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T. Warneke, R. de Beek, M. Buchwitz, J. Notholt, A. Schulz, et al.. Shipborne solar absorption measurements of CO₂, CH₄, N₂O and CO and comparison with SCIAMACHY WFM-DOAS retrievals. Atmospheric Chemistry and Physics, 2005, 5 (8), pp.2029-2034. hal-00295711

HAL Id: hal-00295711

<https://hal.science/hal-00295711>

Submitted on 18 Jun 2008

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Shipborne solar absorption measurements of CO₂, CH₄, N₂O and CO and comparison with SCIAMACHY WFM-DOAS retrievals

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Received: 2 April 2004 – Published in Atmos. Chem. Phys. Discuss.: 16 February 2005

Revised: 1 July 2005 – Accepted: 18 July 2005 – Published: 5 August 2005

Abstract. CO, CH₄, N₂O and CO₂ were retrieved from high resolution solar absorption spectra obtained during a ship cruise from Capetown to Bremerhaven in January/February 2003 by Fourier Transform Infrared (FTIR) spectroscopy. Precisions of better than 0.5% for the column averaged volume mixing ratios (VMR) of CH₄ and CO₂ are achieved using of O₂ as a reference gas. Shipborne FTIR-measurements of CO and data from SCIAMACHY/ENVISAT retrieved by the Weighting Function Modified Differential Optical Absorption Spectroscopy (WFM-DOAS) retrieval algorithm show qualitatively the same latitudinal variations. WFM-DOAS data of CH₄, N₂O and CO₂ measured over sea exhibit a great spread. The spread is significantly reduced for satellite measurements over land and a reasonable agreement can be obtained if the shipborne data are compared with the closest SCIAMACHY measurements over land. The number of comparisons is too small to draw conclusions. However, by including only WFM-DOAS data with small errors the shipborne and WFM-DOAS data compare within 5% for CH₄ and CO₂ and within 30% for N₂O.

1 Introduction

Carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) are the most important human-influenced greenhouse gases. From pre-industrial times until 1998 atmospheric CO₂ has increased by approximately 90 ppmv to 367 ppmv, atmospheric CH₄ has increased by a factor 2.5 to 1745 ppbv and N₂O has increased by 45 ppbv to 314 ppbv. Together, CO₂, CH₄ and N₂O contribute more than 80% to the radiative forcing from the changes in concentrations of all of the long-lived and globally mixed greenhouse gases. Due to their impact on global warming all three gases are addressed in the Kyoto

protocol. While the increase of CO₂ has been mainly attributed to the combustion of fossil fuel and changes of land use, natural as well as anthropogenic sources are responsible for the increase of CH₄ and N₂O. For atmospheric CO₂ concentrations exchange processes with the biosphere and the oceans are highly important because they result in an increase of atmospheric CO₂ at only about half the rate of CO₂ emissions from human activities (IPCC, 2001). However, the spatial distribution and temporal variability of the carbon sinks is still uncertain. In the case of methane the sources are poorly quantified and characterized (IPCC, 2001). Hence better constraints on the sources and sinks of CH₄ and CO₂ are needed to predict future atmospheric CO₂ and CH₄ concentrations that are essential for future climate predictions.

Carbon monoxide (CO) plays an important role in atmospheric chemistry and acts as an indirect greenhouse gas by perturbing the OH–CH₄–O₃ chemistry (IPCC, 2001). It is closely linked to CH₄, because CH₄ oxidation is an important source for CO and the reaction with OH radicals is a common sink for CH₄ and CO. CO sources include fossil fuel combustion, oxidation of methane and nonmethane hydrocarbons and biomass burning.

Satellite total column measurements of CO₂, CH₄, N₂O and CO will provide quantitative information about these gases with a global coverage. These measurements are needed for the prediction of future global warming. In the case of the “Kyoto gases” CO₂, CH₄ and N₂O the measurements can be used to verify national reduction targets of these gases. One important aspect is that CH₄ and CO₂ total column measurements are likely to become important constraints on the geographic and temporal distribution of CH₄ and CO₂ sources and sinks in the future. Currently no satellite instrument is able to achieve the precisions needed to compete with the existing surface network. Among the instruments that are currently in space SCIAMACHY on ENVISAT has the highest potential to achieve this goal, but the retrieval is just in an experimental phase (Howelling et al., 2003).

