cdot x_a}.
\]

For the given \( \lambda_1 \) we subsequently apply the retrieval equation

\[
c o l_{\text{FTIR}} - c o l_{\text{SCIAMACHY}} = (a_{\text{FTIR}} - a_{\text{SCIAMACHY}})^T (\lambda_1 - 1) x_a + x_{\text{trop}}
\]

which describes the iteration of \( V M R_{\text{trop}} \) via \( x_{\text{trop}} \), see Eq. (5) to match the measured columns difference \( c o l_{\text{FTIR}} - c o l_{\text{SCIAMACHY}} \).

The resulting tropospheric mixing ratio \( V M R_{\text{trop}} \) is plotted as a time series in Fig. 11b, and is converted to the tropospheric column (1.077–10 km) within the same figure.
5.4 Partial column averaging kernels for the combined retrieval

In Fig. 12 the partial column averaging kernels are displayed for the combined retrieval by FTIR and SCIAMACHY. They have been calculated by the perturbation approach (see, e.g., Sussmann, 1999) around a typical atmospheric state obtained from the retrievals of the whole time series of this study. One kernel has been calculated for the tropospheric column (1.077–10 km). The kernel for the stratospheric column (10–100 km) of the combined retrieval (Fig. 12) is identical to the total column kernel of the stand-alone FTIR retrieval (Fig. 8). This is a logical consequence of our retrieval set up. These two kernels are showing that two independent pieces of information are obtained by the combined retrieval for the troposphere, and stratosphere, respectively. Note that the tropospheric kernel is able to perfectly monitor possible changes within the free troposphere, but shows a significant underestimation of possible changes in the boundary layer. The same effect can be seen from the total column averaging kernel of the combined retrieval (Fig. 12).

5.5 Discussion of the retrieved tropospheric columns series in terms of validity

First of all, Fig. 11b shows that the retrieved tropospheric columns (1.077 km–10 km) are showing a pronounced annual cycle. It displays a minimum of 0.75 E+15 cm\(^{-2}\), a maximum of 1.54 E+15 cm\(^{-2}\), and an average of 1.09 E+15 cm\(^{-2}\). As discussed earlier in this paper, due to our pollution-clearing criteria, our results should be a measure for clean tropospheric background conditions. For such clean background conditions, columns of the order of 1–3 E+15 were frequently observed by ground-based UV/vis
measurements during a recent extensive validation study of GOME tropospheric nitrogen dioxide in the Po basin (Petritoli et al., 2004). Thus, we have evidence that the tropospheric columns retrieved from combined FTIR and SCIAMACHY retrievals are within a reasonable range of magnitude. This is only a qualitative statement and it means that from our findings we can neither exclude nor find any evidence for an intrinsic principle error in the SCIAMACHY data set.

We repeat, however, that the UB1.5 algorithm was empirically tuned by adding \(1.0 \times 10^{15} \text{ cm}^{-2}\) to the slant columns, which translates to a vertical column offset of \(0.05–0.5 \times 10^{15} \text{ cm}^{-2}\) depending on season (Richter et al., 2004). Due to limited a priori knowledge of the clean background tropospheric NO\(_2\) column (see above) we cannot decide from this study whether this empirical correction to SCIAMACHY has to be refined or not.

A more quantitative validation of our new method could be performed in an upcoming study using collocated SCIAMACHY tropospheric columns retrieved with the Richter and Burrows (2002) method. In fact the two methods are independent (because now the stratospheric background to be removed is that of FTIR and not that retrieved by SCIAMACHY over the Pacific Ocean) so that useful indications on self-consistency and/or validation of the new approach (or limitations of the old one) can be pointed out.

5.6 Discussion of the retrieved tropospheric column in geophysical terms

Now we want to discuss the annual cycle of the background (free) tropospheric columns series which we obtained from the combined retrieval (Fig. 11b), assuming that both FTIR and SCIAMACHY are performing without intrinsic errors. Clearly, the retrieved background free tropospheric columns annual cycle shows a significant phase shift towards earlier times compared to both the stratospheric and the total columns series (\(\text{col}_{\text{FTIR}}\) and \(\text{col}_{\text{combi}}\) in Fig. 11a). On the other hand, the annual cycle of “boundary layer” NO\(_2\) is known to show a symmetric mid-winter maximum due to human fuel combustion related to traffic and heating systems and a broader symmetric summer minimum which is due to the smaller emissions in combination with a reduced NO\(_2\) lifetime in summer (see, e.g., Fig. 6 in Petritoli et al., 2004). Compared to that, our retrieved free tropospheric columns series shows a similar fall-winter increase, but a slower decrease during summer with a minimum in fall. At least the tendency of this delay effect relative to the boundary layer cycle might be tentatively explained by the fact that our retrieved tropospheric columns are representative for the clean (free) troposphere, where the lifetime of NO\(_2\) is significantly higher (up to 10 days) than in the boundary layer (<1 day), see, e.g., IPCC (2001).

6 Conclusions and outlook

Columnar NO\(_2\) retrievals from solar FTIR measurements of the time span July 2002–October 2004 were used synergistically with columnar NO\(_2\) retrieved from SCIAMACHY data by the University of Bremen scientific algorithm UB1.5.

We have presented several new concepts for the data matching between FTIR and satellite measurements of columnar NO\(_2\) for the purpose of validation and synergistic use. A new approach was presented to account for the daytime increase of stratospheric NO\(_2\) and match FTIR data to the time of satellite overpass. This is performed by constructing “virtual coincidences” that make use of the NO\(_2\) daytime increasing rate retrieved from the FTIR data set itself \([+1.02(6) \times 10^{14} \text{ cm}^{-2}\text{h}^{-1}]\). The measured increasing rate shows no significant seasonal variation for our midlatitude data set. This is in contrast to results from stratospheric photochemical model calculations. A pollution-clearing scheme

Fig. 12. Averaging kernels for the combined FTIR and SCIAMACHY retrieval of NO\(_2\), calculated for a solar zenith angle of 20°. Red curve: Tropospheric partial column averaging kernel (calculated for 1.077–10 km). Blue curve: Stratospheric partial column averaging kernel (calculated for 10–100 km). Black curve: Total column averaging kernel for the combined retrieval.
for the SCIAMACHY data was developed to select only pixels corresponding to clean background (free) tropospheric conditions and thus to exclude local pollution hot spots within the 200-km selection radius around the Zugspitze. Furthermore, a generic analytic function was designed in order to better fit obvious deviations of columnar NO$_2$ annual cycles from a sine function. Thereby statistical properties (day-to-day scatter) can be calculated relative to this fitted annual cycle.

From a direct intercomparison (i.e., without correcting for the different sensitivities) we derived the difference between SCIAMACHY and FTIR columns. It varies between 0.60−1.24 E+15 cm$^{-2}$ with an average of 0.83 E+15 cm$^{-2}$. A day-to-day scatter of daily means of $\approx$7−10% could be retrieved in mutual agreement from both FTIR and SCIAMACHY.

We have shown that FTIR gives a nearly unbiased ($<25\%$) maximum bias in case of extreme tropospheric pollution, clean air bias $<1\%$) and highly precise measure of the pure stratospheric column (precision of the daily mean or virtual-coincidence column 4.3%). This is achieved by using measurements from a mountain station, which is located above the possibly polluted boundary layer, and an a priori profile with the tropospheric part set to zero.

Using Zugspitze FTIR soundings set up in this way, we have formulated a combined posteriori retrieval of FTIR and SCIAMACHY for the tropospheric column, based upon the averaging kernels. This combined retrieval was performed under the simplifying assumption that SCIAMACHY and FTIR are operating without intrinsic errors, i.e., the observed differences between SCIAMACHY and FTIR are only due to tropospheric NO$_2$. It yields an annual cycle of the clean background (free) tropospheric column (<10 km) with variations between 0.75−1.54 E+15 cm$^{-2}$, an average of 1.09 E+15 cm$^{-2}$, and an intermediate phase between that of the well known boundary layer and stratospheric annual cycles. Similar column levels have been found from ground-based UV/vis measurements of the background (free) tropospheric column in the Po valley.

Although our combined retrieval was based upon the assumption that both FTIR and SCIAMACHY are operating without errors, there could be some SCIAMACHY errors in reality, of course. However, these errors are minimized by our use of averaging kernels and will only be relevant if the atmospheric conditions deviate strongly from the parameters used in the forward modelling. A validation of our new method could be performed in an upcoming study using collocated SCIAMACHY tropospheric columns retrieved with the Richter and Burrows (2002) reference sector method. Since the two methods are independent useful indications on selfconsistency and/or validation of the new approach could be pointed out.

Our results were shown for our validation application for selected SCIAMACHY pixels without pollution only, but can be also applied to polluted SCIAMACHY data. Our presentation was in the tradition of a point-location time series for the Zugspitze, but can, of course, be converted to a horizontal map of tropospheric NO$_2$ as well. For this, the averaging kernels have to be determined for each measurement independently using the best estimates for albedo, aerosols, clouds and NO$_2$ profile available (Eskes and Boersma, 2003).

We have shown how to use a FTIR mountain site as a reference for combined satellite retrievals of tropospheric NO$_2$ over land. This is a complementary approach in addition to the traditional method using stratospheric reference columns retrieved over sea. The latter is based on the assumption of a longitudinally homogeneous stratospheric NO$_2$ layer. Variations can, however, clearly not be neglected close to the Polar Vortex or during major changes in stratospheric dynamics.

Therefore, our result can be transferred to the use of a group of FTIR stations (preferably mountain sites) within the Network of the Detection of Stratospheric Change (NDSC) as “calibration points” for improved global satellite retrievals of tropospheric NO$_2$ over land. The minimum requirement for such an “integrated global NO$_2$ observing system” would be one FTIR for a horizontal area for which the stratospheric column can be assumed to be constant to a sufficient degree, e.g., for latitudinal bands towards the Pacific with meridional extensions of several hundreds of kilometers.

Finally, we expect that the concepts described in this study can be transferred to a variety of possible combined a posteriori retrievals of further trace species from satellite and ground-based FTIR systems that might be synergistically exploited in near future.

Appendix A: Analytic function to fit NO$_2$ columnar annual cycles

A generic analytic function was designed in order to better fit two obvious deviations of columnar NO$_2$ annual cycles from a sine function. i) Different radii of curvature are observed the minimum and maximum, respectively, and ii) maxima and minima are often delayed or shifted to earlier times, leading to an asymmetry in the peaks and/or minima.

The function is

$$f = b - a + 2a \cdot \left\{ \sin \left( \frac{\pi}{365} \left[ \frac{x-x_0}{1+c \cdot e^{-\left( \frac{x-x_0}{\sigma} \right)^2}} + \frac{\pi}{4} \right] \right) \right\}^\gamma$$

(A1)

with the 7 (fitting) parameters $a$, $b$, $c$, $x_0$, $x_p$, $\sigma$, and $\gamma$.

In order to discuss this function we consider 3 cases.

Case 1. $\gamma=1$, $c=0$.

This reduced case is the sine function

$$f_1 = b + a \cdot \sin \left( \frac{2\pi x-x_0}{365} \right)$$

(A2)
Fig. A1. Schematics to illustrate the analytic function used to fit the annual cycle of NO$_2$ columns, i.e., its deviations from a sine function. (a) Decrease of the radius of curvature around the minimum by using $\gamma$ ($<1$) as a fitting parameter. (b) Shift of maximum to earlier times by a local Gaussian frequency modulation using as fit parameters the strength $c$, the position in time $x_p$, and the width $\sigma$.

**Case 2.** $\gamma < 1$, $c = 0$.

This case describes the decreased radius of curvature around the minimum

$$f_2 = b - a + 2a \cdot \left( \sin \left( \frac{\pi}{365} \left( \frac{x - x_0}{365} + \frac{\pi}{4} \right) \right) \right)^\gamma,$$

(A3)

see Fig. A1a, for an illustration.

**Case 3.** $c \neq 0$, $\gamma = 1$.

This case describes a local Gaussian frequency perturbation with strength $c$, position $x_p$, and width $\sigma$

$$f_3 = b + a \cdot \sin \left( 2\pi \cdot \frac{x - x_0}{365} \cdot \left( 1 + c \cdot e^{-\left( \frac{x-x_p}{\sigma} \right)^2} \right) \right),$$

(A4)

see Fig. A1b, for an illustration.

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Validation of SCIAMACHY AMC-DOAS water vapour columns

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Abstract. A first validation of water vapour total column amounts derived from measurements of the SCanning Imaging Absorption spectroMeter for Atmospheric CHartography (SCIAMACHY) in the visible spectral region has been performed. For this purpose, SCIAMACHY water vapour data have been determined for the year 2003 using an extended version of the Differential Optical Absorption Spectroscopy (DOAS) method, called Air Mass Corrected (AMC-DOAS). The SCIAMACHY results are compared with corresponding water vapour measurements by the Special Sensor Microwave Imager (SSM/I) and with model data from the European Centre for Medium-Range Weather Forecasts (ECMWF).

In confirmation of previous results it could be shown that SCIAMACHY derived water vapour columns are typically slightly lower than both SSM/I and ECMWF data, especially over ocean areas. However, these deviations are much smaller than the observed scatter of the data which is caused by the different temporal and spatial sampling and resolution of the data sets. For example, the overall difference with ECMWF data is only $-0.05 \text{ g/cm}^2$ whereas the typical scatter is in the order of $0.5 \text{ g/cm}^2$. Both values show almost no variation over the year.

In addition, first monthly means of SCIAMACHY water vapour data have been computed. The quality of these monthly means is currently limited by the availability of calibrated SCIAMACHY spectra. Nevertheless, first comparisons with ECMWF data show that SCIAMACHY (and similar instruments) are able to provide a new independent global water vapour data set.

1 Introduction

It is well known that water vapour is one of the most important atmospheric constituents. Most of the atmospheric water vapour is located in the troposphere close to the surface of the Earth. Weather and climate are essentially influenced by the variation of water vapour concentrations. Especially, water vapour is the major greenhouse gas. Therefore, the global distribution of water vapour is a relevant input quantity for global atmospheric models aiming to predict weather or climate.

However, global water vapour distributions are difficult to be obtained. Currently, there are several sources for global water vapour data, all of them having their specific advantages and limitations. In-situ measurements by radio sondes probably provide data with the highest accuracy and the best vertical resolution; however, these measurements only cover a small horizontal area, and the distribution of radio sonde stations over the Earth is rather inhomogeneous. Especially over the oceans and in the southern hemisphere large regions are not covered by radio sonde data.

Remote sensing data from satellite based instruments provide the possibility to fill these gaps, but they are typically limited in vertical and temporal resolution. Water vapour can be measured from space by various techniques. Most commonly used are microwave (MW) sensors like the Special Sensor Microwave Imager (SSM/I) which are able to provide total water vapour columns at a high spatial (horizontal) resolution (Bauer and Schluessel, 1993). However, the MW retrieval is usually constrained to ocean areas.

Instruments operating at other spectral regions like in the near infrared (NIR) – such as e.g. the Moderate Resolution Imaging Spectroradiometer (MODIS) on Aqua/Terra (Gao and Kaufman, 2003) and the Medium Resolution Imaging Spectrometer (MERIS) on ENVISAT (Li et al., 2003) – can derive total water vapour columns also over land.
Unfortunately, in contrast to MW sensors, NIR sensors can not see through clouds which also limits the retrieval.

Another recently developed method for the retrieval of water vapour distributions is the utilisation of data from the Global Positioning System (GPS) satellites (see e.g. Dai et al., 2002).

In addition, several investigations have shown that also measurements performed by the Global Ozone Monitoring Experiment (GOME, see e.g. Burrows et al., 1999) and the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY, see e.g. Bovensmann et al., 1999) in the visible spectral region may be used to derive global water vapour concentrations (Noël et al., 1999, 2002, 2004; Casadio et al., 2000; Maurellis et al., 2000; Lang et al., 2003; Wagner et al., 2003; Buchwitz et al., 2004).

The GOME instrument was started on the second European Remote Sensing Satellite (ERS-2) in 1995 and is still operating (although at somewhat degraded performance and coverage). SCIAMACHY is an extended version of GOME and part of the atmospheric chemistry payload of the European Environmental Satellite ENVISAT which was launched in March 2002. The combination of GOME and SCIAMACHY data already now covers a time span of 9–10 years which may extend even further, depending on the life time of SCIAMACHY (or ENVISAT). In addition, the GOME-2 instruments on the series of operational meteorological satellites Metop (the first one to be launched by the end of 2005) will continue this data set. Therefore, an analysis of these GOME-type instrument data can lead to an additional, independent global water vapour climatology (see also Lang and Lawrence, 2004).

The current paper presents recent results of the so-called “Air Mass Corrected Differential Optical Absorption Spectroscopy” (AMC-DOAS) method which has been applied to SCIAMACHY nadir measurements in the spectral region at about 700 nm. Noël et al. (2004) already showed that it is possible to derive good water vapour total columns from SCIAMACHY measurements using the AMC-DOAS method. However, these results were based on only a small amount of analysed data (some days of measurements). In addition, in the context of the SCIAMACHY/ENVISAT validation program, some first intercomparisons of AMC-DOAS water vapour columns with radio sonde data and ATOVS (Advanced TIROS (Television Infrared Observation Satellite Program) Operational Vertical Sounder) satellite measurements have been performed for a dedicated validation data set (see Timmermans et al., 2004, for details). In the current paper we will extend the validation of the AMC-DOAS water vapour results to a longer period of time, namely the whole year 2003. Furthermore, we will present the first global monthly mean water vapour data from SCIAMACHY.

2 The AMC-DOAS retrieval method

The AMC-DOAS retrieval method has been extensively discussed in Noël et al. (2004). Therefore, only a small summary of the algorithm will be given here.

Similar to the well-known DOAS (Differential Optical Absorption Spectroscopy) approach the AMC-DOAS method derives information about the amount of an atmospheric species from differential absorption structures in sun-normalised radiances. The AMC-DOAS method does not require absolutely calibrated radiances and irradiances, as long as the differential structures are not affected by calibration issues. The method is numerically fast and therefore well suited for operational data processing. The main differences between AMC-DOAS and standard DOAS are as follows:

1. In standard DOAS, which is only applicable in the optically thin case, the absorption depth in the differential spectra is proportional to the absorber amount. Water vapour has highly structured absorption features (saturated and non-saturated lines) which are not resolved by GOME or SCIAMACHY. Therefore, the relation between absorption depth and absorber amount becomes non-linear, which is considered by the AMC-DOAS method.

2. The AMC-DOAS method includes an Air Mass Factor (AMF) correction derived from O₂ absorption features in the same spectral region as the water vapour absorption. This is why the fitting window for the AMC-DOAS water vapour retrieval has been selected to be 688 nm to 700 nm, where both water vapour and molecular oxygen show absorptions of similar strength.

The main purpose of the AMF correction factor is to correct the retrieved water vapour column, but beside this the AMF correction factor can be used as an inherent quality check for the retrieved data. The AMC-DOAS retrieval assumes a cloud-free tropical background atmosphere and does not consider different surface elevations. If the derived AMF correction is too large, this is an indication that these assumptions are not valid (most likely because the observed scene is too cloudy or contains a high mountain area).

Therefore, as in previous studies, only results with an AMF correction factor larger than 0.8 have been taken into account. Currently, the AMC-DOAS retrieval is limited to solar zenith angles (SZAs) below 88°.

Note that in the present study – in contrast to Noël et al. (2004) – no additional scaling factor has been applied to the retrieved columns to better match correlative data. This was no longer necessary after using an updated (narrower) SCIAMACHY slit function of full width at half maximum (FWHM) 0.4 nm. The new slit function width was motivated by the recent analysis of in-flight measurements which revealed differences to the on-ground determined slit functions (Ahlers, 2004). Furthermore, the new slit function leads to
smaller residuals of the AMC-DOAS retrieval which also supports this choice. As a consequence, the AMC-DOAS results do not rely on any other measurement data, e.g. calibration factors derived from comparisons with ground based radio sonde measurements as it is the case for e.g. SSM/I data. The retrieved water vapour columns therefore provide a completely independent data set.

3 Data bases

In the present paper, SCIAMACHY water vapour data are compared with SSM/I measurements and model data from the European Centre for Medium-Range Weather Forecasts (ECMWF).

The SCIAMACHY water vapour data have been derived by applying the AMC-DOAS retrieval method to all available SCIAMACHY nadir data for the year 2003. Because there is no complete consolidated set of SCIAMACHY calibrated spectra (Level 1 data) available yet, the analysis is based on a combination of both consolidated and unconsolidated near-real-time (NRT) data. Even after inclusion of the NRT data there are still larger data gaps, especially in November 2003. In this sense the results presented in the next section are still of preliminary nature.

To avoid a potential influence of the known insufficient radiometric calibration of the current Level 1 data (Skupin et al., 2002, 2003) on the retrieval results, always the same (specially calibrated) solar reference spectrum (provided by J. Frerick, ESA) has been used in the retrieval.

The SSM/I data used in the comparison have been taken from the Daily Gridded Integrated Water Vapour Product provided by the Global Hydrology Resource Center (GHRC) at the Global Hydrology and Climate Center, Huntsville, Alabama. We took only data for the descending orbit part of the DMSP F-14 satellite, because its dayside equatorial crossing time of about 08:00 LT is close to the ENVISAT dayside equatorial crossing time of 10:00 LT. Because SSM/I is a MW sensor, only data over ocean are available.

The ECMWF water vapour columns have been calculated using assimilated meteorological fields (geopotential height, temperature, pressure, and specific humidity) from the operational daily analysis data. These data are provided on a 1.5°×1.5° spatial grid at 60 altitude levels every 6 h. The 6-h values have been combined and integrated over height to derive the total vertical water vapour column. Afterwards, daily averages of the columns have been computed for each grid point. Note that the ECMWF data are not completely independent from SSM/I data because SSM/I results have been assimilated into the ECMWF model.

For the inter-comparison all SCIAMACHY and ECMWF data have been (re-)gridded to the spatial resolution of the SSM/I data which is 0.5°×0.5°.

4 Results

In this section, two types of results will be presented. First, we will show a time series of (globally averaged) deviations between SCIAMACHY total water vapour columns and SSM/I and ECMWF data for the year 2003. Then we will compare global maps of monthly mean water vapour results based on SCIAMACHY and ECMWF data.

4.1 Time series

The time series data have been generated in the following way:

1. Determine collocations of (daily gridded) SCIAMACHY water vapour total columns between 0 and 7 g/cm² (which is about the total range of columns) and correlative data.
2. Compute the absolute differences SCIAMACHY – SSM/I and SCIAMACHY – ECMWF for this collocated data set.
3. Compute the weighted daily means and standard deviations by averaging over all collocated grid points. The weights are chosen to be the cosine of the geographic latitude. The reason for these weights is that the input data are on an equidistant latitude/longitude grid which is not representative for the surface area of the Earth. Therefore, without proper weights, high latitude columns would contribute too much to the global mean.
4. The global monthly means are then derived by averaging the daily means over one month.

The results of this procedure are shown in Figs. 1 and 2. The black circles mark the daily means, the blue vertical lines
are the corresponding daily standard deviations, and the red line denotes the monthly mean.

As can be seen from these figures, the standard deviation of the data is in both the comparisons with SSM/I and ECMWF quite high (about 0.5 g/cm$^2$, maybe somewhat higher for SSM/I data). This magnitude of scatter has been observed before (see e.g. Noël et al., 2004; Lang and Lawrence, 2004). It can be mainly attributed to the large temporal and spatial variability of atmospheric water vapour.

The scatter of the daily mean values is significantly smaller. For the comparison with SSM/I data it is about 0.1–0.2 g/cm$^2$, and even less ($\sim$0.1 g/cm$^2$) for the comparison with ECMWF.

The monthly averages are quite constant over the year 2003. The SCIAMACHY water vapour columns are in the order of 0.2 g/cm$^2$ lower than the corresponding SSM/I results whereas the typical deviation between SCIAMACHY and ECMWF data is only $-0.05$ g/cm$^2$ which is one magnitude lower than the observed daily scatter. Thus, the SCIAMACHY data agree very well with ECMWF data throughout the year.

4.2 Monthly means

Monthly means of SCIAMACHY and ECMWF data have been computed by averaging all available data for a specific month at each grid point. No special weighting is necessary, because only data of the same geolocation are averaged.

Figure 3 shows the resulting means of SCIAMACHY total water vapour column data for the months January, April, July and October 2003, corresponding to different seasons.

The overall picture of the SCIAMACHY monthly means seems quite reasonable. The SCIAMACHY results are quite similar to the corresponding water vapour monthly means derived from ECMWF data displayed in Fig. 4. There is high humidity in the tropics, low humidity at higher latitudes. The movement of the inner tropical convergence zone (ITCZ) with season is clearly visible from the shift of high water vapour columns in the tropics.
For some regions there are no SCIAMACHY water vapour data available (white areas in Fig. 3). Except for those northern or southern regions, where there are no SCIAMACHY data because of a too high solar zenith angle, these gaps are mainly caused by the incomplete SCIAMACHY Level 1 data set; this is especially evident in November 2003 (not shown) where no data over the Atlantic ocean are available. However, there are also some regions where there are no SCIAMACHY water vapour data for the whole year, like over the Himalaya and the Andes. These gaps are not caused by missing Level 1 data but they correspond to regions which are regularly masked out by the AMC-DOAS quality check. This is expected, because the background atmosphere of high mountain areas is extremely different from the one assumed in the retrieval. In fact, this shows that the AMC-DOAS quality check is working correctly, which adds confidence to the SCIAMACHY AMC-DOAS water vapour data product.

There are also some differences between SCIAMACHY and ECMWF data. For example, in summer 2003 the humidity over the Sahara desert is much higher in SCIAMACHY data than expected from the ECMWF model data. This can be seen more clearly in Fig. 5, where the absolute differences between SCIAMACHY and ECMWF water vapour monthly means are plotted. Noting that any deviation below the typical scatter of the water vapour data of 0.5 g/cm² (i.e. the green areas on the plots) can be considered as a good agreement, the difference plots show in general quite encouraging results.

Looking a bit more into the details of Fig. 5 reveals that the agreement between SCIAMACHY and ECMWF data over land seems to be somewhat better than over ocean. Ocean areas are quite noisy in the difference plots. The SCIAMACHY data over ocean tend to be lower than the corresponding ECMWF monthly means. This is in line with the results of the comparison with SSM/I data in the previous subsection. Over the continents, the agreement between both data sets is quite good except for some specific regions at certain times where SCIAMACHY columns are higher than the ECMWF values. This over-estimation of the water vapour content by SCIAMACHY (or the under-estimation by the ECMWF model) seems to occur preferably over desert regions like the above mentioned southern Sahara during summer and western parts of North America. This may indicate an influence of the surface albedo. In addition, the different surface elevation which is is not considered by the AMC-DOAS retrieval may play a role. On the other hand, problems of the ECMWF model data at these regions can also not be excluded, because it is unclear how many real measurements (e.g. radio sonde data) went into the model at these locations.

Furthermore, the different temporal and spatial coverage of SCIAMACHY and ECMWF data may play a role here. As long as there are still large amounts of SCIAMACHY Level 1 data missing no final conclusion on the quality of a monthly mean product can be drawn.
5 Summary and conclusions

A first preliminary validation of SCIAMACHY water vapour columns derived by the AMC-DOAS method has been performed. The interpretation of the results of this effort is somewhat limited by the amount of currently available SCIAMACHY calibrated spectra. Comparisons with SSM/I and ECMWF data for the year 2003 show in general a good agreement. A high scatter of about 0.5 g/cm² is visible throughout the year. This scatter is mainly caused by atmospheric variability which in general makes a validation of water vapour columns more difficult.

The global mean SCIAMACHY AMC-DOAS water vapour columns tend to be lower than the correlative data. The agreement of SCIAMACHY results with ECMWF data is somewhat better than with SSM/I data which confirms previous findings which were based on a smaller data set.

As a first step towards a SCIAMACHY (or GOME-type) water vapour climatology reasonable global maps of monthly mean water vapour columns could be derived. Comparisons with corresponding ECMWF monthly means showed in general a good agreement, although there are some discrepancies especially over ocean and desert areas which require further investigation.

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Comparisons between SCIAMACHY and ground-based FTIR data for total columns of CO, CH$_4$, CO$_2$ and N$_2$O

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Abstract. Total column amounts of CO, CH$_4$, CO$_2$ and N$_2$O retrieved from SCIAMACHY nadir observations in its near-infrared channels have been compared to data from a ground-based quasi-global network of Fourier-transform infrared (FTIR) spectrometers. The SCIAMACHY data considered here have been produced by three different retrieval algorithms, WFM-DOAS (version 0.5 for CO and CH$_4$ and version 0.4 for CO$_2$ and N$_2$O), IMAP-DOAS (version 1.1 and 0.9 (for CO)) and IMLM (version 6.3) and cover the January to December 2003 time period. 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. Particular attention has been given to the question whether SCIAMACHY observes correctly the seasonal and latitudinal variability of the target species. The present results indicate that the individual SCIAMACHY data obtained with the actual versions of the algorithms have been significantly improved, but that the quality requirements, for estimating emissions on regional scales, are not yet met. Nevertheless, possible directions for further algorithm upgrades have been identified which should result in more reliable data products in a near future.

1 Introduction

The SCIAMACHY instrument (Burrows et al., 1995; Bovensmann et al., 1999, 2004) onboard ENVISAT makes nadir observations in the near-infrared (NIR; 0.8–2.38 µm) of the most important greenhouse gases such as water vapour (H$_2$O), carbon dioxide (CO$_2$), methane (CH$_4$), and nitrous oxide (N$_2$O), and of the ozone precursor gas carbon monoxide (CO), which also acts as an important indirect greenhouse gas as it significantly impacts the OH budget. SCIAMACHY is among the first satellite instruments that can measure greenhouse gases in the troposphere on a global scale. Its predecessor instrument GOME (Global Ozone

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Fig. 1. Distribution of stations contributing to the delivery of correlative g-b FTIR data for comparisons with SCIAMACHY products – see also Table 1.

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

<table>
<thead>
<tr>
<th>Station</th>
<th>Lat N</th>
<th>Lon E</th>
<th>Altitude(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ny Alesund</td>
<td>78.91</td>
<td>11.88</td>
<td>20</td>
</tr>
<tr>
<td>Kiruna</td>
<td>67.84</td>
<td>20.41</td>
<td>419</td>
</tr>
<tr>
<td>Harestua</td>
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<td>10.75</td>
<td>580</td>
</tr>
<tr>
<td>Zugspitze</td>
<td>47.42</td>
<td>10.98</td>
<td>2964</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>46.55</td>
<td>7.98</td>
<td>3580</td>
</tr>
<tr>
<td>Egbert</td>
<td>44.23</td>
<td>−79.78</td>
<td>251</td>
</tr>
<tr>
<td>Toronto</td>
<td>43.66</td>
<td>−79.40</td>
<td>174</td>
</tr>
<tr>
<td>Izaña</td>
<td>28.30</td>
<td>−16.48</td>
<td>2367</td>
</tr>
<tr>
<td>Wollongong</td>
<td>−34.45</td>
<td>150.88</td>
<td>30</td>
</tr>
<tr>
<td>Lauder</td>
<td>−45.05</td>
<td>169.68</td>
<td>370</td>
</tr>
<tr>
<td>Arrival heights</td>
<td>−77.85</td>
<td>166.78</td>
<td>190</td>
</tr>
</tbody>
</table>

Monitoring Experiment) does not include the channels in the NIR (Burrows, et al., 1999). IMG (Interferometric Monitor of Greenhouse Gases) flew onboard ADEOS in 1997 to make nadir measurements in the thermal infrared (TIR), but failed after a few months of operation (Kobayashi et al., 1999). At present, MOPITT (Measurements Of Pollution In The Troposphere, Drummond and Mand, 1996) is delivering only CO profile data retrieved from the TIR channels; the expected CH$_4$ products are still unavailable due to instrument calibration problems (MOPITT Web site http://eosweb.larc.nasa.gov/PRODOCS/mopitt/table_mopitt.html). SCIAMACHY measurements in the NIR have the important advantage over TIR measurements that they are sensitive down to the earth’s surface, where most emission sources are located, whereas thermal infrared measurements have a reduced sensitivity in the boundary layer. It is very important therefore to thoroughly investigate the potential capabilities of SCIAMACHY in its NIR channels.

The purpose of the current validation is to identify quantitatively to what extent the SCIAMACHY NIR products generated by various scientific institutes in Europe can be exploited for global geophysical studies. It therefore addresses the consistency of the data to represent the variations of the CO, CO$_2$, CH$_4$ and N$_2$O fields with season, latitude, etc. This is done 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 FTIR spectrometers. Other complementary validation efforts have been made, such as comparisons with data from other satellites, e.g., with CO data from MOPITT, or with analyses from global chemistry models such as TM3 (Heimann and Körner, 2003) or TM5 (Krol et al., 2004), and have been reported by Buchwitz et al. (2005a) and de Beek et al. (2005); Gloudemans et al. (2005); Straume et al. (2005).

The SCIAMACHY data for CO, CH$_4$, CO$_2$ and N$_2$O total columns investigated in this paper have been produced by the algorithms WFM-DOAS v0.5 and v0.4 (Weighting Function Modified DOAS, Institute for Environmental Physics, University of Bremen (Buchwitz et al., 2000, 2004, 2005a, b; de Beek et al., 2006)), IMLM v6.3 (Iterative Maximum Likelihood Method, SRON (Schriwer, 1999; Gloudemans et al., 2005, 2004; de Laat et al., 2006)) and IMAP-DOAS v1.1 and v0.9 (Iterative Maximum A Posteriori-DOAS, University of Heidelberg (Frankenberg et al., 2005a, c)). So far, CO$_2$ and N$_2$O data products have been provided by WFM-DOAS v0.4 only. Only those retrieval products which are open to public use have been validated. The data provided for this validation exercise cover the January to December 2003 time period, and thus offer a much better basis for validation than the limited data set that was available for previous exercises (De
Mazière et al., 2004). Since then, some algorithm updates have also been implemented. For more in depth information about the SCIAMACHY retrieval algorithms and data products, the reader is referred to the above cited references.

The characteristics of the correlative ground-based FTIR data are described in the next section. Section 3 presents the conditions that have been verified for carrying out the comparisons. The comparison methodology and the results of the comparisons are discussed in Sect. 4, successively for CO, CH₄ and N₂O and CO₂. Conclusions are drawn in Sect. 5.

2 The ground-based correlative data

The ground-based (g-b) correlative data are collected from 11 FTIR spectrometers that are operated at various stations of the Network for the Detection of Stratospheric Change (NDSC, http://www.ndsc.ws). They have been submitted to the Envisat Cal/Val database at NILU or directly to BIRA-IASB and have been compiled by us as part of the commitment in the Envisat AO ID 126 “Validation of ENVISAT-1 level-2 products related to lower atmosphere O₃ and NOₓ”.

Figure 1 and Table 1 identify the locations of the contributing stations. While the stations cover almost the entire global latitude band, several regions of specific interest (the tropics, Central Africa, China) are not covered.

The g-b FTIR data are obtained from daytime solar absorption measurements under clear-sky conditions. G-b FTIR data can also be obtained from lunar absorption measurements at near full noon, e.g., in polar night conditions at high northern and southern latitude stations: such lunar absorption data are not included in the present data set however.

Figure 2 shows the database of the CO, CH₄, N₂O and CO₂ g-b data products, respectively, available at BIRA-IASB for the present validation exercise, and the stations for which the respective data was available. For comparison purposes, all data have been converted to average volume mixing ratios (vmrs) using ECMWF pressure data, as explained hereinafter (Eq. 1).

Regarding CO (Fig. 2a) seasonal variations are quite pronounced (amplitude of about 50%), with a maximum by the end of local spring, determined by the availability of OH, which is the major sink for CO. Large excursions in the CO
column amounts are observed at Wollongong: they can probably be attributed to biomass burning events. Also, the ground-based FTIR data (Fig. 2b) clearly illustrate the interhemispheric gradient of CH$_4$ that amounts to $\sim$15% going from the South Pole (Arrival Heights) to the maximum values at northern latitudes (Izaña). One also observes a small seasonal variation of CH$_4$ (of the order of 5%) that is more distinct in the Northern Hemisphere than in the southern one. The CH$_4$ minimum in the Northern Hemisphere occurs at the beginning of the year, i.e., around mid-winter. N$_2$O has a very small seasonal variation; also the variability over the entire data set is less than 15%. The CO$_2$ data set is limited to 3 ground stations, with only very few data at Ny Alesund as seen in Fig. 2d.

Due to the inherent different properties of FTIR and SCIAMACHY measurements, the validation is not straightforward and several issues need to be resolved in order to perform a proper intercomparison. These issues are, (1) how to deal with different ground station altitudes, (2) the data availability, (3) the precision and accuracy of the data, and (4) the difference in observed air masses.

(1) The first issue concerns the difference in altitude between the SCIAMACHY ground pixel height and the FTIR measurement location. Because the target molecules have most of their total concentration in the lower troposphere, the total column amount is strongly dependent on the observatory’s or 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:

$$C_{vmr} = C_{totcol}/(P \times 2.12118e11) \hspace{1cm} (1)$$

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 SCIAMACHY data, using the pressure corresponding to the mean altitude of the observed ground pixel, for these data sets which do not have so-called dry air normalised data products (see Sect. 3). 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, which is the best assumption at hand in the absence of auxiliary information, but still relatively crude. The approximation is best for CO$_2$, having a nearly constant volume mixing ratio throughout the whole atmosphere, relatively good for CH$_4$ and N$_2$O 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 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 vms are multiplied by a profile correction factor prior to any further comparison. This factor was derived by taking the ratio of the calculated TM4 (Meirink et al., 2006) vmr above the mountain station altitude and above ground level (as determined by the model’s orography) at the stations geo-location. Note that the spatial resolution of the model ($2 \times 3^\circ$) 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 2003 day since for several stations a small but clear seasonal dependence of this factor was noticeable (see Fig. 3). The impact of such a correction is only significant for the three high altitude stations as one can see from their mean values listed in Table 2 and on their bias values only. It did not have any significant impact on the scatter or seasonality. No model profile N$_2$O and CO$_2$ data was available, but the impact is deemed to be far less important, nor is any deviant behaviour for the high altitude stations observed.

(2) The second issue (data availability) concerns the amount of available g-b data. One must remember that the g-b FTIR observations require clear-sky conditions. Consequently the g-b FTIR database does not represent a daily coverage, even if most stations are operated on a quasi-continuous basis. This limits of course the number of possible coincidences with SCIAMACHY overpasses. Moreover for some ground-based stations the available data sets do not cover the entire January till December 2003 time period. To maximize data overlap between SCIAMACHY observations and FTIR g-b measurements, and to ensure a statistically significant correlative data set, the SCIAMACHY data that meet the spatial collocation criteria (see Sect. 3) are not compared on the basis of temporal overlap with the g-b data. Instead, we developed an alternative method in which the

<table>
<thead>
<tr>
<th>station</th>
<th>CO mean correction</th>
<th>CH$_4$ mean correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ny Alesund</td>
<td>1.0013</td>
<td>1.0004</td>
</tr>
<tr>
<td>Kiruna</td>
<td>1.0052</td>
<td>1.0015</td>
</tr>
<tr>
<td>Harestua</td>
<td>1.0006</td>
<td>1.0001</td>
</tr>
<tr>
<td>Zugspitze</td>
<td>0.8486</td>
<td>0.9811</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>0.7882</td>
<td>0.9703</td>
</tr>
<tr>
<td>Egbert</td>
<td>1.0078</td>
<td>1.0007</td>
</tr>
<tr>
<td>Toronto</td>
<td>1.0384</td>
<td>1.0028</td>
</tr>
<tr>
<td>Izaña</td>
<td>0.9107</td>
<td>0.9854</td>
</tr>
<tr>
<td>Wollongong</td>
<td>1.0052</td>
<td>1.0005</td>
</tr>
<tr>
<td>Lauder</td>
<td>1.0074</td>
<td>1.0022</td>
</tr>
<tr>
<td>Arrival heights</td>
<td>0.9989</td>
<td>0.9993</td>
</tr>
</tbody>
</table>
SCIAMACHY measurements are compared with the corresponding (in time) interpolated value of a third order polynomial fit through the FTIR g-b data, rather than with the FTIR data themselves. To ensure consistency between all stations, all FTIR data points, if not already daily averages, have been converted to daily averages prior to any further manipulations such as the normalisation using ECMWF daily pressure data and the subsequent 3rd order polynomial fitting procedure. This third order polynomial fit gives a good representation of the seasonal variability (see example in Fig. 4a), but loss of information as to daily variability and as to possible short term events cannot be avoided. Furthermore, locations with strong daily variability may exhibit differences/biases between SCIAMACHY and FTIR if the time of a significant number of FTIR measurements differs a lot from 10:00 h local time, i.e. the SCIAMACHY overpass time. The data comparisons have been limited to the same time periods during which g-b data are available to avoid gross extrapolation errors. This explains why there are no g-b data available for inter-comparisons during the polar night at high-latitude stations. This method, which significantly increases the number of coincident data, allows us to study the latitudinal dependence over a wider range of stations whereas the usual validation method, considering only daily coincidences, failed to provide sufficient, if at all, overlapping data, especially for stations near the poles where the amount of SCIAMACHY data points is limited. The latter is due to the difficulties of cloud filter algorithms to distinguish between ice and clouds and to the high solar zenith angles over these regions leading to low signal to noise ratios, and thus larger errors in the retrieved total columns.

The standard deviations of the ground-based data with respect to their 3rd order fit, or

$$
\text{std} \left( \frac{y_i^{GB} - y_i^{PF}}{y_i^{PF}} \right)
$$

(with $y_i^{GB}$ the individual ground-based daily averaged volume mixing ratios on day i, and $y_i^{PF}$ the corresponding values from the 3rd order polynomial fit) are, on average, 9.5% for CO (the average standard deviation drops to 7.0% when excluding the Wollongong measurements), 1.15% for CH$_4$, and 1.16% for N$_2$O and 1.12% CO$_2$. The individual values per station are provided in Tables 6–9 hereinafter.

(3) The third issue, that of data precision and accuracy, has been discussed partially above. Individual g-b FTIR data for N$_2$O, CO, CO$_2$ and CH$_4$ have a precision in the order of a few percent (<5%). Because of the adopted approach to use interpolated (fit) values instead of original measurement data, the effective precision of the g-b correlative data is set by the values listed in Table 3. It is important to realise that the thus obtained scatter includes the natural day-to-day variability.

Conservative estimates for the accuracies considering the entire FTIR network are 3% for N$_2$O and CO$_2$, and 7% for CO and CH$_4$. Network accuracies are continuously improved over time by adopting some agreements among the contributing stations regarding the choice of spectral data analysis parameters. For example, this has been done recently in the UFTIR project for CO, N$_2$O and CH$_4$ (http://www.nilu.no/uftir).

**Table 3.** Percentage scatter on the daily mean FTIR and SCIAMACHY data, collocated on the large spatial grid. Also indicated are the target precisions set for the SCIAMACHY data. Data marked by * are dry air normalised products, typically denoted by an X such as XCH$_4$.

<table>
<thead>
<tr>
<th></th>
<th>FTIR</th>
<th>WFM-DOAS</th>
<th>IMLM</th>
<th>IMAP</th>
<th>Desired precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>9.49</td>
<td>25.1</td>
<td>22.4</td>
<td>23.5*</td>
<td>5–10</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.15</td>
<td>1.93*</td>
<td>3.14</td>
<td>1.09*</td>
<td>1</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>1.16</td>
<td>9.31*</td>
<td>3.78</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.12</td>
<td>3.78*</td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Fig. 3. Typical examples of TM4 profile correction factors as a function of time. (a, b) TM4 profile correction factor for CH$_4$ and CO Izanä, exhibiting exceptionally strong seasonality. (c) TM4 profile correction factor for CH$_4$ and CO Jungfraujoch, exhibiting a moderate seasonality (an example of Jungfraujoch CH$_4$ is given in Fig. 4b).
(4) 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 (see further in Sect. 3), the pixel size is $30 \times 120 \text{ km}^2$, for Channel 6 products $30 \times 60 \text{ km}^2$ (see Table 4 for the used SCIAMACHY channels for each algorithm). 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 data set, the spatial collocation criteria include all SCIAMACHY pixels centred on the FTIR ground-station coordinates (for the small grid and large grid collocation, respectively – see Sect. 4), 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.

3 The SCIAMACHY data and selection criteria for comparison

The retrieval methods discussed in this paper (WFMD-DOAS (henceforth called WFMD), IMLM and IMAP-DOAS (henceforth called IMAP)) not only use different mathematical retrieval algorithms, but also obtain their data for CO, CH$_4$, N$_2$O and CO$_2$ from different spectral channels and wavelength regions: an overview hereof is given in Table 4. Each of the channels/windows has its own distinct features and associated problems. For instance the SCIAMACHY NIR Channels 7 and 8 are affected by ice layer build-up on the detectors, which is countered by regular decontamination of the instrument (Bovensmann et al., 2004). Also, not all the SCIAMACHY data sets considered for the present comparisons cover the complete year 2003: the IMLM data set contains no data for July and August, and WFMD only contains data from January till October. While the CH$_4$ IMAP data set covers the entire 2003 time period their CO data set lacks measurements for August. Due to the fact that the January to December 2003 time frame includes periods of lower transmission and ice decontamination of the SCIAMACHY instrument, differences in the considered time periods may lead to apparent differences in the final comparison results when evaluating the algorithms. Some differences may also occur because of the seasonal variation of the inter-hemispheric latitudinal gradient of some species, notably CO.

It must also be noted that for WFMD and IMAP, the final data products, henceforth denoted as XCH$_4$, XCO$_2$, XN$_2$O and XCO, are the total column values of said species divided by the total column values of either CO$_2$ (for CH$_4$), O$_2$ (XCO$_2$ and XN$_2$O) or CH$_4$ (XCO), all 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 $XCH_4 = \frac{CH_4 \text{ (molec cm}^{-2})}{368e3 \text{ (ppb)/CO}_2 \text{ (molec cm}^{-2})}$. The only exception is WFMD CO, which uses CH$_4$ measurements (from the same fitting window) to correct the total column values but does not provide dry air normalized XCO vmrs (de Beek et al., 2006). 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. In order to maximize the possibility for such cancellation of retrieval errors, the spectral windows for the retrieval of the species and its dry air proxy must be as close as possible. In the case of XCO and XCH$_4$, the dry air proxies CH$_4$ and CO$_2$ respectively are derived from the same spectral channel. For XCO$_2$ and XN$_2$O, O$_2$ is retrieved from another channel (Channel 4). An additional (small) error is introduced into the normalized product by treating the expected dry air proxy vmr as a constant, neglecting its seasonal and latitudinal variability. Therefore this constant scaling factor is sometimes, but not for this validation, replaced by a variable expected vmr based on a global model (Frankenberg et al., 2006). For the purpose of this validation, in those cases where dry air normalised products are available, these products are used instead of the total column measurements scaled by the ECMWF pressure.

### Table 4. Selection of spectral channels and microwindows for the retrieval of CO, CH$_4$, N$_2$O and CO$_2$ in the different retrieval methods considered.

<table>
<thead>
<tr>
<th></th>
<th>WFMDv0.5 (v0.4 for N$_2$O and CO$_2$)</th>
<th>IMLMv6.3</th>
<th>IMAPv1.1 (v0.9 for CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Channel 8: 2324.2–2334.9 nm</td>
<td>Channel 8: 2324.5–2337.9 nm</td>
<td>Channel 8: 2324.2–2334.9 nm</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Channel 6: 1629.0–1671.0 nm</td>
<td>Channel 8: 2324.5–2337.9 nm</td>
<td>Channel 6: 1630.0–1670.0 nm</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>Channel 8: 2265.0–2280.0 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Channel 6: 1558.0–1594.0 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Selection criteria associated with accepted error levels for the SCIAMACHY data included in the comparisons with ground-based data.

<table>
<thead>
<tr>
<th>Algorithm</th>
<th>Selection criteria (in addition to spatial and temporal collocation criteria)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WFMD</td>
<td>For XN₂O and XCO₂: Cloud-free, Over land (altitude &gt;0), Solar Zenith Angle &lt;85 deg, Error (fitting) &lt;10% for CO₂, &lt;60% for N₂O, only forward scan pixels. For XCH₄ and CO: Only data that are marked as good by the v0.5 data file quality flag</td>
</tr>
<tr>
<td>IMLM</td>
<td>Cloud-free, Albedo ≥ 0.01, Instrument-noise related Error &lt;2E18 molec cm⁻² for CH₄ (~5%) and &lt;1.5E18 molec cm⁻² for CO, Solar Zenith Angle &lt;80 deg</td>
</tr>
<tr>
<td>IMAP</td>
<td>For CH₄ data: [Vertical Column Density of CO₂/\exp(-surface elevation(m)/8500)] &gt; 7E21 molec cm⁻² and variance of fit residual &lt; 0.5%</td>
</tr>
<tr>
<td></td>
<td>For CO data: variance of the fit residual (without weighting) &lt; 0.017, weighted variance of the fit residual between 10 and 0.1, error &lt; 7E17 molec cm⁻² and &lt; 30%</td>
</tr>
</tbody>
</table>

The data products for SCIAMACHY give reliable values only for cloud-free pixels because clouds are not transparent in the NIR (Buchwitz et al., 2000, 2004; Gloudemans et al., 2005; Straume et al., 2005) and thus effectively take over the role of the earth’s surface. Since the highest concentrations of the target species are found close to the earth’s surface, where the air pressure is the highest and where the sources and sinks are located, interpreting cloud-contaminated columns as total columns can lead to large errors in the analysis. The different algorithms investigated here use different cloud detection schemes (Buchwitz et al., 2004, 2005a; de Beek et al., 2006; Gloudemans et al., 2005) resulting in different cloud masks and methods dealing with clouds. In some cases they do not mask all cloudy pixels and in other cases they may be too restrictive, because they cannot distinguish between ice- or snow-covered surfaces and clouds, resulting in loss of data. This implies that some comparisons with g-b FTIR data may still suffer from the presence of clouds in the SCIAMACHY observation. The current IMAP method does not contain a cloud detection algorithm for CO. For XCH₄, IMAP and WFMD filter their measurements based on a lower threshold for the height-corrected CO₂ column: the column must be at least 89% of the expected total column assuming constant CO₂. 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 (see de Beek et al., 2006).

In addition to the above, for low albedo values, the precision of the cloud-free SCIAMACHY data is strongly influenced by the albedo of the observed ground-pixel, because it determines to a large extent the signal-to-noise ratio of the corresponding observed spectra. This explains why data over ocean (water) are less reliable than data over land. Also measurements with a high solar zenith angle (typically at the Earth’s poles), lead to low signal to noise ratios, and thus larger errors in the retrieved total columns. A restriction on the accepted solar zenith angles therefore further limits the size of the comparison data set at northern and southern high-latitude stations.

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 ±2.5° latitude and ±10° longitude of the FTIR ground station (hereinafter indicated as the large collocation grid). Data that have been taken closer to each other (within ±2.5° latitude and ±5° 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.

Additional selection criteria have been applied to the SCIAMACHY data, based on confidence limits as described in the Product Specification Document (available at http://www.sciamachy.org/validation/) or given by the data providers. These confidence limits are different for the different algorithms, because they estimate the errors differently. For example, WFMD includes spectral fit errors in the final error estimate, whereas the error reported by IMLM only accounts for instrument-noise related errors, and therefore appears to be smaller. The additional selection criteria that have been applied to the SCIAMACHY data from each algorithm are listed in Table 5.

In summary, the comparisons are made for dry air normalised products, hereinafter simply called the data, and are limited to (1) cloud-free SCIAMACHY data, according to the individual cloud detection schemes from individual algorithms, (2) having the centre of the SCIAMACHY pixel within the spatial collocation area around the location of the g-b site, as outlined above, and (3) satisfying the additional selection criteria listed in Table 5. 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, as explained in Sect. 2.
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 (Buchwitz et al., 2004; Sussmann and Buchwitz, 2005; Sussmann et al., 2005). The associated smoothing errors for both data sets 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.

4 The comparisons between timeseries of g-b FTIR network and SCIAMACHY data of CO, CH₄, CO₂ and N₂O total column amounts

4.1 Comparison methodology

Time series of the relative differences between the selected SCIAMACHY individual mean vmrs ($x_{SCIA}^j$) and the corresponding values from the 3rd order polynomial interpolation through the normalised g-b FTIR daily network data ($x_{PF}^j$), i.e., $[(x_{SCIA}^j - x_{PF}^j)/x_{PF}^j]$ have been made for all the different SCIAMACHY algorithms and target products. An example for CH₄ from the IMAP algorithm at the Jungfraujoch station is shown in Fig. 4. An overall weighted bias over the considered time period, $b$, was calculated for each target product, algorithm and station, following

$$b = \text{mean}_w \left( \frac{x_{SCIA}^j - x_{PF}^j}{x_{PF}^j} \right)$$

Fig. 4. Time series of CH₄ measurements at Jungfraujoch from g-b FTIR (+) and SCIAMACHY IMAP-DOAS (open squares for large collocation grid; * for small collocation grid). (a) original XCH₄ data points (symbols) and 3rd order polynomial fit through the FTIR ground-based data (solid line). (b) TM4 profile correction factor as a function of time. (c) XCH₄ data points (symbols) after the application of the correction factor and 3rd order polynomial fit through the FTIR ground-based data (solid line). (d) Corresponding time series of relative biases, (SCIAMACHY-FTIR)/FTIR, of IMAP-DOAS versus g-b interpolated data. Listed in the legend are the average bias, the standard deviation and the number of data points for the IMAP-DOAS data sets as well as the average bias and standard deviation of the FTIR data relative to their polynomial fit.
in which the weighted mean, \( \text{mean}_w \), of a data set which consists of \( N \) elements \( x_j \) is given by the general expression
\[
\text{mean}_w(x) = \frac{1}{N} \sum_{j=1}^{N} w_j x_j
\] (4)

with \( w_j \) the weight of the individual data. In our case \( w_j = 1/(\text{err}_j)^2 \) in which \( \text{err}_j \) is the error on the individual measurement as given by the data providers. Note that the definition of the error changes with each algorithm and may or may not include instrument and/or fitting errors. The thus calculated biases are listed in Tables 6 to 9. A globally averaged weighted bias (i.e., a mean over all stations) was calculated as well and is also listed in the same corresponding Tables. The weighted standard errors on the biases reported in Tables 6 to 9 are given by
\[
\frac{3}{\sqrt{N}} \times s_d_w \left( \frac{x_j^{\text{SCIA}} - x_j^{\text{PF}}}{x_j^{\text{PF}}} \right)
\] (5)
in which the weighted standard deviation, \( s_d_w \), of a data set which consists of \( N \) elements \( x_j \) is given by the general expression:
\[
s_d_w(x) = \left[ \frac{N'}{\sum_{j=1}^{N'} w_j (x_j - \bar{x}_w)^2} \right]^{1/2}
\] (6)
with \( N' \), the number of non-zero weights.

