HOCl and Cl$_2$ observations in marine air

M. J. Lawler$^1$, R. Sander$^2$, L. J. Carpenter$^3$, J. D. Lee$^4$, R. von Glasow$^5$, R. Sommariva$^5$, and E. S. Saltzman$^1$

$^1$Department of Earth System Science, University of California, Irvine, CA, USA
$^2$Department of Atmospheric Chemistry, Max-Planck Institute for Chemistry, Mainz, Germany
$^3$Department of Chemistry, University of York, York, UK
$^4$National Centre for Atmospheric Science, University of York, York, UK
$^5$School of Environmental Sciences, University of East Anglia, Norwich, UK

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Abstract. Cl atoms in the marine atmosphere may significantly impact the lifetimes of methane and other hydrocarbons. However, the existing estimates of Cl atom levels in marine air are based on indirect evidence. Here we present measurements of the Cl precursors HOCl and Cl$_2$ in the marine boundary layer during June of 2009 at the Cape Verde Atmospheric Observatory in the eastern tropical Atlantic. These are the first measurements of tropospheric HOCl. HOCl and Cl$_2$ levels were low in air with open ocean back trajectories, with maximum levels always below 60 and 10 ppt (pmol/mol), respectively. In air with trajectories originating over Europe, HOCl and Cl$_2$ levels were higher, with HOCl maxima exceeding 100 ppt each day and Cl$_2$ reaching up to 35 ppt. The increased Cl cycling associated with long distance pollutant transport over the oceans likely impacts a wide geographic area and represents a mechanism by which human activities have increased the reactivity of the marine atmosphere. Data-constrained model simulations indicate that Cl atoms account for approximately 15% of methane destruction on days when aged polluted air arrives at the site. A photochemical model does not adequately simulate the observed abundances of HOCl and Cl$_2$, raising the possibility of an unknown HOCl source.

1 Introduction

The Cl atom is a highly reactive radical which may play a significant role in the oxidative chemistry of the troposphere, particularly over the oceans where there is abundant available chloride. Photochemical cycling of reactive chlorine species can catalytically destroy tropospheric ozone, though this is probably only a minor O$_3$ sink under most conditions. Cl has a roughly 14-fold faster reaction rate constant than OH for reaction with methane and therefore potentially plays a role in controlling the lifetime of this important greenhouse gas (Sander et al., 2006). Cl also has faster rate constants than OH for reactions with non-methane hydrocarbons (NMHCs). NMHCs play an role in the production of tropospheric ozone, which is also a greenhouse gas. However, the abundances of Cl and its precursors are poorly known, and the mechanisms responsible for the oxidation of chloride to more reactive forms (Cl, ClO, Cl$_2$, BrCl, HOCl, ClNO$_2$, etc.; collectively referred to as Cl$_x$) are incompletely understood. It is therefore difficult to assess the impacts of reactive chlorine on tropospheric chemistry and climate.

The Cl atom can be generated in marine air as a result of multiphase photochemical mechanisms. The oxidation of chloride in marine aerosols by various species results in production of gas phase species such as Cl$_2$ and ClNO$_2$ (Finlayson-Pitts, 1983; Finlayson-Pitts et al., 1989; Knipping et al., 2000). These compounds photolyze in the daytime to release Cl atoms. In strongly polluted air, reactive chlorine production is initiated by the reaction of N$_2$O$_5$ with aerosol chloride, as evidenced in both laboratory and field observations (Osthoff et al., 2008; Roberts et al., 2008; Thornton et al., 2010):

\begin{align}
N_2O_5 + Cl^- & \rightarrow ClNO_2 + NO_3^- \\
ClNO_2 + Cl^- & \rightarrow Cl_2 + NO_2^-
\end{align}

Cl activation is less well understood under the low-NO$_x$ conditions typical of marine air masses. Cl atom production and Cl$_x$ cycling may be initiated by the daytime oxidation of HCl (Pechtl and von Glasow, 2007):

HCl + OH $\rightarrow$ Cl + H$_2$O

Correspondence to: M. J. Lawler (mlawler@uci.edu)
This reaction alone is too slow to maintain significant levels of Cl atom for typical HCl levels in the remote atmosphere of less than about 1 ppb (nmol/mol) (Erickson III et al., 1999; Harris et al., 1992). However, Cl can form HOCl via gas phase reactions, and HOCl can react in chloride-containing aerosols to form Cl₂. Cl₂ can then escape to the gas phase and photolyze, releasing Cl atoms which may then reform HOCl. The reactions involved in the hypothesized multiphase autocatalytic cycling for chlorine are shown below (Vogt et al., 1996; Pechtl and von Glasow, 2007).

\[
\begin{align*}
\text{HOCl}_{(g)} & \rightleftharpoons \text{HOCl}_{(aq)} \\
\text{HOCl} + \text{Cl}^- + \text{H}^+ & \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O} \\
\text{Cl}_2(aq) & \rightleftharpoons \text{Cl}_2(g) \\
\text{Cl}_2 + h\nu & \rightarrow 2\text{Cl} \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{HO}_2 & \rightarrow \text{HOCl} + \text{O}_2 \\
\end{align*}
\]

Net:

\[
\text{Cl}^- + \text{H}^+ + \text{O}_3 + \text{HO}_2 + h\nu \rightarrow \text{Cl} + 2\text{O}_2 + \text{H}_2\text{O}
\]

The autocatalytic cycle is promoted by low aerosol pH, which increases the rate of conversion of HOCl to Cl₂ (Reaction R5). The ratio of O₃ to NMHCs is another key parameter in determining the efficiency of Cl cycling. Higher O₃ levels tend to sustain the cycling of reactive Cl₂ by increasing the fraction of Cl atoms that are converted to ClO₂. By contrast, most reactions of Cl with NMHCs produce relatively unreactive HCl, which slows Cl₂ cycling.

