# Analysis and interpretation of satellite measurements in the near-infrared spectral region: Atmospheric carbon dioxide and methane

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# Analysis and interpretation of satellite measurements in the near-infrared spectral region: Atmospheric carbon dioxide and methane

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## Abstract

Carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) are the two most important anthropogenic greenhouse gases. SCIAMACHY on ENVISAT is the first satellite instrument whose measurements are sensitive to concentration changes of the two gases at all altitude levels down to the Earth's surface where the source/sink signals are largest. In the framework of this thesis three years (2003-2005) of SCIAMACHY near-infrared nadir measurements were processed to simultaneously retrieve vertical columns of CO<sub>2</sub> (from the 1.58  $\mu$ m absorption band), CH<sub>4</sub> (1.66  $\mu$ m) and oxygen (O<sub>2</sub> Aband at  $0.76 \,\mu\text{m}$ ) using the scientific retrieval algorithm WFM-DOAS. The latest version of WFM-DOAS, version 1.0, which was developed within the scope of this thesis, has been significantly improved with respect to its accuracy compared to the previous versions while essentially maintaining its high processing speed ( $\sim 1$ minute per orbit, corresponding to  $\sim$ 6000 single measurements, and per gas on a standard PC). The greenhouse gas columns are converted to column-averaged dry air mole fractions, denoted  $XCO_2$  (in ppm) and  $XCH_4$  (in ppb), by dividing the greenhouse gas columns by simultaneously retrieved dry air columns. For XCO<sub>2</sub> dry air columns are obtained from the retrieved  $O_2$  columns. For XCH<sub>4</sub> dry air columns are obtained from the retrieved CO<sub>2</sub> columns because of better cancellation of light path related errors compared to using O<sub>2</sub> columns retrieved from the spectrally distant O<sub>2</sub> A-band.

In order to assess the quality of the retrieved  $XCO_2$ , comparisons with Fourier Transform Spectroscopy (FTS)  $XCO_2$  measurements at two northern hemispheric mid-latitude ground stations are presented. To assess the quality globally, detailed comparisons with global  $XCO_2$  fields obtained from NOAA's  $CO_2$  assimilation system CarbonTracker are carried out. For the northern hemisphere good agreement with the reference data for the  $CO_2$  seasonal cycle and the  $CO_2$  annual increase is found. For the southern hemisphere, where significantly less data are available for averaging compared to the northern hemisphere, the  $CO_2$  annual increase is also in good agreement with CarbonTracker but the amplitude and phase of the seasonal cycle show systematic differences (up to several ppm) arising partially from the  $O_2$  normalisation most likely caused by unconsidered scattering effects due to subvisual cirrus clouds. The retrieved  $XCO_2$  regional patterns at monthly resolution over various regions show clear correlations with CarbonTracker but also significant differences. Typically the retrieved variability is about 4 ppm (1% of 380 ppm) higher but depending on time and location differences can reach or

even exceed 8 ppm. Based on the error analysis and on the comparison with the reference data it can be concluded that the  $XCO_2$  data set can be characterised by a single measurement retrieval precision (random error) of 1-2%, a systematic low bias of about 1.5%, and by a relative accuracy of about 1-2% for monthly averages at a spatial resolution of about  $7^{\circ} \times 7^{\circ}$ . Averaging the SCIAMACHY  $XCO_2$  over all three years provides elevated  $CO_2$  over the highly populated regions of western central Germany and parts of the Netherlands ("Rhine-Main area") as well as for other source regions such as the East Coast of the United States of America or Japan's densely populated and industrialised centres reasonably well correlated with EDGAR anthropogenic  $CO_2$  emissions. The retrieved regional enhancement over the Rhine-Main area is on average 2.7 ppm including an estimated contribution of 1-1.5 ppm due to aerosol related errors and sampling. The remaining signal of about 1.2-1.7 ppm is assumed to be mainly due to anthropogenic  $CO_2$  emissions. This indicates that elevated  $CO_2$  originating from regional anthropogenic  $CO_2$  emissions can be potentially detected from space.

The single measurement retrieval precision of  $XCH_4$  is estimated to be 1.5-1.7%. For 2003 detailed comparisons of the methane product with the TM5 model which has been optimally matched to highly accurate but sparse methane surface observations are presented. After accounting for a systematic low bias of  $\sim 2\%$  agreement with TM5 is typically within 1-2%. It is investigated to what extent the SCIAMACHY  $\text{XCH}_{4}$  is influenced by the variability of atmospheric  $\text{CO}_{2}$  using global  $\text{CO}_{2}$  fields from NOAA's CO<sub>2</sub> assimilation system CarbonTracker showing that the CO<sub>2</sub> corrected and uncorrected XCH<sub>4</sub> spatiotemporal patterns are very similar but that agreement with TM5 is better for the CarbonTracker  $CO_2$  corrected XCH<sub>4</sub>. In line with previous studies (e.g., Frankenberg et al. (2005)) significantly higher methane over the tropics is found compared to the model. Tropical methane is also higher when normalising the  $CH_4$  columns with retrieved  $O_2$  columns instead of  $CO_2$ . In consistency with recent results of Frankenberg et al. (2008b) it is shown that the magnitude of the retrieved tropical methane enhancement is sensitive to changes in spectroscopy and that possible inaccuracies in the HITRAN spectroscopic parameters of water vapour can contribute to a potential overestimation of the tropical methane correlated with high water vapour abundances. Concerning inter-annual variability the analysis shows similar methane spatiotemporal patterns for 2003 and 2004. For 2005 the retrieved methane shows significantly higher variability compared to the two previous years, most likely due to somewhat larger noise of the spectral measurements. First inverse modelling results for methane surface fluxes are presented for the year 2004 performed at the European Commission's Joint Research Centre (EC-JRC) by Peter Bergamaschi.

## **Publications**

#### Journal articles

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Contents

## Motivation and objectives of this thesis

Since the start of the Industrial Revolution human activities affect increasingly the world we live in by changing atmospheric conditions in a significant way. Among the negative anthropogenic effects are destruction of stratospheric ozone, air pollution, and climate change. The atmospheric concentrations of the two most important anthropogenic greenhouse gases carbon dioxide  $(CO_2)$  and methane  $(CH_4)$  are now about 40% and 150%, respectively, higher compared to the pre-industrial levels and are believed, at least for CO<sub>2</sub>, to increase continuously in the future as a result of increasing standard of living and population growth throughout the world. This further increase is predicted to result in a warmer climate with adverse consequences but quantification of the effect requires an accurate understanding of the sources and sinks of the greenhouse gases which is unfortunately limited by the sparse ground-based measurements and economic estimates so far resulting in large uncertainties. However, satellite data, if accurate and precise enough, can be used to deduce strength and spatiotemporal distribution of the sources and sinks by inverse modelling which is based on fitting the model emissions to the satellite observations.

Currently, SCIAMACHY is the only satellite instrument whose  $CO_2$  and  $CH_4$  measurements are sensitive to all altitude levels including the boundary layer due to the near-infrared/shortwave-infrared spectral range which is a prerequisite to obtain information about regional sources and sinks because they are located near Earth's surface, whereas other existing instruments measuring in the thermal infrared are primarily sensitive to middle to upper tropospheric greenhouse gas concentrations. Therefore, SCIAMACHY plays a pioneering role in obtaining a better understanding of the carbon cycle by global near-infrared satellite measurements for other missions planned in the near future.

Thus, the primary objective of this work is the development or rather the further improvement of a retrieval algorithm for the vertical columns of carbon dioxide and methane to obtain column-averaged dry air mole fractions with sufficient accuracy and precision to be useful for inverse modelling, namely about 1% for carbon dioxide and 1-2% for methane, and the production of a global multi-year data set of unprecedented quality. Furthermore, a concurrent high processing speed is indispensable to analyse the huge amount of data in admissible time which is in particular also important for a future potential near real time retrieval.

#### Outline

The thesis is divided in four parts:

Part I covers fundamental background knowledge relevant for the topic including physics and chemistry of the atmosphere, in particular spectroscopic aspects and radiative transfer as well as a description of the SCIAMACHY instrument.

Part II introduces the used retrieval algorithm explicitly and describes the significant improvements compared to previous versions in a detailed way. An error analysis quantifies the sensitivities to different parameters by using simulated measurements.

Part III finally presents the retrieval results of the real satellite data in great detail.

Part IV is the appendix providing supplementary material.

An overview of the mathematical symbols being widely used throughout the thesis is given in the nomenclature.

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# Part I Fundamentals

## 1 Earth's atmosphere

#### 1.1 Structure of the atmosphere

Earth's atmosphere consists of roughly 78% (by volume) nitrogen ( $N_2$ ), 21% oxygen ( $O_2$ ), 0.9% argon and trace amounts of other gases, e.g., on average 380 ppm (parts per million) carbon dioxide ( $CO_2$ ) and 1775 ppb (parts per billion) methane ( $CH_4$ ). Despite their small mixing ratios, these trace gases play an important role in atmospheric physics, especially in the context of natural and anthropogenic greenhouse effect and associated climate change. This mixture of gases is referred to as air and is held to the Earth by gravity. Besides gaseous constituents the atmosphere also contains clouds and aerosols.

Atmospheric pressure is a direct consequence of the weight of the air column above the measurement point. Its average value at sea level is about 1013 hPa. The amount of air molecules per volume decreases approximately exponentially with height dropping by 50% every 5-6 km. From this relation one can conclude that about 90% of all air molecules in the atmosphere are located below an altitude of 17 km.

The atmosphere is divided into different layers according to major temperature variations. The troposphere is the lowest layer of the atmosphere. It extends from the Earth's surface to between 7 km at the poles and 17 km at the equator and is further separated in the boundary layer and the overlying free troposphere. The maximum temperature in the troposphere is usually reached at the surface (about 14°C on average) due to emission of thermal infrared radiation of the Earth and generally decreases with increasing altitude because of adiabatic cooling upon expansion which is caused by the pressure decrease with height. The heating from below leads to a relative instable thermal layering resulting in a good vertical mixing induced by convection. These vertical currents and the presence of most of the total water vapour are the reasons that the troposphere is the layer of the atmosphere where most of the weather takes place. The troposphere is bounded from above by the tropopause which has by definition a negligible temperature gradient and is followed by the stratosphere extending to about 50 km. In the stratosphere the temperature rises again with increasing height because of absorption of ultraviolet solar radiation in the wavelength range between 200 nm and 300 nm by the contained trace gas ozone  $(O_3)$  until it reaches a maximum characterising the stratopause. This



Figure 1.1: Temperature and pressure profiles of the U.S. Standard Atmosphere.

temperature inversion prevents vertical mixing in the stratosphere to a large extent and water vapour amounts are small in this part of the atmosphere. The stratospheric ozone layer protects living organisms on Earth from the harmful solar high energy UV radiation. The following mesosphere which extends to 80-90 km has again a negative temperature gradient. At the mesopause which separates the mesosphere from the thermosphere the temperature reaches an absolute minimum in the atmosphere before it rises again considerably in the adjacent layer. The outermost layer of the Earth's atmosphere - the exosphere - represents the smooth transition to space with continuously decreasing gas density.

Figure 1.1 exemplarily shows the temperature and pressure profiles of the U.S. Standard atmosphere representing an idealised, steady-state atmosphere for moderate solar activity and showing the discussed vertical structure of the atmosphere.

## 1.2 Greenhouse effect and climate change

The natural greenhouse effect is an atmospheric process which warms the Earth enough to support life on it. Solar radiation is reflected or absorbed by the atmosphere, ocean, and land cover. The absorbed radiative energy warms Earth's surface and is then emitted back again to the atmosphere at longer wavelengths in the infrared. A fraction of this thermal infrared emission is strongly absorbed by atmospheric trace gases - the so-called greenhouse gases (which are largely transparent to the incoming solar radiation) - at specific wavelengths characteristic for the respective species. The absorbed radiation is then re-emitted in all directions including the way back towards the surface leading to a net warming of it because the surface temperature rises until the corresponding flux balances the sum of the incoming solar radiation and infrared backradiation re-emitted by the gas molecules.

Species	2005	1750	Increase [%]
CO <sub>2</sub> [ppm]	$379\pm0.65$	$277 \pm 1.2$	37
CH <sub>4</sub> [ppb]	$1774 \pm 1.8$	$715\pm4$	148
N <sub>2</sub> O [ppb]	$319\pm0.12$	$270\pm7$	18

Table 1.1: Increase of atmospheric concentrations of long-lived greenhouse gases since the start of the industrial era. (IPCC: Solomon et al. (2007)).



Figure 1.2: Atmospheric concentrations of  $CO_2$ ,  $CH_4$ , and  $N_2O$  since 1900 and projections to the future based on different emission scenarios (IPCC: Solomon et al. (2007)).

Major greenhouse gases are water vapour ( $H_2O$ ), carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), ozone ( $O_3$ ), and nitrous oxide ( $N_2O$ ). The two most abundant constituents of the atmosphere nitrogen ( $N_2$ ) and oxygen ( $O_2$ ) do not have this capacity. It is estimated that without the greenhouse effect Earth's surface would have a mean temperature of about  $-19^{\circ}C$  which is 33°C less than the actual global mean surface temperature.

The natural amount of several greenhouse gases has increased significantly since pre-industrial times by human activity (see Table 1.1 and Figure 1.2) amplifying the greenhouse effect artificially. This anthropogenic impact is related to emissions of the following principal greenhouse gases: carbon dioxide and methane which are discussed in Sections 1.3 and 1.4 in more detail as well as nitrous oxide and the halocarbons. A further increase of the greenhouse gases is predicted to result in a warmer climate with adverse consequences, such as rising sea levels and an increase of extreme weather conditions (IPCC: Houghton et al. (2001); Solomon et al. (2007)).

Projections of greenhouse gas concentrations to the future depend on the emission scenario chosen, and thus on various assumptions about future socioeconomics,



Radiative forcing of climate between 1750 and 2005

Figure 1.3: Components of radiative forcing of climate change since the start of the industrial era. Because the removal of  $CO_2$  from the atmosphere involves processes that can span long time scales, and thus cannot be expressed accurately with a narrow range of lifetime values, no time scale is given in this case (IPCC: Solomon et al. (2007)).

technological development, and political decisions. Additionally, they are limited to our current knowledge about the climate system and its reaction to perturbations, e.g., to the understanding of the greenhouse gases' sources and sinks. The IPCC Special Report on Emission Scenarios (Nakićenović and Swart, 2000) introduces six illustrative emission scenarios defining four storylines combining the two divergent tendencies of economic (label A) or environmental (B) and global (1) or regional (2) orientation of the future world. The scenario A1 is further divided in alternative developments of energy technologies, namely fossil intensive (A1FI), predominantly non-fossil (A1T), and balanced across energy sources (A1B). The projections for these scenarios are depicted in Figure 1.2 demonstrating a wide range of possible future greenhouse gas concentrations.

Besides the greenhouse gases, there are several other contributions, such as

aerosols or clouds, to climate change. Figure 1.3 summarises the radiative forcings of these components and shows that the overall effect of human activities since 1750 has been extremely likely a warming influence. Radiative forcing refers thereby to the change in the energy balance of the Earth-atmosphere system per unit area. In case of a positive radiative forcing the energy of the system will increase leading to a warming of climate. For a negative radiative forcing the opposite is true. Hence, radiative forcing is a concept quantifying the strength of forcing agents causing climate change. The figure additionally shows the climate efficacy (global mean temperature change per unit forcing relative to  $CO_2$ ), relevant time and spacial scales as well as the degree of scientific understanding of the respective process.

A large factor of uncertainty in the quantification of future global warming are possible feedback effects, e.g., due to decreasing ice cover: Since ice has a higher reflectivity in the ultraviolet spectral region than the underlying land or ocean the melting results in absorption of more heating energy by the exposed surface speeding the warming trend and melting more ice. A similar feedback is expected from the release of the greenhouse gas methane by melting permafrost.

## 1.3 Atmospheric carbon dioxide

The most important anthropogenic atmospheric greenhouse gas carbon dioxide (CO<sub>2</sub>) has increased significantly since pre-industrial times with atmospheric concentration now being about 100 ppm (37%) higher compared to the level of 1750 (see Table 1.1) primarily as a result of fossil fuel combustion, cement production, land use change (mainly deforestation), and biomass burning, thus perturbing the natural global carbon cycle which describes the complex carbon exchange between the major carbon reservoirs (ocean, atmosphere, terrestrial biosphere, and sediments). The corresponding pre-industrial natural fluxes and human-induced perturbations are illustrated in Figure 1.4 pointing out that the anthropogenic fluxes, albeit small compared to the natural fluxes, have changed the carbon content of the different reservoirs measurably since the start of the Industrial Revolution. Atmospheric carbon dioxide concentrations have reached a level of about 380 ppm in 2005, whereas, prior to 1750, the concentration of  $CO_2$  in the atmosphere was rather stable in the range of 260-280 ppm for some thousand years (IPCC: Solomon et al. (2007)). The average residence time of an individual CO<sub>2</sub> molecule in the troposphere is smaller than 10 years while the atmospheric pulse lifetime can be determined by watching the decay of a simulated additional injection of an instantaneous emission pulse to the background burden using global carbon cycle models. This decay can be represented by a sum of exponential functions. The corresponding decay times for the CO<sub>2</sub> response function used in the IPCC report (Solomon et al., 2007) are  $\infty$ ,



Figure 1.4: The global carbon cycle for the 1990s distinguishing between preindustrial natural reservoir sizes or annual fluxes shown in black and anthropogenic perturbations shown in red. GPP denotes the annual gross (terrestrial) primary production (IPCC: Solomon et al. (2007)).

172.9 years, 18.51 years, and 1.186 years assuming a background  $CO_2$  concentration value of 378 ppm. Since carbon dioxide is a long-lived gas, it is relatively well mixed in the atmosphere.

An indicator for the emission source is provided by the isotopic abundance ratio of the two naturally occurring stable isotopes <sup>13</sup>C and <sup>12</sup>C of carbon contained in CO<sub>2</sub>. Each individual source exhibits thereby a characteristic signature. The <sup>13</sup>C/<sup>12</sup>C isotopic ratios of carbon dioxide emissions from fossil fuels are less than in atmospheric CO<sub>2</sub> since plants, which are the origin of the fossilised organic carbon compounds, prefer CO<sub>2</sub> containing <sup>12</sup>C in photosynthesis. Hence, the <sup>13</sup>C/<sup>12</sup>C isotopic ratio in the atmosphere decreases due to increasing fossil fuel emissions (Keeling et al., 2005).

Annual fossil fuel and cement production emissions, which are the dominant  $CO_2$  sources, increased constantly from a mean of  $5.4 \pm 0.3$  GtC/yr in the 1980s over  $6.4 \pm 0.4$  GtC/yr in the 1990s to  $7.2 \pm 0.3$  GtC/yr for the time period 2000-2005 (IPCC: Solomon et al. (2007)) while the emissions from land-use change remained approximately constant averaging  $1.5 \pm 0.5$  GtC/yr (Canadell et al., 2007).



Figure 1.5: Sources, sinks and flux estimates of  $CO_2$  and  $CH_4$ . Anthropogenic influences are shown in orange, natural contributions in teal (IPCC: Solomon et al. (2007)).

About half of the anthropogenic  $CO_2$  emissions has been removed by the terrestrial biosphere and ocean in the 1990s with significantly varying carbon sequestration from year to year as response to steadily rising fossil fuel emissions (Canadell et al., 2007; Crisp et al., 2004). This not only shows the existence of important carbon dioxide sinks, but also suggests a pronounced temporal variation of them. Without these sinks, the amount of carbon dioxide in the atmosphere would have been grown even more.

Global warming could decrease the efficiency of these sinks and thus increase the fraction of anthropogenic  $CO_2$  that remains in the atmosphere leading to a positive feedback effect and an additional increase of atmospheric  $CO_2$ . Therefore the reliable prediction of future atmospheric  $CO_2$  levels and the associated global climate change requires an adequate understanding of the  $CO_2$  sources and sinks and their spatiotemporal distribution. Unfortunately, this understanding has significant gaps and uncertainties are large (see, e.g., Stephens et al. (2007)). Figure 1.5 illustrates the mentioned sources and sinks of carbon dioxide as well as flux estimates and corresponding uncertainties taken from the IPCC report (Solomon et al., 2007).

The current knowledge of the carbon dioxide surface fluxes is limited for example by the sparseness of the ground-based network with a lack of high-frequency surface observations in continental regions particularly outside North America and Europe. Theoretical studies have shown that satellite measurements of  $CO_2$  in combination with models have the potential to significantly reduce  $CO_2$  surface flux uncertainties (Rayner and O'Brien, 2001; Houweling et al., 2004). In order to measure the small changes due to sources and sinks on top of a large background well, the resultant requirements on the accuracy and precision of the measurements of the columnaveraged dry air mole fractions from space are demanding, being of the order of 1% or better (Rayner and O'Brien, 2001; Houweling et al., 2004; Miller et al., 2007a; Chevallier et al., 2007).

Existing satellite instruments whose measurements are sensitive to atmospheric carbon dioxide measure radiances in the thermal infrared (TIR) spectral region such as HIRS (Chédin et al., 2002, 2003) and AIRS (Engelen et al., 2004; Engelen and McNally, 2005; Aumann et al., 2005; Strow et al., 2006) with the exception of SCIAMACHY which measures in the near-infrared (NIR) / short-wave infrared (SWIR) spectral region (Buchwitz et al., 2005a,b, 2006, 2007; Houweling et al., 2005; Bösch et al., 2006; Barkley et al., 2006a,c,b, 2007). Whereas the TIR nadir measurements are primarily sensitive to middle to upper tropospheric  $CO_2$ , the NIR/SWIR nadir measurements are sensitive to all altitude levels, including the boundary layer, which permits the retrieval of  $CO_2$  total columns. High sensitivity to CO<sub>2</sub> concentration variations near the Earth's surface is important in order to get information on regional  $\text{CO}_2$  sources and sinks. SCIAMACHY is the first and currently only satellite instrument which measures reflected solar radiation in the NIR spectral region covering important absorption bands of  $CO_2$  (as well as  $CH_4$ ) and  $O_2$ ). For the near future other satellite missions are planned, most notably OCO (Crisp et al., 2004) and GOSAT (Hamazaki et al., 2004), which will also perform nadir observations in the NIR/SWIR spectral region to retrieve CO<sub>2</sub>.

## 1.4 Atmospheric methane

Methane ( $CH_4$ ) is a potent greenhouse gas and plays important roles in atmospheric chemistry. Considering a time horizon of 100 years, one kilogram of methane warms the Earth 25 times more than a kilogram of carbon dioxide does (IPCC: Solomon et al. (2007)). Increasing  $CH_4$  concentrations lead to increasing concentrations of the pollutant ozone in the troposphere (Dentener et al., 2005). Furthermore,  $CH_4$  consumes the hydroxyl radical, the most important atmospheric cleansing agent (see, e.g., Lelieveld (2006), and references given therein) which removes for example the pollutant carbon monoxide from the atmosphere. Atmospheric methane has more than doubled since pre-industrial times from 715 ppb to about 1775 ppb (see Table 1.1) contributing as much as 20% to the anthropogenic greenhouse effect (IPCC: Houghton et al. (2001); Solomon et al. (2007)). This makes methane the second most important anthropogenic greenhouse gas in the atmosphere after  $CO_2$ . Like carbon dioxide it is long-lived, with a perturbation lifetime (taking chemical feedbacks into account) of about 12 years, and therefore relatively well mixed in the atmosphere.

Sources due to anthropogenic influences include rice cultivation, animal farming, energy production (coal mining and natural gas distribution), waste handling, and biomass burning which exceed natural sources like wetlands, termites, oceans, and hydrates as can be seen in Figure 1.5. Alternatively, methane sources can be divided in biogenic and non-biogenic with the biogenic component being the dominant one. The total estimated mean source strength (582 Tg/yr) is virtually in balance with the total strength of the sinks (581 Tg/yr) (IPCC: Solomon et al. (2007)). However, the uncertainties of the strengths of individual sources and their spatiotemporal variations are quite large.

Besides minor sinks like uptake by soils or photolysis in the stratosphere and mesosphere, the dominant methane sink is the already mentioned tropospheric destruction by the hydroxyl radical OH. Despite having a by far lower concentration in the troposphere than O2, OH starts the oxidation cycles of most compounds emitted to the atmosphere by natural or anthropogenic processes. About 70% of the hydroxyl radical sink in the boundary layer is attributed to oxidation of CO and roughly 15% to oxidation of CH<sub>4</sub> (Warneck, 1999). The dominating reaction chain of methane oxidation is thereby dependent on the availability of NO<sub>x</sub> leading to a net production of ozone (O<sub>3</sub>) in NO-rich environments, whereas in NO-poor environments there is no net production or loss of ozone but a net consumption of the OH radical in one of the two dominating processes (Crutzen, 1994). In NO-rich environments this reaction chain dominates:

$$CH_4 + OH \longrightarrow CH_3 + H_2O \tag{1.1}$$

$$CH_3 + O_2 + M \longrightarrow CH_3OO + M$$
 (1.2)

$$CH_3OO + NO \longrightarrow CH_3O + NO_2$$
 (1.3)

$$CH_{3}O + O_{2} \longrightarrow HCHO + HO_{2}$$
(1.4)  
$$HO_{2} + NO \longrightarrow OH + NO_{2}$$
(1.5)

$$2(NO_2 + hv) \longrightarrow 2(NO + O)$$
(1.6)

$$2(O + O_2 + M) \longrightarrow 2(O_3 + M)$$
(1.7)

net: 
$$CH_4 + 4O_2 \longrightarrow HCHO + H_2O + 2O_3$$
 (1.8)

In NO-poor environments the methylperoxy radical (CH<sub>3</sub>OO) reacts with HO<sub>2</sub> instead, providing one of the following reaction chains:

$$CH_4 + OH \longrightarrow CH_3 + H_2O \tag{1.9}$$

$$CH_3 + O_2 + M \longrightarrow CH_3OO + M$$
(1.10)

$$CH_{3}OO + HO_{2} \longrightarrow CH_{3}OOH + O_{2}$$
(1.11)

$$CH_3OOH + h\nu \longrightarrow CH_3O + OH$$
 (1.12)

$$CH_{3}O + O_{2} \longrightarrow HCHO + HO_{2}$$
(1.13)

net: 
$$CH_4 + O_2 \longrightarrow HCHO + H_2O$$
 (1.14)

 $(1 \ 1)$ 

$$CH_4 + OH \longrightarrow CH_3 + H_2O$$
 (1.15)

$$CH_3 + O_2 + M \longrightarrow CH_3OO + M$$
(1.16)

$$CH_2OO + HO_2 \longrightarrow CH_2OOH + O_2$$
(1.17)

$$CH_{3}OOH + OH \longrightarrow HCHO + H_{2}O + OH$$
 (1.18)

net: 
$$CH_4 + OH + HO_2 \longrightarrow HCHO + 2H_2O$$
 (1.19)

Formaldehyde (HCHO), the first non-radical species formed from methane oxidation, can then further be oxidised to CO whose subsequent oxidation leads to a formation of  $CO_2$ .

Fortunately, methane levels were rather stable during recent years but the reason for this is not well understood. Bousquet et al. (2006) suggested that this stabilisation may be due to a downward trend of anthropogenic emissions between the late 1980s and the late 1990s. They further conclude that year-to-year variability is dominated by wetland emissions and that atmospheric methane concentrations may rise again in the near future if wetland emissions return to their mean 1990s levels. Important issues in this context are climate feedbacks caused by methane release from melting permafrost regions as this amplifies warming trends. Therefore, monitoring of the atmospheric methane is required, and, in order to reliably predict future concentrations, an appropriate understanding of its variable sources and sinks is essential, as in case of  $CO_2$ .

Information on methane sources and sinks can be obtained via inverse modelling from measured atmospheric methane concentrations (Bergamaschi et al., 2005, 2007; Hein et al., 1997; Houweling et al., 1999; Mikaloff Fletcher et al., 2004a,b). These studies revealed that methane surface flux uncertainty reduction strongly depends on the spatial scale with typically significant reduction on the continental scale but only marginal reduction at regional scales due to the sparseness of the ground-based network. Recently Bergamaschi et al. (2005) presented a detailed discussion of the inverse modelling of methane for individual countries by using also continuous surface measurements focusing on Europe.

Detailed regional information on the global scale can be obtained from satellite measurements of the methane vertical column or its column-averaged mixing ratio, provided the satellite data are precise ( $\sim$ 1-2%) and systematic biases, especially regionally dependent biases, can be avoided or are well characterised (Meirink et al., 2006). Very recently, Bergamaschi et al. (2007) reported about the first inverse modelling attempt using satellite data. The methane data set used by Bergamaschi et al. (2007) has been retrieved from the SCIAMACHY instrument using the IMAP-DOAS retrieval algorithm (Frankenberg et al., 2006). Very encouraging results have been obtained but also some problems had been identified, for example, an apparent time dependent latitudinal bias which was attributed recently to a certain extent

to potential inaccuracies in the spectroscopic parameters of methane (Frankenberg et al., 2008a).

For the year 2004 the WFM-DOAS v1.0 SCIAMACHY methane data set presented here has been inverted for methane surface fluxes using a newly developed 4D-VAR inverse modelling scheme (Meirink et al., 2008). The results are presented in Chapter 10.

