

## ***Interactive comment on “A quantitative analysis of the reactions involved in stratospheric polar ozone depletion” by Ingo Wohltmann et al.***

### **Anonymous Referee #3**

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This manuscript presents a comprehensive quantitative evaluation of the chemical reactions involved in lower stratospheric polar ozone depletion. Vortex-averaged abundances and reaction rates of nitrogen, hydrogen, chlorine, bromine, and oxygen species are analyzed over the winter/spring seasons in both hemispheres using a state-of-the-art CTM driven by ERA-I meteorological fields and employing recent laboratory kinetics and photochemical data. Although most of the reaction pathways and cycles important in stratospheric ozone chemistry are well known and little new is revealed in this study, its extensive and detailed nature makes the analysis extremely valuable. In my view, this paper represents a commendable service to the community and merits publication in ACP. That said, I do have a few overall comments and a number of specific corrections or points of clarification that I feel need to be addressed before the paper can be published.

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## General comments:

\* I certainly understand the necessity to focus on individual winters in a study such as this. However, I would like to have seen more discussion of why the specific winters shown were chosen and how dependent the overall results are on this choice. Both the 2004/2005 Arctic and 2006 Antarctic winters were exceptionally cold and/or long-lasting, leading to greater-than-average ozone loss in both hemispheres in those years. The 2004/2005 Arctic winter in particular is not necessarily representative. Yet throughout the manuscript many general statements are made about polar processing in the Arctic based on this one winter. One example appears on P19, L25: “chlorine is activated from December to the beginning of March” — this is simply not true in many Arctic winters (a similar comment is made on P29, L14.) At the least the possibility that some of these results are not universally applicable needs to be acknowledged.

\* The fidelity of the model in reproducing the observed atmospheric state is overstated in my opinion, or at least the seriousness of the discrepancy with HCl is downplayed. The problem with HCl is barely mentioned in the text proper, with detailed discussion of it relegated to the Appendix. This is an important issue that I feel warrants further explication. If the agreement with HCl in the original runs was so poor, then surely the match with ClO (measured by MLS) and ClONO<sub>2</sub> (measured by MIPAS) must have also been severely compromised, but this is not discussed. The degree of agreement after application of an empirical “correction” to the HCl solubility in the model is stated to be “good”, but to me this characterization is overly optimistic (see more detailed comments below), and in fact the comparison between measured and modeled ozone is considerably degraded in the Arctic. The bottom line is that, while the authors note that the HCl issue “introduces some uncertainty in our results”, they make no attempt to quantify that uncertainty.

\* Although this study is inarguably the most in-depth and exhaustive of its kind, some work along these lines has been undertaken in the past but is not referenced here. Not only would it be appropriate to cite more of the earlier work estimating the relative

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contributions from various ozone loss cycles [Frieler et al., GRL 2006 and Kuttippurath et al., ACP 2010 are two recent examples], but a few sentences comparing some of the results from this study to previous findings would also be in order. For instance, do their estimates of the relative importance of the ClO-ClO and ClO-BrO cycles agree with earlier results?

\* More generally, there is a pervasive lack of references to previous work throughout the manuscript. The majority of the conclusions drawn from this study are not new, but most of the discussion is written in a manner that fails to adequately acknowledge that. The first paragraph of the Introduction notes that polar stratospheric ozone depletion “has been the subject of ongoing research for the last 30 years” and that “the chemistry of polar ozone depletion is understood very well”, and a few review articles are cited. In my opinion, however, this does not go far enough. This paper almost functions as a review article itself, and although it obviously cannot encompass 30 years of literature, I feel that it could do a better job of recognizing previous efforts. In fact, the more appropriate degree of referencing in the bromine section (4.4) underscores its lack elsewhere.

Specific substantive comments:

\* P2, L13: Wegner et al. [2013] (also cited in the Appendix) is an abstract, not a peer-reviewed publication, and thus it is not an ideal reference. Have no other published papers discussed this issue?

\* P4, L25–28: It seems that it would have been more natural to perform this analysis, which is based on vortex averages (with the vortex edge defined via modified PV), on isentropic surfaces rather than pressure levels. Some explanation of the use of pressure as a vertical coordinate is warranted.

