*Reply to comments by reviewer three 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 very much for her/his interest in our paper and for very helpful comments. The comments are repeated below in <span style="color:blue">blue</span> 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 all three reviews.

## Review three

<span style="color:blue">**General comments**</span>

<span style="color:blue">The paper entitled: "The impact of dehydration and extremely low HCl values in the Antarctic stratospheric vortex in mid-winter on ozone loss in spring" explores in depth the role of HCL null cycles on maintaining active chlorine in early Antarctic spring. The paper looks into the roles of initial wintertime HCL concentrations (where there is a known discrepancy between models and observations), a correction to the CLO + CH3O2 reaction rate, and dehydration on the HCL null cycles.</span>

<span style="color:blue">Overall, the paper is well written and is a nice addition to literature on Antarctic chlorine partitioning. Further knowledge on the HCL null cycles and the factors that affect them is an important and welcome advancement to the knowledge of Antarctic chlorine partitioning and ozone loss. I have a few comments below that I would like to see addressed. I suggest publication after the following minor revisions.</span>

Thank you very much for these comments on our paper. All comments have been taken into account and a revised version of the paper has been created; in particular, we have restructured the "incorrect A-factor analysis" substantially as suggested.

<span style="color:blue">**Main comments**</span>

<span style="color:blue">The authors present the majority of the results in a concise way, however I found the discussion around the CLO+CH3O2 reaction rates, specifically</span>

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discussion of results of the incorrect A-factor analysis in the methods section, hard to follow. I feel this section can be shortened somewhat or made more concise, especially as results are discussed here but not shown (apart from a few values printed in text). The authors also state in the abstract that there is little difference between the two simulations when using the old (Sander) rates and new (Burkholder) rates. Looking at Figure 2 it looks to me that the differences can be quite significant between the two simulations and remains through to December 1. This may seem insignificant, but such differences after only one reaction is notable. This conclusion is a theme in the other cases investigated as well.

We agree with this comment. In response, we have restructured section 2.3.2; we think that the "incorrect A-factor" analysis is much clearer now. We have also added information of the unit of the rate constant $k$. Further, we agree that the model results (for simulation S4) with the incorrect A-factor should not be discussed in section 2.3.2; we have moved this part to section 3.3 below. There is now a better and clearer discussion of the issue and the error in Eqns. 2 and 3 has been corrected (see also below).

Finally, the review is correct in pointing out that there is the problem that the results on the reaction $ClO + CH_3O_2$ are discussed in the manuscript *but not shown* – this has been changed. The newly added figure 6 now shows the results on the reaction $ClO + CH_3O_2$, so that the accompanying text is much easier to follow.

Is there no role of CLONO2+HCL in spring in maintaining elevated active chlorine? Your box model clearly shows no CLONO2 at all through to December. However, I believe there should be some elevated CLONO2 when spring arrives and therefore this reaction should also play some role. For example Solomon et al. (2015) Figure 3 shows elevated springtime CLONO2 levels from MIPAS observations. The reaction is likely not proceeding as fast as HOCL+HCL, but will the addition of this reaction affect the null cycles in any way? I feel this needs to be at least addressed in the paper.

It is important to point out that the reaction $ClONO_2 + HCl$ was *not* taken out of the system of reactions when the HCl null cycles were identified (Müller et al., 2018). Quoting from Müller et al. (2018) regarding the pathway analysis "As input it [the pathway analysis] requires a set of chemical reaction equations and reaction rates, which are usually provided by a chemical model. Starting from the individual reactions (and their rates) as initial pathways, longer pathways are constructed step by step by connecting shorter

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ones. [...] A rate for each pathway is calculated" (see Lehmann, 2004, for more details). Thus, the HCl null cycles (cycles C1 and C2) have emerged in the pathway analysis (Lehmann, 2004) from the complete chemical set of reactions.

Further, Figure 3 of Solomon et al. (2015) is for 61 hPa, that is for somewhat 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 $ClONO_2$ (MIPAS) are extremely low (similar as in the simulations presented here).

But in any case, we agree with the review that more discussion is necessary; in response we have added the following text to the introduction of the paper.:

"However, at altitudes somewhat greater than 18 km (55 hPa, 430 K) and for conditions in the lower stratosphere closer to the edge of the polar vortex, $HNO_3$ will not continuously be sequestered in PSCs, so that periods with enhanced gas-phase concentrations of $HNO_3$ (compared to the vortex core) will occur. Under such conditions, more $NO_2$ will be available in the gas-phase (e.g., de Laat et al., 2024), enhancing the production of $ClONO_2$, so that reaction R1 will have a much stronger impact on chlorine chemistry. As a result, the chemistry of HCl null cycles will be more complex."

