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# HOCl and Cl<sub>2</sub> observations in marine air

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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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> levels were higher, with HOCl maxima exceeding 100 ppt each day and Cl<sub>2</sub> reaching up to 34 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. The data indicate that Cl atoms accounted for as much as 15% of the methane destruction at this site during the study period. A photochemical model does not adequately simulate the observed abundances of HOCl and Cl<sub>2</sub>, 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. Cl has over tenfold faster reaction rate constants than OH for reactions with methane and non-methane hydrocarbons (NMHCs) (Sander et al., 2006), so Cl may play a significant role in controlling the lifetimes of these climate-relevant gases. However, the abundances of Cl and its precursors are poorly known, and the mechanisms responsible for the oxidation of chloride to more reactive forms

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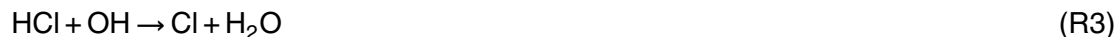


(Cl, ClO, Cl<sub>2</sub>, HOCl, ClNO<sub>2</sub>, etc.; collectively referred to as Cl<sub>x</sub>) are incompletely understood. It is therefore difficult to assess the impacts of reactive chlorine on tropospheric chemistry and climate.

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<sub>2</sub> and ClNO<sub>2</sub> (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 primarily initiated by the reaction of N<sub>2</sub>O<sub>5</sub> with aerosols, as evidenced in both laboratory and field observations (Osthoff et al., 2008; Thornton et al., 2010; Roberts et al., 2008):



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



This reaction alone is too slow to maintain significant levels of Cl atom for typical HCl levels in the remote atmosphere of less than ≈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 Cl<sub>2</sub>. Cl<sub>2</sub> 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 (Pechtl and von Glasow, 2007; Vogt et al., 1996).



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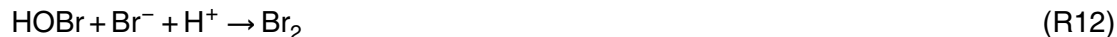


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The autocatalytic cycle is promoted by low aerosol pH, which increases the rate of conversion of HOCl to Cl<sub>2</sub> (Reaction R5). The ratio of O<sub>3</sub> to NMHCs is another key parameter in determining the efficiency of Cl cycling. O<sub>3</sub> tends to increase cycling by conversion of Cl to ClO (Reaction R8), while hydrocarbons tend to dampen cycling by removing Cl atoms.

Analogous aerosol reactions involving HOBr can generate BrCl and Br<sub>2</sub> via the reactions



In photochemical models of marine air, the photolysis of BrCl is a major source of oxidized chlorine in marine air (Pechtl and von Glasow, 2007; Vogt et al., 1996). Surprisingly, BrCl has not yet been detected in coastal or open ocean marine air (Finley and Saltzman, 2008; Lawler et al., 2009). 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, O<sub>3</sub>, and HOCl

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(Behnke et al., 1999; Knipping et al., 2000; Huff and Abbatt, 2000). However, aerosol uptake of HOCl to form Cl<sub>2</sub> 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 Cl<sub>2</sub>, ClNO<sub>2</sub>, and Cl\*, a nonspecific measure of total Cl<sub>x</sub> (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, remote, low-NO<sub>x</sub> environments.

In this study we present the first simultaneous measurements of HOCl and Cl<sub>2</sub> in the marine boundary layer, taken at the Cape Verde islands in the eastern tropical Atlantic ocean. This study follows earlier measurements of Cl<sub>2</sub> 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 ≈50 m from the ocean. Winds were consistently onshore, averaging 7.3 m s<sup>-1</sup> from the northeast, with daytime winds slightly higher than nighttime on days 150–154. There is no local source of pollution upwind of the site. Air mass back trajectories were calculated for the site using the British Atmospheric Data Centre (BADC) Trajectory Service. 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.

