



Global stratospheric hydrogen peroxide distribution from MIPAS-Envisat full resolution spectra compared to KASIMA model results

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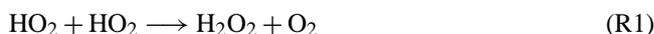
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Abstract. MIPAS-ENVISAT full resolution spectra were analyzed to obtain a global distribution of hydrogen peroxide (H_2O_2) in the stratosphere. H_2O_2 acts as reservoir gas for the HO_x family ($=\text{H}+\text{OH}+\text{HO}_2$) and thus, observations of H_2O_2 provide a better understanding of the HO_x chemistry in the atmosphere. A retrieval approach based on constrained least squares fitting was developed and applied to small dedicated spectral analysis windows with maximum H_2O_2 information and minimum contribution of interfering gases. Due to a low signal to noise ratio in the measured spectra single profiles cannot be used for scientific interpretation and about 100 profiles have to be averaged temporally or spatially. Our retrievals of H_2O_2 from MIPAS measurements provide meaningful results between approximately 20 and 60 km. A possible impact by the high uncertainty of the reaction rate constant for $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ in our 3D-CTM KASIMA is discussed. We find best agreement between model and observations for applying rate constants according to Christensen et al. (2002), however, a mismatch in vertical profile shape remains. The observations were compared to the model results of KASIMA focusing on low to mid latitudes. Good agreement in spatial distribution and in temporal evolution was found. Highest vmr of H_2O_2 in the stratosphere were observed and modeled in low latitudes shortly after equinox at about 30 km. The modelled diurnal cycle with lowest vmr shortly after sunrise and highest vmr in the afternoon is confirmed by the MIPAS observations.

1 Introduction

1.1 Hydrogen Peroxide sources and sinks

Odd hydrogen ($\text{HO}_x = \text{H} + \text{OH} + \text{HO}_2$) is one of the most important gas families in the Earth's atmosphere. It destroys ozone catalytically and is known as cleaning agent of the atmosphere. Hydrogen peroxide (H_2O_2) acts as a reservoir gas for HO_x and therefore plays an important role in atmospheric chemistry. It reduces the amount of the very reactive HO_x radicals. The main source of H_2O_2 is the HO_2 self-reaction:



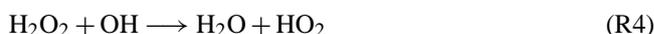
Of minor importance is the three-body reaction:



The main sink in the stratosphere is through photolysis:



The reactions with OH



and with atomic oxygen



destroy H_2O_2 to a smaller extent.

The photochemical lifetime of H_2O_2 varies from approximately 2 days in the lower stratosphere to a few hours in the mesosphere. It is assumed that H_2O_2 is approximately in

photochemical equilibrium with HO_x in a wide range of the middle atmosphere (Brasseur and Solomon, 2005).

Another possible source of H_2O_2 in the stratosphere is transport from the troposphere to the stratosphere. In the troposphere, H_2O_2 is enhanced within biomass burning plumes (Lee et al., 1997). Important sinks in the troposphere are washout by rain, reaction with dissolved SO_2 (Seinfeld and Pandis, 2006) and heterogeneous processes on cloud particles (scavenging) (Holloway and Wayne, 2010).

1.2 Hydrogen Peroxide measurements

To date, there are only a few atmospheric measurements of hydrogen peroxide. Most of them are airborne measurements (e.g. Heikes et al., 1987; Gallagher et al., 1991), mountain top measurements (e.g. Olszyna et al., 1988), measurements at the ground (e.g. Ayers et al., 1992; Gnauk et al., 1997) or ship-borne measurements (e.g. Slemr and Tremmel, 1994) within the troposphere.

There are also some balloon-borne remote measurements in the stratosphere. Chance et al. (1996) measured a peak value of about 120 pptv at an altitude of 32 km over New Mexico. Park and Carli (1991) obtained a slightly higher value at an altitude of 30 km over Texas. Both measurements are in the far infrared spectral region. Waters et al. (1981) obtained a much higher mixing ratio from a balloon-borne microwave sounder than the former mentioned authors.

Papandrea et al. (2005) derived profiles of H_2O_2 from MIPAS-Envisat measurements. They retrieved the logarithm of the volume mixing ratio (vmr) instead of the vmr, which avoids negative mixing ratios but can cause a positive bias when results are averaged.

The retrieval approach described in this paper was developed as to avoid biases as much as possible which may show up when data are averaged. We present global distributions of H_2O_2 and their seasonal and diurnal variation and compare them to the 3 dimensional Chemical Transport Model (3D-CTM) KASIMA.

2 MIPAS-Envisat

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a limb-viewing Fourier transform infrared (FTIR) spectrometer measuring the emission of the Earth's atmosphere (Fischer and Oelhaf, 1996; Fischer et al., 2008). It was launched aboard the environmental satellite (Envisat) on 1 March 2002 into a sun-synchronous polar orbit. It covers a wide mid-infrared spectral region from 685 to 2410 cm^{-1} . In its original measurement mode it was operated with a spectral resolution of 0.025 cm^{-1} . This mode consisted of 17 altitude steps with tangent altitudes between 6 and 68 km (step-width 3 km between 6 and 42 km and at 47, 52, 60, and 68 km). In 2004 the spectral resolution had to be decreased to 0.0625 cm^{-1} due to an instrument failure.

At the same time the spatial resolution was improved. These so-called optimized resolution measurements are performed in numerous different operation modes.

Generation of calibrated, so-called level-1B radiance spectra, is performed by the European Space Agency (ESA) (Nett et al., 2002). The hydrogen peroxide retrievals described in this paper were performed 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) from the full spectral resolution measurements before March 2004.

