Second review of “Chlorine partitioning near the polar vortex ...”

BY NAKAJIMA ET AL.

General

In response to the three reviews, the authors have substantially changed and improved their manuscript. I think that the discussion has improved in many parts of the paper and also the description of the FTIR data is better in the revised version. I think that in particularly adding information on HOCl to the manuscript constitutes a significant improvement of the paper.

However, there are still some issues where I think the paper needs improvement. In my first review I had the point that “the initial Cly correlation needs to be adjusted to 2007 and 2011 – or the adjustment made should be described”. I think this aspect is not completely resolved (see below). Further I stated that “the model behaviour (‘HCl discrepancy’) reported by Grooß et al. (2018) should be discussed in terms of MIROC3.2”. Here there still seems to be discrepancy in opinion, which will require some further discussion (see below). I would be optimistic, however, that this problem can be resolved. Finally, I think the model issue of the transport barrier at the vortex edge needs some attention.

Overall, clearly, the new FTIR measurements presented here are of great scientific interest and are combined in a meaningful way with satellite measurements and model (MIROC3.2) results. In spite of the fact that I recommend a further revision of the paper; I would be optimistic that such a revised version would be further improved and would be close to being accepted by ACP.

Comments in Detail

Year-to-year variability and temporal trend of Cly

As stated in the first review, the main driver for Antarctic ozone loss is the available Cly. The authors now discuss the year-to-year variability in this quantity (Strahan et al., 2014), which is good. However, I think the point of the applicability of the employed empirical relation for Cly (Eq. 2) to the years discussed here (2007, 2011) needs to be addressed in the paper better than in the present draft (see also details below).

There is a statement in the paper that observed Cly in 2011 (2.53 ppbv) was about -5.2% less than the projected Cly from Newman et al. (2007) (2.76 ppbv for 2007 and 2.67 ppbv for 2011). It is not clear to me that the projected values by Newman et al. (2007) were indeed used in the analysis here. Moreover, there is also an alternative projection of Cly values (Engel et al., 2018; WMO, 2019).

HCl remains in the core of the polar vortex in austral winter

In my first review it was stated: "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 $ClONO_2$ 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."

In their reply, the authors state that they "do not agree with the reviewer's opinion that MIROC3.2 CCM shows the same issue". They have added information and discussion on the role of HOCl, which I consider an important improvement. However, if I look at the HCl values at 87.9° in figure 15, I see that HCl remains constant (and above 0.5 ppb) for days 140-160 (this airmass is in darkness as can be seen from Cl_2, panel c). Isn't this the issue discussed by Grooß et al. (2018)? HCl is only close to zero at day $\approx$ 200 (I would argue due to HOx production in sunlight); after this day HOCl starts increasing (see also below).

If the authors really do not agree that they see the "HCl discrepancy", this is only possible if they have a process in the model which removes the remaining HCl in darkness. Which process could there be in the model? Does the model contain some process producing NOx in polar night? The latter point would be very interesting. Another possibility would be that MIROC3.2 does not see this issue because of a too coarse spatial resolution, but this would be a model artefact.

Overestimated transport across the vortex edge in models

The paper originally stated that transport across the vortex edge might be overestimated in the MIROC3.2 model results. This is perhaps no surprise given the relatively coarse (T42) horizontal spatial resolution. I the reply, the authors now state that they "looked at the differences between observed and modeled N_2O gradients at the vortex edge, but could not find apparent differences between them". Thus they do not seem to find the same result as Hoppe et al. (2014) who found that models might overestimate mixing across the vortex edge.

Such a point should not be covered only in passing in the reply. I suggest to include the relevant plots in the reply (which will remain accessible at ACP) or, even better, include this information as an appendix to the paper.

Continuous loss of HCl in the core of the polar vortex

In response to the review comments, the authors have substantially revised the discussion on continuous loss of HCl in the core of the polar vortex. Nonetheless, I would like to come back on a few points of which I think that they could be better represented in the manuscript.

Note that the HCl loss 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). The dynamical process suggested by Solomon et al. (2015) requires light as formation of $ClONO_2$ is involved. This is also true for the explanation for the continuing decline of HCl under sunlit conditions through the formation of HOCl (Grooß et al., 2011; Müller et al., 2018).