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Non-Cl<sub>x</sub> chemical measurements made at the site included NO, NO<sub>2</sub>, NO<sub>y</sub>, O<sub>3</sub>, and CO. NO<sub>y</sub> and NO<sub>2</sub> were measured by catalytic conversion to NO and chemiluminescence detection, with detection limits of 8 ppt (pmol/mol) for NO<sub>2</sub> and 4 ppt for NO<sub>y</sub>. The NO<sub>y</sub> measurement includes a major contribution from aerosol phase nitrate, so (NO<sub>y</sub>-NO<sub>2</sub>-NO) is not an accurate measurement of gas phase HNO<sub>3</sub> alone. Ozone was measured by ultraviolet absorption (Thermo Electron 49i), and CO was measured using a fast response vacuum ultraviolet fluorescence analyzer (Aerolaser 5001). NO<sub>x</sub> levels were low over the whole campaign (<10–120 ppt NO<sub>2</sub> for 97% of points), and ozone ranged from 19–39 ppb. CO 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 AeroTrac 8220). There was often visible sea spray from wave breaking at the coast. Aerosol chemical composition measurements at 30 m showed that the aerosol was usually dominated by salt (K. W. Fomba, personal communication, 2010).

### 3 HOCl and Cl<sub>2</sub> measurement technique

HOCl and Cl<sub>2</sub> were detected using chemical ionization tandem mass spectrometry (CIMS-MS) via formation of a Br<sup>-</sup> 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<sub>2</sub> for the first three days of the study, and 5 ppt HOCl and 2 ppt Cl<sub>2</sub> during the last four days.

Ambient air was drawn from an intake 3 m above ground at 63 L min<sup>-1</sup> through a 2" (5.1 cm) inner diameter (ID) acrylic butyl styrene (ABS) pipe. A subsample of ≈1.3 L min<sup>-1</sup> (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<sup>-1</sup> (STP) of bromoform (CHBr<sub>3</sub>) at its vapor pressure at 23 °C (about 6 mbar) in nitrogen was added to the sampled air, and the mixture passed over a beta-emitting <sup>63</sup>Ni foil. The ionization region was maintained at

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5  $\approx 200$  torr.  $\text{Br}^-$  was the dominant reagent ion produced, and it reacted with  $\text{Cl}_2$  and  $\text{HOCl}$  to form the ion clusters  $\text{Cl}_2\text{Br}^-$  and  $\text{HOClBr}^-$ , 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  
10 set to 9 V (roughly 20 Townsends) to break up weakly-bound clusters. The  $\text{Cl}_2\text{Br}^-$  and  $\text{HOClBr}^-$  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.  $\text{Cl}_2$  was detected using  $\text{Cl}_2\text{Br}^- \rightarrow \text{Cl}^-$  transitions and  $\text{HOCl}$  was detected using  $\text{HOClBr}^- \rightarrow \text{Br}^-$  transitions (Table 1). Data  
15 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  $\text{Cl}_2$  was calibrated in the field every four hours using the output of a  $\text{Cl}_2$  permeation tube (VICI Metronics) and a multi-stage dilution system (Gallagher et al., 1997; Finley and Saltzman, 2006). The  $\text{Cl}_2$  standard was added to the front of the instrument inlet and the final mixing ratio of  $\text{Cl}_2$  in the air stream was  
20 typically 14 ppt. The permeation tube output rate was gravimetrically calibrated in the lab at UC Irvine. A comparison between gravimetric loss and iodometric calibration showed no significant difference between the two methods for a similar  $\text{Cl}_2$  permeation tube from the same manufacturer (Finley, 2007). Instrument sensitivity was assumed to vary linearly between calibrations, except for likely sensitivity step changes, such  
25 as the power outage that resulted in a day-long gap in observations about day 154. Reported standard errors for  $\text{Cl}_2$  mixing ratios include variability in both ambient signal and uncertainty in the instrument sensitivity.

