Emissions Regulations and Food Web Shifts Alter Mercury Signatures of Top Predator Fish

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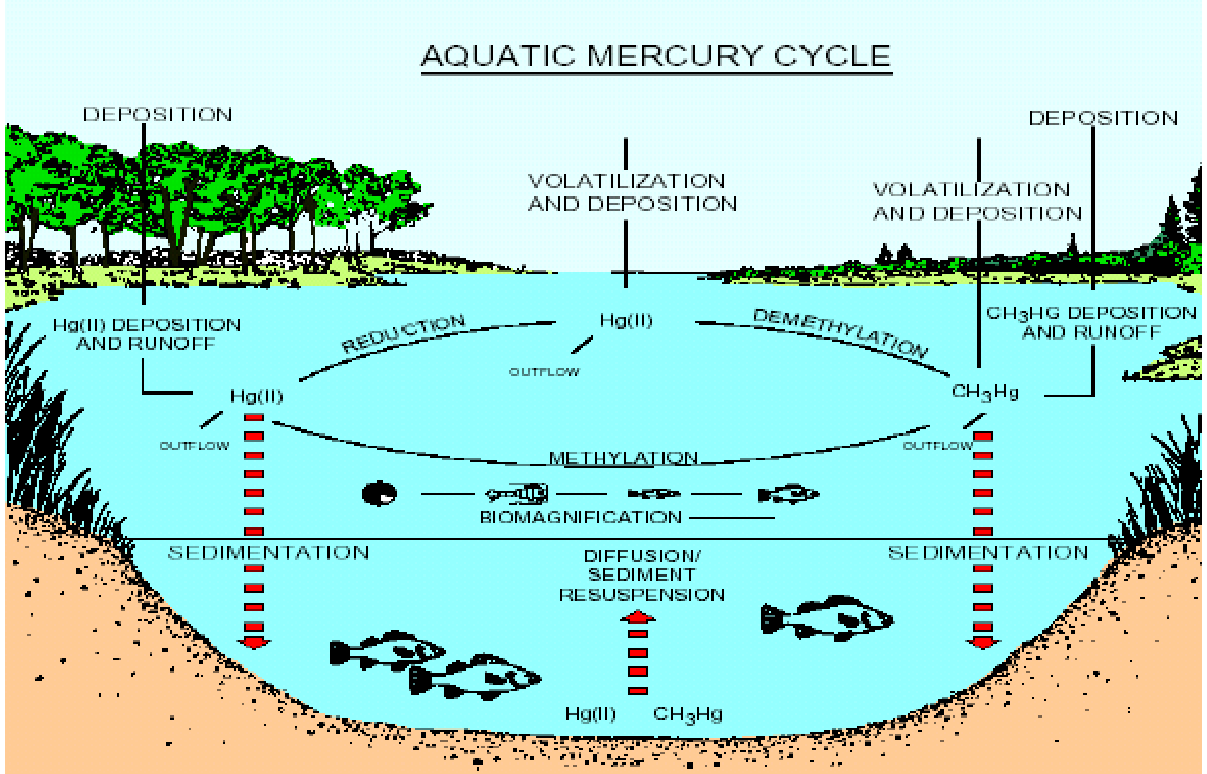
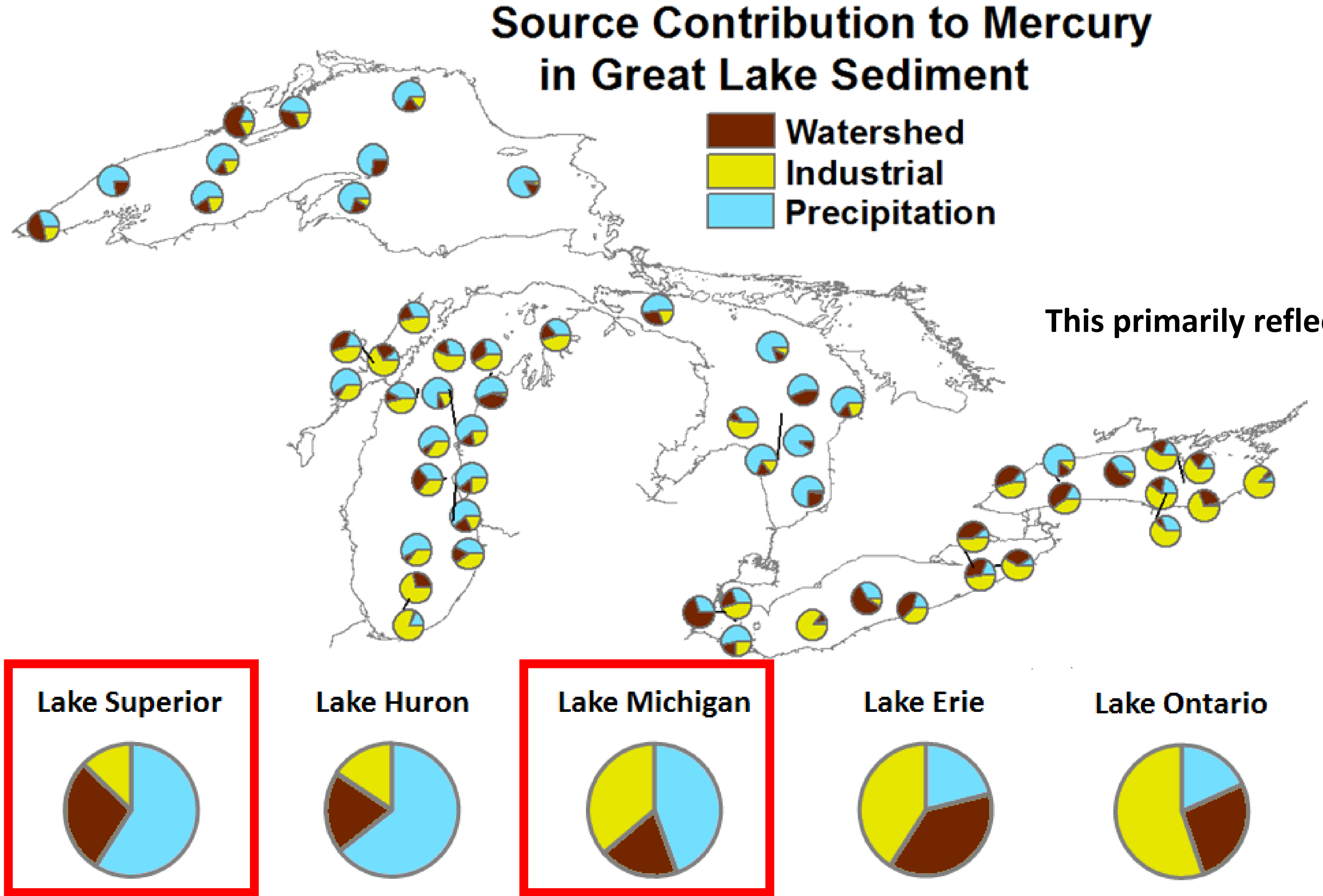
Overarching goal and can we achieve it

- **Can we develop a tool Great Lake resource managers can use to pinpoint sources of Hg to biota?**
  - Historically, what changes (if any) have effectively reduced Hg sources to the Great Lakes?
- Focus
  - Can a biological archive test the utility of sedimentary archives?
    - Are sediments a source of MeHg to fish, or a residual?
- How is this information then translated to resource managers?



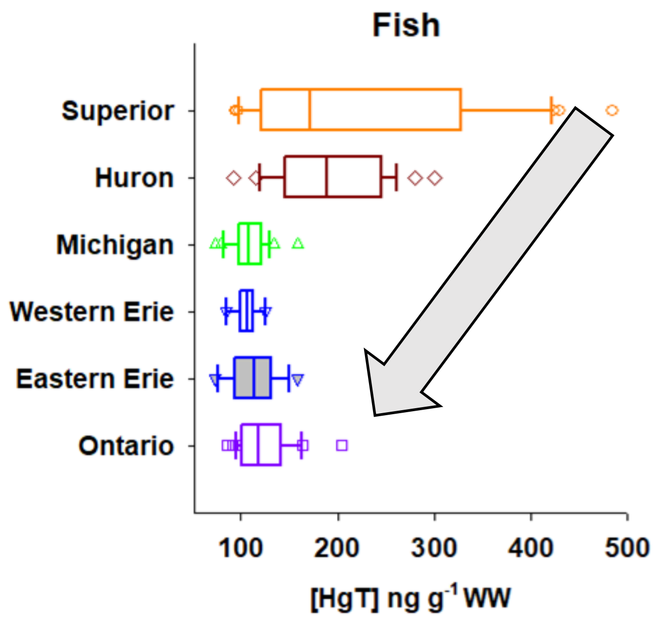
In the Great Lakes, sediments are the final destination