Analogous aerosol reactions involving HOB₃ can generate BrCl and Br₂:

\[
\begin{align*}
\text{HOB} + \text{Cl}^- + \text{H}^+ & \rightarrow \text{BrCl} + \text{H}_2\text{O} \\
\text{HOB} + \text{Br}^- + \text{H}^+ & \rightarrow \text{Br}_2 + \text{H}_2\text{O}
\end{align*}
\]

In photochemical models of marine air, the photolysis of BrCl is a major source of oxidized chlorine in marine air (Vogt et al., 1996; Pechtl and von Glasow, 2007). However, BrCl has not yet been detected in coastal or open ocean marine air (Finley and Saltzman, 2008; Lawler et al., 2009). The BrCl detection limits during these studies were estimated at 2 ppt, which is lower than the nighttime levels predicted by models. BrCl has been observed in the Arctic, where intense reactive halogen cycling involving sea ice occurs (Spicer et al., 2002).

Laboratory experiments have demonstrated molecular and mixed dihalogen production from synthetic halide solutions and surfaces by reactions of OH, O₃, and HOCl (Behnke et al., 1999; Knipping et al., 2000; Huff and Abbatt, 2000). However, aerosol uptake of HOCl to form Cl₂ has not been observed in the laboratory or in ambient air. Field measurements of reactive Cl species in marine air (excluding environments with sea ice) are limited to a few studies of Cl₂, ClNO₂, and Cl⁺, a nonspecific measure of total Clₓ (Spicer et al., 1998; Keene et al., 1993; Pszenny et al., 1993; Finley and Saltzman, 2006; Lawler et al., 2009; Osthoff et al., 2008). The existing data are insufficient to constrain the rate of daytime reactive Cl cycling, or to test current multiphase photochemical models, particularly in remote, low-NOₓ environments.

In this study we present the first simultaneous measurements of HOCl and Cl₂ in the marine boundary layer, taken at the Cape Verde islands in the eastern tropical Atlantic ocean. This study follows earlier measurements of Cl₂ at Cape Verde (Lawler et al., 2009). The data provide new constraints on the rates and mechanisms of reactive Cl cycling and provide precursor-constrained estimates of Cl atom levels in a remote marine environment.

## 2 Field conditions and site characteristics

This study was carried out at the Cape Verde Atmospheric Observatory on the island of São Vicente (hereafter Cape Verde, 16°52’N, 24°52’W) from 30 May to 7 June 2009 (days of year 150–158). The site is located on a rocky coastline about 50 m from the ocean. Winds were consistently onshore, averaging 7.3 m s⁻¹ from the northeast, with daytime winds about 1 m s⁻¹ higher than nighttime on days 150–154. There is no local source of pollution upwind of the site. Air mass back trajectories were calculated using the British Atmospheric Data Centre model for air reaching the field site coordinates at 950 mbar. The back trajectories show that some of the sampled air masses originated in the central Atlantic and some near or over Southwestern Europe prior to subsiding into the boundary layer 2–3 days upwind of the study site (Fig. 1). From late on day 154 to early on day 155 the trajectories indicate transport from the African continent.

Non-Clₓ chemical measurements made at the site included NO, NO₂, NO₃, O₃, and CO. NO₂ and NO₃ were measured by catalytic conversion to NO and chemiluminescence detection, with detection limits of 8 ppt (pmol/mol) for NO₂ and 4 ppt for NO₃. On average, particulate NO₃⁻ contributed 56% of the total NO₃ observed. The total NO₃ measurements may not include all aerosol size ranges and are therefore lower limits. Ozone was measured by ultraviolet absorption (Thermo Electron 49i), and CO was measured using a fast response vacuum ultraviolet fluorescence analyzer (Aerolaser 5001). NOₓ levels were low over the whole campaign (<10–120 ppt NO₂ for 97% of points), and ozone mixing ratios ranged from 19–39 ppb. CO mixing ratios ranged from 85–115 ppb (Fig. 2).

Aerosol optical particle counter measurements were made at 3 m and 30 m on day 140 (20 May 2009) and showed about a 5× total aerosol volume enhancement at the surface (TSI
In these measurements, partition measurements using 24-h filters sampled at 30 m showed wave breaking at the coast. PM10 aerosol chemical composition measurements using 24-h filters sampled at 30 m showed that the aerosol was usually dominated by salt (K. W. Fomba, personal communication, 2010). In these measurements, particulate Na\(^+\) was determined by ion chromatography and ranged from 3.2–5.2 µg m\(^{-3}\) during this study.

### 3 HOCl and Cl\(_2\) measurement technique

HOCl and Cl\(_2\) were detected using chemical ionization tandem mass spectrometry (CIMS-MS) via formation of a Br\(^-\) adduct (Foster et al., 1999). The mass spectrometer was a Thermo Finnigan TSQ Quantum. The instrument detection limits were approximately 30 ppt HOCl and 1 ppt Cl\(_2\) for the first three days of the study, and 5 ppt HOCl and 2 ppt Cl\(_2\) during the last four days.

Ambient air was drawn from an intake 3 m above ground at 63 L min\(^{-1}\) through a 2" (5.1 cm) inner diameter (ID) acrylic butyl styrene (ABS) pipe. The passing efficiency of this inlet was not assessed during this study, but a comparable inlet previously showed a passing efficiency of 85 % for Cl\(_2\) (Finley and Saltzman, 2006). A subsample of about 1.3 L min\(^{-1}\) (at STP, 273 K and 101 kPa) from the air flow was drawn through a stainless steel capillary tube (69 mm long with a 0.51 mm ID) into the mass spectrometer ionization region. A flow of 5–10 ml min\(^{-1}\) (STP) of bromoform (CHBr\(_3\)) at its saturation vapor pressure at 23 °C (about 6 mbar) in nitrogen was added to the sampled air, and the mixture passed over a beta-emitting \(^{63}\)Ni foil. The ionization region was maintained at about 200 torr. Br\(^-\) was the dominant reagent ion produced, and it reacted with Cl\(_2\) and HOCl to form the ion clusters Cl\(_2\)Br\(^-\) and HOClBr\(^-\), respectively. The ionized sample air was drawn through a stainless steel capillary (59 mm long, 0.51 mm ID) into the 0.5 torr declustering region of the mass spectrometer. Collisional declustering was set to 9 V (roughly 20 Townsends) to break up weakly-bound clusters. The Cl\(_2\)Br\(^-\) and HOClBr\(^-\) ion clusters were detected using selected ion reaction monitoring mode. Each cluster was mass-selected by the first quadrupole (Q1), then dissociated by collision with argon (Q2, 15–20 eV) to
yield a daughter ion which was mass selected (Q3) and detected by a dynode/electron multiplier. Cl\textsubscript{2} was detected using Cl\textsubscript{2}Br\textsuperscript{−} → Cl\textsuperscript{−} transitions and HOCl was detected using HOClBr\textsuperscript{−} → Br\textsuperscript{−} transitions (Table 1). Data were collected at the various major halogen isotopomers of these clusters. The signal ratios of the various transitions in ambient air were consistent with natural abundance of the stable halogen isotopes and indistinguishable from those in gas standards. The Cl and Br isotope ratios provide confidence in the identity of the parent ions contributing to the ambient air signals.

