Reply to reviewer #2

We thank anonymous referee #2 for his/her constructive review that helped to improve the contents of our paper. The review comments by anonymous referee #2 are numbered and repeated below as *in italic letters*, followed by our answers.

(1). Although there are likely no severe issues with the data or the simulations, the scientific goal of the manuscript remains completely unclear. I find that it is not sufficient, just to present the observations and simulations without addressing open scientific questions. The authors present no new novel concepts, ideas, or tools. The only thing that is said that they present the first ground based continuous measurements of chlorine species in Antarctica.

We believe that this study contains several new findings in the characteristics of chlorine species over the whole period of Antarctic ozone hole. One is that our measurement was the first continuous measurement of chlorine species related to the ozone hole from the ground in Antarctica. This description was now added in the Abstract and in the Conclusion. Another new finding is that the deactivation pathways from active ClO into reservoir species (HCl and/or $ClONO_2$) in the Antarctica depends on the availability of ambient O_3, and they are different in different altitudes (18 and 22 km in our case), which has never observed in the Antarctic station before. Other new finding is that day-to-day variations in ClO and $ClONO_2$ over Syowa Station are negatively correlated (see (new) Figure 10), associated with the distance between Syowa Station and the inner edge of the polar vortex. These new findings are summarized in the Abstract and Conclusions.

(2). The model data are displayed in addition to the observations but not on the same altitude levels and they are not used to interpret the observations. There is no obvious connection between the simulations and the observations besides two appendix figures that contain the time series of the chlorine compounds and ozone over Syowa station from model and observations.

Yes, you are right. The FTIR and satellite observations are discussed in altitude grid, while the MIROC3.2 CCM output was displayed in a single pressure grid (50 hPa), which was close to the observation altitude of 18 km. The purpose of using the CCM output in this study is to understand the behavior of chlorine species in the whole polar vortex scale (which is now typically shown in (new) Figure 11). By looking at variations of chlorine species in a single station (e.g., (new) Figures 4-9), it is difficult to understand the reason of negative correlation between ClO and $ClONO_2$. The purpose of this study is definitely not the comparison or validation of the MIROC3.2 CCM with observations. Therefore, the comparison between CCM and observations are placed in the Appendix.

(3). With respect to the interpretation of the data, it seems that only few aspects of the observations and the simulations are mentioned. Most of them are in line of what is expected and shown in standard chemistry model

runs over the last two decades. The simulations seem to be in line with the observations. But it remains completely unclear, what the message of the paper is.

As we said above, the main focus of this study is to show whole winter behavior of chlorine species over Syowa Station covering whole ozone hole period. The time series over Syowa Station shows temporal variation of chlorine species over a single station, while the CCM results shows vortex wide spatial distribution of chlorine species. The CCM results are also used to help understanding the characteristics of chlorine species and their (negative) correlations. Moreover, MIROC3.2 CCM succeeded to reproduce the continuous HCl loss in the core of polar vortex in winter period, which was briefly mentioned in the manuscript.

(4). Furthermore, there are many small inaccuracies in the text, some of them are summarized below. Also, many informations are not given precisely, such that the reviewer needs to guess, what the authors meant. Because of the missing scientific concept, I would not recommend the paper for publication in Atmos. Chem. Phys.

Thank you for pointing out inaccuracies in the manuscript. We tried to correct them as much as possible which are described below. The scientific concept of this study is the first observational study of temporal evolution of chlorine species throughout the Antarctic winter, springtime ozone hole period, and recovery phase at Syowa Station, which is located near the edge of the polar vortex.

General

(5). The introductions lists some textbook knowledge but it is not clear, why it is at all important in the context of the manuscript.

Another reviewer also pointed out the shortage of description in the Introduction part. We revised the Introduction part to show more clearly what we want to discuss in this paper.

(6). The use of ClO data as done in this paper is problematic, since one needs to take into account the diurnal cycle typically involving Cl_2O_2 as a nighttime reservoir. Observations (fig 6-12) are likely for different local times and are therefore not comparable. As in the 3-hourly model data of fig 17, no diurnal cycle is visible, it is likely a zonal average over daytime and nighttime data. That is not useful for comparison. Potentially this is the cause of the ClO difference in figs B1 and B2.

We used ClO data from only daytime measurements of Aura/MLS instrument. Since Aura/MLS is in a sun-synchronized orbit, it always observes at 13:45 local time. In the 3-hourly model data in (new) Figure 12, some diurnal cycles are visible in Cl_2O_2 (Fig. 12(b)) and ClO (Fig. 12(d)) data at 68.4S (blue dots) and 71.2S (red dots). The large differences in ClO between CCM and MLS in Figures B1 and B2 might be due to the daily average of the ClO data in the CCM, as you suggested, which is explained in the Appendix B.

(7). Figures 13-16 show the model output on the 50 hPa level for 4 different times. It is not so clear, what can be learned from these figures. Also it would be better to not use a different vertical coordinate (pressure) for the model results as opposed to the observations (altitude).

