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Interactive comment on "Midlatitude ClO during the maximum atmospheric chlorine burden: in situ balloon measurements and model simulations" *by* B. Vogel et al.

B. Vogel et al.

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Reply to the Reviewer 1 (Ross Salawitch) Comments

We thank the reviewer for a very thorough and very helpful review. Following his advice, we have revised the manuscript and made some major revisions.

Major Revisions:

1. For the model simulations, we adjusted the surface area of the background aerosol (SSA = stratospheric sulfuric aerosol) per unit volume A_{SSA} by varying the mixing ratio of H_2SO_4 in ppbv in gas-phase equivalent employing a stratospheric aerosol climatology from SAGE II and CLAES measurements by Baumann et al., 2003. Further, we performed sensitivity studies with A_{SSA} values significant higher and lower than reported by Baumann et al., 2003, however the sensitivity of ClO mixing ratios on the surface area of the background aerosol is not substantial for both flights. The results are shown in a new table (cf. Tab. 5, revised manuscript).

2. We changed the initialization, so that the temporal development of the chemical trace species along each 24-hour backward trajectory are perpetually calculated using the results of the previous model simulation to initialize the following 24-hour simulation, whereas the species CH_4, HCl, H_2O, NO_x, and O_3 derived from measurements are reinitialized to measured values. The conservation of Br_y, Cl_y, and NO_y is warranted between the different cycles. In contrast to the first version of the manuscript, whereby all species was reinitialized to results of the previous model simulation, this yields a better agreement between measurements and simulations for the Aire flight. Further, for the Leon flight the most chemical species converge to a constant volume mixing ratio for a given time in the simulation after approximately 6 – 9 cycles depending on altitude similar to the Aire flight (shown in a new Figure) and in contrast to the previous version of the manuscript. Furthermore, model simulations using different initializations for the partioning between HNO_3 and N_2O_5 (cf. table 1) also converge to the same ClO mixing ratios after approximately 9 cycles as for the Aire flight. However, the measured ClO daylight profile is still underestimated at around 650 K potential temperature. Finally, model simulations with reduced NO_x or HCl values can reproduce measured ClO daylight profile, but simultaneously overestimate the measured night time values.

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Major comments:

1. The aerosol levels that prevailed in 1996 were fairly low, and in 1999 were even lower. This aspect of the "condition of the measurements" should be mentioned in the Introduction, with some appropriate references to aerosol climatology. The value of stratospheric sulfate aerosol loading used in the calculations should be added to Tables 2, 3, and 4. The source of the aerosol data should be indicated in Table 1. If the aerosol surface area information comes from some source other than SAGE II, then the model profile of surface area should be compared to SAGE II, and results of this comparison should be presented, either as a brief discussion or as a brief discussion accompanied by a new figure.

We added this paragraph in the introduction:

"... Furthermore, after the eruption of Mount Pinatubo (June 1991) and the dissipation of the post-Pinatubo aerosol the aerosol levels were low from 1996 to 1999 [e.g., Baumann et al., 2003] simultaneously to the maximum atmospheric chlorine burden."

In model simulations, the surface area of the background aerosol (SSA = stratospheric sulfuric aerosol) per unit volume $\mathrm{A_{SSA}}$ was adjusted by varying the mixing ratio of H_2SO_4 in ppbv in gas-phase equivalent employing a stratospheric aerosol climatology from SAGE II and CLAES measurements by Baumann et al., 2003. The value of stratospheric sulfate aerosol loading used in the simulations is added in Tab. 2,3, and 4. Further, the sensitivity of the model simulations toward the surface area of the background aerosol (SSA =stratospheric sulfuric aerosol) per unit volume

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A_{SSA} was examined. Simulations with A_{SSA} values significant higher and lower than reported by Baumann et al., 2003 were performed (cf. Tab. 5), however the sensitivity of ClO mixing ratios on the surface area of the background aerosol is not substantial.