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Table 1. Microwindows and fitted interfering gases used in the retrieval.

Retrieved gas	Spectral window for fit in cm^{-1}	Fitted interfering gases
CO ₂	6175–6265	H ₂ O
	6297–6382	H ₂ O
CH ₄	6020–6120	H ₂ O, CO ₂
O ₂	7765–8005	OO ₂ , H ₂ O
CO	2111–2112.1	H ₂ O, O ₃ , N ₂ O
	2157.3–2159.15	H ₂ O, O ₃ , N ₂ O
	2157–2163	H ₂ O, O ₃ , N ₂ O
N ₂ O	2441.8–2444.4	CO ₂
	2481.2–2482.5	
	2806.05–2806.55	

Precise measurements from the ground are essential for the validation of satellite data. It is desired to validate satellite measurements over sea and over land because the low surface albedo over sea is a potential source of error in satellite data. FTIR spectroscopy offers the unique ability to measure column averaged volume mixing ratios of about 20 different trace gases simultaneously and for some gases it is possible to retrieve vertical profiles. Recently it has been shown that CH₄ and CO₂ can be measured from the ground with a precision of 0.5% in the near-infrared using O₂ as a reference gas (Yang et al., 2002; Washenfelder et al., 2003).

In this paper we show that CH₄ and CO₂ can be retrieved from shipborne FTIR measurements with precisions of better than 0.5%, which is essential for the validation of high precision satellite measurements. In addition we compare total columns data for CO₂, CH₄, CO, N₂O retrieved from SCIAMACHY by the WFM-DOAS algorithm (Buchwitz et al., 2000; Buchwitz and Burrows, 2004).

2 Experimental and data analysis

Solar absorption Fourier-transform (FT) measurements aboard the research vessel Polarstern have been performed during a cruise on the Atlantic, starting in Capetown (33.9° S, 18.4° E) on 25 January 2003 and ending in Bremerhaven (53.5° N, 8.6° E) on 17 February 2003. Details about the cruise (ANTXX/3) as well as meteorological data can be obtained via the internet from the Alfred-Wegener-Institute (<http://www.awi-bremerhaven.de/MET/Polarstern/GraphInter.html>). The experimental setup is described elsewhere (Notholt et al., 2000).

The spectra were analysed using the line-by-line codes GFIT, developed at NASA/JPL (e.g. Toon et al., 1992). Profiles of pressure, temperature, ozone and relative humidity up to 30 km are taken from ozonesondes that were launched daily from the ship. For CO₂ a constant initial vmr-profile of 370 ppmv was assumed. The initial vmr-profiles for all other

trace gases are based on balloon observations (Toon et al., 1999). The spectral line parameters were taken from an updated version (version April 2003) of the ATMOS database (Brown et al., 1996).

3 Shipborne solar absorption measurements

The retrieval of carbon monoxide (CO) and nitrous oxide (N₂O) from shipborne measurements has been discussed previously (Notholt et al., 2000). Both gases were analysed in the mid-infrared and the resolution of the spectra is 0.005 cm^{-1} . The microwindows used for the retrieval and the fitted interfering gases are given in Table 1.

The CO₂ and CH₄ measurements are converted to column averaged vmrs to achieve a higher precision. The column averaged vmr is also available from WFM-DOAS data. It has been shown that CO₂ and CH₄ can be retrieved from ground based solar absorption spectra with precisions better than 0.5% (Yang et al., 2002; Washenfelder et al., 2003). For the shipborne measurements we follow essentially the ideas of Yang et al. (2002) and Washenfelder et al. (2003). The spectra used for the CO₂ and CH₄ retrieval cover the spectral range from 5800 to 8000 cm^{-1} . In this spectral range also O₂ can be retrieved. This allows calculation of the column averaged VMR's by scaling the CO₂/O₂ (CH₄/O₂) column ratio with the mean O₂ VMR (0.2095). The resolution of the near-IR spectra is 0.075 cm^{-1} (resolution=0.9/retardation). It was aimed to average fifty scans for each spectrum to produce high signal to noise ratios. However, during most days weather conditions permitted only averages of 10–20 scans. 77 spectra were obtained on 11 days during the cruise from Capetown to Bremerhaven. Depending on weather conditions, the time difference between the recordings ranges from minutes to up to 5 h. The microwindows used for the retrieval are different from those by Yang et al. (2002) and Washenfelder et al. (2003). For CO₂ two microwindows, each containing one CO₂-band were used (Table 1). CH₄ was analysed between 6020 cm^{-1} and 6120 cm^{-1} . For our spectra this spectral window proved to be advantageous compared with the one used by Washenfelder et al. (2003), presumably because of the low efficiency of our detector (GaAs-diode) below 6000 cm^{-1} .

