Measurements of HCl in the volcanic plumes of Calbuco (2015) and Raikoke (2019)

Volcanic emissions of HCl

- After $H_2O$, $CO_2$ and $SO_2$, **Hydrogen chloride (HCl)** is the main volcanic gas species, and most important halogen halide (Symonds, Rose and Reed; 1988).

- Important effects on environment/ecosystems/soils/air quality (acidification)

- Chemical tracer of magma degassing and other subsurface processes in both syn-eruptive and quiescent degassing

- Estimated yearly emissions between 1 and 10 Tg. But very little is known on the halogen budget of large-size eruptions

---

**Arc related volcanic emissions of halogens**

HCl/\text{SO}_2\text{ ratios}

- Average HCl/\text{SO}_2: \sim 0.3 – but 4 orders of magnitude variation: from 0.001 (Ertα Ale) to 10 (Montserrat) (Pyle and Mather, 2009)

- Relative ratios vary in time, with applications to volcano monitoring

- Cl is highly soluble, and generally the more volatile gases are exsolved first (\text{CO}_2\text{ before }\text{SO}_2\text{ before }\text{HCl}) (Aiuppa et al, 2009):
  \text{\quad\rightarrow High ratios are associated with the }concluding\text{ stages of basaltic eruptions}
  \text{\quad\rightarrow During periods of reduced magma supply}
  \text{\quad\rightarrow HCl from silicic systems harder to interpret}

- Deposition and plume chemistry adds to the complexity
  - Wet deposition of HCl can be very significant (uptake in clouds, dissolution in condensed water vapour when RH is large; see Aiuppa et al. 2007, Burton et al. 2001)
  - Dry deposition
  - Uptake by (volcanic) ice and ash (see next slide)
  - Heterogeneous (gas-aerosol) reactions (see next slide)
Stratospheric emissions and role

• HCl is the most important Cl reservoir species. In the stratosphere can be transformed to reactive forms, leading to the destruction of ozone.

• Presence of bromide in volcanic plumes leads to “explosion” of reactive halogens (BrO and OClO) via heterogeneous reactions

• Documented stratospheric injections are modest, e.g.
  Augustine 1976: 0.08-0.18 Tg (Johnston, 1980); El Chicon 1982: 0.04 Tg (Mankin et al., 1983); Hekla 2001 (Rose, 2006); MLS ratios ~0.03, a factor 10 lower than what is measured in degassing/smaller tropospheric eruptions

• Direct stratospheric effect of HCl difficult to disentangle from the contribution of volcanic induced heterogeneous reactions that activate Cl reservoir species (ClONO2, HCl).

• Uptake and removal processes
  ▪ Scavenging by liquid supercooled water unimportant (<1%, Textor et al, 2003)
  ▪ Scavenging by ice particles important. Textor et al. (2003) : removes 75% of all initial HCl within the hour. Leaves 25% that reaches the stratosphere but in majority incorporated in those particles.
  ▪ Scavenging of HCl on volcanic ash may or may not important (Gutiérrez et al, 2016; Delmelle et al., 2018)
  ▪ Large uncertainty on stratospheric injections!
Satellite measurements of gases in volcanic plumes