It should be mentioned that the number of correlative data points can vary greatly from station to station (from 0 to several thousands). Due to different selection criteria and cloud filtering procedures for the three algorithms the number of collocations also varies between algorithms and thus precisions may vary accordingly. These numbers of correlative data points are indicated also in Tables 6 to 9. It must be kept in mind that the obtained absolute value of the overall bias can often be explained by slightly wrong slit functions and/or spectral parameters (Gloudemans et al., 2005); in some cases (WFMD v0.4 XN2O and XCO2) the SCIAMACHY data have been scaled according to a chosen reference value (Buchwitz et al., 2005a) (0.66 for N2O and 1.27 for CO2). Similarly the associated error is strongly influenced by the exact choice of error criteria.

We have also evaluated the scatter of the selected SCIAMACHY measurements, \( \sigma_{\text{scat}} \), for each station, algorithm and target species, for comparison with the corresponding ones of the FTIR data. To this end, the individual normalised SCIAMACHY measurements and their respective weights have been weighted averaged per day in order to be comparable with the scatter of the daily averaged FTIR data. Note that while the daily averages for the FTIR data are pure averages in time, the SCIAMACHY averages \( (\sigma_{\text{scat}}^{\text{SCIA}}) \) 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.

A bias of the daily-averaged measurements, \( y_i \), called \( b_{\text{day}} \) hereinafter, has then been calculated using the daily averaged SCIAMACHY values, as
\[
b_{\text{day}} = \text{mean}_w \left( \frac{y_i^{\text{SCIA}} - y_i^{\text{PF}}}{y_i^{\text{PF}}} \right)
\] (7)

Analogous to Eq. (3) \( \sigma_{\text{scat}} \) is then obtained as the statistical 1σ weighted standard deviation, of the daily averaged SCIAMACHY data \( (\sigma_{\text{scat}}^{\text{SCIA}}) \) with respect to the polynomial interpolation of the daily FTIR data, corrected for the daily bias \( (b_{\text{day}}) \), according to:
\[
\sigma_{\text{scat}} = s_d_w \left( \frac{y_i^{\text{SCIA}} - (1 + b_{\text{day}}) y_i^{\text{PF}}}{(1 + b_{\text{day}}) y_i^{\text{PF}}} \right)
\] (8)

The resulting values of \( \sigma_{\text{scat}} \) for the large collocation grid are summarized in Table 3, together with the scatter on the g-b FTIR data and the desired target precision for each species. These targets have been set in order to accurately detect the global sources and sinks of these species, and their evolutions (Barrie et al., 2004; Bréon et al., 2003). The complete set of \( \sigma_{\text{scat}} \) values, including those from small grid collocated measurements, are listed in Tables 6 to 9.

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 Figs. 7, 10, 11, 12 and 13, again for all target products, algorithms 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
\[
\frac{3}{\sqrt{N_k}} \times s_d_w \left( x_{j,k}^{\text{SCIA}} \right)
\] (9)
in which \( N_k \) is the number of individual SCIAMACHY measurements, \( x_{j,k}^{\text{SCIA}} \), for month \( k \).

In the case of CO, we have also calculated monthly mean MOPITT CO data taken over a 2.5 by 10° collocation grid. The MOPITT profile data is used to calculate the total column values above station altitude after which ECMWF pressure data at these station altitudes is used to convert the MOPITT CO total columns into volume mixing ratios. So it was
Table 6. Summary of statistical results of comparisons between SCIAMACHY and FTIR g-b data for (X)CO. Bias is the calculated weighted bias (in %, see Eq. 3) 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. 5). \( n \) is the number of correlative individual SCIAMACHY data. \( \sigma_{\text{scat}} \) is the percentage 1σ weighted standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit (see Eq. 8). \( R \) is the correlation coefficient between the monthly mean SCIAMACHY and FTIR data and \( P \) is the probability of no-correlation.

<table>
<thead>
<tr>
<th>Algorithm → Station ↓</th>
<th>WFMD, SG CO v0.5</th>
<th>WFMD, LG CO v0.5</th>
<th>IMLM, SG CO v6.3</th>
<th>IMLM, LG CO v6.3</th>
<th>IMAP, SG XCO v0.9</th>
<th>IMAP, LG XCO v0.9</th>
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</thead>
<tbody>
<tr>
<td>Ny Alesund Bias</td>
<td>−7.99±3.16</td>
<td>−8.30±2.23</td>
<td>−5.62±37.8</td>
<td>−1.07±33.0</td>
<td>−2.34±2.62</td>
<td>−2.67±1.83</td>
</tr>
<tr>
<td>( n )</td>
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<td>2131</td>
<td>22</td>
<td>30</td>
<td>783</td>
<td>1575</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR=2.57)</td>
<td>21.6</td>
<td>16.7</td>
<td>7.14</td>
<td>15.8</td>
<td>24.7</td>
<td>21.9</td>
</tr>
<tr>
<td>Kiruna Bias</td>
<td>−7.68±3.78</td>
<td>−8.25±2.55</td>
<td>−8.51±25.0</td>
<td>−7.41±17.8</td>
<td>−2.35±3.05</td>
<td>−2.27±2.00</td>
</tr>
<tr>
<td>( n )</td>
<td>994</td>
<td>1956</td>
<td>40</td>
<td>76</td>
<td>632</td>
<td>1252</td>
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<tr>
<td>(( \sigma_{\text{scat}} ) FTIR=5.97)</td>
<td>30.4</td>
<td>21.9</td>
<td>40.7</td>
<td>42.4</td>
<td>29.6</td>
<td>22.8</td>
</tr>
<tr>
<td>Harestua Bias</td>
<td>−2.57±3.54</td>
<td>−4.75±2.62</td>
<td>6.92±20.7</td>
<td>6.07±18.4</td>
<td>−2.03±3.17</td>
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<td>141</td>
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<td>1466</td>
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<td>60.1</td>
<td>27.6</td>
<td>23.7</td>
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<tr>
<td>Zugspitze Bias</td>
<td>−5.29±4.88</td>
<td>−3.96±3.16</td>
<td>11.7±7.30</td>
<td>6.10±4.44</td>
<td>−18.8±2.76</td>
<td>−13.8±1.86</td>
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<td>523</td>
<td>1283</td>
<td>610</td>
<td>1329</td>
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<tr>
<td>(( \sigma_{\text{scat}} ) FTIR=5.96)</td>
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<td>36.0</td>
<td>26.2</td>
<td>26.0</td>
<td>24.7</td>
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<tr>
<td>Jungfraujoch Bias</td>
<td>−2.49±3.23</td>
<td>−2.00±2.24</td>
<td>−4.50±4.91</td>
<td>−7.71±3.32</td>
<td>−9.77±3.17</td>
<td>−10.7±2.13</td>
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<td>950</td>
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<td>1675</td>
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<td>30.7</td>
<td>28.9</td>
<td>27.5</td>
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<td>Egbert Bias</td>
<td>−1.15±2.98</td>
<td>−1.34±2.20</td>
<td>8.67±5.97</td>
<td>7.02±3.98</td>
<td>−8.13±2.22</td>
<td>−9.47±1.72</td>
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<tr>
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<td>2830</td>
<td>774</td>
<td>1705</td>
<td>976</td>
<td>1873</td>
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<tr>
<td>(( \sigma_{\text{scat}} ) FTIR=6.51)</td>
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<td>25.0</td>
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<td>Toronto Bias</td>
<td>−4.99±3.00</td>
<td>−4.92±2.22</td>
<td>6.98±5.70</td>
<td>4.58±3.81</td>
<td>−8.58±2.12</td>
<td>−9.91±1.74</td>
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<td>2699</td>
<td>806</td>
<td>1723</td>
<td>770</td>
<td>1519</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR=6.94)</td>
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<td>26.1</td>
<td>32.7</td>
<td>26.7</td>
<td>27.3</td>
<td>25.3</td>
</tr>
<tr>
<td>Izaña Bias</td>
<td>8.39±3.56</td>
<td>5.65±1.90</td>
<td>−13.5±3.12</td>
<td>−14.8±1.33</td>
<td>−2.01±1.95</td>
<td>−4.58±1.13</td>
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<td>( n )</td>
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<td>410</td>
<td>2290</td>
<td>1097</td>
<td>2910</td>
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<tr>
<td>(( \sigma_{\text{scat}} ) FTIR=6.83)</td>
<td>32.9</td>
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<td>13.7</td>
<td>18.9</td>
<td>17.9</td>
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<tr>
<td>Wollongong Bias</td>
<td>25.7±13.2</td>
<td>18.8±6.02</td>
<td>−19.4±3.95</td>
<td>−21.4±2.15</td>
<td>34.8±11.5</td>
<td>19.2±5.86</td>
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<td>( n )</td>
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<td>894</td>
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<td>432</td>
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<td>32.0</td>
<td>28.4</td>
<td>26.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Lauder Bias</td>
<td>18.9±8.25</td>
<td>22.6±5.83</td>
<td>28.1±31.9</td>
<td>28.7±31.7</td>
<td>40.0±9.00</td>
<td>48.9±6.96</td>
</tr>
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<td>( n )</td>
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<td>1257</td>
<td>66</td>
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<td>23.3</td>
<td>22.8</td>
</tr>
<tr>
<td>Arrival Heights Bias</td>
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<td>18.7±13.9</td>
<td>52.1±38.2</td>
<td>58.6±27.2</td>
<td>56.7±49.5</td>
<td>54.7±31.5</td>
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<td>234</td>
<td>12</td>
<td>23</td>
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<tr>
<td>(( \sigma_{\text{scat}} ) FTIR=4.34)</td>
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<td>41.6</td>
<td>67.1</td>
<td>54.7</td>
<td>34.4</td>
<td>30.8</td>
</tr>
</tbody>
</table>

Global Bias           | −0.61±1.28       | −0.004±0.87      | −11.1±1.76       | −14.7±0.90       | −4.47±0.99       | −4.99±0.68       |
| \( n \)               | 10567            | 22362            | 4719             | 12082            | 6557             | 14418            |
| (\( \sigma_{\text{scat}} \) FTIR=9.49) | 28.2             | 25.1             | 26.5             | 22.4             | 25.8             | 23.5             |
| \( R \)               | 0.79             | 0.86             | 0.79             | 0.83             | 0.53             | 0.53             |
| \( P \)               | 3.85E-19          | 4.12E-27         | 1.81E-13         | 2.30E-16         | 5.33E-6          | 1.64E-6          |

It is also very important to verify whether SCIAMACHY is able to reproduce the seasonal and latitudinal variations of the target species. A separate look at the latitudinal variation in the SCIAMACHY data can be easily derived from Tables 6 to 9 (in combination with Table 1) and is illustrated in Figs. 5 and 8, showing the bias as a function of latitude, per algorithm, for CO and CH\textsubscript{4} respectively.
Table 7. Summary of statistical results of comparisons between SCIAMACHY and ground-based FTIR data for sza corrected and uncorrected WFMD XCH$_4$ Bias is the calculated weighted bias (in %) of the SCIAMACHY data relative to the 3rd order polynomial fit through the ground based FTIR data for WFMD XCH$_4$ before (v0.5) and after the solar zenith angle correction (cor), using the small grid (SG =±2.5° LAT, ±5° LON) and large grid (LG =±2.5° LAT, ±10° LON) spatial collocation criteria (see Eq. 3). The indicated errors represent the weighted standard errors of the ensemble of individual weighted biases (see Eq. 5). n is the number of correlative individual SCIAMACHY data. $\sigma_{scat}$ is the weighted percentage 1σ standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit (see Eq. 8). R is the correlation coefficient between the monthly mean SCIAMACHY and FTIR data and P is the probability of no-correlation.

<table>
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<th>Algorithm →</th>
<th>WFMD, SG XCH$_4$ v0.5</th>
<th>WFMD, LG XCH$_4$ v0.5</th>
<th>WFMD, SG XCH$_4$ cor</th>
<th>WFMD, LG XCH$_4$ cor</th>
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<tr>
<td>Ny Alesund</td>
<td>Bias -3.94±1.90</td>
<td>−5.28±1.33</td>
<td>0.13±1.69</td>
<td>−1.26±1.16</td>
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<tr>
<td></td>
<td>n 39</td>
<td>90</td>
<td>39</td>
<td>90</td>
</tr>
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<td>kiruna</td>
<td>$\sigma_{scat}$ 2.44</td>
<td>3.17</td>
<td>1.81</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>n 2600</td>
<td>4486</td>
<td>2600</td>
<td>4486</td>
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<tr>
<td>harestua</td>
<td>$\sigma_{scat}$ 4.47</td>
<td>4.19</td>
<td>2.37</td>
<td>2.20</td>
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<td>n 1848</td>
<td>2186</td>
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<td>2186</td>
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<td>4.40</td>
<td>2.44</td>
<td>2.35</td>
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<td>1529</td>
<td>3741</td>
</tr>
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<td>8525</td>
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<td>42 072</td>
<td>19 621</td>
<td>42 072</td>
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<td>scat FTIR=0.62</td>
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<td>3.36</td>
<td>2.09</td>
<td>1.93</td>
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<td>4.93E-16</td>
<td>1.79E-19</td>
<td>2.02E-21</td>
</tr>
</tbody>
</table>

Another 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

Table 8. Summary of statistical results of comparisons between SCIAMACHY and FTIR g-b data for (X.CH₄). Bias is the calculated weighted bias (in %) of the SCIAMACHY data relative to the 3rd order polynomial fit through the ground based FTIR data for (X.CH₄, using the small grid (SG=±2.5° LAT, ±5° LON) and large grid (LG=±2.5° LAT, ±10° LON) spatial collocation criteria (see Eq. 3). The indicated errors represent the weighted standard errors of the ensemble of individual weighted biases (see Eq. 5). $n$ is the number of correlative individual SCIAMACHY data. $\sigma_{scat}$ is the weighted percentage 1σ standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit (see Eq. 8). $R$ is the correlation coefficient between the monthly mean SCIAMACHY and FTIR data and $P$ is the probability of no-correlation.

<table>
<thead>
<tr>
<th>Algorithm → Station ↓</th>
<th>WFMD, SG XCH₄ cor</th>
<th>WFMD, LG XCH₄ cor</th>
<th>IMLM, SG CH₄ v6.3</th>
<th>IMLM, LG CH₄ v6.3</th>
<th>IMAP, SG XCH₄ v1.1</th>
<th>IMAP, LG XCH₄ v1.1</th>
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</thead>
<tbody>
<tr>
<td>Ny Alesund Bias</td>
<td>0.13±1.69</td>
<td>-1.26±1.16</td>
<td>/</td>
<td>/</td>
<td>0.09±0.16</td>
<td>0.04±0.11</td>
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<td>($\sigma_{scat, FTIR}=0.62$)</td>
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<td>2.61</td>
<td>/</td>
<td>/</td>
<td>0.80</td>
<td>0.78</td>
</tr>
<tr>
<td>Kiruna Bias</td>
<td>-2.48±0.23</td>
<td>-2.07±0.17</td>
<td>-2.94±5.97</td>
<td>-2.63±4.42</td>
<td>-0.29±0.23</td>
<td>-0.004±0.16</td>
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<td>2.20</td>
<td>5.39</td>
<td>4.55</td>
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<td>1.03</td>
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<tr>
<td>Harestua Bias</td>
<td>-2.50±0.27</td>
<td>-2.33±0.25</td>
<td>-4.94±6.22</td>
<td>-4.33±5.84</td>
<td>0.66±0.25</td>
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<td>($\sigma_{scat, FTIR}=1.12$)</td>
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<td>2.35</td>
<td>9.71</td>
<td>9.59</td>
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<td>1.10</td>
</tr>
<tr>
<td>Zugspitze Bias</td>
<td>-2.02±0.21</td>
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<td>-4.22±0.97</td>
<td>-1.86±0.58</td>
<td>2.39±0.15</td>
<td>2.56±0.10</td>
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<tr>
<td>$n$</td>
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<td>351</td>
<td>945</td>
<td>1063</td>
<td>2387</td>
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<td>($\sigma_{scat, FTIR}=0.76$)</td>
<td>1.67</td>
<td>1.19</td>
<td>6.65</td>
<td>6.49</td>
<td>1.01</td>
<td>1.18</td>
</tr>
<tr>
<td>Jungfraujoch Bias</td>
<td>-3.74±0.12</td>
<td>-3.21±0.08</td>
<td>-4.75±0.61</td>
<td>-4.62±0.41</td>
<td>0.24±0.09</td>
<td>0.23±0.06</td>
</tr>
<tr>
<td>$n$</td>
<td>4247</td>
<td>8525</td>
<td>748</td>
<td>1585</td>
<td>2518</td>
<td>4837</td>
</tr>
<tr>
<td>($\sigma_{scat, FTIR}=0.71$)</td>
<td>1.28</td>
<td>1.31</td>
<td>5.13</td>
<td>4.65</td>
<td>1.09</td>
<td>1.23</td>
</tr>
<tr>
<td>Egbert Bias</td>
<td>-4.56±0.13</td>
<td>-4.75±0.09</td>
<td>-5.58±0.78</td>
<td>-6.10±0.54</td>
<td>-2.21±0.14</td>
<td>-2.36±0.10</td>
</tr>
<tr>
<td>$n$</td>
<td>3774</td>
<td>7516</td>
<td>426</td>
<td>923</td>
<td>1142</td>
<td>2379</td>
</tr>
<tr>
<td>($\sigma_{scat, FTIR}=1.41$)</td>
<td>1.86</td>
<td>1.63</td>
<td>4.72</td>
<td>4.37</td>
<td>1.27</td>
<td>1.18</td>
</tr>
<tr>
<td>Toronto Bias</td>
<td>-3.19±0.14</td>
<td>-3.32±0.10</td>
<td>-4.24±0.82</td>
<td>-4.74±0.55</td>
<td>-1.55±0.16</td>
<td>-1.67±0.11</td>
</tr>
<tr>
<td>$n$</td>
<td>3781</td>
<td>7426</td>
<td>428</td>
<td>960</td>
<td>1108</td>
<td>2315</td>
</tr>
<tr>
<td>($\sigma_{scat, FTIR}=1.69$)</td>
<td>2.06</td>
<td>1.90</td>
<td>5.13</td>
<td>4.43</td>
<td>1.42</td>
<td>1.33</td>
</tr>
<tr>
<td>Izanaora Bias</td>
<td>-3.45±0.12</td>
<td>-5.19±0.08</td>
<td>-1.58±0.41</td>
<td>-2.29±0.15</td>
<td>-1.52±0.07</td>
<td>-1.51±0.04</td>
</tr>
<tr>
<td>$n$</td>
<td>852</td>
<td>4397</td>
<td>400</td>
<td>2275</td>
<td>1880</td>
<td>5929</td>
</tr>
<tr>
<td>($\sigma_{scat, FTIR}=0.55$)</td>
<td>1.17</td>
<td>1.33</td>
<td>2.17</td>
<td>2.12</td>
<td>0.69</td>
<td>0.69</td>
</tr>
<tr>
<td>Wollongong Bias</td>
<td>-3.99±0.26</td>
<td>-4.12±0.12</td>
<td>-3.40±0.35</td>
<td>-3.24±0.19</td>
<td>-0.63±0.17</td>
<td>-0.52±0.10</td>
</tr>
<tr>
<td>$n$</td>
<td>484</td>
<td>1809</td>
<td>927</td>
<td>2474</td>
<td>798</td>
<td>2093</td>
</tr>
<tr>
<td>($\sigma_{scat, FTIR}=1.56$)</td>
<td>1.14</td>
<td>0.83</td>
<td>3.07</td>
<td>2.54</td>
<td>1.44</td>
<td>1.43</td>
</tr>
<tr>
<td>Lauder Bias</td>
<td>-0.77±0.49</td>
<td>-0.77±0.49</td>
<td>0.24±2.58</td>
<td>0.24±2.58</td>
<td>3.08±0.27</td>
<td>3.18±0.22</td>
</tr>
<tr>
<td>$n$</td>
<td>426</td>
<td>426</td>
<td>41</td>
<td>41</td>
<td>257</td>
<td>393</td>
</tr>
<tr>
<td>($\sigma_{scat, FTIR}=0.99$)</td>
<td>1.86</td>
<td>1.86</td>
<td>5.71</td>
<td>5.71</td>
<td>1.36</td>
<td>1.35</td>
</tr>
<tr>
<td>Arrival Heights Bias</td>
<td>-1.19±1.99</td>
<td>-2.89±0.38</td>
<td>-4.61±4.71</td>
<td>-4.69±5.23</td>
<td>4.35±2.33</td>
<td>4.83±1.83</td>
</tr>
<tr>
<td>$n$</td>
<td>41</td>
<td>1470</td>
<td>16</td>
<td>72</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>($\sigma_{scat, FTIR}=1.52$)</td>
<td>3.96</td>
<td>2.83</td>
<td>4.30</td>
<td>12.1</td>
<td>1.05</td>
<td>1.49</td>
</tr>
</tbody>
</table>

provide useful information. The value of this correlation coefficient depends not only on the effective correlation but also on the number of overlapping monthly mean data points. Next to the correlation coefficient $R$, we also tested for the hypothesis of no correlation. The latter is expressed by the $P$-value, also given in Tables 6 to 9, which is the probability of getting a correlation $R$ as large as the observed value by random chance, supposing the true correlation is zero. If $P$ is small, say less than 0.05, then the correlation $R$ is significant. The $P$-value is computed by transforming the correlation to a $t$-statistic having $n$-2 degrees of freedom, with $n$ the number of data points. The calculated $R$ and $P$ values give us a clear indication of how successful SCIAMACHY is in reproducing the overall variations in the g-b FTIR data. These
Table 9. Summary of statistical results of comparisons between SCIAMACHY and FTIR g-b data for WFMD XN\textsubscript{2}O and XCO\textsubscript{2}. Bias is the calculated weighted bias (in \%) of the SCIAMACHY data relative to the 3rd order polynomial fit through the ground based FTIR data for WFMD XCO\textsubscript{2} and XN\textsubscript{2}O, using the small grid (SG =±2.5° LAT, ±5° LON) and large grid (LG=±2.5° LAT, ±10° LON) spatial collocation criteria (see Eq. 3). The indicated errors represent the weighted standard errors of the ensemble of individual weighted biases (see Eq. 5). \( n \) is the number of correlative individual SCIAMACHY data. \( \sigma_{\text{scat}} \) is the weighted percentage 1\( \sigma \) standard deviation of the daily averaged SCIAMACHY measurements towards the bias corrected polynomial FTIR fit (see Eq. 8). \( R \) is the correlation coefficient between the monthly mean SCIAMACHY and FTIR data and \( P \) is the probability of no-correlation.

<table>
<thead>
<tr>
<th>Species →</th>
<th>Station ↓</th>
<th>WFMD, SG XN\textsubscript{2}O v0.4</th>
<th>WFMD, LG XN\textsubscript{2}O v0.4</th>
<th>WFMD, SG XCO\textsubscript{2} v0.4</th>
<th>WFMD, LG XCO\textsubscript{2} v0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ny Alesund*</td>
<td>Bias</td>
<td>−7.84±0</td>
<td>−10.2±7.58</td>
<td>−5.83±1.49</td>
<td>−6.09±1.25</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR CO\textsubscript{2}=0.23)</td>
<td>n</td>
<td>1</td>
<td>2</td>
<td>130</td>
<td>194</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.40)</td>
<td>( \sigma_{\text{scat}} )</td>
<td>0</td>
<td>3.98</td>
<td>4.07</td>
<td>5.36</td>
</tr>
<tr>
<td>Kiruna</td>
<td>Bias</td>
<td>−3.30±2.84</td>
<td>−2.92±2.18</td>
<td>219</td>
<td>406</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.40)</td>
<td>n</td>
<td>219</td>
<td>406</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Harestua</td>
<td>Bias</td>
<td>−3.36±3.05</td>
<td>−3.11±2.60</td>
<td>257</td>
<td>351</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.42)</td>
<td>n</td>
<td>257</td>
<td>351</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zugspitze</td>
<td>Bias</td>
<td>−1.11±2.54</td>
<td>0.43±1.70</td>
<td>255</td>
<td>540</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=0.99)</td>
<td>n</td>
<td>255</td>
<td>540</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jungfraujoch*</td>
<td>Bias</td>
<td>−2.68±1.36</td>
<td>−1.71±0.93</td>
<td>848</td>
<td>1755</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR CO\textsubscript{2}=0.21)</td>
<td>n</td>
<td>848</td>
<td>1755</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.01)</td>
<td>( \sigma_{\text{scat}} )</td>
<td>8.99</td>
<td>8.70</td>
<td>1896</td>
<td>4289</td>
</tr>
<tr>
<td>Egbert*</td>
<td>Bias</td>
<td>2.47±2.12</td>
<td>1.84±1.39</td>
<td>570</td>
<td>1183</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR CO\textsubscript{2}=2.63)</td>
<td>n</td>
<td>570</td>
<td>1183</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.55)</td>
<td>( \sigma_{\text{scat}} )</td>
<td>8.37</td>
<td>7.63</td>
<td>1580</td>
<td>3221</td>
</tr>
<tr>
<td>Toronto</td>
<td>Bias</td>
<td>4.06±2.26</td>
<td>3.42±1.41</td>
<td>543</td>
<td>1167</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.59)</td>
<td>n</td>
<td>543</td>
<td>1167</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Izaña</td>
<td>Bias</td>
<td>4.59±1.62</td>
<td>1.72±0.67</td>
<td>516</td>
<td>1656</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=0.55)</td>
<td>n</td>
<td>516</td>
<td>1656</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wollongong</td>
<td>Bias</td>
<td>−3.62±1.99</td>
<td>−3.52±1.09</td>
<td>136</td>
<td>480</td>
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<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.24)</td>
<td>n</td>
<td>136</td>
<td>480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lauder</td>
<td>Bias</td>
<td>0.95±7.35</td>
<td>0.95±7.35</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.08)</td>
<td>n</td>
<td>73</td>
<td>73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arrival Heights</td>
<td>Bias</td>
<td>15.2</td>
<td>15.2</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.14)</td>
<td>n</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Global</td>
<td>Bias</td>
<td>0.13±0.77</td>
<td>0.20±0.46</td>
<td>−6.91±0.20</td>
<td>−6.95±0.14</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR CO\textsubscript{2}=1.12)</td>
<td>n</td>
<td>3418</td>
<td>7613</td>
<td>3606</td>
<td>7704</td>
</tr>
<tr>
<td>(( \sigma_{\text{scat}} ) FTIR N\textsubscript{2}O=1.16)</td>
<td>( \sigma_{\text{scat}} )</td>
<td>9.51</td>
<td>9.31</td>
<td>3.57</td>
<td>3.78</td>
</tr>
<tr>
<td>R</td>
<td>0.61</td>
<td>0.51</td>
<td>0.38</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>4.89E-6</td>
<td>4.04E-5</td>
<td>0.088</td>
<td>0.057</td>
<td></td>
</tr>
</tbody>
</table>

*CO\textsubscript{2} g-b measurements available for these stations only

variations include the temporal variations as well as the latitudinal variations (with the latter dominating).

Hereinafter the results summarized in the tables and figures are discussed in detail, per molecule.

4.2 Results for CO

All results for CO are listed in Table 6 and shown in Figs. 5 to 7. First of all it must be noted that, while both WFMD and IMLM CO products have been normalised for this validation
with ECMWF pressure data, IMAP XCO is a dry air normalised product using CH$_4$ as a proxy for dry air. The TM4 profile CO data, yielded average correction factors for the normalisation with altitude of 0.85 for Zugspitze, 0.79 for Jungfraujoch and 0.91 for Izaña. All other stations had factors well below 1%, with the notable exception of Toronto (3.8%), which, given its altitude of a mere 174 meters, indicates strong boundary layer concentrations of CO in the model. All mean correction values are listed in Table 2 and typical examples are shown in Fig. 3.

When looking at Fig. 5, the obtained bias is far from constant as a function of latitude. Both IMLM and IMAP seem to exhibit an increasingly larger bias when moving down through the Southern Hemisphere. This effect is less gradual for WFMD, but a clear difference between the Southern Hemisphere and Northern Hemisphere data is noticeable for all algorithms. However, one has to keep in mind the very limited amount of data points for these Southern Hemisphere stations (see Fig. 6), which make an honest quality assessment, let alone the assessment of a trend, very difficult. These bias increases could be related to the difficulties of accurately acquiring the low Southern Hemisphere CO concentrations. Also immediately noticeable is the large difference between the small and large grid IMLM overall biases. As already mentioned, the geographical collocation area can have a significant impact upon the bias. Also the other algorithms exhibit differences in the bias between small and large grids when looking at the data per station. In some cases (Wollongong, which could be related to local biomass burning events) these differences can be substantial, but most differences remain within the order of a few percent.

The overall data scatter around the bias-shifted FTIR polynomial fit, $\sigma_{\text{SCAT}}$, for all algorithms ranges around 23.5% (23.5 for IMAP, 25.1 for WFMD and 22.4 for IMLM), for the large collocation grid, which is $\sim$2.3 times the desired 10% target precision on CO as well as the scatter of the ground-based FTIR data (9.5%). When taking the smaller spatial collocation grid, the scatter increases to around 27%, due to the decrease in data points, which apparently offsets the potential scatter decrease associated with less atmospheric variability in a smaller geographical area. Note that also the scatter, especially for IMLM which has a very limited amount of data points near the poles, can vary strongly from station to station (between 15.8 and 63.7%). Although WFMD measurements exhibit the highest scatter, they also clearly have the highest $R$ (0.86) and lowest $P$ values among the three retrieval methods. Also IMLM exhibits high $R$ values, while those of IMAP are considerably lower. Note that IMAP XCO is derived with an older version of the algorithm (v0.9) than the one used for the XCH$_4$ product (v1.1).

Having such a relatively high scatter complicates the evaluation of the time series of all algorithms (Fig. 7), certainly for those months for which only a limited amount of data is available. Therefore Figs. 7, 10, 11, 12 and 13 do not show months for which there were less than 10 data points available (nor are they included in the calculation of $R$ and $P$). Also included in Fig. 7, are monthly mean MOPITT CO values.

All algorithms appear to have potential given a further decrease in the amount of data scatter. However there are certainly a number of points which need to be looked at more closely. For WFMD for instance, the January (and February) data seems consistently too low for the Northern Hemisphere and too high for the Southern Hemisphere, with respect to the other WFMD data points. The same can be said for IMAP XCO where the underestimation seems to linger into March. In most cases, IMLM has too few data in this period to make a statement. Aberrant behaviour is sometimes also observed for August (Jungfraujoch). In many cases, the September-October data for WFMD and IMAP look suspiciously high. Both January and August feature ice layer decontamination periods and the amount of data for these months are scarce which could (to some extent) be an explanation for the above mentioned deviations. It is hard to detect any systematic offsets for IMLM but significant deviations (although more at random) do occur. From Fig. 6 one can also clearly see that IMLM only retains significant data (due to their strict cloud
filtering algorithm) for mid latitude stations. MOPITT CO on the other hand follows the FTIR seasonality almost perfectly. The correlation coefficient R between the monthly mean MOPITT and FTIR values over the entire network is 0.96, while $P=8.15\times10^{-55}$, which is still better than for any of the SCIAMACHY algorithms. Only for the high latitude Ny Alesund and Arrival Heights stations do we notice a considerable deviation. MOPITT CO however measures in...
the thermal infrared and unlike SCIAMACHY near-infrared capability is unable to look into the boundary layer where the strong local emission sources are located. Most of the current FTIR stations are located at remote areas, where local emission sources are low. However, when we look at the two stations which are not located at such remote locations, Egbert (~70 km from the city of Toronto) and Toronto itself, we see that MOPITT still captures the seasonality extremely well.

In order to truly assess the different capabilities of MOPITT vs. SCIAMACHY CO, it is clear that more independent measurements, especially taken in regions where substantial boundary layer CO concentrations can be expected, are required.

4.3 Results for CH₄

First of all it must be noted that the differences between the algorithm parameters are considerable in the case of CH₄. Both IMAP and WFMD derive CH₄ from Channel 6, while IMLM derives CH₄ from Channel 8 which is affected by an ice layer. Furthermore, the final IMAP and WFMD CH₄ products are dry air normalised XCH₄ (using CO₂ as a proxy for dry air) products, which also allows both algorithms to eliminate the necessity for a rigid cloud detection algorithm and thus retain much more data points. IMLM only keeps measurements that are 100% cloud free, according to their cloud detection algorithm. This striking difference in data quantity is shown in Fig. 9. Therefore the differences between IMLM and WFMD and IMAP are not necessarily related to the retrieval algorithm itself. Another important point is that the WFMD XCH₄ data products have been corrected to compensate for a clear solar zenith angle (sza) dependence which became apparent during the course of this validation exercise (Buchwitz et al., private communication). The corrected XCH₄ is equal to XCH₄ × 0.5 (uncorrected) divided by (0.95 + 0.15 cos (sza)). The impact of this correction is shown in Fig. 10 and Table 7. The cause for this dependence is under investigation but might be due to a calibration error of the Channel 6+ (upper ranges of Channel 6) spectra (as it affects CH₄ but not Channel 6 CO₂ total columns). IMAP, which uses the same spectral windows, has not (yet) been corrected for such dependence; in any case the effect of such dependence, if any, seems far less apparent. This having been said both IMAP and WFMD are investigating to what extent their data could be affected and more importantly what the exact cause of this dependence might be.

From Table 8 and Fig. 11, one can also see that all three algorithms exhibit statistically significant, mostly negative, biases. Especially those of WFMD and IMLM are large, making it more difficult to assess the seasonality. One doesn’t observe any clear latitudinal dependence of the bias for any of the algorithms. However the variability between stations, with respect to the target precision of 1%, is still considerable. Not all variability should be attributed to the SCIAMACHY retrieval algorithms. FTIR CH₄ retrieval is a challenging task and the end results still depend on the microwindows and other retrieval parameters used. A survey of NDSC Egbert and Toronto CH₄ data by Taylor et al. (2005) has shown that interchanging retrieval parameters and microwindows between these stations, could account for a difference of up to 3.3%.

The corrected XCH₄ data yielded correction factors for the normalisation with altitude of 0.98 for Zugspitze, 0.97 for Jungfraujoch and 0.985 for Izaña. All other stations had factors well below 0.3%. While these factors for the high altitude stations are far smaller than those for CO, they are still significant because of the extremely strict target precision of 1%.

A striking feature that can be derived from Table 8 is the low scatter for IMAP XCH₄, (1.09%), approaching the 1% target precision and even better than the 1.15% FTIR scatter. Note that the variability per station ranges between 0.69% (Izaña, thus probably capturing high surface albedo measurements over the Sahara desert) and 1.49% (Arrival Heights, Southern Hemisphere polar station with very limited correlative data points). SCIAMACHY measurements with
precisions of the order of 1.5 to 2% can already contribute considerably to emission uncertainty reduction (Meirink et al., 2006). Certainly IMAP measurements, but also to a lesser extent WFMD, already reach this more relaxed requirement.

When interpreting these numbers one always has to keep in mind that the scatter is not calculated with respect to the FTIR data themselves but to the polynomial fit through these data. Such an approach is certainly valid in cases where the scatter on the SCIA data is much larger than that on the FTIR
Fig. 11. Weighted monthly vmrs for (X)CH$_4$ at all stations as a function of time for the year 2003, for the 3 algorithms (note that for IMLM no XCH4 data was available and ECMWF pressure data was used for the normalisation) 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. (9). No monthly mean data is shown for months which contained fewer than 10 SCIAMACHY measurements.

data itself. When however, the SCIA scatter (1.09%) is becoming similar to that of FTIR (1.15%), as is currently the case, the validity becomes to some extent debatable as one can easily imagine two SCIAMACHY data sets with equal, thus calculated, scatter values, one capturing the FTIR day to day variability perfectly, while the other does the complete opposite. However, as is apparent from Fig. 11, the data quality as it is, while a significant improvement with
previous versions, has not yet obtained the level for which day-to-day variability becomes an issue. Regarding IMLM, the scatter on its CH$_4$ data is the largest, which can to some extent be explained by the fact that the algorithm product is the total CH$_4$ column and that the normalisation has been made using ECMWF pressure data. When applying this
same normalisation procedure to the CH$_4$ column data from IMAP and WFMD, then all algorithms show comparable results. IMLM data then even becomes slightly better than those from WFMD (For LG: $\sigma_{\text{cat}}=3.9\%$ and $R=0.33$) and IMAP ($\sigma_{\text{cat}}=2.1\%$ and $R=0.58$). It is clear that one should normally apply a strict cloud filtering algorithm, before using ECMWF normalised CH$_4$ IMAP and WFMD data, and that this would improve the above mentioned IMAP and WFMD statistics. Still, it is clear that the ice issue problems which plague Channel 8 retrievals of IMLM have been well handled but that the benefits of normalisation, using CO$_2$ as a proxy for dry air, are considerable.

The impact of this dry air normalisation is also apparent in the higher $R$ values of both XCH$_4$ products as compared to IMLM CH$_4$. Strikingly this difference quickly decreases when considering the IMLM data on a large grid ($R=0.70$) rather than on the small grid ($R=0.52$). This large impact of the spatial collocation grid is probably related to the fact that additional monthly mean values for the high latitude stations become valid (derived from more than 9 data points), effectively increasing the range over which the FTIR measurements vary. The sza corrected WFMD data set delivers the best product in this respect, while IMAP XCH$_4$ exhibits a relatively moderate correlation despite the fact that it clearly has the lowest scatter of all the three algorithms. This could be related to the fact that IMAP has no monthly mean ($n>9$) data for Arrival Heights, again decreasing the variability range and thus $R$. But more important facts that could have a negative influence on the correlation coefficient $R$ are the clear overestimation of Lauder data, as well as the facts that IMAP XCH$_4$ often has high values in August, and an apparent opposite seasonal variation in comparison to g-b FTIR at Wollongong.

Due to the limited number of data points for IMLM, one can only do a decent comparison for the mid latitude stations south of Zugspitze to Wollongong and even for those stations the larger scatter complicates matters significantly. This aside, the ability to capture the seasonal variability looks promising, if an increase in data points and reduction in errors could be achieved. Of the three, WFMD, after sza correction, correlates best with the FTIR data, with the very notable exception of Izaña, where the other algorithms clearly outperform WFMD. Also for Toronto, the July–August data look high.

It is clear that there are considerable differences between the three algorithms, all of which show some different weak points. IMLM CH$_4$ clearly suffers from the limited amount of data points and the higher scatter; this to the extent that drawing definite conclusions from the time series plots would be very premature. IMAP XCH$_4$ has the lowest scatter, performs well for the Northern Hemisphere stations but exhibits clear problems for the Southern Hemisphere stations. WFMD has been corrected for its sza dependence, resulting in reasonable agreement (ignoring the bias) with the FTIR data for several stations, but less so for others (most notably Izaña). Further developments that can be expected in the near future are the XCH$_4$ IMLM data retrieved from Channel 6, as well as an in depth investigation into the cause and impact of the solar zenith angle dependence on both IMAP and WFMD algorithms. These developments should further enhance the data quality considerably.

4.4 Results for N$_2$O and CO$_2$

For XN$_2$O and XCO$_2$, only WFMD v0.4 measurements have been available for the present study. Unlike the version 0.5 WFMD data, the v0.4 measurements are still scaled with a constant factor, which is equal to 1.27 for CO$_2$ and 0.66 for N$_2$O. Furthermore, the ground-based data set for CO$_2$ is limited to three stations only, which makes it impossible to draw any conclusions regarding the latitudinal dependence of the CO$_2$ measurements. The N$_2$O ground-based data set covers all stations. Neither for N$_2$O nor for CO$_2$ have we applied a correction to the normalisation using the TM4 profile data. For N$_2$O this profile correction would probably be of the same order as that for CH$_4$. However given the more relaxed precision criteria (10%) and the fact that we observe no systematically different biases for the high altitude stations in the FTIR – SCIAMACHY comparisons, such a correction would not significantly alter the results of the validation. For CO$_2$ with its quasi-constant vmr profile with altitude, such a profile correction would have negligible impact.

The biases for XN$_2$O, which is essentially a by-product of the retrieval of (initial version 0.4) CH$_4$ in Channel 8, are summarized in Table 9. We observe no obvious systematic latitudinal dependence of the bias and the overall bias isn’t statistically significant, although it is statistically significant positive or negative at some individual stations. The spread of the N$_2$O SCIAMACHY measurements, $\sigma_{\text{cat}}$, is a considerable 8 times larger than that of the ground-based FTIR measurements, however they do reach the desired 10% target precision. Also the $R$ and $P$ values indicate a moderate correlation.

From the time profile plots in Fig. 12, it is clear that the variability on the monthly mean data is too large to detect any apparent structured deviations from the temporal evolution. However, again, as with CO, it looks as if the initial data points are lower than the remainder, at least for the Northern Hemisphere, or that the late spring data points are relatively high, depending on your point of view. This is especially striking for Zugspitze and Junfraujoch. But again this could be merely statistical scatter. All in all, it is clear that the current data quality of XN$_2$O needs improvement before it becomes useful for data users, but given the fact that it is a by-product and that efforts to improve its quality are very limited, these initial results are promising for the future development of this product.

For XCO$_2$, we only obtained ground-based FTIR data from three stations. One of them is near the poles (Ny Alesund), another one is a mountainous station (Junfraujoch)
and the third one (Egbert) is only 70 km away from a major city (Toronto). Among them, only the Ny Alesund CO\textsubscript{2} data (immediately submitted as vmrs) are retrieved from near infrared spectra while Jungfraujoch and Egbert use observations in the mid infrared. The near-infrared retrieval benefits from the simultaneous retrieval of O\textsubscript{2} data, thus enabling to deliver dry-air normalised products with a precision that is better than 1%. Table 9 also shows that the XCO\textsubscript{2} results for these stations, albeit the limited data set, are fairly consistent among each other, indicating a significant negative bias of the order of 7% of the SCIAMACHY measurements relative to the 3rd order polynomial fit through the ground-based FTIR measurements. The obtained correlation coefficient \( R \) indicates that there is only a limited degree of correlation and the probability \( P \) is even larger than the 0.05 target value thus stating that the correlation is not statistically significant. This is not surprising given the extremely small number of overlapping monthly mean data points and the corresponding limited variability of the FTIR data. All in all it is extremely difficult to draw conclusions from such a small data set. Figure 13 shows that XCO\textsubscript{2} seems to be correctly capturing the seasonal variations (higher in winter, lower in summer) but also that the SCIAMACHY data exhibit features that are clearly not present in the FTIR data.

The scatter on the XCO\textsubscript{2} data is about 3 times larger than that of the ground-based FTIR measurements and required (target) precision. As with XN\textsubscript{2}O, XCO\textsubscript{2} is in the initial phase of its development and still requires significant improvements before becoming a reliable product. Nevertheless this and other validation exercises (de Beek et al., 2006) already show promising results.

5 Conclusions

The present comparisons between SCIAMACHY data for CO, CH\textsubscript{4}, CO\textsubscript{2}, and N\textsubscript{2}O mean volume mixing ratios from three different algorithms (WFM-DOAS v0.5 (v0.4 for XCO\textsubscript{2} and XN\textsubscript{2}O), IMLM v6.3, and IMAP v1.1 (v0.9 for XCO)) and correlative FTIR g-b data cover the period January to December 2003. The validation approach uses a polynomial interpolation through the g-b FTIR data to increase the number of collocated data. The comparison results show that scientific teams have significantly improved the retrieval algorithms for deriving the total columns of the above-mentioned target species from the instrument’s NIR channels, despite the calibration problems inherent with the spectra (Buchwitz et al., 2000, 2004, 2005a, 2005b; Frankenberg et al., 2005a, 2005c; Gloudemans et al., 2004, 2005).

Overall, for CO and CH\textsubscript{4}, all algorithms give relatively good descriptions of the seasonal and latitudinal variability of the gas species involved. Nevertheless, they still exhibit clear flaws which have to be kept in mind by the data user. It is clear that the capturing of the seasonal variability using the spatial overlap criteria and monthly mean averaging as done in this paper is promising but far from perfect. There are several ways of overcoming some of these remaining issues (averaging over larger time periods and/or larger spatial areas, using scaling (fitting) to additional (in-situ) measurements, etc.) depending on the data user’s specific needs. Calculating the scatter, see Eq. (8), using the SCIAMACHY and FTIR monthly mean values instead of daily mean SCIAMACHY and FTIR polynomial values, did not improve the result. However, the correlative data set, for 11 stations over one year only, becomes too small to make an honest assessment of whether monthly mean values over our collocation grid do reach the target precision. Quantitative studies for monthly averaged SCIAMACHY CO data on spatial scales of a few degrees are very promising (de Laat et al., 2006). It is however beyond the scope of this article, and often beyond the capabilities of our dataset, to validate any of such approaches.

One must be aware of the fact that, due to the use of a polynomial fitting procedure for the g-b data and the smearing over the collocation grid for the satellite data, the obtained
values for the scatter in the SCIAMACHY data include contributions from the natural variability of the considered species. The latter spatial variability includes variations related to topography as well as real variability of the concentrations. This increase of the variability with an enlargement of the collocation grid is often – but not always – offset by an increase in data points.

For CO, the results look promising. The correlation coefficients between g-b FTIR and SCIAMACHY data are relatively high and in general the time series capture the overall seasonal variation. However the relatively high scatter, combined with periods or regions with relatively scarce data (near the poles, Southern Hemisphere, January and August) can cause serious aberrations in the data output of which the data user should be aware. The scatter on the CO data is still at least a factor 2 worse than that of the g-b FTIR measurements and target precision of 10%. Part of the large scatter may be due to natural variability (also present in the FTIR scatter) and part due to low precision of individual SCIAMACHY measurements.

For CH$_4$, the scatter has (almost) reached the target precision of 1% in the case of IMAP, while the other algorithms are still a factor 2 to 3 away. It appears that the IMLM data for CH$_4$ retrieved from Channel 8 exhibit more scatter than the data from both other algorithms, and have the lowest R value of all the algorithms when considering the small grid collocation; they are also less numerous due to the necessity of strict cloud filtering. It is thus very difficult to assess the time series of this product although for those stations for which sufficient data are available it seems to capture the seasonal variability well. Comparisons with ECMWF pressure normalized WFMD and IMAP CH$_4$ show that the ice issue problem of Channel 8 is well handled. WFMD and IMAP XCH$_4$ still harbour structural problems, prompting a solar zenith angle correction factor on the WFMD data. This sza correction improved the comparisons tremendously, but it clearly fails in some cases (e.g., at Izaña). IMAP XCH$_4$ seems to have problems with Southern Hemisphere station data. Both groups are currently investigating the possible causes of this dependence and in how far it could impact the IMAP XCH$_4$ or the future Channel 6 XCH$_4$ IMLM data.

Both XCO$_2$ and XN$_2$O must be looked upon as preliminary data sets as they have received considerably less attention in their development than CO and CH$_4$. For XCO$_2$, the data set is simply too small to make any binding conclusions while for XN$_2$O, even though it has reached the target precision of 10%, the scatter on the data is too large to make any useful comments about possible structural deviations in the time series.

The remaining quantitative uncertainties will probably be reduced in future algorithm improvements, having acquired a better comprehension of the instrument/spectral problems.

Having said that, one must be aware that due to the inherent differences between SCIAMACHY and FTIR observations, the validation is not straightforward. Different measures have been undertaken to limit the impact of these differences but they cannot be completely ignored. Especially the differences in air mass between an FTIR and SCIAMACHY measurement, further accentuated by the necessary use of a relatively large spatial collocation grid, cannot be avoided. With future more accurate SCIAMACHY products, more independent measurements will be needed in order to really make an accurate assessment of SCIAMACHY’s ability to capture the day-to-day variability and ability to measure into the boundary layer. The current FTIR network data set is too limited (in time and space) in this respect. For those stations where one expects significant boundary layer concentrations (Toronto and Egbert) the MOPITT CO data agree surprisingly well with the FTIR g-b data. It would be of great benefit to the scientific community if a comparison between MOPITT, SCIAMACHY and independent data could be performed at additional sites where considerable boundary layer CO concentrations are expected.

It must also be stressed once more that the actual conclusions are based on a limited number of data coincidences, that the collocation criteria were not very stringent, and that a correction for the surface altitude has been applied that may add additional uncertainties. Some comparisons may still suffer from the presence of clouds because of imperfect cloud algorithms associated with the satellite data retrieval. Additional features that have not been taken into account in the comparisons are possible small sensitivity differences due to slightly different total column averaging kernels, spectroscopic uncertainties, etc. All conclusions drawn from this study therefore relate to the end product (or its monthly mean values), if applicable after normalisation, and profile correction as presented in section 2, and not to the algorithm itself since the differences in algorithm parameters and normalisation method can be significant. It is therefore difficult to make a straightforward evaluation of the performances of the three algorithms among them.

The present results based on comparisons for 11 FTIR stations indicate that it is not yet possible to perform quantitative studies on small spatial and temporal (<1 month) scales. In that respect all the data products are to breach a non-negligible gap before reaching the quality requirements for individual SCIAMACHY measurements. However this does not exclude that the actual SCIAMACHY products for CO and CH$_4$ can be used for performing coarse qualitative studies for which lower precisions than the ones listed in Table 3 are required, provided that the data user takes into consideration the issues raised in this and other SCIAMACHY validation papers (De Mazière et al., 2004; Gouldemans et al., 2004; Sussmann and Buchwitz, 2005; Sussmann et al., 2005). An example hereof is the identification of large source and sink areas for CO and CH$_4$ on a global scale, the variability of which is of the order of 200 and 10% respectively, as discussed by Frankenberg et al. (2005c, 2005b) and de Beek et al. (2006).
Based on the conclusions drawn here and in other papers in this same volume, one can state that SCIAMACHY provides an added value to the actually deployed fleet of satellite instruments, especially for tropospheric chemistry research on a global scale, that considerable improvements on the data quality have been achieved but that there are still significant remaining issues to be resolved.

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The impact of SCIAMACHY near-infrared instrument calibration on CH\textsubscript{4} and CO total columns

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Abstract. The near-infrared spectra measured with the SCIAMACHY instrument on board the ENVISAT satellite suffer from several instrument calibration problems. The effects of three important instrument calibration issues on the retrieved methane (CH\textsubscript{4}) and carbon monoxide (CO) total columns have been investigated: the effects of the growing ice layer on the near-infrared detectors, the effects of the orbital variation of the instrument dark signal, and the effects of the dead/bad detector pixels. Corrections for each of these instrument calibration issues have been defined. The retrieved CH\textsubscript{4} and CO total columns including these corrections show good agreement with CO measurements from the MOPITT satellite instrument and with CH\textsubscript{4} model calculations from the MOPITT satellite instrument and with CH\textsubscript{4} model calculations by the chemistry transport model TM3. Using a systematic approach, it is shown that all three instrument calibration issues have a significant effect on the retrieved CH\textsubscript{4} and CO total columns. However, the impact on the CH\textsubscript{4} total columns is more pronounced than for CO, because of its smaller variability. Results for three different wavelength ranges are compared and show good agreement. The growing ice layer and the orbital variation of the dark signal show a systematic, but time-dependent effect on the retrieved CH\textsubscript{4} and CO total columns, whereas the effect of the dead/bad pixels is rather unpredictable: some dead pixels show a random effect, some more systematic, and others no effect at all. The importance of accurate corrections for each of these instrument calibration issues is illustrated using examples where inaccurate corrections lead to a wrong interpretation of the results.

1 Introduction

The SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY)\textsuperscript{1} which was launched on board the ENVISAT satellite on 1 March 2002, has allowed the measurement of global distributions of methane (CH\textsubscript{4}) and carbon monoxide (CO) down to the Earth’s surface. These gases play an important role in tropospheric chemistry and possible climate change. Therefore, a good knowledge of the global distributions of these gases is a prerequisite to fully understand their role in atmospheric chemistry.

Global measurements of CH\textsubscript{4} and CO have also been performed by the MOPITT instrument on board the EOS-TERRA satellite in the near- and thermal infrared (e.g. Drummond and Mand, 1996; Deeter et al., 2003). Up till now, MOPITT has been unsuccessful in retrieving accurate CH\textsubscript{4} total columns from their data. Methane and carbon monoxide have been measured earlier by the Interferometric Monitoring of Greenhouse Gases (IMG) instrument on board the ADEOS satellite (Clerbaux et al., 2003; Barret et al., 2005). Recently, the EOS-AURA satellite was launched, carrying the Tropospheric Emission Spectrometer (TES) instrument, which is currently measuring CH\textsubscript{4} and CO (e.g. Beer et al., 2001). However, retrieved total column products from this instrument are not yet available. Ground-based measurements of CO and CH\textsubscript{4} total columns are available from a number of ground stations, but they do not provide global coverage and a significant fraction of these are at elevated locations. Thus, these stations only measure the total column directly above the station, whereas the larger spatial coverage of a SCIAMACHY ground pixel will mostly also include

\textsuperscript{1}http://envisat.esa.int/instruments/sciamachy/
 contributions from lower (polluted) altitudes, where most of the CO and CH$_4$ resides (de Mazière et al., 2004; Dils et al., 2005).