Instrument sensitivity to Cl\textsubscript{2} was calibrated in the field every four hours using the output of a Cl\textsubscript{2} permeation tube (VICI Metronics) and a multi-stage dilution system (Gal-levy et al., 1997; Finley and Saltzman, 2006). The Cl\textsubscript{2} standard was added to the front of the instrument inlet and the final mixing ratio of Cl\textsubscript{2} in the air stream was typically 14 ppt. The permeation tube output rate was gravimetrically calibrated in the lab at UC Irvine. There is no evidence that the permeation tube mass loss was due to anything other than Cl\textsubscript{2} loss. An iodometric calibration of the permeation tube performed in May 2011 matched the inferred Cl\textsubscript{2} loss from a concurrent month-long mass record to within experimental error. The permeation tube has never released HOCl at measurable levels. Instrument sensitivity was assumed to vary linearly between calibrations, except for likely sensitivity step changes, such as the power outage that resulted in a day-long gap in observations about day 154. Reported standard errors for Cl\textsubscript{2} mixing ratios include variability in both ambient signal and uncertainty in the instrument sensitivity. For each Cl\textsubscript{2} calibration, the uncertainty in sensitivity was calculated as the standard error in averaged Cl\textsubscript{2} standard signal, divided by the mixing ratio of Cl\textsubscript{2} added. The sensitivity standard errors were linearly interpolated between calibrations. The standard error of the calculated mixing ratios was calculated with Gaussian error propagation, incorporating both the standard error in ambient averaged samples and the standard error in interpolated calibration standard error.

The instrument was calibrated for HOCl using a phosphate-buffered solution of NaOCl (0.6–2 mM, pH ≈ 7). Nitrogen was bubbled at 5–20 ml min\textsuperscript{−1} through the solution in a two-port gas-tight glass container, and the output nitrogen flow contained both HOCl and Cl\textsubscript{2}. This output flow was first added to the inlet, to assess the instrument response to each species. Then the bubbler output was routed through a cold (233 K) 1/8\textsuperscript{“} (0.32 cm) outer diameter (OD) teflon tube with HCl condensed onto the walls. This reactor converted the HOCl to Cl\textsubscript{2} while letting Cl\textsubscript{2} pass. After the reactor, the flow was routed to the instrument inlet, and the increase in Cl\textsubscript{2} signal was attributed to a molar equivalent loss of HOCl in the reactor as a result of Reaction (R5) (Foster et al., 1999). This “HOCl as Cl\textsubscript{2}” signal was converted into an HOCl mixing ratio using the instrument sensitivity to Cl\textsubscript{2}, based on the Cl\textsubscript{2} permeation tube. If conversion of HOCl to Cl\textsubscript{2} in the reactor was actually less efficient than assumed, instrument sensitivity was overestimated and ambient HOCl levels were underestimated.

HOCl levels in the standard ranged from 55–438 ppt, but only those near ambient (55–219 ppt) were used to assess instrument sensitivity. Instrument sensitivity was roughly linear in the range of ambient levels, 0–200 ppt. A 3-point (0, 100, and 200 ppt) calibration conducted on day 152 yielded a linear fit with $r^2 = 0.93$. A 3-point (0, 37, and 74 ppt) calibration conducted on day 154 yielded a linear fit with $r^2 = 0.97$. Calibrations were run about once a day, and as for Cl\textsubscript{2}, instrument sensitivity was assumed to vary linearly between calibrations unless it was obvious that a step change had occurred. HOCl sensitivity was more variable than Cl\textsubscript{2} sensitivity, but it varied by less than a factor of 2 between calibrations under similar conditions (see Supplemental Material). One exception was the period between day 155.8 and 156.6, when sensitivity decreased dramatically, most likely due to clogging of the inlet capillary. For the relatively few points above detection during this period, the applied sensitivity was within a factor of 3 of the calibrated sensitivity at day 156.6. HOCl sensitivity was very sensitive to pressure in the ionization region. This pressure was not dynamically controlled and tended to decrease over time. HOCl calibrations...
were done before and after readjusting ion source pressure. Reported standard errors for HOCl measurements include variability in both ambient signal and uncertainty in the instrument sensitivity, using the same approach as described above for Cl₂.

The instrument blank, or background signal, was assessed every hour by passing ambient air through a scrubber composed of glass wool coated with CaCO₃. The instrument blank was assumed to vary linearly between measured blanks. Each interpolated blank was assigned a standard error equal to the sum in quadrature of the standard errors of the two blank measurements on which it was based. Detectability was assessed by using one-sided t-tests ($p=0.05$) to test whether the averaged sample points were greater than the averaged interpolated blank points. The scrubber removes Cl₂ with about 99% efficiency, but a significant fraction of HOCl was found to pass through the scrubber. Over the field measurement period, the HOCl blank signal correlated strongly with the sample signal ($r^2=0.68$, $p<0.001$). A linear least-squares fit showed the blank signal to be 28% of the sample signal over the measurement period. A laboratory test showed 5–10% breakthrough of HOCl through the scrubber, so at least part of the ambient blank signal was likely due to this effect. Because the blank signal was subtracted from the sample signal, the reported HOCl levels are lower limits.

