

Halomethane Fluxes in the Northern Alaskan Coastal Tundra

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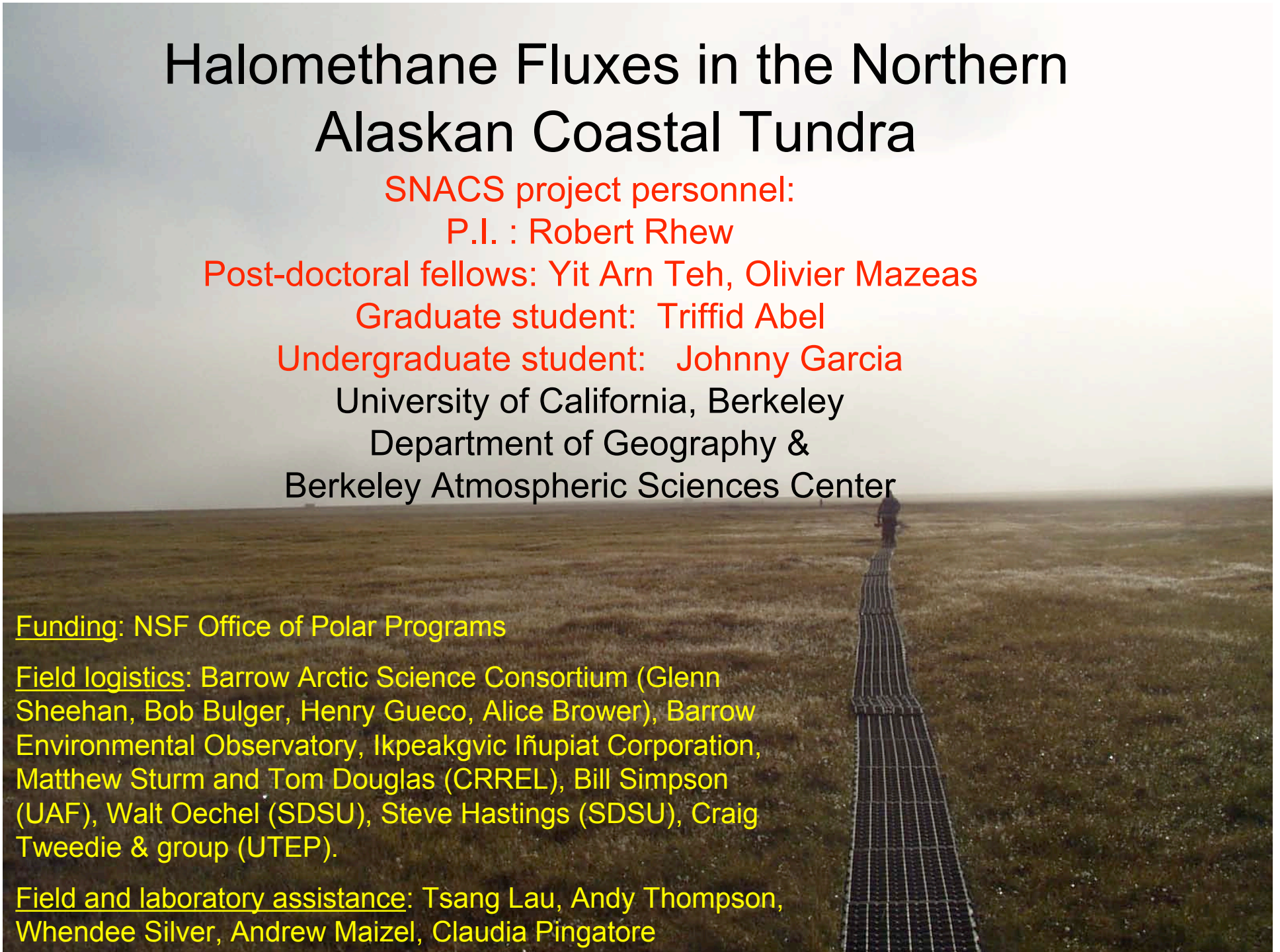
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Field and laboratory assistance: Tsang Lau, Andy Thompson, Whendee Silver, Andrew Maizel, Claudia Pingatore



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 CH₄ 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_3Br , CH_3Cl , CH_3I , and CHCl_3 ?

CH_3Br , CH_3Cl , and CHCl_3 in atmospheric chemistry

- * CH_3Br & CH_3Cl : largest sources of Br & natural Cl to stratosphere, CH_3Br 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 $\bullet\text{OH}$
- * 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_3X 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)

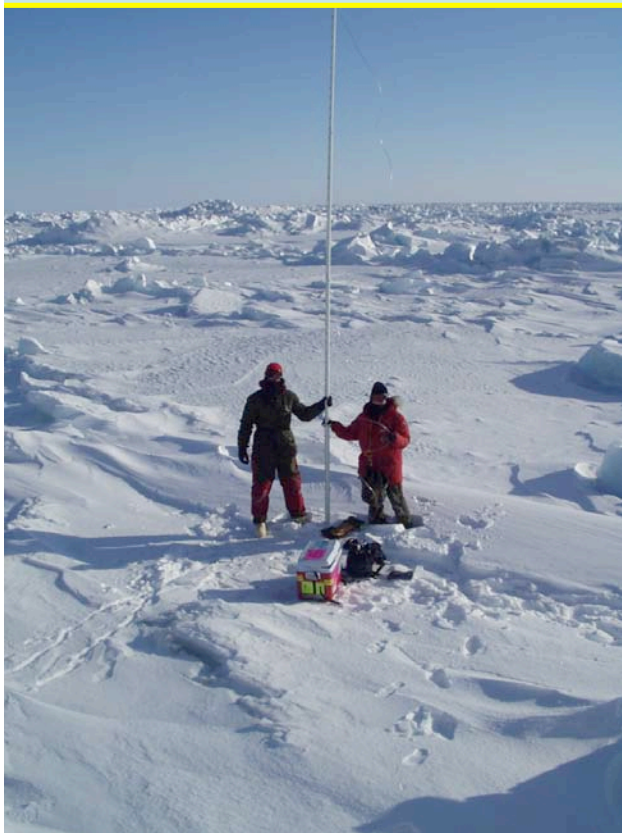
B. First outing: March 23-25, 2005:

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

A. 3/23/05: Lead sample 1,
-12°C, ~20 mph NE winds,
7meters (n=2)

B. 3/24/05: Lead sample 2,
-14° C, ~12 mph NE winds,
~5 meters (n=2)

C. 3/25/05: Tundra sample,
-23° C, ~0-5 mph E to S
winds, 7.5 meters (n=2)



B. March results

Among the halocarbons measured, only CHBr_3 appeared to have significantly higher concentrations than background (2-5x background concentrations in coastal California)

Ratio of gas concentrations compared to Lead 2

Gas	CH_3Cl	CH_2Cl_2	CHCl_3	CH_3Br	CHBr_3
Lead1	1.01	1.01	0.99	0.91	0.51
Lead 2	1.00	1.00	1.00	1.00	1.00
Tundra	1.02	1.01	1.11	1.03	1.16

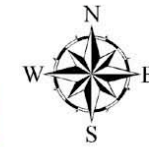
C. Tundra halomethane fluxes in June and August, 2005

2002 Quickbird Satellite Image Barrow, Alaska



Data acquisition made possible with funding from the National Science Foundation Office of Polar Programs, Arctic Research Support and Logistics Program. Copyright Digital Globe, 2002.