The retrievals of CO and CH$_4$ from SCIAMACHY’s near-infrared channel 8 have proven more complex than anticipated, due to the presence of an unexpected ice layer on the detectors, which varies in time. Its effects have been reduced by applying dedicated in-flight decontamination procedures and additional in-flight calibration measurements, as well as improvements to the calibration. However, the quantitative effects of these problems on the retrieved CH$_4$ and CO total columns have only been investigated for very few cases.

This paper focuses on a more systematic investigation of some of the major calibration problems concerning SCIAMACHY’s near-infrared channel 8 and the effects of these problems on the retrieved CH$_4$ and CO total columns from this channel. The problems addressed in this paper are at present not or insufficiently corrected for in the operational SCIAMACHY data provided by ESA/DLR.

Different corrections for these issues have been developed independently by a number of research groups (e.g. Buchwitz et al., 2004b; Frankenberg et al., 2005b; Gloudemans et al., 2004), but the detailed information describing the applied corrections and their impact is often lacking.

Model calculations show that in order to determine e.g. CH$_4$ sources and sinks, and estimate CO emissions from SCIAMACHY measurements, a precision of $\sim$1–2% for CH$_4$ and $\sim$10–20% for CO is required (e.g. Ehret and Kiemle, 2005, S. Houweling and M. Krol, SRON/IMAU, private communication). This paper shows that in order to retrieve total columns with those precisions from channel 8, detailed corrections for all known instrument calibration problems are required. Section 2 discusses the major instrument calibration problems, Sect. 3 describes the retrieval algorithm used, and Sect. 4 shows the retrieval results using SCIAMACHY measurements. The effects of the instrument calibration improvements on the retrieved CH$_4$ and CO total columns are presented in Sect. 5 as well as comparisons of retrievals in different spectral windows of SCIAMACHY’s channel 8. Finally, Sect. 6 discusses all results and the conclusions are summarized in Sect. 7.

2 Instrument calibration

The near-infrared nadir spectra measured by SCIAMACHY’s channel 8 (2265 to 2380 nm) contain absorption lines of CH$_4$, CO, H$_2$O, and N$_2$O. However, the retrieval of

![Fig. 1.](image-url)
these species in this wavelength range is complicated due to the low atmospheric signal compared to the instrument dark signal itself (Fig. 1). This dark signal is the sum of the detector dark signal and the thermal background of the instrument and represents the total measured signal when no light is falling onto the instrument itself. SCIAMACHY measurements show that in case of a strong atmospheric signal, corresponding to a surface albedo of 0.55, the dark signal contribution varies from 30% to 50% at the short wavelength end of channel 8 and 50% to 75% at the long wavelength end. In the case of a lower surface albedo, the corresponding lower atmospheric signal results in an even higher contribution of the dark signal as is shown in Fig. 1. Thus, an accurate instrument calibration (dark signal etc.) is required in order to retrieve meaningful total columns from SCIAMACHY’s channel 8.

Unfortunately, the retrieval within this wavelength range is hampered by a number of instrument-calibration problems. The most important complication in channel 8 is the growth of an ice layer on the detector. This ice layer is due to spurious water absorbed in the ENVISAT satellite frame. Over time, this water evaporates and most of it escapes to space. However, a small portion is trapped by the SCIAMACHY instrument isolation blankets and freezes out onto the near-infrared detectors. The ice layer increases slowly in time up to a thickness of 400 µm and leads to losses in the total measured signal of up to 50% (Lichtenberg et al., 2005). This loss in signal is partially alleviated by heating the detector every 3–6 months, hereby evaporating the ice layer. However, the decrease of the signal behaves differently after each of these decontamination periods (see Fig. 2 and http://atmos.alf.op.dlr.de/projects/scops/ or http://www.sron.nl/www/code/eos/sciamachy/calibration/SCIACALtransmission.php). The consequences of the growing ice layer are threefold:

- The signal-to-noise ratio of the spectra is reduced.
- The instrument thermal background contribution to the total dark signal decreases, as the ice layer also absorbs these photons. In order to deal with this, the total dark signal has been measured every orbit, since October 2002 (Kleipool, 2003a).
- Scattering of light in the ice layer gives rise to extended wings in the slit function.

The latter has a significant effect on the retrieved columns and is the most difficult to correct for, since it varies in time and cannot be determined independently. One possibility to determine a correction for this broadening of the slit function is by using the in-flight measurements from SCIAMACHY’s Spectral Light Source (SLS), which clearly show the presence of broadened wings over time. However, this spectral lamp does not illuminate the whole slit and the overlapping line wings in the SLS spectra complicate the use of these measurements to correct for the broadening of the slit function. In addition, the ice layer is not uniform over the whole channel, so that defining a correction method which is applicable at all wavelengths within channel 8 is complicated. Therefore, a different approach has been adopted in the retrievals presented here, which is described in Sect. 3.

Furthermore, the instrument thermal background and thus the total dark signal also varies within an orbit. This is due to the optical bench heating up on the day side of the orbit. The dark signal is measured upon entering the eclipse near the South Pole, where the contribution of the thermal background signal is largest. This ultimately leads to CH4 total columns that are too high, especially at high Northern latitudes where the actual dark signal deviates most from the measured dark signal (Kleipool, 2004a). The deviation from the measured dark signal varies over the months, since the dark signal is influenced by the thickness of the ice layer.

Lastly, the near-infrared wavelength range in channel 8 is sampled by 1024 detector pixels, a significant fraction of which have turned “dead” or “bad” during the life time of SCIAMACHY (Kleipool, 2004b). A pixel is labelled “dead” when there is no spectral response and “bad” when the spectral response is too noisy or unpredictable. Since neither “dead” nor “bad” detector pixels should be used in the retrievals, both will be referred to as “dead” pixels throughout this paper for simplicity. The most likely causes for this failure of detector pixels are the manufacturing process itself and in-flight radiation damage (Kleipool et al., 2005). The most worrying consequence of this is that the number of dead

\[2\text{Kleipool, Q., Jongma, R., Gloudemans, A. M. S., et al.: Inflight radiation induced degradation of the SCIAMACHY extended wavelength InGaAs near-infrared detectors, in preparation, 2005.}\]
pixels appears to be increasing steadily in time, at a rate of ∼60 pixels per year. This calls for a time-dependent dead pixel mask to be used in the retrieval codes when retrieving total columns from channel 8. In Sect. 5.3 it will be shown that using one dead pixel in the retrieval code, can lead to erroneous results (see also Kleipool, 2004b).

3 Retrieval algorithm

The retrieval method used here is based on an Iterative Maximum Likelihood Method (IMLM) and has been developed at SRON. The retrieval uses a fixed set of climatological atmospheric profiles based on the US standard atmosphere (1976) to compute a model spectrum in terms of optical depths. For each SCIAMACHY ground pixel these profiles are truncated at the mean surface elevation of the pixel.

Once the optical depths are calculated, the earth radiation can be computed in a forward model (Schrijver, 1999, Gloudemans et al., 2005), which is then transformed by an instrument model to represent the radiation detected by the instrument detectors. This modelled spectrum is then fitted – by adjusting the total columns of the different species – to the measured (detector) spectrum in an iterative way. The instrument model also provides an estimate of the instrument noise, from which, by standard statistical methods, an estimate of the instrument-noise related errors in the total columns is estimated to be not more than 1–2%.

All above correction methods, except for the correction for the broadening of the slit function’s wings, are the same as those included in the SCIAMACHY level 1b products patched by SRON4. It is still under investigation how these correction methods can be refined, but further improvements are expected to be small compared to the effects shown in Sect. 5. In addition, a number of improvements to the retrieval approach are foreseen. For example, only a fixed atmospheric temperature profile, the US standard temperature profile, has been used at present, but at the time of writing the inclusion of an ECMWF temperature profile in the IMLM retrieval algorithm is being implemented. The lack of a correct temperature profile can lead to errors in the retrieved CH4 total column of ∼0.35×1018 molec/cm2 for most ground pixels, smaller than the current instrument-noise related precision of the retrievals. The CH4 total columns are mostly off by ∼5% with a maximum error of ∼10% for some isolated cases (Gloudemans et al., 2005). However, this does not affect the effect of the instrument calibration problems presented here, since these are shown as the difference between retrievals with and without correction, both of which use the same temperature profile. Recently, retrievals using ECMWF temperature profiles have been performed for part of the data set presented here. These show indeed that the effects shown in Sect. 5 are not affected by using the fixed US standard temperature profile. Scattering in the atmosphere is not included in the forward model, but is expected to introduce only small corrections of ∼1% for CH4 and ∼2% for CO (Buchwitz and Burrows, 2004). The retrieved CH4 and CO total column data presented in this paper have been cloud masked and thus contain only cloud-free measurements. For this, a cloud mask based on the SCIAMACHY Polarisation Measurement Devices (PMDs) 2, 3, and 4 has been included in the IMLM algorithm. This cloud algorithm is similar to that described by Krijger et al. (2005), except that the distinction between ice/snow covered surfaces is not included. The cloud mask by Krijger et al. (2005) is being implemented at the time of writing.

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4http://www.sron.nl/~richardh/SciaDC/scia_patch_1b/index.html

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www.atmos-chem-phys.org/acp/5/2369/
from the chemistry transport model TM3 on a 2.5° × 2.5° horizontal grid. The CH₄ total columns have been normalized to surface elevation prior to averaging. Right panel: Total columns calculated from the chemistry transport model TM3 on a 2.5° by 2.5° horizontal grid. The total columns have been normalized to surface pressure.

4 Retrieval results

Near-infrared CH₄ and CO total columns from SCIAMACHY have also been reported by others (e.g. Buchwitz et al., 2004a,b, 2005; Frankenberg et al., 2005a,c). Qualitative comparisons have shown that the IMLM results agree well with these other data products (e.g. Gloudemans et al., 2004), even though there are significant differences between the algorithms used and the applied instrument calibration.

In order to investigate the effects of the different instrument calibration problems mentioned in Sect. 2 on the retrieved CH₄ and CO total columns, six months of SCIAMACHY channel 8 data have been analysed. The period September 2003 – February 2004 has been chosen, because the available data result in a good global coverage. The start of this period is right after the August 2003 decontamination (duration: 375 h) and also includes the decontamination period in December 2003/January 2004 (duration 338 h), allowing the investigation of instrument-calibration effects after two different decontamination procedures. Results are shown for retrievals in the channel 8 spectral window between 2321–2334 nm. This window is similar to that used by Frankenberg et al. (2005a). Results for two other spectral windows of channel 8 are discussed in Sect. 5.4. The data presented in this section include corrections for all instrument-calibration problems mentioned in Sect. 2. Section 5 illustrates in more detail the effects on the retrieval of not including these corrections.

4.1 CH₄

Figure 3 shows the monthly-averaged CH₄ results for November 2003. Only cloud-free ground pixels with a high enough signal-to-noise ratio have been included in the SCIAMACHY retrievals. The lack of data over the oceans is due to the fact that the surface albedo is too low, resulting in a signal-to-noise ratio which is too small to perform accurate retrievals. At high latitudes (≥70° N) the signal-to-noise ratio is also too low.

Unfortunately, no independent satellite-based CH₄ total column measurements are available, so that the SCIAMACHY CH₄ total columns can only be compared to total columns from ground-based stations or calculations from atmospheric chemistry transport models. Comparisons of the IMLM total columns with ground-based measurements are presented by Dils et al. (2005), but these do not provide global coverage. Therefore in Fig. 3, the retrieved CH₄ total columns are compared with calculations by the chemistry transport model TM3 from the Royal Netherlands Meteorological Institute (KNMI). A detailed description of the TM3 model used here can be found in Dentener et al. (2003) and references therein. The model includes CH₄ emissions closely following Houweling et al. (1999). These model calculations show a good agreement with in situ measurements (http://www.cmdl.noaa.gov/ccg/) and reproduce the background CH₄ levels well. Although most chemistry transport models do not contain up-to-date emissions and the model resolution is mostly coarser than the resolution of the SCIAMACHY ground pixels (e.g. 2° by 3° as opposed to 120×30 km, i.e. ∼1.1° by 0.27° at the equator) they do provide accurate information on the large scale distribution of CH₄, such as the North-South gradient and well-known continuous or seasonal sources and sinks.

Figure 3 shows that such a qualitative comparison shows good agreement between the monthly-averaged SCIAMACHY data and the corresponding TM3 calculations. For instance, the North-South gradient is clearly visible in the SCIAMACHY data. In addition, many differences can be identified as well, such as the areas in Eastern USA, and the East coast of Australia, which are hardly visible in the TM3 model. The origin of these differences is still under investigation. In Central Africa between ∼10° S and ∼5° N a region with low CH₄ columns is visible which is not in agreement with the TM3 calculations. Since this region is mostly cloudy during this time of the year, this is probably due to
cloudy SCIAMACHY ground pixels that have not been filtered out by the cloud mask included in the IMLM retrieval algorithm. Other persistently cloudy areas such as in the Amazon basin are also clearly identified by the lack of cloud-free SCIAMACHY data. In addition, low CH$_4$ columns are seen in West Africa between $\sim$5–15° N. This area is known for the presence of forest fires and the corresponding smoke may not be picked up by the cloud mask. Smoke and/or clouds shield the CH$_4$ in the lower parts of the atmosphere, resulting in too low CH$_4$ total columns measured by SCIAMACHY. Retrieval of CO$_2$, another well-mixed gas, from SCIAMACHY’s channel 6, also results in too low total columns of a few percent in the same area, using the same cloud mask (W. Hartmann, SRON, private communication).

Figure 4 shows a more quantitative comparison of the monthly-averaged CH$_4$ total columns from the IMLM retrieval algorithm with TM3 for September 2003. Here, the globe has been divided in five-degree latitude bins. All SCIAMACHY data within each latitude bin have been averaged over the whole month and compared to the monthly average of the collocated TM3 CH$_4$ total columns within the same latitude bin. Both data sets have been normalized to surface pressure prior to averaging. The results show a good agreement between latitudes 40° S and 5° S and on the Northern Hemisphere ($\geq$15° N). In both regions the difference between the retrieved CH$_4$ columns and the TM3 calculations is less than $\sim$2%, except for the region North of 65° N, where it is $\sim$5%. This region may suffer from higher solar zenith angles or cloudy ground pixels, resulting in erroneous CH$_4$ columns. The area between 5° S and 15° N is mostly cloudy at this time of the year, as is also seen for November 2003 in Fig. 3, and may also be affected by smoke from the forest fires, resulting in lower CH$_4$ total columns and less collocations with TM3.

Although only comparisons for two months, September and November 2003, are shown here, the other months do give similar results (see also Straume et al., 2005).

4.2 CO

Independent satellite-based CO total column measurements are available, unlike for CH$_4$. Especially for CO, which has strong temporal and spatial variations, such satellite inter-comparisons provide a very valuable validation technique. The MOPITT instrument is currently the only other instrument from which CO total column measurements from space are available. MOPITT uses gas-correlation spectroscopy, based on pressurized cells (Drummond and Mand, 1996), whereas SCIAMACHY uses a grating spectrometer. In addition, SCIAMACHY measures CO in the near-infrared, while MOPITT observes CO in the thermal infrared, where the CO lines are much stronger than in the near-infrared. Thus, measurements from these satellites provide two independent sets of CO total column products, making them very suitable for a first qualitative comparison with the retrieved SCIAMACHY CO total columns. In the near-infrared, the surface reflectance over the oceans is very low, complicating the SCIAMACHY retrievals in these areas. Measurements in the thermal infrared however have a lower sensitivity to the boundary layer, due to small temperature contrasts with respect to the surface. In those cases, a priori information is added to the MOPITT CO measurements. Since this is more likely to happen at night, only day-time MOPITT measurements are taken into account.

Monthly-averaged results for CO compared with measurements by the MOPITT instrument are shown in Figs. 5 and 6 for November and September 2003. Only cloud-free ground pixels with a high enough signal-to-noise ratio have been included in the SCIAMACHY retrievals shown here.

The SCIAMACHY CO total columns for November 2003 shown in Fig. 5 are in reasonably good agreement with the MOPITT measurements of that month. The data sets show a reasonable agreement on both the Northern and Southern Hemisphere, and enhanced CO columns in West and Central Africa and Brazil due to bio-mass burning are seen in both data sets. Similar enhanced CO columns are reported by Frankenberg et al. (2005a), using the same SCIAMACHY data, but using a different retrieval algorithm (Frankenberg et al., 2005b). This is the same region where the low CH$_4$ columns are seen in Fig. 3, providing further evidence for
the low CH₄ columns being due to smoke from forest fires (see Sect. 4.1).

Well-known polluted areas, such as in Asia, are also clearly visible in Fig. 5 as regions with enhanced CO total columns. Mountainous areas, such as the Himalayas and the Andes, show up in both the SCIAMACHY and MOPITT measurements as regions with low CO total columns. Large differences are also observed: the forest fires are more pronounced in the SCIAMACHY data than in the MOPITT measurements, and the retrieved SCIAMACHY total columns also show higher CO values over India and Eastern USA. Part of this difference may come from the fact that the MOPITT measurements are less sensitive to the boundary layer resulting in lower CO total columns (Deeter et al., 2003). In this comparison, the difference in the averaging kernels for the MOPITT and SCIAMACHY instrument has not been taken into account. A more detailed comparison of these two sets of satellite measurements is currently planned in close collaboration with the National Center for Atmospheric Research (NCAR).

A somewhat more quantitative comparison of the IMLM CO total columns with MOPITT is shown in Fig. 6. This figure is constructed in a similar way as Fig. 4 for CH₄. It can be seen that there is a good agreement between the two data sets for September 2003. Differences are generally within 10%, except for the region between ~0° and ~15° N where the differences are up to ~20%. This may be due to the relatively few data points in this area, due to clouds. The standard deviation of the SCIAMACHY measurements is however systematically larger than for the MOPITT data. Part of this may be due to retrieval errors and the rather loose constraints on the signal-to-noise ratio, and part of this may be real: because of the larger sensitivity of SCIAMACHY to the boundary layer, a larger variability in the retrieved CO total columns from individual measurements is expected. A more detailed analysis will help to distinguish between these two.

As is the case for CH₄, the other months in the period September 2003–February 2004 show similar CO

SCIAMACHY–MOPITT comparisons (see also Straume et al., 2005). For January 2004, the quality of the retrieved CO columns cannot be derived from comparisons with MOPITT data, since only a few days of MOPITT data are available for this month.
5 Effects of instrument calibration on the retrieved total columns

5.1 Effects of the growing ice layer

The effect of the broadening of the slit function due to ice growth on SCIAMACHY’s channel 8 detector has been investigated by performing retrievals with and without a correction for the slit function. The applied correction varies from a few % to over 20% of the mean atmospheric signal, depending on the thickness of the ice layer. The resulting CH$_4$ and CO total columns are shown on a daily basis in Fig. 7, since the thickness of the ice layer varies strongly in time. In order to avoid influences of other time-dependent events, such as seasonal variation of CH$_4$ sources and sinks or polluted areas, only the retrieved total columns over the Sahara are taken into account, since the CH$_4$ and CO variation due to atmospheric processes is expected to be low in this region (Houweling et al., 1999). Figure 7a shows the results for CH$_4$, where, for each day, the CH$_4$ total columns are normalized to the mean surface elevation of the corresponding SCIAMACHY pixel and then averaged over the Sahara. Note that this is a larger area than that used to determine the correction for the slit function (see Sect. 3). The difference between retrievals with and without slit-function correction is clearly visible. The CH$_4$ total columns retrieved with a correction for the slit function show an almost constant behaviour in time, in good agreement with calculations by the TM3 model. The trend in the CH$_4$ total columns for retrievals without slit-function correction resembles the loss in the measured total signal for this period, corresponding to the growth of the ice layer (see Fig. 2). The differences between retrievals with and without correction for the slit function range from $\sim$6% shortly after a decontamination to 17.5% four months later, in December 2003. Although this figure only shows results for the Sahara, the retrieved total columns for Australia show the same effect: the differences in the CH$_4$ total columns increase from $\sim$3% at 1 September to 18% in December 2003. The CH$_4$ total columns with the correction for the slit function show good agreement with TM3 model calculations (see also Fig. 3).

Figure 7b shows the results for the retrieved CO total columns. A strong correlation with the loss in the measured total signal due to the growing ice layer, as is present for CH$_4$, cannot be seen for CO, but Fig. 7c shows the difference between the CO total columns retrieved without and with correction for the slit function respectively, relative to the CO total columns with slit-function correction. It can be seen that the relative difference correlates well with the loss in the total signal, indicating that the retrieved CO total columns are also clearly affected by the broadening of the slit function due to the growing ice layer. Differences between retrieved CO total columns with and without correction for the slit function range from $\sim$10% shortly after a decontamination to $\sim$35% four months later in December 2003. Using
the CO total columns over Australia instead of the Sahara, results in similar values. While the differences for CH$_4$ are significantly larger than the current accuracy of the retrieved CH$_4$ total columns of a few %, the differences for CO are comparable to the current accuracy of the retrieved CO total columns (cf. Dils et al., 2005; Straume et al., 2005). However, the clear trend in Fig. 7c strongly suggests that the precision of the CO retrievals is much better than the current CO accuracy. Thus, although the correction for the slit function may seem less important for CO than for CH$_4$, Fig. 7 shows that the total columns of both species are significantly affected by the ice layer.

5.2 Effects of the dark signal orbital variation

Although the orbital variation of the dark signal is much smaller than the slit-function correction, typically $\lesssim 2\%$ of the measured atmospheric signal, it does have an effect on the retrieved columns, especially at Northern latitudes where the deviation of the actual dark signal from the measured dark signal reaches its largest values (Sect. 2). The effect of the variation of the dark signal over the orbit has been tested by performing retrievals with and without a correction for the orbital variation. This correction is taken from the data base set up by Kleipool (2004a). To demonstrate the effect of the orbital variation on the retrieved columns, monthly-averaged data have been investigated for the period September 2003–February 2004. Only the region between longitudes 30° W and 60° E has been investigated, since it has a good data coverage and large regions with high signal-to-noise ratio.

Since both the retrievals with and without correction for the orbital variation do include a correction for the slit function, which is much larger than the orbital variation itself, the two data sets should in principle not show a time-dependent behaviour due to the ice growth. This is true for the retrieved total columns including the correction for the orbital variation, which is done on an orbital basis. However, some time dependency is expected for the retrieved total columns without the correction for the orbital variation. Firstly, the orbital variation is linearly dependent on the measured signal, which decreases in time due to the ice growth. Secondly, the orbital variation is defined as a function of orbit phase, with orbit phase 0 corresponding to the start of the night side. Since phase 0 changes seasonally, this is expected to cause small time-dependent behaviour in the retrieved total columns without a correction for the orbital variation as a function of latitude. Therefore also the differences between the two data sets are expected to show some small time-dependent behaviour.

Figure 8a shows the relative differences between the monthly averaged CH$_4$ total columns without and with correction for the orbital variation respectively, in percentages of the retrieved total columns normalized to the mean surface elevation of the corresponding SCIAMACHY pixel. The data are shown for each month between September 2003 and February 2004. The data shown are the monthly mean total columns. The clear increase in the relative difference can be seen towards Northern latitudes for all months, as expected. The differences for latitudes $\simeq 45^\circ$ N and $\simeq 4$–5% at high Northern latitudes. This is a significant effect, since the differences for latitudes $\simeq 45^\circ$ N and $\simeq 15^\circ$ N (see Sect. 4.1). Similar values for the accuracy of the CH$_4$ total columns are reported by Gloudemans et al. (2004) and Dils et al. (2005).

Figure 8b shows the relative differences between the monthly averaged CO total columns without and with correction for the orbital variation respectively, for each month between September 2003 and February 2004. The data shown are the monthly mean total columns averaged per 5° latitude bin, between longitudes 30° W and 60° E.
The bump between ~15° S and ~10° N correlates well with the change in reflectance in this latitude range. Lower reflectances correspond to a lower signal level, resulting in a larger relative effect of the orbital variation, whereas higher signal levels result in a smaller effect. However, Fig. 8 shows that variations in the reflectance do not cause relative differences of more than ~1%, which is much lower than the differences seen above ~45° N. This strengthens the conclusion that the increase in the relative differences at high Northern latitudes are due to the increase in the dark signal over the orbit. Some differences between the different months are visible, but these are smaller than or comparable to the current accuracy of the CH₄ retrievals and are likely due to a combination of ice growth in time and the seasonal variation of the time of eclipse.

For CO, the effect of the orbital variation of the dark signal is not as evident as for CH₄. In Fig. 8b, a decrease in the relative difference of the CO total columns without and with a correction for the orbital variation, can be seen towards higher latitudes for all months. However, the differences are generally within 15%, corresponding to the accuracy of the monthly-averaged retrieved CO total columns (Sect. 4.2 and Table 1). The apparent trend in the relative differences for CO is opposite to that for CH₄ (Fig. 8). This is probably due to the many CH₄ lines in channel 8, which are often (partially) overlapping with the much weaker and scarcer CO lines. This requires the CO lines to be fitted simultaneously with the CH₄ lines, indicating that the retrieved CO total columns may be influenced by the fit to the CH₄ lines in a non-linear way. Higher CH₄ total columns may fill in part of the CO absorption lines, leading to lower retrieved CO total columns, but lower CH₄ total columns do not necessarily result in higher retrieved CO total columns as e.g. can be seen in Sect. 5.1. Although the effect of the orbital variation does not exceed the current accuracy of the retrieved CO total columns, the clear trend seen for all six months strongly suggests that the precision of the CO retrievals is much better, as is also indicated by the slit-function effect in Sect. 5.1 and Fig. 7. Thus, it is important to also correct the CO total columns for the orbital variation.

5.3 Effects of the dead pixels

The previous sections show that both the orbital variation and the growth of the ice layer result in a systematic, time-dependent effect on the retrieved columns. The dead detector pixels in SCIAMACHY’s channel 8 are not expected to result in systematic effects. Although the number of dead pixels increases in time due to radiation damage (Kleipool et al., 2005²), the effect of dead pixels does not depend on their total number but on their spectral location. A pixel that does not sample (part of) an absorption line, is not expected to have an effect on the retrieved total columns, whereas a pixel that lies at the centre of an absorption line can affect the retrievals in two different ways: it can affect the retrieved total columns of the corresponding molecule and/or the retrieved total column of a different species, since the absorption lines of all molecules are fitted simultaneously.

In the case of CO, only a few absorption lines are present in the wavelength range of channel 8. These lines are most of the time barely above the noise level, many times weaker than the (often overlapping) CH₄ lines in the same spectra. Thus, even without dead pixels, retrieval of CO total columns from SCIAMACHY spectra is difficult. The presence of dead pixels and the corresponding loss of spectral information further complicates the CO retrievals. Unfortunately, a significant number of dead pixels are already located at or near the centre of CO lines. Therefore, there is a realistic possibility that an insufficient number of good detector pixels is left to retrieve accurate CO total columns well before the end of SCIAMACHY’s life time.

On the other hand, the wealth of strong CH₄ lines in the wavelength range of SCIAMACHY’s channel 8, ensures that the CH₄ retrievals are not easily influenced by dead pixels, as long as the dead pixels are not used when fitting the SCIAMACHY spectrum. However, Fig. 9 shows that the CH₄ retrievals are affected significantly, when this is not done correctly.

Thus, in order to perform accurate CO and CH₄ retrievals, a good identification of the dead pixels is required. There are two complications in deriving such a dead pixel mask. The first is the fact that detector pixels are damaged by radiation, mostly resulting in an abrupt change in their dark signal. Although detection of such dead pixels is relatively easy, it
The dead pixel mask used in the current retrievals only masks a pixel if its physical characteristics are bad for more than 25% of this period. This mask has been tested and works well: analyzing retrievals for a whole year, only a few dead pixels have been found that are not masked. For each of these pixels, this is only the case for a period of \(~1\) day, after which each of them is masked correctly. Putting stronger constraints on the physical characteristics leads to a significantly larger number of dead pixels, including pixels that are still performing reasonably, further complicating the retrievals in channel 8. Therefore, it occasionally happens that a dead pixel does not appear in the pixel mask instantly, but only after \(~1\) day. The current dead pixel mask is still being checked regularly and the current constraints may have to be adapted over time, to maintain a good performance.

However, even missing one pixel in the dead pixel mask for such a short period can have a significant effect on the retrievals. An example of this effect is shown for one such pixel, which is dead based on its physical quantities, but does not show up in the dead pixel mask until after \(~0.85\) day or equivalently, 12 SCIAMACHY orbits. This pixel is located at the position of a CH\(_4\) line, but not near a CO line. Figure 10 shows the results for retrievals with and without masking this dead pixel during its \(~0.85\) day period in
February 2004, and then averaging all retrieved CH$_4$ and CO total columns for that whole month. Comparing retrievals with and without masking this pixel clearly shows that it creates artificially low CH$_4$ columns in some areas, but it may not be that obvious that something is wrong from Fig. 10b only. Similarly, looking at Fig. 10d only, may lead to the conclusion that enhanced CO emission is seen over Iraq.

In this case, the retrievals of the individual orbits clearly indicate that something is wrong, by means of the large fit residuals. In fact, most of the time the few dead pixels that are missed are easily identified, since they cause large fit residuals and unrealistic values for the retrieved CH$_4$ and/or CO total columns. However, a few cases have been found where a pixel with truly bad physical characteristics still gives good fit residuals. In particular, RTS pixels with a low noise level could display such a behaviour. Investigation of the effect of one such dead pixel, leads to similar results as seen in Fig. 10: enhanced CO emission is seen over India, which disappears when this pixel is masked out. In the unlikely case that such a pixel is missed by the dead pixel mask, a good way to detect such dead pixels is by comparing retrievals from different wavelength ranges (see Sect. 5.4).

These results indicate that the identification of dead pixels is best done by monitoring their physical behaviour, but inspecting the retrievals afterwards for strange anomalies remains important. Identification of dead pixels by means of fit residuals only appears insufficient and may lead to misinterpretation of the results.

5.4 Effect of retrieval windows

The results presented in the previous sections are based on retrievals in a single spectral window of SCIAMACHY's channel 8 between 2321–2334 nm (hereafter: window 1). Since this is not the only part of channel 8 that contains CO and/or CH$_4$ absorption lines, two other spectral windows, containing both CH$_4$ and CO lines, have been investigated. The results for all three windows are summarized in Table 1.

Window 2 covers the range 2327–2339 nm, and is chosen for the presence of strong CO lines that are relatively unaffected by the dead pixels. It overlaps partially with window 1 which has been used so far and thus similar results are expected. Indeed, the retrieved CH$_4$ total columns are very similar to those from window 1, with monthly-averaged CH$_4$ results also differing from TM3 calculations by $\lesssim$2%. Comparisons of monthly-averaged CO results with MOPITT measurements show a good agreement between the two data sets, with differences within $\sim$15%.

The effect of the orbital variation of the dark signal is also similar to that in window 1, i.e. relative differences of up to $\sim$4–5% for CH$_4$ and up to $\sim$15% for CO at high Northern latitudes.

Window 3 ranges from 2354–2370 nm. This window is similar to the spectral range used by Buchwitz et al. (2004a) and contains CO lines from the $P$-branch, whereas the other windows contain $R$-branch CO lines. The monthly-averaged CH$_4$ total columns compare well with TM3 calculations and with results from the other two windows, although the differences with TM3 of $\lesssim$3% on the Southern Hemisphere are slightly larger than for window 1 and 2, and the deviation from TM3 seems to increase somewhat for high Northern latitudes. Comparisons of monthly-averaged CO results with MOPITT measurements result in deviations of $\sim$30%, larger than for the other two windows. Here, the retrieved CO total columns are mostly lower than those from MOPITT, whereas window 1 shows total columns somewhat larger and window 2 somewhat lower than MOPITT.

The effect of the broadening of the slit function due to the growing ice layer ranges from $\sim$6% to $\sim$18% for CH$_4$ in window 3, comparable to that of the other two windows. Although the atmospheric signal in this wavelength range is lower than in the other two windows, the slit-function broadening causes a relative effect on the CH$_4$ total column, thus explaining the similarity with the other two windows. For CO the difference between retrievals with and without

Table 1. Summary of retrieval results in different spectral windows.

<table>
<thead>
<tr>
<th>Window #</th>
<th>$\lambda$ (nm)</th>
<th>CH$_4$</th>
<th>CO</th>
<th>Ice growth effect</th>
<th>Effect of Orbital variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2321–2334</td>
<td>$\lesssim$2</td>
<td>$\lesssim$15</td>
<td>6–17.5</td>
<td>10–35</td>
</tr>
<tr>
<td>2</td>
<td>2327–2339</td>
<td>$\lesssim$2</td>
<td>$\lesssim$15</td>
<td>8–19.5</td>
<td>15–46</td>
</tr>
<tr>
<td>3</td>
<td>2354–2370</td>
<td>$\lesssim$3</td>
<td>$\lesssim$30</td>
<td>6–18</td>
<td>2–25</td>
</tr>
</tbody>
</table>

a For monthly-averaged total columns only. Differences for daily data are somewhat larger.
b Based on daily averaged total columns over the Sahara (Sect. 5.1).
c Based on monthly-averaged total columns between 30° W and 60° E (Sect. 5.2).
correction for the slit function shows no clear trend in time and ranges from ~2% at the beginning of September 2003 to ~25% around mid December, to ~20% in early January just after the decontamination. This is probably related to the dead pixels in window 3, resulting in few CO lines that are unaffected. One particular pixel, which lies at the center of a strong CO line, causes the retrieval algorithm to give a wrong fit to the remaining detector pixels containing parts of the other CO lines. This probably explains the low retrieved CO total columns for window 3.

The effect of the orbital variation of the dark signal in window 3 is larger than in the other windows and can be up to ~13% for CH$_4$ at high Northern latitudes. For CO, the effect is also larger than in the other windows, up to ~30%, increasing towards Northern latitudes, whereas it is decreasing for the other windows. As for the other windows, the relative difference for CO is comparable to the accuracy of the CO total columns, making the effect of the orbital variation less pronounced for CO than for CH$_4$. The larger effect of the orbital variation and the increasing differences for CO are probably due to the lower atmospheric signal in this wavelength range compared to the other windows (see Fig. 1). The lower signal introduces a larger effect on the retrieved total columns from window 3 for calibration issues with wavelength independent behaviour. The absolute values of the orbital variation of the dark signal show only a weak dependency on wavelength, thus explaining the larger relative differences in window 3. The lower atmospheric signal in window 3 also requires a better calibration, and thus the retrieved CH$_4$ and CO total columns may suffer from larger uncertainties. In addition, the dead pixels may play a role for CO in this window.

The number of dead pixels in all three windows are comparable, but it depends on the spectral location of these pixels whether the retrievals in one window give better results than in the other. The good agreement of the retrieved CH$_4$ total columns in all three windows gives some indication that in terms of dead pixels no window is preferred over another for the considered time period, and that no dead pixels that are important for the CH$_4$ retrievals are missed by the dead pixel mask. For CO, it seems that window 3 is preferred less than window 1 and 2, but using only part of window 3 results in CO total columns that are more in agreement with the results from the other two windows. This is due to a strong H$_2$O line overlapping with one of the stronger CO lines in this window. All three windows contain strong H$_2$O absorptions, but it depends on the position of the lines whether they will influence the retrieved CO and CH$_4$ total columns. In general there is a good correlation between the retrieved H$_2$O total columns from different spectral windows, but there are cases with substantial differences too. This can also influence the retrieved total columns, especially for CO. Thus, using different windows in SCIAMACHY’s channel 8 seems a good way to verify the retrieved CH$_4$ and CO total columns and thus improve their accuracy.

### 6 Discussion

The previous sections show that the growing ice layer, the orbital variation of the dark signal, and the dead pixels can cause significant errors in the retrieved CH$_4$ and CO total columns, when no or inaccurate corrections are taken into account. The nature of each of these effects is different. Whereas the effect of the growing ice layer varies strongly on the order of days, the effect of the orbital variation of the dark signal shows almost no time dependency. Also, both the growing ice layer and the orbital variation cause systematic effects in the retrieved CH$_4$ and CO total columns, whereas the effect of the dead pixels is rather unpredictable: some dead pixels show a random effect, some more systematic, and others no effect at all. Applying accurate corrections for these instrument calibration problems significantly improves the retrieved CH$_4$ and CO total columns.

Although the instrument calibration problems discussed in this paper have the largest impact on the retrieved total columns in SCIAMACHY’s channel 8, additional smaller problems exist. As mentioned in Sect. 2, the dark signal decreases in time due to the growing ice layer and is currently measured for every SCIAMACHY orbit. However, the dark signal measurements are not available for every orbit for which SCIAMACHY data is present, due to incomplete data distribution and different versions of the distributed data. This may lead to small inaccuracies in the retrieved total columns, especially right after decontamination, when the dark signal is dropping fastest due to the ice growth. These are not expected to be larger than a few percent, which is within the current accuracy of the retrieved CH$_4$ and CO columns. Another possible error source is the non-linearity as reported by Kleipool (2003b). For channel 8 this effect is small and errors in the retrieved total columns of less than a few percent are expected. A more detailed calculation of these effects will be provided in a future paper. The instrument calibration issues mentioned in this paper apply to both SCIAMACHY’s channels 7 and 8. Channel 7 also suffers from an additional serious problem, caused by a light leak.

In Sects. 5.3 and 5.4 it is mentioned that comparison of retrievals in different wavelength ranges gives additional information on the accuracy of the retrieved total columns. Here, only retrievals in SCIAMACHY’s channel 8 have been discussed. For CH$_4$, useful independent information can also be derived from SCIAMACHY’s only other near-infrared channel 6, which covers the wavelength range 1000–1750 nm. This channel does not have an ice layer on its detector, and is not hampered by the orbital variation of the dark signal, due to the much higher atmospheric signal in this wavelength range. However, the spectral window containing CH$_4$ lines contains more dead pixels than in channel 8, non-linearity plays an important role, and scattering in the atmosphere complicates the retrieval. Nevertheless, CH$_4$ total column retrievals from channel 6 are foreseen for comparison with the CH$_4$ total columns presented in this paper.
7 Conclusions

In this paper, the effects of three important instrument calibration issues on the retrieved CH$_4$ and CO total columns from SCIAMACHY’s channel 8 are discussed: the broadening of the slit function due to the growing ice layer on the detector, the variation of the dark signal over the orbit, and the dead detector pixels. The main conclusions are as follows:

- The CH$_4$ and CO total columns retrieved with the IMLM retrieval algorithm, including corrections for all known instrument calibration issues, compare well with calculations from the atmospheric chemistry transport model TM3 and independent measurements from the MOPITT instrument on board the EOS-TERRA satellite.

- The slit-function broadening due to the growing ice layer causes a time-dependent systematic effect on both the CH$_4$ and CO total columns. For CH$_4$, this effect is much larger than the precision of $\sim$1–2% required to detect CH$_4$ sources and sinks. The clear trend seen for CO, corresponds well with the loss in the total signal, indicating that also CO is significantly affected.

- The orbital variation of the dark signal also causes a systematic effect, but has only a small time dependency. This effect is much smaller than the effect of the slit function, but is still significant for both CH$_4$ and CO, especially at high Northern latitudes.

- The effect of the dead pixels on the retrieved total columns is unpredictable and depends on the spectral position of each individual dead pixel. Therefore, this effect is difficult to quantify in a general sense. An accurate algorithm which identifies the dead pixels for every orbit is required in order to avoid misinterpretation of the retrieved total columns. The dead pixel mask used in the IMLM retrieval is based on the physical characteristics of the detector pixels and works well. Nevertheless, inspecting the fit residual remains important since it provides additional information. However, a dead pixel mask based on fit residuals only is insufficient.

- Retrievals in different wavelength ranges within SCIAMACHY’s channel 8 give similar results for CH$_4$, but show some differences for CO. This is probably due to the scarcity and weakness of the CO lines in combination with the dead pixels, which complicates the CO retrievals significantly.

- Comparison of retrievals in different wavelength ranges provides a useful tool to detect imperfections in the applied instrument calibration corrections and helps to improve the quality of the retrieved total columns.

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A. M. S. Gloudemans et al.: SCIAMACHY’s impact on CH₄ and CO columns


Carbon monoxide, methane and carbon dioxide columns retrieved from SCIAMACHY by WFM-DOAS: year 2003 initial data set

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Abstract. The near-infrared nadir spectra measured by SCIAMACHY on-board ENVISAT contain information on the vertical columns of important atmospheric trace gases such as carbon monoxide (CO), methane (CH₄), and carbon dioxide (CO₂). The scientific algorithm WFM-DOAS has been used to retrieve this information. For CH₄ and CO₂ also column averaged mixing ratios (XCH₄ and XCO₂) have been determined by simultaneous measurements of the dry air mass. All available spectra of the year 2003 have been processed. We describe the algorithm versions used to generate the data (v0.4; for methane also v0.41) and show comparisons of monthly averaged data over land with global measurements (CO from MOPITT) and models (for CH₄ and CO₂). We show that elevated concentrations of CO resulting from biomass burning have been detected in reasonable agreement with MOPITT. The measured XCH₄ is enhanced over India, south-east Asia, and central Africa in September/October 2003 in line with model simulations, where they result from surface sources of methane such as rice fields and wetlands. The CO₂ measurements over the Northern Hemisphere show the lowest mixing ratios around July in qualitative agreement with model simulations indicating that the large scale pattern of CO₂ uptake by the growing vegetation can be detected with SCIAMACHY. We also identified potential problems such as a too low inter-hemispheric gradient for CO, a time dependent bias of the methane columns on the order of a few percent, and a few percent too high CO₂ over parts of the Sahara.

1 Introduction

Knowledge about the global distribution of carbon monoxide (CO) and of the relatively well-mixed greenhouse gases methane (CH₄) and carbon dioxide (CO₂) is important for many reasons. CO, for example, 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 CH₄. CO also has large air quality impact as a precursor to tropospheric ozone, a secondary pollutant associated with respiratory problems and decreased crop yields. Satellite measurements of CH₄, CO₂, and CO in combination with inverse modeling have the potential to help better understand their surface sources and sinks than currently possible with the very accurate 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 CH₄ and CO₂ 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.

The first CO measurements from SCIAMACHY have been presented in Buchwitz et al. (2004), and first results on CH₄ and CO₂ have been presented in Buchwitz et al. (2005), both papers focusing on a detailed analysis of single day data (except for CO₂ for which also time averaged data have been discussed). Here we present the first large data set of the above mentioned gases obtained by processing nearly a year of nadir radiance spectra using initial versions (v0.4 and v0.41) of the WFM-DOAS retrieval algorithm. WFM-DOAS is a scientific retrieval algorithm which is independent of the official operational algorithm of DLR/ESA.

The SCIAMACHY/WFM-DOAS data set has been compared with independent ground based Fourier Transform Spectroscopy (FTS) measurements. These comparisons, which are limited to the data close to a given ground station,
are described elsewhere in this issue (Dils et al., 2005; Sussmann et al., 2005). Initial comparison for a sub-set of the data can be found in de Maziere et al. (2004); Sussmann and Buchwitz (2005); Warneke et al. (2005). The findings of these validation studies are consistent with the findings that will be reported in this study. Here, however, we focus on the comparison with global reference data.

High quality trace gas column retrieval from the SCIAMACHY near-infrared spectra is a challenging task for many reasons, e.g., because of calibration issues mainly related to high and variable dark signals (Gloudemans et al., 2005), because the weak CO lines are difficult to be detected, and because of the challenging accuracy and precision requirements for CO2 (Rayner and O’Brien, 2001; Houweling et al., 2004) and CH4. 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 of the data products. In this context it is important to point out that other groups are also working on this important topic using quite different approaches (see Gloudemans et al., 2004, 2005; Frankenberg et al., 2005a,b,c; Houweling et al., 2005).

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. Section 4 gives an overview about the processed data mainly in terms of time coverage. The main sections are the three Sects. 5–7 where the results for CO, CH4, and CO2 are separately presented and discussed. The conclusions are given in Sect. 8 and a short summary of our latest developments (v0.5 CO and XCH4) is given in Sect. 9.

2 The SCIAMACHY instrument

The SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) instrument (Burrows et al., 1995; Bovensmann et al., 1999, 2004) is part of the atmospheric chemistry payload of the European Space Agencies (ESA) environmental satellite ENVISAT, launched in March 2002. ENVISAT flies in sun-synchronous polar orbit crossing the equator at 10:00 AM local time. SCIAMACHY is a grating spectrometer that measures spectra of scattered, reflected, and transmitted solar radiation in the spectral region 240–2400 nm in nadir, limb, and solar and lunar occultation viewing modes.

SCIAMACHY consists of eight main spectral channels (each equipped with a linear detector array with 1024 detector pixels) and seven spectrally broad band Polarization Measurement Devices (PMDs) (details are given in Bovensmann et al., 1999). For this study observations of channel 6 (for CO2) and 8 (for CH4, CO, and N2O), and Polarization Measurement Device (PMD) number 1 (~320–380 nm) have been used. In addition, channel 4 has been used to determine the mass of dry air from oxygen (O2) column measurements using the O2 A band. Channels 4, 6 and 8 measure simultaneously the spectral regions 600–800 nm, 970–1772 nm and 2360–2385 nm at spectral resolutions of 0.4, 1.4 and 0.2 nm, respectively. For SCIAMACHY the spatial resolution, i.e., the footprint size of a single nadir measurement, depends on the spectral interval and orbital position. For channel 8 data the spatial resolution is 30×120 km2 corresponding to an integration time of 0.5 s, except at high solar zenith angles (e.g., polar regions in summer hemisphere), where the pixel size is twice as large (30×240 km2). For the channel 4 and 6 data used for this study the integration time is mostly 0.25 s corresponding to a horizontal resolution of 30×60 km2. SCIAMACHY also performs direct (extraterrestrial) sun observations, e.g., to obtain the solar reference spectra needed for the retrieval.

SCIAMACHY is one of the first instruments that performs nadir observations in the near-infrared (NIR) spectral region (i.e., around 2μm). In contrast to the ultra violet (UV) and visible spectral regions where high performance Si detectors have been manufactured for a long time, no appropriate near-infrared detectors were available when SCIAMACHY was designed. The near-infrared InGaAs detectors of SCIAMACHY were a special development for SCIAMACHY. Compared to the UV-visible detectors they are characterized by a substantially higher pixel-to-pixel variability of the quantum efficiency and the dark (leakage) current. Each detector array has a large number of dead and bad pixels. In addition, the dark signal is significantly higher compared to the UV-visible mainly because of thermal radiation generated by the instrument itself. The in-flight optical performance of SCIAMACHY is overall as expected from the on-ground calibration and characterization activities (Bovensmann et al., 2004). One exception is the time dependent optical throughput variation in the SCIAMACHY NIR channels 7 and 8 due the build-up of an ice layer on the detectors (“ice issue”) (Gloudemans et al., 2005). This effect is minimized by regular heating of the instrument (Bovensmann et al., 2004) during decontamination phases. The ice layers adversely influence the quality of the retrieval of all gases discussed in this paper as they result in reduced throughput (transmission) and, therefore, reduced signal and signal-to-noise performance. In addition, changes of the instrument slit function have been observed which introduce systematic errors (Gloudemans et al., 2005). All these issues complicate the retrieval.

3 WFM-DOAS retrieval algorithm

The Weighting Function Modified Differential Optical Absorption Spectroscopy (WFM-DOAS) retrieval algorithm and its current implementation is described in detail.
Fig. 1. Number of orbits per day of the year 2003 processed by WFM-DOAS (blue lines). The maximum number of orbits per day is about 14 (~100%). The red shaded areas indicate the decontamination phases performed to get rid of the ice layer that grows on the near-infrared detectors of channels 7 and 8. Data gaps are due to decontamination but also due to other (mostly ground processing related) reasons.

In short, WFM-DOAS is an unconstrained linear-least squares method based on scaling pre-selected trace gas vertical profiles. The fit parameters are 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 the measured radiances and solar irradiance spectrum, i.e., observed sun-normalized radiance. The WFM-DOAS reference spectra are the logarithm of the sun-normalized radiance and its derivatives. They are computed with a radiative transfer model taking into account line-absorption and multiple scattering (Buchwitz et al., 2000b). A fast look-up table scheme has been developed in order to avoid time consuming on-line radiative transfer simulations. A detailed description of the look-up table is given in Buchwitz and Burrows (2004) (please note that the current version of the look-up table is based on HITRAN2000/2003 line parameters) (Rothmann et al., 2003). A short description is also provided in Buchwitz et al. (2005).

In order to identify cloud-contaminated ground pixels we use a simple threshold algorithm based on sub-pixel information as provided by the SCIAMACHY Polarization Measurement Devices (PMDs) (details are given in Buchwitz et al., 2004, 2005). 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. As a result, ice or snow covered surfaces may be wrongly classified as cloud contaminated. This needs to be improved in future versions of our retrieval method.
The quality of the WFM-DOAS fits in the near-infrared is poor (i.e., the fit residuals are large) when applying WFM-DOAS to the operational Level 1 data products. In order to improve the quality of the fits and thereby the quality of our data products we pre-process the operational Level 1 data products mainly with respect to a better dark signal calibration (see Buchwitz et al., 2004, 2005). In addition, there are indications that the in-orbit slit function of SCIAMACHY is different from the one measured on-ground (Gloudemans et al., 2005) due to the ice layer (see Sect. 2). We use a slit function that has been determined by applying WFM-DOAS to the in-orbit nadir measurements. We selected the one that resulted in best fits, i.e., smallest fit residuum (see Buchwitz et al., 2004, 2005).

4 WFM-DOAS data products: Time coverage

The WFM-DOAS trace gas column data products have been derived by processing all consolidated SCIAMACHY Level 1 operational product files (i.e., the calibrated and geolocated spectra) of the year 2003 that have been made available by ESA/DLR (up to mid-2004). Figure 1 gives an overview about the number of orbits per day that have been processed. The maximum number of orbits per day is about fourteen. As can been seen (blue lines), all 14 orbits were available for only a small number of days. For many days no data were available. Many of the large data gaps are due to decontamination phases (see Sect. 2) which are indicated by red shaded areas. For November and December 2003 no consolidated (i.e., full product) orbit files have been made available (for ground processing related reasons).

5 Carbon monoxide (CO)

CO columns have been retrieved from a small spectral fitting window (2359–2370 nm) located in SCIAMACHY channel 8. The fitting window covers four CO absorption lines. The retrieval is complicated by strong overlapping absorption features of methane and water vapor. The first CO results from SCIAMACHY have been presented in Buchwitz et al. (2004) focusing on a detailed analysis of three days of data of the year 2003. For details concerning pre-processing of the spectra (for improving the calibration), WFM-DOAS v0.4 retrieval, vertical column averaging kernels, quality of the spectral fits, and a quantitative comparison with MOPITT Version 3 CO columns (Deeter et al., 2003; Emmons et al., 2004) we refer to Buchwitz et al. (2004). An initial error analysis using simulated measurements can be found in Buchwitz et al. (2004) and Buchwitz and Burrows (2004) where it is shown that the retrieval errors are expected to be less than about 20%. In Buchwitz et al. (2004) it has been shown that plumes of elevated CO can be detected with single overpass data in good qualitative agreement with MOPITT. Globally, for measurements over land, the standard deviation of the difference with respect to MOPITT was shown to be in the range 0.4–0.6 × 10^18 molecules/cm^2 and the linear correlation coefficient between 0.4 and 0.7. The differences of the CO from the two sensors depend on time and location but are typically within 30% for most latitudes. Perfect agreement with MOPITT is, however, not to be expected for a number of reasons (differences in overpass time, spatial resolution, etc.). In this context it is important to point out that the sensitivity of SCIAMACHY measurements is nearly independent of altitude whereas the sensitivity of MOPITT to boundary layer CO is low. On the other hand, retrieval of CO from SCIAMACHY is not problematic. For example, the WFM-DOAS v0.4 CO columns are scaled with a constant factor of 0.5 to compensate for an obvious overestimation (see Buchwitz et al., 2004, for details). This overestimation is most probably closely related to the difficulty of accurately fitting the weak CO lines in the selected fitting window (note that the CO columns of our new version 0.5 data product, which is retrieved from a different fitting window, are not scaled any more; see Sect. 9 for details). The fit residuals, which are on the order of the CO lines, are not signal-to-noise limited but dominated by (not yet understood) rather stable spectral artifacts.

Figure 2 shows a comparison of tri-monthly averaged WFM-DOAS version 0.4 CO columns with CO from MOPITT (version 3). Because of the low surface reflectivity of water in the NIR (outside sun-glint conditions) the nadir measurements are noisy over the ocean. Therefore, we focus on SCIAMACHY measurements over land. Only these measurements are shown in Fig. 2. The same land mask as used for SCIAMACHY has also been used for MOPITT to ease the comparison. SCIAMACHY data have only been included in Fig. 2 if the CO fit error was less than 60% and when the pixels were cloud free. As can be seen from Fig. 1, there are large SCIAMACHY data gaps. Therefore, the SCIAMACHY data shown in Fig. 2 are not tri-monthly averages obtained from a bias free sampling. For example, the July-September average is strongly weighted towards July and September due to a long decontamination period with no data in August. There are also gaps in the tropical region due to persistent cloud cover. Furthermore, there are no data over Greenland and Antarctica, and over large parts of the Northern Hemisphere in the period January to March. This is partially also due to clouds but mainly due to ice/snow covered surfaces because of the limitations of the cloud detection algorithm.

When comparing the January–March data from SCIAMACHY and MOPITT one can see that there are similarities but also differences. For example, the inter-hemispheric difference is clearly visible for MOPITT but barely visible for SCIAMACHY. Both sensors see low columns over regions of elevated surface topography (Himalaya, Andes and Rocky Mountains) and high columns over the western part of central Africa (where significant biomass burning is going

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The algorithm indicates a cloud free pixel. For MOPITT cloudy pixels are also not included.