Given that there are likely significant quantities of sea salt on the walls of the inlet tubing, the possibility exists for production of Cl₂ or HOCl due to reactions of oxidants on the walls. The oxidant would have to occur at levels of greater than tens of ppt and would need to pass through the carbonate oxidant scrubber. Furthermore, such a process is not likely to give rise to the diel changes in Clₓ speciation observed. Reactive halogens contained in aerosols themselves are not a significant source of interference because the fraction of Clₓ contained in aqueous aerosols is less than $10^{-6}$, given typical marine aerosol loading and the solubilities of Cl₂ and HOCl.

4 Observations

HOCl ranged from $<5$–173 parts per trillion (ppt, pmol/mol), and Cl₂ ranged from $<1$–35 ppt (Fig. 2). The two chlorine species exhibited consistent diel cycles of opposite phase, with high HOCl during daytime, and high Cl₂ levels at night. This pattern is expected as a result of the photochemical production of HOCl during the daytime (Reaction R9), the continuous aerosol-mediated conversion of HOCl to Cl₂ (Reaction R5), and the rapid daytime photolysis of Cl₂ (Maric et al., 1993).

HOCl and Cl₂ levels were high during the first 3 days of the study and lower during the last 4 days. These periods will be referred to as “high Clₓ” and “low Clₓ” days, respectively. The observed variability in Cl₂ and HOCl is likely attributable to changes in air mass origin and chemistry. Clₓ (HOCl + 2 · Cl₂) was positively correlated with both NO₃ ($r^2=0.19$, $p<0.001$) and O₃ ($r^2=0.32$, $p<0.001$). The air mass back trajectories show two air mass regimes during the 8-day measurement period, with a transitional period between them. During the first 2–3 days, air masses originated in the eastern Atlantic, often near or over continental regions, in the lower troposphere. These days showed O₃ levels consistently near or above 30 ppb (mean 34.5 ppb), and rising NO₂ (200–700 ppt). The combination of continental back trajectories, high NO₃ levels, and low NO₂ levels indicates that this is aged polluted air which likely originated in Europe. Cl₂ and HOCl were at their highest levels during these days. During the last three days (low Clₓ days) air masses originated at a variety of elevations over the north Atlantic, spent a few days in the lower troposphere, and entered the marine boundary layer (MBL) about 1 day upwind of the site. During the night of days 156 and 158, NOₓ was at its lowest levels of the measurement period, and O₃ was at its lowest nighttime levels (as low as 20 ppb). These nights showed the lowest Cl₂ mixing ratios of the measurement period.

The Cl₂ levels observed during this study are similar to measurements made at this site during the same season in 2007 using a different CIMS-MS technique. In that study, Cl₂ ranged from $<1$–30 ppt with a similar dependence on air mass origin (Lawler et al., 2009). During the 2007 study, mist chamber measurements of nonspeciated Clₓ ranged from $<14$–101 ppt, with one outlier at 220 ppt (Lawler et al., 2009).

5 Model simulations

Model simulations were carried out using the time-dependent photochemical box model MECCA (Sander et al., 2005) to assess whether the HOCl and Cl₂ observations could be explained by known chemistry and to examine the role environmental conditions play in chlorine cycling. The simulations were intended to model the high Clₓ period, when aged polluted air reached the site. No attempt was made to model the clean marine conditions encountered during the low Clₓ period because observed HOCl and Cl₂ levels were often below the detection limit. A base simulation using realistic conditions and known chemistry (described below) did not fit the observed HOCl and Cl₂ levels well. Further simulations were then carried out to explore possible means to bring the model closer to the observations.

The MECCA model organizes reactions into various categories that can be turned on and off as a group. These simulations employed the tropospheric reaction set, but excluding reactions involving iodine species. Otherwise all chlorine and bromine reactions were included, as were coarse (sea salt) and fine (sulfate) aerosol reactions. The turnover times for sea salt and sulfate aerosol were 2 days and 7 days, respectively. Gas phase reactions of Cl with ethane (C₂H₆), methanol (CH₃OH), acetaldehyde (CH₃CHO), and acetone (CH₃COCH₃) were included based on recommended rate
Table 2. Boundary conditions which were used for all model runs. O₃, CO, and aerosols were based on concurrent measurements. Hydrocarbons and NO₂ were based on measurements in the same season in 2007. Aerosol Cl⁻ and SO₄²⁻ were allowed to vary, so ranges over all the simulations are given.

<table>
<thead>
<tr>
<th>Fixed meteorological conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar parameters</td>
</tr>
<tr>
<td>Temperature (K)</td>
</tr>
<tr>
<td>Relative humidity</td>
</tr>
<tr>
<td>Total column ozone (DU)</td>
</tr>
<tr>
<td>Boundary layer height (m)</td>
</tr>
<tr>
<td>Coarse aerosol liquid water content (m⁻³ water/m⁻³ air)</td>
</tr>
<tr>
<td>Fine aerosol liquid water content (m⁻³ water/m⁻³ air)</td>
</tr>
</tbody>
</table>

Fixed mixing ratios (ppb)

<table>
<thead>
<tr>
<th>O₃</th>
<th>CH₄</th>
<th>NO₂</th>
<th>Methanol</th>
<th>Acetaldehyde</th>
<th>Acetone</th>
<th>Ethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1800</td>
<td>0.015</td>
<td>0.5</td>
<td>0.7</td>
<td>0.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Initial mixing ratios (ppb)

<table>
<thead>
<tr>
<th>CO</th>
<th>HCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Input fluxes (ppb/day)

<table>
<thead>
<tr>
<th>DMS</th>
<th>NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Aerosol components (µg m⁻³)

<table>
<thead>
<tr>
<th>Aerosol Cl⁻</th>
<th>Non-sea-salt SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.3–20.6</td>
<td>0.09–0.37</td>
</tr>
</tbody>
</table>

Table 3. Boundary conditions which were varied for the different MECCA box model runs. HNO₃ and HCl for all cases except new-source + lowacid were based on measurements at Cape Verde in 2007. Here ns is short for newsource.

