Dear reviewer,

thank you for reviewing our manuscript and your helpful comments.

**General comment on HCl**

- We have now considerably expanded the discussion of the HCl discrepancy. There is additional discussion in the introduction and more references. The appendix was moved to the main part of the paper as an additional section. The uncorrected runs are now shown in a supplement and differences are discussed in the main text.

**Specific comments**

- Page 2, line 3: Results for additional pressure levels (70 hPa, 42 hPa, 32 hPa) are available, which were not shown in the manuscript to limit the paper to a reasonable length. We have now included results for additional pressure levels in a supplement and added discussion of the dependence of the results on altitude in several places.

- Page 2, line 7: We assume you refer to Page 3, line 7? Added “dehydration parameterization” to the sentence.

- Page 2, line 15, 16: 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. The winters are Antarctic winter 2011 (as suggested by you) 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.

  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.

- General comment: Moved the paragraph about the Polar Stratospheric Clouds to the model overview.

- Page 3, line 24: The value for the supersaturation in the chemistry module and the dehydration module can be set independently. We have added a note to the manuscript. The value of 0.7 was chosen to give the best possible agreement between modelled and measured water vapor. The value of 0.35 was obtained by comparison of MLS water vapor and temperatures.

  We agree that it would be helpful to have the same values here. The value for the chemistry module is of secondary importance however, since most of the activation normally occurs on STS clouds in our model setup. Thus, it is probably acceptable not to do the model runs again.
• Page 4, line 8–9: We have to admit that this 10% change was not really necessary. We used an initialization file from an earlier study here (Wohltmann et al., 2013) and did notice this too late (after finishing the runs). Since this 10% change does probably not significantly change the results or the agreement to observations, we think it is acceptable not to do the model runs again or to discuss this choice in the paper.

• Page 5, line 1–4: We have now added a supplement with additional pressure levels, see above. In addition, we have changed the title of the paper.

• Page 6, line 6: Done. Thanks for pointing us to this obvious omission.

• Page 11 and 12: Thanks for pointing us to these obvious omissions of important references. We have now added references to these studies in several places. In addition, we have increased the number of citations in the text and of the referenced papers considerably.

• Page 15, line 18: Changed to “HO$x$ chemistry”. “HO$x$ production” was not quite correct here. Added a reference to Figure 8. Extended discussion on the HOCl + HCl reaction considerably (see next comment).

• Page 21, line 14–15: The differences between the ClONO$_2$ + HCl and HOCl + HCl reaction in timing and between hemispheres are a quite interesting point and we have expanded the discussion of this issue in this section considerably.

First, there is a misunderstanding in your comment. The value of 70% refers to an integrated value over all months (i.e. the integral of the colored area for HOCl + HCl in Figure 13 compared to the colored area for ClONO$_2$ + HCl). We have added “integrated over the winter” to the sentence to make that more clear.

The reason for the increased importance of HOCl + HCl is the deactivation of chlorine by the reaction Cl + 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 been 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 ClONO$_2$ + HCl is hindered. We have added discussion of this to the text.

Your statement that ClONO$_2$ is higher in mid-September and October is not quite correct. ClONO$_2$ mixing ratios are near zero from June to November due to the denitrified conditions (see Figure 11, also compare with values in the northern hemisphere). Thus, no explanation is necessary why HOCl+HCl is still more important than ClONO$_2$+HCl on 1 October.

We added figures in the supplement showing that that the 70/30 ratio does not depend on altitude and added a general statement that the results
for the chlorine species do only moderately depend on altitude at the beginning of the section.

- Page 21, line 27: Added reference.

- Figure 19: Actually, vortex means of ozone from MLS and ATLAS compare relatively well in this time period (Figure 22, note that we changed the plots from showing values at 475 K to 54 hPa to be consistent with the rest of the paper). The difference is only slightly larger than the accuracy of the MLS ozone measurements (added bars for the accuracy of the MLS measurements to the figures). The reason that the MLS ozone values slightly differ from the model may be related to the fact that there is a notable overestimation of N₂O in ATLAS compared to MLS in the southern hemisphere in 2006 in October and November (we have now added plots showing N₂O to the manuscript). The overestimation of N₂O points to an overestimation of mixing across the vortex edge, possibly caused by problems in the ERA Interim data. This is supported by an underestimation of HCl. This would however lead to a faster increase in ozone mixing ratios in ATLAS compared to MLS, which is not observed. An alternative hypothesis would be strong upwelling in ERA Interim not existing in reality. In summary, the discrepancies remain an unresolved issue.
Dear reviewer,

thank you for reviewing our paper and your helpful comments.

1 General comments: 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 a supplement. The supplement also contains comparisons to ClO from MLS and ClONO$_2$ from ACE-FTS now. We added some important references that were missing.

It is important to note that this is not a model deficiency specifically related to the ATLAS model, but that discrepancies in HCl between model and observations are 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) or MIMOSA-CHIM (Kuttippurath et al., 2015). Interestingly, the SLIMCAT CTM shows a discrepancy of the same order of magnitude, but with opposite sign. For some models (e.g. KASIMA, CLaMS, see below) we were not able to find sufficient information in the literature. 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 discussion of the problem in the introduction and further references.

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.

1 General comments: CCMs and CLaMS

We disagree with your assertion that this problem does not occur in “state-of-the-art” CCMs and CLaMS, which also seems to imply implicitly that it does not occur in other CTMs in general.

• CCMs: The assertion that the problem is not evident in CCMs is not correct. Fig. 6.32 in the 5th SPARC report (CCMI, Eyring et al., 2010) shows large differences in HCl compared to MLS at the 500 K level, easily exceeding 1 ppb. In May to July, many CCMs overestimate HCl, as it is the case also for ATLAS.

Even more importantly, a comparison to CCMs not nudged to meteorological observations is not very meaningful. It is not possible to decide if differences in HCl between model and measurements are caused by e.g. temperature biases or biases in vortex strength or by problems in the chemistry and microphysics. The comparisons in Eyring et al., 2010 show
large discrepancies between MLS and the models and large differences between models, but it is not clear what the reasons are.

Since it can’t be decided if the problems in the CCMs come from not nudging them, we don’t refer to CCMs in the discussion in the introduction.

- **CLaMS**: Your assertion that the problem does not show up in CLaMS can’t be proven from the existing literature. Either the initialization of the chemical species is too late or comparisons of CLaMS model results for the polar vortex to HCl or ClONO\textsubscript{2} measurements are not shown for the relevant time period. There is just not enough information available to assess if there is the same problem in CLaMS or not.

The initialization in the CLaMS paper that you cite here for the Arctic (Grooß et al., 2002) is too late for the problem to show up (10 February). As far as I understand the paper, Cl\textsubscript{y} is taken from a tracer-tracer relationship, while the partitioning is taken from the Mainz 2-D model (it is however unclear to me from the text if that was done on 10 February or 8 January). That boils down to the question how well this model performs, which could easily overestimate the flux of NO\textsubscript{x} across the vortex edge and hence could overestimate the reformation of ClONO\textsubscript{2}. In addition, there is only a single comparison to HCl for a single ER-2 flight in March, which provides not enough information to assess if there is a problem in this particular run.

We only know of 2 CLaMS publications which deal with the Antarctic winter, where the problem is most pronounced (Grooß et al., 2005, 2011). These studies don’t show the initialization of the chlorine species or their development in May and June. The initialization in Grooß et al. (2005) is too late again for the problem to develop (August) and again depends on the Mainz 2-D model, but comparisons of HCl to measurements are shown. While the initialization in Grooß et al. (2011) is early enough, it shows only the HCl mixing ratio on a single, not representative trajectory and does not compare HCl to measurements. The only hint if the problem is evident in CLaMS is a reply to the reviewer in the discussion of Grooß et al. (2011), which states that CLaMS overestimates HCl (Reviewer 1, reply to major comment 1, C12059), which would point in the direction that CLaMS overestimates HCl as well, in contradiction to what you state in your review.

### 2 Specific comments

- Appendix A: “What happens if the analysis is done with the vortex criterion?”

Unfortunately, the computational effort is much higher when comparing the modelled values to the MLS data under consideration of the vortex tracer criterion. Without the vortex tracer criterion, it is sufficient to calculate simple vortex averages. Considering the criterion requires calculating trajectories from the measurement time and location of every MLS
measurement to the ATLAS output closest in time, sorting out ATLAS points with too low values of the vortex tracer and running the chemical box model forward on the trajectories then. Such point-to-point comparisons of measurements and model for the species measured by MLS were done for the 15th of every month of the simulation and are now shown in a supplement (regardless of the value of the vortex tracer), but were not shown in the original paper to limit the manuscript to a reasonable length. Examples for these plots are attached to this reply for the uncorrected run for 15 June 2006 (Figure 1), the corrected run for 15 June 2006 (Figure 2), the uncorrected run for 15 July (Figure 3) and the corrected run for 15 July 2006 (Figure 4). It can be seen that later in winter, a HCl “collar” region develops in the uncorrected model, where enough NO$_x$ is available to replenish ClONO$_2$. This is not visible either in the MLS data or the corrected run. That means restricting the comparison to the vortex core would make the comparison between the uncorrected run and MLS even worse, with higher values for HCl for the black line in Figure 22 of the manuscript.

Appendix A: “Is there a problem with photolysis rates for twilight conditions?”

We have the impression that the HCl problem is not very sensitive to photolysis reactions. The main problem is the lack of ClONO$_2$ for the HCl + ClONO$_2$ reaction. In addition, if there would be a problem with the photolysis, it should show up in other species as well. Most other species compare well with measurements, however (see supplement). There is some disagreement of the modelled NO$_x$ species to measurements of the ACE-FTS instrument, which by design measures under high solar zenith angles, but this could well be a problem of the unfavourable combination of a large satellite footprint with high gradients in mixing ratios.

If there is a problem is very difficult to tell, since it requires comparison of short-lived species to measurements under twilight conditions. This is difficult, since there are not so many measurements of short-lived species to compare with, the mixing ratios are low in twilight, and for satellite measurements, the satellite footprint will probably cover a relatively large range of solar zenith angles under twilight conditions.

The treatment of photolysis is pretty much standard in ATLAS compared to other models. Photolysis rates in the photolysis tables are calculated up to solar zenith angles of 100 degrees based on the photolysis coefficients given in the JPL catalogue. The spherical geometry is considered in dependence of the altitude. New solar zenith angles are calculated every 30 minutes and are then linearly interpolated to the time steps of the solver.

Appendix A: “Is the problem related to reactions on NAT and ice and the assumption of a constant supersaturation at ECMWF grid point temperatures ignoring mountain wave effects (page 3)?”
Figure 1: HCl at 46 hPa on 15 June 2006 in the uncorrected run. Left: ATLAS, Right: MLS. Bottom: Line plot of model (red) and MLS (black) along the satellite tracks.

Figure 2: HCl at 46 hPa on 15 June 2006 in the corrected run. Left: ATLAS, Right: MLS. Bottom: Line plot of model (red) and MLS (black) along the satellite tracks.
Figure 3: HCl at 46 hPa on 15 July 2006 in the uncorrected run. Left: ATLAS, Right: MLS. Bottom: Line plot of model (red) and MLS (black) along the satellite tracks.

Figure 4: HCl at 46 hPa on 15 July 2006 in the corrected run. Left: ATLAS, Right: MLS. Bottom: Line plot of model (red) and MLS (black) along the satellite tracks.
This probably cannot explain the discrepancies. The problem with the HCl + ClONO\textsubscript{2} reaction is not that it is not fast enough or that the area covered by the reaction is too small, it is simply that there is no ClONO\textsubscript{2} as a reaction partner. It is also very likely not related to the HOCl + HCl reaction. The discrepancy develops in June in the southern hemisphere, but the HOCl + HCl reaction needs sunlight and ClO\textsubscript{x} and does not really start to be important before August. In addition, NAT and ice clouds play a minor role compared to STS clouds in these model runs.

- Page 6, line 17: Do you mean that there is a study that we could cite here or do you mean we should perform a study with MIPAS data? Please clarify. In the first case, can you please give the reference?

- Page 22, Fig. 13: We agree. It is however extremely difficult to find a model parameterization that exactly matches the time evolution and spatial characteristics of HCl from the measurements and is at the same time based on some plausible assumptions about the reason of the HCl discrepancy. Note also that this unfortunately is “state-of-the-art” and that other models show discrepancies in the same order of magnitude (Santee et al., 2008, Brakebusch et al., 2013, Solomon et al., 2015, Kuttippurath et al., 2015). I.e., this is the best one can do with the current knowledge.

