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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The maintenance of elevated active chlorine levels in the Antarctic lower stratosphere through HCl null-cycles" *by* Rolf Müller et al.

Rolf Müller et al.

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We thank the referee for the review and for very helpful comments. We give a point-by-point reply below, where the reviewer comments are repeated in italics.

General remarks

The paper presents a classical process study on important details of the Antarctic ozone hole and is suitable for ACP after minor improvement.

Thank you very much. In the revised version all comments have been taken into ac-

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count.

Specific remarks

Page 3, line 28 and Figure 2: Wouldn't it be better to use for the range of HCHO photolysis branching cases near the experimental uncertainty? The totally unrealistic limits give a larger separation of the curves but what do we learn from that?

We agree and have conducted additional simulations assuming a 20% increase (yellow line in Fig. 1 of this reply) and decrease (light blue line in Fig. 1) of the recommended branching ratio for the radical channel of the formaldehyde photolysis; the value of 20% is deduced from the study of Röth and Ehhalt (2015). The results are shown in Fig. 1 of this reply and will be added to the paper.

However, assuming no HO_2 production in the photolysis of CH_2O (blue line in Fig. 1 leads to very little reduction in HCl between late August and late September. This corroborates the conclusion that the HCl depletion beyond the initial titration against $ClONO_2$ is driven by the radical channel of the CH_2O photolysis. In line with the recommendation of reviewer #1, we have therefore retained the dark blue and red line in the figure.

Page 7 and 8, cycles C3 and C4: These cycles require a lot of ozone. Late September or early October ozone might be too depleted for that and chlorine deactivation starts. Please give some remarks on that, best with typical threshold values. It is too difficult to estimate that from the figures like presented.

The reviewer is correct in pointing out that the net reactions for cycle C3 and C4 require the presence of ozone (three and seven ozone molecules in cycles C3 and C4 respectively). These molecules are required for reaction R9:

$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$

reaction R17:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (2)$$

and reaction R19:

$$OH + O_3 \rightarrow HO_2 + O_2; \quad (3)$$

these reactions are fast enough to sustain cycles C3 and C4 even at low ozone concentrations. However, we agree that it is necessary to include some discussion on the issue to the paper. We have now inserted the following sentences in the text after cycles C3 and C4 are introduced:

"Reactions R9, R17, and R19 are fast enough to sustain cycles C3 and C4 even at the very low ozone concentrations as they occur in late September. For example, in the reference run for 26 September, the diurnal mean ozone mixing ratio is 77 ppb, the rate of reaction R9 is 46 ppb/day, the rate of reaction R17 is 15 ppb/day, and the net rate of reaction R19 is $3.2 \cdot 10^{-2}$ ppb/day directly and 1.1 ppp/day, when it proceeds in two steps (R21 and R9). Therefore, even at extremely low ozone concentrations in late September, the rates of reactions R9, R17, and R19 are not rate limiting for cycles C3 and C4. Under these conditions, the rate limiting reaction for cycle C3 is the radical channel of the photolysis of CH_2O and for cycle C4 the reaction of $O(^1D)$ with water vapour. (Note that reactions R9 and R17 do not constitute the rate limiting step of ozone loss cycles and can therefore not be used to deduce the ozone loss rate)."

Section 3.5: There CLAMS should be mentioned (cited) also in the text and not only in the caption of Fig.4 and in section 2.1.

We agree, the first sentences of section 3.5 read now: "We have repeated the reference run using the CLaMS model (McKenna et al., 2002; Grooß et al., 2005) in box-model mode for multiple trajectories. We employ a set of realistic trajectories passing the South pole at 400 K potential temperature (in late September/early October) including diabatic descent and latitude variations (taken from Grooß et al., 2011)." ...

Technical corrections

Figure 4 might be easier to read with colored curves for the extreme cases. This would be one option to improve Fig. 4; here we have followed the suggestion from reviewer #1 to emphasise the results from the reference run in colour.

Page 14, line 16: Initials messed up? Yes, it should read "A.M.Z." – corrected.

Page 15, line 3: order of words or parentheses wrong. Yes, citation is corrected.

Figure A1: A step of 0.2ppmv and an ordered legend would be better. We agree. The revised version of the plot shows a step of 0.2 ppmv and an ordered legend as suggested.

References

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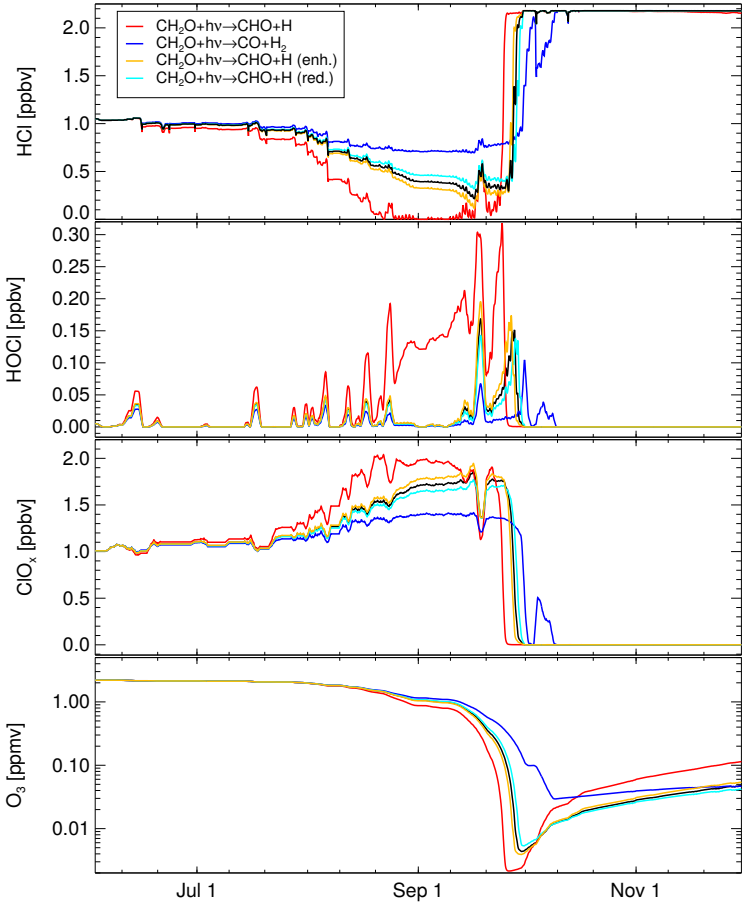

Fig. 1. Improved version of Fig.∼2 showing the effect of realistic estimates of the uncertainty of the branching ratio of the formaldehyde photolysis (light blue and yellow lines).

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