

Interactive comment on “A quantitative analysis of the reactions involved in stratospheric polar ozone depletion” by Ingo Wohltmann et al.

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Dear reviewer,
thank you for reviewing our paper and your helpful comments.

General comments

- **Your general comment 1, Other winters:** We agree that it is important to know how dependent the results are on the choice of the winter. Results for two additional winters are available, which were not shown in the manuscript to limit the paper to a reasonable length: Antarctic winter 2011 and Arctic winter 2009/2010.

We have now added the results for the two missing winters in a supplement. We

have added a new section discussing in how far the results can be generalized and discussing the notable differences between the winters. We have also added results for additional pressure levels to the supplement and discussion of the dependence of the results on altitude in several places.

We added “in this winter”, “2005” or similar in many places in the text to make clear that the results apply to a particular winter.

Actually, the choice of the northern winters was guided by the fact that a large range of possible meteorological conditions would be helpful for interpretation, and the winters 2004/2005 and 2009/2010 were chosen as a colder and a warmer winter. In the Antarctic, conditions are very similar in the different winters, and even the winter 2006 was not that different from the other years.

- **Your general comment 2, HCl discrepancy:** We agree that this is a very important issue and deserves more discussion. We have now moved the discussion to a separate section in the main text and considerably expanded the discussion on the reasons of the discrepancy and its effect on the results. The results of the original uncorrected runs are now shown in the supplement. The supplement also contains comparisons to ClO from MLS and ClONO₂ from ACE-FTS now. In addition, we changed the wording referring to the agreement of the new runs to observations and phrased this more carefully.

It is important to note that this is not a model deficiency specifically related to the ATLAS model, but is a well-known problem in many stratospheric CTMs, e.g. SLIMCAT (Santee et al., 2008), SD-WACCM (Brakebusch et al., 2013, Solomon et al., 2015), MIMOSA-CHIM (Kuttippurath et al., 2015). Unfortunately, discrepancies of this order of magnitude are still “state-of-the-art” in CTM modelling. This points to a gap in our understanding of the chemical and physical processes involved here. Unfortunately, this was not expressed as clearly as it could have been in the original manuscript. We have now added some additional general

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discussion of the problem in the introduction and further references (see specific comment P2, L13).

Unfortunately, discussing this issue in all the detail it deserves is out of the scope of this paper. This issue is so important that it would well deserve its own study summarizing the problems in the different models.

- **Your general comment 3, references:** We have added the references Frieler et al. and Kuttippurath et al. and some discussion. Thanks for pointing us to this obvious omission.
- **Your general comment 4, references:** We agree that some more references in the sections about NO_x , HO_x and ClO_x are helpful to discriminate what are our own results and what are the results of others. We added several new references (e.g. Toon et al., 1986, Stimpfle et al., 2004), including the studies of Portmann et al. (1996) and Douglass et al. (1995), which give a comprehensive overview of many discussed effects, and added numerous additional citations of these references throughout the paper.

We hope you understand that it is out of the scope of this paper to perform a comprehensive literature review, since this would require a lot of literature research for this very broad topic and has already been done in great detail by several authors. This was the reason to cite several textbooks and review papers in the introduction, which contain all the needed references to the original work.

Specific substantive comments

- P2, L13: Some important references were missing here. We have now added more discussion in the introduction and further references for SLIMCAT (Santee et al., 2008), SD-WACCM (Brakebusch et al., 2013, Solomon et al., 2015) and MIMOSA-CHIM (Kuttippurath et al., 2015). We have also added a reference

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to the Ph. D. thesis of T. Wegner, which is available online, and replaces the conference abstract.

Interestingly, the SLIMCAT CTM shows a discrepancy of the same order of magnitude, but with opposite sign. Unfortunately, there seem to be no publications allowing us to assess if e.g. CLaMS or KASIMA show the same discrepancies.

- P4, L25–28: This has technical and “historical” reasons. Originally, the runs were performed to develop a fast model for stratospheric ozone chemistry (SWIFT, see companion paper) and to train the SWIFT model on the modeled reaction rates. SWIFT is formulated on pressure levels (more precisely, the pressure levels of the EMAC model, which is the first model where SWIFT was implemented). For this study, we used the runs which were already existing.

We think it is ok to give no further justification, since neither pressure levels nor isentropic levels are material surfaces.

- P5, L4: The rationale behind this choice was to choose a value as high as possible under the condition that there are still a sufficient number of trajectories at the end of the considered time period to obtain an average (i.e. higher values than 0.7 are not feasible). Since the runs are computationally expensive, we did only perform runs for calculating the reaction rates for the value 0.7 and for no vortex tracer at all. Results for other values of the vortex tracer are only available for the vortex averaged mixing ratios. The runs without the vortex tracer showed reactions happening at the same time in the plots of the vortex averaged reaction rates that clearly would not proceed simultaneously at the same location, making the plots very difficult to interpret. Since the plots with the 0.7 value of the vortex tracer gave a self-consistent picture of the chemistry, we assumed that the remaining trajectory points were sufficiently homogeneous and did not explore this further (this is sort of a binary decision: As soon as reactions important in different parts of the vortex appear at the same time in the plots, they are not

