Responses to Reviewer #3 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 3:

Long et al present a unique global modeling study of the impact of halogen chemistry on tropospheric chemistry. Unlike previous model studies they explicitly model multiphase reactions in deliquesced aerosol particles. All previous global studies used a parameterized treatment of multiphase chemistry. Considerable effort and computing time have gone into these 10-year simulations. Overall, the results are very interesting but appear to (partly drastically) overestimate the impacts. This is likely caused by multiphase reaction cycles that are too efficient. This should have been pointed out and discussed more clearly and suggestions as to what the cause of this overestimate might be should have been made. It is surprising that the breakdown of organic bromine precursors was not included.

To me the real novelty of this study is to go beyond what has been done in previous studies in terms of process-level implementation of the underlying chemistry. However this should have been presented in a more critical way and discussed in more detail - and less optimistically - how this relates to observations. If presented somewhat differently I am sure that this study will serve to show in what direction research into the tropospheric impacts of halogens should go in the future.

Specific comments:
What is the actual reaction mechanism used in the model? This is never explained, the

supplement doesn't contain a listing of the reactions that are used. This definitely needs to be included to understand and evaluate the model results.

The information noted by the reviewer is provided in a companion paper to Long et al. GMD, 2013, wherein the model and chemical mechanism (included as a supplement) are described in detail. The text (Page 6072 Line 17) has been clarified.

Introduction: it is surprising that a brief overview of previous global model studies is missing. Several of these papers are not at all cited in the manuscript. To my knowledge the following are global model studies, that study the impacts of tropospheric halogen chemistry: von Glasow et al (2004), Lary et al (2005a,b), Yang et al (2005), Breider et al (2010), Saiz-Lopez et al (2012), Parrella et al (2012).

As indicated above, 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.

p. 6071, l. 25: Lawler et al 2011 present unique data regarding chlorine speciation in the MBL. One of the current authors is co-author of this study, yet this paper was not mentioned here or below where the chlorine results are discussed.

The following comparison of simulated to observed Cl speciation in the vicinity of Cape Verde has been added:
"Using a similar chemical mechanism and associated observations, Lawler et al. (2009, 2011) investigated Cl speciation in detail at the Cape Verde Atmospheric Observatory (17°N, 25°W). Our results, averaged over May and June model results for the 10-year period, were similar to the *clean* case reported by Lawler et al. (2009) and the *base* and *low-acid* cases reported in Lawler et al. (2011): Our average HNO_3, O_3, and NO_x were 34.5 ($\pm$7.9) pmol mol^{-1}, 24.8 ($\pm$2.5) nmol mol^{-1} and 55.7 ($\pm$12.1) pmol mol^{-1}, respectively. Cl, Cl_2, HOCl and HCl were 3.6 ($\pm$ 1.0) x 10^5 cm^{-3}, 15.8 ($\pm$4.4) pmol mol^{-1}, 2.4 ($\pm$1.2) pmol mol^{-1}, and 683 ($\pm$210) pmol mol-1, respectively. Our simulated HCl is relatively higher but within the range of their observations for the unpolluted MBL. Our simulated atomic Cl in is also higher than that simulated by Lawler et al. (2009- *clean* case; 2011-*base* case), but it's dominant source in our model is BrCl photolysis. Simulated BrCl mixing ratio was 4 pmol mol^{-1} in Lawler et al. (2009), but were not reported by Lawler et al. (2011) and it is unclear if BrCl was considered in their model calculations. However they observed no BrCl above the estimated detection limit of 2 pptv, which are lower than our median simulated mixing ratio for this grid cell of 17.9 ($\pm$3.1) pmol mol^{-1}. Cl_2 (multiplied by a factor of 2 to account for diel cycling in the tropics) was between the *newsource* and *ns+lowacid* cases in Lawler et al. (2011)."

p. 6073, l. 15-17: How are stratiform clouds treated?

This information is detailed in the cited description of CAM (Gent et al., 2009).

Section 3: A discussion as to how modal-CAM-Chem (without halogens) would have been very helpful to assist the reader to put the results with halogen chemistry into context.

We point out that we are *not* using CAM-Chem, but an independently coupled multiphase chemical mechanism that leverages modal-CAM's size-resolved aerosol scheme. A detailed description of the model coupling and chemical scheme are reported in a companion paper (Long et al., GMD, 2013).

p. 6078, l. 2: You probably mean "upper troposphere" as this paper is not about the mesosphere and beyond...

