Responses to Reviewer #1 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 1:

This paper presents a model study on the sensitivity of tropospheric chemical species to marine aerosol-derived inorganic chlorine and bromine. The simulated levels of some reactive halogen species are compared to selected observations and their associated impact, mainly driven by bromine, upon the oxidizing capacity in the troposphere is assessed. The simulated results presented here overestimate bromine levels by far over most of the global troposphere when compared with observations, and hence the suggested influence on O3, HOx, NOx and DMS is almost certainly unrealistic. The authors need to re-evaluate their computed bromine levels so that these are not a factor 2-6 higher than available observations, as reported here. Therefore, I cannot recommend this paper for publication.

Significant deviations between simulated and observed values point to important gaps in current understanding as described in this model. As explained in more detail in the revised manuscript, all other previously published global models of halogen chemistry include parameterizations that prescribe important features of halogen activation and cycling and most of these models do not evaluate some important chemical pathways. Consequently, it is difficult to ascertain whether the underlying behavior of these models is realistic. While we agree and so report in the manuscript that some features the simulated results are not consistent with observations, we disagree that such results do not warrant publication. We explicitly identify major deviations between simulations and observations, evaluate the potential cause(s), and emphasize the need for new research to address outstanding issues unequivocally.

A list of comments follows:

- Simulated bromine concentrations in the lower troposphere:

Table 2 shows a comparison of measured vs modeled total volatile Br. Except in the NE Atlantic the simulations presented here overestimate bromine loadings by a factor that ranges from 2.4 to 6.1 times the reported observations.

Table 3 compared measured and simulated BrO mixing ratios. Given the photochemical nature of the radical, reported BrO measurements would be representative of daytime levels. Overall, the simulations overestimate the measurements. This is particularly certain for the only long timeseries of boundary layer BrO in the tropics, at Cape Verde Islands (Read et al., Nature, 2008), where the observed daytime BrO levels are overestimated by a factor of 2.3.

As discussed in the corresponding section of the manuscript (age 6082 Lines 11 to 15), direct comparisons between point measurements and values averaged over grid cells are inherently problematic particularly for regions with strong gradients such as that within which Cape Verde lies. We agree with the reviewer that simulated daytime mixing ratios of BrO tend to be greater than observations and that the average of BrO mixing ratios simulated during daytime over the grid cell containing Cape Verde is 2.3 times greater than the corresponding average of measured mixing ratios. However, when associated variability is considered, the range in daytime measurements of BrO at Cape Verde (2.5 ± 1.1 or 1.4 to 3.6 pmol mol^{-1}) overlaps the corresponding range of simulated values (5.7 ± 2.4 or 3.3 to 8.1). These uncertainties indicate that averages for measured and simulated BrO at Cape Verde do not differ significantly.

Figure 5 shows the annual mean of PBL BrO mixing ratios. The annual BrO means range from 1 to 4 pmol mol-1 within the tropics. Assuming BrO remains close to zero at night, the approximate simulated daytime tropical annual BrO average (i.e. not peak daytime values) ranges from 2 to 8 pmol mol-1. If a 1 km boundary layer height is assumed, with no BrO in the free troposphere, this converts into a vertical column of approximately 2 x 1013 molecules cm-2. Satellite-derived tropospheric vertical columns (i.e PBL and FT) in the tropics report levels below 2 x 1013 molecules cm-2 (Theys et al., ACP, 2011).

The reviewer's estimate for the BrO vertical column (2x10^{13} cm^{-2}) is based on the maximum for the inferred range in daytime BrO simulated for the tropics (8 pmol mol^{-1}). In response to the reviewer's comment we added the following test starting at Page 6072 Line 16:

"The spatial median mixing ratio for simulated BrO in the tropics (including factor of 2 accounting for day/night ratio as the reviewer has done) was 2.7 (5x10^{-3} - 9.7; mean: 2.9) pmol mol^{-1} for the PBL and 0.14 (2x10^{-3} - 6.8 pmol mol^{-1}; mean: 0.53) pmol mol^{-1} for the FT. This corresponds to a median equivalent vertical column of approximately 0.7 x 10^{13} cm^{-2} for the PBL and 0.7x10^{12} cm^{-2} for the FT. The median total tropospheric column burden was 0.53x10^{13} (0.04x10^{13} – 1.3x10^{13}) cm^{-2} which, is below the 1.5x10^{13} cm^{-2} reported by Theys et al. (2011). Since the range was not reported by Theys et al., it is difficult to evaluate the satellite vertical columns relative to the range in our simulated results. "

Overall, the computed high reactive bromine levels, without including bromocarbons, reported here are not supported by available observations.

