

## Reply to reviewer #3

We thank anonymous [reviewer #3](#) very much for his/her detailed and constructive review that would improve the contents of our paper. The review comments by anonymous [reviewer #3](#) are numbered and repeated below as *in italic letters*, followed by our answers. In the new draft with corrections (supplement file), [red](#), [purple](#), and [blue](#) corrections are the revisions suggested by reviewers [#1](#), [#2](#), and [#3](#), respectively. [Yellow-marked sentences](#) were also added in response to Short Comment #1 by Dr. Adrian Tuck.

### **General**

*(1) It is now more than three decades ago that the Antarctic ozone hole was discovered (WMO, 2019); by now the processes involved in its formation are thought to be understood in some detail. Current state-of-the-art models reproduce the observed springtime ozone loss in the polar stratosphere with good accuracy (e.g., Khosrawi et al., 2009; Chipperfield et al., 2017; WMO, 2019; Froidevaux et al., 2019). Nonetheless, there are open questions in Antarctic chlorine and ozone chemistry. Such questions can be addressed when new observations, such as those reported in the manuscript, become available. Insofar, this manuscript is an important contribution to ACP.*

Thank you for your comment.

*(2) I suggest an extension of the discussion in the manuscript regarding several issues (see in particular detailed comments below). Briefly, the Cly correlation needs to be adjusted to 2007 and 2011 (or the adjustment made should be described, see below) and the model behaviour reported by Grooß et al. (2018) that I think is also found here (namely that the models show HCl remaining in the core of the vortex) should be discussed in terms of MIROC3.2.*

We made some modifications in the text on Cly correlation in 2007 and 2011, considering the differences in available total Cly on those years. The remaining HCl issue in the core of the vortex is now further discussed in the paper.

*(3) Further, the manuscript could make a better contribution to addressing the issue of a “race” between chlorine activation and deactivation (Solomon et al., 2015; Müller et al., 2018; Zafar et al., 2018) and the question of which HCl formation processes are responsible for the observed HCl increase at the end of the ozone hole period.*

We further discussed the issue of a “race” between chlorine activation and deactivation by referring the paper you mentioned.

(4) Overall, the FTIR measurements presented here are certainly of great scientific interest and the measurements are combined in a meaningful way with satellite information. Moreover, a model simulation is included that helps the interpretation of the measurements. Notwithstanding these points, I suggest a substantial extension of the discussions on Antarctic chlorine chemistry in the paper. Provided the (in my view) necessary extensions are done, I would expect that this paper would make a great contribution to ACP.

We extended the discussion on Antarctic chlorine chemistry in the paper as is described below.

### **Comments in Detail**

#### *(5) Year-to-year variability of Cl<sub>y</sub>*

*The main driver for antarctic ozone loss is the available Cl<sub>y</sub> but there is a substantial year-to-year variability in this quantity; this issue is discussed by Strahan et al. (2014). How are the years discussed here (2007, 2011) ranked in the observed variability of Cl<sub>y</sub> (Strahan et al., 2014)? Further, the applicability of the employed empirical relation for Cl<sub>y</sub> to the years discussed here (2007, 2011) needs to be addressed in the paper.*

According to Strahan et al. (2014), 2007 was the year when there were about +4.3% more Cl<sub>y</sub> (2.88/2.76 ppbv), and 2011 was the year when there were about -5.2% less Cl<sub>y</sub> (2.53/2.67 ppbv) than the projected Cl<sub>y</sub> value. This was now described at the end of first paragraph in Section 2.1.

#### *(6) HCl remains in the core of the polar vortex in austral winter*

*The authors find here for the MIROC3.2 CCM that some HCl remains in winter in the core of the polar vortex in darkness. Such a model behaviour is expected as there is not enough ClONO<sub>2</sub> and no light in the core of the vortex. This model behaviour was reported by Grooß et al. (2018) for three models. Further they showed that this model feature is not found in observations of HCl. I suggest stating that the MIROC3.2 CCM shows the same issue – provided that the authors agree. If they do not agree, there should be a discussion of the issue in the paper.*

We do not agree the reviewer's opinion that MIROC3.2 CCM shows the same issue. In the MIROC3.2 simulation, the amount of HCl became nearly zero even in the core of the polar vortex in winter (please see HCl value at 87.9°S in Figure 15). We added discussion on this issue in Section 4.6 by adding new possible cause of the HCl loss by HOCl. The MIROC3.2 HOCl result is now added in Figure 15 (e).