\* P5, L4: A threshold value of 0.7 for the vortex tracer sounds reasonable, but what is this value based on? How sensitive are the results to this value?

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\* P5, L10: There are several previous papers that it would be appropriate to cite for this point, starting with Douglass et al. [JGR 1995].

\* Figure 1: It might be helpful to include the ice frost point in these panels, in addition to the NAT threshold. Then on P13 (L17) this figure could be referred to for the point that the northern hemisphere is not cold enough for significant ice cloud formation. Alternatively (or in addition), a reference needs to be provided in the sentence on P13.

\* Section 3: I'm not convinced that this section is really needed. It mainly presents basic background material that most of this paper's readership will already be familiar with. Of course, it is nice to have for completeness, but it is not crucial. In my opinion it is also inadequately referenced. More importantly, it would be helpful if the phases of polar ozone depletion referred to in the text were marked in the figure panels, making it easier to relate the meteorological conditions shown to the evolution of the chemical species being described.

\* P7, L17: Technically speaking, Figure 2 shows only the changes in HNO<sub>3</sub>, so other information (e.g., a citation) is needed for the attribution of the increase in March to transport.

\* Figure 3: I'm confused by this figure. Why does the effect of PSC sedimentation appear to be so much larger in the northern hemisphere? I realize that this figure shows the rate of change, not the absolute value of HNO<sub>3</sub>, but still . . . There is a pulse of strong denitrification in late December in the Arctic (in this particular year), and then a relatively steady rate of decrease over the next month. The maximum rate of change in the south is much smaller, though a substantial rate of decline lasts longer. It's difficult to perform a seasonal integration of this plot by eye, but I guess it adds up to overall greater denitrification in the Antarctic as seen in Figure 2? Or am I misinterpreting this plot? A sentence of clarification on this point would be good, because at first glance the results in Figure 3 seem surprising.

\* P11, L21: It would be good to remind readers that this discussion is specifically

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relevant to the polar lower stratosphere, and that NO<sub>x</sub> plays a bigger role at higher altitudes [e.g., Kuttippurath et al., 2010].

\* Figure 6: The reaction BrO+NO is shown in this figure but does not seem to be discussed in the text at all (unless I missed it) – it is written out in Section 4.4 (R37), but this figure is not referred to there. If this reaction is worth showing in a figure, then it probably should get a sentence somewhere.

\* P17, L3–4 and Figure 9: “In the southern hemisphere, the change between conditions rich in ClO<sub>x</sub> and rich in NO<sub>x</sub> can be seen in a change in the relative partitioning (Figure 9)”. It’s not clear to me exactly what period is being talked about here, since I see no dramatic change in the relative partitioning between OH and HO<sub>2</sub>, except perhaps briefly in mid-October? Also, note typo (“partitoning”).

\* P19, L22: Given that some attention has been devoted to the equilibrium between ClO and its dimer in the last decade (see, for example, the discussion in the 2010 WMO Ozone Assessment), it seems odd to me to include only this one quite old reference. In addition, brief discussion of the temperature dependence of the ClO/Cl<sub>2</sub>O<sub>2</sub> relationship would be appropriate here.

\* P19, L25–27: According to Figure 12 (and previous literature), in the southern hemisphere chlorine remains activated well into October. Also, is there an explanation for the interhemispheric difference in peak ClO<sub>x</sub> values? Is the finding that maximum ClO<sub>x</sub> values in the Arctic exceed those in the Antarctic consistent with results published previously?

\* P21, L13–17: What factors give rise to the interhemispheric difference in the importance of the HOCl+HCl reaction (I note that it is stated on P15 that HOCl mixing ratios can reach 0.15 ppb in both hemispheres)? Also, Figure 13 indicates that this reaction dominates in the northern hemisphere in early February, so a similar shift takes place there as well, at least temporarily.

