Multiphase Halogen Chemistry in the Tropical Atlantic Ocean

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ABSTRACT: We used a one-dimensional model to simulate the chemical evolution of air masses in the tropical Atlantic Ocean, with a focus on halogen chemistry. The model results were compared to the observations of inorganic halogen species made in this region. The model could largely reproduce the measurements of most chlorine species, especially under unpolluted conditions, but overestimated sea salt chloride, BrCl, and bromine species. Agreement with the measurements could be improved by taking into account the reactivity with aldehydes and the effects of dimethyl sulfide (DMS) and Saharan dust on aerosol pH; a hypothetical \( \text{HOX} \rightarrow \text{X}^- \) aqueous-phase reaction could also improve the agreement with measured Cl\(_2\) and HOCl, especially under semipolluted conditions. The results also showed that halogens speciation and concentrations are very sensitive to cloud processing. The model was used to calculate the impact of the observed levels of halogens: Cl atoms accounted for 5.4–11.6% of total methane sinks and halogens (mostly bromine and iodine) accounted for 35–40% of total ozone destruction.

INTRODUCTION

The tropical marine boundary layer (MBL) is a region of particular interest for atmospheric chemistry: high levels of solar radiation, along with high temperatures and relative humidities, result in a highly oxidizing environment. It is estimated that the tropical atmosphere accounts for up to 80% of the global oxidation of methane (the second most important greenhouse gas) and that ~25% of the global oxidation of methane occurs in the tropical MBL.1 Halogen species (chlorine, bromine, iodine) are known to play an important role in the chemical processes of the MBL, particularly with regard to the nitrogen and ozone cycles, sulfur chemistry and particle formation: an overview of halogen chemistry and its impact on atmospheric chemical processes can be found in ref 2. Measurements of these species in the tropical region are sparse, but a number of recent studies3–13 have reported observations of several halogen species in the tropical Atlantic Ocean. These studies suggested that halogen chemistry is responsible for a large fraction (~30%) of ozone destruction in the Tropics6 and up to 7% of the global methane destruction.9

In this paper, we used the one-dimensional chemical model MISTRA to study halogen chemistry in the tropical Atlantic Ocean and the evolution of the chemical composition of air masses traveling across the ocean to the islands of Cape Verde, 900 km West of the coast of Africa. We compared the model results to the database of published observations of halogen species from this region with the objective of testing our understanding of halogen chemistry and of quantifying the impact of the observed halogens levels on ozone (O\(_3\)) and methane (CH\(_4\)).

METHODS

Model. MISTRA is a one-dimensional model of the MBL. The model includes a description of meteorological and microphysical processes in the MBL and is described in detail in refs 14 and 15. Version 7.4.1 of MISTRA includes a number of improvements over the previous version,16,17 particularly with regard to the gas-phase chemical mechanism; the aqueous-phase mechanism was the same as in ref 17. Details of the model and of its setup, together with a list of the gas-phase reactions, are provided in the Supporting Information.

The model was run in Lagrangian mode (i.e., following an air mass) for five days under different scenarios; the first two days were used as spin-up time and therefore discarded from the analysis of the results. The model scenarios were developed by applying cluster analysis to the back-trajectories of air masses arriving at the Cape Verde Observatory (CVAO, see below) and to the measurements of gas and aerosol chemical markers at CVAO.18,19 The back-trajectories were calculated by the British Atmospheric Data Centre (http://badc.nerc.ac.uk/) and
the average chemical conditions of each scenario are shown in Table 1. The scenarios represent the following:

**LOCAL:** Air masses slowly moving around Cape Verde at low altitude; rich in sea salt, poor in ozone precursors.

**OCEAN:** Air masses from the Northwest that have been over the Atlantic Ocean for five days or more before arriving at Cape Verde.

**AMERICA:** Fast-moving oceanic air masses which originated over North America and arrived at Cape Verde traveling at high altitude; still contained ozone precursors, but depleted in NO$_x$ (= NO + NO$_2$). Some spring-time air masses from Europe had similar chemical composition.