## 2 Infrared spectroscopy

The contents of this chapter is largely adopted from standard textbooks (Haken and Wolf, 2006; Barrow, 1962; Herzberg, 1989, 1991).

## 2.1 Basics of spectroscopy

Spectroscopy deals with the interaction between matter and electromagnetic radiation through absorption, emission, and scattering of the latter. Radiation can be characterised by its energy which is linked to frequency by Planck's relation E = hv. The electromagnetic spectrum (Figure 2.1) classifies all possible electromagnetic radiation according to specific wavelength or rather frequency ranges. These quantities can be converted by the simple formula  $v = c/\lambda$ . Commonly used in spectroscopy is also the wavenumber defined as  $\tilde{v} = 1/\lambda$ .

The part of the electromagnetic spectrum between the visible and microwave regions is referred to as the infrared spectrum commonly being subdivided in spectroscopy as follows: The region from  $0.7 \,\mu\text{m}$  to  $1.4 \,\mu\text{m}$  is denoted near-infrared (NIR), the short-wave infrared (SWIR) ranges from  $1.4 \,\mu\text{m}$  to  $3 \,\mu\text{m}$ , and the interval from  $3 \,\mu\text{m}$  to  $15 \,\mu\text{m}$  is called thermal infrared (TIR), while the spectral interval from  $15 \,\mu\text{m}$  to  $1 \,\text{m}$  is referred to as far-infrared (FIR).

Molecular absorption spectra result from conversion of radiative energy to excitation of the molecule by rotational, vibrational or electronic transitions. The spacings of available energy levels of the molecule have to match the energy of the incident radiation, otherwise the species will be transparent to that radiation. While



Figure 2.1: The electromagnetic spectrum.

rotational energies of the molecule correspond to the far-infrared or microwave region, vibrational energies are located in the NIR/SWIR or TIR region. Electronic transitions correspond to energies in the visible, ultraviolet or X-ray wavelength range.

Besides the strong absorption features of  $CO_2$  and  $CH_4$  in the thermal infrared (which are characteristic for greenhouse gases), these molecules also absorb in the NIR/SWIR spectral region. The differentiation between NIR and SWIR is somewhat arbitrary and in this study near-infrared therefore refers to the entire spectral range from 0.7  $\mu$ m to 3  $\mu$ m to simplify matters covering all considered absorption bands of oxygen, carbon dioxide, and methane relevant for the retrieval presented here.

In contrast to thermal infrared spectroscopy which uses thermal emission from the earth's surface and the atmosphere, near-infrared spectroscopy benefits from the absorption of reflected, backscattered or transmitted solar radiation in the atmosphere and is normally based on corresponding coupled rotational and vibrational excitation of the molecules with the vibrational spectra containing fine structure according to the rotational sublevels. Due to the coupling the spectra exhibit high complexity. Rarely, also electronic transitions such as in oxygen are involved.

## 2.2 Molecular rotations and vibrations

A molecule which consists of n atoms has 3n degrees of freedom, whereof three are translational and three are rotational in a nonlinear molecule. A linear molecule only has two rotational degrees of freedom because the degree of freedom associated with spinning along the line of centres of the atoms is frozen out which is due to the very small moment of inertia I along this axis and the inverse dependence of energy on it according to (with J being the total angular momentum quantum number)

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1)$$
 (2.1)

resulting in very widely spaced rotational energy levels greater than the binding energy. The remaining degrees of freedom then correspond to fundamental vibrations amounting to 3n-5 in the linear and 3n-6 in the nonlinear case. The actual amount of spectral bands due to fundamental vibrational modes can be smaller because of degeneration caused by symmetry.

Commonly observed near-infrared transitions are of rotational-vibrational nature. The corresponding spectra are a result of transitions from rotational levels of a specific vibrational state (described by the vibrational quantum number v) to rotational levels of another vibrational state without changing the electronic state  $((v',J') \leftarrow (v'',J''))$ . For the absorption to take place, there has to be a periodic change in the electric dipole moment of the molecule during the vibration, otherwise the corresponding band is not observed in the infrared absorption spectrum (infrared-inactivity).

Assuming that the interaction between rotation and vibration is negligible, the rotational and vibrational contributions to the energy of the molecule can be considered independently. Using the approximations of harmonic oscillator and rigid rotor one gets therewith for a symmetric top molecule ( $I_A \neq I_B = I_C$ ) having two equal principal moments of inertia

$$E_{vib,rot} = E_{vib} + E_{rot} = \left(v + \frac{1}{2}\right)hv_0 + hcBJ(J+1) + hc(A-B)K^2$$
(2.2)

where *A* and *B* are the rotational constants with respect to the moments of inertia about the axis of symmetry and about an axis perpendicular to the axis of symmetry. v is the vibrational quantum number,  $v_0$  the vibration frequency, *J* the quantum number of the total angular momentum, and K = -J, ..., J the quantum number of the component of angular momentum about the axis of symmetry (i.e., projection of **J** on the symmetry axis).

Vibrational modes in a symmetric top differ according to the orientation of the oscillating dipole moment relative to the top axis and the corresponding bands are referred to as parallel and perpendicular. The selection rules are  $\Delta v = \pm 1$  and

parallel bands: 
$$\Delta J = \pm 1;$$
  $\Delta K = 0$  for  $K = 0$   
 $\Delta J = 0, \pm 1;$   $\Delta K = 0$  for  $K \neq 0$   
perpendicular bands:  $\Delta J = 0, \pm 1;$   $\Delta K = \pm 1$ .

Pure rotational transitions ( $\Delta v = 0$ ) are also possible if the molecule has a permanent electric dipole moment.

Special cases of the symmetric top are linear  $(I_B=I_C; I_A=0)$  and spherical top  $(I_A=I_B=I_C)$  molecules. For linear molecules holds K=0 (no rotation about the molecular axis accordant to the frozen out rotational degree of freedom mentioned above) and for spherical tops A=B so that (2.2) reduces to

$$E_{vib,rot} = \left(v + \frac{1}{2}\right)hv_0 + hcBJ(J+1) , \qquad (2.3)$$

respectively. The degeneracy of each energy level is 2J+1 in the linear case and  $(2J+1)^2$  for spherical tops. According to the selection rules given above,  $\Delta J = \pm 1$  for parallel bands of linear molecules (i.e., stretching vibrations) whereas for perpendicular bands which are associated to a change of dipole moment perpendicular to the molecular axis (i.e., bending vibrations) also  $\Delta J = 0$  is possible. Transitions with  $\Delta J = -1$  and  $\Delta J = +1$  are referred to as P-branch and R-branch, respectively; transitions with  $\Delta J = 0$  are denoted as the Q-branch, which is - if present - rather strong because of many overlapping lines due to  $\Delta B/B'' \ll 1$  concentrated near the



Figure 2.2: Schematic rotational-vibrational molecular spectral band and corresponding transitions. The P- and R-branches are consequences of transitions with  $\Delta J = -1$  and  $\Delta J = +1$ , respectively. In local thermodynamic equilibrium there is typically only thermal population in the lowest vibrational state with v'' = 0. The relative amplitudes of the spectral lines scale as the population of the rotational sublevels J'' (Haken and Wolf, 2006).

band center between the P- and R-branches. The involved transitions are illustrated in Figure 2.2.

Unlike linear molecules where a Q-branch is only allowed for bending vibrations or when the molecule has a triplet ground state, i.e., unpaired electron spins contributing to angular momentum about the molecular axis, for a spherical top there is a Q-branch for both parallel and perpendicular bands. The Q-branches of different *K*-values all lie on top of each other (only very slightly displaced due to centrifugal distortion) with P- and R-branches to either side as in the linear case. For a general symmetric top with  $I_A \neq I_B$  the PQR-branches of a perpendicular band would be spread out according to *K* due to  $\Delta K = \pm 1$  and (2.2) leading to a very complex spectrum with spacing 2(A-B) of the Q-branches but since A=B for a spherical top they overlap near the band center because the energy levels do not depend on *K*.

The rigid rotor approximation predicts lines with a constant distance of 2*B* in the observed spectrum, whereas realistic measurements reveal slightly decreasing spacing in the R-branch as the wavenumber increases and increasing spacing in the P-branch as the wavenumber decreases due to the fact that bonds in molecules are not entirely rigid because of the vibrational coupling. Anharmonicity additionally causes overtone bands resulting from  $\Delta v = \pm 2, \pm 3, \pm 4, \ldots$  with decreasing intensity.

Besides the selection rules, the relative amplitude of the spectral lines in a given band depends on the degree of degeneracy and the population of the rotational level of the lower state (v'', J''). In local thermodynamic equilibrium the thermal population is given by the Boltzmann distribution, hence

$$\frac{N_J}{N_0} = \frac{g_J}{g_0} \exp\left(-\frac{E_J - E_0}{k_B T}\right) = g_J \exp\left(-\frac{hcBJ(J+1)}{k_B T}\right)$$
(2.4)

with degeneracy  $g_J$ , i.e., number of states having energy  $E_J$ . For small J the degeneration term ((2J+1) for linear and  $(2J+1)^2$  for spherical top molecules) dominates and the population  $N_J$  increases with J, whereas for greater J the population decays exponentially with increasing J. Thus, a population maximum is obtained for a specific J depending on temperature and rotational constant. Since there is typically no thermal population in the upper state ( $\nu', J'$ ) the spectral line intensities scale as the population of the rotational sublevels of the lower vibrational state according to (2.4) with J = J''. The intensities of transitions can also be affected by nuclear spin in molecules with inversion symmetry. Given for example the linear molecule  ${}^{12}C^{16}O_2$ , the exchange of the identical  ${}^{16}O$  nuclei corresponds to a symmetric total wave function if J is even and to a antisymmetric wave function if J is odd. Since the nuclei have zero spin, the Bose-Einstein statistics requires symmetric behaviour under nuclear exchange explaining why only spectral lines originating from energy levels with even J are observed.



Figure 2.3: Potential curves for the lowest electronic states of molecular oxygen.

## 2.3 The molecules $O_2$ , $CO_2$ , and $CH_4$

#### Oxygen

Due to molecular orbital theory the ground state of molecular oxygen has two unpaired electrons with parallel spin, each in one of the two antibonding  $2p\pi^*$ orbitals resulting in a total spin S=1. Hence, the ground state  $O_2(^{3}\Sigma_{g})$  is a triplet state and there are two low-lying excited metastable singlet states  $O_2(^1\Delta_g)$  and  $O_2({}^1\Sigma_{\sigma}^+)$  with zero total spin leading to strong absorption bands in the near-infrared  $(\Delta v = 0, 0 \leftarrow 0)$  at 7882 cm<sup>-1</sup> and 13122 cm<sup>-1</sup> (A-band) associated with the electronic transitions  $O_2(^1\Delta_g) \leftarrow O_2(^3\Sigma_g^-)$  and  $O_2(^1\Sigma_g^+) \leftarrow O_2(^3\Sigma_g^-)$ , respectively. In this respect molecular oxygen differs from most other molecules which normally only have electronic transitions in the visible, ultraviolet or X-ray region of the electromagnetic spectrum such as N<sub>2</sub> which has a singlet ground state. The relevant electronic states of molecular oxygen and the corresponding spin configuration of the  $2p\pi^*$ -orbitals are shown in Figure 2.3. Besides the O<sub>2</sub> A-band, which is used in this study to retrieve the total column amount of oxygen, the electronic transition  $O_2({}^1\Sigma_g^+) \leftarrow O_2({}^3\Sigma_g^-)$  also leads to additional absorption features in the visible spectral region, namely the O<sub>2</sub> B-band ( $\Delta \nu = 1, 1 \leftarrow 0$ ) and the O<sub>2</sub>  $\gamma$ -band  $(\Delta v = 2, 2 \leftarrow 0)$ . As a homonuclear diatomic molecule, oxygen has no permanent or vibrational induced electric dipole moment and thus no pure rotational or rotationalvibrational transitions in the optical spectrum.



Figure 2.4: Stretching and bending vibrational modes for  $CO_2$ : symmetric stretch  $\tilde{v}_1$ , asymmetric stretch  $\tilde{v}_3$ , and doubly-degenerate bending mode  $\tilde{v}_2$  (bending in the plane of the paper and bending in and out of the plane of the paper).

As the electronic state is changed for all these transitions, the corresponding rotational constants B' and B'' are generally no longer approximately equal. Therefore the Q-branches do not have to be concentrated to small wavelength intervals near the band center anymore and can exhibit strong overlaps with the other rotational branches. The branches are labeled  ${}^{\Delta N}\Delta J$  with J being the quantum number of the total angular momentum and N the quantum number of the angular momentum without spin. For the O<sub>2</sub> A-band transition holds B' < B'' and dipole transitions are of <sup>R</sup>R, <sup>R</sup>Q, <sup>P</sup>P, and <sup>P</sup>Q type (Herzberg, 1989). The overlap of the <sup>P</sup>P and <sup>P</sup>Q branches leads to the P wing line doublets visible in Figure 2.5. The overlapped weak band with band center around 771 nm corresponds to the transition  $O_2({}^{1}\Sigma_{g}^{+}, \nu' = 1) \leftarrow O_2({}^{3}\Sigma_{g}^{-}, \nu'' = 1)$ .

#### Carbon dioxide

Carbon dioxide (CO<sub>2</sub>) is a linear molecule with three normal modes of vibration, namely besides a doubly-degenerate bending mode  $\tilde{v}_2 = 667 \text{ cm}^{-1}$ , non-degenerate symmetric ( $\tilde{v}_1 = 1388 \text{ cm}^{-1}$ ) and asymmetric ( $\tilde{v}_3 = 2349 \text{ cm}^{-1}$ ) stretching modes. The symmetrical stretch  $\tilde{v}_1$  is an infrared-inactive mode because this vibration induces no change in the dipole moment of the molecule. Since  $\tilde{v}_2$  is a bending mode of a linear molecule, the Q-branch is observable in the corresponding spectral band. As carbon dioxide has no permanent dipole moment, a pure rotational spectrum is not existent.

Because  $\tilde{v}_1 \simeq 2\tilde{v}_2$ , CO<sub>2</sub> shows large Fermi resonance with spectral bands grouped in polyads. The different bands of CO<sub>2</sub> are described by the notation  $(v_1v_2^lv_3)_r$  where the vibrational quantum number  $v_i$  is associated with the vibrational fundamental mode i,  $l=v_2, v_2-2, ...$  is an integer representing the quantised vibrational angular momentum associated with the degenerated bending mode, and  $r \in [1, 2, ..., v_1+1]$  is the rank of the level in the Fermi resonating  $(v_1+1)$ -ad consisting of the levels  $(v_1v_2^lv_3), ((v_1-1)(v_2+2)^lv_3), ..., (0(v_2+2v_1)^lv_3)$  sorted by decreasing wavenumber and denoted by Roman numerals.

Relevant for the near-infrared CO<sub>2</sub> retrieval considered in this study is the absorption band at 6348 cm<sup>-1</sup> due to the transition from the ground state (00<sup>0</sup>0) to the vibrational level (30<sup>0</sup>1)<sub>II</sub> = (22<sup>0</sup>1) of the Fermi tetrad corresponding to the combination of the asymmetric stretching mode  $\tilde{v}_3$  and overtones of  $\tilde{v}_1$  and  $\tilde{v}_2$ .

#### Methane

Methane (CH<sub>4</sub>) is a tetrahedral spherical top molecule having four normal modes of vibration: a non-degenerate symmetric stretching mode  $\tilde{v}_1 = 2917 \text{ cm}^{-1}$ , a doubly-degenerate bending mode  $\tilde{v}_2 = 1534 \text{ cm}^{-1}$  as well as a stretching mode  $\tilde{v}_3 = 3019 \text{ cm}^{-1}$  and a bending mode  $\tilde{v}_4 = 1306 \text{ cm}^{-1}$  both being triply degenerated due to symmetry.  $\tilde{v}_1$  and  $\tilde{v}_2$  are infrared-inactive modes. The wavenumbers of the fundamental vibrations satisfy the simple approximate relation  $\tilde{v}_1 \simeq 2\tilde{v}_2 \simeq \tilde{v}_3 \simeq 2\tilde{v}_4$ leading to vibrational levels grouped into so-called polyads  $P_n$  defined by

$$n = 2(v_1 + v_3) + v_2 + v_4 , \qquad (2.5)$$

where  $v_i$  are the vibrational quantum numbers, and named by using the Greek prefix corresponding to the number of vibrational levels (Boudon et al., 2006)

$$N(n) = \frac{1}{24}(n+3)\left(n+4+(n \mod 2)\right)\left(n+2-(n \mod 2)\right)$$
(2.6)

in a given  $P_n$ , such as Pentad (5 levels) for  $P_2$  or Octad (8 levels) for  $P_3$ . Each set of vibrational quantum numbers ( $v_1v_2v_3v_4$ ) defines a vibrational level containing a certain number of sublevels due to the degenerated normal vibrations. Vibrational angular momentum quantum numbers  $l_i$  associated with the degenerated fundamental modes needed to identify the sublevels unambiguously are omitted here in the notation for the sake of simplicity.

In the retrieval of methane described later, the absorption band corresponding to the transition from the ground state (0000) to a sublevel of the overtone of the triply-degenerate  $\tilde{v}_3$  vibration, namely (0020), at 6005 cm<sup>-1</sup> in the tetradecad  $P_4$  is used. This band, which overlaps to some extent with other weaker bands of the methane tetradecad, lies close to the used CO<sub>2</sub> band.
Molecule	${ ilde v}_1$	$\tilde{v}_2$	$\tilde{v}_3$	$\tilde{v}_4$
$CO_2$	1388	667	2349	-
CH <sub>4</sub>	2917	1534	3019	1306

Table 2.1: Wavenumbers of the fundamental vibrational modes of carbon dioxide and methane. Infrared-inactive modes are shaded in gray, doubly-degenerate modes are shown in bold, and triply-degenerate modes in bold italic.



Figure 2.5: Transmittances of oxygen, carbon dioxide, and methane at 900 hPa and 280 K in specific spectral intervals. Shown are the O<sub>2</sub> A-band  $O_2({}^{1}\Sigma_{g}^{+}) \leftarrow O_2({}^{3}\Sigma_{g}^{-})$ , the CO<sub>2</sub> band  $(30^{0}1)_{II} \leftarrow (00^{0}0)$ , and the band of the methane tetradecad at 6005 cm<sup>-1</sup> overlapped by other weak methane bands.

2 INFRARED SPECTROSCOPY

# **3** The SCIAMACHY instrument on ENVISAT

### 3.1 The Environmental Satellite ENVISAT

The European environmental satellite ENVISAT (Figure 3.1) built by a European industrial consortium on behalf of the European Space Agency (ESA) was launched on March 1, 2002 on a Ariane-5 rocket from Kourou in French Guiana into a sunsynchronous near polar orbit in descending node having an equator crossing time of 10:00 a.m. local time. With dimensions of  $26 \text{ m} \times 10 \text{ m} \times 5 \text{ m}$  and a total mass of 8140 kg it is the largest and concomitantly the most powerful European Earth Observation satellite yet built observing and monitoring the Earth's Atmosphere, land, ice, and oceans with ten different instruments onboard. These are the Radar Altimeter 2 (RA-2), the MicroWave Radiometer (MWR), the Doppler Orbitography and Radiopositioning Integrated by Satellite (DORIS), the Laser RetroReflector (LRR), the Advanced Synthetic Aperture Radar (ASAR), the MEdium Resolution Imaging Spectrometer (MERIS), the Advanced Along Track Scanning Radiometer (AATSR), the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), the Global Ozone Monitoring by Occultation of Stars (GOMOS), and the SCanning Imaging Absorption spectroMeter of Atmospheric CHartographY (SCIAMACHY), which is used in this study. The different instruments complement each other concerning application ranges, spectral coverage, and measurement principles facilitating synergistic use by providing a wealth of information about the Earth system. An orbit period of ENVISAT lasts 100.6 min resulting in  $14\frac{11}{35}$  orbits per day and a ground track repeat cycle of 35 days, i.e., 501 Orbits.

## 3.2 The SCIAMACHY instrument

SCIAMACHY (greek:  $\sigma \kappa \iota \alpha \mu \alpha \chi \iota \alpha$ , "fighting shadows"), which is a multi-national contribution of Germany, The Netherlands, and Belgium to ENVISAT, is a passive imaging grating spectrometer that measures reflected, backscattered and transmitted solar radiation upwelling from the top of the atmosphere (Burrows et al., 1990; Burrows and Chance, 1991; Burrows et al., 1995; Bovensmann et al., 1999; Gottwald et al., 2006). The spectral region from 214 nm to 1773 nm is measured contiguously in six channels, and there are two additional channels covering the regions 1934-2044 and 2259-2386 nm (see Table 3.1 and Figure 3.5).



Figure 3.1: ENVISAT in the European Space Research and Technology Centre, ESTEC (photos by ESA).

SCIAMACHY measures in three different viewing modes. In nadir mode the field of view faces downward to the Earth's surface scanning across the sub-satellite track, thus observing the atmospheric column directly below the instrument, whereas in limb mode scattered light above the horizon is measured as function of tangent height allowing the determination of trace gas profiles. The limb/nadir matching provides the possibility to measure the same atmospheric volume both in nadir and limb within one orbit yielding in principle three-dimensional information about the atmosphere. Occultation measurements are performed in limb geometry with the sun or the moon directly in the instrument's field of view tracking sunrises and moonrises through the atmosphere.

The optical configuration of SCIAMACHY is shown in Figure 3.2. The incoming light entering the instrument alternatively via the nadir, limb or subsolar port depending on scan mode is focussed on the entrance slit of the spectrometer. After leaving a predisperser prism a geometrical channel separator splits the resulting weakly dispersed intermediate spectrum and directs the light depending on the spectral range to the 8 spectral channels using reflective optics and dichroic mirrors. The sophisticated design of optical components along the light paths prevents stray light to a large extent. Each spectral channel comprises a individual grating focusing optics and a 1024 element monolithic diode array of the appropriate material, namely Silicon for the detectors of channel 1-5 whereas InGaAs is used for the



Figure 3.2: Optical configuration of SCIAMACHY (Gottwald et al., 2006).

Channel	Spectral range [nm]	Resolution [nm]	Detector material	Temperature range [K]
1	214-334	0.24	Si	204.5-210.5
2	300-412	0.26	Si	204.0-210.0
3	383-628	0.44	Si	221.8-227.8
4	595-812	0.48	Si	222.9-224.3
5	773-1063	0.54	Si	221.4-222.4
6	971-1773	1.48	InGaAs	197.0-203.8
7	1934-2044	0.22	InGaAs	145.9-155.9
8	2259-2386	0.26	InGaAs	143.5-150.0

Table 3.1: Characteristics of SCIAMACHY's spectral channels.

channels 6-8 instead because the band gap of silicon is too large to be utilised for detectors in this spectral range. The detector material of the upper part of channel 6 (called channel 6+) as well as the channels 7 and 8 had to be doped with a higher fraction of Indium compared to the rest of channel 6 to be sensitive to wavelengths beyond 1600 nm. However, the associated larger lattice constant of the InGaAs light detection layer is in mismatch with the lattice constant of the InP substrate in this case resulting in a reduced performance in terms of detector dark current and number of usable pixels. In order to achieve the desired signal-to-noise performance all channels are cooled with temperatures being lowest (about 150 K) for channels 7 and 8. The predisperser prism also reflects fully polarised light perpendicular with respect to the instrument optical plane under the Brewster angle which is splitted and directed to 6 broad band channels of the Polarisation Measurement Device (PMD) monitoring at high spatial resolution (the PMD diodes are read out much faster than the main channel detector arrays) and thus providing subscene information which can be used for example to identify cloud contaminated ground scenes. A seventh PMD channel measures the 45° polarisation component of extracted light uncoupled from the channels 3-6 light path by a beam splitter.

During every orbit calibration measurements are made during the eclipse, followed by a solar occultation and limb atmospheric measurement. On the Earth's day side SCIAMACHY performs alternate nadir and limb observations with a swath width of 960 km (see Figure 3.3). These measurements can be inverted to obtain a large number of atmospheric data products (Bovensmann et al., 1999) (see also Figure 3.4). As a result of SCIAMACHY's observation of greenhouse gas overtone absorptions in the near-infrared/short wave infrared (NIR/SWIR) solar backscattered spectrum, SCIAMACHY is the first and currently only satellite instrument that yields the vertical columns of carbon dioxide and methane with high sensitivity



Figure 3.3: Nadir and limb scanning strategy of SCIAMACHY.



Figure 3.4: The spectral range and corresponding data products of SCIAMACHY compared to GOME.



Figure 3.5: Simulated SCIAMACHY nadir spectrum.

down to the Earth's surface (Buchwitz et al., 2005a). As the integration time for the detectors is optimised around an orbit, the horizontal resolution of the nadir measurements depends on orbital position and spectral interval, but is typically 60 km across track by 30 km along track for the methane, carbon dioxide, and oxygen absorption features in the spectral fitting windows used in this study. When using the standard alternating Limb/Nadir scan option global coverage at the equator is achieved within 6 days.

Overall, the in-flight optical performance of SCIAMACHY is very similar to that predicted from the pre-flight on ground characterisation and calibration activities. One exception is a time dependent optical throughput variation in the SCIAMACHY NIR/SWIR channel 7, which has many resolved  $CO_2$  absorption features, and channel 8, which has many  $CH_4$  absorption features. This results from the in-flight deposition of ice on the cooled detectors. As ice absorbs and scatters at these wavelengths this adversely affects the trace gas retrieval by reducing the signal-to-noise ratio and changing the instrument function (Gloudemans et al., 2005; Buchwitz et al., 2005b). As shown in Figure 3.5, the WFM-DOAS version 1.0 results have been derived using  $CO_2$  and  $CH_4$  absorption features in channel 6 (1000-1750 nm) and  $O_2$  A-band absorption in channel 4 (605-805 nm), which are not affected by an ice-layer, as their detectors operate at higher temperatures.

# 4 Radiative transfer in the atmosphere

#### 4.1 Relevant atmospheric processes

In order to retrieve information about atmospheric constituents from reflected or backscattered sunlight by satellite observations, the measurements have to be compared to simulated top-of-atmosphere spectral radiances computed by a forward radiative transfer model not only accounting for molecular absorption, but also for other atmospheric processes including, amongst others, Rayleigh scattering, aerosol extinction, and ground surface reflection. Compared to the highly structured gaseous absorptions, the spectral features of the other processes are usually relatively smooth.

#### Molecular absorption

The absorption of a molecule is described by its absorption cross-section k exhibiting unique spectral signatures characteristic for the respective molecule. As we have seen in Chapter 2 the absorption spectra of the greenhouse gases carbon dioxide and methane in the near-infrared are due to overtones and combinations of rotational-vibrational transitions. In general the absorption cross-section depends on pressure and temperature. Its product with the concentration n of the molecule is referred to as the absorption coefficient  $\alpha$  whose integration along the finite light path gives the corresponding optical density  $\tau$ . Following Beer-Lambert's law,

$$L_{\lambda}(s) = L_{\lambda 0}(s) \exp\left(-\int_{s_1}^{s_2} k_{\lambda}(s)n(s)ds\right) \quad , \tag{4.1}$$

the monochromatic radiance  $L_{\lambda}$  decays exponentially with respect to  $\tau$  neglecting other absorbers, scattering and surface reflection.

If individual spectral lines are not fully resolved, i.e., when spectrometers detect radiation convolved with a broader instrument function, the linear relation between the logarithm of transmittance, which is defined as the ratio of transmitted to incident radiance, and the optical density is no longer valid.

The spectral transmittances of different atmospheric gases absorbing in the nearinfrared are shown in Figure 4.1.



Figure 4.1: Transmittances of absorbers in the near-infrared spectral range according to HITRAN 2004 for U.S. Standard Atmosphere vertical columns, a pressure of 900 hPa, and a temperature of 282 K (corresponding to U.S. Standard Atmosphere conditions at 1 km). Monochromatic transmittances are shown in gray, convolved transmittances (gaussian instrument function, FWHM 0.2 nm) in black.

#### **Rayleigh and Raman scattering**

Rayleigh scattering describes the elastic scattering of electromagnetic radiation by molecules or particles whose characteristic dimension is very small compared to the wavelength of the incident radiation  $(2\pi r \ll \lambda)$ . It therefore applies to scattering of solar radiation by air molecules. The Rayleigh scattering phase function normalised to  $4\pi$  describing the angular distribution of the scattered light is given by

$$\varphi_{R}(\vartheta) = \frac{3}{2} \frac{(1+d) + (1-d)\cos^{2}\vartheta}{2+d}$$
(4.2)

with scattering angle  $\vartheta$  and depolarisation factor d. The Rayleigh scattering coefficient  $\sigma_R$  which is obtained by multiplication of the Rayleigh scattering cross-section and the air density n(p, T) is proportional to  $\lambda^{-4}$  leading to considerably decreasing intensity of Rayleigh scattered light with increasing wavelength which is the reason for the blue colour of the sky in the daytime.

A small fraction of the solar radiation is also scattered inelastically by Raman scattering resulting in less deep Fraunhofer lines in scattered solar radiation compared to the direct sun light spectrum (Grainger and Ring, 1962). This Raman filling-in of spectral lines is known as the Ring-effect.