0 2.5 5 7.5 Kilometers



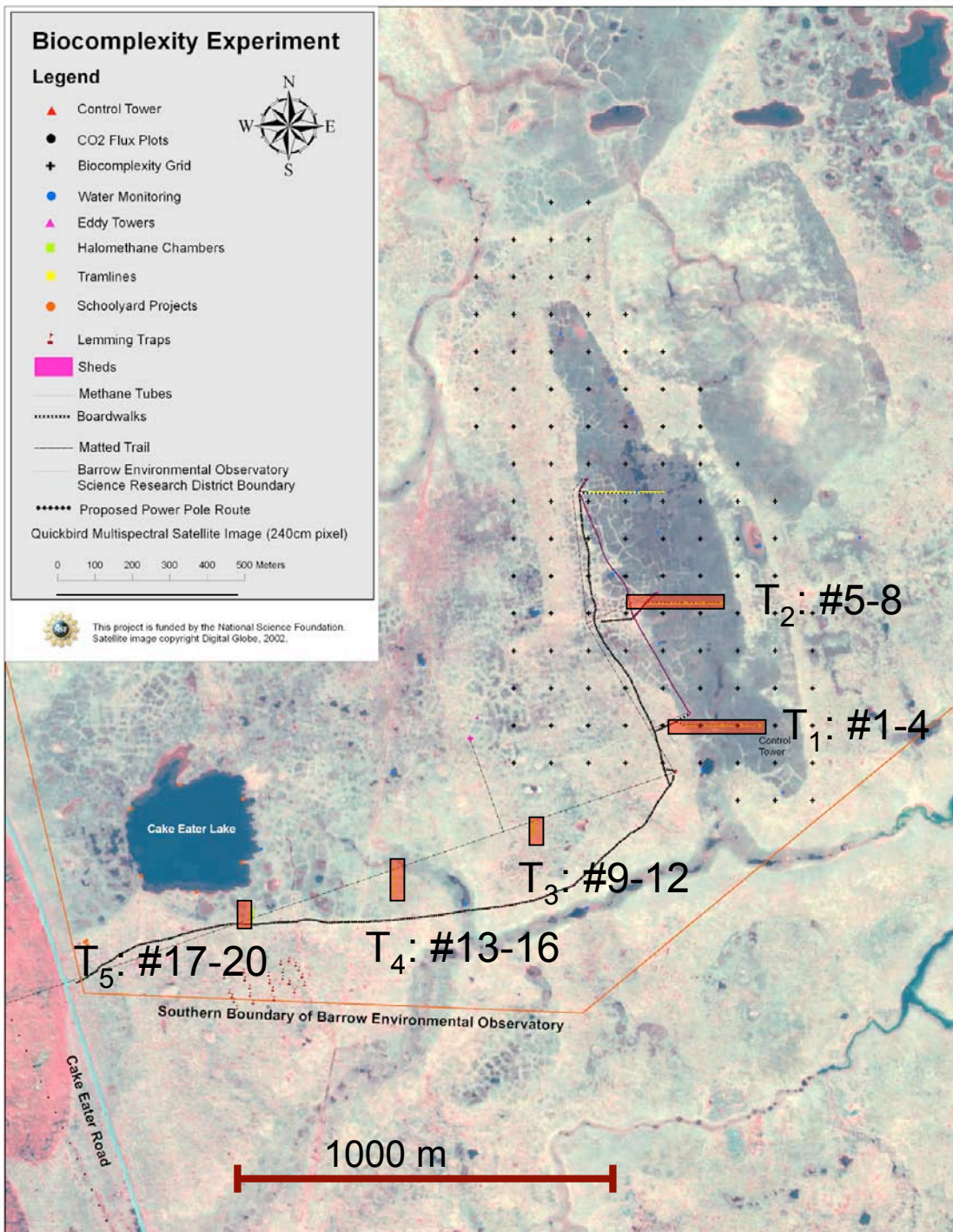
Barrow Environmental Observatory

ELSON LAGOON

CHUKCHI SEA

BEAUFORT SEA

*courtesy of
Allison Gaylord
(Nuna Tech)*



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_3Cl , CH_3Br

CH_3I , CHCl_3

CH_4 , CO_2 , N_2O



biological:

vegetation (species, functional type)

biomass (g dry wt/m²)

(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

environmental/biogeophysical:

microtopography

flux chamber T (°C)

ambient air T (°C) and P (mbar)

soil T @ 5cm (°C)

soil T @ 10 cm (°C)

soil H₂O content (#9-20 Aug)

halide content (surface H₂O)