<table>
<thead>
<tr>
<th>Model run</th>
<th>Added HOCl source (midday value, ppt h⁻¹)</th>
<th>HOCl(aq) sink</th>
<th>αHOCl</th>
<th>HCl (ppb)</th>
<th>HNO₃ (ppb)</th>
<th>Gas phase halogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>base case</td>
<td>0</td>
<td>No</td>
<td>0.1</td>
<td>0.6</td>
<td>0.1</td>
<td>Yes</td>
</tr>
<tr>
<td>newsource</td>
<td>54</td>
<td>No</td>
<td>0.1</td>
<td>0.6</td>
<td>0.1</td>
<td>Yes</td>
</tr>
<tr>
<td>ns+sink</td>
<td>79</td>
<td>Yes</td>
<td>0.1</td>
<td>0.6</td>
<td>0.1</td>
<td>Yes</td>
</tr>
<tr>
<td>ns+lowalpha</td>
<td>54</td>
<td>No</td>
<td>0.002</td>
<td>0.6</td>
<td>0.1</td>
<td>Yes</td>
</tr>
<tr>
<td>ns+lowacid</td>
<td>59</td>
<td>No</td>
<td>0.1</td>
<td>0.08</td>
<td>0.01</td>
<td>Yes</td>
</tr>
<tr>
<td>nohalogen</td>
<td>0</td>
<td>No</td>
<td>0.1</td>
<td>0.6</td>
<td>0.1</td>
<td>No</td>
</tr>
</tbody>
</table>

constants (Sander et al., 2006). Ozone, methane, HNO₃, HCl, NO₂, and non-methane hydrocarbons were held at fixed levels which were identical for all the simulations. Initial conditions are listed in Tables 2 and 3. The model reached a pseudo-steady state condition after a few model days, and conditions on day 9 of the run were used for analysis.

5.1 Base simulation (base case)

A simulation dubbed base case was run with best-guess environmental conditions and standard model chemistry. O₃ and sea salt particle abundances were based on measurements made during the campaign. Levels of NMHCs, acidic gases, and NO₂ were based on measurements made during previous studies at Cape Verde (Read et al., 2009; Lawler et al., 2009).
The fixed levels of HNO₃ and HCl are the primary control on coarse (sea salt) aerosol acidity and result in a coarse aerosol pH of 3.4. The initial HCHO mixing ratio (300 ppt) is within the range of values found by Still et al. (0.13–1.15, 2006) in the MBL. The DMS flux maintains a 13–35 ppt DMS diurnal cycle, and the NH₃ flux maintains NH₃ levels of about 130 ppt, within the wide range of values in the MBL (Quinn et al., 1987). Under these conditions, the model achieves a maximum of only 23 ppt HOCl (Fig. 3, Table 4), whereas ambient levels were often over 100 ppt. Increasing O₃ and gas phase acids results in higher HOCl levels, but very extreme conditions would need to prevail for the model to reach 100 ppt HOCl. O₃ in the base case is 45 ppb, already higher than the maximum observed level of 40 ppb, so it does not make sense to increase this further to try to increase HOCl levels. Two independent perturbations to the base case were performed to assess the sensitivity of the model results to levels of HCl and NMHCs. Increasing HCl contributes to both aerosol acidity via aerosol uptake and to Cl atom production via HCl + OH. NMHCs reduce the rate of Cl₂ cycling by removing Cl atoms. Fixing model gas phase HCl at 10 ppb results in HOCl levels comparable to observations, but HCl never exceeded 700 ppt during the same season in 2007. Eliminating all NMHCs results in only a 50 ppt HOCl maximum. The base case simulation does not demonstrate good agreement with the HOCl observations, even when modified with major perturbations aimed at improving agreement. The underestimation of HOCl levels is even more severe when one considers that BrCl is a major source of Cl atoms in the model, contributing to HOCl formation and reaching 24 ppt at night. As noted above, observations do not support such high BrCl levels in the MBL (Finley and Saltzman, 2008; Lawler et al., 2009).

5.2 New Cl₂ source (newsource)

Another model simulation was run with the same boundary conditions as the base case, but including a hypothetical daytime HOCl source. The HOCl source in this newsource simulation was a light-dependent chloride oxidation reaction generating gas-phase HOCl:

\[ P_{\text{HOCl}} = c \cdot j_{O_3(O^1D)} \cdot Cl^-_{\text{aerosol}} \]  \hspace{1cm} (R13)

Here \( c = 0.04 \) and \( j_{O_3(O^1D)} \) is the rate constant for photolysis of O₃ to produce O³D.

A midday source strength of 54 ppt h⁻¹ was required to achieve 96 ppt HOCl at midday (Fig. 3, Table 4). This is a strong source, but nonetheless a conservative estimate of the Cl₂ source required. Several-fold larger rates of Cl₂ oxidation to Cl₁ would be required if the Cl₅ species formed were something other than HOCl. In that case the observed HOCl would have to be formed in the gas phase via Reactions (R8–R9) after photolysis of the aerosol-derived Cl₅ species. This means of forming HOCl is inefficient because a large fraction of Cl forms the unreactive reservoir species HCl. Cl₂ reached a nighttime maximum of 41 ppt in this simulation (Fig. 3, Table 4).

If the HOCl production at Cape Verde were due to the aerosol uptake of a gas phase, photochemically derived oxidant, it would require a very large oxidant flux. For example, under Cape Verde conditions, the nighttime OH-aerosol collision rate is estimated to be only 20 ppt h⁻¹. Even if every such collision somehow oxidized Cl⁻ to form HOCl, it would not be sufficient. Photolytic aerosol production of OH from nitrate or dissolved organic matter appears to be orders of magnitude too slow (Takeda et al., 2004; Anastasio and Newberg, 2007). O₃, NO₂, and H₂O₂ each have sufficiently large fluxes to the aerosols, but would require some form of surface-, photo-, or catalyst-enhanced reaction mechanisms to generate HOCl, as their reaction rates with Cl⁻ in bulk aqueous solution are negligible.