#### Aerosol extinction

The concept of aerosols refers to airborne liquid droplets, particulate matter (PM), or combinations of these exhibiting typical radii between  $0.01 \,\mu\text{m}$  and  $10 \,\mu\text{m}$ . Besides natural occurrences, about 10% of the total amount of aerosols in the atmosphere is of anthropogenic origin. The main contribution of aerosols to radiative transfer in the solar spectral region is scattering. Apart from desert dust, soot, and volcanic ash, absorption of aerosols generally only plays a minor role.

The scattering of spherical aerosols comparable in size with the wavelength of incident radiation  $(2\pi r \approx \lambda)$  is well described by Mie theory. In contrast to the Rayleigh scattering coefficient the aerosol extinction coefficient  $\kappa_A$  cannot be derived analytically due to complex dependencies between the involved microphysical parameters and the variety of composition and shape. However, the wavelength dependence of aerosol extinction is estimated to be  $\lambda^{-a}$  with typical Ångstrom exponent  $a \in [0, 1.5]$  depending on considered wavelength range and aerosol scenario (Hess et al., 1998).

The angular distribution of the scattered light is described by the aerosol scattering phase function  $\varphi_A$  which depends on the aerosol type and usually shows a complex dependence on the scattering angle and wavelength. However, it generally has a strong forward peak and is often parametrised by the Henyey-Greenstein approximation (normalised to  $4\pi$ )

$$\varphi_A(\vartheta) = \frac{1 - g^2}{(1 + g^2 - 2g\cos\vartheta)^{3/2}}$$
(4.3)

with asymmetry factor  $g \in [-1, 1]$  defining how strongly and in which direction the phase function is peaked. For g = 0 the scattering is isotropic.

For cloud particle scattering  $(2\pi r \gg \lambda)$  the scattering coefficient  $\sigma$  is approximately constant with wavelength, giving clouds the white or rather achromatic gray colour.

#### Surface reflection

Given a reflecting surface illuminated by a light source under zenith angle  $\theta'$ , the ratio of reflected radiant flux density (integrated radiance *L* over the half-space) to incident radiant flux density (irradiance)  $E = E_0 \cos \theta'$  defines the albedo of the surface

$$\rho = \frac{\int_{\Omega = 2\pi} L \cos \theta \, d\Omega}{E} \quad , \tag{4.4}$$

where  $\Omega$  is the solid angle and  $\theta$  the angle between reflection direction and the surface normal (Figure 4.2). Hence, albedo is the fraction of incident radiation that is reflected by a surface, with  $\rho \in [0, 1]$  being a dimensionless quantity. In case of a Lambertian surface, the reflected radiance *L* is isotropic and therefore independent of the viewing geometry which simplifies the relation to

$$\rho = \frac{L \int_{\Omega = 2\pi} \cos \theta \, d\Omega}{E} = \frac{\pi L}{E} \quad . \tag{4.5}$$

The albedo is characteristic for a particular material and usually depends on wavelength for natural surface types (e.g., see Figure 8.2).

In the general case of a non-Lambertian surface the reflection can be described by a Bidirectional Reflectance Distribution Function (BRDF)  $\tilde{\rho}(\theta', \phi', \theta, \phi)$  depending on the direction of incident and reflected radiation.

#### 4.2 Radiative transfer equation

The radiative transfer equation in its most general form describes the change in radiance (radiant flux per area and solid angle in a given direction)

$$L = \frac{d^2 \Phi}{\cos \theta \, d\Omega dA} \tag{4.6}$$



Figure 4.2: Reflection on a surface.

in an infinitesimal path element ds along the direction **s** in the atmosphere (Lenoble, 1993)

$$\frac{dL_{\lambda}(\mathbf{s})}{ds} = \kappa_{\lambda} \left( J_{\lambda}(\mathbf{s}, L) - L_{\lambda}(\mathbf{s}) \right) .$$
(4.7)

The extinction coefficient  $\kappa$  is the sum of the absorption coefficient  $\alpha$  and the scattering coefficient  $\sigma$ , while *J* denotes the so-called source function which can be splitted in two terms, the scattering source function  $J^{sc}$  and the emission source function  $J^{em}$ . Thus, the radiative transfer equation, which completely defines the radiance for specified boundary conditions, describes the loss of photons due to absorption along the light path or scattering out of the beam and the gain caused by local sources or scattering into the beam.

Introducing the single scattering albedo

$$\varpi = \frac{\sigma}{\kappa} \in [0, 1] \tag{4.8}$$

the scattering source function is obtained from the phase function  $\varphi$  by

$$J_{\lambda}^{sc}(\mathbf{s},L) = \frac{\varpi_{\lambda}}{4\pi} \int \varphi_{\lambda}(\mathbf{s},\mathbf{s}')L_{\lambda}(\mathbf{s}')d\Omega' \quad .$$
(4.9)

Although being generally more complex, in case of local thermodynamic equilibrium the emission source function is given by

$$J_{\lambda}^{em} = (1 - \boldsymbol{\varpi}_{\lambda}) L_{\lambda}^{B}(T) , \qquad (4.10)$$

where  $L_{\lambda}^{B}(T)$  is the black-body radiance at temperature *T*. Hence, the emission source function is independent of the direction **s** in this case.

If source terms are negligible  $(J_{\lambda} = 0)$ , (4.7) reduces to

$$\frac{dL_{\lambda}}{L_{\lambda}} = -\kappa_{\lambda} ds \quad , \tag{4.11}$$

giving Beer-Lambert's law

$$L(s) = L_0 e^{-\tau(s)} \quad , \quad \tau(s) = \int_{s_1}^{s_2} \kappa(s) ds \tag{4.12}$$

describing the exponential attenuation of incoming radiation  $L_0$  due to extinction with  $\tau$  being the slant optical density of the atmosphere corresponding to the given finite light path.

#### 4.3 The radiative transfer model SCIATRAN

SCIATRAN (Rozanov et al., 2002) is a radiative transfer program developed at the University of Bremen to allow fast and accurate simulation of top-of-atmosphere radiance spectra in satellite geometry as measured by SCIAMACHY covering the spectral interval of about 240-2400 nm. Calculations can be done in line-by-line or in the fast exponential sum fitting correlated-k modus with supported correlated-k parameters related to the SCIAMACHY spectral channels (Buchwitz et al., 2000a). The associated line parameters of the gaseous absorbers were updated to HITRAN 2004 (Rothman et al., 2005) within the framework of this thesis and cover a variety of trace gases including oxygen, carbon dioxide, and methane which are needed for this study.

The pseudo-spherical mode (plane-parallel atmosphere, solar source term calculated in spherical geometry) gives accurate results for a solar zenith angle of less than about 92° and a near-nadir viewing geometry with a line-of-sight angle up to  $\pm 35^{\circ}$ . Multiple scattering is fully taken into account in the computation of radiances and weighting functions, i.e., the derivatives of the radiances with respect to atmospheric and surface parameters.

Aerosol scenarios can be parameterised in two different ways. The simple LOW-TRAN aerosol model based on Shettle and Fenn (1979) allows some basic scenarios using predefined aerosol types in four height layers with constant boundaries (boundary layer, troposphere, stratosphere, and mesosphere) and Henyey-Greenstein approximation of the aerosol phase function. For each layer several predefined reference vertical profiles of the aerosol extinction coefficient exist.

In the alternative and more powerful SCIATRAN aerosol parametrisation, different aerosol components can be mixed ad libitum in arbitrarily many height layers and Mie phase function or Henyey-Greenstein approximation can be used optionally. It can handle arbitrary extinction or particle density profiles and humidity can be chosen from eight predefined values compared to four in LOWTRAN.

Earth's surface is treated as a Lambertian reflector with constant or wavelength dependent albedo and altitude can be specified with respect to sea level.

# Part II Retrieval Algorithm

# **5** Introducing WFM-DOAS

## 5.1 Selection of the retrieval technique

The retrieval of long-lived and therefore relatively well-mixed gases such as carbon dioxide and methane is challenging as only the small variations on top of a large background yield information on their surface sources and sinks. The retrieval algorithm has therefore to be accurate and, in addition, sufficiently fast to process the large amounts of data produced by SCIAMACHY. Hence, the choice of the retrieval technique has to be matched ideally to the specific requirements of the problem by balancing the assets and drawbacks of the different approaches in the selection process.

In remote sensing there are in principle two different well-established methods in retrieval theory, the Differential Optical Absorption Spectroscopy (DOAS) and Optimal Estimation (OE) (Rodgers, 2000). Another possibility would be the design and training of a neural network, which, however, might be considered as unsatisfying from a physical point of view. A conceptual comparison of the different approaches is presented in Table 5.1. The Optimal Estimation ansatz offers the opportunity of accounting for correlations of errors and providing regularisation by the usage of a priori knowledge rendering large deviations from the prior unlikely. However, a priori constraints are problematic because one has to avoid the retrieval results being artificially biased towards the prior knowledge which is important particularly with regard to the analysis of the seasonal cycle and the annual increase of the greenhouse gases. In contrast to a profile retrieval, the retrieval of vertical columns is furthermore relatively well-conditioned because of the small number of free fit parameters permitting to dispense with regularisation. Since the retrieval errors of the vertical columns relevant for this study and of the other fit parameters are assumed to be independent, the possibility of allowing correlations of errors is not necessary. Taking everything into account, including the fact that Optimal Estimation is the slowest of the mentioned techniques, the above considerations turn the balance to a unconstrained DOAS approach.

At the University of Bremen the Weighting Function Modified Differential Optical Absorption Spectroscopy (WFM-DOAS) retrieval technique (Buchwitz, 2000; Buchwitz et al., 2000b), which is described in this chapter, has been developed for the retrieval of strong absorbing gases and was further improved as part of this thesis.

Technique	Processing speed	Error estimate	Error correlations	A priori constraints
WFM-DOAS	Fast	Yes	No	No
Neural Networks	Fast	No	No	No
<b>Optimal Estimation</b>	Slow	Yes	Yes	Yes

Table 5.1: Comparison of different retrieval techniques.

#### 5.2 The standard DOAS equation

Considering a surface of albedo  $\rho$  and a light path corresponding to a top-ofatmosphere measurement of reflected solar radiation (satellite geometry, see Figure 4.2) in a plane-parallel atmosphere, Beer-Lambert's law (4.12) can be rewritten as

$$L = \rho \frac{E_0 \cos \theta'}{\pi} e^{-\tau} \tag{5.1}$$

using the nomenclature of Chapter 4. Assuming a spectral window with specific gaseous absorption, the slant optical density can be split into the sum

$$\tau(\lambda) = \tau_g(\lambda) + \tau_r(\lambda) \tag{5.2}$$

with slant optical density of the narrow band absorption  $\tau_g$  of the considered species and residual optical density  $\tau_r$  of the other processes. Because of the smooth broad band dependencies on wavelength of the Rayleigh scattering coefficient  $\sigma_R \propto \lambda^{-4}$  and the aerosol extinction coefficient  $\kappa_A \propto \lambda^{-a}$  (see Chapter 4),  $\tau_r$  can be approximated by a low-order polynomial as function of wavelength if the spectral window is small enough. Hence, the logarithm of the sun-normalised radiance  $I(\lambda)$ can be written as

$$\ln I(\lambda) = \ln \left(\frac{\pi L(\lambda)}{E_0(\lambda)}\right) = -\tau_g(\lambda) + \ln \left(\rho(\lambda)\cos\theta'\right) + \sum_{j=0}^N \tilde{a}_j \lambda^j$$
$$= -\tau_g(\lambda) + \sum_{j=0}^N a_j \lambda^j$$
(5.3)

using (5.1), (5.2), and the assumption that the albedo term also shows only broad band spectral features and thus can be approximated by a low-order polynomial, too.

Assuming that the absorption cross-section k is independent of height and hence, does not depend on temperature and pressure, the slant optical density respecting

the gaseous absorption is given by

$$\tau_g(\lambda) = \int_{s_1}^{s_2} k(\lambda) n(s) ds = k(\lambda) \int_{s_1}^{s_2} n(s) ds = k(\lambda) S$$
(5.4)

with trace gas number density n and slant column S which can be converted in the desired vertical column

$$V = \int_0^{z_0} n(z) dz \tag{5.5}$$

via division by the air mass factor A = S/V describing the absorption enhancement due to the slant light path. If scattering is neglected the air mass factor is only dependent on the viewing geometry,

$$A = \frac{1}{\cos \theta'} + \frac{1}{\cos \theta} \quad , \tag{5.6}$$

but generally depends explicitly on wavelength and is not exactly known because the actual light path is unknown due to multiple scattering.

With this notation (5.3) becomes the standard DOAS equation:

$$\ln I(\lambda) = -VA_{\lambda}k(\lambda) + \sum_{j=0}^{N} a_{j}\lambda^{j} . \qquad (5.7)$$

The wavelength dependent air mass factor  $A_{\lambda}$  is usually approximated by a constant value taking into account scattering properties in the respective wavelength range.

However, the strong absorption lines of the considered gases in the near-infrared are highly pressure and temperature dependent, so that (5.4) is not satisfied and the standard DOAS algorithm is not applicable. This drawback can be tackled by a weighting function modified (WFM) DOAS approach using linearisation points.

#### 5.3 Linearisation and weighting functions

A linear relation between  $\ln I(\lambda)$  and the vertical column cannot be derived without any assumption because *V* is not an independent parameter in the radiative transfer equation. This can be seen by the fact that the sun-normalised radiance depends on the number density vertical profile n(z) of the absorber rather than on its vertical column amount because the absorption coefficient is given by

$$\alpha_{\lambda}(z) = n(z)k_{\lambda}(z) \quad . \tag{5.8}$$

Actually, the same vertical column can be achieved by different profiles and thus can occur concurrently with different sun-normalised radiances.

However,  $\ln I(\lambda)$  can be expanded by a functional Taylor series with respect to the absorption coefficient around  $\bar{\alpha}_{\lambda}(z)$ , thus

$$\ln I(\lambda, \alpha_{\lambda}(z)) = \ln I(\lambda, \bar{\alpha}_{\lambda}(z)) + \int_{0}^{z_{0}} \frac{\delta \ln I(\lambda, \alpha_{\lambda}(z))}{\delta \alpha_{\lambda}(z)} \bigg|_{\bar{\alpha}_{\lambda}(z)} \delta \alpha_{\lambda}(z) dz$$
(5.9)

in first order approximation neglecting linearisation error.

Assuming that the variation of the absorption coefficient is only due to variation of the number density profile

$$\delta \alpha_{\lambda}(z) = k_{\lambda}(z) \delta n(z) \quad , \quad \delta n(z) = n(z) - \bar{n}(z)$$
 (5.10)

equation (5.9) becomes

$$\ln I(\lambda, n(z)) = \ln I(\lambda, \bar{n}(z)) + \int_0^{z_0} w_{\lambda}(z) \delta n(z) dz$$
(5.11)

with the height dependent weighting function  $w_{\lambda}$  being defined by the functional derivative

$$w_{\lambda}(z) = \frac{\delta \ln I(\lambda, n(z))}{\delta n(z)} \bigg|_{\bar{n}(z)} .$$
(5.12)

In order to introduce the vertical column V as a variable, one assumes that the variation in the number density can be achieved by a scaling of the original profile:

$$n(z) = C\bar{n}(z) \tag{5.13}$$

As a consequence the same scaling relation is true for the vertical columns ( $V = C\bar{V}$ ), hence

$$n(z) = \frac{V}{\bar{V}}\bar{n}(z) \tag{5.14}$$

and (5.11) can be rewritten as

$$\ln I(\lambda, n(z)) = \ln I(\lambda, \bar{n}(z)) + \int_0^{z_0} w_\lambda(z) \left(\frac{V}{\bar{V}} - 1\right) \bar{n}(z) dz \quad . \tag{5.15}$$

With the columnar weighting function *W* which is defined by

$$W(\lambda) = \frac{\int_0^{z_0} w_{\lambda}(z)\bar{n}(z)dz}{\bar{V}}$$
(5.16)

the logarithm of the sun-normalised radiance can then be considered locally as a linear function of the absorber's vertical column rather than a functional of its number density profile:

$$\ln I(\lambda, V) = \ln I(\lambda, \bar{V}) + W(\lambda)(V - \bar{V}) \quad . \tag{5.17}$$

So far we have only considered a single absorber and neglected other atmospheric processes whose variation can also cause a variation in the sun-normalised radiance. This can be taken into account by introducing additional weighting functions for each considered parameter, respectively. Although, the Rayleigh scattering coefficient, aerosol extinction coefficient, and surface albedo term only show broad band spectral dependence, their weighting functions can contain spectral features of the absorbers due to scattering which enhances the light path (see Appendix B). Assuming that the spectral dependence of the weighting functions corresponding to scattering parameters and albedo can be approximated to first order by a polynomial, the linearisation of the logarithm of the sun-normalised radiance is given by

$$\ln I(\lambda, \mathbf{V}) = \ln I(\lambda, \bar{\mathbf{V}}) + \sum_{j=1}^{J} W_j(\lambda)(V_j - \bar{V}_j) + \sum_{i=0}^{N} b_i \lambda^i$$
(5.18)

where the components of vector  $\mathbf{V}$ , denoted  $V_j$ , are the vertical columns of all trace gases which have absorption lines in the selected spectral region.

#### 5.4 Inversion and WFM-DOAS equation

We have seen in the previous section that the logarithm of the sun-normalised radiance can be assumed locally as a linear function of the vertical column under the scaling assumption of the vertical profiles of the absorbing gases if the linearisation point  $\bar{\mathbf{V}}$  is close enough to  $\mathbf{V}$ .

In case of the SCIAMACHY retrieval one wants to determine the vertical column amounts from the measured sun-normalised radiance. As a forward model the discretisation of the deduced relation is used, since SCIAMACHY provides radiances at discrete wavelength values. Hence, the modelled radiation is given by

$$\ln I_{\lambda_l}^{mod}(\mathbf{V}, \mathbf{b}) = \ln I_{\lambda_l}^{mod}(\bar{\mathbf{V}}) + \sum_{j=1}^{J} \frac{\partial \ln I_{\lambda_l}^{mod}}{\partial V_j} \bigg|_{\bar{V}_j} (V_j - \bar{V}_j) + P_{\lambda_l}(\mathbf{b})$$
(5.19)

with the center wavelength  $\lambda_l$  of detector pixel number l and vector of polynomial coefficients **b** of polynomial P. A derivative with respect to a vertical column refers thereby to the change of the top-of-atmosphere radiance caused by a scaling of a pre-selected absorber concentration vertical profile.

Since the number of spectral points is greater than the number of parameters to retrieve, the problem is overconstrained and a linear least-squares approach is suitable for the retrieval of the desired vertical columns. In the process the radiative transfer model is fitted to the logarithm of the observed sun-normalised radiance  $I^{obs}$  by minimising the difference between observation and model, i.e., the

"length" of fit residuum vector **RES** (with components  $RES_l$ ), for all spectral points  $\lambda_l$  simultaneously. The least-squares WFM-DOAS equation is then

$$\sum_{l=1}^{m} \left( \ln I_{\lambda_{l}}^{obs} - \ln I_{\lambda_{l}}^{mod}(\hat{\mathbf{V}}, \hat{\mathbf{b}}) \right)^{2} \equiv \|\mathbf{RES}\|_{2}^{2} \to \text{ min.}$$
(5.20)

where the model is given by (5.19) and the fit parameter vectors or vector components are indicated by a hat. The fit parameters are the desired trace gas vertical columns  $\hat{V}_j$  and the polynomial coefficients. An additional fit parameter also used (but for simplicity omitted in the equations given above) is the shift (in Kelvin) of a pre-selected temperature profile. This fit parameter has been added in order to take the temperature dependence of the trace gas absorption cross-sections into account.

The least-squares problem can also be expressed in the following vector/matrix notation. Given a forward model by

$$\mathbf{y} = \mathbf{A}\mathbf{x} + \mathbf{e} \tag{5.21}$$

with *m*-dimensional measurement vector **y**, *n*-dimensional state vector **x**,  $(m \times n)$  weighting function matrix **A**, and model error **e**, the most probable inference  $p(\mathbf{x}|\mathbf{y})$  is obtained by minimising  $\chi^2 = \|\mathbf{y} - \mathbf{A}\mathbf{x}\|_2^2$  with respect to **x**. The solution is

$$\hat{\mathbf{x}} = \mathbf{C}_{\mathbf{x}} \mathbf{A}^T \mathbf{y}$$
,  $\mathbf{C}_{\mathbf{x}} = (\mathbf{A}^T \mathbf{A})^{-1}$  (5.22)

where  $C_x$  is the covariance matrix of solution  $\hat{x}$ . The errors of the retrieved columns are estimated as follows (Press et al., 1992):

$$\sigma_{\hat{V}_j} = \sqrt{\frac{(\mathbf{C}_{\mathbf{x}})_{jj}\chi^2}{m-n}} , \qquad (5.23)$$

where  $(\mathbf{C}_{\mathbf{x}})_{jj}$  is the *j*-th diagonal element of the covariance matrix, *m* is the number of spectral points in the fitting window and *n* is the number of linear fit parameters.

#### 5.5 Correlated *k*-distributions

Because of the highly wavelength dependent molecular absorptions an exact numerical integration of the radiative transfer equation is very computing time intensive. Hence, one is in need of a faster and nonetheless accurate solution in order to have the ability to process the large amount of forward model data needed for the retrieval. This is archived by the correlated *k*-distribution method (Buchwitz, 2000; Buchwitz et al., 2000a) which virtually yields the same sun-normalised radiances and weighting functions as computed in line-by-line mode after convolution with the instrument function (see Appendix B).



Figure 5.1: Demonstration of the transformation  $(\lambda, k_{\lambda}) \mapsto (g, k_g)$  from a rapidly varying to a monotonically increasing absorption cross-section in *g*-space.

The idea is to approximate the mean transmittance in a sufficiently small wavelength interval  $\Delta\lambda$  (smaller than the instrument resolution) by a weighted sum of subinterval-transmissions. If  $\Delta\lambda$  is so small that the absorption cross-section of a given absorber is the only varying optical parameter in this interval, the mean transmittance only depends on the occurrence frequency of particular cross-section values rather than the exact wavelength dependence of the cross-section. Therefore, the wavelength axis might as well be transformed to a probability axis. With the corresponding probability variable being defined by

$$g(k) = \int_0^k f(k')dk' \in [0,1] , \qquad (5.24)$$

where f(k')dk' is the fraction of the wavelength interval occupied by absorption cross-sections between k' and k' + dk', the inverse k(g), the so-called k-distribution, is a monotonically increasing function (Goody and Yung, 1989).

The transformation of the rapidly varying absorption cross-section  $k(\lambda)$  to a k-distribution in g-space which is demonstrated in Figure 5.1 allows an efficient numerical evaluation of the mean transmittance. The term "correlated" refers to the assumption that for a vertically inhomogeneous atmosphere the ordering transformation  $(\lambda, k_{\lambda}) \mapsto (g, k_g)$  remains constant which is an approximation for any real atmosphere because of the pressure and temperature dependence of the absorption cross-sections. However, if the cross-sections for different layers are well correlated which is the case in this study, the corresponding transformations are quite similar justifying this assumption.

The mean transmittance in the interval can then be written as

$$T(n) = \frac{1}{\Delta\lambda} \int_{\lambda_1}^{\lambda_2} \exp\left(-\int_0^{z_0} n(z)k_\lambda(z)dz\right) d\lambda$$
$$= \int_0^1 \exp\left(-\int_0^{z_0} n(z)k_g(z)dz\right) dg$$
$$\approx \int_0^1 \exp\left(-\sum_{i=1}^{N_z} k_{g,i}V_i\right) dg \quad ,$$
(5.25)

with  $V_i$  being the column in layer *i*. By dividing the *g*-axis in *M* subintervals where the variation of  $k_g$  is relatively small, the transmittance can be rewritten as a weighted sum of subinterval-transmittances with weights  $a_j$  and representative subinterval-cross-sections  $k_i$ :

$$T \approx \sum_{j=1}^{M} a_j \exp\left(-\sum_{i=1}^{N_z} k_{j,i} V_i\right) \quad . \tag{5.26}$$

The cross-sections  $k_j$  are obtained by a non-linear least squares fit known as the ESFT (Exponential Sum Fitting of Transmittance functions) method (Wiscombe and Evans, 1977).

Thus, by using the correlated *k*-distribution method the radiative transfer computations can be performed with far fewer calculations in *g*-space compared to the original wavelength space. Therefore, correlated-*k* calculations are much more computationally efficient than line-by-line models while being sufficiently accurate at the same time if the wavelength interval is chosen small enough.

#### 5.6 Look-up table approach

Although the correlated-*k* method is much faster than a line-by-line model, it is still not fast enough to process all forward calculations needed for the vast number of individual measurements separately in admissible time. Therefore, in order to avoid time-consuming on-line radiative transfer simulations, a fast look-up table scheme has been implemented. The pre-computed spectral radiances and their derivatives (e.g., with respect to trace gas concentration and temperature profile changes) depend on solar zenith angle, surface elevation (pressure), surface albedo, and water vapour amount to consider possible non-linearities caused by the high variability of atmospheric water vapour. The reference spectra are computed with the radiative transfer model SCIATRAN (see Section 4.3) for assumed (e.g., climatological) "mean"

columns  $\bar{\mathbf{V}}$  depending on surface elevation. Multiple scattering is fully taken into account.

For a specific satellite measurement (characterised by the parameters solar zenith angle, surface elevation, and surface albedo) the appropriate modelled radiance and weighting functions which are used in the fitting procedure are deduced by multidimensional interpolation of the neighbouring reference spectra in parameter space. The required surface albedo is retrieved beforehand by comparing the measured sun-normalised radiance at a selected wavelength, in a transparent region of the fitting window where no significant gaseous or particulate absorptions occur, to pre-calculated radiances for different surface albedos.

The reference spectra are calculated for water vapour amounts corresponding to the U.S. Standard Atmosphere scaled by 0.5, 1.0, 1.5, 2.0, and 4.0. If  $H_2O$  is an interfering gas in the fitting window the algorithm starts with an assumed scaling factor of 1.0, i.e., with the U.S. Standard Atmosphere water vapour amount. If the ratio of retrieved water vapour column after the fit and U.S. Standard Atmosphere  $H_2O$  is closer to another scaling factor the process is repeated with the corresponding reference spectrum. Usually convergence is achieved after at most one iteration step.

## 5.7 Column-averaged dry air mole fractions

The carbon dioxide and methane vertical columns are retrieved using small spectral fitting windows in the near-infrared (1558-1594 nm and 1630-1671 nm, respectively) located in SCIAMACHY channel 6, whereas oxygen is retrieved from a spectrally distant fitting window (755-775 nm,  $O_2$  A-band) in SCIAMACHY channel 4 (see Figure 3.5). Interfering gas for the  $CO_2$  fit is  $H_2O$ , whereas interfering gases for the  $CH_4$  fit are  $H_2O$  and  $CO_2$ . Example fits are depicted in Figure 5.2 and in more detail (also showing the fit residua and fitted weighting functions) in Appendix C.

As the considered gases are long-lived and therefore well mixed in the atmosphere, the vertical columns are dominated by topography and surface pressure. Thus, the rather small source and sink signals are not identifiable in the vertical columns. However, by normalising with the air column, which can be determined by a simultaneously measured gas with less variability, the small differences between the well correlated columns can be observed in the column-averaged mole fraction (Figure 5.3).

For carbon dioxide column-averaged dry air mole fractions are derived by normalising the  $CO_2$  columns with the oxygen columns retrieved simultaneously from the  $O_2$  A-band. Oxygen is an accurate proxy for the air column because its mole fraction is well known and has negligibly small variations. The column-averaged



Figure 5.2: Example fits of O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>. Symbols correspond to the measurement and the solid line to the fitted radiative transfer model.

mole fraction  $XCO_2$  is computed as follows:

$$XCO_{2} = \frac{CO_{2}^{col}}{(O_{2}^{col}/O_{2}^{mf})} , \qquad (5.27)$$

where  $CO_2^{col}$  is the retrieved absolute  $CO_2$  column (in molecules/cm<sup>2</sup>),  $O_2^{col}$  is the retrieved absolute  $O_2$  column (in molecules/cm<sup>2</sup>), and  $O_2^{mf}$  is the assumed (column-averaged) mole fraction of  $O_2$  used to convert the  $O_2$  column into a corresponding dry air column and is equal to 0.2095.

In contrast to carbon dioxide, the improved version of the WFM-DOAS data product of column-averaged methane dry air mole fractions presented here, uses simultaneously retrieved  $CO_2$  instead of  $O_2$  as a proxy for the air column because of better cancellation of path length related retrieval errors. This assumes that  $CO_2$  is significantly less variable than methane, and that the optical light paths for the two absorbers are, at least in first order, the same for the two spectral fitting windows which are located close to one another in SCIAMACHY channel 6 (Frankenberg et al., 2006). The column-averaged mole fraction XCH<sub>4</sub> is computed as follows:

$$XCH_4 = \frac{CH_4^{col}}{(CO_2^{col}/CO_2^{mf})}$$
, (5.28)

where  $CH_4^{col}$  is the retrieved absolute methane column (in molecules/cm<sup>2</sup>),  $CO_2^{col}$  is the retrieved absolute  $CO_2$  column (in molecules/cm<sup>2</sup>), and  $CO_2^{mf}$  is the assumed (column-averaged) mole fraction of  $CO_2$  used to convert the  $CO_2$  column into a corresponding dry air column. For  $CO_2^{mf}$  a constant value of 370 ppm is assumed. Therefore, normalising with carbon dioxide introduces a small systematic error associated with the variation of the  $CO_2$  column-averaged dry air mole fractions. This can be improved to a certain extent using modelled  $CO_2^{mf}$  fields, for example from



Figure 5.3: Source and sink detection with column-averaged dry air mole fractions.

the CarbonTracker assimilation system (Peters et al., 2007). A detailed discussion of the impact of assuming a constant carbon dioxide mole fraction follows later in Section 10.3.

