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Authors

Lawler, M. J
Sander, R.
Carpenter, L. J
et al.

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HOCl and Cl₂ observations in marine air

M. J. Lawler¹, R. Sander², L. J. Carpenter³, J. D. Lee⁴, R. von Glasow⁵, R. Sommariva⁵, and E. S. Saltzman¹

¹Department of Earth System Science, University of California, Irvine, CA, USA

²Department of Atmospheric Chemistry, Max-Planck Institute for Chemistry, Mainz, Germany

³Department of Chemistry, University of York, York, UK

⁴National Centre for Atmospheric Science, University of York, York, UK

⁵School of Environmental Sciences, University of East Anglia, Norwich, UK

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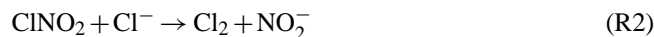
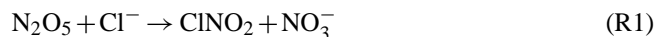
Abstract. Cl atoms in the marine atmosphere may significantly impact the lifetimes of methane and other hydrocarbons. However, the existing estimates of Cl atom levels in marine air are based on indirect evidence. Here we present measurements of the Cl precursors HOCl and Cl₂ in the marine boundary layer 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 Cl₂ 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 Cl₂ levels were higher, with HOCl maxima exceeding 100 ppt each day and Cl₂ 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 Cl₂, 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 O₃ 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 a 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, Cl₂, BrCl, HOCl, ClNO₂, 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 Cl₂ and ClNO₂ (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 N₂O₅ with aerosol chloride, as evidenced in both laboratory and field observations (Osthoff et al., 2008; Roberts et al., 2008; Thornton et al., 2010):

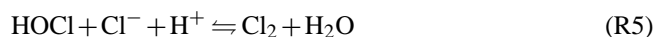


Cl activation is less well understood under the low-NO_x conditions typical of marine air masses. Cl atom production and Cl_x cycling may be initiated by the daytime oxidation of HCl (Pechtl and von Glasow, 2007):

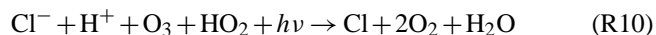


Correspondence to: M. J. Lawler
(mlawler@uci.edu)

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).

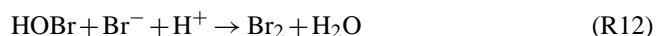
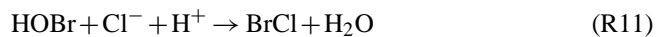


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The autocatalytic cycle is promoted by low aerosol pH, which increases the rate of conversion of HOCl to Cl₂ (Reaction R5). The ratio of O₃ to NMHCs is another key parameter in determining the efficiency of Cl cycling. Higher O₃ levels tend to sustain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

Analogous aerosol reactions involving HOBr can generate BrCl and Br₂:



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 Cl_x (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-NO_x 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

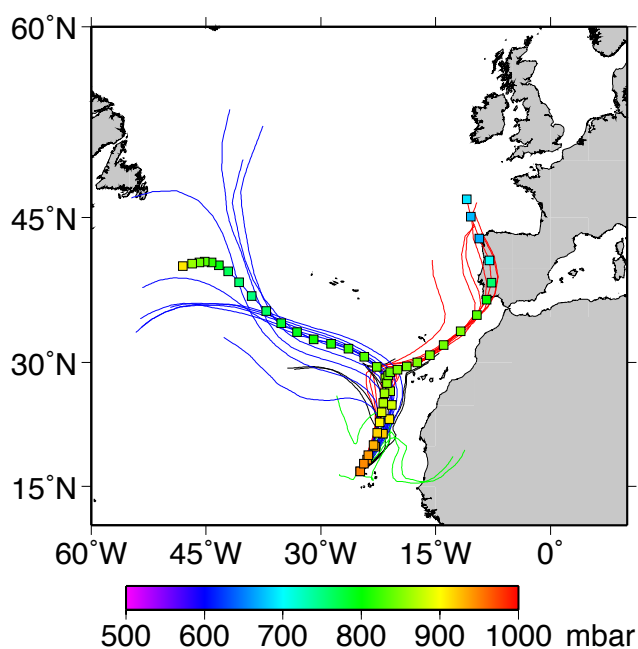
This study was carried out at the Cape Verde Atmospheric Observatory on the island of São Vicente (hereafter Cape Verde, 16°52' N, 24°52' W) from 30 May to 7 June 2009 (days of year 150–158). The site is located on a rocky coastline about 50 m from the ocean. Winds were consistently on-shore, averaging 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-Cl_x chemical measurements made at the site included NO, NO₂, NO_y, O₃, and CO. NO_y and NO₂ were measured by catalytic conversion to NO and chemiluminescence detection, with detection limits of 8 ppt (pmol/mol) for NO₂ and 4 ppt for NO_y. On average, particulate NO₃⁻ contributed 56% of the total NO_y observed. The total NO_y 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). NO_x 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

Table 1. Ambient halogen-containing isotopomers monitored by chemical ionization MS/MS during this study using Br^- as the reagent ion. Parent and fragment ions used in detection are shown.