As is mentioned above, the purpose of showing this figure (new Figure 11) is to show that the time series over Syowa Station includes both chemical evolution and dynamical effect of the spatial distribution due to the movement of the vortex edge, because Syowa Station is located at relatively lower latitude (69S). See the difference in ClO and $ClONO_2$ values at the location of Syowa Station (shown by stars in Fig. 11) between Sep. 1 and Sep. 6. These situations are difficult to understand by only looking at data over single station like in Figs. 4-9. In order to show general characteristics of the situation relative to the location of polar vortex, difference in altitude grid would not affect a lot.

(8). fig 10/11 shows Cl_y (MLS) relative to Cl_y (MLS N_2O), even though that should be described more clearly. In the context Cl_y (without star) is defined as ClO + $ClONO_2$ + HCl. However, there are no $ClONO_2$ observations of MLS. This needs to be clarified.*

$ClONO_2$ was measured by MIPAS. In order to show Cl_y (FTIR) and Cl_y (MLS) more clearly, we added new equations (3) and (4) in the text.

Details

(9). page 1/line 16 "is not well understood." I don't think that this statement is justified.

I think this statement is valid. For example, there are several issues related to Antarctic chlorine chemistry which are not fully well understood yet. For example, recent studies by Grooß et al. (2018, ACP), Müller et al. (2018, ACP), and Zafar et al. (2018, Tellus) raised some new questions which need to be understood in future.

(10). 1/22 PSC saturation temperature: you likely mean "PSC existence temperature."

Yes. It was corrected as suggested.

(11). 2/3: "from active chlorine" or "from ClO"?

It was corrected to 'from active chlorine into …'

(12). 2/17: the expression "inert chlorines" for HCl and $ClONO_2$ is not typical, please use the wording "chlorine reservoirs" (as in 3/31).

They are corrected to ‘chlorine reservoirs’.

(13). 3/4-14: The chlorine deactivation into $ClONO_2$ or HCl is mentioned, but not that it depends on ozone (Douglass et al. 1997, Grooß et al., 2005 JAS, Grooß et al., 2011 etc;).

Now, the chlorine deactivation processes into $ClONO_2$ or HCl depending on ambient ozone amount is described in the Introduction using Douglass et al. (1995) and Grooß et al. (2011) as references.

(14). 3/19: the phrase "super-recovery" is not ideal. It is sometimes used for ozone but not often for $ClONO_2$.

We rephrased ‘super-recovery’ into ‘additional increase of $ClONO_2$ than initial value’ throughout the manuscript.

(15). 3/22: ozone has been monitored before the discovery of the ozone hole. (otherwise the ozone hole would not have been discovered).

You are right. However, it is also true that measurement quality and quantity on ozone and related atmospheric trace gas species have increased a lot after the discovery of the ozone hole. In order to avoid your point, the word ‘intensively’ was added in the manuscript.

(16). 4/18: "analysis" Do you mean retrieval of tracer profiles from the FTIR spectra?

Yes. It was corrected to ‘retrieval’.

(17). 4/22: how many layers exactly?

We checked the SFIT2 program and found that it was actually constructed with 47 layers. It was corrected in the text.

(18). 5/12: As you only show 14 coincident measurements within a period of 3 months, I would not call this chapter "Validation."

Initially we compared FTIR profiles with MLS O_3 measurements, which gave much more comparison cases (~50 like the case for HNO_3 or HCl). However, there was a suggestion to compare with ozonesondes rather than MLS, because the accuracy of ozonesonde profiles are much more reliable than satellite measurements. Since ozonesonde measurements were done only once per week, there were only 14 coincidences in total. Nevertheless, we believe that comparison with ozonesondes is better than with satellite measurements.

(19). 5/31: You show results from MLS Version 3.3 data. Why do you not use version 4.x?

At the time when we have done this study, MLS Version 3.3 was the latest data product. In the technical documentation of MLS data products (Livesey et al., 2018), it was stated that there are some improvements for MLS Ver. 4.2 compared with Ver. 3.* product, such as improved composition profiles in cloudy regions, or more suitable reference surface for geopotential heights. However, there are only minor changes in the data product for the focus of this study (O_3, ClO, HCl, and HNO_3).

(20). 6/8: How exactly do you identify the coincident CALIPSO PSCs? Orbit within a certain distance from Syowa station? PSCs of what type at what altitude?

The nearest CALIPSO orbit to Syowa Station was selected. The maximum distance between Syowa Station and the nearest CALIPSO orbit is about 500 km, and the maximum time difference is +/- 12 hours. Any type of PSCs at any altitude were counted. The description was added.

(21). 6/12-15: This seems to be a speculation. It is not clear how this statement is proven in this context.

You are right. The description was rephrased as 'This may be due to other reason, …'.

(22). 6/16: You use the term "temporal variations" several times, where I think it is (only) a time series.

We changed 'temporal variation' into 'time series' at several places.