# 6 Improved retrieval technique

The latest version of WFM-DOAS, version 1.0 (Schneising et al., 2008, 2009), which was developed within the scope of this thesis, has been significantly improved with respect to its accuracy compared to the previous versions (v0.4x, v0.5) while essentially maintaining its high processing speed ( $\sim$ 1 minute per orbit, corresponding to  $\sim$ 6000 individual measurements, and per gas, on a standard PC). As a result the constant scaling factors of 1.27 and 0.85, which were introduced in the previous versions to correct systematically underestimated CO<sub>2</sub> columns and systematically overestimated O<sub>2</sub> columns, are not needed anymore. These scaling factors used in the previous WFM-DOAS versions were chosen such that the carbon dioxide and oxygen columns were within experimental error close to their expected value of about  $8 \cdot 10^{21}$  molecules/cm<sup>2</sup> and  $4.5 \cdot 10^{24}$  molecules/cm<sup>2</sup>, respectively, for cloudfree scenes with a surface elevation corresponding to sea level. The new version WFM-DOAS 1.0 yields the expected values for the CO<sub>2</sub> and O<sub>2</sub> columns without scaling. Additionally, the solar zenith angle (SZA) dependent bias problem of XCH<sub>4</sub> v0.5 of several percent is significantly reduced (see also the discussion in Buchwitz et al. (2006)). This chapter discusses the main changes in the algorithm with which this quality enhancement was achieved.

### 6.1 Consideration of albedo variability

A significant improvement is the better consideration of albedo variability in the retrieval algorithm. The surface albedo is specifically retrieved in each fitting window separately to consider its wavelength dependence in combination with an extended look-up table of reference spectra. The wavelength dependent surface albedo retrieval is based on comparing the measured sun-normalised radiance at selected wavelengths  $\lambda_0$  in a trans-



Figure 6.1: Albedo retrieval.

parent region of each fitting window where no significant gaseous or particulate absorptions occur (see Figure 6.1), to pre-calculated radiances  $I^{mod}(\lambda_0)$  for different surface albedos. Figure 6.2 shows albedo retrieval results for the fitting windows of oxygen, carbon dioxide, and methane, respectively.



Figure 6.2: Albedos retrieved in transparent regions of the  $O_2$ ,  $CO_2$ , and  $CH_4$  fitting windows, respectively, considering only cloud free (and snow and ice free) ground scenes. Different surface types are clearly distinguishable.

The retrieved surface albedo is used to account for the dependence of the topof-atmosphere radiance on the surface albedo. In comparison, for computational simplicity, the previous WFM-DOAS versions used a constant wavelength independent surface albedo of 0.1. The extended look-up table includes surface albedos of 0.03, 0.1, and 0.3 and an interpolation/extrapolation scheme is used to obtain the model radiance and its derivatives for the retrieved surface albedo in each fitting window.

This improved treatment of surface albedo was essential to remove the need for an  $O_2$  column scaling factor as in previous versions of WFM-DOAS where a constant albedo of 0.1 was assumed and a surface spectral reflectance weighting function (derivative) was included for the  $O_2$  column fit to minimise errors related to the variability of the surface spectral reflectance. However, the albedo weighting function is correlated with the oxygen weighting function which led to systematically overestimated  $O_2$  columns. The new approach removes the need for a weighting function for surface albedo in WFM-DOAS v1.0 and a scaling of the  $O_2$  columns is no longer necessary.

#### 6.2 Surface elevation changes

Besides the better consideration of surface albedo variability, additional progress concerning data quality was achieved by taking surface elevation changes better into account. To this end, an extended look-up table scheme for surface elevation (mean surface pressure) has been implemented. The previous versions of WFM-DOAS used pre-calculated radiances and derivatives for surface elevations of 0 km, 1 km, 2 km, and 3 km in combination with a simple next neighbour approach. Now an extended database covering also an altitude of 4 km is used in combination with an interpolation/extrapolation scheme to determine the radiance and its derivatives appropriate for the average surface elevation of each ground scene. This significantly reduces the associated error of the retrieved columns (as discussed in detail in Section 8.3) which could be as large as a few percent in version 0.4 (Buchwitz et al., 2005a).

The obvious improvement is visualised in Figure 6.3 which shows the difference of retrieved SCIAMACHY and modelled CarbonTracker (details concerning Carbon-Tracker are given in Section 9.1) carbon dioxide as function of surface elevation. It can be seen that the jumps associated with the nearest neighbour approach are no longer existent when interpolating the reference spectra with respect to altitude.



Figure 6.3: Difference of retrieved SCIAMACHY and modelled CarbonTracker carbon dioxide for a specific orbit showing the positive effect of the newly implemented surface elevation interpolation technique. The steps due to the nearest neighbour approach of the previous versions disappear.

#### 6.3 Calibration issues

The current WFM-DOAS version also benefits from the usage of newly calibrated Level 1-Files (spectra) version 5. The SCIAMACHY Level 1 product is a geophysical product, describing the measured spectral radiance in units of photons/s/cm<sup>2</sup>/nm/ steradian as a function of wavelength in units of nanometers. By contrast the previous version's data products were based on the Level 1 version 4 calibrated spectra.

Figure 6.4 visualises the improved calibration using example fits of carbon dioxide for selected ground scenes. As can be seen, the version 1.0 fits are considerably better also providing far more realistic  $CO_2$  vertical columns than the version 0.4 columns which were systematically underestimated and thus have been corrected to first order by scaling with the constant factor 1.27. For clarification the v0.4 column amounts given in the figure are unscaled. Using the new Level 1 product this source of error due to calibration problems of the version 4 spectra is now negligible superseding the need for a scaling factor of the carbon dioxide vertical columns.

Furthermore, a solar zenith angle (SZA) dependent bias problem of  $XCH_4$  v0.5 of several percent could be significantly reduced by using the newly calibrated Level 1b-Files (see also Buchwitz et al. (2006)).



Figure 6.4: Improved  $CO_2$  fit results of WFM-DOAS version 1.0 compared to the previous version 0.4 due to calibration improvement. A scaling factor for the  $CO_2$  vertical columns is no longer needed.

## 6.4 Update of spectroscopy

The spectroscopic data used as input for the radiative transfer model calculations were updated to HITRAN 2004 (Rothman et al., 2005), whereas the previous version was based on the line parameters for  $O_2$ ,  $CO_2$ ,  $CH_4$ , and  $H_2O$  described in HITRAN 2000/2001 (Rothman et al., 2003). HITRAN is an acronym for high-resolution transmission molecular absorption database containing all import spectroscopic parameters for over 1,700,000 spectral lines for a multitude of molecules, including oxygen, carbon dioxide, methane, and water vapour which are used in this study. The HITRAN database has become a widely used international standard in atmospheric remote sensing applications.

	v0.4/0.5	v1.0				
Calibration						
Level 1b	v4	v5				
Reference Spectra						
Spectroscopic Data Included Albedos Included Altitudes	HITRAN 2000/2001 0.1 0km, 1km, 2km, 3km	HITRAN 2004 0.03, 0.1, 0.3 0km, 1km, 2km, 3km, 4km				
Algorithm						
Albedo Retrieval Albedo Treatment Altitude Treatment	– One Fixed Albedo Nearest Neighbour	√ Interpolation Interpolation				

Table 6.1: Summary of the main improvements in WFM-DOAS version 1.0, the different colors correspond to the solution of the following problems of previous versions: CO<sub>2</sub> scaling factor, O<sub>2</sub> scaling factor, and XCH<sub>4</sub> SZA bias.
## 7 Quality flags

In order to separate out ground scenes affected by clouds or poor spectral fits, quality flags marking successful measurements are set for each single measurement, i.e., for each observed ground scene. It has to be pointed out that neither the spectral fitting method nor the quality filtering puts any constraints on the retrieved methane or carbon dioxide columns or mole fractions in the sense that the retrieved or accepted values are forced to lie in a pre-defined range of values.

### 7.1 Carbon dioxide filter criteria

For the column-averaged dry air mole fraction of carbon dioxide, measurements satisfying the following criteria are classified as being good by the WFM-DOAS retrieval and are subsequently used for the analysis described in this thesis:

- The root-mean-square (RMS) of the fit residuum (relative difference between measurement and model after the fit) in the  $CO_2$  fitting window has to be less than 0.25%.
- The RMS of the fit residuum in the  $O_2$  fitting window has to be less than 2%.
- The  $CO_2$  column fit error has to be less than 2.5%.
- The observed scene has to be nearly cloud free. Cloud contaminated ground scenes are identified using a threshold algorithm based on sub-pixel information provided by the SCIAMACHY Polarisation Measurement Device (PMD) channel A detecting enhanced backscatter in the UV as described in Section 7.3. In addition it is required that the retrieved O<sub>2</sub> column has to be larger than 90% of the assumed a-priori O<sub>2</sub> column (determined from surface elevation and the known mixing ratio of O<sub>2</sub>).
- The solar zenith angle (SZA) has to be less than 75° (as the signal gets weaker for high SZAs and the sensitivity to changes of the absorber amount in the boundary layer decreases with increasing SZA (saturation)).
- The ground pixel must be over land (as the signal-to-noise ratio is typically significantly worse over water).

- The ground pixel must be a forward scan pixel (as the horizontal resolution of the backward scan pixel is four times larger (typically 240 km across track compared to 60 km for the forward scan)).
- The surface elevation has to be less than 5 km as higher altitudes are not covered by the current look-up table.
- The ground scene must not exhibit strong aerosol contamination. The aerosol filtering will be described in Section 7.4.

#### 7.2 Methane filter criteria

For the column-averaged dry air mole fraction of methane, the quality criteria classifying good measurements are the following:

- The root-mean-square (RMS) of the fit residuum in the  $CH_4$  fitting window has to be less than 0.4%.
- The  $CH_4$  column fit error has to be less than 4%.
- The RMS of the fit residuum in the CO<sub>2</sub> fitting window has to be less than 0.25%.
- The CO<sub>2</sub> column fit error has to be less than 2.5%.
- The observed scene has to be nearly cloud free, as defined by a retrieved O<sub>2</sub> column larger than 90% of the assumed a-priori O<sub>2</sub> column (determined from surface elevation and the known mixing ratio of O<sub>2</sub>) and a RMS of the fit residuum in the O<sub>2</sub> fitting window of less than 2%.
- The SZA has to be less than 75°.
- The ground pixel must be a forward scan pixel (as the horizontal resolution of the backward scan pixel is four times larger (typically 240 km across track compared to 60 km for the forward scan)).

In case of normalising methane with oxygen, which has been done additionally for the purpose of comparison and to discuss to what extent the SCIAMACHY methane product is influenced by  $CO_2$  (see Chapter 10), the aerosol as well as the PMD cloud filter are added (Sections 7.3,7.4) and only ground pixels over land are considered.

#### 7.3 PMD cloud filter

Since the precision and accuracy requirements on carbon dioxide to be useful for inverse modelling are even higher than for methane and the proxy for the light path  $(O_2)$  is spectrally distant, cloud contaminated scenes are supplementary identified and discarded in case of XCO<sub>2</sub> by using a simple single threshold algorithm on sub-scene information of SCIAMACHY's Polarisation Measurement Device (PMD) channel A covering the spectral region 310-365 nm in the UV (Buchwitz et al., 2005a). As all PMDs, channel A is non-integrating and read out every 1/40 sec. The main channel ground scene is flagged cloud contaminated when at least for one sub-scene the threshold criterium is violated. The cloud identification is based on detecting enhanced backscatter, which might also be caused by enhanced aerosol loading or very high surface reflectivity (e.g., snow and ice), in the mentioned spectral region. To this end, each PMD readout is divided by the cosine of the solar zenith angle to obtain a quantity proportional to top-of-atmosphere reflectivity which is then compared to the pre-defined threshold value.

Channel A was chosen from the six available PMDs because it benefits from the relatively high atmospheric penetration depth of solar UV radiation while having lower sensitivity to Earth's surface than the other PMD channels at the same time.

The PMD channel A cloud identification used in WFM-DOAS is reasonable as it is well correlated with other cloud retrieval algorithms, e.g., the FRESCO+ retrieved effective cloud fraction using  $O_2$  A-band measurements (Koelemeijer et al., 2001). An exemplary comparison of daily SCIAMACHY data is shown in Figure 7.1. As can be seen the allowed PMD reflectivities correspond approximately to cloud fractions of at most 10%.

An analysis revealed that the PMD cloud filter is stable for the considered time period 2003-2005 showing no upward trend of ground scenes flagged cloud free with time due to a potential degradation of the PMD detector.

#### 7.4 Aerosol filtering

Unaccounted variability of aerosols and clouds (including cirrus) in the retrieval is an important error source for  $CO_2$  measurements from space (Tolton and Plouffe, 2001; O'Brien and Rayner, 2002; Kuang et al., 2002; Dufour and Bréon, 2003; Buchwitz and Burrows, 2004; Buchwitz et al., 2005a; Christi and Stephens, 2004; Mao and Kawa, 2004; Houweling et al., 2005; van Diedenhoven et al., 2005; Barkley et al., 2006a; Aben et al., 2006; Bril et al., 2007) as aerosols are highly variable and their optical properties (e.g., vertical profiles of phase function, extinction and scattering coefficients) are not known for each scene observed from satellite.





cloudfree, LOS<30, SZA<7

## SCIAMACHY (FRESCO+) - 20030831



- Figure 7.1: Daily cloudfree scenes as detected by the PMD channel A threshold algorithm used in WFM-DOAS compared to scenes with less than 10% effective cloud
  - fraction as retrieved by the FRESCO+ algorithm using  $O_2$  A-band measurements (Koelemeijer et al., 2001).

This results in aerosol and cloud related errors which are difficult to quantify. Figure 7.2 illustrates that unrealistically enhanced values appearing in the retrieved carbon dioxide mole fraction are correlated with enhanced levels of UV-absorbing aerosols as retrieved by Earth Probe/TOMS (Herman et al., 1997) obtained from http://toms.gsfc.nasa.gov/.

The absorbing aerosol index (AAI) is a measure of the departure of an observed reflectance spectrum

$$\rho_{\lambda} = \frac{\pi L_{\lambda}}{E_0 \cos \theta'} \tag{7.1}$$

(using the notation of Chapter 4; thus,  $\theta'$  is the solar zenith angle) from that of a simulated pure Rayleigh scattering clear-sky scene without aerosols being defined as the positive part of the residue

$$r_{\lambda_{0},\lambda} = -100 \left( \log_{10} \left( \frac{\rho_{\lambda}}{\rho_{\lambda_{0}}} \right)^{obs} - \log_{10} \left( \frac{\rho_{\lambda}}{\rho_{\lambda_{0}}} \right)^{Ray} \right)$$
(7.2)

for two wavelengths  $\lambda < \lambda_0$  in the ultraviolet spectral region. Thus, the AAI depends on the difference of the slopes of observed and simulated Rayleigh reflectances between  $\lambda$  and  $\lambda_0$ .

Aerosol types detected by the TOMS AAI include desert dust, smoke and volcanic ash even over bright surfaces while being insensitive to clouds and weakly UV-absorbing aerosols. During June 2003 the Absorbing Aerosol Index (AAI) is high over the Sahara due to desert dust storms. During this month the SCIAMACHY carbon dioxide data product also shows high values and good correlation with the aerosol index. During November AAI is low and the SCIAMACHY XCO<sub>2</sub> is not enhanced. This comparison shows that the retrieved carbon dioxide mole fraction can exhibit large (few percent) errors in case of strong desert dust storms.

To remove aerosol contaminated retrieved  $XCO_2$  for cases of high aerosol load, primarily over deserts (mainly Sahara), an additional quality criterion for the global analysis of  $XCO_2$  is applied by rejecting ground scenes where the TOMS aerosol index is greater than a specific threshold.

In this context it is interesting to investigate whether the effect of overestimated  $CO_2$  mole fractions in case of strong desert dust storms is dominated by errors of the  $CO_2$  or the  $O_2$  column. Figure 7.3 shows the  $XCO_2$  data product over the Sahara obtained using the simultaneously retrieved  $O_2$  column compared to that derived using model  $O_2$  columns computed from surface pressure obtained from meteorological analysis:

$$O_2^{\text{mod}} = \frac{p^{\text{mod}}}{1013 \,\text{hPa}} \cdot 4.5 \cdot 10^{24} \,\frac{\text{molec}}{\text{cm}^2} \tag{7.3}$$



Figure 7.2: Demonstration of enhanced  $XCO_2$  in the presence of specific aerosols. The left panels shows SCIAMACHY  $XCO_2$  not filtered for aerosol contamination (top: June 2003, bottom: November 2003). The two panels on the right show the Absorbing Aerosol Index (AAI) data product from TOMS/Earth Probe.

Assuming that the computed oxygen column obtained from meteorological (ECMWF) surface pressure is accurate, it can be concluded that the enhanced  $CO_2/O_2(mod)$  ratio over the Sahara must be due to an (at least relative to the surrounding areas) overestimated  $CO_2$  column, which is consistent with the findings of Houweling et al. (2005) who showed by simulated retrievals that aerosol-induced path length enhancements can explain unrealistically enhanced carbon dioxide columns in the presence of desert dust.

Figure 7.3 additionally shows that the  $CO_2$  column error cancels partially when computing the ratio with the measured  $O_2$  columns. Therefore it can be concluded that aerosols due to strong desert dust storms are causing an overestimation of both the  $CO_2$  and  $O_2$  columns but affecting  $CO_2$  to a greater extent so that the errors do not cancel completely in  $XCO_2$ . As can be seen, the  $XCO_2$  field is smoothest (and probably most realistic) if the aerosol filter is applied and if the retrieved  $CO_2$  is normalised using the retrieved  $O_2$  columns due to better cancellation of errors when the retrieved  $O_2$  is used to compute  $XCO_2$ . Therefore, it is concluded that the  $XCO_2$  shown in the bottom left panel is the most accurate of the four  $XCO_2$  data sets shown here.



Figure 7.3: Comparison between two SCIAMACHY  $XCO_2$  data products. On the left hand side the standard  $XCO_2$  data product is shown which is based on normalising the measured  $CO_2$  column by the simultaneously measured  $O_2$  column without (top) and with (bottom) AAI (aerosol) filtering applied. On the right hand side the measured  $CO_2$  is normalised using model  $O_2$  columns obtained from CarbonTracker meteorological (ECMWF) surface pressure.

Figure 7.4 illustrates the aerosol filtering globally, leading to a significantly better agreement with independent global reference data by removing scenes with overestimated  $XCO_2$ , which is obvious when comparing, for example, with CarbonTracker  $XCO_2$  shown in Figure 9.2.

As WFM-DOAS v1.0 uses a single constant aerosol scenario and aerosol variability is only accounted for to first order by the inclusion of a low order polynomial in the WFM-DOAS fit, perceptible deviations under extreme conditions are expected (Buchwitz and Burrows, 2004; Buchwitz et al., 2005a). Other groups use somewhat different but also highly simplified approaches to deal with aerosol variability. For example in FSI/WFM-DOAS (Barkley et al., 2006a,c,b, 2007) three "climatological" aerosol scenarios (maritime, rural, and urban) are used (instead of one as in WFM-DOAS) depending on the location of the satellite footprint. This approach is not considered to be superior compared to the approach presented here as it also



363.5 366.0 368.5 371.0 373.5 376.0 378.5 381.0 383.5 386.0 388.5



does not take aerosol variability fully into account and might introduce additional complications such as discontinuities of the retrieved carbon dioxide near cities and coast lines.

Future studies will show to what extent aerosol related errors can be reduced by taking aerosol variability better into account in the radiative transfer used to determine  $XCO_2$  but at present there is only an identification of aerosols and filtering of the data to remove strongly aerosol contaminated scenes.

For the methane mole fractions aerosol filtering is not necessary because, due to the normalisation with  $CO_2$ , path length related errors cancel to a large extent as a result of neighbouring fitting windows. This is confirmed by the sensitivity study presented in the next chapter.

## 8 Sensitivity and error analysis

#### 8.1 Averaging kernels

In contrast to nadir measurements in the thermal infrared spectral region which are primarily sensitive to middle to upper tropospheric greenhouse gas concentrations, the significant advantage of the near-infrared spectral region is the sensitivity to all altitude levels, including the boundary layer, which is important to get information on regional sources and sinks because the corresponding concentration variations are largest in the lower troposphere near the Earth's surface.

The sensitivity of the SCIAMACHY retrievals to different atmospheric layers is demonstrated by the vertical column averaging kernels (Figure 8.1) which are obtained by applying the WFM-DOAS retrieval algorithm to simulated nadir spectra corresponding to perturbed and unperturbed carbon dioxide and methane vertical profiles. The perturbed profiles differ from the unperturbed ones by adding an additional constant number of the respective molecule at a given altitude z. The averaging kernels are defined as the derivative of the retrieved column with respect to the true column, thus

$$AK(z) = \frac{d\hat{V}}{dV^{t}}(z) = \frac{\hat{V}_{p} - \hat{V}_{u}}{V_{p}^{t} - V_{u}^{t}}(z)$$
(8.1)

where  $V_u^t$  is the true column of the unperturbed vertical profile,  $V_p^t$  is the true column of the perturbed vertical profile, and  $\hat{V}_u$  and  $\hat{V}_p$  are the retrieved columns of the unperturbed and perturbed profiles, respectively.

The retrieval is sensitive to concentration changes at altitudes where the averaging kernels are on the order of 1, thus significantly larger than zero. As can be seen in Figure 8.1 this is in particular true for the boundary layer. While the shape of the averaging kernels is characteristic for the instrument, the spectral region, and the given gas, the absolute values also depend on the retrieval algorithm. The decreasing sensitivity with increasing altitude can be explained by saturation of strong absorption lines not resolved by the instrument associated with different line-shapes at the respective pressure levels (Goody and Yung, 1989). The pressure broadened lines at lower altitudes show less saturation (in the line center) and therefore absorb more effectively exhibiting more sensitivity to concentration changes than the narrower lines in upper parts of the atmosphere.



Figure 8.1: SCIAMACHY/WFM-DOAS CO<sub>2</sub> and CH<sub>4</sub> averaging kernels.

#### 8.2 Instrument noise

The retrieved carbon dioxide, methane, and oxygen vertical columns exhibit a random error due to instrument noise depending on the signal-to-noise ratio and thus on surface albedo and characteristics of the detector of the respective channel. Taking into account the different detector materials in channel 6 below 1590 nm, where the  $CO_2$  fitting window is mainly located, and above 1590 nm (the so called channel 6+), where the  $CH_4$  fitting window is located, results in a theoretical single measurement precision of 0.7% of the retrieved  $CO_2$  column and 1.5% of the retrieved  $CH_4$  column for a typical surface albedo of land of about 0.2 and a solar zenith angle of 50°. The much better signal-to-noise ratio in the  $O_2$  A-band spectral region (around 760 nm in SCIAMACHY channel 4) results in a considerably smaller random error of the  $O_2$  column of about ~0.3%. Therefore, the theoretical single ground pixel retrieval precision due to instrument noise can be estimated to be about 1% for  $XCO_2$  and 1.7% for  $XCH_4$  on average using radiative transfer simulations and the instrument's signal-to-noise performance.

The single ground pixel retrieval precision of the real in-orbit measurements is estimated by determining daily standard deviations of the retrieved  $XCO_2$  and  $XCH_4$  for several locations. Because of the orbit geometry this basically corresponds to the

standard deviation of all the data from a single overpass at around 10:00 a.m. local time. The daily standard deviations determined from all the SCIAMACHY  $XCO_2$  and  $XCH_4$  retrievals at a given location are averaged for all days where at least 10 measurements pass the quality filter in a radius of 350 km around that location. This average standard deviation can be interpreted as an upper limit of the single ground pixel retrieval precision. This analysis was performed for Park Falls (USA), Bremen (Germany), and Darwin (Australia) providing a consistent estimate of the  $XCO_2$  precision error of about 5-6 ppm, respectively, which corresponds approximately to 1.5% and is therewith close to the expected theoretical value. In case of  $XCH_4$  a consistent estimate of the precision error of about 25-30 ppb, respectively, is obtained, which corresponds approximately to 1.5-1.7%, in good agreement with the theoretical estimate of 1.7% given above.

#### 8.3 Albedo and surface elevation

To investigate the sensitivity of WFM-DOAS to albedo changes and the accuracy of the albedo retrieval the algorithm was tested on simulated SCIAMACHY measurements obtained from radiative transfer calculations. Table 8.1 shows the corresponding vertical column retrieval errors of oxygen, carbon dioxide, and methane, respectively, demonstrating the clear improvement compared to the previous versions of WFM-DOAS. Moreover, the albedo retrieval obviously works fine in all three fitting windows showing very good agreement with the true albedo used in the radiative transfer simulation. Because of the improved albedo treatment in WFM-DOAS version 1.0, with albedo retrieval and the extended look-up table interpolation/extrapolation method, the albedo related XCO<sub>2</sub> and XCH<sub>4</sub> errors shown in Table 8.2, which could be as large as a few percent in the previous version, are now significantly reduced and essentially negligible (absolute value  $\lesssim 0.1\%$ ) for typical albedos assumed to be wavelength independent in a given spectral fitting window. These errors of the mole fractions are calculated from the vertical column retrieval errors as follows:

$$\epsilon_{\text{XCO}_2} = \frac{1 + \epsilon_{\text{CO}_2}}{1 + \epsilon_{\text{O}_2}} - 1 \quad , \quad \epsilon_{\text{XCH}_4} = \frac{1 + \epsilon_{\text{CH}_4}}{1 + \epsilon_{\text{CO}_2}} - 1 \quad .$$
 (8.2)

This essentially shows the accurate implementation of the new albedo retrieval and reference spectra interpolation/extrapolation method. However, the albedos of surfaces typically occurring in retrievals of real satellite data can depend significantly on wavelength which is accounted for in the further analysis. Table 8.3 shows the retrieval errors for different natural surface types taking the full spectral albedo dependence (also within the small spectral fitting windows) into account. As can be

		WFMD v1.0 WFMD v0.4/0.5		
A <sup>t</sup>	Â	column ret	trieval error [%]	
02				
0.003	0.003	0.89	-60.14 (-24.87)	
0.03	0.030	0.01	-29.41 (-6.03)	
0.05	0.050	-0.02	-17.10 (-2.03)	
0.08	0.080	-0.01	-5.37 (-0.19)	
0.10	0.100	0.01	0.00 (0.01)	
0.15	0.150	-0.16	9.06 (-0.54)	
0.20	0.200	-0.18	14.76 (-1.41)	
0.30	0.300	0.01	21.66 (-2.84)	
0.40	0.398	0.31	25.81 (-3.75)	
CO <sub>2</sub>				
0.003	0.003	0.63	-10.18	
0.03	0.030	-0.01	-2.59	
0.05	0.050	-0.05	-1.29	
0.08	0.080	-0.04	-0.37	
0.10	0.100	-0.01	-0.01	
0.15	0.150	-0.13	0.55	
0.20	0.200	-0.13	0.90	
0.30	0.300	-0.01	1.39	
0.40	0.399	0.18	1.76	
CH <sub>4</sub>				
0.003	0.003	0.59	-8.82	
0.03	0.030	0.03	-2.16	
0.05	0.050	-0.01	-1.05	
0.08	0.080	0.00	-0.28	
0.10	0.100	0.03	0.02	
0.15	0.150	-0.07	0.49	
0.20	0.200	-0.08	0.79	
0.30	0.300	0.02	1.20	
0.40	0.399	0.18	1.51	

Table 8.1: Retrieved albedos  $\hat{A}$  and vertical column retrieval errors for different true albedos, a solar zenith angle of 50°, and a surface elevation corresponding to sea level for the new WFM-DOAS version 1.0 compared to the previous versions. The values in brackets are valid for retrievals where the albedo weighting function has been included in the fit such as for the WFMD v0.4/0.5 data product by default to reduce albedo related O<sub>2</sub> column errors.