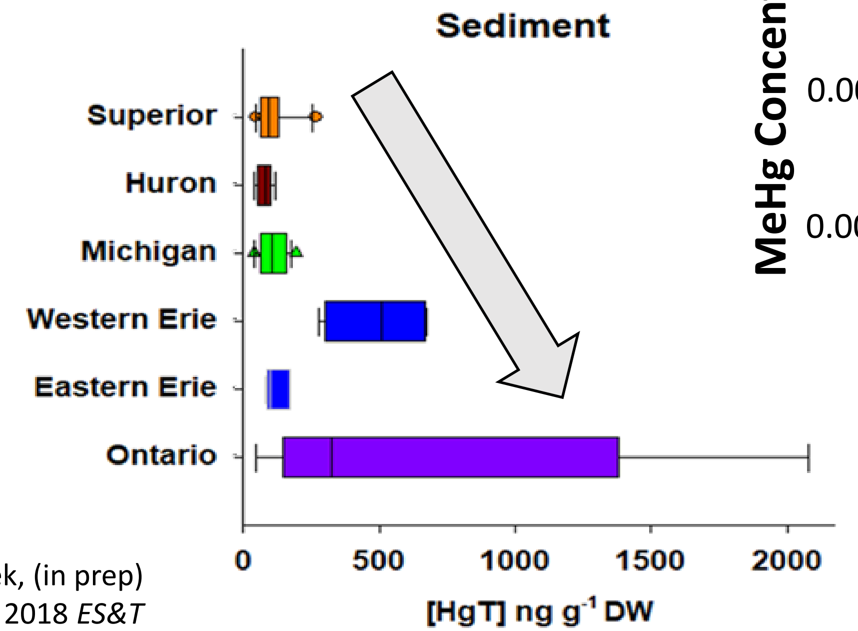


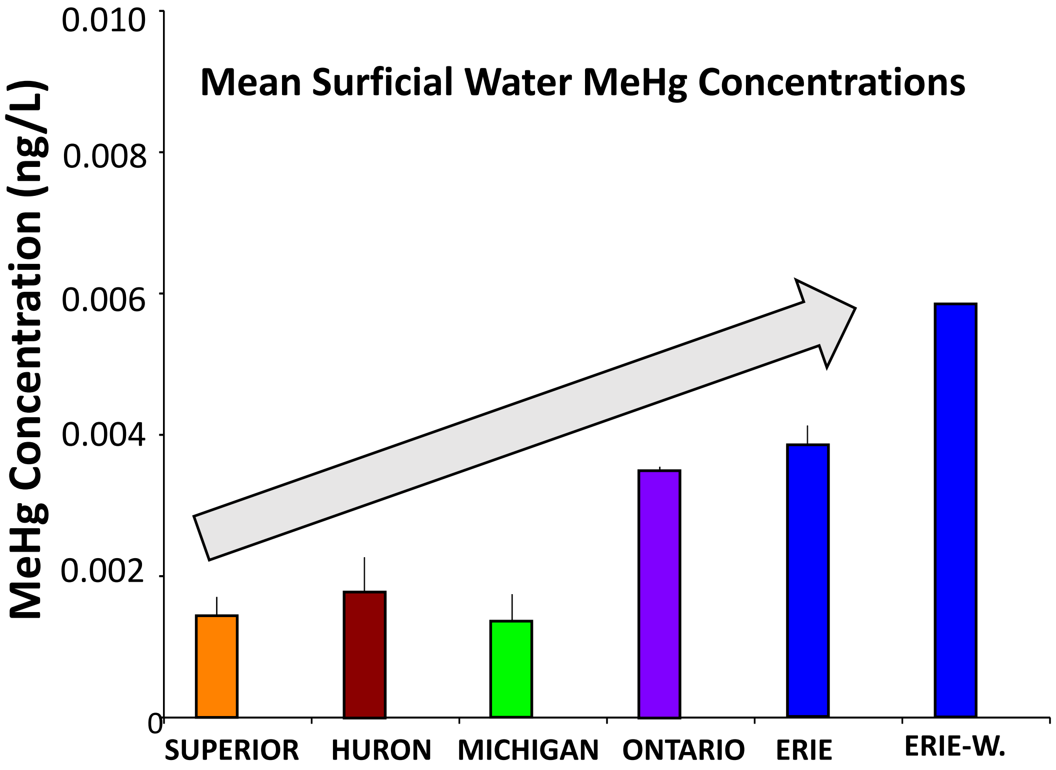
This primarily reflects inorganic Hg

Comparing [Hg] between GLs

- Key finding:
  - Trends in fish [HgT] are opposite to sediment [iHg] and water [MeHg] concentrations.
  - 1) due to enhanced BAF in TP1 biota[1].
  - 2) due to differing fish growth rates[2].



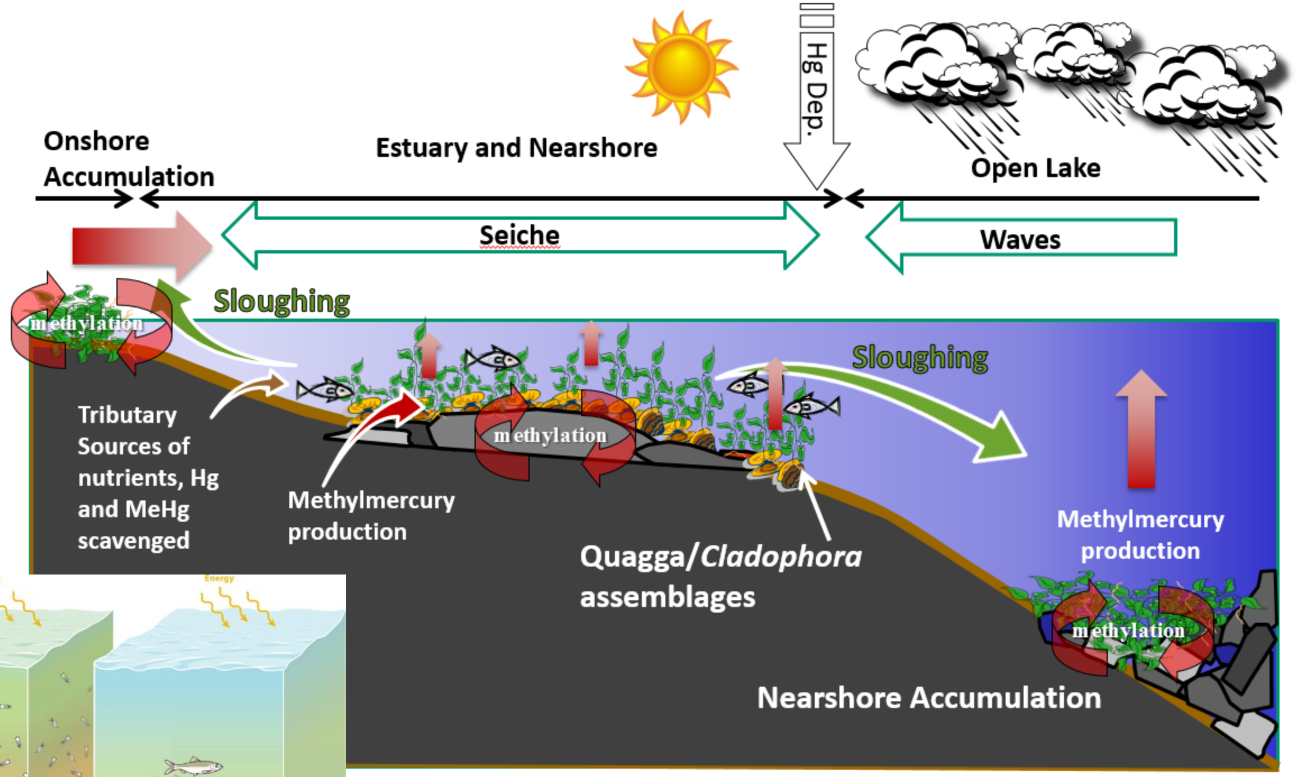




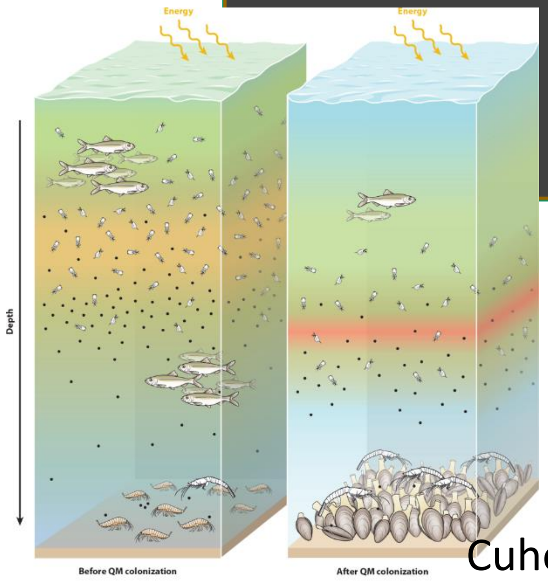
1. Ogorek, (in prep)
2. Zhou, 2018 *ES&T*

Changes to Hg within LM and the broader GLs

- Early 1970s Implementation of the Clean Air Act and initial stages of the Clean Water Act
- Late 1980's implementation of SO_x & NO_x controls
- **Early 2000's Infestation of Quagga Mussels**
- 2010 US implements Mercury and Air Toxics Standards and widespread conversion to natural gas



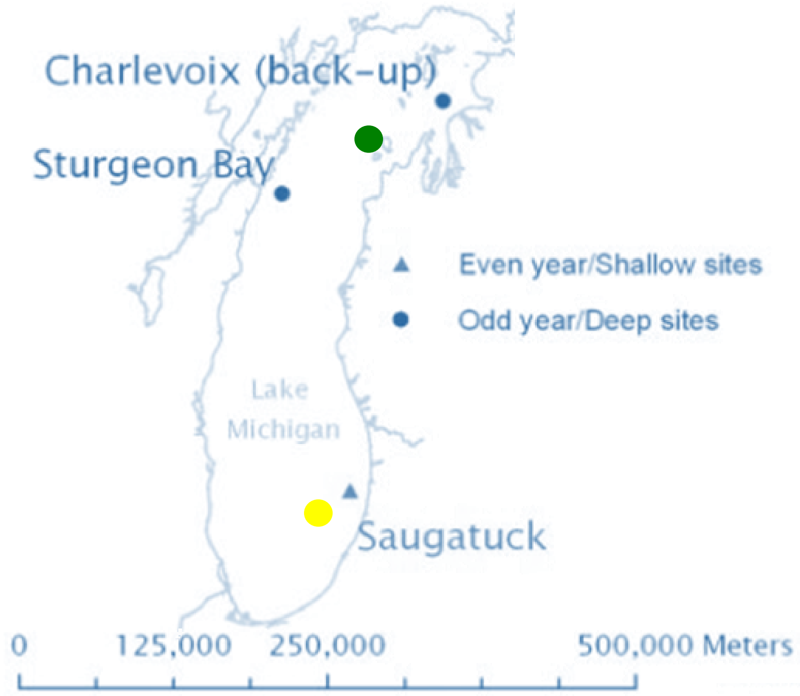
Lepak, 2015

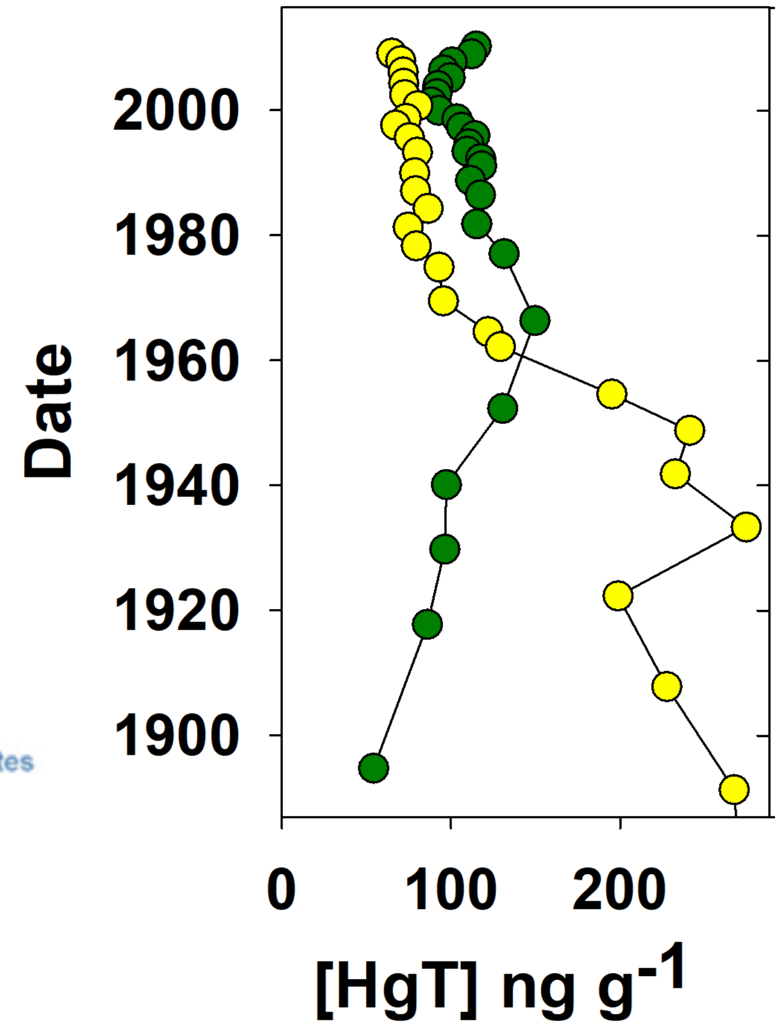


Cuhel, 2013

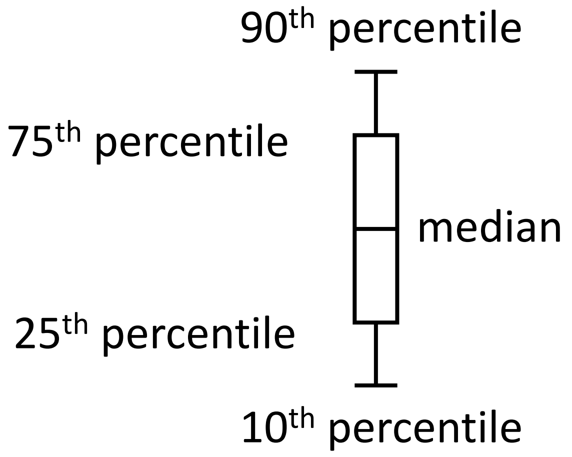
Sediment cores are the typical archives

- Useful for monitoring inorganic Hg deposition – reconstruction studies
  - The residue Hg
- Begin to better understand the temporal stability evolution of Hg source portfolios

