

Interactive comment on “Latitudinal variation in the multiphase chemical processing of inorganic halogens and related species over the eastern North and South Atlantic Oceans” by W. C. Keene et al.

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Authors response to comments by Anonymous Reviewer 1

We thank the reviewer for his/her their thorough evaluation and constructive recommendations for improving the manuscript. Paraphrased versions of the comments (in italics) and our responses to each are listed below.

The indicated page, line, figure, and table numbers refer to the original version of the manuscript.

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General Comments:

Manuscript is unnecessarily hard to read. Re-write to avoid repetition and unnecessary details.

As described below in response to more specific comments, the manuscript has been revised to improve readability.

Is there a treatment of trace gas exchange between the FT and the MBL?

The composition of the FT and the corresponding strength of the inversion were not characterized during the campaign and, consequently, the exchange of material between the FT and the MBL along the cruise track was largely unconstrained by observations. The entrainment flux of O₃ was specified as described in Section 2.5 (page 11,899, lines 23–24). The approaches used to parameterize exogenous sources (including but not limited to entrainment from the FT) for oxidized N, non-sea-salt S, and NH₃ are described explicitly in Section 2.5 (page 11,901, line 2 through page 11,902, line 6). In response to the reviewer’s comment, we have added the exogenous source fluxes to Table 2. We have also added the following statement regarding CH₄ to Section 2.5 (page 11,899, starting on line 24):

“Mixing ratios of CH₄ were held constant (i.e., exogenous sources were assumed equal to internal sinks).”

Results for the N-AFR regime differ from previously published work [Read et al., 2008]. O₃ simulated destruction is larger than reported by Read et al. How do author explain discrepancies between simulated and measured O₃?

Possible explanations for divergence between simulated processes related to O₃ in our study relative to those reported by Read et al. (2008) are discussed in the original manuscript. For BrO, see page 11,914, lines 2 to 15. For OH and HO₂, see page 11,914, line 26 through page 11,915, line 11. For Br activation and cycling see page 11,924, line 14 through page 11,925, line 2 and page 11,926, line 25 through page

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11,927, line 8.

Possible causes for divergence between simulated and measured O₃ are discussed on page 11,915, lines 12 to 25.

Have the authors carried out sensitivity runs on the combined impact of O₃ depletion of bromine, chlorine, and iodine chemistries? Considering the predicted O₃ destruction of 63 percent with bromine and chlorine, does the inclusion of iodine lead to close to total O₃ destruction in the current model configuration?

As indicated on pages 11,914 and 11,915 (line numbers cited above), the concentrations and turnover rates of sea salt in the N-AFR simulation were substantially greater than those at Cape Verde and, consequently, it is reasonable to expect that chemical processes involving Br would have greater influences on O₃ in our N-AFR simulations relative to those inferred by Read et al. based on observations at Cape Verde. In addition and as described in the manuscript (page 11,914, line 26 through page 11, 915, line 11), Read et al. did not consider the large indirect influences on HO_x/NO_x photochemistry associated with the formation and processing of halogen nitrates. Other factors that contribute to differences between the two studies are also discussed in the above mentioned section of the manuscript. Consequently, results of the two studies are not directly comparable in terms of either the nature of the chemical regime or the underlying processes that were evaluated.

We point out in the manuscript that the absence of iodine chemistry represents an important source of uncertainty in our simulations and agree with the reviewer that sensitivity runs to evaluate processes involving iodine would be a useful contribution to the literature. However, because no iodine species were measured during this campaign, no observational constraints are available and, consequently, the simulations would be largely exploratory and their interpretation rather speculative. In addition, the manuscript is already quite long. Adding more model results and associated interpretations would increase length further and, in our view, dilute the primary focus on

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evaluating observationally constrained components of the multiphase system.

Recognizing the importance of a more detailed evaluation that includes processes involving iodine compounds, we have initiated plans to collaborate with investigators affiliated with the Cape Verde Observatory in a study that incorporates our modeling approach parameterized with the more comprehensive suite of observations generated during the summer 2007 and 2009 field experiments at the observatory. This effort would also draw on a subset of our measurements from the portion of the Polarstern cruise in the vicinity of Cape Verde. From our perspective, this more rigorous approach would generate results considerably more useful than those from an essentially unconstrained sensitivity study.

The authors mention that halogens in their N-AFR simulations lead to lower OH values, 5 percent to 12 percent with respect to the “no halogens” run and in disagreement with calculations by Read et al. Could this effect be the result of the significant difference between the halogen-catalysed O₃ depletion as predicted in both paper?

As described in the manuscript (page 11,914, line 26 through page 11, 915, line 11), we attribute these differences primarily to the fact that Read et al. did not consider the influences of halogen nitrate formation and processing on the lifetime of NO_x. If NO_x mixing ratios had been held constant in our “with halogens” versus “no halogens runs” (as they were by Read et al.), our results would have more similar to those reported by Read et al.

In general, the authors should be more cautious regarding statements on the effects of halogens (bromine and chlorine only) on the chemistry, for instance on HO_x, considering the unrealistically large O₃ depletion rates calculated here.

We do not assume that the simulated results are fully representative of ambient conditions. Indeed, we point out explicitly that the model does not accurately capture some important measured characteristics of the multiphase system and, consequently, we infer that the simulated influences of Br on oxidation processes probably represent up-

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per limits (see for example the Method Section, page 11,902 lines 16 to 24; Results and Discussion, page 11,924, line 14 through page 11,925, line 2; and Summary and Conclusions, page 11,926, line 25 through page 11,927, line 8). In response to the reviewer's comment, we also added the following text (in italics) to the abstract.

“Measured particulate Br⁻ (median enrichment factor = 0.25) was greater and volatile inorganic Br less than simulated values suggesting that the halogen activation mechanism in the model overestimated Br-radical production and associated influences.”

The fact that some key observations are not consistent with predications based on current models indicates an important gap in our understanding of halogen-radical chemistry in marine air as implemented in these models.

Minor Comments:

Page 11,893, line 4: “(but not others,” ?? please correct.

The text has been changed to, “. . . in some coastal regions (e.g., O'Dowd et al., 2002) but not in others (e.g., Russell et al., 2007) . . .”

The definition of Cl is given on page 11,907, please define at the beginning of the manuscript.*

The modeled species that were summed to yield simulated mixing ratios of Cl* are defined on page 11,903. The species that have been demonstrated experimentally to contribute to measured mixing ratios of Cl* are specified on page 11,894, line 27. The text on both pages has been revised to clarify this distinction:

Mentioned to Fig. 2a, b, c, d, etc. is made across the manuscript and Fig. 2 caption however the letters are not written on the plot.

The letter designator is depicted in the upper right corner of each panel.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 11889, 2009.

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