The diurnal variation of the column ratios CO₂/O₂ and CH₄/O₂ is reduced by up to a factor 5 compared to the diurnal variation of the CO₂ and CH₄ columns. This is expected because many systematic errors are common to CO₂ (CH₄) and O₂ (e.g. surface pressure, zenith angle, instrumental line shape) and will partially cancel in the CO₂/O₂ (CH₄/O₂) ratio. Assuming a constant O₂ volume mixing ratio (VMR) in the atmosphere the column averaged volume mixing ratios of CO₂ (CH₄) can be obtained by scaling the column ratio CO₂/O₂ (CH₄/O₂) by the VMR of O₂. The diurnal variation is smaller than 0.4% for CO₂/O₂ and smaller than 0.75% for the CH₄/O₂ (Fig. 1). However, for the vast majority of the

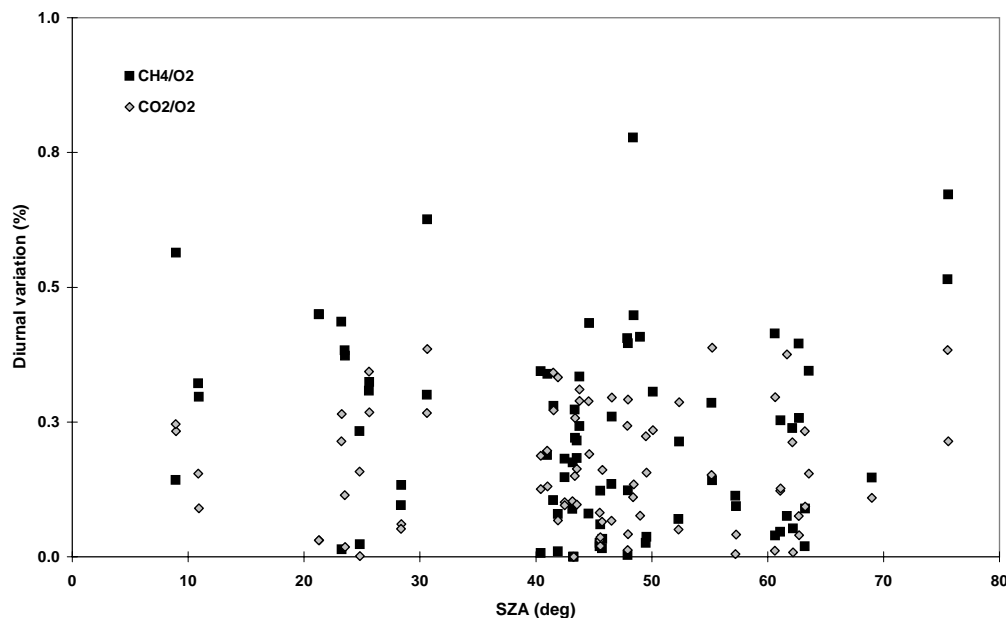


Fig. 1. Diurnal variations of the CO₂ and CH₄ ratios. The diurnal variation is defined as $100 \times \text{abs} \left(\frac{x}{\langle x \rangle} - 1 \right)$ where x is one measurement, $\langle x \rangle$ the mean of the day and abs stands for absolute value.

CH₄/O₂ measurements the diurnal variation is smaller than 0.5%. Using the daily variation as a measure of precision it can be concluded that the column averaged VMR of CH₄ can be measured with a precision of better than 0.5% and the column averaged VMR of CO₂ with a precision of better than 0.4%. Currently no satellite instrument can achieve this precision and it is also sufficient for the validation of proposed future satellite instruments that are dedicated to CO₂ measurements.