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The instrument was calibrated for HOCl using a phosphate-buffered solution of NaOCl (0.6–2 mM, pH  $\approx$  7). Nitrogen was bubbled at 5–20 ml min<sup>-1</sup> through the solution in a two-port gas-tight glass container, and the output nitrogen flow contained both HOCl and Cl<sub>2</sub>. 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<sub>2</sub> while letting Cl<sub>2</sub> pass. After the reactor, the flow was routed to the instrument inlet, and the increase in Cl<sub>2</sub> 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<sub>2</sub>" signal was converted into an HOCl mixing ratio using the instrument sensitivity to Cl<sub>2</sub>, as assessed using the Cl<sub>2</sub> perm tube. The HOCl mixing ratio in the standard ranged from 55–438 ppt, but only levels near ambient mixing ratios (55–219 ppt) were used to assess instrument response. Instrument response was roughly linear in the range of ambient mixing ratios, 0–200 ppt. Calibrations were run about once a day, and as for Cl<sub>2</sub>, instrument sensitivity was assumed to vary linearly between calibrations except for likely step changes. HOCl sensitivity was more variable than Cl<sub>2</sub> sensitivity, but it varied by less than 90% between calibrations under similar conditions. 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 response was very sensitive to pressure in the ionization region. This pressure was not dynamically controlled and was subject to some drift. Reported standard errors for HOCl mixing ratios include variability in both ambient signal and uncertainty in the instrument sensitivity.

The HOCl calibration assumes complete conversion of HOCl to Cl<sub>2</sub> in the reactor. If conversion was actually less efficient, instrument sensitivity was overestimated and ambient HOCl levels were underestimated. This potential source of bias therefore cannot be responsible for the unexpectedly high HOCl levels observed.

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The instrument blank, or background signal, was assessed every hour by passing ambient air through a scrubber composed of glass wool coated with  $\text{CaCO}_3$ . The scrubber removes  $\text{Cl}_2$  with  $\approx 99\%$  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 to calculate mixing ratios, the reported HOCl mixing ratios are lower limits.

## 4 Observations

HOCl ranged from  $<5$ –173 parts per trillion (ppt, pmol/mol), and  $\text{Cl}_2$  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  $\text{Cl}_2$  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  $\text{Cl}_2$  (Reaction R5), and the rapid daytime photolysis of  $\text{Cl}_2$  (Maric et al., 1993).

HOCl and  $\text{Cl}_2$  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  $\text{Cl}_x$ ” and “low  $\text{Cl}_x$ ” days, respectively. The observed variability in  $\text{Cl}_2$  and HOCl is likely attributable to changes in air mass origin and chemistry.  $\text{Cl}_x$  ( $\text{HOCl} + 2 \cdot \text{Cl}_2$ ) was positively correlated with both  $\text{NO}_y$  ( $r^2 = 0.19$ ,  $p < 0.001$ ) and  $\text{O}_3$  ( $r^2 = 0.32$ ,  $p < 0.001$ ). 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  $\text{O}_3$  levels consistently near or above 30 ppb (mean 34.5 ppb), and rising  $\text{NO}_y$  (200–700 ppt).  $\text{Cl}_2$  and HOCl were at their highest levels during these days. During

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the last three days (low  $\text{Cl}_x$  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)  $\approx 1$  day upwind of the site. During the night of days 156 and 158,  $\text{NO}_y$  was at its lowest levels of the measurement period, and  $\text{O}_3$  was at its lowest nighttime levels (as low as 20 ppb). These nights showed the lowest  $\text{Cl}_2$  mixing ratios of the measurement period.

The  $\text{Cl}_2$  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, when  $\text{Cl}_2$  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  $\text{Cl}_x$  ranged from  $<14$ –101 ppt, with one outlier at 220 ppt (Lawler et al., 2009). The 2007 data are consistent with the existence of significant levels of daytime HOCl at Cape Verde.

## 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  $\text{Cl}_2$  observations could be explained by known chemistry and examine the role environmental conditions play in chlorine cycling. The simulations were intended to model the high  $\text{Cl}_x$  period, when aged polluted air reached the site. No attempt was made to model the clean marine conditions encountered during the low  $\text{Cl}_x$  period because observed HOCl and  $\text{Cl}_2$  levels were often below the detection limit. The model included bromine and chlorine chemistry in the gas phase and in seasalt and sulfate aerosols. Ozone, methane,  $\text{HNO}_3$ , HCl,  $\text{NO}_2$ , 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.

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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. Gas phase reactions of Cl with ethane (C<sub>2</sub>H<sub>6</sub>), methanol (CH<sub>3</sub>OH), acetaldehyde (CH<sub>3</sub>CHO), and acetone (CH<sub>3</sub>COCH<sub>3</sub>) were included based on recommended rate constants (Sander et al., 2006).