3 Model description

We compare the measured H_2O_2 fields to the model results of KASIMA (Karlsruhe Simulation Model of the Middle Atmosphere). KASIMA is a 3D-CTM. It includes the stratospheric chemistry and is able to simulate physical and chemical effects in the middle atmosphere (Kouker et al., 1999; Ruhnke et al., 1999; Reddmann et al., 2001). The model is based on the solution of the primitive meteorological equations in spectral formulation and uses the pressure altitude z , with $z = -H \ln(p/p_0)$, as the vertical coordinate. Here p is the pressure, $H (= 7\text{ km})$ is the atmospheric-scale height and $p_0 = 1013\text{ hPa}$. For the simulations in this paper we use a horizontal resolution of T21 ($5.6^\circ \times 5.6^\circ$) and 63 layers reaching from 7 to 120 km. Below 18 km the operational analysis from ECMWF (European Centre for Medium-Range Weather Forecasts) are used, from 18 to 48 km temperature, divergence and vorticity are relaxed to the ECMWF analysis. Between 48 km and the upper boundary the prognostic part of the model is used. A numerical time step of 12 min is used for the dynamic part of the model and a time step of 4 minutes for the chemistry part in the experiments. For HO_x , NO_x , ClO_x , BrO_x and O_x a family approach is used. The chemistry in KASIMA which is calculated up to 90 km on a rectangular grid includes all important species in the stratosphere as the oxygen-, nitrogen-, hydrogen-, chlorine- and bromine families. The 63 species in KASIMA interact by 127 gas phase reactions, 53 photolysis and 10 heterogeneous reactions. The reaction rates are from Sander et al. (2003). Photolysis rates are calculated online by the fast-j2-scheme from Brian and Prather (2002), supplemented by Lyman- α photolysis of O_2 , CH_4 , CO_2 , and H_2O using the Lyman- α actinic flux parameterization of Reddmann and Uhl (2003).

4 Hydrogen Peroxide spectral signatures

In the mid-infrared spectral region, which is covered by the spectral range of MIPAS, hydrogen peroxide shows weak emission lines between about 1210 cm^{-1} and 1300 cm^{-1} (Fig. 1). All these lines belong to the H_2O_2 ν_6 band centered at 1266 cm^{-1} . The spectroscopic data are taken from the latest update for H_2O_2 (based on measurements from (Perrin

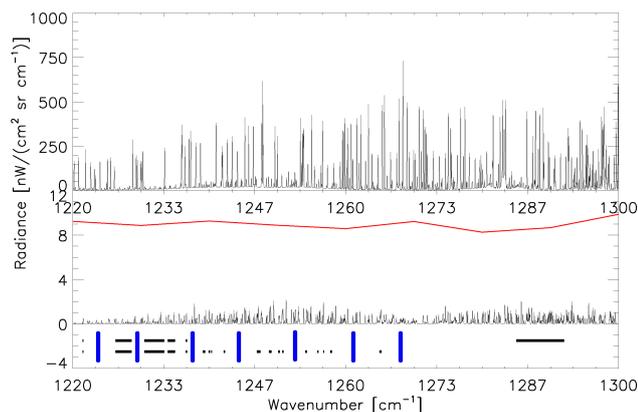


Fig. 1. Top: Simulated spectrum for tropical conditions and all gases included. Bottom: Contribution of Hydrogen Peroxide (note the different scale). Calculations are done for a tangent altitude of 35 km. The red line in the bottom figure shows the typical spectral noise in the MIPAS measurements. Black horizontal bars represent the microwindows used for data analysis; bottom: below 44.5 km tangent altitude, top: above 44.5 km tangent altitude. All sub-microwindows in between a pair of vertical blue bars belong to one main microwindow.

et al., 1995) and (Klee et al., 1999)) in the HITRAN 2004 molecular spectroscopic database (Rothman et al., 2005). The challenge of the hydrogen peroxide retrieval is the very weak signal of the emission lines in comparison to the instrument noise which in this spectral region is much higher than the H_2O_2 signal (Fig. 1).

Figure 1 (top) shows that there are several strong spectral lines from other gases in the wavenumber range of the spectrum of hydrogen peroxide. These spectral lines are mainly from methane, nitrous oxide and water vapor transitions. The continuum like signature between 1230 cm^{-1} and 1260 cm^{-1} is due to N_2O_5 and that between 1275 cm^{-1} and 1290 cm^{-1} is due to CF_4 .

5 Retrieval setup

For the retrieval, 19 narrow spectral regions (19 sub-microwindows which are combined to 8 main microwindows) have been selected by visual inspection between 1220 cm^{-1} and 1265 cm^{-1} , which is the lower end of MIPAS band B and includes the P-branch of the H_2O_2 ν_6 band. These microwindows are applied up to tangent altitudes of 44.5 km. The main criterion for the selection was high sensitivity to hydrogen peroxide and low interference by other gases (von Clarmann and Echle, 1998). Unfortunately the R-branch could not be used in the lower stratosphere for our retrieval because the lines of the interfering gases are too dense. Above 44.5 km an additional microwindow from 1285 cm^{-1} to 1292 cm^{-1} was applied. The microwindows between 1237 cm^{-1} and 1265 cm^{-1} were not used in this al-

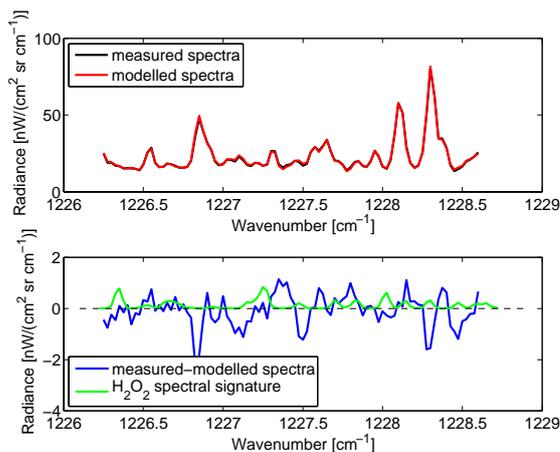


Fig. 2. Different spectra averaged between 20° N and 20° S in about 30 km; Shown is main microwindow 2; Top: measured spectra (black), modelled spectra (red); Bottom: difference between measured and modelled spectra (blue), H_2O_2 spectral signature (green)

titude region due to absorption cross sections of N_2O_5 being potentially of low quality for low pressures. Since the hydrogen peroxide contribution is so small, the contribution of other gases needed to be considered and HOCl , N_2O_5 and COF_2 abundances had to be retrieved jointly in order to minimize related error propagation. CH_4 , N_2O , H_2O , O_3 , ClONO_2 and HNO_3 had to be retrieved before the hydrogen peroxide retrieval in better suited spectral ranges and the results had to be considered in our H_2O_2 retrieval. For all the other gases in this spectral region climatological volume mixing ratio profiles were used.