Ambient Species	Parent Ion	Parent Mass	Fragment Ion	Fragment Mass
HO^{35}Cl	$\text{HO}^{35}\text{Cl}^{79}\text{Br}^-$	131	$^{79}\text{Br}^-$	79
HO^{35}Cl	$\text{HO}^{35}\text{Cl}^{81}\text{Br}^-$	133	$^{81}\text{Br}^-$	81
HO^{37}Cl	$\text{HO}^{37}\text{Cl}^{79}\text{Br}^-$	133	$^{79}\text{Br}^-$	79
HO^{37}Cl	$\text{HO}^{37}\text{Cl}^{81}\text{Br}^-$	135	$^{81}\text{Br}^-$	81
$^{70}\text{Cl}_2$	$^{70}\text{Cl}_2^{79}\text{Br}^-$	149	$^{35}\text{Cl}^-$	35
$^{70}\text{Cl}_2/^{72}\text{Cl}_2$	$^{70}\text{Cl}_2^{81}\text{Br}^-/^{72}\text{Cl}_2^{79}\text{Br}^-$	151	$^{35}\text{Cl}^-$	35
$^{72}\text{Cl}_2$	$^{72}\text{Cl}_2^{79}\text{Br}^-$	151	$^{37}\text{Cl}^-$	37
$^{72}\text{Cl}_2/^{74}\text{Cl}_2$	$^{72}\text{Cl}_2^{81}\text{Br}^-/^{74}\text{Cl}_2^{79}\text{Br}^-$	153	$^{37}\text{Cl}^-$	37

**Fig. 1.** 6-day back trajectories for air reaching the Cape Verde Atmospheric Observatory measurement site, given every 6 h for all time periods that Cl_2 and HOCl were measured. Trajectory trace colors show different time periods by day of year (day 150.0 is 30 May 2009, 00:00 local times). Red: 150.25–152.25, black: 152.5–153.75, green: 154.75–155.75, blue: 156.00–158.5. Colored squares indicate air parcel elevation in mbar for trajectories on two characteristic days. Trajectories are from the British Atmospheric Data Centre, using the ECMWF archive data.

AeroTrac 8220). There was often visible sea spray from 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, par-

ticulate Na^+ was determined by ion chromatography and ranged from 3.2–5.2 $\mu\text{g m}^{-3}$ 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_2Br^- 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_2Br^- 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

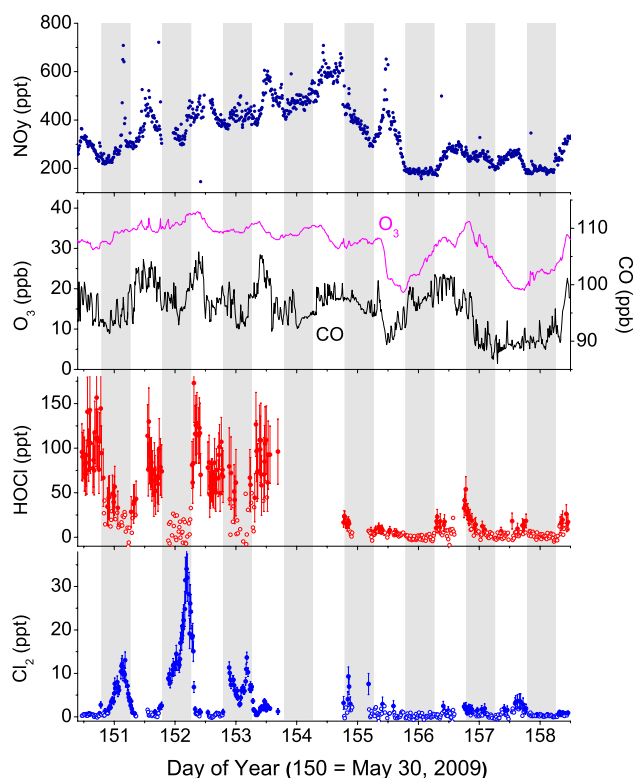


Fig. 2. NO_y , O_3 , CO, HOCl, and Cl_2 during the 2009 Cape Verde field campaign. For HOCl and Cl_2 , open circles indicate measurements below detection limit. Each point is a 15-min average, and error bars are one standard error of the mean. Shaded vertical bars represent nighttime hours. The day-long gap in HOCl and Cl_2 data about day 154 was due to a power outage.

