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T. Steck, N. Glatthor, T. von Clarmann, H. Fischer, J. M. Flaud, et al.. Retrieval of global upper tropospheric and stratospheric formaldehyde (H₂CO) distributions from high-resolution MIPAS-Envisat spectra. *Atmospheric Chemistry and Physics*, 2008, 8 (3), pp.470. hal-00328564

HAL Id: hal-00328564

<https://hal.science/hal-00328564>

Submitted on 18 Jun 2008

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Retrieval of global upper tropospheric and stratospheric formaldehyde (H_2CO) distributions from high-resolution MIPAS-Envisat spectra

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Received: 2 August 2007 – Published in Atmos. Chem. Phys. Discuss.: 18 September 2007

Revised: 11 December 2007 – Accepted: 3 January 2008 – Published: 1 February 2008

Abstract. The Fourier transform spectrometer MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) on Envisat measures infrared emission of the Earth's atmosphere in a limb viewing mode. High spectral resolution measurements of MIPAS are sensitive to formaldehyde from the upper troposphere to the stratopause. Single profile retrievals of formaldehyde are dominated by a 60% noise error; however zonal mean values for 30 days of data during 8 September 2003 and 1 December 2003 reduces this error by a factor of 20 or more. The number of degrees of freedom for single profile retrieval ranges from 2 to 4.5 depending on latitude and number of cloud-free tangent altitudes. In the upper tropical troposphere zonal mean values of about 70 parts per trillion by volume (pptv) were found, which have been attributed to biomass burning emissions. In the stratosphere, formaldehyde values are determined by photochemical reactions. In the upper tropical stratosphere, formaldehyde zonal mean maximum values can reach 130 pptv. Diurnal variations in this region can be up to 50 pptv. Comparisons with other satellite instruments show generally good agreement in the region of upper troposphere and lower stratosphere as well as in the upper stratosphere.

2000). The main sources of H_2CO in the troposphere are biomass burning, anthropogenic, and biogenic emissions as well as methane oxidation. It is destroyed via photolysis and reaction with OH. In continental boundary layers, non-methane hydrocarbons (NMHCs) emitted by biogenic and anthropogenic sources usually dominate over methane as a source of H_2CO (Munger et al., 1995). In the stratosphere, the H_2CO profile results from an equilibrium between production by methane oxidation and destruction as described above (Brasseur and Solomon, 1986), which means that a diurnal variation in formaldehyde abundances is expected in the stratosphere where production and destruction processes are dominated by photochemistry.

The first stratospheric measurements of formaldehyde were made with a ground-based Fourier Transform infrared (FTIR) instrument (Barbe et al., 1979). Global distributions of H_2CO columns have been derived with the GOME (Global Ozone Monitoring Experiment) instrument (Burrows et al., 1999; Chance et al., 2000) which are dominated by the tropospheric signal. Vertically resolved satellite measurements of H_2CO have been made recently with the sub-millimeter radiometer (SMR) aboard the Odin satellite (Ricaud et al., 2007), with an altitude region of about 35 to 50 km, and with the Atmospheric Chemistry Experiment – Fourier Transform Spectrometer (ACE-FTS) (Coheur et al., 2007) with focus on the upper tropospheric and lower stratospheric (UTLS) region. In the following we show that MIPAS has the potential to provide day and night profile information of formaldehyde from the upper troposphere to the stratopause on a global scale.

1 Introduction

1.1 Formaldehyde sources, sinks and measurements

Formaldehyde (H_2CO) is a principal intermediate in the oxidation of hydrocarbons in the troposphere (Chance et al.,



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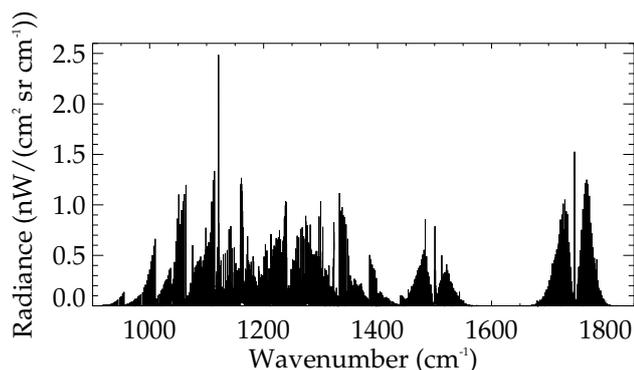


Fig. 1. Simulated H_2CO spectrum at 16.4 km tangent altitude with only H_2CO in the atmosphere for tropical conditions; based on new spectroscopic data (Perrin et al., 2003).

1.2 MIPAS-Envisat description

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a Fourier transform infrared (FTIR) spectrometer measuring the emission of the Earth's atmosphere in limb-viewing mode (Fischer and Oelhaf, 1996; Fischer et al., 2007). MIPAS was launched on the environmental satellite Envisat on 1 March 2002 into a sun-synchronous polar orbit with equatorial local crossing times of 10:00 (descending node) and 22:00 (ascending node). MIPAS was operated in its original measurement mode with high spectral resolution of 0.025 cm^{-1} from July 2002 to March 2004. Flight altitude of Envisat is 800 km and one orbit takes about 100 min allowing to measure 72 limb sequences per orbit with a sampling of about 550 km along track. With these characteristics, MIPAS is able to provide vertical profiles of temperature and a large number of trace gases globally during day and night. The nominal observation mode comprises 17 tangent altitudes per limb sequence from 6 to 68 km (3 km step-width between 6 and 42 km, and at 47, 52, 60, and 68 km). The 3 km step-width was chosen due to the vertical instantaneous field-of-view (FOV) of MIPAS, which is about 3 km, while the across track FOV is about 30 km. The generation of calibrated radiance spectra, the so-called level 1B data, is performed by the European Space Agency (ESA) (Nett et al., 2002). ESA additionally provides vertical profiles of temperature and 6 key species (H_2O , O_3 , HNO_3 , CH_4 , N_2O , and NO_2), the so-called Level 2 product. Furthermore, there are several institutes which have developed retrieval codes to determine trace gases beyond the ESA key species. The formaldehyde distributions described in this paper were derived with the retrieval processor of the Institut für Meteorologie und Klimaforschung (IMK) and the Instituto de Astrofísica de Andalucía (IAA) (von Clarmann et al., 2003).

