Responses to Reviewer #2 Comments on

Sensitivity of Tropospheric Chemical Composition to Halogen-Radical Chemistry Using a Fully Coupled Size-Resolved Multiphase Chemistry/Global Climate System

I: Halogen Distributions, Aerosol Composition, and Sensitivity of Climate-Relevant Gases

Authored by Long et al.

We thank the reviewer for their thoughtful comments and recommendations for improving the manuscript. Each comment (in italics) followed by our corresponding response to that comment is listed below. Unless otherwise noted, line numbers refer to those in the previous un-revised version of the manuscript.

General Comment:

Each of the reviewers felt that the original version of the manuscript did not adequately address the implications of divergence between our results and observations and previous model investigations. In addition to responding to specific concerns along these lines (detailed below), we have added a dedicated subsection at the beginning of Results (Section 3) entitled "Overview Comparisons with Observations and Previous Model Studies" that provides a more integrated evaluation of consistencies and inconsistencies and their associated implications. As indicated in response to a comment by reviewer 1, we have also expanded the introduction and added a table to better frame our work in the context of previous 3-D modeling efforts.

Review 2:

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 chemistry 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 discussed on page 6077, 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, whichdon'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).

The median Antarctic PBL O_3 mixing ratio was 7.4 nmol mol^{-1} (3.7 – 8.1 nmol mol^{-1}). This is about a factor of two lower than observations, and consistent with the impact of high emissions of Br associated with high sea salt emissions from the Southern ocean.

The median Arctic PBL O_3 mixing ratio was 16 nmol mol^{-1} (15 – 28 nmol mol^{-1}). For stations in this region, modeled O_3 mixing ratios were low by about 10% (or about 1 to 1.5 nmol mol^{-1}; not shown). As noted above, text describing the differences between our bromine release scheme and mechanism and those of Parrella et al. (2012) and Saiz-Lopez et al. (2012) has been added. We emphasize that our mechanism represents a more complete, processes-level treatment of reactive halogen emissions from sea-salt aerosol whereas the two studies cited by the reviewer are based on parameterized chemical schemes that prescribe important aspects of halogen activation and cycling. As such, unambiguous interpretation of causes for differences in simulated O_3 is problematic.

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 longerlived 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.

As per the review's recommendation, we have added a paragraph and table to the Introduction and a new section at the beginning of the Results section that summarizes major differences between 3-D global models of halogen chemistry and their associated implications.

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 total bromine radicals.

This section summarizes the primary reactions which govern Br partitioning in the simulation. A discussion of the net effects of these reaction on other species such as O_3 is not addressed explicitly but is discussed later in the manuscript. Reactions R1 through R4 describe that pathways through which Br is recycled in the FT, and the relative contribution of the latter pathway to the total.

In response to the reviewer's comment, the text starting on line 16 on page 6078 of the original manuscript has been changed to the following:

"In the NH-FT, $BrO + NO \rightarrow Br + NO_2$ competes with R3 to recycle Br at approximately equal proportions as the effect of R3 and R4 together.

In the mid and high latitude FT of the NH and SH, 7% to 15% of HOBr is converted to BrCl via the multiphase pathway involving accumulation mode aerosol…"

Also, the phrase, "not completely inactive", is not a double-negative in this sense, and is grammatically permissible. We prefer to retain this structure to emphasize that, in the absence of significant amounts of aerosol liquid water, one might expect heterogeneous cycling to be negligible using the MECCA mechanism. To a large extent, this is the case. Yet, our results indicate that "slightly active" or "not totally inactive" heterogeneous Br cycling does occur.

P6079: L5: The reviewer is correct and the text has been changed to:

"Reactions R1 through R4 and R5 through R8 complete the autocatalytic cycle."