The text has been revised as recommended.

p. 6079, l. 8: Delete "above the surface".

The text has been revised as recommended.

p. 6079, l. 11: "moded" ◊ "modeled"

The text has been corrected.

p. 6079, l. 15/16: I think this conclusion is a bit optimistic given that this is based on 2 studies only.

We agree and have changed the word 'demonstrates' to 'suggests'. The reproduction of large-scale observations is of particular importance in the context of global-scale halogen cycling.

p. 6080, l. 12-18: While this explanation is plausible it would have been good to see some quantification or other support for it. Are there any field data that can be used to confirm this?

To our knowledge, there are no data that support this explanation outside of the consistent observation of Br enrichments in the MBL. Sufficient data are presented (in the supplement and throughout the text) to verify that the species involved in the enrichment pathways are present and capable of cycling in the manner simulated by the model. It should be emphasized that this is a large-scale dynamic process and thus difficult to quantify. We note in the discussion that this result points out the need for speciated Br observations in the FT.

Tables 4/5: I'm very surprised about the emphasis on Br atoms. The reaction of Br + O3 is not a sink for odd oxygen which should be the metric used here. Most of the produced BrO photolyses back to Br and O3.

Table 4 (now Table 5) is presented within the context of Br speciation, rather than within Br's role in O_3 and odd O cycling. Table 5 (now Table 6), on the other hand, is presented within the context of the role of halogens in the destruction of O_3, either direct or indirect.

p. 6084, l. 15-25: Thornton et al discuss in depth the mismatch between measured particulate chloride and ClNO2 and argue that rapid repartitioning of gaseous HCl is the actual source for ClNO2. What is the chlorine source in the model? Does repartitioning play a role?

As indicated in the methods section, all Cl in the model is produced in association with primary marine aerosol. HCl partitions with all aerosol size fractions based on its thermodynamic properties. In response to the reviewer's comment, the text has been revised to clarify this point at Page 6084 Line 18:

"The simulated distribution of $ClNO_2$ over N. America (Fig. 6) is also generally consistent with production patterns based on the GEOS-Chem model (Thornton et al., 2010). In all cases, the condensation of HCl sustained $ClNO_2$ production when Cl^- concentrations were low over inland continental regains consistent with recent observations (Young et al., 2013). $ClNO_2$ mixing ratios simulated by *Hal* are generally higher and extend over broader geographic regions downwind from continents relative those simulated by Erickson et al. (1999), and compare well with limited observations …"

p. 6084, l. 28: I didn't understand this adjustment.

For all species presented in this model, statistics are based on monthly averaged model output, which masks signals due diurnal cycling of photochemically active species such as $ClNO_2$. The adjustment due to day length accounts for the fact that $ClNO_2$ rapidly photolyzes during the daytime and, thus, accumulates to significant levels in the dark. This is described in detail starting on page 6082 line 2, within the context of BrO. To clarify this point, the text has been revised as follows:

"Simulated $ClNO_2$ mixing ratios within the corresponding grid cell, which like BrO were adjusted by a factor reflecting the season and latitude adjusted ratio of daytime to nighttime were 302 ($\pm$88.4) pmol mol^{-1} …"

p. 6085 Lawler et al (2011) presented unique data from Cape Verde regarding chlorine speciation. It is very surprising that this paper is not mentioned especially given that one of the current authors is co-author of this study.

As mentioned above, text comparing our results with these data has been added.

p. 6087, l. 19-20: I don't understand this statement/reaction sequence, please explain.

This sentence was a fragment of a re-write that was mistakenly included in the previous version. The revised text now reads:

"Second, the accelerated rate of NO_2 oxidation by halogen species (section 3.3.3) in combination with increased NO in the vicinity of high HO_2 mixing ratios and lower O_3, led to a net decrease in both OH and HO_2."

p. 6090: The discussion should include a discussion of ageing of sea salt aerosol and the related change in pH and hence in the importance of the reaction S(IV) + O3. This was explained in detail in Chameides and Stelson (1992, and other papers since, e.g. von Glasow 2006) and is key for the production of S(VI) in sea salt. Alexander et al (2005) included this very elegantly in a

global study.

