

Reply to comments by reviewer two 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 in all three reviews.

Review two

General comments

The manuscript describes new modelling simulations of Antarctic ozone depletion using the well-regarded CLaMS model with meteorological fields from ECMWF.

Building on previous work by much the same team, the same techniques as previously used are again made use of to study the effects of making specific improvements to a number of the parameters of the simulation, namely updated reaction rates and more realistic values for water vapour and HCl as seen in observations. The authors find that with these changes, the model still simulates extremely low ozone in late September, as required to match observations.

While this could be seen as a null result which doesn't add very much to our understanding of polar ozone depletion, it is good science to investigate the effect of all such potential issues in previous work and to assess the sensitivities of the earlier results.

The subject matter of polar ozone depletion is central to the scope of ACP and I believe the manuscript is suitable for publication after some fairly easy revisions.

Thank you very much for these comments on our paper. Indeed, we agree that it constitutes "good science" to investigate the effect of potential issues in previous work. All comments in the review have been taken into account

and a revised version of the paper has been created.

My only major concern is that, while I find the manuscript is very clearly written, in the sense that each individual sentence is well-written and easily understood, the broader narrative is not very clearly expressed.

The entire paper has been revised with this comment in mind. See below for changes in detail.

I would like to see several points being better discussed for the benefit of the reader.

The abstract and the introduction need to explain better that this work is building on previous results. Similarly, the core method of using a single reference trajectory to evaluate the model output needs to be discussed (the readers shouldn't have to refer to the older papers) and the strengths and weaknesses of this approach outlined.

This is a valid point. However, the abstract is restricted in length (according to ACP standards) so there are limits to what is possible in the abstract. Nonetheless, we state in the abstract now in response: "Simulations of Antarctic chlorine and ozone chemistry in previous work show that in the core of the Antarctic vortex (16–18 km, 85–55 hPa, 390–430 K) HCl null cycles (initiated by reactions of Cl with CH₄ and CH₂O) are effective."

In the introduction, there is more room for discussion; we state now:

"In the present study, we extend earlier work on HCl null cycles (Grooß et al., 2011; Müller et al., 2018; Zafar et al., 2018) investigating the chemical processes in the core of the Antarctic vortex in the lower stratosphere (16–18 km, 85–55 hPa, 390–430 K), where extremely low ozone molar mixing ratios in spring are reached regularly (Solomon et al., 2005; Johnson et al., 2023). [...] The earlier work (Grooß et al., 2011; Müller et al., 2018) was based on a detailed examination of a single trajectory and an analysis of multi-trajectory simulations. Here we do *not* employ a three-dimensional model version [...], which is based on global or hemispheric meteorological fields and includes atmospheric mixing (e.g., Poshyvailo et al., 2018; Grooß and Müller, 2021; Sonnabend et al., 2024)."

Further, in response to this review, there is also a more detailed discussion of the multi-trajectory analysis in section 3.4 now.

The authors don't explain why unrealistic choices of water vapour (in particular) and HCl were used in the older work – according to section 2.2.1, two 2018 papers used 4.1 ppm but the observations listed giving a lower

concentration were generally well known before 2018.

First, we agree with the comment that regarding initial water vapour; clearly the issue of Antarctic dehydration was known prior to 2018 (e.g., Kelly et al., 1989; Vömel et al., 1995; Nedoluha et al., 2002; Jiménez et al., 2006, and other references in the submitted manuscript). The initial value of 4.1 ppm chosen in previous work (Müller et al., 2018; Zafar et al., 2018) was too high for an entire Antarctic winter. Such a value is however appropriate for conditions on 1 June, but dehydration occurs thereafter in the Antarctic stratosphere (although this dehydration is not represented in the trajectory model employed here). In response to this comment, these arguments are now better discussed in section 2.2.1. In particular, this issue should be resolved here by showing the simulation with a lower (dehydrated) initial value for H_2O , which is close to observations. However, assuming somewhat higher initial water vapour mixing ratios does not seem completely irrelevant considering the case of the Honga volcanic eruption raised in review one. (And we have refrained from a discussion in the paper *why* particular choices were made in previous work).