ambient PAR

GPS coordinates

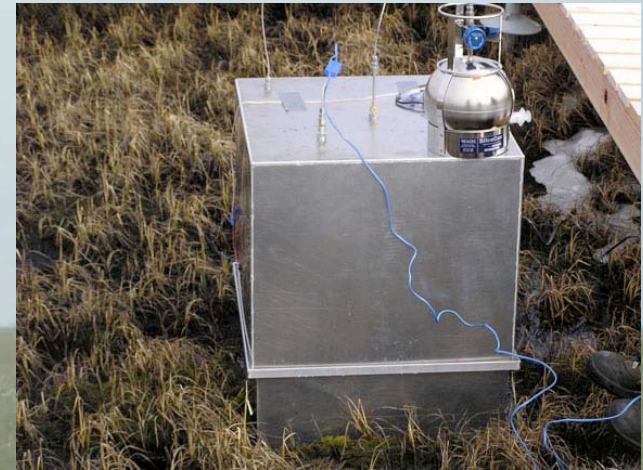

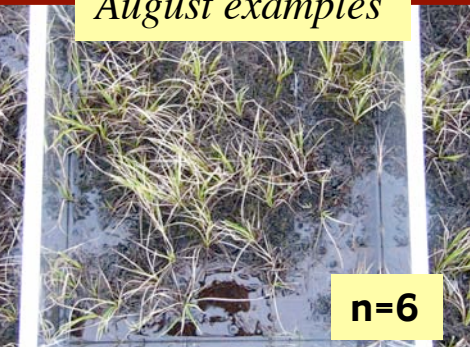

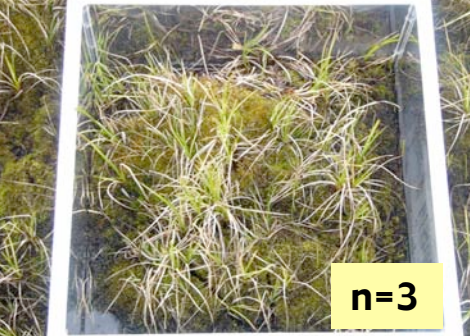

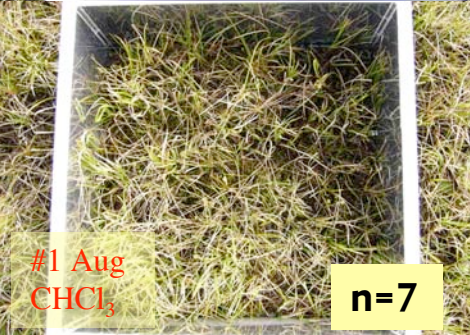

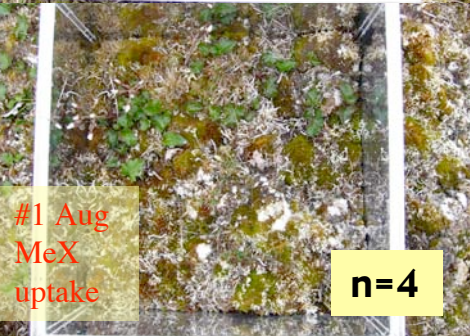


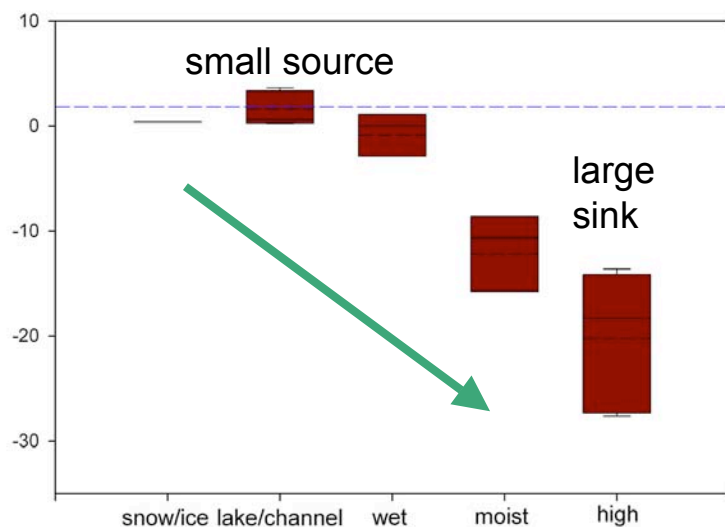
photo courtesy of Steve Hastings

<u>topographic feature</u>	<u>vegetation</u>	June examples	August examples
lake/channel: >50% standing water	<i>Carex aquatilis</i> , <i>Dupontia fisherii</i>	 <p>#1 Jun CH₄ n=6</p>	 <p>n=6</p>
wet tundra: <50% standing water	mix of lake/channel and high tundra plants	 <p>n=3</p>	 <p>n=3</p>
moist tundra: low center polygons	<i>Carex aquatilis</i> , <i>Eriophorum</i> spp., <i>Dupontia fisherii</i> ,	 <p>#1 Jun CHCl₃ n=4</p>	 <p>#1 Aug CHCl₃ n=7</p>
high tundra: high center polygons	<i>Sphagnum</i> moss, lichens, <i>Petasites frigidus</i> , <i>Luzulu arctica</i>	 <p>#1 Jun MeX uptake n=5</p>	 <p>#1 Aug MeX uptake n=4</p>

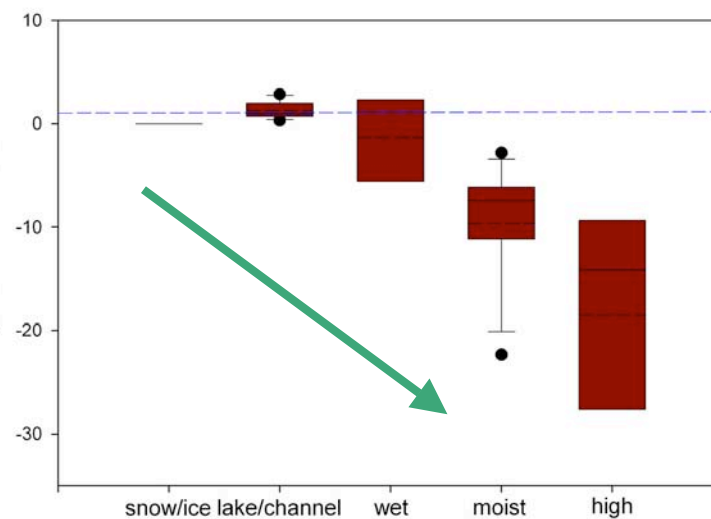
CH₃Br and CH₃Cl uptake rates increase with decreasing moisture

CH₃Br
(nmol/m²/d)

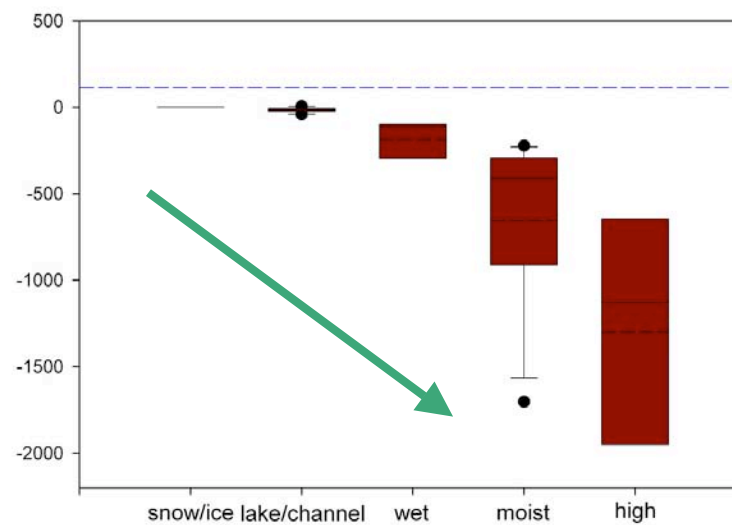
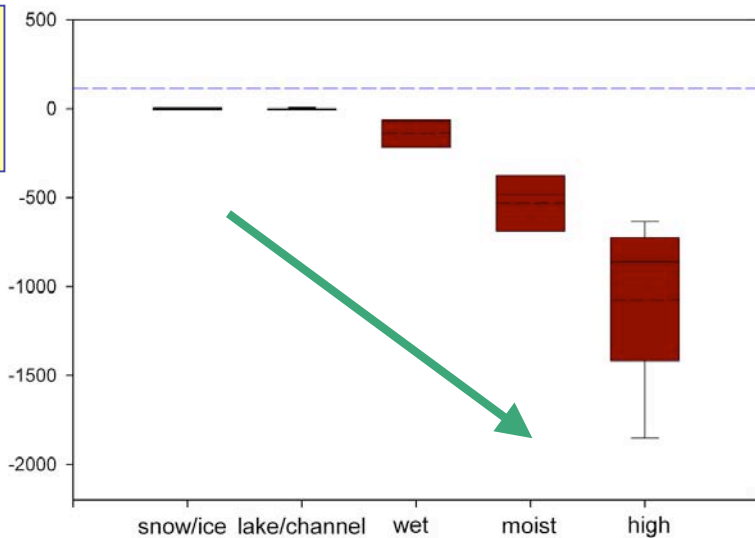
June 2005



August 2005



CH₃Cl
(nmol/m²/d)

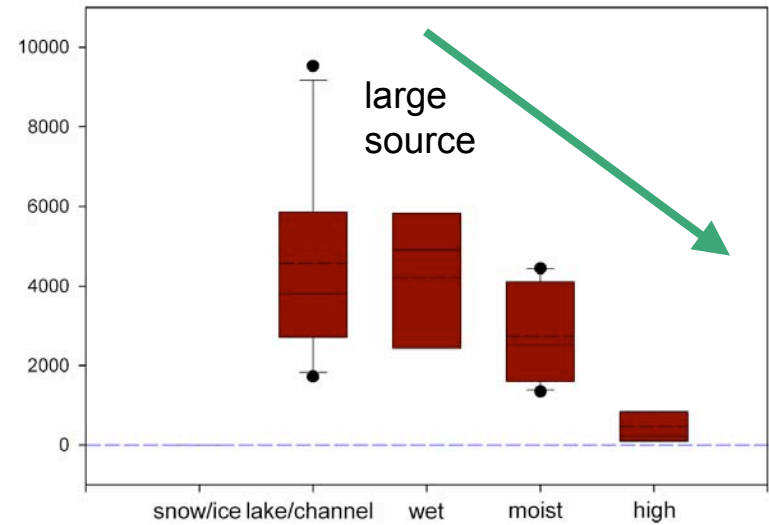
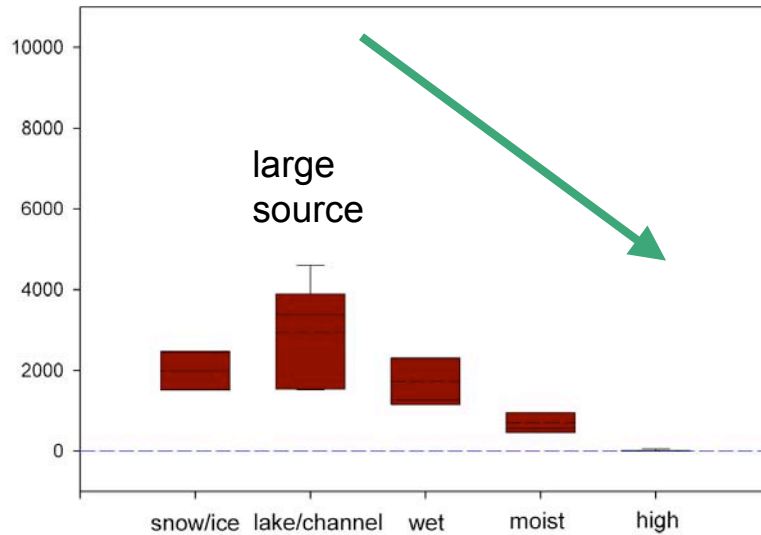