A more plausible candidate might be the oxidation of aerosol Cl⁻ via organic photosensitization. The photoexcited triplet state of various substituted quinones can oxidize chloride and bromide, as shown in both synthetic solutions and natural waters (Scharf and Weitz, 1979; Gratzel and Halman, 1990; Jammoul et al., 2009). Such reactions could provide the required Cl₂ source if the photosensitizers comprise a few percent of the total aerosol dissolved organic carbon (DOC). However, whether such reactions could directly result in HOCl, rather than Cl₂, is not clear.

The hypothetical HOCl source results in higher Cl₂ levels due to reactions in acidic aerosols (Reaction R5). The newsource model Cl₂ averaged over 2 ppt in the daytime. This is higher than measured on days 150 and 151, when daytime Cl₂ averaged 0.4 and 0.7 ppt, respectively. Observed
nighttime Cl\(_2\) levels were also generally higher in this model run, and the rate of increase of Cl\(_2\) at nightfall is faster. It appears that the conversion of HOCl to Cl\(_2\) was less efficient in the real atmosphere than in the model. Potential explanations include (1) a sink of HOCl in aerosols (e.g. to organic reaction), (2) inefficient uptake of HOCl onto aerosol (due to an organic surface film), or (3) an aerosol pH distribution effect (i.e. a population of less acidic aerosols that convert Cl\(_2\) back into HOCl). Each of these possibilities would reduce the rate of Cl\(_2\) production and result in lower Cl\(_2\) levels, as demonstrated by the following model simulations.

### 5.3 New Cl\(_x\) source with aerosol HOCl sink (newsource + sink)

The MECCA model, and in fact all published tropospheric halogen models, assume that there are no significant sinks of reactive chlorine in marine aerosols. However, it is well known that natural waters are reactive to added chlorine, a process commonly referred to as “chlorine demand” in the water treatment literature. We suggest that fresh marine aerosols likely exhibit a similar chlorine demand. In natural waters, chlorine demand kinetics are described by two parallel first-order loss processes (fast and slow), leading to the production of various oxidized bromine and bromocarbon species (Wong and Davidson, 1977). Marine aerosols differ from other natural waters in that bromide levels are lower due to oxidation and volatilization (Sander et al., 2003). Hence, in aerosols the potential exists for direct interaction of reactive chlorine species with dissolved organics without bromine as an intermediate. The fast loss rate constant for chlorine in natural waters has not been measured precisely, Jaworske and Helz (1985) examined the loss rate of oxidized bromine added to natural waters, and observed lifetimes of less than 7 ms. They determined that the bromine-reactive species in natural estuary water were present at concentrations of about 1 × 10\(^{-5}\) M, roughly 2–4 % of the total dissolved organic carbon, and exhibited reactivity similar to that of fulvic acids. For the purposes of this discussion, we assume that reactive chlorine has a similar reactivity in sea salt aerosols.

The chlorine demand hypothesis was examined by constructing a model run containing both the HOCl source (as in the newsource simulation) and an irreversible aerosol sink for reactive chlorine (newsource + sink). This sink was parameterized as follows:

\[
\text{HOCl} + C_{\text{Clsink}} \rightarrow \text{products} \quad (R14)
\]

with a bimolecular rate constant of 2.2 × 10\(^4\) M\(^{-1}\) s\(^{-1}\), the rate of the reaction of HOCl with phenol (Gallard and Von Gunten, 2002). \(C_{\text{Clsink}}\) was assumed to be present in fresh sea salt aerosols at 160 mM and was lost only via Reaction (R14). During the daytime, \(C_{\text{Clsink}}\) is depleted and it becomes a negligible sink for HOCl at midday. Overnight, \(C_{\text{Clsink}}\) reaches 29 mM. If \(C_{\text{Clsink}}\) had a molar mass of 100, this would correspond to about 5 % of the sea salt mass. For comparison, Middlebrook et al. (1998) estimated average total organic mass in aerosols at Cape Grim, Tasmania, to be around 10 % of the sea-salt content. If Cape Verde sea salt aerosols were similar, then the Cl\(_x\)-reactive fraction would have to be a large fraction of the total organic matter in sea salt. Introducing this new aerosol sink of HOCl into the model reduces the daytime gas phase HOCl levels by about 20 %. To compensate for this loss, the newsource + sink HOCl source was increased to 79 ppt h\(^{-1}\) at midday to result in an HOCl maximum of 108 ppt. This simulation shows decreased nighttime Cl\(_2\) levels (18 ppt maximum) relative to

---

**Table 4.** Mixing ratios and rates for four model runs at day 9, by which time the model has reached pseudo-steady state. Mean HOCl and Cl\(_2\) observations during the high Cl\(_x\) period are given for comparison. The midday observational means for HOCl and Cl\(_2\) include all data between 10:00–14:00 LT, including points below detection. One standard deviation is shown.

