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

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[1] 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 fates 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 (Cl_x: Cl, Cl₂, HOCl, ClO, etc.) is potentially important to tropospheric photochemistry, but its abundance is poorly quantified. Cl atoms have >10^x 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:

The net impact of Cl on tropospheric ozone depends primarily on NO_x levels. Under high-NO_x conditions, the oxidation of hydrocarbons by Cl results in ozone production due to enhanced formation of peroxy radicals [Knipping and Dabdub, 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; McInnes *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]:

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

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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 (○), Iberian Influenced (△), Dusty (□), and Open Ocean-hss (▽). Trajectories are numbered by day of year (143 arrived 00:00 May 23, 2007).

pollutant levels and the intensity of reactive chlorine cycling in MBL air.

2. Field Site and Conditions

[7] 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

[8] Cl₂ 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 ⁶³Ni beta-emitting foil to form Cl₂⁺ ions from atmospheric Cl₂. Cl₂⁺ 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 I₃[−] by absorbance. The mean detection limit (DL) was 1.9 ± 0.7 ppt (1σ) for reported 15-minute means. BrCl was also monitored but was not detected above the estimated <2 ppt DL.

[9] Gas-phase Cl*, water-soluble forms of volatile inorganic Cl and oxidized N (dominated by and hereafter referred to as HCl and HNO₃, 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-μm-diameter aerosols and in-line Teflon filters removed sub-μm 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, HNO₃, and HCOOH were 14, 26, 12, and 29 ppt, respectively.

[10] 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].

[11] NO_x was sampled 3m above ground (13m above sea level) and quantified with a chemiluminescence NO detector with a photolytic NO₂ converter with a DL of <14 ppt for reported NO_x (10-minute means), and O₃ 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

[12] Cl₂ levels ranged from <2 to 30 ppt (Figure 2), with a mean value of 4 ppt. Cl₂ exhibited a marked diel cycle, with nighttime maxima and daytime minima. During the periods with highest nighttime Cl₂ levels (e.g., days 156–157), Cl₂ was occasionally detectable during daylight hours. Cl₂ and HNO₃ were positively correlated at night, but Cl₂ and NO_x were not correlated. Cl* is a measure of photolyzable inorganic chlorine, which in this environment is equivalent to Σ(2Cl₂ + HOCl). Cl* ranged from <14 to 222 ppt Cl and was almost always greater than 2Cl₂. Cl* and Cl₂ exhibited similar temporal trends.

[13] Cl₂ 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)

[14] 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)

Table 1. Summary of Air Mass Types^a

	Open Ocean-lss	Open Ocean-hss	Iberian Influenced	Dusty
Days in MBL	1.5–2.5	2–2.5	3–4.5	~2
HNO ₃ (ppt)	<12–25	<12–35	<12–124	<12–30
HCOOH (ppt)	95–275	<29–243	91–796	<29–131
Na (nmol m ⁻³)	74–181	123–256	119–186	82–247
Al (nmol m ⁻³)	1.1–3.7	2.2–5.6	2.6–7.4	1.9–20.8
Cl ₂ (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
O ₃ (ppb)	31–46	25–41	27–39	27–39
NO _x (ppt)	<14–51.0	<14–30.2	<14–19.1	<14–22.6

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

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 (up to 796 ppt), ~35 ppb O₃, and moderate aerosol Na (119–186 nmol m⁻³; Table 1). These air masses exhibited the highest nocturnal Cl₂ levels (up to 30 ppt) and, occasionally, detectable midday Cl₂ levels (1–3 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 (Cl_x and Br_x) 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-hss/lss and Iberian Influenced air

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.

Figure 3. Modeled mean boundary layer O_3 , Cl , Cl_2 , and HOCl . *Polluted* case (red dashed), *Clean* case (solid black). Time intervals labeled show range of MBL transit times of Open Ocean and Iberian air mass types before observation at Cape Verde. Dots emphasize model data that should be compared to Open Ocean and Iberian Influenced observational data. Gray shading indicates night.

mass types, respectively. The two cases were initialized using the following mixing ratios: *Clean* - 20 ppt NO_x , 35 ppt HNO_3 , 0.5 ppb NMHC, 45 ppb O_3 , and 80 ppt SO_2 , and *Polluted* - 0.8 ppb NO_x , 8 ppt HNO_3 , 2 ppb NMHC, 75 ppb O_3 , and 0.5 ppb SO_2 . The initial sulfate aerosol concentration was higher in the polluted case. Back trajectories suggest that model days 3–4.5 and 1.5–2.5 should be compared to observations for the *Polluted* and *Clean* cases, respectively.

