Polar Halogen Chemistry

Udo Frieß
Institute of Environmental Physics
University of Heidelberg, Germany

CREATE Summer School 2013
Lecture A, Tuesday, July 17
The Role of Halogens in the Polar Troposphere
- Outline -

- A short historical review on polar halogens
- Where do halogens come from?
- The Impact of halogens on tropospheric chemistry
- BrO in polar regions
- Impact of halogen radicals on the mercury cycle
- IO in polar regions
- Outlook:
  Open questions and challenges
1981: First indications that something strange is going on in the Arctic atmosphere

Samuel Oltmans:
Surface ozone measurements in clean air
JGR, 1981

"The most stunning day-to-day changes in surface ozone occur at Barrow during the spring. It is not unusual for daily ozone values to fluctuate from near zero to 30 or 40 nbar. The near zero values may persist up to a couple of days. It is not clear where air so depleted of ozone originates."
When compared to the natural background levels, the results presented in this paper indicate that the bromine concentrations in the Arctic troposphere are the highest found anywhere in the world. The source or sources that feed bromine into the Arctic remain to be identified. Long range transport of anthropogenic bromine, perhaps associated with the Arctic haze phenomenon, represents a possible source term. Natural biogeochemical surface emissions are also probably important.
1986: Observation of anti-correlation between bromine and ozone

Nature, 1986

emphasize the need for more diagnostic measurements. In view of the very efficient $O_3$ depletion that was observed and which we have considerable difficulty in modelling, it may be asked whether heterogeneous reactions on ice crystals could enhance $BrO_3$ production and catalytic ozone destruction, in the way that probably occurs for $ClO_3$ in the Antarctic lower stratosphere during springtime$^{27,28}$.

In conclusion, we would like to re-emphasize that more measurements are needed in the Arctic atmosphere during polar sunrise to elucidate the mechanism of ozone destruction. The Arctic atmosphere is a unique laboratory in which to study the chemical behaviour of anthropogenic and natural substances in the presence and absence of light. There is much to be learned from studies on this part of the globe about the biogeochemical cycles of ozone, nitrogen and sulphur oxides, as well as the cycles of the halogens Br and I.
Relationship between BrO and surface ozone
Neumayer Station, Antarctica

Frieß et al., JGR, 2004
Polar BrO from Satellite

Tropospheric BrO over the poles as seen from GOME

Arctic
20.04.1997

Antarctic
18.09.1997

Wagner et al., JGR, 2001
BrO from GOME-2 Satellite

Holger Sihler, IUP Heidelberg
Halogen in Polar Regions: Where do they come from?

1. Heterogeneous release from sea salt surfaces
2. Photochemical destruction of halocarbons (e.g., CH$_3$Br, CH$_3$I, CH$_2$I$_2$, ...) emitted by macroalgae and phytoplankton
3. Direct emission of I$_2$ by algae
4. Reaction of ozone with dissolved organic matter at the ocean surface
Natural precursors of reactive halogens in the atmosphere

Halocarbons produced by macroalgae (in ng per g wet algae and day)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Laminaria saccharina</th>
<th>Desmarestia aculeata</th>
<th>Fucus distichus</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Br₂</td>
<td>8.2</td>
<td>0.9</td>
<td>8.1</td>
</tr>
<tr>
<td>CHBr₃</td>
<td>71.5</td>
<td>3.4</td>
<td>17.4</td>
</tr>
<tr>
<td>CHBrCl₂</td>
<td>0.07</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>CHBr₂Cl</td>
<td>1.8</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>CH₃I</td>
<td>0.2</td>
<td>0.14</td>
<td>0.8</td>
</tr>
<tr>
<td>CH₂I₂</td>
<td>4.1</td>
<td>1.6</td>
<td>0.08</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>0.2</td>
<td>0.04</td>
<td>0.16</td>
</tr>
<tr>
<td>CH₃CH₂CH₂I</td>
<td>0.0</td>
<td>0.02</td>
<td>0.15</td>
</tr>
<tr>
<td>CH₃CHICH₃</td>
<td>0.0</td>
<td>0.14</td>
<td>0.8</td>
</tr>
<tr>
<td>CH₃I</td>
<td>0.2</td>
<td>0.14</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Lifetime and abundance of brominated and iodinated halocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Approx. lifetime</th>
<th>Mixing ratio [ppt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃Br</td>
<td>8 months</td>
<td>10</td>
</tr>
<tr>
<td>CH₂Br₂</td>
<td>4 months</td>
<td>&lt; 1.5</td>
</tr>
<tr>
<td>CH₂BrCl</td>
<td>5 months</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>CHBr₂Cl</td>
<td>1.2 months</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>CHBr₃</td>
<td>1.2 months</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>CHBrCl₂</td>
<td>1.2 months</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>CH₃I</td>
<td>5 days</td>
<td>2.4</td>
</tr>
<tr>
<td>C₃H₇I</td>
<td>40 hours</td>
<td>0.43</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>5 hours</td>
<td>n.d.</td>
</tr>
<tr>
<td>CH₂I₂</td>
<td>5 minutes</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Algae as a source for polar halogen radials?
Impact of Halogens on Tropospheric Chemistry