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- usable anymore).
- P5, L10: Added reference.
 - Figure 1: Added a line for the ice frost point. Added reference to the figure at P13, L17.
 - Section 3: We would like to keep the section. We agree that it is not crucial, but it may be helpful for a reader new to the stratospheric community that uses this study as an overview paper and is helpful for assessing the results shown later.
We changed the reference for the phases from Solomon et al. (1999) to Portmann et al. (1996), which is to our knowledge the first paper introducing these four phases (this was also requested by another reviewer).
We are not sure if it is a good idea to mark the phases in the figure panels. It is difficult to assign exact dates to the phases, since there is no abrupt change between the phases, but it is more like a continuous process (e.g. what is the beginning of the third phase? How much sunlight is needed? What are the thresholds for the mixing ratios of ClO_x or Cl_2 ?). In addition, it will make the figures quite busy.
 - P7, L17: The rate of change of HNO_3 by denitrification and chemistry shown in Figure 3 is negative or near zero in March (and end of February). The net rate of change of HNO_3 in Figure 2 is positive. The only possible explanation is that the difference is caused by transport and mixing, since the net rate of change is the sum of the changes by chemistry, denitrification, transport and mixing. Added a note to the sentence.
 - Figure 3: The confusion arises because Figure 2 shows net changes (i.e. including transport and mixing), while Figure 3 shows only the chemical change and the change by denitrification. I.e., a seasonal integration would not result in the

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changes seen in Figure 2, see also the discussion in section 2.5. We hope the discussion in 2.5 is sufficient as clarification.

- P11, L21: Added a sentence discussing this.
- Figure 6: In all plots, all reactions that can be distinguished from the zero line at plot resolution are shown. Not all of these reactions are discussed in the text, e.g. the $\text{OH} + \text{HO}_2\text{NO}_2$ reaction in Figure 8 is not discussed, too. The rationale behind this is that we wanted to concentrate on the important reactions in the text (e.g. the reactions that are necessary to calculate sufficiently correct equilibrium mixing ratios) and not to get lost into details that obscure the main results. Nevertheless, showing the reactions in the plots is some additional information for readers interested in the details that does not hurt.

In addition, we think it is not a good idea to mention Figure 6 in section 4.4, since Figure 6 concentrates on nitrogen and section 4.4 concentrates on bromine.

- P17, L3–4 and Figure 9: In the original submitted version, the change was clearly visible in a figure showing the percentages. The fraction of OH changes from about 20% to about 40% at the start of October. We were however asked to remove this figure and some other figures in the prereview. We have now added these figures again in the supplement and added a reference to these figures in the text. Corrected typo.
- P19, L22: We considerably extended the discussion here. Removed the reference to Wayne. Note that there was already some discussion on this later in the ozone section, but we agree it doesn't hurt to discuss this here, too. Added a sentence on the temperature dependence of the ClO/ClOOCl equilibrium at night.
- P19, L25–27: October: We agree. Do you want us to change anything here?

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Peak ClO_x values: This is quite an interesting point, and we have added some discussion on the supposed reasons to the manuscript. It seems to us this is related to the higher Cl_y modeled in the northern hemisphere (Figure 11), which is probably caused by the stronger descent in the northern hemisphere. Added some discussion to the text describing Figure 11 (start of 4.3.1). In addition, there is also more activation from HCl into ClO_x in the northern hemisphere, even though the initial values for HCl and ClONO_2 are similar. Added discussion for this at the end of 4.3.1. This is clearly caused by the $\text{HCl} + \text{ClONO}_2$ reaction (Figure 13) and it seems that there is more ClONO_2 reformation in the northern hemisphere (yellow area, Figure 17). Added discussion for this in 4.3.2 (“HCl loss” section).

In addition, added a remark that the higher ozone depletion in the southern hemisphere is mainly caused by the longer time period of activation and not by higher ClO_x values to the ozone section 4.5.

- P21, L13–17: This is also an interesting point. The reason for this is the deactivation of chlorine by the reaction $\text{Cl} + \text{CH}_4$ (caused by the low ozone values), which provides HCl and produces HO_x (see Portmann et al., 1996, Crutzen et al., 1992). This can clearly be seen in the rising HCl levels in September in the southern hemisphere (Figure 11) and in the increased HO_x levels (Figure 9). In contrast, deactivation is into ClONO_2 in the northern hemisphere, keeping HCl levels low. Since the southern hemisphere is more denitrified, activation by $\text{ClONO}_2 + \text{HCl}$ is hindered. Added discussion of this to the text.
- Figure 13 and L1–4: Is $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ shown in Figure 13?

Basically, yes. You are correct, that was an unnoticed inconsistency, caused by the use of net reactions for the methane oxidation. The reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ has in very good approximation the same reaction rate as the net reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_2\text{O} + \text{HO}_2$. Only the net reaction can be shown

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here, since the reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ is not in the chemistry scheme (and CH_3 is not a modelled species). To avoid confusing the reader, we have changed the legend in the plot to the reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$.