#### *(7) Overestimated transport across the vortex edge in models*

*The paper states that transport across the vortex edge might be overestimated in models. I think here is the potential for the paper to make an important contribution. The issue that models might overestimate mixing into the vortex edge has been discussed (e.g.) by Hoppe et al. (2014); indeed for the same Eulerian transport scheme as employed in MIROC3.2. Observations of N<sub>2</sub>O (and the N<sub>2</sub>O gradient might help to elucidate the model issue. In any case a bit more discussion on this point is warranted.*

We looked at the differences between observed and modeled N<sub>2</sub>O gradients at the vortex edge, but could not find apparent differences between them. The coarse resolution of MIROC3.2 CCM (T42) may be the cause of overestimation of ClONO<sub>2</sub> transport across the polar vortex.

*(8) Continuous loss of HCl in the core of the polar vortex*

*The authors state the following conclusion in the paper: “Continuous loss of HCl was seen at 87.9 S between days 160 and 200 even after the disappearance of the counterpart of heterogeneous reaction (R1) (Figure 15(e)). The cause of this continuous loss was unknown until recently, where a hypothesis was proposed that includes the effect of decomposition of particulate HNO<sub>3</sub> by some process like ionisation caused by galactic cosmic rays during the winter polar vortex (Grooß et al., 2018). Solomon et al. (2015) proposed a new mechanism on this issue: Continuous transport of ClONO<sub>2</sub> from the subpolar regions near 55-65 S to higher latitudes near 65-75 S provides a flux of NO<sub>x</sub> from more sunlit latitudes into the polar vortex. Our result is consistent with the mechanism indicated by some sporadic increase in ClONO<sub>2</sub> at around days 158, 179, and 189 at 76.7 S as shown in Figure 15(f)”.*

*First, the processes described by Grooß et al. (2018) and Solomon et al. (2015) are very different: Grooß et al. (2018) describe a polar night process, whereas Solomon et al. (2015) describe a dynamical process (acting later in the course of the existence of the polar vortex), which needs light nonetheless as formation of ClONO<sub>2</sub> is involved.*

*Further note that Grooß et al. (2018) discussed the transport mechanism and concluded that it cannot explain the so-called ‘HCl-discrepancy’. Of course the present manuscript might come to a different conclusion but I think a more extensive evaluation of the arguments put forward by Grooß et al. (2018) is necessary here. In this context, Fig. 15 of the manuscript could be important; could it be that the ‘discrepancy’ reported by Grooß et al. (2018) is also noticeable in panel (e) of Fig. 15?*

*Second, an alternative explanation for the continuing decline of HCl could be the formation of HOCl under sunlit conditions which would allow HCl to decline to zero values (Grooß et al., 2011; Müller et al., 2018). If the authors cannot develop a preference for one of these mechanisms based on their data/observations, I suggest to state both alternatives in the discussion in the paper.*

*This issue reflects the importance of the reaction  $\text{HCl} + \text{HOCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$  (R4); early papers (Prather, 1992; Crutzen et al., 1992) have pointed to the importance of this reaction for bringing down the HCl concentrations in the polar vortex in Antarctica.*

*Finally, the transport of ClONO<sub>2</sub> from the vortex edge to the vortex core does not occur in isolation; inspection of Fig. 15 would suggest to me that mixing from the vortex edge would transport an amount of x ppb of ClONO<sub>2</sub> but at the same time an amount of x ppb HCl as well. Thus there is no net removal of HCl by “mixing”. As stated above –the easiest solution would be to discuss both alternative explanations. Further, these alternative are not necessarily contradictory; both mechanisms could contribute partly to the observed HCl decline.*

