Gas phase acid, ammonia and aerosol ionic and trace element concentrations at Cape Verde during the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) 2007 intensive sampling period

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Abstract. We report mixing ratios of soluble reactive trace gases sampled with mist chambers and the chemical composition of bulk aerosol and volatile inorganic bromine (Br\textsubscript{g}) sampled with filter packs during the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) field campaign at the Cape Verde Atmospheric Observatory (CVAO) on São Vicente island in the tropical North Atlantic in May and June 2007. The gas-phase data include HCl, HNO\textsubscript{3}, HONO, HCOOH, CH\textsubscript{3}COOH, NH\textsubscript{3}, and volatile reactive chlorine other than HCl (Cl\textsuperscript{*}). Aerosol samples were analyzed by neutron activation (Na, Al, Cl, V, Mn, and Br) and ion chromatography (SO\textsubscript{4}\textsuperscript{2−}, Cl\textsuperscript{−}, Br\textsuperscript{−}, NH\textsubscript{4}\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, and Ca\textsuperscript{2+}). Content and quality of the data, which are available under doi:10.5281/zenodo.6956, are presented and discussed.

1 Introduction

Multiphase halogen chemistry impacts important, interrelated chemical processes in marine air. Bromine activation chemistry leads to catalytic ozone destruction and modification of oxidation processes including HO\textsubscript{x} and NO\textsubscript{x} cycling. Spatiotemporal variability in many reactants, products and reaction pathways are poorly characterized, rendering uncertain the global significance of tropospheric halogen chemistry.

2 Data set description and access

RHaMBLe was a large-scale investigation of reactive halogen cycling and associated impacts on oxidation processes in the marine boundary layer over the eastern North Atlantic Ocean (Lee et al., 2010). As part of RHaMBLe, (Reactive Halogens in the Marine Boundary Layer) an intensive 25 day process study was conducted during spring 2007 at the Cape Verde Atmospheric Observatory (Fig. 1) on the windward shore of São Vicente Island (16.8° N, 24.9° W) in the tropical, eastern North Atlantic (Fig. 2). Data from this field intensive campaign coupled with measurements within the surrounding region and at the observatory during other periods have been used to address a range of topics including...
halogen-mediated destruction of ozone (Read et al., 2008), pollution-enhanced production of Cl radicals and associated influences on oxidation processes (Lawler et al., 2009), the cycling of reactive nitrogen oxides (Lee et al., 2009), and the composition and processing of aerosols (Allan et al., 2009), among others. Herein, we report a suite of soluble reactive trace gases, volatile inorganic bromine, and ionic and elemental aerosol constituents measured from the top of the observatory’s 30 m tower during the RHaMBLe campaign.

The complete data set is available in NASA Ames format\(^1\) from the Zenodo repository service under doi:10.5281/zenodo.6956. In addition, we also provide comma-separated-values (csv) files of the full data set in the Supplement.

### 3 Instruments and methods

All air volumes reported here are normalized to standard temperature and pressure (273 K and 1.013×10\(^5\) Pa).

\(^1\)http://badc.nerc.ac.uk/help/formats/NASA-Ames
probably contributions from $\text{ClNO}_3$, $\text{ClNO}_2$, $\text{BrCl}$, ClO, and Cl). Available evidence (Keene et al., 1993; Maben et al., 1995) indicates that this sampling technique reliably discriminates volatile inorganic Cl from Cl associated with both particles and organic gases and that it quantitatively differentiates between HCl and other forms of volatile inorganic Cl. However, the speciation of Cl* cannot be determined unequivocally. Mist solutions were analyzed on site by IC.

