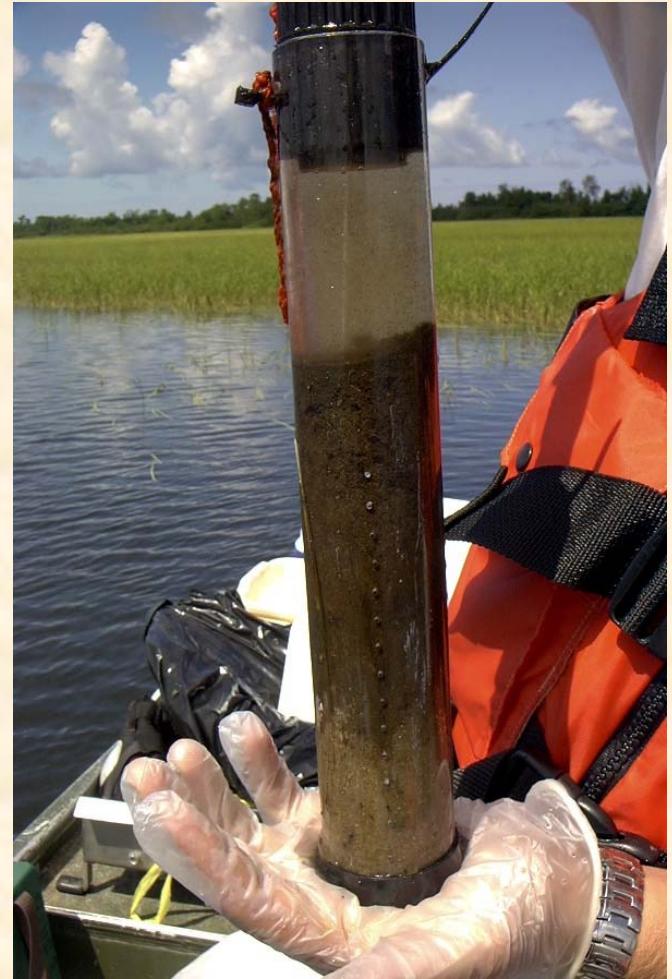


# Methylmercury Production and Incorporation into the Lower Food Web of Contrasting Nearshore Environments of Chequamegon Bay, WI



Jacob Ogorek, Kris Rolfhus, Roger Haro, and James Wiener

River Studies Center and Chemistry Dept.  
University of Wisconsin-La Crosse



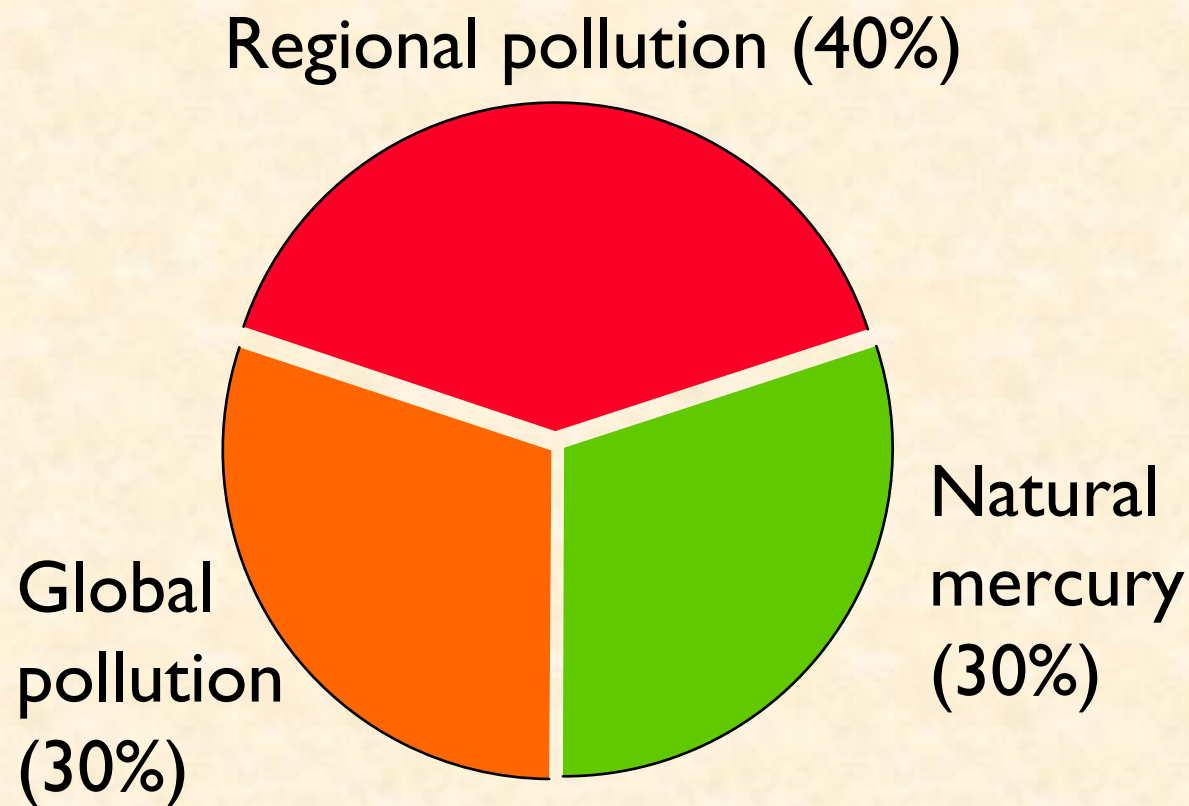
## Why are we concerned about mercury?

