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Atmospheric
Chemistry
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Discussions

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 2

We thank the reviewer for his/her 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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The paper is somewhat difficult to read and sometimes the relevant information is hard to extract.

As described in more detail above and below, the manuscript has been revised to improve readability.

General Comments:

Some parts of the manuscript should be rewritten in order to make the paper easier to read and understand. Section 3 in particular should be reorganized so that the measurements, model/measurement comparisons, and results from each model (with and without halogens) are clearly separated. Reduce text by using tables to present model/measurement comparisons. The objective of the modeling study should also be declared explicitly.

In response to the reviewer's recommendation, we have reorganized Section 3. Because ACP allows only "three levels of sectioning . . . e.g. 3, 3.1 and 3.1.1," we eliminated the original title for section 3.2 (Multiphase MBL Composition and Processing) on page 11,903, line 18 and consolidated lines 19 through 24 with Section 3.1. The new Section 3.2 is now entitled European Influenced, Section 3.3 is North African Influences, and so on. Subsections discussing measured characteristics (e.g., 3.2.1) and simulated characteristics (e.g., 3.2.2) are now differentiated. However, we feel that it would be most efficient to compare model results with measurements and to compare model results both with and without halogen chemistry in the same subsection. In our view, partitioning this material into separate subsections would be cumbersome and inefficient. As recommended subsequently by reviewer 2, we have also consolidated summary statistics (medians and ranges) for major analytes into a new table to facilitate comparisons with the simulated results. The original Table 2 has been revised accordingly to eliminate redundancy. Finally, we have revised the beginning of Section 2.5 (starting on page 11,899, line 2) to explicitly state the objective of the model calculations.

Describe mist-chamber measurements in greater detail. How many chambers were used and what was measured in each? What was the sampling interval and how often were filters changes? Give collection efficiencies, detection limits and precisions for each species. Specify whether data were corrected for sampling efficiency and the filter.

The text in section in Section 2.2.1 (starting on line 7) has been revised to more clearly describe the mist-chamber sampling system. Briefly, HCl, HNO3, NH3, HCOOH, and CH3COOH were sampled with a single set of tandem mist chambers each of which contained deionized water. Cl* was sampled in a single set of tandem mist chambers, which contained acidic (upstream) and alkaline (downstream) mist solutions. Total volatile inorganic Cl was sampled in a single set of tandem mist chambers each of which contained alkaline mist solution. As indicated on page 11,894, lines 7 to 8, air "was sampled over two-hour intervals." In-line filters were changed daily. The average detection limit for each analyte has been added. Relative precision varied as a function of concentration so only typical ranges are reported. Because collection efficiencies were close to 100 percent, corrections for inefficient sampling were not needed. There is no correction associated with the filter.

Section 2.4 describes the calculation of aerosol pH, dry deposition fluxes of aerosols, and emissions of particulate Cl and Br. Were these calculations used to parameterize the box-model calculations? If so, this should be stated clearly.

As descried in Section (2.4) and depicted in Figure 3, size-resolved pHs were calculated directly from the measured phase partitioning of HCl. The legend for Figure 3 has been expanded to clarify that the pHs depicted in panels h and p correspond to those inferred directly from measurements. In addition, as discussed in both the Results and Discussion section (see for example page 11,907, lines 3 to 28, among others) and Summary and Conclusions section (11,926, lines 6-8) and depicted in Figure 9, size-resolved aerosol pHs were also simulated independently in the model; the legend for Figure 9 has been revised to clarify that the plots depicted simulated results. The size-

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resolved pHs that were inferred directly from the measured phase partitioning of HCl were not used to parameterize the model. As indicated in Section 2.5 (page 11,899, line 25), "The model was initialized with externally mixed populations of unreacted sea salt . . ."

As described in Section 2.5, the calculated dry-deposition fluxes were used to parameterize the model. In response to the reviewer's recommendation, we added the following statement to the end of Section 2.4 to emphasize this point:

"As described in detail below, the dry-deposition fluxes of size-resolved aerosols and soluble gases calculated from measurements based on the above approaches were used to parameterize turnover rates for aerosols and exogenous source strengths for N and S gases in the model."

We have also revised all figure legends to explicitly indicate whether the corresponding plots depict measured, directly calculated, or simulated results.

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. Of 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 section 2.4. The same clarification is needed when discussing the particle pH (e.g., on page 11,907).

Under steady-state conditions in the absence of precipitation, the size-resolved emissions fluxes of Cl- and Br- associated with sea-salt aerosol can be inferred directly from the corresponding calculated dry-deposition fluxes of conservative tracers such as Na+ and the respective sea-salt ratios. However, the dry-deposition fluxes of total (volatile + particulate) inorganic Cl and Br do not necessarily scale directly with the corresponding emission fluxes of particulate Cl- and Br- as suggested by the reviewer. For example, in the S-ATL regime, the aerosol was substantially debrominated (median EF(Br-) = 0.14) and volatile inorganic Br (Brt) dominated the dry-deposition flux of total (volatile

+ particulate) inorganic Br (see Fig. 6). The dry-deposition flux of Brt was calculated from the measured Brt mixing ratios, meteorological conditions, and surface-ocean temperature based on Valigura [1995]. With the exception of common meteorological variables (wind velocity, temperature, and relative humidity), the corresponding size-resolved particulate Br- emissions were calculated completely independently based on the measured size-resolve Na+ concentrations following Hummelshøj et al. [1992]. The fact that the median emission flux of particulate Br- and the correspond deposition flux of total (volatile + particulate) inorganic Br are approximately equal indicates that the measurements and the flux calculations are internally consistent and, thereby, supports the hypothesis that sea-salt production was the dominant source for inorganic Br in this regime. In response to the reviewer's recommendation, the phase "calculated as described in Section 2.4" has been added to the legends for Figures 5 and 6.