- Figure 13 and L1–4: Are net changes being referred to (for HCl and ClONO₂)?

Yes. Added a reference to the green line to the text. We hope it is sufficiently clear that the change rate of a species (e.g. HCl or ClONO₂) (as opposed to the change rate by a single reaction) is always the net change by all reactions.

- Figure 13 and L1–4: When ClONO₂ is mentioned, is Figure 16 referred to?

It does not matter if Figure 16 or 17 is referred to, since the net change indicated by the green line is exactly the same in both figures. Added reference to both figures.

- Figure 13 and L1–4: Changed one of the colors.

- (1) P31, L16–17: We hope that the polar maps of model results and MLS observations shown in the supplement are sufficient to resolve this comment.

- (2) P31, L19–20: We think it is appropriate to write “satisfactory”. We do not state that the agreement is “good” or “excellent”. To go to the other extreme and to state that the agreement is “bad” or “unsatisfactory” certainly would not be appropriate: Differences for most species are below 10 % most of the time, and for many species MLS and the model agree better than the accuracy of the satellite data. Given the current state-of-the-art in CTM modelling, that is certainly not less than can be expected.

We are not of the opinion that the agreement of ozone to observations is considerably degraded. The agreement is still better than 10 % and only slightly different from the uncorrected run.

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- (3) P31, L25–L26: Added a figure showing N_2O . We agree that this omission was causing the reader to wonder why we don't show the plot. In addition, the discussion in the text was expanded. Two changes were applied to the figures: added bars for the accuracy of the MLS measurements to all plots, and changed the plots from showing values at 475 K to 54 hPa, to be more consistent with the other figures.

Most of the time, the agreement between N_2O from MLS and the model is good and there is no indication that there are differences in descent or mixing that would cause differences in other species (e.g. HCl) between model and observations. There is an overestimation of N_2O compared to MLS in the southern hemisphere in October and November, which is however after the period of interest here.

The reason of the overestimation of N_2O in the southern hemisphere is not certain. Given the vertical N_2O gradient and the N_2O gradient over the vortex edge, it seems likely that the problem is related to an overestimation of mixing over the vortex edge and not to differences in descent. Possibly, there are some problems in the Interim data used to drive the model.

Note that the change in HCl solubility in the new runs improves the agreement of N_2O to observations due to more chemical depletion of N_2O .

- (4) P33, L8–10: We have phrased that more carefully. Corrected typo.

Minor points

- P3, L29: Done.
- P4, L4: Done.
- P4, L10: Added “ Br_y ”.

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- P4, L25: Done.
- P5, L3–4: Done.
- P5, L7: Done.
- P6, L3: Done.
- P6, L10: Done.
- P7, L8: Changed to “evaporate”.
- P7, L19: Done.
- P7, L21: Done.
- P9, L3: Done.
- P9, L11–12: Done.
- P11, L4: Done.
- P11, L11: Added “that these are the relevant reactions”.
- P11, L16: Done.
- P12, L1: Done.
- P12, L13–14: Deleted sentence.
- P14, L4: Split into two sentences.
- P15, L16: Done.
- P15, L20: First comment: Done. Second comment: No change.

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- P16, L5: Deleted “to illustrate that”.
- P16, L6: Done.
- P16, L8: Done.
- P16, L12: Done.
- P17, L1: Done.
- P17, L3: Done.
- P17, L10–12: Done.
- P19, L4: Done.
- P21, L28: Added references to Portmann et al. (1996) and Santee et al. (2008).
- P22, L9: Done.
- P22, L10: Corrected.
- P23, L4: Done.
- P23, L7: Done.
- P25, L2: Deleted reference to the color.
- P25, L8: Done.
- P25, L10: Done.
- P25, L14: Done.
- P25, L16–17: Added reference, see P21, L28. Changed wording as suggested.

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- P26, Figure 17: In fact, this was a regression introduced by changes done in response to the prereview. Changed back the pink color in Figure 16 to blue. Now, blue is used for the reaction $\text{ClONO}_2 + \text{HCl}$ in Figures 13, 16 and 17 consistently. Instead, pink is used now for $\text{ClONO}_2 + h\nu$ in Figure 16, which causes no inconsistency with other figures as far as we can see.
- P28, L13: Done.
- P28, bottom: All reactions changed to the format used at P19. Also changed R38 to be consistent.
- P29, Figure 20: Changed the red line to a green line, assigned a different color to the O cycle and added an area for the remainder. Changed “negligible” to “small” in the caption. In addition, added an area for ozone production, which is almost exclusively from $\text{O}_2 + h\nu$.
- P29, L6: Done.
- P29, L8: Done.
- P29, L9: Done.
- P30, L13: Done.
- P30, L16–17: Done.
- P31, L3: Done.
- P31, L9: We would like to keep “desirable”. Unfortunately, it is still “state-of-the-art” in stratospheric CTMs that there are large discrepancies between measured and modeled values for some species (e.g. Kuttippurath et al., 2015 or Santee et al., 2008).

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- P31, L10: Done.
- P31, L24: Done.
- P31, L25: Done.
- P33, L5–6: Done.

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