

Interactive comment on “HOCl chemistry in the Antarctic stratospheric vortex 2002, as observed with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS)” by T. von Clarmann et al.

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General comments

This paper studies in detail polar stratospheric chlorine chemistry, with a focus on HOCl, above the Antarctic in September-October 2002. I found its content original and interesting, especially in view of the following points:

1) The Antarctic 2002 fall season presented aspects typical both of the Southern Hemisphere (single vortex) and of the Northern Hemisphere (weaker, episodic vortices with lower ozone depletion). Hence the specific period and region analysed here do not reduce the paper to a simple case study.

2) HOCl observations are scarce, especially from spaceborne instruments. Its inclusion in an extensive dataset of co-located chemical observation, i.e. the MIPAS-IMK retrievals, is an important step for in-depth studies of polar stratospheric chemistry, both quantitatively and qualitatively. This is precisely the point made by this study.

3) It is important for stratospheric chemistry modelling to have evaluations of chemical rate constants that are based on "real-world" observations. Here it is shown that the values recommended by the latest JPL compilation for the reaction rate of $\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$ are probably less appropriate than those reported by Stimpfle et al. (1979).

I found the paper well written and relatively well structured with an excellent introduction and a relatively good presentation of the observations. While this study is certainly worth publication in *Atmospheric Chemistry and Physics*, I found that three important topics lack detailed description and clear explanations, the third one possibly requiring additional investigation. First, the selection, coverage and representativity of the observations are not well discussed. Second, the set-up of the KASIMA model simulation is not explained very well, and could even contain mistakes. Finally, I found no clear discussion about the possible causes for the disagreement between the observations and the model in the lower stratosphere. These three points are briefly discussed below, with more details in the Specific comments.

1) The process of selection of the observations, i.e. the determination of the edge of the polar vortex, is not described properly. There is no figure to report the geographical and temporal distribution of the selected observations with respect to the vortex area and evolution. While the manuscript mentions repeatedly the irregular spatial sampling of the dataset, there is almost no discussion about the specific impact(s) to expect from this irregular sampling.

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2) The set-up of KASIMA deserves some further explanations:

- Is the model output (fig. 3–6) interpolated to the location of the observations prior to averaging over the vortex area, or is the vortex average obtained from the model gridpoints? In the second case, the irregular sampling of MIPAS observations would prevent any meaningful quantitative comparison.
- What is the strength of the nudging towards ECMWF analyses, and the validity of the resulting dynamical fields?
- The reinitialisation of chemical fields to MIPAS observations on 17-18 September is justified by an (unexplained) underestimation of heterogeneous chemistry prior to the observation period. But the reinitialisation seems contradicted by some figures (see specific comments below), opening the possibility of a mistake in the chemical set-up.

3) The large model underestimation of lower stratospheric HOCl and ClO is attributed to the absence of heterogeneous chemistry in the simulation, due to the absence of PSCs in the model run. This absence of modelled PSC during the observation period is simply mentioned, and its causes are not explored. Some attempt should be made to explain this model deficiency, including especially a description of the parameterization (or microphysical modelling?) of PSC abundances used in KASIMA.

Specific comments

- Abstract, p. 18968, lines 6–9: this sentence is too long and difficult to read. Consider revision.
- Abstract, p. 18968, line 20: the words “comparison with a model run where no PSCs appeared during the observation period suggests that ...” can be understood only after careful reading of the relevant section. This sentence should be revised.
- Introduction, p. 18969, reactions (R8) and (R9): since these are heterogeneous

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reactions, it would be nice to indicate (through subscripts) which species are in gas phase, and which species are condensed.

- Introduction, p. 18969, line 14: "there do not exist many experimental data which can be used to study ...": consider revision.

- MIPAS measurements, p. 18971, lines 25-26: "For definition of the vortex edge, a procedure similar to that described by Nash et al. (1996) was used ...". This procedure should actually be described, including the origin and the horizontal resolution of the dynamical data used to define the vortex edge. As explained in the general comments, the results of this procedure (and of corresponding data selection) should be illustrated. I recommend plotting maps of the vortex edge at 1000K and 475K for a few dates in the observation period, overlaid with the locations of the selected MIPAS profiles. The first time series plots (figure 3) should also include the number of MIPAS profiles used per day. These additional plots would allow a brief discussion about the irregular spatial sampling of the dataset and its expected impact.

- MIPAS measurements, p. 18972, line 7: "HOCl, ClO and ClONO₂ mean values ...". This should also include HNO₄.