In Fig. 2 a closer look at main microwindow 2 is shown. Our retrieval residual shown there is not correlated with the H_2O_2 signatures.

The retrieval procedure follows a scheme analog to that described by Rodgers (2000) but with a Tikhonov smoothing matrix (Tikhonov, 1963) instead of the climatological covariance matrix as constraint:

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

where \mathbf{x} is the retrieval vector, \mathbf{K} the partial derivatives of the spectral grid points with respect to the retrieval vector (Jacobian), \mathbf{S}_y is the covariance matrix representing measurement noise, \mathbf{R} the regularization or constraint matrix, \mathbf{y} the vector of measured spectral radiances used, \mathbf{F} the forward model, \mathbf{x}_a the a priori profile, and i the iteration index. In the case of convergence problems, Eq. (1) is modified by inclusion of a Levenberg-Marquardt term (Levenberg, 1944; Marquardt, 1963) to force the iteration towards smaller but safer steps of the parameter update (see von Clarmann et al. (2003) for formal details).

The grid used for the retrieval has an altitude spacing of 1 km up to 44 km and of 2 km between 44 and 70 km. The tangent point spacing of MIPAS is 3 km and therefore coarser than our retrieval grid. To avoid retrieval instabilities as a consequence of this choice, the retrieval was stabilized by a (Tikhonov, 1963) type smoothing constraint in an altitude-dependent implementation by (Steck, 2002). Due to the very low signal-to-noise ratio we had to choose a rather high regularization strength resulting in a low number of degrees of freedom. The regularization is stronger in the upper stratosphere. It is weakest in the middle stratosphere where we expect the maximum volume mixing ratio of H_2O_2 . Lowest measurement altitudes used were around 20 km because otherwise oscillations in our profiles occurred which were caused by unsuccessful fitting of measurements at lower altitudes and upward error propagation due to the retrieval scheme. The shortcoming of this retrieval approach is that we cannot derive information about H_2O_2 from the troposphere which would be interesting for the understanding of the ozone budget of the troposphere for which hydrogen peroxide plays an important role.

As initial guess the climatological profiles from Kiefer et al. (2002) and Remedios et al. (2007) were used. As a priori profile we use an all-zero profile to avoid any artificial structures in the hydrogen peroxide profile not caused by the measurements. It should be noted that this choice does not cause a systematic negative bias of the results because the absolute amount lies in the nullspace of our regularization matrix which constrains only the differences between adjacent profile points. The setting for microwindows, constraint and a-priori profiles are chosen time and latitude-independent. All variations of structures in the retrieved distributions originate from the measurements and are not artificial structures from the retrieval setup.

With this approach more than 99.9 % of our H_2O_2 retrievals converge.

6 Retrieval

6.1 Retrieval for synthetic spectra

The retrieval setup was validated by retrieval of H_2O_2 from synthetic spectra. These spectra were calculated with the Karlsruhe Optimized and Precise Radiative transfer Algorithm (KOPRA) (Stiller et al., 2002). We used the H_2O_2 profile shown in Fig. 3. All the other gases were set to their climatological values.

With this calculated spectrum a retrieval as described in Section 5 was performed. The result is a profile of H_2O_2 (Fig. 3 red line) with a vertical resolution coarser than the input profile. Both profiles have their maximum in about the same altitude and differences are due to different vertical resolution. Results from real measurements are expected to be worse because of instrumental noise, probably less-than-

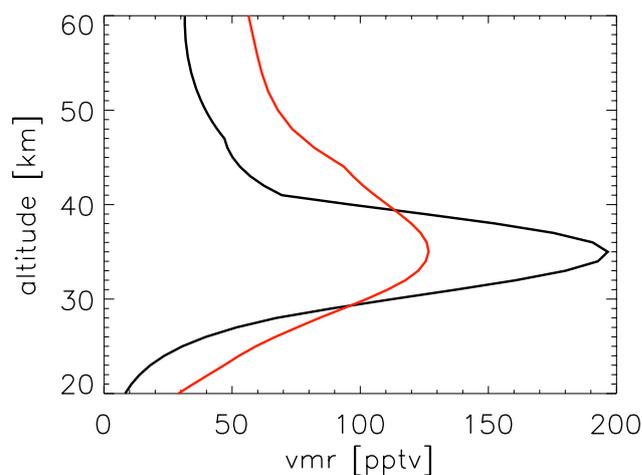


Fig. 3. Results for retrieval with synthetic spectra; black line: profile used to generate the synthetic measurements; red line: retrieval result.