### 3.2 Filter-pack sampling and chemical analysis

Using a modification of the technique by Rahn et al. (1976), total aerosol and inorganic gases were sampled using filter packs with 3 filters (Fig. 5). Particles were sampled on dry 47 mm diameter Whatman 41 cellulose filters that were positioned upstream (W1 in Fig. 5). Each filter was precleaned with deionized water (DIW) and dried prior to the campaign. Alkaline-reactive trace gases were sampled on moist tandem Rayon filters (SKU 64007, Leader Evaporator), impregnated with an alkaline solution ($10 \text{g LiOH and } 10 \text{mL glycerol per } 100 \text{mL}$), positioned in tandem downstream (R1 and R2 in Fig. 5). Filters from the same lot were used for all samples, blanks, and analytical standards. Sample and field blank filters were mounted in 47 mm diameter Nuclepore polycarbonate cassettes. Seven samples were collected each day with sample changes keyed to sunrise and sunset and other change times adjusted such that sampling interval durations were similar (3 to 4 h). The airflow was about 80 standard liters per minute (SLPM) and monitored with a mass flow meter. Field blanks were obtained once per day at different times. Each field blank was loaded, deployed, exposed briefly (few seconds) to ambient air, recovered, processed,
Table 1. Data summary. Here, DL is the detection limit. N(tot) and N(<DL) are the total number of data points and the number below the DL, respectively.

<table>
<thead>
<tr>
<th>Substance</th>
<th>minimum</th>
<th>maximum</th>
<th>median</th>
<th>DL*</th>
<th>N(tot)</th>
<th>N(&lt;DL)</th>
<th>unit</th>
</tr>
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<td>HCl</td>
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<td>613</td>
<td>206</td>
<td>26</td>
<td>212</td>
<td>13</td>
<td>pmol mol⁻¹</td>
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<tr>
<td>Cl⁺</td>
<td>&lt;DL</td>
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<td>21</td>
<td>14</td>
<td>212</td>
<td>79</td>
<td>pmol mol⁻¹</td>
</tr>
<tr>
<td>HNO₃</td>
<td>&lt;DL</td>
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<td>14</td>
<td>12</td>
<td>212</td>
<td>90</td>
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<tr>
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<td>&lt;DL</td>
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<td>18</td>
<td>3</td>
<td>212</td>
<td>51</td>
<td>pmol mol⁻¹</td>
</tr>
<tr>
<td>HCOOH</td>
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<td>128</td>
<td>29</td>
<td>212</td>
<td>68</td>
<td>pmol mol⁻¹</td>
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<tr>
<td>CH₃COOH</td>
<td>&lt;DL</td>
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<td>78</td>
<td>44</td>
<td>212</td>
<td>68</td>
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<table>
<thead>
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<th>Unit</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
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<td>µg m⁻³</td>
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<td>0.031</td>
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<td>0.39</td>
<td>6.84</td>
<td>2.6</td>
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<td>0.752</td>
<td>0.432</td>
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<td></td>
<td>147</td>
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<tr>
<td>Cl deficit</td>
<td>µg m⁻³</td>
<td>1.21</td>
<td>6.96</td>
<td>3.17</td>
<td></td>
<td></td>
<td>147</td>
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<tr>
<td>V</td>
<td>ng m⁻³</td>
<td>&lt;DL</td>
<td>2.21</td>
<td>0.68</td>
<td>0.26</td>
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<td>16</td>
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<tr>
<td>Mn</td>
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<td>26.3</td>
<td>8.39</td>
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<td></td>
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<td>11.3</td>
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<tr>
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<td>16.8</td>
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<td>29.2</td>
<td>5.48</td>
<td></td>
<td></td>
<td>147</td>
</tr>
</tbody>
</table>

* For IC and for chloride from NAA, the blanks’ analyses indicated two distinct subsets with quite different concentrations of several ions. Individual detection limits were calculated for these subsets.

and analyzed using procedures identical to those for samples. Between each use filter cassettes were completely disassembled, cleaned with dilute Liquinox solution, rinsed with DIW and dried in a clean bench. Exposed filters were transferred to clean polyethylene envelopes, frozen, and transported to and stored frozen at the University of New Hampshire (UNH) prior to preparation for analysis.

