Ozone Chemistry in the High-Latitude Boundary Layer

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Outline

• Brief history of boundary layer ozone loss phenomenon

• In situ observations of BrO at Arctic sites

• Preliminary results from Antarctic experiments in 2002 and 2004
Brief History

• Springtime ozone loss observed at many sites around Arctic since 1970s
Barrow, AK Ozone Record

Data courtesy NOAA CMDL
Brief History

- Springtime ozone loss observed at many sites since 1970s
- Early studies suggested link to “Arctic Haze” – pollution transported from Europe and Asia
- Filterable Br correlated with ozone loss
Barrie et al., *Nature*, 1988
Brief History

- Later studies show some correlation between ozone loss and presence of BrO

Tuckerman et al., *Tellus*, 1997
Ozone Loss in the Arctic

- Natural chemistry in the Arctic caused by bromine episodically removes $O_3$ near the surface every spring
- Allows other gases to build up to unnaturally high levels, including mercury and certain hydrocarbons

\[
\begin{align*}
2 (Br + O_3 & \rightarrow BrO + O_2) \\
BrO + BrO & \rightarrow 2Br + O_2 \\
2 O_3 & \rightarrow 3 O_2
\end{align*}
\]
Where does bromine come from?

“leads” spray deposits
salt on snowy surfaces

frost flowers
made of brine
< 150 km

O3 + BrO → Br2 + O2

Br2 + hv → 2Br

BrO + HOx → HOBr

HOBr + Br^- + H^+ → Br2 + H2O

O3 + Br → O2 + BrO

BrO + BrO → Br2 + O2

Br2 + hν → 2Br
“Bromine Explosion”

\[ \text{HOBr}_{(aq)} + \text{Br}^-_{(aq)} + \text{H}^+_{(aq)} \rightarrow \text{H}_2\text{O}_{(aq)} + \text{Br}_2(g) \]

\[ \text{Br}_2 + h\nu \rightarrow 2\text{Br} \]

\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]

\[ \text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2 \]

**Net:** \[ \text{H}^+ + \text{Br}^- + \text{HO}_2 + \text{O}_3 \rightarrow \text{Br} + \text{H}_2\text{O} + 2\text{O}_2 \]

[Fan and Jacob, 1992]
“Bromine Explosion”

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\text{Br}_2 + h\nu \rightarrow 2\text{Br}
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\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2
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\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2
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\text{Net: } \text{H}^+ + \text{Br}^- + \text{HO}_2 + \text{O}_3 \rightarrow \text{Br} + \text{H}_2\text{O} + 2\text{O}_2

[Fan and Jacob, 1992]
<table>
<thead>
<tr>
<th>Source</th>
<th>pH</th>
<th>Cl/Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea Water</td>
<td>7.6 - 8.2</td>
<td>650</td>
</tr>
<tr>
<td>Frost flowers, measured</td>
<td>8.1 – 8.7</td>
<td>269-367</td>
</tr>
<tr>
<td>Surface snow, measured</td>
<td>5.4 – 7.3</td>
<td>13-980</td>
</tr>
</tbody>
</table>

[Kalnajs and Avallone 2006]
Why should we care?

• Bromine activation is widespread
BrO is widespread
Why should we care?

• Bromine activation is widespread

• Bromine may react with gaseous mercury (Hg₀), converting it to forms that are deposited into ecosystems
Correlation of Mercury with Ozone

Schroeder et al., *Nature*, 1998
Why should we care?

• Bromine activation is widespread

• Bromine may react with gaseous mercury (Hg\(^0\)), converting it to forms that are deposited into ecosystems

• Possible climate implications of boundary layer ozone loss
• Tropospheric Ozone has significant climate forcing at poles

• ODEs affect arctic ozone budget

• Antarctic is cleaner than arctic → study non-anthropogenic contribution

• ODEs play a role in aerosol formation → ice core interpretation

JJA tropospheric ozone forcing above pre-industrial levels [L.J. Mickley 2001]
In Situ Measurements of Halogens

• Prior to 1996, all observations of halogens had been made either by long-path spectroscopy (DOAS) or by collection and analysis of aerosols or air samples.