For SCIAMACHY infrared only data have been averaged where the CO fit error is less than 60% and where the PMD1 cloud identification algorithm indicates a cloud free pixel. For MOPITT cloudy pixels are also not included.

SCIAMACHY CO columns over the Sahel region is not yet exactly understood but it is very likely that this is an overestimation due to systematic artifacts (caused by, for example, aerosol). This is supported by the fact that our new version 0.5 CO WFM-DOAS data product, which is shortly described in Sect. 9, shows significantly lower values over this region compared to v0.4. The version 0.5 CO columns are less sensitive to errors related to average light path (or observed airmass) uncertainty resulting from the unknown distribution of scattering material (aerosols, clouds) in the atmosphere and/or surface reflectivity variability. The reason for this is that the CO v0.5 column is normalized by the methane column obtained from the same spectral fitting window resulting in (at least partial) canceling of errors. Also over large on during the dry season), south-east Asia, parts of Europe, and the south-eastern part of the United States of America. Over South America and the northern part of Australia SCIAMACHY sees elevated CO not observed by MOPITT.

During April to June both sensors see elevated CO over large parts of the Northern Hemisphere (eastern part of the US, Canada, western Europe and large parts of Russia (the observed pattern are, however, not exactly identical), south-east Asia and parts of China. Over India and parts of south-east Asia SCIAMACHY sees elevated CO not seen by MOPITT. The largest difference over the Northern Hemisphere occurs over the western part of central Africa where the CO retrieved from SCIAMACHY is significantly higher than the CO from MOPITT. The reason for the elevated

Fig. 2. Tri-monthly averaged CO columns over land from SCIAMACHY/ENVISAT (left) and MOPITT/EOS-Terra (right). Only the columns over land are shown because the quality of the SCIAMACHY CO columns over water is low due to the low reflectivity of water in the near-infrared. For SCIAMACHY only data have been averaged where the CO fit error is less than 60% and where the PMD1 cloud identification algorithm indicates a cloud free pixel. For MOPITT cloudy pixels are also not included.

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In summary, the agreement with MOPITT is reasonable but there are large differences at certain locations during certain times of the year. More investigations are needed to explain the observed differences taking into account the different altitude sensitivities of both sensors.

6 Methane (CH$_4$)

The methane columns have been retrieved from a small spectral fitting window (2265–2280 nm) located in SCIAMACHY channel 8 which covers several absorption lines of CH$_4$ and several (much weaker) absorption lines of nitrous oxide (N$_2$O) and water vapor (H$_2$O). The main scientific application of the methane measurements of SCIAMACHY is to obtain information on the surface sources of methane. The modulation of methane columns due to methane sources is only on the order of a few percent. This is much weaker than the variation of the methane column due to changes of surface pressure/surface elevation (because methane is well-mixed the methane column is highly correlated with the total air mass over a given location and, therefore, with surface pressure). To filter out these much larger disturbing modulations, the methane columns need to be normalized by the observed airmass to obtain a so called dry air column averaged mixing ratio of methane (denoted XCH$_4$). To accomplish this, oxygen (O$_2$) columns have been retrieved in addition to the methane columns. From the oxygen columns the airmass can be calculated using its constant mixing ratio of 0.2095. The O$_2$ columns used to compute the WFM-DOAS v0.4 XCH$_4$ data product have been retrieved from the SCIAMACHY measurements in the O$_2$ A band spectral region (around 760 nm; channel 4).

First CH$_4$ results from SCIAMACHY have been presented in Buchwitz et al. (2005) focusing on a detailed analysis of four days of data of the year 2003. For details concerning pre-processing of the spectra (to improve the calibration), WFM-DOAS (v0.4) processing, averaging kernels, quality of the spectral fits, an initial error analysis (see also Buchwitz and Burrows, 2004), and a quantitative comparison with global models we refer to that study. According to the error analysis errors of a few percent due to undetected cirrus clouds, aerosols, surface reflectivity, temperature and pressure profiles, etc., are to be expected. It has been shown in Buchwitz et al. (2005) that the WFM-DOAS Version 0.4 methane columns have a time dependent (nearly globally uniform) bias of up to –15% (low bias of SCIAMACHY) for one of the four days that have been analyzed. The bias is correlated with the time after the last decontamination performed to get rid of the ice layers on the detector. Therefore, Buchwitz et al. (2005) concluded that the bias might be due to the “ice-issue” (see Sect. 2). This is consistent with the finding of Gloudemans et al. (2005) that the ice build-up on the detectors results in a broadening of the instrument slit function (the wider the slit function compared to the assumed
Typically, the weak methane source signal is difficult to be clearly detected with single overpass or single day SCIAMACHY data. For accurate detection of methane sources averages have to be computed. Because of the time dependent bias of the WFM-DOAS v0.4 methane columns this is, however, not directly possible.

In the following we describe how we have processed the SCIAMACHY data to get an improved version of our methane data product (Version 0.41) by applying a bias correction to the v0.4 methane columns. We assume that the data can be sufficiently corrected by dividing the columns by a globally constant scaling factor which only depends on time (on the day of the measurement). The correction factor has been determined as follows: For each day all cloud free v0.4 XCH₄ measurements over the Sahara have been averaged. The ratio of these daily average mixing ratios to a constant reference value (chosen to be 1750 ppbv) is approximately the methane bias (because methane is not constant this is not exactly the methane bias and a certain systematic error is introduced by this assumption). This time dependent methane bias is shown in Fig. 3 (black diamonds). This bias shows a similar time dependence as the independently measured channel 8 transmission loss also shown in Fig. 3 (red diamonds). The transmission has been determined by averaging the signal of the channel 8 solar measurements normalized to a reference measurement at the beginning of the mission. The varying transmission is a consequence of the varying ice layer on the detectors. Figure 3 shows a third curve, the (daily) correction factor (magenta diamonds). The correction factor curve has been obtained by linearly transforming the transmission curve. The coefficients of the linear transformation have been selected such that a good match is obtained with the methane bias curve. In order to correct the WFM-DOAS v0.4 methane columns for the systematic errors introduced by the ice layer the correction factors are applied as follows: All v0.4 methane columns of a given day have been divided by the correction factor for this day. The corrected WFM-DOAS v0.4 methane columns are the new WFM-DOAS v0.41 (absolute) methane columns.

In order to generate the new WFM-DOAS v0.41 XCH₄ product a second modification has been applied: Instead of normalizing the methane columns by the oxygen column retrieved from the 760 nm O₂ A band (as done for v0.4 XCH₄), they have been normalized by the CO₂ columns retrieved from the 1580 nm region (for details on CO₂ retrieval see Sect. 7). Using CO₂ rather than O₂ for normalizing the
methane columns has been first proposed by Frankenberg et al. (2005c) (the approach has been presented earlier, namely at the ENVISAT Symposium, Salzburg, Austria, September 2004).

The reason why normalizing methane by CO\textsubscript{2} rather than O\textsubscript{2} is expected to give better results for XCH\textsubscript{4} is that the CO\textsubscript{2} band is located spectrally much closer to the CH\textsubscript{4} band than the O\textsubscript{2} A band. Retrieval errors due to aerosols, residual cloud contamination, surface reflectivity uncertainties, etc., are expected to be the more similar, the more similar the radiative transfer is (including all parameters that influence the radiative transfer such as surface albedo). In general, this requires that the two spectral intervals from which the two columns are retrieved are spectrally located as close as possible next to each other (there are exceptions, of course, for example in case of spectral absorption features). As the CO\textsubscript{2} band is located spectrally much closer to the CH\textsubscript{4} band than the O\textsubscript{2} A band. 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The comparison with the model simulations shows similarities but also differences. Very interestingly and in qualitative agreement with the model simulations, the measurements show high CH\textsubscript{4} mixing ratios in the September to October 2003 average over India, southeast Asia, and over the western part of central Africa, which are absent or significantly lower in the March to April average. In the model the high columns over these regions are a result of methane emissions mainly from rice fields, wetlands, ruminants, and waste handling. The good agreement with the model simulations indicates that SCIAMACHY can detect these emission signals. Similar findings have been reported in Frankenberg et al. (2005c). However, there are also differences compared to the model simulations. For example, in the March–April average the SCIAMACHY data are a few percent higher over large parts of northern South America. Over large parts of the Northern Hemisphere the SCIAMACHY data are a few percent lower.

We have also compared monthly averaged v0.41 XCH\textsubscript{4} with (the throughput-based) bias corrected v0.4 XCH\textsubscript{4} to assess the impact of normalizing by CO\textsubscript{2} (as done for v0.41) compared to normalizing by O\textsubscript{2} (as done for v0.4). For example for October 2003 this comparison showed significant differences. The extended plumes of high v0.41 XCH\textsubscript{4} over India, China, and central Africa (similar as those shown in Fig. 4) do not show up so clearly in the v0.4 XCH\textsubscript{4}. In addition, there are also large differences at other places with the v0.4 XCH\textsubscript{4} being more “noisy” (more inhomogeneous) than v0.41 XCH\textsubscript{4}. This confirms that cancellation of errors is better for v0.41 XCH\textsubscript{4} (normalization by CO\textsubscript{2}) than for v0.4 XCH\textsubscript{4} (normalization by O\textsubscript{2}). The impact of using the O\textsubscript{2} measurements to obtain column averaged mixing ratios is further discussed in Sect. 7 where it has been used to obtain XCO\textsubscript{2}.

Figure 5 shows a quantitative comparison of the global daily data with the TM5 model, the correlation coefficient and the bias for the two versions of SCIAMACHY XCH\textsubscript{4} data products, namely v0.4 and v0.41. As can be seen, the bias is significantly smaller for the v0.41 data, although not zero. There still appears to be a systematic bias due to the ice issue indicating that the bias correction applied to generate...
the v0.41 data is not perfect. Also the correlation with the model results is typically significantly better for the version 0.41 data.

7 Carbon dioxide (CO$_2$)

The CO$_2$ columns have been retrieved using a small spectral fitting window (1558–1594 nm) located in SCIAMACHY channel 6 (which is not affected by an ice layer). This spectral region covers one absorption band of CO$_2$ and weak absorption features of water vapor. As for methane v0.4 (air or O$_2$-normalized CO$_2$ columns have been derived, the dry air column averaged mixing ratios XCO$_2$. First results of CO$_2$ from SCIAMACHY have been presented in Buchwitz et al. (2005). For details concerning pre-processing of the spectra (for improving the calibration), WFM-DOAS (v0.4) processing, vertical column averaging kernels, quality of the spectral fits, and a quantitative comparison with global model simulations we refer to Buchwitz et al. (2005). An initial error analysis using simulated measurements is given in Buchwitz et al. (2005) and Buchwitz and Burrows (2004). According to this analysis, errors of a few percent due to undetected
cirrus clouds, aerosols, surface reflectivity, temperature and pressure profiles, etc., are to be expected. To compensate for a not yet understood systematic underestimation of the initially retrieved CO₂ columns the WFM-DOAS v0.4 CO₂ columns have been scaled with a constant factor of 1.27 (see Buchwitz et al., 2005, for details). The factor has been chosen to make sure that the CO₂ column is near its expected value of about 8 × 10^{21} molecules/cm² for a cloud free scene with a surface elevation close to sea level and moderate surface albedo. In Buchwitz et al. (2005) it has been shown that the WFM-DOAS v0.4 CO₂ (scaled) columns agree with model columns within a few percent (range −3.7% to +2.0%). Because of the scaling factor a meaningful comparison with reference data should focus on variability in time and space and not on the absolute level. Also the v0.4 O₂ columns, used to compute XCO₂, are scaled (by 0.85). The reason for the about 15% overestimation of the originally retrieved O₂ columns is currently unclear. The factor has been chosen to make sure that the O₂ column is near its expected value of about 4.5 × 10^{24} molecules/cm² for a cloud free scene with a surface elevation close to sea level and moderate surface albedo. In a recent paper of van Diedenhofen et al. (2005) an overestimation of 2–5% over scenes with moderate to high surface albedo is found when comparing their SCIAMACHY O₂ columns with actual meteorological data. They found that 2% can be explained by an offset on the measured reflectance and argue that the remaining overestimation is likely due to aerosols. Taking this into account our retrievals are still overestimated by 10%. At present we cannot offer an explanation for this discrepancy. The investigation of this will be a focus of our future work. For now we have to state that the v0.4 CO₂ and O₂ columns are scaled resulting in a quite large scaling factor for XCO₂ of 1.49 (=1.27/0.85). Because of this we focus on variability rather than on absolute XCO₂ levels when comparing our XCO₂ to reference data.

In Buchwitz et al. (2005) it has been shown that the spatial and temporal pattern of the retrieved column averaged mixing ratio is in reasonable agreement with the model data except for the amplitude of the variability. The measured variability is about a factor of four higher than the variability of the model data (about 6% compared to about 1.5% for the model data). This is also confirmed in this study which provides more details on this finding. In this context it is important to note that an overestimation of the retrieved variability of about a factor 2.2 (at maximum) may be explained as follows: The SCIAMACHY/WFM-DOAS CO₂ column averaging kernels (shown in Buchwitz et al., 2005) peak in the lower troposphere and have a maximum value of about 1.5. This means that the retrieved variability is overestimated by 50% (e.g., 3 ppmv instead of 2 ppmv) if this column variability is entirely due to variability in the lower troposphere (note that the averaging kernels typically decrease with altitude and reach 1.0 (i.e., no over- or underestimation) around 400 hPa (~7 km); above 400 hPa they are less than 1.0). The scaling factor of 1.49 which is currently applied to the retrieved XCO₂ may also contribute to an enhancement of the retrieved variability. This however requires that the initially retrieved columns are off by a constant offset rather than a constant scaling factor (this aspect needs further investigation). The averaging kernels in combination with the scaling factor might explain at maximum a factor of 2.2 (=1.5 × 1.49) overestimated variability. The different resolution of the SCIAMACHY measurements (60 × 30 km²) and the model simulations (1.8 × 1.8 deg) also contribute to a difference in the observed and the modeled variability. Further study is needed to identify the origin of the scaling factors for CO₂ and O₂. Also the averaging kernels need to be taken into account when comparing with reference data. The factor of 2.2 however can only partially explain the observed variability. At least a factor of 2 higher observed variability still needs to be explained.

In the following we present a detailed comparison of the retrieved XCO₂ with TM3 model simulations. TM3 3.8 (Heimann and Körner, 2003) is a three-dimensional global atmospheric transport model for an arbitrary number of active or passive tracers. It uses re-analyzed meteorological fields from the National Center for Environmental Prediction (NCEP) or from the ECMWF re-analysis. The modeled processes comprise tracer advection, vertical transport due to convective clouds and turbulent vertical transport by diffusion. Available horizontal resolutions range from 8 × 10 deg to 1.1 × 1.1 deg. In this case, TM3 was run with a resolution of 1.8 × 1.8 deg and 28 layers, and the meteorology fields were derived from the NCEP/DOE AMIP-II reanalysis. CO₂ source/sink fields for the ocean originate from Takahashi et al. (2002), for anthropogenic sources from the EDGAR 3.2 database and for the biosphere from the BIOME-BGC model (Thornton et al., 2002) with inclusion of a simple parameterization of the diurnal cycle in photosynthesis and respiration. For SCIAMACHY the averages have been computed using only the cloud free pixels with a XCO₂ error of less than 10%. Shown in Fig. 6 are only the data over land because of the problems with measuring over the ocean in the near-infrared (see Sect. 5).

For SCIAMACHY Fig. 6 shows absolute column averaged mixing ratios of CO₂ in the range 335–385 ppmv. For TM3 “uncalibrated” XCO₂-offsets are shown which are in the range 0–13.7 ppmv. These offsets do not include the (current) background concentration of CO₂. Therefore, not the absolute values but only the variability in space and time should be compared. The model simulations show low CO₂ columns (compared to the mean column) over the Northern Hemisphere in July 2003 compared to higher values in May and September. This is mainly due to uptake of CO₂ by the biosphere which results in minimum columns around July. Qualitatively the SCIAMACHY data show a similar time dependence with also lower columns in July compared to May and September. Thus the general time dependence of the SCIAMACHY retrievals is consistent with the model simulations.
Fig. 6. Comparison of SCIAMACHY XCO$_2$ (left) with TM3 model simulations (right). For SCIAMACHY all cloud free measurements over land have been averaged where the CO$_2$ column fit error is less than 10%. For TM3 monthly averaged XCO$_2$-offsets are shown. These offsets do not include the background concentration of CO$_2$. Therefore, only the spatial and temporal variability should be compared. Two different scales have been used, one for SCIAMACHY ($\pm$25 ppmv) and one for the model simulations ($\pm$6.85 ppmv), to consider the 3–4 times higher variability of the SCIAMACHY data compared to the model data.

Figure 6 shows that over large parts of the (mostly western) Sahara SCIAMACHY sees “plumes” of relatively high CO$_2$ (red colored areas) not present in the model simulations. These few percent too high CO$_2$ mixing ratios may result from the high surface reflectivity over the Sahara in combination with aerosol variability. This is qualitatively consistent with the analysis of Houweling et al. (2005) who performed a detailed study on the impact of aerosols and albedo on SCIAMACHY CO$_2$ column retrievals. We are optimistic that this problem can be substantially reduced in future versions of our retrieval algorithm which currently only considers first order effects of albedo and aerosol variability (mainly by including a polynomial in our WFM-DOAS fit). Currently, for the radiative transfer simulations, a constant surface albedo of 0.1 is assumed and only one aerosol scenario. According to the error analysis presented in Buchwitz et al. (2005) the XCO$_2$ error is estimated to be +4.5% (16 ppmv overestimation) if the albedo is 0.3 instead of 0.1 (for a solar zenith angle of 50°). Depending on the aerosol scenario and on a number of other parameters the actual error might be...
somewhat higher or lower. This indicates that the high values seen by SCIAMACHY over the Sahara may be explained by retrieval algorithm limitations as the current version does not take albedo and aerosol variations fully into account.

To provide more confidence that the uptake (and release) of CO$_2$ by the biosphere can be observed with SCIAMACHY, the year 2003 XCO$_2$ data set has been investigated in more detail. This is important, because the estimated retrieval errors are on the same order as the few ppmv XCO$_2$ variations shown by the model. It has to be made sure that the observed XCO$_2$ modulations are not an artifact resulting from, e.g., solar zenith angle dependent errors. Figure 7 shows a detailed comparison of the daily data as well as for time averaged data (using a 31 days running mean) for the entire year 2003 data set.

Before we discuss the first three panels we will discuss the bottom part of Fig. 7. The last three panels show the mean difference between SCIAMACHY (black) and TM3 (blue),
SCIAMACHY data (shown in black) have been obtained as follows: Two regions have been defined (each 20 deg latitude series has been subtracted. The blue curve has been obtained by applying the same procedure to the TM3 model data. Annotation: which are denoted region 1 (the reference region) and region 2 (both regions are shown in Fig. 9 where, for example, the reference region is detected). For each region its daily average XCO2 has been determined (considering only measurements over land). The daily time series for the reference region has been subtracted from the time series of region 2 (only if data were available for both regions; if not the day was ignored). The time series of the XCO2 difference has been smoothed (21 days running mean). Finally, the mean of the time series has been subtracted. The blue curve has been obtained by applying the same procedure to the TM3 model data. Annotation: _r_ denotes Pearson’s linear correlation coefficient and _s_ is a scaling factor obtained from a linear least squares fit of the SCIAMACHY time series to the TM3 time series (2.47 means that the SCIAMACHY XCO2 anomaly time series has to be divided by 4.7 to match the TM3 time series). The middle and the bottom panels show the corresponding time series for two other regions denoted regions 3 and 4 (shown in Fig. 9).

The first three panels of Fig. 7 show that the SCIAMACHY data (shown in black) have been obtained as follows: Two regions have been defined (each 20 deg latitude × 20 deg longitude) which are denoted region 1 (the reference region) and region 2 (both regions are shown in Fig. 9 where, for example, the reference region is shown as green rectangle). For each region its daily average XCO2 has been determined (considering only measurements over land). The daily time series for the reference region has been subtracted from the time series of region 2 (only if data were available for both regions; if not the day was ignored). The time series of the XCO2 difference has been smoothed (21 days running mean). Finally, the mean of the time series has been subtracted. The blue curve has been obtained by applying the same procedure to the TM3 model data. Annotation: _r_ denotes Pearson’s linear correlation coefficient and _s_ is a scaling factor obtained from a linear least squares fit of the SCIAMACHY time series to the TM3 time series (2.47 means that the SCIAMACHY XCO2 anomaly time series has to be divided by 4.7 to match the TM3 time series). The middle and the bottom panels show the corresponding time series for two other regions denoted regions 3 and 4 (shown in Fig. 9).

The first three panels of Fig. 7 show that the SCIAMACHY observations are significantly correlated with the model results. The time dependence of the observed XCO2 cannot be explained by a solar zenith angle dependent error. Over the Northern Hemisphere the minimum solar zenith

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angle occurs at summer solstice (21 June; around day 170), i.e., close to the day where the XCO$_2$ values cross the zero line and change sign. A solar zenith angle dependent error would be symmetric around summer solstice, but the curves are anti-symmetric with respect to this day. This means that the observed XCO$_2$ is not significantly influenced by a solar zenith angle dependent error. A significant error due to the changing solar zenith angle was not to be expected as the solar zenith angle dependence of the radiative transfer is explicitly taken into account for WFM-DOAS retrievals. Similar arguments can be given for atmospheric temperature related errors. Temperature variability is taken into account because a temperature weighting function is included in the WFM-DOAS fit.

Now we will focus on the regional scale. A comparison between observed and modeled XCO$_2$ for regions of size 20 deg latitude times 20 deg longitude yields similar sinusoidal curves (not shown here) as displayed in the first two panels of Fig. 7 for the hemispheric averages. In order to better highlight regional differences we have compared differences between time series from two regions. Typical results are shown in Fig. 8. We have selected a smaller interval for the time averaging (21 days) compared to the interval used for Fig. 7 (31 days) to better display the regional differences.

The top panel of Fig. 8 shows the observed time series (in black) and the model time series (in blue). These curves are the difference of the time series of two regions, region 2 and region 1 (region 1 is denoted the reference region in the

Figure 9. Correlation coefficient $r$ (top panel) and scaling factor $s$ (bottom panel) for SCIAMACHY and TM3 time series of regional XCO$_2$ differences (see Fig. 8 for a detailed explanation). The green area indicates the reference region (region 1). Details for regions 2–4 are shown in Fig. 8. The correlation coefficient is only shown for those regions where the final time series comprises at least 70 days. The scaling factor (bottom panel) is only shown for a subset of the regions shown in the top panel, namely only for regions where the correlation coefficient is larger than 0.7.
following). The spatial positions of both regions (and of the regions 3 and 4 investigated in the remaining two panels) are shown in Fig. 9. As in Fig. 7 all curves are shown as anomalies. As can be seen, the measured and the modeled curve are significantly correlated \( r=0.88 \). The main difference is the amplitude. The SCIAMACHY curve has been divided by a scaling factor \( s \), which is 4.7. This value has been determined by a linear least-squares fit. The middle and the bottom panels show the same comparison for two other regions (shown in Fig. 7) but using the same reference region (region 1). Figure 7 shows the extension of this analysis to the entire globe (but restricted to land surfaces) using the same region 1 as reference region as used for the detailed results shown in Fig. 8. Shown in the top panel, which displays the correlation coefficient \( r \) (see Fig. 8), are only those regions where at least 70 days with measurements were available in this region and (for the same days) also in the reference region. The bottom panel show the scaling factor \( s \) (see Fig. 8) for the sub-set of the regions shown in the top panel where the correlation coefficient is larger than 0.7 (otherwise the scaling does not make too much sense). The top panel shows that significant correlations exist for most regions between observed and modelled \( XCO_2 \). The bottom panel shown that the scaling factor is mostly in the range 3–7 and always less than 9. This analysis confirms earlier results obtained with the same data set also indicating that the retrieved \( XCO_2 \) variability is typically significantly larger than the variability of the model simulations (typically larger than a factor of 2 which might be explained by the averaging kernels and the applied scaling factor). This analysis also indicates that SCIAMACHY seems is able to capture regional \( XCO_2 \) differences which is important for the main application of these measurements, namely the detection and quantification of regional sources and sinks of \( CO_2 \).

### 8 Conclusions

Nearly one year (2003) of SCIAMACHY nadir measurements have been processed with the WFM-DOAS retrieval algorithm (v0.4, for methane also v0.41) to generate a number of data products: vertical columns of \( CO \), \( CH_4 \), and \( CO_2 \). In addition, \( O_2 \) columns have been retrieved to compute dry air column averaged mixing ratios for the relatively well-mixed greenhouse gases \( CH_4 \) and \( CO_2 \), denoted \( XCH_4 \) and \( XCO_2 \), respectively. The data products have been compared with independent measurements (\( CO \) from MOPITT) and model simulations (\( CH_4 \) and \( CO_2 \)).

For the \( CO \) columns the agreement with MOPITT is mostly within 30% (Buchwitz et al., 2004). SCIAMACHY detects enhanced concentrations of \( CO \) due to biomass burning similar as MOPITT. SCIAMACHY seems to systematically overestimate the \( CO \) columns over large parts of the Southern Hemisphere at least for certain months where MOPITT sees systematically lower columns in the Southern Hemisphere compared to the Northern Hemisphere. This discrepancy is most probably related to the difficulty of accurately fitting the weak \( CO \) lines covered by SCIAMACHY (see Sect. 9).

The WFM-DOAS Version 0.4 methane columns have a time dependent bias of up to about \(-15\%\) related to ice build-up on the channel 8 detector. Using a simple bias correction an improved methane data product (v0.41) has been generated. The comparison with model simulations shows agreement within a few percent (mostly within 5%). The comparison indicates that SCIAMACHY can detect elevated methane columns resulting from emissions from surface sources such as rice fields and wetlands over India, southeast Asia and central Africa. Similar findings have been reported in Frankenberg et al. (2005c).

The (scaled) WFM-DOAS Version 0.4 \( CO_2 \) columns show agreement with model simulations within a few percent (mostly within 5%). The comparison indicates that SCIAMACHY is able to detect low columns of \( CO_2 \) resulting from uptake of \( CO_2 \) over the Northern Hemisphere when the vegetation is in its main growing season. Over highly reflecting surfaces such as over the Sahara SCIAMACHY seems to systematically overestimate the \( CO_2 \) column averaged mixing ratio of \( CO_2 \) by a few percent most probably because of limitations of the current version of the retrieval algorithm (simplified treatment of albedo and aerosol variability).

A summary of our findings from the comparisons with independent data shown here and elsewhere (Buchwitz et al., 2004, 2005; Cloudemans et al., 2004; de Maziere et al., 2004; Dils et al., 2005; Sussmann et al., 2005; Sussmann and Buchwitz, 2005; Warneke et al., 2005) is given in Table 1 which shows our current best estimates of precision and accuracy of our v0.4x data products.

<table>
<thead>
<tr>
<th>Data product</th>
<th>Horizontal resolution [km²]</th>
<th>Estimated precision (scatter) [%]</th>
<th>Estimated accuracy (bias) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CO ) (v0.4)</td>
<td>30×120</td>
<td>10–20</td>
<td>10–30 (mostly positive)</td>
</tr>
<tr>
<td>( XCH_4 ) (v0.4)</td>
<td>30×120</td>
<td>1–6</td>
<td>2–15 (mostly negative)</td>
</tr>
<tr>
<td>( XCH_4 ) (v0.41)</td>
<td>30×120</td>
<td>1–4</td>
<td>2–5</td>
</tr>
<tr>
<td>( XCO_2 ) (v0.4)</td>
<td>30×60</td>
<td>1–4</td>
<td>2–5</td>
</tr>
</tbody>
</table>
products. This work has already started and the latest status is shortly summarized in the next section.

9 Outlook

Recently (May 2005), we have reprocessed the year 2003 data for CO and XCH$_4$ with a new version (v0.5) of the WFM-DOAS retrieval algorithm. Our initial analysis indicates that at least some of the major problems identified for the v0.4x data products discussed in this paper have been solved. For example, the v0.5 CO is retrieved from an optimized fitting window and is not scaled any more (the v0.4 product was scaled with the factor 0.5). The v0.5 CO is normalized with the methane column retrieved from the same fitting window. This approach results (at least partially) in canceling of errors which are common to both gases (e.g., errors due to slit function changes caused by the ice issue, partial clouds, aerosols). For v0.5 XCH$_4$ the methane column is obtained from channel 6 which is not affected by the ice issue. More details concerning the v0.5 CO and methane data products are given in a separate paper (de Beek et al., 2005).

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Validation of ENVISAT/SCIAMACHY columnar methane by solar FTIR spectrometry at the Ground-Truthing Station Zugspitze

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Abstract. Methane total-vertical column retrievals from ground-based solar FTIR measurements at the Permanent Ground-Truthing Station Zugspitze (47.42\(^{\circ}\)N, 10.98\(^{\circ}\)E, 2964 m a.s.l.), Germany are used to validate column averaged methane retrieved from ENVISAT/SCIAMACHY spectra by WFM-DOAS (WFMD) version 0.4 and 0.41 for 153 days in 2003. Smoothing errors are estimated to be below 0.10% for FTIR and 0.14% for SCIAMACHY -WFMD retrievals and can be neglected for the assessment of observed bias and day-to-day-scatter. In order to minimize the altitude-difference effect, dry-air column averaged mixing ratios (XCH\(_4\)) have been utilized. From the FTIR-time series of XCH\(_4\) an atmospheric day-to-day variability of 1% was found, and a sinusoidal annual cycle with a \(\approx 1.6\%) amplitude. To obtain the WFMD bias, a polynomial fitted to the FTIR series was used as a reference. The result is WFMD v0.4/FTIR=1.008\(\pm\)0.019 and WFMD v0.41/FTIR=1.058\(\pm\)0.008. WFMD v0.41 was significantly improved by a time-dependent bias correction. It can still not capture the natural day-to-day variability, i.e., the standard deviation calculated from the daily-mean values is 2.4% using averages within a 2000-km radius, and 2.7% for a 1000-km radius. These numbers are dominated by a residual time-dependent bias correction. Standard deviations of the daily means, calculated from the individual measurements of each day, are excluding time-dependent biases, thus showing the potential precision of WFMD daily means, i.e., 0.3% for a 2000-km selection radius, and 0.6% for a 1000-km selection radius. Therefore, the annual cycle as well as possibly the day-to-day variability could be captured under the prerequisite of further advanced time-dependent bias corrections, or the use of other channels, where the icing issue is less prominent.

1 Introduction

The atmospheric trace species methane (CH\(_4\)) contributes by 15% to the anthropogenic greenhouse forcing, and has recently been included into the list of the so called “Kyoto gases”. It has thus become mandatory to better understand and monitor its spatiotemporal distribution on a global and centennial scale. In particular, the locations and strengths of the CH\(_4\) sources are not sufficiently quantified yet (IPCC, 2001). An obstacle for the quantification of surface sources is that measurements of small variations on top of a large background of this well-mixed gas are required. Therefore, measurements with both high precision and global coverage are needed.

High-precision measurements of in-situ mixing ratios are realized by surface-sampling sites of the GAW (Global Atmosphere Watch) and NOAA/CMDL (National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory) networks. By the inverse modeling of these in-situ measurements the global atmospheric CH\(_4\) cycle has been characterized and the average uncertainties of CH\(_4\) source magnitudes could be reduced by more than one third (Hein et al., 1997).

Ground-based solar FTIR (Fourier Transform Infrared) spectrometry sites operated within the NDSC (Network for the Detection of Stratospheric Change) are yielding vertical total columns of CH\(_4\). The Zugspitze FTIR is a so called Primary-Status instrument within the NDSC, which certifies both operationality and data quality on a highest level. These ground-based total-column measurements are crucial for the validation of the upcoming satellite missions dedicated to the measurement of greenhouse gases, and are likely to become important constraints on the geographic and temporal distribution of CH\(_4\) sources and sinks in the future.

Satellite-borne remote sounders are also providing total columns and have the potential to add the required information on the global distribution of CH\(_4\) to the highly precise ground-based networks, but strongly rely upon careful
ground-truthing. The first global maps of CH$_4$ columns have been retrieved from IMG/ADEOS thermal infrared (TIR) nadir spectra (Kobayashi et al., 1999). The results show qualitatively the expected variability, for example the North-South hemispheric gradient (Clerbaux et al., 2003). The CH$_4$ amounts retrieved from TIR nadir observations are relatively insensitive to changes within the lower troposphere, however.

Meanwhile, another satellite instrument has achieved the potential to retrieve global information on CH$_4$, i.e., the Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY (SCIAMACHY), which is a UV/visible/near-infrared spectrometer onboard ENVISAT launched in 2002 (Bovensmann et al., 1999). Due to the near-infrared (NIR) spectral domain the SCIAMACHY nadir measurements of CH$_4$ are highly sensitive to concentration changes at all altitude levels, including the boundary layer (see Sect. 3).

In this paper we focus on the validation of the SCIAMACHY scientific total-column product retrieved at the University of Bremen by the Weighting Function Modified DOAS (WFMD) algorithm (Buchwitz and Burrows, 2004; Buchwitz et al., 2005a, b), which utilizes an iterative spectral fitting by scaling of an US-standard a priori profile. CH$_4$ has been retrieved from the 2265–2280 nm spectral region. Simultaneously, oxygen (O$_2$) columns have been retrieved from the oxygen A band (around 760 nm). This enables the dry-air column averaged mixing ratio, denoted as XCH$_4$, to be determined: XCH$_4$=CH$_4$-column/O$_2$-column×0.2095, where 0.2095 is the O$_2$ mixing ratio of dry air. This normalization is a means of significantly improving the attainable measurement precision, because many systematic errors are common to the CH$_4$ and O$_2$ spectrometric retrievals, respectively, and thus cancel out (e.g., errors in pressure or zenith angle are propagating in a similar way to the retrieved columns of CH$_4$ and O$_2$). Our validation study refers to version 0.4 of the WFMD product 2003 data set, that has been released via the internet on 6 September 2004, including all consolidated SCIAMACHY level-1B products available for 2003, i.e., 153 days from the time period January 2003–October 2003. Additionally, we validate the version 0.41 XCH$_4$ data update, released on 30 September 2004, which includes an a-posteriori time-dependent bias correction, based on a channel-8 throughput analysis. Our study is the first validation of this (WFMD version 0.41) promising attempt to compensate for the time-dependent slit function changes due to the SCIAMACHY-channel 8 ice-build up. (XCH$_4$ version 0.41 also utilizes a normalization by CO$_2$ rather than O$_2$, which has the advantage of being retrieved in a spectral domain that is spectrally more closely neighbored to the target species). The SCIAMACHY CH$_4$ scientific product plays a key role for the users community, since there has been no operational product for CH$_4$ released by ESA yet.

An initial comparison of WFMD CH$_4$ retrievals to global models showed that the measured column amounts agree with the model columns within a few percent. For individual measurements the standard deviations of the difference with respect to the models were found to be in the range of 100–200 ppbv (5–10%) for XCH$_4$ (Buchwitz et al., 2005a). Early characterization studies of SCIAMACHY scientific products have also been presented at the Second Workshop on the Atmospheric Chemistry Validation of ENVISAT (ESA, 2004).

In this paper we want to promote the validation and maturation of SCIAMACHY XCH$_4$ by comparing the WFMD v.04 and v.04.1 retrievals to the ground-based correlative solar FTIR data of the clean air site Zugspitze. The goal of this paper is i) to thereby assess the overall bias of WFMD v0.4 and 0.41, ii) characterize the time-dependent bias (ice issue) in detail, in particular the intended effect from the version 0.4 to 0.41 update, and ii) to address the question, to which degree the precision of the WFMD retrievals allows to reflect the true atmospheric variability of CH$_4$ in a realistic manner – both for the version 0.41 at hand, and under the assumption that the problem of time-dependent bias could be further reduced in future WFMD-data updates.

2 The correlative ground-data set from Zugspitze solar FTIR

Validation is performed using the ground-based data that are being recorded by the NDSC-Primary Status solar FTIR instrument at the Zugspitze (47.42° N, 10.98° E, 2964 m a.s.l.) continuously. The Zugspitze-FTIR instrument and retrieval-set up has been described in detail elsewhere (Sussmann et al., 1997; Sussmann, 1999). Briefly, a high-resolution Bruker IFS 120 HR Fourier Transform Spectrometer is operated with an actively controlled solar tracker, and liquid-nitrogen cooled MCT (HgCdTe) and InSb detectors.

The Zugspitze CH$_4$ total columns are retrieved by using non-linear least squares spectral fitting software (SFIT) initially developed at NASA Langley Research Center (Rinsland et al., 1984). For the CH$_4$ total-column retrievals we applied a strong smoothness constraint based upon a VMR a priori profile obtained from balloon-borne FTIR measurements (provided by G.C. Toon, JPL/NASA). We have chosen this conservative approach for the validation purpose of this paper, i.e., we are not performing a full profile retrieval (e.g., via optimal estimation). This is because there are still unresolved spectroscopic problems for CH$_4$, like line mixing, that can propagate into erroneous profiles retrievals via the forward model, leading to subsequent errors in the retrieved columns. This effect is minimized by applying a strong smoothness constraint to the retrievals. The HITRAN-2000 molecular line parameters compilation was used (Rothmann et al., 2003), and daily p-T-profiles from the Munich radio sonde station (located 80 km to the north of the Zugspitzte) have been utilized.

For the CH$_4$ column retrievals two different spectral domains from routine-measurement operations were utilized, i.e., a MCT-detector domain micro-window at
Table 1. Statistics of XCH$_4$ data scatter for FTIR and WFMD v0.41 measurements and time periods as indicated in Fig. 5. The index for the number of measurement days is $i$. First column: $AV_{i}(n_{i})$, i.e., average of the numbers $n_{i}$ of individual measurements during each measurement day. Second column: $AV_{i}(\sigma_{i})$, i.e., average of the “single-value standard deviations” calculated from the individual measurements for the different days. 3rd column: $AV_{i}(\sigma_{i}/\sqrt{n_{i}})$, i.e., average of the “standard deviations of the daily mean values” calculated from the individual measurements for the different days. 4th column: Standard deviations of daily means calculated from the daily-means data sets as shown in Fig. 5a, i.e., normalized to the annual cycle (polynomial fit to FTIR). 5th column: Standard deviations of daily means calculated from the daily-means data sets as shown in Fig. 5b, i.e., after applying an empirical time-dependent bias-correction (polynomial fit to WFMD v0.41). SCIAMACHY data were taken within a 2000-km pixel-selection radius around the Zugspitze for each day (“SCIA 2000”), and a 1000-km selection radius (“SCIA 1000”), respectively.

<table>
<thead>
<tr>
<th></th>
<th>$AV_{i}(n_{i})$</th>
<th>$AV_{i}(\sigma_{i})$</th>
<th>$AV_{i}(\sigma_{i}/\sqrt{n_{i}})$</th>
<th>$\sigma$ of daily means corrected for ann. cycle (Fig. 5a)</th>
<th>$\sigma$ of daily means incl. empirical time-dependent bias correction (Fig. 5b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zugspitze FTIR</td>
<td>12.3</td>
<td>1.3%</td>
<td>0.4%</td>
<td>1.0%</td>
<td>–</td>
</tr>
<tr>
<td>SCIA 2000</td>
<td>249</td>
<td>5.2%</td>
<td>0.3%</td>
<td>2.4%</td>
<td>1.6%</td>
</tr>
<tr>
<td>SCIA 1000</td>
<td>85</td>
<td>5.4%</td>
<td>0.6%</td>
<td>2.7%</td>
<td>2.4%</td>
</tr>
</tbody>
</table>

1201.80–1202.65 cm$^{-1}$, (859 spectra recorded on 133 measurement days in 2003; each spectrum resulted from integrating 8 interferometric scans with a 250-cm optical path difference within 20 min) and an InSb-detector domain micro-window at 2835.55–2835.85 cm$^{-1}$ (781 spectra recorded on 133 measurement days in 2003; each spectrum resulted from 5 scans with a maximum optical path difference of 175 cm integrated within 10 min). I.e., on average 6.5 MCT-spectra and 5.8 InSb spectra were recorded per day, yielding 6.5+5.8=12.3 retrieved columns per day. The accuracies and precisions for CH$_4$ vertical-column retrievals from single ground-based FTIR measurements are well characterized and understood and have been estimated from sensitivity studies to be below 6.5% and 2.5%, respectively, see, e.g., Zander et al. (1989). The actual numbers depend somewhat on changing geophysical parameters like the actual solar zenith angle. Daily mean columns were calculated using the arithmetic mean of the individual columns. From the above error numbers the precision of a daily-mean column from our FTIR retrievals is estimated to be below 2.5%/sqrt(12.3)=0.7%. We will show in Sect. 4.2.1 below, that we find an even smaller number of 0.4% for the precision of a daily mean XCH$_4$ columns derived directly from our real FTIR measurements.

We calculated Zugspitze XCH$_4$, i.e., air-column averaged mixing ratios for the validation purpose of this paper by dividing the FTIR CH$_4$ columns by the air columns calculated from the daily radio soundings. Note that alternatively, other authors have used for the ground-based retrievals a normalization to O$_2$ columns measured by FTIR at the same time (Washenfelder et al., 2003), i.e., an analogous approach as described for the satellite retrievals above.

3 Validation approach

First we focus on investigating the bias of absolute XCH$_4$ values. The retrieval of WFMD version 0.4 XCH$_4$ includes an empirical column scaling factor, i.e., an O$_2$ column scaling factor of 0.85 (no scaling factor for CH$_4$), which will be validated. Version 0.41 XCH$_4$ data include a time-dependent bias correction in order to account for the icing issue of SCIAMACHY channel 8, and a normalization to CO$_2$ instead of O$_2$, which both will be validated.

Subsequently, validation focus will be put in our study on precision and dynamic response of the SCIAMACHY retrievals. I.e., we will investigate, whether the atmospheric day-to-day variabilities, which are dominated by dynamically induced tropopause movements, can be retrieved from the SCIAMACHY data. Furthermore, we find from the Zugspitze FTIR measurements, that the amplitude of the sinusoidal XCH$_4$ annual cycle (dominated by the tropopause annual cycle) is only slightly larger than the standard deviation of the day-to-day scatter (see Sect. 4). Therefore, it is challenging to investigate the potential of the SCIAMACHY retrievals to reflect the dynamic response to this weak annual cycle in spite of limited precision and time dependent biases due to the detector-icing issue.

Our approach to this is as follows. Individual WFMD retrievals in the near-infrared spectral domain are showing a significant scatter. The reasons are discussed in detail by Buchwitz and Burrows (2004) and Buchwitz et al. (2005a). Therefore, our validation approach is investigating to what extent the quality of SCIAMACHY data allows to approach the true variability of CH$_4$ columns as a function of the amount of the averaging of individual measurements performed in time and space. For this purpose, we are using daily-mean pixel averages within a stepwise increased selection radius around the Zugspitze ground site. The goal is to thereby stepwise reduce the scatter of the daily means by statistically averaging over increasing ensembles of pixels.
One might argue that also source and sink regions may be more and more included into the ensemble while increasing the selection radius, and this could potentially be compensating the statistical effect of reducing the scatter of the daily means. However, this effect is obviously weaker than the reduction of scatter by the statistical effect of increasing the averaging ensemble, as our test of the statistical parameters in Sect. 4 (Table 1) below is proving.

Since we are using selection radii of up to 2000 km around the Zugspitze, i.e., daily averages of CH$_4$ values from all the SCIAMACHY pixels available within this radius for that day, the question arises how i) the absolute XCH$_4$ values, ii) the amplitude of their annual cycle, and iii) the day-to-day variability of the 2000-km averages compare to the corresponding quantities seen in the column time series above the center site (i.e., the Zugspitze). Ad i) we state that we expect no significant bias (i.e., less than a few percent) between the daily average column averaged mixing ratio above a single site (e.g., 47° N, 11° E), and an average over a 2000-km radius around that site on that day. The argumentation for this is as follows. First of all, we obtained a standard deviation of the individual SCIAMACHY column averaged mixing ratios of ≈5.2% using all pixels per day within the 2000-km selection radius (Sect. 4.2.3, Table 1). Using this value we derive an estimate of the standard deviation of the true individual XCH$_4$ values within the 2000-km radius of ≈4% per day. This is obtained assuming a quadratic error superposition of the true scatter together with the known statistical SCIAMACHY error sources, i.e., instrumental noise causing an ≈1% error (Buchwitz et al., 2005a) as well the so-called-retrieval noise of ≈3% (the latter resulted from a comparison to models in Buchwitz et al., 2005b). We state that this variability of ≈4% within the 2000-km selection circle is dominated by regional sources and sinks, and this scattering effect appears strongly reduced by a factor in the order of ≈10, considering the “standard deviation of the mean value” of all radius-2000-km values, as done in Sect. 4.2.3 below (Table 1). From these considerations it is obvious, that we do not expect any significant bias between the column averaged mixing ratio obtained at the Zugspitze site (which shows a day-to-day variability of only ≈1% and is located in the free troposphere and is therefore representative for a wider horizontal area), versus that obtained from the 2000-km radius average. In particular, it becomes clear that the current study focusing upon characterization of a time-dependent bias of SCIAMACHY in the order of ≈10%, is not significantly affected by any possible bias due to the horizontal averaging. As an additional effect, the well known north-south gradient in the tropopause altitude results in an absolute tropopause increase of ≈2 km between the northern and the southern border of our selection circle. However, this transfers only to a gradient of XCH$_4$ of ≈2% expected between the northern and southern borderer. The underlying relation for the change of XCH$_4$ with the tropopause altitude was derived using an ensemble of radio-sonde pressure-temperature profiles with differing tropopause altitudes, together with a methane volume mixing ratio profile that was iteratively distorted according to varying tropopause altitudes (vertical scale linearly compressed or stretched below and above the tropopause, respectively, or vice versa). I.e., there is a small north-south increase of the columns within our selection radius on the ≈2% level, but since it is to a good approximation a linear increase, this does not introduce any significant bias to the 2000-km average versus the center-site value, considering the magnitude of the effect we are investigating in this study, i.e., the ≈10% time-dependent bias effects. Ad ii) we expect the amplitude of the annual cycle in the 2000-km radius daily averages to be very close to the magnitude of the amplitude at the center (Zugspitze) site. For an explanation, we make reference to the FTIR station at Izaña (Teneriffa, 28° N, −16° E) which shows an amplitude of the annual cycle of ≈1% (I. Kramer, personal communication, 2005), which is within the same order of magnitude as the Zugspitze amplitude of ≈1.6% (see Sect. 4.2.1), and shows the same phase. Since the annual cycles both at the center site (Zugspitze) and at the southern boarder site (Izaña) are in the same order of ≈1–2%, and they are showing the same phase, we conclude, that the amplitude of the annual cycle of the full 2000-km CH$_4$ average is also within this same order of ≈1–2%, i.e., it is by no means expected to be completely different in amplitude or phase. Ad iii) we state that the day-to-day variability of the 2000-km radius average is probably in the same order of magnitude as that above the center (Zugspitze) site (≈1%), with a tendency to be smaller. We derive this from the consideration that day-to-day variabilities of column averaged methane are caused by tropopause movements due to synoptic planetary-wave activity, and this effect might be somewhat reduced due to averaging, when using the 2000-km radius mean XCH$_4$ values, compared to when using individual-site values.

Another issue of the validation approach is how to reduce the impact of varying ground altitudes of the different satellite pixels that are averaged on one hand, and the (higher) altitude of the Zugspitze mountain site on the other hand. We solve this problem by focusing our validation study on CH$_4$ data, i.e., the column averaged mixing ratios. This quantity does not depend on the average pixel ground-level altitude, assuming a constant mixing ratio with altitude. This approximation does not introduce significant additional errors, as measured CH$_4$ profiles are typically showing nearly constant volume mixing ratios as a function of altitude up to the tropopause. Deviations from this behavior are in the few per cent range, with a tendency to approach perfectly constant mixing rations as a function of altitude after averaging of only a few profiles.

Related to this issue, one might argue whether a high-altitude mountain site or a low-altitude ground site, located in the boundary layer, is to be preferred for satellite validation of tropospheric species like CH$_4$. On the one hand, as discussed above, for a high-altitude site the altitude difference...
relative to the satellite-pixel ground altitude has to be properly considered, which may introduce errors on the percent level. On the other hand, a high-altitude site like the Zugspitze located above the boundary layer has the advantage to be representative for a much wider horizontal area, and that is exactly what the satellite data are – we will show below that not only the pixel size of the satellite data (60×30 km footprint), but even larger horizontal averages, e.g., selection radii in the order of 1000 km, have to be considered for the validation purposes.

Finally, an important issue in intercomparing two different remote-sounding systems (satellite versus ground) is to properly take their altitude-dependent sensitivities, i.e., their averaging kernels (Rodgers, 1990) into account. In case of strongly differing kernels, neglecting the effect of different smoothing errors can result in intercomparison errors in the order of the natural variability of the trace-gas columns (Rodgers and Connor, 2003). However, in our case we encounter the nearly ideal situation, that the ground-based (FTIR) and satellite (SCIAMACHY) instruments are both sampling the CH4 columns with nearly the same total-column averaging kernels as shown in Fig. 1, i.e., both being close to the ideal uniform sampling. The FTIR kernel shown is a weighted mean of the two (slightly differing) FTIR kernels we obtain from utilizing the two different spectral micro-windows from alternating MCT and InSb measurements as described in Sect. 2. This mean was weighted by the number ratio of all spectra of the two different spectral domains used in our study (i.e., 859/781, see Sect. 2). The resulting effective FTIR kernel shows only minor differences relative to the SCIAMACHY-WFMD kernel, e.g., at the 700 hPa level, there is a slight under-estimation of the natural variability of ≈13% by FTIR, and a slight overestimation of ≈14% by SCIAMACHY (Fig. 1). In the stratosphere the situation is reversed, with the underestimations/overestimations increasing with altitude. However, due to the decreasing air-number density the latter does not quantitatively impact the total columns retrieved. To prove this quantitatively, we calculated the smoothing errors \( \sqrt{\mathbf{S}_a^T \mathbf{S}_a (\mathbf{a}_{\text{FTIR}} - \mathbf{a}_{\text{ideal}})} \) for the total columns using the kernels (vectors \( \mathbf{a}_{\text{FTIR}} \) and \( \mathbf{a}_{\text{WFMD}} \)) shown in Fig. 1, and the total-column kernel \( \mathbf{a}_{\text{ideal}} \) of an ideal remote-sounding system with \( a_{T_{\text{ideal}}} = (111...1) \). For \( \mathbf{S}_a \) we adapted a best-estimate variance-covariance matrix of the atmospheric CH4 variabilities. The relative vertical change of the diagonal elements (variances) were adopted from results of the Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA). The absolute values of the variances were then scaled in order to reflect the total-column day-to-day variability found by our FTIR measurements (this procedure will be detailed with numbers in Sect. 4 below). For the off-diagonals (covariances) a Gaussian-shaped interlayer correlation with length of 2.5 km was used. Thereby we end up with smoothing errors of 0.10% for FTIR and 0.14% for SCIAMACHY WFMD, respectively. These errors are small relative to the bias found between FTIR and SCIAMACHY WFMD, and relative to the differences in day-to-day scatter encountered for FTIR and WFMD, respectively during our intercomparisons of Sect. 4. For consistency reasons, we briefly state that we do not distinguish between smoothing errors of CH4 columns and XCH4, respectively, i.e., we are neglecting the smoothing error contribution from the CO2 retrieval (being part of the WFMD XCH4 retrieval) throughout this paper. This simplification is valid because the natural variability of column averaged CO2 is known to be significantly (≈ factor 4) smaller than for CH4 (Buchwitz et al., 2005a). All in all, our validation results are not impacted significantly by smoothing errors. In Sects. 4.1.2 and 4.2.2 we will add absolute numbers as to this (small) smoothing-error effect on the bias and relative day-to-day scatter we obtained during our intercomparison study.

It is noteworthy, that the SCIAMACHY retrievals (and also the ground-based measurements) are perfectly sensitive down to the lower troposphere. This is indicated by the kernels in Fig. 1 showing numbers significantly above zero. This is due to the near-infrared spectral domain utilized for the SCIAMACHY retrievals, and is advantageous over thermal-IR satellite retrievals which are showing a reduced sensitivity in the boundary layer.

Fig. 1. Total-column averaging kernels for Zugspitze FTIR (red line) and SCIAMACHY-WFMD CH4 retrievals (blue line) calculated for a solar zenith angle (SZA) of 60°.
4 Validation results

4.1 Overall bias

4.1.1 Correlative study FTIR versus WFMD: bias

Figure 2a shows all SCIAMACHY WFMD XCH$_4$ data currently available (i.e., versions 0.4 and 0.41). Each SCIAMACHY data point is the average of all pixels from one day within a 2000-km radius around the Zugspitze. Cloud flagged pixels have been removed, and we restricted the WFMD data to a maximum threshold of 10% in the individual retrieval errors reported. Additionally, a flag for erroneous retrievals had been added with the version 0.41 release, and, subsequently, we excluded all error-flagged data for both versions (i.e., 0.4 and 0.41) for this study. Zugspitze FTIR daily-mean XCH$_4$ data are shown in the same plot. A 3rd order polynomial fit to the FTIR data nicely shows the XCH$_4$ annual cycle with a $\approx 1.6\%$ amplitude.

In order to obtain the bias of the SCIAMACHY WFMD data relative to the FTIR data we normalized the SCIAMACHY data by the 3rd order polynomial fit to the FTIR data. The result is shown in Fig. 2b. Note, that we do not investigate pairwise “coincidences”, as performed in many validation studies. Rather, we herewith propose the approach of fitting a polynomial to the reference series (FTIR) that is subsequently used as a reference. This approach allows to compare time series even in case of alternating time-gaps, which would not allow for the use of “coincidences”. This is partially the case for our time series of SCIAMACHY (measurement gaps due to decontamination phases) and FTIR (measurement gaps due to the clear-sky requirement). From Fig. 2b we retrieve an overall XCH$_4$ bias for WFMD v0.4/FTIR=1.008$\pm$0.019 and WFMD v0.41/FTIR=1.058$\pm$0.008. The statistical errors of the biases given are $3\times$ standard deviation/sqrt(n), where n=126 is the number of the WFMD data points.