## 5.1 Best guess simulation (*base case*)

A simulation dubbed *base case* was run with best-guess environmental conditions and standard model chemistry. Model inputs are listed in Tables 2 and 3. O<sub>3</sub> and sea salt particle abundances were based on measurements made during the campaign. Levels of NMHCs, acidic gases, and NO<sub>2</sub> were based on measurements made during previous studies at Cape Verde (Read et al., 2009; Lawler et al., 2009). Under these conditions, the model achieves a maximum of only 23 ppt HOCl (Fig. 3, Table 4). Increasing O<sub>3</sub> 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. For example, HCl would need to be present at levels of ≈10 ppb if it were responsible for the HOCl levels observed. HCl never exceeded 700 ppt during the same season in 2007. O<sub>3</sub> in the *base case* was fixed at 45 ppb, already higher than the observed maximum of 40 ppb during the measurement period. Eliminating all NMHCs results in HOCl levels of only 50 ppt. It seems likely that an unknown, additional source of Cl<sub>x</sub> exists in the MBL.

## 5.2 New Cl<sub>x</sub> 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:

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$$P_{\text{HOCl}} = c \cdot j\text{O}_{3(\text{O}^1\text{D})} \cdot \text{Cl}^-_{\text{aerosol}} \quad (\text{R13})$$

Here  $c$  is a constant and  $j\text{O}_{3(\text{O}^1\text{D})}$  is the rate constant for photolysis of  $\text{O}_3$  to produce  $\text{O}^1\text{D}$ .

A midday source strength of  $54 \text{ ppt h}^{-1}$  was required to achieve 96 ppt HOCl at mid-day (Fig. 3, Table 4). This is a strong source, but nonetheless a conservative estimate of the  $\text{Cl}_x$  source required. Several-fold larger rates of  $\text{Cl}^-$  oxidation to  $\text{Cl}_x$  would be required if the  $\text{Cl}_x$  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  $\text{Cl}_x$  species formed in aerosol. This means of forming HOCl is inefficient because a large fraction of Cl forms the unreactive reservoir species HCl. It is also worth noting that BrCl is the dominant source of Cl atom in the model, contributing to HOCl formation and reaching 24 ppt in the *base case* run. As noted above, BrCl has not been observed in marine air (Finley and Saltzman, 2008; Lawler et al., 2009).  $\text{Cl}_2$  reached a nighttime maximum of 41 ppt (Fig. 3, Table 4).

If the HOCl production at Cape Verde was 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  $20 \text{ ppt h}^{-1}$ . Even if every such collision somehow oxidized  $\text{Cl}^-$  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).  $\text{O}_3$ ,  $\text{NO}_2$ , and  $\text{H}_2\text{O}_2$  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  $\text{Cl}^-$  in bulk aqueous solution are negligible.

A more plausible candidate might be the oxidation of aerosol  $\text{Cl}^-$  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 (Gratzel and Halmann, 1990; Scharf and Weitz, 1979; Jammoul et al., 2009). Such reactions could provide the required  $\text{Cl}_x$  source if the photosensitizers comprise a few percent

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of the total aerosol dissolved organic carbon (DOC). However, whether such reactions could directly result in HOCl, rather than Cl<sub>2</sub>, is not clear.

The hypothetical HOCl source results in higher Cl<sub>2</sub> levels due to reactions in acidic aerosols (Reaction R5). The newsource model Cl<sub>2</sub> averaged over 2 ppt in the daytime.

This is higher than measured on days 150 and 151, when daytime Cl<sub>2</sub> averaged 0.4 and 0.7 ppt, respectively. Observed nighttime Cl<sub>2</sub> levels were also generally higher in this model run, and the rate of increase of Cl<sub>2</sub> at nightfall is faster. It appears that the conversion of HOCl to Cl<sub>2</sub> 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<sub>2</sub> back into HOCl). Each of these possibilities would reduce the rate of Cl<sub>2</sub> production and result in Cl<sub>2</sub> levels, as demonstrated by the following model simulations.