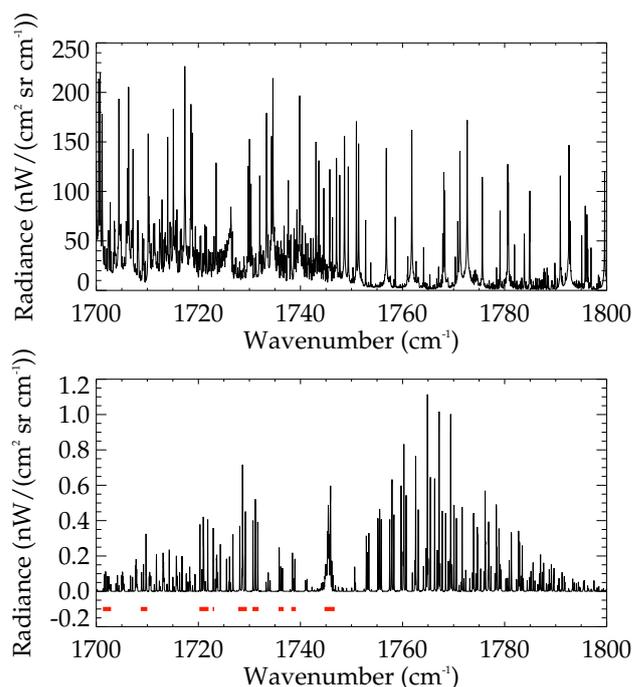


Fig. 2. Top: Simulated spectrum at 16.4 km tangent altitude; tropical conditions, all gases included. Bottom: Formaldehyde contribution only (note the different scale). The noise equivalent spectral radiance of the measurement is in the order of $3\text{ nW}/(\text{cm}^{-2}\text{ sr cm}^{-1})$. Red horizontal bars represent the microwindows used for data analysis.

2 Formaldehyde spectral signatures

In the mid-infrared spectral region, formaldehyde shows weak emission lines between about 900 and 1850 cm^{-1} (Fig. 1) with the most prominent band centered around 1750 cm^{-1} . Due to the lowest instrumental noise level there, this region is used in the retrieval based on new spectroscopic data (Perrin et al., 2003; Sharpe et al., 2004) which are thought to be more accurate and contain more spectral lines compared to previous data. The challenge of the H_2CO retrieval is the very weak signal of the emission lines compared to the instrumental noise which is about $3\text{ nW}/(\text{cm}^{-2}\text{ sr cm}^{-1})$ at the relevant spectral region.

Figure 2 (top) shows the simulated formaldehyde spectrum at 16.4 km tangent altitude for tropical atmospheric conditions. The spectrum is dominated by water vapor lines and minor ozone and nitric acid signatures. The H_2CO contribution is shown in Fig. 2 (bottom) which is given by the residual spectrum. The residual spectrum is the difference between the spectra at 16.4 km with and without formaldehyde considered in the simulation. For these conditions the formaldehyde contribution is below the instrumental noise of about $3\text{ nW}/(\text{cm}^{-2}\text{ sr cm}^{-1})$.

3 Retrieval setup

For the retrieval, 9 narrow spectral regions (microwindows) have been selected by visual inspection between 1700 cm⁻¹ and 1750 cm⁻¹, which is the upper end of MIPAS channel C (see Table 1). The main criterion for the selection was high sensitivity to formaldehyde and low interference by other gases. Since the formaldehyde contribution is so small, the contribution of other gases still needs to be considered even after careful microwindow selection. Many gases need to be retrieved jointly in order to limit propagation of related errors in particular in the UTLS region. These interfering gases are: H₂O, O₃, HNO₃, ClONO₂, and PAN.

The retrieval procedure follows a scheme similar to that described by Rodgers (2000):

$$\mathbf{x}_{i+1} = \mathbf{x}_i + (\mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i + \mathbf{R})^{-1} \times [\mathbf{K}_i^T \mathbf{S}_y^{-1} (\mathbf{y} - \mathbf{F}(\mathbf{x}_i)) - \mathbf{R}(\mathbf{x}_i - \mathbf{x}_a)], \quad (1)$$

where \mathbf{x} is the retrieval vector, \mathbf{K} the partial derivatives of the spectra with respect to the retrieval vector (Jacobian), \mathbf{S}_y the covariance matrix due to measurement noise, \mathbf{R} the regularization or constraint matrix, \mathbf{y} the measurement vector, \mathbf{F} the forward model, \mathbf{x}_a the a priori profile, and i the iteration index.