- Human health risks (>300,000/yr in US alone, USEPA est.)
  - Methylmercury is a developmental neurotoxin—high fetal sensitivity
- Mobility in the environment
  - Chemical reactions keep it active in environment
  - Long atm residence time—non-point sources
- Bioaccumulation and biomagnification in food webs
  - Million-fold concentration increase (water to fish)
  - Largest increase in lower food web
- Anthropogenic forcing
  - Currently est. 50-75% emissions

# The Aquatic Mercury Problem: a Methylmercury Problem

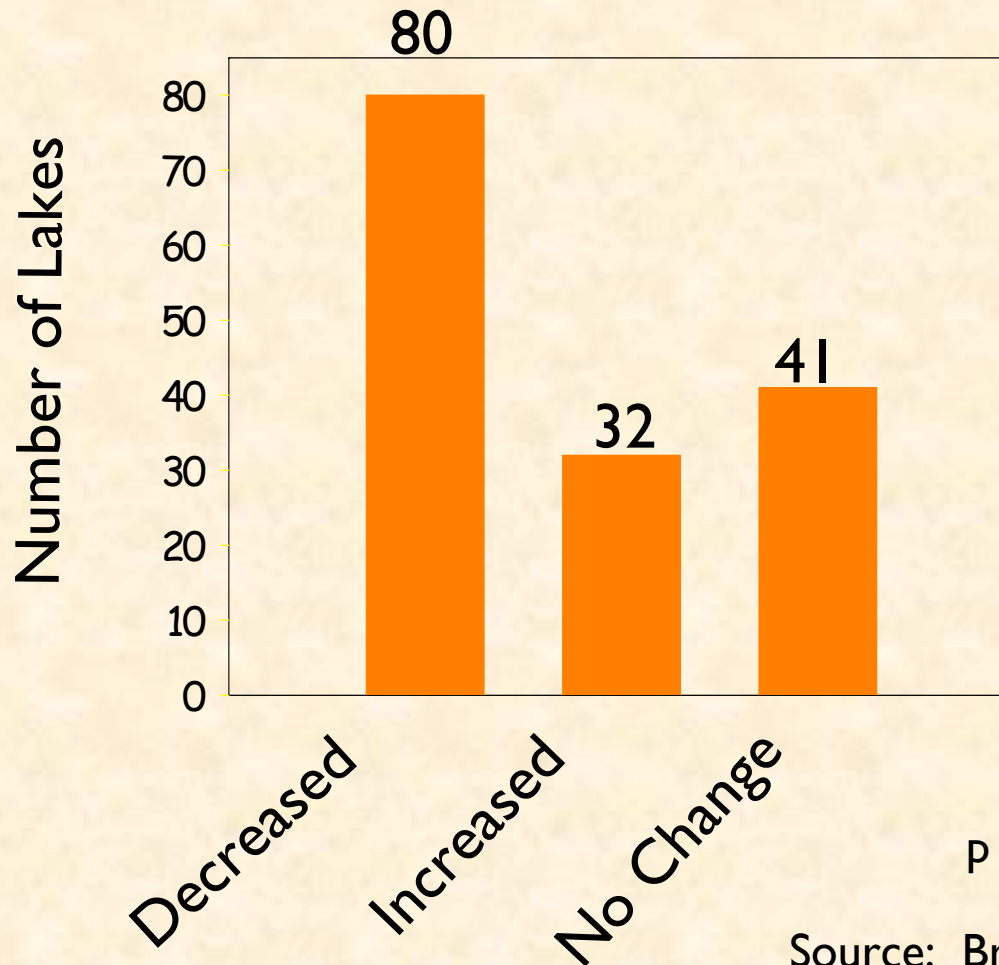
- Methylmercury readily crosses biological membranes & bioaccumulates in exposed organisms
- Produced naturally by sulfate-reducing bacteria in aquatic sediments and wetlands (other bacteria?)
  - Require oxic/anoxic interfaces, source of organic matter for food, mercury substrate for  $\text{Hg(II)} \rightarrow (\text{CH}_3)\text{Hg}^+$
  - Microbial reactions, organic matter supply are temperature dependent (high T, high reaction rates)
  - Shallow, organic sediments more conducive to Hg methylation