We agree to the reviewer that the processes described by Grooß et al. (2018) and Solomon et al. (2015) are

very different, and transport mechanism cannot fully explain the so-called ‘HCl-discrepancy’. We also checked our MIROC3.2 CCM model result on HOCl and found that HOCl certainly plays an important role in winter HCl continuous loss. Therefore, we added new column showing HOCl amount by MIROC3.2 CCM in Figure 15 (e) and added discussion on the HOCl issue in Section 4.6. However, we still believe that the transport of ClONO<sub>2</sub> from the vortex edge toward inside the vortex would partly explain the continuous loss of HCl in the polar vortex in early winter period (June-July), because there are much more ClONO<sub>2</sub> available at the edge region of the polar vortex, while there are almost no HCl at this place (please see HCl and ClONO<sub>2</sub> values at the edge of polar vortex on June 24, 2007 in Figure 13).

(9) *“Race” between chlorine activation and deactivation*

*An aspect of polar ozone and chlorine chemistry, where different concepts are discussed in the literature is the maintenance of enhanced levels of active chlorine during the time period (September and early October) when rapid ozone loss occurs. One concept is the one of a “race” between chlorine activation and deactivation, i.e., a competition of the heterogeneous reactions R1, R2, and R4 and gas-phase reformation of HCl and ClONO<sub>2</sub> (R12, R13) (Solomon et al., 2015). The other concept is the one of so-called “HCl null-cycles”, where the formation of HCl (R13) is followed by immediate reactivation of HCl (Müller et al., 2018; Zafar et al., 2018). (See also the discussion in WMO, 2019). The measurements presented in this manuscript might help to shed some light on these issues – this could be a contribution of this paper. Alternatively, if the measurements presented here cannot contribute to discriminating between the two discussed processes, this could also be a result of the paper (which should be mentioned).*

We believe that our MIROC3.2 CCM model results also supports the “HCl null-cycles” by our HCl and HOCl results shown in Figures 15(d) and 15(e). We added description on “race” between chlorine activation and deactivation at the end of Section 4.6.

(10) *Formation of HCl – Antarctic deactivation*

*The presented observations demonstrate that the deactivation in the Antarctic is through formation of HCl and that the deactivation is rapid. This is good and important. However, it is also stated that the formation of HCl is via the reaction  $CH_4 + Cl \rightarrow HCl + CH_3$  (R13). I agree that this HCl formation is “common wisdom” (e.g. Crutzen et al., 1992; Douglass et al., 1995). However the authors have also mentioned the reaction  $CH_2O + Cl \rightarrow HCl + CHO$  (R14). What is the evidence that the observed formation of HCl is indeed via R13? Further, it should be taken into account that there is also reactivation of chlorine even if reactions R14 and R13 occur at a considerable rate (Müller et al., 2018; Zafar et al., 2018). Again, the paper could make a contribution here, but at least there should be more discussion of all the processes playing a role here.*

At the beginning, we did not notice the importance of reaction (R14) in our draft. Now both reactions (R13) and/or (R14) are mentioned for the possible mechanisms of chlorine deactivation into HCl.

(11) *Negative correlation between ClO and ClONO<sub>2</sub>*

*The cause of the negative correlation between ClO and ClONO<sub>2</sub> (e.g. Fig. 10) is discussed as being caused by the distance of Syowa station relative to the vortex. I do not think that this is entirely correct. The main reason for the negative correlation is that ClO is converted into ClONO<sub>2</sub> and vice versa. (However the rather large scatter in Fig. 10 should also be acknowledged.) Given this fact, the higher values of ClONO<sub>2</sub> seem to preferentially occur closer to the vortex edge (so that the location of Syowa indeed is relevant).*

We agree to the reviewer that the negative correlation is because of the conversion between ClO and ClONO<sub>2</sub>, and one way (ClO + NO<sub>2</sub> + M → ClONO<sub>2</sub> + M) reaction is limited due to the loss of NO<sub>2</sub> by denitrification by PSCs inside the polar vortex. We explained this issue in Section 4.3 by adding new reactions (R17) and (R18).