The retrieval is performed on a fine vertical grid with 1 km distance up to 44 km and 2 km above. Since the retrieval grid is finer than the tangent altitude spacing, the retrieval is stabilized by a first order Tikhonov smoothing constraint (Tikhonov, 1963):

$$\mathbf{R} = \alpha \mathbf{L}_1^T \mathbf{L}_1, \quad (2)$$

where α is the strength of the constraint and \mathbf{L}_1 the first order derivative matrix (as discussed by Steck (2002)), which smoothes the solution without pushing it towards the a priori profile. The regularization strength α is determined by finding a trade-off between the number of degrees of freedom, which is given by the trace of the averaging kernel \mathbf{A} (Rodgers, 2000)

$$\mathbf{A} = (\mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i + \mathbf{R})^{-1} \mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i \quad (3)$$

and the noise induced error (Steck, 2002)

$$\mathbf{S}_n = (\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{R})^{-1} \mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} (\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{R})^{-1}, \quad (4)$$

where \mathbf{S}_n is the error covariance matrix due to instrumental noise, and where \mathbf{K} is evaluated for the final result of \mathbf{x} after convergence. A regularization strength α of 10⁴ has been selected as a reasonable trade-off between the number of degrees of freedom and the noise error. The sensitivity $\Delta \mathbf{x}_b$ of the retrieval in terms of standard deviation to uncertain parameters b is estimated as

$$\Delta \mathbf{x}_b = (\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{R})^{-1} \mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K}_b \sigma_b, \quad (5)$$

where \mathbf{K}_b is the sensitivity of the measurements to the uncertain parameter b , and where σ_b is the uncertainty of b in terms

Table 1. Microwindows for MIPAS formaldehyde retrievals.

MW	begin (cm ⁻¹)	end (cm ⁻¹)
1	1701.3	1702.9
2	1708.7	1710.0
3	1720.2	1722.0
4	1722.8	1723.1
5	1727.8	1729.5
6	1730.6	1731.8
7	1735.7	1736.7
8	1738.2	1739.1
9	1744.7	1746.7

of standard deviation. The following uncertainties have been assumed: spectral shift: 0.0005 cm⁻¹; gain calibration: 1%; line of sight uncertainty in terms of elevation pointing: 150 m; temperature 0.4–1.0 K, depending on altitude; uncertainties in spectroscopic data, conservatively estimated at 8%; instrument line shape in terms of modulation efficiency uncertainty: 3%.

As initial guess, the profile from the U.S. standard atmosphere 1976 is used. As a priori profile we use a zero profile to avoid any artificial structures in the formaldehyde profile not caused by the measurements. Thus, the linear retrieval equation (Rodgers, 2000)

$$\hat{\mathbf{x}} = \mathbf{A} \mathbf{x}_t + (\mathbf{I} - \mathbf{A}) \mathbf{x}_a, \quad (6)$$

where $\hat{\mathbf{x}}$ is the estimated and \mathbf{x}_t is the true H₂CO profile, simplifies to $\hat{\mathbf{x}} = \mathbf{A} \mathbf{x}_t$ for $\mathbf{x}_a = 0$. This means that in linear approximation the retrieved H₂CO profile is a smoothed version of the true profile.

All settings (microwindows, constraint, initial guess and a priori profiles) are chosen time and latitude-independent. This is again to ensure that all structures visible in the retrieved distributions originate from the measurements and are not artefacts resulting from the retrieval setup.

4 Single profile retrieval and diagnostics

The retrieval procedure described above has been applied to real MIPAS measurements. Figure 3 shows an example for single profile retrieval of formaldehyde for MIPAS-Envisat orbit 8194 on 24 September 2003, at 14° S/46° W, which is right over Brazil. The profile shows maximum values in the UTLS region of 180 parts per trillion by volume (pptv) and near the stratopause of 140 pptv, which are both of reasonable size. However, the profile shows some oscillations and the retrieval error caused by measurement noise is rather large with values of about 70 pptv leading to percentage errors larger than 100% except for the altitude regions with maximum formaldehyde (about 60%).

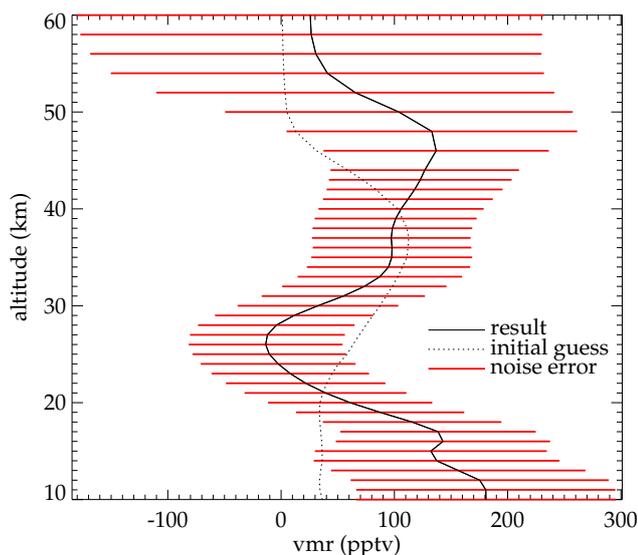


Fig. 3. Formaldehyde retrieval result (solid) (orbit 8194, 24 September 2003, 14° S/46° W) with error bars (red) and initial guess (dotted).