Second, regarding initial HCl, this issue was not well established prior to 2018 (Wohltmann et al., 2017; Grooß et al., 2018). Indeed, the processes causing the low winter HCl are not yet established today. Overall, we argue that this paper makes an important point stating that neither the initial H_2O nor the initial HCl have a significant impact on Antarctic chlorine chemistry and ozone depletion (corroborating the findings of earlier studies, Müller et al., 2018; Zafar et al., 2018).

The authors also don't suggest any other ways the new simulations could be tested other than the effect on the ozone concentration at the end of the reference trajectory – for example, wouldn't there be some observational consequences of the much greater surface area of ice clouds shown in figure 3?

We agree and have now added (in section 3.2) to the paper: “There should be observational consequences of the very different ice surfaces in simulations S2 and S3 (Fig. 3), i.e. observations should allow discriminating between the hypotheses about initial water vapour in simulations S2 and S3.” Further (section 3.3.1), we have added now: “Differences in the temporal development of HOCl, ClO_x , and HCl between simulations S3 and S4 are greater than for ozone and thus might possibly be simpler to detect in satellite observation than a different temporal development of ozone.”

Section 3.4 was not very clear in terms of the motivation, the details of the method or what exactly the results were showing, and needs some particular extra work.

We agree that the motivation for the multi-trajectory simulation in section 3.4 needs to be clearer. The point is that the reference trajectory is typical for the conditions in the vortex core in the lower stratosphere. We have added to following text to the paper: “In the discussions above, one particular (reference) trajectory was considered. Nonetheless, this trajectory is representative for the conditions in the core of the Antarctic vortex at 16–18 km (85–55 hPa, 390–430 K). To demonstrate this, we selected here twenty one trajectories passing the South Pole (in late September/early October) at the 400 K potential temperature level; these trajectories include diabatic descent and latitude variations.”

Regarding the results, it is stated in the paper that “all trajectories show strongly enhanced values of ClO_x over the period of strong ozone loss in August and September, consistent with suppressed values of HCl”.

There is some repetition in the text which could be cleaned up.

Thanks for pointing this out – we have revised the text throughout the paper.

The references are very thorough.

Thanks for this comment. We have also invested some effort in keeping the references correct and up-to date.

Specific comments:

Lines 2-11 Please re-write the abstract to better describe the purpose of the paper

The purpose of the paper is now clearer in the abstract: “ Here we investigate the impact of the observed dehydration in Antarctica, [. . .]; however the efficacy of HCl null cycles is not affected. Moreover, also when using the observed very low HCl molar mixing ratios in Antarctic winter as initial values; HCl null cycles are efficient in maintaining low HCl (and high ClO_x) throughout winter/spring.” (see also comments above).

Line 52 Please state the reactions you are referring to here

Done, we state now: “. . . in spite of increasingly rapid formation of HCl in the gas phase (through the reactions of Cl with CH_4 and CH_2O Müller

et al., 2018).”

Line 55 Please state the phase of this reaction

Done, we state now: “(which occurs on the surfaces of nitric acid trihydrate (NAT) and ice particles or within supercooled (liquid) ternary solutions and cold liquid aerosol particles)”

Lines 56-57 please state or refer to the specific reactions

Done, we have added now: “. . . through the reactions of Cl with CH₄ and CH₂O . . .”

Line 75-76 “the uptake of HNO₃ on ice particles” has not been mentioned until now

We agree and have provided more background here (including a new citation). The text in the manuscript reads now: “Ice clouds are very efficient in sequestering HNO₃ from the gas-phase (e.g. Hynes et al., 2002), thus a lower occurrence of ice clouds in the model reduces substantially the uptake of gas-phase HNO₃ on ice particles”.

Line 87 This reaction has not been previously mentioned either

We agree, we have removed the mentioning of this reaction (ClO + CH₃O₂) in line 87. The reaction is now discussed in the introduction below reaction R2.

Lines 98-101 How does the model know what the surface areas are of these different types of clouds though?