### Specific comments

Lines 53-55. Does CLONO2+HCL also play a role in maintaining elevated chlorine? See more extensive discussion above. We agree and have added the following text: "However, at altitudes somewhat greater than $\approx$ 18 km (55 hPa, 430 K) and for conditions in the lower stratosphere closer to the edge of the polar vortex, $HNO_3$ will not continuously be sequestered in PSCs, so that periods with enhanced gas-phase concentrations of $HNO_3$ (compared to the vortex core) will occur. Under such conditions, more $NO_2$ will be available in the gas-phase (e.g., de Laat et al., 2024), enhancing the production of $ClONO_2$, so that reaction R1 will have a much stronger impact on chlorine chemistry. As a result, the chemistry of HCl null cycles will be more complex." (see also above).

Lines 179 and 182. I believe these equations should be A*exp(-E/RT) not A*exp(-R/ET)? Based on Figure 1 and Table 3 it looks like this is just a typo, but please check. The reviewer is right, Eqns. 2 and 3 in the submitted

version were not correct. The error has been corrected and the Arrhenius equation is now better explained, so that there should not be any remaining misunderstandings. Figure 1 and Table 3 were calculated using the correct formula. Thanks very much for catching this.

Section 3.1. I would like to see this section expanded on a little to explain why there are differences when changing from the older to newer rate recommendations.

The difference between simulations S1 and S2 are minor (most visible in the bottom plot with ozone on a logarithmic scale, see Fig. 2); However, we have added a sentence on the somewhat different development of $ClONO_2$ in simulations S1 and S2 to the discussion here. Canty et al. (2016) have already provided a detailed discussion of updates to JPL recommendations by Burkholder et al. (2015). In response to the comment we state now in the paper: "...(although there are a few periods with more $ClONO_2$ for an initial water vapour molar mixing ratio of 4.11 ppm, Fig. 2). This has consequences for chemical ozone depletion (Fig. 2). There is a slightly lower minimum value of ozone ($\approx$ 10 ppb lower) for an initial water vapour molar mixing ratio of 4.11 ppm."

Line 225. The authors state: "Further, a substantial difference in initial water vapour mixing ratios does not result in a substantial difference of polar chlorine chemistry and ozone loss (Fig. 4). There is a slightly lower minimum value of ozone ($\approx$ 10 ppb lower) for an initial water vapour mixing ratio of 4.11 ppm." Again this seems a quite significant change to me. Some discussion of why this isn't would be welcome here.

We agree that more discussion is warranted here. We have reworked the entire section. The main point is that the HCl null cycles do not depend on the actual rate constant of the heterogeneous reaction $HOCl + HCl \longrightarrow$ ; in other words $HOCl + HCl \longrightarrow$ is still "fast enough" independent of the initial water vapour. We state now in the paper: " The rate constant of heterogeneous reactions is influenced strongly by the type of the available PSC particles. The efficacy of the HCl null cycles, however, is limited by the rates of the reactions of Cl with $CH_4$ and $CH_2O$ [...]. The HCl null cycles are relevant for the maintenance of high levels of active chlorine (Müller et al., 2018)". In response to review one, we have also added a section on the eruption of the Honga volcano, where a further discussion of initial water vapour is provided.

Line 240-245. The earlier onset of ozone loss here is interesting and I

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would like to see it discussed more. This to me is quite substantial especially when early winter HCL conditions is something that fully coupled models can't simulate accurately at the moment, as you mention in the paper.

Again, we agree that more discussion is warranted here. We have revised the relevant section of the manuscript. In particularly, we have added to the text: "However, there is clearly an earlier onset of ozone depletion when $HCl_{initial} = 0$ is employed, with the difference between simulation S3 and S4 notable in late August/early September."

### Technical corrections

Line 193. Please remove "a" from "to a much larger value". Thanks, sentence is reformulated.

Line 295. Suggest rewording "Further, while ozone depletion is somewhat enhanced under these conditions, ozone depletion is not strongly affected" as it currently sounds contradictory. Thanks, the sentence is simpler and clearer now: "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)."

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