<table>
<thead>
<tr>
<th>Sensor</th>
<th>H2O</th>
<th>CO2</th>
<th>CO</th>
<th>SO2</th>
<th>HCl</th>
<th>BrO</th>
<th>ODO</th>
<th>CH4/Cl</th>
<th>Timespan</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOMS*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1978-2005</td>
<td>1, 2</td>
</tr>
<tr>
<td>SBUV* (P)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1978-present</td>
<td>3, 4</td>
</tr>
<tr>
<td>HIRS*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1978-present</td>
<td>5</td>
</tr>
<tr>
<td>GOME</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1995-2003</td>
<td>6, 7, 8</td>
</tr>
<tr>
<td>MODIS*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1999-present</td>
<td>9, 10</td>
</tr>
<tr>
<td>ASTER</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1999-present</td>
<td>11, 12, 13</td>
</tr>
<tr>
<td>MOPITT</td>
<td></td>
<td></td>
<td></td>
<td>15%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1999-present</td>
<td>14</td>
</tr>
<tr>
<td>SCIAMACHY (L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2002-2012</td>
<td>8.15, 16</td>
</tr>
<tr>
<td>MIPAS (L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2002-2012</td>
<td>17</td>
</tr>
<tr>
<td>AIRS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2002-present</td>
<td>18, 19</td>
</tr>
<tr>
<td>ACE (L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2003-present</td>
<td>20</td>
</tr>
<tr>
<td>SEVIRI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2004-present</td>
<td>21</td>
</tr>
<tr>
<td>OMI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2004-present</td>
<td>16, 22, 23, 24</td>
</tr>
<tr>
<td>MLS* (L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1991-2001; 2004-present</td>
<td>25, 26, 27, 28</td>
</tr>
<tr>
<td>TES (P)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2004-present</td>
<td>29</td>
</tr>
<tr>
<td>GOME-2*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2006-present</td>
<td>16, 30, 31</td>
</tr>
<tr>
<td>IASI*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2006-present</td>
<td>14, 32, 33</td>
</tr>
<tr>
<td>OMPS*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2011-present</td>
<td>34</td>
</tr>
<tr>
<td>VIIRS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2011-present</td>
<td>35</td>
</tr>
<tr>
<td>CrIS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2011-present</td>
<td>36</td>
</tr>
<tr>
<td>AHI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2015-present</td>
<td>37</td>
</tr>
<tr>
<td>GOSAT (P)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2009-present</td>
<td>38</td>
</tr>
<tr>
<td>OCO-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2014-present</td>
<td>39</td>
</tr>
</tbody>
</table>

**Table 7**

HCl and SO2 mixing ratios measured by Aura/MLS in volcanic clouds.

<table>
<thead>
<tr>
<th>Volcano</th>
<th>Eruption Date</th>
<th>HCl (ppbv)</th>
<th>SO2 (ppbv)</th>
<th>Pressure (hPa)</th>
<th>HCl/SO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manam</td>
<td>Jan 27, 2005</td>
<td>4–6</td>
<td>279</td>
<td>68–100</td>
<td>0.01</td>
</tr>
<tr>
<td>Anatahan</td>
<td>Apr 6, 2005</td>
<td>3.5</td>
<td>133</td>
<td>100</td>
<td>0.02</td>
</tr>
<tr>
<td>Soufriere Hills</td>
<td>May 20, 2006</td>
<td>3</td>
<td>200</td>
<td>68</td>
<td>0.01</td>
</tr>
<tr>
<td>Chaitén</td>
<td>May 6, 2008</td>
<td>1.6</td>
<td>28</td>
<td>147</td>
<td>0.03</td>
</tr>
<tr>
<td>Okmok</td>
<td>Jul 12, 2008</td>
<td>5</td>
<td>212</td>
<td>147</td>
<td>0.01–0.02</td>
</tr>
<tr>
<td>Kasatochi</td>
<td>Aug 7, 2008</td>
<td>5–6</td>
<td>392</td>
<td>68–215</td>
<td>0.01–0.014</td>
</tr>
<tr>
<td>Redoubt</td>
<td>Mar 26, 2009</td>
<td>4–5</td>
<td>175</td>
<td>100–215</td>
<td>0.02</td>
</tr>
<tr>
<td>Sarychev Peak</td>
<td>Jun 15, 2009</td>
<td>7–9</td>
<td>529</td>
<td>32–215</td>
<td>0.03</td>
</tr>
<tr>
<td>Merapi</td>
<td>Nov 5, 2010</td>
<td>6–7</td>
<td>172</td>
<td>100–215</td>
<td>0.03</td>
</tr>
<tr>
<td>Cordón Caulle</td>
<td>Jun 4, 2011</td>
<td>2–3</td>
<td>77</td>
<td>147–215</td>
<td>0.03</td>
</tr>
<tr>
<td>Nabro</td>
<td>Jun 15, 2011</td>
<td>9</td>
<td>306</td>
<td>46–215</td>
<td>0.03</td>
</tr>
<tr>
<td>Paluweh</td>
<td>Feb 2, 2013</td>
<td>2.2</td>
<td>129</td>
<td>100–215</td>
<td>0.01</td>
</tr>
<tr>
<td>Kétut</td>
<td>Feb 14, 2014</td>
<td>7</td>
<td>398</td>
<td>32–147</td>
<td>0.01</td>
</tr>
<tr>
<td>Sangeang Api</td>
<td>May 31, 2014</td>
<td>2–3</td>
<td>53</td>
<td>146</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Ratios a factor 10 lower than what is measured in-situ – in degassing/smaller tropospheric eruptions