## Estimated Sources of Mercury Deposited in Northeastern Minnesota in past 150 years



Engstrom & Swain, 1997

# Trends in Fish-Mercury Levels in 153 Minnesota Lakes



## Methods:

Fish last sampled in 1995 or later.

More than 5 years between collections.

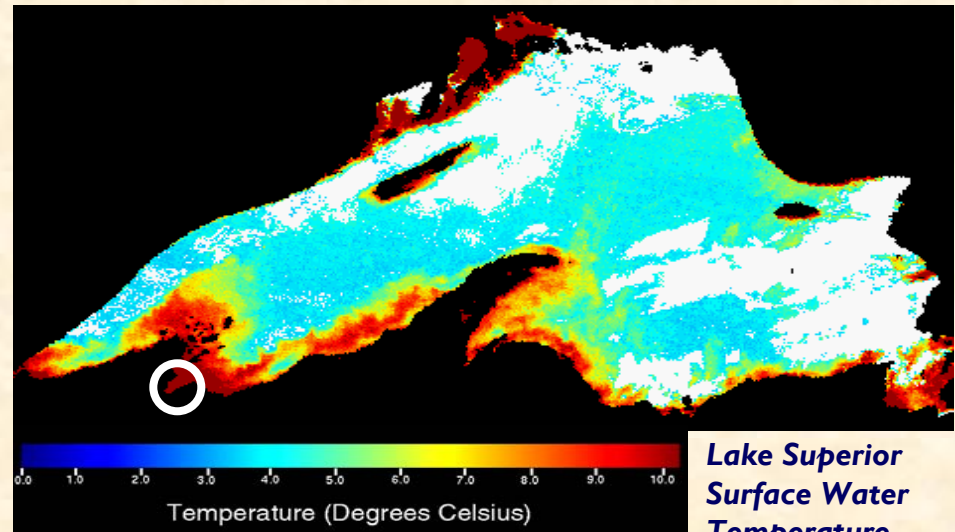
Northern pike or walleye of standard total length.