yield a daughter ion which was mass selected (Q3) and detected by a dynode/electron multiplier. Cl_2 was detected using $\text{Cl}_2\text{Br}^- \rightarrow \text{Cl}^-$ transitions and HOCl was detected using $\text{HOClBr}^- \rightarrow \text{Br}^-$ 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_2 was calibrated in the field every four hours using the output of a Cl_2 permeation tube (VICI Metronics) and a multi-stage dilution system (Gallagher et al., 1997; Finley and Saltzman, 2006). The Cl_2 standard was added to the front of the instrument inlet and the final mixing ratio of Cl_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_2 loss. An iodometric calibration of the permeation tube performed in May 2011 matched the inferred Cl_2 loss from a concurrent month-long mass record to within experimen-

tal 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_2 mixing ratios include variability in both ambient signal and uncertainty in the instrument sensitivity. For each Cl_2 calibration, the uncertainty in sensitivity was calculated as the standard error in averaged Cl_2 standard signal, divided by the mixing ratio of Cl_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, $\text{pH} \approx 7$). Nitrogen was bubbled at 5–20 ml min^{-1} through the solution in a two-port gas-tight glass container, and the output nitrogen flow contained both HOCl and Cl_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" (0.32 cm) outer diameter (OD) teflon tube with HCl condensed onto the walls. This reactor converted the HOCl to Cl_2 while letting Cl_2 pass. After the reactor, the flow was routed to the instrument inlet, and the increase in Cl_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_2 " signal was converted into an HOCl mixing ratio using the instrument sensitivity to Cl_2 , based on the Cl_2 permeation tube. If conversion of HOCl to Cl_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_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_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 Cl_x speciation observed. Reactive halogens contained in aerosols themselves are not a significant source of interference because the fraction of Cl_x 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 Cl_x” and “low Cl_x” days, respectively. The observed variability in Cl₂ and HOCl is likely attributable to changes in air mass origin and chemistry. Cl_x (HOCl + 2 · Cl₂) was positively correlated with both NO_y

($r^2 = 0.19$, $p < 0.001$) 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 NO_y (200–700 ppt). The combination of continental back trajectories, high NO_y levels, and low NO_x 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 Cl_x 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, NO_y 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 Cl_x 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 Cl_x period, when aged polluted air reached the site. No attempt was made to model the clean marine conditions encountered during the low Cl_x 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.

<i>Fixed meteorological conditions</i>	
Solar parameters	30 May, 17° N latitude
Temperature (K)	296
Relative humidity	0.8
Total column ozone (DU)	300
Boundary layer height (m)	1000
Coarse aerosol liquid water content (m ⁻³ water/m ⁻³ air)	1.2 × 10 ⁻¹⁰
Fine aerosol liquid water content (m ⁻³ water/m ⁻³ air)	1.1 × 10 ⁻¹²
<i>Fixed mixing ratios (ppb)</i>	
O ₃	45
CH ₄	1800
NO ₂	0.015
Methanol	0.5
Acetaldehyde	0.7
Acetone	0.3
Ethane	0.7
<i>Initial mixing ratios (ppb)</i>	
CO	100
HCHO	0.3
<i>Input fluxes (ppb/day)</i>	
DMS	0.07
NH ₃	0.035
<i>Aerosol components (μg m⁻³)</i>	
Aerosol Cl ⁻	18.3–20.6
Non-sea-salt SO ₄ ²⁻	0.09–0.37

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

Model run	Added HOCl source (midday value, ppt h ⁻¹)	HOCl _(aq) sink	α _{HOCl}	HCl (ppb)	HNO ₃ (ppb)	Gas phase halogens
<i>base case</i>	0	No	0.1	0.6	0.1	Yes
<i>news-source</i>	54	No	0.1	0.6	0.1	Yes
<i>ns+sink</i>	79	Yes	0.1	0.6	0.1	Yes
<i>ns+lowalpha</i>	54	No	0.002	0.6	0.1	Yes
<i>ns+lowacid</i>	59	No	0.1	0.08	0.01	Yes
<i>nohalogen</i>	0	No	0.1	0.6	0.1	No

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 Cl_x 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 Cl_x source (*newsourc*)

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 *newsourc* simulation was a light-dependent chloride oxidation reaction generating gas-phase HOCl:



Here $c = 0.04$ and $j_{\text{O}_3(\text{O}^1\text{D})}$ is the rate constant for photolysis of O₃ to produce O¹D.

