Reply to comments by reviewer one 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 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 by the reviewer.

Reviewer one

Summary: The paper addresses three questions: What is the impact of updates to previous recommendations on chemical kinetics on Antarctic ozone depletion? Furthermore, while dehydration strongly regulates Antarctic stratospheric water vapour, its impact on ozone depletion is small. And thirdly, an HCl null cycle and a further cycle starting with $CH_2O + Cl \longrightarrow HCl + CHO$ contribute substantially to keeping HCl low and ClO_x high, hence leading to enhanced ozone depletion.

I learnt a few things reading the paper. I had not thought about the two null cycles and their role in sustaining ozone depletion. The prevailing view is that $CH_4 + Cl$ is a termination reaction for ozone depletion, not the start of yet another cycle of ozone depletion and a null cycle for HCl. Also the typo / order-of-magnitude error in the reaction $ClO + CH_3O_3$ is good to know about – that might be wrong in many chemistry models. The paper represents good, solid work, enhancing our understanding of chemical kinetics of the Antarctic polar vortex. Of course this topic is sometimes considered to be fairly mature, but this paper presents a fresh take on this subject. I don't have many comments to make; the method is fairly straightforward. It involves trajectory calculations simulating atmospheric chemistry under Antarctic conditions and testing the sensitivity of the results to assumptions on initial values for HCl and water, and for correcting the typo in the rate coefficient.

I recommend publication of the paper in ACP subject to addressing the small, technical comments below.

Thank you very much for your comments on our paper. All your comments have been taken into account when producing a revised version of the paper.

Comments:

Table 1: Here and throughout the text, I suggest to put "volume" in front of "mixing ratio", and to use units of ppmv, ppbv, etc, instead of ppm and ppb. Otherwise these can be misunderstood.

We certainly agree with the reviewer that a confusion of volume and mass mixing ratios should be avoided. Thus, the manuscript must be changed. However, our concept in the paper is that molar mixing ratios are shown; molar mixing ratios are identical to volume mixing ratios for an ideal gas. And the deviation of most gases discussed in our manuscript from an ideal gas behaviour can hardly be measured. We have changed the manuscript. In Table 1, we now say "molar mixing ratio" in the caption, and, more importantly perhaps, we now say "molar mixing ratios" throughout the manuscript. We have also inserted the following explanation "(Molar mixing ratios are identical to volume mixing ratios in the case of an ideal gas)" into the introduction of the paper now.

Section 3.2: Can a line be drawn from the small impact of the initial value of H_2O on chlorine and ozone to the (thus far) small impact of the increased water vapour in the stratosphere since the Hunga-Tonga Hunga-Haapai eruption? There had been some expectation in the community that this would increase ozone depletion, but the 2023 season was quite ordinary.

We agree with this comment and we have extended Sec. 3.2. The reviewer is correct in pointing out the relevance of our results in section 3.2. to the Hunga eruption. Indeed, the impact on Antarctic ozone is small as implied by the reviewer comment.

In response to the comment we have added the following discussion to the manuscript in section 3.2:

"The initial water vapour in the Antarctic vortex assumed here and the related model results (. . .) are discussed below regarding the interpretation of water vapour injections into the stratosphere by volcanic eruptions. In

January 2022, the eruption of the Hunga underwater volcano injected a huge, unprecedented in the observational record, amount of water vapour into the mid-stratosphere (Wohltmann et al., 2023; Fleming et al., 2024; Zhou et al., 2024).

The impact of this water vapour enhancement on Antarctic ozone has been assessed through model studies. (Fleming et al., 2024) find that the excess H_2O is projected to increase polar stratospheric clouds and springtime halogen-ozone loss, enhancing the Antarctic ozone hole by 25–30 DU. Wohltmann et al. (2023) find that the direct chemical effect of the increased water vapour on vortex average Antarctic ozone depletion in June through October was minor (less than 4 DU). Zhou et al. (2024) confirm this conclusion but find somewhat more ozone loss caused by the injected water vapour ($\approx$ 10 DU) at the vortex edge. The observation of a small impact of water vapour injected into the stratosphere on polar ozone loss is consistent with the notion put forward in this paper that low temperatures in the vortex, which occur regularly in the Antarctic, limit the atmospheric water vapour to the water vapour saturation pressure over ice and thus remove any anomalies through dehydration before they can affect ozone loss.

The impact of the stratospheric water vapour enhancement through the Hunga eruption on Antarctic ozone has further been assessed in the analysis of satellite observations (Santee et al., 2024). It was observed that the Hunga eruption increased the vertical extent of PSC formation and chlorine activation in early Austral winter in the Antarctic vortex in 2023 (the Antarctic season influenced most strongly by the Hunga eruption). Nonetheless, ozone depletion in the Antarctic in 2023 was unremarkable throughout the lower stratosphere (Santee et al., 2024).

The very minor impact of the huge water vapour injections into the stratosphere by the the Hunga volcano on Antarctic ozone in the 2023 season (Wohltmann et al., 2023; Fleming et al., 2024; Zhou et al., 2024; Santee et al., 2024) is consistent with the very small impact of initial water vapour in mid-winter and the subsequent formation of ice PSC particles in the model simulations presented here. First, the low temperatures in the lower stratosphere in the core of the Antarctic vortex determine mid-winter water vapour (independent of the amount of water vapour present at the time of the formation of the vortex). Second, even if higher water vapour mixing ratios prevailed in mid-winter, chlorine activation and chemical ozone loss remain practically unaltered (Fig. 4 of the submitted manuscript).

Minor comments:

L17: You want to add that the temperature range refers to potential temperature, the vertical coordinate in CLaMS.
Thanks, “potential temperature” has been added.

L23: Replace “although” with “notwithstanding” Done.

L60: Conventional wisdom has it that NAT is important here too. Please comment. I suggest to replace ”ice particles” with ”PSC particles”

We agree with this comment. We changed the wording and say PSC particles now; here is the new text: “Heterogeneous chlorine activation, enhanced concentrations of active chlorine and subsequent ozone loss occur frequently in the polar regions. Under exceptional circumstances chlorine activation also occurs in the mid-latitudes for conditions of low temperatures and enhanced water vapour. The surfaces for heterogeneous reactions might be provided for example by stratospheric PSC particles, stratospheric sulphate aerosol particles (potentially enhanced by volcanic eruptions or climate intervention) or by wildfire smoke injected into the stratosphere. . . ”

L116: Replace “on” with “to” Done.

References

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