**EUROPE:** Air masses from Europe (typically in summer) or from Northwestern Africa (via the Iberian peninsula) arriving at Cape Verde traveling along the African coast; contained comparatively high levels of ozone precursors and acid gases (HNO$_3$), sometimes Saharan dust.

**AFRICA:** Air masses from Northwestern Africa and Sahara arriving at Cape Verde from the East (typically in winter); contained Saharan dust and comparatively high levels of ozone precursors. The increase in the MBL height from the coast to the ocean caused the formation of clouds in the model.

### Table 1. Average Mixing Ratios of Selected Species in the BASE Scenarios (CO and O$_3$ in ppb, All Other Species in ppt)

<table>
<thead>
<tr>
<th>species</th>
<th>LOCAL</th>
<th>OCEAN</th>
<th>AMERICA</th>
<th>EUROPE</th>
<th>AFRICA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>105</td>
<td>110</td>
<td>150</td>
<td>130–140</td>
<td>130</td>
</tr>
<tr>
<td>O$_3$</td>
<td>25</td>
<td>30</td>
<td>40</td>
<td>35–40</td>
<td>35</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>15</td>
<td>20–25</td>
<td>15–20</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>60</td>
<td>20</td>
<td>15</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>ethene</td>
<td>450</td>
<td>500</td>
<td>1200</td>
<td>750–1000</td>
<td>1050</td>
</tr>
<tr>
<td>ethene</td>
<td>20–30</td>
<td>20–30</td>
<td>80</td>
<td>20–25</td>
<td>30</td>
</tr>
<tr>
<td>DMS</td>
<td>20</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

Typical trajectories for each scenario are shown in Figure S1. Due to the remoteness of the study region, chemical conditions in some scenarios—namely the OCEAN, AMERICA, and LOCAL scenarios—were similar (Table 1), although they described geographically different air masses. The AFRICA scenario will be discussed separately, because it was the only one with clouds. MISTRA was run for each scenario with different sources are largely consistent with those obtained, under similar conditions, by refs 9 and 16; however, they contrasted with the model results by ref 13, who

### RESULTS AND DISCUSSION

**Comparison with Observations. Inorganic Chlorine.** Gas-phase HCl and Cl$^+$ ($\approx 2 \times$ Cl$_2$ + HOCl) were measured with tandem mist-chamber samplers onboard the Polarstern$^8$ and at CVAO.$^9$ Gas-phase Cl$_2$ and HOCl were measured by atmospheric pressure chemical ionization tandem mass spectrometry (APCI/MS/MS) at CVAO.$^{9,13}$ Chloride (Cl$^-$) in submicrometer and supermicrometer aerosol was measured onboard the Discovery and at CVAO with multistage impactors;$^7$ bulk aerosol Cl$^-$ was measured with multistage impactors onboard the Polarstern.$^8$ The concentrations of particulate Cl$^-$ reported by these studies were similar to those observed in the Gulf of Guinea.$^{23}$

Modeled concentrations of HOCl and HCl were within the range of the measurements in all scenarios. The model could also reproduce lower levels of HCl in the LOCAL scenario (more processed air masses), compared to the OCEAN and AMERICA scenarios (Figure 1a–c). In the unpolluted scenarios (OCEAN, AMERICA, LOCAL), modeled concentrations of Cl$_2$ were within the range of the measurements, but the BASE case underestimated Cl$^+$ by $\sim$30% (Figure 1d); note that, while ref 13 defined Cl$^+$ as $2 \times$ Cl$_2$ + HOCl, other inorganic chlorine species might be included in this measurement,$^8$ which could partially explain the model-measurements discrepancy.

In the semipolluted scenario (EUROPE), the model overestimated the measurements of Cl$_2$ by a factor of 2–3, also causing the overestimation of Cl$^+$ during night-time (Figure 1a, d). During day-time, when Cl$^+$ was dominated by HOCl, modeled Cl$^+$ was within the range of the measurements. The model results for the EUROPE scenario were consistent with those obtained, under similar conditions, by refs 9 and 16; however, they contrasted with the model results by ref 13, who
could reproduce measured Cl\textsubscript{2} under “polluted” conditions, but underestimated HOCl by at least a factor of 5. The reason for the discrepancy between the two models is likely related to aerosol acidity.