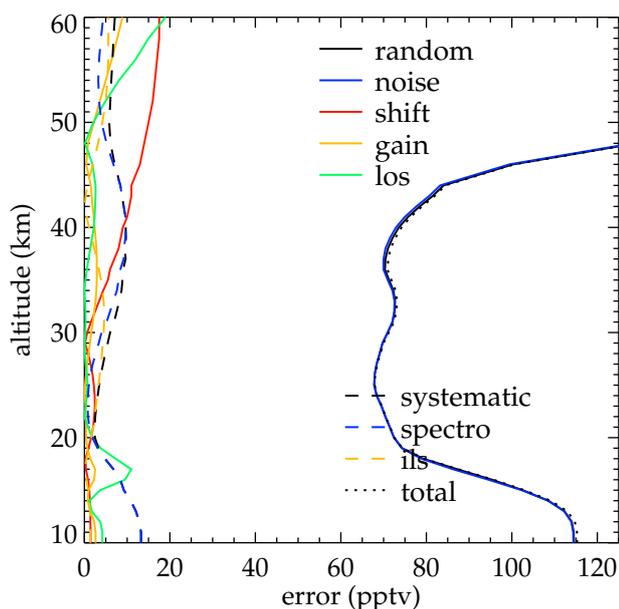


Fig. 4. Error analysis of formaldehyde retrieval (24 September 2003, 14° S/46° W). Error sources from top to bottom: total random error (solid black), measurement noise (solid blue), spectral shift (solid red), gain calibration uncertainty (solid yellow), line-of-sight (LOS) uncertainty (solid green), total systematic error (dashed black), spectroscopic data uncertainties (dashed blue), instrumental line shape (ILS) (dashed yellow), and total error (dotted black).

A detailed error analysis is given in Fig. 4. Due to the small formaldehyde signatures and large instrumental noise, as discussed in Section 2, the measurement noise induced er-

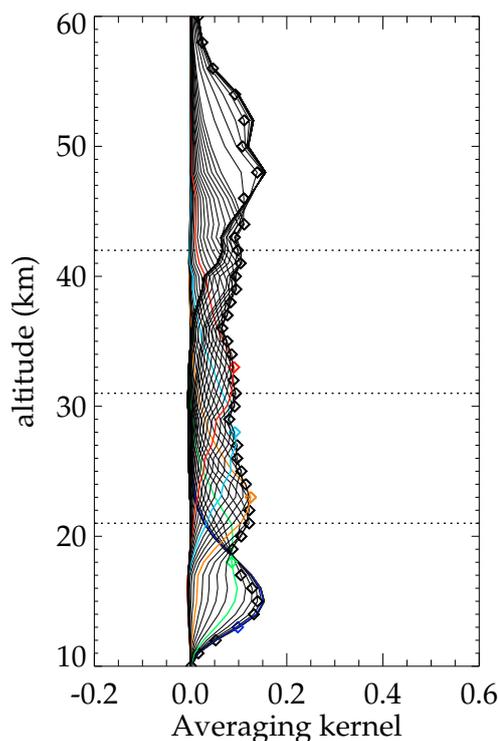


Fig. 5. Formaldehyde averaging kernels; some altitudes are highlighted in colors; dotted horizontal lines delimit the altitude regions characterized by one degree of freedom each, which is derived from the sum of the diagonal elements of the averaging kernel matrix (diamonds).

ror (Fig. 4, solid blue) is the dominating error source with values between 70 and 115 pptv in the altitude region from 10 to 47 km. The noise error includes uncertainties caused by the joint-retrieval of the interfering species H_2O , O_3 , HNO_3 , ClONO_2 , and PAN. The error due to spectral shift (Fig. 4, solid red) exceeds 10 pptv at 40 km altitude and further increases with altitude. In a wide altitude range, the systematic errors are dominated by uncertainties in spectroscopic data, which are conservatively estimated at 8% (Fig. 4, dashed blue). For single profile retrieval, however, this error becomes negligible compared to the noise error. Further errors due to gain calibration, instrumental line shape (ILS) and line-of-sight (LOS) uncertainties are mainly below 10 pptv for the complete altitude range.

The formaldehyde averaging kernel \mathbf{A} (Fig. 5) shows sensitivity to the true profile from the UTLS region up to the stratopause. The dotted horizontal lines in Fig. 5 delimit the altitude region of every single degree of freedom with a total number of 3.9, which is given by the trace of \mathbf{A} . The averaging kernels show that MIPAS is also sensitive to the UTLS region with about one piece of information. The vertical resolution is estimated at about 11 km. The averaging kernel also shows that there is basically no information in the

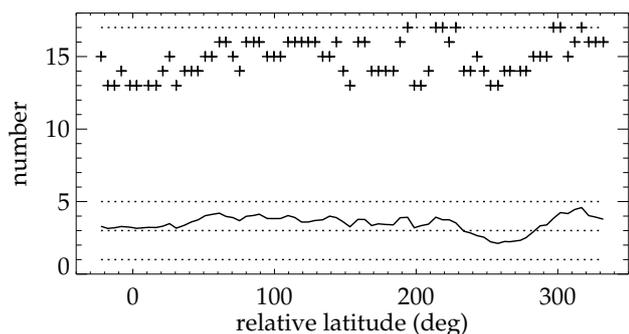


Fig. 6. Degrees of freedom (solid line) and number of cloud-free tangent altitudes (crosses) along orbit 8194 (24 September 2003). The values on the abscissa have the following meaning: 0° and 180° correspond to the equator, 90° to the north pole, and 270° to the south pole. Dotted lines are for guidance only.

retrieval above 60 km and below 10 km, although for this geolocation the lowest tangent altitude is at 7.9 km. This means that the atmosphere becomes optically opaque.