### 5.3 New Cl<sub>x</sub> 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 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

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present at concentrations of  $\approx 1 \times 10^{-5}$  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 Cl has a similar reactivity in seasalt 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:



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).  $\text{C}_{\text{Clsink}}$  was assumed to be present in fresh sea salt aerosols at 160 mM and was lost only via Reaction (R14). During the daytime,  $\text{C}_{\text{Clsink}}$  is depleted and it becomes a negligible sink for HOCl at midday. Overnight,  $\text{C}_{\text{Clsink}}$  reaches 29 mM. If  $\text{C}_{\text{Clsink}}$  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 seasalt aerosols were similar, then the  $\text{Cl}_x$ -reactive fraction would have to be a large fraction of the total organic matter in seasalt. 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  $79 \text{ ppt h}^{-1}$  at midday to result in an HOCl maximum of 108 ppt. This simulation shows decreased nighttime  $\text{Cl}_2$  levels (18 ppt maximum) relative to the *newsource* case, bringing the model more in line with observations in that regard (Fig. 3). However, daytime  $\text{Cl}_2$  is still higher than observed on days 151 and 152, and the early nighttime  $\text{Cl}_2$  increase is earlier and more rapid than observed (Fig. 3).

#### 5.4 New $\text{Cl}_x$ source with low HOCl uptake coefficient (*newsource*+*lowalpha*)

In the *newsource* 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  $\alpha_{\text{HOCl}} = 0.002$  (*newsourc* + *lowalpha*), yields  $\gamma_{\text{HOCl}} = 0.0017$  and shows much better agreement with the field observations in terms of  $\text{Cl}_2$  levels and the rate of evening conversion of HOCl to  $\text{Cl}_2$  (Fig. 3).  $\text{Cl}_2$  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 *newsourc* 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.

### 5.5 New $\text{Cl}_x$ source with lower acidity levels (*newsourc* + *lowacid*)

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

The fact that  $\text{Cl}_x$  levels are observed to be higher in aged polluted air supports the idea that aged, very acidic aerosols contribute to  $\text{Cl}_x$  cycling. However, the model generates too much  $\text{Cl}_2$  when it is forced to have the observed high HOCl levels. This may indicate that  $\text{Cl}_2$  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

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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<sub>2</sub> balance towards HOCl.

To explore this idea in a simplistic way, a *newsourc* + *lowacid* model simulation was run. This was identical to the *newsourc* simulation but the fixed levels of gas phase HCl and HNO<sub>3</sub> 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 *newsourc* case due to higher aerosol phase Cl<sup>-</sup> (see Reaction R13). The results of this case were similar to those found in the *newsourc* + *lowalpha* case. HOCl reaches a maximum of 107 ppt, and this simulation showed slower nighttime growth of Cl<sub>2</sub> and lower levels of both nighttime and daytime Cl<sub>2</sub>, more in line with observations. Cl<sub>2</sub> is maintained at 0.5 ppt at noon and reaches 22 ppt at night.

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

A *nohalogen* simulation was also run, using the same initial conditions as the *base case* but excluding gas phase chlorine and bromine species. The *newsourc*+*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 *newsourc* + *lowacid* case, primarily due to Brx cycling. Similarly large enhancements in Cape Verde ozone destruction due to Brx and Ix 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*.

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All cases which included gas phase halogen chemistry showed a  $\text{NO}_x$  loss rate about three times higher than in the *nohalogen* case. This difference is primarily due to aerosol uptake of  $\text{ClNO}_3$  and  $\text{BrNO}_3$  to form  $\text{NO}_3^-$ .

## 5.7 Discussion of modeling results

5 We ran a total of 6 box model simulations with the goal of understanding the HOCl and  $\text{Cl}_2$  observations during the high  $\text{Cl}_x$  period at Cape Verde. These simulations included a *base case* based on known chemistry, four simulations which included a hypothetical photochemical aerosol source of HOCl, and one simulation with no gas phase reactive halogens. The simulations which best represented the observations  
10 were the *newsourc* + *lowalpha* and *newsourc* + *lowacid* runs. Each of these runs included the hypothetical additional source of HOCl and a means to hinder the rapid conversion of HOCl to  $\text{Cl}_2$  in 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  
15  $\text{Cl}_x$ .