- Influence on ozone depletion in the troposphere:

Previous modeling studies using different well-established global halogen models have reported much lower ozone loss percentages due to bromine chemistry. von Glasow et al., ACP (2004) reported 12-18% of tropospheric ozone loss due to bromine chemistry. The global study of Yang et al., JGR (2005) reported 4-6% bromine-driven ozone reduction in the tropical troposphere. Saiz-Lopez et al., ACP (2012), which concerned only with the tropics, reported 6-20% ozone reduction in the tropical troposphere due to combined bromine and iodine chemistry. Recently, Parrella et al., ACP (2012) have reported a global 6.5% global reduction in tropospheric ozone. The simulations in this paper report reductions global tropospheric ozone of 65%, being around 40-60% in the tropics. Furthermore, this is achieved here without including in the model the bromine loading that would arise in the upper troposphere when considering the photochemical breakdown of short-lived bromocarbons.

It is unclear exactly what the reviewer means by “well-established” in the context of other global halogen models. As noted by Reviewer 3, “unlike previous model studies (we) explicitly model multiphase reactions in deliquesced aerosol particles. All previous global studies used a parameterized treatment of multiphase chemistry.” Reviewer 3 goes on to point out that our “process-level implementation of the underlying chemistry … will serve to show in what direction (such) research … should go in the future.” Because parameterizations used in previous studies typically correspond to highly simplified treatments, it is not necessarily surprising that our results diverge substantially. For example, von Glasow et al. (2004) prescribed generic sources of Br that are constrained based on concentrations of inorganic Br in the free troposphere as inferred from measurements of BrO and an assumed lifetime for inorganic Br of 1 to 2 weeks. They did not consider Br activated from marine aerosol and, for this reason, characterize “all related consequences for photochemistry (as) lower limits.” Thus, their reported reductions in O_3 due to bromine chemistry of “up to 18% in zonal, annual mean values and up to 40% regionally” should be viewed as minimal. Yang et al. (2005) adopt from the literature a wind-speed dependent production function for marine aerosol. Based on reported measurements of particulate Br^- depletions in ambient air, they assume that (1) at lower latitudes (30^o N to 30^o S), 50% of the Br^- production flux associated with marine aerosol is converted to Br_2 and, (2) at higher latitudes, a seasonally variable fraction (averaging 50% over the year) of particulate Br^- is activated. However, numerous measurements indicate typically greater Br^- depletions in ambient marine aerosol at both lower and higher latitudes (e.g., Pszenny et al., 2004, JGR; Keene et al., 2009, ACP; among others). In addition, this parameterization scheme does not consider radical recycling via multiphase pathways other than HOBr + Br^- in acidic solution and $BrNO_3$ hydrolysis. In this regard, box model calculations suggest that the production and processing of $ClNO_3$ is a major sink for NO_x and thus O_3, particularly in the topics (Keene et al., 2009). Consequently, the Yang et al. parameterization may underestimate the Br activation flux and associated impacts. In addition, to clarify one point, Yang et al. reported a 4% to 6% reduction in ozone averaged over the global troposphere (not the tropical troposphere as mentioned by the reviewer) and up to 30% reduction in the high-latitude southern troposphere. Saiz-Lopez et al.

(2012) "assume that the rate-limiting step (in halogen activation) is the uptake of inorganic halogen species onto aerosols." They utilized a parameterization reported by Ordóñez et al. (2012) based on prescribed uptake coefficients and branching ratios for production of Br_2, BrCl, and IBr. In a supplement, Ordóñez et al. discuss several inherent limitations in this parameterization scheme and state that explicit treatment of halogen activation "is out of the scope of this paper." In addition, no specific justification for the parameterization scheme (in particular, the assumed branching ratios) is reported in either paper although Ordóñez et al. indicate that these reactions are "needed to reproduce observed BrO in the marine boundary layer." Parrella et al. (2012) adopted the Yang et al. (2005) production parameterization scheme based on the assumption that 50% of marine-derived Br^- is activated and, perhaps not surprisingly, their estimated impacts on O_3 are similar to those reported by Yang et al. (2005). Potential limitations in this approach are the same as those noted above for Yang et al.