2. Tables 2, 3, and 4 provide a detailed level of documentation of the calculations. However, certain important parameters are not given. These include: temperature (or pressure), H2O, CO, and, as noted above, surface area. This information should be added to these tables.

In table 2,3, and 4 the parameters H_2O, CO, A_{SSA}, temperature, pressure, and altitude are added.

3. Since I have access to HALOE data, and have conducted many simulations using a similar approach, I have checked the profiles of CH4, Cly, and NOx used in this analysis versus my version of the HALOE data and of tracer-tracer relations.

Overall, the model input specification used here is fine. The Leon flight poses a special challenge, given the large variability in CH4 for air inside the vortex compared to extra vortex air. The authors have pursued a reasonable approach given the unfortunate loss of data from the whole air sampler system for the Leon flight. It looks like the level of NOx given in Tables 3 and 4 is less than NOx reported by HALOE. I suspect the reason for this is the nature of the calculation: even though the model is initialized by HALOE NOx, the value of NOx is allowed to change over the 9 cycles of iteration.

This statement bring us to change the initialization, so that the temporal development of the chemical trace species along each 24-hour backward trajectory are perpetually calculated using the results of the previous model simulation to initialize the following 24-hour simulation, whereas the species CH_4, HCl, H_2O, NO_x, and O_3 derived from

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measurements are reinitialized to measured values (cf. above, Major Revisons).

It would be quite helpful to add a new figure, similar to Figure 4, but for the Leon flight at 650 K (region of largest apparent discrepancy between measured and modeled ClO). Indeed, a two panel version of this new figure, one for "vortex" and one for "midlatitude", would be helpful. Finally, for the two new panels as well as the present version of Figure 4, it would be helpful to denote, perhaps as an asterisk or circle tied to the Cycle 000 curve, the initial values of all calculated species (I know this info is already contained in the figures, but it would be easier to read if a symbol were used to draw attention to the initial values).

In the revised manuscript, a new Figure 5 is added, similar to Figure 4, but for the Leon flight for both the midlatitude and the vortex case. Further, figures 4 and 5 are in color, so that the initial values of the species are better to read.

The time evolution of NOx shown in the 7th panel of Figure 4, as well as what I infer will be the time evolution of NOx that will be seen at 650 K and higher THETA levels for the Leon flight, is somewhat of a concern for the interpretation of the data. For the region of largest disagreement, the 650 K level of the Leon flight, it would be helpful if the authors could comment on whether the discrepancy gets worse (or better) if the HALOE measurement of NOx is correct: e.g., how would modeled ClO change if the model were forced to go through HALOE NOx, as well as forced to satisfy constraints for Cly, O3, and NOy? This comment ties into the importance of surface area, since the NOx/NOy ratio at 650 K over Leon is controlled largely by heterogeneous reactions. I infer from Case 1 vs Case 3 for the Leon flight that basically, if HALOE data for NOx are assumed to be correct, that the discrepancy between measured and modeled ClO largely is explained. But, I am not sure I am interpreting Case 1 versus Case 3 correctly.

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We added a paragraph in Section 3.2.1 in which the sensitiviy on the NO_x values is described: “Further in the lower stratosphere, ClO is inversely correlated with NO_2 [Stimpfle et al.,1994]. In a sensitivity study, the initial NO_x mixing ratios were reduced by about 20 % (equivalent to approximately the minimum NO_x mixing ratios measured by HALOE), whereby the same NO_y was used as in case 1 and 2 (see case 5 and 6, Fig. 8). Nonetheless the measured ClO daylight values are still underestimated or are at the lower limit of the uncertainty of the ClO measurements by the simulations after 9 cycles and simultaneously the measured ClO night time values are at the upper limit of the measurements.”