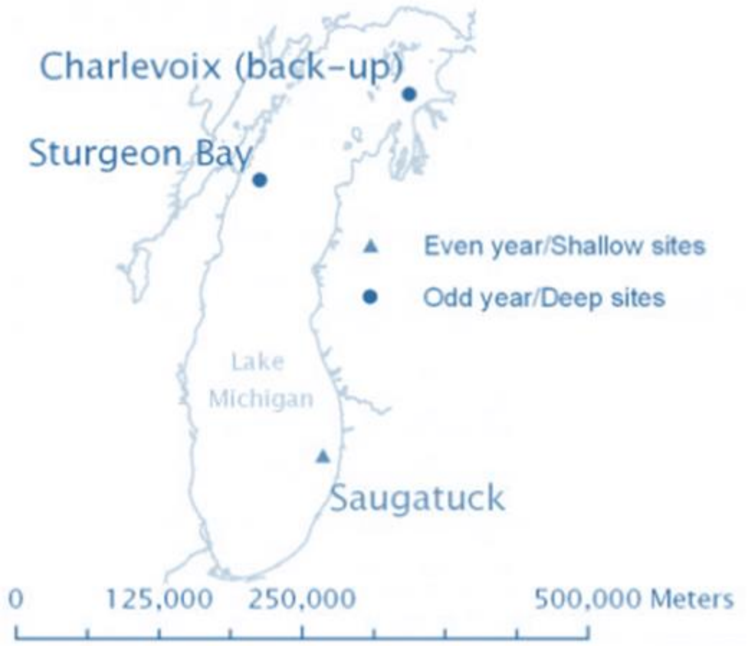


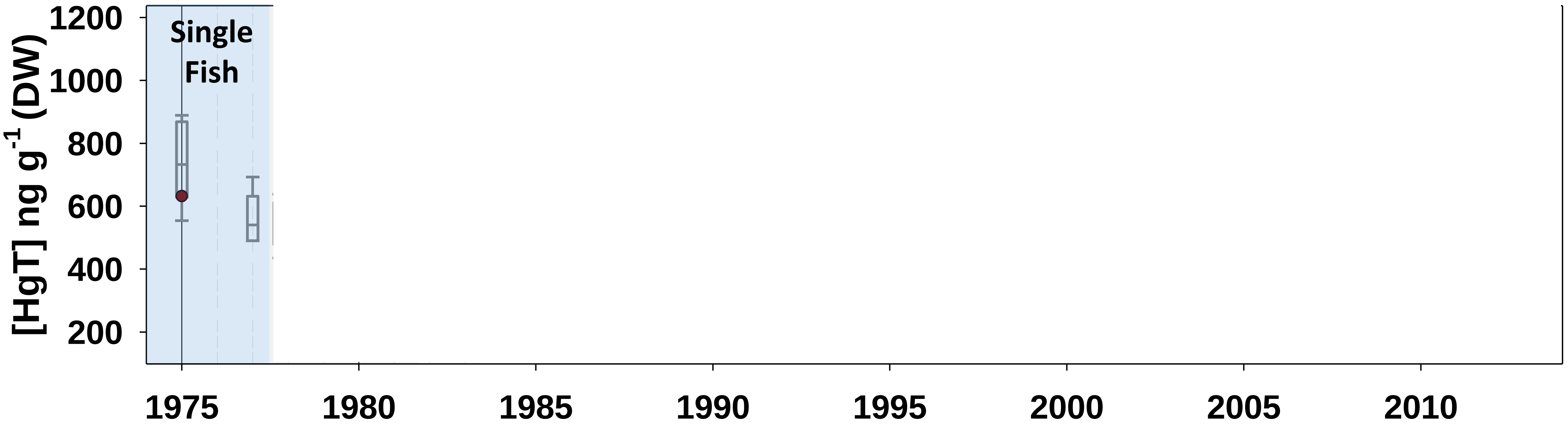


Temporal [HgT] data



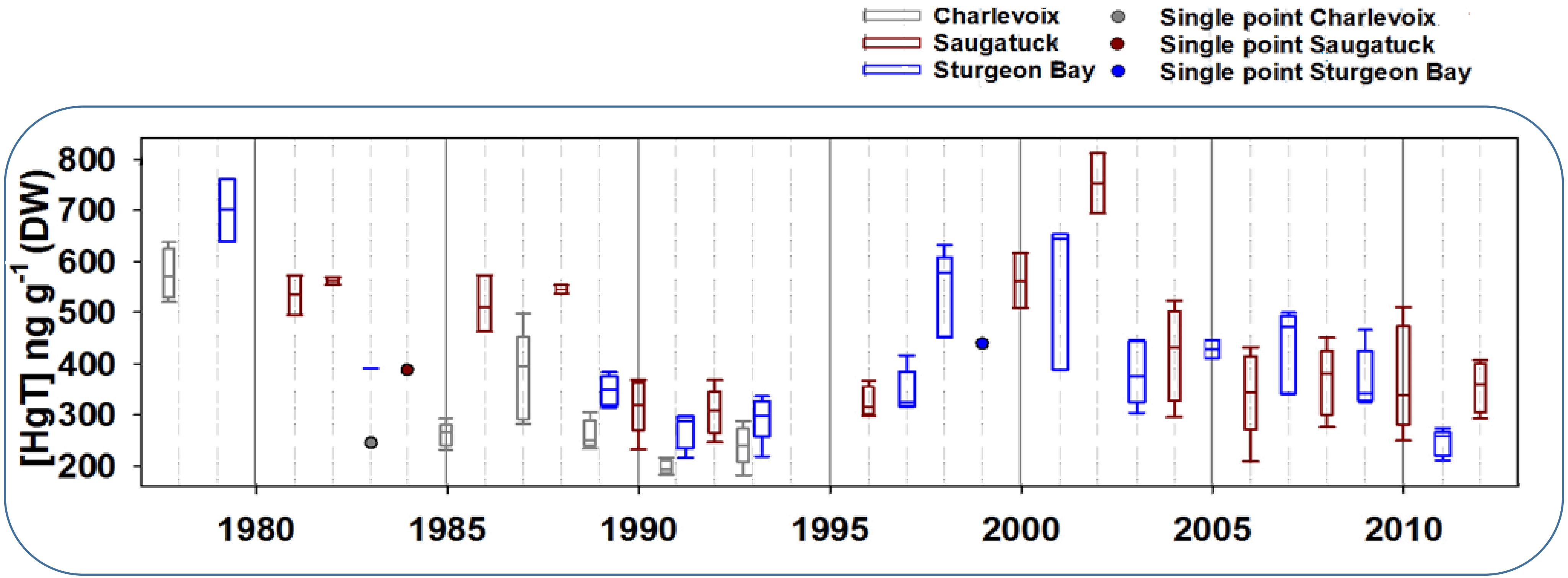
Charlevoix
Saugatuck
Sturgeon Bay
Single point Charlevoix
Single point Saugatuck
Single point Sturgeon Bay

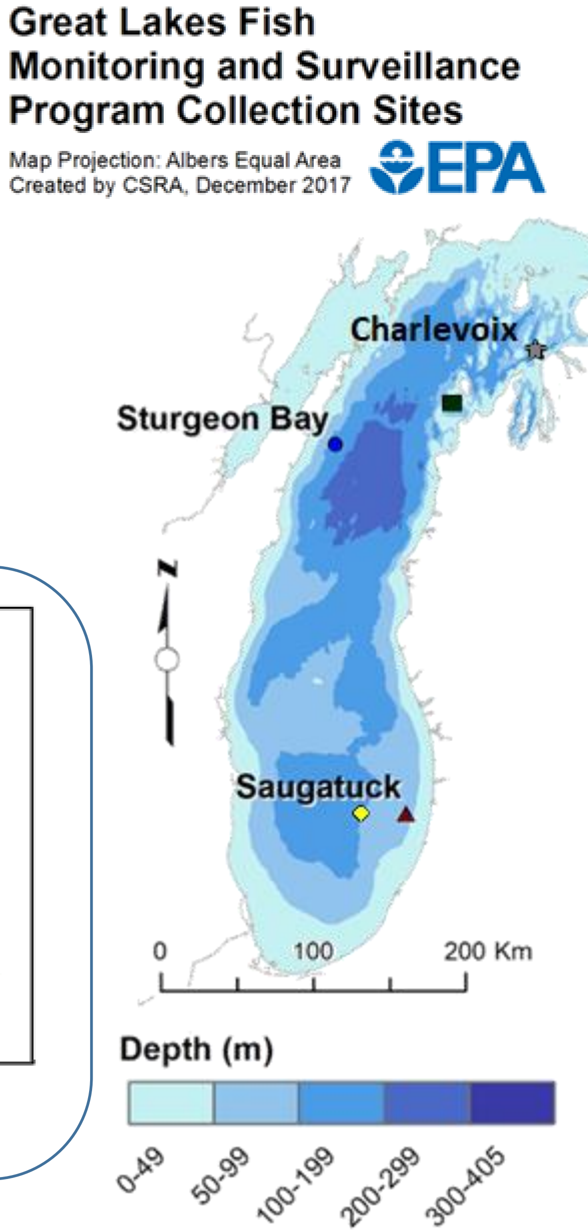




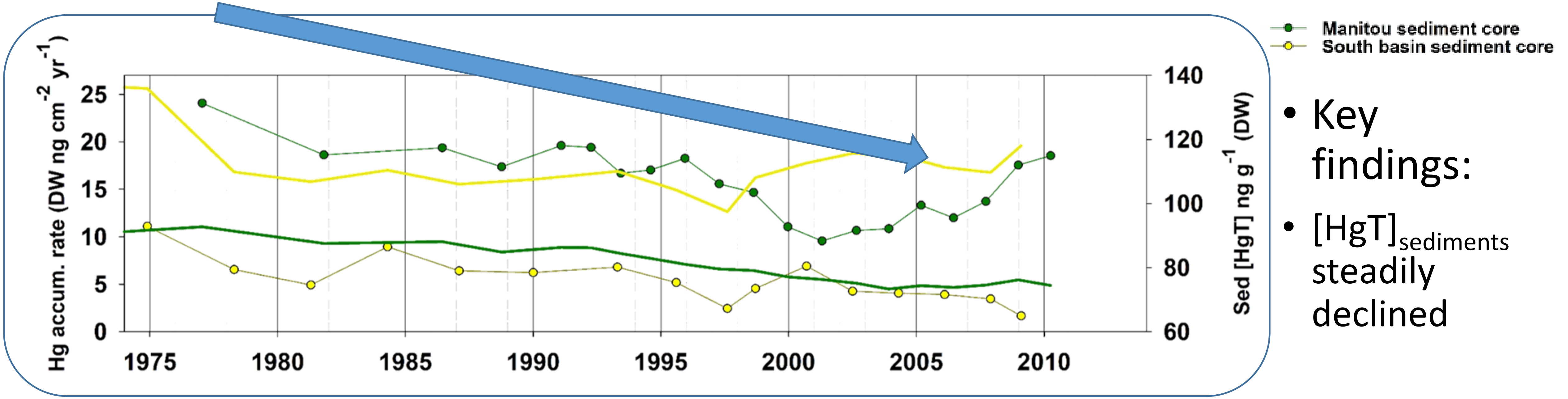
Tracing Dietary Shifts and Mercury Sources to Lake Michigan Lake Trout Over 35 Years – to be submitted *PNAS*

- Key findings:
  - Hg mitigation decreased [HgT] from 1978 – 1994.
  - Following 1996, $[HgT]_{lake\ trout}$ trends did not match $[HgT]_{sediment}$ trends.