- Page 37, Wegner reference: We have to admit that citing this conference abstract was a little bit unfortunate, since it is not publicly available and there are at least two published studies on the HCl discrepancy in SD-WACCM, which we could have cited. We have added two references for SD-WACCM (Brakebusch et al., 2013, Solomon et al., 2015) and we have added a reference to the Ph. D. thesis of T. Wegner, which is available online.

3 Technical corrections

- Thanks for pointing me to the incorrect year. City has been added.

References

- Eyring et al. (2010), SPARC Report No. 5
- Grooß et al. (2011), Atmos. Chem. Phys., 11, 12217–12226
- Kuttippurath et al. (2015), Atmos. Chem. Phys., 15, 10385–10397
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 ClONO$_2$ 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 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 Friele 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\textsubscript{x}, HO\textsubscript{x} and ClO\textsubscript{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 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 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\textsubscript{x} or Cl\textsubscript{2}?). In addition, it will make the figures quite busy.

- P7, L17: The rate of change of HNO\textsubscript{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\textsubscript{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 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 OH + HO$_2$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?

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 HCl + 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 Cl + CH₄ → HCl + CH₃ (caused by the low ozone values), which provides HCl and produces HOₓ (see Portmann et al., 1996, Crutzen et al., 1992). This can clearly been seen in the rising HCl levels in September in the southern hemisphere (Figure 11) and in the increased HOₓ levels (Figure 9). In contrast, deactivation is into ClONO₂ in the northern hemisphere, keeping HCl levels low. Since the southern hemisphere is more denitrified, activation by ClONO₂ + HCl is hindered. Added discussion of this to the text.

Figure 13 and L1–4: Is Cl + CH₄ → HCl + CH₃ 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 Cl + CH₄ → HCl + CH₃ has in very good approximation the same reaction rate as the net reaction Cl+CH₄ → HCl+CH₂O+HO₂. Only the net reaction can be shown here, since the reaction Cl+CH₄ → HCl+CH₃ is not in the chemistry scheme (and CH₃ is not a modelled species). To avoid confusing the reader, we have changed the legend in the plot to the reaction Cl + CH₄ → HCl + CH₃.

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 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.

- (3) P31, L25–L26: Added a figure showing N\textsubscript{2}O. 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O in the southern hemisphere is not certain. Given the vertical N\textsubscript{2}O gradient and the N\textsubscript{2}O 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\textsubscript{2}O to observations due to more chemical depletion of N\textsubscript{2}O.

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

Minor points

- P3, L29: Done.
- P4, L4: Done.
- P4, L10: Added “Br\textsubscript{y}”.
- 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.
• 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.

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 ClONO$_2$ + HCl in Figures 13, 16 and 17 consistently. Instead, pink is used now for 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 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).

P31, L10: Done.

P31, L24: Done.

P31, L25: Done.

P33, L5–6: Done.
A quantitative analysis of the reactions involved in stratospheric polar ozone depletion in the polar vortex core

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Abstract. We present a quantitative analysis of the chemical reactions involved in polar ozone depletion in the stratosphere, and of the relevant reaction pathways and cycles. While the reaction pathways and cycles involved in polar ozone depletion are well known, quantitative estimates of the importance of single-individual reactions or reaction cycles are rare. In particular, there is no comprehensive and quantitative study of the reaction rates and cycles averaged over the polar vortex under conditions of heterogeneous chemistry so far. We show time series of reaction rates averaged over the core of the polar vortex in winter and spring for all relevant reactions and indicate which reaction pathways and cycles are responsible for the vortex-averaged net change of the key species involved in ozone depletion, that is ozone, chlorine species (ClOₓ, HCl, ClONO₂), bromine species, nitrogen species (HNO₃, NOₓ) and hydrogen species (HOₓ). For clarity, we focus on one Arctic winter (2004/2005) and one Antarctic winter (2006) in a layer in the lower stratosphere around 54 hPa, and show results for additional pressure levels and winters in a supplement. Mixing ratios and reaction rates are obtained from runs of the ATLAS Lagrangian Chemistry and Transport Model (CTM) driven by ECMWF ERA Interim reanalysis data. An emphasis is put on the partitioning of the relevant chemical families (nitrogen, hydrogen, chlorine, bromine and odd oxygen) and activation and deactivation of chlorine.

1 Introduction

The After the discovery of the ozone hole (Farman et al., 1985), the chemistry of polar ozone depletion in the stratosphere has been the subject of ongoing research for the last 30 years (see e.g. articles, review papers and text books by Solomon et al., 1986, Wayne et al., 1995, Portmann et al., 1996, Brasseur et al., 1999, Solomon, 1999, Brasseur and Solomon, 2005, and the reports of the World Meteorological Organization, WMO, 2011, Müller, 2012, Solomon et al., 2015). In general, the chemistry of polar ozone depletion is understood very well (see e.g. the recent overview in or the special issue of the RECONCILE¹ project in this journal, Müller, 2012, or von Hobe et al., 2013). Remaining issues, such as uncertainties in the formation pathways of Polar Stratospheric Clouds (PSCs) or uncertainties in the contribution of the different cloud types to chlorine activation (e.g. Lowe and MacKenzie, 2008; Peter and Grooß, 2012; Wohltmann et al., 2013), do not pose a serious challenge to the generally accepted basic theory.

¹Reconciliation of essential process parameters for an enhanced predictability of Arctic stratospheric ozone loss and its climate interactions
While the reaction pathways and reaction cycles that are involved in ozone depletion are well known (e.g. Portmann et al., 1996; Solomon, 1999; Müller, 2012), quantitative estimates of the importance of single reactions or reaction cycles are rare, and are limited to case studies or certain aspects of the chemical system (e.g. Portmann et al., 1996; Grenfell et al., 2006; Frieler et al., 2006) or apply mainly to conditions undisturbed by heterogeneous chemistry (e.g. Brasseur and Solomon, 2005).

Here, we give a comprehensive overview of the temporal evolution of the vortex-averaged reaction rates and mixing ratios and associated reaction pathways and cycles for one Arctic winter (2004/2005) and one Antarctic winter (2006) in a layer in the lower stratosphere around 54 hPa. Results for additional winters and pressure levels can be found in a supplement. Vortex-averaged mixing ratios and reaction rates are obtained from runs of the Lagrangian (trajectory-based) ATLAS Chemistry and Transport Model (Wohltmann and Rex, 2009; Wohltmann et al., 2010). Since results cannot be based on direct observations due to a lack of measurements of the mixing ratios of minor species and reaction rates, only a model-based approach is feasible. The most important model parameters that influence the vortex-averaged rates are the initial mixing ratios, the laboratory measurements of the rate coefficients of the reactions (taken from Sander et al., 2011) and the meteorological data that drive the model, which are taken from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA Interim reanalysis (Dee et al., 2011). A detailed study of the uncertainties is outside the scope of this paper, but some of the major uncertainties will be noted. For a study of the uncertainties, see e.g. Kawa et al. (2009).

Good Reasonable agreement of the modeled and observed mixing ratios for many species gives us confidence that our results represent the real atmosphere well in most cases (see Appendix the basic validation against observations in Section 6 and extensive additional comparisons of the model to measurements in the supplement). There was however a significant overestimation of HCl compared to measurements in our original model runs, which has also been observed in other models. While we apply a correction like SD-W ACCM (Brakebusch et al., 2013; Wegner, 2013; Solomon et al., 2015) or MIMOSA-CHIM (Kuttippurath et al., 2015), Interestingly, the SLIMCAT CTM shows a discrepancy of the same order of magnitude, but with opposite sign in a recent publication (Santee et al., 2008).

Hence, we consider the differences in HCl between models and observations as “state-of-the-art” in current CTMs and apply an empirical correction to bring the HCl mixing ratios in closer agreement to observations. The correction is based on changing the HCl solubility, which is a possible cause for this discrepancy—this. This introduces some uncertainty in our results (see Appendix)—which are explored in Section 6 and by comparisons to the uncorrected runs shown in the supplement. However, a detailed discussion of this important issue would deserve its own study.

While it is easy to identify the gross production or loss of a species by single reactions, it is difficult to identify what causes the net loss or production of a species (e.g. Lehmann, 2002). Often, the reactions that directly produce or remove a species of interest are part of a complicated chain of reactions, frequently involving reaction cycles. Many of these cycles will consume as much of a species as they produce (null cycles, equilibria), others will lead to a net loss of the species (loss cycles). Numerous loss cycles in the stratosphere are catalytic cycles, i.e. they destroy the species of interest with the help of another species that is constantly recycled in the loss cycle. To complicate things further, cycles may share species and reactions. Hence, it is of crucial importance to know the reaction cycles and pathways in the chemical system to actually understand the underlying reasons for the loss or production of a species, and these relationship are discussed in the following.
In Section 2, the methods and the model are introduced. The section contains a description of the ATLAS model and the setup of the runs and explains the method to obtain vortex-averaged reaction rates. In Section 3, we give an overview of the typical evolution of polar ozone chemistry in winter to provide a foundation for the following discussion. Section 4 discusses reactions and partitioning sorted by chemical families, that is nitrogen, hydrogen, chlorine, bromine and oxygen compounds. Section 5 explores in how far the results can be generalized to other years. Section 6 discusses the HCl discrepancy and gives a short discussion of validation of other species with observations. Section 7 contains the conclusions.

Results of this study are extensively used in a companion paper (Wohltmann et al., 2017) to develop a fast model for polar ozone chemistry.

2 Model and methods

2.1 Model overview

ATLAS is a global Chemistry and Transport Model (CTM) based on a Lagrangian (trajectory-based) approach. A detailed description of the model can be found in Wohltmann and Rex (2009) and Wohltmann et al. (2010). Updates to the chemistry module and polar stratospheric cloud module are described in Wohltmann et al. (2013). The model includes a gas-phase stratospheric chemistry module, heterogeneous chemistry on polar stratospheric clouds and a particle-based Lagrangian denitrification module and a dehydration parameterization. The chemistry module comprises 47 active species and more than 180 reactions. Absorption cross sections and rate coefficients are taken from recent JPL recommendations (Sander et al., 2011). In addition to the binary background aerosol, the model simulates three types of Polar Stratospheric Clouds, that is supercooled ternary HNO$_3$/H$_2$SO$_4$/H$_2$O solutions (STS), solid clouds composed of nitric acid trihydrate (NAT), and solid ice clouds.

2.2 Model setup

Model runs are driven by meteorological data from the ECMWF ERA Interim reanalysis (Dee et al., 2011). The initial horizontal model resolution is 150 km. The runs use the hybrid pressure-potential temperature coordinate of the model, which is a pure potential temperature coordinate above 100 hPa. The vertical range of the model domain is 350 K to 1900 K. Vertical motion is driven by diabatic heating rates from ERA Interim. Two model runs are started, one for the northern hemispheric winter, and one for the southern hemispheric winter. The run for the northern hemisphere starts on 1 October 2004 and ends on 31 March 2005. The run for the southern hemisphere starts on 1 April 2006 and ends on 30 November 2006. Model data before 15 November 2004 or 1 May 2006 are not used for analysis to allow for a spin up of the mixing in the model and for a sufficiently stable vortex in the northern hemisphere.

In addition to the binary background aerosol, the model simulates three types of Polar Stratospheric Clouds, that is supercooled ternary. Results for two additional winters (2009//solutions (STS), solid clouds composed of nitric acid trihydrate (NAT), and solid ice clouds 2010 in the northern hemisphere and 2011 in the southern hemisphere) are only shown in the supplement.
The number density of NAT particles in the runs is set to 0.1 cm\(^{-3}\), the number density of ice particles is set to 0.01 cm\(^{-3}\) and the number density of the ternary solution droplets is set to 10 cm\(^{-3}\). A supersaturation of HNO\(_3\) over NAT of 10 (corresponding to about 3 K supercooling) is assumed to be necessary for the formation of the NAT particles. A detailed discussion of the rationale behind these choices can be found in Wohltmann et al. (2013). For ice particles, a supersaturation of 0.35 is assumed based on Microwave Limb Sounder (MLS) satellite measurements of H\(_2\)O (Waters et al., 2006) and ECMWF temperatures.

The treatment of conditions where both NAT and STS clouds are allowed to form has changed compared to Wohltmann et al. (2013). Since mixed NAT/STS clouds are commonly observed (e.g. Pitts et al., 2011), they can now form in the model to allow for a more realistic behaviour, see Nakajima et al. (2016) for details.

The settings for the polar stratospheric clouds largely favor the formation of liquid clouds (binary liquids and STS clouds) over the formation of NAT clouds and activation of chlorine predominantly occurs on liquid clouds in the model runs.