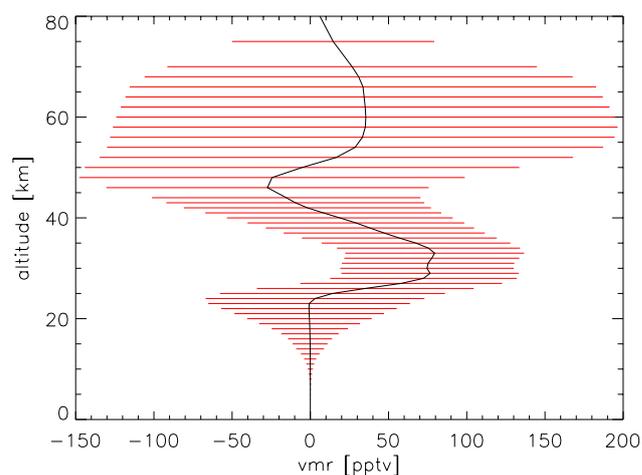


Fig. 4. Hydrogen peroxide retrieval result (solid line) (orbit 7791, 27 August 2003, tropics). Error bars represent propagated measurement noise.

perfect spectroscopic information of each gas (the same spectroscopy was used for the forward calculation and the retrieval) and potential contributions of gases not considered in our retrieval.

6.2 Retrieval from measured spectra

In a next step the retrieval procedure described above was applied to measured MIPAS spectra. Figure 4 shows an example for a single profile retrieval of hydrogen peroxide for MIPAS-Envisat orbit 7791 on 27 August 2003 at $3^\circ \text{S}/154^\circ \text{W}$. The profile shows maximum values in the middle stratosphere of 80 parts per trillion by volume (pptv) and insignificant negative values in the upper stratosphere.

In our retrieval we accept negative values by intention, because high noise can result in negative retrieved mixing

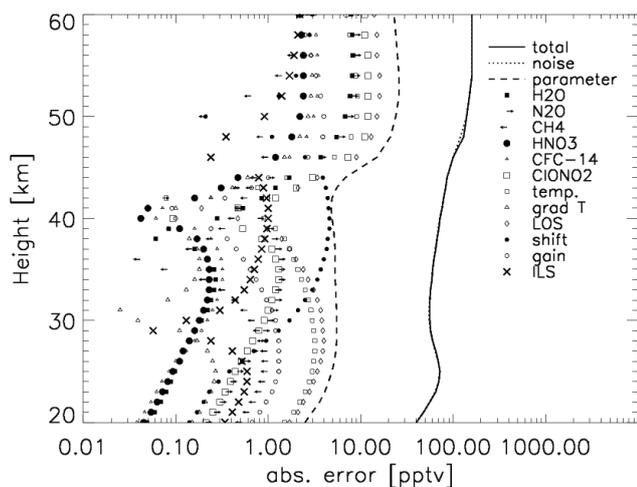


Fig. 5. Error analysis of hydrogen peroxide retrieval (orbit 7791, 27 August 2003, tropics). Error sources from top to bottom: total error (solid line), noise error (dotted line) (mostly overlapped by total error), total parameter error (dashed line) containing errors due to vmr uncertainties of other gases: H_2O , N_2O , CH_4 , HNO_3 , CF_4 and ClONO_2 , error due to temperature uncertainty and uncertainty of the temperature gradient, line-of-sight (LOS) uncertainty, spectral shift uncertainty, gain calibration uncertainty, and residual uncertainty of the instrumental line shape (ILS).

ratios. A retrieval of the logarithm of volume mixing ratio as Papandrea et al. (2005) did would avoid negative, thus unphysical, values but would produce a positive bias in case of averaging. Smallest mean values retrieved by Papandrea et al. (2005) are slightly lower than 30 pptv. Assuming that the possible bias is constant with altitude would imply that the bias in their retrievals is less than about 10 % of the maximal mixing ratio of H_2O_2 .

6.3 Error analysis

The total expected error consists of the error due to measurement noise, called noise error below, parameter error and smoothing error (Rodgers, 2000).

For a single H_2O_2 profile the noise error is by far the largest. In the example error budget (Fig. 5) the total error is dominated by the noise error (total error and noise error are nearly identical in the figure). In the lower stratosphere the noise error is about 40 pptv and increases in the higher stratosphere to values of approximately 150 pptv. As the noise error can be assumed to be randomly distributed, averaging can be applied to reduce the statistical error. In this paper we used daily means or means of the whole time series for latitude bins of 5° .

The parameter error is less important for H_2O_2 . It contains uncertainties of parameters of the forward calculations. For example, errors in the vmrs of interfering gases, which are used in the H_2O_2 retrieval, cause errors in the H_2O_2 retrieval. The largest error sources are uncertainties in ClONO_2 , N_2O ,

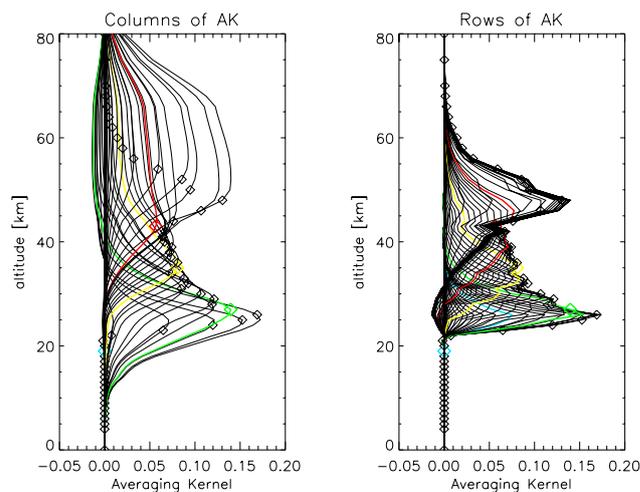


Fig. 6. Typical MIPAS Averaging Kernel (A) in the tropics for H_2O_2 . Altitudes marked for better illustration: 19 km (turquoise), 27 km (green), 35 km (yellow) and 43 km (red). The diamonds indicate the altitude the averaging kernels refer to.

and H_2O . The error due to uncertainty of ClONO_2 is about 15 pptv in the higher stratosphere, N_2O and H_2O uncertainties are contributing with roughly 10 pptv to the parameter error. Another important parameter error is the error due to temperature uncertainty which is about 10 pptv in the upper stratosphere. In the polar regions the parameter error is much smaller (about 2 to 3 pptv) than elsewhere and does not play a role at all. This error is partly randomly distributed and partly systematic depending on the type of error in the source. There is no evidence of any systematic day/night difference in the uncertainty of the former mentioned gases, therefore there is also no day/night difference in uncertainty of H_2O_2 .