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 Cl_x source required. Several-fold larger rates of Cl⁻ oxidation to Cl_x would be required if the Cl_x 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 Cl_x species. This means of forming HOCl is inefficient because a large fraction of Cl forms the unreactive reservoir species HCl. Cl₂

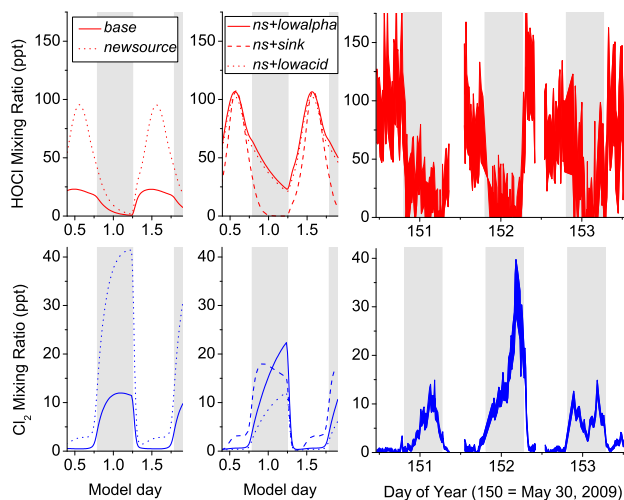


Fig. 3. Model results (left and center panels) for Cl₂ and HOCl compared to observed high Cl_x period data (right panels). Observational data shaded area is within mean ±1 standard error. Red: HOCl, blue: Cl₂. Shaded vertical bars represent nighttime hours. Model day and day of year whole numbers are midnight.

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 noontime 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 Halmann, 1990; Jammoul et al., 2009). Such reactions could provide the required Cl_x 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 *newsourc* 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

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 Cl₂ observations during the high Cl_x period are given for comparison. The midday observational means for HOCl and Cl₂ include all data between 10:00–14:00 LT, including points below detection. One standard deviation is shown.

Mixing ratios (ppt)	Model Scenario				Observations
	base	newsourc	ns+lowacid	nohalogen	
Midday HOCl max	23.1	95.5	106.8	0	83.3±23.6
Midday Cl ₂	0.50	2.45	0.54	0	1.2±1.0
Nighttime Cl ₂ max	12.0	41.4	22.3	0	20.2±11.9
Mean Cl atom (cm ⁻³)	1.41×10 ⁴	2.61×10 ⁴	2.19×10 ⁴	0	
Rates (ppb/day)					
Cl + O ₃ reaction	0.63	1.16	0.97	0	
Br + O ₃ reaction	4.45	4.33	4.34	0	
ΣO ₃ loss	6.68	7.16	7.00	4.67	
CH ₄ loss to Cl	0.21	0.38	0.32	0	
CH ₄ loss to OH	1.77	1.80	1.82	1.66	
ΣCH ₄ loss	2.01	2.20	2.17	1.69	
ΣNO _x loss	0.112	0.130	0.122	0.040	

nighttime Cl₂ levels were also generally higher in this model run, and the rate of increase of Cl₂ at nightfall is faster. It appears that the conversion of HOCl to Cl₂ 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 Cl₂ back into HOCl). Each of these possibilities would reduce the rate of Cl₂ production and result in lower Cl₂ levels, as demonstrated by the following model simulations.

5.3 New Cl_x source with aerosol HOCl sink (*newsourc + 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 low 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 *newsourc* simulation) and an irreversible aerosol sink for reactive chlorine (*newsourc + sink*). This sink was parameterized as follows:



with a bimolecular rate constant of $2.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, the rate of the reaction of HOCl with phenol (Gallard and Von Gunten, 2002). C_{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_{ClSink} is depleted and it becomes a negligible sink for HOCl at midday. Overnight, C_{ClSink} reaches 29 mM. If C_{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 *newsourc + 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 Cl₂ levels (18 ppt maximum) relative to

the *newsorce* case, bringing the model more in line with observations in that regard (Fig. 3). However, daytime Cl₂ is still higher than observed on days 151 and 152, and the early nighttime Cl₂ increase is earlier and more rapid than observed (Fig. 3).