\* Figure 13 and L1–4: I find this figure and accompanying discussion confusing. Are the first two (presumably net) production reactions the same as those mentioned in the caption for Figure 8 (the reactants of the second one are not written the same in the legend to Figure 13 as they are in the caption to Figure 8)? If so, then they need to be explained in a similar manner here. Is the  $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$  reaction (R33) that mainly accounts for the production of HCl shown in Figure 13? When it is stated that “chemical change rates of both HCl and  $\text{ClONO}_2$  decrease to zero in November in the southern hemisphere”, are net changes (i.e., the green line) being referred to? When  $\text{ClONO}_2$  is mentioned, is Figure 16 being referred to? All of this should be clarified. Finally, the two pale blue colors in this figure are indistinguishable (I realize that one region is shown positive and the other negative, but nevertheless different colors should be used).

\* Appendix A: several related points:

(1) P31, L16–17 note that the vortex averages shown in Figures 21 and 22 do not take into account the vortex tracer criterion, as the figures in the main text do. However, it might be interesting to add such lines to these plots; although they could not be directly compared to the satellite measurements, they would allow assessment of how much difference that filter makes.

(2) P31, L19–20 state that apart from the HCl problem, “the agreement of model and observations for other species like ozone, water vapour or  $\text{HNO}_3$  is quite satisfactory”. This seems like a slightly optimistic characterization to me. Agreement with ozone is considerably degraded in the northern hemisphere in the “corrected” runs, and the match with  $\text{H}_2\text{O}$  is not very close in either simulation, especially in the Antarctic. Even with the adjustment, the agreement with MLS HCl is not very good in either hemisphere.

(3) P31, L25–26: “the good agreement of most other species with measurements, including the tracer  $\text{N}_2\text{O}$  (not shown)”. Why not show  $\text{N}_2\text{O}$ , since MLS measures it?

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Given that the agreement for the other species is characterized as “good”, its omission causes the reader to wonder whether N<sub>2</sub>O looks even worse.

(4) P33, L8–10: “The HCl mixing ratios of the model runs with the changed Henry constant agree well with the satellite measurements for the southern hemisphere and the northern hemisphere after beginning of January, but a discrepancy remains in December”. I disagree with this characterization. Modeled HCl from the “corrected” runs really does not agree “well” with MLS HCl in the southern hemisphere in any part of the season, except on a few days here and there where the curves cross. Similarly, it is an overstatement to say that modeled and measured HCl agree well in the northern hemisphere after the beginning of January – the curves simply cross then, and a substantial discrepancy is seen in February as well as December. Only at the end of the winter in the Arctic (March) do modeled and measured HCl agree well. Also note typo (“discrepany”).

Minor points of clarification, wording / figure suggestions, and grammar / typo corrections:

- P3, L29: I think it might be better to say “The settings for the polar stratospheric cloud parameterizations” or something similar.
- P4, L4: “. . . 2006 for the northern and southern hemispheres, respectively”
- P4, L10: It is not clear what “All values” is referring to – Bry?
- P4, L25: Delete the comma and change “which” to “that”
- P5, L3–4: This sentence would read better as: “We only include in the vortex mean those parcels for which the vortex tracer has a value greater than 0.7”
- P5, L7: Would be better as “This leads not only to”
- P6, L3: “both methods” → “the two methods”
- P6, L10: Shouldn’t this be “the main player in the chemistry of lower stratospheric

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ozone depletion”?

- P7, L8: Since as PSCs dissipate they release HNO<sub>3</sub> (and H<sub>2</sub>O) back to the gas phase, is “dissolve” really the best word here? Maybe “evaporate” or “sublimate” would be better

- P7, L19: It might be better to delete “changes by” in front of “denitrification”

- P7, L21: Would be better as: “lower temperatures (Figure 1), leaving almost no NO<sub>y</sub>”

- P9, L3: “of the production” would be better

- P9, L11–12: Might be better as “and net production of extended NO<sub>x</sub> from HNO<sub>3</sub> occurs”

- P11, L4: “. . . March or October in the northern and southern hemispheres, respectively”

- P11, L11: What does “this” refer to – the daytime equilibrium between NO and NO<sub>2</sub>?