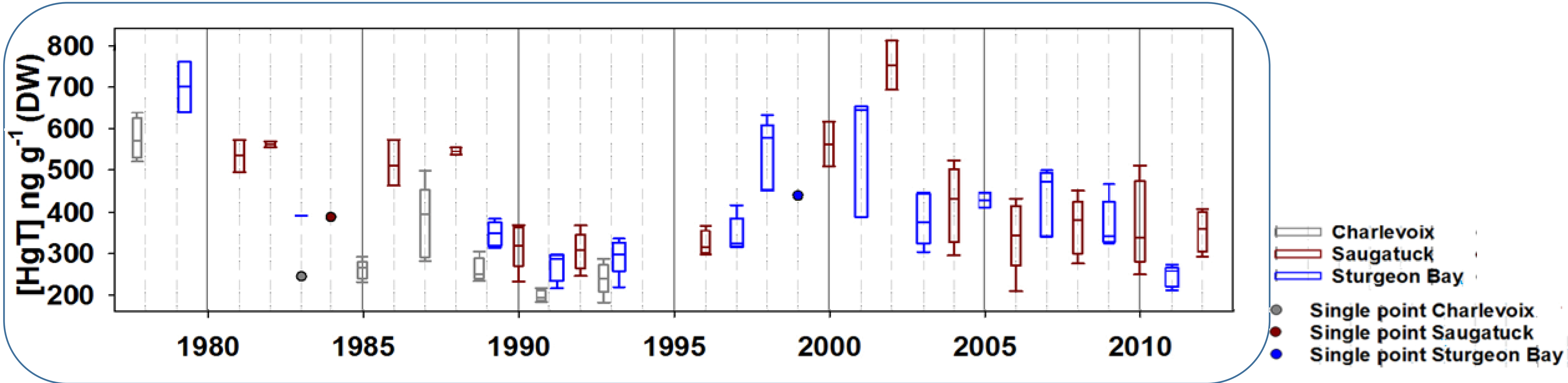




Fish HgT does not trend with Hg loading rates

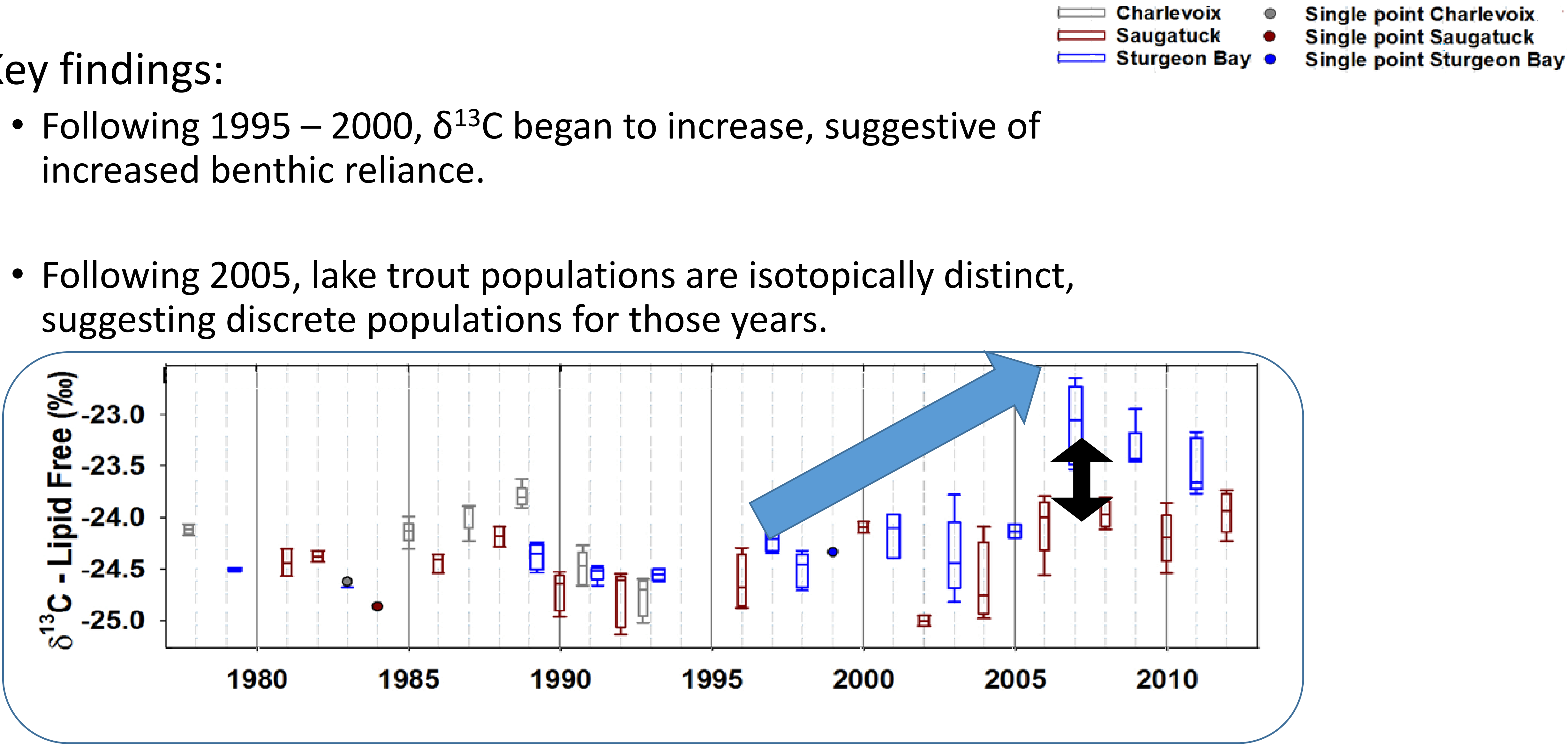


- Key findings:
- $[HgT]_{sediments}$ steadily declined



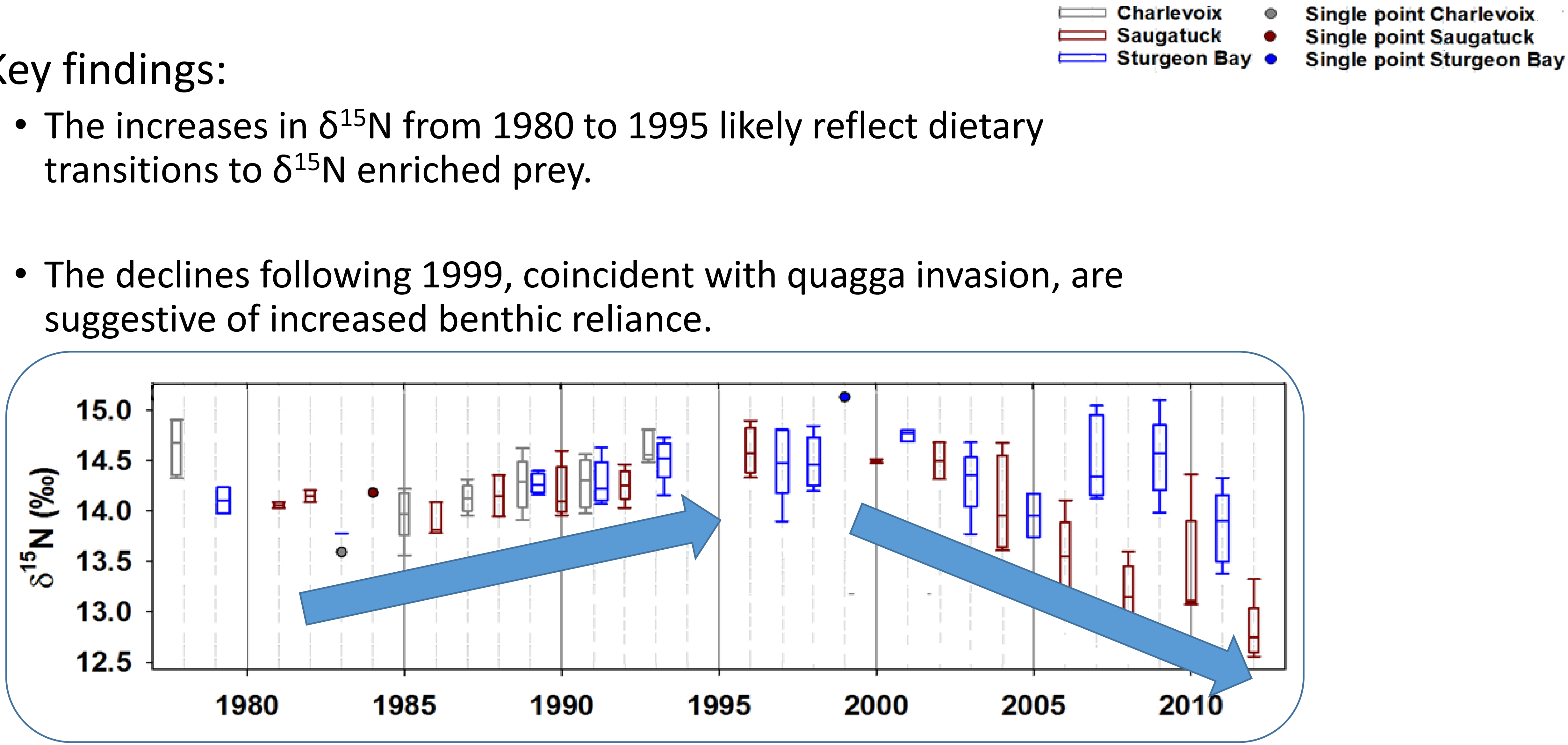
Carbon stable isotope ratios in lake trout

- Key findings:
  - Following 1995 – 2000, $\delta^{13}C$ began to increase, suggestive of increased benthic reliance.
  - Following 2005, lake trout populations are isotopically distinct, suggesting discrete populations for those years.