The vertical resolution is described by the averaging kernel matrix (**A**) (Rodgers, 2000):

$$\mathbf{A} = (\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \mathbf{R})^{-1} \mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} \quad (2)$$

In case of H_2O_2 a rather strong regularization was applied to stabilize the retrievals. Therefore our averaging kernel (**A**) diagonal values are small and the resulting vertical resolution is quite low. In Fig. 6 representative averaging kernels are shown. Up to about 40 km the averaging kernels are well-behaved, since they are rather symmetric and peak at their nominal altitude. Above 40 km, information from above the nominal altitude contributes to the retrieval and thus the retrieval renders a distorted image of the true atmosphere. For H_2O_2 we only can use vmrs between about 20 km and 60 km height. The corresponding vertical resolution, which is the full width at half maximum of an averaging kernel row in a specific height, is about 8 km in the lower stratosphere and increases to about 35 km in the upper stratosphere. During polar night, when the temperatures are lower, the vertical resolution becomes even worse, while during polar day,

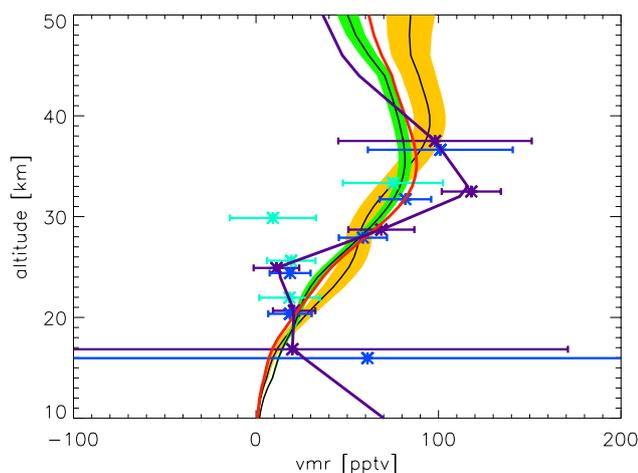


Fig. 7. Comparison of H_2O_2 balloon-borne observations (Chance et al., 1996) (asterisks: September 1989; violet: afternoon; blue: night; light blue: morning) and MIPAS observations (yellow: September 2002; green: September 2003) all showing 1-sigma error bars; balloon measurements were made above Fort Sumner (34.5°N), while MIPAS measurements are zonal means between 30°N and 40°N . The solid violet line is the interpolated balloon-borne profile, while the red line is the violet profile convolved with the MIPAS A.

the vertical resolution is better. Comparison of H_2O_2 MIPAS measurements with models must be done by application of the MIPAS A to the model results. The result is the modeled H_2O_2 distribution as it would be seen by MIPAS.

6.4 Comparison with other measurements

In order to put our measurements into context we compared to balloon-borne H_2O_2 profiles, and the H_2O_2 distributions retrieved from MIPAS by Papandrea et al. (2005).

Chance et al. (1996) performed a balloon-borne measurement of H_2O_2 in the far infrared spectral range in September 1989 in Fort Sumner in New Mexico (34.5°N). They measured a vmr of 118 ± 16 pptv at 32.5 km at a balloon flight in the afternoon and 82 ± 14 pptv at 31.7 km during night. On the following morning they measured 75 ± 27 pptv in 33.3 km altitude. In September 2002 zonal mean vmrs from MIPAS data reach from 71 ± 13 to 97 ± 10 pptv in an altitude of 32 km between latitudes of 32.5°N and 37.5°N . In September 2003 the vmrs cover a range from 71 ± 10 to 86 ± 12 pptv. Thus MIPAS vmr of H_2O_2 seems to be lower than the balloon-borne measurements. Figure 7 compares the balloon-borne measurement with our MIPAS results, including 1-sigma error bars and considering the different vertical resolution by applying the MIPAS As to the balloon-borne profiles (red line). Within the error bars and considering the inter-annual variability above 35 km which is obvious from the 2002 and 2003 mean profiles, the two measurements are in good agreement.

Another balloon-borne measurement of hydrogen peroxide in the far infrared spectral range is available from Park and Carli (1991). Their measurement took place in June 1983 over Texas. They retrieved a mean vmr of about 130 pptv in an altitude of 30 km for a 5-km-thick layer. The estimated error is 60%. Within the error bars this measurement is in agreement with our retrieved vmr.

Kaye and Jackman (1986) inferred mixing ratios of H_2O_2 from several measured profiles of other trace gases not including HO_x with the help of a chemistry model. They derived higher vmr in the summer hemisphere and highest vmr around equinox which both is in agreement with our observations. However their vmrs are much higher than the vmr obtained from MIPAS measurements, while they are comparable to our KASIMA model results (see Sect. 7).

Waters et al. (1981) obtained an abundance of 1.1 ± 0.5 ppbv from a balloon-borne microwave sounder. This value is much higher than our retrieved result or the results from other balloon-borne measurements. However, they described their results as tentative.

In comparison to the MIPAS results by Papandrea et al. (2005) we have in general a lower vertical resolution in the uppermost stratosphere and lower mesosphere but a higher vertical resolution below. Their volume mixing ratios in the mid-latitudes are about the same as ours. Their maximum values in the tropics reach vmrs above 330 pptv, which is much higher than our maximum of about 130 pptv at the same time. This can partly be explained by different vertical resolutions. A quantitative analysis, however, could not be performed since the vertical resolutions vary differently with altitude, and simply convolving the profiles by Papandrea et al. (2005) with the As of our retrievals or vice versa would not adequately take into account the different retrieval characteristics.