- P11, L16: It would be good to add “(see Figure 5)” after “northern hemisphere”

- P12, L1: “dominating” → “dominant”

- P12, L13-14: “ClO drops to even lower values after October due to missing ozone” – is ClO really meant here? I think this might be referring to ClONO<sub>2</sub>. Also, “severely depleted” would be better than “missing”

- P14, L4: Add “or” before “OH”. This is a somewhat awkward sentence; it might be better to break it up: “. . . production from CH<sub>4</sub> oxidation plays an important role; it can be initiated by . . . and then continues . . .”

- P15, L16: It would be helpful to add “(see Figure 11)” after “activated”

- P15, L20: “within HO<sub>x</sub>” or “between the HO<sub>x</sub> species” would be better than “inside HO<sub>x</sub>”. In addition, although it is generally helpful to the reader when reactions from earlier in the paper are repeated in a later section, in this case these reactions were in-



roduced only a few lines before. So here it might be OK to simply say “The partitioning within HO<sub>x</sub> is determined mainly by R21, R22, and . . .”

- P16, L5: What does “that” refer to – the fast equilibrium between OH and HO<sub>2</sub>?
- P16, L6: “and ClO+HO<sub>2</sub> is replaced” → “with ClO+HO<sub>2</sub> replaced”
- P16, L8: It would be good to add “(Figure 9)” after “hemispheres”
- P16, L12: “in” → “to a”
- P17, L1: “. . . September in the northern and southern hemispheres, respectively); see Figure 5”
- P17, L3: Rather than the specific timing (“in spring (end of March)”), the important point is “after chlorine is deactivated”
- P17, L10–12: It would be helpful to add equation numbers (R17 and R20) after the reactions given in L10, especially since the latter is referred to in L11. Similar comment for L12 (R23)
- P19, L4: “are dissolved” → “is dissolved”. Also, I assume that this is what is represented by the “HCl (cloud)” pink region in Figure 11, but it might be good to explicitly state that in the caption
- P21, L28: “This can be seen in the fact that . . .”. Actually, it is not seen in this paper, since the late spring / summer period is not shown in any figure. A reference is needed here
- P22, L9: “a part” → “part”
- P22, L10: It is stated that “the other channel is into ClO”, but I think that “Cl” is meant (i.e., R24). Also, use either “about” or “~”, not both
- P23, L4: “over” → “through” or “via”
- P23, L7: It might be good to refer back to Figure 13 for the Cl+CH<sub>4</sub> reaction

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- P25, L2: “yellow” → “gold” (there is a yellow area, but it shows O+ClONO<sub>2</sub>)
- P25, L8: Add “or” before “OH”. Also, “dominating” → “dominant”
- P25, L10: “is dominating” → “dominates”
- P25, L14: “Then” → “At that time”
- P25, L16–17: Again, summer conditions in the Arctic are not shown here, so a reference is needed. Also, “rates” → “rates of change”, “occured” (typo), add “directly” before “into HCl”
- P26, Figure 17: For consistency, it would be nice if the region denoting the ClONO<sub>2</sub>+HCl reaction were shown in pink, as it was in Figure 16 (the Cl+ClONO<sub>2</sub> regions are in the same color in both figures)
- P28, L13: “dominating” → “dominant”
- P28, bottom: A minor point, but this is the third different format used to write R31 (see P19 and P22)
- P29, Figure 20: Why use a red line here when a green line was used for net changes in previous similar figures? It would be better to assign a different color for the O cycle and use green for net rates in this figure as well. In addition, the caption states that the contribution of other cycles is negligible, but is that really true in aggregate, given that the red line falls outside the colored contours? Perhaps a “remaining unspecified reactions” region should be added, as done elsewhere
- P29, L6: “is able to work” → “is effective”, or something similar
- P29, L8: It would be better to enclose the reaction numbers in parentheses
- P29, L9: “photolysis” → “photolysis rate constant”
- P30, L13: Add “for one specific winter in each hemisphere” after “54 hPa”
- P30, L16–17: Delete “numbers for”

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- P31, L3: “are” → “is”
- P31, L9: I would say it is “necessary”, not “desirable”
- P30, L10: “backed up” → “substantiated” or “confirmed”
- P31, L24: “over” → “across”
- P31, L25: “over” → “through” or “via”
- P33, L5–6: “a good agreement of” → “good agreement between”

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