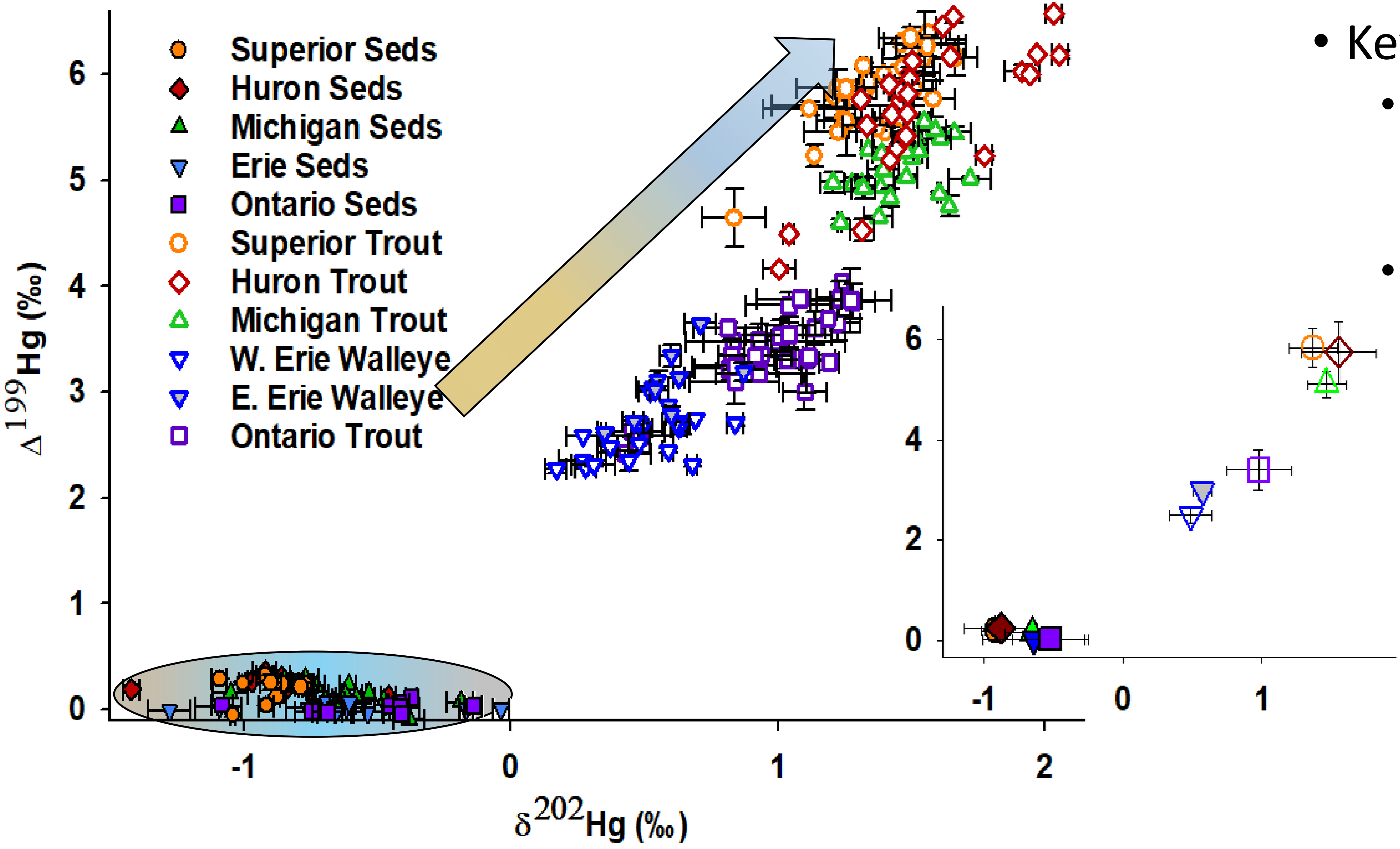


Nitrogen stable isotope ratios in lake trout

- Key findings:
  - The increases in $\delta^{15}N$ from 1980 to 1995 likely reflect dietary transitions to $\delta^{15}N$ enriched prey.
  - The declines following 1999, coincident with quagga invasion, are suggestive of increased benthic reliance.



Comparing Hg isotopes between GL fishes

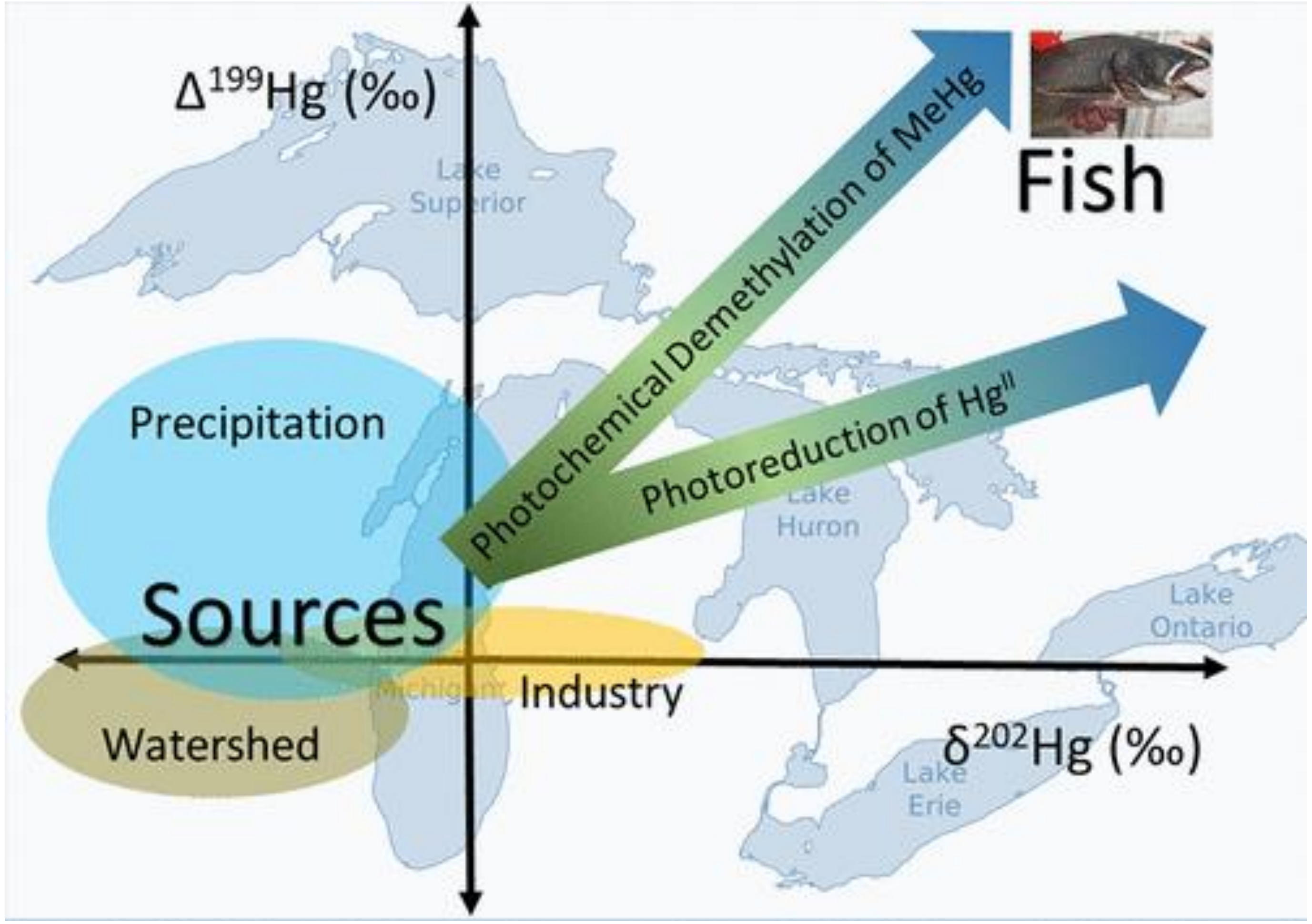


- Key findings:
  - Lakes group into two regions.
  - Fish are distinct from sediments

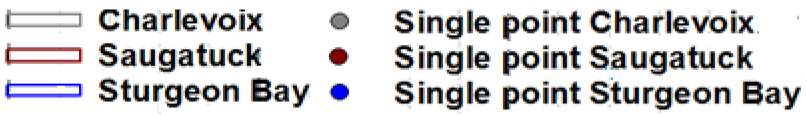
Factors Affecting Mercury Stable Isotopic Distribution in Piscivorous Fish of the Laurentian Great Lakes – *ES&T 2018*

- Compared fish to a collection of water quality parameters.

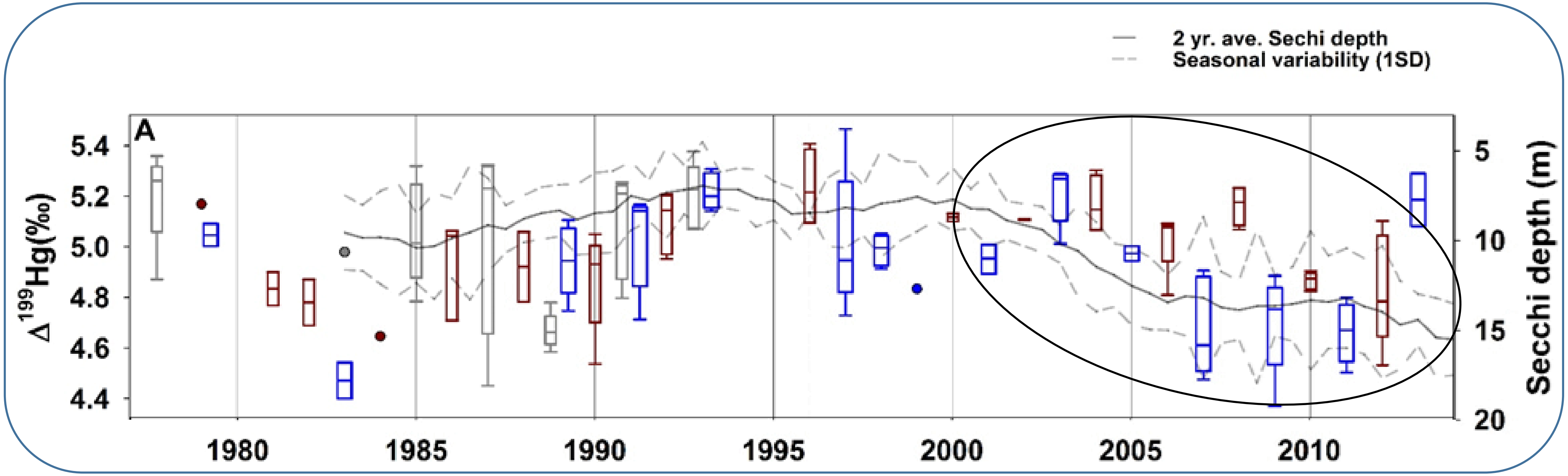
- Key findings:
  - δ^{202}Hg and Δ^{199}Hg are tied to the depth of the chlorophyll maxima.
  - Atmospheric signals are similar across lakes.



