Pollution-enhanced reactive chlorine chemistry in the eastern tropical Atlantic boundary layer

M. J. Lawler, B. D. Finley, W. C. Keene, A. A. P. Pszenny, K. A. Read, R. von Glasow, and E. S. Saltzman

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This study examines atmospheric reactive chlorine chemistry at the Cape Verde Atmospheric Observatory in the eastern tropical Atlantic. During May–June, 2007, Cl2 levels ranged from below detection (≈2 ppt) to 30 ppt. Elevated Cl2 was associated with high HNO3 (40 to 120 ppt) in polluted continental outflow transported in the marine boundary layer (MBL) to the site. Lower Cl2 was observed in recently subsided air masses with multiday free tropospheric oceanic trajectories and in air containing Saharan dust. Model simulations show that the observations of elevated Cl2 in polluted marine air are consistent with initiation of Cl chemistry by OH + HCl and subsequent heterogeneous, autocatalytic Cl cycling involving marine aerosols. Model estimates suggest that Cl atom reactions significantly impact the fluxes of methane and dimethylsulfide at Cape Verde and are moderately important for ozone cycling. Citation: Lawler, M. J., B. D. Finley, W. C. Keene, A. A. P. Pszenny, K. A. Read, R. von Glasow, and E. S. Saltzman (2009), Pollution-enhanced reactive chlorine chemistry in the eastern tropical Atlantic boundary layer, Geophys. Res. Lett., 36, L08810, doi:10.1029/2008GL036666.

1. Introduction

[2] Reactive chlorine (Cl2; Cl, Cl2, HOCl, ClO, etc.) is potentially important to tropospheric photochemistry, but its abundance is poorly quantified. Cl atoms have >10x higher reaction rate constants than OH with climate-active gases such as dimethylsulfide (DMS), methane, and non-methane hydrocarbons (NMHCs) [Sander et al., 2006]. Atomic chlorine can cause ozone loss via catalytic pathways such as:

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \] (1)

\[ \text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 \] (2)

\[ \text{HOCl} + \nu \rightarrow \text{OH} + \text{Cl} \] (3)

The net impact of Cl on tropospheric ozone depends primarily on NOx levels. Under high-NOx conditions, the oxidation of hydrocarbons by Cl results in ozone production due to enhanced formation of peroxo radicals [Knipping and Dabab, 2003].

[3] Several approaches have been used to assess the importance of reactive chlorine chemistry in marine air, including observations of aerosol chloride depletion [Keene et al., 1990; Mclnnes et al., 1994], Eulerian [Jobson et al., 1994; Pszenny et al., 2007] and Lagrangian [Wingenter et al., 1996] field studies of hydrocarbon ratios, laboratory studies [Behnke et al., 1993; Knipping et al., 2000], and model simulations [von Glasow et al., 2002]. Estimates of marine boundary layer (MBL) Cl atom levels range from <103 to >105 cm−3.

[4] Few direct observations of reactive chlorine gases in marine air have been reported. Cl* (the sum of Cl2 and HOCl) has been measured at mixing ratios of up to 420 ppt (pmol mol−1) in polluted coastal New England air [Keene et al., 2007]. Spicer et al. [1998] reported up to 150 ppt Cl2 in onshore flow in Long Island, and Finley and Saltzman [2006] reported mixing ratios up to 15 ppt Cl2 in polluted coastal California air. Recently, Osthoff et al. [2008] reported up to 1200 ppt ClNO2 in highly polluted air off Houston, Texas. These coastal measurements provide evidence of active chlorine cycling in polluted air. However, reactive chlorine levels are highly variable, and the controlling factors are not well understood.

[5] Multiphase photochemical models suggest that reactive halogen compounds can be generated in marine air via autocatalytic mechanisms [Vogt et al., 1996]:

\[ \text{HOCl}(g) \rightarrow \text{HOCl}(aq) \] (4)

\[ \text{HOCl}(aq) + \text{Cl}^- + \text{H}^+ \rightarrow \text{Cl}_2(g) \] (5)

\[ \text{Cl}_2 + \nu \rightarrow 2\text{Cl} \] (6)

Atomic Cl (and Br) subsequently regenerate HOCl (and HOBr) via reactions (1) and (2). Model calculations suggest that Br should dominate the halogen chemistry in clean marine air but that Cl chemistry is enhanced via aerosol acidification under more polluted conditions [von Glasow et al., 2002; Pechtl and von Glasow, 2007].