We can and do discuss our results in the context of the above studies. However, based on the above rationale, we would not characterize simulated results from these previous 3-D modeling efforts to be particularly reliable or "well-established" benchmarks against which our model calculations should be judged. As reported in the discussion paper and in a previous journal article (Keene et al., 2009, *ACP*), we recognize that the MECCA chemical scheme tends to overestimate rates of Br activation and cycling. However, this process-level scheme is not constrained by prescribed aspects of halogen activation and recycling processes. In response to the reviewer's comment (and as noted under "General Comments" above), we have added a new section that provides a more comprehensive evaluation of this issue. We have also added the following paragraph to the introduction (Page 6072 Line 11) and an associated table to better frame our work in the context of previous 3-D modeling efforts:

"Several previous 3-D modeling efforts have evaluated impacts of halogen cycling on climate-relevant atmospheric species. von Glasow et al. (2004) simulated influences of Br radicals produced from the degradation of generic bromine-containing organic precursors on chemical processes in the troposphere. However, that study did not consider Br activated from marine aerosol and, consequently, the authors characterized related consequences for photochemistry as lower limits. Yang et al. (2005) and Parrella et al., (2012) evaluated influences of inorganic Br originating from both marine aerosol and the photochemical degradation of organic precursors. Production from marine aerosol was based on the assumption that 50% of the associated Br^- is activated. However, measurements indicate that Br^- deficits relative to conservative sea-salt constituents integrated over particle size distributions often exceed 50% (e.g., Pszenny et al., 2004; Keene et al., 2009). In addition, these parameterization schemes do not consider radical recycling via multiphase pathways other than HOBr + Br^- in acidic solution and $BrNO_3$ hydrolysis. In particular, the production and processing of $ClNO_3$ is an important sink for NO_x thereby contributing to net O_3 destruction (Keene et al., 2009). Consequently, these studies may also underestimate the overall importance of Br chemistry. Saiz-Lopez et al. (2012) simulated impacts of Br, Cl, and I chemistry in the tropical marine troposphere based on the assumption that the rate-limiting step in halogen activation is the uptake of inorganic halogen species by aerosols. They utilized a parameterization based on uptake coefficients for Br, Cl, and I species and prescribed branching ratios for the associated production of halogen-atom precursors reported by Ordóñez et al. (2012). As acknowledged by Ordóñez et al. (2012), the reliability of this parameterization scheme is uncertain because it does not consider influences of important factors that regulate halogen activation and recycling including solution acidity (e.g., Keene et al., 1998) and depletion of particulate-phase halides (e.g., Fickert et al., 1999). The sensitivity of model performance to this parameterization scheme was not reported. No previous 3-D modeling efforts have simulated impacts of inorganic Br cycling on tropospheric chemistry based on a process-level treatment of the underlying multiphase transformations that regulate the activation and cycling of inorganic halogens. To provide context for subsequent comparisons between results reported herein and those from the previous modeling efforts summarize above, major aspects of halogen-radical chemistry that were considered in each study are summarized in Table 1."

The following sentence was also inserted into the subsequent paragraph (Page 6072 Line 17):

"This comprehensive chemical scheme explicitly evaluates the multiphase production and processing of inorganic Br and Cl."

Figure 9 shows two runs with vertical profiles of mean O_3 compared to boundary layer measurements. Although the agreement with observations is good, this may well be not for the right reasons: halogens destroy 20 ppbv of O_3 in this simulation. This is an order of magnitude larger O_3 destruction (i.e. approx. 2 ppbv) than what was measured at Cape Verde Islands when combining bromine with iodine chemistry (Read et al., Nature, 2008).