Comparing water clarity, Δ^{199}Hg and diets

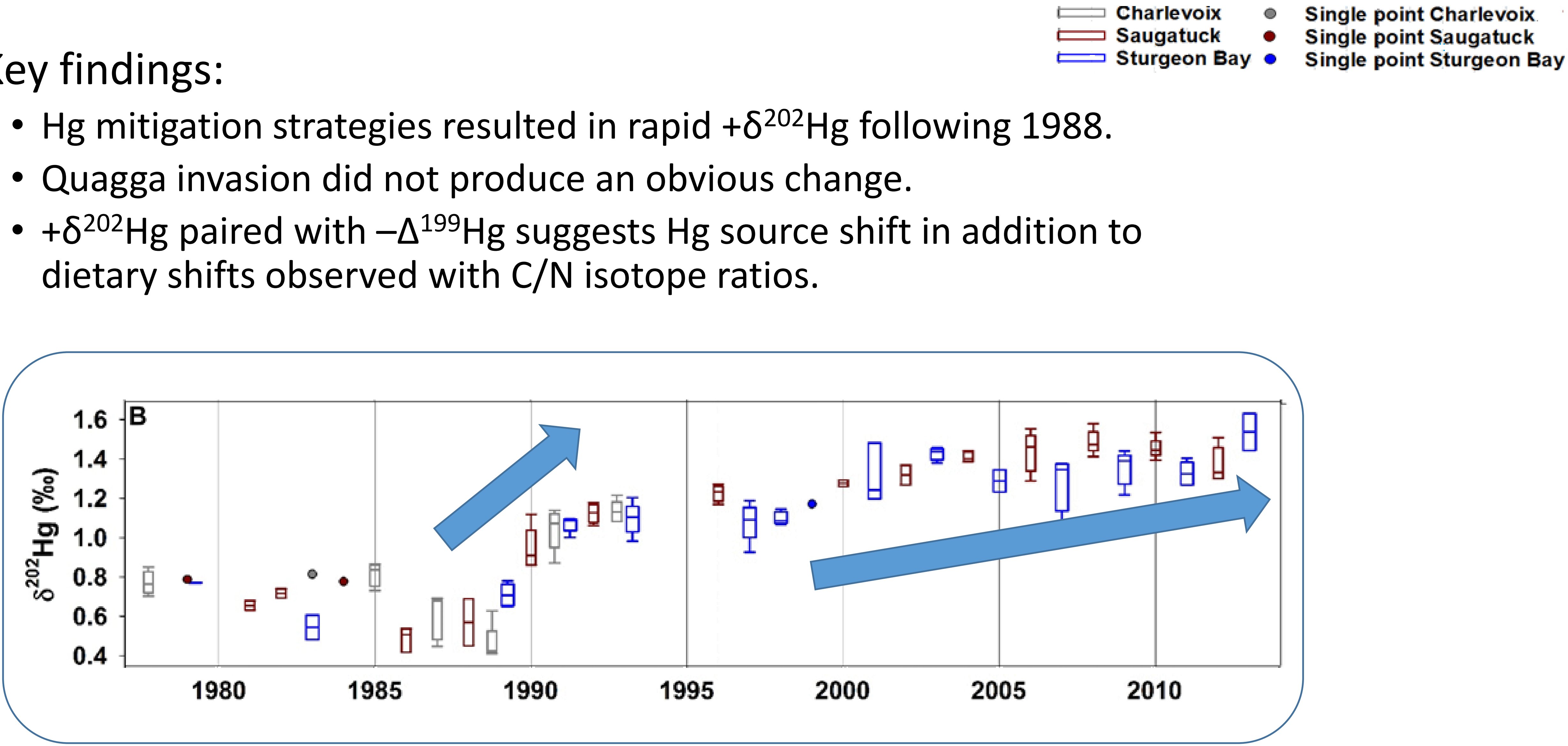


- Key findings:
  - Hg mitigation strategies resulted in +Δ^{199}Hg from 1983 – 1995.
  - Quagga invasion (2000) led to increased Secchi depth.
  - Increased water clarity did not increase Δ^{199}Hg, due to dietary shifts.

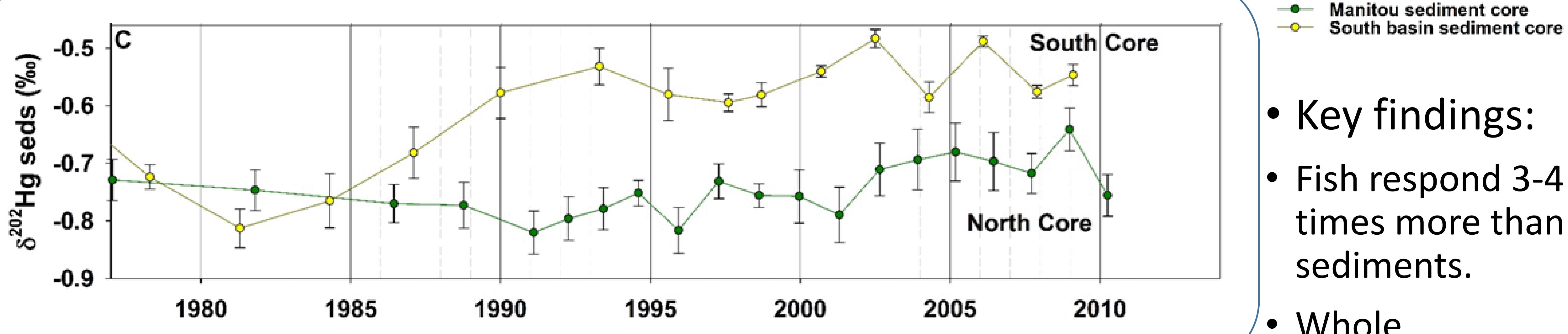


Tracing sources of Hg to trout with δ^{202}Hg

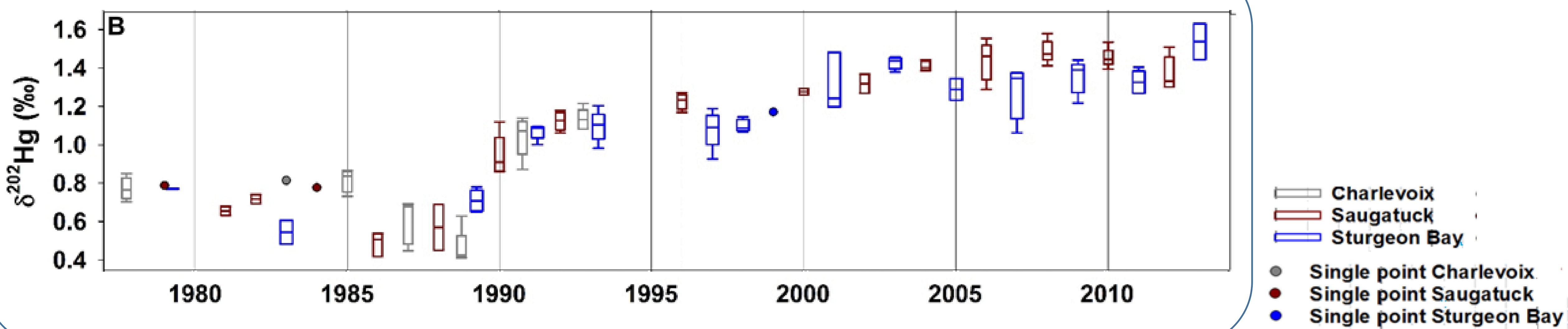
- Key findings:
  - Hg mitigation strategies resulted in rapid +δ^{202}Hg following 1988.
  - Quagga invasion did not produce an obvious change.
  - +δ^{202}Hg paired with –Δ^{199}Hg suggests Hg source shift in addition to dietary shifts observed with C/N isotope ratios.



Ecosystem response to a Hg source shift



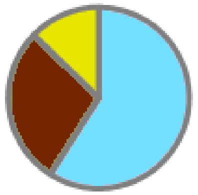
- Key findings:
- Fish respond 3-4 times more than sediments.
- Whole ecosystem response.



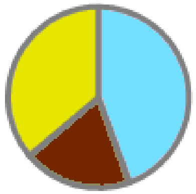
So what can we expect in LS?

- Landscape differences –
  - Less urbanized, less ag.