<table>
<thead>
<tr>
<th>Mixing ratios (ppt)</th>
<th>base</th>
<th>newsource</th>
<th>ns+lowacid</th>
<th>nohalogen</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Midday HOCl max</td>
<td>23.1</td>
<td>95.5</td>
<td>106.8</td>
<td>0</td>
<td>83.3±23.6</td>
</tr>
<tr>
<td>Midday Cl(_2)</td>
<td>0.50</td>
<td>2.45</td>
<td>0.54</td>
<td>0</td>
<td>1.2±1.0</td>
</tr>
<tr>
<td>Nighttime Cl(_2) max</td>
<td>12.0</td>
<td>41.4</td>
<td>22.3</td>
<td>0</td>
<td>20.2±11.9</td>
</tr>
<tr>
<td>Mean Cl atom (cm(^{-3}))</td>
<td>1.41×10(^4)</td>
<td>2.61×10(^4)</td>
<td>2.19×10(^4)</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rates (ppb/day)</th>
<th>Cl + O(_3) reaction</th>
<th>Br + O(_3) reaction</th>
<th>(\sum)O(_3) loss</th>
<th>CH(_4) loss to Cl</th>
<th>CH(_4) loss to OH</th>
<th>(\sum)CH(_4) loss</th>
<th>(\sum)NO(_x) loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.63</td>
<td>4.45</td>
<td>6.68</td>
<td>0.21</td>
<td>1.77</td>
<td>2.01</td>
<td>0.112</td>
</tr>
<tr>
<td></td>
<td>1.16</td>
<td>4.33</td>
<td>7.16</td>
<td>0.38</td>
<td>1.80</td>
<td>2.20</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td>0.97</td>
<td>4.34</td>
<td>7.00</td>
<td>0.32</td>
<td>1.82</td>
<td>2.17</td>
<td>0.122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.040</td>
</tr>
</tbody>
</table>
the *newsoure* case, bringing the model more in line with observations in that regard (Fig. 3). However, daytime Cl$_2$ is still higher than observed on days 151 and 152, and the early nighttime Cl$_2$ increase is earlier and more rapid than observed (Fig. 3).

### 5.4 New Cl$_x$ source with low HOCl uptake coefficient (*newsoure*+lowalpha)

In the *newsoure* case, about 10% of gas phase HOCl that contacts an aerosol undergoes reactive uptake ($\gamma = 0.1$). The fraction $\gamma$ is controlled by aqueous phase reaction rates and the mass accommodation coefficient ($\alpha$). The model uses $\alpha_{\text{HOCl}} = 0.5$, based on laboratory measurements of uptake of HOBr on NaCl and NaBr aerosols (Abbatt and Waschewsky, 1998; Wachsmuth et al., 2002). Recent experiments with aerosols generated from acidified natural seawater show a lower $\gamma_{\text{HOCl}}$ of 0.0004–0.0018 and unusual relative humidity dependence (Pratte and Rossi, 2006). These observations and some model simulations suggest that organic surface films may inhibit HOCl uptake (Smoydzin and von Glasow, 2007). A simulation with $\alpha_{\text{HOCl}} = 0.002$ (*newsoure*+lowalpha), yields $\gamma_{\text{HOCl}} = 0.0017$ and shows much better agreement with the field observations in terms of Cl$_2$ levels and the rate of evening conversion of HOCl to Cl$_2$ (Fig. 3). Cl$_2$ reaches only about 0.5 ppt at midday and 22 ppt at night. The lower accommodation coefficient results in daytime HOCl levels slightly greater than those in the *newsoure* case (up to 107 ppt). Imposing similar changes in the HOBr uptake efficiency would also have significant impacts on halogen chemistry in the model, but this possibility was not explored in these simulations. In particular, model overestimation of aerosol HOBr uptake could at least partially explain why models tend to overestimate Br$_x$ cycling in aerosols (Sander et al., 2003; Smoydzin and von Glasow, 2007; Keene et al., 2009).

### 5.5 New Cl$_x$ source with lower acidity levels (*newsoure*+lowacid)

Aerosol acidity affects modeled chlorine cycling by increasing the rate of conversion of HOCl to Cl$_2$ (Reaction R5). Lower aerosol pH favors this reaction, resulting in lower HOCl/Cl$_2$ ratios in aerosols. Uptake and release of HOCl and Cl$_2$ from aerosols in turn influence the gas phase HOCl/Cl$_2$ ratio. Consequently, model simulations with more acidic aerosols have a lower HOCl/Cl$_2$ ratio in the gas phase. Sea salt aerosols originate at pH ≈ 8 but rapidly acidify due to the uptake of gas phase acids and aqueous oxidation of S(IV) (Chameides and Stelson, 1992; Erickson et al., 1999). Under the aged polluted air conditions at Cape Verde (i.e. with HNO$_3$ ≈ 100 ppt), the model predicts that fresh sea salt aerosols reach a pH of 3 in minutes.

The fact that Cl$_x$ levels are observed to be higher in aged polluted air supports the idea that aged, very acidic aerosols contribute to Cl$_x$ cycling. However, the model generates too much Cl$_2$ when it is forced to have the observed high HOCl levels. This may indicate that Cl$_2$ production is too strongly favored in the highly acidic model aerosols. It is likely that sea salt aerosol pH decreases with increasing elevation in the MBL (von Glasow and Sander, 2001). In the surface layer where our measurements were made, it is possible that less acidic sea salt aerosols push the HOCl-Cl$_2$ balance towards HOCl.

To explore this idea in a simplistic way, a *newsoure*+lowacid model simulation was run. This was identical to the *newsoure* simulation but the fixed levels of gas phase HCl and HNO$_3$ were reduced to 80 ppt and 10 ppt, respectively. The resulting sea salt aerosol pH was 4.3, higher than the pH 3.4 aerosols of all the other simulations. The imposed HOCl source was 9 % higher than in the *newsoure* case due to higher aerosol phase Cl$^-$ (see Reaction R13). The results of this case were similar to those found in the *newsoure*+lowalpha case. HOCl reaches a maximum of 107 ppt, and this simulation showed slower nighttime growth of Cl$_2$ and lower levels of both nighttime and daytime Cl$_2$, more in line with observations. Cl$_2$ is maintained at 0.5 ppt at noon and reaches 22 ppt at night.

### 5.6 Base conditions with no gas phase halogens (*nohalogen*)

A *nohalogen* simulation was carried out, using the same initial conditions as the *base case* but excluding gas phase chlorine and bromine species. This approach is useful for directly comparing certain impacts of halogens, but it is not useful for understanding the net oxidative impacts of halogens in the MBL. For example, the presence of halogens draws down NO$_3$ levels, which would in turn result in lower O$_3$ levels. Fixing NO$_x$ and O$_3$ prevents this effect from being realized in the model runs. The *newsoure*+lowacid simulation showed a 28 % increase in total daily methane loss relative to the *nohalogen* case (Table 4). The increase is due to methane oxidation by the Cl atom (67 %) and increased OH (33 %). Ozone loss was enhanced by 50 % in the *newsoure*+lowacid case, primarily due to Br$_x$ cycling. Similarly large enhancements in Cape Verde ozone destruction due to Br$_x$ and I$_x$ have been inferred previously (Read et al., 2008). If the missing HOCl in the model were provided by a Cl atom precursor rather than by a direct source of HOCl, Cl$_2$ atom concentration and its impacts on methane and ozone loss would be roughly 5-fold greater. This is due to the inefficient conversion of Cl atom to HOCl. In that case, Cl$_2$ would compete with OH as the dominant methane oxidant. However, under the assumption that the missing HOCl was directly released from aerosols, the additional HOCl source only increases total methane oxidation by 8 % relative to the *base case*.