Using tandem impregnated filters allowed to calculate the collection efficiency ε for volatile inorganic bromine Br₂⁺:

\[ \varepsilon = \frac{m_1}{m_{tot}} = \frac{m_2}{(m_{tot} - m_1)}. \]

Here, \( m_1 \) and \( m_2 \) are the masses deposited on the first and second impregnated filter, respectively, and \( m_{tot} \) is the total mass that would be deposited at 100% collection efficiency. Rearranging the equations and inserting the known values of \( m_1 \) and \( m_2 \) yields a collection efficiency of

\[ \varepsilon = 1 - \frac{m_2}{m_1} \]

and a total mass of

\[ m_{tot} = \frac{m_1}{1 - \frac{m_2}{m_1}}. \]

All filters were analyzed by neutron activation analysis (NAA) using a procedure based on that described by Uematsu et al. (1983). Standards were prepared by spotting aliquots of a NIST-traceable mixed element standard solution (Ultra Scientific, North Kingstown, RI) on blank filter circles. Standards, samples and field blanks were each
Figure 6. Time series of the filter pack data, analyzed by NAA. The red lines denote the detection limit and the blue lines denote sea water composition, i.e., EF = 1 and deficit = 0.

spiked with 20 ng of indium in dilute nitric acid (as an aliquot of a NIST-traceable standard solution; Ultra Scientific) as internal flux monitor, sealed in a clean polyethylene envelope and subsequently irradiated at the Rhode Island Nuclear Science Center (RINSC) for 300 s at a nominal flux of \(4 \times 10^{12} \text{ cm}^{-2} \text{s}^{-1}\) thermal neutrons. Following irradiation, samples were allowed to decay for approximately 5 min during which they were transferred to non-irradiated envelopes, and counted for 900 s live time on a Ge(Li) gamma-ray spectrometer. From the particle filters, data were obtained for six elements: Na, Al, Cl, Mn, V, and Br. Using Eq. (3), gaseous Br data were obtained from the impregnated filters. All laboratory manipulations of cassettes and filters prior to irradiation were carried out in class 100 clean benches by personnel wearing unpowdered plastic gloves.

About three years after the NAA analysis, the radioactivity had decreased to a safe level, and it was possible to handle the samples again. The aerosols on the particle filters were extracted under sonication in DIW. The ionic species \(\text{SO}_4^{2-}\), \(\text{Cl}^-\), \(\text{Br}^-\), \(\text{NH}_4^+\), \(\text{Na}^+\), \(\text{K}^+\), \(\text{Mg}^{2+}\), and \(\text{Ca}^{2+}\) were determined by high-performance ion chromatography (IC) using procedures similar to those described by Keene et al. (2009). Data for samples were corrected based on median concentrations of analytes recovered from handling blanks \((n = 10)\).

To estimate the detection limits for the filter pack aerosol samples, we used Eq. (14) of Currie (1995). An element or ion was deemed detected if its mass (NAA) or extract concentration (IC) exceeded its minimal detectable value estimated via

\[
\text{DL} = 2 \cdot t_{\alpha, \nu} \cdot s_0, \tag{4}
\]

where DL is the detection limit (minimal detectable value), \(t\) is the value of Student’s \(t\) statistic for probability level \(\alpha\) and \(\nu\) degrees of freedom (i.e., number of blanks), and \(s_0\) is the standard deviation of mass or concentration values determined in the \(N\) blanks analyzed. The choice of \(\alpha = 0.025\) corresponds to rejecting a null hypothesis of “not detected” at the 95% confidence level. The average sampled air volume for all samples of 12.4 m\(^3\) STP \((0^\circ \text{C}, 1 \text{ atm})\) was assumed for all calculations.

For IC, the blanks’ analyses indicated two distinct subsets of blanks of \(N = 3\) and \(N = 20\), respectively, with quite different concentrations of several ions. For NAA, chlorine appeared to have the same two subsets. For other elements determined no distinct subsets were apparent.

The phase partitioning of HCl and NH\(_3\) with aerosol solutions is pH dependent, and aerosol pH typically varies as a function of size. Because the pH of aerosols sampled in bulk on a filter may diverge from the pH of the aerosol size fractions with which most Cl\(^-\) and NH\(_4^+\) is associated in ambient air, these species are subject to artifact phase changes when sampled in bulk (e.g., Keene et al., 1990). Consequently, the absolute concentrations and associated enrichment factors and deficits relative to sea salt that are reported herein may not be representative of those for ambient aerosols during the campaign.

