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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sensitivity of tropospheric chemical composition to halogen-radical chemistry using a fully coupled size-resolved multiphase chemistry/global climate system – Part 1: Halogen distributions, aerosol composition, and sensitivity of climate-relevant gases" *by* M. S. Long et al.

Anonymous Referee #2

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This manuscript describes global modeling of atmospheric chemistry with inclusion of halogen chemistry. Use of global modeling to understand how inclusion of halogen chemistry affects the Earth system is a valuable goal, and this work makes progress on the topic. Because many halogen reactions are heterogeneous and involve aerosol surfaces, the model includes a modal aerosol model. A model run with halogen chem-

istry turned on, called "Hal" is compared to the "noHal" run, which has halogen reactions turned off. Generally, the inclusion of halogen chemistry appears to shift the results in reasonable directions, and often brings the results closer to observations. The manuscript also includes a significant effort to verify the results by comparison to field observations of halogens and related species. Because of the complexity of halogens, some halogen related processes are not included in the model, which makes it a bit difficult to be assured that the model is fully relevant to atmosphere. Additionally, the halogen reactions in the chemical model appear to be quite active, leading to what seems to be a larger than real set of impacts of halogen chemistry. Some of the feedbacks related to halogen and coupled non-halogen reactions (e.g. NOx and HOx reactions) are well described, but some of the discussions are difficult to follow and could have their clarity increased. Lastly, this modeling effort seems to indicate regions where halogen chemistry should be explored or there is a high sensitivity to specific halogen related processes. A discussion of how this modeling result might inform field researchers would be valuable. Below are specific comments on sections of the manuscript where improvement could be made.

It is discussed on page 6077 that the MECCA scheme overestimates rates of Br cycling. It is clear from later comparisons that this is true, but the fact that the scheme is too aggressive leads to difficulty in accepting the results of the model. Specifically, it appears in Figure 7 that inclusion of halogen chemistry causes essentially complete destruction of ozone over the Southern Oceans surrounding the Antarctica. It appears that the tip of South America is within this ozone removed area; does the result agree with observations in that location. Similarly, Arctic ozone is highly depleted, apparently into single-digit nmol / mol mixing ratios. Can these be compared to observations? How were the locations used in Table 6 chosen? While the sites used in this table seem to show Hal is better than NoHal, they seem to avoid the locations discussed above. There are two recent halogen modeling efforts, Saiz-Lopez et al., ACP 2012, referenced here, and Parrella et al., ACP 2012 (which is not referenced, but should be). Both of those models appear to have more moderate halogen chemical effects, which

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don't appear to zero ozone at locations where I think that ozone is probably observed. Discussions around page 6086 should be enhanced through reference to these other two paper. For example, Parrella et al. report in their Fig. 6 depletions of ozone of roughly 1-6 nmol / mol due to bromine chemistry. These should be compared to the present results (which appear much larger and are annually averaged, while Parrella report seasonal results).

Also on page 6077, but additionally spread through the manuscript, various halogen sources are included in this model or are not included, and the inclusion or lack of inclusion is compared to other modeling efforts. I think it would be valuable to clearly spell out, and in one place, what is and isn't included in this model and in other efforts (e.g. van Glasow et al., 2004, Saiz-Lopez et al., 2012, and Parrella et al., 2012. Sources that appear to be relevant are: 1) Sea salt aerosol, 2) short and longer-lived organic Br species, 3) Sea ice-derived halogens, 4) Stratospheric-tropospheric exchanged halogens. On this last point, on page 6078, line 2, the authors indicate that the model's stratosphere has no long-lived organic halogen sources, leading to less stratospheric halogen burden, but then the model is tuned in the stratosphere to give reasonable ozone. Although this practice probably adjusts stratospheric chemistry to give observed results, it doesn't appear to say that halogens exchanged between the stratosphere and troposphere don't have effects on upper tropospheric chemistry.

On page 6078, the chemistry might be made more clear. For example, reactions R1 and R2 do "recycle" Br, but they do it with no net effect on ozone (they are a "null cycle"). However, reactions R3 + R4 then R1 (not listed) are an ozone-destroying cycle. The discussion of reactions in the middle of the page includes percent values that are hard to follow because the FT is discussed, then high latitude FT, then MBL – the discussion jumps around. I think this could be written more clearly. The phrase "Multiphase recycling is not completely inactive in the FT" uses two negatives. On page 6079, line 5 seems to say that R8 is not needed in the autocatalytic cycle, but I think R8 is needed, while R7 followed by photolysis maintains reactive Br, but does not increase

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total bromine radicals.

Discussion in multiple parts of the paper seem to indicate that "traditional" marine aerosol sea salt sources (e.g. wind-speed driven sea spray) are included while Polar-specific (e.g. sea-ice related) halogen sources are not included. However, some comparisons in the manuscript compare their results to observations that are likely affected by sea-ice related halogen sources. E.g. on pg 6079, Roscoe et al., 2012 and McElroy et al., 1999 BrO observations in polar regions are discussed, and high BrO abundances are related to modeled high BrO abundances. However, the current effort seems to lack important polar halogen sources. Another point where this topic seems to be apparent is in Fig. 4. First, when this figure is discussed, the presence or absence of a reasonable stratospheric BrO abundance in the model should be discussed. It seems like their model has no stratospheric BrO, possibly due to lack of long-lived organic Br precursors. Second, the maximum BrO appears be be seen over Greenland, and not over sea ice as satellites typically observe. Possibly their model only has FT BrO, and if that is true, then it might be possible that FT BrO is really maximizing over Greenland. Do observations indicate this effect? If not, then the modeling effort might point to a need to explore FT halogens to verify this result. On page 6081, there is discussion of OMI BrO. Please clarify here whether stratospheric BrO is in their column or not (or if it is too low due to lack of organic-Br sources of stratospheric bromine). Why are 9 of the 12 months shown, but three are missing? Specifically, SON are the Austral spring, where halogens are often observed in the Antarctic region.