Figure 6 (solid line) shows the variation of the number of degrees of freedom along the complete orbit 8194. The number of independent pieces of information varies between 2 and 4.5 depending on latitude and number of cloud-free tangent altitudes (crosses). Near the southern winter pole (Fig. 6, about 270°), the number of tangent altitudes not affected by clouds is reduced to 13 due to polar stratospheric clouds. Together with the low temperatures in this region and the resulting low signal, the number of degrees of freedom has a minimum and is close to 2. The mean number of degrees of freedom for this orbit is about 3.5.

5 Global MIPAS formaldehyde data

The error analysis of the single profile retrieval has shown large random errors which are dominating the error budget. To reduce this error component and to obtain more reliable data, averaging over a larger ensemble of data is the obvious way to go. Between 8 September 2003 and 1 December 2003, 30 days of data have been analyzed which cover about 420 orbits or more than 29 000 geolocations.

5.1 Zonal means

Zonal mean formaldehyde data is shown in Fig. 7. Averages have been taken for latitude bins of 5° leading to about 500 to 1000 profiles per bin. This means a reduction of the random error (i.e. measurement noise and the randomly varying parameter errors including spectral shift, gain calibration uncertainty, line of sight uncertainties and temperature) by a factor of about 20 to 30. For the averaging only altitudes are used which are within the cloud-masked tangent altitude range and where the corresponding diagonal value of the averaging ker-

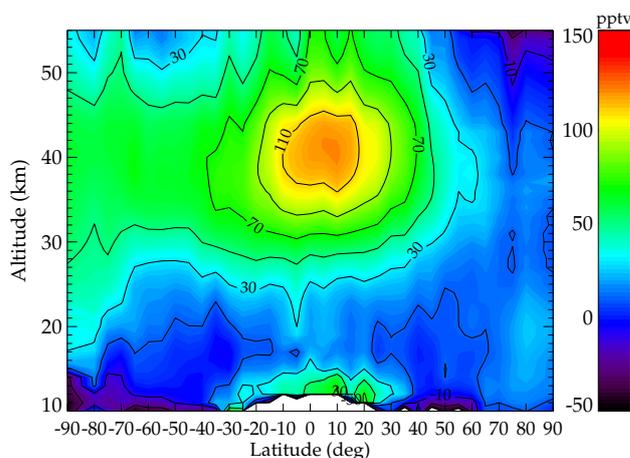


Fig. 7. Zonal mean of formaldehyde for the period 8.9.2003–1.12.2003. Zonal averages are taken for 5° latitudinal bins. White areas mean no data available or values are outside the plotting range.

nel is above a given threshold (0.03). Care has been taken to avoid sampling artefacts due to diurnal variation (see below). In order to avoid biasing the zonal means towards daytime or nighttime values, depending on the unbalanced availability of daytime and nighttime measurements, the zonal mean has been calculated as the average of the daytime mean and the nighttime mean distribution. There actually are slightly more daytime than nighttime measurements available.

In the upper tropical tropopause region, mean values exceed 60 pptv. These larger values are attributed mainly to urban and industrial pollution and biomass burning emissions. MIPAS has detected enhanced values also in other pollutants like PAN (Glatthor et al., 2007), C_2H_6 , and ozone (von Clarmann et al., 2007). Due to the very weak emission lines, MIPAS can measure enhanced formaldehyde mainly in the tropical troposphere, where lower tropospheric air is transported to higher altitudes.

In the upper stratosphere a prominent maximum is visible at around 40 km altitude with values of about 130 pptv in the tropics. The stratospheric values in the southern hemisphere are smaller than in the tropics but much larger compared to the northern hemisphere. This is likely connected with different illumination conditions and different availability of OH. In the northern winter upper stratosphere low temperatures cause an extremely low signal, which makes the formaldehyde retrieval even more difficult and prone to error propagation. These degraded retrievals are characterized by unrealistic negative mixing ratios.

5.2 Diurnal variations

Since MIPAS is measuring the atmospheric emission, the zonal mean data (Fig. 7) can be divided into day- and nighttime measurements. Daytime measurements (Fig. 8) show

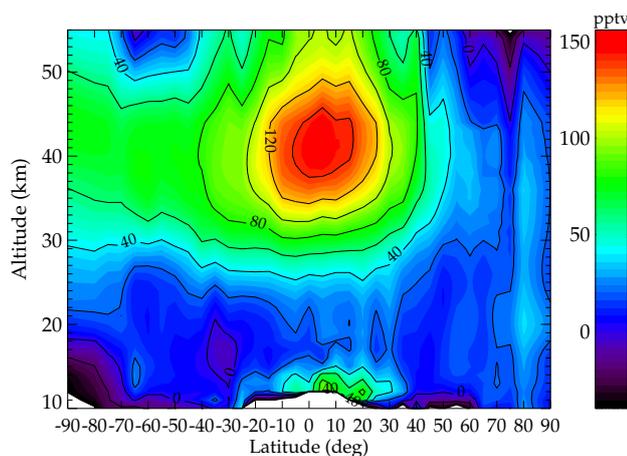


Fig. 8. Zonal mean of daytime formaldehyde for the period 8.9.2003–1.12.2003. For more details see Fig. 7.