The Lagrangian particle model is used to simulate the nucleation, growth, sedimentation and evaporation of large NAT particles. These particles are formed with a nucleation rate of 7.8×10\(^{-6}\) particles per h and cm\(^3\) and an initial radius of 0.1 µm, wherever a supersaturation of 10 for HNO\(_3\) is exceeded. Dehydration by falling ice particles is simulated by a simple new algorithm that irreversibly removes all ice above a given supersaturation, which is set to 0.7 here (note that the value 0.35 given above is only used in the chemistry module, the value in the dehydration module is set separately).

H\(_2\)O, N\(_2\)O, HCl, O\(_3\), CO and HNO\(_3\) are initialized from all measurements of the MLS instrument performed during 1 November 2004 and 1 May 2006 for the northern and southern hemispheres, respectively. CH\(_4\) is initialized from a monthly mean HALOE (Halogen Occultation Experiment) climatology (mean of the years 1991–2002) as a function of equivalent latitude and pressure (Grooß and Russell III, 2005). NO\(_x\) is initialized from the monthly mean HALOE data set by putting all NO\(_x\) into NO\(_2\). ClONO\(_2\) is calculated as the difference between Cl\(_y\) and HCl. Cl\(_y\) is taken from a Cl\(_y\)-N\(_2\)O tracer-tracer correlation from ER-2 aircraft and Triple balloon data (Grooß et al., 2002). As in Wohltmann et al. (2013), we increase the amount of ClONO\(_2\) by 10 % at the expense of HCl, see the discussion there. BrONO\(_2\) is assumed to contain all Br\(_y\), which is taken from a Br\(_y\)-CH\(_4\) relationship from ER-2 aircraft and Triple balloon data in Grooß et al. (2002). All Br\(_y\) values are scaled with a constant factor to give maximum values of 19.9 ppt.

2.3 Production and loss rates

Reaction rates are calculated for every reaction separately in the ATLAS model. For this purpose, one artificial species per reaction is introduced to the model, which is produced at the same rate as the other products of the reaction. For instance, a reaction of the type

\[ A + B \rightarrow C + D \]

is modified to

\[ A + B \rightarrow C + D + P \]
where P is an artificial product species. The mixing ratio of the artificial product species is reset to zero every 24 hours. This way, P directly gives the 24 h averaged rates of production of the species C and D by this reaction and the 24 h averaged loss rates of the species A and B. The 24 h time period is used to capture the diurnal cycle of the photochemically active species. For technical reasons, heterogeneous reaction rates with the same chemical equation, but on different surface types are added together in a single reaction rate.

2.4 Vortex averages

Production and loss rates are averaged over all air parcels of the model inside the polar vortex, which are situated in a layer between 61.3 hPa and 47.4 hPa. The logarithmic mean level of this layer is at 54 hPa. The vortex edge is assumed to be situated at the 36 PVU contour of modified potential vorticity (PV) in the northern hemisphere and at the −36 PVU contour in the southern hemisphere. Modified PV is calculated from the potential vorticity field of the ERA Interim reanalysis according to Lait (1994), with \( \theta_0 = 475 \text{ K} \). The supplement shows results for the additional pressure levels 32 hPa, 42 hPa and 70 hPa.

In order to obtain a more consistent picture of the ozone chemistry in the vortex, we exclude air parcels that experience a too high amount of mixing with extra-vortex air during the course of the model run. This basically limits our results to the core of the vortex. For that purpose, we initialize a “vortex tracer” as an artificial chemical species near the start of the model run (15 November in the northern hemisphere, 1 May in the southern hemisphere), which is set to 1 inside the vortex and to 0 outside the vortex. The vortex tracer is then transported and mixed like any other species in the model and can take any value between 0 and 1. We only include air parcels in the vortex mean, where those parcels for which the vortex tracer has a value greater than 0.7. This value was chosen as a compromise between obtaining a sufficient number of trajectories for averaging and a set of trajectories that is chemically sufficiently homogenous.

Without the vortex tracer, analysis would get much more complicated. An example may illustrate this: In the southern vortex, air masses rich in NO\(_y\) are mixed into the edge region of the vortex during the course of the winter, while in the core of the vortex, air masses are depleted of nitrogen species due to denitrification. This does not only lead to differences in mixing ratios of the nitrogen species over the vortex, but also to different reactions being important in different parts of the vortex. For example, while very low ozone values are reached in the core of the vortex since deactivation into ClONO\(_2\) is hindered, ozone values at the edge are higher and chlorine is also deactivated into ClONO\(_2\) (“collar”, see e.g. Douglass et al., 1995).

2.5 Different air masses

The 54 hPa level is not a material surface and we look at different air masses at different points of time, due to mixing, the movement of the isentropes relative to the pressure level and the additional sinking of the air masses relative to isentropes due to diabatic cooling. A similar caveat applies to the definition of the vortex edge. As a consequence of these transport effects, the temporal derivative of the vortex-averaged mixing ratio of a chemical species may deviate from the vortex-averaged chemical net production change of this species.
Unfortunately, it is difficult to look at the same air mass over the course of several months, since an air mass with a well defined extent at the beginning of the winter will completely lose its identity due to mixing and transport during the course of the winter.

### 2.6 Equilibria

In many cases, two species $X$ and $Y$ with short lifetimes are in a fast equilibrium with each other, and will not change their mixing ratios if the external conditions do not change. For example, consider two fast reactions of the form

$$X + Z_1 \rightarrow Y + \ldots$$
$$Y + Z_2 \rightarrow X + \ldots$$

Then, assuming that the change of the mixing ratios is zero

$$\frac{d[X]}{dt} = -k_1[X][Z_1] + k_2[Y][Z_2] = 0 \quad (1)$$

where $[X]$ is the concentration of $X$ and $k_1$ and $k_2$ are the reaction constants, we obtain equilibrium conditions like

$$\frac{[X]}{[Y]} = \frac{k_2[Z_2]}{k_1[Z_1]} \quad (2)$$

Similar equations can be derived for more complex reaction systems. We use the equilibrium conditions in the following not only to show relationships between mixing ratios of different species, but also to determine the reactions involved in an equilibrium: For a given set of species, we start with a small set of reactions involved in the equilibrium derived from the vortex-averaged reaction rates, and calculate the mixing ratios of the species from the equilibrium conditions. Then, we compare these mixing ratios with the mixing ratios in the output of the model. If the mixing ratios determined by both methods do not agree with each other, we add reactions until we reach good agreement with a set of reactions as small as possible.

### 3 Short overview of the chemical evolution

The evolution of the chemistry of polar ozone depletion can be divided into several phases (see also, for an overview first defined by Portmann et al., 1996). For orientation, Figure 1 shows the evolution of temperature and sunlight in both hemispheres.

After the polar vortex forms in late autumn and early winter in response to the cooling of the atmosphere in the beginning of polar night, air masses in the vortex are well isolated from mid latitudes (e.g. Solomon, 1999). In the first phase in early winter, chlorine, the main player in the chemistry of lower stratospheric ozone depletion, is present mainly in the form of passive reservoir gases such as HCl and ClONO$_2$ (e.g. Solomon, 1999). Chemical activity is low due to the lack of sunlight in the polar night. This period lasts from the forming of the vortex until the first polar stratospheric clouds form.
In the second phase, HCl and ClONO₂ are transformed from passive reservoir gases to Cl₂ through heterogeneous reactions on the surface of polar stratospheric clouds (e.g. Solomon et al., 1986), which condense when temperatures in the polar night get cold enough. A second effect of the clouds can be the removal of large quantities of HNO₃ and H₂O by sedimentation (denitrification and dehydration, e.g. Toon et al., 1986, Fahey et al., 1990), which can prolong ozone loss later in spring (e.g. Portmann et al., 1996). In the model setup used here, activation predominantly occurs on liquid STS clouds and only to a lesser part on solid NAT clouds. Unfortunately, observations of PSCs are not detailed enough to sufficiently constrain the ratio of activation on STS versus NAT clouds, and there is also uncertainty in other parameters like size distribution, number densities and required supersaturation. However, chlorine activation and ozone loss are robust quantities with respect to most changes in PSC parameterizations (Wohltmann et al., 2013).

The third phase starts when sunlight comes back, enabling catalytic cycles to destroy ozone in large quantities. Cl₂ is transformed to Cl and ClO by photolysis. Then ozone is removed mainly by the catalytic ClO dimer cycle and the catalytic ClO–BrO cycle (e.g. Solomon, 1999). The second cycle makes ozone destruction sensitive to the amount of bromine and to bromine chemistry. At the same time, reactions that deactivate active chlorine and that are dependent on sunlight gain importance. Hence, there is a constant competition between activation and deactivation in this phase, as long as it is cold enough (e.g. Portmann et al., 1996; Solomon et al., 2015).

In the fourth phase, when temperatures rise in spring and PSCs dissolve, chlorine is deactivated into the reservoir gases again and ozone loss significantly decreases.
Figure 2. Vortex-averaged partitioning of NO\textsubscript{y} species for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Species NO\textsubscript{3}, Br\textsubscript{2}O\textsubscript{2}, Cl\textsubscript{2}O\textsubscript{2} and N are not shown due to their small mixing ratios.

4 Budgets of the chemical families and chemical evolution arranged by families

4.1 Nitrogen species

NO\textsubscript{y} is defined as the sum of all nitrogen containing species except for the long-lived source gas N\textsubscript{2}O, which is the source of all other nitrogen species in the stratosphere. N\textsubscript{2}O has both natural and anthropogenic sources in the troposphere (e.g. WMO, 2011; Montzka, 2012). Figure 2 shows the partitioning of NO\textsubscript{y} at 54 hPa. The majority of NO\textsubscript{y} is in the form of HNO\textsubscript{3} in the considered altitude range. This is due to the fact that removal of HNO\textsubscript{3} by photolysis and OH is not very efficient at these altitudes. The initial level of HNO\textsubscript{3} is about 13 to 14 ppb in both hemispheres and the initial NO\textsubscript{y} is about 1 ppb higher. Figure 2 shows that the mixing ratio of HNO\textsubscript{3} (and NO\textsubscript{y}) declines to about 3 ppb in February 2005 in the northern hemisphere and increases again in March due to transport (see Figure 3, which shows that the rate of change by chemistry is small in this time period). In contrast, HNO\textsubscript{3} decreases to about 0.5 ppb (with NO\textsubscript{y} at 1 ppb) in the southern hemisphere after June 2006. The rate of change of HNO\textsubscript{3} is not dominated by chemical changes, but by changes by denitrification, i.e. the irreversible removal of HNO\textsubscript{3} by sedimenting cloud particles (e.g. Toon et al., 1986; Fahey et al., 1990), as shown in Figure 3. Denitrification is much more severe in the southern hemisphere due to the lower temperatures, leaving almost no reservoir Cl\textsubscript{2}O\textsubscript{2} is limited by the mixing ratio of Cl\textsubscript{y} (less than 3.5 ppb). Thus, Cl\textsubscript{2}O\textsubscript{2} never contributes more than about 25 \% to NO\textsubscript{y}. The supplement shows that NO\textsubscript{y} increases with height from 10 ppb at 70 hPa to 18 ppb at 32 hPa, but that the majority is always in the form of HNO\textsubscript{3}.

NO\textsubscript{x} is defined as the sum of the short-lived and reactive species NO, NO\textsubscript{2}, NO\textsubscript{3} and 2 N\textsubscript{2}O\textsubscript{5}, which only form under sunlit conditions from the longer lived HNO\textsubscript{3}. Only a small part of NO\textsubscript{y} is in the form of NO\textsubscript{x} under sunlit conditions, typically less
Figure 3. Vortex-averaged net chemical reaction rate of HNO$_3$ (red) for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa and sum of the vortex-averaged change by sedimentation and the net chemical reaction rate (blue).

