**Atmospheric
Chemistry
and Physics
Discussions**

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.

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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 $ClONO_2$ 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 $ClO+NO_2$, the formation of HOCl by the reaction $ClO+HO_2$ is the important

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_2 production caused by the CH_4 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 $ClO+CH_3O_2$.

Detailed answer to Reviewer 2

Specific comments

We agree with most of the criticism of reviewer 2 and changed the wording in the revised version as suggested. Exceptions are listed below.

page 22174, line 2: *In this first sentence of the abstract, it might be worth mentioning that the ozone mixing ratios measured by the ozonesondes are essentially below the detection limit of the instruments and so it is quite likely that the ozone concentration is actually zero.*
We agree that the ozone mixing ratios may likely be below the detection limit of the ozone sondes. However, the presented simulations suggest that minimum ozone would be a few ppbv, not zero. In the revised manuscript mention that the observations are below the detection limit, as suggested.

page 22174, line 4: *This is a bit ambiguous. I think that it would make more sense to say "increase to above 1 ppm".*

We agree, but the 1 ppmv value for ozone is true for 70 hPa, not below. We changed the text accordingly.

page 22175, line 1-3: *incomprehensible wording*
The aim was to mention that few observations of ozone above 1 ppm, e.g. in late September to mid November was caused by transport. In fact they are caused by the 2002 vortex split, when the polar vortex was not above the South Pole. This was clarified in the revision.

page 22175, line 9: *I don't think that it is accurate to say that the ozone depletion is limited to values near 10 ppb. This is almost certainly close to or below the detection limit of the ozonesonde. So the ozone may well have gone to zero. And then of course no explanation is needed as to why ozone doesn't go below zero. Maybe the simple story is that well known chemistry drives ozone to zero concentration. I don't think that you need to make a big story about that...*
The model simulations do suggest that the minimum ozone mixing ratios are in the range of 4 to 10 ppbv, not zero. Before this study it was not clear to us that the well known ozone depletion cycles work down to such low ozone mixing ratios. That the low ozone values trigger the chlorine deactivation was also not exactly mentioned previously to our knowledge. Although the papers by Douglass et al. (1995) and Grooß et al. (1997) describe the basic principles. In any case, our model results provide a suggestion for the minimum ozone values reached in the Antarctic spring. It would be interesting to test these suggestions with measurements more accurate than ozone sondes.

page 22175, line 22: *How were the temperature data used to calculate the trajectories? More importantly, what diabatic ascent/descent rates were used in the trajectory calculations? Were these also obtained from ECMWF?*
The temperature data from ECMWF operational analyses were interpolated onto the time and location of the trajectory. The diabatic descent (or ascent) rates

were calculated from a radiation code (Morcrette, 1991; Zhong and Haigh, 1995) for a cloud-free atmosphere based on temperature from the ECMWF operational analyses and climatological ozone and water vapour profiles (Grooß and Russell, 2005). We did clarify this in the revised version.

page 22175, line 22: *I am not sure what the 'long time span' refers to? Is this the months over which the trajectory calculations are made?*
yes, from June to November, clarified in the revised version.

Fig. 2, caption: *The first sentence doesn't make sense. What does "Trajectory simulations through ozone sonde" mean? The caption refers to "ozone (green)" in panel (c). There is no green trace in panel (c). The ClONO₂ concentration in panel (e) seems to be uniformly zero. Why not just leave it off the plot and say that it is zero.*
For clarification, we changed the text to the following: "Box model simulations along a trajectory passing through the location of the ozone sonde observation of 10 ppbv on 73 hPa on 24 September 2003." We corrected the caption of panel (c). It is true that $ClONO_2$ is close to zero. As indicated above, the production of HOCl is more important. To elucidate this, we changed figures 2e and 4b to include HOCl instead of $ClONO_2$.

Fig. 2: *Figure 2 is too small to see the details...*
We will ask the production department of ACP to enlarge the figures 2 and 4 to page-wide size in the final version.

page 22177, line 14: *But quite a few days after the ozonesonde showed the 10 ppb value.*
Yes. This is mentioned now in the revised manuscript.

page 22178, line 3: *Regarding 'occurs in the short time period of only about one day'. This point has already been made in the paragraph above.*
The sentence was rephrased to avoid this repetition "The fast chlorine deactivation into the reservoir HCl can be elucidated by looking at the net chlorine

activation and deactivation rates that are shown in panel f of Fig. 2"

page 22179, line 8: *Why is this a positive feedback? ...*
The point here is that the net chlorine deactivation rate increases with decreasing ozone mixing ratio. As indicated above, it was not correctly described in the submitted paper. The mechanism works as follows. Increase of Cl concentration leads to faster CH_4 and CH_2O oxidation. From that, there is an increased HO_2 production (due to CH_3O_2+ClO and CH_2O+Cl). This causes an increased HOCl production and thus an increase in the chlorine activation rate through HOCl+HCl. We agree that the word feedback may not be appropriate. We clarified this mechanism in detail in the revised version.

page 22180, line 3: *Figure 5 labels are not consistent with the text.*
The legend in the figure is correct, it was an error in the text.

page 22181, line 1: *Incomprehensible wording*
We admit that the wording was somewhat inappropriate. The initial chlorine activation from the 3-D version may not simulate the correct $HCl/ClONO_2$ ratio, with the consequence that potentially the initial chlorine activation of the box model simulation could be different. Or there may be some variability of that parameter. This is the reason for this sensitivity study. We rephrased the beginning of the paragraph as: "The simulated development of ozone mixing ratios also depend on the initial chlorine activation. This was investigated..."

page 22185, line 14: *Incomprehensible wording*
To clarify the point to be made here, we revised the entire paragraph and rephrased the sentence as: "It is caused by the typical climatological temperature increase in spring, that leads to an increase of potential temperature on a constant pressure level. The change in potential temperature at 70 hPa between 1 October and 1 December is about 38 K. Since in spring the airmasses stay

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on slowly descending potential temperature levels, the time series of observations on constant pressure levels in Fig. 1 corresponds to different altitude origin. Therefore we compare the simulations with data on potential temperature levels."

page 22185, line 22: *I don't agree with this assumption that 'to first order, similar ozone loss would be expected for an air parcel starting at the pole and ending at latitude x compared with an air parcel starting at latitude x and ending at the pole for the same time period'...*
We see the point, but we don't agree completely. The example trajectories in October and November stay in the vortex at latitudes between about 65° and 90°N while different trajectories frequently pass near the South pole throughout the whole period. Note also that the noontime solar elevation increases from pole to mid-latitude, while the time of solar hours per day increases from mid-latitude to the pole. Therefore we conclude that to the first order the typical solar irradiance is similar on the mentioned trajectories. We included this argument in the revised version.

Grammar and typographical errors

All grammar and typographical errors were corrected as suggested. The revised manuscript was also proof-read in detail by a native speaker.