7 Results and comparison with model

We analyzed the data for 190 days between September 2002 and March 2004 for all of which MIPAS full resolution measurements were available. For the comparison with the model we applied the corresponding MIPAS A to the model profiles. Only profiles within 350 km and 2 h of a MIPAS geolocation were considered. For detailed comparison we have chosen an altitude of 30 km. This height is near the maximum of the volume mixing ratio profile. In addition the errors in terms of standard error of the mean are lowest at altitudes between 30 and 40 km with a value of 10 pptv. Below this altitude the errors are slightly higher, above they increase to values up to 80 pptv in 55 km in the Northern Hemisphere summer.

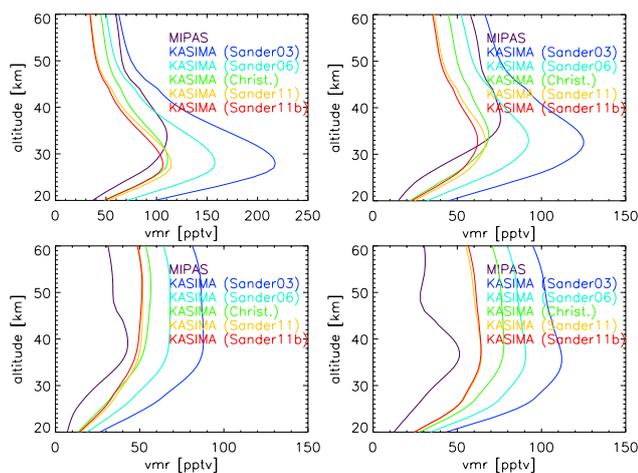


Fig. 8. Mean profiles for MIPAS measurements (purple) and KASIMA model results with MIPAS A applied with JPL recommendation for R1 from Sander et al. (2003) (blue), Sander et al. (2006) (turquoise), Christensen et al. (2002) (green), Sander et al. (2011) (orange) and Sander et al. (2011) with updated HO_x reactions (red); top left: 20° S to 20° N; top right: 30° N to 60° N; bottom left: 70° N to 90° N; bottom right: 70° S to 90° S.

7.1 Sensitivity to the HO₂ + HO₂ reaction

There is a large difference in absolute vmr between KASIMA default model run with the reaction rate for R1 from Sander et al. (2003) and MIPAS with almost twice as much H₂O₂ in KASIMA than in MIPAS. The reason for this difference is not completely understood but there are some hints. Sensitivity tests show that the H₂O₂ vmr is rather sensitive to a different photolysis rate of H₂O₂ in KASIMA and to different reaction rates for HO₂ + HO₂, and thus uncertainties of the corresponding reaction rates may contribute to the difference between observations and model. For example Christensen et al. (2002) suggest a much different reaction rate for (R1) compared to Sander et al. (2003). For the temperature conditions in the middle stratosphere, the reaction rate according to Christensen et al. (2002) is only about half the value of Sander et al. (2003). In Fig. 8 the results from five KASIMA model runs, one with the reaction rate from Christensen et al. (2002), one with the reaction rate from Sander et al. (2003), one with the reaction rate from Sander et al. (2006), one with the reaction rate from Sander et al. (2011) and one with all HO_x reaction rates changed to Sander et al. (2011) are compared to MIPAS observations. The figure covers the whole time period of the high resolution MIPAS measurements of H₂O₂. With the recommended reaction rate from Sander et al. (2003) the mixing ratio in the model is higher than observed by MIPAS in the whole altitude range and in each latitude bin. Up to about 30 km there is a factor of about 2 between these two mean profiles in the tropics. Above 30 km the difference is decreasing to almost perfect match in about 60 km. If we use the updated reaction rate

from Sander et al. (2006) the agreement in general becomes better but H₂O₂ mixing ratios in the model are still too high. In midlatitudes the mixing ratio in general is smaller and in higher altitudes the difference remains higher. In the polar regions the difference between observation and model result is growing with altitude up to a factor of three. If the reaction rate from Christensen et al. (2002) is used, modelled results are closer to MIPAS observations. In the tropics and midlatitudes the maximum vmrs are about the same in the model run and in the observations but the maximum in the model is about 5 km lower in altitude. In the upper stratosphere the model now produces too low vmr. The vmr in the polar regions are reduced in all altitudes compared to the Sander et al. (2003) and Sander et al. (2006) reaction rates, but remain too high in comparison to MIPAS observations. Using reaction rate from Sander et al. (2011) gives very similar results to Christensen et al. (2002). Biggest influence can be seen in southern polar region where the mixing ratios are getting closer to MIPAS observations. Changing all other HO_x reactions in KASIMA to Sander et al. (2011) (red profile in Fig. 8) has only a very small impact on our model results.

For all the following model results we show the results from our KASIMA model run with the reaction rate according to Christensen et al. (2002).

The model shows an additional maximum in H₂O₂ vmr in the upper mesosphere (not shown). Highest vmrs there are up to 500 pptv. If we use reaction rate from Sander et al. (2003) the maximum is much more pronounced (vmr up to 4000 pptv). Unfortunately, the MIPAS measurement is not sensitive to H₂O₂ at these altitudes.

7.2 Annual cycle

Figure 9 presents a time-altitude cross section for inner tropics (top: MIPAS, bottom: KASIMA). It shows a seasonal variation and an interannual variation is indicated. The white areas indicate time periods and altitudes where the diagonal element of the **A** is below a threshold of 0.03. The highest vmrs are found in the middle stratosphere. In the altitude range between 25 km and 40 km an annual cycle is present. Highest vmrs are reached shortly after equinox in October and April (also see Fig. 10, top).