Chlorine is released from sea salt via two main mechanisms:

1. Acid displacement of HCl—following aerosol acidification, e.g., by HNO\textsubscript{3} uptake (ref 24 and references therein)—and/or halogen activation via an autocatalytic cycle:25 Briefly, if X and Y are Cl and/or Br:

   \[
   \text{HOX} \rightarrow \text{HOX}_{aq} \quad (1)
   \]

   \[
   \text{HOX}_{aq} + Y_{aq} + H^{+} \rightarrow XY_{aq} + \text{H}_{2}O_{aq} \quad (2)
   \]

   \[
   XY_{aq} \rightarrow XY \quad (3)
   \]

   \[
   XY + h\nu \rightarrow X + Y \quad (4)
   \]

   \[
   X + O_{3} \rightarrow XO + O_{2} \quad (5)
   \]

   \[
   XO + \text{HO}_{2} \rightarrow \text{HOX} \quad (6)
   \]

   The cycle is initiated with the oxidation of X\textsuperscript{−} in sea salt to form HOX by reaction with OH, O\textsubscript{3}, or HSO\textsubscript{5}\textsuperscript{−} (ref 14).

   Aerosol acidity determines the displacement of HCl and the equilibrium between HOCl and Cl\textsubscript{2} (eq 2). At lower pH, Cl\textsubscript{2} formation is favored, so the higher acidity of sulfate aerosol in the EUROPE scenario (pH ~1 in MISTRA vs pH ~3 in ref 13) might explain why MISTRA predicted higher concentrations of Cl\textsubscript{2} than the ref 13 model. Additionally, sea salt acidity increases with altitude,26 so vertical transport of Cl\textsubscript{2} from the top of the MBL might explain high Cl\textsubscript{2} mixing ratios at the surface, a process which was not accounted for in the box model used by ref 13.

   The concentration of modeled Cl\textsuperscript{−} in sulfate aerosol was largely within the measured range in all scenarios (Figure 1e), but the model generally overestimated Cl\textsuperscript{−} in sea salt (by a factor of 5−10). Bulk aerosol Cl\textsuperscript{−}, which is mostly sea salt, showed better agreement, although the variability in the measurements was very large and the measured median concentration was still a factor of 2−3 lower than the model (Figure 1f). This might suggest that dechlorination of aerosol proceeded too slowly in the model, although if that were the case, the model would predict higher Cl\textsubscript{2} concentrations than shown in Figure 1a, thus increasing the model-measurements discrepancy. Another possibility, which will be further discussed below, is that the sea salt flux in the model was too high. Oxidation of halides by chlorophyll on the sea surface has also been proposed (e.g., by ref 27) as possible source of chlorine (and bromine) in the MBL, although information is not yet sufficient to implement this process in MISTRA.

**Inorganic Bromine.** Gas-phase BrO was measured by long-path differential optical absorption spectroscopy (LP-DOAS) at CVAO\textsuperscript{6,11} and by multiaxis differential optical absorption measurement.
spectroscopy (MAX-DOAS) onboard the Polarstern and the Poseidon. Total gas-phase inorganic bromine (Br\textsubscript{inorg} = HBr + HOBr + Br\textsubscript{NO} + Br\textsubscript{NO\textsubscript{2}} + 2 \times Br\textsubscript{2} + 2 \times Br\textsubscript{O} + Br + Br\textsubscript{O\textsubscript{2}} + BrCl + IBr) was measured with tandem mist-chamber samplers onboard the Polarstern. Bulk aerosol bromide (Br\textsuperscript{−}) was measured with multistage impactors onboard the Polarstern and, during RHAMBLE\textsuperscript{7,12} onboard the Discovery and at CVAO; similar values for particulate Br\textsuperscript{−} were also observed in the Gulf of Guinea by ref 23.