The rate of  $\text{Cl}_x$  cycling and the partitioning of HOCl and  $\text{Cl}_2$  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 seasalt 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  
20 could be important. For example, Cl cycling in acidic aerosols aloft could generate  $\text{Cl}_2$ . Freshly generated seasalt aerosols near the surface are likely less acidic, so  $\text{Cl}_2$  mixed downward into the surface layer could undergo conversion to HOCl. The vertically resolved MISTRA model was used to simulate  $\text{Cl}_2$  chemistry at Cape Verde (Lawler et al., 2009). In that study a time-dependent model run yielding  $\approx 30$  ppt of nighttime  
25  $\text{Cl}_2$  exhibited HOCl daytime maxima of  $\approx 60$  and  $\approx 30$  ppt on the preceding and following days. This supports the basic conclusion of our model studies, that additional oxidation of  $\text{Cl}^-$  is needed in order to explain the HOCl levels at Cape Verde.

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We speculate that photosensitized reactions involving organic matter could provide additional oxidation of aerosol  $\text{Cl}^-$  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  $\text{Cl}^-$  to form  $\text{Cl}_2^-$ , which disproportionates to form  $\text{Cl}_2$  (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  $\text{HOCl}^-$  dissociates rapidly to OH and  $\text{Cl}^-$ . We have found no evidence in the literature of an aqueous phase reaction channel for the direct formation of HOCl from Cl without involving  $\text{Cl}_2$  as an intermediate. Given the short diffusion time scale for aerosols, most of the  $\text{Cl}_2$  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  $\text{Cl}_x$  would lead to unrealistically high gas phase  $\text{Cl}_2$  levels, unless there exists some other aqueous path to HOCl from  $\text{Cl}^-$ . Laboratory studies of photosensitized chloride oxidation in seawater and aerosols are needed to investigate this question.

If all seasalt aerosols contain organics capable of photosensitized oxidation of  $\text{Cl}^-$  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  $\text{Cl}_x$  observational period do not support such a large source in clean marine air.

The rapid and efficient recycling of HOCl to  $\text{Cl}_2$  that occurs in the model was not supported by observations. We explored three possible explanations for this: an aerosol  $\text{Cl}_x$  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. However, the low acidity option appears the most appealing because it does not require dramatic changes to aerosol composition and chemistry. It may only require a more detailed treatment of aerosols in the model. This issue should be addressed in a future modeling study.

## 6 Implications

The observations of HOCl and Cl<sub>2</sub> at Cape Verde provide direct evidence for rapid Cl<sub>x</sub> 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<sub>2</sub> levels are considerably higher in aged polluted air than in air with open ocean back trajectories, consistent with model predictions and previous Cl<sub>2</sub> and Cl\* measurements. The rates and mechanisms of Cl<sub>x</sub> cycling at Cape Verde are not yet fully understood, and the model simulations suggest that Cl<sub>x</sub> cycling occurs more rapidly than predicted by current models.

The relationship between pollutants and Cl<sub>x</sub> levels suggests that human-driven changes in ozone, NO<sub>y</sub>, and aerosol loading and chemistry have altered Cl atom levels, and hence, the reactivity of the atmosphere. Cl chemistry resulting from reactions of N<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> has decreased to negligible levels and ClNO<sub>2</sub> 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<sub>x</sub> cycling.

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

Ambient Species	Parent Ion	Parent Mass	Fragment Ion	Fragment Mass
$\text{HO}^{35}\text{Cl}$	$\text{HO}^{35}\text{Cl}^{79}\text{Br}^-$	131	$^{79}\text{Br}^-$	79
$\text{HO}^{35}\text{Cl}$	$\text{HO}^{35}\text{Cl}^{81}\text{Br}^-$	133	$^{81}\text{Br}^-$	81
$\text{HO}^{37}\text{Cl}$	$\text{HO}^{37}\text{Cl}^{79}\text{Br}^-$	133	$^{79}\text{Br}^-$	79
$\text{HO}^{37}\text{Cl}$	$\text{HO}^{37}\text{Cl}^{81}\text{Br}^-$	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

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**Table 2.** Boundary conditions which were used for all model runs. O<sub>3</sub>, CO, and aerosols were based on concurrent measurements. Hydrocarbons and NO<sub>2</sub> were based on measurements in the same season in 2007.