Now we take a closer look at an altitude of 30 km. The temporal evolution of the H₂O₂ distribution in KASIMA (Fig. 10, middle) is very similar to the temporal evolution in the MIPAS measurements (Fig. 10, top). The time-latitude cross sections of daily means are calculated in latitude bins of 5 degrees. Both show the highest vmr in the inner tropics shortly after equinox. In the tropics and subtropics the H₂O₂ volume mixing ratio over the year is highest for lowest midday solar zenith angles. The lower volume mixing ratios at the end of 2003 and beginning of 2004 are represented by KASIMA as well. The described patterns do not change if we use reaction rates from Sander et al. (2003) to

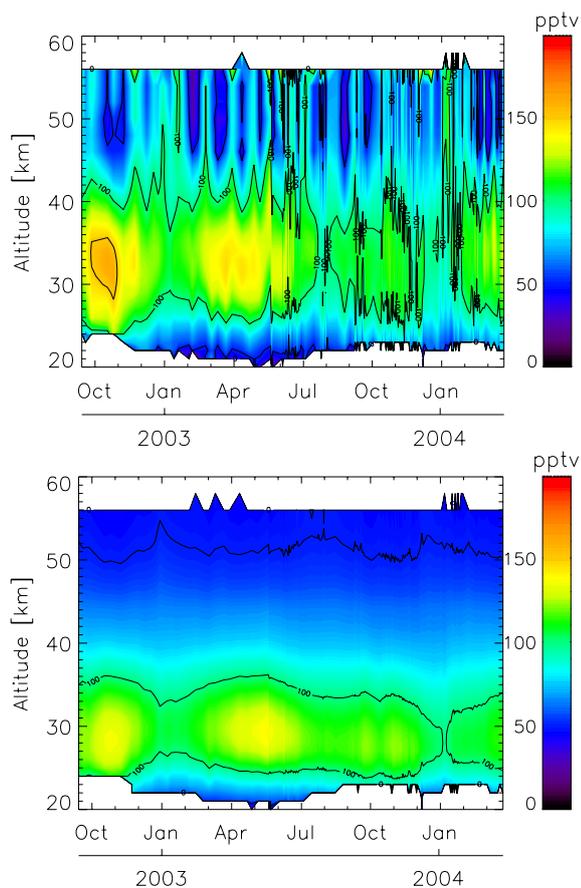


Fig. 9. Top: Timeseries of MIPAS H_2O_2 daily zonal mean vmr averaged between 10°N and 10°S ; Bottom: same for KASIMA results with MIPAS A applied

Sander et al. (2011) instead of the reaction rate from Christensen et al. (2002).

In the observations and in the model an interannual variability is present. Higher vmr are observed in the end of 2002 and in the beginning of 2003. This interannual variability can be assigned to a change in OH vmr. Our model produces higher OH vmr after the mid of 2003. As mentioned in the beginning of this paper OH is one of the main sinks of H_2O_2 . OH itself for longer timeperiods is closely correlated with H_2O . H_2O mixing ratios from MIPAS observations in an altitude of 30 km are shown in Fig. 10 (bottom). The vmrs until June 2003 in the inner tropics are lower than after June 2003. This change in the H_2O vmr is almost certainly due to a change in the QBO phase.

In the polar regions the volume mixing ratios are much lower in this altitude region. Shorter term changes in the mixing ratios there are not discussed in this paper because of possible influences by energetic particle precipitation. The overall discrepancy there between model and MIPAS observations (see also Fig. 10) are probably due to still unresolved

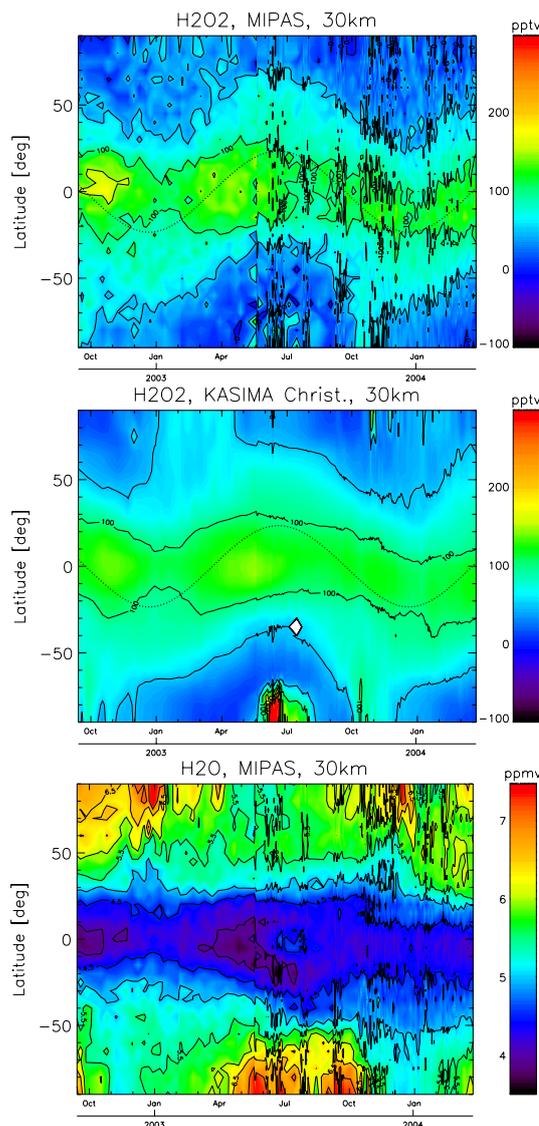


Fig. 10. Temporal evolution of the daily zonal means of the volume mixing ratio in 30 km of: (top) H_2O_2 as observed by MIPAS; (middle) H_2O_2 modeled by KASIMA with reaction rate constant from Christensen et al. (2002) for R1; vmr on MIPAS geolocations with MIPAS A applied; Additionally for H_2O_2 the latitude where the sun reaches zenith position for that day is shown (black dotted) (bottom) H_2O as observed by MIPAS.

issues regarding reaction rates and related atmospheric conditions determining those.