[20] The *Polluted* case exhibited very active Cl chemistry, with Cl_2 levels reaching 125 ppt over the second night (Figure 3). On the 4th and 5th nights (3.5 and 4.5 days into the run) Cl_2 levels reached 30 and 17 ppt (Figure 3), respectively, in good agreement with the observations at Cape Verde. Simulated HOCl was roughly 50 ppt during the daytime 4 days into the run (Figure 3), and the sum of HOCl and 2Cl_2 in the model (~ 30 – 70 ppt) was in reasonable agreement with Cl^* (Table 1). HCl in this simulation was ~ 550 ppt, in good agreement with the observed range of 400–600 ppt. The modeled Cl chemistry is initiated by acid displacement of HCl from seasalt aerosol and the subsequent reaction $\text{HCl} + \text{OH} \rightarrow \text{Cl}$. This process enables the heterogeneous autocatalytic cycling described in reactions (1)–(6) [Pechtl and von Glasow, 2007].

[21] In the *Clean* case, a maximum of 6 ppt of Cl_2 was generated after 1.5 days, and 7.5 ppt after 2.5 days (Figure 3). The lower Cl_2 levels in the *Clean* case are a consequence of less HCl being available to react with OH to release Cl atoms and of the slower Cl cycling in less-acidified aero-

sols. This result is in rough agreement with the observations at Cape Verde under the Open Ocean-lss conditions and slightly lower than observations under Open Ocean-hss conditions (Table 1). Simulated midday HOCl after 2 days was about 20 ppt, and $\text{HOCl} + 2\text{Cl}_2$ was ~ 15 – 20 ppt, somewhat lower than observed Cl^* (<14 – 84) under Open Ocean conditions. Model predictions of HCl were ~ 250 ppt, within the range of the observed levels.

[22] BrCl levels were ~ 10 ppt under *Polluted* conditions and ~ 4 ppt under *Clean* conditions, both higher than observed levels (<2 ppt). This discrepancy may indicate that the model overestimates the extent of bromide depletion in sea salt aerosols, causing a shift from Br_2 production to BrCl production.

6. Impacts on Methane, DMS, and Ozone

[23] For the *Polluted* case four days into the run, the simulated 24-hr mean Cl concentration was $3.5 \times 10^4 \text{ cm}^{-3}$. At this concentration and a temperature of 25°C , the lifetime of CH_4 in the MBL would be about 9 years with respect to Cl oxidation [Sander et al., 2006]. If the mean Cl levels in the *Polluted* case were present year-round in a 1 km deep MBL from 30°N to 30°S , the global atmospheric lifetime of CH_4 with respect to oxidation by Cl atoms ($\tau_{\text{CH}_4-\text{Cl}}$) would be ~ 150 years, as compared with $\tau_{\text{CH}_4-\text{OH}}$ of ~ 10 years [Lawrence et al., 2001]. In that scenario, low latitude MBL Cl would represent $\sim 7\%$ of the global CH_4 sink. For the *Clean* case two days into the run, Cl levels were roughly 4 times lower, and the same calculation gives $\tau_{\text{CH}_4-\text{Cl}}$ of ~ 600 years ($\sim 2\%$ of the global CH_4 sink).

[24] The Cl levels estimated in these model runs would also impact the fate of DMS at Cape Verde. In the *Clean* case on day 2, DMS oxidation occurs primarily via OH (54%), with BrO and Cl accounting for 36% and 9%, respectively. In the *Polluted* case on day 4, Cl is more important, accounting for 24% of DMS oxidation, with BrO and OH oxidizing 26% and 48% respectively. The total DMS oxidation rate is similar in the two cases. The oxidation of DMS by Cl may affect the distribution of oxidation products (DMSO , DMSO_2 , MSA , SO_2 , MSA), with implications for aerosol growth and CCN formation. The $\text{Cl} + \text{DMS}$ and $\text{OH} + \text{DMS}$ reactions both proceed via addition and abstraction, but the lifetime and fate of the Cl -DMS adduct are not known [Stickel et al., 1992].

[25] Cl_x chemistry was responsible for 5% of total O_3 destruction under day 2 *Clean* conditions and 18% under day 4 *Polluted* conditions. HO_x chemistry was the dominant O_3 sink in both cases, with Br_x contributing 11% in the *Clean* case and 12% in the *Polluted* case. These model results are similar to those based on long-term measurements of BrO and IO at Cape Verde [Read et al., 2008], which indicate that the combined influences of transformations involving Br_x and I_x account for $\sim 30\%$ 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_x measurements and observationally-constrained aerosol pH calculations are needed to quantitatively assess the mechanisms involved in this process.

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