HCl only observed from Limb measurements (UTLS)

Hydrogen chloride spectrum

Measured with ground-based FTIR


• Its spectral band is located **unfavourably in terms of source radiation:**
  - Thermal emission too low to be useful
  - Solar reflected radiation weak -> measurement possible in daytime

• Its spectral band is located **favourable in terms of competing absorbers:**
  - A few water and methane interferences
Satellite measurements of HCl using its SWIR band

Currently only IASI covers this band, but only partially (645-2760 cm\(^{-1}\))

But retrieval will be challenging:

- weak background signal (daytime only)
- doesn’t cover the strongest lines
- low signal to noise

First IASI observations of HCl

Unambiguous identification of HCL in the volcanic plumes of Raikoke and Calbuco
Raikoke

Where: Kuril Islands  
Type: (basaltic) arc volcano  
Elevation: 551 m  
Eruptions: VEI ≥4 eruptions in 765, 1778, 1924 and 2019

21 June 2019 eruption

- Start of eruption around 1750 UTC (Himawari-8 +infrasound)  
- Duration ~15h  
- 1-2 Tg SO$_2$  
- Injection altitudes >15 km
No HCl detected!
(neither at low or high altitude)

Total mass: 29.26 kt
Total mass: 0.00 kt


Raikoke
(a) SO2 column

Total mass: 1189.36 kt

(b) HCl column

Total mass: 0.00 kt

(c) SO2 altitude

(d) Ash detection confidence

Nighttime

Raikoke
HCl detected below 6km, up to 100 DU! 

Raikoke
Two example spectra, in either part of the plume

Raikoke
Large variability in ratios, from <0.05 (estimate) to > 50
Calbuco

Where: southern Chile
Type: (basaltic) andesitic arc volcano
Elevation: 2,015 m
Eruptions: History of moderately explosive to sub-plinian eruptions throughout the Holocene. 13 eruptions in 20th century, last one in 1972

22-23 April 2015 eruption

- <3h precursory seismic activity
- Triggered by continued crystallisation of a cooling magma, which led to second boiling and (over)pressurisation of the system, and rapid onset of the eruption (Arzilli et al. 2019).
- Two eruption pulses (of 1.5 and 6 h duration)
- 300 – 400 kt SO$_2$
- 0.3 – 0.9 km$^3$ erupted tephra (sub-plinian, VEI 4)
- Injection altitudes >15 km (twice)
- Caused measurable destruction of ozone (Solomon et al., 2015)

Calbuco

(a) SO2 column

(b) HCl column

(c) SO2 altitude

(d) Ash detection confidence

Total mass: 91.74 kt

Nighttime

Total mass: 0.00 kt

(a) SO2 column

(b) HCl column

(c) SO2 altitude

(d) Ash detection confidence

Calbuco

Nighttime
In large part of the plume, no SO$_2$ is detected!

Possible explanation: Gas that was scavenged (e.g., by ice or ice-ash mixtures) at higher altitudes in the eruption column fell out to lower altitudes where it was released upon sublimation. The high ratio would reflect the ‘scavenging efficiency’ which is higher for HCl than for SO$_2$. 

Calbuco
Conclusions

• Large HCl plumes observed in both eruptions at low altitude near the final stages of the eruptions

• Some very high HCl/SO₂ ratios measured, 10 and above

• No HCl is observed in the high altitude parts, leading to a low upper bound on the (gaseous) HCl/SO₂ ratio (<0.05).

• Relative low stratospheric ratios as measured by MLS confirmed

• A combination of scavenging, plume chemistry, uptake by ice particles and variable emission ratios likely explain the observed variations.

• The large Calbuco HCl plume is likely the result of sublimation from ice fall