Figure 4. Vortex-averaged chemical reaction rates of reactions changing extended NO$_x$ (NO + NO$_2$ + NO$_3$ + 2N$_2$O$_5$ + ClONO$_2$ + BrONO$_2$ + HO$_2$NO$_2$) for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Production reactions are shown positive and are separated by a line in the legend from the loss reactions, which are shown negative. The net change of extended NO$_x$ is shown as a green line. Reactions with rates which cannot be distinguished from the zero line at plot resolution are not shown.

than 21.5 ppb in the northern hemisphere and less than 0.750.5 ppb in the southern hemisphere at 54 hPa. The supplement shows that NO$_x$ increases from about 0.5 ppb at 70 hPa to 2.5 ppb at 32 hPa due to increasing radiation. For the following discussion, it is reasonable to define an “extended” NO$_x$, which also includes ClONO$_2$ (and, much less importantly, BrONO$_2$ and HO$_2$NO$_2$), since these species are in very fast equilibria with the “classical” NO$_x$ species under sunlit conditions.
The extended NO\textsubscript{x} mixing ratios can be changed by a number of reactions. Vortex-averaged reaction rates of these reactions for the northern and southern hemisphere are shown in Figure 4. Extended NO\textsubscript{x} is almost exclusively produced from HNO\textsubscript{3} under sunlit conditions by photolysis and reaction with OH

\[
\text{HNO}_3 + h\nu \rightarrow \text{NO}_2 + \text{OH} \quad \text{(R1)}
\]

\[
\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3^- \quad \text{(R2)}
\]

See e.g. Portmann et al. (1996). The OH reaction contributes about 60\%–80\% to the production of the production (cf. Figure 7 in Portmann et al., 1996). Extended NO\textsubscript{x} is lost to HNO\textsubscript{3} mainly by the heterogeneous reactions

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_3 \quad \text{(R3)}
\]

\[
\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3 \quad \text{(R4)}
\]

and by the gas-phase reaction

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad \text{(R5)}
\]

The reaction N\textsubscript{2}O\textsubscript{5} + H\textsubscript{2}O proceeds on the background aerosol, not only when polar stratospheric clouds are present. When sunlight comes back to the vortex in spring, reactions R1–R2 are not in equilibrium with R3–R5 and produce net production of extended NO\textsubscript{x} from HNO\textsubscript{3} occurs (e.g. Portmann et al., 1996). Due to the denitrified conditions in the southern hemisphere, much less NO\textsubscript{x} is produced there (e.g. Douglass et al., 1995). While the rates of the reactions changing extended NO\textsubscript{x} increase by a factor of 4 from 70 hPa to 32 hPa (see supplement), the relative importance of the reactions does not change.

Note that the introduction of an extended NO\textsubscript{x} does not work very well under polar night conditions, since ClONO\textsubscript{2} is not in equilibrium with the classical NO\textsubscript{x} then, which can be seen in the fact that extended NO\textsubscript{x} is lost in polar night due to heterogeneous reaction of ClONO\textsubscript{2}, although no NO or NO\textsubscript{2} is present.

Figure 5 shows the partitioning of extended NO\textsubscript{x} during daytime and at night. Daytime averages are defined over the parts of the vortex where the solar zenith angle is smaller than 80° and nighttime averages are defined over parts of the vortex where the solar zenith angle is larger than 100° (note that this means that the areas for the daytime average and the nighttime average may not be coincident). Except for early winter, NO\textsubscript{x} proper is only present in appreciable quantities after the start of March or October 2005 or October 2006 in the northern and southern hemispheres, respectively. During daytime, the partitioning between NO and NO\textsubscript{2} is so fast that steady state conditions can be assumed (e.g. Douglass et al., 1995). The three reactions that determine the equilibrium are

\[
\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R6)}
\]
Figure 5. Vortex-averaged partitioning of extended NO$_x$ species for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Top row: Daytime averages (parts of the vortex where the solar zenith angle is smaller than 80°). Bottom row: Nighttime averages (parts of the vortex where the solar zenith angle is larger than 100°). Days without sufficient data for averaging are not shown (grey bars).
ClO + NO → Cl + NO₂ \hspace{1cm} (R7)

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}. \] \hspace{1cm} (R8)

Figure 6 shows the formation and loss rates of NO to illustrate that these are the relevant reactions (the corresponding plots for NO₂ look identical, but mirrored). The equilibrium condition derived from these reactions is

\[
\frac{[\text{NO}]}{[\text{NO}_2]} = \frac{k_{R8}}{k_{R6}[\text{O}_3] + k_{R7}[\text{ClO}]].
\] (3)

In the southern hemisphere during daytime, the fraction of NO compared to NO₂ is much higher than in the northern hemisphere (80%–90% NO and 10%–20% NO₂ in the southern hemisphere, and 20%–40% NO and 60%–80% NO₂ in the northern hemisphere, see Figure 5 and percentage plots in the supplement). The relative partitioning is approximately constant between 70 hPa and 32 hPa (see supplement). The higher NO levels are caused by the much lower ozone levels in the southern hemisphere (see Figure 19), which shifts the equilibrium by hindering the O₃ + NO reaction (e.g. Douglass et al., 1995). At night, no NO is present, since the reaction NO₂ + hν does not take place. NO₃ only plays a negligible role for does not significantly contribute to the budget of NOₓ due to the fast reaction into NO₂ by

\[ \text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O} \] \hspace{1cm} (R9)

during daytime and into N₂O₅ at night (see discussion of R13).

Despite the relatively low mixing ratios, NOₓ plays an important role in ozone chemistry, the chemistry of polar ozone depletion (the gas phase catalytic NOₓ cycle is in general an important contributor to stratospheric ozone chemistry, e.g. outside of the vortex and in higher altitudes than discussed here). In addition to the equilibrium between NO and NO₂, there is a fast equilibrium between NO₂ and ClONO₂ under sunlit conditions, so that all three species are coupled. ClONO₂ is to a good approximation in an equilibrium between

\[ \text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_3 \] \hspace{1cm} (R10)

\[ \rightarrow \text{ClO} + \text{NO}_2 \] \hspace{1cm} (R11)

and

\[ \text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \] \hspace{1cm} (R12)

see e.g. Portmann et al. (1996). Reaction R10 is the dominating branch of the ClONO₂ photolysis. The equilibrium condition for ClONO₂ can be written as

\[
[\text{ClO}][\text{NO}_2] = \frac{k_{R10} + k_{R11}}{k_{R12}}[\text{ClONO}_2].
\] (4)
Figure 6. Vortex-averaged chemical reaction rates of reactions changing NO for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa to illustrate NO\textsubscript{x} partitioning. Production reactions are shown positive and are separated by a line in the legend from the loss reactions, which are shown negative. The net change of NO is shown as a green line.

Alternatively, since NO and NO\textsubscript{2} are in equilibrium, this can also be expressed in terms of NO

\[
[C\text{IO}][\text{NO}] = \frac{(k_{R10} + k_{R11})k_{R8}[\text{ClONO}_2]}{k_{R12}(k_{R6}[\text{O}_3] + k_{R7}[\text{ClO}])}.
\]  

Production of NO\textsubscript{x} from HNO\textsubscript{3} in spring will increase NO\textsubscript{2}. In turn, ClONO\textsubscript{2} will increase almost instantly at the expense of NO\textsubscript{2} to match the equilibrium condition again. In this sense, ClONO\textsubscript{2} is produced from HNO\textsubscript{3} via NO\textsubscript{x} in spring (e.g. Portmann et al., 1996). This is an important deactivation pathway for active chlorine in the northern hemisphere, since it consumes ClO.

There is a striking difference in ClONO\textsubscript{2} production in spring between the northern and southern hemisphere. While ClONO\textsubscript{2} increases to 2 ppb in the northern hemisphere, it stays below 0.1 ppb in the southern hemisphere due to the strongly denitrified conditions there. The hindrance of the deactivation path via ClONO\textsubscript{2} under denitrified conditions prolongs the period of ozone loss, since the other deactivation path via the reaction Cl + CH\textsubscript{4} is only effective under low ozone levels (see section 4.3.2 e.g. Douglass et al., 1995, Portmann et al., 1996), see Section 4.3.2. ClONO\textsubscript{2} stays relatively constant in March 2005 in the northern hemisphere after the initial increase, since the decrease in ClO is compensated by an increase in NO\textsubscript{2}. In the southern hemisphere, drops to even lower values after October due to missing ozone.

The mixing ratio of N\textsubscript{2}O\textsubscript{5} is governed by

\[
\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \tag{R13}
\]

\[
\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO}_3 \tag{R14}
\]
Figure 7. Vortex-averaged mixing ratios of H$_2$O and CH$_4$ for the Arctic winter 2004/2005 and the Antarctic winter 2006 at 54 hPa.

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \to \text{HNO}_3 + \text{HNO}_3. \tag{R3}
\]

At night N$_2$O$_5$ is produced slowly by reaction R13, with NO$_3$ produced by

\[
\text{NO}_2 + \text{O}_3 \to \text{NO}_3 + \text{O}_2. \tag{R15}
\]

During daytime, no N$_2$O$_5$ is produced, since the NO$_3$ produced by reactions R10 and R15 is easily photolyzed. However, N$_2$O$_5$ is only slowly depleted during daytime, so that N$_2$O$_5$ levels during daytime and at night are comparable in the northern hemisphere (up to 30% of classical NO$_x$ is in N$_2$O$_5$). In the southern hemisphere, low ozone levels hinder the production of N$_2$O$_5$. The produced N$_2$O$_5$ can react back to the reservoir HNO$_3$ via reaction R3 (see Figure 4).

4.2 Hydrogen species

The sources for HO$_x$ = OH + HO$_2$ are mainly H$_2$O, CH$_4$ and HNO$_3$. The source for stratospheric water is humid tropospheric air “freeze-dried” at the tropopause and sources for CH$_4$ are both natural (e.g. wetlands) and anthropogenic (e.g. WMO, 2011; Montzka, 2012). CH$_4$ is slowly oxidized to H$_2$O in the stratosphere (e.g. Hanisco, 2003; see also below). Figure 7 shows that the mixing ratio for H$_2$O is between 2 ppm and 6 ppm at 54 hPa and that CH$_4$ has a mixing ratio of about 1 ppm. The decrease of H$_2$O in July 2006 in the southern hemisphere is caused by dehydration by sedimenting cloud particles, similar to the situation for HNO$_3$. The northern hemisphere in 2005 is not cold enough for the formation of a significant amount of ice clouds (Figure 1).

Production and loss processes of HO$_x$ are fairly complicated (Hanisco, 2003). Figure 8 shows the production and loss rates of an extended HO$_x$ at 54 hPa, where we have included some species that are not a net source or sink of HO$_x$ over a diurnal cycle (extended HO$_x$ = OH + HO$_2$ + H + HOCl + HOBr + HO$_2$NO$_2$). Particularly in the southern hemisphere, production
Methane oxidation is modelled by simplified net reactions in ATLAS, the reactions denoted as methane oxidation in the legend are 

\[ \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_2\text{O} + \text{HO}_2 \text{ and } \text{Cl} + \text{CH}_2\text{O} \rightarrow \text{HCl} + \text{CO} + \text{HO}_2. \]

from CH$_4$ oxidation, which can be initiated by

\[ \text{X} + \text{CH}_4 \rightarrow \text{XH} + \text{CH}_3 \tag{R16} \]

with X = Cl, O($^1$D), OH and plays an important role. It then continues with a complicated chain of reactions involving CH$_2$O (see Hanisco, 2003, for more details), plays an important role. The maximum yield of this reaction chain is 4 HO$_x$ per CH$_4$, but the yield is normally lower (Hanisco, 2003). For example, the HCl formed by R16 with X = Cl lowers the yield of the reaction chain starting with this reaction because of the reaction

\[ \text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}. \tag{R17} \]

Reaction of water with O($^1$D)

\[ \text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{OH} \tag{R18} \]

and photolysis of HNO$_3$

\[ \text{HNO}_3 + h\nu \rightarrow \text{NO}_2 + \text{OH} \tag{R1} \]

can also produce HO$_x$. Sinks are the recombination into water

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \tag{R19} \]
and the reactions

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad \text{(R5)} \]

\[ \text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3 \quad \text{(R2)} \]

5

\[ \text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2. \quad \text{(R20)} \]

\[ \text{HO}_x \text{ is in equilibrium with HOCl under sunlit conditions and when chlorine is activated } (\text{e.g. Portmann et al., 1996}) \]

\[ \text{HOCl} + h\nu \rightarrow \text{Cl} + \text{OH} \quad \text{(R21)} \]

10

\[ \text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2. \quad \text{(R22)} \]

Hence, the heterogeneous reaction

\[ \text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \quad \text{(R23)} \]

is also a sink for \( \text{HO}_x \). The rates of the reactions changing extended \( \text{HO}_x \) increase by a factor of 4 from 70 hPa to 32 hPa (see supplement). The relative importance of the reactions does not change with the exception of methane oxidation, which becomes less important with increasing height.