[6] Here we report measurements of gas phase Cl2, Cl*, acids and particulate species at Cape Verde Atmospheric Observatory (CVAO) in the eastern tropical Atlantic. The goals of the study were to assess the importance of reactive chlorine in marine boundary layer air and to elucidate halogen activation mechanisms. The data encompass a variety of air mass types and suggest a relationship between...
levels were extremely low (<30 ppt 95% of the time), 2\, converter with a DL of <14 ppt for levels ranged from <2 to 30 ppt (Figure 2), with was measured using atmospheric pressure chem- and HNO\(_2\) Representative seven-day back trajectories for mixing ratios varied on time scales of a few days was measured at \(L_08810\) was occasionally detectable during daylight hours. Cl* ranged from <14 to 222 4\, levels (e.g., days 156– were not correlated. Cl* is a measure of photo-

Figure 1. Representative seven-day back trajectories for air arriving at CVAO at midnight (local time: GMT – 1) at 950 mbar. Air mass types: Open Ocean-lss (\(\bigcirc\)), Iberian Influenced (\(\triangle\)), Dusty (\(\square\)), and Open Ocean-hss (\(\triangledown\)). Trajectories are numbered by day of year (143 arrived 00:00 May 23, 2007).

2. Field Site and Conditions

Air was sampled about 50m from the ocean on the windward northeast coast of São Vicente Island, Republic of Cape Verde (16.848°N, 24.871°W), from May 20 to June 9, 2007 (day of year 140–160). Northeasterly trade winds maintained onshore air flow throughout the campaign. Boundary layer heights were estimated at 500–1200 m based on daily soundings at Sal Island (16.73°N, 22.95°W) and local aircraft soundings [Read et al., 2008]. The boundary layer was well mixed and capped by a strong inversion. Skies were mostly clear with occasional periods of scattered cumulus clouds. Moderate levels of African dust were observed on days 147–151, but no major dust outbreaks occurred during the campaign. There were no local sources of pollution upwind of the site other than occasional ship plumes, and NO\(_x\) levels were extremely low (<30 ppt 95% of the time), with rare, brief (~1 hr) excursions of <900 ppt.

3. Analytical Methods

Cl\(_2\) was measured using atmospheric pressure chemical ionization tandem mass spectrometry (APCI/MS/MS) [Finley and Saltzman, 2006]. The inlet was located at about 3m above ground (13m above sea level). Ambient air was drawn through a 3m long, multi-stage laminar flow inlet and ionized using a \(^{60}\)Ni beta-emitting foil to form Cl\(_2\) ions from atmospheric Cl\(_2\). Cl\(_2\) was mass filtered, then collisionally dissociated to Cl\(^+\), which was mass filtered and detected. The instrument blank was assessed by sampling ambient air through carbonate-coated glass wool. The instrument was field-calibrated using gas standards (14–57 ppt) generated from a permeation tube calibrated both gravimetrically and by reacting its output with a neutral KI solution and measuring the production of I\(_2\) by absorbance. The mean detection limit (DL) was 1.9 ± 0.7 ppt (1\(\sigma\)) for reported 15-minute means. BrCl was also monitored but was not detected above the estimated <2 ppt DL.

Gas-phase Cl*, water-soluble forms of volatile inorganic Cl and oxidized N (dominated by and hereafter referred to as HCl and HNO\(_3\), respectively), and HCOOH were sampled atop a 30m tower (40m above sea level) over 2-hour intervals with tandem mist-chamber systems [Keene et al., 2007]. Inertial size-fractioning inlets removed super-\(\mu\)m diameter aerosols and in-line Teflon filters removed sub-\(\mu\)m aerosols from sample air. Exposed mist solutions were analyzed on site by ion chromatography and data were corrected for dynamic handling blanks. DLs for Cl*, HCl, HNO\(_3\), and HCOOH were 14, 26, 12, and 29 ppt, respectively.

Bulk particulate Na, Al, and Mn were sampled atop the tower on a nominal 3-hour schedule using precleaned 47 mm diameter Whatman 41 filters [Pszenny et al., 2004; Keene et al., 2007]. The filters were analyzed for total Na, Al, and Mn by neutron activation [Rahn et al., 1976; Keene et al., 2007].