Minor comments:

1. Several places it is stated that the discrepancy between modeled and measured ClO, at 650 K over Leon, is "up to a factor of two approximately". However, on page 888, it is stated "all other ratios ... are in the interval 1.0 +/- 0.5 including the discrepancy found in the ClO daylight profile at around 650 K for the Leon flight. It does not appear that the mean difference between modeled ClO (about 100 pptv) and measured ClO (about 175 K) is quite large enough to be described as "about a factor of 2".

We corrected this and removed the statement “about a factor of 2”.

2. Somewhere in the paper, the authors should comment on the odd result that calculated ClO using "vortex profiles" over Leon at 650 K is less than calculated ClO using "mid-latitude" profiles, despite more Cly in the vortex profiles. Presumably, this difference is driven by the higher levels of NOx in the vortex profile.

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We added in Sect. 3.2: "...In general the simulations for midlatitudes conditions are somewhat lower than for vortex conditions above 700 K and somewhat higher below, except at 500 K (see Fig. 8). We note that although the Cl_y values are for vortex conditions higher than for midlatitude conditions simulated ClO mixing ratios for case 2 are less than for case 1 between 600 and 700 K. Presumably, this difference is driven by higher NO_x mixing ratios for vortex conditions...."

3. The last three sentences of the abstract are confusing. 3d to last says the model "substantially overestimates" measured ClO. The 2nd to last says "no indication ... [of] ... substantial uncertainties". The last sentence again returns to a thought of "substantial overestimation". The last part of this abstract will be very confusing until colleagues read the paper. I believe the glass is much more than "half full": e.g., I think the comparisons show overall "excellent" , or perhaps "very good" agreement. I suggest some modification of the abstract. In my view, I think the overall good agreement should be emphasized and then the exceptions can be noted. Regardless, the abstract will confuse many if the overall message of the last few sentences is so self-contradictory.

We have rewritten the last part of the abstract:

" ... Model simulations for the flight launched in Aire 1999 show an excellent agreement with the ClO measurements. For the flight launched in Leon 1996, an overall good agreement is found, whereas the flight is characterized by a more complex dynamical situation due to a possible mixture of vortex and non vortex air. We note that for both flights at solar zenith angles greater than $86^\circ - 87^\circ$ simulated ClO mixing ratios are higher than observed ClO mixing ratios. However, the present findings indicate that no

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substantial uncertainties exist in midlatitude chlorine chemistry of the stratosphere."

4. page 877, line 16, "was" should be "were"

This is corrected.

5. page 877, line 19, perhaps a paper reporting recent measurements of ClO from the POLARIS mission (e.g., Stimpfle et al., 1999 or some other paper) can be added to the two citations already given. This Stimpfle paper is the same one that is cited elsewhere.

The Stimpfle et al., 1999 is added.

6. page 878, lines 20 to 27: perhaps the findings of Sen et al. (JGR, 104, 26653, 1999), who examined ClONO2/HCl and ClONO2/Cly using balloon

The Sen et al., 1999 paper is added into the introduction.

7. page 880, line 6: it is not clear what "the Island" means.

It was meant "Iceland"

8. page 880, lines 10 and 11: need a comma after "consequence". Most importantly, nothing is obvious to me from Figure 1 unless color is used. Black and white for these PV maps really doesn't work. Is there a cost associated with use of color for an on-line journal ?!?

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The comma is added. Further, in the most figures color is used now.

9. page 880, line 13: need a comma after "ClO mixing ratios"

The comma is added.

10. page 880, lines 14-15: this sentence is awkward and should be revised to read something like: During descent, both a nighttime and sunrise profile of ClO were measured. During ascent, only a daytime profile was derived.

We removed this sentence and wrote only: ''For both balloon flights a flight profile was employed to study in detail the sunrise evolution of the ClO mixing ratios (see Figure 2)."

11. page 881, lines 9 and 10: perhaps state "so ozone measurements could not be obtained for all altitudes".

We rewrote: "The signal of the ozone sonde was jammed, so ozone measurements could not be obtained for all altitudes."