4.1.2 Estimate of intercomparison error: impact on bias

We briefly want to estimate, whether the bias of 5.8% found for WFMD v0.41 can be partially affected by the slightly differing averaging kernels, and the different a priori profiles used for FTIR and WFMD, respectively. Therefore, we calculated the term $a_{FTIR}^T (x_{a,FTIR} - x_{a,WFMD})$/total column=0.74% and the analogous term, i.e., $a_{WFMD}^T (x_{a,WFMD} - x_{a,FTIR})$/total column=0.93%, where $a$ are the total-column averaging kernel vectors and $x_a$ are the vectors of the a priori profiles. The numbers obtained indicate that the effect from slightly differing a priori profiles and averaging kernels is only a minor contribution to the observed bias of WFMD v0.41.
4.2 Time-dependent bias, precision, and variability

4.2.1 Precision and variability of the FTIR column data set

Figure 3 shows the FTIR data set (together with WFMD v0.4, WFMD v0.41), but now plotted as anomaly, i.e., the daily mean data are normalized with respect to their overall average. First, it is obvious that the FTIR data are monitoring a sinusoidal annual cycle with a ≈1.6% amplitude. The dominant cause for this is the corresponding annual cycle of the tropopause altitude. Second, it is obvious that the FTIR daily-mean data are showing some scatter of ≈1% around this sinusoidal cycle. We will show below that this variability is not caused by limited precision of the FTIR measurements but is dominated by the true atmospheric day-to-day variability caused by the dynamic effect of planetary-wave activity.

In the following we want to investigate statistical parameters describing the scatter of the FTIR data in detail. Table 1 gives in the first 3 columns the statistical numbers describing the “individual” (FTIR) measurements within one measurement day. On average over the ensemble of $i=133$ FTIR measurement days, 12.3 FTIR column measurements have been performed per day. As a measure for the precision of individual FTIR measurements, the overall average of the standard deviations $\sigma_i$ of the individual measurements of each day is given in Table 1, i.e., $AV_i(\sigma_i)$=1.3% for FTIR. Furthermore, as a measure for the statistical error for one FTIR daily-mean value, the overall average for the daily “standard deviations of the mean value”, i.e., $AV_i(\sigma_i/\sqrt{n_i})$ calculated from the individual measurements is given in Table 1. $AV_i(\sigma_i/\sqrt{n_i})$ equals 0.4% for FTIR.

Now we discuss the standard deviations calculated from the FTIR “daily-mean” data. Of course, prior to this calculation from the daily means, the FTIR time series has to be normalized with respect to its obvious annual cycle. See, e.g., Fig. 4 for the result of this normalization. Table 1 shows in column 4 that the resulting standard deviation for FTIR is 1%.

Finally, we want to discuss the obvious discrepancy between the standard deviations we calculated from the daily mean data (1% for FTIR, see Table 1), and the average statistical error of the daily means calculated from the individual measurements, which is $AV_i(\sigma_i/\sqrt{n_i})=0.4\%$ for FTIR. Clearly the numbers indicate, that the standard deviation of 1% obtained from the FTIR daily means is dominated by true atmospheric day-to-day-variability due to tropopause movements, and not by the statistical error (due to limited single-measurement precision) which is only $AV_i(\sigma_i/\sqrt{n_i})=0.4\%$.
4.2.2 Estimate of intercomparison error: impact on variability

Here we like to address the question, to which degree possible differences in the day-to-day variability observed by the FTIR and WFMD, respectively might be attributed to smoothing errors. In the following we present a simple but quantitative estimate for FTIR and WFMD retrievals.

We write the variance of daily-mean total columns \(c_{\text{FTIR}}\) observed by FTIR as \(\sigma^2(c_{\text{FTIR}}) = a_{\text{FTIR}}S_a + \sigma^2(\varepsilon_{\text{FTIR}})\), where vector \(a_{\text{FTIR}}\) is the total-column averaging kernel, and \(S_a\) is the a priori variance-covariance matrix described in Sect. 3 above. The term \(a_{\text{FTIR}}^T S_a a_{\text{FTIR}}\) describes the variance due to the true variability of the atmosphere, smoothed by the measurement. By the second term \(\sigma^2(\varepsilon_{\text{FTIR}})\), we denote all further contributions which do not originate from the true variability of the atmosphere, i.e., contributions due to any kind of random-type measurement errors. Using \(\sigma(c_{\text{FTIR}}) = 1\%\) from Table 1, and using for the error term \(\sigma(\varepsilon_{\text{FTIR}}) = \tau\varepsilon_{\text{FTIR}}\), we find that we should hold \(\sqrt{a_{\text{FTIR}}^T S_a a_{\text{FTIR}}} / \text{total column} = 0.92\%\). We now use \(a_{\text{FTIR}}\) of Fig. 1 and scale \(S_a\) to fulfill this relation. (See Sect. 3 for the adopted principle shape of \(S_a\).) Using the resulting best-estimate \(S_a\) we calculate for WFMD analogously \(\sqrt{a_{\text{WFMD}}^T S_a a_{\text{WFMD}}} / \text{total column} = 0.93\%\). For an ideal observing system with \(a_{\text{ideal}} = (111\ldots1)\) we would obtain \(\sqrt{a_{\text{ideal}}^T S_a a_{\text{ideal}}} / \text{total column} = 0.94\%\). These numbers tell us that FTIR is underestimating the true variability by a factor of 0.92/0.94=0.98 and WFMD by a factor of 0.93/0.94=0.99 due to the smoothing effect. These underestimations are both similar to each other, and small in absolute terms. This means that possible differences in the day-to-day variability observed by the FTIR and WFMD, respectively (as discussed in the next Section) do not contain significant contributions from smoothing errors.

4.2.3 Correlative study FTIR versus WFMD: Time-dependent bias, precision, and variability

Figure 2b shows that the time-dependent bias correction introduced with version 0.41 for \(X\text{CH}_4\) WFMD, in order to account for the icing issue, did result in a significant reduction in the time dependence of the bias relative to version 0.4. This holds for both the time dependencies on the monthly scale, i.e., in between the various decontamination phases (marked by red vertical lines in Fig. 2b), as well as for the overall time dependence of the bias on the annual scale, as indicated by the linear fits in Fig. 2b.

Figure 3 again shows the three data sets (FTIR, WFMD v0.4, WFMD v0.41) but now plotted as anomalies, i.e., each data set is normalized with respect to its overall average. This shows even more obvious than Fig. 2a, that the changes associated with the version 0.41 update succeeded in significantly reducing the time-dependent bias compared to version 0.4. However, Fig. 3 also shows, that there is still a residual time dependence also in the version 0.41 data, which is clearly related to the decontamination cycles.

Figure 4 shows the WFMD v0.41 daily data both averaged for a selection radius of 1000 km around Zugspitze, as well as for a 2000-km radius. Note, that in Fig. 4 all three data sets have additionally been normalized to the annual cycle, i.e., the 3rd order polynomial fit to the FTIR data shown in Fig. 3. Figure 4 shows that the scatter of the daily WFMD data clearly exceeds the scatter of the FTIR daily means. It can also be seen that the WFMD data for a 1000-km selection radius are showing a higher scatter compared to the WFMD data for a 2000-km selection radius, as expected.

The question arises whether the scatter of the WFMD data in Fig. 4 is limited by systematic issues like a residual time-dependent bias due to the icing issue, or by the limited precision of the individual column retrievals, i.e., the limited signal-to-noise ratio of the SCIAMACHY spectra. This is further investigated in Fig. 5a. We restrict here to SCIAMACHY data out of one uninterrupted measurement period between two decontamination phases, i.e., the period 25 May–12 August 2003. We have chosen this time period, because here a systematic time dependence of WFMD-selection-radius-2000-km data can be most clearly identified, see Fig. 5a. Figure 5a shows a polynomial (2nd order) fit to this time dependence of the WFMD-selection-radius-2000-km data, which reflects a residual time-dependent bias of \(\approx3\%/\text{month}\). In Fig. 5b the WFMD data (both for 1000-km and 2000-km selection radii) are empirically normalized to this time dependence.

Having eliminated all residual systematic time dependence on an empirical best-effort basis (Fig. 5b), the next step is to investigate the statistical parameters describing the scatter of the WFMD version 0.41 data in comparison to the scatter of FTIR data in full detail. First, Table 1 gives the statistical numbers describing the “individual” measurements for FTIR and WFMD v0.41. While the number of days for which FTIR data exist (133) is comparable to the number of data for which WFMD data exist, Table 1 shows that average \(\bar{\sigma}_i(n_i)\) of the number \(n_i\) of daily measurements are quite different, i.e., 12.3 FTIR measurements per day on average versus 249 and 85 individual WFMD measurements per day for a 2000-km and a 1000-km selection radius, respectively. As a measure for the precision of the individual measurements \(\bar{\sigma}_i(n_i)\), i.e., the overall average of the standard deviations of the individual measurements of each day is given in Table 1. The precisions are quite different, i.e., \(\bar{\sigma}_i(n_i) = 1.3\%\) for FTIR, and a factor of 4 lower precisions are encountered for WFMD, i.e., \(\bar{\sigma}_i(n_i) = 5.2\%\) and 5.4% for calculation of \(\bar{\sigma}_i(n_i)\) from the 2000-km and 1000-km selection ensembles, respectively. Note, that the WFMD single-measurement standard deviations are nearly identical (5.2 versus 5.4%), i.e., nearly independent on the size of the selected ensemble (1000-km versus 2000-km selection radius), as expected for an ideal random ensemble.

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Furthermore, as a measure for the statistical error for one daily mean value, the overall average for the daily “standard deviations of the mean value”, i.e., $AV_i(\sigma_i/\sqrt{n_i})$ calculated from the individual measurements is given in Table 1. $AV_i(\sigma_i/\sqrt{n_i})$ equals 0.4% for FTIR, and for WFMD 0.6% and 0.3% for the 1000-km and the 2000-km selection radii, respectively. Note again, that this factor-of-two reduction of $AV_i(\sigma_i/\sqrt{n_i})$ on doubling the selection radius nicely reflects what we would expect for an ideal statistical ensemble. This confirms our assumption of Sect. 3, that the possible effect that also source and sink regions may be more and more included into the ensemble while increasing the selection radius might potentially compensate for the intended reduction of the standard deviation of the daily mean value (by increasing the selection radius), is quantitatively negligible. All in all we have found with a selection radius somewhere between 1000–2000 km the threshold, where the statistical errors of WFMD-daily-mean data become comparable to the ones of the FTIR, i.e. in the order of 0.5%. Note, that we had obtained a related result validating the species CO in our recent work (Sussmann and Buchwitz, 2005).

Now we discuss the standard deviations calculated from the daily mean data. Table 1 shows in column 5 and 6 the results with and without our empirical correction for a residual systematic time dependence (see Figs. 5a and b). As an important result, it can be seen from Table 1, that in fact the scatter of the WFMD-selection-radius-2000-km-data had been limited by a residual systematic time dependence. This results from the finding that the standard deviation of daily means could be reduced from 2.4% to 1.6% by our simple and merely illustrative empirical time-dependent bias correction of Fig. 5b. Note, that this is now close to the day-to-day variability of ≈1% observed at the Zugspitze site. However, as stated earlier, an even smaller true day-to-day variability is expected for a 2000-km mean value due to the averaging effect (Sect. 3). I.e., there appears to be still some potential for further improvements.

Finally, we want to discuss the obvious discrepancy between the standard deviations we calculated from the daily-mean data (1% for FTIR and 1.6% for 2000-km-WFMD after correcting for annual cycle and time-dependent bias, see Table 1), and the average statistical errors of the daily means calculated from the individual measurements, which is $AV_i(\sigma_i/\sqrt{n_i})=0.4%$ for FTIR, and $AV_i(\sigma_i/\sqrt{n_i})=0.3%$ for 2000-kmWFMD, and $AV_i(\sigma_i/\sqrt{n_i})=0.6%$ for 1000-kmWFMD, see Table 1. Interpretation is easy for FTIR, where no time-dependent drift is expected. Here clearly the numbers indicate that the standard deviation of 1% obtained from the FTIR daily means is dominated by true atmospheric day-to-day-variability due to tropopause movements, and not by the statistical error (due to limited single-measurement precision) which is only $AV_i(\sigma_i/\sqrt{n_i})=0.4%$. Interpretation for the satellite data is not so straight forward. Here, we have to stress that the statistical error for a daily mean value, i.e., $AV_i(\sigma_i/\sqrt{n_i})$ is calculated from the individual measurement data obtained
during the individual measurement days, i.e., it can in principle not describe time-dependent drifts on the weekly or monthly scale. Therefore the conclusion from our statistical numbers given above can only be, that WFMD data have the potential – as to their precision – to retrieve natural variabilities down to the 0.3% level for a 2000 km selection radius and down to the 0.6% level for a 1000 km selection radius "if" all systematic type time-dependent drifts would/could be eliminated.

5 Conclusions

Solar FTIR measurements at the Permanent Ground-Truthing Station Zugspitze (47.42° N, 10.98° E, 2964 m a.s.l.), Germany were used to validate the EN-VISAT/SCIAMACHY Scientific Data Product for XCH$_4$ retrieved at the University of Bremen, i.e., the near infrared WFMD-DOAS version 0.4 and 0.41 products.

The averaging kernels of the ground-based FTIR technique turned out to be similar shaped as the SCIAMACHY WFMD kernels, which both maintain a nearly uniform sampling down to the lower troposphere. Therefore, both a direct comparison of absolute column levels (bias) and the intercomparison of the day-to-day scatter is possible without introducing significant intercomparison errors from smoothing errors, which have been estimated to be below 0.10% for FTIR and 0.14% for SCIAMACHY WFMD retrievals, respectively.

In order to account for the altitude difference between the ground altitudes of the satellite pixels and the Zugspitze, XCH$_4$ columns have been used for both the satellite and ground-based data sets for the intercomparison. This approach eliminates the effect of the altitude difference for the case of a constant volume mixing ratio throughout the altitude range to be accounted for. This assumption should hold for the case of the lower tropospheric CH$_4$ profile within the per cent level.

Analysing the 2003-time series of the Zugspitze FTIR, we characterized the natural variability of XCH$_4$. It displays a 1% day-to-day variability and a sinusoidal annual cycle with a $\approx 1.6\%$ amplitude which is both dominated by related tropopause movements.

In order to obtain the bias of the SCIAMACHY WFMD data relative to the FTIR data we used a new approach, i.e., we did not investigate pairwise "coincidences" (satellite versus ground), which are limited in number in case of data series with time-gaps (e.g., decontamination phases, clear sky restrictions). Therefore, we fitted a polynomial to the reference series (FTIR) that is subsequently used as a reference. We obtained an overall XCH$_4$ bias for WFMD v0.4/FTIR=1.008±0.019 and WFMD v0.41/FTIR=1.058±0.008.

Finally, we investigated whether WFMD is capable of reflecting the natural atmospheric variability of XCH$_4$ as characterized by FTIR. WFMD version 0.41 shows up with a break through in data quality relative to version 0.4 due to an a-posteriori time-dependent bias correction, that is based on a channel-8 throughput analysis. However, version 0.41 is still not yet able to capture the natural day-to-day variability on the $\leq 1\%$ level because the standard deviation calculated from the daily-mean values is 2.4% using averages within a 2000 km radius, and 2.7% for a 1000 km radius. We have shown by a merely illustrative (additional) empirical time-dependent bias correction, that it is not the precision of the daily means, but the residual time-dependent bias of WFMD v0.41 ($\approx 3\%/month$) what currently limits data quality – and that this can still be improved (e.g., from 2.4% to 1.6% by our illustrative empirical time-dependent bias correction).

From analysis of the statistics of the individual measurements, we have shown that WFMD data have the potential – as to their pure precision, i.e., neglecting any time-dependent biases – to retrieve natural variabilities down to the 0.3% level for averaging data within a 2000 km selection radius and down to the 0.6% level for a 1000 km selection radius "if" all systematic type time-dependent drifts would/could be eliminated. This means that the XCH$_4$ annual cycle as well as possibly the atmospheric day-to-day variability could be captured under the prerequisite of further successful advanced time-dependent bias corrections, or the use of other channels, where the icing issue might be less prominent.

Acknowledgements. The authors like to thank A. Rockmann (IMK-IFU) for maintaining the Zugspitze FTIR measurements. Funding by BMBF/DLR as part of the German SCIAMACHY validation program (GCVOS) via contract DLR 50 EE 0007 and by the EC within the project UFTIR (contract EVK2-CT-2002-00159) is gratefully acknowledged. This work is contributes to the ESA-ENVISAT-Validation-Project TASTE and is part of the EC-Network of Excellence ACCENT-TROPOSAT-2.

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Evidence of systematic errors in SCIAMACHY-observed CO\textsubscript{2} due to aerosols

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Abstract. SCIAMACHY CO\textsubscript{2} measurements show a large variability in total column CO\textsubscript{2} over the Sahara desert of up to 10\%, which is not anticipated from in situ measurements and cannot be explained by results of atmospheric models. Comparisons with colocated aerosol measurements by TOMS and MISR over the Sahara indicate that the seasonal variation of SCIAMACHY-observed CO\textsubscript{2} strongly resembles seasonal variations of windblown dust. Correlation coefficients of monthly datasets of colocated MISR aerosol optical depth and SCIAMACHY CO\textsubscript{2} vary between 0.6 and 0.8, indicating that about half of the CO\textsubscript{2} variance is explained by aerosol optical depth. Radiative transfer model calculations confirm the role of dust and can explain the size of the errors. Sensitivity tests suggest that the remaining variance may largely be explained by variations in the vertical distribution of dust. Further calculations for a few typical aerosol classes and a broad range of atmospheric conditions show that the impact of aerosols on SCIAMACHY retrieved CO\textsubscript{2} is by far the largest over the Sahara, but may also reach significant levels elsewhere. Over the continents, aerosols lead mostly to overestimated CO\textsubscript{2} columns with the exception of biomass burning plumes and dark coniferous forests. Inverse modelling calculations confirm that aerosol correction of SCIAMACHY CO\textsubscript{2} measurements is needed to derive meaningful source and sink estimates. Methods for correcting aerosol-induced errors exist, but so far mainly on the basis of theoretical considerations. As demonstrated by this study, SCIAMACHY may contribute to a verification of such methods using real data.

1 Introduction

Remote sensing of CO\textsubscript{2} is gaining scientific interest due to advances in technology that are now starting to make such measurements feasible. CO\textsubscript{2} is receiving special attention as a candidate for remote sensing because of its important role in global warming and in the global carbon cycle. Our knowledge of CO\textsubscript{2} concentration in the atmosphere is currently based on sparse ground-based flask sampling networks (GLOBALVIEW-CO\textsubscript{2}, 2004) mostly at remote marine locations and networks of continuous measurements in developed countries, for example in Europe (CarboEurope-IP, 2004) and the United States (NACP, 2002). Although these monitoring networks continue to expand, they remain limited by lack of measurements in several parts of the world particularly in the tropics. In the near future, remote sensing is likely to step in and become an important part of global CO\textsubscript{2} observing systems due to the unique contribution of being able to fill the gaps in the surface measurement network. The challenge of small atmospheric gradients of CO\textsubscript{2} necessitates that detection be done with high measurement accuracy (~1\% or better). The motivation for this study is to determine the conditions that need to be fulfilled for short wave infrared measurements in order to meet this requirement.

First attempts to measure CO\textsubscript{2} from space were published by Chédin et al. (2002a,b) using thermal infrared (TIR) channels of NOAA-TOVS, followed by Crevoisier et al. (2004) and Engelen et al. (2004) who applied a similar methodology to AIRS. These measurements largely reproduce in situ measured seasonal cycles in the tropics. CO\textsubscript{2} measurements in the short wave infrared (SWIR) from SCIAMACHY were first reported by Buchwitz et al. (2005), and show realistic global patterns but seasonal cycle amplitudes that are
overestimated by ~4 times. Note that these studies should be considered first exploratory attempts, because none of the instruments were originally designed to measure CO₂ concentrations. The first dedicated CO₂ missions will be the Orbiting Carbon Observatory (OCO) and the Greenhouse gases Observing SATellite (GOSAT) both planned for launch in 2008 (http://oco.jpl.nasa.gov/, http://www.jaxa.jp/). OCO will make use of CO₂ absorption bands (1.6 and 2.0 µm) that are also detected by SCIAMACHY, although the OCO spectral resolution will be higher. Nevertheless, OCO might benefit from experience with SCIAMACHY.

This study aims at validation of SCIAMACHY CO₂ retrieval at 1.6 µm (channel 6). In particular we focus on large variability in column CO₂ that is observed over the Sahara desert. The Sahara is a logical starting point for validation as its bright surface favors the measured signal to noise ratio, and measurement coverage is extensive owing to a high percentage of cloud free measurements. Atmospheric CO₂ in this region is expected to behave rather predictably in absence of any significant surface sources and sinks. Concentrations should largely follow the background as observed at low to mid latitudes of the Northern Hemisphere, as contractions should largely follow the background as observed at presence of any significant surface sources and sinks. Concentrations in this region is expected to behave rather predictably in absence of any significant surface sources and sinks. Concentrations should largely follow the background as observed at low to mid latitudes of the Northern Hemisphere, as contractions should largely follow the background as observed at presence of any significant surface sources and sinks.

SCIAMACHY was launched in March 2002 onboard ENVISAT (Bovensmann et al., 1999). Its 8 detector channels cover the UV-Visible-SWIR wavelength range. Our CO₂ retrieval makes use of channel 6, which measures at a 30×60 km² resolution and a spectral resolution of 1.48 nm. The instrument scans in across track direction with a 960 km swath alternating between limb and nadir mode. Global coverage is reached in ~6 days.

CO₂ columns have been retrieved using the so-called Iterative Maximum Likelihood Method (IMLM) (Schrijver, 1999). First, the model albedo is scaled such that the integral over the modelled spectral window equals that of the measurements. Next, the CO₂ column is fitted to the measured spectrum using least squares optimization, after which the model spectrum is recalculated. These steps are repeated until convergence is achieved, i.e. when the relative change in the parameters is less than 1 %. Usually 2–4 iterations are needed to satisfy this criterion. The retrieved CO₂ column is normalized to 1013 hPa. For this purpose, a high resolution elevation map is used (ETOP05 tbase.bin, http://aero.ist.utl.pt/~a) to calculate the average surface elevation over the SCIAMACHY footprint. The normalization factor is calculated from the hydrostatic equation using the footprint elevation in combination with the coincident ECMWF vertical temperature profile, surface pressure, and orography.

As observed spectra we use calibrated SCIAMACHY top of the atmosphere radiances (level 1). Cloud contaminated measurements and back scans are excluded. The cloud detection algorithm makes use of SCIAMACHY’s broadband polarization measurement devices (PMD 2, 3 and 4) as described by Kriger et al. (2005). The retrieval uses a spectral window covering a continuous set of detector pixels ranging from 1563 nm to 1585 nm. This window contains part of the CO₂ absorption band at 1.6 µm and a few significant H₂O spectral lines. Contributions from other molecules can be neglected. The measurements are corrected for the orbit specific dark signal. Note that the temporal variations in dark signal that have been reported for SCIAMACHY retrieval in channel 8 (Gloudemans et al., 2005) do not affect this window. Channel 7 also contains a strong CO₂ band, but suffers from ice formation on the detectors and many dead and bad pixels. All detector pixels within our spectral window functioned properly, which was a reason to limit the CO₂ retrieval to this part of the observed spectrum.

The model that is used to fit the observed spectra calculates the line-by-line absorption of CO₂ and H₂O in the Earth’s atmosphere according to Beer’s Law. Rayleigh scattering and scattering by aerosols are ignored in this model. To simulate the SCIAMACHY instrument, the forward model is multiplied by the instruments pixel sensitivity, quantum efficiency.

2 Methods

2.1 SCIAMACHY

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slit function and Modtran Solar spectrum (Berk et al., 1999). A study by Frankenberg et al. (2004) showed that the CO₂ retrieval is sensitive to the local vertical temperature profile. Therefore, ECMWF-derived temperature and pressure data on 1°×1° have been applied to calculate high spectral resolution CO₂ and H₂O cross-sections. In addition, ECMWF-derived water vapor has been used because the CO₂ column retrieval was found to be sensitive to H₂O. The 6 hourly ECMWF profiles are interpolated to the SCIAMACHY local overpass time (10:00 am equator crossing time). The absorption cross-sections of the two most abundant CO₂ and H₂O isotopomers have been taken from the Hitran 2000 database (Rothman et al., 2003). The contributions of the remaining isotopomers of less than 0.4% for CO₂ and less than 0.04% for H₂O have been neglected. A Voigt line shape has been assumed for all lines.

To study the effect of aerosol scattering on the retrieved CO₂ column, the retrieval algorithm is tested against synthetic spectra that include the effects of aerosol (multiple-) scattering. The synthetic spectra are calculated using a radiative transfer model, which accounts for Rayleigh and Mie (multiple-) scattering (Hasekamp and Landgraf, 2002, 2005). The line-by-line calculation of the CO₂ optical depth followed the same procedure as is used to retrieve CO₂. A log-normal bimodal particle size distribution is used which allowed the same procedure as is used to retrieve CO₂ (multiple-) scattering (Hasekamp and Landgraf, 2002, 2005).

Table 1. Aerosol size distribution and scattering properties.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sea salt</th>
<th>Soot</th>
<th>Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>log n</td>
<td>0.052</td>
<td>0.030</td>
<td>0.074</td>
</tr>
<tr>
<td>σ log</td>
<td>1.697</td>
<td>2.030</td>
<td>1.537</td>
</tr>
<tr>
<td>Rm₁₆</td>
<td>1.400</td>
<td>1.357</td>
<td>1.794</td>
</tr>
<tr>
<td>Im₁₆</td>
<td>1.56×10⁻³</td>
<td>9.82×10⁻⁴</td>
<td>6.48×10⁻¹</td>
</tr>
<tr>
<td>Rm₀₅₅</td>
<td>1.530</td>
<td>1.381</td>
<td>1.750</td>
</tr>
<tr>
<td>Im₀₅₅</td>
<td>5.50×10⁻³</td>
<td>3.70×10⁻⁹</td>
<td>4.40×10⁻¹</td>
</tr>
<tr>
<td>Coarse mode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n log</td>
<td>0.670</td>
<td>0.240</td>
<td>0.511</td>
</tr>
<tr>
<td>σ log</td>
<td>1.806</td>
<td>2.030</td>
<td>2.203</td>
</tr>
<tr>
<td>Rm₁₆</td>
<td>1.400</td>
<td>1.357</td>
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<td>5.50×10⁻³</td>
<td>3.70×10⁻⁹</td>
<td>4.40×10⁻¹</td>
</tr>
<tr>
<td>Fine mode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fraction</td>
<td>4.35×10⁻³</td>
<td>1.53×10⁻²</td>
<td>1.70×10⁻⁴</td>
</tr>
</tbody>
</table>

n log, σ log: central value and standard deviation of the log-normal size distribution (µm). Rm₁₆, Im₁₆: Real and imaginary part of the index of refraction at “x” µm. Fraction: Fractional contribution of the coarse mode to the number concentration.

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2.2 Aerosol measurements

Data from two aerosol measuring satellites have been used in this study: The Aerosol Index (AI) of the Earthprobe Total Ozone Mapping Spectrometer (TOMS) (Herman et al., 1997; Torres et al., 1998), and Aerosol Optical Depth (AOD) as measured by the Multi-angle Imaging Spectrometer (MISR) (Kahn et al., 2005). Although MISR provides a more quantitative estimate of the aerosol load (i.e., the optical thickness), the TOMS-data aerosol index product has a much better statistical sampling: TOMS covers 90% of the globe each day, whereas MISR has only 3–4 revisits per month. We were not able to use TOMS for a quantitative analysis as it cannot provide aerosol optical depth without additional information on aerosol type and height distribution (Torres et al., 1998).

The footprint of TOMS varies between 50×50 km² in nadir to 250×150 km² at extreme off nadir (Prospero et al., 2000). We have used an interpolated data product at 1.25°×1°. The TOMS aerosol index is defined as:

\[ AI = -100 \log \left( \frac{(I_{340}/I_{380})_{\text{meas}}}{(I_{340}/I_{380})_{\text{mod}}} \right), \]

where “meas” refers to the observed ratio of radiances, and “mod” to a model with an aerosol free atmosphere. Over deserts, UV radiation is absorbed at the ground and the signal detected by TOMS is mainly due to Rayleigh scattering. UV absorbing aerosols, such as soot and mineral dust, are detected by absorption of UV light that is backscattered from the layer beneath. Because of this, the sensitivity of TOMS AI to aerosols increases about proportionally with aerosol layer height, while any aerosol below ~1000 m is unlikely to be detected. Despite this limitation, good correlation between TOMS AI and in situ measurements has been found (Chiapello et al., 1999; Hsu et al., 1999). The data used in this study have been downloaded from http://toms.gsfc.nasa.gov/ep/toms/ep_v8.html.

The MISR instrument measures continuously in different directions, allowing the instrument to differentiate between aerosols and the Earth’s surface. Cameras are aimed at nine angles in the orbital plane ranging from 70° to 70° forward detecting 4 narrow spectral bands. The instrument has a spatial resolution of 1.1×1.1 km². The product we used was averaged to 0.5°×0.5° (downloaded from http://eosweb.larc.nasa.gov/PRODOCS/misr/table_misr.html). A comparison with ground-based measurements of the Acid Aerosol RObotic NETwork (AERONET) (Holben et al., 1998) indicates that for arid conditions the MISR AOD product has an 8% uncertainty at 18×18 km² reducing to 5% at 50×50 km², without any obvious systematic biases or trend (Martonchik et al., 2004; Kahn et al., 2005).

2.3 Global extrapolation

The global and seasonal variation of aerosol-induced retrieval errors has been calculated using the radiative transfer modelling approach described in Sect. 2.1 using global
maps of surface albedo and aerosol optical thickness. Four different classes of aerosol have been distinguished: mineral dust, soot, sea salt, and sulfate aerosol. Table 1 summarizes the aerosol class-specific size and scattering properties that have been used. MODIS-derived global White Sky albedo maps have been used for 1.64 µm on 0.5°×0.5° horizontal resolution for each month of the year 2001 (http://modis.gsfc.nasa.gov/). This level 3 product has been constructed using a land cover description for data gap filling (see Fig. 1). The seasonal and global distribution of aerosol optical depth for each aerosol class has been taken from output of the LMDz model (Hauglustaine et al., 2004). We have used monthly averaged aerosol columns at 3.75×2.5° horizontal resolution (see Fig. 1).

For each 0.5°×0.5° grid box located over the continents monthly averaged aerosol errors have been calculated according to the local albedo and aerosol optical depth. The calculations are limited to the continents because the low surface albedo of the sea surface prevents any useful SCIAMACHY measurements over the oceans, neglecting the potential use of occasional sun glint measurements. To reduce computation time, lookup tables have been prepared for each aerosol class, spanning the range of realistic values of albedo and AOD at intervals of 0.1. As a further simplification, the total aerosol error is calculated as the sum of the contributions of each aerosol class. These simplifications are justified by calculated relations between AOD and CO₂ that do not deviate much from linearity for a common range of albedo of 0.1–0.4 and AOD<0.3 (see Fig. 4). AOD values >0.3 are mainly encountered in regions where a single aerosol class dominates, as is the case, for example, for mineral dust over the Sahara.

The global and monthly maps of aerosol error have been used to quantify the impact of aerosols on the CO₂ sources and sinks that would be obtained if SCIAMACHY CO₂ measurements were used for inverse modelling. The inverse modelling procedure follows a classical Bayesian approach (see e.g. Tarantola (1987)). The same set-up has been used as described in Houweling et al. (2003), where details can be found. In short, atmospheric transport is calculated using the Eulerian Tracer Model 3 (TM3) by Heimann and Körner (2003). The state vector consists of monthly fluxes for each 8°×10° degree grid box of the transport model. Realistic prior CO₂ fluxes and uncertainties have been prescribed (see Houweling et al. (2003)). Simulated SCIAMACHY measurements have been averaged in weekly intervals on 8°×10°. A 1% uncertainty has been assumed for single column measurements. Two inverse modelling calculations have been carried out: (A) with, and (B) without an error due to aerosols. The only difference between these inversions is that in inversion A the aerosol error is added to the measurements. The impact of the aerosol errors on the results of the inversion is quantified by the difference in calculated posterior flux of inversion A and B.

3 Results

3.1 Correlation of CO₂ and Dust measurements

Figure 2 shows the peculiar phenomenon of large CO₂ variability as it was initially observed. It also points out the location of our study domain extending from 20° W–50° E and 15° N–35° N covering a large fraction of the Sahara desert. Monthly values were obtained by averaging SCIAMACHY measurements that fall within the same 0.5°×0.5° grid box. Cloud-free measurements were selected with a CO₂ retrieval uncertainty <1%, which is satisfied for about 75% of the measurements within our study region (or ~15,000 measurements per month). CO₂ varies between fairly realistic column depths of ~8×10^21 molec./cm² to values as high as 9×10^21 molec./cm² (or column mean mixing ratios between 370 and 415 ppm), spanning a range of about 10%. For comparison, air samples collected by NOAA/ CMDL at Assekerem (23°10′N, 5°25′E, 2728 m a.s.l.) show variations in CO₂ that barely exceed 1% around an average value of 375 ppm for 2003. Since the CO₂ variability higher up in the atmosphere should not be much larger than near the surface, we can only conclude that SCIAMACHY largely overestimates CO₂ variability pointing at a highly significant source.
Fig. 2. Colocated measurements of SCIAMACHY CO$_2$ (a, c) and TOMS AI (b, d) for July 2003 (a, b) and October 2003 (c, d).
Although TOMS AI has proven to be a useful qualitative indicator of large scale variations in windblown dust we move to MISR for a more detailed and quantitative analysis. At the price, however, of a lower measurement coverage of MISR compared with TOMS which reduces the number of SCIAMACHY colocations (from 14,000 to about 3500 per month). Figure 3 presents colocations of SCIAMACHY CO$_2$ and MISR AOD for July and October 2003, confirming a relationship between these parameters. Pearson correlation coefficients range from 0.6 to 0.8 indicating that AOD explains about 50% of the observed variance in CO$_2$. Part of the remaining variance is explained by variations in surface albedo, which, as we will show later, influences the optical path in the presence of aerosols. To limit the influence of surface albedo, data were selected with measured (apparent) albedo values between 0.45 and 0.65. Another part of the variance is explained by errors in the CO$_2$ column normalization. Since the normalization correction is not a linear function of surface elevation, the sub-footprint scale orography variations do not cancel out in the footprint mean. If scattering on aerosol particles is taken into account the surface extrapolation function becomes even more complex and difficult to correct. To reduce the impact of these errors we discard measurements in 0.5° grid box where the standard deviation of 1×1 km$^2$ orography exceeds 100 m. In addition to these specific filtering rules, the same selection procedure was followed as in Fig. 2. Selection by scan angle may seem another logical choice given the angular dependence of aerosol scattering. Even though the swath of SCIAMACHY in nadir covers angles between roughly −30 to 30 degrees, no clear relationship was found between scan angle and retrieved CO$_2$. Therefore, scan angle selection has been ignored to maximize the number of colocated measurements.

### 3.2 Relation between CO$_2$ retrieval and aerosol

Radiative transfer model calculations were carried out to study the relationship between windblown dust and SCIAMACHY-retrieved CO$_2$. The aim of these calculations is to find out whether aerosol-induced pathlength deviations can explain the size of observed CO$_2$ variations. The upper panel of Fig. 4 presents results of these model calculations, showing the calculated CO$_2$ retrieval error as function of surface albedo and aerosol optical depth. For bright surfaces and low optical depths surface reflection dominates. Under these conditions, an increase of AOD leads to increased perturbation of the optical path, on average extending the optical pathlength. Towards darker surfaces and higher optical depths the average altitude at which photons are scattered back to space increases, thereby reducing the mean optical pathlength.

The calculated size of the path length deviation is sensitive to the vertical profile of aerosol. Published in situ and remote sensing measurements of dust over the Sahara and the West Atlantic Ocean indicate that dust layers extend to 600 hPa, or

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![Graph showing relation between colocated SCIAMACHY CO$_2$ and MISR AOD measurements (550 nm) over the Sahara for July 2003 (a) and October 2003 (b).](image-url)
Fig. 4. Model simulated relation between mineral dust aerosol and retrieved column CO$_2$ for different surface albedos (a), and comparison with SCIAMACHY measurements (b) for July (red) and October (green) over the Sahara. Solid lines, model calculations for July; dashed lines, model calculations for October.

about 5 km altitude, in summer (Karyampudi et al., 1999; de Reus et al., 2000). In addition, the first 1–2 km show lower dust load, which is true in particular for the marine boundary layer along the west coast of Africa in summer (Karyampudi et al., 1999; Haywood et al., 2003). Over land the vertical distribution is highly variable with occasional intensive dust plumes near the surface and remnants of previous dust events higher up. Due to lack of detailed local information, our computations assume a layer of evenly distributed dust extending from the surface to 5 km in July and 3 km in October. The lower mixing depth in October is in line with seasonal variations in the vertical dust profile as simulated by the LMDz model. The sensitivity of pathlength deviation (and thus CO$_2$ mixing ratio) to mixing height is demonstrated in Fig. 4 by the differences between the calculations for July (0–5 km, solid lines) and October (0–3 km, dashed lines).

Besides mixing height, the calculations for July and October differ also by the assumed temperature, humidity and solar zenith angle. However, the influence of these other factors is only minor.

The lower panel of Fig. 4 compares modeled and measurement-derived CO$_2$ columns. For this purpose, the measurements shown in Fig. 3 have been averaged into bins of 0.1 AOD. The figure shows only the modelled curves for surface albedos that span the same range as the apparent albedos determined from the SCIAMACHY measurements. Note that there is a difference between surface albedo and the apparent albedo as seen by SCIAMACHY, which is a combination of aerosol and surface reflectance. Over the bright surface of the Sahara dust aerosols reduce the apparent albedo. The difference between surface albedo and apparent albedo ranges between insignificant values at low AOD to $\sim$0.05 at AOD=2. This explains why modelled (surface) albedos for 0.5 to 0.7 are shown, while the measurements represent (apparent) albedos between 0.45 and 0.65. As can be seen in Fig. 4 the observed and model derived relations between CO$_2$ and AOD are in reasonable agreement. The sensitivity of the modelled CO$_2$ column to the vertical aerosol profile may largely account for the large standard deviations of the measurements. In line with the model calculations, the measurements show lower values in October than in July, although the measured difference seems slightly less.

3.3 Global extrapolation

This subsection addresses the question of how significant aerosol-induced errors in SCIAMACHY-observed CO$_2$ are on the global scale. The upper panel of Fig. 5 shows annually averaged CO$_2$ errors as calculated by the procedure that was outlined in Sect. 2.3. The radiative transfer model calculations assume that the aerosol optical thickness is distributed evenly over a globally uniform 1 km thick boundary layer decaying towards higher altitudes with the third power of pressure. This procedure has been applied to all aerosol classes except dust, which has been evenly distributed over the first 3 km only.

Fig. 5. Model simulated annually averaged error in continental CO$_2$ concentrations due to aerosol.
Not surprisingly, the largest errors are found over the deserts, owing to the high surface albedo in combination with relatively large aerosol loads. These conditions are satisfied most over the Sahara desert. High aerosol optical thicknesses are also predicted for some parts of Asia but the errors in CO2 are lower because of a lower surface albedo (see Fig. 1). The relatively coarse dust and sea salt particles scatter SWIR radiation more efficiently than the much smaller sulfate and soot particles. The influence of sea salt particles, however, remains limited in the absence of SCIAMACHY measurements over the oceans. As can be seen in Fig. 5 the sign of the annual mean aerosol error is predominantly positive. The model predicts that, for aerosol classes other than soot, CO2 columns will be overestimated for surface albedos >0.1, which is generally the case over land (see Fig. 1). Nevertheless, monthly maps of aerosol error (not presented) show reductions of column CO2 in regions with intensive biomass burning, explained by absorption of radiative scattering on soot particles, and in dense boreal coniferous forests with low surface albedo.

Inverse modelling calculations confirm that the aerosol-induced errors in the measured CO2 total column are too large to allow meaningful source and sink estimates. Generally, large errors are found with a pronounced maximum over the Sahara. The posterior fluxes have been integrated annually over the 22 continental scale TRANSCOM regions (Gurney et al., 2002). For North Africa several Pg of carbon are needed to bring the model in agreement with the measurements. Even for Temperate North America (the contiguous United States) an error of 0.4 Pg/yr is found, exceeding the uncertainty of inverse modelling estimates for this region on the basis of the surface monitoring network reported by Gurney et al. (2002). In practice, one would decide to ignore the data over deserts and use the remaining data to obtain improved flux estimates. For SCIAMACHY this means a reduction of the number of available data by as much as about 33%, which is explained by the predominantly cloud free conditions over deserts. Still, our inversion results show errors in the annual CO2 flux of a few tenths of a Pg carbon for several continental TRANSCOM regions. This is explained partly by incomplete filtering of desert dust contaminated data and partly due to other sources of aerosol. These results confirm that the influence of aerosols on SCIAMACHY retrieved CO2 are a global problem, that must be corrected to allow a meaningful interpretation.

4 Discussion

In the previous section we have demonstrated a reasonable correspondence between SCIAMACHY-retrieved CO2 and TOMS and MISR observed dust over the Sahara. The question arises of how good the correlation should be if pathlength perturbation by dust aerosols were the main mechanism explaining the observed CO2 variability. We have tried to quantify the influence of other potential sources of error by correlating SCIAMACHY CO2 with orography, apparent and surface albedo, column mean temperature, and specific humidity. None of these parameters could explain a significant part of the remaining variance. Our claim that the vertical distribution is an important factor is mainly supported by the sensitivity of our multiple scattering calculations to the assumed aerosol vertical profile. Besides this, the correlation between TOMS and MISR data hints in the same direction. Those correlations are comparable with the correlation between SCIAMACHY and MISR. Like SCIAMACHY, TOMS AI is sensitive to the vertical distribution of aerosol, although the relationship is quite different. In cases where both MISR and TOMS show high dust load SCIAMACHY CO2 tends to be notably high as well, which might be explained by a combination of high albedo, high dust load and the occurrence of dust at higher elevation. Part of the remaining variance may also be explained by undetected cirrus clouds, although this should only play a minor role over the Sahara owing to the large scale subsidence of air at these latitudes suppressing cloud formation.

When comparing Fig. 2 and 3 it may seem that TOMS AI correlates better with SCIAMACHY CO2 than MISR AOD. If the same data selection procedure is followed to compute correlations between SCIAMACHY and TOMS, however, it turns out that these correlations are in fact lower by ∼r=0.1. It looks like the correlation on the scale of a few 100 km2 is higher than that on the scale of the measurements. This may be explained by errors comparing different data products resulting from differences in footprints and overpass time, which might average out partially at larger scales. While the vertical distribution of dust remains a plausible candidate to explain the remaining variance, we cannot exclude contributions from other processes that are currently overwhelmed by dust in our data but, in absence of dust, may nevertheless be significant at the high level of accuracy that is required for CO2. For example, our calculated aerosol errors do not seem to explain the underestimated SCIAMACHY-observed CO2 seasonal cycle of 20 ppm in the retrievals versus 5 ppm in the model reported reported by (Buchwitz et al., 2005), hinting at some other significant source of error.

Our global assessment points out that aerosol-induced errors of ~10% of the CO2 column, as found over the Sahara, are not representative for the rest of the world but rather should be considered a worst case. Nonetheless, averaged over all continents, the error amounts to ~3 ppm, which is substantially higher than the 1 ppm that was previously published by Dufour and Breon (2003), who took only single scattering (either by aerosols or by the earth surface) into account. As a consequence of the use of such a simplified radiative transfer model, Dufour and Breon (2003) [as well as O’Brien and Rayner (2002)] only report underestimation of CO2 due to aerosols, while our multiple scattering calculations point to a more complex behavior related to surface albedo supporting the model analysis by Mao and Randolph.

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Kawa (2004) and resulting in overestimation for most conditions encountered over the continents. The fact that we can largely explain the SCIAMACHY CO₂ measurements over the Sahara confirms that our current approach is probably more realistic. Although the importance of multiple scattering over bright surfaces and high aerosol loads of the Sahara may seem obvious, according to our results, it should also be taken into account elsewhere. Nevertheless, our global approach is also limited, in particular, by the simplified treatment of the vertical aerosol profile. For example, a layer of enhanced aerosol optical thickness near the tropopause that is predicted by the LMDz model has been neglected as sensitivity tests suggest that its impact should only be minor. Analysis of SCIAMACHY CO₂ and aerosol measurements in other regions could provide further insight, and has been planned as a next step.

What are the options for correcting the SCIAMACHY CO₂ data product for aerosols? One possibility is to include an aerosol scattering algorithm in the CO₂ retrieval, which, for SCIAMACHY, would require additional information on the local aerosol optical depth and its vertical distribution, as well as information on the local surface albedo. Further information could be gained from CO₂ absorption around 2.0 μm. Those wavelengths, however, are measured by another SCIAMACHY channel which suffers from ice layer formation (see Gloudemans et al., 2005) and possibly other calibration problems (see Lichtenberg et al., 2005) introducing significant complications. The use of O₂ absorption in the O₂ A-band has been proposed to directly measure the CO₂/O₂ mixing ratio (O’Brien and Rayner, 2002; Dufour and Breon, 2003; Buchwitz et al., 2005). Therein lies the advantage that this parameter can easily be converted to the dry air mixing ratio, which is the relevant parameter for atmospheric modelling. It has been suggested that the same procedure would eliminate aerosol-induced pathlength deviations. However, this has not yet been proven for SCIAMACHY measurements and problems are expected to arise from different scattering properties at 0.7 μm (O₂-A) and 1.6 μm (CO₂) (see van Diedenhoven et al., 2005). In summary, there are options to correct SCIAMACHY CO₂ measurements for aerosols, which call for further investigation. Uncorrected or partially corrected CO₂ measurements might still be valuable in regions with moderate surface albedo and relatively low aerosol loads.

What is the relevance of our findings for other satellite missions aiming at measuring CO₂? Towards longer wavelengths aerosol scattering will become less important, which is why aerosols are not expected to complicate CO₂ measurements in TIR. However, AIRS measurements do show a significant influence of desert dust on the observed infrared brightness temperatures, with potential implications for CO₂ measurements at these wavelengths (Pierangelo et al., 2004). For the OCO mission a combination of measurements at 0.7 μm (O₂-A), 1.6 μm (CO₂) and 2.0 μm (CO₂) has been proposed at high spectral resolution (0.075 nm) to correct for the effect of scattering layers on the apparent CO₂ content. According to the theoretical study by Kuang et al. (2002) this approach should allow a precision of ~0.3–2.5 ppm for aerosol optical thicknesses less than 0.3. Although SCIAMACHY cannot be used to fully test the OCO approach, it might nevertheless be possible to verify certain assumptions of theoretical performance assessments, for example, related to the path length perturbation due to aerosol scattering when measuring in sun glint. A potential alternative option in SWIR is the use of active instrumentation, such as a Differential Absorption Lidar (DIAL). In this case the delay between the emission and detection of laser pulses provides a measure of path length, which could in principle be used to strongly reduce the influence of aerosols.

5 Conclusions

We have analyzed SCIAMACHY measurements of total column CO₂ showing large variability over the Sahara. The correlation of SCIAMACHY CO₂ and coincident TOMS AI and MISR AOD measurements provides strong evidence that the unrealistically large CO₂ variability of 10% (37 ppm) of the total column is caused by mineral dust aerosol. Radiative transfer model calculations show that aerosol-induced pathlength enhancement can explain the size of the observed variations. Aerosol optical depth explains about 50% of the observed CO₂ variability. Model calculations show large sensitivity of the CO₂ column to the aerosol vertical profile, which seems the most likely candidate to explain the remaining variance. A model-based extrapolation to regions outside the Sahara leads to the conclusion that aerosols will mostly increase SCIAMACHY-observed CO₂ mixing ratios over continents, by 3 ppm on average. Reverse modelling calculations clearly point out that such errors are too large to allow improved source and sink estimates. However, further analysis of SCIAMACHY measurements is needed to confirm the model predicted size of aerosol-induced errors outside the Sahara. The outcome of this study has important implications for future instruments aiming at measuring CO₂ from space at SWIR wavelengths, and may be used to verify theoretical assessments of methods to account for pathlength perturbation by aerosol scattering.

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Geophysical validation of SCIAMACHY Limb Ozone Profiles

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Abstract. We discuss the quality of the two available SCIAMACHY limb ozone profile products. They were retrieved with the University of Bremen IFE’s algorithm version 1.61 (hereafter IFE), and the official ESA offline algorithm (hereafter OL) versions 2.4 and 2.5. The ozone profiles were compared to a suite of correlative measurements from ground-based lidar and microwave, sondes, SAGE II and SAGE III (Stratospheric Aerosol and Gas Experiment).

To correct for the expected Envisat pointing errors, which have not been corrected implicitly in either of the algorithms, we applied a constant altitude shift of −1.5 km to the SCIAMACHY ozone profiles.

The IFE ozone profile data between 16 and 40 km are biased low by 3–6%. The average difference profiles have a typical standard deviation of 10% between 20 and 35 km.

We show that more than 20% of the SCIAMACHY official ESA offline (OL) ozone profiles version 2.4 and 2.5 have unrealistic ozone values, most of these are north of 15° S. The remaining OL profiles compare well to correlative instruments above 24 km. Between 20 and 24 km, they underestimate ozone by 15±5%.

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files, the SBUV climatology (altitude. Averaging kernels are provided. For the a priori pro-

MACHY state is retrieved, in units of number density against vertical grid with resolution of about 3 km up to 50 km, and 5 km above.

Figure 1 shows an example of the averaging kernels for the IFE product. Evidently, the limb retrieval has a high vertical resolution (sharp averaging kernels), especially around the ozone maximum at approximately 20 km.

The squares in Fig. 1 show the altitude assignment of each of the elements in the ozone profile. Between 15 and 45 km the kernels peak at the assigned altitude of a profile element. SCIAMACHY is insensitive to ozone below 12 km, which is reflected in the averaging kernel shapes in Fig. 1. The IFE retrieval takes into account some layers below that altitude in order to obtain smooth tropospheric profiles. This is evidently not measurement information.

IFE limb ozone profile retrievals are based on the Chappuis bands of ozone (von Savigny et al., 2005a), which are in the visible wavelengths. Retrievals are performed from SCIAMACHY level 0 files using the SCARIAYs radiative transfer model (Kaiser, 2001). One ozone profile per SCIAMACHY state is retrieved, in units of number density against altitude. Averaging kernels are provided. For the a priori profiles, the SBUV climatology (McPeters, 1993) is used.

ESA offline DLR retrievals (hereafter OL) are based on ozone absorption exclusively in the ultraviolet window of 319–333 nm. Four ozone profiles per state are retrieved. The available data consist of the 2002 data described in Brinksma et al. (2004), and two recent subsets: data between 20 September 2004 and 27 November 2004 (hereafter OL2.4) and data from 7 December 2004 and onward (in this paper through 17 February, hereafter OL2.5). Although the version numbers differ, the processor and all inputs relevant for ozone profile retrievals were identical (S. Hilgers, DLR, personal communication, 2005). These data are relatively recent at the time of writing, hence the number of collocations with ground and balloon instruments is limited, because for many locations, data were not yet available in databases. For the OL data sets, we will only consider the ozone profiles in units of number density (which we derive from the listed partial columns) against altitude. Averaging kernels for the offline algorithm are not contained in the product or publicly available.

In an earlier paper, validation of the offline algorithm version 2.1 applied to the validation reference data set (383 selected SCIAMACHY limb states from 18 July through 16 December 2002), and the IFE algorithm version 1.6, applied to available level 0 states between July and December 2002 was discussed based on comparisons to correlative instruments (Brinksma et al., 2004). Conclusions were that the OL2.1 as well as IFE1.6 profiles agreed within about 10% for the 20–40 km region when compared with ground-based data, and within about 20% when compared with satellite data. However, the standard deviations on the differences between SCIAMACHY and correlative instruments were rather large (10–40%). The results were dominated by uncertainties in the altitude assignment, caused by Envisat pointing inaccuracies, which are discussed in Sect. 2. Another problem was that the data set was too small to get good statistics. In the current paper, we present the status of the most recent algorithm versions, based on recent SCIAMACHY measurements in which the pointing problem should be less.

A number of more recent validation studies on IFE version 1.6 have been performed. Bracher et al. (2005) compared IFE1.6 data from October and November 2003 with MIPAS-IMK and GOMOS-ACRI data products. The three retrievals mutually agreed within 15% between 22 and 38 km. Comparisons with ozone sondes by Segers et al. (2005) show that IFE1.6 and sondes differ 10–15% in the 10–30 km range, after application of an overal shift of 2 km to correct for the pointing error. The analysed period is August–December 2002. They also showed that the gradients in ozone (below as well as above the ozone number density maximum) were too steep. Palm et al. (2005) compared IFE1.6 data between August 2002 and August 2003 with two microwave radiometers in Bremen and Ny-Ålesund and concluded that they agree within the expected covariance of the intercomparison, after shifting the SCIAMACHY profiles downward with 1.5 km. A preliminary comparison with FTIR for only a few collocations showed large deviations, especially below 20 km. Comparisons of IFE1.6 data with ASUR measurements for 11 flights in September 2002, February 2003 and March 2003 (Kuttipurath et al., 2004) result in deviations ranging from −12 to +15% between 20 and 40 km, after subtraction of a constant positive bias of 12% in the ASUR data. The pointing error in this study was accounted for by applying a retrieved tangent height error following Kaiser et al. (2004). De Clercq et al. (2004) compared IFE1.6 data between July and December 2002 with measurements from ozone sondes, lidars and microwave radiometers. Deviations between 18 and 40 km range from −30% to +30%, which is mainly caused by Envisat’s altitude registration error (see Sect. 2).
Recently, data processed with a newer algorithm, namely IFE version 1.61, have become available. Since these data are considerably different from the previous version, we will limit the discussion to version 1.61 only. The validated data set consists of five months of data (all available orbits during January, March, May, September, and November 2004).