$p < 0.05$ , two-tailed test

Source: Bruce Monson, MN PCA

# A Focus on Lake Superior...

- Large
- Cold
- Relatively unproductive
- Small watershed/surface area ratio

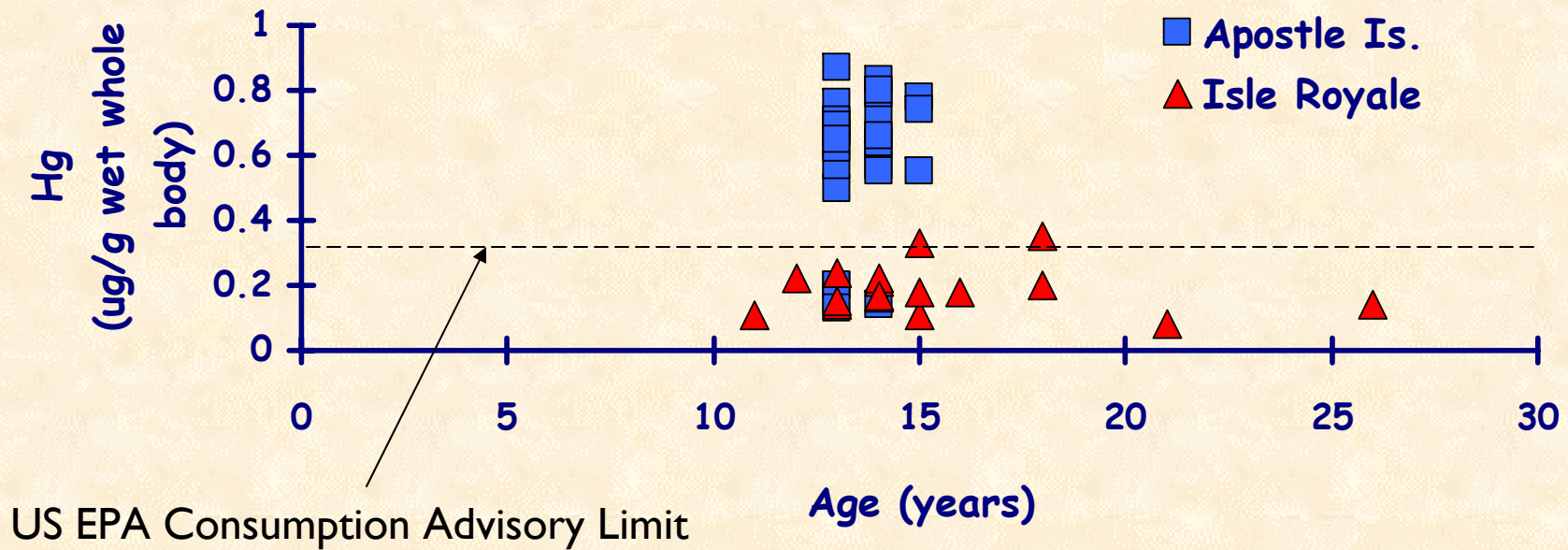


*Lake Superior  
Surface Water  
Temperature  
(Image from MTU-  