All cases which included gas phase halogen chemistry showed a NO$_x$ loss rate about three times higher than in the
nohalogen case. This difference is primarily due to aerosol uptake of ClNO3 and BrNO3 to form NO5.

5.7 Discussion of modeling results

The model simulations described above show that a base case simulation with realistic environmental conditions and known chemistry significantly underestimates HOCl levels during the high Clx measurement period. The simulations which best represented the observations were the new-source + lowalpha and newsource + lowacid runs. Each of these runs included a hypothetical additional source of HOCl and a means to hinder the rapid conversion of HOCl to Cl2 in model aerosols. The MECCA modeling results show that it is not possible to simulate the high observed levels of HOCl in aged polluted air at Cape Verde without imposing unrealistic boundary conditions or introducing a new source of Clx.

The rate of Clx cycling and the partitioning of HOCl and Cl2 in the model are both sensitive to aerosol pH and abundance. It is noteworthy that these simulations involved a single, well-mixed box, and the aerosol sea salt and sulfate modes are each well mixed. Hence, the processes of vertical mixing or aerosol aging are not well represented and it is possible that vertical gradients in gas phase or aerosol chemistry could be important. For example, Cl cycling in acidic aerosols aloft could generate Cl2. Freshly generated sea salt aerosols near the surface are likely less acidic, so Cl2 mixed downward into the surface layer could undergo conversion to HOCl. The vertically resolved MISTRA model was used to simulate Cl2 chemistry at Cape Verde (Lawler et al., 2009). In that study a time-dependent model run yielding about 30 ppt of nighttime Cl2 exhibited HOCl daytime maxima of about 60 and 30 ppt on the preceding and following days. This supports the basic conclusion of our model studies, that additional oxidation of Cl− is needed in order to explain the HOCl levels at Cape Verde.

We speculate that photosensitized reactions involving organic matter could provide additional oxidation of aerosol Cl− in the marine boundary layer. Such reactions presumably result in production of Cl atoms, which do not directly form HOCl in aqueous solution. Cl atoms likely react with Cl− to form Cl2−, which disproportionate to form Cl2 (Eqs. 15–16) (Jayson et al., 1973; Jacobi et al., 1999).

\[
\begin{align*}
\text{Cl} + \text{Cl}^- & \rightarrow \text{Cl}_2^- \\
\text{2Cl}_2^- & \rightarrow \text{Cl}_2 + 2\text{Cl}^- \\
\text{Cl} + \text{H}_2\text{O} & \rightarrow \text{HOCl}^- + \text{H}^+ 
\end{align*}
\]

(R15) (R16) (R17)

Newly formed Cl can also react with water

but this reaction is much slower than Reaction (R15), and HOCl− dissociates rapidly to OH and Cl−. We have found no evidence in the literature of an aqueous phase reaction channel for the direct formation of HOCl from Cl without involving Cl2 as an intermediate. Given the short diffusion time scale for aerosols, most of the Cl2 produced in an aerosol would escape to the gas phase before it could hydrolyze to form HOCl via Reaction (R5). Thus, the photosensitizer source of Clx would lead to unrealistically high gas phase Cl2 levels, unless there exists some other aqueous path to HOCl from Cl−. Laboratory studies of photosensitized chloride oxidation in seawater and aerosols are needed to investigate this question.

If all sea salt aerosols contain organics capable of photosensitized oxidation of Cl− to form HOCl, then this process should occur in both clean and polluted air masses. The hypothetical HOCl source included in the model runs would result in HOCl levels above 70 ppt even under clean air conditions. The measurements of HOCl from the low Clx observational period do not support such a large source in clean marine air. For the photosensitizer hypothesis to explain the observations would require the photosensitizers to be present at higher levels in polluted air than in clean air.

The rapid and efficient recycling of HOCl to Cl2 that occurs in the model was not supported by observations. We explored three possible explanations for this: an aerosol Clx sink, lower than expected uptake rates of HOCl, and less acidic aerosols. We are not able to definitively confirm or refute any of these possibilities. They may all be involved in controlling Clx cycling in marine air.

6 Implications

The observations of HOCl and Cl2 at Cape Verde provide direct evidence for rapid Clx cycling in the marine boundary layer, with daytime Cl atom sources that are large enough to impact ozone and methane destruction in the MBL. HOCl and Cl2 levels are considerably higher in aged polluted air than in air with open ocean back trajectories, consistent with model predictions and previous Cl2 and Cl* measurements. The rates and mechanisms of Clx cycling at Cape Verde are not yet fully understood, and the model simulations suggest that Clx cycling occurs more rapidly than predicted by current models.

The relationship between pollutants and Clx levels suggests that human-driven changes in ozone, NOx, and aerosol loading and chemistry have altered Cl atom levels, and hence, the reactivity of the atmosphere. Cl chemistry resulting from reactions of N2O5 can have a significant impact on photochemistry in continental and highly polluted coastal regions (Thornton et al., 2010; Osthoff et al., 2008). This study suggests that human influence on Cl chemistry continues for several days over the oceans, even after N2O5 has decreased to negligible levels and ClNO2 production is no longer significant. Assessing the impact of this chemistry on climate and global air quality will require field measurements over a broader range of oceanic and atmospheric conditions, and a more thorough understanding of the mechanisms involved in Clx cycling.
Supplement related to this article is available online at:

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