

***Interactive comment on* “Global stratospheric hydrogen peroxide distribution from MIPAS-Envisat full resolution spectra compared to KASIMA model results” by S. Versick et al.**

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

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heterogeneous processes

On page 33513 also heterogeneous processes on cloud particles should be mentioned (scavenging).

We will add this information in the text.

ClONO₂

In section 6.3, concerning ClONO₂, it should be distinguished between day and night. At daytime there is almost no ClONO₂ in the upper stratosphere due to photolysis.

It is true that there is a difference in ClONO₂ between day and night. However, the shown error is not influenced by the mixing ratio of ClONO₂, but by the uncertainty in

C16247

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our ClONO₂ retrieval. We cannot see a day/night difference in the uncertainty of our ClONO₂-Retrieval therefore there will be no day/night difference in our error estimation for H₂O₂ due to ClONO₂. Therefore we will not show error plots for day and night.

Sander2011

2 Section 7.1 should be rearranged. A run using an outlier of laboratory data (due to artifacts, known since 2003 in the model community) cannot be a 'standard model run'. In this section also Sander et al (2011), including the discussion therein, should be cited, their recommendation for the H₂O₂ is closer to Christensen et al (2002) than the other sources. There are also changes in sink reactions. An additional sensitivity study might be useful to be included in Fig.7.

We additionally have performed two model runs with reaction rate constants from Sander et al (2011). For the first run we only changed the reaction constants for the source reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$. The results we obtain are similar to those with the reaction rate from Christensen. For the second model run we updated all HOx reactions to Sander et al. (2011). The impact on our H₂O₂ mixing ratios also is very small. In both cases the influence on H₂O₂ mixing ratio during southern polar winter in the southern polar region is largest. But mixing ratios there still remain way to high.

We will show additional mean profiles in figure 7.

Mesospheric values

The mesospheric values appear to be rather high compared to other studies, was that based on Christensen et al (2002) as stated in the sentence before? Is there a hint on it in the older retrieval scheme mentioned?

Thanks for this hint. The mesospheric values given in the paper are accidentally from our model run with JPL03 reaction rate. With Christensen et al (2002) the mesospheric maximum remains but is getting much lower (app. 500 pptv). We will fix this in our final version of the paper and we will also mention that there is a large impact on H₂O₂ abundances in the mesosphere by changing reaction rates from Sander et al. (2003) to Christensen et al. (2011). We will change the text to: "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 upto 4000 pptv). Unfortunately the MIPAS measurement is not sensitive to H₂O₂ in these altitudes."

There are no hints in the older retrieval scheme because they are even less sensitive in higher altitudes than compared to our retrieval.

Diurnal cycle

In section 7.3 the spatial and time difference are inconsistent. 250km should correspond to about 10 minutes (1h is more than 1500km at equator). The description of Fig.11 is only valid for equinox conditions, here more details are needed. It might be also useful to show a figure with the latitudinal dependence of the diurnal cycle for 2 seasons.

For to technical reasons we had to choose a model output timestep of 6 hours. To reduce the uncertainty due to noisy profiles we have chosen our spatial and time difference in a way that we get many profiles but only introduce a small error due to horizontal inhomogenities. With a model output timestep of 6 hour a time difference of 1 hour means that we are using roughly one third of our observations for this comparison. A spatial difference of 250 km corresponds to about nearest model gridpoint in the equator region in our model run.

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Figure 11 is indeed only valid for equinox conditions. This is automatically fulfilled at the equator during the whole year. We show the results for a small latitude band around the equator as mentioned in the text therefore we only induce a small error.

We investigated latitudinal dependence in several month. The latitudinal dependence is very weak in an altitude of 30 km. Due to limited data (much shorter timeperiod) we get bad statistics and we prefer to not show latitudinal dependence because there is almost no additional information.

We will add latitude and season shown in the figure caption.