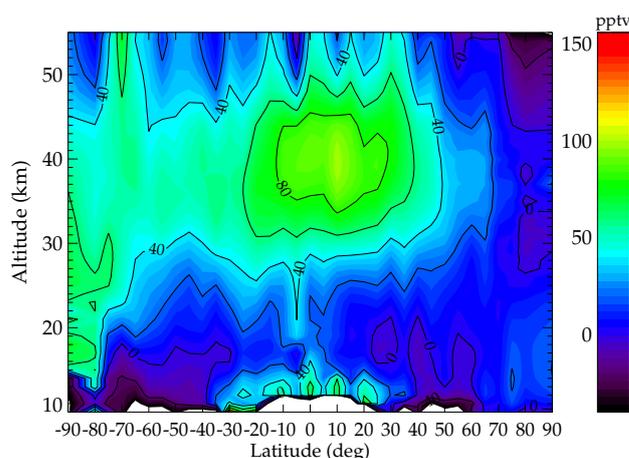


Fig. 9. Zonal mean of nighttime formaldehyde for the period 8.9.2003–1.12.2003. For more details see Fig. 7.

enhancements in the stratosphere with maximum values of more than 150 pptv. For nighttime measurements (Fig. 9), formaldehyde stratospheric maximum values are reduced to values below 100 pptv. This diurnal variation is also seen in H_2CO fields modeled with the Modular Earth Sub-model System (MESSy) (Jöckel et al., 2005) (<http://www.messy-interface.org/>). In the southern polar lower stratosphere, the nighttime values are larger than those at daytime. One might speculate that this is connected to the special chemistry in the polar vortex, where the relative weight of the different source and sink reactions might be different than under normal conditions. This issue certainly deserves further investigation.

While photochemistry plays the dominating role particularly in the upper stratosphere, in the upper troposphere also transport is important to understand the formaldehyde mixing ratios and may outweigh the diurnal variations there.

6 Comparison with other satellite instruments

In order to put our results into the context of previously published measurements of H_2CO , we compare the MIPAS results with those from ACE-FTS (Coheur et al., 2007) and Odin-SMR (Ricaud et al., 2007), as well as REPROBUS model calculations (Lefèvre et al., 1994; Ricaud et al., 2007). While this comparison is not meant as quantitative validation, it still gives an idea of the general agreement between the measurements.

6.1 Comparison with ACE-FTS

ACE-FTS is operating in the infrared between 750 and 4400 cm^{-1} at a spectral resolution of 0.02 cm^{-1} (Bernath et al., 2005). ACE-FTS is a solar occultation instrument measuring a maximum of 15 sunrises and 15 sunsets a day. The

altitude range spans from the upper troposphere to the mesosphere at an average vertical resolution of 4 km.

On 8 October 2005, ACE-FTS measured a vertical profile of H_2CO in a biomass burning plume (Coheur et al., 2007), using another spectral region ($3.6\text{ }\mu\text{m}$). In the altitude range between 12 and 20 km, which represents approximately one degree of freedom of the MIPAS measurement, the estimated partial zenith column amount derived from the ACE-FTS profile is $1.33 \times 10^{14}\text{ H}_2\text{CO molecules/cm}^2$. The zonal mean partial zenith column amount at this altitude derived from MIPAS measurements at 10°N , also within a belt of enhanced mixing ratios of pollutants, between 8 September and 10 December 2003, is $(1.52 \pm 0.35) \times 10^{14}\text{ molecules/cm}^2$. Given possible inconsistencies between the spectroscopic data in the two spectral domains, such a result is very encouraging, suggesting reasonable overall agreement of the measured mixing ratios and comparability of the atmospheric situations covered.

6.2 Comparison with Odin-SMR

Odin-SMR is a limb-viewing instrument aboard the Odin satellite launched on 20 February 2001 into a 600 km sun-synchronous orbit (Murtagh et al., 2002). The formaldehyde analysis is based on a weak rotational transition line at 576.7083150 GHz (Ricaud et al., 2007). The signal-to-noise ratio is increased by averaging about 1000 spectra within vertical layers of 2 km width leading to profile retrieval in the upper stratosphere.

For the comparison, the Odin-SMR measurements from 19 to 20 September 2005 were used. Table 2 contains averaged partial zenith column amounts from 37–49 km altitude within three latitude bands: $90^\circ\text{ S}–45^\circ\text{ S}$, $30^\circ\text{ S}–30^\circ\text{ N}$, and $45^\circ\text{ N}–90^\circ\text{ N}$. This altitude range is represented by approximately one degree of freedom of the MIPAS measurements. These data are compared to MIPAS averaged partial

Table 2. Partial zenith column amounts (37–49 km) in units of 10^{12} molecules H_2CO per cm^2 . Odin-SMR values are averaged for the period 19 to 20 September 2005, REPROBUS values are averaged for September 2005, and MIPAS values are averaged for the period 8 September 2003 to 1 December 2003.

latitude	Odin-SMR	REPROBUS	MIPAS
90° S–45° S	2.86	2.76	2.91±0.10
30° S–30° N	5.66	9.37	7.74±0.17
45° N–90° N	5.20	4.41	1.94±0.29

zenith column amounts (8 September 2003 to 1 December 2003) and three-dimensional chemical-transport model monthly average (September) calculated by REPROBUS (Lefèvre et al., 1994; Ricaud et al., 2007).

For latitudes south of 45° S, MIPAS and Odin-SMR values agree within the MIPAS standard error (Table 2, first row). Also the agreement with REPROBUS is reasonable. In the tropical region (–30° S to +30° S), the discrepancies are somewhat larger but MIPAS falls just between the Odin-SMR and REPROBUS results. The MIPAS standard error of the mean does not explain the differences but it does not include any systematic components such as spectroscopic data uncertainties, which are not reduced by averaging. Further, no Odin-SMR uncertainties have been considered. Largest discrepancies are observed for latitudes north of 45° N. Here MIPAS partial zenith column amounts are more than a factor of two lower than those of Odin-SMR and REPROBUS. This apparent disagreement is attributed to seasonal variation; contrary to Odin-SMR and REPROBUS data, the MIPAS average, which spans from 8 September to 1 December, includes polar winter data which push the seasonal mean towards much lower values (Fig. 7). Of course due to inter-annual variability and different averaging periods no perfect agreement can be expected.