Surface in-situ measurements of CO₂ and CH₄ are routinely performed by the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) at land-based sampling stations. These measurements are highly accurate (0.1 ppmv). Data have been collected approximately during the time of the passage of the ship from several NOAA/CMDL-stations along the route (CCGG, 2003). These stations include Mace Head (Ireland), Terceira Island, Tenerife Island, Ascension Island and Crozet Island. The sampling altitude varies between sea level and 2360 m a.s.l. and the stations are in some cases far away from the ships position. An additional problem is that a comparison of the column averaged mixing ratio with in situ measurements is only correct if the vertical mixing ratio profile is uniform. This is approximately true for CO₂ but not for CH₄. The volume mixing ratio of CH₄ strongly decreases in the stratosphere due to oxidation by O(¹D), OH and Cl. Despite these problems the in situ data from NOAA/CMDL provide the best available information about the expected latitudinal variation of CH₄ and CO₂ for the time of the cruise. The retrieved shipborne column averaged volume mixing ra-

tios are unreasonable high compared to the surface data. The source of the bias has not completely resolved, but it is assumed that a large part of the bias arises from errors in the spectroscopic linelist used for the retrieval of the shipborne data. The retrieved shipborne column averaged volume mixing ratio of CH₄ is scaled with a factor 0.9 and the CO₂ with 0.957. This factor was empirically determined by minimizing the bias between the surface and the column data. The scaling factors are different from those reported in Warneke et al. (2005). The reasons for the differences are different spectral and solar linelists. In the following comparison we always refer to the scaled shipborne data.

4 Comparison of shipborne measurements with WFM-DOAS retrievals from SCIAMACHY near infrared spectra

For the retrievals of CO, CH₄, CO₂, H₂O, and N₂O from SCIAMACHY/ENVISAT near-infrared spectra the Weighting Function Modified Differential Optical Absorption Spectroscopy (WFM-DOAS) retrieval algorithm has been developed at the University of Bremen (Buchwitz et al., 2000; Buchwitz and Burrows, 2004). WFM-DOAS version 0.4 scientific products recently released (available from <http://www.iup.physik.uni-bremen.de/sciamachy/NIRNADIRWFMDOAS/>) have been used for the comparison of CO, CH₄, CO₂, and N₂O vertical columns.

WFM-DOAS – data are available for 5 days of the cruise. Only the longitudinally closest WFM-DOAS retrievals

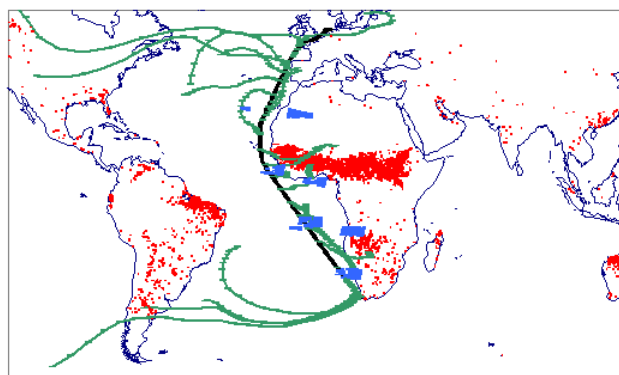


Fig. 2. Ship track (black), backward trajectories (green) at 850 hPa and closest available WFM-DOAS-retrievals (blue). The red dots indicate fires (from MODIS Rapid Response).

within 3° – latitude bands around the ships position have been taken into consideration. The considered WFM-DOAS retrievals are indicated by the blue areas in Fig. 2. Each area consists of a high number of WFM-DOAS retrievals. The blue areas indicate measurements over land and over sea. Land and sea WFM-DOAS data have been compared separately with the shipborne data. The WFM-DOAS data also state an error for each datapoint. Only data with an error below a certain threshold were included. A higher threshold results in a larger spread of the data and a smaller threshold results in a lower number of included datapoints. This demonstrates that the error indicated in the WFM-DOAS data is a qualitatively sensible measure of the precision. In our case the error threshold of the included data is a trade-off between the spread in the data and the number of days for which data can be included. The error threshold was empirically determined by minimising the spread of the data and ensuring that at least three of the five days are included. The error threshold was determined for each dataset separately and is for CO_2 7% over sea and 7.4% over land, 60% for CO over sea, 7% for CH_4 over sea and 30% for N_2O over land. For CO and CH_4 over land the spread did not depend on the threshold and all data were included.

For all compared gases the spread in the WFM-DOAS data is larger over sea than over land (Fig. 3). This is due to the lower surface albedo over the oceans compared to land resulting in a lower signal to noise ratio in the measurements over the oceans.