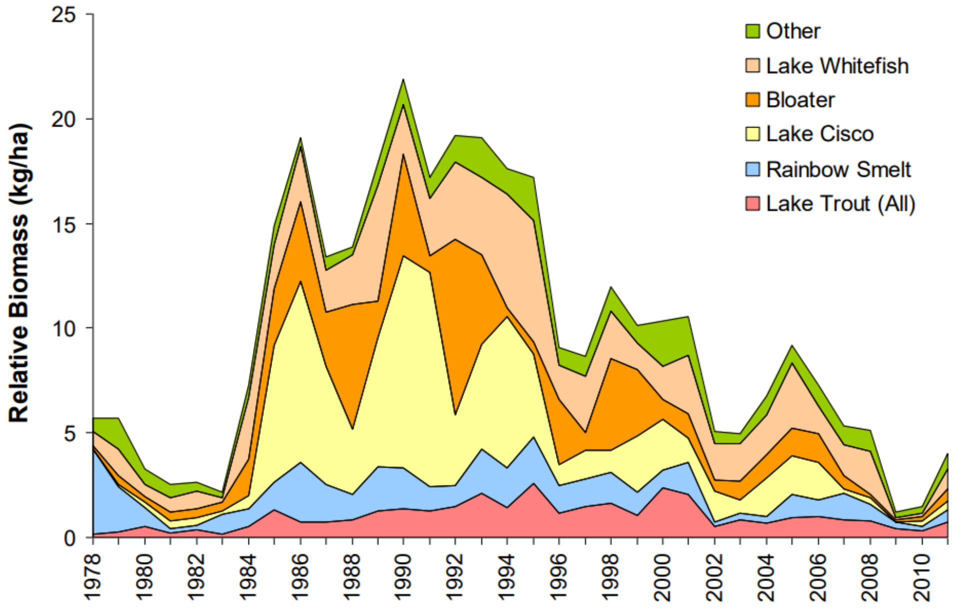
Lake Superior



Lake Michigan

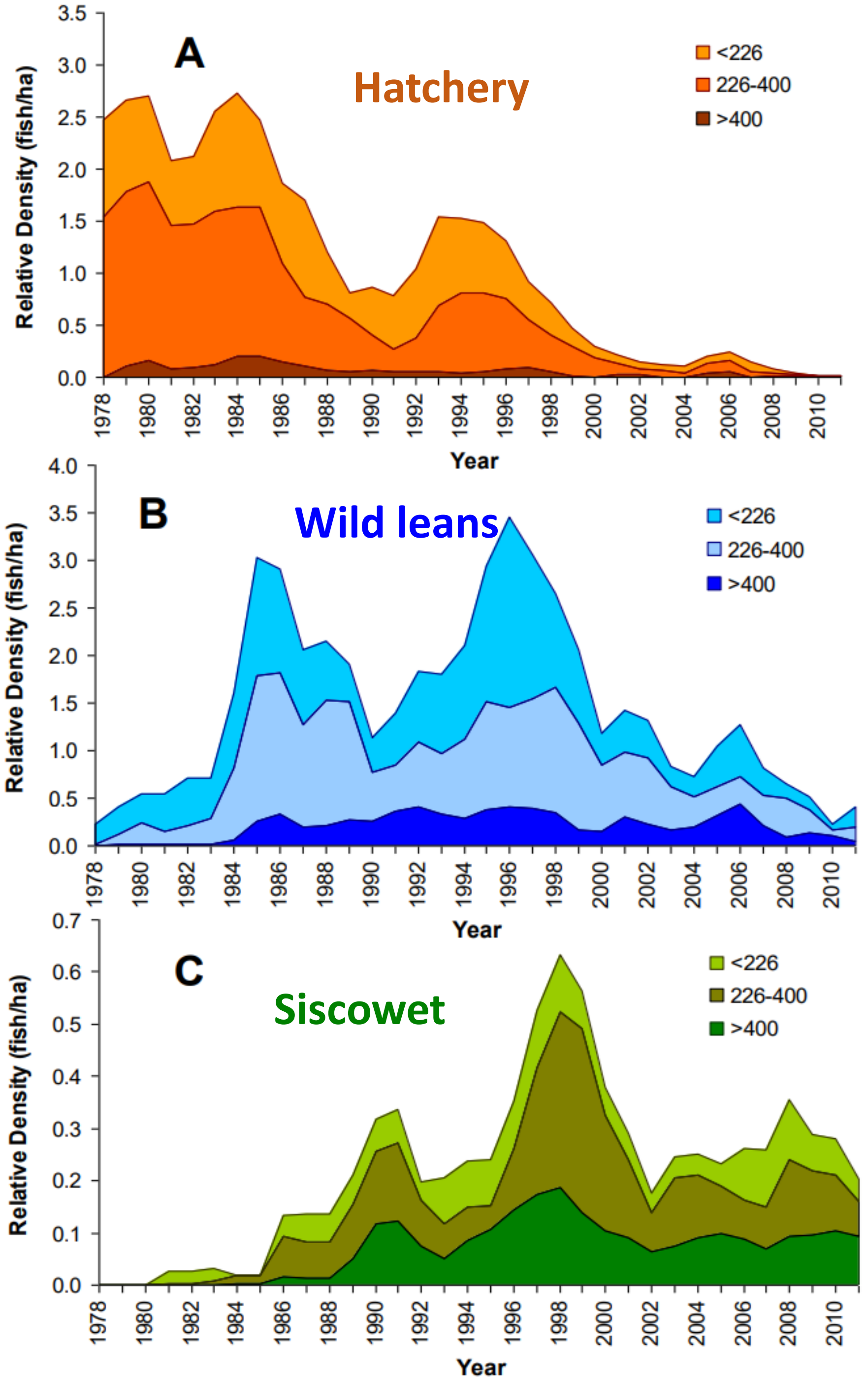


- Invasive species differences –



Gorman 2011

- Lake Trout differences



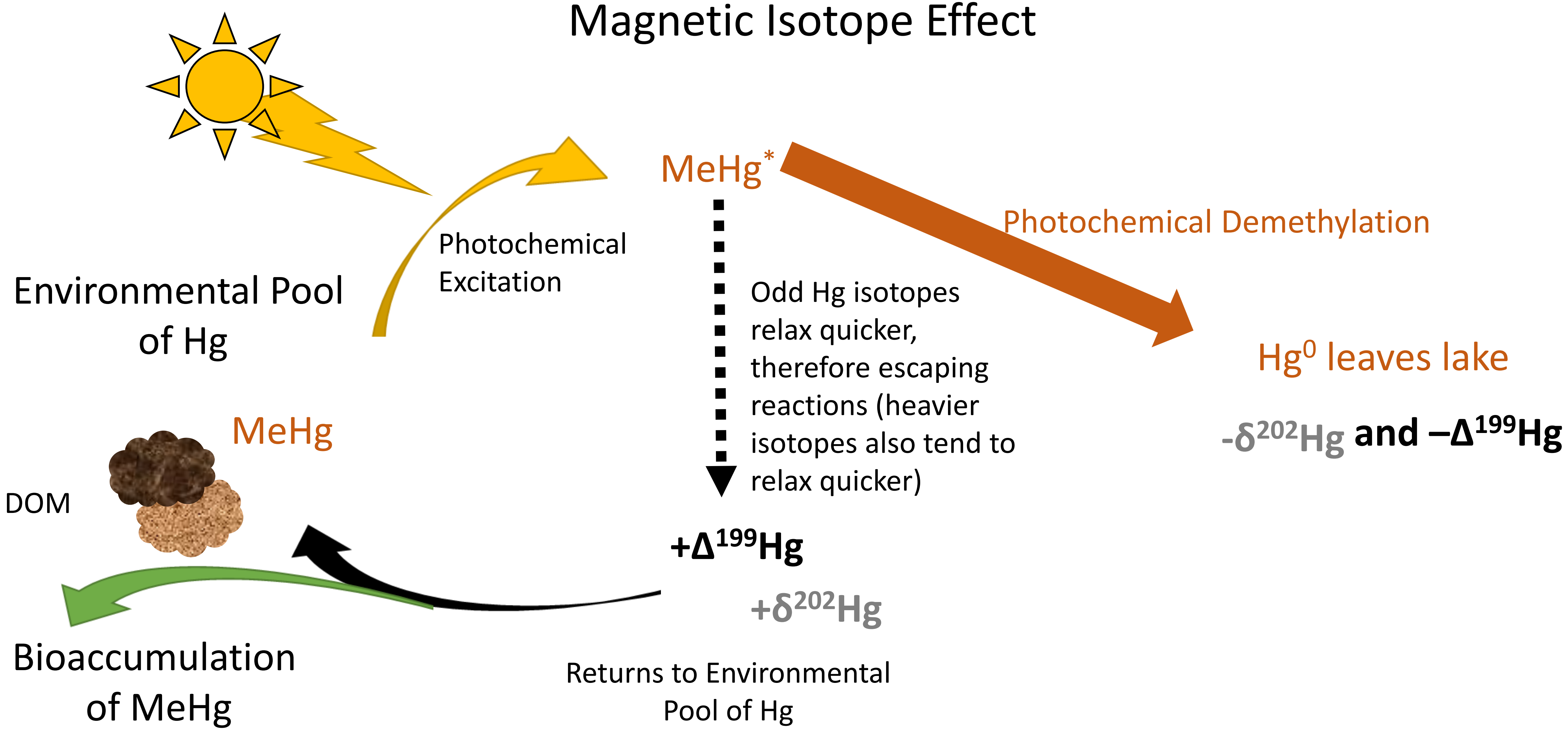
Acknowledgements

- Jim Hurley and Dave Krabbenhoft
- Beth Murphy - US EPA Great Lakes National Program Office
- Joel Hoffman - US EPA Office of Research and Development
- The entire USGS MRL staff
- And **YOU** here in attendance on a Friday morning at 8AM!!!

How does nature change Hg isotopic distributions?

Mass Independent Fractionation – Odd isotopes (odd-MIF)

Magnetic Isotope Effect



High Precision Determination of Mercury Isotopic Composition Using MC-ICP-MS

- Allows for the qualitative and semi-quantitative assessment of sources of Hg and processes it may undergo
- In ambient conditions tracking naturally occurring stable Hg isotopes

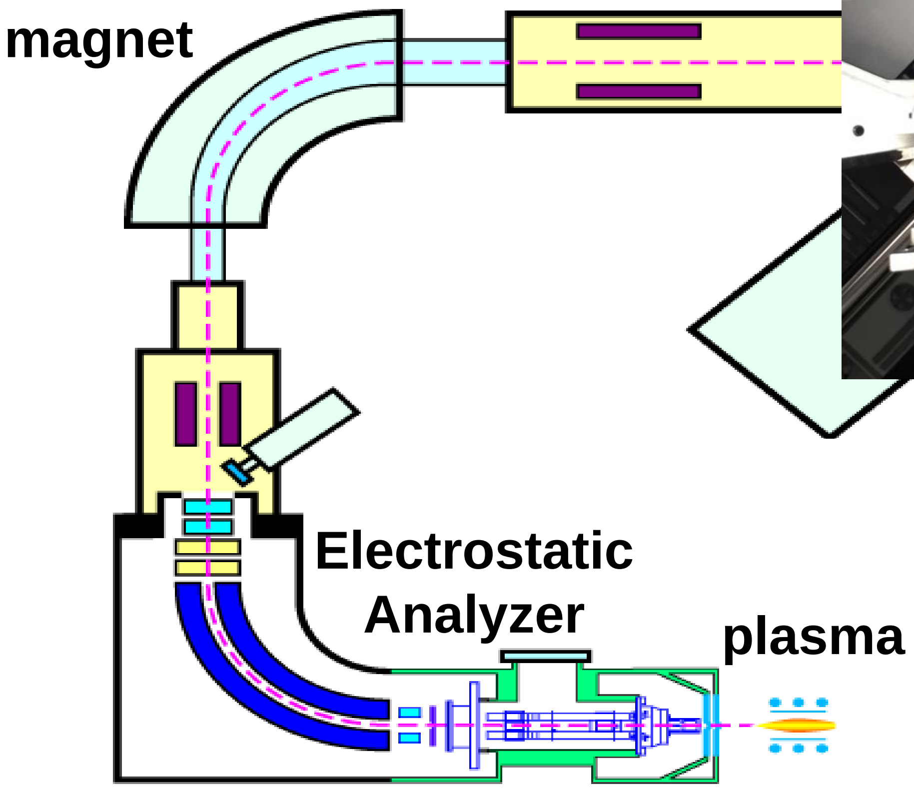
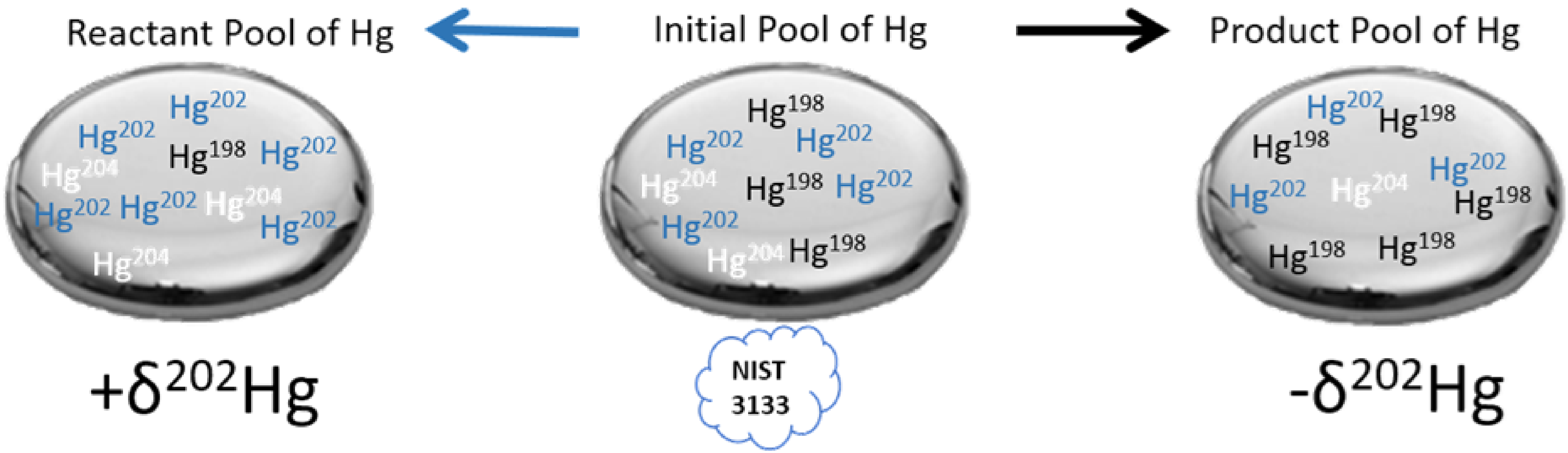


Image by Thermo

How does nature change Hg isotopic distributions?