Albedo	CH <sub>4</sub> column error [%]	CO <sub>2</sub> column error [%]	O <sub>2</sub> column error [%]	XCH <sub>4</sub> error [%]	XCO <sub>2</sub> error [%]
0.003	0.59	0.63	0.89	-0.04	-0.26
0.03	0.03	-0.01	0.01	0.04	-0.02
0.05	-0.01	-0.05	-0.02	0.04	-0.03
0.08	0.00	-0.04	-0.01	0.04	-0.03
0.10	0.03	-0.01	0.01	0.04	-0.02
0.15	-0.07	-0.13	-0.16	0.06	0.03
0.20	-0.08	-0.13	-0.18	0.05	0.05
0.30	0.02	-0.01	0.01	0.03	-0.02
0.40	0.18	0.18	0.31	0.00	-0.13

Table 8.2: Results of the error analysis for different constant albedos performed by applying WFM-DOAS version 1.0 to simulated SCIAMACHY spectra. The results are valid for a solar zenith angle of  $50^{\circ}$  and a surface elevation corresponding to sea level.

seen, the retrieval errors are well below one percent for typical surfaces with the exception of  $XCO_2$  in the case of snow where the very high albedo (close to 1) in the  $O_2$  fitting window leads to a somewhat higher error. However, snow- and ice-covered surfaces are typically filtered out as a side-effect of the PMD cloud detection used in the carbon dioxide mole fraction retrieval. Otherwise an observable  $XCO_2$  underestimation would be expected. The albedo related errors for surface types with albedos higher than 0.3 in at least one fitting window can be further reduced by adding additional albedos to the reference spectra in the future.

The retrieval error due to surface elevation (mean surface pressure) variations caused by the pressure dependence of the absorption cross sections is also significantly reduced due to the better consideration of surface elevation changes by using the new altitude interpolation/extrapolation scheme of reference spectra. As was shown qualitatively in Section 6.2 the nearest neighbour approach of the previous WFM-DOAS versions led to quite large errors for surface elevations being right between the values used for the reference spectra computation, e.g., for altitudes of about 0.5 km or 1.5 km. This problem was overcome by the improved surface elevation treatment of WFM-DOAS version 1.0. For a quantitative investigation the retrieval was performed on simulated SCIAMACHY spectra for a surface elevation of 400 m, a solar zenith angle of 50°, and an albedo of 0.1. The vertical column retrieval errors of  $O_2$ ,  $CO_2$ , and  $CH_4$  are listed in Table 8.4 showing an obvious improvement when switching to the new version. The associated errors of the mole fractions using WFM-DOAS v1.0 are 0.3% for XCO<sub>2</sub> and 0.1% for XCH<sub>4</sub>.

Surface type	CH <sub>4</sub> [%]	$\mathrm{CO}_2~[\%]$	O <sub>2</sub> [%]	XCH <sub>4</sub> [%]	XCO <sub>2</sub> [%]
Sand (Entisol)	0.23	0.13	0.03	0.10	0.10
Soil (Mollisol)	0.37	0.41	0.13	-0.04	0.28
Deciduous (Aspen)	-0.01	0.22	0.17	-0.23	0.05
<b>Conifers-Meadow</b>	0.04	-0.01	0.11	0.05	-0.12
Rangeland	0.04	-0.11	-0.04	0.15	-0.07
Open Ocean	0.09	0.06	0.16	0.03	-0.10
Medium Snow	0.65	0.37	1.83	0.28	-1.43

Table 8.3: As Table 8.2 but for the spectral albedos of natural materials shown in Figure 8.2 taken from the ASTER and USGS spectral libraries.



Figure 8.2: Spectral albedos of different natural surface types. Reproduced from the ASTER Spectral Library through the courtesy of the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California (©1999, California Institute of Technology) and the Digital Spectral Library 06 of the U.S. Geological Survey.

	Â	WFMD v1.0 column ret	WFMD v0.4/0.5 rieval error [%]
0,	0.100	-0.49	-4.82
$CO_2$	0.100	-0.16	-2.26
CH <sub>4</sub>	0.100	-0.04	-1.25

Table 8.4: Retrieved albedos and vertical column retrieval errors for a surface elevation of 400 m, a solar zenith angle of 50°, and an albedo of 0.1 for the new WFM-DOAS version 1.0 compared to the previous versions.

#### 8.4 Aerosols

To estimate the retrieval error due to aerosols several aerosol scenarios have been defined (Tables 8.5, 8.6). The default scenario used for the look-up table calculation can be characterised as follows: Maritime aerosol in the boundary layer, tropospheric visibility and humidity 23 km and 80%, respectively, background stratospheric, and normal mesospheric conditions. Besides the rather extreme scenario with strongly enhanced aerosol in the boundary layer (urban aerosol in the boundary layer with visibility of only 2 km and relative humidity of 99%), three additional more typical scenarios are considered (using Mie phase function instead of the Henyey-Greenstein parametrisation used for the look-up table default and the extreme scenario): (i) "OPAC background" consists of continental clean aerosol in the boundary layer and the free troposphere (99.998% water soluble), (ii) "OPAC urban" has continental polluted aerosol in the boundary layer (31.399% water soluble and 68.6% soot) and continental average aerosol (45.79% water soluble and 54.2% soot) in the free troposphere, and (iii) "OPAC desert" consists of desert aerosol (93.19% mineral (nucleation mode) and 6.81% mineral (accumulation mode)) in the boundary layer and the continental clean aerosol type in the free troposphere.

For these three realistic scenarios the  $XCO_2$  sensitivity to aerosols is less than 1%. However, in extreme situations (e.g., very high boundary layer aerosol) the error can be as high as about 5% because the sensitivity in the  $O_2$  A-band is significantly larger in these cases than in the near-infrared spectral region where the  $CO_2$  and  $CH_4$  fitting windows are located. Therefore strongly aerosol contaminated scenes are filtered out as described in Section 7.4. The  $XCH_4$  error due to aerosols is considerably less than 1% for all scenarios even for the extreme one. When normalising methane with oxygen, however, which is occasionally done in the following for comparison purposes or to investigate potential impacts of carbon dioxide on the  $XCH_4$  retrieval, strongly aerosol contaminated scenes have to be filtered out as in case of  $XCO_2$ .

Aerosol scenario		756 nm	1560 nm	1630 nm
LUT default	ASOD:	0.24669	0.17369	0.16981
	AAOD:	0.00291	0.00307	0.00313
OPAC background	ASOD:	0.09353	0.02211	0.01977
	AAOD:	0.00315	0.00293	0.00262
OPAC urban	ASOD:	0.16420	0.04794	0.04414
	AAOD:	0.02373	0.01411	0.01324
OPAC desert	ASOD:	0.22740	0.17568	0.16852
	AAOD:	0.01406	0.00419	0.00402
Extreme in BL	ASOD:	2.12661	0.91676	0.87507
	AAOD:	0.13324	0.07892	0.07829
	RSOD:	0.02674	0.00145	0.00122

Table 8.5: Aerosol scattering (ASOD) and aerosol absorption vertical optical depth (AAOD) in the  $O_2$ ,  $CO_2$ , and  $CH_4$  fitting windows for the aerosol scenarios used in the error analysis. For comparison the Rayleigh scattering vertical optical depth (RSOD) has also been included. The default values used for the WFM-DOAS look-up table (LUT) are given in the first two rows.

Aerosol scenario	CH <sub>4</sub> [%]	CO <sub>2</sub> [%]	O <sub>2</sub> [%]	XCH <sub>4</sub> [%]	XCO <sub>2</sub> [%]
OPAC background	-0.60	-0.73	0.26	0.13	-0.99
OPAC urban	-0.57	-0.70	-0.05	0.13	-0.65
OPAC desert	-0.08	-0.14	-0.49	0.06	0.35
Extreme in BL	-0.89	-1.16	-6.50	0.27	5.71

Table 8.6: Results of the error analysis for various aerosol scenarios. The results are valid for an albedo of 0.1, a solar zenith angle of 50°, and a surface elevation corresponding to sea level.

Subvisual Cirrus	CH <sub>4</sub> [%]	CO <sub>2</sub> [%]	O <sub>2</sub> [%]	XCO <sub>2</sub> [%]	XCH <sub>4</sub> [%]
Albedo 0.1:					
SOD 0.01	-0.33	-0.58	-3.12	2.62	0.25
SOD 0.02	-0.58	-0.78	-6.09	5.65	0.20
SOD 0.03	-0.73	-0.89	-8.91	8.80	0.16
Albedo 0.3:					
SOD 0.01	0.43	0.18	-1.17	1.37	0.25
SOD 0.02	0.92	0.71	-2.31	3.09	0.21
SOD 0.03	1.50	1.33	-3.41	4.91	0.17

Table 8.7: Results of the error analysis for undetected subvisual cirrus clouds at 12 km with different assumed scattering optical depths (SOD) for different surface albedos. The results are valid for a solar zenith angle of 50°, and a surface elevation corresponding to sea level.

#### 8.5 Subvisual cirrus

The retrieval error due to undetected subvisual thin cirrus clouds is hard to estimate because it depends amongst other things on the scattering vertical optical depth, cloud top height, albedo, and the way the cirrus clouds are modelled. In this error analysis cirrus clouds are modelled as a scattering layer of 1 km vertical extent centered at a specific height with a scattering vertical optical depth independent of wavelength which is reasonable because the particle size is much larger than the wavelength. The results for a scattering layer centered at a height of 12 km and different vertical optical depths and surface albedos are listed in Table 8.7 showing that such a scattering layer typically leads to a considerable underestimation of the oxygen vertical columns increasing with increasing optical depth of the layer and decreasing albedo. The specification of a realistic error estimate is complicated because it is uncertain which maximal vertical optical depths are allowed by the quality filter before the fit gets too bad or the cirrus cloud is detected by the PMD cloud algorithm. Nevertheless the residual retrieval error after quality filtering due to subvisual thin cirrus clouds can probably reach several percent for XCO<sub>2</sub> while for XCH<sub>4</sub> the error is well below 1%. Hence, the resulting XCO<sub>2</sub> overestimation has the potential to become rather large in the presence of subvisual thin cirrus clouds not detected by the quality filter especially over dark surfaces.

CH <sub>4</sub> [%]	CO <sub>2</sub> [%]	O <sub>2</sub> [%]	XCH <sub>4</sub> [%]	XCO <sub>2</sub> [%]
1.18	0.04	-0.38	1.14	0.42
1.30	0.17	0.67	1.13	-0.50
0.99	-0.15	-0.55	1.14	0.40
1.25	0.47	0.66	0.78	-0.19
0.34	-0.54	-0.68	0.88	0.14
	CH <sub>4</sub> [%] 1.18 1.30 0.99 1.25 0.34	$\begin{array}{c} {\rm CH}_4[\%] & {\rm CO}_2[\%] \\ \\ 1.18 & 0.04 \\ 1.30 & 0.17 \\ 0.99 & -0.15 \\ 1.25 & 0.47 \\ 0.34 & -0.54 \end{array}$	$\begin{array}{c} {\rm CH}_4[\%] & {\rm CO}_2[\%] & {\rm O}_2[\%] \\ \\ 1.18 & 0.04 & -0.38 \\ 1.30 & 0.17 & 0.67 \\ 0.99 & -0.15 & -0.55 \\ 1.25 & 0.47 & 0.66 \\ 0.34 & -0.54 & -0.68 \end{array}$	$\begin{array}{c c} \mathrm{CH}_{4}\left[\%\right] & \mathrm{CO}_{2}\left[\%\right] & \mathrm{O}_{2}\left[\%\right] & \mathrm{XCH}_{4}\left[\%\right] \\ \\ 1.18 & 0.04 & -0.38 & 1.14 \\ 1.30 & 0.17 & 0.67 & 1.13 \\ 0.99 & -0.15 & -0.55 & 1.14 \\ 1.25 & 0.47 & 0.66 & 0.78 \\ 0.34 & -0.54 & -0.68 & 0.88 \end{array}$

Table 8.8: Retrieval errors resulting from applying WFM-DOAS to various model atmospheres valid for an albedo of 0.1, a solar zenith angle of 50°, and a surface elevation corresponding to sea level. The analysed atmospheres differ from the U.S. Standard Atmosphere used as reference with respect to temperature, pressure, water vapour and methane profiles.

#### 8.6 Profile variability

In order to examine the sensitivity to vertical profile variations of temperature, pressure, and trace gases, simulated spectra for several model atmospheres (extracted from MODTRAN (Berk et al., 1998)) have been generated while the WFM-DOAS look-up table is based on the U.S. Standard Atmosphere. The analysed atmospheres differ from the U.S. Standard Atmosphere with respect to temperature, pressure, water vapour and methane profiles (see Appendix D). The resulting retrieval errors are shown in Table 8.8. As can be seen, the  $XCO_2$  errors are less than 1% for all cases.

The investigation of errors resulting from profile variability has been extended focussing on an error analysis relevant for the  $CO_2$  seasonal cycle. To specify the errors originating from unconsidered variability of temperature and trace gas profiles (WFM-DOAS uses a single profile in each case for the retrieval), simulated spectra have been generated using ECMWF temperature and water vapour profiles as well as carbon dioxide profiles from NOAA's CarbonTracker model (details in Section 9.1). Park Falls was chosen as a reference location for this study because it is assumed to be approximately representative for northern hemispheric mid-latitudes and because the choice of this site is helpful in estimating the error of the retrieved XCO<sub>2</sub> seasonal cycle when comparing with the Park Falls FTS (see Section 9.4).

As one can see in Figure 8.3, the  $CO_2$  and  $O_2$  vertical column errors due to temperature profile variability cancel to a large extent when calculating the  $CO_2$  to  $O_2$  column ratio, i.e., the  $CO_2$  mole fraction, because both absorption bands respond similar to temperature changes. The water vapour profile related error is negligible because the spectral fitting windows have been selected such that interference with water vapour absorption is small. Additionally a weighting function (radiance



Figure 8.3: Results of an error analysis of the SCIAMACHY  $XCO_2$  retrievals based on simulated retrievals focusing on the error of the  $CO_2$  seasonal cycle. For each month simulated spectra have been computed using different vertical profiles of temperature, water vapour, and  $CO_2$ . The time dependent temperature and water vapour profiles are from ECMWF; the  $CO_2$  profiles are from CarbonTracker. The first three panels show the retrieval errors for the  $CO_2$  and  $O_2$  column (in red and blue, respectively) and for  $XCO_2$  (black) due to respective profile variability. The bottom panel shows the total error when all three error sources are combined.

derivative) for water absorption is included in the  $CO_2$  fit and an iteration regarding water vapour is implemented in the algorithm further minimising this error. From the three error sources investigated, the dominating error is the carbon dioxide vertical profile variability error (being defined as the deviation of the retrieved  $XCO_2$  from the true  $XCO_2$ ) which is about 0.8% peak-to-peak (note that this error can be reduced if the  $CO_2$  vertical profile is (approximately) known by taking into account the SCIAMACHY WFM-DOAS  $CO_2$  retrieval averaging kernels, which characterise the altitude sensitivity of the  $CO_2$  retrievals (see Section 8.1)). When all three error sources are considered together, the total  $XCO_2$  retrieval error is 1.0% peak-to-peak. These findings are consistent with a similar error analysis for WFM-DOAS performed by Barkley et al. (2006a) restricted to  $CO_2$  total column retrieval.

#### 8.7 Summary

We have seen that the WFM-DOAS near-infrared retrieval of greenhouse gases benefits from the sensitivity to trace gas concentration changes in all altitude levels including the boundary layer. Besides instrument noise there are several other error sources and sensitivity to them is typically less than 1%.

It can be concluded from the error analysis that the sensitivity of  $XCH_4$  to most of the considered parameters influencing the radiative transfer is smaller when normalising methane with carbon dioxide instead of oxygen because of the much smaller spectral distance of the  $CH_4$  and  $CO_2$  fitting windows and, therefore, better cancellation of errors. Hence, the  $O_2$ -normalised methane product is only used sporadically for comparison and to draw qualitative conclusions.

The error analysis also shows that the  $XCH_4$  obtained using  $CO_2$  has smaller relative errors than the absolute methane columns due to cancellation of errors. Using (assumed error free) surface pressure information from meteorological analysis to convert the measured methane columns to  $XCH_4$ , the relative  $XCH_4$  errors would be (nearly) identical to the relative errors of the  $CH_4$  columns. Therefore estimating the air column using simultaneously measured  $CO_2$  typically results in a higher quality  $XCH_4$  than using, for example, meteorological surface pressure.

The same is mostly true for  $XCO_2$  and the normalisation with simultaneously measured  $O_2$  instead of surface pressure. However, for specific scenarios, the  $XCO_2$  error can also be higher than the  $CO_2$  vertical column error but these scenes are often discarded anyway by the quality filter (e.g., aerosol contamination or snow-and ice-covered surfaces). A remaining potential problem associated with the  $O_2$  normalisation is the presence of subvisual thin cirrus clouds.

# Part III Retrieval Results

## 9 Carbon dioxide results

This chapter is mainly based on the results presented in Schneising et al. (2008). All SCIAMACHY spectra (Level 1b version 5 converted to Level 1c by the ESA SciaL1C tool using the standard calibration) for the years 2003, 2004, and 2005 which have been made available by ESA/DLR, have been processed using the improved retrieval algorithm WFM-DOAS version 1.0.

To assess the quality of the measured WFM-DOAS  $CO_2$  mole fractions comparisons with local and global independent data are performed. In particular, extensive use is made of comparisons with the XCO<sub>2</sub> obtained from the global CO<sub>2</sub> assimilation system CarbonTracker (Peters et al., 2007) which is briefly introduced in the following section.

#### 9.1 Usage of CarbonTracker

CarbonTracker has been developed by NOAA ESRL in cooperation with many partners. CarbonTracker (see also http://www.esrl.noaa.gov/gmd/ccgg/ carbontracker/) is a reanalysis of the recent global surface fluxes of carbon dioxide, as estimated from a large set of atmospheric  $CO_2$  mole fractions produced via a data assimilation system using an Ensemble Kalman Filter technique. The underlying atmospheric transport model TM5 (Krol et al., 2005) with 25 vertical layers is driven by meteorological data from ECMWF and the assimilation has been performed using a resolution of  $6^{\circ} \times 4^{\circ}$ .

The CarbonTracker  $XCO_2$  field as used for this study has been sampled in space and time as the SCIAMACHY satellite instrument measures. The SCIAMACHY altitude sensitivity has been taken into account by applying the SCIAMACHY  $CO_2$ column averaging kernels (Section 8.1) to the CarbonTracker  $CO_2$  vertical profiles using the formula

$$XCO_{2}^{CT} = \frac{1}{p_{0}} \sum_{l} \left( \overline{XCO}_{2}^{l} + AK^{l} (XCO_{2}^{CT^{l}} - \overline{XCO}_{2}^{l}) \right) \Delta p^{l}$$
(9.1)

where *l* is the index of the vertical layer,  $AK^l$  the averaging kernel,  $\overline{\text{XCO}}_2^l$  the a-priori mole fraction (370 ppm in all altitude layers) and  $\text{XCO}_2^{\text{CT}^l}$  the simulated mole fraction of layer *l*.  $\Delta p^l$  is the pressure difference between the upper and lower boundary

of layer l and  $p_0$  denotes surface pressure. The difference between applying or not applying the SCIAMACHY averaging kernels is quite small, typically less than 1 ppm.

Concerning the accuracy of CarbonTracker, NOAA's comparison to about 14,000 independent aircraft vertical profiles sampled mostly over North America shows agreement within one standard deviation of  $\pm 1.9$  ppm over multiple years, distributed as  $\pm 1.5$  ppm in winter, and  $\pm 2.7$  ppm in summer; biases are within 0.5 ppm in each season and nearly zero for the multiyear average (Wouter Peters, NOAA, personal communication; see also the CarbonTracker product evaluation website http://www.esrl.noaa.gov/gmd/ccgg/carbontracker/profiles. php showing agreement within typically  $\pm 4$  ppm). For all comparisons with Carbon-Tracker the SCIAMACHY CO<sub>2</sub> data have been scaled by a constant factor of 1.015 to compensate a small systematic bias between the two data sets, which is, however, uncritical for application in inverse modelling as constant biases can be corrected relatively easily, especially if they are known. A similar low bias is also observed relative to Fourier Transform Spectrometers (see Section 9.4). There are several possible causes for a relatively small overall bias, e.g., errors of the spectroscopic data (e.g., line intensity errors) but also the assumed aerosol scenario as a single aerosol scenario with a relatively high aerosol optical depth is used for the reference spectra.

#### 9.2 Yearly averages

Figure 9.1 shows, as an example, the  $CO_2$  and  $O_2$  total column annual averages for the year 2003. It can be seen that the spatial variations are very similar (correlation coefficient r=0.98) because both gases are long-lived and therefore well mixed in the atmosphere; hence the columns are primarily reflecting Earth's topography.

The small  $CO_2$  source and sink signals one is primarily interested in are hidden in the tiny differences between the  $CO_2$  columns and the  $O_2$  columns. These signals can be made visible by computing  $XCO_2$ , i.e., the column-averaged dry air mole fraction of  $CO_2$  as introduced in Section 5.7, which is the ratio of the  $CO_2$  column and the dry air column. The dry air column is obtained by dividing the  $O_2$  column (shown in the bottom panel) by 0.2095, which is the mixing ratio of  $O_2$  in dry air. The corresponding SCIAMACHY XCO<sub>2</sub> for 2003 is shown in Figure 9.2. For all three quantities derived from SCIAMACHY, the  $CO_2$  and  $O_2$  columns and  $XCO_2$ , the same filtering criteria have been applied.

The resulting annual composite averages for  $XCO_2$ , which meet the classification 'good' defined in Chapter 7, are shown in Figure 9.2 (left hand side panels) compared to the corresponding CarbonTracker  $XCO_2$  shown in the right hand side panels exhibiting qualitatively reasonable agreement between the two data sets although



Figure 9.1:  $CO_2$  (top) and  $O_2$  (bottom) total vertical columns for the year 2003 as retrieved from SCIAMACHY. Both gases are long-lived and therefore well mixed in the atmosphere; hence the columns of the two gases are well correlated (r=0.98) and the spatial patterns primarily reflect the Earth's topography.



Figure 9.2: Three years of SCIAMACHY carbon dioxide column-averaged dry air mole fractions (left) as retrieved by WFM-DOAS version 1.0 (WFMDv1.0) compared to NOAA's CarbonTracker (right) sampled as SCIAMACHY measures. The color scales are different for SCIAMACHY and CarbonTracker to consider the higher variability of the SCIAMACHY XCO<sub>2</sub> (±12.5 ppm) compared to CarbonTracker (±6.0 ppm).

the retrieved  $XCO_2$  spatial pattern is about a factor of two more variable (about  $\pm 12$  ppm for SCIAMACHY compared to about  $\pm 6$  ppm for CarbonTracker).

A significant part of the  $CO_2$  spatial variations shown in Figure 9.2 result from the irregular sampling of the SCIAMACHY  $XCO_2$ . For example, the mid and high latitudes of the northern hemisphere are strongly weighted towards late spring, summer, and early autumn, where  $CO_2$  is known to be much lower than for the (true) yearly average. This uneven weighting is due to the significantly higher cloud cover in winter but also because of larger solar zenith angles and snow coverage. As a result, most of the measurements in winter are automatically filtered out by the implemented quality filtering scheme in these regions.

The largest XCO<sub>2</sub> values in the yearly averages as retrieved from SCIAMACHY

are over the tropical regions. Although CarbonTracker sampled as SCIAMACHY measures also shows regionally elevated  $XCO_2$  over parts of the tropics, the satellite derived  $XCO_2$  is significantly higher, e.g., over central Africa and over the northern part of South America. This may partially be due to retrieval errors caused by undetected subvisual cirrus clouds (see Section 8.5; a detailed discussion of this aspect is given in Section 9.4) which occur frequently over this region (Liu, 2007).

#### 9.3 Annual increase

As can be seen in Figure 9.2, the  $CO_2$  pattern as retrieved from SCIAMACHY is similar for all years but shifted upwards from one year to the next due to a general quite homogeneous increase of the retrieved  $CO_2$  with time. This can also be seen in the CarbonTracker XCO<sub>2</sub>.

Figure 9.3 shows monthly mean composite values of XCO<sub>2</sub> retrieved from SCIA-MACHY, averaged over  $\pm 20^{\circ}$  latitude bands, centred at the latitudes of two selected ground based stations, namely Mauna Loa (20°N) and Mace Head (53°N). The average surface observations at the two stations, based on weekly flask sampling, are also shown (obtained from ftp://ftp.cmdl.noaa.gov/ccg/co2/flask/month/). A quantitative comparison of the surface observations and the column-averaged satellite XCO<sub>2</sub> is not possible because of the different spatiotemporal sampling of the different types of measurements and retrievals resulting in different seasonal cycles with respect to phase and amplitude (Olsen and Randerson, 2004; Warneke et al., 2005). However, a direct comparison of the satellite XCO<sub>2</sub> and the CarbonTracker XCO<sub>2</sub> is possible using the CarbonTracker results obtained by averaging Carbon Tracker in the same way as the satellite observations. Within the two latitude bands, the phase of the XCO<sub>2</sub> seasonal cycle as retrieved from satellite and modelled by CarbonTracker is in good agreement. The retrieved amplitude of XCO<sub>2</sub> is however somewhat larger, especially in the latitude band centred at Mauna Loa, with typical deviations being within 2 ppm (0.5% of 380 ppm). The surface observations and CarbonTracker show that the amplitude of the  $CO_2$  seasonal cycle is larger at higher latitudes, i.e., at the latitude of Mace Head, 53°N, compared to the latitude of Mauna Loa, 20°N. This increase of the amplitude of the CO<sub>2</sub> seasonal cycle with increasing latitude is also observed by the satellite. As also shown, the annual CO<sub>2</sub> increase, retrieved by the satellite, is in reasonable agreement with CarbonTracker and similar to the increase observed by the two ground stations, being on the order of 1-3 ppm/year depending on time and latitude. This demonstrates that it is possible to observe the long-term increase of CO<sub>2</sub> from space. From the comparison with CarbonTracker one can conclude that the systematic error of the annual increase as obtained from the satellite data is less than about 1 ppm/year.



Figure 9.3: Comparison between satellite and CarbonTracker XCO<sub>2</sub> for two latitude bands. The top panels show a comparison of seasonal averages (based on monthly mean anomalies smoothed using a 3 months running average). Shown is the retrieved XCO<sub>2</sub> (blue; left axis) and the CarbonTracker XCO<sub>2</sub> (green; left axis) for two latitude bands of width  $\pm 20^{\circ}$  centred at a latitude of 19.53°N corresponding to Mauna Loa, Hawaii, USA, (left) and a latitude of 53.33°N corresponding to Mace Head, Ireland (right). Also shown are the CO<sub>2</sub> measurements based on flask sampling (red; right axis) at the two stations Mauna Loa (MLO; 19.53°N, -155.58°E, altitude: 3397 m) and Mace Head (MHD; 53.33°N, -9.90°E, altitude: 25 m). The bottom panels show the corresponding yearly mean anomalies as horizontal lines. For each data set the difference between two contiguous years has been computed (2004-2003 and 2005-2004) and the corresponding numbers are given in the bottom panels. They correspond to the year-to-year CO<sub>2</sub> increase in the corresponding latitude band (first two rows; for SCIAMACHY (blue) and CarbonTracker (green)) or locally at the two ground stations (last row; for the ground stations (red)).

The observed  $CO_2$  increase is also demonstrated by the linear fits shown in the hemispherical comparison in Figure 9.5, which are almost identical to CarbonTracker for both hemispheres, and amounts to about 1.0% from the beginning of 2003 to the end of 2005. In this context it is important to point out, as already explained earlier, that no a-priori information is used about increasing  $CO_2$  in the retrieval procedure.

#### 9.4 Seasonal cycle

To validate the retrieved XCO<sub>2</sub> data, the SCIAMACHY WFM-DOAS version 1.0 XCO<sub>2</sub> has been compared with Fourier Transform Spectrometer (FTS) measurements performed at Park Falls, Wisconsin, USA (Washenfelder et al., 2006) (obtained from http://www.tccon.caltech.edu/) and at Bremen, Germany (Macatangay et al., 2008). Figure 9.4 shows the comparison between the FTS and SCIAMACHY data sets for both locations based on monthly averages. For the XCO<sub>2</sub> data from SCIAMACHY a radius of 350 km around the measurement site has been selected and the monthly composite is made of XCO<sub>2</sub> data classified as 'good', which fall within this region. The data are plotted as anomalies, i.e., with SCIAMACHY and FTS mean values subtracted (on average the SCIAMACHY data are about 1-2% lower than FTS; the exact biases are given in Figure 9.4, see d%). To maximise the number of SCIAMACHY data points a slightly relaxed WFM-DOAS quality criterion is used (allowing an  $O_2$  fit residuum RMS up to 0.025 instead of the standard value of 0.02). As can be seen, despite the larger scatter of the single measurement of SCIAMACHY  $XCO_2$  good agreement is obtained for the monthly composite averages with respect to the amplitude and the phase of the seasonal cycle of  $CO_2$  over Park Falls. The correlation coefficient between the two data sets is 0.94. For the standard quality filtering with somewhat less data points available for comparison, the correlation coefficient is 0.88. The agreement with the FTS in Bremen is somewhat worse (r=0.73) most likely because of the larger variability of the atmospheric CO<sub>2</sub> in northern Germany with many local sources compared to Park Falls. Assuming that the time dependence of the total peak-to-peak XCO<sub>2</sub> measurement error from the error analysis in Section 8.6 is perfectly correlated with the CO<sub>2</sub> seasonal cycle, which is not exactly the case, the upper bound of the error of the amplitude of the measured CO<sub>2</sub> seasonal cycle due to the examined error sources is estimated to be 0.5% or 2 ppm (half of the total  $XCO_2$  peak-to-peak measurement error determined in Section 8.6).