12. The variation of the O3 abundances for the Aire flight is a bit confusing. Perhaps a new table, giving values of O3 from the sonde, from HALOE, from the 2D model, and for the two simulations (e.g., case a and case b) could be added for the 14 trajectories already detailed for this flight. Or, somehow, some other indication of the ozone differences should be provided. I did not fully understand the discussion on page 883, lines 13 to 26. Also, I don't see any indication in the figures or tables (but

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perhaps I have missed something) that shows the difference between ozone for case a compared to case b.

We removed this paragraph.

13. page 884, line 18: should add a semi-colon after "simulations".

We added the semi-colon.

14. page 885, line 24: there are two 600 and 650 K points "during daylight", so perhaps state something like: except between 600 and 650 K during the most sunlit portion of the flight (SZA about 67 deg).

The entire paragraph is revised: ''For both midlatitude and vortex conditions, simulations and measured ClO mixing ratio show a good agreements during float and night time. During daylight, simulations are at the lower limit of the uncertainties of the ClO measurements and significantly underestimate the measurements at around 650 K potential temperature during the most sunlit portion of the flight (SZA about 67°)....."

15. page 886, lines 1 to 6. First sentence says "ClO is sensitive to O3". Last sentence says "sensitivity of ClO ... on O3 ... determined this way ... is negligible". This is a confusing paragraph. Figure 6 shows some sensitivity of ClO to ozone. The paragraph should better reflect the figure.

The entire paragraph is removed.

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16. One problem with the speculation of the cause of the discrepancy between measured and modeled ClO at 600 to 650 K for the Leon flight is that, if the explanation is caused by a process such as pressure dependence of J_{ClONO2}, then this should affect comparisons of ClO at 600 to 650 K for the Aire flight. The only robust result common to both flights is the apparent tendency for the model to overestimate ClO during twilight. Even this is tricky, as the Air flight at 87 deg shows a different result than the Leon flight at 87 deg. I think the discussion of J_{ClONO2} should include a brief statement that the Aire comparisons, for 600 to 650 K, agree with standard photochemistry.

In Section 3.2, we added a brief statement that for the Aire flight the comparisons for 600 to 650 K, agree with standard photochemistry: "Nevertheless, we analyzed further reasons independent of the initialization of the model simulations and the dynamic conditions of the flight that could explain the uncertainties for the Leon flight, although the simulations of the Aire flight show an excellent agreement with the measurements and thus indicate that no substantial uncertainties exist in midlatitude chlorine chemistry."

Also, while I am not suggesting any change to Figure 9, this figure can be misleading in that the amount of extra ozone loss implied by the model at SZAs between 87 and 90 deg, compared to that implied by the data for the same SZAs, is tiny compared to 24 hr average ozone loss. The reference to Riviere et al. [2003] at the top of page 889 suggests a larger type of discrepancy. Riviere et al.'s observations challenge conventional thinking. I would say the problems noted by Figure 9 are in a different class of modifications to our thinking; e.g, they suggest perhaps a fine refinement. Anyway, it is OK to cite Riviere's work, but I feel the paper overall tends to focus a bit too much on the minor discrepancies and should, upon revision, perhaps present a more balanced view of (in my view) the overall excellent agreement between modeled

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and measured ClO. On the other hand, I realize progress is made by searching for discepancies, and then understanding them. The authors should take this comment into consideration and proceed with a presentation they are completely comfortable with.

Thank you for this helpful comment. We revised the entire manuscript having regard to this comment.

17. Captions of Figures 6 and 7 should include description which ClO uncertainties are shown (e.g., are they precision, or accuracy, or both) and whether these are 1-sigma, 2-sigma, etc.

This was already mentioned in the caption of Figure 3: "1 σ accuracy for the ClO measurements is approximately 20 – 23 % (gray bars)." We refer in Fig. 6 and 8 (before Fig. 6 and 7) to Figure 3.

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