\[ \text{HO}_x \text{ levels are about 1 to 4 ppt at 54 hPa under sunlit conditions in both hemispheres (Figure 9). Maximum values increase from 3 ppt at 70 hPa to 7 ppt at 32 hPa. At night, no } \text{HO}_x \text{ is present, since there is no production and } \text{HO}_x \text{ recombines into water and } \text{HNO}_3 \text{ (Figure 8). HOCl can reach mixing ratios of up to 0.15 ppb at 54 hPa in both hemispheres, as long as chlorine is activated (see Figure 11). Figure 9 shows that } \text{HO}_x \text{ does not simply scale with the amount of sunlight, } \text{HNO}_3, \text{ H}_2\text{O and CH}_4: \text{ In the southern hemisphere, } \text{HO}_x \text{ shows a peak under conditions of both chlorine activation and sunlight, related to the fact that reactions like } \text{Cl} + \text{CH}_4 \text{ and } \text{HOCl} + \text{HCl play a role in } \text{HO}_x \text{ production chemistry (Figure 8, see also the discussion in Section 4.3.2 related to } \text{HCl}). \]

Figure 9 also shows the partitioning of \( \text{HO}_x \). Similar to \( \text{NO}_x \), there is a fast equilibrium between \( \text{OH} \) and \( \text{HO}_2 \). The partitioning is determined mainly by

\[ \text{HOCl} + h\nu \rightarrow \text{Cl} + \text{OH} \quad \text{(R21)} \]

\[ \text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 \quad \text{(R22)} \]

\[ \text{ClO} + \text{OH} \rightarrow \text{Cl} + \text{HO}_2 \quad \text{(R24)} \]
Figure 9. Vortex-averaged partitioning of HO$_x$ species for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Daytime averages (parts of the vortex where the solar zenith angle is smaller than 80°). Nighttime averages are near zero and not shown. Days without sufficient data for averaging are not shown (grey bars).

$$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$$  \hspace{1cm} (R25)

$$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$$  \hspace{1cm} (R26)

$$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}.$$  \hspace{1cm} (R27)

Figure 10 shows the rates of HO$_2$ production and loss to illustrate that (the corresponding plots for OH look similar, but mirrored, and with ClO + HO$_2$ is replaced by HOCl + hν).

The rates of the reactions partitioning HO$_x$ increase by a factor of 4 from 70 hPa to 32 hPa again (see supplement), the relative importance of the reactions does not change except for the reaction R24 getting less important with increasing altitude.

The production and loss rates of HO$_x$ proper are dominated by the reactions R21 and R22 which form the equilibrium with HOCl (not shown).

The equilibrium is mainly on the side of HO$_2$ in both hemispheres (see Figure 9, e.g., Hanisco, 2003). The fraction of OH is somewhat higher in the southern hemisphere (about 20%–40%) than in the northern hemisphere (about 10%–20%), see also percentage plots in the supplement. The relative partitioning is approximately constant with altitude (see supplement).
Figure 10. Vortex-averaged chemical reaction rates of reactions changing HO$_2$ for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa to illustrate HO$_x$ partitioning. Production reactions are shown positive and are separated by a line in the legend from the loss reactions, which are shown negative. The net change of HO$_2$ is shown as a green line.

Absolute OH levels are of relatively similar magnitude in both hemispheres (up to 1 ppt in the southern hemisphere and up to 0.5 ppt in the northern hemisphere).

Equations for the equilibrium values of OH, HO$_2$ and HOCl can be derived from reactions R21 to R27. The ratio of OH and HO$_2$ under sunlit conditions in the northern hemisphere and in the southern hemisphere before mid-September is in to a good approximation given by

$$\frac{[\text{OH}]}{[\text{HO}_2]} = \frac{k_{R25}[\text{O}_3] + k_{R22}[\text{ClO}] + k_{R27}[\text{NO}]}{k_{R26}[\text{O}_3] + k_{R24}[\text{ClO}]}.$$  (6)

That is, the ratio depends only on O$_3$, ClO and NO. The equation can be simplified to

$$\frac{[\text{OH}]}{[\text{HO}_2]} = \frac{k_{R25}[\text{O}_3] + k_{R22}[\text{ClO}]}{k_{R26}[\text{O}_3] + k_{R24}[\text{ClO}]}.$$  (7)

under conditions when chlorine is activated and no NO is present (before March, see Figure 5, before March 2005 and mid-September 2006 in the northern and southern hemisphere, respectively) and to

$$\frac{[\text{OH}]}{[\text{HO}_2]} = \frac{k_{R25}[\text{O}_3] + k_{R27}[\text{NO}]}{k_{R26}[\text{O}_3]}.$$  (8)

in spring in the northern hemisphere (end of March) in the northern hemisphere 2005, after chlorine is deactivated. In the southern hemisphere, the change between conditions rich in ClO$_x$ and rich in NO$_x$ can be seen in is marked by a change in the relative partitioning (Figure 9), partitioning of OH from about 20% to about 40% at the start of October (see percentage plots in the supplement). A similar discussion and expressions for mid-latitudes can be found in Cohen et al. (1994).

Under sunlit conditions and when chlorine is activated, the equilibrium of HOCl is given by

$$[\text{HOCl}] = \frac{k_{R22}}{k_{R21}} [\text{ClO}][\text{HO}_2].$$  (9)
At night, HOCl remains constant (except for heterogeneous processing), since neither the photolysis reaction nor the ClO + HO2 reaction can proceed.

HOx is relevant for ozone depletion, since the reactions HCl + OH → H2O + Cl (R17) and ClO + OH → HCl + O2 (R20) play a role in chlorine activation and deactivation (note that the second reaction differs from reaction R24 in the products). In addition, chlorine can be activated by the heterogeneous HOCl + HCl (R23) reaction.

4.3 Chlorine species

4.3.1 Overview and partitioning

When the polar vortex forms, the majority of chlorine is present in the form of HCl and the remainder is present in the other important reservoir gas ClONO2 (e.g. Solomon, 1999; Santee et al., 2008). Figure 11 shows the partitioning between the various inorganic chlorine species (Cly). The available amount of Cly is about 2.7 to 3.3 ppb in the considered altitude range (the increase at 54 hPa. The increase of Cly is due to transport from above). Due to the stronger descent in the northern hemisphere, Cly increases to values that are about 0.3 ppb higher in the northern hemisphere in 2005 than in the southern hemisphere in spring 2006, although the initial values are similar. This increases the chlorine potentially available for ozone depletion in the northern hemisphere compared to the southern hemisphere. In both hemispheres, the initial mixing ratio of HCl is about 2 ppb at 54 hPa (75% of Cly) and the initial mixing ratio of ClONO2 is about 0.7 ppb (see also Santee et al., 2008). Cly is produced by photolysis and reaction with O(1D) from chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and similar species of mainly anthropogenic origin (e.g. WMO, 2011; Montzka, 2012). The relative partitioning inside Cly is approximately constant between 70 hPa and 32 hPa (with only a slight increase in Cly with altitude, see supplement), so that most of the following discussion applies to the entire altitude range.

In early winter, passive reservoir gases HCl and ClONO2 are transformed to Cl2 through heterogeneous reactions on the surface of polar stratospheric clouds (e.g. Solomon et al., 1986), starting in December 2004 in the northern hemisphere and May in May 2006 in the southern hemisphere. Since the major reaction that transforms the reservoir gases to Cl2 is HCl + ClONO2 (e.g. Solomon et al., 1986, see also Section 4.3.2), the amount of chlorine that can be activated is limited by the mixing ratio of the less abundant ClONO2 (e.g. Portmann et al., 1996). While some ClONO2 can be regenerated by the reaction ClO + NO2 + M and some HCl can be activated by the reaction HOCl + HCl, this is not sufficient to remove all HCl over the course of the winter, and total HCl mixing ratios consistently stay larger than 0.5 ppb in our model runs, while ClONO2 decreases to near zero values. Due to the applied correction to the HCl solubility (see Appendix Section 6), up to 0.5 ppb of HCl is dissolved in STS droplets in the southern hemisphere at 54 hPa (more with increasing altitude).

When sunlight starts to come back, Cl2 is quickly transformed to the active chlorine species ClO and its dimer Cl2O2 by photolysis of Cl2

\[ \text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl} \]  

(R28)
Figure 11. Vortex-averaged partitioning of inorganic chlorine species (Cl\textsubscript{y}) for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Top row: Daytime averages (parts of the vortex where the solar zenith angle is smaller than 80\(^\circ\)). Bottom row: Nighttime averages (parts of the vortex where the solar zenith angle is larger than 100\(^\circ\)). Days without sufficient data for averaging are not shown (grey bars). Species ClNO\textsubscript{2} and BrCl are not shown due to their small mixing ratios. The area labeled “HCl (cloud)” shows HCl dissolved in STS droplets due to the applied correction to the HCl solubility (see section 6).
immediately followed by the reaction

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]  

(R29)

to produce ClO. The time between first activation and the first sunlight becomes apparent in a Cl\(_2\) peak in December and May 2004 and May 2006 in Figure 11.

Under polar conditions, the dimer of ClO plays an important role. Reactions that determine the ratio of ClO and its dimer Cl\(_2\)O\(_2\) are

\[ \text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \]  

(R30)

\[ \text{Cl}_2\text{O}_2 + h\nu + \text{M} \rightarrow 2\text{Cl} + \text{O}_2 + \text{M} \]  

(R31)

\[ \text{Cl}_2\text{O}_2 + \text{M} \rightarrow \text{ClO} + \text{ClO} + \text{M} \]  

(R32)

Reactions R30 and R31 are also part of the ClO dimer ozone loss cycle (see Section 4.5). Note that reaction R31 includes an intermediate step over ClOO not shown here. Figure 12 shows the partitioning of ClO\(_x\) = ClO + 2Cl\(_2\)O\(_2\) at 54 hPa. Active chlorine is mainly present in the form of Cl\(_2\)O\(_2\) at night and in the form of ClO during daytime (e.g. Stimpfle et al., 2004; WMO, 2011). At night, only small levels of ClO (10% of ClO\(_x\) in our model) are maintained by the interplay between the forward and backward reaction R32 and R30 (see also, p. 2836 reaction R32 (thermal dissociation) and backward reaction R30 (e.g. Stimpfle et al., 2004; WMO, 2011). The nighttime equilibrium is highly temperature dependent (e.g. Stimpfle et al., 2004), and higher temperatures shift the equilibrium towards ClO at night (see Figure 12). During daytime, most Cl\(_2\)O\(_2\) is photolyzed into Cl which reacts to ClO and there is an equilibrium between ClO and Cl\(_2\)O\(_2\) by the photolysis reaction R31 and reaction R30 (e.g. WMO, 2011). About 70% of ClO\(_x\) is present as ClO during daytime in all altitudes in our model (Figure 12 and supplement). This is in good agreement with the 60%–70% inferred from direct aircraft observations of ClO and ClOOCI by Stimpfle et al. (2004). Modelled ClO values are also in reasonable agreement with MLS measurements in the northern hemisphere in 2005 and in the southern hemisphere in 2006 (see supplement).

There is a long history of studies investigating the reactions R30 to R32, which are central for polar ozone depletion and have been uncertain for a long time (e.g. Molina and Molina, 1987; Burkholder et al., 1990; Stimpfle et al., 2004; Frieler et al., 2006; Schofield et al., 2008; Kremser et al., 2011; Canty et al., 2016). Recently, a study of the photolysis cross section of Cl\(_2\)O\(_2\) challenged the understanding of polar ozone depletion and caused a thorough reinvestigation of the chemistry of ozone depletion (see WMO, 2011, 2.2.2 and references therein). The uncertainties have been resolved (Kawa et al., 2009; WMO, 2011; von Hobe and Stroh, 2012; Canty et al., 2016), but the Cl\(_2\)O\(_2\) photolysis is still one of the reactions that causes the largest uncertainties in ozone depletion (Kawa et al., 2009). In addition, there is also some uncertainty in the nighttime
Figure 12. Vortex-averaged partitioning of ClO$_x$ for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Top row: Daytime averages (parts of the vortex where the solar zenith angle is smaller than 80$^\circ$). Bottom row: Nighttime averages (parts of the vortex where the solar zenith angle is larger than 100$^\circ$). Days without sufficient data for averaging are not shown (grey bars).

Equilibrium between ClO and Cl$_2$O$_2$ (Kawa et al., 2009; Canty et al., 2016), but this is not relevant for the amount of ozone depletion.

When chlorine is activated from December (from December 2004 to the beginning of March 2005 in the northern hemisphere and from May to September 2006 to September 2006 in the southern hemisphere), ozone is removed by the ClO dimer cycle and the ClO–BrO cycle (see section e.g. Solomon, 1999, see also Section 4.5). ClO$_x$ peaks at about 2.4 ppb in the northern hemisphere and at about 2.0 ppb in the southern hemisphere at 54 hPa, with little variation from 70 hPa to 32 hPa (see supplement).
The higher peak values of ClO$_x$ in the northern hemisphere are caused not only by the higher Cl$_x$ values (Figure 11), but also by the more efficient activation of HCl into ClO$_x$ in the northern hemisphere, which provides about 0.1–0.2 ppb additional chlorine from HCl compared to the southern hemisphere (see discussion in the section “HCl loss” below).

