

## ***Interactive comment on “Stratospheric ozone chemistry in the Antarctic: what controls the lowest values that can be reached and their recovery?” by J.-U. Grooß et al.***

**J.-U. Grooß et al.**

j.-u.grooss@fz-juelich.de

Received and published: 18 November 2011

We thank both reviewers for their constructive and detailed reviews. With very few exceptions (see below) the suggestions have been incorporated into the revised manuscript. Further details are discussed below. Comments of the reviewers are partly repeated *in italic letters* for clarification.

Both reviewers pointed to the fact, that ClONO<sub>2</sub> in the simulation is always close to zero and to the somewhat incomprehensible explanation. Therefore, we investigated the individual chlorine deactivation reactions and recognised indeed that instead of the reaction ClO+NO<sub>2</sub>, the formation of HOCl by the reaction ClO+HO<sub>2</sub> is the important

C12058

reaction in this cycle of chlorine deactivation and chlorine activation. Thus, Figures 2 and 4 and the explanation was corrected accordingly. From the discussion about the chemical mechanisms inspired by the reviewers comments some further insights were included into the paper, especially under the conditions of interest here (1) the HO<sub>2</sub> production caused by the CH<sub>4</sub> oxidation cycle and the resulting increased HOCl production, (2) the role of the ozone depletion cycle involving HOCl photolysis that was originally proposed by Solomon et al. (1986), and (3) the critical role of the reaction ClO+CH<sub>3</sub>O<sub>2</sub>.

### **Detailed Answer to Reviewer 1**

Major corrections

- 1) *The paper mainly focuses on chemistry of the Antarctic ozone hole. It would be good to mention or show how good the modelled chemical species (i.e., HCl, ClO, ClONO<sub>2</sub>) are from CLaMS 3D-CTM in the Antarctic polar region.*

We compared the 3-D model simulations with the publication of Santee et al., 2008, in which satellite observations were compared with the SLIMCAT model. Although this publication is discussing a different winter, we would expect similar behaviour of chlorine activation. The vortex average HCl mixing ratios of this CLaMS simulation show a decrease in June and July that is too slow in contrast to the SLIMCAT simulation that shows too fast HCl decrease. However, the problems of the CLaMS 3-D simulation are not central to the conclusions of the paper as it is (only) used for the initialisation of the box-trajectory models. The sensitivity studies with respect to initialisation are therefore important.

- 2) *The box model simulation is based on one trajectory in 2003 (Figure 2, 4) but it seems to me that the result is very sensitive to the chosen trajectory by looking at Fig. 9. The*

C12059

simulated ozone from box model run is similar at 400 K but there are large differences at 375 K and 450 K if we look at the red lines in Fig. 9.

Indeed, one major conclusion of this study is this sensitivity. Even for identical trajectories and simulations that only differ by the initial ozone mixing ratio the development of ozone mixing ratios are different. Depending very sensitively on factors like chemical initialisation, temperature history, the “turning point” (time and minimum ozone mixing ratio) when complete deactivation into HCl is reached varies significantly. However, the mechanisms for chlorine deactivation are similar in all examined trajectories.

The lines in figure 9c and 9d that show not very strong ozone depletion correspond to simulations with probably unrealistically strong dehydration (below 2 ppmv H<sub>2</sub>O) and denitrification (below 2 ppbv). The consequence of that was that the NAT PSC period ended already in early October before the very low ozone mixing ratios could be reached. Unlike the mechanism described in the paper, along these trajectories rather slow deactivation into the chlorine reservoirs was simulated. We attribute that to problems of the 3-D simulation. The initial chlorine activation of some trajectories is also not realistic when compared with observations. In the revised version we increased initial H<sub>2</sub>O and for these air parcels to be at least 2 ppmv H<sub>2</sub>O and 2 ppbv. We also initialised HCl and ClONO<sub>2</sub> from a climatology of the ACE-FTS experiment. The comparison between the box model simulations and the observation has improved from that.

- 3) In Figure 9, it looks that the CLaMS 3D CTM largely underestimates the observed ozone in the lowermost stratosphere (375 K and 400 K) early August (i.e. the ozonesonde data shows ozone value is about 1 ppmv at 375 K and over 1 ppmv at 400 K early August but the modelled ozone from CLaMS 3D-CTM is about 0.4 ppmv at 375 K and 1 ppmv at 400 K). It would be better to explain this in the paper.

Part of the difference between South Pole ozone sondes and CLaMS ozone minimum at latitudes 75-90° can be explained by the latitudinal ozone gradient.