- Catalytic ozone destruction
- Mercury oxidation → Hg deposition
- DMS oxidation → Cloud formation, impact on climate
- OIO polymerisation → New particle formation
- Impact on oxidising capacity

![Diagram showing the impact of halogens on tropospheric chemistry](Diagram.png)

- X, Y ∈ [Cl, Br, I]
The Bromine Explosion

Heterogeneous bromine release on sea salt surfaces

\[
\begin{align*}
\text{BrO} + \text{HO}_2 & \rightarrow \text{HOBr} + \text{O}_2 \\
\text{HOBr}(g) + \text{Br}^- (aq) + H^+ & \rightarrow \text{Br}_2 (g) + H_2O \\
\text{Br}_2 + h\nu & \rightarrow 2\text{Br} \\
2\text{Br} + 2\text{O}_3 & \rightarrow 2\text{BrO} + \text{O}_2
\end{align*}
\]

→ One gaseous BrO molecule releases up to two BrO molecules per cycle
→ Exponential increase in gas phase BrO

Catalytic ozone destruction – Formation of ozone depletion events (ODE)

\[
\begin{align*}
\text{Br} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2 \\
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{BrO} + \text{HO}_2 & \rightarrow \text{HOBr} + \text{O}_2 \\
\text{HOBr} + h\nu & \rightarrow \text{Br} + \text{OH} \\
2\text{O}_3 & \rightarrow 3\text{O}_2
\end{align*}
\]

Important at high BrO levels
Ozone destruction rate $\sim [\text{BrO}]^2$

\[
\begin{align*}
2\text{Br} + 2\text{O}_3 & \rightarrow 2\text{BrO} + 2\text{O}_2 \\
\text{BrO} + \text{BrO} & \rightarrow 2\text{Br} + \text{O}_2 \\
2\text{O}_3 & \rightarrow 3\text{O}_2
\end{align*}
\]

Important at low BrO levels
Ozone destruction rate $\sim [\text{BrO}]$

\[
\begin{align*}
\text{Br} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2 \\
\text{I} + \text{O}_3 & \rightarrow \text{IO} + \text{O}_2 \\
\text{BrO} + \text{IO} & \rightarrow \text{Br} + \text{I} + \text{O}_2 \\
2\text{O}_3 & \rightarrow 3\text{O}_2
\end{align*}
\]

Interhalogen reactions (Br/Cl; Br/I) can increase the rate of ozone destruction
Prerequisites for the bromine explosion

Why does it only happen in polar spring?

1. **Radiative cooling** leads to a very stable boundary layer with reduced vertical mixing
2. **Sunlight** is needed to drive the photochemistry
3. **Brine production** leads to surfaces with high salinity and increased in Br/Cl ratio
4. **Acidification** is required because bromine explosion requires low pH (<7)
5. **Low temperatures** lead to **carbonate precipitation** in the sea ice. This reduces the buffer capacity and facilitates acidification
6. **Large surface areas** for heterogeneous chemistry can be provided by frost flowers and windblown ice/snow particles
Frost flowers
A potential source for reactive bromine in polar regions

Kaleschke et al., GRL, 2004

However, the total surface area of frost flowers is probably too small to explain the amount of BrO release.
Which processes contribute to bromine release?