5.4 New Cl_x source with low HOCl uptake coefficient (*newsorce+lowalpha*)

In the *newsorce* case, about 10% of gas phase HOCl that contacts an aerosol undergoes reactive uptake ($\gamma = 0.1$). The fraction γ is controlled by aqueous phase reaction rates and the mass accommodation coefficient (α). 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 γ_{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 $\alpha_{\text{HOCl}} = 0.002$ (*newsorce + lowalpha*), yields $\gamma_{\text{HOCl}} = 0.0017$ and shows much better agreement with the field observations in terms of Cl₂ levels and the rate of evening conversion of HOCl to Cl₂ (Fig. 3). Cl₂ 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 *newsorce* 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 (*newsorce + lowacid*)

Aerosol acidity affects modeled chlorine cycling by increasing the rate of conversion of HOCl to Cl₂ (Reaction R5). Lower aerosol pH favors this reaction, resulting in lower HOCl/Cl₂ ratios in aerosols. Uptake and release of HOCl and Cl₂ from aerosols in turn influence the gas phase HOCl/Cl₂ ratio. Consequently, model simulations with more acidic aerosols have a lower HOCl/Cl₂ ratio in the gas phase. Sea salt aerosols originate at pH \approx 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 HNO₃ \approx 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 Cl₂ when it is forced to have the observed high HOCl levels. This may indicate that Cl₂ 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-Cl₂ balance towards HOCl.

To explore this idea in a simplistic way, a *newsorce + lowacid* model simulation was run. This was identical to the *newsorce* simulation but the fixed levels of gas phase HCl and HNO₃ 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 *newsorce* case due to higher aerosol phase Cl⁻ (see Reaction R13). The results of this case were similar to those found in the *newsorce + lowalpha* case. HOCl reaches a maximum of 107 ppt, and this simulation showed slower nighttime growth of Cl₂ and lower levels of both nighttime and daytime Cl₂, more in line with observations. Cl₂ 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_x levels, which would in turn result in lower O₃ levels. Fixing NO_x and O₃ prevents this effect from being realized in the model runs. The *newsorce+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 *newsorce + 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 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 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 ClNO_3 and BrNO_3 to form NO_3^- .

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 Cl_x measurement period. The simulations which best represented the observations were the *new-source + lowalpha* and *newsources + lowacid* runs. Each of these runs included a hypothetical additional source of HOCl and a means to hinder the rapid conversion of HOCl to Cl_2 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 Cl_x .

The rate of Cl_x cycling and the partitioning of HOCl and Cl_2 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 Cl_2 . Freshly generated sea salt aerosols near the surface are likely less acidic, so Cl_2 mixed downward into the surface layer could undergo conversion to HOCl. The vertically resolved MISTRA model was used to simulate Cl_2 chemistry at Cape Verde (Lawler et al., 2009). In that study a time-dependent model run yielding about 30 ppt of nighttime Cl_2 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 Cl_2^- , which disproportionates to form Cl_2 (Eqs. 15–16) (Jayson et al., 1973; Jacobi et al., 1999).



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 Cl_2 as an intermediate. Given the short diffusion time scale for aerosols, most of the Cl_2 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 Cl_x would lead to unrealistically high gas phase Cl_2 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 Cl_x 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 Cl_2 that occurs in the model was not supported by observations. We explored three possible explanations for this: an aerosol Cl_x 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 Cl_x cycling in marine air.

6 Implications

The observations of HOCl and Cl_2 at Cape Verde provide direct evidence for rapid Cl_x 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 Cl_2 levels are considerably higher in aged polluted air than in air with open ocean back trajectories, consistent with model predictions and previous Cl_2 and Cl^* measurements. The rates and mechanisms of Cl_x cycling at Cape Verde are not yet fully understood, and the model simulations suggest that Cl_x cycling occurs more rapidly than predicted by current models.

The relationship between pollutants and Cl_x levels suggests that human-driven changes in ozone, NO_y , and aerosol loading and chemistry have altered Cl atom levels, and hence, the reactivity of the atmosphere. Cl chemistry resulting from reactions of N_2O_5 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 N_2O_5 has decreased to negligible levels and ClNO_2 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 Cl_x cycling.

Supplement related to this article is available online at:
[http://www.atmos-chem-phys.net/11/7617/2011/
acp-11-7617-2011-supplement.pdf](http://www.atmos-chem-phys.net/11/7617/2011/acp-11-7617-2011-supplement.pdf)

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