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 Polarspecific (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.*

In response to the reviewer's comment we have revised the text beginning on Page 6081 Line 24 of the original manuscript as follows:

"These peaks typically occur over the polar ice-caps and are believed to be due to "bromine explosions" during Arctic springtime (Simpson et al., 2007; Piot and von Glasow, 2008). Corresponding surface BrO mixing ratios fall within observed ranges (e.g. Table 2). For example, simulated BrO for May and June across all 10 years ranged from 0.9 to 3.5 pmol mol-1, which after accounting for daylight to nighttime ratios, correspond to most of the observed 1 to 5 pmol mol-1 BrO at Summit, Greenland (Stutz et al., 2011). BrO over Greenland is controlled by a combination of downwelling and subsequent activation of HBr in the FT. While all hypothesized sources specific to the Arctic are not considered here, the results depicted in Fig. 4 provide potentially useful background values for estimating the contribution to total Br from sources other than activation pathways involving marine aerosol (e.g., reactions involving brine films on surfaces, frost flowers, organobromine precursors, downwelling of stratospheric BrO, etc.)."

Regarding the discussion of OMI on page 6081, the text has been clarified as follows,

"It is difficult to partition observations into relative contributions of BrO from different altitudes to the total column abundance and it is necessary to constrain either stratospheric or tropospheric column burdens in order to ascertain the potential contribution of the other. Vertically integrated simulated tropospheric BrO (Fig. 4) ranged from…"

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 mostof 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?*

Figure 2 is not referenced until L23 of page 6080. This is after the discussion of FT EF(Br) on P6079 L17 through P6080 L7, and is not meant to be considered with this part of the text. The caption for Fig. 2 now clearly states that simulated data reflect results from the model surface layer.

This section beginning on page 6079 line17 has been revised as follows:

" Br enrichments in sub-µm aerosol have been observed throughout the MBL (e.g., Sander et al., 2003) but until now models have been unable to explain them. For example, in a CAABA box model, MECCA chemistry predicts efficient activation of particulate Br- in all aerosol size fractions (e.g., Keene et al., 2009) and, thus, no significant Br enrichment of marine aerosol within the MBL. Our simulations produced these enrichments and suggest that they are driven by the complex cycling of Br species between the PBL and FT. In the model, significant amounts of relatively insoluble forms of Br_t are detrained from the MBL and accumulate in the FT whereas most of the highly soluble parent aerosol is largely confined to the MBL. Simulated Br cycling in the FT leads to enrichments in particulate Br relative to inorganic sea salt (i.e., EF(Br) > 1) throughout most of the FT (see Supplement Tables S1 and S2). Br accumulates in FT aerosols via two principal pathways:

1) Secondary Br- is formed via the oxidation of aqueous SO_2 (in the form of HSO_3^- and SO_3^{2-}) by HOBr.
2) HBr condenses onto newly formed and preexisting aerosol.

The subsequent transport and entrainment of condensed or condensable reaction products back into the PBL accounts for the Br enrichment of sub-µm aerosol size fractions measured within the PBL. The role of this dynamic process is evident in a slight but statistically significant ($p<0.10$) negative correlation between HBr and model vertical velocity (not shown). Within the PBL, the incorporation of secondary Br- into fine-mode particles formed via nucleation, and subsequent coagulation into accumulation-mode particles likely affects EF(Br) across the size distribution, as well. However, since the model does not distinguish between fresh and aged aerosols, the relative contributions of different pathways to simulated EF(Br) in the PBL cannot be quantified explicitly."

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.

We agree with the reviewer and have revised the original text starting on (Page 6096 Line 26) as follows:

“Despite some of the inherent limitations discussed above, estimated impacts of sea-salt derived Cl and Br on HO_x, NO_x, O_3, and S in the NH and the tropical SH are generally consistent with observations and thus provide useful context for planning future research efforts. In addition, large deviations between simulated and measured species over the high-latitude southern ocean point to important gaps in current understanding. For example:

> 1) The model’s prediction of observed phenomena like a BrO maximum in the Antarctic and Arctic free-troposphere, spring-time reactive Br explosions, and Br enrichments of PBL aerosols suggests a strong role for large-scale dynamics in halogen-cycling, yet very few speciated measurements of Br and Cl exist in the FT.
>
> 2) The large influence of halogen cycling in the SH-MBL, while likely over-estimated, highlights large uncertainties in current marine aerosol production flunctions and, more generally, air-sea exchange processes in energetic sea states.
>
> 3) Laboratory-based investigations into why BrCl emission is predicted but, based on very limited data, not observed, and what potential role organic reactions may play are important.