7) Fig 11 about the diurnal cycle The authors only showed 30km data comparison. I think it is worth to show another altitude, for example 50km, where both model and MIPAS H₂O₂ show difference between day and night.

The comparison shown in figure 10 is between altitudes of 20 km and 60 km. Figure 11 only shows model results. The model results which are not at 10 a.m. or 10 p.m. local time can not be evaluated by our MIPAS measurements. Furthermore in figure 11 we only can show model results which are not convolved with MIPAS AK. But in higher altitudes this will have a large impact because in MIPAS results you see a mixture of different altitudes. Therefore we don't think it is worth to show other altitudes.

Microwindows

P 33516, L 19: Looking at Fig. 1 it seems that some microwindows are too narrow to be considered microwindows (even if it is a bit hard to see details from this figure), they rather seem almost "individual spectral points". My concern here is how can you correctly reproduce the spectral line shape inside these so narrow microwindows? It could be helpful to add a table with the microwindows boundaries.

It is true that it is hard to reproduce the spectral line shape in very small microwindows.

Therefore we combined some submicrowindows to in total 8 main-microwindows. The spectra is fitted to those main-microwindows. And of course there are no individual spectral points. We will add the information of main-microwindows in our figure. We also changed the text accordingly.

1) P33516: about the spectral range and the microwindow selection The spectral range in the text (Line 6) is 1210 – 1320 cm⁻¹, while the range shown in Fig 1 is 1220 – 1300 cm⁻¹. Suggest change the Fig to make it consistent. Also, the microwindows shown in Fig 1 have various widths, some may include several spectral lines, while the others may be tiny and hard to see from the figure. I think the authors should show at least one or two examples of such microwindows and add them as additional panels or “closeup” modes of Fig 1. Since the signal to noise ratio is very low, it would be very important to see the retrieval residual and compare with the H₂O₂ spectral lines to ensure that the residual is random in nature.

It is true that there are no additional microwindows at larger wavenumbers than 1300 cm⁻¹. We will fix this in the text.

We will show one main-microwindow with all sub-microwindows included for better illustration. In this figure we will also include the retrieval residual.

Convergence Problems

P 33517, L 19: Could you provide a statistic of occurrence of these convergence problems?

Sorry, we do not have this, because this has no effect on the results, and in most cases the retrievals converge after a few Levenberg-Marquardt steps. Since activation of the Levenberg-Marquardt scheme does not affect our results, and since it is switched off for the last iteration anyway, we have no statistics on this. We, however, do have statistics

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on the overall fraction of non-converged retrievals. For the data-set provided, more than 99.9% of the retrievals have converged (with switched-off Levenberg-Marquardt scheme in the last iteration) while less than 0.1% of the retrievals failed. We will include this information in the paper.

Retrieval instabilities

P 33518, L 3: What is the main cause of instability of a retrieval below 20 km: too many cloudy spectra, or maybe too high systematic errors? Does this happens at every latitude and/or period of the year? Could you please comment on that.

At lower tangent altitudes the spectra become more opaque, and the ratio between the target signal and the background signal by continuum emission and the wings of interfering lines becomes too weak for a robust retrieval. These effects are generally more pronounced in humid atmospheres.

logarithmic retrieval

P 33519, L 14: I have a comment on the sentence “retrieval of the logarithm of volume mixing ratio. . .would produce a positive bias in case of averaging”. The authors are right to say that it is possible to generate a bias when retrieving $\log(\text{vmr})$ instead of vmr . However it seems that in the cited paper the bias is not so evident. It can be noticed (e.g. from its fig.5) that there are regions where the averaged vmr is at least lower than 0.03 ppbv, so the bias should not be greater than this value. This should be mentioned in the paper.

The possible bias does not depend on the minima of the retrieved vmr , it depends on the statistical error of the retrieval. However, if the statistical error is independent of

time and place you are right, the bias can not be larger than the smallest retrieved mixing ratio (in this case about 0.03 ppbv).