Mass Dependent Fractionation (MDF)

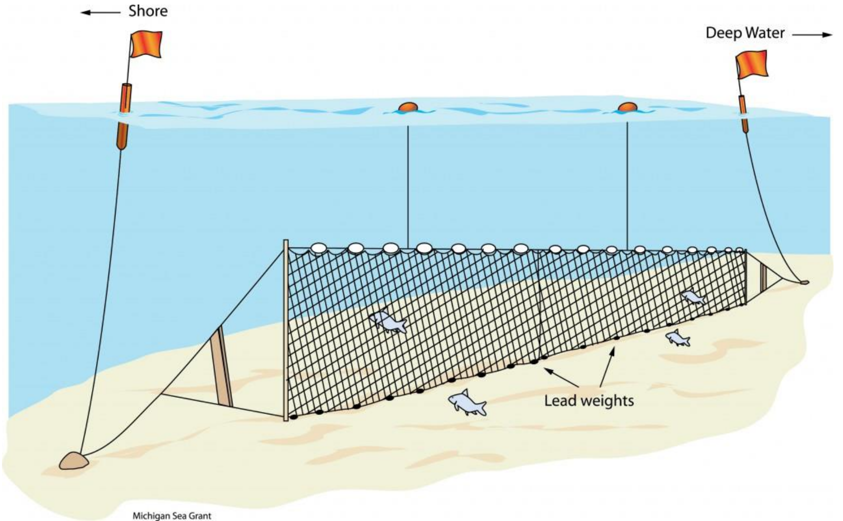
Light isotopes kinetically react faster and therefore enrich in the product pool.



$$\delta^{202}Hg(‰) = \left\{\left[\frac{^{202}Hg\,/\,^{198}Hg_{sample}}{^{202}Hg\,/\,^{198}Hg_{NISTSRM\,3133}}\right]-1\right\}\times 1000$$

Sample “Collection”

- 1970 – present day fish archive
  - Includes:
    - Trout, salmon and moderate prey species
    - All 5 Great Lakes and tributaries
    - Gill netted
  - Purpose:
    - determine what trends might be happening in the lakes as well as how the lakes are responding to emerging chemicals in the ecosystem.
  - Kept frozen in -20°C freezers as whole body wet composites

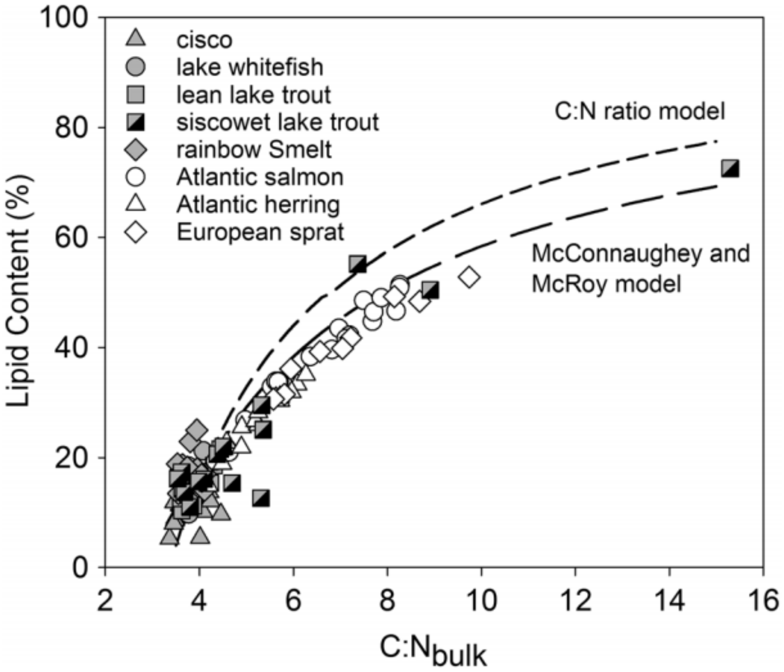


Lipid
δ^{13}C Correction

Based on lipid extraction and mathematical modeling

Methylene chloride/methanol solvent mixture to extract ^{13}C-depleted lipids in white tissue

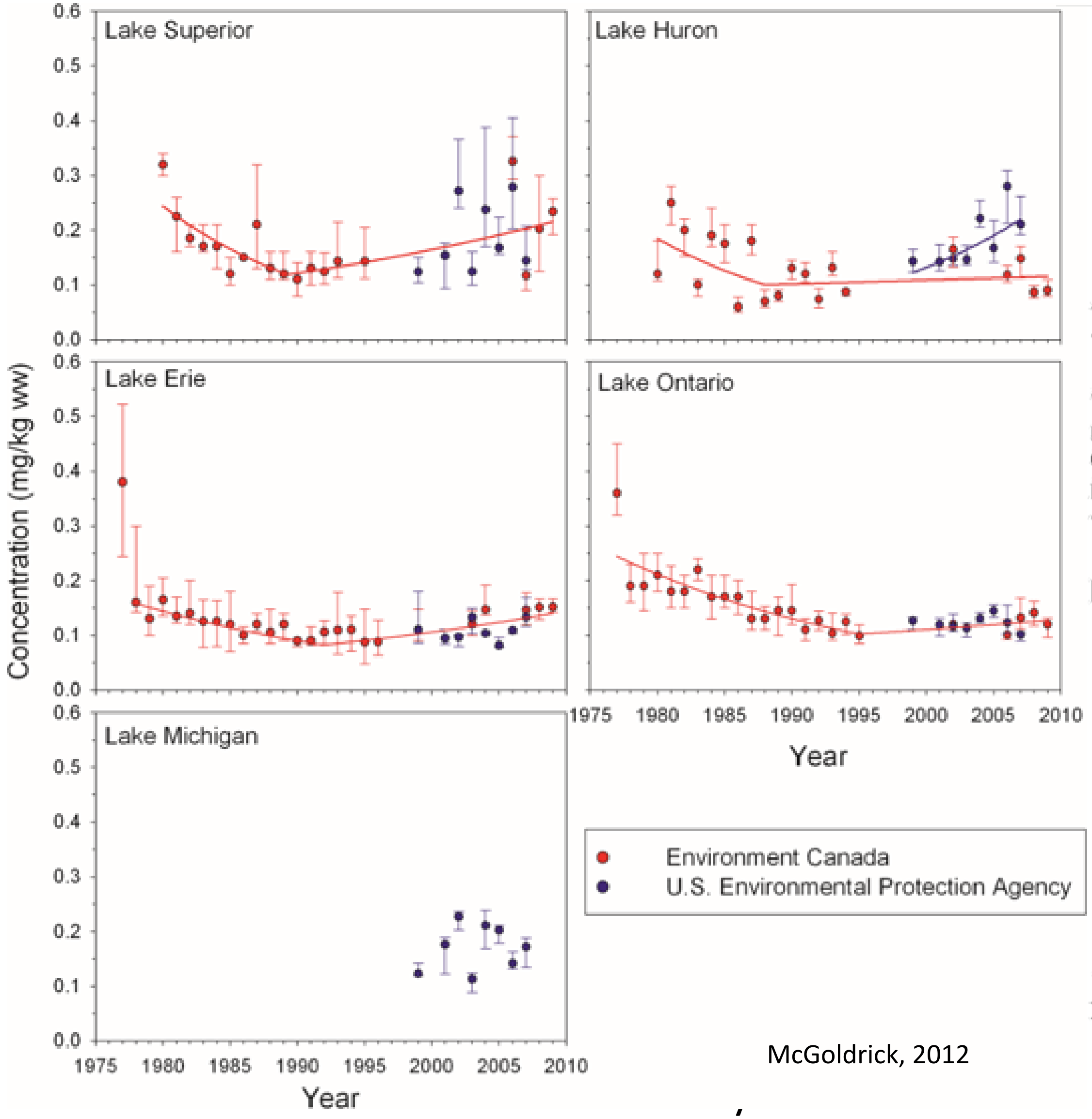
Largely lipids are absent of N therefore major no change is evident through extraction



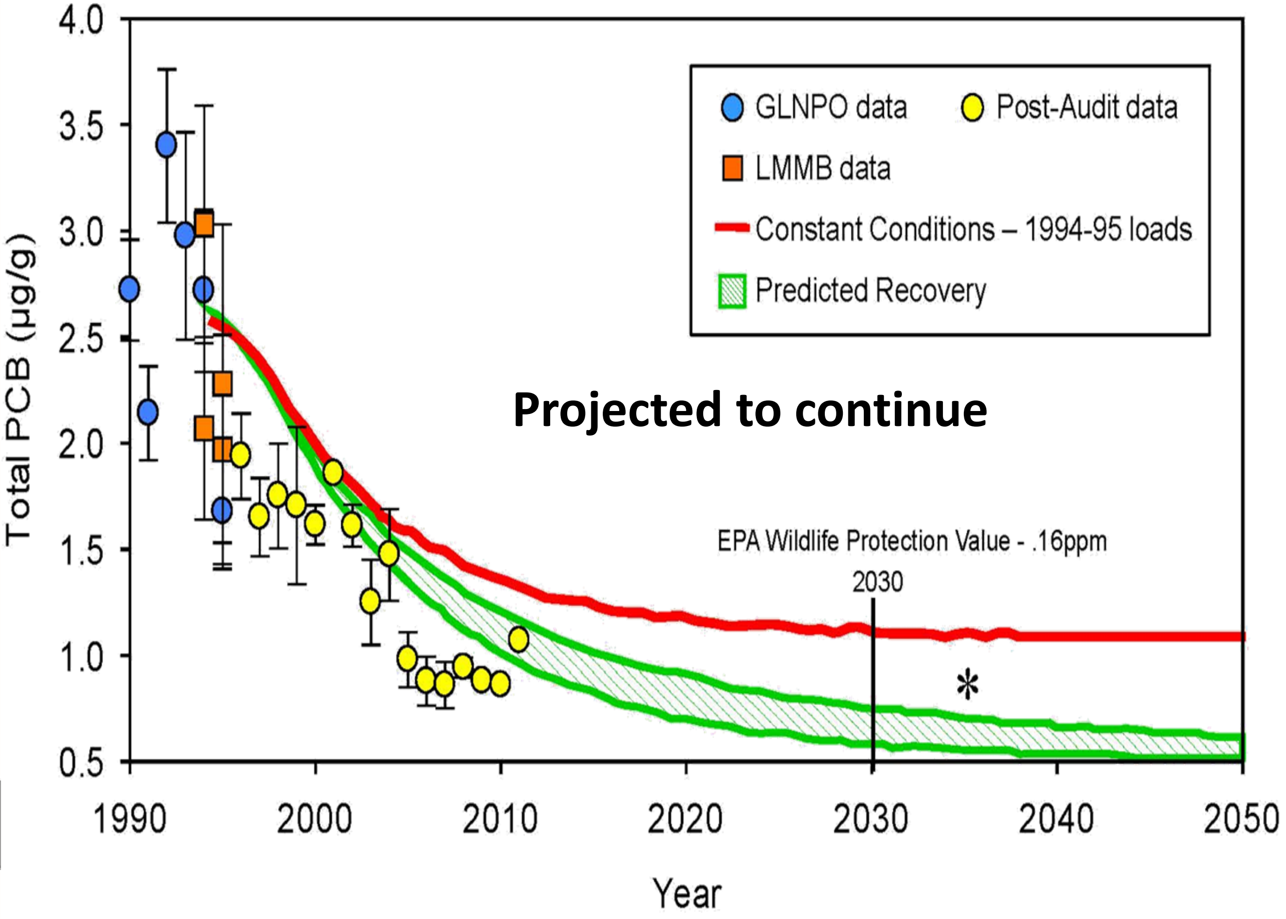
Hoffman 2016

- $\delta^{13}C_{lipid\ free} = \delta^{13}C_{bulk} + [\Delta\delta^{13}C_{lipid} * (C:N_{lipid\ free} - C:N_{bulk})] / C:N_{bulk}$
  - $C:N_{lipid\ free}$ = published molar ratio = 3.5
  - $\Delta\delta^{13}C_{lipid}$ do to lipid formation = -6.5‰

Successes in part due to GLFMSP in organic contaminants



McGoldrick, 2012



*Assume whole fish PCB levels will have declined enough by 2035 that lake trout fillets will have fallen into the unlimited consumption category, .05ppm, set by the Great Lakes Consortium for Fish Consumption Advisories .

Beth Murphy - 2014