2 Envisat pointing

A study of the Envisat pointing accuracy showed that differences of up to 3 km were found between the on-board orbit propagator and the retrieved pointing (from the UV limb radiances) for the period up to December 2003 (Kaiser et al., 2004). This was confirmed in the studies of De Clercq et al. (2004) and Segers et al. (2005) who estimated the shift by optimising the correlation of the SCIAMACHY profiles, applying different altitude shifts, with ground-based measurements. The tangent height retrieval for 2004 (von Savigny et al., 2005b) showed that even after the Envisat orbit model improvement in December 2003 an offset of about 1 km is present in the SCIAMACHY level 1 data sets, with the resulting pointing systematically too high. Indications for a seasonal (sinusoidal) variation with an amplitude of about 220 m were found in 2004. Compared to the amplitude before December 2003 of about 800 m this is a significant improvement. Several further pointing anomalies due to, e.g., star tracker failure etc. were found, but none of them occurred during the months considered here. More information on the spatial and temporal variation of the tangent height errors can be found in (von Savigny et al., 2005b).

The best way to correct for the error caused by the pointing inaccuracy, would be to correct before or during the retrieval. However, neither the IFE nor the OL data described in this paper have implicit pointing corrections. There is a need to correct at least in a provisional way, in order to be able to assess as well as possible the quality of the SCIAMACHY ozone profiles. An earlier validation paper (Brinksma et al., 2004), that covered ozone profiles in the second half of 2002, was inconclusive due to the Envisat platform pointing inaccuracy. The reason is that errors in altitude and errors in ozone concentration cannot always be distinguished.

Since the variation on the pointing inaccuracy itself is typically only 220 m (von Savigny et al., 2005b), it is reasonable to apply a constant altitude shift to the SCIAMACHY profiles before the comparisons are performed. Sensitivity studies with the IFE retrieval code showed that for tangent height offsets of less than about 4 km, the difference between shifting the retrieved profile and a proper tangent height correction before the retrieval is only a few percent for altitudes between 15 and 40 km.

In order to find the appropriate value for this shift, we optimised the correlation between individual ozone sondes and the IFE profiles by applying different shifts, similar as was done by Segers et al. (2005). The resulting most optimal individual shifts are shown in Fig. 2. The spread in the shifts is much larger than the expected variation in the pointing inaccuracy. This should be expected, because differences between sondes and SCIAMACHY profiles are not only caused by pointing errors. The average shift is approximately −1.5 km. Therefore we chose this value for the constant altitude shift in this paper.

3 Correlative data sets

An overview of the correlative data sets used to study the quality of the IFE and OL data is presented in Table 1. We do not discuss the validation based on airborne campaigns conducted in 2002 and 2003 (Kuttipurath et al., 2004), because no SCIAMACHY profiles were retrieved with version IFE1.61 or OL 2.4/2.5 in that timespan.

3.1 Lidar

Stratospheric ozone profiles measured by the lidars at primary NDSC sites are regularly compared to measurements by other instruments, and also to a travelling lidar. This
ensures their high quality measurements (e.g., McPeters et al., 1999; McDermid et al., 1998). Typical accuracies for stratospheric ozone lidar instruments are 2% for the 20 to 35 km region, and 5–10% for other altitudes (e.g., Keckhut et al., 2004). Lidar profiles are reported with a resolution of 300 m, however the correlation length is typically a few kilometers (ranging from at least 1 km in the tropopause to at most 8 km at 50 km. Lidar measurements were taken at various midlatitude and one tropical locations, see Table 2.

### 3.2 Microwave instruments

#### 3.2.1 Mauna Loa and Lauder Microwave

The instruments are groundbased microwave spectrometers observing atmospheric thermal emission at 110.8 GHz. They record the spectral lineshape of an ozone rotational transition every 20 min at about 10° to 20° elevation. Observations continue 24 h a day whenever weather permits. An ozone mixing ratio profile (in ppmv) from 56 hPa to 0.05 hPa (about 70 km altitude). Accuracy and precision for the previous version of SAGE II are characterised by Wang et al. (2002) shows an agreement within 10% of SAGE II profiles with ozone sondes measurements from the tropopause up to 30 km. SAGE II v6.1 profiles slightly overestimate (less than 5%) ozone between 15 to 20 km. Extensive validation of an older version of SAGE II (version 5.96) show SAGE II to be within 7% at 20 to 50 km with correlative measurements of the rotational transmission line at 273 GHz. The typical integration time for one profile is about 1 h and the uncertainty in the retrieved profiles due to standing waves and systematic errors amounts to at least 1 ppmv (Kopp et al., 2003). Errors due to thermal noise are almost negligible due to the integration of the measured spectra.

#### 3.3 Sondes

Balloon based ozone sondes are launched on a regular basis from globally distributed stations. A sonde samples the atmosphere up to about 30 km with a resolution of ten to hundred meters, depending on the balloon and sonde type. Ozone is measured using electro chemical cells. In a comparison study by McPeters et al. (1999) it was shown that due to uncertainties in the composition of the chemical solutions, the ozone measurements from two individual sondes could show a difference of 1–2%, and that sondes agree with lidar, microwave and other measurements within 5% in the 20–45 km region.

### 3.4 SAGE II

The longest record of satellite high-resolution profile measurements has been made by the solar occultation instrument Stratospheric Aerosol and Gas Experiment (SAGE II) which was launched on the Earth Radiation Budget Satellite (ERBS) in October 1984 and is still operational and collecting data. SAGE II uses solar occultation to measure the attenuation of solar radiation between the satellite (McCormick, 1987). The inversion uses the “onion-peeling” approach to yield 1-km vertical resolution ozone profiles with a horizontal resolution of about 200 km (Mauldin et al., 1985; Chu et al., 1989). SAGE II has a repeat cycle of slightly more than a month and a vertical resolution of about 1 km. From SAGE II measurements ozone number concentrations at the 0.60 µm wavelength channel are derived (focusing on 15–60 km). Accuracy and precision for the previous version of SAGE II (version 6.1) are characterised by Wang et al. (2002) at 16 and 53 km with an accuracy between 5 and 7% and a precision between 3.2 and 6.7%. Validation by Wang et al. (2002) shows an agreement within 10% of SAGE II profiles with ozone sondes measurements from the tropopause up to 30 km. SAGE II v6.1 profiles slightly overestimate (less than 5%) ozone between 15 to 20 km. Extensive validation of an older version of SAGE II (version 5.96) show SAGE II to be within 7% at 20 to 50 km with correlative measurements (Cunnold et al., 1989). The version 6.2 of SAGE II was improved in respect to the previous version by adjustment to the aerosol clearing and by the correction of channels 520 and 1020 nm for absorption of the oxygen dimer (information on SAGE II can be found at http://www-sage2.larc.nasa.gov).

<table>
<thead>
<tr>
<th>Location</th>
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<th>lon</th>
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<tr>
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</tr>
<tr>
<td>Hohenpeissenberg</td>
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<td>11.0</td>
</tr>
<tr>
<td>Observatoire Haute Provence</td>
<td>43.9</td>
<td>5.7</td>
</tr>
<tr>
<td>Tsukuba</td>
<td>36.1</td>
<td>140.1</td>
</tr>
<tr>
<td>Table Mountain</td>
<td>34.4</td>
<td>−117.7</td>
</tr>
<tr>
<td>Mauna Loa</td>
<td>19.5</td>
<td>−155.6</td>
</tr>
<tr>
<td>Lauder</td>
<td>−45.0</td>
<td>169.7</td>
</tr>
</tbody>
</table>
3.5 SAGE III

The Stratospheric Aerosol and Gas Experiment III (SAGE III) was launched on 10 December 2001. The instrument makes use of solar-occultation measurements, similar to those described for SAGE II above. SAGE III solar products (version 3.0) were released in mid 2004, and this is the version used in this paper. They have been intercompared with the SAGE II, HALOE, POAM III satellite instrument, and with sondes and ground-based instruments. Compared with SAGE II, a difference of 1–2% in the northern hemisphere, and about 3% in the southern hemisphere is found. These errors are independent of altitude (Taha et al., 2004).

4 SCIAMACHY IFE ozone profile validation

4.1 Validation approach

IFE ozone profile data retrieved from all available level 0 orbits during January, March, May, September, and November 2004 were compared with ground-based lidar, microwave radiometer, and sondes. They were also compared with SAGE II and SAGE III data. Collocation criteria were a maximum distance of 1000 km, and maximum time difference of 12 h (20 h for nighttime instruments) between SCIAMACHY overpass and correlative measurement. For SAGE III, the distance criterion was replaced by 3° latitude and 10° longitude. Within these limits, the nearest match between the SCIAMACHY and correlative data was selected for each individual measurement (except for comparisons with lidar, where one lidar measurement was allowed to be collocated with multiple IFE profiles, as long as the collocation criteria were met). The number of collocation profiles for the different correlative data sets are given in Table 1.

4.2 Validation results

In this subsection, we will first present comparisons in which averages were made over multiple location, and then show a few examples at unique locations.

Collocations between lidar and IFE are found only at mid-latitudes and one tropical location. Averaged over all collocations, we conclude that the IFE ozone profiles are lower than the lidar profiles by about 3% (16–40 km; see Fig. 3). The average difference profile has a zigzag shape with maxima around 31 and 24 km, minima around 40, 20 and 27 km, the value varying between −10% and +10%. This shape stems from an oscillation in the IFE ozone profiles, which are likely a consequence of the fact that the air volumes sampled by SCIAMACHY at different tangent heights are not exactly aligned vertically. The maximum ozone number densities are in general too high (about 8%) compared to the lidar ozone profiles. In the lower stratosphere (18–23 km), the IFE ozone concentrations are too low.

IFE data were also compared with SAGE II data, results are shown in Fig. 4. This was done both for the original SAGE data, as well as for SAGE data that were convolved using the IFE averaging kernels and a prioris. SAGE II collocations with IFE are mostly between 60° S and 60° N, with only
Fig. 4. As Fig. 3, but now with respect to SAGE II (884 collocations). For SAGE II, original profiles are shown, as well as profiles convolved with the IFE averaging kernels using also the IFE a priori profiles.

Fig. 5. As Fig. 4, but now with respect to SAGE III (1071 collocations).

a few collocations in the polar regions. Averaged over all collocations, we see that IFE is about 6% lower than SAGE II (averaged over 16–40 km), with averaging kernels applied. Best results are found between 30 and 35 km.

As in the comparisons with lidar, we see the characteristic profile shape with IFE ozone number densities often too low around 27 km (7%). In the lower stratosphere (18–22 km), again the IFE ozone concentrations are too low, in comparisons with SAGE II also between 16 and 18 km.

Figure 5 shows comparisons with SAGE III. This comparison results in a larger bias (~9% between 16 and 40 km) than the comparison with SAGE II (both with averaging kernels applied). Intercomparisons between the two SAGE instruments indicate that SAGE III is biased with respect to SAGE II: SAGE III ozone number densities are 2% higher between 15–40 km, SAGE II has a known bias below 15 km (see Sect. 3.5).

The average difference between IFE1.61 and SAGE-II profiles depends on the solar zenith angle (sza) of the SCIAMACHY measurement. In Fig. 6, where comparisons are grouped into 10° sza bands, evidently the characteristic zigzag shape is present for all sza ranges, with a slight variation in the altitude of the maxima and minima within 2 km.

~ For sza between 50° and 90°, the average IFE1.61 ozone number densities are smaller than the SAGE-II
Fig. 6. Shown here are comparisons between IFE1.61 and SAGE II, convolved with the IFE averaging kernels, grouped into 10 degree solar zenith angle bands (which are shown on top of the plots). The number of collocations ‘n’ are indicated in each plot.
values almost everywhere between 15 and 40 km. The average difference profiles are rather flat, with values ranging from $-10\%$ to 0, except for the lower levels of profiles with SZA above 80° ($+15\%$ at 16 km) and with SZA between 50° and 60° ($-25\%$ at 17 km).

- For SZA between 20° and 40°, the IFE1.61 profiles are on average closer to the SAGE-II profiles. The average deviation is $-1.7\%$ between 20 and 40 km, but the peaks in the difference profile just below the ozone maximum are more pronounced, ranging from $-18\%$ at 20 km to $+7\%$ at 24 km. Below 18 km the positive difference becomes rapidly larger.

- For SZA between 40° and 50°, there is no significant difference between IFE1.61 and SAGE-II profiles between 23 and 37 km, where the zigzag shape is absent. Below 23 km the difference grows to $-30\%$ at 17 km.

We also grouped comparisons with lidar into solar zenith angle groups, namely below 30° (56 collocations), 30°–60° (235 collocations), and 60°–90° (72 collocations). Solar zenith angles below 30° and between 30° and 60° give results that are very similar to those shown in Fig. 3. The 60°–90° SZA’s show worse results, with IFE results biased low by 7% over the 15–40 km region.

When looking for a latitude dependence, we see something similar, midlatitude results are biased low by about
Fig. 7. As Fig. 3, but now with respect to lidar and microwave, and only for the Mauna Loa location (44 lidar-microwave-SCIAMACHY collocations).

Fig. 8. As Fig. 3, but now with respect to microwave, only for the Merida (Venezuela) location, 15 collocations. ‘Unsmoothed data’ refer to comparison between original IFE and microwave results, ‘smoothed data’ refer to a comparison where IFE data were smoothed using the microwave radiometer averaging kernels.

7% (15–40 km, 257 collocations), tropical results (containing only Mauna Loa) are not consistently biased but do differ significantly from the lidar data (one sigma level, 106 collocations). In Fig. 7, we show IFE data over Mauna Loa that were collocated with lidar as well as microwave measurements, and therefore have fewer collocations (44). There is no significantly different result with respect to microwave than there is with respect to lidar. In Fig. 8, an example of comparisons at another tropical location (Mérida, Venezuela) is shown. These comparisons are not consistent with those at Mauna Loa above 37 km.

Table 3. Numbers of OL profiles with extreme values (either below zero or above $8.0 \times 10^{12}$ cm$^{-3}$).

<table>
<thead>
<tr>
<th>lats</th>
<th>total</th>
<th>min &lt; 0.0</th>
<th>max &gt; 8.0</th>
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<tbody>
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<td>2725</td>
<td>206 (7.5%)</td>
<td>972 (35%)</td>
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<tr>
<td>[-15, 30]</td>
<td>4938</td>
<td>2935 (60%)</td>
<td>0 (0%)</td>
</tr>
<tr>
<td>[-90, -15]</td>
<td>11127</td>
<td>59 (0.5%)</td>
<td>1 (0%)</td>
</tr>
</tbody>
</table>

www.atmos-chem-phys.org/acp/6/197/

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There were no significantly different validation results found between each of the five months for which the IFE data were retrieved.

5 SCIAMACHY offline ozone profile verification and validation

The data set discussed here consists of OL2.4 (20 September–27 November 2004) and OL 2.5 (7 December 2004 and onward, in this paper, through 17 February 2005). Although the data are given in terms of partial columns as well as mixing ratios as a function of altitude and pressure, we will only use the partial columns, and convert these to number densities (see the remarks in Appendix A). The collocation criteria were the same as those for the IFE data.

For the OL data, unlike the IFE data, four SCIAMACHY profiles are retrieved within one state.

5.1 Verification of SCIAMACHY offline data

Verification of the OL data shows that within the current data set, about 35% of the retrieved profiles at latitudes north of 30° N show unrealistically high ozone concentrations between about 15 and 25 km. Also, about 7.5% of the profiles north of 30° N, and 60% of the profiles between 15° S and 30° N, show negative values around the tropopause region. Detailed numbers are shown in Table 3.

In Fig. 9, bottom panel, we show examples of such unrealistic profiles for one orbit, and in the top panel we show at which locations this type of profile was found, with an indication of the most extreme (either negative or positive) value. Note that if a profile was realistic, it is not plotted. We were not able to find what caused these retrieval errors, we only verified that there was no link to ground albedo (which was assumed to be 0.3 across the globe) or to the “state IDs” (which are settings for the integration time and number of spectra taken per tangent height). Evidently, there is a clear latitude dependence (see Table 3). Also a longitudinal dependence was found, extreme positive values above 30° N were found over Asia and the Atlantic (see Fig. 9), but almost never over Europe or North America.

OL2.5 and the a priori profiles used in this retrieval were both compared with collocated sondes between 40 and 70° N. The OL data set was first filtered to remove all profiles that had either ozone number densities below zero or above $8 \times 10^{12}$ cm$^{-3}$. Also the collocated correlative data for these cases were filtered out. The results are shown in Fig. 10: the a prioris compare better with sondes than the retrieval. In the wavelength window where the retrieval is performed (319–333 nm) almost no light is returned from the atmosphere below about 24 km (this height depends on latitude and time of year), which is evident from radiative transfer studies, e.g., see Flittner et al. (2000), that show weighting functions at 322 nm. This might explain the result.

From Fig. 10 it is not clear whether the match between sondes and retrieval above 27 km is a coincidence or a retrieval result. The average of the unshifted retrievals almost perfectly match the average a priori, and the average a priori is shifted about 1.5 km with respect to the average sonde profile. So even if the retrieval would just return the a priori the match to the sondes would be good.

5.2 Validation of SCIAMACHY offline data

As was outlined in Sect. 2, we chose to apply a downward shift of 1.5 km to all SCIAMACHY data to correct provisionally for the Envisat pointing inaccuracy. To assess the quality of the OL2.4 and OL2.5 data above 24 km, comparisons...
with ground based lidar and microwave were made, as well as with SAGE II. Averaging kernels were not available. Outliers like those discussed in the previous subsection were removed from the averages. Results below 24 km confirm that the ozone maximum is underestimated (by up to 20% at 20 km).

In Fig. 11 we show comparisons of OL2.4 and OL2.5 (together) with lidar. The number of collocations was 86 and 192, respectively. We see that OL profiles above 24 km agree with lidar results to within 2σ. They disagree significantly between 20 and 24 km (15±5% too low).

These results are consistent with comparisons performed with SAGE II and microwave (not shown). A similar latitude dependence that was described for the IFE data (Sect. 4.2) was evident from the OL (2.4 and 2.5 together) to SAGE II comparisons: at the NH mid latitudes, SCIA OL profiles seem to deviate more than in the other regions. Retrievals in the SH do not show this latitude dependence.

The retrieval above 40 km and below 15 km will stay close to the a priori. It is therefore expected that the altitude shift applied to the retrieved profile causes the ozone values to be smaller than the a priori above 40 km, and larger than the a priori below 15 km. When we assume that the a priori is close to the true profile for these heights, we would expect the altitude shifted SCIAMACHY profile to have smaller values than the true profile above 40 km, and larger values than the true profile below 15 km. This is indeed what can be seen in Figs. 10 and 11.

6 Conclusions and outlook

We validated the SCIAMACHY ozone profiles retrieved using the IFE algorithm version 1.61 with various correlative instruments. The standard deviation of the differences is typically 10% between 20 and 35 km. The IFE profiles are biased low by 3 to 6% with respect to lidar and SAGE II, respectively. There is a solar zenith angle dependence in these results, which is discussed in detail. For solar zenith angles below 30° (typically in the tropics) the average bias between 20 and 40 km is −1.7% compared to SAGE II.

The IFE algorithm is under development. A future version will probably include a radiative-transfer based correction for the inaccurate Envisat pointing, which was described in an earlier paper (Kaiser et al., 2004).

More than 20% of the OL ozone profiles version 2.4 and 2.5 have unrealistic ozone values, most of these are north of 15° S. The remaining OL profiles compare well to lidar and SAGE II above 24 km. Between 20 and 24 km, they underestimate ozone by 15±5%. There are indications that the retrieval is very restrained to the a priori. A new offline algorithm is currently under development (DLR, private communication, 2005). In this new OL algorithm, a different fit window, similar to that now used in the IFE algorithm, will be applied.
Appendix A

Remarks on SCIAMACHY offline data set

Since documentation of the offline data is currently not available, we will make a few remarks for the benefit of potential users of these data.

- Profiles are reported in terms of partial columns and in mixing ratio. Mixing ratio profiles were generated from the partial columns using a very crude temperature and pressure climatology, and are therefore subject to large errors. Users who need mixing ratio units can get more accurate results by converting the reported partial columns into number density, and then into mixing ratio using appropriate (e.g., NCEP or ECMWF) temperature and pressure profiles.

- The temperature and pressure profiles reported in the files are climatological values and were not retrieved.

- The averaging kernels of the profiles are not reported. This means that true validation cannot be carried out. The a priori can be deduced by applying the reported iterative change to the profile in each of the retrieval steps backwards.

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Spatial and temporal characterization of SCIAMACHY limb pointing errors during the first three years of the mission

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Abstract. Limb scattering retrievals of atmospheric minor constituent profiles require highly accurate knowledge of the tangent heights during the measurements. The limb scattering measurements of the Scanning Imaging Absorption spectroMeter for Atmospheric Cartography (SCIAMACHY) on Envisat are affected by tangent height errors of up to 2 km. This contribution provides a summary of the temporal and spatial variation of the SCIAMACHY limb pointing errors during the first three years of the SCIAMACHY mission. The tangent height errors are retrieved from the limb measurements in the UV-B spectral range. A seasonal modulation of the monthly mean tangent height offsets is identified with amplitudes of 800 m (220 m) before (after) the improvement of the Envisat orbit propagator model in December 2003. Even after the December 2003 orbit model improvement a constant offset component of about 1 km is present. Furthermore, pointing discontinuities are identified that coincide with the daily updates of the on-board orbit propagator model. In order to reduce the errors in ozone profile retrievals caused by pointing errors to less than 5%, the tangent heights have to be known to within 250 m.

1 Introduction

UV/visible limb scattering is a powerful technique to remotely sense the chemical composition of the terrestrial atmosphere. It combines global coverage – typical of nadir backscatter measurements (e.g., with TOMS (Total Ozone Mapping Spectrometer) (Heath et al., 1975) or GOME (Global Ozone Monitoring Experiment) (Burrows et al., 1999) – with a high vertical resolution on the order of 2–3 km – typical of solar occultation measurements (e.g., with SAGE (Stratospheric Aerosol and Gas Experiment) (McCormick et al., 1989) or POAM (Polar Ozone and Aerosol Measurement) (Lucke et al., 1999)). In the past few years a series of new atmospheric remote sensing instruments applying the limb scattering method was launched: SOLSE/LORE (Shuttle Ozone Limb Sounding Experiment/Limb Ozone Retrieval Experiment) flying on NASA’s space shuttle in 1997 and again in 2003 (McPeters et al., 2000; Flittner et al., 2000), OSIRIS (Optical Spectrograph and InfraRed Imager System) on Odin (Llewellyn et al., 2004), SAGE III (Rault, 2005) on a Meteor-3M spacecraft, and SCIAMACHY on the European environmental satellite Envisat (Bovensmann et al., 1999). Furthermore, the limb scattering technique will also be employed by the future OMPS (Ozone Mapping and Profiling Suite) mission on a NPOESS (National Polar-Orbiting Operational Environmental Satellite) satellite, scheduled for launch in 2008. Satellite-based limb scattering measurements were used already more than 2 decades ago for observations of mesospheric ozone profiles (Rusch et al., 1984) and upper stratospheric NO₂ profiles (Mount et al., 1984) using the UV spectrometer on SME (Solar Mesosphere Explorer). Yet, the greatly enhanced computing power now makes profile retrievals possible for extended altitude ranges (and also other constituents), since spherical radiative transfer (RT) models can be run online in full multiple scattering mode.

One of the main issues for all existing limb scattering instruments is the accuracy with which the tangent heights (THs) can be reconstructed (von Savigny et al., 2004a). The requirements on the knowledge of orientation and position of the spacecraft are particularly strict for limb viewing instruments, because of the large distance between the satellite and the sampled air volume (about 3000 km). For instance, an angular difference of only 1 min of arc translates to a TH difference of about 1 km. Furthermore, tangent errors of only a few hundred meters can lead to significant errors in the retrieved trace gas profiles: 500 m TH error leads to errors in the retrieved ozone concentrations of up to 10%.
in the stratosphere (von Savigny et al., 2005b) and up to 20% in the mesosphere (Rohen et al., 2005). The reason for the larger errors in the mesosphere is the larger vertical gradient, i.e., smaller scale height, of mesospheric ozone number density, at least up to the middle mesosphere. Near the secondary ozone maximum in the upper mesosphere, the ozone scale height will of course become larger again. The retrieval errors associated with pointing errors strongly depend on the shape of the minor constituent profile and will differ to a certain extent from species to species.

It has been recognized early during the SCIAMACHY mission that the TH information in the data files is affected by errors of up to 3 km (von Savigny et al., 2003; Kaiser et al., 2004). Several different pieces of evidence indicated that the TH information in the data files was erroneous: (a) The stratospheric ozone concentration peak in SCIAMACHY ozone profile retrievals appeared at unrealistically high altitudes (near 30 km) in many cases and ozone profile comparisons with independent methods showed a fairly systematic altitude offset; (b) the noctilucent cloud (NLC) signatures apparent in the limb radiance profiles (von Savigny et al., 2005) near the summer-mesopause at high latitudes occurred at altitudes that were higher than the present knowledge (NLCs occur at a remarkably constant altitude of about 82–84 km in the northern hemisphere); (c) elevation mirror discontinuities during solar occultation measurements coinciding with the switch-on of the sun tracker showed systematic differences between the predicted and the actual sun position (S. Noël, pers. comm.); (d) CO₂ (near 1560 nm) and O₂ (b-band) retrievals from solar occultation measurements also showed systematic TH offsets (Meyer et al., 2005). Although the pointing offsets present in the solar occultation measurements are in good agreement with the offsets observed in limb mode in terms of sign and seasonal variation, there may be different pointing error contributions from sources specific for each observation geometry. For example, there may be different misalignments of the optical axes with respect to the platform reference system.

Furthermore, the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding, another limb-viewing instrument on Envisat (Fischer and Oelhaf, 1996)) team identified pointing errors and pointing discontinuities in the MIPAS limb measurements and von Clarmann et al. (2003) published the first evidence for problems with the Envisat attitude. As MIPAS is located on the other side of the spacecraft its viewing direction is opposite to the SCIAMACHY limb viewing direction.

Limb pointing errors may be a consequence of several different problems and combinations thereof: (a) incorrect knowledge of the orientation as well as the position of the satellite platform; (b) misalignments between the instrument optical axis and the satellite platform; (c) thermal drifts of the optical bench and/or individual optical components; (d) erroneous positioning of the scanning mirrors. Schwab et al. (1996) presented a pre-launch limb pointing error budget for SCIAMACHY that included all relevant sources of pointing error including thermal distortions, scanner alignment, effects of launch vibrations, ageing, misalignments between the different structural spacecraft and instrument components, as well as spacecraft attitude errors. The estimated total limb pointing error in elevation direction including systematic, harmonic and random errors originating from the spacecraft and the instrument is 0.061° corresponding to a TH error of about 3.4 km. The total systematic error estimate is 0.035°, the total harmonic error estimate is 0.021°, and the total random error is estimated to be 0.005°. The spacecraft and instrument portions of the total elevation pointing error estimates are 0.048°, and 0.034°, respectively.

To investigate the apparent pointing errors a pointing retrieval from the limb measurements themselves was implemented based on the well established “knee” technique (Sioris et al., 2003; Kaiser et al., 2004) in the UV spectral range. The main purpose of this paper is to complement the special issue of Atmospheric Chemistry and Physics on SCIAMACHY calibration, validation and first results with a detailed description of the retrieved spatial and temporal characteristics of the SCIAMACHY limb pointing errors. High pointing accuracy is a crucial prerequisite not only for all scientific applications – e.g., studying polar chemical ozone loss in both hemispheres – but also for algorithm diagnostics/improvements and all validation activities. The paper is structured as follows: Sect. 2 provides a brief overview of the numerical method to retrieve pointing information from limb scattering observations in the UV-B spectral range. In Sect. 3 a detailed description of the temporal and spatial pointing variability is given. Section 4 illustrates with sample stratospheric O₃ profile retrievals how the retrieval accuracy can be improved by performing a pointing retrieval prior to the minor constituent profile retrieval. Conclusions are presented in Sect. 5.

2 Method and data set

The method used to perform limb pointing retrievals from SCIAMACHY limb scattering observations is based on the now well established knee-technique (Janz et al., 1996; Merkel et al., 2001; Sioris et al., 2003; Kaiser et al., 2004). Basically, the maximum (i.e., the “knee”) in the UV limb radiance profiles caused by absorption in the Huggins/Hartley bands of O₃ (Sioris et al., 2003; Kaiser et al., 2004) or Rayleigh extinction (Janz et al., 1996; Merkel et al., 2001) provides a suitable signature for pointing retrievals. For the present analysis the TRUE (Tangent height Retrieval by UV-B Exploitation) (Kaiser et al., 2004) code (Version 1.4) is employed. It uses the SCIAMACHY UV limb scattering measurements in the 295 nm to 305 nm spectral range and THs ranging from about 35 km to 50 km. This TH range includes the knees of the wavelengths considered. The TH retrieval is based on SCIAMACHY Level 1 data. An optimal
estimation scheme is used together with the radiative transfer code SCIRAYS (Kaiser and Burrows, 2003) to adjust a constant TH offset:

\[ \text{TH offset} = \text{engineering TH} - \text{retrieved TH} \]

The engineering THs are the ones provided in the Level 1 data sets. For all TH retrievals shown here, the background atmosphere climatology in Nagatani and Rosenfield (1993) and the UGAMP (Universities Global Atmospheric Modeling Programme) (Li and Shine, 1995) O3 profile climatology – based on 5 years of SME, SAGE II, and SBUV O3 measurements – are used. A more detailed description of the TRUE method itself is given in Kaiser et al. (2004) and will not be repeated here.

In the used spectral window (295 nm to 305 nm) the knee in the limb radiance profiles is solely due to absorption by O3. Thus, the pointing retrieval is only possible if the atmospheric O3 profile is known or can be estimated with high accuracy. Conversely, the most important source of error of the retrieved THs is an inaccurate O3 profile. Particularly the altitude range between about 40 and 55 km is crucial for the spectral range considered here. Sensitivity studies showed (see Kaiser et al. (2004)) that scaling the O3 profile by factors of 0.8 and 1.2 leads to differences in the retrieved THs of up to 1 km. Scaling the O3 profile by factors of 0.5 and 2.0 leads to differences of up to 3 km. Therefore, the absolute accuracy of the retrieval technique is generally not better than about 1–2 km if mid-latitudes – with significant latitudinal and zonal variability in the O3 field, particularly in the winter hemisphere with its enhanced planetary wave activity – are considered. But, if the stratospheric O3 field is horizontally relatively homogeneous, then a relative retrieval precision of 300 m or better can be achieved. Since stratospheric and lower mesospheric O3 is particularly variable at mid- and high latitudes, but generally less in the tropics, only SCIAMACHY limb measurements between 20° N and 20° S are used. For all orbits analyzed a mean TH offset for this latitude range was determined. Thus, for each orbit a single TH offset was derived and is shown in the following figures. It must be noted that by looking at the TH offsets only at tropical latitudes a possible latitudinal dependence of the TH offset cannot be investigated.

It was also tested how errors in the O3 absorption cross sections affect the TH retrievals. If the absorption cross sections are changed by ±2% then the TH retrievals differ by about 60 m on average. The retrieved THs are smaller (larger) if the cross sections are reduced (increased).

Another important error source are differences between the actual atmospheric density profile and the used climatological density profile. This is because the Rayleigh-scattering cross section is proportional to atmospheric density. A sensitivity analysis using several orbits showed that perturbing the density profile by 5% leads to a mean difference in the retrieved TH offsets of 20 m with a standard deviation of about 120 m. The maximum difference for an individual limb measurement was about 400 m.

Spatial straylight, i.e., radiation entering the instrument from outside its nominal field of view, could not be identified in the spectral range and the tangent height range used here.

For further information on the error budget of the pointing retrievals see Kaiser et al. (2004).

### 3 Results

#### 3.1 General overview

Figure 1 shows the retrieved TH offsets for all orbits – between July 2002 and February 2005 – available at IUP/IFE Bremen and averaged over the tropical limb measurements as described in Sect. 2. The derived TH errors cover the range between about −0.5 km and 2.5 km, and there is (a) significant scatter in every month (about ±0.5 km), and (b) an apparent seasonal variation in the TH offsets. Summer 2003 shows a gap in the coverage lasting from 26 May 2003 until 12 September 2003. Due to a software error, the Level 0 data taken during this period was not processed by the Level 0–1b processor, and therefore the SCIAMACHY Level 1 files did not contain any limb data. However, this gap will be closed after the next reprocessing of the Level 1b data set is completed.

The amplitude of the seasonal variation is suddenly reduced in December 2003. This is due to an improvement
of the orbit propagator model onboard the Envisat spacecraft, that was implemented on 13 December 2003 (Duesmann et al., 2004). The on-board orbit propagator model is used to determine attitude and position of the spacecraft on-board Envisat, and its output is employed to control the limb elevation and azimuth mirror position. The on-board orbit propagator model is re-initialized twice per day, when the so-called orbit state vector (a 38 parameter vector) is uploaded to the spacecraft. An inconsistency of coordinate systems between the software used to calculate the state vectors on-board and the software controlling the SCIAMACHY scan-mirror position based on the output of the on-board orbit model led to the pronounced seasonal variation in the platform attitude errors and consequently in the SCIAMACHY TH errors. On-board the True of Date (TOD) coordinate system was used, whereas the state vector was calculated in the Mean of 2000 (MO2K) coordinate system.

Apart from the seasonal variation and the usual variability of the retrieved TH offsets there are also several additional pointing anomalies. On 21/22 June 2004 during the orbits 12071 to 12086 negative TH offsets between $-1$ and $-2$ km were retrieved. This anomaly was due to a star tracker failure. On 11–13 December tests were carried out to investigate the performance of the improved on-board orbit model. These tests also led to significant TH errors. More variability than usually was also observed in November 2003, May 2003, and several months in 2002. It is important to note in this context, that in 2003 and particularly 2002 the number of available orbits was significantly smaller than in 2004 and 2005. This can also be seen in Table 1, that presents an overview of the monthly mean TH offsets, their standard deviations and the number of orbits used in this study.

3.2 Seasonal variation between July 2002–November 2003

The seasonal variation of the monthly mean TH offsets for the period before the December 2003 improvement of the Envisat orbit model is shown in Fig. 2, together with a model fit composed of a linear and a sinusoidal term. Note that the shown error bars correspond to the standard deviations of the retrieved TH offsets about the monthly mean value. The variability mainly originates from the longitudinal variation discussed in Sect. 3.4. All parameters (i.e., $c_1$, $c_2$, $c_3$, $c_4$, $c_5$) were fitted for. The derived constant offset (black dotted line), the linear increase (blue solid line) and the sinusoidal variation (red dashed line) are shown separately and superimposed (black solid line). The amplitude ($c_3$) of the sinusoidal variation is about 800 m, the fitted period ($2\times c_5$) is 11.7 months − consistent with an annual variation within the error bars − and the phase ($c_4$) is about 7 months with respect to the beginning of year 2002. Amplitude, period and phase of the sinusoidal variation are in very good agreement with pointing retrievals from the two other atmospheric chemistry sensors on Envisat (Saavedra et al., 2005): GOMOS (Global Ozone Monitoring by Occultation of Stars) and MIPAS (Michelson Interferometer for Passive Atmospheric Sounding). The reported annual variation in pitch pointing errors derived from both instruments is between $3\times 10^{-2}$ and $4\times 10^{-2}$ degrees, corresponding to about 1.5–2 km, in excellent quantitative agreement with the annual variation of about 1.6 km (two times the amplitude of 800 m) found in this study. Note that the pointing information from MIPAS and GOMOS is derived using entirely different techniques. GOMOS is a stellar occultation instrument and the difference between the predicted and the actual position of stars on the CCD detector can be used to accurately determine pointing information. The MIPAS pointing measurements used by Saavedra et al. (2005) are the weekly star passage measurements. The good agreement between SCIAMACHY, GOMOS and MIPAS pointing retrievals is a confirmation of the validity of the results presented here.

The apparent annual variation in the TH offsets was caused by the coordinate system inconsistency mentioned above. This coordinate system inconsistency was eliminated with the December 2003 orbit propagator model update.

3.3 Seasonal variation between December 2003–January 2005

As mentioned before the amplitude of the seasonal variation of the TH offset after December 2003 is markedly smaller than before. The monthly mean TH offsets together with the model fit is shown in Fig. 3. The linear term ($c_2$) is about a factor of 3 smaller than before December 2003. The amplitude of the sinusoidal component was found to be about...
Table 1. Monthly tangent height offset statistics.

<table>
<thead>
<tr>
<th>Month</th>
<th>Year offset/km</th>
<th>Std. dev. /km</th>
<th>Number of orbits</th>
<th>Month</th>
<th>Year offset/km</th>
<th>Std. dev. /km</th>
<th>Number of orbits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jul 2002</td>
<td>0.57</td>
<td>0.45</td>
<td>17</td>
<td>Nov 2003</td>
<td>1.57</td>
<td>0.33</td>
<td>163</td>
</tr>
<tr>
<td>Aug 2002</td>
<td>0.89</td>
<td>0.40</td>
<td>71</td>
<td>Dec 2003</td>
<td>0.90</td>
<td>0.50</td>
<td>166</td>
</tr>
<tr>
<td>Sep 2002</td>
<td>1.40</td>
<td>0.30</td>
<td>26</td>
<td>Jan 2004</td>
<td>1.04</td>
<td>0.24</td>
<td>294</td>
</tr>
<tr>
<td>Oct 2002</td>
<td>1.38</td>
<td>0.21</td>
<td>34</td>
<td>Feb 2004</td>
<td>1.04</td>
<td>0.23</td>
<td>261</td>
</tr>
<tr>
<td>Nov 2002</td>
<td>1.43</td>
<td>0.21</td>
<td>34</td>
<td>Mar 2004</td>
<td>1.20</td>
<td>0.24</td>
<td>375</td>
</tr>
<tr>
<td>Dec 2002</td>
<td>0.84</td>
<td>0.37</td>
<td>31</td>
<td>Apr 2004</td>
<td>1.22</td>
<td>0.22</td>
<td>391</td>
</tr>
<tr>
<td>Jan 2003</td>
<td>0.44</td>
<td>0.40</td>
<td>132</td>
<td>May 2004</td>
<td>1.12</td>
<td>0.17</td>
<td>405</td>
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<tr>
<td>Feb 2003</td>
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<td>0.37</td>
<td>136</td>
<td>Jun 2004</td>
<td>0.92</td>
<td>0.43</td>
<td>361</td>
</tr>
<tr>
<td>Mar 2003</td>
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<td>0.19</td>
<td>158</td>
<td>Jul 2004</td>
<td>0.73</td>
<td>0.24</td>
<td>307</td>
</tr>
<tr>
<td>Apr 2003</td>
<td>0.06</td>
<td>0.26</td>
<td>166</td>
<td>Aug 2004</td>
<td>0.68</td>
<td>0.24</td>
<td>334</td>
</tr>
<tr>
<td>May 2003</td>
<td>0.21</td>
<td>0.52</td>
<td>94</td>
<td>Sep 2004</td>
<td>0.83</td>
<td>0.27</td>
<td>399</td>
</tr>
<tr>
<td>Jun 2003</td>
<td>—</td>
<td>—</td>
<td>0</td>
<td>Oct 2004</td>
<td>0.83</td>
<td>0.23</td>
<td>199</td>
</tr>
<tr>
<td>Jul 2003</td>
<td>—</td>
<td>—</td>
<td>0</td>
<td>Nov 2004</td>
<td>1.03</td>
<td>0.20</td>
<td>302</td>
</tr>
<tr>
<td>Aug 2003</td>
<td>—</td>
<td>—</td>
<td>0</td>
<td>Dec 2004</td>
<td>1.06</td>
<td>0.21</td>
<td>247</td>
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<tr>
<td>Sep 2003</td>
<td>1.67</td>
<td>0.25</td>
<td>91</td>
<td>Jan 2005</td>
<td>1.12</td>
<td>0.24</td>
<td>326</td>
</tr>
<tr>
<td>Oct 2003</td>
<td>1.68</td>
<td>0.23</td>
<td>184</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

220 m. The fitted period \((2 \times c_5)\) of the sinusoidal variation is only about 9 months. However, within the error bars the derived variation of the mean TH offsets is also in agreement with a period of 12 months. At present, we cannot state with certainty that the 9 month period is real.

An important question is, whether the remaining seasonal variation after the December 2003 orbit model update is real or a consequence of possible seasonally varying differences between the used ozone climatology and the actual ozone profiles. In principle, it is conceivable that the seasonal variation is at least partly due to the ozone climatology used. A 5% difference in the upper stratospheric and lower mesospheric ozone concentrations is sufficient to cause a 250 m difference in the retrieved TH offsets. However, the sun-acquisition observations during solar occultation (see (c) in Sect. 1) also yield a remaining seasonal variation after December 2003 with an amplitude of about 250 m, in agreement with the amplitude derived from the TRUE retrievals within the scatter of both data sets. In summary, we think that the remaining seasonal variation after December 2003 is to a large extent real.

Moreover, a constant component \((c_1)\) of about 1 km is present. This offset may be due to a misalignment of the limb optical axis with respect to the platform, or due to a remaining problem with the orbit propagator model. It is also conceivable that temporal inconsistencies in the data processing cause the offset. Considering that the entire spacecraft performs a pitch-rotation by 360° in about 100 min (one orbit period), a TH offset of 1 km translates to a temporal error of only about 0.25 s. The origin of this offset is further investigated and a correction will be implemented in a future version of the SCIAMACHY Level-0-to-1 processor. Important in this context is the comparison of SCIAMACHY limb O₃ profile measurements in 2004 with an extensive set of independent measurements (Brinskma et al., 2005) that also yielded an altitude offset of about 1–1.5 km.

In summary, the pointing retrievals suggest that the December 2003 improvement of the orbit propagator model led to (a) a reduced seasonal variation, (b) a reduced linear change, and (c) an increased constant offset component of the TH offsets.
3.4 Longitudinal variation of the TH offsets

Kaiser et al. (2004) report sudden limb pointing discontinuities of up to 2.5 km that occur within a few limb measurements, i.e., within a few minutes. Furthermore, Kaiser et al. (2004) find that the discontinuities are in very good agreement in terms of magnitude and sign – considering that MIPAS and SCIAMACHY look in opposite directions – with pointing discontinuities derived from MIPAS limb-emission measurements in September 2002 using the method of von Clarmann et al. (2003). These discontinuities coincide in time with updates of the on-board orbit model that occur twice per day, always approximately at the same geographical locations: (a) around 60°–70° W between about 20° N and the equator – corresponding to the Caribbean and/or the northern part of South America – and (b) around 100° E and 45° S, i.e., south-west of Australia. For easier reference the updates are called Caribbean and Australian updates in the following sections. To check if pointing discontinuities occur systematically at these locations, the longitudinal variation of the 20° N to 20° S mean TH offset is shown in Fig. 4 for several months before and after the orbit model improvement in December 2003.

A closer inspection of Fig. 4 shows that for the months before December 2003 (left column) the Caribbean update (near 60° W) is in many cases associated with considerable pointing discontinuities, reaching values of about 2 km for example in May 2003. However, the magnitude of the discontinuities differs significantly from day to day. The impact of the Australian update on the TH offsets is not as obvious, but manifests itself in many cases in a bump around 100° E. Its magnitude is also highly variable but generally less than about 0.5 km. After the Australian update the retrieved TH errors increase almost linearly from orbit to orbit (the longitudinal of the equator crossings move from east to west), until the Caribbean update takes place, and the THs are corrected again. Although this appears to be a repeating pattern a simple parametrization that would allow for an analytical TH correction is not possible due to the apparent random variability of the magnitude of the discontinuities.

Interestingly the months after December 2003 exhibit a distinctly different longitudinal variation of the mean tropical TH offsets. The large pointing discontinuities previously associated with the Caribbean updates are not present any more. However, the Australian update now shows a more pronounced TH jump with values of up to about 800 m, and even more in a few cases.

It is important to realize that some of the features present in the retrieved longitudinal variation of the TH offsets may in part be retrieval artifacts originating from differences between the actual middle atmospheric O$_3$ profile and the assumed climatological and zonally averaged UGAMP O$_3$ profile. Any zonal variation in the true atmospheric O$_3$ field will introduce a zonal variation in the TH retrievals to a certain extent. However, there is no doubt that the retrieved pointing discontinuities, that coincide exactly with the daily updates of the on-board orbit propagator model are real and not spuriously introduced by differences between the O$_3$ climatology and the actual O$_3$ profile. Furthermore, the panels a) – e) of Fig. 4 show for many days a nearly linear increase of the TH offset between the Australian and the Caribbean update. This behavior is consistent with a slow pointing drift from orbit to orbit, until the pointing is corrected again, and indicates that the pointing retrieval is precise to within a few hundred meters.

4 Improvement of O$_3$ profile retrievals by pointing correction

In this section the improvement of the stratospheric O$_3$ profile retrievals applying the derived TH offsets is investigated with a sample coincident measurement with the LIDAR (McDermid et al., 1995; Leblanc and McDermid, 2000) at Table mountain (California, USA). The SCIAMACHY stratospheric O$_3$ profiles are retrieved exploiting the Chappuis absorption bands of O$_3$ using the technique (Stratozone version 1.61) described in von Savigny et al. (2005a). With this method stratospheric O$_3$ profiles can be retrieved in the 15–40 km altitude range with a vertical resolution of about 4 km and a theoretical accuracy of about 5–10% (von Savigny et al., 2005b). We use a limb measurement on 20 September 2004 (Orbit 13379) with a mean tangent point location of 35.8° N/−122.2° E made at 18:10:55 UTC. The location of the LIDAR instrument is 34.4° N/−117.7° E, and the measurement was made at 06:14:00 UTC. The time difference between the measurements is therefore 12:05 h. This fairly large difference in time may in principle cause differences in the sampled O$_3$ profiles. However, at the relatively low latitude considered here the longitudinal variation of the stratospheric O$_3$ field are fairly small.

The TRUE pointing retrieval for orbit 13379 yielded a TH offset of 1.13 km. The comparison between the LIDAR profile and the SCIAMACHY retrievals is shown in Fig. 5. Since the LIDAR profile has a significantly higher vertical resolution, it was convolved with the SCIAMACHY averaging kernels. Apparently, the SCIAMACHY O$_3$ profile with corrected THs is in much better agreement than the uncorrected profile. In Fig. 6 the relative differences between SCIAMACHY and the LIDAR profiles as well as the relative difference between the pointing corrected and uncorrected SCIAMACHY profiles are shown. For this comparison the SCIAMACHY retrievals as well as the convolved LIDAR profiles were interpolated onto a regular 2 km altitude grid. The pointing corrected SCIAMACHY profile agrees to within about 10% with the collocated LIDAR measurement, whereas the uncorrected retrieval differs by up to 33%, and it shows a systematic high bias above the O$_3$ concentration peak and a systematic low bias below the peak. This is indicative of a vertical displacement of the retrieved profile.
Fig. 4. Longitudinal variation of the retrieved mean tropical TH offsets for several months before (left column) and after (right column) the orbit model update in December 2003. For the months before December 2003 the repeating discontinuity at about 60° W – where the updates of the on-board orbit model take place – is clearly visible. After December 2003, the longitudinal variation of the pointing offsets is different. Although the Caribbean discontinuity is gone, the signature at around 100° E is more pronounced. The outliers in June 2004 are due to the previously mentioned pointing anomaly on 21/22 June.
The retrieved TH offset of 1.13 km leads to relative differences between the corrected and the uncorrected O₃ profiles of up to 25% above the O₃ concentration peak and up to 20% below the peak. In order to reduce the retrieval error due to pointing errors to less than 5%, the TH accuracy has to be better than about 250 m. Note, that sensitivity tests showed that if the TH offset is less than about 3 km, then the O₃ profile retrieved without prior TH correction may just be shifted vertically. The difference in O₃ concentrations between prior TH correction and TH correction after the O₃ profile retrieval is only a few percent within the 15–40 km altitude range.

Only an individual comparison with an independent method is shown here and one may argue that this is not representative for the majority of the O₃ profile retrievals. However, Brinksma et al. (2005) presented a comprehensive comparison of stratospheric O₃ profiles (Stratozone version 1.61) retrieved with the retrieval scheme used here with O₃ profiles measured with several different ground-based and satellite-based instruments. The SCIAMACHY limb data used in the Brinksma et al. (2005) study was not corrected for pointing errors using the TRUE TH offset retrievals, but a constant TH offset of 1.5 km was subtracted from all tangent heights. It was found that the applied tangent height offset — although less accurate than an orbit-per-orbit correction using the TRUE pointing retrievals — leads to a significant improvement of the profile comparisons. The offset-corrected O₃ concentrations were on average 3–6% lower than SAGE II (about 900 coincident measurements in January, March, May, September and November 2004) between 16 and 40 km with standard deviations of the differences of about 10% between 20 and 35 km. Although the absolute value of the constant TH offset correction of 1.5 km used in Brinksma et al. (2005) differs from the constant offset component c₁=1.04 km obtained for 2004 by several hundred meters, the validation results can be considered as a confirmation that the SCIAMACHY engineering TH are systematically wrong in 2004. Note, that a 1.5 km TH shift leads to differences in the O₃ concentrations between 15 and 40 km of up to 25%.

From a general point of view one may criticize our approach of using an ozone climatology for pointing retrievals that are then used to improve the SCIAMACHY ozone profile retrievals. However, the approach taken here — to use pointing retrievals at low latitudes, where the stratospheric
ozone field is not that variable – has shown to significantly improve the comparisons with independent ozone profile measurements, and is at present the best tangent height correction we can provide. Furthermore, the TRUE retrievals may help to identify further reasons for the remaining pointing errors including both software errors in the calculation of the engineering tangent heights and instrumental problems, e.g., misalignments. The correction of these possible errors may eventually lead to a further improvement of the engineering tangent height accuracy.

5 Conclusions

Pointing errors are the main source of error for trace gas retrievals from limb scattering observations. Without accurate TH (tangent height) information the retrieved profiles cannot be fully validated, and not be used for most scientific applications. An overview of the spatial and temporal behavior of the pointing errors of SCIAMACHY limb scattering observations during the first 3 years of the mission has been presented. The TRUE method was applied to derive a mean TH offset – averaged over the tropical limb measurements – for each orbit. The main conclusions are:

1) The retrieved TH offsets exhibit a seasonal variation, both before and after the December 2003 improvement of the orbit propagator model. Before December 2003 the amplitude of the seasonal variation was about 800 m, and it is significantly reduced to about 220 m after December 2003.

2) The constant offset component increased from about 0.5 km before December 2003 to about 1 km after December 2003. The presence of a tangent offset of about 1 km after the December 2003 orbit model improvement is in good agreement with comprehensive validation results for the year 2004 (Brinksma et al., 2005).

3) The retrieved TH offsets show discontinuities of up to 2 km that coincide in time with updates of the on-board orbit propagator model. These updates occur two times per day. Before December 2003 the Caribbean update was associated with more pronounced discontinuities, whereas the Australian update manifested itself in bumps of generally less than 0.5 km. After December 2003 the longitudinal variation of the TH offsets differs from the period before. The pointing discontinuity associated with the Australian update is now more pronounced, and the Caribbean discontinuity has almost vanished.

4) A pointing correction performed prior to the trace gas profile retrievals significantly improves the accuracy of the profile retrievals. A TH error of only 500 m leads to errors in the derived O3 concentration of 10% and more at certain altitudes. In order to reduce the profile retrieval errors due to TH errors to less than 5%, the TH accuracy has to be better than about 250 m.

The pointing retrievals presented here are not used for a correction of the operational SCIAMACHY limb data products. Instead, the historic data set will be reprocessed with an updated version of the Level-0-to-1 processor that includes a correction for the coordinate system inconsistency that led to the strong seasonal variation before the December 2003 orbit model update. The cause of the constant offset component of about 1 km after December 2003 is presently being investigated and will be corrected for in a future version of the Level-0-to-1 processor.

Acknowledgements. We are indebted to all members of the SCIAMACHY team whose efforts made this analysis possible. We particularly thank Drs. S. Noël (IUP/IFE), M. Gottwald (DLR), E. Krieg (DLR), B. Duesmann (ESA), J. Frerick (ESA) and C. Sioris (SAO) for helpful discussions. This study was in part funded by the University of Bremen, the German Ministry of Education and Research BMBF (grant 07UFE12/8) and the German Aerospace Center DLR (grant 50EE0027). Some of the retrievals were performed at the HLRN (High Performance Computing Center North). The HLRN service and support is gratefully acknowledged.

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References


Validation of IFE-1.6 SCIAMACHY limb ozone profiles

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Abstract. The IFE-1.6 scientific data set of SCIAMACHY limb ozone profiles is validated for the period August–December 2002. The data set provides ozone profiles over an altitude range of 15–45 km. The main uncertainty in the profiles is the imprecise knowledge of the pointing of the instrument, leading to retrieved profiles that are shifted in altitude direction. To obtain a first order correction for the pointing error and the remaining uncertainties, the retrieved profiles are compared to their a-priori value and ozone sondes based on absolute distance and equivalent latitude criteria. A vertical shift of the satellite profiles with 2 km downward is found to be an appropriate correction for the data set studied. A total root-mean-square difference between limb profiles and sondes of 10–15% remains for the stratospheric ozone profile after application of the correction. Small biases are left above and below the ozone maximum at mid latitudes, where the vertical gradients in the retrieved product are in general too strong.