- Model calculations, p. 18972, line 17: "A horizontal resolution of T21 ($2.84^\circ \times 2.84^\circ$) has been used." T21 corresponds to (approximately) $5.6^\circ \times 5.6^\circ$ while $2.84^\circ \times 2.84^\circ$ corresponds to T42. What is the actual horizontal resolution used here? This is especially important in view of the results by Strahan and Polansky (2006, Atmos. Chem. Phys., 6, p.2895), who showed that a horizontal resolution of $2^\circ \times 2.5^\circ$ is necessary to properly isolate the air masses in CTM simulations of the polar vortex - a result that is expected to hold for a GCM like KASIMA, and that would certainly invalidate the use of a T21 horizontal resolution.

- Model calculations, p. 18973: the description of the chemical module does not include any reference or description about the parameterization (or microphysical modelling?) used for the abundance of PSCs allowing heterogeneous chemistry. This omission

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prevents any in-depth discussion about the cause of the disagreement between model and observation in the lower stratosphere (section 5.2).

- Model calculations, p. 18973, line 7: the chemical rate constants use an outdated version of the JPL compilation (Sander et al., 2003). Could the current compilation (Sander et al., 2006) significantly change any results presented here ?

- Model calculations, p. 18973, lines 10–17: this chemical reinitialisation procedure is one of the major issues arising in the comparison between model and observations:

+ It seems justified by the underestimation of heterogeneous chemistry prior to the observation period, but this justification is given much later in the text and should be moved here.

+ The dates chosen for the reinitialisation (beginning of the observation period) are problematic in any case. In most quantitative comparisons between models and chemical observations, the CTM is reinitialized at least a few weeks *before* the observation period, in order to let the model some time to find its own state (especially for longer-lived species as ClONO₂). Is this choice for the reinitialization date also related to the availability of MIPAS observations ?

+ Finally, the effect of this reinitialisation does *not* appear on several time series plots, where the observed and modelled values coincide on 18 September for HOCl *only* (see, e.g., middle stratospheric ClONO₂ on fig.3 and lower stratospheric ClO on fig. 5). Either the reinitialisation was not performed as described, or the description of the procedure is not correct.

- Figure 2 is quite difficult to read. As the other referee, I suggest further time averaging of the vertical profiles.

- Figures 3 and 5: it is difficult to see the difference between the two model simulations. I suggest using several colors in each panel - even though it would lead to another color coding than in figure 4 and 6.

- Figures 4 and 6: the disagreement between observations and model is obscured by

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the different vertical scale for the model results, due to the inclusion of modeled HCl. For figure 4 at least this is not necessary, it would suffice to mention in the text that the modeled sum [ClO+ClONO₂+HOCl+HCl] remains constant at 3.5 ppbv.

- Gas phase chemistry regime, p. 18975, lines 21–28: the significance of the high (24 September) and low (26 September) ClO abundances is discarded on the basis of larger error bars non-random spatial sampling. The first argument does not hold when one compares directly the values on 24 September (0.7 ppbv) with the values on 26 September (0.3 ppbv): these two error bars do not overlap. The second argument can not be verified due to the lack of plot showing the distribution of the observations (see above). My personal guess is that this day-to-day variability is real, related to the strongly perturbed dynamical situation of these dates, and can not be reproduced by the model due to its low horizontal resolution.

- Gas phase chemistry regime, p. 18976, lines 10–13: “While around 20 September modeled [HCl] strongly increases at the cost of [ClO+ClONO₂+HOCl], there is no obvious decrease of the latter species in the MIPAS measurements.” Modeled [HCl] increases by 0.2 ppbv while modeled [ClO+ClONO₂+HOCl] decreases from 1.2 to \simeq 1 ppbv. Measured [ClO+ClONO₂+HOCl] starts at 1 ppbv. Hence I think that this disagreement is due to the initial disagreement in ClONO₂. See comment above on the reinitialization procedure.

- Heterogeneous chemistry regime, p. 18977, line 6: “No substantial diurnal variation was observed here”. Does that mean that there is no substantial difference between the MIPAS observations at 10 AM and the observations at 10 PM ?

- Heterogeneous chemistry regime, p. 18978, lines 8-18: the whole paragraph is unclear and should be re-written with a focus on the cause of the absence of heterogeneous chemistry in the model simulation. Here are some further questions raised by the text:

+ “no PSCs appear in the model run during the observation period” - but do *any* PSCs

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appear in the model run? If yes, until what date ? Höpfner et al., 2004, observe PSCs until 21 September

+ "the part of HOCl also reproduced by the model must have been generated from previously heterogeneously generated ClO" - but both species are supposed to have been reinitialised to MIPAS observations on 17 and 18 September?

+ Line 15: the reinitialization date is now reported as 16 September?

+ Line 16: the necessity for the reinitialization procedure must be moved to the model description.

- Heterogeneous chemistry regime, p. 18978, lines 18-20: "Poor reproduction of measured ClO values, however, also leaves room for speculation that the quantitative understanding of ClO dimer chemistry is insufficient (von Hobe et al., 2007)." In view of all the remarks above, I do not think that this speculation is necessary to explain the disagreement between model and observations.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 18967, 2008.

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