—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.

This line has been revised as follows:

“…which leads to the production of organic compounds that may contribute to aerosol production and growth…”

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 apressure above...).

In line 26, “between levels” has been removed from this sentence.
Line 29 now reads, “below an altitude corresponding to 867 mb”

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

The text has been corrected.

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

Per a prior comment, this section has been rewritten as indicated above.

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

This sentence has been changed to, "The coarse model resolution relative to such gradients in these regions limits the reliability of comparisons between observed and simulated values…"

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

Volcanic emissions are per the monthly-varying AEROCOM emissions database operating on a one-hour time-step, and cycle through the 2000 calendar year. This is not an historical simulation, so no specific eruptions are known to be included in the emissions. The reviewer is directed to Long et al., GMD, 2013 (and references therein) for details regarding emissions.

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-.

This section has been revised to clarify the point:

"Differences between aerosol pH in *Hal* versus *NoHal* simulations reflect the influence of HCl phase partitioning on aerosol solution acidity. Acid displacement of HCl by HNO_3 and other relatively more soluble acids that accumulated as marine aerosols age transfers acidity from the aerosol solution to the gas phase and thereby sustains higher solution pHs in the *Hal* simulation. Conversely, in *NoHal*, Cl is chemically inert, HCl does not volatilize as aerosols acidify with age, and, thus, acidity associated with condensed acids accumulates in the aerosol resulting in relatively lower pHs (not shown)."

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).

This sentence focuses specifically on the impacts of $ClNO_2$ and not N_2O_5. Text has been revised as follows to clarify this point:

"Thus, this pathway (R11→R12→R9→R10) acts as both a source for halogen radicals and a nocturnal reservoir for NO_x that efficiently extends its atmospheric lifetime and thereby enhancing O_3 production relative to that predicted in the absence of R9 and R10 (as in NoHal)."

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

The sentence has been changed as suggested.

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

The sentence now states, "…is one of the primary sources…"

p6094, line 21 – clarify "significant"

In response to the reviewer's comment, "significant amounts" has been removed from the sentence.

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.

The activation of halogen-radical precursors is acid catalyzed (e.g., Keene et al., 1998). In the absence of sufficient acidity to titrate marine alkalinity, strong winds that produce high concentrations of marine aerosols will not lead to significant halogen-radical chemistry. The text in question has been revised as follows to clarify this point:

"…The continued expansion of the human population and global-scale industrialization will certainly result in increased emissions of acids and acid precursors. Halogen activation and radical recycling is acid catalyzed (Keene et al., 1998). The results reported herein suggest that throughout most of the unpolluted Southern Hemisphere, halogen radical chemistry is already important. The increased acidification of marine aerosol in this region would lead to increased activation of halogen species with associated implications. It has been hypothesized that modest increases in acidity in this region would yield disproportionately large increases …"

p6096, lines 9-14 are awkwardly worded.

The text have been reworded:

"Although the feedbacks associated with changes in sea-salt emission associated with climate change cannot be assessed directly from this study, our results imply that they would be important. Available evidence suggests that greater sea-salt emissions is associated with greater Br activation and associated radical chemistry and influences on tropospheric composition."

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.

This line was erroneous and has been removed.

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?).

The purpose and context of this figure is with regards to BrO explosions at the poles. The caption has been revised as follows to clarify that the figure depicts the vertical column burden of tropospheric BrO

“Figure 4. Vertically integrated tropospheric BrO (10^{13} cm^{-2}) for the northern and southern hemispherices (NH, SH) polar regions, averaged over winter (DJF), spring (MAM; March-April-May), and summer (JJA).”

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".

The legend has been corrected.

p6128 Fig. 12 – clarify that "percent deviation" means Hal versus noHal
The text has been revised as recommended.