• In situ measurements provide higher temporal resolution, and potentially higher spatial resolution.
Measurement Sites

- PSE 2000
- ARCTOC

Map showing measurement sites in the Arctic region.
Instruments

ARCTOC '96
Ny Ålesund, April-May

Polar Sunrise 2000
Alert, May

1 m

25 cm
ARCTOC '96 BrO

Avallone et al., *JGR*, 2003
Alert 2000 BrO

Avalone et al., JGR, 2003
Lessons from in situ BrO measurements

BrO + BrO,
ClO + BrO

Ozone Lifetime
Ozone Lifetime

[Graph showing the percentage of occurrence of ozone lifetime for ARCTOC '96 and Alert 2000 across different time intervals.]
Ozone Lifetime

![Graph showing the distribution of ozone lifetime with labels for Chemistry and Transport]
Aerosol

Sea Ice

Sea Water

< 150 km

O₃

BrO + BrO → Br₂ + O₂

O₃ + Br → O₂ + BrO

Br₂ + hν → 2Br

BrO + HOₓ → HOBr

BrO + HOₓ → HOBr

Br

Br⁻ + Cl⁻

Atmosphere

Frost Flowers

Snow Pack

Br⁻ + Br⁻ + H⁺ → Br₂ + H₂O

HOBr + Br⁻ + H⁺ → Br₂ + H₂O
What about the Antarctic?
What about the Antarctic?
Questions about Antarctic boundary layer ozone

• Does surface ozone loss happen in the Antarctic?

• If so, can we explain it? Is it due to bromine?
Ozone loss in Antarctica?

[Graph showing the trend of ozone concentrations over time with labels for Ozone (ppb) on the y-axis and Date on the x-axis. The graph indicates a peak in ozone concentration followed by a decline, typical of the ozone hole in Antarctica.]
Ozone loss in Antarctica? Yes, but...

Not as deep or dramatic at McMurdo as in the Arctic
Measurements at Arrival Heights

Winfly 2002
First Results

![Graph showing Ozone and NOx levels over time with a storm period highlighted]
Is there BrO at McMurdo?

Yes, but…
- There’s something else present - not the form we expected
- Continuing data analysis and lab work

So for 2004 season….
2004 Field Season Goals

• “Clean Air” site – near Pegasus runway
• Continue to monitor “pollution tracers”
• Measure ozone fluxes from/to snow surface
• Sample snow for chemical content
Field Site - Fish Hut #12

monitoring

fluxes
Ozone Behavior

![Ozone Behavior Graph](image)
Ozone in town – for contrast
Ozone Behavior

23 - 26 October

Direction?
Wind speed?
Blowing snow?
Ozone Surface Flux

• Definition: Number of molecules per second crossing a surface parallel to the ground.
• Expressed as a deposition velocity – average vertical velocity of an ozone molecule
Vertical Profiles of Ozone

• Can we learn about the chemistry of ozone from its vertical profile?

• Ran a tethered balloon using a Univ. Wyoming ozonesonde
Flux Measurements

10 Hz (0.1 sec) measurements of ozone and $CO_2$
Flux Measurements
Aerosol

Sea Water

Sea Ice

Frost Flowers

Atmosphere

Snow Pack

\[ \text{Br} \]

\[ \text{Cl}^- \]

\[ \text{Br}^- \]

\[ \text{O}_3 \]

\[ \text{BrO} + \text{BrO} \rightarrow \text{Br}_2 + \text{O}_2 \]

\[ \text{O}_3 + \text{Br} \rightarrow \text{O}_2 + \text{BrO} \]

\[ \text{Br}_2 + \text{hv} \rightarrow 2\text{Br} \]

\[ \text{BrO} + \text{HO}_x \rightarrow \text{HOBr} \]

\[ \text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O} \]
Outstanding Issues

• What is the real source of bromine to the atmosphere? Is direct BrO release from the snowpack important?
• What is the role of aerosols in ODEs?
• Are inter-halogen reactions important (Iodine?)
• Do these ODEs occur by the same mechanism in the Arctic and Antarctic?