Among the investigated gases the best agreement between the shipborne and the WFM-DOAS data are observed for CO. Deviations between the datasets are smaller than the observed latitudinal variation (Fig. 3). The most striking feature in both datasets is the CO enhancement between the equator and 10° N. Trajectory calculations reveal biomass burning in West Africa as the apparent source of this enhancement (Fig. 2). WFMDOAS data show that during the time of the cruise enhanced CO can be observed over large parts of the

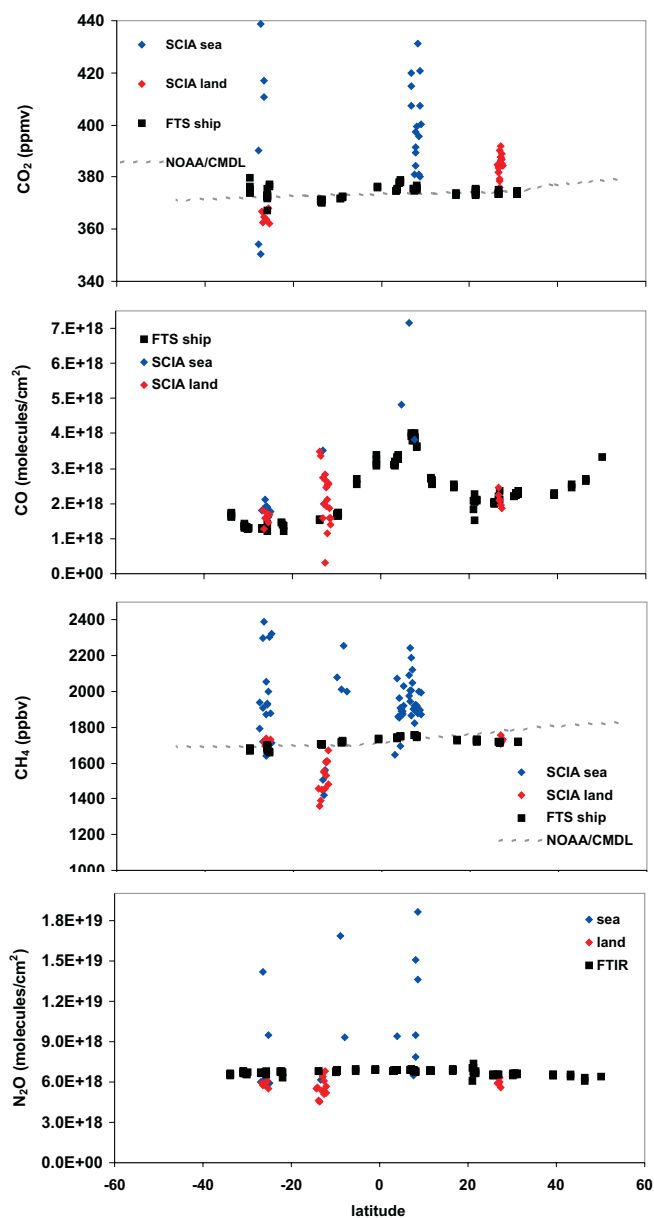


Fig. 3. Comparison of WFM-DOAS-retrievals (blue over sea and red over land) with shipborne data (black rectangles). Only cloud-free WFM-DOAS data with an error smaller than a certain value were taken into account. The maximal errors for the data that were included are for CO_2 7% over sea and 7.4% over land, 60% for CO over sea, 7% for CH_4 over sea and 30% for N_2O over land. For CO and CH_4 over land all data were included. Due to its large spread no N_2O over sea were included. The shipborne data for CO_2 are scaled with a factor 0.957 and the CH_4 data with a factor 0.9. The dotted grey line represents NOAA/CMDL surface sampling data connects data measured during the cruise at stations closed to the cruise track. Stations included are Mace Head (Ireland), Terceira Island, Tenerife Island, Ascension Is. and Crozet Island.

African continent in the latitude band between the equator and 10° N (Fig. 4). This coincides with the biomass burning (Fig. 2) which is typical for that region during the considered time of the year. The deviations between the WFM-DOAS data and the shipborne data between the equator and 10° N result most likely from the different sampling locations. Between 12° S and 15° S the WFM-DOAS CO data show a larger spread than at other latitudes, which is also valid for the other investigated gases.