### 4 Data summary

A detailed analysis of the data is beyond the scope of a paper in this journal. Here, we only present the data and draw some basic conclusions. Table 1 lists minimum, maximum, average, and median values, and Figs. 6, 7, and 8 show time series of the measurements.

Regarding the analytical techniques applied here, we found very good correlations between Na and Cl measured by NAA vs. IC (Fig. 10) coupled with slopes and intercepts...
that are statistically indistinguishable from 1.0 and 0.0, respectively. This indicates that (1) virtually all particulate Na and Cl were in the forms Na\(^+\) and Cl\(^-\), respectively, and (2) Na\(^+\) and Cl\(^-\) in samples did not deteriorate while stored for 3 yr.

Correlations between selected data are shown in Fig. 10. A good correlation can indicate a common origin. The relative concentrations of Na, Mg and K are the same as for sea salt. The correlation between Al and Mn points towards crustal dust. The presence of volatile acids at detectable mixing ratios indicates that aerosols were either acidic or rapidly acidified throughout the campaign. A good correlation between the acids HCOOH and CH\(_3\)COOH (Fig. 10) suggests common sources and/or processing.

In the context of reactive halogens, the main focus of the campaign, a few definitions are needed for the evaluation of the results. Adopting the equations from Sander et al. (2003) and using the seawater mass ratios ([Cl]/[Na])\(_{\text{seawater}}\) = 1.8 kg kg\(^{-1}\) and ([Br]/[Na])\(_{\text{seawater}}\) = 0.0062 kg kg\(^{-1}\), we define the enrichment factors \(\text{EF}(X)\) for X = Cl and Br as
Figure 10. Scatter plots. The first column shows comparisons between filter pack samples analyzed by neutron activation (prefix FP_NAA) and ion chromatography (prefix FP_IC), respectively, with a 1:1 line in green. The second and third columns show correlations between selected data, where the prefix MC refers to mist chamber data, and a blue line indicates the sea water composition. Finally, the last column shows correlations to the derived quantities enrichment factor and deficit, as defined in Sect. 4. The units of all plots are the same as listed in Table 1. Regression lines in red are only shown if \( r^2 > 0.3 \).

\[
\text{EF}(X) = \frac{[X]/[Na]}{([X]/[Na])_{\text{seawater}}},
\]

(5)

where square brackets denote mass concentrations. Another useful quantity is the absolute deficit, which is defined as

\[
\text{deficit} = \left[ [Na] \times \left( \frac{[X]}{[Na]} \right)_{\text{seawater}} \right] - [X].
\]

(6)

We also define the quantity \( \Delta Br \), which is the difference between gas-phase bromine and the bromine deficit. The following are our main conclusions regarding measured halogens.

- Values for total bromine analyzed by NAA are higher than those for bromide analyzed by IC. This indicates that some aerosol bromine is in a form other than \( Br^- \).
- \( \text{EF}(Br) \) was not correlated with particulate \( Na^+ \). Absolute deficits of particulate \( Br \) and mixing ratios of gas-phase bromine (\( Br_g \)) increased with increasing sea-salt concentrations. These relationships together with the presence of acidic gases at detectable levels indicate that sufficient acidity was available to titrate sea-salt alkalinity and sustain halogen activation over the full range of sea-salt loadings during the experiment.
- \( Br_g \) concentrations are almost always higher than absolute deficits of particulate \( Br \) (the difference is shown as “delta \( Br \)” in Fig. 6). This implies that \( Br_g \) has a longer atmospheric lifetime than the parent aerosol. This has also been observed in a previous campaign (Keene et al., 2009).
- Systematic diel variability was not evident in either the aerosol \( Br \) enrichment factor nor inorganic gaseous \( Br \) (Fig. 9). This is in contrast to previous measurements in the MBL at Hawaii (Sander et al., 2003) and over the eastern Atlantic (Keene et al., 2009).

**Supplementary material related to this article is available online at** http://www.earth-syst-sci-data.net/5/385/2013/essd-5-385-2013-supplement.zip.

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References