In the EUROPE scenario the model overestimated the observations of BrO by one or more ppt, while in the other scenarios BrO was generally within the range of the observations, although it tended to increase with time (Figure 1g); the typical BrO peaks at dawn and dusk were several ppt larger than observed.\textsuperscript{11} The model results were in broad agreement with the observations by ref 5, but in contrast with the observations by ref 10, who reported BrO below detection limit upwind of CVAO and very high BrO mixing ratios (up to 10.2 ppt) between Cape Verde and the African coast; however, it is likely that the latter were affected by local emissions not included in the model. Br\textsubscript{inorg} was generally overestimated by the model (Figure 1h): in the EUROPE scenario, Br\textsubscript{inorg} was overestimated by about a factor of 2, while in the other scenarios it was overestimated by a factor of 10.

Bulk aerosol Br\textsuperscript{−} was broadly in agreement with the observations by ref 12, but not with those by ref 8 who reported higher (factor of 2−4) bromide concentrations. It must be noted that the two data sets showed large variability—especially the ref 8 data set—and they might not be directly comparable due to the differences in sampling times and the possibility of instrumental artifacts.\textsuperscript{12} The EUROPE scenario showed the best agreement with the ref 12 observations (Figure 1i), while the other scenarios slightly overestimated the observations, especially during the day. This was consistent with the comparison to BrO measurements, as the scenario with larger BrO (EUROPE) also showed lower particulate Br\textsuperscript{−} and vice versa. The model predicted higher concentrations of Br\textsuperscript{−} during the day in all scenarios (Figure 1i); although this was not apparent from the observations, some studies in tropical regions have reported an inverse diurnal cycle,\textsuperscript{23,28} which could be related to in-cloud processes\textsuperscript{15} (clouds were absent in the BASE case, except in the AFRICA scenario; see below).

BrCl was not detected at CVAO; MISTRA predicted 20−40 ppt of BrCl during the night and up to 3 ppt during the day (Figure 1j), well above the detection limit of the instrument (∼2 ppt\textsuperscript{8,15}). Enhanced levels of gas-phase BrCl (or Br\textsubscript{2}) could explain the overprediction of Br\textsubscript{inorg}. This was likely caused by the model overestimating bromide depletion in sea salt, as the Br\textsuperscript{−}/Cl\textsuperscript{−} ratio determines whether BrCl or Br\textsubscript{2} are preferentially released (via HOBr + Cl\textsuperscript{−} or HOBr + Br\textsuperscript{−}, ref 29). In the atmosphere, the release of bromine (as BrX) could also be slowed by the presence of dissolved organic matter (DOM), which may compete with Br\textsuperscript{−} for the reaction with HOBr. An additional explanation for the discrepancy is that the model overestimated aqueous-phase BrCl formation (eq 2) or underestimated aqueous-phase BrCl destruction (via BrCl + Br\textsuperscript{−} + H\textsuperscript{+} → Br\textsubscript{2} + Cl\textsuperscript{−}). The latter is less likely, as the concentrations of bulk aerosol Br\textsuperscript{−} were reasonably well reproduced by the model (Figure 1i). Another possible cause for the discrepancy is that reactions with oxygenated hydrocarbons (e.g., aldehydes) converted inorganic bromine into organic bromine,\textsuperscript{30} a process which was likely underestimated in the model (see below).

Because the only measured gas-phase bromine species was BrO, it is difficult to assess whether other bromine species could be reproduced by the model. It must be noted that the measurements of BrO and of Br\textsubscript{inorg} were taken in different years (2006−2007 and 2003, respectively) and there were large differences among the observations of BrO at CVAO,\textsuperscript{11} onboard the Polarstern,\textsuperscript{5} and onboard the Poseidon.\textsuperscript{10} The discrepancies might simply indicate strong variability of bromine in the tropical MBL, although this is impossible to ascertain without multiyear observations of bromine species.

Inorganic Iodine. Gas-phase I\textsuperscript{2}O was measured by long-path differential optical absorption spectroscopy (LP-DOAS) at CVAO.\textsuperscript{6,11} The mixing ratios of I\textsuperscript{2}O at CVAO averaged 1.4 ± 0.8 ppt;\textsuperscript{9} these values cannot be explained using the fluxes of iodinated hydrocarbons measured in the Cape Verde region,\textsuperscript{11,31} but require the assumption of an unknown iodine source with an atmospheric lifetime comparable to that of CH\textsubscript{3}I or I\textsubscript{2}. The nature of this source remains a subject of debate;\textsuperscript{25,52,33} since we addressed this question in great detail in ref 31, here we assumed a constant oceanic I\textsubscript{2} flux (1.9−2.2 × 10\textsuperscript{4} molecules cm\textsuperscript{−2} s\textsuperscript{−1}), so that the mixing ratio of I\textsuperscript{2}O was 1−1.5 ppt in the IOD case, consistent with the observations (Figure S6).