**CH₄ emissions follow a similar pattern.
CHCl₃ is emitted at all sites, highest at moist tundra sites**

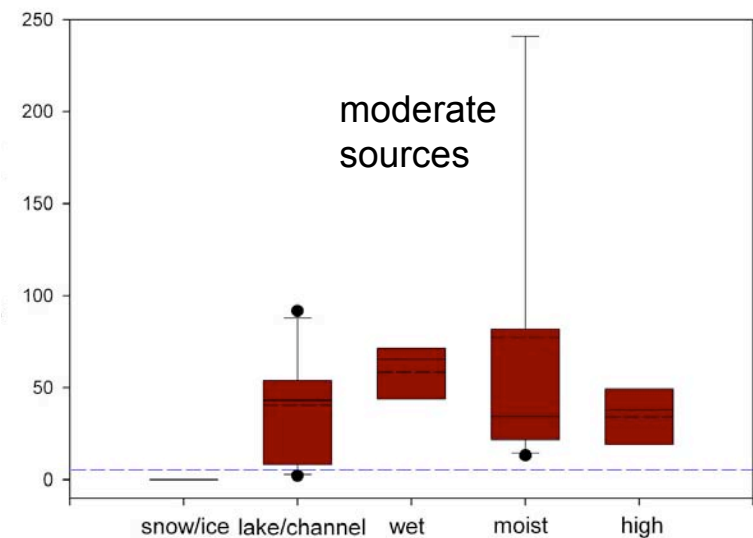
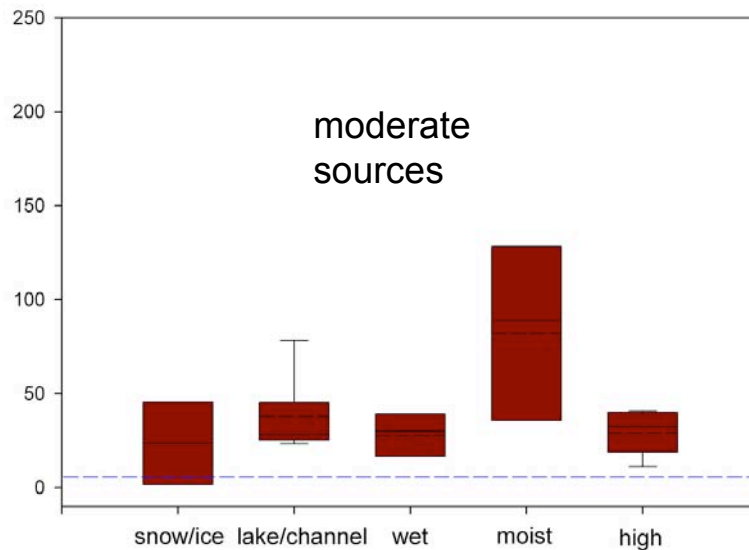
June 2005

August 2005

CH₄
(μmol/
m²/d)



CHCl₃
(nmol/
m²/d)



Can these fluxes be significant on the larger scale?

	CH₄ ($\mu\text{mol}/\text{m}^2/\text{d}$)	CH₃Cl ($\text{nmol}/\text{m}^2/\text{d}$)	CH₃Br ($\text{nmol}/\text{m}^2/\text{d}$)	CHCl₃ ($\text{nmol}/\text{m}^2/\text{d}$)
1. flooded	3800	-9.3	1.4	39
2. wet tundra	2800	-160	-1.0	41
3. moist tundra	2000	-610	-11	79
4. high tundra	210	-1200	-19	31

	CH₄ (Tg/yr)	CH₃Cl (Gg/yr)	CH₃Br (Gg/yr)	CHCl₃ (Gg/yr)
average cover*	23	-16	-0.5	3.7
% of atm burden**	0.5%	0.4%	0.3%	2%
% of source/sink**	4%	0.4%	0.2%	1%

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

** 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.

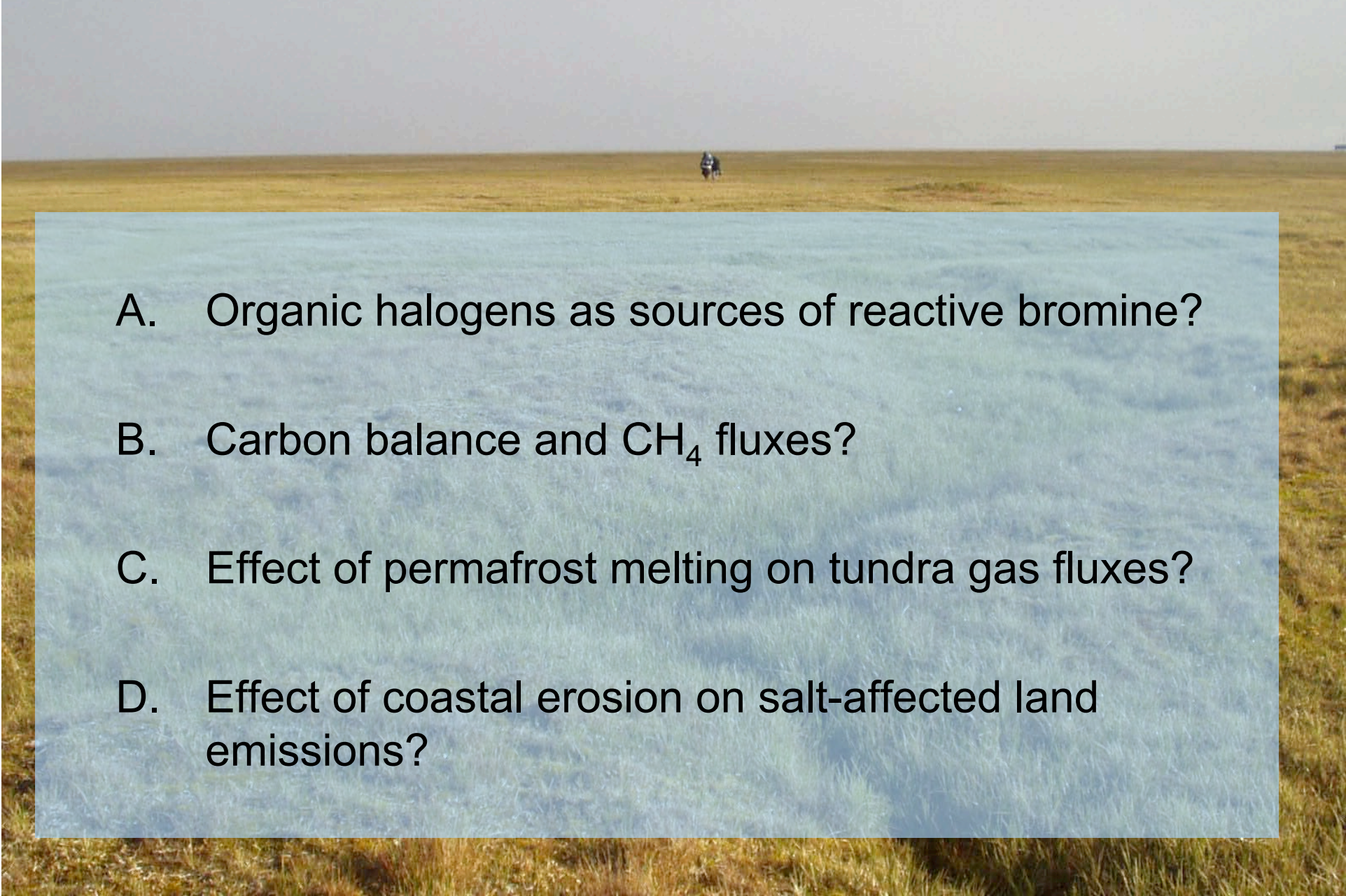
Future directions

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 CH₄ 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 O₃ (and Hg deposition?)