*(12) Near zero values of ozone*

*The observations of ozone reported here (ozone sonde measurements) show very low values in October. Such near zero values of ozone have been reported before (Solomon et al., 2005); are the ozone values reported here compatible with the reported low ozone values? Perhaps the ozone values could be replotted on a log-scale as is the earlier publication (Solomon et al., 2005) – perhaps it is too much to show such plots in the paper, but an electronic supplement might be an alternative.*

Yes, the near zero ozone values in October at 18 km in 2007 and 2011 are typical in these years at Syowa Station. We think that the current linear scale for the ozone values (Figures 4 and 5) are better to show temporal variation of ozone throughout the winter-spring than log-scale. Even Solomon et al. (2005) used linear scale in Figure 2.

*(13) FTIR measurements*

*The FTIR measurements are a major contribution of this paper. This is why I suggest to make the data available for other researchers as well. Further Toon and Farmer (1989) have reported measurements of the HOCl integrated vertical column abundance, which was inferred from high resolution infrared solar spectra measured by the JPL MkIV interferometer from the NASA DC-8 aircraft during flights over Antarctica in September 1987. Would the current set-up also allow measurements of HOCl? Even quantifying an upper limit might be helpful. Other species of potential interest would be methanol or formaldehyde.*

We are working to put our FTIR data (in hdf format) in the data repository of our institute and put DOI number for it. Hopefully, it will be realized within this September.

Thank you for the information of HOCl paper by Toon and Farmer (1989). We looked at the spectra taken at Syowa Station for the period when the most HOCl amount is expected. However, it is very hard to distinguish the spectral feature of HOCl in those spectra, because of the weak absorption by HOCl and small amount of HOCl in the atmosphere. We may work to retrieve HOCl from Syowa FTIR data by co-adding several spectra and reducing noise in future work. It requires a bit too much effort for the current work.

*(14) Model description*

*The results of the MIROC3.2 model make an important contribution to the study. However, the model documentation is not sufficient. There is a short paragraph (on p. 15) and the reference to Akiyoshi et al. (2016). But even after consulting these pieces of information, many aspects of the model remain unclear. Which photolysis scheme is used for the calculations presented here; is the scheme using spherical geometry?*

*I think a reference to the employed scheme would be appropriate. Which solver is employed for solving the set of differential equations that result from the considered chemical scheme? How exactly (which surfaces?) is heterogeneous chemistry (including particle formation) treated in the model?*

*Further, it is not clear which reactions (and which species) have been considered in the presented model calculations. But this aspect could be important. I think it would be very helpful (and very easy) to add the information in question (e.g. add a list of reactions as an electronic appendix) to the paper.*

A more detailed description of MIROC3.2 is now described in Appendix in addition to some more citations.

#### *(15) Data Availability*

*There is no data availability statement in this paper. According to the rules of ACP such a statement should be added to the final version of the paper. This point would both regard all observations (including FTIR, ozone sondes and the satellite information shown in the plots of the paper) and the model results. It is up to ACP, but I believe that making the data (in particularly the unique FTIR data) available would enhance the impact of this paper.*

We are working to put our FTIR data (in hdf format) in the data repository of our institute and put DOI number for it. Hopefully, it will be realized within this September. Also, MIROC3.2 CCM model results can be obtained from the CCMI site. The doi information was now described in the “Data availability:” statement.

#### **Details**

*(16) p. 2, l. 10: “and the observed”*

It was corrected as suggested.

*(17) p. 2, l. 11: add a citation for the observed ozone hole magnitude*

We added Figure 4-6 in WMO (2019) for citation.

*(18) p. 3, l. 5: citations for these reactions? In particularly, R14 is often mentioned regarding chlorine deactivation.*

We added Groß et al. (2011) and Müller et al. (2018) for the citations.

(19) p 3, l 8: R14 is not often mentioned as a HCl forming reaction; suggest adding a reference. Perhaps also for R 12 and R 13.

We added Grooß et al. (2011) and Müller et al. (2018) for the citations.