In our paper we will add the following sentence: "Smallest mean values retrieved by Papandrea et al. are slightly lower than 30 pptv. Assuming that the possible bias is constant with altitude would imply that the bias is less than about 10% of the maximal mixing ratio of H₂O₂."

Differences in pole regions

-P 33524, L2: have you got some indications to explain the high difference between MIPAS and the model around pole regions?

6) P33525, Line 6: The authors avoid discussions on the discrepancies at polar region in Fig 9 by saying that it may be affected by the "energetic particle precipitation". But the "energetic particle precipitation" does not penetrate as deep as 30 km to affect H₂O₂ in Fig 9. Its influences are mostly in the mesosphere. I think the discrepancy here is again related to the unresolved/undiscussed discrepancy between modeled and retrieved H₂O₂ vertical profiles (as shown in Fig 7). It is fine that if the authors can not make any solid conclusions on it. But it is worth mentioning it in the conclusions.

Ref. #3 is right, energetic particle precipitation (EPP) only penetrates in rare cases as deep as 30 km into the atmosphere. But this does not mean that we can not see effects in 30 km due to EPP. The vertical resolution of our MIPAS in pole regions is rather bad compared to tropical conditions. Therefore the signal of H₂O₂ is smeared out and you also can see it further downwards. For example during the southern polar winter 2003 we see effects due to energetic electron precipitation in KASIMA above 40 km (direct effect above 50 km, then transported a little bit downwards). After applying MIPAS Averaging Kernel to our model results you can see effects down to about 25 km. In an altitude of 30 km we have mixing ratios of about 350 pptv during this particular

C16253

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winter (in MIPAS about 50 pptv). Major effects due to the discrepancy between our probably unrealistic high model results and MIPAS are during EPP in our model (e.g. June 2003). During other time periods the differences are much smaller. We therefore still believe that the main difference in polar regions is due to EPP.

Figure 4

- *Fig 4: what does the title “error budget for 25” means?*

25 is the number which identifies the species H_2O_2 in our processor. This is internal information not relevant to the reader and thus will be removed.

Figure 5

- *Fig 5: the meaning of the lines colour is not explained in the caption.*

There is no real meaning of the lines colour. There are just some altitudes marked for better illustration. We will add the altitudes to the figure caption.

Negative values

2) P33519, Line 8-16: about the negative values in the profile Does the negative feature present in both daytime and nighttime profiles of MIPAS H_2O_2 ? Does the negative feature change with latitude or change with time of year? These may be useful information for the reader as well. Also, it may help evaluate whether it is a consistent bias of the measurement.

We did some frequency distributions for our retrieved H_2O_2 vmr under similar conditions. They all look like a normal distribution and are therefore believed to be of random nature. This also means negative values appear more often during time periods and in latitudes where are low H_2O_2 mixing ratios expected. Figure 3 is showing just one example. The negative feature there changes in each profile. After averaging a lot of profiles there is no negative feature present in our profiles as can be seen for example in figure 7.

Daily means

3) P33521, Line 8-10: Is the “daily mean vmrs from MIPAS data” here refers to daytime zonal mean only? If so, please specify it and please mention the satellite overpass time at the corresponding latitudes as well. A few pages later, when discussing the diurnal variation, the authors do mention the 10am and 10pm times, but here the description is not clear.

No, daily mean here refers to daily zonal mean and not daytime zonal mean. We will change this in our text to "zonal mean".

Missing error bars

4) The comparison in Fig 7: The MIPAS profiles does not show the uncertainty (or error bars). I understand that the error bars might be very big and dominating. But this is important information to be included in the comparison plots (or at least mentioned in the caption and the text). Also the model results should include some uncertainty ranges as well. A good way to do it is to use the recommended uncertainty ranges of the key chemical reaction in the several kinetic references. This uncertainty in reaction

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rate should produce a corresponding uncertainty in the model results. With these “error bar” information included in Fig 7, the discussion will be more meaningful.