Similar results have been reported for a comparison of SCIAMACHY  $CO_2$  retrieved using FSI/WFM-DOAS (Barkley et al., 2007) with the Park Falls FTS data. Based on a comparison of daily data, Barkley et al. (2007) report correlation coefficients in



Figure 9.4: Comparison of the satellite XCO<sub>2</sub> (blue) with ground based Fourier Transform Spectroscopy (FTS) measurements (red) for Park Falls, Wisconsin, USA (top), and Bremen, northern Germany (bottom). Also included are corresponding CarbonTracker results (green). Shown are comparisons of XCO<sub>2</sub> anomalies, i.e., the corresponding mean values have been subtracted. All quality-filtered SCIA-MACHY measurements within a radius of 350 km around the ground station are considered for the comparison. The thin light blue vertical bars correspond to the standard deviation of the SCIAMACHY data within a given month, i.e., correspond to the measured single ground pixel XCO<sub>2</sub> variability. The thicker (darker) blue vertical bars are an estimate of the statistical error of the SCIAMACHY monthly mean  $XCO_2$ . The red bars show the standard deviation of the FTS data. The following numbers have been computed based on the monthly averages: d%is the mean difference SCIAMACHY-FTS in percent, s% denotes the standard deviation of the difference in percent, and r is the correlation coefficient. Note that these numbers are valid for the absolute  $XCO_2$ , i.e., not for the anomalies, and for SCIAMACHY XCO<sub>2</sub> which has not been scaled by 1.015 (therefore d%quantifies the systematic bias of the SCIAMACHY XCO<sub>2</sub> relative to the FTS).

the range 0.36-0.73 (their Table 1) depending on spatial collocation with typically higher correlation for the more relaxed spatial collocation limits. For monthly mean data Barkley et al. (2007) also report a correlation coefficient of 0.94 as found here for WFM-DOAS. Similar remarks apply to the 1-2% low bias of the SCIAMACHY XCO<sub>2</sub> relative to the Park Falls FTS. Furthermore, also the scatter of the single ground pixel XCO<sub>2</sub> retrievals of the two independently generated SCIAMACHY data sets is similar.

A hemispheric comparison of the WFM-DOAS version  $1.0 \text{ XCO}_2$  with Carbon-Tracker based on daily data is shown in Figure 9.5. As can be seen, the retrieved  $\text{XCO}_2$  seasonal cycle over the northern hemisphere shows good agreement with CarbonTracker (r=0.86). The northern hemispheric amplitude of the seasonal cycle retrieved by SCIAMACHY (6 ppm) is however somewhat larger than for Carbon-Tracker (4 ppm) which is consistent with the findings for the latitude bands around the two northern hemispherical ground-stations considered in the previous section.

The seasonal variation, as measured by SCIAMACHY, is however significantly different for the southern hemisphere concerning both amplitude (4-5 ppm for SCIAMACHY compared to 1-2 ppm for CarbonTracker) as well as phase. Olsen and Randerson (2004) report a seasonal amplitude of  $\sim$ 3 ppm for southern hemispheric Africa and South America derived from independent model simulations. Figure 9.5 shows that the SCIAMACHY XCO<sub>2</sub> over the southern hemisphere is significantly noisier (larger scatter of the daily means) compared to the northern hemisphere. This is because of the smaller (ice and snow free) landmass in the southern hemisphere, to which the SCIAMACHY data are restricted, resulting in less data available for averaging. This may contribute to the larger differences to CarbonTracker over the southern hemisphere compared to the northern hemisphere but probably cannot explain the significantly different seasonal cycles. Figure 9.6 shows the column amounts of SCIAMACHY carbon dioxide and oxygen in comparison to CarbonTracker (computed from surface pressure and  $CO_2$  mole fraction). The deviations from CarbonTracker of the column amounts have a very similar structure in the northern hemisphere and cancel to a large extent when computing the mole fraction XCO<sub>2</sub> leading to the good agreement demonstrated in Figure 9.5. In the southern hemisphere the small additional negative offset in both columns cancels perfectly when computing the ratio while the deviation of the retrieved SCIAMACHY XCO<sub>2</sub> seasonal variations from CarbonTracker is primarily due to a systematic underestimation of the retrieved O<sub>2</sub> columns during southern hemispheric summer (December/January).

The main reason for the deviation of the retrieved carbon dioxide mole fractions in the southern hemisphere is most probably the higher weight on ground scenes with occurrences of subvisual cirrus clouds (scattering optical depth less than about 0.03) which are a potential significant error source leading to a possible



Figure 9.5: Comparison of the SCIAMACHY (black) and CarbonTracker (red) XCO<sub>2</sub> for the northern hemisphere (top), the southern hemisphere (middle) and for the interhemispheric XCO<sub>2</sub> difference (bottom). For the comparison both the daily SCIAMACHY and CarbonTracker data have been gridded on a common  $0.5^{\circ} \times 0.5^{\circ}$  latitude/longitude grid. The symbols show the daily average of all coincident grid cells in the corresponding hemisphere. For SCIAMACHY all measurements have been averaged for which the WFMDv1.0 quality flag indicates a 'good' measurement. The solid lines represent a 90 days running average and the straight lines the corresponding linear fits further demonstrating the increase of XCO<sub>2</sub> with time. For each hemisphere the following numbers have been computed based on the (not smoothed) daily averages: d% is the mean difference SCIAMACHY–CarbonTracker in percent, s% denotes the standard deviation of the difference in percent, and r is the correlation coefficient. Note that the SCIAMACHY XCO<sub>2</sub> has been scaled with 1.015 to compensate for an approximately 1.5% low bias relative to CarbonTracker (as demonstrated by d%which is essentially zero).



Figure 9.6: As Figure 9.5 but for the column amounts of carbon dioxide (left) and oxygen (right). The SCIAMACHY  $CO_2$  has been scaled with 1.015. The deviations of the  $CO_2$  and  $O_2$  columns from CarbonTracker have a very similar structure in the northern hemisphere (top) and cancel to a large extent when computing the mole fraction  $XCO_2$  leading to the good agreement between SCIAMACHY and CarbonTracker demonstrated in the previous figure. In the southern hemisphere (bottom) the small additional negative offset in both columns cancels nearly perfectly when computing the ratio.

overestimation of the carbon dioxide mole fractions due to the  $O_2$  normalisation (see Section 8.5). Actually, the difference of the retrieved and modelled seasonal cycle over the southern hemisphere with maximum in December/January and minimum in July/August is highly correlated (r=0.94) with the strong seasonal variations of the subvisual cirrus fraction (approximately sampled as SCIAMACHY measures) as concluded using preliminary subvisual cirrus retrievals (provided by E. Martins, LMD/IPSL, France; Martins et al., Subvisual cirrus clouds at global scale from CALIPSO lidar observations, poster presented at EGU 2008, Vienna, Austria) based on Level 1 v2.01 CALIPSO data (see Figure 9.7). This analysis is based on the assumption that the broad scale features (e.g., monthly hemispheric averages) of the subvisual cirrus occurrences are representative also for other years as the CALIPSO data set is covering a different time period (June 2006 - March 2008).

Another possible contribution to the deviation of the resulting SCIAMACHY XCO<sub>2</sub>



Figure 9.7: Hemispherical correlation of SCIAMACHY-CarbonTracker XCO<sub>2</sub> with CALIPSO subvisual thin cirrus fraction approximately sampled as SCIAMACHY measures based on monthly averages. Whereas for the northern hemisphere (top) the subvisual cirrus fraction is rather constant throughout the year, the strong seasonal variations in the southern hemisphere (bottom) are highly correlated with the difference of the retrieved and modelled XCO<sub>2</sub> seasonal cycle.

seasonal variations from CarbonTracker in the southern hemisphere could be a SZA (or airmass) dependent error resulting for example from neglecting polarisation in the radiative transfer (Natraj et al., 2007) or from errors in the spectroscopic data, e.g., errors of the air-broadened half width of the  $CO_2$  and/or  $O_2$  absorption lines, as discussed in Washenfelder et al. (2006) for the Park Falls  $XCO_2$  FTS measurements. Such kind of errors can contribute to the differences shown in Figure 9.5 but probably cannot fully explain the difference to CarbonTracker over the southern hemisphere because of the much better agreement with CarbonTracker over the northern hemisphere. If a SZA dependent error for example due to errors in the spectroscopic data would be the only reason for the difference of the SCIAMACHY and CarbonTracker seasonal cycles, then the difference should be similar for both hemispheres except for a six months phase shift. This however is not the case.

Nevertheless, spectroscopic errors may contribute to the differences shown in Figure 9.5 and the sensitivity of the retrieved  $XCO_2$  to changes in the  $CO_2$  and  $O_2$  absorption line width is estimated. Why can line width errors result in a SZA dependent  $CO_2$  or  $O_2$  column retrieval error? This can be explained by increasing "saturation" of the depth of non-resolved strong absorption lines with increasing absorber amount along the light path (Goody and Yung, 1989). Here saturation

refers to the decrease of the sensitivity of the (logarithm of the) measured spectrum to changes in the absorber amount along the light path, for example due to an increasing SZA. As a wider line shows less saturation (in the line center) compared to a narrower line (assuming identical line intensities and line shape functions), and because the SZA dependence of the saturation will be different for the two lines, a line width error may result in a SZA dependent retrieval error. Therefore one typically would expect an underestimation (overestimation) of the retrieved column which increases with increasing SZA, if the line width is in reality narrower (wider) than assumed for the retrieval (a narrower monochromatic line is deeper compared to an equivalent wider line, but if the lines are strong and not resolved, the opposite is true after convolution with the instrument function). The discussed effects are illustrated by supplementary material in Appendix E. To quantify this error retrievals based on simulated spectra for a range of solar zenith angles for different assumed air-broadened line width errors were performed (assuming that the width of all lines change identically by a certain percentage). The reported values are for the two extreme solar zenith angles, namely 15° (which is approximately the lowest SZA encountered by SCIAMACHY) and 75° (the upper limit accepted for this study). If all CO<sub>2</sub> lines would (in reality) be narrower by 1% compared to the air-broadened line widths currently assumed for retrieval (HITRAN 2004, (Rothman et al., 2005)), this would result in retrieved  $CO_2$  columns being underestimated by ~0.4% for a SZA of  $15^{\circ}$  and by ~0.5% for a SZA of  $75^{\circ}$ , i.e., the underestimation increases with increasing SZA, in agreement with the discussion given above, by 0.1% for  $CO_2$ . For  $O_2$  a larger offset, but a negligible SZA dependence compared to  $CO_2$  is found. This means that the SZA dependent part of the XCO<sub>2</sub> error appears to be dominated by the SZA dependent part of the CO<sub>2</sub> column error, i.e., 0.1% if the line widths would be off by 1%. This investigation was repeated for a range of line width errors and SZAs with the result that the SZA dependent part of the XCO<sub>2</sub> error depends to a good approximation linearly on the assumed line width error resulting in an approximately 0.5 ppm XCO<sub>2</sub> error (peak-to-peak) per 1% line width error (the results for Lauder, New Zealand, are shown in Figure 9.8). This means that the differences to CarbonTracker over the southern hemisphere of about 6 ppm peak-to-peak would correspond to an air-broadened line width error of 12% which is higher, but not very much higher, than the uncertainty of the spectroscopic data which are 5-10% for  $CO_2$  (2-5% for  $O_2$ ). The retrieved  $XCO_2$  over the southern hemisphere (or, more precisely, the difference to CarbonTracker) is (anti-)correlated with the SZA, which has a maximum in winter, i.e., in the middle of the year. This is not true, however, for the northern hemisphere, as the difference to CarbonTracker is not symmetric with respect to the middle of the year. From this one can conclude that a SZA dependent error, for example due to spectroscopic errors, may contribute significantly to the differences between the SCIAMACHY and CarbonTracker XCO<sub>2</sub>



Figure 9.8: Sensitivity of the retrieved SCIAMACHY  $XCO_2$  with respect to the  $CO_2$  air-broadened line width for Lauder, New Zealand. Each curve corresponds to a different assumed error of the air-broadened line width. The blue curve, for example, corresponds to a line width error of 5% (g\*0.95 means that a true line width is assumed which is 0.95 times the line width assumed for the  $XCO_2$  retrieval). All errors are shown as percentage errors (negative values correspond to an underestimation of the retrieved  $XCO_2$ ) and as anomalies, i.e., the mean value of each curve has been subtracted to highlight the time (SZA) dependence of the potential retrieval error (Figure: M. Reuter).

shown in Figure 9.5 but cannot explain all the differences.

Figure 9.9 shows global bi-monthly maps of the  $XCO_2$  spatial pattern observed when sampling the seasonal cycle during its (northern hemispheric)  $XCO_2$  maximum and minimum time periods. Significant seasonal variability is visible in both the SCIAMACHY and the CarbonTracker data. This variability of the  $CO_2$  spatial pattern is dominated by the seasonal uptake and release of  $CO_2$  by the northern hemisphere terrestrial biosphere, resulting in much lower  $XCO_2$  during July/August compared to May/June in the northern hemispheric mid and high latitudes covered by, e.g., the boreal forests. Figure 9.9 shows that both data sets, SCIAMACHY and CarbonTracker  $XCO_2$ , are clearly correlated. The SCIAMACHY data show however significantly larger variability; for this reason two different color scales have been used for Figure 9.9 (±14 ppm for SCIAMACHY compared to ±9 ppm for CarbonTracker).


Figure 9.9: Bi-monthly averages of the SCIAMACHY  $XCO_2$  (left) compared to CarbonTracker (right). Shown are only those measurements for which the WFM-DOAS quality flag indicates a good measurement. Note that different color scales have been used for SCIAMACHY (±14 ppm) and CarbonTracker (±9 ppm).

## 9.5 Regional pattern

To enable a more detailed comparison on the regional scale, Figures 9.10 and 9.11 show monthly composite averages of the satellite data and CarbonTracker over large parts of the northern hemisphere, namely USA, Canada and Eurasia. The horizontal resolution of the maps shown in Figures 9.10 and 9.11 is  $7^{\circ} \times 7^{\circ}$ . The data are shown as anomalies, i.e., the mean value has been subtracted for each map to be able to better compare the spatial pattern. As can be seen, the two independent XCO<sub>2</sub> data sets are clearly correlated in space and time indicating that the satellite data capture spatiotemporal atmospheric CO<sub>2</sub> variability on a regional scale. Many of the larger scale features which show up in the CarbonTracker XCO<sub>2</sub> are also visible in the satellite data, for example the extended region of low XCO<sub>2</sub> over eastern Canada in August 2005 and the relatively high XCO<sub>2</sub> over the



## USA & Canada (mid-west/east)

Lat: 25 to 60, Lon: -110 to -65

Figure 9.10: The spatial pattern of XCO<sub>2</sub> over parts of the United States of America and Canada. The XCO<sub>2</sub> field is shown here as anomaly, i.e., the XCO<sub>2</sub> mean value has been subtracted for each panel. The first column shows the XCO<sub>2</sub> as retrieved from SCIAMACHY. The second column shows the CarbonTracker XCO<sub>2</sub> using an appropriate (different) color scale. The last column also shows the CarbonTracker XCO<sub>2</sub> but using the same color scale as has been used for the satellite data. The red rectangles indicate the spatial positions of observation sites used in CarbonTracker. The rows correspond to different months of the year 2005. The spatial resolution is  $7^{\circ} \times 7^{\circ}$ . The root mean square (RMS) differences between SCIAMACHY and CarbonTracker for the region shown are: July: 2.3 ppm (0.6%), August: 2.2 ppm (0.6%), and September: 2.9 ppm (0.8%).



Figure 9.11: As Figure 9.10 but for Europe, Asia and parts of northern Africa. The RMS differences between SCIAMACHY and CarbonTracker for the region shown are: July: 4.3 ppm (1.2%), August: 4.0 ppm (1.1%), September: 5.0 ppm (1.3%).

southern USA in particular in July and August. There are however also significant differences. The differences with respect to CarbonTracker shown in Figures 9.10 and 9.11 cannot be explained by a possible SZA dependent retrieval error discussed in the previous section, as the variation of the SZA is small for the maps shown in Figures 9.10 and 9.11 (especially in the east to west direction where the SZA is essentially constant) and because only  $XCO_2$  anomalies are shown, i.e., the  $XCO_2$  mean value (which could be affected by a SZA dependent error) has been subtracted for each map. Typically the retrieved variability in the SCIAMACHY data product is about 4 ppm (~1% of 380 ppm) higher compared to CarbonTracker. But depending on time and location the differences can exceed 8 ppm. Similar conclusions can be drawn for other time periods (2003 and 2004) and other regions (e.g., South

America), not shown here. A clear interpretation of the differences to CarbonTracker cannot be offered at present. As discussed in Section 9.1 the estimated accuracy of CarbonTracker is about a few ppm. In the error analysis of the WFM-DOAS retrieval algorithm presented in Section 8 several error sources have been identified which may contribute to the overall error of a single measurement. Most of the individual errors are typically less than 1% for a single measurement but the results shown in Figures 9.10 and 9.11 are averages over many individual measurements. The random error (precision) is probably very small, much smaller than 1%, but it is difficult to reliably estimate the systematic error which remains after averaging many individual measurements; the overall systematic error can be smaller but also larger than 1%. One can however assume that the errors of the CarbonTracker and the satellite  $XCO_2$  are uncorrelated. In this case the 1-3% systematic differences between the satellite and the CarbonTracker XCO<sub>2</sub> anomalies may be interpreted as an estimate of the relative accuracy of the satellite XCO<sub>2</sub>. This difference however also includes modelling errors. Based on this one may conclude that the relative accuracy of the satellite  $XCO_2$  is about 1-2%.

In order to determine if regionally elevated CO<sub>2</sub> originating from anthropogenic CO<sub>2</sub> emissions can be potentially detected, all the SCIAMACHY XCO<sub>2</sub> retrievals for the years 2003-2005 are averaged. Figure 9.12 shows the resulting map (resolution  $0.5^{\circ} \times 0.5^{\circ}$ ) for Germany and surrounding countries (top left panel). As can be seen, the SCIAMACHY XCO<sub>2</sub> correlates reasonably well with population density (CIESIN/CIAT, 2005) and EDGAR anthropogenic CO<sub>2</sub> emissions (EDGAR 3.2 Fast Track 2000 data set (32FT2000) (Olivier et al., 2005)). All three data sets show an extended region of high values covering the region central western Germany and parts of the Netherlands and Belgium, in the following referred to as the "Rhine-Main area". Similarly, enhanced  $CO_2$  is also visible over other anthropogenic source regions such as the East Coast of the United States exhibiting enhanced values along the highly urbanised and industrialised coastal area from Boston, Massachusetts, to Washington, D.C. when three years of data are averaged. Drawing on the example of Central Europe, Figure 9.12 shows that the retrieved regional XCO<sub>2</sub> enhancement over the Rhine-Main area is on average 2.7 ppm (0.7%) as concluded by comparing the mean values in the two rectangular regions approximately representing the Rhine-Main area (red) and a reference background area (green) shown in Figure 9.12 (top left panel).

In this context it has to be pointed out that there is of course not a simple one to one relationship between the retrieved  $XCO_2$  enhancement and anthropogenic emissions because the signal is a mixture of the latter, (residual) biogenic features (mainly due to the imperfect sampling) and possible retrieval errors. Therefore the  $CO_2$  seasonal cycle in combination with inhomogeneous sampling as well as path length issues, e.g., aerosol variability, might contribute to the observed pattern.



Figure 9.12: SCIAMACHY XCO<sub>2</sub> over Germany and the U.S. East Coast (left,  $0.5^{\circ} \times 0.5^{\circ}$  gridded, scaled with 1.015) during 2003-2005 compared to population density (middle) (CIESIN/CIAT, 2005) and anthropogenic CO<sub>2</sub> emissions (right, EDGAR 32ft2000,  $1^{\circ} \times 1^{\circ}$ ) (Olivier et al., 2005). Also shown are the regions used to quantify the regional CO<sub>2</sub> enhancement over the Rhine-Main area (red and green rectangle).

What is the expected anthropogenic  $XCO_2$  signal? In Palmer et al. (2008) maps of the contribution of North American anthropogenic CO<sub>2</sub> emissions to monthly mean CO<sub>2</sub> column-averaged mixing ratios over the U.S. are shown derived using the GEOS-Chem model (their Figure 4, left hand side panels) for April-September 2003. The model has been sampled as SCIAMACHY (using a filtering of the SCIAMACHY retrievals as implemented in the FSI-WFM-DOAS algorithm which is (although similar) independent of the algorithm and results shown here). In that paper it is shown that especially over the highly populated areas along the U.S. East Coast the anthropogenic XCO<sub>2</sub> enhancement often exceeds 1 ppm and often reaches 2 ppm at the model resolution of  $2.0^{\circ} \times 2.5^{\circ}$ . Although the EDGAR CO<sub>2</sub> emissions along the U.S. East Coast are comparable with the emissions in the Rhine-Main area (typically the emissions are in the range 30-70 Tg/year per  $1^{\circ} \times 1^{\circ}$  grid cell over the highly populated areas) the two regions may not be exactly comparable. For Europe, Houweling (2008) has used CarbonTracker at  $1^{\circ} \times 1^{\circ}$  resolution and concludes that 1 ppm over the Rhine-Main area is the maximum enhancement to be expected. Both estimates based on model simulations at relatively high spatial resolution are lower than the 2.7 ppm enhancement shown in Figure 9.12.



Figure 9.13: Illustration of the examined contributions of inhomogeneous sampling in combination with seasonal  $CO_2$  variations (top, ratio SCIA-MACHY/CarbonTracker and mean daily SCIAMACHY anomaly) and path length errors (bottom, SCIAMACHY methane normalized by  $O_2$  and MODIS/Terra aerosol optical depth at 550 nm approximately sampled as SCIAMACHY measures).

Because of the mismatch of the resolutions, correlations between SCIAMACHY  $(0.5^{\circ} \times 0.5^{\circ})$  and CarbonTracker (4° latitude × 6° longitude) regarding sub-grid XCO<sub>2</sub> features can be used to identify the contribution of sampling in connection with seasonal variations and the CO<sub>2</sub> increase with time. Assuming that Carbon-Tracker captures the seasonal cycle well and does not resolve the features under consideration the biogenic (seasonal cycle) influence can be minimised by analysing the daily ratio SCIAMACHY/CarbonTracker. Another independent approach to this end is the averaging of daily anomalies (obtained by subtracting the mean value of the SCIAMACHY XCO<sub>2</sub> from all the daily observations over the region of interest before averaging). The corresponding comparison for Central Europe is illustrated in the upper panels of Figure 9.13. As can be seen, the pattern of enhanced values

over the Rhine-Main region is still clearly visible in both data sets indicating that this particular feature is more than coincidence. A quantitative analysis based on the two regions of Figure 9.12 reveals that the regional enhancement is nearly unchanged if the seasonal variations are filtered out indicating that the contribution of inhomogeneous sampling to the observed pattern over the Rhine-Main area is small. By contrast the elevated  $CO_2$  retrieved over northern Germany and southern Denmark which is not well correlated with population density and the EDGAR  $CO_2$  emissions actually disappears or is less pronounced in the mean daily anomaly and SCIAMACHY/CarbonTracker ratio, respectively, indicating that this retrieved  $CO_2$  enhancement is probably an effect of inhomogeneous sampling.

The analysis of the contribution of path length induced errors to the observed pattern, e.g., caused by residual aerosol over urban areas missed by the quality filtering, is much more difficult as the impact of aerosol depends on the amount, height, shape, and size distribution of the particles, which are unknown. If one assumes OPAC background aerosol (aerosol optical depth of 0.19 at 550 nm) with the exception of OPAC urban aerosol (additional pollution in the boundary layer and the free troposphere leading to an aerosol optical depth of 0.38 at 550 nm) over the urbanised and industrialised areas under consideration (both scenarios are described in Section 8.4) one would expect an overestimation of 0.11% (about 0.5 ppm) taking the realistic albedos in the different fitting windows in this region into account (see Table 9.1). Although the choice of these aerosol scenarios seems reasonable one may argue that the real error is larger because the above estimate is derived from simulated measurements assuming certain aerosol characteristics. To estimate the contribution of aerosols from real SCIAMACHY data XCH, normalised by O<sub>2</sub> is analysed because, in principle, path length related errors should affect  $XCO_2$  and  $XCH_4(O_2)$  similarly due to the O<sub>2</sub> normalisation and the neighbouring fitting windows of CO<sub>2</sub> and CH<sub>4</sub> which is also confirmed by the error analysis and the estimated theoretical aerosol induced overestimation discussed above (see also Table 9.1). Thus, path length errors might be identified via correlations between  $XCH_4(O_2)$  and  $XCO_2$ . However, this is only approximately true as methane has its own variability. The bottom left panel of Figure 9.13 shows that there is no obvious one to one correlation of  $XCH_4(O_2)$  with the retrieved enhanced  $XCO_2$ pattern discussed above (although part of the elevated CO<sub>2</sub> over the Rhine-Main area may be due to aerosol in particular over the region south of Cologne and parts of northern Belgium where  $XCH_4(O_2)$  is also enhanced). Similar conclusions can be drawn from the comparison with MODIS/Terra aerosol optical depth at 550 nm also shown in Figure 9.13. This gives evidence that aerosol related errors may contribute to the elevated CO<sub>2</sub> retrieved over the Rhine-Main area but cannot entirely explain the retrieved CO<sub>2</sub> pattern over this anthropogenic source region. This alternative  $XCH_4(O_2)$  approach using the two regions (Rhine-Main and background) from the

Aerosol scenario (Ruhrgebiet)	CH <sub>4</sub> [%] (A 0.16)	CO <sub>2</sub> [%] (A 0.14)	O <sub>2</sub> [%] (A 0.20)	XCO <sub>2</sub> [%]	XCH <sub>4</sub> (O <sub>2</sub> ) [%]
OPAC urban OPAC background	$-0.73 \\ -0.88$	$-0.82 \\ -0.97$	-0.43 -0.47	-0.39 -0.50	-0.30 -0.41
overestimation (urban-background)				0.11	0.11

Table 9.1: Estimated overestimation due to aerosols (relative systematic error urban area versus surroundings) valid for the retrieved spectral albedo of the German Ruhrgebiet (approximately the German part of the Rhine-Main area as defined for this study), a solar zenith angle of 50°, and a surface elevation corresponding to sea level. As can be seen  $XCH_4(O_2)$  and  $XCO_2$  are affected similarly.

top panel of Figure 9.12 provides that on average only a fraction of about 0.9 ppm of the observed  $XCO_2$  enhancement can be attributed to path length errors.

Overall it is concluded from the combined analysis of real SCIAMACHY data and simulated retrievals that the elevated CO<sub>2</sub> over the Rhine-Main region has an estimated uncertainty of about 1-1.5 ppm due to aerosols and sampling contributions. The remaining signal of about 1.2-1.7 ppm is assumed to be mainly due to anthropogenic emissions. This indicates that elevated CO<sub>2</sub> originating from regional anthropogenic CO<sub>2</sub> emissions can be potentially detected using measurements from space. The expected signal (order 1 ppm) is however close to the detection limit of the SCIAMACHY retrievals even if three years of data are averaged. As has been shown, the single measurement precision is about 1-2% corresponding to about 4-7 ppm. In order to detect a signal on the order of 1 ppm the (single measurement) precision has to be improved by at least a factor of 7. Assuming that the precision improves with the square root of the number of measurements added this means that more than 50 measurements need to be averaged per  $0.5^{\circ} \times 0.5^{\circ}$  grid cell before a 1 ppm signal can be detected at this resolution. For the three years average this is achieved for nearly the entire region shown in the top panel of Figure 9.12 (except for coastal areas including parts of the Netherlands) but not for one year averages. For the south-western part of the Netherlands, for example, there are nearly no data during 2004 and the elevated  $CO_2$  over the Netherlands is mainly due to 2003 data (slight elevation) and 2005 data (significant elevation). As a consequence the elevated  $CO_2$  over the Netherlands is less stable (e.g. with respect to smaller averaging time periods) compared to the German part of the Rhine-Main area where significantly more data are available and where we observe regionally elevated CO<sub>2</sub> also in yearly averages.

To minimise the uncertainty due to real methane variations in the  $XCH_4(O_2)$ 



Figure 9.14: Residual signal *R* according to (9.2) for the year 2003 compared to anthropogenic  $CO_2$  emissions.

approach it would be desirable to separate path length induced errors from real variability. However, this differentiation cannot be achieved without assumptions. Assuming that the TM5 methane model (see Section 10.1) describes the methane variability over the considered region well, deviations of  $XCH_4(O_2)$  from the model might be interpreted as path length errors which could then be quantified via the ratio  $XCH_4(O_2)/XCH_4^{TM5}$ . As already mentioned  $XCO_2$  is expected to be affected to a comparable extent. Hence, the pattern visible in the data set described by the residual signal

$$R = \frac{\text{XCO}_2^{\text{SCIA}}/\text{XCO}_2^{\text{CT}}}{\text{XCH}_4^{\text{SCIA}}(\text{O}_2)/\text{XCH}_4^{\text{TM5}}}$$
(9.2)

should be unaffected by biogenic influences and path length issues to a large extent under the assumptions made. Since the methane model is only available for 2003 so far, the analysis of R is restricted to this year. Moreover, because of the involvement of methane additional filter criteria as described in Section 7.2 have to be applied. These both limitations lead to significant less data per grid cell compared to the 2003-2005 averages shown before and therewith to a greater impact of random error so that the number of measurements per grid cell to reach the required precision is generally not achieved. Therefore the data has to be smoothed and it cannot be expected to obtain exactly the same pattern as in Figure 9.12. Nevertheless, the coarse residual signal attributed to emissions which is shown in Figure 9.14 for the year 2003 exhibits enhanced values over anthropogenic source regions namely western Germany, the East Coast of the United States of America, and Japan's densely populated and industrialised centres.