(20) p. 3, l 21: in all years?

It was corrected as suggested.

(21) p. 3, l. 28: “sometimes” is not right, is it? It happens in the Arctic always if chlorine activation occurs, I’d argue. Probably the first observations of this phenomenon were reported by von Clarmann et al. (1993); Oelhaf et al. (1994).

We deleted “sometimes” here. von Clarmann et al. (1993), Muller et al. (1994), and Oelhaf et al. (1994) are already listed here.

(22) p 4, l. 5: citation for the FTIR measurement? How much can we learn about the vertical resolution from Fig. 1?

Rinsland et al. (1988) was added as a citation of FTIR measurement. The typical vertical resolution was added in Table 2.

(23) p 4, l. 22: Farman et al. (1985) did not show ozone sonde measurements. By the way, another ozone sonde measurement was conducted in 1985 by Gernandt (1987).

We modified the description at Halley Bay. Since this part describes the first ozone hole measurements in Antarctica, we did not mention Gernandt (1987).

(24) p. 5, l 1: I think a further advantage is also the location inside and outside of the vortex core and the inner vortex transport barrier.

We added description on the advantage of Syowa Station here.

(25) p. 7, l. 19: 4.5 ppm is not the best value if dehydration occurs.

This is the typical value before the occurrence of dehydration. We used this value to show the initial condition of PSC occurrence at the beginning of the winter.

(26) p. 7, l. 30: *have these ozone sondes been compared in sonde comparison studies?*

Yes, they participated in the Juelich Ozone Sonde Intercomparison Experiment (JOSIE)-2000. We added citation of JOSIE-2000 (Smit and Straeter, 2004) in the citation.

(27) p. 8, l. 4: *Such an empirical relation is not valid for arbitrary years: it should be explained how the adjustment to the conditions of 2007 and 2001 has been done (it is necessary to both correct N<sub>2</sub>O and Cl<sub>y</sub>).*

We agree with the reviewer that this empirical relation should be modified for 2007 and 2011 by the change of Cl<sub>y</sub> values. We added description on this issue in the text.

(28) p 8., l. 14: *the issue of a transport barrier within the Antarctic polar vortex was also discussed by Lee et al. (2001). The transport barrier within the Antarctic polar vortex in the early vortex can also be seen in ILAS measurements (Tilmes et al., 2006).*

The transport barrier issue is now added in the text, in addition to the citations (Lee et al., 2001; Tilmes et al., 2006).

(29) p 8., l. 28: *Within the vortex (but at the boundary) much lower HCl would be expected than outside of the vortex. Is this not seen by the FTIR measurements?*

The HCl value at the boundary region are in between the outside and inside the polar vortex. The gradual change of HCl was observed. We modified the text in this part.

(30) p. 9, l. 3: *what is the uncertainty range of the FTIR measurements? (report a ± here).*

Typical errors of the FTIR measurements are now shown in new Table 1 (old Table 2).

(31) p. 9, l. 21: *inside, but in the core or at the edge?*

We defined three categories; inside, boundary region, and outside the polar vortex. The data we showed for Figures 8 and 9 are for the first category (inside the polar vortex) data.

(32) p. 9., l. 26: *“partitioning” is not really clear; I believe you mean HCl/Cl<sub>y</sub>.*

We rewrote to “ratio of HCl to Cl<sub>y</sub>\*”.

(33) p. 9, l. 33: *probably not via R13, see above.*



We rewrote to “via reactions (R13) and/or (R14)”

(34) p. 11, l. 17: “systematically smaller”: could you quantify this statement?

We rewrote to “systematically smaller by 20-40% compared with ...”

(35) p. 11, l. 19: faster mixing in the model than in the real world might indeed be an issue (see above).

In this part, smaller downward advection and/or faster horizontal mixing are proposed for the explanation of discrepancies in HCl and Cl<sub>y</sub> between the model and the observations.

(36) p. 11, l. 21: for which year is the correlation – the correlation needs to be adjusted to the years in question here (2007 and 2011).