NO\(_x\) was sampled 3m above ground (13m above sea level) and quantified with a chemiluminescence NO detector with a photolytic NO\(_2\) converter with a DL of <14 ppt for reported NO\(_x\) (10-minute means), and O\(_3\) was measured at 3m via UV absorption and is reported as 15-minute means. Air mass back trajectories were calculated using the British Atmospheric Data Centre (BADC) trajectory service.

4. Observations

Cl\(_2\) levels ranged from <2 to 30 ppt (Figure 2), with a mean value of 4 ppt. Cl\(_2\) exhibited a marked diel cycle, with nighttime maxima and daytime minima. During the periods with highest nighttime Cl\(_2\) levels (e.g., days 156–157), Cl\(_2\) was occasionally detectable during daylight hours. Cl\(_2\) and HNO\(_3\) were positively correlated at night, but Cl\(_2\) and NO\(_x\) were not correlated. Cl* is a measure of photo-lyzable inorganic chlorine, which in this environment is equivalent to \(\sum(2\text{Cl}_2 + \text{HOCI})\). Cl* ranged from <14 to 222 ppt Cl and was almost always greater than 2Cl\(_2\). Cl* and Cl\(_2\) exhibited similar temporal trends.

Cl\(_2\) mixing ratios varied on time scales of a few days in association with changes in atmospheric circulation. Eight-day air mass back trajectories, acidic gases, and aerosol chemistry were used to classify the study period in terms of four air mass types: Iberian Influenced, Open Ocean-low seasalt (-lss), Dusty, and Open Ocean-high seasalt (-hss) (Figure 1). In general, air mass types remained coherent for a few days at a time.

4.1. Open Ocean-low seasalt (-lss)

These air masses typically originated in the subtropical or midlatitude free troposphere over the western North Atlantic ocean or North America, circulated around a mid-Atlantic high pressure system, and subsided into the boundary layer 1.5–2.5 days north of Cape Verde (days 142–144, Figure 1). These air masses reached Cape Verde without passing over Europe and exhibited low (mostly <12 ppt)
HNO₃, 95–275 ppt HCOOH, high (~43 ppb) O₃, and low to moderate seasalt (74–181 nmol m⁻³ Na, Table 1). Nocturnal Cl₂ mixing ratios were usually below 5 ppt (Table 1 and Figure 2).

### 4.2. Open Ocean-high seasalt (-hss)

[15] Elevated levels of seasalt (up to 256 nmol m⁻³ Na) were observed on days 152–154 (Table 1). These air masses originated over the central or eastern North Atlantic, skirted the West African coast northeast of Cape Verde, and entered the MBL 2–2.5 days upwind of the site (Figure 1). Acid gas levels were low (~15 ppt HNO₃, <29 ppt HCOOH), and O₃ mixing ratios were ~35 ppb. Cl₂ had nighttime maxima of 5–15 ppt (Table 1 and Figure 2).

### 4.3. Iberian Influenced

[16] These conditions occurred when free tropospheric air from the central North Atlantic subsided into the boundary layer over Iberia 3–4.5 days upwind of Cape Verde (days 141 and 156–158, Figure 1). This air was characterized by elevated levels of HNO₃ (up to 124 ppt) and HCOOH, and O₃ mixing ratios were ~35 ppb. Cl₂ had nighttime maxima of 5–15 ppt (Table 1 and Figure 2).

### 4.4. Dusty

[17] Dusty air was sampled on days 147–151 and was characterized by elevated levels of Al and Mn (Table 1). Most air mass trajectories during this period originated in the free troposphere over the Northwestern Sahara, then passed over Iberia before subsiding into the boundary layer ~2 days north of Cape Verde (Figure 1). HNO₃ mixing ratios were near the 12 ppt DL, HCOOH levels were usually <29 ppt, O₃ levels were ~35 ppb, and Na increased from low to high levels (82–247 nmol m⁻³). Cl₂ levels were near the DL, except for day 150 when nocturnal mixing ratios reached 13 ppt (Table 1 and Figure 2). Days 140 and 159 were transitional between Polluted, Open Ocean-lss, and Open Ocean-hss conditions. For these days, Cl₂ nighttime maxima ranged from 10–15 ppt. Day 146 was transitional between Open Ocean-lss and Dusty conditions. Day 145 uniquely had an eight-day back trajectory entirely in the MBL, with low Cl₂, low acids, and low seasalt.