4.3.2 Reservoir HCl

Figure 13 shows the time evolution of the vortex-averaged reaction rates of all relevant reactions that change HCl at 54 hPa. The supplement shows that the rates and relative importance of the reactions are similar from 70 hPa to 32 hPa, so that the following discussion applies to the entire altitude range. In early winter (up to the end of December 2004 in the northern hemisphere and up to the end of July 2006 in the southern hemisphere), HCl is removed by heterogeneous reactions on polar stratospheric clouds and active chlorine is produced. When sunlight returns, this is followed by a phase of competition between HCl removal by heterogeneous reactions and deactivation of ClO$_x$ into HCl by gas-phase reactions (e.g. Portmann et al., 1996; Solomon et al., 2015), most pronounced in August 2006 in the southern hemisphere. In the southern hemisphere, this is followed by a phase of deactivation of active chlorine into HCl by the Cl + CH$_4$ reaction in September to October (e.g. Douglass et al., 1995). Finally, when sunlight comes back, the gas-phase loss reaction HCl + OH becomes important and competes with the production by Cl + CH$_4$. In the southern hemisphere, HCl is near equilibrium during this time, while in the northern hemisphere, chlorine that was initially deactivated into ClONO$_2$ is slowly transformed into HCl.

HCl loss (chlorine activation)

The most important heterogeneous loss reaction for HCl is

\[ \text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3 \]  \hspace{1cm} (R4)

Another heterogeneous activation channel for HCl is

\[ \text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}. \]  \hspace{1cm} (R23)

While this reaction plays a smaller role in the northern hemisphere in 2005, the reaction is important in the southern hemisphere in the months August and September in 2006. In the southern hemisphere, the HOCl + HCl reaction accounts for about 70% of the HCl activation by heterogeneous reactions (integrated over the winter) and in the northern hemisphere it accounts for about 30%. HOCl only exists in significant amounts when chlorine is activated. In the southern hemisphere, this causes there is a shift from activation by ClONO$_2$ + HCl in early winter to activation dominated by HOCl + HCl later in spring. The reason for this is the deactivation of chlorine by the reaction Cl + CH$_4$ in the southern hemisphere (caused by the low ozone values, see next section below), which provides HCl and produces HO$_x$ and in turn HOCl (for a detailed discussion, see Crutzen et al., 1992, Portmann et al., 1996). 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 mainly into ClONO$_2$ in the northern hemisphere, keeping HCl levels low. Since the southern hemisphere is more denitrified, activation by ClONO$_2$ + HCl
Figure 13. Vortex-averaged chemical reaction rates of reactions involving HCl for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Production reactions are shown positive and are separated by a line in the legend from the loss reactions, which are shown negative. The net change of HCl is shown as a green line. Reactions with rates which cannot be distinguished from the zero line at plot resolution are not shown.

is hindered. Note that the net effect of Cl + CH₄ and HOCl + HCl is a net chlorine deactivation in the southern hemisphere (green line in Figure 13).

It is evident that initially about 0.1–0.2 ppb more HCl is removed in the northern hemisphere in 2005 than in the southern hemisphere in 2006 (Figure 11), although the temperatures are lower in the southern hemisphere and the initial values of HCl and ClONO₂ are similar. Figure 13 shows that the reason is that the ClONO₂ + HCl reaction activates more HCl in the northern hemisphere. This is caused by reformation of ClONO₂ after the initial depletion in the northern hemisphere (see Figure 17 below), which is much smaller in the southern hemisphere.

The only other reaction that removes HCl in relevant quantities is the gas-phase reaction with OH, which is only important under sunlit conditions:

\[ \text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}. \]  

(R17)

In the northern hemisphere, the reaction is relevant in late winter (March) 2005. For the southern hemisphere, the reaction is relevant in October 2006 and later.

HCl production (chlorine deactivation)

HCl is only produced by reactions that are indirectly dependent on sunlight. Deactivation of active chlorine occurs mainly into HCl in the southern hemisphere but predominantly into ClONO₂ in the northern hemisphere. The reason for this is that deactivation into ClONO₂ is hindered in the southern hemisphere by strong denitrification (absence of NO₂), while normally it would be the preferred pathway of deactivation (e.g. Douglass et al., 1995; Portmann et al., 1996).
In the long term, the partitioning of HCl and ClONO$_2$ in spring and summer favors HCl (e.g. Portmann et al., 1996; Santee et al., 2008). This can be seen in the fact that in the northern hemisphere, HCl is produced from ClONO$_2$ in spring after ClO$_x$ has been deactivated into ClONO$_2$ some time earlier (see also section 4.3.3 and Figure 17), while in the southern hemisphere, active chlorine is deactivated mainly into HCl. The chemical change rates of both HCl and ClONO$_2$ decrease to zero in November in the southern hemisphere (green lines in Figures 13, 16 and 17). The reaction

$$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \quad \text{(R33)}$$

is the main production reaction for HCl in both hemispheres (e.g. Portmann et al., 1996). In addition, it is responsible for deactivation under ozone hole conditions in the southern hemisphere. The reaction

$$\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2 \quad \text{(R20)}$$

becomes similar in importance to Cl + CH$_4$ as a production process for HCl around late February 2005 in the northern hemisphere, and plays a smaller role earlier and later in winter. In the southern hemisphere, the reaction is not negligible around September and October 2006. The reaction is responsible for a part of the chlorine deactivation in both hemispheres. The reaction ClO + OH has two product channels. The channel into HCl yields about $\approx 88\%$ of the products (the other channel is into Cl).

**The role of Cl in HCl production**

The rate of the Cl + CH$_4$ reaction is proportional to the mixing ratio of Cl. Figure 14 shows the mixing ratio of Cl for both hemispheres. Figure 15 shows that Cl is determined by the two source reactions

$$\text{Cl}_2\text{O}_2 + h\nu + \text{M} \rightarrow 2\text{Cl} + \text{O}_2 + \text{M} \quad \text{(R31)}$$

$$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \quad \text{(R7)}$$

and a reaction that removes Cl

$$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2. \quad \text{(R29)}$$

Reaction R31 is coupled to the catalytic ClO dimer cycle. Cl levels are considerably higher in the southern hemisphere due to a lack of ozone, which hinders the recombination to ClO (e.g. Douglass et al., 1995). This favors the deactivation of active chlorine via the Cl + CH$_4$ reaction (e.g. Portmann et al., 1996). Cl shows a very distinct behaviour in the southern hemisphere. It does not just increase with the amount of sunlight, but shows a peak in September, followed by a near constant plateau. This curve shape is approximately repeated in the curves of the reaction rate of the Cl + CH$_4$ reaction (Figure 13), since CH$_4$ is relatively constant. Figure 15 shows that the peak in Cl mixing ratios in the southern hemisphere is related to reaction R31, i.e. the catalytic ozone destruction. In contrast, the plateau is related to the NO$_x$ reaction R7 (see also Wayne et al., 1995, p. 2836).
Figure 14. Vortex-averaged Cl mixing ratios for the Arctic winter 2004/2005 and the Antarctic winter 2006 at 54 hPa.

Figure 15. Vortex-averaged chemical reaction rates of reactions involving Cl for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Production reactions are shown positive and are separated by a line in the legend from the loss reactions, which are shown negative.
Figure 16. Vortex-averaged chemical reaction rates involving ClONO$_2$ for the Arctic winter 2004/2005 and the Antarctic winter 2006 at 54 hPa. Production reactions are shown positive and are separated by a line in the legend from the loss reactions, which are shown negative. The net change of ClONO$_2$ is shown as a green line. Reactions with rates which cannot be distinguished from the zero line at plot resolution are not shown.

4.3.3 Reservoir ClONO$_2$

Figure 16 shows the reaction rates of the most important reactions changing ClONO$_2$. The reaction rates increase by a factor of 2 from 70 hPa to 32 hPa in 2004/2005, but are more constant in 2009/2010 (see supplement). As discussed in section 4.1, the gross change rates of ClONO$_2$ are dominated by a near equilibrium between the reactions

\[ \text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_3 \]  
\[ \rightarrow \text{ClO} + \text{NO}_2 \]  

(R10)

and

\[ \text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \]  

(R12)

under sunlit conditions (e.g. Portmann et al., 1996). Net changes of ClONO$_2$ are induced by changes in NO$_x$ which shift the equilibrium (e.g. Portmann et al., 1996).

The net change of ClONO$_2$ is one order of magnitude smaller than the gross rates. Figure 17 shows the net effect of R10–R12 (yellow area) and all other reactions that play a role in changing ClONO$_2$. These reactions, which are all loss reactions, remove ClONO$_2$ either by heterogeneous reactions or gas-phase reactions of ClONO$_2$ with a radical. The most important heterogeneous reaction is the same as for HCl

\[ \text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3. \]  

(R4)
**Figure 17.** Vortex-averaged chemical reaction rates involving ClONO$_2$ for the Arctic winter 2004/2005 and the Antarctic winter 2006 at 54 hPa. In contrast to Figure 16, the net production rate of the fast cycle ClONO$_2$ + $hv$ → Products / ClO + NO$_2$ + M → ClONO$_2$ + M is shown. This cycle is separated by a line in the legend from the loss reactions. The green line shows the net change of ClONO$_2$ by chemistry. Reactions with rates which cannot be distinguished from the zero line at plot resolution are not shown.

The reactions of ClONO$_2$ with a radical are of the type

$$\text{ClONO}_2 + X \rightarrow X\text{Cl} + \text{NO}_3$$

(R34)

where X is X = O, Cl, OH X = O, Cl or OH. The reaction with Cl is the dominating reaction. The relative importance of these reactions is approximately constant from 70 hPa to 32 hPa (see supplement).

In early winter in the polar night (December 2004 in the northern hemisphere, May and June 2006 in the southern hemisphere), the loss of ClONO$_2$ by heterogeneous reactions dominates, leading to the activation of chlorine. After the complete depletion of ClONO$_2$, this is followed by a phase with only small production and loss, due to near-zero levels of both NO$_x$ and ClONO$_2$. The peak in production in early spring in the northern hemisphere (end of February and beginning of March 2005) is caused by the net production of extended NO$_x$ from HNO$_3$ and is the main deactivation pathway for active chlorine in the northern hemisphere. Then (e.g. Douglass et al., 1995; Portmann et al., 1996). At that time, ClONO$_2$ is out of equilibrium and more ClONO$_2$ is produced by ClO + NO$_2$ than is lost by photolysis. In the southern hemisphere, the rates are much lower due to the strongly denitrified conditions. In late March 2005, ClONO$_2$ is lost in the northern hemisphere and finally converted to HCl, which is the favored reservoir under summer conditions (e.g. Portmann et al., 1996; Santee et al., 2008). In the southern hemisphere, the rates of change are low in late October and November, since the deactivation already occurred directly into HCl.
4.4 Bromine species

Sources of inorganic bromine, which has both natural and anthropogenic sources, are mainly halons and methyl bromide, but also some short-lived species (e.g. WMO, 2011; Montzka, 2012). Inorganic bromine (Br_y) levels in the stratosphere are about 20 ppt at maximum (e.g. WMO, 2011), with marginally lower levels in the altitude range considered here. Bromine chemistry is still somewhat uncertain due to uncertainties in the reaction constants (Sander et al., 2011; von Hobe and Stroh, 2012).

Atomic bromine is released from the source gases mainly by photolysis. Under sunlit conditions, it is in equilibrium with BrO. The relevant reactions are

\[ \text{Br} + O_3 \rightarrow \text{BrO} + O_2 \]  
(R35)

\[ \text{BrO} + h\nu \rightarrow \text{Br} + O \]  
(R36)

\[ \text{BrO} + \text{NO} \rightarrow \text{NO}_2 + \text{Br} \]  
(R37)

\[ \text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + O_2. \]  
(R38)

Reactions R35 and R38 are directly involved in the ClO–BrO cycle, see Section 4.5.