KITES  
Web Site)*

Prediction: Methylation of Hg(II) is not a major issue,  
Fish concentrations generally low...

Fish consumption advisories exist for walleye, lake trout...

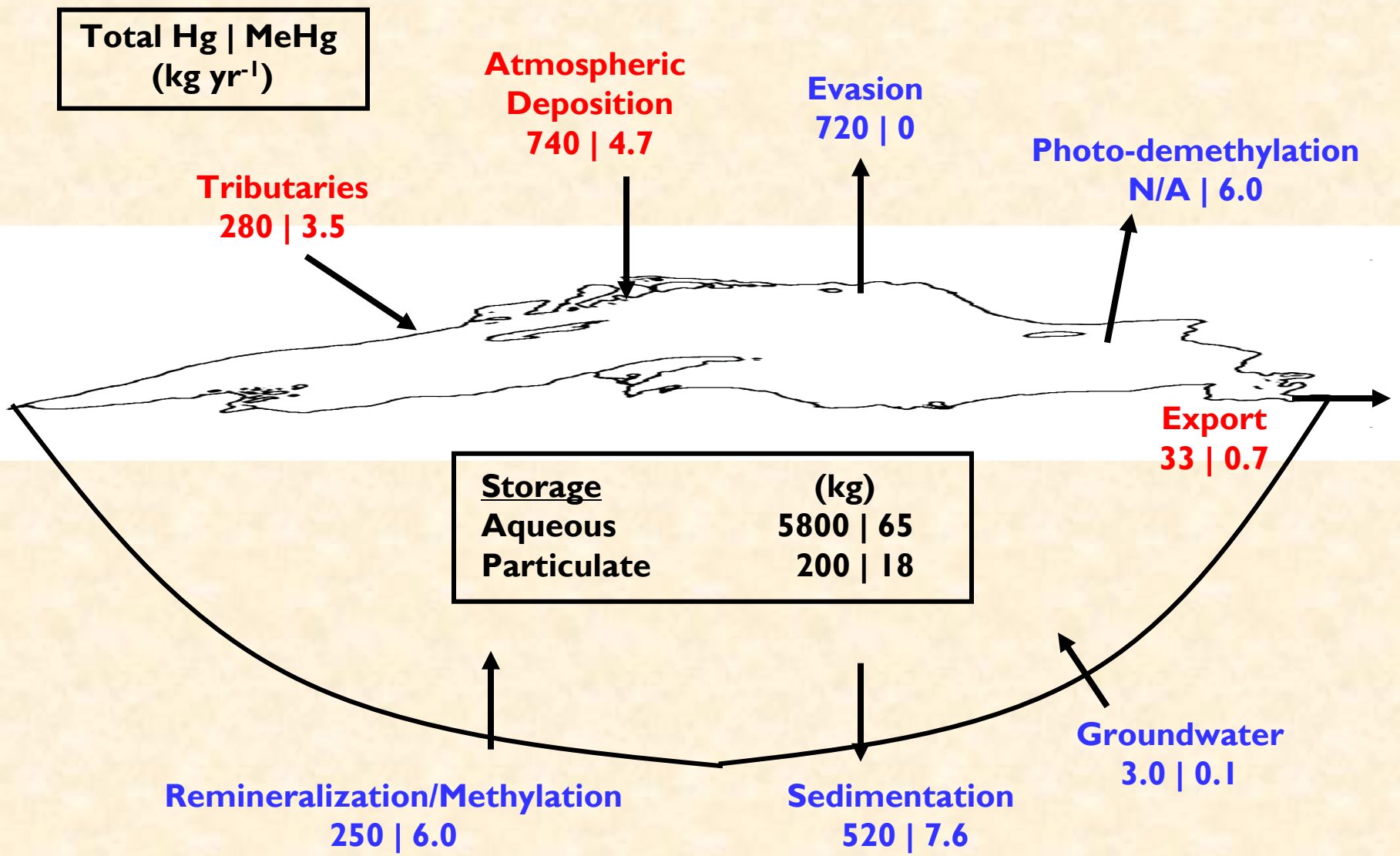
### Observed Hg vs Age for Lake Trout in Lake Superior



Sources:  
WI DNR  
R. Harris (Tetra Tech)

# Lake Superior Mass Balance

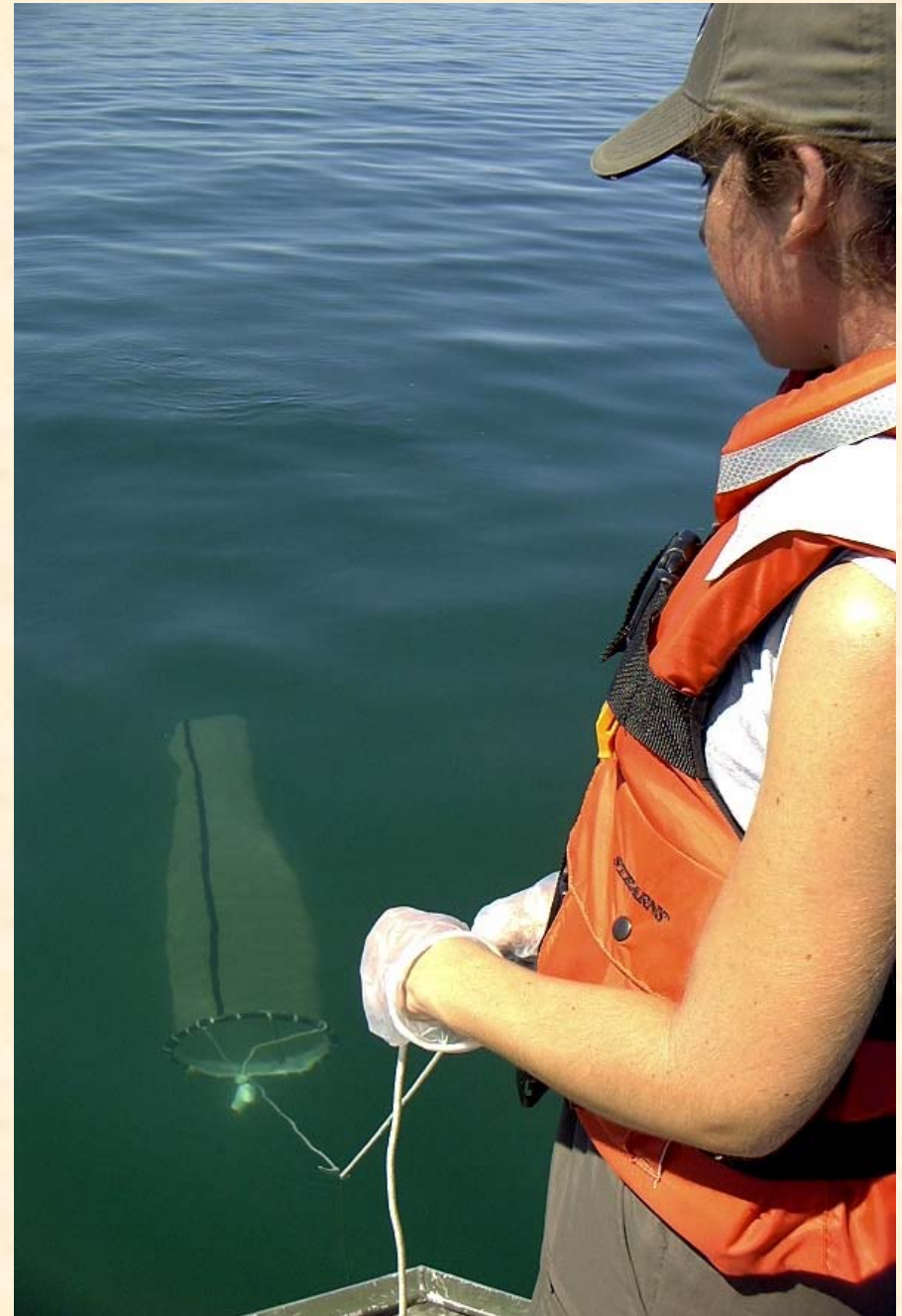
More Confident  
Less Confident

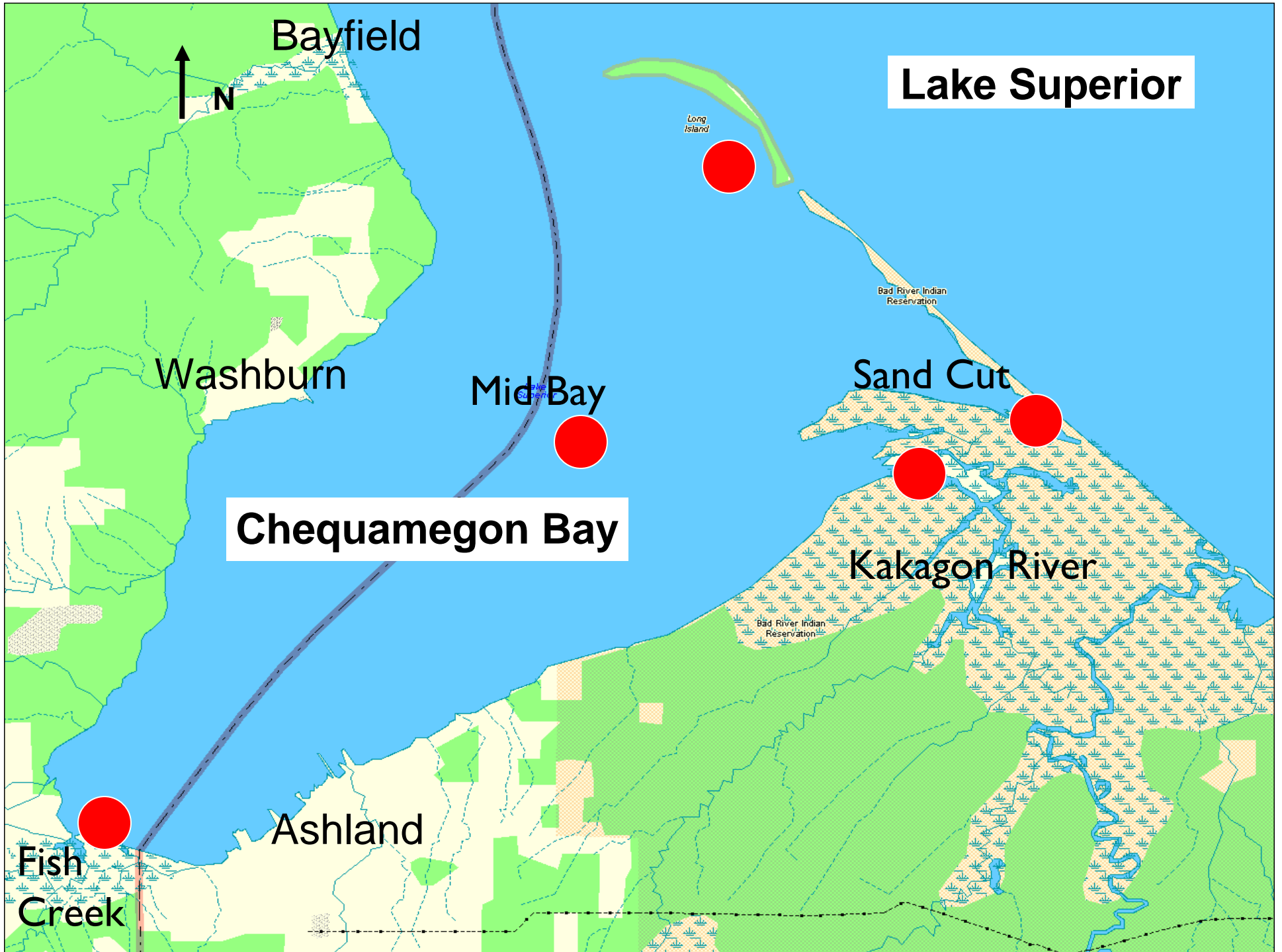


“Methylmercury  
Production and Transfer  
to Benthic Food Webs in  
Nearshore and Wetland  
Environments of  
Southern Lake Superior”

(WI Sea Grant Program)

- Sedimentary MeHg production
- Benthic trophic transfer
- Watershed vs. pelagic sources
- Eurasian Ruffe





# How Does Chequamegon Bay Compare?

<u>Compartment</u>	<u>Voyageurs (MN)</u>	<u>Cheq. Bay</u>	<u>Open L Sup<sup>b</sup></u>
<b>Water (ng/L)</b>			
THg	0.3-4.8 <sup>a</sup>	0.3-2.1	0.5
MeHg	< 0.04-0.30	0.05-0.27	0.003-0.013
Mean % MeHg	8	18	1
<b>Surficial Sediment (ng/g dw)</b>			
THg	102-364 <sup>c</sup>	5-59	83
MeHg	0.04-0.25	0.004-1.60	0.21
Mean % MeHg	--	1.7	0.25

<sup>a</sup> M. Brigham, unpublished data. USGS.

<sup>b</sup> Rolfhus et al., 2003. Environ. Sci. Technol.

<sup>c</sup> Wiener et al., 2006. Environ. Sci. Technol.

# How Does Chequamegon Bay Compare?

Methylmercury Concentration, median (range)

<u>Compartment (ng/g dw)</u>	<u>Voyageurs (MN)</u>	<u>Cheq. Bay</u>	<u>Open L Sup</u>
Benthic Macroinvertebrates	79 (9-177)	25 (0.5-774)	--