Iodine is known to accumulate in aerosol, as iodate (IO\textsubscript{3}−) or iodide (I\textsuperscript{−}) ions. In the IOD case (Figure S7), the model predicted that most of particulate iodine was in the form of IO\textsubscript{3}− (up to 1 × 10\textsuperscript{−10} mole m\textsuperscript{−3} in sulfate aerosol and up to 7 × 10\textsuperscript{−11} mole m\textsuperscript{−3} in sea salt) and underestimated the observations of I\textsuperscript{−} (refs 3,4,7) by 6−7 orders of magnitude in submicrometer aerosol and 2−3 orders of magnitude in supermicrometer aerosol. The IO\textsubscript{3}−/I\textsuperscript{−} ratio could be brought closer to the observed ratio by including an aqueous-phase reaction of HOI with DOM, as discussed in ref 17.

Investigation of the Model-Measurements Discrepancies. The comparison between the results of the BASE and IOD cases and the observations made in the tropical Atlantic Ocean highlighted several discrepancies:

- Under unpolluted conditions (OCEAN, AMERICA, and LOCAL scenarios), the BASE case could reproduce the concentrations of all measured Cl species, except for sea salt Cl\textsuperscript{−} which was overestimated by up to a factor of 5−10; the model also tended to overestimate BrO, Br\textsubscript{inorg} and bulk aerosol Br\textsuperscript{−}.
- Under semipolluted conditions (EUROPE scenario), the BASE case could reproduce observed concentrations of HCl and HOCl, but not of Cl\textsubscript{2} and underestimated by several ppt the mixing ratios of BrO and Br\textsubscript{inorg} modeled Cl\textsuperscript{−} in sea salt and bulk aerosol Br\textsuperscript{−} were overestimated, but were closer to the observations than under unpolluted conditions.
- In all scenarios, the BASE case predicted a night-time mixing ratios of 20−40 ppt of BrCl, which was not observed.

These issues will be discussed hereafter using a number of test cases with modified mechanisms/scenarios. The test cases were run only for the OCEAN and EUROPE scenarios, because of the similarity of the chemical conditions in the OCEAN, AMERICA, and LOCAL scenarios (Table 1).

The objective of the test cases was to investigate the importance of the following factors: (1) aerosol pH, which
controls the formation and release into the gas-phase of XY species, (2) reactions of Br with aldehydes, which affect the partitioning of bromine, (3) parametrization of the sea salt flux, which determines the overall levels of chlorine and bromine, (4) impact of Saharan dust on halogen activation, (5) uncertainties in aqueous-phase chemistry, which impact the formation/destruction of BrCl and Br₂, and (6) effect of in-cloud processing.

**DMS Levels.** The observations of dimethyl sulfide (DMS) made at CVAO were typically below 20–30 ppt, but previous observations in the tropical and subtropical Atlantic Ocean have often found higher mixing ratios (50–300 ppt), especially in air masses coming from upwelling regions. The BASE case was modified with DMS levels increased by a factor of 10 (∼200–250 ppt). Day-time HOCl decreased by 30–35% (OCEAN scenario) and ∼25% (EUROPE scenario), while night-time Cl₂ decreased by ∼45% (OCEAN scenario) and ∼30% (EUROPE scenario). The model results were still in the range of the observations in the OCEAN scenario, but the decrease in Cl₂ was not enough to reconcile the model and the measurements in the EUROPE scenario (test DMS in Figure 2).

Elevated DMS concentrations caused an increase in aqueous-phase acidity due to increased formation and uptake on aerosol of SO₂ and H₂SO₄, the main oxidation products of DMS. With faster acidification of the aerosol, acid displacement was the dominating process to activate chlorine leading to higher concentrations of gas-phase HCl (about a factor of 2) and slower release of XY via the autocatalytic cycle (eqs 1–6).