For MIPAS profiles just the opposite is the case: The error bars (in terms of standard error of the mean) after averaging are very small and almost will not be visible. In figure 10 we provide a 3-sigma error bar for daytime and nighttime means. Here both are averaged and the error bar therefore will be even smaller. In the plot you just will see a thicker line, therefore we will not show error bars in this plot.

Giving a meaningful error estimation for the model results is not that easy. Most chemical reactions depend on two values: one pre-exponential factor and on the activation energy in the exponent. Therefore it is not possible to linearly interpolate the uncertainties in those numbers to the model result. Furthermore reactions can strongly depend on temperature which itself has an uncertainty. Additionally changing one reaction influences other reactions which can change dynamics. The only way to give a meaningful error estimation for model results is to do a Monte Carlo simulation with the 3D-model. This definitely will take so much time that it won't be done for this paper.

The standard error of the mean for KASIMA (same error estimation than for our observations) is even smaller than for MIPAS.

Different vertical profiles

More importantly, the authors didn't address the different vertical profiles of H_2O_2 before MIPAS and various model calculations at the near polar regions in both southern and northern hemispheres. The shapes, not only the values, are different. And I suspect that such difference in profile shape can not be explained by adjusting one simple chemical reaction rate.

It is true that it is not that simple to change the profile shape in the model that it fits MI-

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PAS observations. A wrong temperature or pressure dependence of the reaction rate however will change the profile shape. Uncertainties in temperature dependence in reaction rates for H_2O_2 suggests that it is not completely clear if the reaction is faster with increasing or decreasing temperature. This definitely will influence the profile shape. We also can speculate on photolysis as a reason for the wrong profile shape. For example in the currently recommended crosssections for H_2O_2 photolysis there are some overlapping wavenumber parts with ozone photolysis. An error in ozone photolysis therefore can propagate into the H_2O_2 profile. Additionally subsidence during polar winter and particle precipitation can influence the vertical shape of the profile. This is beyond the scope of this paper and therefore will not be discussed in detail.

overhead sun

5) Fig 9, the annual variation Since the H_2O_2 mostly follows the overhead sun, it's the best to overplot the corresponding SZA (solar zenith angle) so that it can be easily shown.

We will add the position of the overhead sun in figure 9.

Technical corrections

- Fig 2: for uniformity with the other figures, the units of measure should be placed between square brackets.

We will change this.

- Fig 6: "30° N and 40° N zonal means": does it mean that the curve is the "zonal mean of measurements from 30° to 40° N"? Also, for uniformity with the other figures, the

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units of measure should be placed between square brackets.

We change the description to "zonal mean of measurements between 30 and 40N". The units will be placed in square brackets.

Page 33515, line 26: grammar. Page 33516, line 17: better write CF4 (is that meant?). Page 33524, line 28: which JPL? Page 33530, line 3: incomplete, typos. Page 33527, line 5; page 33529, line 8: subscript! Figure 5, caption: define symbols and colors. Figure 11, caption: which latitude and season?

JPL refers to all tested versions. We will add this information in the text.

We added the informations and corrected typos/grammar.

P33515, Line 7: "measurements before 2005" is a little confusing. The earlier paragraph mentioned that the spectral resolution changed in 2004 and the data discussed here are only data before that. So please include the specific date or at least the month of the cutoff date and make it consistent throughout the text.

We exchange 2005 by March 2004.

P33523, Line15: "whole time period of MIPAS" Again, the authors mentioned earlier that they only use data before the resolution change in 2004. So the statement here is confusing. Please explain.

We change this sentence to: "The figure covers the whole time period of the high resolution MIPAS measurements of H₂O₂."

"3d-Chemical Transport Model" in a number of places in the text: I assume it means "3 dimensional". Suggest to use "3D (3 dimensional) " when it's first introduced.

We will explain 3D at its first appearance and change 3d to 3D.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 33511, 2011.