1 Introduction

The SCIAMACHY (SCanning Imaging Absorption SpectroMeter for Atmospheric CartograpHY) instrument on board of Envisat (Environmental Satellite) measures Earth reflectance spectra between 220 and 2380 nm. SCIAMACHY combines high spectral and spatial resolutions with nadir as well as limb mode (Bovensmann et al., 1999).

Ozone profiles are retrieved from limb scattered radiance spectra by two research groups. The ESA Off-Line (OL) product is retrieved by DLR (German Aerospace Center). At time of writing, only a limited amount of OL profiles has become available for the second half of 2002 (version 2.0), spatially limited to locations around validation stations. Recently, a first set of profiles with global coverage has become available for the period December 2004–January 2005 (version 2.5). The scientific product of IFE (Institute of Remote Sensing, University of Bremen) has a much better spatial and temporal coverage. Sets of IFE profiles with global coverage have become available for the periods August–December of 2002 and 2003, processed with algorithm version 1.6 (von Savigny et al., 2005).

The main uncertainty in both the OL and IFE data sets is related to an error in the knowledge of the pointing of SCIAMACHY. If the pointing is not precisely known, it is uncertain from which layers of the atmosphere the instrument receives limb-scattered light. As a result, an ozone profile retrieved from the limb radiance spectra might be positioned at the wrong altitude grid. An estimation of the pointing is made by the on-board orbit propagator model and is provided with the SCIAMACHY Level 1 data (calibrated Level 0 (reflectance spectra) data). The actual pointing can be retrieved by examining the maximum in the UV limb radiance profiles caused by absorption of ozone (Kaiser et al., 2004). This method is reliable in the tropics, but at mid latitudes, where the ozone profile shows much larger variations, the pointing can not be retrieved accurately in this way. For the period up to December 2003, differences up to 3 km were found between the on-board and retrieved pointing, with dependence on longitude, latitude, and season (von Savigny et al., 2004). In December 2003, the on-board orbit propagator has been improved significantly. However, pointing retrievals from the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) instrument on board of Envisat still showed a pole to pole variation in the pointing offset of 1–1.5 km.

The target of this study is to provide insight in the pointing error present in the ozone profiles by comparison with ozone sondes. Application of a vertical shift as a correction of the pointing error is used to identify the remaining quality of the product. Although such a correction can not be a substitute for accurate pointing retrieval at the base of
the retrieval process (Level 0), it will give insight in the biases present in the profile product apart from the pointing. Since identification of spatial variations in pointing offset requires a global data set, the IFE-1.6 for 2002 has been used in this study. A first validation of this set by comparison with ground-based (lidar, sondes, microwave) and satellite data showed good results; average differences between 20 and 40 km were within about 10% (Brinksma et al., 2004). These results were largely influenced by the pointing errors, showed also in the large standard deviations on the differences.

### 2 IFE v1.6 SCIAMACHY limb ozone profiles

The IFE v1.6 ozone profiles are retrieved from SCIAMACHY Level 0 data. The retrieval algorithm uses the SCIRAYS radiative transfer model (Kaiser, 2001) based on wavelengths in the Chappuis band (Flittner et al., 2000). The quantity retrieved is ozone number density in \(10^{12} \text{ cm}^{-3} \) as a function of altitude. A-priori ozone profiles are taken from a SBUV (Solar Backscatter UV) climatology (McPeters, 1993), and provided as a separate data set. The IFE algorithm uses the Optimal Estimation Method (OEM; Rodgers, 2000) for the inversion from radiances to ozone profiles (von Savigny et al., 2005).

The SCIAMACHY measurements are insensitive for ozone below 12–14 km, since light transmission towards the instrument from below this altitude is almost impossible due to absorption by ozone and clouds and Rayleigh extinction. The retrieval algorithm provides however ozone concentrations different from the a-priori already from an altitude of 7 km; some extra points between 7 and 12–14 km are taken into account too, in order to obtain smooth profiles in the troposphere. Above 45 km, no measurable signal is produced due to the low ozone concentrations found here. Due to the different sensitivities, the retrieved ozone profile is not the same as the true profile. The retrieved profile \( y' \) is related to the (discrete representation of the) true profile \( y \) by the a-priori profile \( y^a \) and the averaging kernel matrix:

\[
y' = y^a + A(y - y^a)
\]

All profiles \( y, y^a, \) and \( y' \) are vectors defined on a discrete set of retrieval heights. The discrete representation of the (continuous) true profile is created using averages over altitude layers surrounding the retrieval heights; a point in the continuous profile grid contributes to the average computed for the most near-by retrieval height. The averaging kernel matrix \( A \) has zero or almost zero rows at altitudes where the instrument is not or less sensitive to ozone. The remaining part of the kernel has the form of a band matrix, collecting a weighted average of points in the true profile into a point in the retrieved profile. The averaging kernel therefore smooths strong vertical fluctuations in the true profile, to account for the limited vertical resolution of the instrument. Unfortunately, the averaging kernel is not provided with the IFE-1.6 product. A-priori profiles and averaging kernel matrices will however accompany the retrieved profiles in future releases of the IFE data set. To prepare the validation for future releases, an averaging kernel is simulated by a matrix which is identity matrix between 7 and 45 km and zero elsewhere. Applied in convolution Eq. (1), this approximate kernel ensures that a retrieved profile is equal to the a-priori at the lower and upper levels. Although this is a rather simple approximation, it is the best that can be done with the available information. The approximated kernel simply selects the altitude range for which the retrieval is sensitive, without any smoothing.

### 3 Comparison with a-priori

A simple experiment to obtain first insight in the quality of the IFE-1.6 data set is to compare the product with its own a-priori, in this case the SBUV climatology (McPeters, 1993). The a-priori profile is used in the retrieval as an unbiased first guess of the true profile. A structural bias between a-priori and retrieved profiles indicates that either the a-priori is biased, or the retrieval is biased, or both.

Figure 1 shows the zonal bias between IFE-1.6 and its a-priori for August 2002 (similar results have been obtained for the other months). For almost all latitudes, a clear negative bias is found just below the ozone maximum, as well as a positive bias just above it. These biases indicate that the IFE profiles place the ozone maximum at an altitude that is too high. This displacement of the ozone layer altitude is a clear result of the pointing error.
The longitudinal variation in the bias is limited, except for latitude band [80° S, 60° S] as shown in Fig. 2. The bias between IFE profiles and climatology is here negative at western longitudes, and positive at eastern longitudes. This variation can be explained by the fact that the Antarctic polar vortex is not perfectly centered around the South Pole, but shows in general a displacement towards the Atlantic Ocean (an orography effect of the Andes mountains and Antarctic plateau; see also Fig. 9). This result indicates that the IFE product contains information on the ozone profile even for complex events as the polar vortex.

From the difference between IFE profiles and a-priori it is possible to obtain insight in the pointing uncertainty. A first order impact of a pointing error is that a profile retrieved with wrong-pointing has the correct shape, but is defined on a wrong, in the vertical shifted grid. This neglects the fact that parts of the retrieved profile are equal or close to the a-priori profile, which is independent of the pointing. However, since the a-priori parts of the retrieved profile contain only a minor part of the total ozone, a useful correction for the profiles retrieved with wrong-pointing is to simply apply a proper altitude shift (see also Fig. 8).

For each of the retrieved profiles, an optimal correction has been obtained, defined as the vertical shift that provides the lowest root-mean-square difference between the shifted retrieved profile and the a-priori. The result is shown in Fig. 3. According to the a-priori profiles, the pointing error shows a strong pole-to-pole variation for this period. The pointing correction is on average zero near the north pole, but increases strongly to about −3 km at southern mid latitudes, to decrease again towards the south pole.

A clear longitudinal variation could not be observed in the corrections. Since a small longitudinal dependency was observed in the actual pointing retrieval (von Savigny et al., 2004), this is related to the large spread in the found corrections. The longitudinal dependency of biases will be subject of further study when larger data sets have become available.

Note that the vertical offset found here is not an accurate quantitative estimate of the actual pointing error, since the quality of the a-priori profiles has not been studied in detail. The SBUV climatology is known to contain large uncertainties; although this not necessarily influences the retrieval, new versions of the retrieval method will be based on an improved climatology. The qualitative estimate of the pointing error found here will however be confirmed by the comparison with ozone sondes carried out in the next sections.

4 Comparison with sondes

The IFE-1.6 profiles have been compared to ozone sonde measurements. A database has been created collecting all available sonde measurements for the period under investigation from the WOUDC (World Ozone and UV Data Centre), NILU (Norwegian Institute for Air Research), and NDSC (Network for the Detection of Stratospheric Change) data bases. Figure 4 shows the locations of the ground stations from which sondes are available. The coverage is the best on northern hemisphere mid latitudes, but also the tropics and the southern hemisphere show a reasonable coverage.

In principle all sonde measurements are used for the validation. The following criteria are however used to reject data:

- Sondes that did not reach an altitude of at least 20 km are rejected.
Fig. 4. Locations of ground based stations from which sondes are available.

- All data above 10 hPa is rejected; higher in the atmosphere, the quality of sonde measurements becomes doubtful because of instrument failure.

- If a sonde shows a data gap over more than 3 km, the profile is truncated below the gap.

- If the measured ozone concentration suddenly drops to zero, the profile is truncated at the measured maximum.

Pairs of sondes and nearby IFE profiles have been selected using the co-location criteria that the center of the satellite footprint is less than 1000 km away from the station, and that the launch and measurement times differ less than 12 h. With this criteria, about 400 pairs of co-located satellite and sonde profiles have been selected (on a total of about 17 000 IFE profiles available for August–December 2002).

Sonde measurements can only be meaningful compared to retrieved profiles if the impact of the retrieval on a true profile (convolution with averaging kernel) is applied to the sonde profile too. This has been obtained by 1) extending the sonde profile to the top of the atmosphere with the a-priori profile (discontinuities are in general small and therefore not treated specially); 2) averaging the high resolution sonde+extension to the retrieval height grid, and 3) convolution with the (simulated) averaging kernel following Eq. (1). The convolved sonde is therefore equal to the a-priori above the 10 hPa level (about 30 km) where no sonde measurements are used, and below 7 km where the retrieval is insensitive to ozone.

Figure 5 shows the bias and root-mean-square (RMS) of the differences between the retrieved IFE profiles and convolved sondes, defined by:

$$\text{bias} = \frac{1}{n} \sum_{i=1}^{n} (x_i - y_i), \quad \text{rms} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (x_i - y_i)^2}$$

where $x$ is a retrieved IFE measurement, $y$ is a (convolved) sonde measurement, and $n$ the number of measurements. Similar as for the comparison with the a-priori profiles, the negative bias just below the ozone maximum indicates the existence of a height displacement in the IFE profiles. A positive bias above the ozone maximum exists only for the tropics, but since it is located above 30 km it is almost completely caused by the bias between retrieved and a-priori profile, and therefore not a result of validation with independent data.

Variations in longitudinal direction could not be identified due to the lack of a dense station network at all longitudes in at least one of the latitude bands. However, such variations are not expected to be found here, since even comparison
with the longitude invariant a-priori profiles did not show a clear longitudinal dependence in bias and RMS difference for most latitudes.

To obtain insight in the value of the pointing error, an optimal height shift for the IFE profiles has been obtained for the co-located profiles in a similar way as for the comparison with the a-priori profiles. The sondes, extended to the top of the atmosphere, have been averaged on several shifted retrieval height grids, convolved with the averaging kernel, and compared with the retrieved profile; the height shift that leads to the lowest RMS difference is regarded as the optimum. Figure 6 shows the optimal height shifts as a function of latitude. Some upward shifts have been obtained for sonde profiles with a low ozone maximum (flat profile) or with strong vertical gradients (ozone hole conditions and stratospheric intrusions), which can be regarded as an artefact of the method. The optimization could benefit from having a proper averaging kernel matrix available, such that strong gradients in the sondes are smoothed before comparison with the retrieval. The spread in the optimal shifts is too large to identify a statistically significant latitudinal trend as in Fig. 3. However, a first order correction of $-2.0\text{ km}$ is found to be a useful first order correction at all latitudes.

Figure 7 shows the bias and RMS difference between IFE-1.6 profiles and convolved sondes after height correction of the IFE profiles with the previously found optimal shifts. As expected, the negative bias below the ozone maximum resulting from the pointing error has disappeared. A large bias is left in the tropical upper stratosphere, caused by the bias between a-priori and retrieved profiles, as observed in Fig. 1. Small biases are introduced below 7 km and above 30 km where the convolved sondes are set to the a-priori, caused by the fact that during correction, the complete retrieved profile is shifted in the vertical, regardless whether parts of it are equal to the a-priori. Neglecting these a-priori related effects, the most important remaining bias concerns a structural underestimation of the concentrations in the ozone layer at mid-latitudes. Investigation of individual IFE and sonde profiles in these regions shows that the ozone gradients below and above the ozone maximum are too strong in the IFE profiles; see illustration in Figs. 8 and 5. A part of this bias might be explained from not having the averaging kernel matrix available for the comparisons, but this cannot explain the entire effect; in fact, kernels could even increase this bias by smoothing the sondes profiles such that their gradients become less strong rather than stronger.

Comparison of Fig. 5 with Fig. 7 shows a dramatic decrease in RMS difference after pointing correction. This is an indication that the majority of the error in the IFE profiles arises from the pointing error. The RMS difference after height correction is almost constant over the ozone layer, with a value of $0.4\text{ cm}^{-3}$ (about 10%). The largest RMS
differences are found in the tropical upper stratosphere due to the a-priori bias, and near the Antarctic polar vortex. Investigation of the IFE and sonde profiles in the latter region shows that the retrieval is in general able to retrieve the strong gradients present in the ozone profiles here, but is not able to estimate the amplitudes correctly.

5 Comparison with sondes using equivalent latitude

A drawback of co-located satellite profiles with sondes using distance and time criteria is the low number of data pairs that is left for comparison, since the number of measurement stations is limited. A method to increase the number of co-located data points in the stratosphere is the use of equivalent latitude as co-location criterion rather than distance. Equivalent latitude is a useful tool in atmospheric science to decide whether two points are part of the same large scale air volume or not (Allen and Nakamura, 2003; Good and Pyle, 2004).

The concept of equivalent latitude exploits the fact that in the stratosphere, on a time scale of days, air parcels are transported along lines of constant potential temperature ($\theta$) and potential vorticity (PV). The altitude above which this is true is determined by the stability of air; we use a lower border for $\theta$ of 330 K. As a consequence, if two parcels of air on the same $\theta$-level have the same PV, they are likely to have the same origin. Potential vorticity has a strong zonal character, since transport and mixing in longitudinal direction is much stronger than in latitudinal direction. Since PV increases from south to north, it is possible to map the PV axis to a latitude axis from $-90^\circ$ to $+90^\circ$, assigning an “equivalent latitude” to each PV value. The mapping is such that given a fixed PV, the equivalent latitude encloses a polar cap starting at the south pole that covers an area equal to the area covered by all air parcels with a lower PV. In this way, similar equivalent latitude means similar PV means similar origin, and, since on a time scale of days stratospheric ozone concentrations are almost constant, it also means similar ozone concentrations.

In this study, equivalent latitude is used to compare retrieved ozone concentrations with sondes that measured the same air volume; see the illustration in Fig. 9. Profiles of equivalent latitude as a function of $\theta$ and altitude are obtained for each individual retrieved profile and each sonde launched. These meteorological profiles are obtained by interpolation of ECMWF (European Centre for Medium-Range Weather Forecasts) meteorological fields of $\theta$, PV and geo-potential height in space and time. For each individual point in one of the retrieved profiles, the following steps are taken. First, the $\theta$-level and equivalent latitude at the corresponding altitude are obtained by interpolation of the meteorological profiles. Second, for all sondes launched within 24 h, the equivalent latitude and ozone concentrations are obtained on the computed $\theta$-level by interpolation of the meteorological profiles, respectively averaging the high resolution sonde profile over a small altitude interval. This large time interval is allowed since even sondes launched at the other side of the earth might sample the same air as the satellite instrument. Third, only those sonde concentrations are selected for which the equivalent latitude differs less than 2.5 degrees form the equivalent latitude of the profile. This corresponds
to a virtual meridional distance of 250 km, which is much smaller than the 1000 km criterion used for co-location by distance; this smaller distance is however required to ensure that SCIAMACHY and sondes sample the same volume of air even if the longitudes are far apart from each other.

The comparison between retrieved and sonde profiles is now not on profile-to-profile base, but rather on point-to-point base. Only if the retrieval location is close to the location of the sonde station, it is possible that for each point in the retrieved profile a sonde measurement can be obtained within the desired equivalent latitude range. If the horizontal distance corresponding to the equivalent latitude criterion is larger than the 1000 km criterion used for direct co-location, the set of retrieval/sonde pairs found with the equivalent latitude method is simply an extension of the distance-based validation set. The point-to-point character of the comparison is a problem if the averaging kernels are rather broad. For convolution of sonde measurements with such a kernel it is necessary that the sonde is within the desired equivalent latitude range over an altitude range equal to the width of the kernel. In our study, this is not a problem however, since the averaging kernels are simulated with an identity matrix in the kernel. In our study, this is not a problem however, since the horizontal distance over an altitude range equal to the width of the kernel.

A drawback of the point-to-point character of the equivalent latitude method is the impossibility to compute a height correction for the pointing error as applied in the previous sections. Therefore, an overall vertical shift of −2.0 km has been applied to all IFE profiles. The results from the previous section showed that this is a useful first order correction for the pointing error.

For the period August–December 2002, about 27 000 pairs of retrieval and sonde profile points matching the chosen time and equivalent latitude criteria have been selected. The 27 000 pairs originate from 11 000 of the 17 000 available IFE profiles. Thus, on average 2.5 profile point per IFE profile can be compared with sondes data, for more than 60% of the total number of profiles. These numbers show immediately the advantage of using equivalent latitude for co-location rather than absolute distance. Using the latter method, 400 co-located profiles were found with about 4000 data points (the IFE profiles have 10 points between the lower sensitivity bound and the top of the sondes). The data volume is therefore increased with a factor 6, and might be increased further since the chosen co-location criteria are rather strong.

The large data volume allows computation of statistics over smaller temporal ranges than the 5 month period used in the previous section. Figure 10 shows the bias as a function of latitude and height for each month in August–December 2002. The vertical boundaries between which the bias is sampled are determined by the θ=330 K level at the bottom and 10 hPa pressure top of the sondes. The bias has been computed in almost all latitude bands, since the equivalent latitude criterion allows comparison of retrieved and sonde profiles even near the poles. A lack of IFE profiles hampered the bias computation for December at the mid latitudes.

The zonal pattern of the biases is similar to the pattern found in Fig. 7. A negative bias around the stratospheric ozone maximum is visible at all latitudes during all months, as a result of the too strong vertical gradient in the IFE product. Especially for October it is clear that the amplitude of the ozone maximum is almost unbiased. A positive bias is visible in the lower stratosphere for tropical and northern latitudes, which decreases slowly in time. Removal of both biases will be subject of future study. The overall root-mean-square difference has a value of 0.4 to 0.6 cm−3 in the stratospheric ozone layer (10 to 15%). This is slightly larger than the 10% RMS difference obtained in the previous section, and can be explained from using an overall altitude shift of 2 km to all IFE profiles, rather than optimizing the shift for each individual comparison. Variation of the applied altitude corrections show that for shifts of 1.5 km or smaller, strong negative biases below the ozone maximum remain as seen for uncorrected profiles too. For shifts larger than 3 km, a small positive bias is introduced below the ozone maximum.
at all latitudes, indicating that the ozone maximum in the IFE profiles is too low for this choice.

6 Summary and conclusions

The IFE-1.6 ozone profiles form the first set of limb measured ozone profiles retrieved from SCIAMACHY with global coverage. The data set provides stratospheric ozone profiles between 15 and 45 km. The set studied here covers the period August–December 2002. The major uncertainty in the set arises from an imprecise knowledge of the pointing of SCIAMACHY.

Comparison of the retrieved profiles with the a-priori profiles used in the retrieval shows that due to the pointing error, the IFE profiles are strongly biased below and above the ozone maximum. According to the results of the comparisons with the a-priori profiles, the size of the pointing offset shows a strong pole-to-pole variation.

Comparison of IFE profiles and nearby ozone sondes shows that the pointing error is in the order of 1–3 km. A clear pole-to-pole trend could not be identified due to the limited number of co-located profiles. After a first order correction for the pointing error, the remaining RMS difference is for most latitudes in the order of 10%. The only exception is the dynamically active region around the Antarctic vortex where a RMS difference of 20% remains; although the shape of the profile is in general retrieved correctly, the extreme values need improvement. At mid-latitudes, a part of remaining error is caused by a bias in the gradients of the ozone layer, that are too strong in the IFE profiles in comparison with the sonde measurements. This bias will be investigated in more detail when averaging kernels have become available with future releases. Application of the kernels will smooth the profile, and might have a large impact on the comparison results.

Co-location of retrieved and sonde profiles in terms of equivalent latitude provides a large data set of satellite and sonde measurements that can be compared with each other. The number of data points in this set is much larger than obtained with co-location by distance. A comparison between the IFE profiles and sondes using equivalent latitude showed that an overall vertical shift of 2 km provides a satellite product that is almost bias free around the ozone maximum during selected months, but shows too strong gradients above and below. The remaining RMS difference after the correction is 10–15%.

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Inter-comparison of stratospheric O$_3$ and NO$_2$ abundances retrieved from balloon borne direct sun observations and Envisat/SCIAMACHY limb measurements

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Abstract. Stratospheric O$_3$ and NO$_2$ abundances measured by different remote sensing instruments are intercompared: (1) Line-of-sight absorptions and vertical profiles inferred from solar spectra in the ultra-violet (UV), visible and infrared (IR) wavelength ranges measured by the LPMA/DOAS (Limb Profile Monitor of the Atmosphere/Differential Optical Absorption Spectroscopy) balloon payload during balloon ascent/descent and solar occultation are examined with respect to internal consistency. (2) The balloon borne stratospheric profiles of O$_3$ and NO$_2$ are compared to collocated space-borne skylight limb observations of the Envisat/SCIAMACHY satellite instrument. The trace gas profiles are retrieved from SCIAMACHY spectra using different algorithms developed at the Universities of Bremen and Heidelberg and at the Harvard-Smithsonian Center for Astrophysics. A comparison scheme is used that accounts for the spatial and temporal mismatch as well as differing photochemical conditions between the balloon and satellite borne measurements. It is found that the balloon borne measurements internally agree to within ±10% and ±20% for O$_3$ and NO$_2$, respectively, whereas the agreement with the satellite is ±20% for both gases in the 20 km to 30 km altitude range and in general worse below 20 km.

1 Introduction

Stratospheric NO$_x$ (=NO+NO$_2$) is responsible for up to 70% of the stratospheric O$_3$ loss (Crutzen, 1970; Portmann et al., 1999). NO$_x$ reactions dominate the catalytic destruction of O$_3$ between 25 and 40 km altitude via

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  
(R1)

\[ \text{NO}_2 + h \cdot \nu \rightarrow \text{NO} + \text{O} \]  
(R2)

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \]  
(R3)

Reactions (R1) and (R2), account for more than 90% of NO$_x$ chemistry in the lower stratosphere (Del Negro et al., 1999; Cohen et al., 2000). Thus, NO$_2$ and O$_3$ measurements are of primary importance to study the photochemistry of stratospheric O$_3$. Recent studies by Dufour et al. (2005) indicate that for selected geophysical conditions the agreement between measured and photochemically modeled O$_3$ and NO$_x$ is better than 10%. Accordingly, high precision measurements are required to constrain or to be compared with photochemical models.

Past observations of these key species involve in-situ as well as optical remote sensing instrumentation operated from ground, aircraft, balloons and satellites, exploiting the fact that O$_3$ and NO$_2$ absorb electromagnetic radiation in various wavelength ranges. Pioneering work on monitoring atmospheric O$_3$ abundances has been conducted by Dobson...
As far as vertical profiling of trace gases is concerned, historically first the solar occultation technique (e.g. Mauldin et al., 1985; Russell III et al., 1988; Camy-Peyret et al., 1993; Sasano et al., 1993) was applied to the UV/visible and IR spectral ranges and only more recently the satellite-borne UV/visible skylight limb technique became available (e.g. Mount et al., 1984; Rusch et al., 1984; Burrows et al., 1995; von Savigny et al., 2003; Sioris et al., 2003; Rozanov et al., 2005b).

The SCanning Imaging Absorption spectrometer for Atmospheric CHartography (SCIAMACHY) instrument onboard the European Envisat satellite is a UV/visible/near-IR spectrometer designed to measure direct and scattered sunlight in various viewing directions (Burrows et al., 1995; Bovensmann et al., 1999). An exciting new feature of SCIAMACHY is to probe the atmosphere in subsequent and spatially overlapping nadir and limb scanning observations. This will eventually allow to discriminate between the measured total atmospheric column amounts (nadir) and total stratospheric columns obtained from integrated stratospheric profiles to yield tropospheric column amounts of the targeted gases (Sioris et al., 2004; Sierk et al., 2006).

Here, we present O$_3$ and NO$_2$ stratospheric profiles retrieved from SCIAMACHY skylight limb observations using first retrieval exercises developed at the Universities of Bremen (IUP-Bremen) and Heidelberg (IUP-Heidelberg) and at the Harvard-Smithsonian Center for Astrophysics (Harvard). The present study aims at estimating the accuracy of the inferred vertical profiles of stratospheric O$_3$ and NO$_2$ by comparison to the corresponding data retrieved from traditional balloon borne solar occultation measurements performed by the LPMA/DOAS (Limb Profile Monitor of the Atmosphere/Differential Optical Absorption Spectroscopy) balloon payload (Camy-Peyret, 1995; Ferlemann et al., 1998; Harder et al., 1998; Bösch et al., 2003). For ENVISAT validation purposes, LPMA/DOAS has been deployed at different launch locations and in different seasons during the recent past. It allows us to perform simultaneous measurements of targeted gases in various wavelength ranges covering the UV to the IR.

Therefore in a first exercise, the internal consistency of the LPMA/DOAS observations is checked by comparing slant column amounts of O$_3$ and NO$_2$ (taken from the balloon to the sun) inferred from the visible and IR spectral ranges. Since instrumental setup and retrieval algorithms are inherently different for the DOAS and LPMA instrument but the line-of-sight is inherently the same, inferred line-of-sight absorptions are compared and discussed with respect to precision and accuracy of the instruments. Further, the vertical profiles are analyzed regarding altitude resolution and implications for satellite validation. In the second part, the balloon borne profiles of O$_3$ and NO$_2$ are compared with collocated profiles inferred from SCIAMACHY skylight limb observations. Spatial and temporal coincidences of the balloon and satellite borne measurements are identified using air mass trajectory calculations based on ECMWF analyses. In addition, for the photochemically short-lived NO$_2$ radical, the diurnal variation is modelled on the calculated air mass trajectory in order to consider the different daylight hour of the satellite and the balloon borne observations. Finally, after accounting for the spatial and temporal mismatch as well as the differing photochemical conditions, the balloon and satellite borne measurements are inter-compared and discussed with respect to inherent errors and possible further improvements of the involved algorithms. A schematic drawing which illustrates the presented comparison and validation strategy is shown in Fig. 1.

## 2 Methods

### 2.1 O$_3$ and NO$_2$ profiles inferred from LPMA/DOAS observations

Since details on the instrumental setup and performance of the French/German LPMA/DOAS balloon payload have been reported elsewhere (Camy-Peyret, 1995; Ferlemann et al., 1998), only a short description of the instrumental features important for the present study is given here. The payload is mounted on an azimuth-controlled gondola and comprises a sun-tracker (Hawat et al., 1998) and three optical spectrometers which analyze direct sunlight over virtually the entire wavelength range from the UV to the mid-IR. Sunlight is collected by the automated sun-tracker (beam diameter 10 cm), which points to the center of the solar disk within 30 arcsec. It directs the inner core (beam diameter 5 cm) of the solar beam into a Fourier Transform spectrometer (FT-IR) operated by LPMAA (effective field of view FOV$\approx0.2^\circ$) while two small telescopes (diameter 1 cm each, effective field of view FOV$\approx0.53^\circ$) mounted into the beam’s outer fringe feed the collected sunlight into the two DOAS spectrometers via glass fibre bundles. This optical setup guarantees that the UV/visible (DOAS) and IR (LPMA, FT-IR) spectrometers analyze direct sunlight which traversed almost the same atmospheric air masses, (except for the slightly different effective FOV of both spectrometers). The measurements are performed during balloon ascent/descent and in solar occultation geometry with moderate spectral resolution in the UV/visible (UV: FWHM$\approx0.5$ nm, visible: FWHM$\approx1.5$ nm) and high spectral resolution in the IR (apodized resolution $\approx0.02$ cm$^{-1}$).

In addition to the spectrometers observing direct sunlight a small versatile UV/visible spectrometer has been operated in limb scattering geometry aboard the same balloon gondola since 2002. The instrumental setup, performance and first results are published in Weidner et al. (2005). The inferred O$_3$ and NO$_2$ abundances show overall good agreement with the data inferred from the direct sun measurements.

The retrieval of O$_3$ and NO$_2$ profiles from LPMA/DOAS measurements is split in two steps. First the trace gas
concentrations integrated along the line-of-sight (Slant Column Densities (SCDs)) are inferred from individual solar spectra. Then the SCDs are inverted to vertical profiles of the respective trace gases.

2.1.1 DOAS O$_3$ and NO$_2$ SCD retrieval

The UV/visible spectra recorded by the two DOAS spectrometers are analyzed for trace gas absorptions applying the DOAS retrieval algorithm (Platt, 1994; Stutz and Platt, 1996). Each spectrum is evaluated with respect to a solar reference spectrum guaranteeing the removal of solar Fraunhofer lines. The solar reference spectrum usually is the spectrum for which the air mass along the line-of-sight and the residual trace gas absorption are minimal. The residual absorption in the solar reference is determined using Langley’s extrapolation to zero air mass.

O$_3$ SCDs are retrieved from the differential structures in the Chappuis absorption band between 545 nm and 615 nm where the temperature and pressure dependence of the O$_3$ absorption cross section taken from Anderson et al. (1992) is negligible (Burkholder et al., 1994; Orphal, 2003). Remaining trace gas absorptions are dealt with by simultaneously fitting two NO$_2$ absorption cross sections recorded at T=218 K and T=238 K in the laboratory, wavelength aligned to cross sections from Voigt et al. (2002) and orthogonalized with respect to each other. Further, an oxygen dimer (O$_4$) absorption cross section taken from Hermans (2002) and an H$_2$O absorption cross section generated from HITRAN 2000 (Rothman et al., 2003) by convolution to our spectral resolution are considered. Rayleigh and Mie scattering are accounted for by including a third order polynomial in the fitting procedure. In addition we allow for a first order polynomial which is subtracted from the measured intensity before any algebraic manipulation to correct for instrumental straylight. In the final evaluation the relative wavelength alignment of the absorption cross sections and the solar reference spectrum is fixed and only the measured spectrum is allowed to shift and stretch.

The line-of-sight absorptions of NO$_2$ are inferred from the 435 nm to 485 nm wavelength range. Interfering absorption features come from O$_4$ (Hermans, 2002) and O$_3$. Two O$_3$ absorption cross sections recorded in the laboratory at T=230 K and T=244 K, aligned to cross sections from Voigt et al. (2001), are orthogonalized and fitted simultaneously. Broad band spectral features are represented by a fourth order polynomial. Instrumental straylight correction and wavelength alignment are treated as in the case of the O$_3$ analysis. Additional complications arise from the temperature dependence of the NO$_2$ absorption cross section while the pressure dependence is negligible at our spectral resolution (Pfeilsticker et al., 1999; Orphal, 2003). The NO$_2$ analysis is performed using absorption cross sections recorded in our laboratory scaled and aligned to convolved cross sections from Harder et al. (1997) at T=217 K, T=230 K, T=238 K and T=294 K. The resulting four sets of NO$_2$ SCDs are linearly interpolated to the effective NO$_2$ concentration weighted temperature along the line-of-sight for each spectrum.

The error bars of the retrieved SCDs are estimated via Gaussian error propagation from the statistical error given by the fitting routine, the error in determining the residual absorber amount in the solar reference spectrum and the errors of the absorption cross sections (1% for O$_3$, 4% for NO$_2$). For NO$_2$ additional errors coming from unaccounted features of the temperature dependence of the absorption cross...
section (2%) and from the convolution to our spectral resolution (1%) are taken into account. The statistical error comprises the 1-σ fitting error, errors coming from systematic residual absorption features and from shift and stretch of the fitted spectrum. The error of the residual absorber amount in the solar reference spectrum is dominated by the estimated accuracy (5%) of the overhead air mass. The errors of the retrieved \( \text{O}_3 \) SCDs are governed by the latter error contribution while, for \( \text{NO}_2 \), fitting errors become important when \( \text{NO}_2 \) abundances are very low. In total, typical accuracies of the DOAS \( \text{O}_3 \) and \( \text{NO}_2 \) measurements are better than 5% and 10%, respectively.

Typical optical densities range between \( 10^{-1} \) and \( 10^{-3} \) for both gases. All DOAS data presented in this study originate from spectra in the visible wavelength range. \( \text{NO}_2 \) SCDs are also retrieved in the 370 nm to 390 nm wavelength range measured by the UV spectograph. As \( \text{NO}_2 \) SCDs inferred from the UV and the visible do not differ significantly, only data inferred from the visible spectograph are shown exhibiting smaller error bars. Evaluating \( \text{O}_3 \) in the UV is difficult due to the strong temperature dependence and the strong absorption (optical densities \( \simeq 1 \)) below 350 nm which renders the DOAS approach questionable (Frankenberg et al., 2005). For further information on the spectral retrieval see Harder et al. (1998, 2000), Ferlemann et al. (1998, 2000), and Bösch et al. (2003).

2.1.2 LPMA \( \text{O}_3 \) and \( \text{NO}_2 \) SCD retrieval

The SCD retrieval of \( \text{O}_3 \), \( \text{NO}_2 \), \( \text{NO} \), \( \text{HNO}_3 \), \( \text{N}_2\text{O} \), \( \text{CH}_4 \), \( \text{HCl} \), \( \text{CO}_2 \) and \( \text{ClONO}_2 \) is performed simultaneously using a multi fit of 6 to 11 micro-windows. The possibility to retrieve all species depends on the actual filters and beam splitters used for the FT-IR measurements. The target micro-windows for \( \text{O}_3 \) and \( \text{NO}_2 \) are 3040.03 cm\(^{-1}\) to 3040.85 cm\(^{-1}\) and 2914.36 cm\(^{-1}\) to 2915.16 cm\(^{-1}\), respectively. Typically the \( \text{O}_3 \) absorption lines in the main target window become saturated during deep solar occultation reducing the sensitivity of the retrieval to changes in \( \text{O}_3 \) abundances along the line-of-sight. Thus, an additional micro-window between 1818.09 cm\(^{-1}\) and 1820.98 cm\(^{-1}\) with non-saturated \( \text{O}_3 \) absorption features is added if available. Interfering absorbers in the \( \text{O}_3 \) and \( \text{NO}_2 \) target windows are \( \text{H}_2\text{O} \), \( \text{CO}_2 \), \( \text{NO} \), \( \text{CH}_4 \) and \( \text{H}_2\text{O} \), \( \text{O}_2 \), \( \text{CH}_4 \), respectively. Additional information on ozone SCDs comes from weak absorption in the micro-windows dedicated to \( \text{NO}_2 \) (2914.36–2915.16 cm\(^{-1}\)), and \( \text{CO}_2 \) (1933.89–1940.00 cm\(^{-1}\)). For \( \text{NO}_2 \), weak absorption in the HCl micro-window (2944.71–2945.11 cm\(^{-1}\)) improves the SCD retrieval. Based on absorption line parameters from HITRAN 2004 (Rothman et al., 2005) and a reasonable a priori guess for the trace gas profiles, a forward model calculates synthetic spectra which are fitted to the measured ones by a non-linear Levenberg-Marquardt algorithm. The calculation of the synthetic spectra relies on atmospheric parameters taken from nearby radiosonde launches and climatological and meteorological model data. Fitting parameters include a polynomial of up to third order, a zero order wavelength shift and several parameters to adjust the instrumental line shape (ILS). All auxiliar ILS parameters are determined separately in various test runs and finally set to a fixed value for all spectra during a balloon flight.

The error bars comprise the statistical error of the fitting routine (1-σ), the uncertainty in determining the instrumental line shape (~5%), the error coming from the ambient atmospheric parameters (<1%) and their impact on the spectroscopic parameters and the stated error bars of the latter (5% to 10% for \( \text{O}_3 \), 2% to 5% for \( \text{NO}_2 \) (Rothman et al., 2005)). In total the systematic contribution to the SCD error is estimated to 10% for both gases. Since the pre-flight alignment and in-flight stability of the LPMA instrument improved during the suite of considered balloon flights between 1996 and 2003, the analysis of earlier balloon flights usually yields larger errors than analysis of the more recent ones. Typical errors of the retrieved \( \text{O}_3 \) SCDs range between 10% and 15% and are dominated by the accuracies of the spectroscopic parameters and the estimated accuracy of the instrumental line shape function. The errors of the \( \text{NO}_2 \) SCDs range between 10% and 25%. As in the case of the DOAS error budget, fitting errors become important for \( \text{NO}_2 \) when its abundances are very low e.g. for the flight from Kiruna in February 1999, where \( \text{NO}_2 \) SCDs are close to the detection limit of the LPMA instrument. For earlier work on LPMA data see Payan et al. (1998, 1999) and Dufour et al. (2005).

2.1.3 LPMA/DOAS \( \text{O}_3 \) and \( \text{NO}_2 \) profile retrieval

Each spectrum yields an \( \text{O}_3 \) and \( \text{NO}_2 \) SCD according to the specifications described above. Vertical trace gas profiles are inferred separately from the measurements during balloon ascent and solar occultation. We refer to the respective set of SCDs as the measurement vector \( y \). In keeping with the standard notation the true trace gas profile is denoted \( \hat{x} \) (Rodgers, 2000). The forward model which links the measurements and the vertical profile is straight forward to obtain by raytracing the path of the incoming light from the sun to the detector. Assuming a spherical, layered atmosphere including refraction, the elements \( K_{ij} \) of the weighting function matrix \( K \) are given by the ratio of the slant path through layer \( j \) and the height of layer \( j \) for the observation geometry of spectrum \( i \). The inversion problem can be stated in linear form

\[
y = Kx + \epsilon, \tag{1}
\]

where \( \epsilon \) represents the measurement error. A variety of methods exists to invert the weighting function matrix \( K \) and to calculate a retrieved vertical trace gas profile \( \hat{y} \) given the measurements \( y \). Vertical trace gas profiles from balloon borne measurements shown here are generated using a
linear Maximum A Posteriori inversion algorithm described in Rodgers (2000)
\[ \hat{x} = (K^T S_e^{-1} K + S_a^{-1})^{-1} (K^T S_e^{-1} y + S_a^{-1} x_a) \] (2)
where the superscript $T$ indicates transposed matrices. A priori, $S_a$, as well as measurement covariance matrices, $S_e$, are assumed to be diagonal. The a priori profile $x_a$ is taken from the satellite retrievals described below or from the SLIMCAT chemical transport model (Chipperfield, 1999). Error propagation is handled by calculating the corresponding error covariance matrix $\hat{S}$ via
\[ \hat{S} = (K^T S_e^{-1} K + S_a^{-1})^{-1}. \] (3)
The square roots of the variances $\hat{S}_{ii}$ represent the errors attributed to the retrieved trace gas profile $\hat{x}$.

The quality of the retrieval can be characterized by the averaging kernel matrix $A$ which gives the relation between the true trace gas profile $x$ and the retrieved one $\hat{x}$
\[ \hat{x} = x_a + A (x - x_a) + \text{error terms}. \] (4)
For the Maximum A Posteriori retrieval $A$ is given through
\[ A = \hat{S} K^T S_e^{-1} K. \] (5)
The width of averaging kernels given by the rows of $A$ is a measure for the altitude resolution of the measurement. As altitude resolution depends on the weighting function matrix $K$ and measurement error $S_e$, the altitude resolution of the retrieved trace gas profiles is different for the three sensors presented in this study. When comparing trace gas profiles the differing altitude resolution can be accounted for by degrading the altitude resolution of the high resolution profile. First, the profile inversion of the high resolution measurement is performed on the same altitude grid as the inversion of the low resolution data set, then the resulting trace gas profile $\hat{x}_h$ is smoothed by the averaging kernel matrix of the low resolution measurement $A_l$. Accordingly, the smoothed trace gas profile $\hat{x}_s$ is given by
\[ \hat{x}_s = x_a + A_l (\hat{x}_h - x_a), \] (6)
where $x_a$ is the a priori profile simultaneously used for both retrievals (Connor et al., 1994; Hendrick et al., 2004). Whenever smoothed profiles are shown in this study they are generated according to Eq. (6).

2.2 $O_3$ and NO$_2$ profiles inferred from Envisat/ SCIAMACHY limb observations

The SCIAMACHY instrument, which was put into a sun-synchronous orbit onboard the European Envisat satellite on 28 February 2002, is a UV/visible/near-IR spectrometer (220 nm–2380 nm, FWHM: 0.2 nm–1.5 nm) designed to measure either direct sunlight during solar occultation, direct moonlight during lunar occultation or sunlight scattered by the Earth’s atmosphere in nadir or limb direction (e.g. Burrows et al., 1995; Bovensmann et al., 1999). In limb scattering mode SCIAMACHY scans the Earth’s atmosphere vertically in steps of 3.3 km from the ground to about 100 km tangent height (vertical field of view at tangent point, FOV ≃ 2.8 km, horizontal field of view at tangent point, FOV ≃ 110 km). In addition a horizontal scan is performed at each tangent height covering in total about 960 km at the tangent point. Here, results obtained by the LPMA/DOAS balloon payload since 2003 are used to validate SCIAMACHY limb observations.

$O_3$ and NO$_2$ profiles are inferred from SCIAMACHY limb measurements using algorithms developed at the university of Bremen (IUP-Bremen). In the case of NO$_2$, also data retrieved at the Harvard Smithsonian Center for Astrophysics (Harvard) and a limited data set retrieved by the university of Heidelberg (IUP-Heidelberg) are available. To our knowledge no official ESA products are on hand to be compared with the presented data.

2.2.1 IUP-Bremen $O_3$ retrieval

The stratospheric ozone profiles are derived from SCIAMACHY limb scattering observations with the Stratozone code (version 1.62) using the method described in von Savigny et al. (2005c). The altitude range from about 15–40 km can be covered with this technique with a vertical resolution of about 4 km. The retrieval technique exploits the absorption in the Chappuis bands of ozone using only three discrete wavelengths as described in Flttnert et al. (2000). A non-linear optimal estimation (OE) scheme drives the radiative transfer model SCIARA YS (Kaiser and Burrows, 2003), which is run online to calculate weighting functions and to forward-model the limb radiance profiles. The main error sources are incorrect knowledge of the stratospheric aerosol loading, surface albedo, cloud cover, as well as tangent height errors (von Savigny et al., 2005b). The estimated total error between 15 and 35 km is about 8–14%. The SCIAMACHY limb observations are affected by errors in the tangent height information of up to 2.5 km (von Savigny et al., 2005a), particularly before the improvement of the orbit propagator model on-board the Envisat spacecraft in December 2003. Note that tangent height errors of only 500 m lead to errors in the ozone concentrations of up to 10%. For the stratospheric ozone profile retrievals presented here a tangent height offset for each orbit was derived from the limb measurements in the UV-B spectral range prior to the ozone profile retrieval, using the method described in Kaiser et al. (2004). The precision of the tangent height retrieval method is about 200–300 m.

2.2.2 IUP-Bremen NO$_2$ retrieval

The forward simulations of the SCIAMACHY limb measurements and the calculations of the appropriate weighting functions are performed employing the SCIATRAN radiative
transfer model (Rozanov et al., 2005a,b), assuming cloud free conditions. In spherical mode the SCIATRAN model calculates the limb radiance properly considering the single scattered radiance and using an approximation to account for multiple scattering. Vertical distributions of NO$_2$ are retrieved from SCIAMACHY limb measurements using the spectral information in the 420–470 nm wavelength interval. To improve the retrieval quality the vertical profiles of O$_3$ are estimated in combination with NO$_2$ retrievals using the same spectral information. Limb measurements performed at tangent heights from 12 to 40 km are considered. To reduce the impact of the Fraunhofer structure and incorrect instrument calibration all selected limb scans are divided by the reference limb measurement obtained at a tangent height of about 43 km. To account for broadband features resulting from unknown scattering properties of the atmosphere as well as instrument calibration issues, a cubic polynomial is deduced from all spectral ratios. The temperature dependent absorption cross sections of O$_3$ and NO$_2$ measured by the SCIAMACHY PFM Satellite Spectrometer are used in the forward model (Bogumil et al., 1999). Pressure and temperature profiles are taken from the corresponding ECMWF data. The SCIAMACHY pointing errors are accounted for by applying appropriate tangent height corrections obtained using the TRUE retrievals (Kaiser et al., 2004). The retrieval is performed as described in Rozanov et al. (2005b) using a two-step retrieval procedure. During the preprocessing step which is done for each tangent height independently a possible misalignment of the wavelength grids of the limb spectra, of the reference spectrum and of the forward model is accounted for. Additionally, known corrections, namely, undersampling, Ring spectrum, stray light correction and instrument calibration functions, are applied. The main retrieval step is based on the solution of Eq. (1) employing the optimal estimation technique. Different from the description given in Sect. 2.1.3, the measurement vector $y$ contains the differences between ratios of simulated and measured differential limb spectra at all tangent heights selected for the retrieval with all corrections from the preprocessing step applied. The state vector $x$ contains relative differences of trace gas number densities (with respect to a priori values) at all altitude layers for all gases to be retrieved. The final solution is found employing the information operator approach (Hoogen et al., 1999; Rozanov, 2001) which ensures an additional noise filtering, resulting in more stable profiles.

2.2.3 Harvard NO$_2$ retrieval

The Harvard-SAO algorithm is described in Sioris et al. (2004) and references therein. Cloud top height is retrieved from channel 6 and is used to define the lower limit of the retrieval. Tangent height (TH) registration is determined by the multi-wavelength ~305 nm knee method (Sioris et al., 2003). The calculated orbital median TH offset is applied to all limb scans if greater than the orbital standard deviation of the TH offsets. The NO$_2$ fitting window consists of 256 pixels in the 434–495 nm range and the simulations are performed at SCIAMACHY channel 3 spectral resolution (0.5 nm), leading to 114 wavelengths in the same fitting window. The analysis uses a classic two-step approach: spectral fitting followed by inversion of SCDs to a number density profile. The reference spectrum is the co-addition of all spectra between the retrieval upper altitude limit (∼40 km) and 70 km. Absorption cross sections included in the fitting process are NO$_2$ and O$_3$ from Bogumil et al. (2003), and the collisional oxygen dimer (O$_3$) from Greenblatt et al. (1990). The temperature dependence of the NO$_2$ and O$_3$ absorption cross section is handled by performing three runs with absorption cross sections corresponding to $T=203$ K, $T=223$ K, $T=243$ K (Bogumil et al., 2003). At each tangent height the run which exhibits the smallest errors is chosen for profile retrieval. The inversion of the SCDs to number density profiles is direct, thus a priori is not required in the retrieval range.

2.2.4 IUP-Heidelberg NO$_2$ retrieval

The IUP-Heidelberg uses a two step approach to retrieve NO$_2$ vertical profiles from SCIAMACHY limb spectra (Kühl, 2005), see also Krecz et al. (2005) and Haley et al. (2004). First, the SCD of the considered absorber is deduced by Differential Optical Absorption Spectroscopy (Platt, 1994). In the second step the SCDs for the different tangent heights are inverted to concentration profiles by an optimal estimation method (Rodgers, 2000). The DOAS retrieval for NO$_2$ is performed in the 420–450 nm spectral range. The measured and calibrated spectral information from SCIAMACHY is analyzed with respect to a pseudo top-of-the-atmosphere (TOA) reference spectrum taken as average of SCIAMACHY measurements at tangent heights between 40 to 46 km to infer the SCDs. Considered trace gas absorption cross sections are NO$_2$ at 223 K from Bogumil et al. (2003), O$_3$ at 241 K from Bogumil et al. (2003), H$_2$O at 273 K from Rothman et al. (2003), O$_3$ at 298 K from Greenblatt et al. (1990). In addition we account for the Ring effect (Grainger and Ring, 1962), instrumental straylight and broadband spectral features by considering a calculated Ring spectrum and the inverse of the TOA reference as fitting parameters. The vertical trace gas profiles are obtained using the same approach as in the case of the balloon borne retrieval, see Sect. 2.1.3. The weighting function matrix $K$ is calculated by the fully spherical 3-dimensional Monte Carlo radiative transfer model “Tracy” (von Friedenburg, 2003; Weidner et al., 2005), assuming a cloud cover at 10 km altitude. Sensitivity studies show that the impact of clouds on the retrieval of stratospheric NO$_2$ is negligible. Using the maximum a posteriori technique the vertical trace gas profile is inferred from Eq. (2), where the measurement vector $y$ represents the measured SCDs and the vector $\hat{x}$ the retrieved profile. Our studies show the possibility to retrieve information about the NO$_2$ concentration in the altitude range from
approximately 15 km to 40 km where averaging kernels are larger than 0.7. The accuracy in this altitude range is approximately 15–25%. Tangent height corrections are performed according to the monthly averaged SCIAMACHY pointing errors given in von Savigny et al. (2005a).

2.3 Air mass trajectory modelling

Balloon borne measurements exhibit several inherent constraints with respect to the time and location of the balloon launch. Balloon launches are possible at a few sites around the world, only. The launching possibility depends on the local surface weather conditions and the balloon’s trajectory is determined by the tropospheric and stratospheric wind fields. Furthermore, the LPMA/DOAS payload is supposed to be launched temporally close to local sunset or sunrise as LPMA/DOAS performs measurements during solar occultation. In practise, these constraints make it difficult to get a direct temporal and spatial coincidence with individual satellite measurements such as SCIAMACHY limb observations. In part, the use of air mass trajectory models can help to overcome the shortcomings in balloon borne satellite validation (Bacmeister et al., 1999; Lu et al., 2000; Danilin et al., 2002a,b).

For that purpose, an air mass trajectory model is applied within the framework of Envisat/SCIAMACHY validation (Langematz et al., 1987; Reimer and Kaupp, 1997). It uses the operational ECMWF analyses and forecasts given every 6 h on a 2.5°×2.5° latitude/longitude grid. Forward and backward trajectories are calculated on isentropic levels from the surface up to 1600 K with interpolation between the levels. The internal time step is 10 minutes and the diabatic and climatological heating rates are based on Newtonian cooling. The results (trajectory points) are stored for each hour.

Backward and forward trajectories start at the balloon measurement locations. For the remote-sensing payload LPMA/DOAS these starting points are the balloon location and the tangent points for balloon ascent and solar occultation, respectively. For post-flight analysis air mass trajectory models are calculated for up to 10 days forward and backward in time, but for balloon flight planning purposes the time range is limited by the available ECMWF forecasts: the latest analysis is from 12:00 UT the day before, forecasts are available every 6 h up to 72 h into the future.

The actual geolocations of Envisat/SCIAMACHY observations are provided by the SCIAMACHY Operational Support Team (SOST) through its website (http://atmos.raf.op.dlr.de/projects/scops/). For each Envisat orbit, overpass time, geolocation and detailed measurement specifications (e.g. swath, measurement duration, ground pixel size) can be downloaded. For the air mass trajectory based matching technique only the area covered by the tangent points of SCIAMACHY limb is considered. This information is used to find satellite measurement points along the individual air mass trajectories, for which the spatial and temporal mismatch is as small as possible. The match criteria are chosen based on the experience of the ozone Match experiment (von der Gathen et al., 1995). The maximum time mismatch between the satellite observation and the air mass trajectory started at the balloon observation is one hour and the maximum area mismatch is 500 km with respect to the center of the SCIAMACHY limb ground pixel. In case, no Envisat/SCIAMACHY observation satisfies these limits, the distance criterion is weakened to a maximum spatial mismatch of 1000 km.

2.4 Photochemical modelling

On timescales important for this study, i.e. the time between satellite and correlative balloon borne measurement (<1 day), the photochemical variation of O3 is found negligible. Hence, we focus our modelling on the photochemical variation of NO2. For the impact of the photochemistry of NO2 on solar occultation measurements and validation studies see also Kerr et al. (1977), Roscoe and Pyle (1987) and Bracher et al. (2005). We use output from a simulation of the SLIMCAT 3-D off-line chemical transport model (CTM) (Chipperfield, 1999) to initialize a 1-D chemistry model of the stratosphere. SLIMCAT output of run 323 is saved at 00:00 UT every 2 days interpolated to the launching sites of the balloon flights. Both photochemical models include a comprehensive set of the relevant gas-phase and heterogeneous reactions as given by the JPL-2002 report on Chemical Kinetics and Photochemical Data (Sander et al., 2003). The 1-D chemistry model is an updated version of the model used in Bösch et al. (2003). Stratospheric chemistry is modelled on 19 potential temperature (Θ) levels between Θ=336 K (≃11 km) and Θ=1520 K (≃42 km). Aerosol loadings are taken from Deshler et al. (2003) as recommended by Dufour et al. (2005). Photolysis rates are interpolated with respect to pressure, temperature, overhead ozone and solar zenith angle (SZA) from a lookup table where the actinic fluxes are calculated as recommended by Lary and Pyle (1991) and validated for JNO2 by Bösch et al. (2001).