(23). 6/16: define the expression Cl_y.*

Cl_y* is defined a few lines below (inferred inorganic chlorine) and in equation (2).

(24). 6/17: add "for all ground-based and satellite based observations used in this study" (or similar).

The description was added in the manuscript as suggested.

(25). 8/5 ratios of each species with respect to Cl_y.*

It was now rephrased as suggested.

(26). 9/1ff: It has not been said over what time the data were collected, how the anticorrelation was evaluated (MIPAS and MLS have different orbits).

MLS and MIPAS data were sampled on the same day at the nearest orbit for both satellites to Syowa Station.

The maximum differences between these two satellites' observational times and locations are 9.0 hours in time and 587 km in distance. Mean differences are 6.8 hours in time and 270 km in distance, respectively. This information is now described in the manuscript.

(27). page 9/line 1-6 (anti-correlation of MIPAS $ClONO_2$ and MLS ClO, fig 12): If is said that this is due to the PV (eq. latitude) dependence. Could it also be that this occurs because of the time dependence of the deactivation throughout the days 220-260? The slope of the regression line is not given in the text nor a statement of what would be expected from the model. What does this slope or correlation mean scientifically? This correlation in the phase of chlorine deactivation is definitely no surprise.

The slope of the regression line is now shown on the (new) Figure 10. It is about -1.0 for all panels, which is expected if we assume constant Cl_y value in the polar vortex. As we described in the manuscript, this negative correlation between $ClONO_2$ and ClO is the result of relative distance between Syowa Station and polar vortex edge, not because of the time dependence of the chlorine deactivation.

(28). 9/24 'About 50% ozone depletion was seen throughout the polar vortex.' This statement is inaccurate. Do you mean at the 50 hPa level equally from the vortex edge to the core? Or also at the other levels? It is at least rather hard to read a number of percentage ozone loss from this figure.

We agree that this statement is inaccurate. We now rephrased to: 'Development of ozone depletion was seen in the polar vortex.'

(29). 9/33f 'Inside the polar vortex,depletion of O_3, NO_2, HNO_3, and $ClONO_2$ continued' Most of the species are already near zero. It is not clear from the figure how you see continuing depletion. Also I would not expect further ozone depletion, if active chlorine returned more or less to zero.

We agree. We now rephrased to: 'Inside the polar vortex, O_3, NO_2, HNO_3, and $ClONO_2$ showed very low values.'

(30). 10/23-28: The continuous loss of HCl seems to look differently than in the study by Grooß et al. that you mention. The conclusions of that study are not given properly. It is not clear, whether you include an additional process like ionisation by cosmic rays or cross vortex edge $ClONO_2$ flow due to Solomon et al. in your model. Or does the HCl just deplete because of the large diffusivity that is present due to the low model resolution (2.8×2.8 degrees)?

At the time when we submitted this paper, the paper of Grooß et al., (2018) was in the discussion phase of ACPD. Now, Grooß et al., (2018) was published in ACP, and the conclusion was a bit modified. We modified the draft to more accurately refer the conclusion of new Grooß et al., (2018) paper in ACP. In our MIROC3.2 CCM run, we did not include any ionization process by cosmic rays. We agree with you on that *'the HCl just deplete because of the large diffusivity that is present due to the low model resolution (2.8×2.8 degrees)'*. In addition, our model uses a hybrid sigma-pressure levels for the vertical coordinates. This also may lead to a larger diffusivity than in the theta coordinates.

(31). 11/18f: I do not see this good agreement between model and FTIR in the figures.

You are right. We now rephrased to: 'The modeled O_3 and day-to-day variations of HCl and $ClONO_2$ are in good agreement with FTIR and satellite observations.

(32). figure 5: How was T_{NAT} and T_{ice} derived? What data for HNO_3 and H_2O were used?

We calculated T_{NAT} and T_{ice} by assuming 6 ppbv HNO_3 and 4.5 ppmv H_2O. The explanation was added in the manuscript.

(33). figure 12: There must be something wrong with the colour coding of the PV in the panels. I would expect about a factor 2 difference in PV between 18 and 22 km and also PV values significantly below -85PVU at 22 km.

We checked the actual PV values used in this plot. Actually, the PV values for this figure ranged as follows: (new) Figure 10 (a): -61.4 ~ -76.3, (b): -61.1 ~ -78.6, (c): -60.4 ~ -80.5, (d): -61.2 ~ -82.7. Therefore, we used the same color scales for both 18 and 22 km.

(34). figure 17: Three-hourly zonal-mean temporal variations'What do you mean by variations? It only looks like zonal mean values.

The description was now rephrased as: 'Three-hourly zonal-mean time series of …'

(35). figures B1/B2: Here the model is labelled CTM. Is it really? In the paper you always talk about a CCM.

CCM is correct. The label was corrected in the figures.

Typos/grammar

(36). 6/12: other reason -> őther reasons'or ăn other reason"

Corrected to: 'other reasons'.

(37). 8/32 shows

Corrected as suggested.