

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.

Anonymous Referee #2

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This paper reports measurements of inorganic halogens in the gas- and aqueous-phase during a cruise in the eastern Atlantic Ocean. The results of a box-model study are used to interpret the measurements and investigate the chemistry of chlorine and bromine in the marine boundary layer. Simultaneous observations of these species in both phases, under different conditions and on regional scale, are needed in order to understand the proper role of halogens in the marine troposphere. Therefore the subject of the paper is appropriate for publication in ACP and would advance our understanding of these processes. However the paper is somewhat difficult to read and

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sometimes the relevant information is hard to extract. I do recommend that the paper is published in ACP, provided that the authors address the following issues:

GENERAL COMMENTS

- I suggest that some parts of the manuscript are rewritten in order to make the paper easier to read and understand. Section 3, in particular, should be reorganized so that the discussion of the measurements, the model/measurements comparison and the results from each model (with and without halogens) are clearly separated. The section could also benefit from some reduction in the text, for example by using tables to present the model/measurements comparison - see below. The objectives of the modelling study should also be declared explicitly.
- Since a large part of the manuscript is based on the mist chamber measurements - and even though the instrument has been described in other papers - some more detail should be given in section 2.2.1. It should be described more clearly how many chambers there were (four?), what was measured in each one (two measuring HCl and HNO₃, one measuring Cl* and one Cl total?), what was the sampling interval (sampled for 2 hours or every 2 hours?) and how often were the filters changed. Besides, the collection efficiencies, precisions and detection limits should be given for each species/parameter, and not as a range, and it should be specified whether the data were corrected for the sampling efficiency and the filter.
- Section 2.4 describes the calculation of aerosol pH, dry-deposition fluxes of aerosol and emissions of particulate Cl and Br. Were these calculations used to parametrize the box-model as described in the following section (and shown in Table 2)? If so, this should be stated clearly. Also, in section 3 it is stated several times that the emissions of sea-salt Br and Cl are approximately balanced by the dry deposition fluxes. If the emissions were calculated from the dry deposition fluxes, this is not surprising. If these calculations were not used in the model, then it should be specified that the comparison is between the model-calculated values and the values calculated as described in

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section 2.4. The same clarification is needed when discussing the particle pH (e.g. on page 11907).

- During the discussion of each regime it is mentioned that iodine chemistry was not included in the model, although it might be important. While the exclusion of iodine is probably due to lack of sufficient information during this particular cruise, iodine oxides have been measured in the eastern Atlantic and some discussion of how their presence might affect the paper's main conclusion seems necessary. Sensitivity runs are mentioned on page 11910, but only with reference to HNO₃/NO₂ and not many details are given. Also, it is mentioned on page 11915 that rates of O₃ entrainment could be underestimated in the model. Was the sensitivity of the model to this parameter assessed? Could the author please add some quantitative detail about the sensitivity analysis performed and comment on the potential impact of iodine chemistry.

- The comparison between the model and the measurements is mostly done in the text citing the medians of measurements. For example on page 11906 it is stated that HNO₃ was within the range measured and the median is given. Sometimes the range of measurements is given (e.g. for HCl on the same page), which is more appropriate when comparing the model to the measurements. Please always give the range, and the median only where necessary. A table similar to Table 3 with the measured medians, averages and ranges, would make the manuscript easier to read and less wordy and facilitate the comparison with the model. Also, maxima and minima of some measurements are sometimes mentioned, without giving the numbers, and referring instead to the relevant figure (e.g., page 11911, lines 20-22, and elsewhere in the manuscript). Please state the numbers where appropriate.

SPECIFIC COMMENTS

- The authors describe four regimes encountered during the cruise, but there is no mention of the variability within each regime. For example, some of the trajectories identified as N-AFR clearly originated in Europe (Fig. 1), which presumably had some

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influence on the composition of the air masses. Some comment about this might be added to the paper.

- It is mentioned in section 2.5 that the model contains the oxidation mechanism of NMHCs, but it is not specified how many and which ones. From the information in the supplement it seems only DMS was included. This should be clarified.

- Also, in section 2.5 it is stated that the model is parametrized to the median values of some measurements. Does this mean that the model is constrained to the measured medians values, or that these medians are the initial values? Also, NO₂ has an "assumed value" of 2e-11 mol/mol. Since this parameter is important for the following discussion, it should be specified how this assumption was made (literature, perhaps?).

- The model is set to a median MBL depth, but in a previous section it is said that the MBL depth is estimated using a variety of measurements. It should be clarified whether the estimates were used only to obtain a campaign median value and, if this parameter has a significant effect on the model results, what was its variability.

- page 11917 (line 16) and on page 11920 (line 18): these statements are rather generic. Please add more quantitative information.

TECHNICAL CORRECTIONS

- In several places in the manuscript "physiochemical" should be replaced with "physico-chemical".

- In the abstract, line 12: "to the low 4 s for ITCZ"?

- page 11893, line 8: "importance, reactive halogens".

- page 11897, lines 1-3: This paragraph is a bit convoluted. It is stated that with the exception of size resolved concentration of Br⁻, data for Br⁻ are based on bulk samples. Please rephrase this sentence.

- page 11897, line 14 (and elsewhere), please use GMT or UTC, instead of Z.

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- page 11899, line 6: please change "transformations" to "reactions".
- figures 4, 5 and 6: please state more clearly which of the plotted parameters were measured and which calculated and/or modelled.

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

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