The WFM-DOAS data for CO₂ over sea show a high spread of up to 90 ppmv. This high spread cannot be real considering a maximal seasonal amplitude of the column of less than 15 ppm. Over land CO₂ ranges from 362 ppmv to 368 ppmv at 25° S–28° S and from 375 ppmv to 391 ppmv at 25° N–28° N. The mean of the included data at 25° S–28° S is 365±2.2 ppmv and 384.6±3.8 ppmv at 25° N–28° N. The deviation between the WFM-DOAS and the shipborne data is less than 4% at these latitudes. The CH₄ WFM-DOAS data over sea exhibit a large spread and the majority of datapoints is higher than the shipborne data. Similar to CO the CH₄ data over land show a larger spread between 12° S and 15° S than at other latitudes. A deviation between satellite and shipborne measurement of up to 20% is observed in this latitude band. By lowering the error threshold to 4% the data between 12° S and 15° S are excluded. At the remaining two latitude bands the WFM-DOAS data over land and the shipborne CH₄ agree within 2.5%. In the case of N₂O the WFM-DOAS data over land are significantly lower than the shipborne data and the spread is higher than the latitudinal variation. Due to its high spread the WFM-DOAS data over sea is not shown.

5 Conclusions

High resolution solar absorption spectra were obtained during a ship cruise from Capetown to Bremerhaven in January/February 2003 by FTIR spectroscopy. It has been demonstrated that column averaged volume mixing ratios (VMR) of CH₄ and CO₂ can be retrieved with precisions of better than 0.5% from these spectra by using O₂ as a reference gas.

Recently released SCIAMACHY WFM-DOAS scientific products of CO, CH₄, N₂O and CO₂ are compared with the shipborne data. In the case of CO the agreement between shipborne and satellite data is very good in the sense that the data show qualitatively the same latitudinal variation and that the difference between shipborne and satellite data is smaller than the latitudinal variation. WFM-DOAS data of CH₄, N₂O and CO₂ measured over sea exhibit a large spread. A better agreement can be obtained if the shipborne data are compared with the closest SCIAMACHY measurements over land. A crucial point for the comparison is the definition of an error threshold filter applied on the WFM-DOAS results. At the expense of the number of included datapoints

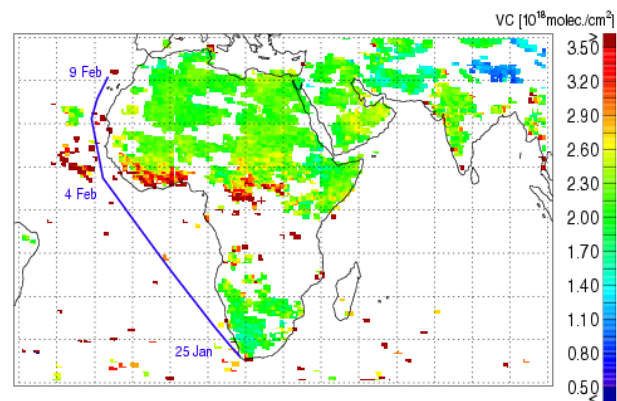


Fig. 4. CO vertical columns from SCIAMACHY WFM-DOAS-retrievals (Version 0.4). The plot includes all available WFM-DOAS data for the duration of the cruise (24, 27, 30, 31 January 2003 and 3, 4, 8 February 2003). Only cloudfree measurements with an error <60% were used.

the shipborne and the WFM-DOAS data for CH₄ and CO₂ can be brought into an agreement of 5%. N₂O shows the strongest deviation between shipborne and satellite data of up to 30%. However, for all gases the number of comparisons is too small for statistical analyses in order to achieve further quantitative conclusions about the agreement.

Acknowledgements. We would like to thank G. Toon from the Jet Propulsion Laboratory in Pasadena for many helpful comments. We wish to thank the British Atmospheric Data Centre for the calculation of trajectories and access to ECMWF data and the MODIS Rapid Response developed by NASA's Goddard Space Flight Center and the University of Maryland for the fire data. We are grateful to the NOAA Climate Monitoring and Diagnostics Laboratory for providing free access of surface data. Last but not least we would like to thank the German Ministry for Research and Education (BMBF) that funded this work via the DLR-Bonn (Grants 50EE0013 and 50EE0014).

Edited by: U. Platt

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