### 5. Model Simulations

[18] Numerical simulations were carried out to assess the extent to which multiphase halogen cycling mechanisms can explain the observed association between Cl₂ and pollutants. A one-dimensional Lagrangian model with detailed gas phase and aerosol halogen (Clₓ and Brₓ) reactions was used (MISTRA [von Glasow et al., 2002]). The complete chemical mechanism is reported in the supplement to Pechtl et al. [2006]. For the present study, iodine chemistry was turned off. The model includes dynamics, thermodynamics, and a detailed microphysical module that handles seasalt generation at the ocean surface, calculates particle growth explicitly, and accounts for interactions between radiation and particles. Boundary conditions were chosen such that no clouds formed. Each model run simulated the advection of an air column in the MBL over the ocean for five days, with initialization at 13:00.

[19] Two simulations were carried out, dubbed “Clean” and “Polluted” cases, to represent the conditions in the observed Open Ocean-lss and Iberian Influenced air

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**Table 1. Summary of Air Mass Types**

| Air Mass Type       | Open Ocean-lss | Open Ocean-hss | Iberian Influenced | Dusty |
|---------------------|----------------|----------------|-------------------|-------|
| Days in MBL         | 1.5–2.5       | 2–2.5         | 3–4.5             | ~2    |
| HNO₃ (ppt)          | <12–25        | <12–35        | <12–124           | <12–30|
| HCOOH (ppt)         | 95–275        | 29–243        | 119–186           | 82–247|
| Na (nmol m⁻³)       | 74–181        | 123–256       | 119–186           | 82–247|
| Al (nmol m⁻³)       | 1.1–3.7       | 2.2–5.6       | 2–7.4             | 1–10.8|
| Cl₂ (ppt)           | <1.8–10.6     | <0.9–18.0     | <1.5–30.1         | <0.7–13.0|
| Cl* (ppt)           | <14–62        | <14–84        | <14–101, 222      | <14–64|
| HCl (ppt)           | 134–426       | 97–581        | 145–613           | 49–354|
| O₃ (ppb)            | 31–46         | 25–41         | 27–39             | 27–39 |
| NO₂ (ppt)           | <14–51.0      | <14–30.2      | <14–19.1          | <14–22.6|

*Full ranges given except for NOₓ, for which 5%–95% range is given due to rare large spikes; one Cl* outlier noted.

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**Figure 2.** Gas-phase Cl₂, HCl, HNO₃, and particulate Na at Cape Verde during May-June, 2007. Points above and below Cl₂ and HNO₃ detection limits (DLs) indicated. Gray shading indicates night.
polluted air in the MBL over the eastern Tropical Atlantic. In particular, higher Cl levels were observed in aged polluted air than in clean marine air, most likely as a result of aerosol acidification. Therefore, the combined influences of transformations involving Br$_x$ and I$_x$ account for ~30% of the total O$_3$ loss with 11% of the total attributed to Br$_x$ alone.

7. Conclusions

[26] This study suggests a link between chlorine cycling and the advection of polluted air in the MBL over the eastern tropical Atlantic. In particular, higher Cl$_2$ levels were observed in aged polluted air than in clean marine air, most likely as a result of aerosol acidification. Therefore,
regions of very active chlorine chemistry over the oceans are likely to be spatially heterogeneous and time-varying. Simultaneous gas-phase, speciated Cl\textsubscript{x} measurements and observationally-constrained aerosol pH calculations are needed to quantitatively assess the mechanisms involved in this process.

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B. D. Finley, M. J. Lawler, and E. S. Saltzman, Department of Earth System Science, University of California, Irvine, 3325 Croul Hall, Irvine, CA 92697-3100, USA. (mlawler@uci.edu)

W. C. Keene, Department of Environmental Sciences, University of Virginia, Clark Hall, Charlottesville, VA 22904, USA.

A. A. P. Pszenny, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, 39 College Road, Durham, NH 03824, USA.

K. A. Read, Department of Chemistry, University of York, Woodhouse Lane, York LS2 9JT, UK.

R. von Glasow, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK.