Halomethane Fluxes in the Northern Alaskan Coastal Tundra

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Field and laboratory assistance: Tsang Lau, Andy Thompson, Whendee Silver, Andrew Maizel, Claudia Pingatôre
Linking gas exchange to other SNACS projects

I. Our project
   A. Introduction: What we are looking at and why?
   B. March: Air composition near ice leads and over tundra
   C. June-August: Tundra fluxes by microtopography

II. Possible linkages with other projects & our tentative plans
   A. Organic halogens as sources of reactive bromine?
   B. Carbon balance and CH$_4$ fluxes?
   C. Effect of permafrost melting on tundra gas fluxes?
   D. Effect of coastal erosion on salt-affected land emissions?
A. Is the Alaskan coastal tundra an important source or sink of CH$_3$Br, CH$_3$Cl, CH$_3$I, and CHCl$_3$?

CH$_3$Br, CH$_3$Cl, and CHCl$_3$ in atmospheric chemistry

* CH$_3$Br & CH$_3$Cl: largest sources of Br & natural Cl to stratosphere, CH$_3$Br a Montreal Protocol gas, used in agriculture.
* CHCl$_3$: minor Cl source to stratosphere, few % of reactive Cl in troposphere (Gradel and Keene, 1995), reactions with •OH
* Global budgets of these compounds poorly known (WMO, 2003)

Why the northern Alaskan coastal tundra?

* Tropical and temperate coastal ecosystems are large sources of methyl halides (Yokouchi et al., 2001; Rhew et al., 2001).
* Temperate peatlands are sources of CH$_3$X and CHX$_3$ (Dimmer et al., 2001; Varner, 1999; Carpenter et al., 2005)
* >50% CHCl$_3$ emissions estimated to emanate from 30-90° N, but very limited tundra measurements (Khalil and Rasmussen, 1999; O’Doherty et al., 2001)
* Background concentrations measured at Barrow (NOAA/CMDL)
B. First outing: March 23-25, 2005:

Pressurized air samples collected near ice leads and over tundra. Analyzed at SIO for a range of halogenated compounds.

<table>
<thead>
<tr>
<th>Date</th>
<th>Sample Type</th>
<th>Temperature</th>
<th>Wind Speed</th>
<th>Distance (m)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/23/05</td>
<td>Lead sample 1</td>
<td>-12°C</td>
<td>~20 mph</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>3/24/05</td>
<td>Lead sample 2</td>
<td>-14°C</td>
<td>~12 mph</td>
<td>~5</td>
<td>2</td>
</tr>
<tr>
<td>3/25/05</td>
<td>Tundra sample</td>
<td>-23°C</td>
<td>~0-5 mph</td>
<td>7.5</td>
<td>2</td>
</tr>
</tbody>
</table>
B. March results

Among the halocarbons measured, only CHBr₃ appeared to have significantly higher concentrations than background (2-5x background concentrations in coastal California)

<table>
<thead>
<tr>
<th>Gas</th>
<th>CH₃Cl</th>
<th>CH₂Cl₂</th>
<th>CHCl₃</th>
<th>CH₃Br</th>
<th>CHBr₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead1</td>
<td>1.01</td>
<td>1.01</td>
<td>0.99</td>
<td>0.91</td>
<td>0.51</td>
</tr>
<tr>
<td>Lead 2</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Tundra</td>
<td>1.02</td>
<td>1.01</td>
<td>1.11</td>
<td>1.03</td>
<td>1.16</td>
</tr>
</tbody>
</table>
C. Tundra halomethane fluxes in June and August, 2005
Tundra research infrastructure courtesy of a biocomplexity experiment on carbon uptake, storage and release (Oechel, Tweedie, Gamon, and Oberbauer)

20 flux chamber sites

5 transects with 4 sites each, covering a range of microtopographic features:

1. snow/ice
2. drained lake/channels
3. wet tundra
4. low (moist) tundra
5. high (drier) tundra

map courtesy of Allison Graves Gaylord
What we measured

gas fluxes
CH$_3$Cl, CH$_3$Br
CH$_3$I, CHCl$_3$
CH$_4$, CO$_2$, N$_2$O

environmental/biogeophysical:
microtopography
flux chamber T(°C)
ambient air T (°C) and P (mbar)
soil T @ 5cm (°C)
soil T @ 10 cm (°C)
soil H$_2$O content (#9-20 Aug)
halide content (surface H$_2$O)
ambient PAR
GPS coordinates

biological:
vegetation (species, functional type)
biomass (g dry wt/m$^2$)
(sites #9-20 only)
total aboveground
total sphagnum
total vascular
total grass/sedges
live above-ground
live sphagnum
live vascular
live grass/sedges
digital photographs

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total grass/sedges
live above-ground
live sphagnum
live vascular
live grass/sedges
digital photographs
<table>
<thead>
<tr>
<th>Topographic Feature</th>
<th>Vegetation</th>
<th>June Examples</th>
<th>August Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake/Channel: &gt;50% Standing Water</td>
<td>Carex aquatilis, Dupontia fisherii</td>
<td>n=6</td>
<td>n=6</td>
</tr>
<tr>
<td>Wet Tundra: &lt;50% Standing Water</td>
<td>Mix of lake/channel and high tundra plants</td>
<td>n=3</td>
<td>n=3</td>
</tr>
<tr>
<td>Moist Tundra: Low Center Polygons</td>
<td>Carex aquatilis, Eriophorum spp., Dupontia fisherii</td>
<td>n=4</td>
<td>n=7</td>
</tr>
<tr>
<td>High Tundra: High Center Polygons</td>
<td>Sphagnum moss, lichens, Petasites frigidus, Luzulu arctica</td>
<td>n=5</td>
<td>n=4</td>
</tr>
</tbody>
</table>
CH$_3$Br and CH$_3$Cl uptake rates increase with decreasing moisture.

**CH$_3$Br** (nmol/m$^2$/d)

**June 2005**

- small source
- large sink

**August 2005**

- small source
- large sink

**CH$_3$Cl** (nmol/m$^2$/d)

- June 2005
- August 2005
CH₄ emissions follow a similar pattern. CHCl₃ is emitted at all sites, highest at moist tundra sites.

**June 2005**

<table>
<thead>
<tr>
<th>Source Type</th>
<th>CH₄ (µmol/m²/d)</th>
<th>CHCl₃ (nmol/m²/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>snow/ice</td>
<td>2000</td>
<td>50</td>
</tr>
<tr>
<td>lake/channel</td>
<td>4000</td>
<td>100</td>
</tr>
<tr>
<td>wet</td>
<td>2000</td>
<td>50</td>
</tr>
<tr>
<td>moist</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>high</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

**August 2005**

<table>
<thead>
<tr>
<th>Source Type</th>
<th>CH₄ (µmol/m²/d)</th>
<th>CHCl₃ (nmol/m²/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>snow/ice</td>
<td>2000</td>
<td>50</td>
</tr>
<tr>
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</tr>
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<td>wet</td>
<td>2000</td>
<td>50</td>
</tr>
<tr>
<td>moist</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>high</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>
Can these fluxes be significant on the larger scale?

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$ (µmol/m$^2$/d)</th>
<th>CH$_3$Cl (nmol/m$^2$/d)</th>
<th>CH$_3$Br (nmol/m$^2$/d)</th>
<th>CHCl$_3$ (nmol/m$^2$/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. flooded</td>
<td>3800</td>
<td>-9.3</td>
<td>1.4</td>
<td>39</td>
</tr>
<tr>
<td>2. wet tundra</td>
<td>2800</td>
<td>-160</td>
<td>-1.0</td>
<td>41</td>
</tr>
<tr>
<td>3. moist tundra</td>
<td>2000</td>
<td>-610</td>
<td>-11</td>
<td>79</td>
</tr>
<tr>
<td>4. high tundra</td>
<td>210</td>
<td>-1200</td>
<td>-19</td>
<td>31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$ (Tg/yr)</th>
<th>CH$_3$Cl (Gg/yr)</th>
<th>CH$_3$Br (Gg/yr)</th>
<th>CHCl$_3$ (Gg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>average cover*</td>
<td>23</td>
<td>-16</td>
<td>-0.5</td>
<td>3.7</td>
</tr>
<tr>
<td>% of atm burden**</td>
<td>0.5%</td>
<td>0.4%</td>
<td>0.3%</td>
<td>2%</td>
</tr>
<tr>
<td>% of source/sink**</td>
<td>4%</td>
<td>0.4%</td>
<td>0.2%</td>
<td>1%</td>
</tr>
</tbody>
</table>

* assume active season of 90 days, tundra s.a. = 7.3 x 10$^{12}$ m$^2$

** budget estimates from IPCC (2001), WMO (2003), and O’Doherty (2001)
Summary

**CH₃Br and CH₃Cl**

The northern coastal Arctic tundra is not a significant source of methyl halides.

While some production is observed, overall the tundra is a sink for CH₃Br and CH₃Cl, and a minor source of CH₃I.

Consumption rates are related to CH₄ emissions (soil redox conditions) and amount of above-ground biomass (sphagnum moss).

CH₃Br and CH₃Cl uptake rates are strongly correlated.

**CHCl₃**

The tundra is a regionally (and perhaps globally) significant source of chloroform.

**Future directions**

Is the tundra a source/sink for other halogenated VOCs?

Do lower latitude tundra ecosystems have larger flux rates?

Will Arctic warming cause a significant shift in emissions / uptake rates?
II. Possible linkages with other SNACS projects & our tentative plans for 2006

A. Organic halogens as sources of reactive bromine?

B. Carbon balance and CH$_4$ fluxes?

C. Effect of permafrost melting on tundra gas fluxes?

D. Effect of coastal erosion on salt-affected land emissions?
A. Biogenic Bromine: links with O$_3$ (and Hg deposition?)

**Fig. 1 in Salawitch, R. (2006), Biogenic Bromine, Nature 439, 275-277.**
A. Organic halogens as sources of reactive bromine?

1. There appears to be a mystery CHBr$_3$ source, but not necessarily from the ice lead
2. A springtime terrestrial source of bromoform? (preliminary analyses from summer flux chambers do not see high CHBr$_3$)
3. Links with O$_3$ reaction and Hg deposition? MeX and MeHg?
4. Plans: finish developing methods to measure CH$_2$Br$_2$, CHBr$_3$, including standards dilution line by May, 2006. In September, 2006: Measure fluxes over sunlit snow and ambient air samples, compare to wind trajectories. Abiotic or biotic sources?
Currently we measure CH$_4$ in order to link halomethane fluxes with soil redox conditions, but CH$_4$ is extremely important to measure in its own right.

Collaborative plans:


2. Coordinate with Jerry Brown and Schoolyard project: Develop a floating chamber system to measure CH$_4$ fluxes from Cakeeater Lake.

3. Compare CH$_4$ fluxes from boardwalk with Yoshi’s eddy correlation measurements.
C. Effect of permafrost melting on tundra trace gas emissions on the Arctic Coastal Plain

CO$_2$, CH$_4$ and methyl halide fluxes are strongly linked to the hydrology of the region.

Monitoring the changes in microtopography: Will the tundra become wetter or drier as the permafrost melts, and how will this feed back to trace gas fluxes? Who is developing a large scale picture of changing permafrost and hydrology?

Topography: ice-wedge polygons (65% coverage), rest covered by shallow N-S oriented lakes, drained lake basins, gently sloping terrain (J. Brown et al., 1980).
D. Effect of coastal erosion on salt-effected land emissions?

Our research sites were coastal tundra, but did not include the salt tolerant species found closest to the coast. These coastline ecosystems may be degraded by erosion, or the amount of salt input on land may be affected.

Research plan: Arrange helicopter transport to other coastal tundra ecosystem types (outside of the BEO). Investigate the fluxes from salt-affected tundra. A better analogue to the temperate and tropical regions?
-- end --
II. Methods

Flux chamber air sampling:
2 component, vented, dark static (195 L, 0.271 m²)

t = 1, 20, 40 min. samples and ambient air samples

1L electropolished st. steel or
3L SilcoCans canisters

Laboratory analyses at UC-Berkeley:
GC/MS (Agilent 6890N/ 5973 inert MSD)
glass beads cryotrap + cryofocus
60m DB-VRX capillary column
(15m pre-column)
28 to 100 temperature ramp
see Aydin et al., 2002

Standard calibration:
whole air from Trinidad Head, CA
AGAGE/SIO calibration scale
J. Mühle and R. Weiss

Flux calculations
concentration vs time
positive slopes: linear regressions
negative slopes: ln(conc) vs time
1st order uptake rate constants
normalize to background concs.
multiply by # moles of air in chamber,
divide by surface area.
B. Correlation between \( \text{CH}_3\text{Cl} \) and \( \text{CH}_3\text{Br} \) uptake vs \( \text{CH}_4 \) emissions

- \( \text{CH}_4 \) emissions used as a proxy for soil redox conditions.
- Uptake rates also correlated with sphagnum moss biomass.
- Aerobic sites consume more methyl halides.
- Microbes on live or dead vegetation surfaces?
- Sphagnum moss layer a ‘filter’ for \( \text{CH}_3\text{Br} \) and \( \text{CH}_3\text{Cl} \)?
CH$_3$I production

June 2005

August 2005
CH$_3$Cl vs CH$_3$Br uptake rates are correlated

\[ y = 55.6 \times -70.6 \]
\[ R^2 = 0.89 \]

Uptake rates calculated using 1$^{\text{st}}$ order uptake rate constants and normalized to $C_{o(\text{MeCl})} = 536$ ppt and $C_{o(\text{MeBr})} = 10.4$ ppt hence, $C_{o(\text{MeCl})} \cdot C_{o(\text{MeBr})} = 51.5$
CH$_3$Cl and CH$_3$Br uptake vs. sphagnum moss biomass

No correlation with vascular plants.

Aerobic bacteria on live or senescent plant surfaces?

Sphagnum moss layer a ‘filter’ for CH$_3$Br and CH$_3$Cl?
IV. Results compared to other ecosystems

- **CH$_3$Cl shrubland max. uptake** (Rhew et al., 2001)

- **Ave. CH$_3$Br uptake rates** in tropical rainforest/savanna, boreal forest soils. (Shorter et al., 1995)

- **CH$_3$I emissions minor** compared to rice paddies (~930, Redeker & Cicerone, 2004)

- **CHCl$_3$ emissions from temperate peatlands** (Dimmer et al., 2001)