In response to the reviewer's comment, the following text has been added to the manuscript on page 6090 starting on line 1:

"As for most other multiphase 3-D models, limitations in the capabilities of current high-performance platforms effectively preclude explicit evaluation of the chemical evolution of freshly produced particles as a function of age. Aerosols of each size fraction emitted during each time step are mixed with preexisting aerosols in that size fraction and the bulk composition adjusted accordingly. Freshly produced marine aerosol are alkaline but, in most marine regions, acids and acid precursors (SO_2, HNO_3, HCl, HCOOH, and CH_3COOH) are present at levels sufficient to titrate marine-derived alkalinity associated with all but the largest aerosols within tens of minutes after emission (e.g., Erickson et al., 1999). Consequently, in most marine regions, most aerosols in ambient air are acidic (e.g., Erickson et al., 1999; Keene et al., 2009). As a result, when fresh alkaline aerosols are mixed with preexisting acidic aerosols in the model, the fresh alkalinity is immediately titrated and, thus, chemical processes that are limited to alkaline conditions are not resolved. In alkaline aerosol solutions, oxidation of S(IV) by O_3 is the dominant source for nss SO_4^{2-}; rates are diffusion limited (Chameides and Stelson, 1992; Keene et al., 1998). SO_2 solubility and its associated aqueous-phase oxidation by O_3 decreases with increasing acidity and, consequently, this pathway becomes unimportant after the initial alkalinity has been titrated and pH drops (Chameides and Stelson, 1992; Keene et al., 1998). In most regions, the rapid acidification of fresh aerosol limits nss SO_4^{2-} production from S(IV) oxidation by O_3 (Erickson et al., 1999). However, in more remote regions where continental sources of acids are relatively less important and high wind velocities over long fetch sustain high fluxes of marine aerosols and associated alkalinity, such as the MBL over the high latitude southern ocean, the O_3 pathway may be relatively more important. Because our model structure does explicitly resolve S(IV) oxidation in freshly produced marine aerosol, simulated rates of SO_2 oxidation and nss SO_4^{2-} production reported herein are considered lower limits."

p. 6091, l. 1-5: I don't quite understand this, please explain more. I don't see how this difference should be responsible for the very pronounced differences between these studies.

From our perspective, differences between our results and those reported by von Glasow et al. (2002) are not as pronounced as the reviewer suggests. A direct quantitative comparison would require that we differentiate periods of clear and cloudy skies within a single set of results, which unfortunately we are not able to do. If we were able to quantify a partitioning between clear and cloudy conditions, our respective results would probably be reasonably similar. In response to the reviewer's comment, the section in question has been revised as follows:

"Differences between our results and those reported by von Glasow et al. (2002) were due in part to the inability to differentiate between cloudy and non-cloudy conditions in our monthly-mean model datasets whereas von Glasow et al. (2002) were able to explicitly differentiate processes under clear-sky and cloudy conditions."

General: The use of the word "deviations" is confusing. Please rephrase as "difference" or similar.

We appreciate the reviewer's preference. However, based on considerable discussion among authors this prior to initial submission, we prefer to retain the term *deviation*, which is explicitly defined in Eq. (1).

Table 3: Please explain the calculations in more detail/clarity, in the caption or in the text. Is "simulated" a 24h average? What does the ratio "day/night" show, is it the ratio of BrO at day to that at night?? How is the "estimated daytime mean" derived?

An explanation of the calculations is now clarified in footnotes to the Table 3 (now Table 4):
- [a] Maximum daytime values reported by Read et al (2008). Nighttime values were below detection limits (0.5 – 1.0 pmol mol-1)
- [b] Simulated values are based on averages of monthly-mean data output by CAM.
- [c] Since the simulated results are based on monthly means, and assuming BrO is close to zero during nighttime, the ratio of daylight hours to nighttime hours at the specified location and time is used to scale to a daytime BrO mean value.
- [d] Estimated daytime mean is the simulated mean multiplied by the day/night factor as described in foot-note (c)"

Figures 3 and 4 are too small.

Sept./Oct./Nov. (SON) has been added to Fig. 4 the figure has been revised. Font and graphics sizes have been increased for both Figures.

References:
- There are a lot of mistakes in the references. Some papers are referenced in a different way in the text as in the bibliography. Saiz-Lopez et al 2012 is referred to interchangeably as Saiz-Lopez et al 2011 or 2012. Von Glasow et al (2004) is referred to as "von Glasow (2004)" and "von Glasow et al (2004)" in the text but in the bibliography a different paper is cited (von Glasow and Crutzen, 2004).

References have been corrected.