Figure 18 shows the partitioning between the various inorganic bromine species at 54 hPa, which is very similar from 70 hPa to 32 hPa (see supplement). Bromine is mostly present in the form of HOBr and BrONO_2 at night before chlorine activation starts. In contrast to the less reactive chlorine, these are not real reservoir gases, since they easily photolyze into Br and react further to BrO during daytime, which gives bromine a great potential to destroy ozone despite the low mixing ratios (e.g. Lary, 1996; Solomon, 1999). BrO is a dominant species during daytime (e.g. Lary, 1996), except in October and November in the southern hemisphere, when the reaction Br + O_3 is hindered by the low ozone levels and Br mixing ratios are significant. Heterogeneous reactions play only a minor role and are not needed for activation (e.g. Lary et al., 1996; Wayne et al., 1995). As long as chlorine is activated, almost all bromine is in the form of BrCl at night (e.g. Lary et al., 1996; von Hobe and Stroh, 2012). BrCl is produced by the reaction

\[ \text{BrO} + \text{ClO} \rightarrow \text{BrCl} + O_2. \]  
(R39)

During daytime, most of this BrCl is transformed to Br by photolysis

\[ \text{BrCl} + h\nu \rightarrow \text{Br} + \text{Cl} \]  
(R40)

followed by transformation to BrO by reaction R35.
Figure 18. Vortex-averaged partitioning of inorganic bromine species for the Arctic winter 2004/2005 (left) and the Antarctic winter 2006 (right) at 54 hPa. Top row: Daytime averages (parts of the vortex where the solar zenith angle is smaller than 80°). Bottom row: Nighttime averages (parts of the vortex where the solar zenith angle is larger than 100°). Days without sufficient data for averaging are not shown (grey bars).
Figure 19. Ozone mixing ratios for the Arctic winter 2004/2005 and the Antarctic winter 2006 at 54 hPa.

4.5 Oxygen species

Figure 19 shows the vortex-averaged mixing ratios of ozone for the northern and southern hemisphere. Ozone stays relatively constant at values between 1.5 ppm and 2.5 ppm in the northern hemisphere in 2006, since the change by ozone depletion is nearly cancelled by transport of air rich in ozone from above and over the vortex edge. In contrast, ozone values decrease from 2.5 ppm to less than 0.5 ppm at 54 hPa in the southern hemisphere in 2006, both due to weaker transport and larger ozone depletion. While the initial ozone value of 2.5 ppm in the northern hemisphere in 2004/2005 is relatively constant with height, the value at the end of the winter varies from 1 ppm at 70 hPa to 3 ppm at 32 hPa due to changes in ozone depletion, production and transport (see supplement). In the warmer winter 2009/2010, values are more similar at the end of the winter and less ozone depletion is observed (see supplement).

O₃ is in a very fast equilibrium with O. The dominant cycle is part of the well-known Chapman chemistry (Chapman, 1930)

\[ O_3 + h\nu \rightarrow O + O_2 \]  \hspace{1cm} (R41)

\[ O + O_2 + M \rightarrow O_3 + M. \]  \hspace{1cm} (R42)

We follow the usual convention here to treat O₃ and O together as odd oxygen Oₓ (e.g. Brasseur and Solomon, 2005; Solomon, 1999). Since O mixing ratios are low, the chemical rate of change of Oₓ is nearly the same as the rate of change of ozone.
Odd oxygen is destroyed by several catalytic cycles. It is well known (e.g. Solomon, 1999) that the two dominant cycles in anthropogenic polar ozone depletion by halogens are the ClO dimer cycle (first proposed by Molina and Molina, 1987)

\[
2 (\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2) \quad \text{(R29)}
\]

\[
\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \quad \text{(R30)}
\]

\[
5 \quad \text{Cl}_2\text{O}_2 + h\nu + \text{M}_2 \rightarrow 2 \text{Cl} + \text{O}_2 + \text{M} \quad \text{(R31)}
\]

\[
2 \text{O}_3 \rightarrow 3 \text{O}_2
\]

and the ClO–BrO cycle (first proposed by McElroy et al., 1986)

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad \text{(R29)}
\]

\[
\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \quad \text{(R35)}
\]

\[
10 \quad \text{BrO} + \text{ClO} + \text{M} \rightarrow \text{Br} + \text{Cl} + \text{O}_2 + \text{M} \quad \text{(R38)}
\]

\[
2 \text{O}_3 \rightarrow 3 \text{O}_2.
\]

The ClO dimer cycle is able to work effective, because the Cl\textsubscript{2}O\textsubscript{2} photolysis, which produces Cl and not ClO, is fast compared to the competing Cl\textsubscript{2}O\textsubscript{2} loss reaction Cl\textsubscript{2}O\textsubscript{2} + M (Wayne et al., 1995, p. 2836). The uncertainty of the rate constant coefficient of the Cl\textsubscript{2}O\textsubscript{2} photolysis \text{R34--R31} and the rate constant coefficient of the BrO + ClO reaction \text{R38--R38} are two of the parameters which produce the largest uncertainties with respect to ozone loss in models (e.g. Frieler et al., 2006; WMO, 2011), although much of the uncertainty in the photolysis rate coefficient has been resolved recently (Kawa et al., 2009; von Hobe and Stroh, 2012; Canty et al., 2016).

Figure 20 shows the contribution of the different catalytic cycles to the net chemical rate of change of ozone. For this purpose, the reaction rates of the rate limiting step of the reaction cycles have been used. This is possible here without ambiguities, since all rate limiting reactions are only involved in one cycle.

Typical peak loss rates vary between 40–60 ppb per day and are similar in both hemispheres in the altitude range 70 hPa to 32 hPa for these two winters (compare also the peak values of ClO\textsubscript{x} discussed earlier and the supplement). Somewhat higher values of up to 70 ppb are only seen in 42 hPa and 32 hPa in the southern hemisphere. Hence, the higher ozone depletion in the southern hemisphere is mainly caused by the much longer time period in which ClO\textsubscript{x} is activated, Photochemical production of ozone is evident in March 2005 in the northern hemisphere and in October and November 2006 in the southern hemisphere and increasing with altitude (see supplement).

As long as appreciable amounts of ClO exist (January to February 2005 in the northern hemisphere, June to September 2006 in the southern hemisphere), the ClO–ClO cycle contributes about 50% to the net ozone loss and the ClO–BrO cycle contributes about 40%–40% in all altitudes (see supplement). These values compare well with the results of Kuttippurath et al. (2010) at 475 K and for 2005 (see 50% ClO–ClO to 30% ClO–BrO) and with the results of Frieler et al. (2006) (50% ClO–ClO to 30%–50% ClO–BrO, but for years different from 2005). See also Grenfell et al., 2006, for case studies of the partitioning.
Loss cycles of the form

\[ \begin{align*} 
X + O_3 & \rightarrow XO + O_2 \\
XO + O & \rightarrow X + O_2 \\
O + O_3 & \rightarrow O_2 + O_2 
\end{align*} \]

where \( X = \text{OH}, \text{H}, \text{NO}, \text{Cl}, \text{Br} \), which dominate in most latitudes and seasons, only play a minor role in the polar lower stratosphere due to the relatively low production of atomic oxygen by photolysis (e.g. von Hobe and Stroh, 2012). The ClO–O cycle contributes about 10\% at 54 hPa and increases in importance with altitude, in agreement with e.g. Kuttippurath et al. (2010).

The most important null cycle acting on odd oxygen apart from reactions R41 and R42 is the nitrogen cycle

\[ \begin{align*} 
O_3 + NO & \rightarrow NO_2 + O_2 & \text{(R6)} \\
NO_2 + h\nu & \rightarrow NO + O & \text{(R8)} \\
O_3 & \rightarrow O_2 + O. 
\end{align*} \]

We have given a quantitative analysis of the reactions involved in polar ozone depletion in the stratosphere. For clarity, this study focuses on vortex averages in a layer around 54. The reactions and reaction cycles involved in polar ozone depletion are well known, but quantitative estimates of the partitioning of the chemical families or the importance of single reactions and reaction cycles are rare. To our knowledge, this is the first comprehensive study providing quantitative results averaged over

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**Figure 20.** Vortex-averaged net chemical change of odd oxygen by different catalytic cycles. The red–green line shows the net chemical change rate of ozone, which nearly equals the change rate of odd oxygen at this altitude. The contribution of the different catalytic cycles to the ozone loss is shown by the reaction rates of their rate limiting step. Only the three most important cycles are shown, the contribution of other cycles is negligible. The ozone increase in the right panel, ozone production, which is caused almost exclusively by the \( \text{O}_2 + h\nu \) reaction, is shown in cyan.
the polar vortex under conditions perturbed by heterogeneous chemistry. The main aim of this study is to quantify numbers for
the partitioning of , and , the relative importance of production and loss reactions and-

5 Interannual variability

In addition to the runs for the Arctic winter 2004/2005 and the Antarctic winter 2006, we performed model runs for the Arctic
winter 2009/2010 and the timing of the reactions. Some selected findings are: The dimer cycle contributes about 50 to the
vortex averaged ozone loss at 54 in both hemispheres, while the cycle contributes about 40. In Antarctic winter 2011 to get at
least an idea of the interannual variability of the reaction rates and partitioning and to assess if the results can be generalized.
Figures for the additional years can be found in the supplement.

Since meteorological conditions are usually very similar in the southern hemisphere, there is a clear shift from chlorine
activation by the ClONO$_2$ + HCl reaction in early winter to activation by the HOCl + HCl reaction later in winter. HOCl + HCl
accounts for about 70% of the activation of HCl in from year to year, the results do not change significantly for the Antarctic winter
2011 compared to 2006, and the same discussion as for the winter 2006 applies. Except for rare cases as the vortex split in
2002, the dates, magnitudes of the values and the relative partitioning will also be applicable to other southern winters.

The northern winters 2004/2005 and 2009/2010 were taken as examples for a colder and a warmer winter and reflect
the larger meteorological variability in the southern hemisphere, while it accounts for 30% of the activation in the northern
ehemisphere. Peaks at 2.0 – 2.5. About 70% is present as ClO during daytime at 54, levels peak at 4. is mainly produced from
oxidation in the southern hemisphere, while in the northern hemisphere, production by and play comparable roles. The
partitioning between and results in 20 – 40 in the southern hemisphere and in 10 – 20 in the northern hemisphere. NO$_x$ levels
are smaller than 2 in the northern hemisphere and smaller than 0.75 in the southern hemisphere due to the denitrified conditions
there. The partitioning between and during daytime results in 80 – 90 in. The main differences are in the southern hemisphere and
20 – 40 in the northern hemisphere. The higher levels are caused by the much lower ozone levels in the southern hemisphere.
60 – 80% of the production of in spring are caused by the HNO$_3$ + OH reaction, the remainder is caused by the HNO$_3$ + $h$ reaction.
Deactivation of by the formation of in the northern hemisphere is caused by a shift in the fast equilibrium between
and timing of the changes in reaction rates and mixing ratios. The first main difference is a later activation of chlorine (end
of December 2010 compared to start of December 2005), reflected e.g. in the timing of the heterogeneous reaction rates. The
second main difference is an earlier deactivation by an earlier stratospheric warming in February. That means an earlier increase
in e.g. ClONO$_2$, which in turn is caused by the production of NO$_x$ or HO$_x$ and the associated reaction rates, and an earlier
decrease in ClO$_x$. The timing of activation and deactivation can vary greatly between different northern winters, from winters
with no chlorine activation and heterogeneous ozone depletion at all to winters that stay cold until April.

The absolute values of the reaction rates and mixing ratios, the relative partitioning inside the chemical families and the
relative importance of reactions remain similar for most species for these two northern winters. One of the notable exceptions
is of course ozone, which shows less depletion in a warm winter like 2009/2010. This comparison suggests that the relative
partitioning and the relative importance of reactions can be generalized to other northern winters, but that the absolute values
of ozone depletion and of several reaction rates will differ. Results of this study are extensively used in a companion paper to
develop a fast model for polar ozone chemistry.

6 Model validation: HCl discrepancy between model and measurements

It is desirable that the results of the ATLAS model agree well with observations to increase the confidence in the model results
for minor species and reaction rates which cannot be backed up confirmed by observations. It is out of the scope of this study
to give a comprehensive model validation against observations, and the reader but we include an extensive set of comparisons
to observations of the MLS (e.g. Santee et al., 2008) and ACE-FTS (e.g. Bernath, 2017) satellite instruments in a supplement
to provide additional information for the interested reader. In addition, the reader is referred to Wohltmann et al. (2010) and
Wohltmann et al. (2013) for a detailed validation. We will.

Since there is reasonable agreement between measurements and the ATLAS model for many species, we will restrict
discussion on the notable differences between ATLAS and observations and show only some selected results here in the main
text. The focus is on a prominent disagreement between modeled mixing ratios of HCl and observations.