Although the total amount of chlorine released from sea salt increased, it was mostly stored in relatively unreactive form (HCl) and the release of reactive halogen species was suppressed, leading to lower/unchanged levels of reactive chlorine and bromine. Because the aerosol in the EUROPE scenario was already more acidic than that in the OCEAN scenario (because of higher HNO₃) the effect was less pronounced in the EUROPE scenario.

**Aldehydes Levels.** The BASE case predicted comparatively low levels of HCHO (300–400 ppt in the OCEAN, AMERICA, and LOCAL scenarios and 400–500 ppt in the EUROPE scenario) and CH₃CHO (5–15 ppt), because of the low concentrations of hydrocarbons at CVAO. Some observations support the presence of higher mixing ratios of aldehydes in the MBL: ref 36 measured 350–550 ppt of HCHO (peaking at ∼1.8 ppb) by LP-DOAS and ref 22 measured 500–1000 ppt of CH₃CHO at CVAO. The BASE case was run with increased HCHO and CH₃CHO mixing ratios (∼500 and ∼900 ppt, respectively). Day-time HOCl decreased by 70–75% and night-time Cl₂ decreased by ∼50% (test ALD in Figure 2); BrO and BrCl (Figure S8) also decreased by ∼40% and ∼20%, respectively.
In the presence of higher levels of aldehydes, Cl\textsubscript{2} mixing ratios were still within or closer to the range of the observations (in the OCEAN and EUROPE scenario, respectively), HOCl was underestimated by 5–30 ppt and BrCl was >10–20 ppt (Figure S8). Because of the high reactivity with Br, aldehydes were very efficient in reducing the tendency of the model to overestimate bromine; however, Br\textsubscript{Br2oog} was still outside the range of the observations. The reason is that the reactions with aldehydes converted bromine into a more stable form (HBr) and decreased the levels of reactive Br and slowing down the autocatalytic cycle (as already noted by ref 30), without changing total gas-phase bromine. Although MISTRA v7.4.1 does not include long-chain hydrocarbons, stable brominated oxygenates may form from their reaction with Br:30 in this case, bromine would be converted into organic form, causing the decrease of both reactive bromine and of Br\textsubscript{Br2oog}.

Sea Salt Flux. The model results were sensitive to the sea salt flux: an overestimation of this parameter could explain the overestimation of aerosol Cl\textsuperscript{−} and, hence, of BrCl (eq 2). Decreasing the sea salt flux in the model brought modeled BrCl below the instrumental detection limit—consistent with the observations—but it also caused an almost linear decrease of all other halogen species, reducing the overall agreement with the observations.

Saharan Dust. Saharan dust events are common in the Cape Verde region, especially in winter.18,19 The BASE case was modified to include a simple parametrization of Saharan dust: assuming that the uptake of a molecule on dust can be described as a pseudo-first-order process with \( k_{\text{dust}} = (A \gamma \tau) / \sqrt{\pi} \) (where \( A \) = dust surface area, \( \tau \) = mean molecular speed, and \( \gamma \) = uptake coefficient of molecule, Table S1). The surface area of Saharan dust is highly variable and depends on the intensity of the event: for this test case, we assumed \( A = 300 \) \( \mu \text{m}^2 / \text{cm}^3 \).38,39

The main impact of dust is the change in the pH of sea salt aerosol; due to the large \( \gamma_{\text{INO}} \) on dust (0.1, ref 40), acidification of sea salt proceeded much slower than in the absence of dust, resulting in higher pH (\( \sim 6 \)) and slower activation of halogens via the autocatalytic cycle (eqs 1–6). Day-time HOCl decreased by 25–30%, night-time Cl\textsubscript{2} decreased by 50–60% (test dust Figure 2) and BrCl decreased by 30–40% (Figure S8). Acid displacement was a minor process at pH \( \sim 6 \), resulting in an HCl concentration four times lower than in the BASE case. As a consequence, in the presence of dust, modeled Cl\textsubscript{2} decreased to within the range of the measurements, but the model overestimated HOCl and HCl by 10–50 ppt and BrCl was >20 ppt. The effect of Saharan dust is strongly dependent on the surface area (which is very variable) and on the uptake coefficients (the database of which is very limited).