7.3 Diurnal cycle

It is not possible to measure the full diurnal cycle with a satellite-instrument like MIPAS-ENVISAT because above the equator it only measures at 10 a.m. and 10 p.m. local time (LT). Therefore we present a day/night difference for MIPAS. For the comparison with KASIMA we reduced the allowed spatial difference to 250 km and the time difference to

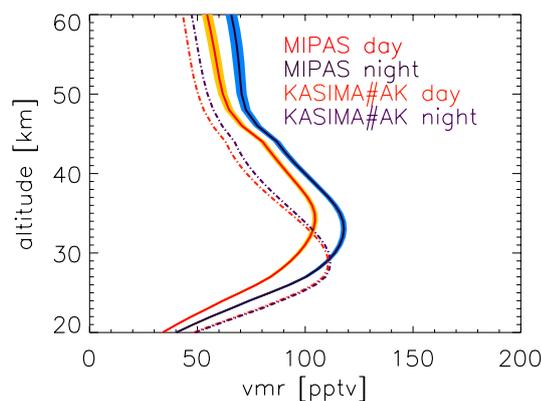


Fig. 11. Day (red) and nighttime (blue) H_2O_2 vmr for MIPAS (solid) and KASIMA with MIPAS A applied (dash-dotted) averaged between 20°N and 20°S for the full data period; For MIPAS the 3-sigma error bar is shown.

1 h. Profiles were averaged between 20°N and 20°S . So we do not expect strong effects due to seasonal changes. To exclude such effects we also looked at smaller timeperiods and got the same results.

Figure 11 shows that the vmr for H_2O_2 in KASIMA are higher than in MIPAS in the lower stratosphere during day and night and are lower in the mid and upper stratosphere. The nighttime vmr measured by MIPAS is higher than MIPAS daytime vmr by about 15%. The 3-sigma error bars do not overlap. The differences are significant on the 99%-confidence level. The difference in KASIMA is much smaller and almost is not present but night values are also higher than day values.

The diurnal cycle of H_2O_2 as represented by the KASIMA model (no Averaging Kernel applied) in the tropics at 30 km altitude is shown in Fig. 12. Between 18:00 LT (sunset) and 06:00 LT (sunrise) local time, the H_2O_2 mixing ratio is almost constant. In the morning the vmr is decreasing until about 08:30 LT. Afterwards the H_2O_2 vmr is rising to its maximum at 14:30 LT. In the late afternoon the vmr is decreasing to its night value. Besides photolysis these changes can be attributed to OH and HO_2 which both have very short lifetimes, are mainly influenced by sunlight and do change little during night.

The vmr of H_2O_2 in the model at 22:00 LT is higher than at 10:00 LT. The “diurnal cycle” therefore is in qualitatively good agreement between KASIMA model results and MIPAS measurements. There is also good agreement with the day/night variation shown by Papandrea et al. (2005), however they showed, for reasons not known, an even stronger “diurnal cycle” than in our MIPAS results. Chance et al. (1996) “did not see evidence for diurnal variation of H_2O_2 ”. However, some hints that their results are in good agreement with our model results are presented in their paper. They performed three balloon measurements, one in the morning, one in the afternoon and one during night. In the morning they

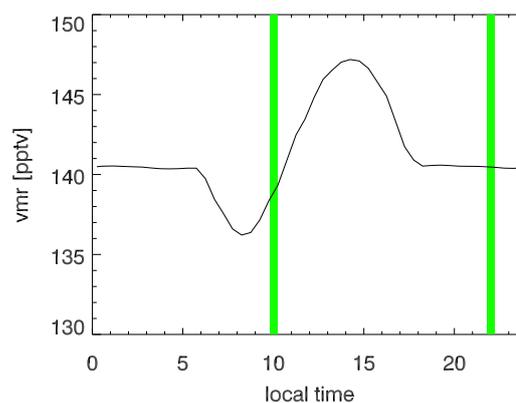


Fig. 12. Diurnal cycle of H_2O_2 vmr in KASIMA in dependency of local time in 30 km; vmr is averaged for the whole data period between 10°N and 10°S ; The vertical lines mark MIPAS measurement times.

measured the lowest vmr and in the afternoon the highest. During night their measured vmr was in between. They had large error bars so the differences were not significant. But the temporal change of their mean values is in agreement with KASIMA model results.

While for MIPAS measurements in the whole altitude range the nighttime vmr is higher than daytime vmr, this is not the case for KASIMA. The diurnal cycle is modified at different altitudes in different ways. However, the H_2O_2 vmr at 22:00 LT is always higher than at 10:00 LT. Therefore the diurnal cycle in KASIMA is in good agreement with MIPAS measurements, however, the night-day-difference in KASIMA is smaller.

8 Conclusions

We have presented global distributions of H_2O_2 retrieved from MIPAS-Envisat spectra. The profiles cover an altitude range from about 20 km to 60 km. The analysed data set consists of 190 days from September 2002 to March 2004. The total error for single profiles is very high but dominated by random error components which can be reduced by averaging. The retrieved profiles are qualitatively in good agreement with older balloon-borne measurements and with results from the 3D-CTM KASIMA. Potential reasons for the differences in the model are inappropriate reaction and photolysis rates. In a comparison of model runs with reaction rates for $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ from Christensen et al. (2002) and Sander et al. (2003) the model performed much better with the first mentioned reaction rate. Our data shows highest vmr in the tropics in 30 km. During the annual cycle, highest vmr is reached just after equinox. The absolute abundance of H_2O_2 in the tropics is driven by the H_2O abundance and thus, is modulated, similar to H_2O , by the QBO; however, H_2O_2 vmrs are lower in the QBO phase when H_2O

provides higher values, due to OH produced from H₂O as major H₂O₂ sink. The 10 a.m./10 p.m. differences observed by MIPAS can be qualitatively reproduced by the KASIMA model which shows a complicated diurnal cycle in the stratosphere. H₂O₂ vmr is decreasing after sunrise and increasing in the late morning till afternoon. Using Sander et al. (2011) for R1 reaction rates gives very similar results to using reaction rates from Christensen et al. (2002). In our next paper we will discuss the influence of energetic particle events on H₂O₂ in polar regions.

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