Temperature is key here. We have extended the model description to address this point. In particular, we state in the paper now: “NAT particles are assumed to form at a supersaturation of 10 from liquid ternary solutions or from ice evaporation. Ice is formed in the model at the equilibrium temperature (no supersaturation). The initial density of liquid (binary) aerosol particles is assumed to be 10 cm⁻³. The condensable material for liquid ternary particles, NAT and ice is determined from the equilibrium with the gas-phase.”

Table 1 – how have these values been determined though? In particular, how have you decided the Bromine concentration?

We agree that more information on the initial conditions should be given in the paper. In response, we have added to following text: “The values for key species at the start of the simulation on 1 May 2003 at 430 K potential temperature for O₃, HNO₃, and N₂O are based on MIPAS-Envisat obser-

vations; further, tracer correlations of N_2O with Cl_y , Br_y , and NO_y were employed (see Grooß et al., 2011, for details). With the exception of H_2O , the initial values used here are identical to those used in earlier work (Müller et al., 2018; Zafar et al., 2018).”

Lines 120-139 The reader is left to puzzle why the 2018 papers used 4.1 ppm when there was such an abundance of observational data available to support a lower value – this point should be briefly discussed, otherwise it sounds strange.

We agree that adding some discussion is warranted here, which was done (see above). We also agree with the reviewer that the process of Antarctic dehydration was established prior to 2018 (e.g., Kelly et al., 1989; Vömel et al., 1995; Nedoluha et al., 2002; Jiménez et al., 2006, and other references in the submitted manuscript). Clearly, the initial value of 4.1 ppm chosen in previous work (Müller et al., 2018; Zafar et al., 2018) was too high for an entire Antarctic winter. (As is stated in the paper now, section 2.2.1). This issue is resolved here by showing the simulation with a lower (dehydrated) initial value for H_2O , which is close to observations. However, assuming somewhat higher initial water vapour mixing ratios does not seem completely irrelevant considering the case of the Honga volcanic eruption raised in review one. (And we have refrained from a discussion in the paper *why* particular choices were made in previous work).

Line 148 – I don’t think you quite mean “it must be a process missing in the models”. You next state it could be a temperature bias in the meteorological fields, which isn’t a missing process in the models.

Yes, this is correct; we have removed “(but it must be a process missing in the models)” from the manuscript.

Line 220 What do you mean by “the occurrence heterogeneous reactions”?

We agree that our formulation was not good. We are more explicit now and say in the paper: “This 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. Although it is important for the efficacy of the HCl null cycles that temperatures are sufficiently low so that particles are present and heterogeneous reactions occur. . .”

Figure 2 – A general question about the method – the trajectory is calculated for months but its path could not possibly be accurately determined for such a long period of time – does this matter?

It does not matter. However, it is correct pointing out that a trajectory cannot be accurately determined for a long period of time. Nonetheless, accurately following an air parcel is also not possible in a classic three-dimensional model (e.g., excessive mixing across transport barriers or comparisons over several months on a pressure surface). However, following an air parcel (as done here) allows a pathway analysis to be conducted, which is more difficult in a three-dimensional framework. An important point is that the trajectory discussed in the main part the results section (independent of the details of the trajectory) is representative for the conditions in the core of the vortex in the lower stratosphere (see the point below).

Lines 225-271 Section 3.4 is not explained well enough, you need to better motivate this section for the reader, explain what exactly the different trajectories are, and discuss what it shows.

We agree, section 3.4 (in particular the motivation) has been changed, see also response on this point above. Further the paper states regarding this issue: “As in the reference simulation, the period of rapid ozone loss [...] ends abruptly with chlorine deactivation through very rapid formation of HCl [...]. After deactivation, HCl values remain high and practically unchanged in the box model simulation”. We are confident that section 3.4 is now better motivated and explained.

Lines 296-298 This sentence reads very awkwardly at the moment and needs some minor re-wording. “...while ozone depletion is somewhat enhanced ...ozone depletion is not strongly affected”

We agree – the sentence has been changed; we dropped “while ozone depletion is somewhat enhanced under these conditions”; the sentence now reads “...ozone depletion is not strongly affected by the initial values of HCl...”

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