Iodine chemistry is not included in the model, although if might be important. Some discussion of how their presence might affect the papers main conclusion seems necessary. What was the sensitivity of the model to iodine chemistry and O3 entrainment? Please add details about the sensitivity analysis that was performed.

We explicitly point out in the manuscript that a number of poorly constrained factors (including I chemistry and O3 entrainment) introduce uncertainty into the simulated results (for example, see page 11,902, lines 16 to 24; page 11,910, lines 18-21; page 11,915, lines 16 to 25). As described above in response to a similar comment by Reviewer 1, we consider a detailed evaluation of the sensitivity of results to largely unconstrained factors to be beyond the scope of this study. Also, as indicated above, we think it more appropriate to investigate these and related factors in the context of a follow-up study based on a broader ensemble of measurements that include iodine species.

In response to the reviewer's recommendation to add additional details regarding the sensitivity runs, the following statement was added to page 11,902, starting on line 15:

“In addition to the primary simulations described above, the model was run over ranges of conditions to evaluate the sensitivity of results to (1) the approach employed to vertically scale size-resolve aerosols and (2) variability in the ratio of HNO3 to NO2 in the source term. Results of these runs are briefly discussed where appropriate below.”

The comparison between the model and the measurements is mostly done in the text citing the medians of measurements. Sometimes the range of measurements is given, which is more appropriated when comparing the model to the measurements. Please always give the range and the median only when necessary. A table similar to 3 with the measured medians, averages, and ranges would make the manuscript easier to read and less wordy. Also, maxima and minimum of some measurements are sometimes mentioned without giving the numbers and referring instead to the relevant figure. Please state the numbers where appropriate.

As recommended, a new Table reporting medians and ranges of conditions for each regime has been added and cited as appropriated in the text. Table 2 has also been revised to eliminate redundancy.

Specific Comments:

Add comment about how variability in transport within each regime influenced composition of the air masses.

In response to the reviewer’s recommendation, we revised the text on page 11,903, lines 19 to 22 as follows:

“The major physicochemical characteristics of MBL air along the cruise track (Fig. 2, 3, [Williams et al., 2007]) varied substantially *both within and* among transport regimes as functions of upwind emissions of precursors, length and duration of fetch over the ocean, associated meteorological drivers (primarily wind velocity and RH), and chemical processing.”

It is mentioned in Section 2.5 that the model contains the oxidation mechanism for

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NMHCs, but it is not specific how many and which ones. From the information in the supplement it seems only DMS was included. This should be clarified.

In response to the reviewer's recommendation, we revised the text on page 11,899, lines 8 to 9 as follows:

"Because iodine and NMHC species were not measured during the cruise, their reactions were switched off for these simulations."

Section 2.5 states that the model is parameterized to the median values of some measurements. Does this mean that the model is constrained to the measured median 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?).

Table 2 has been revised to differentiate between parameterization of the model and initialization of conditions. The text in Section 2.5 was also revised accordingly. As described later in Section 2.5 (page 11,901, lines 2 to 29), the model includes exogenous sources for NO2 so the initial mixing ratio had no influence on dynamics of the system at steady state.

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?

Median MBL depths for each regime have been added as a footnote in Table 2. As indicated in the text, "to minimize sources of variability among results for different regimes, MBL depth for each simulation was set to the median value for the entire cruise." Because aerosol turnover rates vary as functions of MBL depth, adopting a constant depth for all regimes influenced these rates. Although the sensitivity to this parameterization was not evaluated explicitly, we do not believe that it influenced results substantially.

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Page 11,917 (line 16) and on page 11,920 (line 18): These statements are rather generic. Please add more quantitative information.

The first statement has been changed to, "Cl- concentrations associated with the smallest aerosol size fraction in the EURO regime (median of 0.8 nmol m-3; Fig. 3j) were near the average detection limit (1.0 nmol m-3), which contributed to large uncertainties in estimating pHs for this size fraction based on HCl partitioning."

The second statement has been changed to, "Cl2 peaked at 2.0 pmol mol-1 and accounted for 12 percent of Cl* before dawn (Fig. 8)."

Technical Corrections

Change physiochemical to physio-chemical.

According to *Webster's Ninth New Collegiate Dictionary*, the correct word is "physicochemical", which is not hyphenated. The text has been revised.

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

The text has been changed to "($\sim$3.0 for EURO to $\sim$4.5 for ITCZ)."

Page 11,893, line 8: "importance, reactive halogens".

The text has been changed to "Despite the potential importance of reactive halogen chemistry . . ."

Page 11,897, lines 1-3. This paragraph is a bit convoluted. Rephrase to clarify.

This section (including the preceding sentence) has been revised as follows:

"Reported concentrations of total particulate Br-, Na+, and nss SO42- are based on aerosol sampled in bulk. Because they are not conservative in bulk samples, reported concentrations of total particulate Cl-, NO3-, and NH4+ are based on values summed over all size fractions sampled with the cascade impactor."

Additional Changes

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Simulated ClNO2 mixing ratios and relative importance of ClNO2 photolysis as a source for atomic Cl have been added to Table 3.

The major sources and sinks for OH and HO2 and the other major sinks for O3 have been added to Table 3. Text elaborating on the nature of differences in OH and HO2 between the 'with halogens' and 'no halogens' runs has been added to Section 3.

The description of the model in the supplemental material has been revised to more clearly distinguish between aqueous-phase and heterogeneous reactions.

Other minor revisions have been implemented to clarify the presentation and several typos have been corrected.

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

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