If available the 1-D model is initialized at 00:00 UT with SLIMCAT output of the same day at the balloon launch site. If output is not available on the day of the balloon flight, we decide whether to take output from the day before or after the flight by comparing the measured O3, NO2 and if available CH4 and N2O profiles to the modelled ones and choosing the output which produces better agreement with the measurement. While the model is run with fixed pressures and temperatures for each Θ level taken from the meteorological support data of the balloon flight, the SZA timeline is taken from the air mass trajectory calculations to guarantee that the photochemical evolution of the modelled air mass corresponds to the true evolution between initialization of the model, satellite measurement and balloon borne observation. For simplicity a single representative SZA timeline is chosen for all Θ levels. In addition O3, NO2, NO and N2O5

www.atmos-chem-phys.net/6/1293/2006/ Atmos. Chem. Phys., 6, 1293–1314, 2006
Fig. 2. Slant Column Densities of O₃ (panels a and b) and NO₂ (panels c and d) retrieved from LPMA (red triangles) and DOAS (black boxes) direct solar spectra measured at Kiruna on 23 March 2003, during balloon ascent (panels a and c) and sunset (panels b and d). Each panel consists of two sub-panels showing the measured SCDs on the left and the corresponding relative errors and deviations (blue open stars), i.e. SCD(DOAS) / SCD(LPMA) - 1, on the right. For clarity not all DOAS data points are shown.

are scaled at initialization in a way that the model can reproduce the balloon borne O₃ and NO₂ profiles in the evening (Bracher et al., 2005).

In general, each spectrum measured by SCIAMACHY as well as by the balloon borne instruments is a composite of several photochemical conditions since the SZA varies along the line-of-sight through the atmosphere. All satellite measurements presented here are conducted in the morning far from sunset or sunrise where the photochemical variation of NO₂ is weak. Hence, we assume a fixed SZA for the SCIAMACHY observations. However, the time-lag to the validation measurements is on the order of several hours and balloon borne profiles are inferred from measurements close to sunset when the photochemical variation of NO₂ is strongest. Introducing the photochemical weighting factors $\kappa_{kj}$, balloon observations are scaled to the photochemical conditions of the satellite measurements. Given the model data along the SZA timeline of a given air mass trajectory, $\kappa_{kj}$ is defined by

$$\kappa_{kj} = \frac{a_{kj}}{b_j},$$

where $b_j$ is the modelled NO₂ concentration at altitude $j$ and the SZA of the SCIAMACHY measurement and $a_{kj}$ the modelled NO₂ concentration at altitude $j$ and SZA $k$. When tracing the light through the atmosphere from the sun to the balloon borne detector, each point on the line-of-sight can be identified through its altitude and its local SZA. Assuming a layered atmosphere the slant path through layer $j$ at local SZA $k$ is multiplied by $\kappa_{kj}$. Hence, we obtain a photochemically corrected weighting function matrix $\tilde{K}$. Replacing $K$ by $\tilde{K}$ in Eq. (1) and solving the inversion problem as described in Sect. 2.1.3 yields the balloon borne trace gas profile scaled to the photochemical conditions of the satellite measurement.

Following a similar approach as in Bracher et al. (2005) the modelling error is estimated by sensitivity studies. For the flight from Kiruna on 24 March 2004, several model runs are performed along a representative air mass trajectory varying model parameters important for the photochemical
variation of NO$_2$. These parameters include the O$_3$ profile (−33%, +50%), overhead ozone (±74%), the temperature for each Θ-level (±7 K), the rate constants of Re-
actions (R1) and (R2) (±20%), the aerosol surface area (±40%) and the γ-coefficient for N$_2$O$_2$ uptake on liquid aerosol (−50%, +100%). For each run two photochemically

traced trace gas profiles are generated corresponding to a back-
ward and a forward satellite match in the morning before and after the balloon flight, respectively. The root mean
square deviation of the vertical profiles from the standard run
yields the estimate of the modelling error. The modelling
error increases from less than 10% at balloon float altitude to
20% at 20 km altitude. Between 20 km and balloon float al-
titude the error is governed by the factors which influence the
photolysis of NO$_2$ via Eq. (R2). The modelling error for the
backward match grows to 30% at 15 km and up to 50% be-
low 15 km, mainly due to the sensitivity of NO$_3$ chemistry to
the O$_3$ profile through Eq. (R1). The modelling error of the
forward match calculations remains constant at 20% down to
15 km. Below 15 km it rises up to 35% caused by sensitivity
to the O$_3$ profile. Whenever photochemically corrected trace
gas profiles are shown the modelling error is added applying
Gaussian error propagation.

3 Internal LPMA/DOAS comparison

3.1 Comparison of LPMA/DOAS O$_3$ and NO$_2$ Slant Col-
umn Densities

Table 1 summarizes the geophysical conditions of the bal-
loon flights chosen for the comparison of the LPMA/DOAS
O$_3$ and NO$_2$ SCDs. We present data of six joint
LPMA/DOAS balloon flights where the corresponding geo-
physical conditions range from high-latitude winter and sum-
mer to mid-latitude fall comprising measurements inside as
well as outside the northern polar vortex. Due to bad data
quality or instrumental malfunction and the considerable ef-
fort necessary for data re-analysis we restrict the comparison
study to six out of the 13 flights conducted to date.

The quality of the LPMA/DOAS comparison is illustrated
in Fig. 2 showing O$_3$ and NO$_2$ SCDs as well as the corre-
sponding errors and relative deviations inferred from obser-
vations at Kiruna on 23 March 2003. The particular flight is
chosen as an example since all data sets are available allow-
ing for a consistent comparison. In addition, relative devi-
ations between LPMA and DOAS SCDs are presented as his-
tograms in Figs. 3 and 4 for the six considered balloon flights.
Relative deviations are calculated by linear interoplation of
the DOAS data to the measurement instances of LPMA.

The general agreement of LPMA and DOAS O$_3$ SCDs is
on the order of 10%. Maximum deviations of up to 30% are observed when slant columns are very low and governed
by the O$_3$ abundances above balloon float altitude indicat-
ing a problem when applying Langley’s method to retrieve
the residual absorber amount in the DOAS solar reference
spectrum. For some of the earlier balloon flights the rela-
tive deviations for solar occultation measurements are as
large as 20%. During solar occultation the measured O$_3$ IR-
asorption lines in the LPMA standard retrieval window be-
come saturated. In order to increase retrieval sensitivity we
include a micro-window exhibiting weak, unsaturated O$_3$ ab-
sorption. Unfortunately the latter micro-window is not avail-
able for some of the flights due to usage of spectral filters
which cut the respective spectral region. The statistical anal-
ysis of all 1032 data points yields that in average DOAS O$_3$
SCDs are larger by 6.1% than the LPMA data. The stan-
dard deviation of the relative deviation between LPMA and
DOAS amounts to 8.0%, see Fig. 3.

The comparison of NO$_2$ SCDs is more difficult to assess.
The NO$_2$ measurements during balloon ascent of the earlier
flights from Leon in 1996 and Kiruna in 1997 are hard to
compare as LPMA data are very noisy. Data retrieved from
balloon ascent of the more recent flights at Kiruna in 2001
and in 2003 are less noisy although the NO$_2$ slant column
abundances show similar values. This suggests that the pre-
flight optical alignment of the FT-IR improved during the se-
ries of presented balloon flights. For the flights at Kiruna
and at Gap in 1999, NO$_2$ slant columns are close to the de-
tection limit of the LPMA retrieval causing large error bars.
The agreement on NO$_2$ SCDs inferred form solar occultation
is on the order of 20%. The maximum deviation up to 50%
occur for the flight from Kiruna in 1999 where NO₂ abundances are very low. In this case, stratospheric temperatures were well below 217 K and an extrapolation of the Harder et al. (1997) data has to be used when accounting for the temperature dependence of the NO₂ absorption cross sections. However, an extrapolation error alone cannot account for the observed discrepancy which has been tested using the NO₂ cross section from Bogumil et al. (2003) at 203 K. The statistical analysis of all 1016 data points reveals a mean deviation of +3.7% between DOAS and LPMA with a large standard deviation of 24.5%, see Fig. 4 lower panel. As some of the LPMA data are noisy or close to the detection limit we performed another statistical analysis excluding all data where the corresponding SCDs show errors larger than 25%. The resulting set of 753 data points exhibits a mean relative deviation between DOAS and LPMA of +6.6% and 14.0% standard deviation, see Fig. 4 upper panel. Overall the combined error bars are a reasonable estimate for the LPMA/DOAS agreement on NO₂ measurements.

3.2 Comparison of LPMA/DOAS O₃ and NO₂ profiles

Section 3.1 discussed the level of agreement between the O₃ and NO₂ SCDs inferred from LPMA and DOAS measurements. In this section O₃ and NO₂ data again taken from balloon ascent and sunset of the flight at Kiruna on March 23, 2003, are chosen to illustrate the characteristics of the profile inversion technique. SCDs are inverted to vertical trace gas profiles via Eq. (2). The profile retrieval is characterized by the corresponding averaging kernel matrices given by Eq. (5). The O₃ and NO₂ profiles presented in the upper panels of Figs. 5.1 and 5.2, respectively, are retrieved using diagonal a priori covariance matrices with variances corresponding to 30% error of the a priori profiles. LPMA data are inverted on a 2-km altitude grid. DOAS data are generated on the same altitude grid as the satellite retrievals which corresponds to 1 km grid spacing between 10 and 45 km altitude and coarser below and above. In addition DOAS profiles are shown which are smoothed applying Eq. (6) to match
Fig. 5.1. Vertical O$_3$ profiles (panel a and b) and corresponding averaging kernels (panel c and d) retrieved from balloon ascent (panel a and c) and sunset (panel b and d) for the flight from Kiruna on 23 March 2003. LPMA data (red triangles) are retrieved on a 2 km, DOAS data (grey diamonds) on a 1 km altitude grid. In addition smoothed DOAS data are shown (black boxes). The green stars represent the O$_3$ a priori profile. The averaging kernels of the SCIAMACHY O$_3$ retrieval are plotted (blue circles) for comparison.

The retrieved O$_3$ profiles, Figs. 5.1 and 5.2, reproduce the general behavior of the underlying SCDs shown in Fig. 2. LPMA data underestimate the DOAS data during balloon ascent below 22 km. Above, the agreement is good. During sunset O$_3$ concentrations retrieved from LPMA spectra tend to be higher than those retrieved from DOAS spectra and the shapes of the considered profiles are somewhat different. The general agreement is on the order of the combined error bars as already indicated by the underlying SCDs.

The averaging kernels of the DOAS O$_3$ profile retrieval, Fig. 5.1c and d, are well shaped in the altitude range between 10 km and 30 km for both, the balloon ascent and sunset measurements. Hence, profile retrieval is possible with 1 km to 2 km altitude resolution in the respective altitude range. The LPMA averaging kernels are reasonably well shaped between 17 km and balloon float altitude for both viewing geometries and allow for profile retrieval there. Below 17 km, there is essentially no information on the O$_3$ profile from LPMA measurements, which draws the retrieved profile toward the a priori. Consequently, also the smoothed DOAS profile is drawn toward the LPMA and a priori profile. Filamented structures in the lower stratosphere, e.g. Fig. 5.1b around 15 km, cannot be resolved by the LPMA and smoothed DOAS measurements while they are well resolved by the standard DOAS retrieval. The corresponding altitude resolution of the LPMA balloon ascent and solar occultation measurements improves from about 3 km at 17 km to about 2 km at balloon float altitude. The decrease in altitude resolution for lower altitudes is mostly due to the smaller number of contributing measurements during the beginning of balloon ascent and the increase in vertical averaging by the effective field-of-view of the instruments when the line-of-sight penetrates deeper into the atmosphere during sunset.
Fig. 5.2. Vertical NO$_2$ profiles (panel a and b) and corresponding averaging kernels (panel c and d) retrieved from balloon ascent (panel a and c) and sunset (panel b and d) for the flight from Kiruna on 23 March 2003. LPMA data (red triangles) are retrieved on a 2 km, DOAS data (grey diamonds) on a 1 km altitude grid. In addition smoothed DOAS data are shown (black boxes). The green stars represent the O$_3$ a priori profile. The averaging kernels of the SCIAMACHY NO$_2$ retrieval are plotted (blue circles) for comparison.

The comparison of NO$_2$ vertical profiles for balloon ascent, Fig. 5.2a, reveals an underestimation of the DOAS by the LPMA data over the entire retrieved altitude range. In the lower stratosphere the discrepancy is substantial and larger than the error bars. For sunset, Fig. 5.2b, LPMA overestimates the DOAS data between 31 km and 25 km. Below 25 km LPMA and DOAS agree well.

The averaging kernels indicate that it is possible to retrieve NO$_2$ vertical profiles in the range between 12 km and balloon float altitude at about 30 km from DOAS measurements during balloon ascent and sunset exhibiting 5 km to 1 km altitude resolution. However, the NO$_2$ averaging kernels are less well shaped than those of the O$_3$ retrieval since the underlying NO$_2$ SCDs have larger errors. Hence, in contrast to the O$_3$ retrieval, there is a significant decrease in altitude resolution below 20 km. LPMA measurements during balloon ascent and solar occultation allow for profile retrieval between 17 km and 30 km altitude with 5 km to 2 km altitude resolution. Due to the larger errors of the NO$_2$ SCDs, altitude resolution for the NO$_2$ profile retrieval is worse than for the O$_3$ retrieval. Comparing the averaging kernels of the LPMA and DOAS data sets it becomes evident that smoothing is most significant below 20 km altitude where LPMA measurements yield only little or no information on the NO$_2$ vertical profile. The secondary (and real) maximum at about 15 km altitude seen in the DOAS unsmoothed data is not present in the LPMA retrieval. Hence, according to Eq. (6) the smoothed DOAS profile is drawn toward the a priori.

For both gases, SCIAMACHY averaging kernels are smaller than 0.5 and significantly broader than the grid spacing indicating that on the selected retrieval grid the retrieved profile points are not independent. Correspondingly, SCIAMACHY’s altitude resolution amounts to 3 km to 5 km in the retrieved altitude range.
Table 2. Compendium of joint LPMA and DOAS O$_3$ and NO$_2$ profile measurements and Envisat/SCIAMACHY overpasses. BA and SO indicate balloon ascent and solar occultation measurements, respectively.

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<th>Geophysical condition</th>
<th>Available datasets</th>
<th>Satellite coincidence orbit, date, time/UT</th>
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3.3 Conclusions on the LPMA/DOAS comparison and implications for satellite validation

As presented in Sects. 3.1 and 3.2, O$_3$ and NO$_2$ abundances inferred from LPMA/DOAS measurements in the IR and visible spectral ranges agree roughly within ±10% for O$_3$ and ±20% for NO$_2$. Observed discrepancies can be due to instrumental and retrieval related shortcomings of either technique. The LPMA Fourier Transform spectrometer inherently exhibits smaller signal-to-noise-ratio (SNR ≃10$^2$) than the grating spectrometers operated by DOAS (SNR ≃10$^3$) causing significantly smaller detection limit and higher precision of the DOAS measurements. In the visible spectral range where the Sun’s intensity peaks the typical integration time for individual spectra is less than 1 s, whereas in the IR it takes about 50 s to record a single interferogram. Hence, the DOAS instruments sample the atmosphere with a much higher rate than the LPMA FT-IR. Taking into account the respective errors of the considered trace gases it is evident that altitude resolution is significantly better for the DOAS observations. When the apparent size of the solar disk becomes large during solar occultation the smaller field of view of the FT-IR (FOV ≃0.2$^\circ$) partly compensates the high integration times and large errors compared to the DOAS measurements (FOV ≃0.53$^\circ$). On the other hand the small field of view of the FT-IR renders the intensity of the measured interferograms very sensitive to small pointing errors of the sun-tracker as the solar irradiance is not uniform across the solar disk (Bösch et al., 2003). According to Fig. 3 and 4 LPMA O$_3$ and NO$_2$ SCDs are low biased with respect to the corresponding DOAS SCDs. For both trace gases the typical errors of individual measurements are larger than the bias. Errors of the absorption cross sections with respect to magnitude or pressure and temperature dependencies would directly cause a bias. Especially the DOAS retrieval of NO$_2$ might exhibit shortcomings when accounting for the temperature dependence of the NO$_2$ absorption cross section, since the interpolation is performed linearly using four reference temperatures, only. In the IR spectral range, errors in the spectroscopic parameters and the ambient temperature and pressure data propagate into the shape of the absorption lines causing systematic errors of the retrieved trace gas SCDs. Correlations between the various fitting parameters considered for the spectral retrieval are minimized but, still, might cause small unaccounted systematic errors in both data sets. Summing up the arguments, the O$_3$ and NO$_2$ stratospheric profiles inferred from DOAS measurements appear to be better suited for validation purposes than the LPMA data particularly as the former exhibit smaller error bars and better altitude resolution. Nonetheless, stratospheric FT-IR measurements are indispensable since the majority of trace gases important for a comprehensive understanding of stratospheric photochemistry do not absorb in the UV/visible.
4 Validation of SCIAMACHY O$_3$ and NO$_2$ profiles

4.1 Observations

The validation study reports on four LPMA/DOAS balloon flights, three from ESRANGE, Kiruna, Sweden, and one from Aire sur l’Adour in southern France conducted since 2003. The analysis of a fifth balloon flight at Teresina, Brazil, in June 2005 is currently in preparation. For each balloon flight a satellite coincident measurement is identified in the morning before and after the balloon flight using the trajectory matching technique described in Sect. 2.3. In the following we refer to these coincidences as backward and forward coincidences. If trace gas profiles inferred from balloon ascent and solar occultation are available the satellite coincidences are identified separately. For each balloon flight Table 2 provides information on the measurement site, the geophysical condition, the SZA range covered by the balloon borne observations, the available data sets and some details on the selected SCIAMACHY limb scans. Besides orbit number, time and date of the satellite measurement, the matching altitude range, the distance with respect to the air masses probed by the balloon borne instruments and the time delay between satellite overpass and balloon flight are given.

In general we succeed in identifying satellite coincidences in the altitude range from about 20 km to 30 km. In some cases the characteristics of the satellite coincidences are not perfect for validation purposes, e.g. for the flight from Kiruna in 2004 where the coincident altitude range is below 20 km and for the flight from Kiruna on 4 March 2003, where the forward coincidence is restricted to a small altitude range. Nevertheless, remembering that coincidence criteria are somewhat arbitrary the balloon and satellite borne trace gas profiles are compared in the whole retrieved altitude range. For the flight from Aire sur l’Adour on 9 October 2003, the match criterion is weakened to a maximum spatial mismatch of 1000 km, as no coincidence is found applying the 500 km criterion. Furthermore assuming the weakened match criterion, the satellite overpass in the morning of 9 October coincides directly with the balloon measurement locations. Hence, the backward model calculations for this flight are not performed along the SZA timeline given by air mass trajectory calculations, but are carried out along the SZA timeline corresponding to air masses stationary at Aire sur l’Adour.

The retrieved vertical trace gas profiles for O$_3$ and NO$_2$ are shown in Figs. 6 and 7, respectively. Satellite observations in the morning before and after the balloon flight are compared to balloon borne trace gas profiles. We present smoothed and in the case of NO$_2$ also photochemically corrected balloon borne profiles. For reference vertical profiles without photochemical correction at full altitude resolution are plotted. In the case of O$_3$, in-situ sonde data are included if available. The O$_3$ sonde data are taken from an electrochemical cell either deployed onboard the gondola or launched from the ground station shortly after balloon launch. The relative deviations between the satellite and balloon borne measurements are assessed in Figs. 8 and 9 for O$_3$ and NO$_2$, respectively.

LPMA data are available for the two flights at Kiruna in 2003, only. DOAS data are lacking for 4 March 2003, due to instrumental malfunction. According to the findings of Sect. 3.2, DOAS O$_3$ and NO$_2$ profiles are retrieved on the same altitude grid as the satellite profiles. As the altitude resolution of the DOAS retrieval is significantly better, DOAS profiles are smoothed to match the satellite’s coarser altitude resolution except for NO$_2$ at balloon ascent below 20 km where no smoothing is applied. LPMA trace gas profiles are generated on a 2-km altitude grid applying no smoothing as the satellite’s altitude resolution does not differ significantly. Satellite borne O$_3$ profiles are inferred using the IUP-Bremen retrieval algorithm. SCIAMACHY NO$_2$ profiles are generated by the IUP-Bremen and Harvard retrieval. In two cases also NO$_2$ profiles inferred by the IUP-Heidelberg are available. Relative deviations between balloon and satellite borne observations are calculated for the trace gas profiles retrieved at the IUP-Bremen and the balloon borne DOAS measurements, except for the observations at Kiruna on 4 March 2003, where LPMA data are used in the absence of available DOAS measurements.

4.2 Discussion

4.2.1 O$_3$ validation study

The internal consistency of the validation data set has been discussed in Sect. 3.1 where a bias of +6.1% between DOAS and LPMA O$_3$ measurements is detected. The corresponding standard deviation of the deviations between the two datasets is 8.0%. Accordingly, the inferred vertical profiles mostly agree to within the combined error bars of both data sets. In all cases the agreement between in-situ sonde and remote sensing balloon borne O$_3$ data is good. Sometimes even highly filamented structures, e.g. Fig. 6e, can be observed simultaneously in the high resolution balloon borne and the in-situ observations.

Figures 6 and 8 show the O$_3$ satellite validation study. In most cases SCIAMACHY limb O$_3$ profiles agree to within ±20% with the validation data set in the 20 km to 30 km altitude range. The agreement ranges from close to perfect as for the observations at Kiruna on 4 March 2003, Fig. 6a, to fair as in the case of Fig. 6d, Aire sur l’Adour on 9 October 2003, where the agreement in the considered altitude range is on the order of 30%, only, and the profile shape is rather different for satellite and balloon borne data. The relative deviations show a systematic underestimation of the balloon borne by the satellite borne profiles at 24 km to 28 km altitude. The underestimation decreases and sometimes changes to overestimation when going up to 31 km and down to 20 km. This finding is similar to conclusions of Brinksma et al. (2005).
Fig. 6. Comparison of O₃ profiles inferred from SCIAMACHY limb observations with correlative balloon borne measurements. Panels (a) to (f) correspond to observations at (a) Kiruna on 4 March 2003, at Kiruna on 23 March 2003, during (b) balloon ascent and (c) sunset, at (d) Aire sur l’Adour on 9 October 2003 and at Kiruna on 24 March 2004, during (e) balloon ascent and (f) sunset. The left and right sub-panels correspond to backward and forward coincidences. Satellite data are shown as blue circles. Smoothed DOAS data are plotted as black boxes, LPMA data as red triangles. The grey diamonds represent DOAS O₃ profiles at full altitude resolution without smoothing. If available, O₃ profiles measured by an electrochemical cell onboard the gondola during balloon ascent are shown as green line. The dashed green lines correspond to O₃ profiles inferred from stand-alone in-situ sondes launched from the ground station shortly after balloon launch. The altitude range between the horizontal dotted lines represents the range where coincident air masses are found. Unfortunately on 24 March 2004, only forward match data are available for SCIAMACHY. For better visibility, only selected error bars are shown.
Fig. 7. Comparison of NO\textsubscript{2} profiles inferred from SCIAMACHY limb observations with correlative balloon borne measurements. Panels (a) to (f) correspond to observations at (a) Kiruna on 4 March 2003, at Kiruna on 23 March 2003, during (b) balloon ascent and (c) sunset, at (d) Aire sur l’Adour on 9 October 2003 and at Kiruna on 24 March 2004, during (e) balloon ascent and (f) sunset. The left and right sub-panels correspond to backward and forward coincidences. Satellite data inferred by IUP-Bremen are shown as blue full circles, inferred by Harvard as open magenta circles, inferred by IUP-Heidelberg as green open stars. Photochemically corrected and smoothed DOAS data are plotted as black boxes, photochemically corrected LPMA data as red triangles. The grey diamonds represent balloon borne profiles at full altitude resolution without photochemical correction which are taken from the DOAS data except for the flight from Kiruna on 4 March 2003, where LPMA data are used. The altitude range between the horizontal, dotted lines represents the range where coincident air masses are found. For better visibility, only selected error bars are shown.
Fig. 8. Relative deviations between satellite and balloon borne measurements of O$_3$ profiles. Filled and open symbols correspond to backward and forward coincidences, respectively. Observation sites and conditions are indicated in the legend. The mean deviation of all coincident data in the 20 km–31 km altitude range is 4.3% with 10.8% standard deviation. The grey lines indicate the mean at $+0.043$ and the one and two times standard deviation boundaries with respect to the 20 km–31 km altitude range. The grey error bars indicate the mean combined errors of the satellite and balloon borne observations. Note the broken abscissa.

where a zigzag shape of the deviations between a validation data set (lidar, SAGE II) and the IUP-Bremen O$_3$ retrieval is observed, indicating that O$_3$ concentrations at 27 km inferred from SCIAMACHY limb are too low. Albeit different corrections for tangent height errors are already included in the SCIAMACHY retrievals there might be a remaining small tangent height error causing the observed deviations. The combined error bars of the balloon and satellite borne observations are on the order of the observed standard deviation of all coincident measurements in the 20 to 30 km altitude range. However, a number of data points differ by more than the combined error bars which might point to a systematic error as suggested above.

Below 20 km SCIAMACHY O$_3$ profiles underestimate the balloon borne data in most cases and cannot reproduce the frequently highly filamented O$_3$ profiles observed especially at high latitudes during winter, e.g., Fig. 6e and f. The balloon flights from Kiruna on 23 March 2003, and on 24 March 2004, have been conducted close to the polar vortex edge where the gradients in O$_3$ concentration are large on small spatial scales. When identifying coincident balloon and satellite measurements, the air mass trajectory calculations allow for a sizeable mismatch in space and time. Spatial mismatch of up to 500 km is possible and, hence, the influence of horizontally inhomogeneous air masses can be important close to the polar vortex edge. Further, SCIAMACHY measurements represent an average over a 960 km wide horizontal area, whereas the LPMA/DOAS measurements average the horizontal trace gas distribution along the line-of-sight from the balloon to the sun. Deviations as in Fig. 6e and f might originate from the difference in horizontal averaging. Good agreement is found for the backward coincidences in Fig. 6b and c. However, the forward coincident measurements in Fig. 6b, c, e and f show large deviations between satellite and balloon borne data. Since the uncertainty of the air mass trajectory calculations increases with increasing time-lag to initialization of the trajectory model, the influence of horizontally inhomogeneous air masses might be enhanced for the forward calculations where the time-lag is about ten hours larger than in the backward case. Unfortunately, there are no DOAS or LPMA data available for the observations below 19 km at the mid-latitudinal station Aire sur l’Adour, but SCIAMACHY limb profiles and the corresponding profiles inferred from in-situ O$_3$ sondes agree well, see Fig. 6d. Figure 8 reveals that the combined error bars cannot explain the observed discrepancies below 20 km altitude.

4.2.2 NO$_2$ validation study

The internal agreement of the balloon borne NO$_2$ measurements has been assessed in Sects. 3.1 and 3.2. When neglecting noisy data, we observe a bias of $+6.6\%$ of the DOAS with respect to the LPMA observations, the standard deviation of the relative differences is 14.0%. Accordingly, the
LPMA/DOAS observations in Fig. 7b and c mostly lie within the combined error bars. Nonetheless, for the flight from Kiruna on 23 March 2003, LPMA underestimates the DOAS profile for balloon ascent and overestimates it for sunset as already seen in Fig. 5.2. Remarkable agreement can be observed for DOAS profiles retrieved from measurements during balloon ascent and sunset which are scaled to the photochemical regime of the same SCIAMACHY observation, proofing the validity of our photochemical as well as meteorological approach.

The comparison between NO$_2$ profiles inferred from the SCIAMACHY limb measurements and the validation data set is presented in Figs. 7 and 9. Although a detailed comparison of the different retrieval exercises is beyond the scope of the present study, we note that the internal agreement of the satellite data is variable. NO$_2$ profiles inferred by IUP-Bremen and IUP-Heidelberg show good agreement. Deviations are observed for 9 October 2003, Fig. 7d, at 30 km altitude and for 24 March 2004, Fig. 7e, below 20 km. In some cases, e.g. Fig. 7d, the Harvard NO$_2$ retrieval yields smaller trace gas concentrations than the IUP-Bremen algorithm around 25 to 27 km altitude. In one case, the backward coincidence in Fig. 7e and f, where SCIAMACHY was operating in a non-nominal measurement mode and pointing could not be verified, the Harvard profiles are offset by +2 km to +3 km with respect to the other satellite data. For the forward coincidence at Kiruna in 2004, agreement is good. In the following we refer our discussion to the IUP-Bremen records as the latter agree best with the balloon borne data. Implications for the Harvard and IUP-Heidelberg retrievals can be inferred easily.

In the 20 km to 30 km altitude range the agreement between the balloon borne NO$_2$ profiles and the satellite observations is on the order of 20% and most often well represented by the combined error bars. The latter amount to about 1.5 to 3 times the observed standard deviation between the two data sets for all coincident datapoints in the considered altitude range. No clear trend can be observed except for the backward observations at Kiruna on 4 March 2003, Fig. 7a, where an altitude offset of +2 km to +3 km of the SCIAMACHY with respect to the LPMA data is clearly visible. The same might be true for the forward coincidences at Kiruna in 2004, Fig. 7e and f, but the offset is not as clear as for the forward comparison.

Below 20 km the level of agreement is variable. Similar to the O$_3$ comparison, the backward coincidences in Fig. 7b, c, e and f reveal moderate deviations whereas the corresponding forward coincidences exhibit larger differences between the satellite and the balloon borne measurements. Further, as can been seen in Fig. 7e, the SCIAMACHY limb profiles retrieved by the IUP-Bremen, IUP-Heidelberg and Harvard algorithms exhibit sizeable discrepancies below 20 km. This indicates that for low altitudes the SCIAMACHY retrieval might depend on the actual parameters, e.g. a priori information, used. The latter finding is supported by the characteristics of the corresponding averaging kernels, Fig. 5.2, which grow wider below 20 km altitude. The combined relative errors shown in Fig. 9 increase dramatically with decreasing altitude since, there, the absolute abundances of NO$_2$ are very low. The relative errors of SCIAMACHY NO$_2$ measurements below 15 km typically are larger than 50%. Adding the rather large modelling error and the error of the balloon borne measurements, the combined error bars are often on the order of the observed deviation. Despite the large combined error bars, a systematic underestimation of the balloon by the satellite borne data is obvious.

5 Conclusions

Stratospheric O$_3$ and NO$_2$ abundances inferred from different sensors are inter-compared.

In the first part of this study line-of-sight absorptions and vertical profiles retrieved from the UV/vis DOAS spectrometer and the LPMA FT-IR both performing balloon borne direct sun measurements during balloon ascent and solar occultation are compared. The general agreement is ±10% and ±20% for O$_3$ and NO$_2$, respectively. The observations in the visible wavelength range exhibit higher precision and better altitude resolution than the FT-IR measurements due to lower instrumental noise and higher sampling frequency. In solar occultation, the smaller field of view of the FT-IR partly compensates the deficiency in altitude resolution. A small bias between the data inferred from the visible and from the IR observed for both gases could be explained by errors of the spectroscopic parameters, i.e. absorption cross sections and their pressure and temperature dependencies, or remaining correlations between the retrieval parameters. However, the bias lies within the errors of individual measurements.

The second part of this study addresses the validation of O$_3$ and NO$_2$ stratospheric profiles inferred from SCIAMACHY skylight limb observations based on the balloon borne data set presented in the first part. An air mass trajectory model is used to identify coincident balloon and satellite borne measurements. The balloon borne trace gas profiles are treated appropriately to match the altitude resolution of the satellite sensor and in the case of NO$_2$ by means of a 1-D stratospheric chemistry model to match the photochemical conditions of the satellite measurements. Typical deviations between SCIAMACHY observations and balloon borne data amount for both considered gases to 20% in the 20 km to 30 km altitude range, somewhat depending on the retrieval algorithm. In the case of O$_3$ our observations support findings of a previous study (Brinksma et al., 2005) indicating that the IUP-Bremen O$_3$ retrievals are systematically low between 24 km and 28 km altitude. Below 20 km the agreement worsens for both gases due to the lower sensitivity of the satellite retrieval, uncompensated horizontal variations of the trace gases and in the case of NO$_2$, modelling uncertainty. Since the origin of the discrepancies observed at low altitudes
cannot be unambiguously attributed to the satellite retrievals or the validation strategy, it is important for future studies to keep the spatial and temporal mismatch between satellite and validation measurements as small as possible. The internal agreement of the satellite NO₂ retrieval exercises developed by IUP-Bremen, Harvard and IUP-Heidelberg, is promising.

Finally, the present study provides a data set which can contribute to the improvement and the validation of future official ESA algorithms currently under development.

The presented balloon borne profiles are made available to the public via our web-site http://www.iup.uni-heidelberg.de/institut/forschung/groups/atmosphere/stratosphere/.

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Detection and mapping of polar stratospheric clouds using limb scattering observations

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Abstract. Satellite-based measurements of Visible/NIR limb-scattered solar radiation are well suited for the detection and mapping of polar stratospheric clouds (PSCs). This publication describes a method to detect PSCs from limb scattering observations with the Scanning Imaging Absorption spectrometer for Atmospheric Cartography (SCIAMACHY) on the European Space Agency’s Envisat spacecraft. The method is based on a color-index approach and requires a priori knowledge of the stratospheric background aerosol loading in order to avoid false PSC identifications by stratospheric background aerosol. The method is applied to a sample data set including the 2003 PSC season in the Southern Hemisphere. The PSCs are correlated with coincident UKMO model temperature data, and with very few exceptions, the detected PSCs occur at temperatures below 195–198 K. Monthly averaged PSC descent rates are about 1.5 km/month for the −50° S to −75° S latitude range and assume a maximum between August and September with a value of about 2.5 km/month. The main cause of the PSC descent is the slow descent of the lower stratospheric temperature minimum.

1 Introduction

Polar stratospheric clouds are of fundamental importance for the formation of the Antarctic ozone hole (Farman et al., 1985) that occurs every year since the early 1980s in Southern Hemisphere spring. PSCs act as hosts for heterogeneous reactions that transfer chlorine from the reservoir compounds HCl and ClONO\(_2\) to Cl\(_2\) (Molina et al., 1987). This process occurs throughout the polar night. When solar radiation reaches the polar lower stratosphere again, Cl\(_2\) is photolyzed to active Cl that participates in a series of catalytic ozone destruction cycles (e.g. Solomon, 1999). The formation of PSCs requires temperatures of less than about 195 K for PSC types Ia (NAT, nitric acid tri-hydrate; crystalline) and Ib (ternary solution of HNO\(_3\), H\(_2\)SO\(_4\) and H\(_2\)O; liquid), and less than about 188 K for PSC type II (H\(_2\)O ice).

Several different techniques were applied in the past to remotely sense PSCs. In terms of ground-based methods there are passive spectrometers measuring scattered solar radiation (e.g. Sarkissian et al., 1994; Enell et al., 1999), as well as active LIDAR systems (e.g. Santacesaria et al., 2001). Satellite remote sensing techniques to detect PSCs include solar occultation (McCormick et al., 1989; Fromm et al., 1997; Nedoluha et al., 2003), stellar occultation (Vanhellemont et al., 2005), limb scattering (von Savigny et al., 2005a), and IR emission spectroscopy (Spang et al., 2005). Ground-based measurements can provide continuous observations with high temporal resolution, but are limited to a certain location. The spatial coverage of satellite observations depends on the method used, but it is a common feature of most satellite methods, that a certain air volume may only be sampled once every several days/weeks. The solar occultation measurements generally provide PSC extinction profiles at different wavelengths with high vertical resolution, but can only be performed during orbital sunsets/sunrises. The geographical coverage of solar occultation measurements on a given day is therefore rather limited. Limb scattering observations are limited to the sunlit part of the Earth, whereas stellar occultation and IR emission can in principle be applied both on the sunlit and the dark side of the Earth.

First results on PSC measurements with SCIAMACHY limb scattering observations were already presented in von Savigny et al. (2005a). In this paper we present a more comprehensive description of the PSC detection method and its performance using the 2003 Southern Hemisphere (SH) PSC season as a sample data set. The paper is structured as follows: in Sect. 2 a brief description of the SCIAMACHY instrument and the limb scattering geometry is given, followed

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SCIAMACHY on Envisat

SCIAMACHY, the Scanning Imaging Absorption spectroMeter for Atmospheric Cartography (Bovensmann et al., 1999) is one of ten scientific instruments on board the European Space Agency’s (ESA) environmental satellite Envisat. Since its successful launch on 1 March, 2002 Envisat orbits the Earth in a polar, sun-synchronous orbit with a 10:00 LST (local solar time) descending node. SCIAMACHY performs spectroscopic observations of scattered, reflected and transmitted solar radiation in three different observation geometries: Nadir, occultation and limb scattering. In this study only SCIAMACHY limb scattering observations are used. In limb viewing mode, the tangent height range from 0 km to about 100 km is covered in tangent height steps of 3.3 km. At each tangent height step an azimuthal, i.e., horizontal scan is performed corresponding to 960 km at the tangent point. The instantaneous field of view in limb mode is about 2.6 km vertically and 110 km horizontally at the tangent point. The spectral range from about 220 nm up to 2380 nm is covered with a wavelength-dependent spectral resolution of 0.2–1.5 nm. On the sunlit side of the Earth limb and nadir measurements are performed alternately, leading to about 25 limb measurements per orbit. The spatial extent of the limb ground pixels is about 1000 km perpendicular to the flight (and viewing) direction and 500 km parallel to the flight direction.

It has to be mentioned that the SCIAMACHY limb measurements during 2003 were affected by pointing errors of up to 3 km caused by inaccurate knowledge of the spacecraft’s attitude and/or position. As a first order pointing correction 1.5 km were subtracted from the tangent heights provided in the Level 1 data files. More information on the pointing problem can be found in von Savigny et al. (2005b).

3 Methodology

PSC particles act as scatterers of solar radiation and therefore affect the measured limb radiance profiles. Since the PSC particle sizes are not small compared to the wavelength of the solar radiation in the UV/Visible/NIR spectral range, the spectral dependence of their scattering coefficient differs from the Rayleigh $\lambda^{-4}$ spectral dependence. Hence, the ratio (i.e., color ratio or color index) of limb radiances at two wavelengths will provide a sensitive indicator for the presence of PSCs. The following aspects have to be considered when selecting a pair of wavelengths suitable for detecting PSCs with a color index approach using limb scattering observations: (a) the wavelengths should not be affected by molecular absorption, or at least as little as possible; (b) the wavelengths must not be shorter than about 400 nm, since the atmosphere becomes optically thick at UV wavelengths for lower stratospheric tangent heights. This is because of the $\lambda^{-4}$ wavelength dependence of Rayleigh scattering and below 320 nm also because of the absorption in the Huggins and Hartley bands of $O_3$. Please note that 400 nm is only an approximate threshold. The longer the wavelength, the larger is the altitude range where the atmosphere between the tangent point and the instrument is optically thin in terms of Rayleigh extinction.

The following wavelengths were chosen: $\lambda_1 = 1090$ nm (SCIAMACHY channel 6) which is just short of a H$_2$O absorption band ranging from about 1100 nm to 1170 nm; $\lambda_2 = 750$ nm (SCIAMACHY channel 4) between a H$_2$O absorption band centered at 725 nm and the O$_2$ A-band ($b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$) band at around 760 nm. In order to improve the signal to noise ratio we used radiances integrated

![Limb radiance spectra for SCIAMACHY channels 4 (upper panel) and 6 (lower panel) for a sample limb observation. Large radiances correspond to low tangent heights and vice versa. The most prominent feature in channel 4 is the O$_2$ A band at 760 nm, that appears as an absorption feature at low tangent heights and as an emission at higher tangent heights (not shown here). A more detailed description of the spectral features appearing in the spectra can be found in Kaiser et al. (2004).]
over ±5 nm intervals around $\lambda_1$ and $\lambda_2$. Figure 1 shows sample limb radiance spectra for channels 4 and 6.

In a first step the color index of the limb radiances $I(\lambda, TH)$ at $\lambda_1$ and $\lambda_2$ is simply determined by

$$R_c(TH) = \frac{I(\lambda_1, TH)}{I(\lambda_2, TH)}$$

(1)

with TH denoting the tangent height. This approach is similar to the one used for PSC detection with ground-based UV/Visible spectrometers (e.g. Sarkissian et al., 1994).

In a second step a color index ratio $\Theta(TH)$ between two adjacent tangent heights is determined from the color index profiles:

$$\Theta(TH) = R_c(TH)/R_c(TH+\Delta TH)$$

(2)

where $\Delta TH=3.3$ km is the SCIAMACHY tangent height step. PSCs are detected if the color index ratio $\Theta(TH)$ exceeds a certain threshold. Figure 2 shows color index profiles $R_c(TH)$ and color index ratio profiles $\Theta(TH)$ for two sample measurements with and without PSCs in the field of view. The use of the color index ratio instead of the color index has proven advantageous, since the color index ratio can be forward-modeled with radiative transfer (RT) calculations even if the measurements are not calibrated. Therefore, radiative transfer calculations can be used as a guide to find an optimum threshold for PSC detection. In order to estimate the range of color index ratios $\Theta(TH)$ occurring in a PSC-free stratosphere – only due to Rayleigh scattering and stratospheric sulphate aerosol – we performed simulations with the RT model LIMBTRAN (Griffioen and Oikari- nen., 2000) for the following scenarios: (a) a pure Rayleigh atmosphere without aerosols, (b) stratospheric background aerosol conditions, (c) moderate volcanic and (d) high volcanic aerosol conditions and for the solar zenith angle (SZA) range from $30^\circ$ to $90^\circ$, and the solar azimuth angle (SAA) range from $30^\circ$ to $90^\circ$, and the solar azimuth angle (SAA) range from $20^\circ$ (forward scattering) to $160^\circ$ (backward scattering). These SZA and SAA ranges include all possible SCIAMACHY limb viewing geometries. The standard MODTRAN aerosol extinction coefficient profiles were used and a Henyey-Greenstein phase function with an asymmetry parameter of $g=0.7$.

Figure 2 shows contour plots of the modeled color index ratios $\Theta(TH)$ between 12 and 30 km altitude for the stratospheric aerosol scenarios (a)–(d). The maximum modeled color index ratio $\Theta(TH)$ for the possible SCIAMACHY viewing angles are $1.1$ for case (a), $1.2$ for case (b), $1.3$ for case (c), and $1.7$ for case (d) for the 15 to 30 km altitude range. Therefore, the threshold for PSC detection requires some a priori knowledge of the stratospheric aerosol loading. For the present study – for a low stratospheric aerosols loading – a PSC detection threshold for the color index ratio of $\Theta=1.3$ was employed. This implies that optically thin PSCs may not be detected, and the derived statistics is somewhat biased to optically thicker PSCs. Lower color index ratio threshold values ($\Theta=1.15$, $1.2$, $1.25$) were also tested and led to a significant number of spurious PSC detections. Also shown in Fig. 3 are the viewing angles of SCIA-MACHY limb measurements on different days in Southern Hemisphere Winter/Spring 2003.

Most aspects of the viewing angle dependence of the modeled color index ratios in Fig. 3 can be understood qualitatively.

- For a fixed SZA the Rayleigh scattering phase function is symmetrical with respect to SAA=90$^\circ$, whereas the Mie-phase function favors forward scattering. Therefore, we expect the contour plot for the Rayleigh-only scenario (a) to be more symmetrical with respect to an azimuth angle of 90$^\circ$ than the scenarios (b)–(d). Figure 3 shows that this is the case.

- For enhanced stratospheric aerosol loading (scenarios c and d) the asymmetry of the Mie phase function will become more important, leading to small color index ratios for large solar azimuth angles (backward scattering) and large color index ratios for small solar azimuth angles (forward scattering).

- In all four cases, the maximum color index ratios increase for setting sun, i.e., if the SZA approaches 90$^\circ$. This is due to the fact, that the Rayleigh extinction coefficient and generally also the Mie-extinction coefficient at 750 nm is larger than at 1090 nm. Therefore, the atmosphere is optically thicker at 750 nm than at 1090 nm and the color index ratio increases as the SZA approaches 90$^\circ$.

In order to avoid false PSC identifications due to ordinary cirrus clouds it was required that the enhancement in the color index ratios has to occur at least 3 km above the climatologically tropopause heights taken from Randel et al. (2000).
The advantages of this PSC detection method are (a) that the threshold for PSC detection can be determined independently with radiative transfer calculations, and (b) that no additional temperature threshold (e.g., \( T < 200 \, \text{K} \) as in Poole and Fritts, 1994) has to be imposed. In terms of (a), the PSC detection methods applied to solar occultation measurements (Poole and Fritts, 1994; Fromm et al., 1997; Hayashida et al., 2000), require empirical aerosol extinction profiles without PSCs to determine the natural variability.

4 Results and discussion

In order to show that the aerosol signatures identified in the limb radiance measurements are indeed caused by PSCs we investigate in the following sections the geographical distribution, the temporal and latitudinal variation of the derived PSC altitudes as well as the temperatures at the altitude of the detected PSCs during the 2003 PSC season in the Southern Hemisphere.

4.1 PSC maps

PSC maps for the Southern Hemisphere on selected days between June and November 2003 are shown in Fig. 4. The circles indicate locations of SCIAMACHY limb scattering observations. Black solid circles correspond to measurements without PSC detections and the open circles show detected PSCs. The underlying color contours show the UKMO temperature fields for the corresponding days at the 550 K potential temperature level. The temperature field is an approximate indicator as to where PSCs can be expected. However, 550 K (about 22 km) is generally not identical to the PSC altitude – as will be shown in Sect. 4.2 the PSCs descend slowly as the winter progresses. Therefore, apparent outliers – e.g., the PSCs detected almost above the south pole on 27 September, 2003 at temperatures between 200 K and 205 K temperature – are not necessarily PSC occurrences at unrealistically high temperatures. Only up to 10 of the 14 daily orbits are shown for the individual days in Fig. 4. This is because not all the orbits measured are currently available for analysis at IUP/IFE Bremen.
For most days, the detected PSCs occur within the area of sufficiently low temperatures, i.e., roughly below 195 K. The shape of the area covered by PSCs nicely tracks the slowly rotating area of the lower stratospheric temperature minimum. For example, on 20 August 2003 both the vortex and the PSC covered area are slightly elongated and oriented parallel to the 60°–240° meridian. A week later on 27 August 2003 the vortex and the PSC covered area have rotated by about 90°.

Thus, PSCs are detected in the expected Antarctic regions for sufficiently low temperatures. Note, that due to the used detection method thin PSCs may not be detected. A potential improvement would be the use of color index ratio detection thresholds that are a function of the SZA.

4.2 Temporal evolution of PSC altitude

By “PSC altitude” we mean the top tangent height for which the color index ratio $\Theta(TH)$ exceeds the threshold of $\Theta=1.3$. Since it contains no information about the vertical extension of the PSC, the PSC altitude is a measure for the PSC top altitude and not for the mean PSC altitude. Note that the actual PSC top altitude will be larger – roughly by about half.
a tangent height step, i.e., 1.5 to 2 km – than the PSC altitudes shown here, since we use the TH, where the color index ratio exceeds $\vartheta=1.3$ to determine the PSC altitude.

Figure 5 shows the temporal change of the monthly mean and zonally averaged PSC altitudes for different latitude bands. The latitudinal variation of the monthly mean zonally averaged PSC altitudes is shown in Fig. 6 for July to October 2003. For the higher latitude ranges SCIAMACHY limb measurements were possible only later in the SH winter/spring (see incomplete coverage in Fig. 5), since the high latitude air volumes were not illuminated before.

The color contours show the corresponding mean UKMO temperature field determined by averaging the UKMO temperature profiles extracted for the date, time and location of each individual PSC observation. Obviously both the PSC altitudes and the altitude of the temperature minimum descend slowly with time, and these altitudes are in very good agreement.

The slow descent of PSCs as the winter progresses has also been reported in other studies, using ground-based LIDAR and solar occultation measurements. Santacesaria et al. (2001) report on a 9 year (1989–1997) PSC climatology based on LIDAR observations at the French Antarctic base in Dumont d’Urville (66.40° S, 140.01° E). The authors discuss three possible reasons for the PSC descent. First, the sedimentation of the PSC particles, which – stated by Santacesaria et al. (2001) – can be excluded as an explanation for the apparent descent, since the sedimentation speeds are too large. PSC type II particles can indeed reach sedimentation velocities on the order of 1 km/day, which is significantly larger than the observed PSC descent rates. However, the sedimentation velocities of type I PSCs are smaller – as small as 10 m/day – and may be consistent with an apparent PSC descent rate of 1.5–2.5 km/month. Secondly, the slow diabatic descent of the HNO$_3$ and H$_2$O distributions. This process leads to descent rates of less than 0.5 km/month, and is therefore not strong enough to solely cause the observed descent. Thirdly, the descent of the lower stratospheric temperature minimum. Our PSC observations together with the UKMO temperature data strongly indicate that the stratospheric temperature is the main driver for the PSC descent.

The PSC descent rates derived from our measurements for 2003 are: 2.5 km/month for the 50° S–60° S latitude band, 2.0 km/month for the 60° S–70° S latitude band, and 1.2 km/month for latitudes between 70° S and 80° S. Interestingly, the descent rates increase with decreasing latitude. These values are in very good agreement with the LIDAR measurements by Santacesaria et al. (2001) at Dumont d’Urville yielding about 2.0 – 2.5 km / month. It is important to realize that these threshold temperatures are not constant, but depend on the amount of molecular species the PSC are composed of, i.e., HNO$_3$ and 1.2 km / month for latitudes between 70° S and 80° S. Inter-

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**Fig. 5.** Temporal evolution of mean PSC altitudes for different latitude bands superimposed to the averaged UKMO temperature profiles at the locations of the SCIAMACHY limb measurements.
d’Urville yielding about 2.0–2.5 km/month. It is important to note, that we use a derived PSC altitude that is more representative for the PSC top altitude, whereas Santacesaria et al. (2001) show mid-cloud altitudes. However, Santacesaria et al. (2001) mention explicitly that the descent rates derived from the cloud tops do not differ significantly from the mid-cloud altitude descent rates. A PSC descent with rates of about 2.0 km/month was also observed in POAM II solar occultation measurements (Fromm et al., 1997) during Southern Hemisphere springs of 1994–1996. The latitudes of the occultation observations varied slowly between about 65° S and 88° S from June to October. Vanhellemont et al. (2005) recently presented measurements of the extinction by stratospheric background aerosols and PSCs with GOMOS (Global Ozone Monitoring by Occultation of Stars), another remote sensing instrument on Envisat. Although no PSC descent rates were derived, the observed PSC descent is in good agreement with the results presented here.

From the very good agreement of descent rates of the temperature minimum and the PSC descent rates derived in this study it appears that the temporal variation of the lower stratospheric temperature structure is the main driver of the PSC descent.

4.3 Distribution of temperature at PSC altitudes

Generally, type I PSCs are assumed to form at temperatures below about 195 K, and type II PSCs at temperatures below 188–190 K. It is important to realize that these threshold temperatures are not constant, but depend on the amount of the molecular species the PSC are composed of, i.e., HNO₃, H₂SO₄ and H₂O. For all PSCs detected in 2003 the temperature at the PSC altitudes and their locations were extracted from the UKMO temperature fields and are presented as histograms for different months in Fig. 7. July 2003 is not shown here, since only 3 PSCs were detected in this month. This low number is due to the fact that the SH polar cap was not illuminated and therefore SCIAMACHY limb scattering measurements were not possible. The average temperatures at the PSC altitudes are around 190 K in August, September, and October 2003, and assume a minimum value of 189.5 K in September. In November no PSCs were detected in agreement with temperatures of generally more than 215 K at the 550 K potential temperature level (see Fig. 4). The derived temperatures of around 190 K, at which PSCs are most likely to occur are in very good agreement with previous studies. Santacesaria et al. (2001) report the highest PSC occurrence frequency at a temperature of 189 K. Poole and Fritts (1994)
In this manuscript we have investigated the detection of PSCs and for the first time the temporal variation of PSC altitudes using limb scattering measurements. This has been achieved with a limited number of wavelengths. As the in-flight calibration of SCIAMACHY is improved, we anticipate the extension of the wavelength range to be used to study stratospheric aerosol, PSCs, and cirrus clouds. PSC type II and cirrus clouds consist of ice particles. In this respect a phase index approach has already been demonstrated to allow the distinction of tropospheric liquid water and ice clouds using Nadir measurements at wavelengths around 1.6 micron (Kokhanovsky et al., 2005). There are several other regions where liquid water and ice absorb in the 0.7–2.4 micron region. These absorption signatures may be employed for the detection of type II PSCs. This, as well as the use of SCIAMACHY polarization measurements, is presently under investigation. Another important question is whether the SCIAMACHY limb scattering observations with their wide spectral range allow the distinction between type Ia and type Ib PSCs. The principal constituents, i.e., HNO₃ and H₂SO₄ have no usable absorption/emission features in the SCIAMACHY spectral range. However, the derivation of PSC particle radii – which is easily possible with noctilucent clouds (NLCs) in the UV spectral range (von Savigny et al., 2004), where the strong absorption of solar radiation in the Hartley and Huggins bands of O₃ lead to negligibly small multiple scattering and surface reflection contributions – in combination with the measurements of the degree of linear polarization may allow to distinguish between type Ia and Ib. This is also the subject of ongoing investigations.

In summary, a method to detect PSCs from limb scattering observations in the Visible/NIR spectral range was presented. The method is based on a color index approach and has been applied to SCIAMACHY limb scattering measurements during the 2003 PSC season in the Southern Hemisphere. PSC descent rates of 1.0–2.5 km/month were derived, and descent rates were found to increase with increasing latitude. The good correlation between PSC altitude and the altitude of the lower stratospheric temperature minimum leads to the conclusion that the temporal change of the stratospheric temperature field is the main driver behind the observed descent. Concluding, satellite measurements of limb-scattered solar radiation in the Visible/NIR spectral range are a sensitive technique to detect and map PSCs.

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