7 Summary and conclusions

We have demonstrated that high spectral resolution measurements of MIPAS on Envisat are sensitive to formaldehyde. These emission lines are weak compared to the instrumental noise; nevertheless vertical distributions from the upper troposphere to the stratopause have been derived on basis of most recent spectroscopic data. Formaldehyde single profile retrieval is formally possible, however with a large noise error (more than 60%), which is the dominant error source. The number of degrees of freedom for single profile retrieval ranges from 2 to 4.5 depending on latitude and number of cloud-free tangent altitudes.

For the period from 8 September 2003 to 1 December 2003, 30 days of data have been analyzed which cover 420 orbits or more than 29 thousand geolocations. To reduce

the large noise error component, profiles have been averaged leading to a reduction of the noise error to 4% or less, depending on atmospheric variability and the actual abundance. In the upper tropical troposphere, enhanced formaldehyde values of about 70 pptv were measured which have been attributed to pollution by urban or industrial sources or biomass burning emission. In the stratosphere, formaldehyde production and destruction is dominated by photochemical reactions. Zonal mean profiles show a prominent maximum in the upper tropical stratosphere with values up to 130 pptv, which are decreasing towards the poles. Zonal mean values in the upper tropical stratosphere show differences between day and night of up to 50 pptv.

Comparison with other satellite instruments (ACE-FTS and Odin-SMR) reveals reasonable agreement. ACE-FTS partial zenith column amounts measured in the upper troposphere/ lower stratosphere region in a biomass burning plume in 2005 fall within the MIPAS autumn 2003 zonal mean plus/minus its standard error. Further, under comparable atmospheric conditions the MIPAS results are in good to reasonable agreement with Odin-SMR measurements and REPROBUS calculations.

Acknowledgements. We thank ESA for providing the MIPAS spectra (Level-1B data). The simulations were performed on the national super computer HP XC6000 at the High Performance Computing Center Stuttgart (HLRS) under the project MIPAS.

Edited by: M. van Roozendael

References

- Barbe, A., Marché, P., Secroun, C., and Jouve, P.: Measurements of Tropospheric and Stratospheric H_2CO by an Infrared High Resolution Technique, *Geophys. Res. Lett.*, 6, 463–465, 1979.
- Bernath, P. F., McElroy, C. T., Abrams, M. C., Boone, C. D., Butler, M., Camy-Peyret, C., Carleer, M., Clerbaux, C., Coheur, P.-F., Colin, R., DeCola, P., De Mazière, M., Drummond, J. R., Dufour, D., Evans, W. F. J., Fast, H., Fussen, D., Gilbert, K., Jennings, D. E., Llewellyn, E. J., Lowe, R. P., Mahieu, E., McConnell, J. C., McHugh, M., McLeod, S. D., Michaud, R., Midwinter, C., Nassar, R., Nichitiu, F., Nowlan, C., Rinsland, C. P., Rochon, Y. J., Rowlands, N., Semeniuk, K., Simon, P., Skelton, R., Sloan, J. J., Soucy, M.-A., Strong, K., Tremblay, P., Turnbull, D., Walker, K. A., Walkty, I., Wardle, D. A., Wehrle, V., Zander, R., and Zou, J.: Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, 32, L15S01, doi: 10.1029/2005GL022386, 2005.
- Brasseur, G. and Solomon, S.: *Aeronomy of the Middle Atmosphere*, Atmospheric Science Library, D. Reidel Publishing Company, Dordrecht, Holland, 2nd Edn., 1986.
- Burrows, J. P., Weber, M., Buchwitz, M., Rozanov, V., Ladstätter-Weißmayer, A., Richter, A., de Beek, R., Hoogen, R., Bramstedt, K., Eichmann, K.-U., Eisinger, M., and Perner, D.: The Global Ozone Monitoring Experiment (GOME): Mission Concept and first scientific results, *J. Atmos. Sci.*, 56, 151–175, 1999.