The effect of different Cl<sub>y</sub> values between the correlation year (1997) and our observations (2007 and 2011) is now described in the text.

(37) p. 11., l. 32: Note that the onset of heterogeneous chemistry occurs very likely before PSCs form and that PSCs do not form at NAT equilibrium. You could formulate: temperatures low enough for the onset of heterogeneous chemistry.

We rewrote as suggested.

(38) p. 11., l. 32: NO<sub>2</sub> does not condense (it needs to be chemically converted first).

We rewrote to “NO<sub>2</sub> was converted into HNO<sub>3</sub> via reaction (R17), and HNO<sub>3</sub> ...”

(39) p 12, l. 2: “Some HCl remains” this is expected in the model as there is not enough ClONO<sub>2</sub> (as stated here) and no light in the core of the vortex. This model behaviour was also shown by Grooß et al. (2018) and I suggest stating that the MIROC3.2 CCM shows the same issue (see also above).

We added the statement “as was also shown by CLaMS model simulation by Grooß et al. (2018)” here.

(40) p. 12, l. 16: Note that HCl remains low even under these conditions, when a relatively fast rate of reaction R13 should occur in the stratosphere. HCl-null cycles (Müller et al., 2018) could be an explanation.

We added explanation of HCl-null cycles (Müller et al., 2018) here.

(41) p 12, l. 21: How sure can we be that the recovery is via R13??

We rewrote to “reactions (R13) and/or (R14)”.

*(42) p. 13., l. 10: compare Grooß et al. (2018)*

We cannot compare our Figure 15 result with Grooß et al. (2018), because Figure 15 deals with the year in 2007, while Grooß et al. (2018) deals with the year in 2011.

*(43) p 13, l. 22: Again, how sure can we be that the recovery is via R13?? What about R14? What about other possible HCl forming reactions?*

We rewrote to “reactions (R13) and/or (R14)”.

*(44) p 13, l. 25 and below: The processes described by Grooß et al. (2018) and Solomon et al. (2015) should be distinguished: Grooß et al. (2018) describe a polar night process, whereas Solomon et al. (2015) describe a dynamical process which needs light nonetheless as formation of ClONO<sub>2</sub> is involved.*

We now distinguished processes by Grooß et al. (2018) and Solomon et al. (2015) and rewrote this part. Also, a process with HOCl was now described. Also, see our answer to your comment (8).

*(45) p. 14, l. 9: could you quantify “well below”*

We rewrote to “fell ~4K below ...”. We also added this explanation in the first paragraph of Section 4.1

*(46) p. 14., l. 13: the reason for the negative correlation is the conversion of ClO to ClONO<sub>2</sub> (see above).*

Even the conversion of ClO to ClONO<sub>2</sub> occurs, it is related to the availability of NO<sub>2</sub>, which is proportional to the relative distance to the vortex edge. We added the word “relative” here and in the abstract.

*(47) p. 14, l. 21: As discussed above, it is not sure that the transport of ClONO<sub>2</sub> is the only possible explanation for the behaviour of HCl.*

We added the possibility of the heterogenous reaction with HOCl here and in the abstract.

*(48) p. 14., l. 23: NO<sub>x</sub> rich would also mean rich in HCl – correct?*

No, not always. NO<sub>x</sub> rich airmass can produce ClONO<sub>2</sub> by reaction (R12), but not always rich in HCl.

*(49) p 15., l. 14: Sander et al 2010 or 2011? (see reference list).*

It was Sander et al. (2011), not (2010). Thank you for your comment.

(50) p. 16., l. 20: *Stimpfle*

It was corrected as suggested.

(51) p. 17, l. 29: 1977?

It was 1997, not 1977.

(52) p. 20, l. 10: *Karin Labitzke*

It was corrected as suggested.

(53) p 22, l. 2: *activation (no hyphen)*

Hyphen was deleted.

(54) p. 24, 25: *Could you add the information on the vertical resolution of the FTIR measurements to one of these tables?*

Vertical resolutions of the FTIR measurements were added in Table 2.

(55) p. 39: *pane -> panel*

It was corrected as suggested.