Finally, $ClONO_2$ is not enhanced at the vortex edge in June or May (see Figs. 13 and 14). Also transport of $ClONO_2$ from the vortex edge to the vortex core does not occur in isolation but in mid-winter likely mixes in air with enhanced HCl and ozone (see below and first review). A very different issue again is the mixing of 'out-of-vortex' air; first, this is less likely and, second, it would certainly bring in non-activated air with substantial concentrations of HCl.

Model description

In response to my first review, the authors have substantially extended the model description. However, the detailed description of the heterogeneous reactions is in Japanese and the paper still does not contain a list of reactions (e.g. add a list of reactions as an electronic appendix). Perhaps a bit more could be done regarding model description. As discussed below, some model behaviour raises the questions, exactly which reactions are taken into account in the model formulation.

Data Availability

A data availability statement has now been added to this paper. I think in particular making the FTIR data available is very helpful. You might want to add statements regarding MLS, MIPAS and MIROC3.2.

Some details regarding the revised version

- p 1, l 21: $ClONO_2$ was almost depleted; but what about HCl?
- p 1, l 25 "comprehensive behaviour" is unclear, what is meant here?
- p. 3, l 6: perhaps you want to add a reference here for R 12 also? Santee et al. (2008) would be a possibility.
- p. 3, l 22: replace 'formation' by 'existence'
- p. 8, l 31: This relation (Eq. 2) is only true for conditions of 1997. Assuming that N_2O is constant, the Cly calculated from this equation is only valid for 1997.

Correct? So one needs to take into account the temporal trend of Cly between 1997 and 2007 or 2011. In reality there are also temporal changes of N_2O that should be taken into account. Only thereafter the adjustments suggested by Strahan et al. (2014) should be taken into account.

- p 9, l 5: state here to which figure the 'light shaded region' etc belongs.
- p 9, l 16: "was occurred" $\longrightarrow$ "occurred"
- p 10, l 20: 'ratio of HCl' etc – this is unclear. I think you mean mixing ratio here? Or HCl/Cly ratio? This should be clarified. (similar in l. 29).
- p. 11, l 32: taken *up* by PSCs (or similar)
- p 12, l 2 (R18): there is also the reaction $HNO_3 + OH \longrightarrow NO_3 + H_2O$
- p 12, l. 27: this is indeed not unlikely, however the change of stratospheric Cly between 1997 and 2007 as well as between 1997 and 2011 can be quantified and should not be ignored.
- 13, l 8: note that enhanced $ClONO_2$ is *not* seen in June!
- p 13, l 11: not only CLaMS but also SD-WACCM and TOMCAT/SLIMCAT
- p 14, l 21: "the decrease of HCl stopped ..." – I think the authors have an important point here. But is this not the model behaviour reported by Grooß et al. (2018)? And a model behaviour which is *not* in agreement with HCl observations. I suggest more discussion here.
- p. 15, l 2: note that there is also HOCl production in the gas-phase ($ClO + HO_2$; the details might depend on the HO_2 production in the photolysis of CH_2O, see e.g. Müller et al. (2018). I would be interesting to analyse here in detail the assumptions in the MIROC3.2 model.
- p. 15., l 7: I think cycles C3 and C4 are not defined in the manuscript. I suggest to include a brief explanation here not just a reference.
- p. 15, l 19: For this interpretation, it is important to take into account that the poleward transport of $ClONO_2$ by mixing (this is the point here if I understand the text correctly) does not occur in isolation. The impact of such mixing depends on the time period considered. In deep winter mixing would not transport only $ClONO_2$, but also HCl and ozone. On the other hand, in June (Fig. 13) there is no enhancement of $ClONO_2$ at the vortex edge, so what could be the effect of mixing of vortex edge air in June?
- p 16, l 10: PSCs do not *form* at NAT saturation temperature a stated in this sentence. In general; I suggest using the same wording throughout the paper for this issue. Be clear if you mean onset of heterogeneous chemistry, PSC formation/existence etc. For example it is NAT saturation temperature, not NAT PSC saturation temperature.

- p 16, l 15: ‘comprehensive behaviour’?
- Fig 13: It is difficult to see two white circles here – I can see only one.
- Fig 14: It is difficult to see two white circles here for August and October – I can see only one. The last sentence of the caption is difficult to understand. The dotted line for 5 July 2011 is confusing – is it correct? It looks rather different than the various chemical species. Is the point here that on 5 July 2011 only an inner vortex edge is defined but no actual vortex edge?

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