Aqueous-Phase Chemistry. One way to resolve the inconsistencies between the observations of HOCl, Cl\textsubscript{2} and BrCl is to introduce a “brake” in the halogen activation cycle. The key reaction of the cycle is eq 2: any process that interferes with this reaction would stop or slow the release of XY in the gas phase. The BASE case was modified to include an additional (hypothetical) aqueous-phase reaction: HOX + A → X\textsuperscript{−}, with pseudo-first-order rate coefficients of \( 1 \times 10^5 \) s\textsuperscript{−1} for \( X = \text{Cl} \) and \( 1 \times 10^5 \) s\textsuperscript{−1} for \( X = Br \). One potential candidate for hypothetical reactant A is DOM: there is evidence for a similar reaction involving iodine, which helps reconcile the modeled and measured IO\textsubscript{3}\textsuperscript{−}/I\textsuperscript{−} ratio (see above and ref 17).

With the HOCl + A → X\textsuperscript{−} reaction, modeled HOCl decreased by \( \sim 20\% \) (OCEAN scenario) and \( \sim 15\% \) (EUROPE scenario), while Cl\textsubscript{2} decreased by \( \sim 65\% \) and \( \sim 40\% \) in the OCEAN and EUROPE scenarios, respectively (test HOCL in Figure 2). With the HOBBr + A → Br\textsuperscript{−} reaction, modeled HOCl decreased by 10–15% and Cl\textsubscript{2} decreased by \( \sim 80\% \) and \( \sim 25\% \) in the OCEAN and EUROPE scenarios, respectively (test HOBBr in Figure 2). However, the models still predicted mixing ratios of BrCl >10–15 ppt (Figure S8). The impact was dependent on the choice of the rate coefficients, but the model showed that both these reactions—particularly HOCl + A → Cl\textsuperscript{−}—would be very effective in decreasing the concentration of Cl\textsubscript{2}, without causing a similar decrease in the concentration of HOCl, which would be consistent with the observations.15 The effect would be larger in the unpolluted scenario (OCEAN), where aerosol acidity was lower and the activation cycle was dominant over acid displacement as mechanism for the release of halogens to the gas-phase.

Cloud Chemistry. Clouds did not form in the BASE and IOD cases, but the observations made at CVAO indicated that cumulus clouds could be present at the top of the MBL. In the AFRICA scenario, which simulated air masses arriving at CVAO from the East, the MBL height increased with time, in accord with the observations which showed lower boundary layer heights near the coast than over the ocean.20 This caused the slow vertical expansion of the MBL and cloud formation at the top of the MBL (Figure S9).

Upon formation of clouds, chemical conditions in the model changed dramatically, with \( \text{SO}_2, \text{H}_2\text{SO}_4, \) and most halogen species (especially HOX) being quickly taken up on water droplets. The model was run with and without iodine and Saharan dust, with little difference in the results. While modeled BrCl dropped below the detection limit of the instrument, there was no agreement with the observations of other halogen species (HOCl, Cl\textsubscript{2}, and BrO). Chloride concentrations in sea salt decreased by a factor of 2–5, resulting in better agreement with the observations (Figure S10), but the diurnal cycle of bulk aerosol Br\textsuperscript{−} did not change (unlike in ref 15). It must be stressed that the model cannot reproduce the cumulus clouds observed in the study region, but only stratiform clouds: therefore, this scenario only indicates the importance of cloud processing for halogen chemistry, highlighting the need for further research in this area.

Discussion. The analysis of the test cases suggests that more than one process may be responsible for the observed model—measurements discrepancies. Increased acidification of sea salt, either due to increased levels of DMS or to the impact of Saharan dust, improved the agreement with measured Cl\textsubscript{2}, but had little impact on modeled bromide. Agreement with chlorine and bromine species could be improved by including in the model hypothetical aqueous-phase reactions that convert HOX to X\textsuperscript{−}. Information on these reactions is missing, so they should be considered speculative at the moment.