On pages 6079 and 6080, there are discussions of EF(Br), which I found to be confusing and the choice of Fig. 2 seemed strange. Specifically, if I take a look at Fig. 2, I see the model generally has EF(Br) < 1 at non-polar latitudes. However, as the manuscript starts discussion of EF(Br) on page 6079, there are discussions of EF(Br)>1. It appears that the FT is being discussed, not what is shown Fig. 2, but the order seemed strange and difficult to follow. As I see it, EF(Br)>1 is more relevant to Fig. 3. The whole set of mechanistic discussions on the bottom of page 6079 and through most

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of page 6080 were difficult to follow. Use of more consistent labeling of species and more explicit reference to reactions would help. for example, HBr is sometimes called HBr, sometime HBr(g). Are these different? Is Br in aerosol different from Br-? What is "secondary Br-"? Does the model explicitly track Br- that has been activated and then deactivated? At the bottom of page 6080, "strong subsidence in the high (Southern?) latitudes" is discussed, but I cannot follow the mechanistic discussions well enough to tell if this is consistent. Is what is trying to be said that Br- originally on sea salt aerosol particles gets converted to gases (depleting Br- compared to sea salt on the large particles), and some Br remains in the gas phase, giving overall EF(Br)<1, but as the gas-phase Br species convert back to HBr and HBr sticks to particles, it will stick to the largest surface area (e.g. smaller) particles, leading to EF(Br) >1 in the sub-micron particles?

In the Discussion in general, some of the unique predictions of this model comparisons could be pointed out as possible areas to be studied in the field. For example, Southern ocean marine-halogen derived Br and ozone depletion is very severe in this model. Do observations exist there? If not, it is a place where study would be indicated. Direct observations of aerosol Br (e.g. EF(Br)) in the FT, as well as BrO and ozone, particularly in the polar regions are indicated by this modeling.

—Minor comments / Typographical errors—

Around p6071, line 26 – This could be misread to imply that methane oxidation leads to condensible organic compounds, while it was probably meant that the NMHC oxidation leads to particle growth and/or formation. Please try to reword.

Page 6075, Line 26 says "between levels", but only one level appears to be listed? Below, on line 29, clarify that "below 867mb" means at an altitude below (i.e. at a pressure above...).

Page 6078, line 12 – the "triplet P" shows the 3 (triplet) as subscript when it should be a superscript.

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Page 6079, Lines 17-19. This sentence is confusing. Can it be clarified by making more explicit reference to specific chemical species?

p6081, line 10 "What does "constrains the reliability of comparisons" mean?

p6083, line 2 – How are volcanoes treated in the model? Only slow degassing? Are historic eruptions included?

p6083, line 17 – I'm not sure I get this. I think of acid displacement as production of an acid gas from a weak conjugate acid in solution. For example, for deliquesced sea salt aerosol, NaCl is present as Na+ and Cl-. If you then add H2SO4, it dissociates to 2H+ and SO42- and sulfuric is a stronger acid than hydrochloric, so the H+ increase pushes the equilibrium H+ + Cl- <=> HCl (aq) towards the dissolved HCl, which then pushes the Henry's law solubility to release HCl(g). True that the other product is a sodium salt of sulfuric acid (NaHSO4 if equal moles of NaCl react with H2SO4), but it is the acidity of the sulfuric acid that drives the pH more acidic and thus displaces the chloride. Possibly NaHSO4 is a weaker acid than H2SO4, but they both must be quite strong acids to displace Cl-.

p6088, line 11 – The Cl pathway is a halogen radical source and nocturnal reservoir, but the heterogeneous hydrolysis pathway is a loss of NOx and removes ozone, reducing daytime radical burdens (e.g. Brown et al., 2006).

p6090, line 11 – Consider replacement of "mediation" with "moderation". Median is also used in the same sentence.

p6093, line 9 – CO is also a key source of O3.

p6094, line 21 – clarify "significant"

p6095, line 26 – This section discusses anthropgenic acids, then Southern Oceans halogen chemistry. Presumably the prevalence of halogens in the Southern Oceans is due to strong winds and sea salt sources, not acid pH.

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p6096, lines 9-14 are awkwardly worded.

p6118, middle of caption. I don't understand the "maxima and minima are of data within 1.5 times the 25th - 75th quartile range". Needs better wording.

p6120 – This figure caption needs more information about what parts of the BrO column are really being shown. I think this is mostly FT BrO, and that stratospheric BrO is probably absent or very underrepresented, and BL events are probably missing. Clarify in text and make appropriate notes or reference to text here. Why are 9 of 12 months shown? Why are the midlatitudes not shown reasonbly (the NH figure cuts off in middle European latitudes, and the SH figure seems to go to NH midlatitudes?).

p6126 – I think that the caption and figure labels are not consistent. The figures a and b say "with Hal" while c and d say "with noHal". The caption says a and c are "Hal" and B and D are "noHal".

p6128 Fig. 12 – clarify that "percent deviation" means Hal versus noHal

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 6067, 2013.