<i>Fixed meteorological conditions</i>	
Solar parameters	May 30, 17° N latitude
Total column ozone (DU)	300
Boundary layer height (m)	1000
Coarse aerosol liquid water content (m <sup>-3</sup> water/m <sup>-3</sup> air)	$1.2 \times 10^{-10}$
Fine aerosol liquid water content (m <sup>-3</sup> water/m <sup>-3</sup> air)	$1.1 \times 10^{-12}$
<i>Fixed mixing ratios (ppb)</i>	
O <sub>3</sub>	45
CH <sub>4</sub>	1800
NO <sub>2</sub>	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 <sub>3</sub>	0.035

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**Table 3.** Boundary conditions which were varied for the different MECCA box model runs.  $\text{HNO}_3$  and HCl for all cases except *newsource* + *lowacid* were based on measurements at Cape Verde in 2007. Here *ns* is short for *newsource*.

Model run	Added HOCl source (midday value, $\text{ppt h}^{-1}$ )	HOCl <sub>(aq)</sub> sink	$\alpha_{\text{HOCl}}$	HCl (ppb)	$\text{HNO}_3$ (ppb)	Gas phase halogens
<i>base case</i>	0	No	0.1	0.6	0.1	Yes
<i>newsource</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

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**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<sub>2</sub> observations during the high Cl<sub>x</sub> period are given for comparison. The midday observational means for HOCl and Cl<sub>2</sub> include all data between 10:00–14:00 local time, including points below detection. One standard deviation is shown.

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

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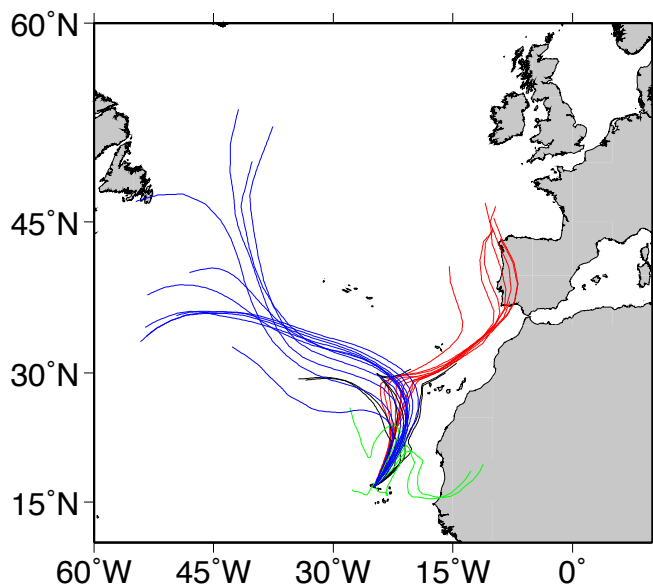
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**Fig. 1.** 6-day back trajectories for air reaching the Cape Verde Atmospheric Observatory measurement site, given every 6 h for all time periods that  $\text{Cl}_2$  and HOCl were measured. Colors show different time periods by day of year (day 150.0 is 30 May 2009, 00:00 local). Red: 150.25–152.25, black: 152.5–153.75, green: 154.75–155.75, blue: 156.00–158.5. Trajectories are from the British Atmospheric Data Centre, using the ECMWF archive data.