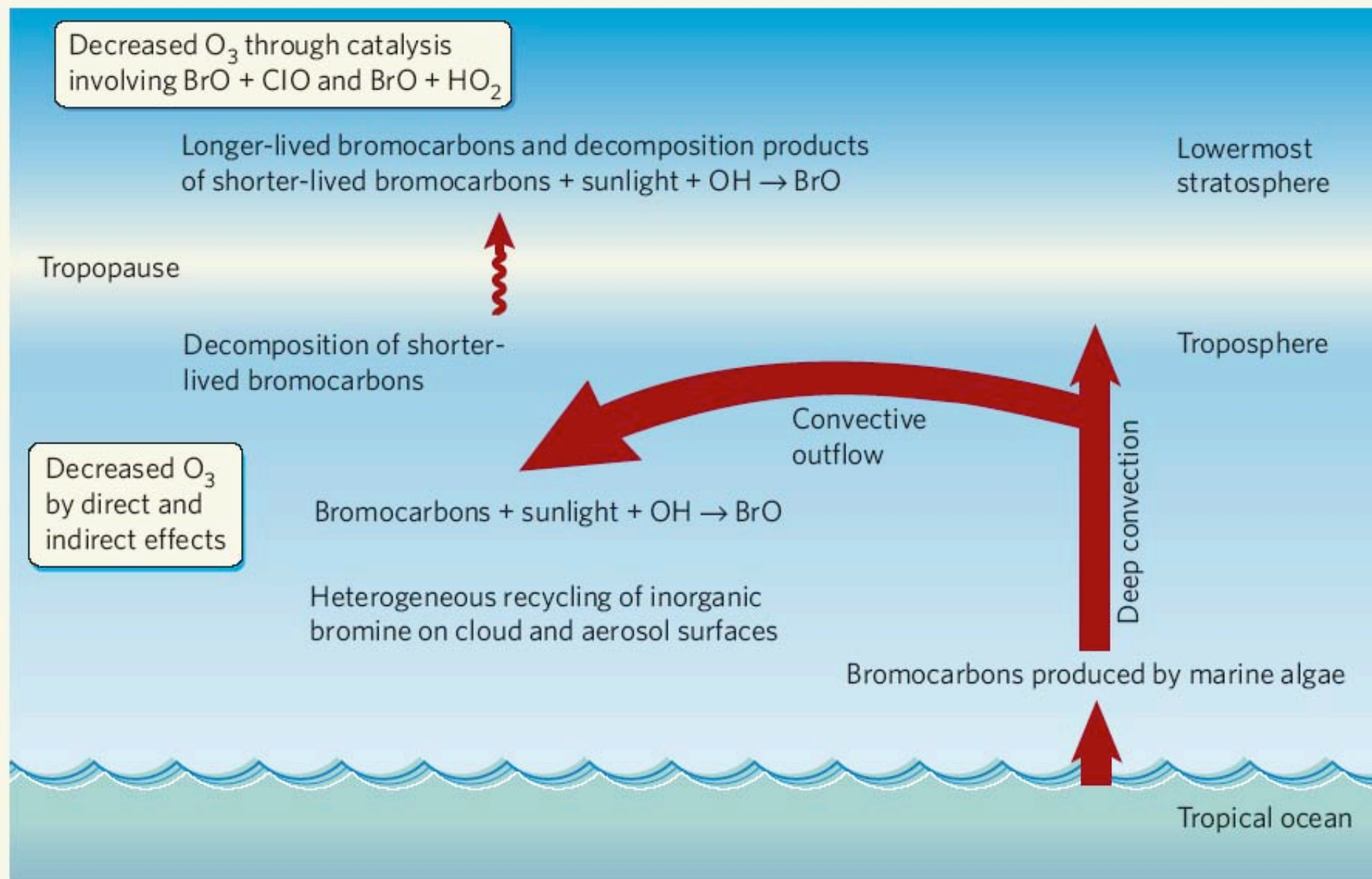
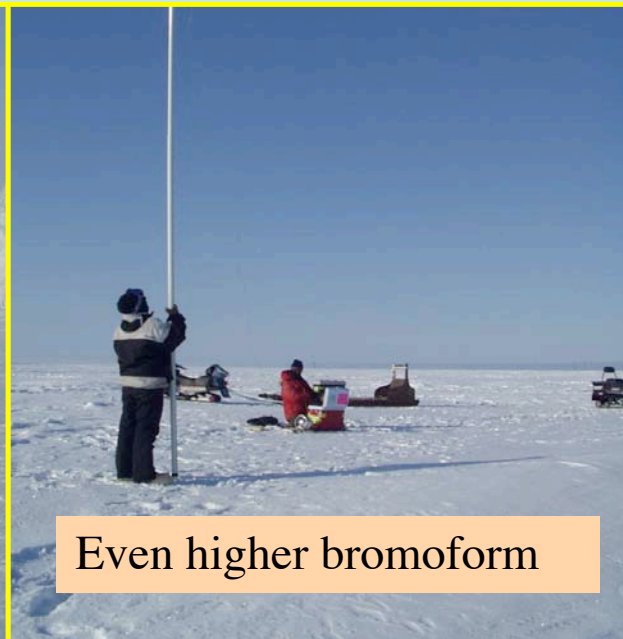
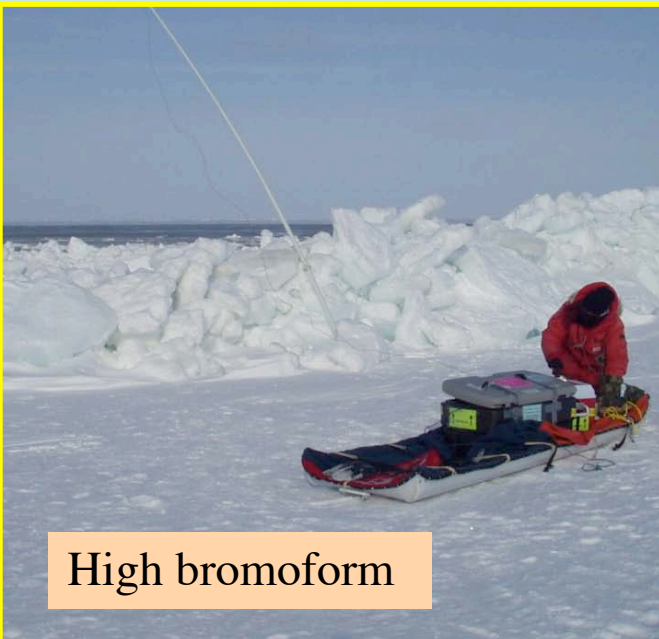


Fig. 1 in Salawitch, R. (2006), *Biogenic Bromine*, *Nature* **439**, 275-277.

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_2Br_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?



B. Carbon balance and CH₄ fluxes

Currently we measure CH₄ in order to link halomethane fluxes with soil redox conditions, but CH₄ is extremely important to measure in its own right.