(a) Nilas

(b) Open lead cloud

(c) Frost flowers

Steffen et al., ACP, 2008
1. Direct release of reactive bromine from brine and frost flowers
2. Uptake of brine by blowing snow and subsequent release of reactive bromine
3. Dispersion of saline frost flowers and subsequent release of reactive bromine
4. Deposition and accumulation of snow and ice crystals with high salinity on the snowpack and subsequent bromine release
First direct measurement of reactive bromine release from Arctic snow

Pratt et al., Nature Geosciences, 2013

Barrow, Alaska, 2012
BrO, Ozone and Aerosols
Barrow, Alaska, 2009

Frieß et al., JGR, 2011
BrO, Ozone and Aerosols
Barrow, Alaska, 2009

GOME-2 BrO

MAX-DOAS BrO profiles

BrO surface mixing ratio

BrO vertical column

Surface ozone

MAX-DOAS aerosol profiles

Frieß et al., JGR, 2011
Surface BrO and Aerosols

- Direct correlation between BrO and enhanced aerosol extinction
- Clear indication for bromine activation on aerosol particles and/or blowing snow

Frieß et al., JGR, 2011
Dependence of GOME-2 Tropospheric BrO on Temperature and Wind Speed

- **February/March:**
  - More BrO at low temperatures (< -25°C)

- **April/May:**
  - More BrO at high temperatures (≈ -10°C)

- **Probability of BrO release as a function of temperature**

- **February/March:**
  - No significant dependence on wind speed

- **April/May:**
  - More BrO at high wind speed

Sihler et al., AMT, 2012
Modelling polar bromine chemistry

- MISTRA: 1D photochemical model
- A column of air parcels is moved over different surfaces (snow, frost flowers, open lead)
- Chemistry inside the boxes modelled using a detailed photochemical scheme
- Model accounts for vertical mixing

Piot and von Glasow, ACP, 2008
Modelling polar bromine chemistry

Piot and von Glasow, ACP, 2008
Impact of bromine radicals on atmospheric mercury

Steffen et al., ACP, 2008
Mercury in the Arctic

Steffen et al., ACP, 2008
First indications for iodine enrichment in the Antarctic

HALOGENS IN ANTARCTIC METEORITES
G. Dreibus and H. Wänke, Max-Planck-Institut für Chemie, Saarstrasse 23, 6500 Mainz, F.R. Germany

The discovery of Antarctic meteorites offers the opportunity to study meteorites which have been kept in one of the cleanest and most sterile environments on Earth. Nevertheless, many of these stones are badly weathered. Therefore macroscopically, stony meteorites from Antarctica are classified in respect to their degree of weathering and fracturing. We have determined halogen concentrations in polymict eucrites, howardites, diogenites, shergottites and a C2-chondrite from the Allan Hills and Elephant Moraine regions in Victoria Land and the Yamato Mountains. Surprisingly, we found in all polymict eucrites from the Elephant Moraine locality extremely high iodine concentrations of 11-15 ppm, compared to a mean iodine content of 0.07 ppm in non-antartic eucrites (Dreibus et al., 1979). Similarly the chlorine content in all Antarctic eucrites

Dreibus and Wänke, 1983

Heumann et al., 1987
First detection of IO in the Antarctic troposphere

Frieß et al, GRL, 2001
Tropospheric IO: Why is it only in the Antarctic and not in the Arctic?

Schönhardt et al., ACP, 2008
Tropospheric IO: How can it reach the interior of the Antarctic continent?

Schönhardt et al, ACP, 2012
Antarctic snowpack as a reservoir for IO?

MAX-DOAS measurements at Neumayer

Estimated IO mixing ratio in the snowpack

Assuming an iodine snow:air ratio of 50:50 yields > 100 ppb of gaseous iodine

Frieß et al, ACP, 2010
Halogens in the Troposphere: Summary

- Sources of halogens:
  - Sea ice
  - Snowpack
  - Brine
  - Frost flowers
  - Blowing snow
  - Sea salt aerosols
  - Biogenic production (algae, phytoplankton)

- Main impacts:
  - Ozone destruction
  - Mercury oxidation and input of toxic mercury into fragile ecosystems
  - Modification of the HO/HO$_2$ and NO/NO$_2$ ratio
  - Oxidative capacity of the atmosphere
  - Cloud formation (via DMS oxidation)
  - New particle formation (via I$_x$O$_y$ clustering)
Halogens in the Troposphere: Open questions and challenges

- What happens to polar BrO in a world of changing climate?
  - Less multi-year sea ice
  - More first-year sea ice with higher salinity
  - More BrO emission from sea ice???
- What exactly are the sources, release and recycling mechanisms for polar bromine?
- Is there an impact of polar BrO on mid-latitudes via spill-out effects?
- Why is IO found in Antarctica, but not in the Arctic?