Reply to comments by reviewer two (second round) on

The impact of dehydration and extremely low HCl values in the Antarctic stratospheric vortex in mid-winter on ozone loss in spring

by Yiran Zhang-Liu et al.

We thank the reviewer again for her/his interest in our paper and for very helpful additional comments. The comments are repeated below in blue and a point-by-point response is given in normal font and black colour.

The paper has been revised in view of the comments in this second round of comments.

Review two (second round)

General comments

I would like to thank the authors for addressing my previous comments. I think the paper has been improved from the previous version. I am happy for this paper to be accepted after the following minor comments have been addressed.

Thank you!

Following my previous comment about ClONO2 + HCL reaction, the author's response states: "Further, Figure 3 of Solomon et al. (2015) is for 61 hPa, that is for some- what higher altitudes than studied here (roughly 75-80 hPa for the period of strongest ozone depletion). Also, for days 220 to 250 (Fig. 3), the observed values of ClONO2 (MIPAS) are extremely low (similar as in the simulations presented here)." I appreciate the author's reasoning regarding the ClONO2 + HCl reaction not being as important at lower altitudes for days 220-250, However, the null cycles presented in the paper seen to show active chlorine maintenance through to the end of September ($\sim$ day 275) in their Figures 4 and 5. I suspect by the end of September ClONO2 concentrations will be greater than HOCl even at lower altitudes (although that is clearly not shown in your box model, so I could be wrong)? I think a little more expansion of their explanation (which I agree with for earlier time periods at lower altitudes) needs to be made for the later time period too. I would be nice to have some confirmation using observations: ACE-FTS has measurements of ClONO2 that extent as low as ~10 km at high Southern latitudes during August and September that could be used to confirm that ClONO2 is or is not important during the later time period.

Thanks for these remarks. First, we should point out that a follow up study is planned, which will address the $ClONO_2$ issue in more detail. However, clearly, this paper needs to be complete. For the conditions considered in this paper, the temporal development of both HOCl and $ClONO_2$ is shown for the entire period (including end of September; $\sim$ day 275, see e.g., Fig. 2 but also Figs. 4 and 5, panels c and d). At the end of September (for the conditions considered here), $ClONO_2$ is almost zero, while HOCl is about 0.1 ppb (or more) as long as ClO_x is elevated.

However this issue needs to be better explained/discussed, so we have added to the text (at the end of section 3.3.1): "Under the conditions discussed here, values of $ClONO_2$ remain strongly depressed (close to zero, with few exceptions; Fig. 5, panel d). This statement is true for the entire simulated period, including the period of strongest ozone loss throughout September. This observation is consistent with the dominance of the HCl null cycles that do not involve the heterogeneous reaction R1 (Müller et al., 2018, see also appendix A)."

Line 54. The author's state "so that there is no full activation in this step". There is still complete activation though I believe? We just don't understand why it is occurring? It's likely still due to reaction R1. Or do you mean only in the model?

The reviewer is correct here. We mean "in the model" and this is clarified by saying explicitly in the paper now: "In the Antarctic lower stratosphere, the initial concentrations of HCl are greater than those of $ClONO_2$ (Jaeglé et al., 1997; Santee et al., 2008; Nakajima et al., 2020). Thus, in the absence of chemical processes leading to a further loss in HCl, there is no full activation in this step. Such a behaviour is found in models (Grooß et al., 2018)."

Line 379-381 and Lines 405-409. The author's state: "Further, ozone depletion is not strongly affected by the initial values of HCl (and also the minimum values of Antarctic ozone reached are similar) consistent with Grooß et al. (2018)." Figure 5 to me shows that ozone depletion is strongly affected, maybe the minimum values are similar, but the earlier onset when HCl = 0 looks like a large difference to me. I thank the authors for including discussion of this in the relevant section, but I think it should also be mentioned here and in the conclusions. Something like "Initial values of HCl are seen to impact the timing of onset of ozone depletion and the timing of maximum ozone loss, but don't significantly impact the minimum values."

We agree. In response, we have changed the text in the discussion: "Further, ozone depletion is affected by the initial values of HCl, namely the timing of maximum ozone loss. However, the minimum values of Antarctic ozone reached are similar, consistent with Grooß et al. (2018)" and in the conclusions: "Further, ClO_x is enhanced throughout winter and spring, and HCl molar mixing ratios remain very low until rapid chlorine deactivation occurs into HCl. Also the strength of the ozone loss rate and the timing of maximum ozone loss is affected by the initial value of HCl, but not the minimum ozone value (consistent with Grooß et al., 2018); the simulated ozone minimum values differ by ≈ 10 ppb".

Line 388-390: Does this sentence: "Second, the HCl null cycles require the heterogeneous reaction R2 ($HCl + HOCl \longrightarrow Cl_2 + H_2O$) to proceed at a substantial rate" contradict the earlier statement on Line 258-259: "This finding is consistent with the notion that the rate constant of the heterogeneous reactions within HCl null cycles is of little relevance for the efficacy of the HCl null cycles"?

Thanks for pointing this out. Indeed "substantial" is not correct here. In the revised version of the paper it is stated now: "Second, the HCl null cycles require the heterogeneous reaction R2 ($HCl + HOCl \rightarrow Cl_2 + H_2O$) to proceed; i.e., temperatures need to be sufficiently low."

References

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