Collaborative plans:

1. Coordinate with Craig Tweedie: transects of CH₄ and halomethane fluxes from Nome (28Jul-1Aug), Ivotuk (2 Aug-5 Aug) to Barrow (6Aug-18Aug).
2. Coordinate with Jerry Brown and Schoolyard project: Develop a floating chamber system to measure CH₄ fluxes from Cakeeater Lake.
3. Compare CH₄ fluxes from boardwalk with Yoshi's eddy correlation measurements

C. Effect of permafrost melting on tundra trace gas emissions on the Arctic Coastal Plain

CO₂, CH₄ 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).

2005.07.25

D. Effect of coastal erosion on salt-affected 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

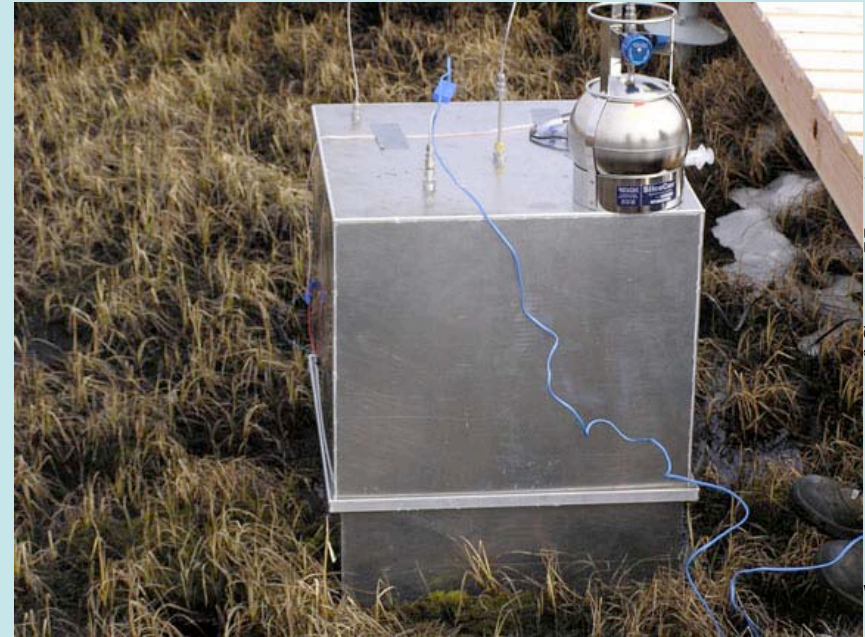


photo courtesy of Steve Hastings

flux calculations

concentration vs time

positive slopes: linear regressions

negative slopes: ln(conc) vs time

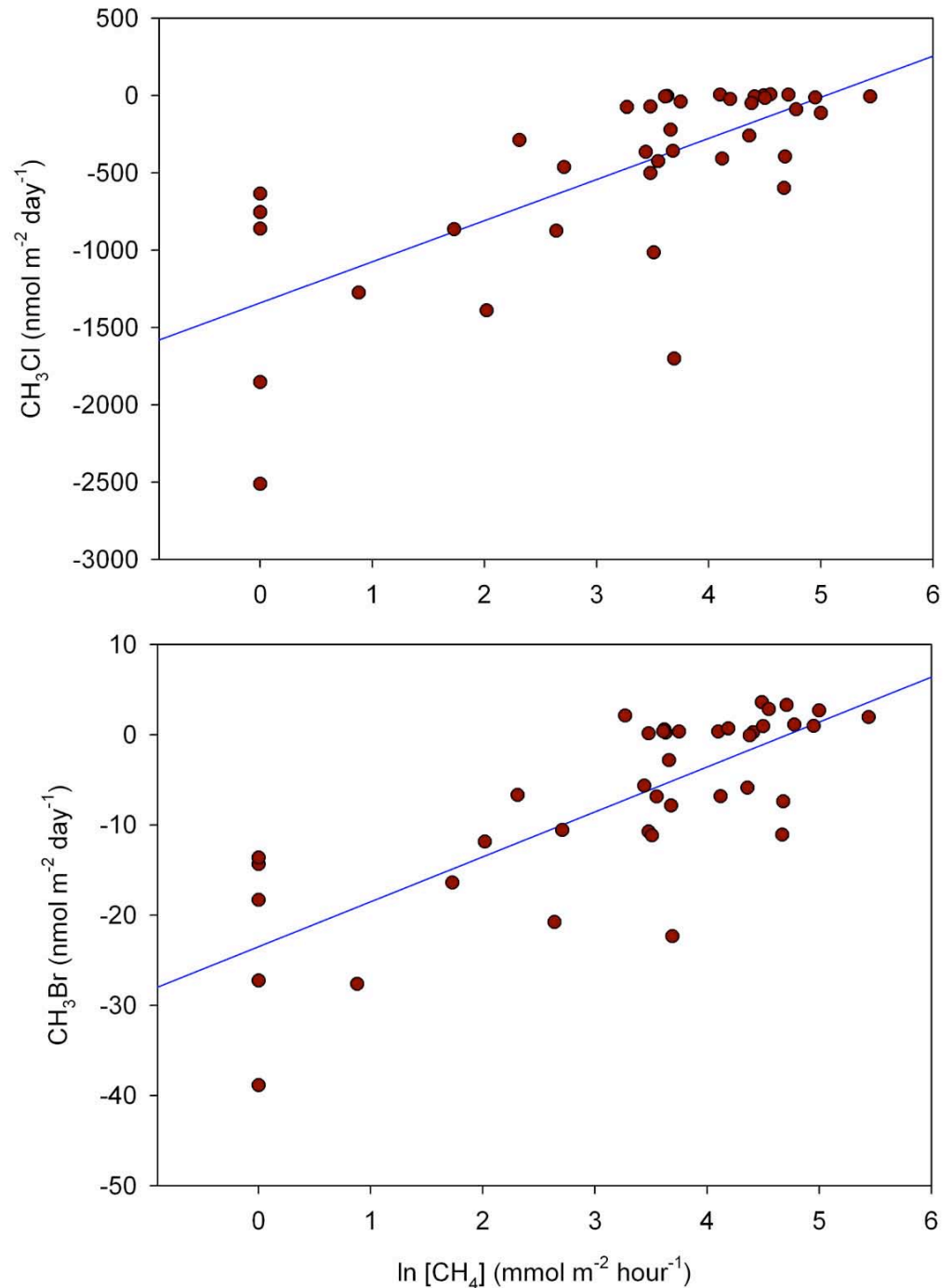
1st order uptake rate constants

normalize to background concs.

multiply by # moles of air in chamber,
divide by surface area.

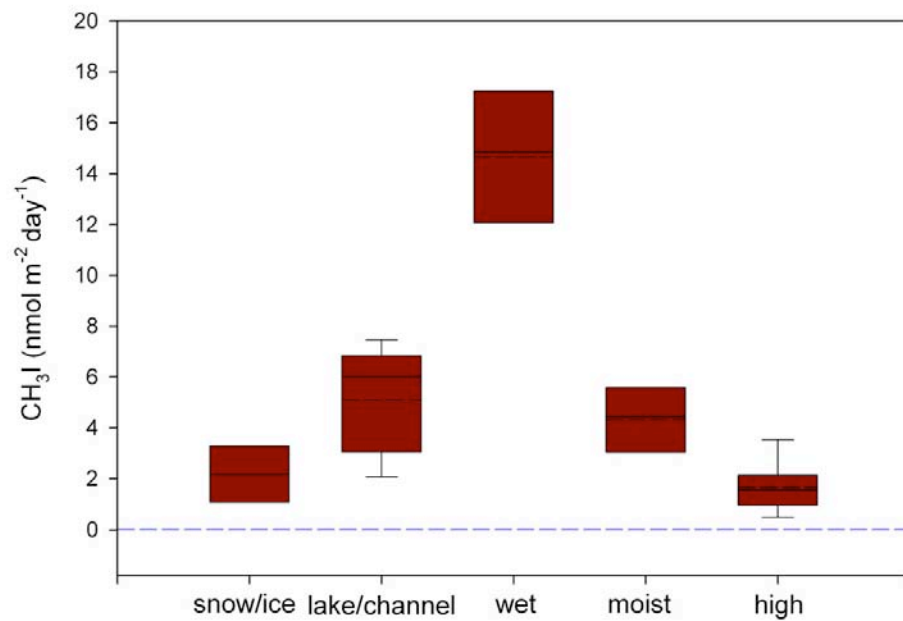
B. Correlation between CH_3Cl and CH_3Br uptake vs CH_4 emissions

- 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 CH_3Br and CH_3Cl ?