% as MeHg		24-96%	
Seston	(1-32)	(2-11)	(3-10) <sup>a</sup>
Zooplankton	(30-280)	(22-66)	(15-50) <sup>a</sup>
Age-I Yellow Perch	(182-942)	(61-153)	--
Age-I Eurasian Ruffe	--	(46-113)	--

<sup>a</sup> Back et al., 2003. Sci. Tot. Environ.

# Conclusions

- Mercury concentrations in Chequamegon Bay are sufficient to account for elevated fish content in largest piscivores
- Inland lakes > Cheq. Bay > open Lake Superior in all food web compartments
- Differences between sample sites originate at base of the food web (water and sediment)
  - Bottom-up influence on higher trophic levels
- Methylation rates highest in wetland/trib complexes
  - Surface 0-1 cm highest rates in spike/incubation experiments
- Wetland influence, coupled with transport, results in high methylmercury throughout the lower food web
  - Tributaries deliver atmospheric mercury, organic matter, sulfate
  - Wetland without tributary is moderate in concentration
- Warming trends in regional climate may exacerbate methylation along southern margin of Lake Superior, greater fish mercury content

## **Acknowledgments**

Wisconsin Sea Grant Program

UW-La Crosse River Studies Center

UW-Madison Env Sci Tech

US EPA GLNPO

Bad River Band of LS Chippewa