- Chance, K., Palmer, P. I., Spurr, R. J. D., Martin, R. V., Kurosu, T. P., and Jacob, D. J.: Satellite observations of formaldehyde over North America from GOME, *Geophys. Res. Lett.*, 27, 3461–3464, 2000.
- Coheur, P.-F., Herbin, H., Clerbaux, C., Hurtmans, D., Wespes, C., Carleer, M., Turquety, S., Rinsland, C. P., Remedios, J., Hauglustaine, D., Boone, C. D., and Bernath, P. F.: ACE-FTS observation of a young biomass burning plume: first reported measurements of C_2H_4 , C_3H_6O , H_2CO and PAN by infrared occultation from space, *Atmos. Chem. Phys.*, 7, 5437–5446, 2007, <http://www.atmos-chem-phys.net/7/5437/2007/>.
- Fischer, H. and Oelhaf, H.: Remote sensing of vertical profiles of atmospheric trace constituents with MIPAS limb-emission spectrometers, *Appl. Opt.*, 35, 2787–2796, 1996.
- Fischer, H., Birk, M., Blom, C., Carli, B., Carlotti, M., von Clarmann, T., Delbouille, L., Dudhia, A., Ehlfalt, D., Endemann, M., Flaud, J. M., Gessner, R., Kleinert, A., Koopmann, R., Langen, J., López-Puertas, M., Mosner, P., Nett, H., Oelhaf, H., Perron, G., Remedios, J., Ridolfi, M., Stiller, G., and Zander, R.: MIPAS: an instrument for atmospheric and climate research, *Atmos. Chem. Phys. Discuss.*, 7, 8795–8893, 2007, <http://www.atmos-chem-phys-discuss.net/7/8795/2007/>.
- Glatthor, N., von Clarmann, T., Fischer, H., Funke, B., Grabowski, U., Höpfner, M., Kellmann, S., Linden, A., Milz, M., Steck, T., and Stiller, G. P.: Global peroxyacetyl nitrate (PAN) retrieval in the upper troposphere from limb emission spectra of the Michelson Interferometer for Passive Atmospheric Sounding MIPAS, *Atmos. Chem. Phys.*, 7, 2775–2787, 2007, <http://www.atmos-chem-phys.net/7/2775/2007/>.
- Jöckel, P., Sander, R., Kerkweg, A., Tost, H., and Lelieveld, J.: Technical Note: The Modular Earth Submodel System (MESSy) – a new approach towards Earth System Modeling, *Atmos. Chem. Phys.*, 5, 433–444, 2005, <http://www.atmos-chem-phys.net/5/433/2005/>.
- Lefèvre, F., Brasseur, G. P., Folkins, I., Smith, A. K., and Simon, P.: Chemistry of the 1991–1992 stratospheric winter: Three-dimensional model simulations, *J. Geophys. Res.*, 99, 8183–8195, 1994.
- Munger, J. W., Jacob, D., Daube, B., Horowitz, L., Keene, W., and Heikes, B.: Formaldehyde, glyoxal, and methylglyoxal at a rural mountain site in central Virginia, *J. Geophys. Res.*, 100, 9325–9334, 1995.
- Murtagh, D., Frisk, U., Merino, F., Ridal, M., Jonsson, A., Stegman, J., Witt, G., Eriksson, P., Jiménez, C., Megie, G., de la Nöe, J., Ricaud, P., Baron, P., Pardo, J. R., Hauchcorne, A., Llewellyn, E. J., Degenstein, D. A., Gattinger, R. L., Lloyd, N. D., Evans, W. F. J., McDade, I. C., Haley, C. S., Sioris, C., von Savigny, C., Solheim, B. H., McConnell, J. C., Strong, K., Richardson, E. H., Leppelmeier, G. W., Kyrölä, E., Auvinen, H., and Oikarinen, L.: An overview of the Odin atmospheric mission, *Can. J. Phys.*, 80, 309–319, doi:10.1139/P01-157, 2002.
- Nett, H., Perron, G., Sanchez, M., Burgess, A., and Mossner, P.: MIPAS inflight calibration and processor validation, in: EN-VISAT Calibration Review – Proc. of the European Workshop, 9–13 September 2002, ESTEC, Noordwijk, The Netherlands, CD-ROM, vol. SP-520, edited by: Sawaya-Lacoste, H., ESA Publications Division, ESTEC, P.O. Box 299, 2200 AG Noordwijk, The Netherlands, 2002.
- Perrin, A., Keller, F., and Flaud, J.-M.: New analysis of the ν_2 , ν_3 , ν_4 and ν_6 bands of formaldehyde $H_2^{12}C^{16}O$, Line positions and intensities in the 5–10 μm spectral region, *J. Mol. Spectrosc.*, 221, 192–198, 2003.
- Ricaud, P., Alexandre, D., Barret, B., Flochmoën, E. L., Motte, E., Berthet, G., Lefèvre, F., and Murtagh, D.: Measurements of mid-stratospheric formaldehyde from the Odin/SMR instrument, *J. Quant. Spectroscop. Radiat. Transfer*, 107, 91–104, 2007.
- Rodgers, C. D.: Inverse Methods for Atmospheric Sounding: Theory and Practice, Vol. 2, in: Series on Atmospheric, Oceanic and Planetary Physics, edited by: Taylor, F. W., World Scientific, 2000.
- Sharpe, S. W., Johnson, T. J., Sams, R. L., Chu, P. M., Rhoderick, G. C., and Johnson, P. A.: Gas-phase databases for quantitative infrared spectroscopy, *Appl. Spectrosc.*, 58, 1452–1461, 2004.
- Steck, T.: Methods for determining regularization for atmospheric retrieval problems, *Appl. Opt.*, 41, 1788–1797, 2002.
- Tikhonov, A.: On the solution of incorrectly stated problems and method of regularization, *Dokl. Akad. Nauk. SSSR*, 151, 501–504, 1963.
- von Clarmann, T., Glatthor, N., Grabowski, U., Höpfner, M., Kellmann, S., Kiefer, M., Linden, A., Mengistu Tsidu, G., Milz, M., Steck, T., Stiller, G. P., Wang, D. Y., Fischer, H., Funke, B., Gil-López, S., and López-Puertas, M.: Retrieval of temperature and tangent altitude pointing from limb emission spectra recorded from space by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), *J. Geophys. Res.*, 108, 4736, doi:10.1029/2003JD003602, 2003.
- von Clarmann, T., Glatthor, N., Koukouli, M. E., Stiller, G. P., Funke, B., Grabowski, U., Höpfner, M., Kellmann, S., Linden, A., Milz, M., Steck, T., and Fischer, H.: MIPAS measurements of upper tropospheric C_2H_6 and O_3 during the Southern hemispheric biomass burning season in 2003, *Atmos. Chem. Phys.*, 7, 5861–5872, 2007, <http://www.atmos-chem-phys.net/7/5861/2007/>.