The agreement with BrO could be improved by increasing the levels of aldehydes, although this caused the model to underestimate chlorine species. The role played by aldehydes in partitioning bromine to stable organic forms could not be addressed with MISTRA—which lacks a complete organic chemistry mechanism—but might explain some of the discrepancies. Changes in the sea salt flux and cloud processing could decrease significantly the concentrations of BrCl and of sea salt chloride, but it also removed most of the other halogen species from the gas phase.
Impact on Methane and Ozone. The presence of halogen species in the tropical MBL has significant effects on the concentrations of methane and ozone. Methane sinks are controlled by the concentrations of OH and Cl: in the IOD case these were $8.2 - 10.2 \times 10^6$ molecules cm$^{-3}$ and $2.9 - 8.2 \times 10^4$ molecules cm$^{-3}$, respectively. Therefore the lifetime of CH$_4$ (considering only daylight hours) with respect to OH was 184.5–230 days and with respect to Cl was 3.9–10.9 years, depending on the scenario. This indicates that Cl accounted for 5.4–11.6% of total methane loss in the Cape Verde region, in accord with previous estimates.$^9$

The Cape Verde region is typically under ozone destruction conditions, due to the low levels of NO$_x$: diurnal ozone loss was observed at CVAO$^{6,21}$ with average values of 3.3 ± 2.6 ppb/day. The BASE cases could reproduce ozone destruction during the day, although the calculated destruction rates were higher than the observations by a factor of 2–3 (depending on the scenario: 6–14 ppb/day). The comparison of the diurnal ozone loss rates of the BASE and IOD cases indicated that iodine contributed additional loss of 0.5–1 ppb/day. The over-estimation of ozone loss by MISTRA was expected, as the model also overestimated the levels of chlorine and bromine (Figure 1).

The model results were used to identify the main processes responsible for ozone destruction in the Cape Verde region. Ozone destruction can occur both by direct reaction and indirectly, by destroying its sources: to account for this, the odd oxygen family ($O_x = O_3 + O^{1P} + O^{1D} + NO_2 + 2 NO_3 + 3 N_2O_5 + HO_2NO_2 + ClO + 2 Cl_2O_2 + 2 OCIO + BrO + IO + 2 I_2O_2$) was defined to account for the species that are readily transferred to $O_x$.$^{14}$ The net $O_x$ loss rates were calculated for 12:00 of day 3 of the simulation and are shown in Figure 3 for the IOD case (OCEAN and EUROPE scenarios).

In both scenarios, the destruction of $O_x$ was driven by reactions involving HO$_x$ (especially HO$_2$, H$_2$O) and halogens, while reactions involving NO$_x$ and hydrocarbons had the net effect of forming O$_3$. HO$_x$ reactions (mostly $O^{1D} + H_2O$ and $O_3 + HO_2$) accounted for up to 60–65% of the total net $O_x$ loss, while halogens accounted for 35–40% (mostly via XO + HO$_2$ → HOX). The main halogen species destroying O$_3$ was bromine (~30–40% of halogens net $O_x$ loss); the contribution of iodine was the same in all scenarios—as iodine levels were similar (see above)—and accounted for ~20–30% of halogens net $O_x$ loss. Because of iodine’s relatively large vertical gradient, iodine contribution to $O_x$ loss became less important than chlorine’s above 600 m (OCEAN scenario) and 100 m (EUROPE scenario). The EUROPE scenario had larger concentrations of reactive chlorine (Figure 1) and therefore the contribution of chlorine to $O_x$ loss (almost 50% of halogens net $O_x$ loss) was a factor of 2 larger in the EUROPE scenario; chlorine also had a large vertical gradient—as a consequence of decreasing pH with altitude$^{26}$—and therefore was the largest halogen contributor to $O_x$ loss above 650 m (only in the EUROPE scenario; in the OCEAN scenario, chlorine levels were too low and bromine was the main contributor up to the top of the MBL).

**ASSOCIATED CONTENT**

Supporting Information

Three tables and ten figures. This material is available free of charge via the Internet at http://pubs.acs.org/.

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