## **10** Methane results

This chapter is based in essence on results published in Schneising et al. (2009). All SCIAMACHY spectra (Level 1b version 5 converted to Level 1c using the standard calibration) for the time period 2003-2005 which have been made available by ESA/DLR, have been processed using the improved retrieval algorithm WFM-DOAS version 1.0.

The quality of the global WFM-DOAS  $CH_4$  mole fractions is assessed by performing comparisons with local and global independent reference data. Particularly, for the year 2003  $CH_4$  model simulations, based on the TM5 model which has been optimised versus highly accurate surface methane measurements from the NOAA/ESRL network (Bergamaschi et al., 2007), are useful for comparison. Moreover, first inverse modelling results are obtained for the year 2004 using the WFM-DOAS version 1.0 data set.

## 10.1 Usage of the TM5 model

The TM5 model (Krol et al., 2005) is a two-way nested atmospheric zoom model using off-line transport based on ECMWF meteorological fields. The tropospheric standard version of TM5 with 25 vertical layers has been used in this study. While the inversion has been performed using the  $6^{\circ} \times 4^{\circ}$  coarse resolution, the model has been rerun with the optimised emissions at global resolution of  $3^{\circ} \times 2^{\circ}$ , and 6 embedded zoom regions over major continental areas (North America, South America, Europe, Africa, Asia, and Australia), simulated with high resolution of  $1^{\circ} \times 1^{\circ}$ . For the comparison the Scenario S1 of Bergamaschi et al. (2007) based on the surface measurements from the NOAA network and the new wetland inventory of J. O. Kaplan (EC-JRC, Institute for Environment and Sustainability) is used. The CH<sub>4</sub> inversion is based on the synthesis inversion technique. To account for small differences in the altitude sensitivity of the SCIAMACHY measurements the SCIAMACHY averaging kernels (Section 8.1) are applied to the TM5 model output when computing the column-averaged methane mole fraction:

$$\operatorname{XCH}_{4}^{\operatorname{TM5}} = \frac{1}{p_0} \sum_{l} \left( \overline{\operatorname{XCH}}_{4}^{l} + AK^{l} (\operatorname{XCH}_{4}^{\operatorname{TM5}l} - \overline{\operatorname{XCH}}_{4}^{l}) \right) \Delta p^{l}$$
(10.1)



Figure 10.1: CH<sub>4</sub> a-priori profile.

where *l* is the index of the vertical layer,  $AK^l$  the averaging kernel,  $\overline{\text{XCH}}_4^l$  the a-priori mole fraction (1750 ppb below 6 km and decreasing above, see Figure 10.1) and  $\text{XCH}_4^{\text{TM5}l}$  the simulated mole fraction of layer *l*.  $\Delta p^l$  is the pressure difference between the upper and lower boundary of layer *l* and  $p_0$  denotes surface pressure.

# 10.2 Comparison with local and global reference data

The retrieved WFM-DOAS annual composite averages for  $XCH_4$ , which meet the classification 'good' defined in Chapter 7, are shown in Figure 10.2. Thereby, as for all results presented in this section, a constant value of 370 ppm of the carbon dioxide mole fraction was assumed when computing  $XCH_4$ . Significant features which are apparent in the  $XCH_4$  fields of all three years are a clearly visible interhemispheric gradient and significantly enhanced  $XCH_4$  over known methane source regions such as South-East Asia (e.g., wetlands, rice paddies, ruminants) and large parts of Russia and tropical South America and Africa (e.g., wetlands).

A comparison of the SCIAMACHY WFM-DOAS version 1.0 methane product with European Fourier Transform Spectrometers (FTS) located at seven ground stations has been performed by Dils et al. (2006) for the years 2003 and 2004 showing reasonable to good agreement between the two data sets with an average correlation of about 0.7 over all stations. The standard deviation of the difference between the data sets is about 1.5%. The latter includes the error of the SCIAMACHY



XCH4 SCIAMACHY (WFMDv1.0)

Figure 10.2: Three years of SCIAMACHY methane column-averaged dry air mole fractions as retrieved by WFM-DOAS version 1.0 (WFMDv1.0). Shown are yearly averages for 2003 (top), 2004 (middle), and 2005 (bottom).



Figure 10.3: European Fourier Transform Spectrometers used in the SCIAMACHY methane validation performed by Dils et al. (2006).

measurements, the FTS measurement error, and the error of the comparison method. In addition, a small regionally constant bias of SCIAMACHY of about 2-3% has been identified as compared to the FTS measurements. The bias in 2004 is somewhat higher than in 2003 which is due to the  $CO_2$  increase with time (see Section 9.3) which is not accounted for in the WFM-DOAS standard product which assumes a constant  $CO_2$  mole fraction of 370 ppm. Biases need to be minimised as much as possible when the data are going to be used for inverse modelling of methane sources and sinks. Constant (or nearly constant) biases can be relatively easily corrected for in coupled inversions including also surface measurements as high-accuracy reference (Bergamaschi et al., 2007). The validation shows that both the correlation and scatter as well as the bias have improved significantly with the version 1.0 data set compared to version 0.5.

The global comparison with the TM5 model for the year 2003 average is shown in Figure 10.4. The comparisons of latitudinal averages in Figure 10.6, of global seasonal averages in Figure 10.7, and of regional time series in Figure 10.9 are performed for both the standard product and the corrected data set taking modelled  $CO_2$  variability of CarbonTracker into account which will be further discussed in the following section. As can be seen, agreement with the TM5 model is typically within 1-2% (approximately 17-34 ppb) with the exception of large parts of the tropics where significantly higher  $XCH_4$  is observed as compared to the model especially when considering seasonal averages. This is qualitatively consistent with the finding of higher column-averaged  $CH_4$  mole fractions over tropical regions detected by the independent retrieval algorithm of Frankenberg et al. (2005, 2006), compared



#### XCH4 SCIAMACHY (WFMDv1.0) - 2003

Figure 10.4: Comparison of SCIAMACHY/WFMDv1.0 XCH<sub>4</sub> (top) with TM5 model simulations (bottom left) for the year 2003. The SCIAMACHY data have been scaled with 1.02 to compensate for a systematic offset between the two data sets. The TM5 model data have been sampled in time and space as the SCIAMACHY instrument measures and the SCIAMACHY averaging kernels have been applied to TM5. The bottom right panel shows the difference between SCIAMACHY and TM5. to the inverse model simulations of scenario S1 in Bergamaschi et al. (2007), suggesting higher tropical emissions than assumed by TM5 which is also supported by independent aircraft measurements over the Amazon basin (Miller et al., 2007b). However, the high methane levels over the tropics are now considered to be lower than initially retrieved due to a recent update in the near-infrared water vapour spectroscopy (Frankenberg et al., 2008b). The impact of the new spectroscopic data on the WFM-DOAS retrievals, particularly with regard to the retrieved magnitude of the tropical enhancement, agreement with model simulations, and quality of the fits, is discussed in Section 10.7.

It has been suggested that the high tropical methane observed by SCIAMACHY may be due to emissions from living plants (Keppler et al., 2006). However, the potential role of plants has become now further controversial after a recent study by Dueck et al. (2007) questioning the measurements of Keppler et al. (2006). Using an independent method based on <sup>13</sup>C labelling and laser-based measurements, Dueck et al. (2007) did not find evidence for substantial  $CH_4$  emissions of plants under aerobic conditions while Keppler et al. (2008) confirm their earlier work by providing evidence that methoxyl groups of pectin can act as a source of atmospheric  $CH_4$  under aerobic conditions. Nevertheless, the contribution of emissions from plants to the global methane budget remains uncertain.

## 10.3 Impact of CO<sub>2</sub> variability on XCH<sub>4</sub>

Although  $CO_2$  is less variable than  $CH_4$ , it is not constant and therefore variations in  $CO_2$ , especially its seasonal cycle, introduce a small error in the retrieved  $XCH_4$ . This can be taken into account by considering modelled column-averaged mole fractions of  $CO_2$  instead of assuming a globally constant mole fraction when computing  $XCH_4$ , i.e., by using modelled  $CO_2^{mf}$  in (5.28) instead of a constant value. This approach has been introduced by Frankenberg et al. (2006). This ideally requires that the  $CO_2$  distribution is well known everywhere, which is not the case. The effect of using modelled  $CO_2$  variations using the CarbonTracker assimilation system is depicted in Figures 10.5–10.9 (here modelled  $CO_2^{mf}$  is the column-averaged mole fraction of  $CO_2$ , i.e.,  $XCO_2$ , obtained from the CarbonTracker  $CO_2$  mixing ratio vertical profiles computed taking the SCIAMACHY  $CO_2$  averaging kernels into account).

The global average of the standard deviation of the difference of retrieved and modelled column-averaged methane mole fractions, which is 1.7% when correcting for  $CO_2$  variability by the usage of assimilated CarbonTracker mole fractions (1.8% when assuming constant  $CO_2$ ) is consistent with the single ground scene XCH<sub>4</sub> retrieval precision error of SCIAMACHY derived in Section 8.2. Averaging over *N* independent retrievals reduces the random error and the resulting estimated



Figure 10.5: Estimated statistical error associated with the WFM-DOAS retrieval obtained by averaging the relative standard deviation of the difference SCIA–TM5 over all *N* available annual retrievals for each grid cell (*N* is shown in the top panel) via division by  $\sqrt{N}$  (bottom left panel without CO<sub>2</sub> correction; bottom right panel with CO<sub>2</sub> correction). By comparison with Figure 6.2 one observes an anti-correlation with the retrieved near-infrared albedo because the number of measurements classified good increases with albedo due to a better signal-to-noise ratio of the spectra.

relative statistical error, which is calculated by division by  $\sqrt{N}$ , is shown in Figure 10.5. Additionally the observed quite systematic low bias of the WFM-DOAS data drops from 2% to 1% when using CarbonTracker XCO<sub>2</sub> to estimate the dry air column. It can be seen in Figures 10.6, 10.7, and 10.9 that for most seasons and most regions the differences (after accounting for this bias by appropriate scaling) between using a constant and the modelled XCO<sub>2</sub> are small but may reach about 1% in the northern hemisphere in spring time locally when the expected CO<sub>2</sub> seasonal cycle has its maximum. These Figures show that the disregard of the seasonal variations of CO<sub>2</sub> may result in higher retrieved seasonal methane variations than in the CarbonTracker-corrected data product. This effect is in particular observable over northern hemisphere mid-latitudes where the impact of the CO<sub>2</sub> correction



Figure 10.6: Comparison of latitudinal averages of SCIAMACHY WFM-DOAS methane retrievals (black) and TM5 simulations (red) for the entire year 2003 (left) and for the four seasons as also used for Figure 10.7. For the comparison both the SCIAMACHY and TM5 data have been gridded on a common  $0.5^{\circ} \times 0.5^{\circ}$  latitude/longitude grid. The shaded areas illustrate the standard deviations. The bottom panels show the difference SCIA–TM5 and a quadratic polynomial fitted to it. For SCIAMACHY the solid lines correspond to considering CarbonTracker CO<sub>2</sub> for the computation of XCH<sub>4</sub>, whereas the dotted lines correspond to assuming a constant CO<sub>2</sub> mole fraction. As can be seen, the consideration of the seasonal CO<sub>2</sub> variability from CarbonTracker in the SCIAMACHY XCH<sub>4</sub> product leads to a better agreement with the TM5 model simulation concerning seasonal variability and seasonal latitudinal bias. Note that the SCIAMACHY XCH<sub>4</sub> has been scaled with 1.01 (CO<sub>2</sub> from CarbonTracker) and 1.02 (CO<sub>2</sub> constant), respectively, to compensate for a systematic low bias relative to the TM5 model.



Figure 10.7: Seasonal averages for the year 2003 of measured and modelled methane (from top to bottom: January-March (JFM), April-June (AMJ), July-September (JAS), and October-December (OND) seasons). The first column shows the WFMDv1.0 methane based on using a constant  $CO_2$  mole fraction for the XCH<sub>4</sub> computation. The second column shows SCIAMACHY methane obtained using XCO<sub>2</sub> from the CarbonTracker assimilation system. The last column shows modelled TM5 methane.



Figure 10.8: Six regions selected for a comparison of the SCIAMACHY and TM5 methane column averaged mole fractions shown in Figure 10.9: North America (USA), Europe (EUR), Tropical South America (TSAM), Sahara (SAH), South-East Asia (SEA), and Australia (AUS).



Figure 10.9: Comparison of the SCIAMACHY methane (black) with TM5 model simulations (red). The six left panels show the comparison for the six regions displayed in Figure 10.8 for the standard SCIAMACHY XCH<sub>4</sub> computed using a constant CO<sub>2</sub>. For the comparison both the daily SCIAMACHY and TM5 data have been gridded on a common  $0.5^{\circ} \times 0.5^{\circ}$  latitude/longitude grid. The symbols show the daily averages of all coincident grid cells in a given region. For SCIAMACHY all measurement have been averaged for which the WFMDv1.0 quality flag indicates a good measurement. The solid lines represent a 30 days running average. For each region the following numbers have been computed based on the (not smoothed) daily averages: d% is the mean difference SCIA–TM5 in percent, s% denotes the standard deviation of the difference in percent, and r is the correlation coefficient. To assess the impact of assuming a constant carbon dioxide mole fraction the six right panels show the same comparison but using CarbonTracker CO<sub>2</sub> for the computation of the measured XCH<sub>4</sub>. As can be seen from a comparison of the left and the right panels, the differences are relatively small, although not zero. The CarbonTracker correction leads generally to better agreement with the TM5 model, especially over the northern hemisphere where the  $CO_2$  seasonal cycle is more pronounced. Note that the SCIAMACHY XCH<sub>4</sub> has been scaled with 1.02 (left six panels) and 1.01 (right six panels) to compensate for a systematic low bias relative to the TM5 model.

on seasonal methane variability can be as large as about 30 ppb when comparing summer to spring XCH<sub>4</sub> changes (see AMJ and JAS seasons in Figure 10.6). Figure 10.6 additionally shows that the usage of modelled  $CO_2$  variability reduces an elsewise more pronounced seasonal latitudinal bias compared to TM5. Hence, it can be concluded that taking the modelled  $CO_2$  variations into account in the XCH<sub>4</sub> product generally results in a better agreement with the methane model and is therefore better suited for quantitative examinations or inverse modelling. Assuming a constant  $CO_2$  would also introduce a superposed decreasing methane trend when studying the methane evolution over longer time periods due to increasing atmospheric  $CO_2$  concentrations (Section 9.3, Buchwitz et al. (2007); Houghton et al. (2001); Solomon et al. (2007)). Thus, in the following the CarbonTracker corrected WFM-DOAS XCH<sub>4</sub> product is solely used.

#### 10.4 Regional pattern

As shown in Figure 10.7, major methane source regions are South-East Asia, in particular China and India, central Africa, and the northern part of South Amercia. Figures 10.10-10.12 show a comparison between seasonal averages of the SCIA-MACHY and TM5  $XCH_4$  for these three source regions. In order to focus on the spatial pattern of methane the data are shown as anomalies, i.e., the mean value has been subtracted for each map separately. Comparisons for these regions are also shown in Bergamaschi et al. (2007) for SCIAMACHY methane retrieved with the IMAP-DOAS algorithm (Frankenberg et al., 2006) and TM5. The comparison of the results shown here with the results shown in Bergamaschi et al. (2007) reveals that the two independent SCIAMACHY methane data products (obtained with WFM-DOAS (WFMD) and IMAP-DOAS (IMAP)) are quite similar but not exactly identical. If one compares, for example, Figure 10.10 with Figure 7 of Bergamaschi et al. (2007) one can see that both data products show the highest methane over India and China in the second half of 2003 around July-September with only slightly elevated methane during January-March (see also the time series for South-East Asia shown in Figure 10.9). Major methane sources in this region are rice paddies, wetlands, and ruminants (for a detailed discussion see Bergamaschi et al. (2007)). Concerning the details of the spatial pattern there are however also differences resulting from the different retrieval algorithms and the different quality filtering applied to the data prior to averaging. The SCIAMACHY/IMAP methane shows, for example, lower methane over large parts of India and China during October-December relative to July-September whereas TM5 still shows relatively high methane also during October-December. In contrast, the SCIAMACHY/WFMD methane shown in 10.10 agrees with TM5 reasonably well also during October-December.



Figure 10.10: Comparison of seasonal XCH<sub>4</sub> averages over South-East Asia between SCIAMACHY (top) and TM5 (bottom). To better highlight the spatial pattern the data are shown as anomalies, i.e., the mean value has been subtracted for each map separately. The (unscaled) SCIAMACHY XCH<sub>4</sub> has been corrected for CO<sub>2</sub> variations using CarbonTracker. The SCIAMACHY data have been gridded on a  $0.5^{\circ} \times 0.5^{\circ}$  latitude/longitude grid and TM5 has been sampled as SCIAMACHY measures using the same grid. The SCIAMACHY methane averaging kernels have been applied to TM5. Shown are tri-monthly averages for the year 2003 (from left to right: January-March (JFM), April-June (AMJ), July-September (JAS), and October-December (OND)).

Similar conclusions, namely that the two SCIAMACHY methane data products are similar but not exactly identical, can be drawn for other regions, e.g., Africa shown in Figure 10.11, to be compared with Figure 9 of Bergamaschi et al. (2007), and South America shown in Figure 10.12, to be compared with Figure 8a of Bergamaschi et al. (2007). These figures show that despite the fact that both methane data products, SCIAMACHY/WFMD and SCIAMACHY/IMAP, are not exactly identical, significantly higher tropical methane is retrieved from SCIAMACHY compared to TM5.

Concerning SCIAMACHY's discovery of unexpectedly high tropical methane it is important to exclude the possibility that the retrieved elevated tropical  $XCH_4$  is an artifact of the  $CO_2$  normalisation used to compute the  $XCH_4$ . To investigate this, the standard  $XCH_4$  data product, which is influenced by  $CO_2$ , is compared to alternative







Figure 10.12: As Figure 10.10 but for South America.

 $XCH_4$  data products not influenced by  $CO_2$ . The alternative  $XCH_4$  data products are obtained by dividing the retrieved methane columns by dry air columns obtained from (i) simultaneously retrieved  $O_2$  columns (as used for the  $XCO_2$  data product described in Section 9) and (ii) using dry air columns obtained from meteorological surface pressure.

Figure 10.13 shows that the elevated methane over the tropics is also visible when using measured  $O_2$  instead of measured  $CO_2$ . According to Figure 10.13 using O<sub>2</sub> instead of CO<sub>2</sub> results in even higher retrieved tropical XCH<sub>4</sub>, but this is probably due to the larger measurement error expected for using O<sub>2</sub> instead of  $CO_2$ , in particular in the presence of subvisual thin cirrus clouds (see Chapter 8). The retrieved methane is also larger over the tropics compared to TM5 when the analysis is restricted to, for example, August-November 2003, i.e., for the time period discussed in Frankenberg et al. (2005), regardless of whether CO<sub>2</sub> or O<sub>2</sub> is used for normalisation of the methane columns. Tropical methane is also enhanced when methane is normalised by meteorological surface pressure instead of measured  $CO_2$  or  $O_2$ . This is illustrated exemplarily in 10.14 for Southern America where the deviation of the retrieved methane mole fractions from the model is largest. The fact that the retrieved methane enhancement is stable under the change of normalisation method gives evidence that methane is actually higher over tropical rain forests than expected by the TM5 model pointing to an unconsidered or significantly underestimated known methane source (firstly suggested by Frankenberg et al. (2005)). At least it can be excluded that the enhancement is introduced artificially by the  $CO_2$  normalisation. In this context it is also important to point out that the high tropical methane (compared to TM5) has also been observed using an entirely different methane spectral fitting window. This has been shown in Buchwitz et al. (2005b) using WFM-DOAS version 0.41 applied to methane absorption lines located in SCIAMACHY channel 8 (2265-2280 nm). The results reveal that the elevated tropical methane compared to the model is nearly independent of the CO<sub>2</sub> (CarbonTracker) correction as shown in, e.g., Figures 10.6 and 10.7. In summary, it can be concluded that the elevated tropical methane observed by SCIAMACHY appears to be a robust feature. For the Amazon basin it has also been recently confirmed using airborne measurements that methane emissions in this region appear to be higher that hitherto known (Miller et al., 2007b). Although this result is consistent with the findings of Frankenberg et al. (2005) it is important to point out that the retrieved tropical XCH<sub>4</sub> enhancement is only about 2%, i.e., a fairly small signal. Therefore one has to be careful with a quantitative interpretation especially because the absolute magnitude of the enhancement decreases to a certain extent when using updated water vapour line parameters accounting for spectroscopic interferences with methane in the considered spectral range (Frankenberg et al. (2008b), see also Section 10.7).



Figure 10.13: Comparison between two different SCIAMACHY XCH<sub>4</sub> data products. The top panel shows the CarbonTracker-corrected XCH<sub>4</sub> obtained by normalising the measured methane columns by simultaneously measured CO<sub>2</sub> columns. The bottom panel shows XCH<sub>4</sub> obtained by normalising the measured methane columns by simultaneously measured O<sub>2</sub> columns.



Figure 10.14: Illustration of the (meteorological surface) pressure-normalised vertical columns over South America. All three columns show similar systematic structures while in  $CH_4$  an additional enhancement over Colombia and Venezuela is observable; in particular there is no  $CO_2$  degradation in this region compared to the rest of South America giving evidence that the elevated methane is not an artifact of the  $CO_2$  normalisation.

## 10.5 Interannual variability

The latitudinal averages and global annual composite averages of three years of SCIAMACHY XCH<sub>4</sub> retrievals, when accounting for CO<sub>2</sub> variability by modelled carbon dioxide from CarbonTracker, are shown in Figure 10.15. As can be seen, the spatial pattern and the latitudinal dependence of the retrieved XCH<sub>4</sub> is quite similar for 2003 and 2004. Over the northern hemisphere the methane is about 1% higher in 2005 compared to 2003 and 2004 in contrast to the surface observations (see, e.g., http://www.esrl.noaa.gov/gmd/aggi/). The regional analysis of the interannual variability for the three years displayed in Figure 10.16 shows similar seasonal cycles but also larger scatter of the SCIAMACHY XCH<sub>4</sub> in the year 2005. Figure 10.17 suggests that this scatter is due to the retrieved methane columns and not due to carbon dioxide as the root-mean-square (RMS) of the spectral fit residua (a measure of the instrument noise) is larger for methane for 2005 compared to the two previous years whereas for CO<sub>2</sub> the RMS is rather stable.

Figure 10.18 shows that the standard deviations of the spectral fit residua are larger for 2005 compared to the two previous years especially in the wavelength range where the methane absorption is largest (Q-branch at 1666 nm). Hence, the significant higher variability of the retrieved XCH<sub>4</sub> is most likely due to somewhat



Figure 10.15: Latitudinal averages (left) and global annual composite average maps (right) of three years of SCIAMACHY XCH<sub>4</sub> retrieved by WFM-DOAS version 1.0 using CarbonTracker to account for CO<sub>2</sub> variability.

larger noise of the spectral measurements in 2005 compared to the two previous years. It is known that the SCIAMACHY near-infrared detectors are on average degrading with time (this holds especially for channels 7 and 8 not used for this study and for channel 6+ used for this study for methane column retrieval; channel 6, used for  $CO_2$  column retrieval, is in contrast very stable). A detailed discussion of this is given in Kleipool et al. (2007) where it is also shown that the behaviour of the individual detector pixels is quite complicated including the possibility that degrading pixels recover. For the future it is planned to process a longer time series to investigate how the performance of the channels behaves after 2005.



Figure 10.16: Time series of SCIAMACHY methane for the years 2003 (red), 2004 (green), and 2005 (blue) for the six regions shown in Figure 10.8. The symbols denote daily averages, the solid lines represent a 30 days running average.



Figure 10.17: Time series of methane columns (top panel) and carbon dioxide columns (third panel) and the corresponding root-mean-square (RMS) of the fit residua (= relative difference between measurement and radiative transfer model after the fit) in the Sahara in a radius of 800 km around 25°N, 10°E. The second panel shows the RMS of the  $CH_4$  fit, the bottom panel shows the RMS of the  $CO_2$  fit. All single measurements passing the quality filter are shown as grey dots while the black square symbols denote daily averages.



Figure 10.18: Analysis of the cause of the larger scatter of the retrieved methane columns in 2005. The top panel shows the temporal evolution of the standard deviations of the fit residua of all retrievals passing the quality filter for six selected nadir states covering a specific Arabian region (a nadir state corresponds to about one minute nadir observations; the spatial regions covered by these states are shown in the bottom panel). The dotted grey lines shows the spectral positions of the methane absorption features (i.e., the methane weighting function (radiance derivative) scaled by the retrieved methane column; right axis). The top panel shows that the standard deviation, especially at two detector pixels (pixel number 894 and 895 of channel 6) which are located where the strongest methane absorption occurs, is considerably higher in 2005 (blue) compared to 2003 (red) and 2004 (green) indicating a possible degradation of these detector pixels especially in terms of larger noise. The middle panel shows the averages of the fit residua (shown as anomalies, i.e., with mean value subtracted) for the same six nadir states. As there are no obvious systematic differences for the different years it appears that the degradation is mainly random rather than systematic.

## 10.6 Inverse modelling results

For the year 2004 the WFM-DOAS v1.0 SCIAMACHY XCH<sub>4</sub> data set presented in this thesis has been inverted combined with NOAA surface measurements for methane surface fluxes (Peter Bergamaschi, EC-JRC, personal communication) using a newly developed four-dimensional variational (4D-VAR) inverse modelling scheme. TM5 has been used as underlying atmospheric transport model. The inverse modelling scheme is referred to as TM5-4DVAR in the following. TM5-4DVAR allows optimisation of emissions on the model grid scale and assimilation of satellite observations at high spatial and temporal resolution (Meirink et al., 2008).

Figure 10.19 compares the SCIAMACHY WFM-DOAS retrieved mole fractions, corrected for a time dependent latitudinal bias (polynomial fits) which was also illustrated in Figure 10.6, to the posterior model simulations. The corresponding a priori and optimised a posteriori emissions resulting from the inversion as well as the inversion increment are shown in Figure 10.20. SCIAMACHY data are only used in the latitude range 50°S - 50°N because at higher latitudes TM5 in the stratosphere can differ considerably from observations with potential significant impact on the simulated XCH<sub>4</sub>. This restriction also reduces possible systematic errors due to the seasonal differences in the amount of available SCIAMACHY data at higher latitudes. Additionally, only satellite data departing by at most 250 m from the TM5 surface are utilised reducing the model representativeness error. The inversion leads for example to an increase of emissions from the tropics and from Chinese wetlands or rice paddies as well as to a decrease of emissions from Northern India and the Middle East. The total emissions increase from 516.5 Tg a priori to 520.1 Tg a posteriori. The increase of tropical emissions is potentially overestimated due to possible inaccuracies in the spectroscopic parameters provided by HITRAN as the magnitude of the retrieved tropical methane enhancement is sensitive to the choice of spectroscopy (Frankenberg et al. (2008b), see also the discussion in Section 10.7).

The main findings can be shortly summarised as follows: (i) The methane fluxes obtained by applying TM5-4DVAR to the SCIAMACHY IMAP-DOAS version 1.1 XCH<sub>4</sub> data set (Frankenberg et al., 2006) are consistent (nearly identical) with the methane fluxes obtained from this data set using the alternative synthesis inversion method presented in Bergamaschi et al. (2007). This verifies the implementation of the new TM5-4DVAR inverse modelling scheme. (ii) The methane fluxes obtained by applying TM5-4DVAR to the WFM-DOAS v1.0 methane data set presented here are consistent with the methane fluxes obtained by applying TM5-4DVAR to the IMAP-DOAS v1.1 methane data set. From this one can conclude that the two SCIAMACHY methane data sets which have been generated using two independently developed retrieval algorithms (WFM-DOAS v1.0 and IMAP-DOAS v1.1) give very similar results in terms of retrieved methane surface fluxes. However, a source



Figure 10.19: SCIAMACHY WFM-DOAS methane and corresponding TM5-4DVAR inverse model results for the year 2004. The left panels show the SCIAMACHY methane, the TM5-4DVAR a priori, the SCIAMACHY methane corrected for the latitudinal bias illustrated in the right panels, and the TM5-4DVAR a posteriori inverse model results (Figure courtesy of P. Bergamaschi, EC-JRC-IES).