C12060

Ozone mixing ratios in the vortex core are larger than in mid-latitudes. In the simulation there are occurrences of small filaments of mid-latitude origin south of 75°S. To exclude those mid-latitude filaments, we now plot the minimum for 75-90°S equivalent latitude instead of latitude. However, it is clear that there are still minimum ozone values in August below the envelope of the ozone sonde observations. On the 375 K and the 400 K level, about 5% and 1% of the CLaMS air parcels are below this envelope in August, respectively. This is a problem of the model initialisation at the lower levels. However, this deficiency of the 3-D model simulation does not affect the conclusions of this paper. In the revised version, we include this explanation.

We also estimated the effect of diabatic descent on the 500 K level (Fig. 9d). We found that the main part of the difference in ozone increase between model and data can be explained by the diabatic descent of about 20 K. The lower envelope of the South Pole observations on 1 December is around 340 ppbv on the 480 K and 480 ppbv on the 500 K potential temperature level.

- 4) Figure 1. The low ozone mixing ratio value (0.4 ppmv) around 1 July between 2000-2004 period can not be found from Figure 7a of Solomon et al. (2005). I think your ozonesonde data from the South pole station at 70 hPa should have the same source for the periods 1990-1999 and 2000-2004 as Solomon et al. (2005). Please double check the data.

We thank the reviewer for this hint. The mentioned point was caused by mistake by an interpolation of a sonde that contained no data between 9 and 20 km. Therefore, the entire data set was checked for vertical gaps in the ozone sonde data and two further ozone profiles with similar gaps were found. These 3 points were also excluded from the plot. Similarly, the data displayed in figure 9 were checked again, but there was no such error in the displayed time frame.

- 5) Figure 2. The caption of panel (c) is wrong. You also need to add “solid line for O<sub>2</sub>+hv, dot line for P(O<sub>3</sub>)” in Fig.2 (g). Is it possible to get the time series of PV values from this trajectory? Can you also explain why the simulated ClONO<sub>2</sub> field is always near zero

C12061

during the simulation period from the box model run? Why there is still some activation rate mid October since ClOx is near zero since early October?

The caption of Fig. 2 was updated accordingly. The trajectory stays in the vortex core as the average equivalent latitude of this trajectory is 77°S with a standard deviation of 5°. We include this information but no additional plot of PV or equivalent latitude. ClONO<sub>2</sub> is always very close to zero, as long as PSC surfaces are available. The displayed activation/deactivation rate also includes gas-phase reactions. In October and November, these reactions activate chlorine, namely the reaction HCl+OH (~84%) and the photolysis of ClONO<sub>2</sub>(~15%), that is immediately followed by the deactivation reaction.

- 6) Figure 3. It would be better to move Figure 3 before Figure 2. Then move the sentences in P22177-P22178 "Figure 3 shows..." after line 6 page 22176.

We did not change the order of the figures. The (now corrected) schematic in Figure 3 is shown to explain the model results displayed in figure 2 (and 4) and it does not make sense to move this in the model description section. However, we changed the formulations of the explanations in Section 3.1. as also indicated above. We hope that the interpretation of the results is now much clearer.

- 7) Figure 5 labels are not consistent with the text.

This is corrected in the revised version. the labels on the plot were correct.

- 8) The plot titles were removed from the figure and mentioned in the caption as suggested

#### Minor corrections

The mentioned items 1-6, 10-14 and 16-17 were corrected as suggested by the reviewer.

C12062

- 7) The photolysis rates are updated every hour, all photochemical parameters are taken from JPL06 except for the Cl<sub>2</sub>O<sub>2</sub> cross sections which are taken from Hobe et al., 2009, scaled with factor 1.48 to match the observation of Lien et al., 2009. This is now explicitly mentioned in the revised paper.
- 8) The liquid aerosol profiles were given as equivalent H<sub>2</sub>SO<sub>4</sub> volume mixing ratio derived from a fit to SAGE-II data (Grooß et al., 2005).
- 9) The initialisation of the 3-D model simulation was based on MIPAS-Envisat data of O<sub>3</sub>, N<sub>2</sub>O, and HNO<sub>3</sub>. Correlations with N<sub>2</sub>O were used to initialise Cl<sub>y</sub> (Grooß et al., 2002), Br<sub>y</sub> (Grooß et al., 2002)+10% and NO<sub>y</sub> (Grooß et al., 2005). The remaining species and the family partitioning was initialised from the Mainz 2-D model (Grooß, 1996). The CLaMS simulation was forced by the ECMWF operational analyses in a 1°×1° resolution.
- 15) The simulations suggest that ozone mixing ratios fall below the detection limit of about 10 ppbv at 70 hPa as also pointed out by reviewer 2. So the minimum ozone value may likely be below 10 ppbv. For the plotted results the initial ozone mixing ratio does not matter as the ozone increase rate for the shown reaction chains does not depend on ozone mixing ratio. Between 1 October and 30 November, ozone is increasing at a rate of above 1 ppbv per day and the plotted ozone increase would not be different.