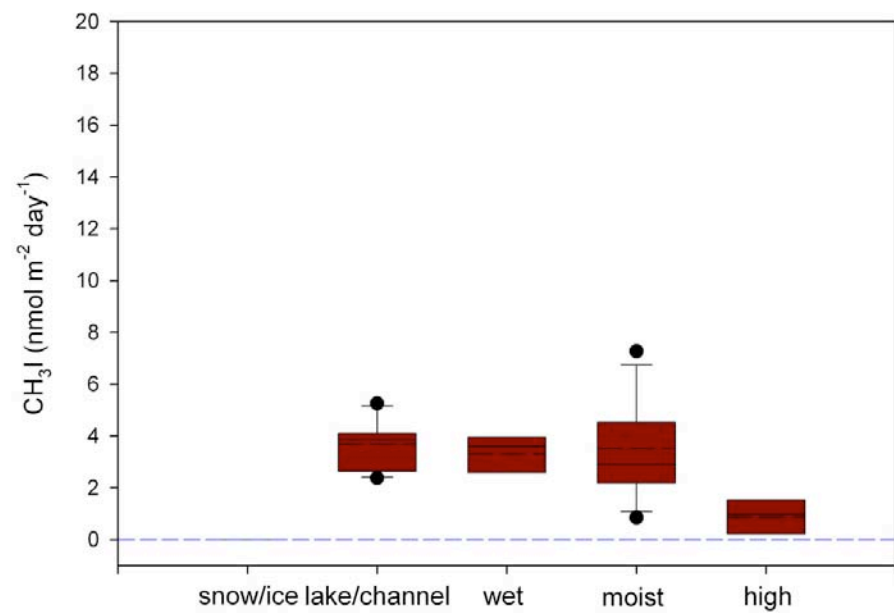


CH₃I production

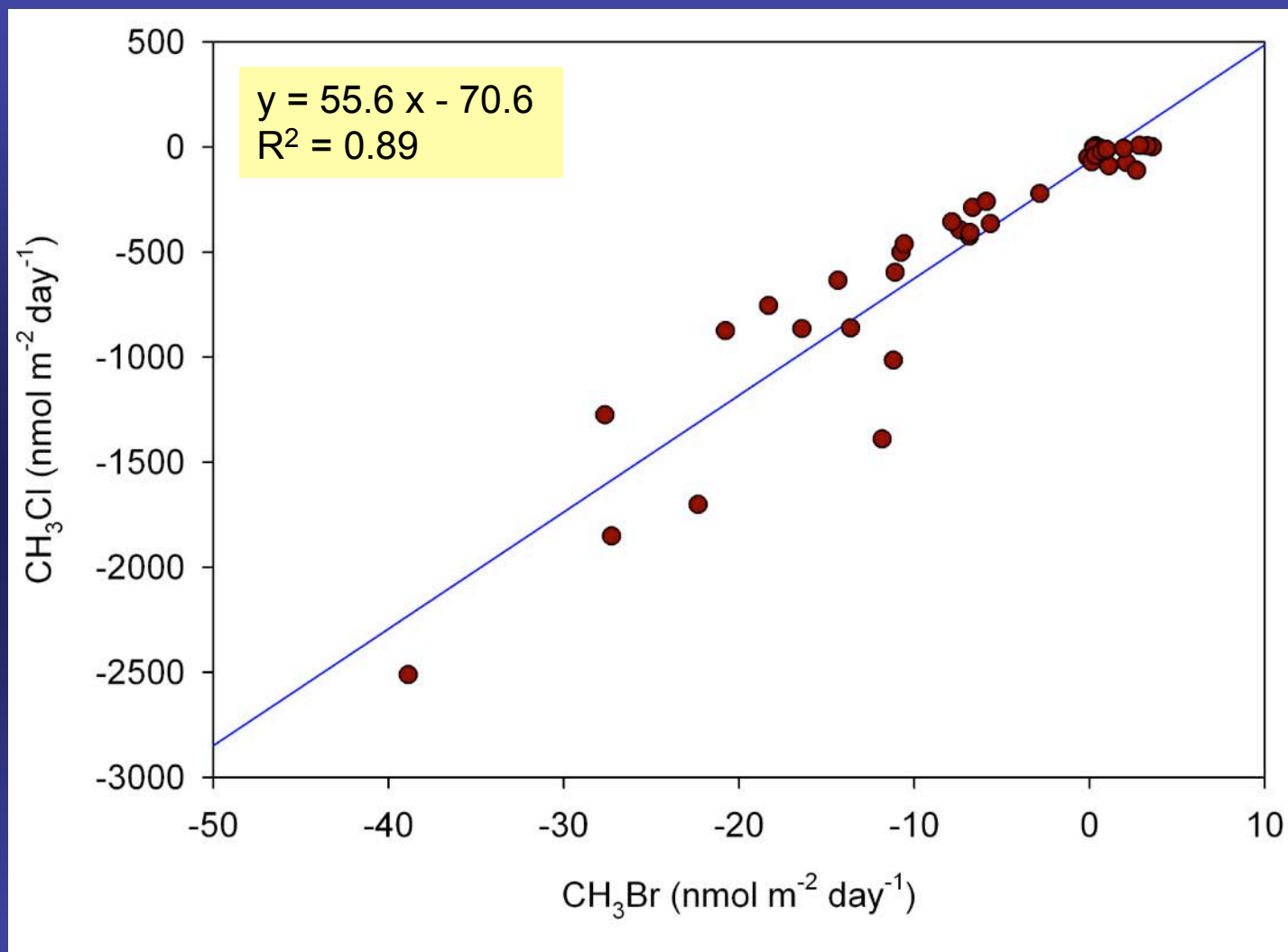
June 2005



August 2005



CH₃Cl vs CH₃Br uptake rates are correlated



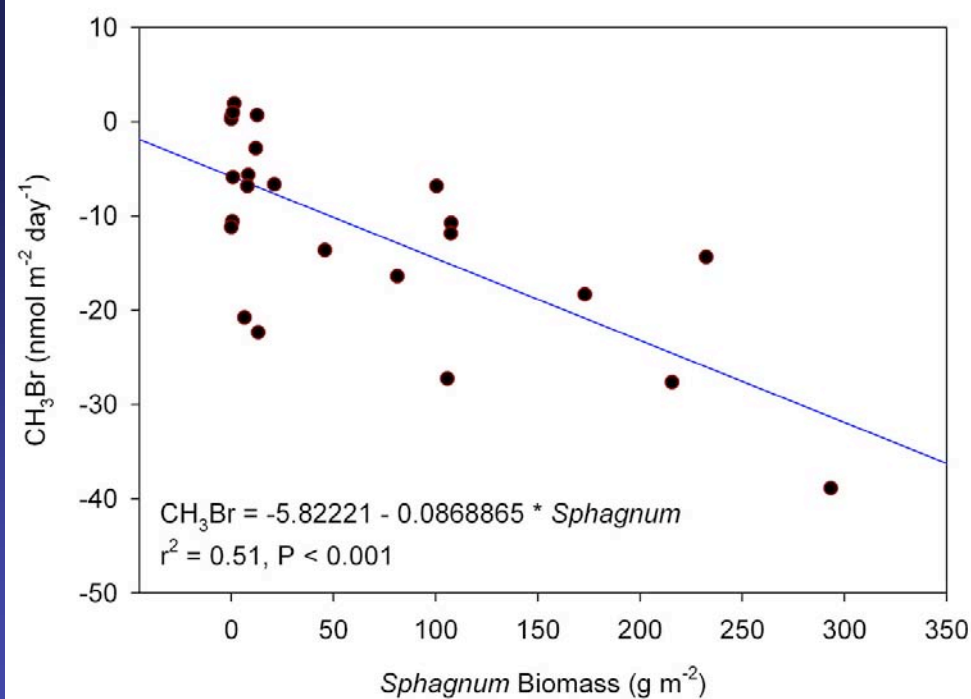
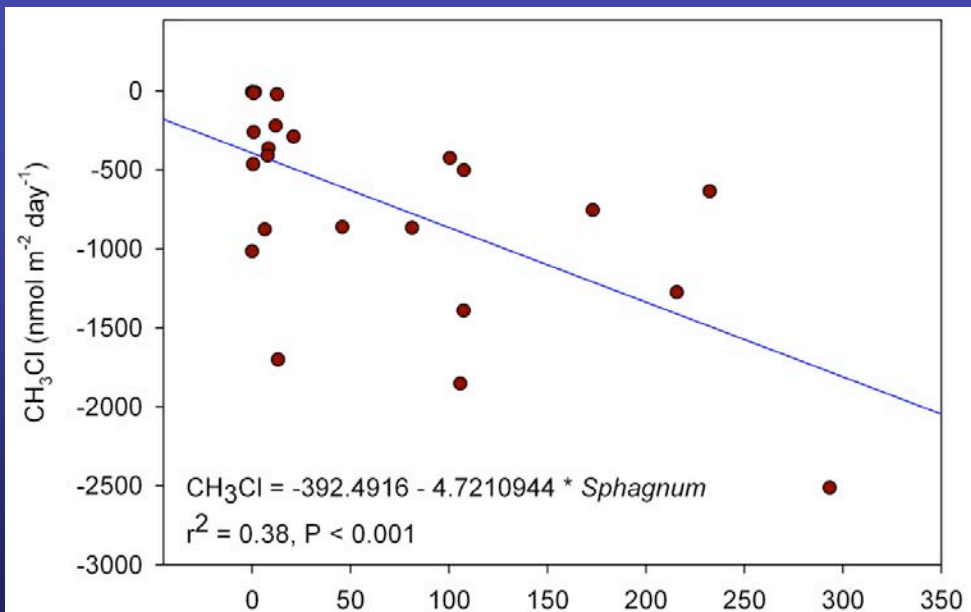
Uptake rates calculated using 1st order uptake rate constants and normalized to $C_{o(\text{MeCl})} = 536$ ppt and $C_{o(\text{MeBr})} = 10.4$ ppt
hence, $C_{o(\text{MeCl})} \cdot C_{o(\text{MeBr})} = 51.5$

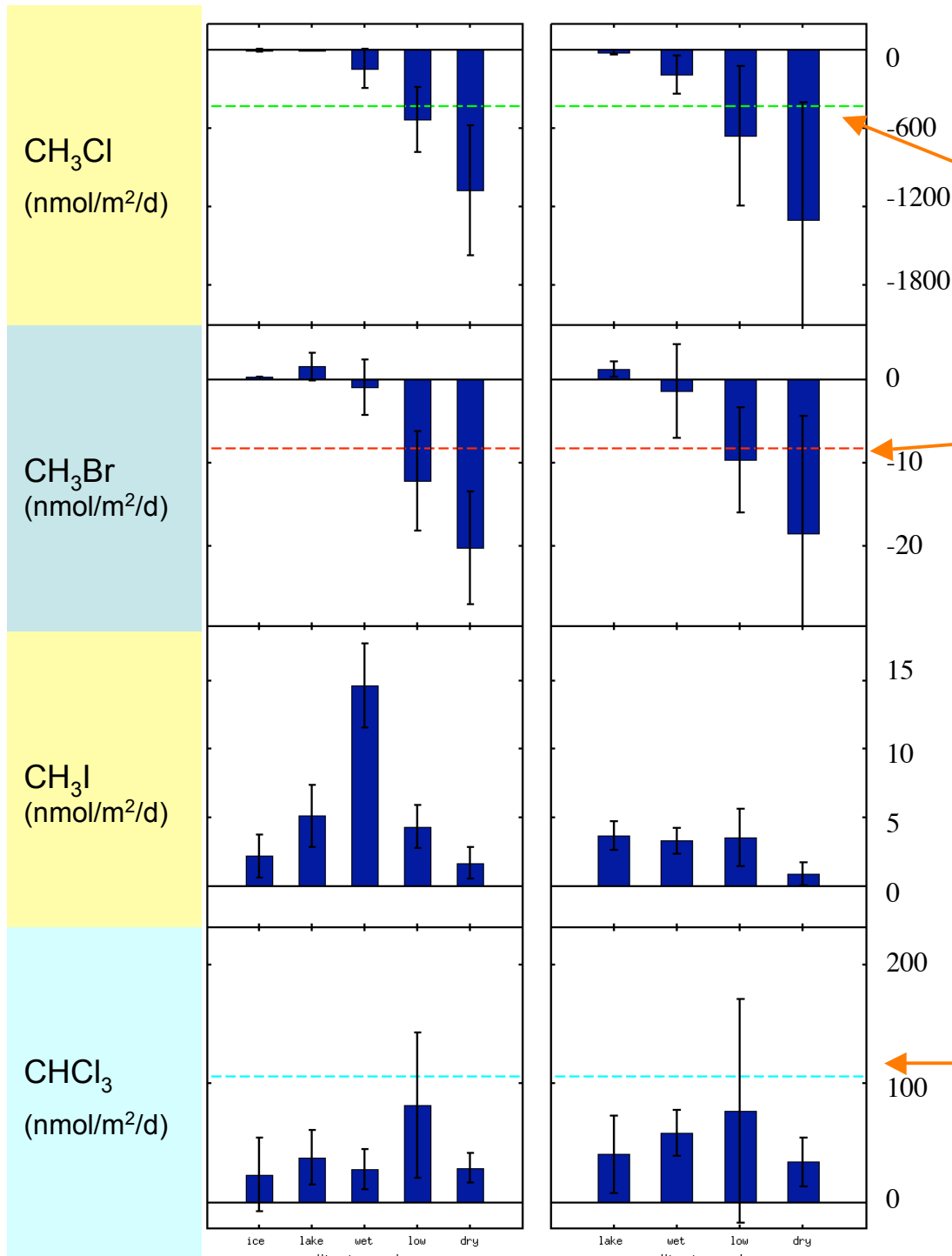
CH₃Cl and CH₃Br uptake vs. sphagnum moss biomass

No correlation with vascular plants.

Aerobic bacteria on live or senescent plant surfaces?

Sphagnum moss layer a 'filter' for CH₃Br and CH₃Cl?





IV. Results compared to other ecosystems

CH₃Cl shrubland max. uptake (Rhew *et al.*, 2001)

Ave. CH₃Br uptake rates in tropical rainforest /savanna, boreal forest soils. (Shorter *et al.*, 1995)

CH₃I emissions minor compared to rice paddies (~930, Redeker & Cicerone, 2004)

CHCl₃ emissions from temperate peatlands (Dimmer *et al.*, 2001)