6.1 HCl discrepancy between model and measurements

Figure 21 and 22 show a comparison of the vortex-averaged mixing ratios of some important species (ozone, water vapor $O_3$,
H$_2$O, HNO$_3$, and HCl, HCl and N$_2$O, blue and black lines) with corresponding vortex averages measured by the MLS satellite
instrument (red circles,e.g. Santee et al., 2008, red circles with bars for the accuracy, version 3 data). Note that the vortex
averages do not take into account the vortex tracer criterion -(as in the main part of the paper, preceding sections) to facilitate
comparison with MLS (the supplement contains comparisons with MLS at individual locations for more detailed information).
The blue lines denote the runs actually used in this paper (with a 5 K offset to HCl solubility), and the black lines denote an
earlier version of the model runs. the uncorrected model runs (without any change to HCl solubility).

It is obvious that the earlier version significantly overestimates runs without a change to the HCl solubility significantly
overestimate HCl, a behaviour also observed in other models. Apart from this like SD-WACCM (Brakebusch et al., 2013;
Wegner, 2013; Solomon et al., 2015) or MIMOSA-CHIM (Kuttippurath et al., 2015). Interestingly, the SLIMCAT CTM shows
a discrepancy of the same order of magnitude, but with the opposite sign in a recent publication (Santee et al., 2008), while in
an older version, species mixing ratios depend on the model resolution (Chipperfield et al., 1997).

Apart from the discrepancy in HCl, the agreement of model and observations for other species like ozone, water vapour or
HNO$_3$ is quite satisfactory. The reason for this the HCl discrepancy is unknown, but several solutions are possible:

- The initial amount of ClONO$_2$ in the model is underestimated, which hinders the HCl + ClONO$_2$ reaction. This is
(discussed in Santee et al., 2008; Brakebusch et al., 2013; Wegner, 2013). ClONO$_2$ only represents about 30% of
inorganic chlorine at the start of the winter and is clearly the limiting species of the reaction. An underestimation in
ATLAS is however unlikely, since it is not supported by measurements of ClONO$_2$ by ACE-FTS (not shown here see
supplement) and would require increasing the ClONO$_2$ mixing ratios by more than 100 %.
Figure 21. Vortex-averaged mixing ratios of O$_3$, H$_2$O, HCl and HNO$_3$ for the Arctic winter 2004/2005. The red dots show MLS satellite measurements, the blue lines show the ATLAS runs used in this paper and the black line shows the original runs which are not empirically corrected for the HCl discrepancy.
Figure 22. Comparison of vortex-averaged mixing ratios for the Antarctic winter 2006
Less NO$_x$ is transported across the vortex edge in the model compared to the real atmosphere, which impedes the reformation of ClONO$_2$ and HCl depletion via the HCl + ClONO$_2$ reaction. While this (discussed in Solomon et al., 2015) is likely very dependent on the transport and mixing scheme used in the model, and Eulerian (grid-based) models will show differences to Lagrangian (trajectory-based) models here due to the lower numerical diffusion in the latter. The underestimation of HCl in SLIMCAT (Santee et al., 2008) and the dependency of the species abundances on model resolution in the same model (Chipperfield et al., 1997) may point into this direction.

While it cannot be excluded that less NO$_x$ is transported across the vortex edge in ATLAS compared to the real atmosphere, the good agreement of most other species in ATLAS with measurements, including the tracer N$_2$O (not shown Figure 21 and 22), suggests that this option is unlikely. As long as errors in subsidence do not compensate for errors in mixing, this also means that the discrepancy cannot be caused by differences in subsidence between model and real atmosphere.

Note that there is a marked discrepancy in N$_2$O between MLS and the model in the southern hemisphere in October and November, which is however after the period of interest here. The reason for this discrepancy is unknown, but a possible reason could be overestimation of mixing across the vortex edge in ERA Interim in this time period.

HCl is taken up in PSCs and sediments out of the observed layer (discussed in Wegner, 2013). This is not supported by either the temporal or the spatial evolution of HCl.

An unknown heterogeneous reaction is depleting HCl. This cannot be excluded, but some boundary conditions need to be fulfilled, e.g. the reaction needs to involve HCl and it must not change the mixing ratios of other observed species too much.

There is a temperature bias in the ERA Interim data compared to the real atmosphere or a water vapor bias in the model (discussed in Brakebusch et al., 2013; Wegner, 2013; Solomon et al., 2015). The solubility of HCl in STS droplets is underestimated a strong function of both temperature and water vapor. The discussion in Simmons et al. (2014) and our own comparisons at the station Ny Ålesund suggest that the bias between ERA Interim and radiosonde data is less than 0.3 K in the considered altitude range and cannot explain the differences between MLS and ATLAS. The water vapor data is in good agreement between MLS and ATLAS (Figure 21 and 22) and is also not likely to cause the differences in HCl.

The parameterized solubility of HCl in STS droplets is underestimated (discussed in Brakebusch et al., 2013; Wegner, 2013). This is a promising possibility (since it does not affect most other species, consistent with the reasonable agreement of the other species to measurements), but it requires changes to the solubility that are above the stated uncertainties of the solubility parameterization by Luo et al. (1995) that is used in the model.

Since there is not enough evidence to narrow down this list to a likely candidate, we decided on an empirical approach: We introduced a temperature offset for the calculation of the Henry constant of HCl and changed the offset until we obtained a
good agreement of measured and modeled HCl, which was the case for an offset of −5 K. The effect of the changed Henry constant is twofold: First, it increases the amount of HCl dissolved in STS droplets. Second, it increases the rates of the heterogeneous reactions (even if only small amounts of HCl are dissolved) by changing the γ values. Brakebusch et al. (2013) and Solomon et al. (2015) did take the approach to introduce a temperature bias, but we opted here for a different solution, since introducing a temperature bias would have an additional direct effect on reaction rates in the model.

The HCl mixing ratios of the model runs with the changed Henry constant agree well considerably better than before with the satellite measurements for the southern hemisphere in both hemispheres. A larger discrepancy remains in December in the northern hemisphere.

In addition to the results for the corrected runs, the supplement shows the same figures for the uncorrected runs to assess the impact of the changes in HCl solubility. The main difference is considerably less chlorine activation in both hemispheres (e.g. the peak value of ClO for the northern winter 2004/2005 at 54 hPa changes from 2.5 ppb to 1.5 ppb). This corresponds to higher mixing ratios of the reservoir gases and lower reaction rates of HCl and ClONO₂. In the northern hemisphere, the reduced chlorine activation leads to reduced ozone loss (e.g. the mixing ratio of ozone at 70 hPa at the end of March 2005 increases from 1 ppm to 1.5 ppm). However, in the southern hemisphere, chlorine activation is still sufficient to deplete ozone to near zero values. Most other findings remain largely unaffected, including: the relative importance of reactions, the relative partitioning and the results for the NOₓ and the northern hemisphere after beginning of January, but a discrepancy remains in December–HOₓ chemistry.

### 6.2 Other notable differences

The supplement shows maps of comparisons to MLS satellite observations at 46 hPa for the northern winter 2004/2005 and the southern winter 2006. The maps show all measurements on the 15th of every month for the species ClO, HCl, H₂O, HNO₃, N₂O and O₃. Additionally, comparisons to ACE-FTS measurements are shown for the southern winter 2006 as a function of equivalent latitude and altitude. Species are H₂O, O₃, CH₄, HCl, ClONO₂, N₂O, NO, NO₂, N₂O₅ and HNO₃. In general, agreement is reasonable both for the spatial patterns and the absolute values, with the following exceptions:

- An underestimation of HNO₃ outside of the vortex by the model compared to both MLS and ACE-FTS, which is however outside of the region of interest here and may be related to the initialization.

- An overestimation of O₃ outside of the vortex by the model, which may be related to the underestimation of HNO₃ (less ozone depletion by NOₓ).

- A significant overestimation of ClONO₂ around 600 K by the model compared to ACE-FTS in the southern hemisphere, very likely caused by the initialization (there is only a limited amount of measurements of ClONO₂ and initialization is based on a tracer relationship).
7 Conclusions

We have given a quantitative analysis of the reactions involved in polar ozone depletion in the stratosphere. For clarity, this study focuses on vortex averages in a layer around 54 hPa for one specific winter in each hemisphere, with additional winters and pressure levels shown in a supplement. The chemistry of polar ozone depletion is well known, but quantitative estimates of the partitioning of the chemical families or the importance of single reactions and reaction cycles are rare. To our knowledge, this is the first comprehensive study providing quantitative results averaged over the core of the polar vortex under conditions perturbed by heterogeneous chemistry. The main aim of this study is to quantify the partitioning of HO\textsubscript{x}, NO\textsubscript{x} and ClO\textsubscript{x}, the relative importance of production and loss reactions and the timing of the reactions. Some selected findings are:

- Our results suggest that the relative partitioning inside chemical families and the relative importance of reactions in the northern winter 2004/2005 and the southern winter 2006 can be generalized to other winters. The absolute values of ozone depletion, the absolute values of the reaction rates and the timing of changes will differ, particularly in the northern hemisphere.

- The ClO dimer cycle contributes about 50\% to the vortex-averaged ozone loss at 54 hPa in both hemispheres, while the ClO--BrO cycle contributes about 40\%, in good agreement with earlier studies (e.g. Frieler et al., 2006; Kuttippurath et al., 2010). The ClO--O contributes about 10\% at 54 hPa and increases in importance with altitude at the expense of the ClO dimer and ClO--BrO cycle.

- In the southern hemisphere, there is a clear shift from chlorine activation by the ClONO\textsubscript{2} + HCl reaction in early winter to activation by the HOCl + HCl reaction later in winter. HOCl + HCl accounts for about 70\% of the activation of HCl in the southern hemisphere at 54 hPa in 2006 (integrated over time), while it accounts for only 30\% of the activation in the northern hemisphere in 2005. The reason for this is the deactivation of chlorine by the reaction Cl + CH\textsubscript{3} in the southern hemisphere (caused in turn by the low ozone values), which provides HCl and produces HO\textsubscript{x} (see e.g. Crutzen et al., 1992, Portmann et al., 1996). This can clearly be seen in rising HCl levels in September in the southern hemisphere and in increased HO\textsubscript{x} levels.

- ClO\textsubscript{x} peaks at 2.0 ppb at 70 hPa and at 2.5 ppb from 54 hPa to 32 hPa in the northern hemisphere in both 2005 and 2010. The peak values in the southern hemisphere in 2006 and 2011 are lower (2.0 ppb at 54 hPa and 42 hPa) due to less transport from above and less reactivation of ClONO\textsubscript{2} than in the northern hemisphere. Hence, the higher ozone depletion in the southern hemisphere is mainly caused by the much longer time period in which ClO\textsubscript{x} is activated. About 70\% of ClO\textsubscript{x} is present as ClO during daytime at 54 hPa, in good agreement with e.g. Stimpfle et al. (2004).
- HOx levels peak at 4 ppt. HOx is mainly produced from CH4 oxidation in the southern hemisphere, while in the northern hemisphere, production by HNO3, CH4 and H2O play comparable roles. The partitioning between OH and HO2 results in 20%–40% OH in the southern hemisphere and in 10%–20% OH in the northern hemisphere.

- NOx levels are smaller than 2 ppb in the northern hemisphere and smaller than 0.75 ppb in the southern hemisphere due to the denitrified conditions there. The partitioning between NO and NO2 during daytime results in 80%–90% NO in the southern hemisphere and 20%–40% NO in the northern hemisphere. The higher NO levels are caused by the much lower ozone levels in the southern hemisphere (e.g. Douglass et al., 1995).

- 60%–80% of the production of NOx in spring is caused by the HNO3 + OH reaction at 54 hPa in the northern hemisphere, the remainder is caused by the HNO3 + hν reaction (cf. Portmann et al., 1996). Deactivation of ClOx by the formation of ClONO2 in the northern hemisphere is caused by a shift in the fast equilibrium between ClO, NO2 and ClONO2, which in turn is caused by the production of NOx (e.g. Portmann et al., 1996).

Results of this study are extensively used in a companion paper (Wohltmann et al., 2017) to develop a fast model for polar ozone chemistry.

Acknowledgements. This work was supported by the BMBF under the FAST-O3 project in the MiKliP framework programme (FKZ 01LP1137A) and in the MiKliP II programme (FKZ 01LP1517E). This research has received funding from the European Community’s Seventh Framework Programme (FP7/2007–2013) under grant agreement no. 603557–603557 (StratoClim). We thank Peter von der Gathen for providing the Ny Ålesund temperature analysis. We thank ECMWF for providing reanalysis data.
References