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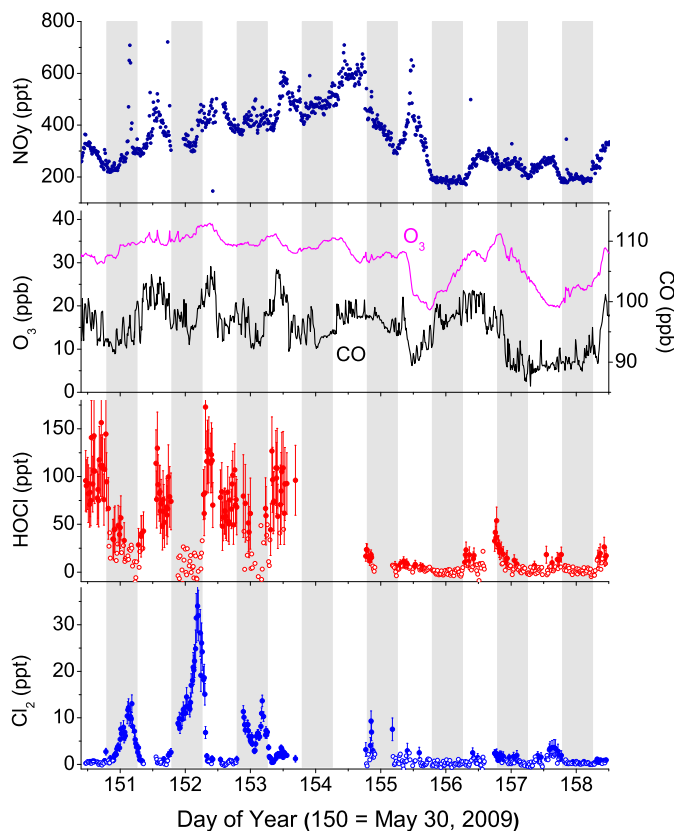
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**Fig. 2.**  $\text{NO}_y$ ,  $\text{O}_3$ ,  $\text{CO}$ ,  $\text{HOCl}$ , and  $\text{Cl}_2$  during the 2009 Cape Verde field campaign. For  $\text{HOCl}$  and  $\text{Cl}_2$ , open circles indicate measurements below detection limit. Each point 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  $\text{HOCl}$  and  $\text{Cl}_2$  data about day 154 was due to a power outage.

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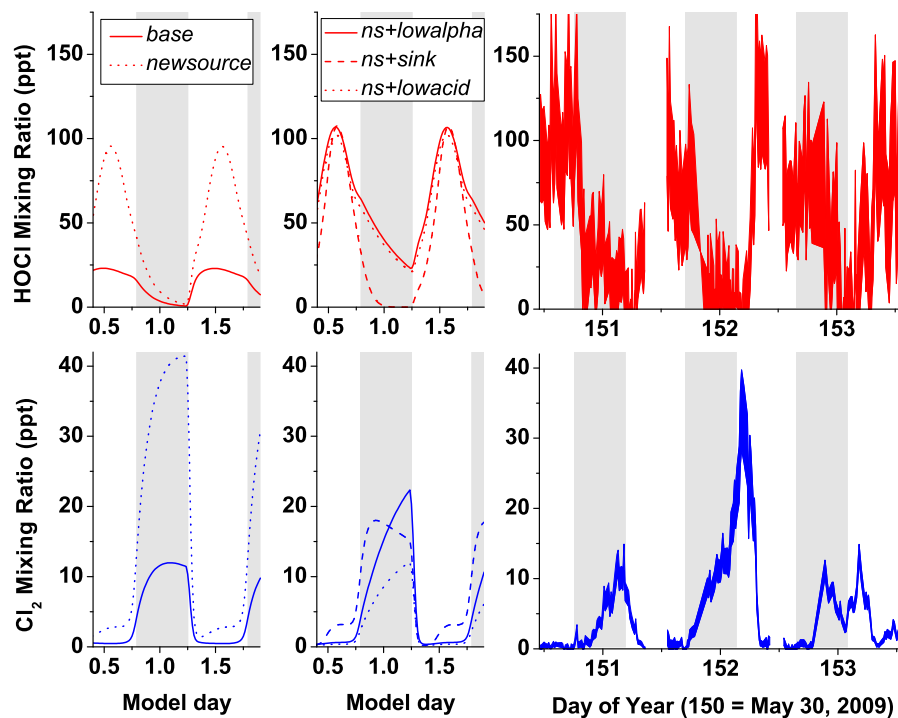
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**Fig. 3.** Model results (left and center panels) for  $\text{Cl}_2$  and HOCl compared to observed high  $\text{Cl}_x$  period data (right panels). Observational data shaded area is within mean  $\pm 1$  standard error. Red: HOCl, blue:  $\text{Cl}_2$ . Shaded vertical bars represent nighttime hours. Model day and day of year whole numbers are midnight.

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