Figure 10.20: Global emissions obtained from the TM5-4DVAR inversion for the year 2004 using SCIAMACHY WFM-DOAS methane and NOAA surface measurements. Shown are the a priori emissions (top panel), a posteriori emissions (middle panel), and the inversion increment, i.e., a posteriori - a priori emissions (bottom panel) (Figure courtesy of P. Bergamaschi, EC-JRC-IES).

inversion using an updated IMAP-DOAS version, based on spectroscopic parameters by Frankenberg et al. (2008a) and manually modified water vapour parameters of Jenouvrier et al. (2007), leads to a considerable decrease of the estimated elevated tropical emissions being more consistent with inversions based on NOAA surface measurements only (Frankenberg et al., 2008b). The impact of spectroscopy on WFM-DOAS methane is expected to be similar and is discussed in the following section.

## **10.7** Sensitivity to spectroscopy

To analyse the sensitivity of the WFM-DOAS methane retrievals to spectroscopy, particularly with regard to the absolute magnitude of the retrieved tropical enhancement linked to possible inaccuracies in the HITRAN spectroscopic data and an associated potential methane overestimation in cases of high water vapour abundances due to unaccounted spectroscopic interferences (Frankenberg et al., 2008b), the entire  $CH_4$  data set was reprocessed (referred to as WFM-DOAS v1.1 in the following) using updated methane (Frankenberg et al., 2008a) and water vapour line parameters (Jenouvrier et al., 2007) in the associated near-infrared fitting window without changing anything else. In contrast to Frankenberg et al. (2008b) the Jenouvrier water vapour spectroscopic parameters were taken as is without manually adjusting broadening coefficients, pressure shifts or line strengths. For missing shift or broadening parameters, standard values were assumed universally. The differences in absorption between the HITRAN and the updated spectroscopy are visualised in Appendix F.

Figure 10.21 shows that the positive correlation with total water vapour amount of the deviation of the retrieved methane from the TM5 model simulation is reduced to some extent over the Sahara and vanishes almost completely over Australia. Thereby, the water vapour data set used for the comparison is retrieved from SCIAMACHY spectral measurements in the visible wavelength region (Noël et al., 2004). The considered time period from January through July 2003 was chosen to avoid methane transport from the strong Asian source regions at the end of the year. However, as can be seen in Figure 10.22, using the updated spectroscopy results in a dubious positive correlation of the RMS of the  $CH_4$  fit residuum with specific humidity which is not existent for the HITRAN spectroscopy. Additionally, the systematic low bias of the SCIAMACHY data relative to the model is further increased after the update of spectroscopy.

Figure 10.23 shows a comparison of WFM-DOAS v1.0 and v1.1 yearly averages for the year 2003 of measurements passing the quality filter simultaneously for both spectroscopies appropriately scaled to be on average on the same level as the model



Figure 10.21: Frequency distribution of the methane ratio SCIAMACHY/TM5 as function of the water vapour amount for the HITRAN spectroscopy (left) compared to the updated spectroscopy of Frankenberg et al. (2008a) and Jenouvrier et al. (2007) over Australia (top) and the Sahara (bottom). Also given are the linear fit parameters  $a_0$  and  $a_1$ .



Figure 10.22: As Figure 10.21 but for the RMS of the  $CH_4$  fit residuum as function of the water vapour column. Using the new spectroscopy leads to a positive correlation of the RMS of the  $CH_4$  fit residuum with specific humidity.


Figure 10.23: Comparison of the two methane data sets using HITRAN (top left) and updated spectroscopy (top right). The difference is shown in the bottom left and the corresponding TM5 model simulation in the bottom right panel.

(scaling factors 1.01 for v1.0 and 1.03 for v1.1), as well as the difference of the two retrieval versions which only differ in methane and water vapour spectroscopic parameters. As can be seen, the main difference between the two data sets is the decrease (by about 1%) of the absolute magnitude of the tropical enhancement in better agreement with the model when using the updated spectroscopy.

The WFM-DOAS v1.1 global annual composite averages of retrieved XCH<sub>4</sub> (using CarbonTracker to account for CO<sub>2</sub> variability) as well as the seasonal averages for 2003 are shown in Figures 10.24 and 10.25, respectively. A comparison with Figures 10.15 and 10.7 confirms that the updated spectroscopy results in a better agreement with the model concerning tropical enhancement but also in less data over the tropics. This is in line with the findings linked to Figures 10.21 and 10.22 as the correlation of methane with water vapour is reduced and the fits are getting systematically worse in cases of high water vapour abundances when using the updated spectroscopy (see also Appendix F for a comparison of mean spectral fit residua and corresponding standard deviations using the different spectroscopic



XCH4 SCIAMACHY (WFMDv1.1)

Figure 10.24: Global annual composite average maps of three years of SCIAMACHY XCH<sub>4</sub> retrieved by WFM-DOAS version 1.1 using updated methane and water vapour spectroscopy and CarbonTracker to account for  $CO_2$  variability.



Figure 10.25: Seasonal averages for the year 2003 of measured and modelled methane using updated spectroscopy (from top to bottom: January-March (JFM), April-June (AMJ), July-September (JAS), and October-December (OND) seasons). The first column shows the WFMDv1.1 methane based on using a constant CO<sub>2</sub> mole fraction for the XCH<sub>4</sub> computation. The second column shows SCIAMACHY methane obtained using XCO<sub>2</sub> from the CarbonTracker assimilation system. The last column shows modelled TM5 methane. A comparison with Figure 10.7 reveals that the updated spectroscopy results in a better agreement with the model concerning tropical enhancement but also in less data over the tropics.



Figure 10.26: As Figure 10.9 but using updated spectroscopy. Note that the SCIAMACHY XCH<sub>4</sub> has been scaled with 1.043 (left six panels) and 1.03 (right six panels) to compensate for a systematic low bias relative to the TM5 model.

parameters). Thus, the occasional very high humidity over the tropics apparently leads to lower quality fits associated to the new line parameters not passing the filter criteria described in Chapter 7 anymore. Concerning interannual variability Figure 10.24 additionally demonstrates (when comparing with Figure 10.15) that the retrieved methane elevation in 2005 relative to 2003/2004 ascribed to somewhat larger noise of the spectral measurements, which is inconsistent with surface observations, is even increasing when using the updated spectroscopy reinforcing the impression of less stability of the spectral fits. Nevertheless, the better agreement of WFMD v1.1 with the model concerning tropical methane sources is generally also valid as regards latitudinal biases or regional time series as shown in Figure 10.26. For example the seasonal variations over Australia agree perceptibly better with TM5 than for the HITRAN line parameters (see Figure 10.9 for comparison) in line with the findings of Frankenberg et al. (2008a).

The analysis has revealed the assets and drawbacks of the updated spectroscopy according to line parameters by Frankenberg et al. (2008a) and Jenouvrier et al. (2007) indicating that the HITRAN and the new spectroscopy are both potentially suf-

fering from inaccuracies adversely affecting the retrieval results albeit in a different way. It has become clear that the accurate knowledge of spectroscopic parameters is very important with respect to precise quantification of regional enhancements over source regions and corresponding fluxes obtained via inverse modelling as small changes in spectroscopy can have a significant impact on the retrievals in cases of spectroscopic interferences of different absorbers because the SCIAMACHY resolution does not resolve individual absorption lines. This has to be borne in mind in future retrievals and is in principle crucial for all gases with demanding accuracy requirements especially for the long-lived and therefore well mixed greenhouse gases.

#### 11 Conclusions and outlook

#### Conclusions

This thesis presented and discussed a multi-year global data set of atmospheric carbon dioxide and methane column-averaged dry air mole fractions retrieved from the spectral near-infrared nadir observations of the SCIAMACHY instrument onboard the European environmental satellite ENVISAT using the significantly improved version 1.0 of the retrieval algorithm WFM-DOAS and benefiting from the simultaneous retrieval of  $CH_4$ ,  $CO_2$ , and  $O_2$  vertical columns.

The quality of the global SCIAMACHY  $XCO_2$  data set has been assessed by a combination of an error analysis using simulated retrievals, comparisons with a limited number of independent  $XCO_2$  measurements obtained using ground-based FTS, and comparisons with  $XCO_2$  from NOAA's global assimilation system CarbonTracker.

The largest differences with respect to the reference data which have been identified were over the Sahara where SCIAMACHY  $XCO_2$  is overestimated by a few percent under conditions of highly elevated desert dust storm aerosol as identified using TOMS/Earth Probe Absorbing Aerosol Index (AAI) (Herman et al., 1997). It was shown that  $XCO_2$  has smaller errors in this case than the absolute  $CO_2$ columns due to cancellation of errors when dividing the retrieved  $CO_2$  columns by simultaneously retrieved  $O_2$ . However, this does not fully eliminate all aerosol related errors. Therefore, a threshold filter based on the AAI to remove strongly aerosol contaminated scenes was introduced and applied as a quality criterion for the retrieved carbon dioxide mole fractions.

Currently, the carbon dioxide column-averaged dry air mole fraction is only measured at a few ground stations and only recently by a new network of FTS stations (see, for example, the Total Carbon Column Observing Nework (TCCON) website: http://www.tccon.caltech.edu). The comparison of the SCIAMACHY  $XCO_2$  with the  $XCO_2$  FTS measurements at Park Falls, Wisconsin, USA and Bremen, Germany, which are both part of TCCON, showed good agreement with respect to the amplitude and the phase of the  $CO_2$  seasonal cycle for the monthly composite averages.

To assess the quality of the data globally, comparisons with the recently released output of NOAA's global assimilation system CarbonTracker have been performed. To enable a meaningful comparison, the CarbonTracker data have been sampled in space and time as SCIAMACHY measures and the SCIAMACHY averaging kernels have been applied to CarbonTracker to take the altitude sensitivity of the SCIA-MACHY  $CO_2$  retrievals into account. In general, reasonable to good agreement with CarbonTracker was found, for example concerning the increase of carbon dioxide with time globally and concerning the  $CO_2$  seasonal cycle over the northern hemisphere where a large uptake of atmospheric  $CO_2$  is observed typically in July and August. This uptake is attributed primarily to vegetation during the growing season, i.e., by the terrestrial biosphere. On the regional scale the satellite data show in general similar spatial pattern as CarbonTracker but exhibit typically higher variability.

From the comparison with the limited reference data it was inferred that the SCIAMACHY  $XCO_2$  data set over land can be characterised by a systematic low bias of about 1.5% as concluded from the mean difference relative to the FTS and CarbonTracker, and by a relative accuracy of about 1-2% for monthly averages at a horizontal resolution of  $7^{\circ} \times 7^{\circ}$  as concluded from the comparison of regional  $XCO_2$  anomalies with CarbonTracker. Furthermore the single ground pixel retrieval precision is estimated to be about 1-2% (~6 ppm) as concluded, for example, from the mean of the standard deviations of the daily SCIAMACHY  $XCO_2$  at given locations.

When averaging the SCIAMACHY  $XCO_2$  over all three years we find elevated  $CO_2$  over the highly populated area of western central Germany and parts of the Netherlands ("Rhine-Main area") and other regions (U.S. East Coast, parts of Japan, e.g., around Tokyo), reasonably well correlated with EDGAR anthropogenic  $CO_2$  emissions, indicating that regionally elevated  $CO_2$  arising from regional anthropogenic  $CO_2$  emissions can be potentially detected from space.

For the global SCIAMACHY XCH<sub>4</sub> detailed comparisons with global model simulations using the TM5 model were performed, which has been optimised versus highly accurate but sparse surface measurements from the NOAA/ESRL network (scenario S1 from Bergamaschi et al. (2007)). The comparison results are consistent with the findings of Dils et al. (2006) who performed a comparison of the SCIAMACHY XCH<sub>4</sub> with FTIR XCH<sub>4</sub> measurements at seven European ground stations. As the SCIAMACHY XCH<sub>4</sub> is obtained using simultaneously retrieved CO<sub>2</sub> columns as a proxy for the light path it was investigated to what extent the SCIAMACHY XCH<sub>4</sub> data product is influenced by CO<sub>2</sub> variability. For this purpose CO<sub>2</sub> fields from NOAA's CO<sub>2</sub> assimilation system CarbonTracker were used leading to the result that the regional patterns of methane are only marginally affected by CO<sub>2</sub> but that using CarbonTracker helps to reduce seasonal and latitudinal XCH<sub>4</sub> biases caused by CO<sub>2</sub> variability. Therefore, for most of the results presented in this thesis, the SCIAMACHY XCH<sub>4</sub> has been corrected for CO<sub>2</sub> variability (using CarbonTracker).

From the comparison with TM5 and an error analysis of the retrieval algorithm it was inferred that the SCIAMACHY XCH<sub>4</sub> data set can be characterised by (i) a single ground pixel retrieval precision of about 1.7% as concluded, for example, from the mean of the standard deviations of the daily data at a given location being consistent with the standard deviation of the retrieved XCH<sub>4</sub> relative to the model and European FTS measurements and (ii) a systematic low bias of about 1% as concluded from the mean difference relative to TM5 (after CO<sub>2</sub> correction). The underestimation of the SCIAMACHY XCH<sub>4</sub> of about 2% when assuming a constant CO<sub>2</sub> mole fraction of 370 ppm (i.e., without CO<sub>2</sub> correction) is consistent with the findings of Dils et al. (2006). After scaling the methane mole fractions appropriately to account for the low bias, agreement with the model is typically within about 1-2%.

In agreement with previous studies (Frankenberg et al., 2005, 2006; Buchwitz et al., 2006) significantly higher methane was found over the tropics compared to the model. Concerning the ongoing discussion of the discovery of a new methane source or a significantly underestimated known source (e.g., wetland emissions) in the tropics (Keppler et al., 2006; Crutzen et al., 2006; Houweling et al., 2006; Bergamaschi et al., 2007; Miller et al., 2007b; Dueck et al., 2007; Keppler et al., 2008) it appears unlikely that the elevated tropical methane measured by SCIA-MACHY is caused artificially in the retrieval by lower than assumed tropical CO<sub>2</sub>. This is an important conclusion as the SCIAMACHY column-averaged mole fraction of methane is obtained by normalising with simultaneously measured CO<sub>2</sub> to reduce systematic light path related errors. This conclusion is based on the finding that enhanced tropical methane is also observed when using a SCIAMACHY XCH<sub>4</sub> data product not influenced by  $CO_2$ . However, the magnitude of the retrieved tropical methane enhancement is sensitive to the choice of spectroscopic parameters and might be overestimated as the usage of an updated spectroscopy by Jenouvrier et al. (2007) and Frankenberg et al. (2008a) accounting for spectroscopic interferences with water vapour results in about 1% lower tropical methane mole fractions unfortunately connected with less stable fit results in the presence of high humidity.

Concerning interannual variability similar methane spatio-temporal patterns are found for 2003 and 2004. For 2005 the retrieved methane shows significantly ( $\sim$ 2%) higher variability compared to the two previous years, most likely due to larger noise of the spectral measurements.

In summary, it was shown that significant progress has been made in our understanding and the quality of the carbon dioxide and methane data products derived from the SCIAMACHY nadir observations. For carbon dioxide the new WFM-DOAS data set comes considerably closer to the demanding accuracy and precision requirements of 1% or better needed for significant CO<sub>2</sub> surface flux uncertainty reduction. The somewhat relaxed requirements for methane of 1-2% are already satisfied by the current WFM-DOAS  $XCH_4$  data set and for the year 2004 the WFM-DOAS v1.0 SCIAMACHY methane mole fraction data set presented here has been inverted for methane surface fluxes coupled with NOAA surface measurements using the 4D-VAR inverse modelling scheme developed by Meirink et al. (2008).

#### Outlook

To further improve the accuracy of the retrieval algorithm it is intended, for example, to take updates of the spectroscopic line parameters of all involved absorbers into account in the future as the sensitivity study in the framework of this thesis and the results of Frankenberg et al. (2008b) have shown exemplified by methane that specific retrieval results can depend significantly on the choice of spectroscopy in cases of spectroscopic interferences. The current look-up table scheme of the forward model is based on spectroscopic parameters of the HITRAN 2004 database (or alternatively on an updated spectroscopy by Jenouvrier et al. (2007) for water vapour and Frankenberg et al. (2008a) for methane) which could be potentially improved by future laboratory measurements. Once these data are available the revision of the WFM-DOAS look-up table is straightforward and no changes in the retrieval algorithm are necessary.

The second kind of improvements like better consideration of meteorological parameters (e.g., by taking advantage of temperature, pressure, and water vapour vertical profiles from meteorological analysis) could quite easily be implemented when using time consuming on-line radiative transfer calculations for the forward model but require more fundamental changes and ideas if one wants to maintain the fast look-up table approach because the look-up table grows exponentially with the number of involved parameters which therefore have to be minimised. The optimisation process to find out which parameters and how much corresponding reference values or profiles should be included preferentially in future look-up tables could be performed with the help of on-line calculations focussing on small data sets limited to specific locations where independent reference data from surface measurements are available for comparison and assessment of accuracy. Thus, the main challenge for this class of updates will be the significant further improvement of accuracy without increasing the processing time by many orders of magnitude.

A third kind of possible future improvements deals with problems which are hard to be thoroughly solved in principle even when using on-line radiative transfer calculations because of unavailability of all the relevant information with respect to atmospheric scatterers. This category includes light path variations caused by the variability of aerosols and clouds affecting the  $XCO_2$  retrieval while for  $XCH_4$  these errors cancel to a large extent. The treatment of clouds (especially cirrus)

and aerosols (apart from filtering out contaminated scenes) in the  $XCO_2$  retrieval is difficult and needs further study because the radiative transfer is wavelength dependent and depends on the amount, height, shape, and size distribution of the particles. Although not trivial, a combined nadir and limb retrieval seems worth considering to identify subvisual cirrus.

Another future application could be the utilisation of the WFM-DOAS retrieval algorithm on satellite data provided by the upcoming OCO (NASA) and GOSAT (JAXA) greenhouse gas missions.

Part IV Appendix

### A Instrument function

For the calculation of the forward model data a Gaussian instrument function given by

$$f(\lambda) = a \cdot \exp\left(-\frac{(\lambda - \lambda_0)^2}{2b^2}\right)$$
 (A.1)

with constants  $a, b \in \mathbb{R}^+$  was assumed with which the calculated reference spectra are convolved.  $\lambda_0$  is thereby the center wavelength and b can be expressed by the full width at half maximum

$$FWHM = 2b\sqrt{2\ln 2}$$
(A.2)

which is the only free parameter of the slit function and is chosen to be 0.45 nm for SCIAMACHY's channel 4 where the oxygen fitting window is located and 1.4 nm for channel 6 where the used carbon dioxide and methane absorption features are located. The parameter a is defined by the normalisation requirement

$$1 = \int_{-\infty}^{\infty} f(\lambda) d\lambda = ab\sqrt{2\pi} \quad . \tag{A.3}$$



Figure A.1: Instrument function for the SCIAMACHY channels 4 and 6.

A INSTRUMENT FUNCTION

# B Line-by-line and correlated-k radiances and weighting functions

To demonstrate the accuracy of the radiative transfer when using the fast correlated k-distribution method described in Section 5.5 the corresponding SCIATRAN results are compared exemplarily to line-by-line calculations in this appendix. As can be seen by the examples for a solar zenith angle of 50° and an albedo of 0.1 shown in Figures B.1–B.6 the correlated k-distribution method virtually yields the same sun-normalised radiances and weighting functions as computed in line-by-line mode in all fitting windows after convolution with the appropriate instrument function for the respective SCIAMACHY channel (see Appendix A) justifying the processing time saving ansatz. The good agreement is ensured by the choice of a sufficiently small wavelength interval  $\Delta \lambda$  and enough summands M in the weighted sum of subinterval-transmittances (see Section 5.5 for details). Table B.1 lists the chosen sizes of these intervals being on the order of about an eighth of the FWHM characterising the instrument resolution. Hence, the resulting wavelength grid of the simulation is about four times finer than the grid of the measurement (as the SCIAMACHY sampling corresponds to about two pixels per FWHM) minimising errors due to wavelength interpolation.

Absorber	Microwindow	FWHM	$\Delta\lambda$	Μ
	[nm]	[nm]	[nm]	
02	755-775	0.45	0.05	5
$\bar{CO}_2$	1558-1594	1.40	0.20	5
$CH_4$	1630-1671	1.40	0.20	5

Table B.1: Overview of the relevant correlated-k parameters. Given are the instrument resolution in the corresponding fitting window, the size of the wavelength interval  $\Delta \lambda$  and the number of subintervals *M* used in the exponential sum (see Section 5.5 for details).



Figure B.1: High resolution (red) and convolved (black) radiance and weighting functions for the oxygen fitting window calculated in line-by-line mode.



Figure B.2: As Figure B.1 but calculated in correlated-k mode.



Figure B.3: High resolution (red) and convolved (black) radiance and weighting functions for the carbon dioxide fitting window calculated in line-by-line mode.



Figure B.4: As Figure B.3 but calculated in correlated-k mode.





Figure B.5: High resolution (red) and convolved (black) radiance and weighting functions for the methane fitting window calculated in line-by-line mode.



Figure B.6: As Figure B.5 but calculated in correlated-k mode.

#### C Example fit and albedo retrieval results

This appendix shows in detail typical WFM-DOAS spectral fit results. In addition to the gas of interest spectral absorption features (i.e., radiance derivatives or weighting functions) of interfering gases are also included in the fit, namely water vapour in the  $CO_2$  and  $CH_4$  fitting windows and  $CO_2$  in the  $CH_4$  fitting window. Additional fit parameters also used is the shift (in Kelvin) of a pre-selected temperature profile to take the temperature dependence of the absorption cross-sections into account and a low order polynomial (not shown). The left panels show the measured (diamond symbols) and modelled (solid line) sun-normalised radiances as well as the corresponding fit residua. The right panels show the contributions of the different fit parameters along with the "parameter fit residua" (symbols) being defined as the sum of the (overall) residuum and the fitted spectral structures of the respective parameter. Figures C.1–C.3 depict the results for a rangeland ground scene in Iran and Figures C.4–C.6 for a vegetated ground scene in Central Europe.



Figure C.1:  $O_2$  example fit for a ground scene in Iran.



Figure C.2: As Figure C.1 but for the  $CO_2$  fitting window.



Figure C.3: As Figure C.1 but for the CH<sub>4</sub> fitting window.



Figure C.4:  $O_2$  example fit for a ground scene in Central Europe.



Figure C.5: As Figure C.4 but for the  $CO_2$  fitting window.



Figure C.6: As Figure C.4 but for the  $CH_4$  fitting window.



Figure C.7: Retrieved albedos for the two ground scenes compared to spectral albedos taken from the USGS spectral library.

Figure C.7 shows that the retrieved albedos in the different fitting windows for the two considered example ground scenes exhibit good agreement with corresponding spectral albedos from the USGS spectral library.

### **D** MODTRAN model atmospheres

This appendix shows the vertical profiles for the model atmospheres (extracted from MODTRAN (Berk et al., 1998)) used in the error analysis in Section 8.6. The carbon dioxide and methane profiles are adjusted to concentration increases in the meantime by appropriate scaling so that the surface concentrations are 370 ppm and 1750 ppb, respectively. The corresponding vertical columns are given in Table D.1. The WFM-DOAS reference spectra are calculated using the U.S. Standard Atmosphere.



Figure D.1: Vertical profiles of the considered model atmospheres.

Atmosphere	H <sub>2</sub> O	CH <sub>4</sub>	CO <sub>2</sub>	0 <sub>2</sub>
U.S. Standard mid-latitude winter mid-latitude summer sub-artic winter sub-artic summer	$\begin{array}{r} - \\ 4.78 \cdot 10^{22} \\ 2.87 \cdot 10^{22} \\ 9.90 \cdot 10^{22} \\ 1.40 \cdot 10^{22} \\ 7.03 \cdot 10^{22} \\ \end{array}$	$\begin{array}{c} 3.65 \cdot 10^{19} \\ 3.54 \cdot 10^{19} \\ 3.51 \cdot 10^{19} \\ 3.52 \cdot 10^{19} \\ 3.47 \cdot 10^{19} \end{array}$	$7.97 \cdot 10^{21} \\ 8.01 \cdot 10^{21} \\ 7.99 \cdot 10^{21} \\ 7.96 \cdot 10^{21} \\ 7.94 \cdot 10^{21} \\ 8.01 \cdot 10^{21} \\ 8.01$	$\begin{array}{c} 4.50 \cdot 10^{24} \\ 4.52 \cdot 10^{24} \\ 4.51 \cdot 10^{24} \\ 4.50 \cdot 10^{24} \\ 4.49 \cdot 10^{24} \\ 4.9 \cdot 10^{24} \end{array}$
tropical	$1.39 \cdot 10^{23}$	$3.66 \cdot 10^{19}$	$8.00 \cdot 10^{21}$	$4.52 \cdot 10^{24}$

Table D.1: Vertical columns of the model atmospheres in molecules per  $\rm cm^2$ .

## E Spectroscopy-related SZA dependent retrieval errors

This appendix includes supplementary material demonstrating the dependence on the solar zenith angle of potential spectroscopy-related retrieval errors for strong absorption lines not resolved by the instrument discussed in Section 9.4. Figure E.1 shows that the SZA dependence is negligible in case of weak absorption lines even when the line is not resolved by the instrument and Figure E.2 demonstrates that an noticeable SZA dependence in case of strong absorption lines only occurs if the spectral line is not resolved by the instrument.



Figure E.1: Spectroscopy-related error for a weak absorption line not resolved by the instrument.



Figure E.2: Spectroscopy-related error for a strong absorption line resolved (a) and not resolved (b) by the instrument.

# F Comparison of HITRAN and updated spectroscopy

Figures F.1 and F.2 visualise the differences in absorption between the HITRAN and updated spectroscopy by Frankenberg et al. (2008a) and Jenouvrier et al. (2007) used for the sensitivity study in Section 10.7. The column amounts are chosen to represent tropical conditions with high water vapour abundance. As can be seen, Jenouvrier et al. (2007) have identified new weak water vapour lines (see also Table F.1). Moreover, further systematic differences, albeit small after convolution with the instrument function, of the updated spectroscopy compared to HITRAN exist. Although the differences at SCIAMACHY resolution look marginal, they can affect the methane retrievals perceptibly due to spectroscopic interferences and the high variability of atmospheric water vapour (see Section 10.7).

Figure F.3 illustrates that the update of spectroscopy is generally associated with worse fit results originating from the long wave end of the fitting window close to the Q-branch where the differences of the high resolution  $H_2O$  transmittance to HITRAN as shown in Figure F.1 are largest. Shown are the mean fit residua for a typical orbit considering all measurements passing the quality filter for both spectroscopic data sets. The simultaneously observed higher standard deviation of the fit residua compared to HITRAN is in line with the finding of newly appearing positive correlation of the RMS of the  $CH_4$  fit residuum with atmospheric water vapour amount when switching to the updated spectroscopic parameters (see Section 10.7) because the high variability of humidity thus leads to more variable residua.

	Isotope	Abundance [%]	# Lines in microwindo v1.0 v1.1		
CH <sub>4</sub>	<sup>12</sup> CH <sub>4</sub> <sup>13</sup> CH <sub>4</sub>	98.83 1.11	527 46	527 46	
H <sub>2</sub> O	$\begin{array}{c} H_2^{16}O\\ HD^{16}O \end{array}$	99.73 0.03	112 2	238 37	

Table F.1:	Isotopic	abundances	and	number	of lines	in tł	ne metha	ane fitting	window
(1630-1	.671 nm)	contained in	the	differen	t spectro	oscoj	pic data	sets.	



Figure F.1: Comparison of the  $CH_4$  (left) and  $H_2O$  (right) cross-sections and transmittances according to the HITRAN (black) and updated spectroscopic parameters by Frankenberg et al. (2008a) and Jenouvrier et al. (2007), respectively (green). The transmittances are shown in high resolution (middle) and after convolution with the instrument function (bottom).



Figure F.2: Comparison of the  $CH_4$  and  $H_2O$  transmittances according to the HITRAN and updated spectroscopic parameters focussing on spectroscopic interferences in the Q-branch of the  $2\tilde{v}_3$  methane band.



Figure F.3: Typical mean spectral fit residua and corresponding standard deviations (for Orbit 08663 in October 2003) using the different spectroscopic parameters.

### Nomenclature

For the sake of clarity the following overview lists the mathematical symbols used consistently throughout the thesis.

- $\alpha$  Absorption coefficient
- $\kappa$  Extinction coefficient
- $\lambda$  Wavelength
- v Frequency
- $\tilde{v}$  Wavenumber
- $\Omega$  Solid angle
- $\phi$  Azimuth angle
- $\varphi$  Phase function
- $\varpi$  Single scattering albedo (=  $\sigma/\kappa$ )
- $\rho$  Reflectivity, Albedo
- $\sigma$  Scattering coefficient
- au Optical density
- $\theta$  Zenith angle
- $\vartheta$  Scattering angle
- AK Averaging kernels
- *B* Rotational constant
- c Speed of light
- *E* Irradiance
- *h* Planck constant

- $\hbar$  Reduced Planck constant (=  $h/2\pi$ )
- *I* Sun-normalised radiance or moment of inertia
- *J* Total angular momentum quantum number
- *k* Absorption cross-section
- *L* Radiance
- *p* Pressure
- *S* Slant column
- *T* Transmittance
- *V* Vertical column
- *v* Vibrational quantum number
- $XCH_4$  Column-averaged dry air mole fraction of methane
- $\mathrm{XCO}_2~\mathrm{Column}$  -averaged dry air mole fraction of carbon dioxide
- z Altitude
- $z_0$  Height of the atmosphere
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