Certainly, some of this divergence between our results and those reported by Read et al. relates to the fact that the MECCA chemical scheme as currently configured tends to overestimate rates of Br cycling in marine air. However, as discussed in more detail by Keene et al. (2009), Read et al. evaluated influences of Br and I chemistry on O_3 based on comparison of model calculations with versus without halogen chemistry. For both sets of calculations, NO_x was constrained to the same measured mixing ratio. The formation and processing of halogen nitrates with halogen chemistry turned on accelerates the oxidation of NO_x significantly relative to the conventional HO_x/NO_x photochemical pathways (i.e., with halogen chemistry turned off). In effect, by holding NO_x constant for both sets of calculations, the authors added a greater amount of NO_x to the system at each time step with halogen chemistry turned on relative to that added with halogen chemistry turned off. Consequently, Read et al. evaluated only the direct destruction of O_3 via reaction with halogen atoms; they did not consider the large indirect impact of NO_x destruction on O_3. When both direct and indirect influences are considered, the data from Cape Verde suggest greater impacts of halogen chemistry on O_3 than inferred by Read et al. In contrast, our simulations, account for both influences, which contributes to the differences noted by the reviewer.

In Fig 7, the annual mean of PBL ozone reduction from 40S to 90S ranges from 80 to 100% in the Hal simulation. What are the simulated levels of PBL ozone in this area when including halogens? They must be very close to zero all year long.

Modeled O_3 mixing ratios in the PBL over the high-latitude southern ocean ranged from 2.0 to 25 nmol mol^{-1} with a median of 5.3 nmol mol^{-1} These simulated values are a factor of approximately two lower than corresponding observations. The most likely cause for these differences relates to overestimates of marine aerosol production fluxes under high-wind conditions over the SH. The following text has been added (Page 6095 Line 1) to address this issue:

“In contrast to the relatively good agreement between simulated and measured O_3 in other regions, comparisons in the SH MBL below 45°S indicate that the model systematically under-predicts O_3 concentrations by up to 93% (Figs. 7 and 10). As noted above, comparisons between simulated aerosol loadings and AOD over the high-latitude southern ocean (Jaegle et al., 2011) suggest that simulated aerosol production based on wind-speed-dependent parameterizations such as that used for this study (Long et al., 2011) and the associated impacts of halogen chemistry in this region may be too high. In addition, comparison of simulated aerosol concentrations south of 45°S with measured concentrations of marine aerosol (Prospero et al., 1989; Savoie et al., 1989, 1993; Arimoto et al., 1996) reveal consistent over-prediction by factors of 1.95 to 12.5 (not shown). Between 45°S and 80°S, modeled Br_t, Br, and Br_2 correlated strongly with sea salt mass (R^2 of 0.49, 0.77 and 0.42, respectively), which is consistent with the fact that that Br is controlled primarily by Br_2 emission from marine aerosol, its subsequent photolysis, and the cycling to Br via BrO self-reaction (Table 4). Based on the above, we infer that the primary caused for the over-predicted loss of O_3 due to halogen reactions in this region is an over-estimate of marine aerosol production.”

Influence on DMS: This study reports a reduction of DMS of a factor of 5 when including halogens. Would this agree with DMS observations? A recent report by Breider et al., GRL (2010) have suggested an annual decrease of 16% in the DMS levels. In this reviewer’s view, the overestimation of bromine in the model is most likely due to an over efficient halogen-marine aerosol recycling mechanism. This in turn has inevitably led to the abovementioned unrealistic overestimations in the impact of this chemistry on the oxidizing capacity of the troposphere.

This is an important point, and it is likely that some of the DMS influence is an over-prediction due to an over-efficiency in Br cycling. But, we have added a discussion to the text (Page 6095 Line10) outlining our argument that the likely cause for an over-estimation of halogen’s influence on DMS is too much sea-salt emission in the high southern ocean.

”As with O_3, it is likely that the estimates of DMS and S(IV) oxidation in the high southern latitudes is overestimated due primarily to an overestimation of sea-salt emission, and subsequent activation of associated halogens. A decrease in sea salt emission of 40%, per estimates by Jaegle et al. (2011), yielding a proportional decrease in available reactive Br and Cl would reduce this impact by approximately a factor of two.”

We also note that our mechanism permits an indirect influence on DMS oxidation via reductions in both OH and NO_3, both of which is not accounted for in Breider et al. (2010). Halogen cycling resulted in an approximate factor of 5 decrease in both NO_3 and OH, which if linearly accounted for in DMS oxidation, would diminish the relative impact of BrO + DMS as a DMS sink. Overall, we feel that this is a major point of this study: That indirect pathways (e.g. via impacts on HO_x and NO_x partitioning) are an important and unaccounted for factor in assessing halogen cycling