

Understanding Sources of Mercury in the St Louis River, MN using Stable Isotope Approaches

Sarah E Janssen*, Joel Hoffman, Greg Peterson, Ryan Lepak,
Mark Pearson, Anne Cotter, David Krabbenhoft

*USGS Mercury Research Lab
sjanssen@usgs.gov



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Simplified Hg Cycle

Emissions

$\text{Hg(II)} \leftarrow \text{Hg(0)}$

Deposition

Watershed Runoff

Hg point source
(current or legacy)

Hg

Hg

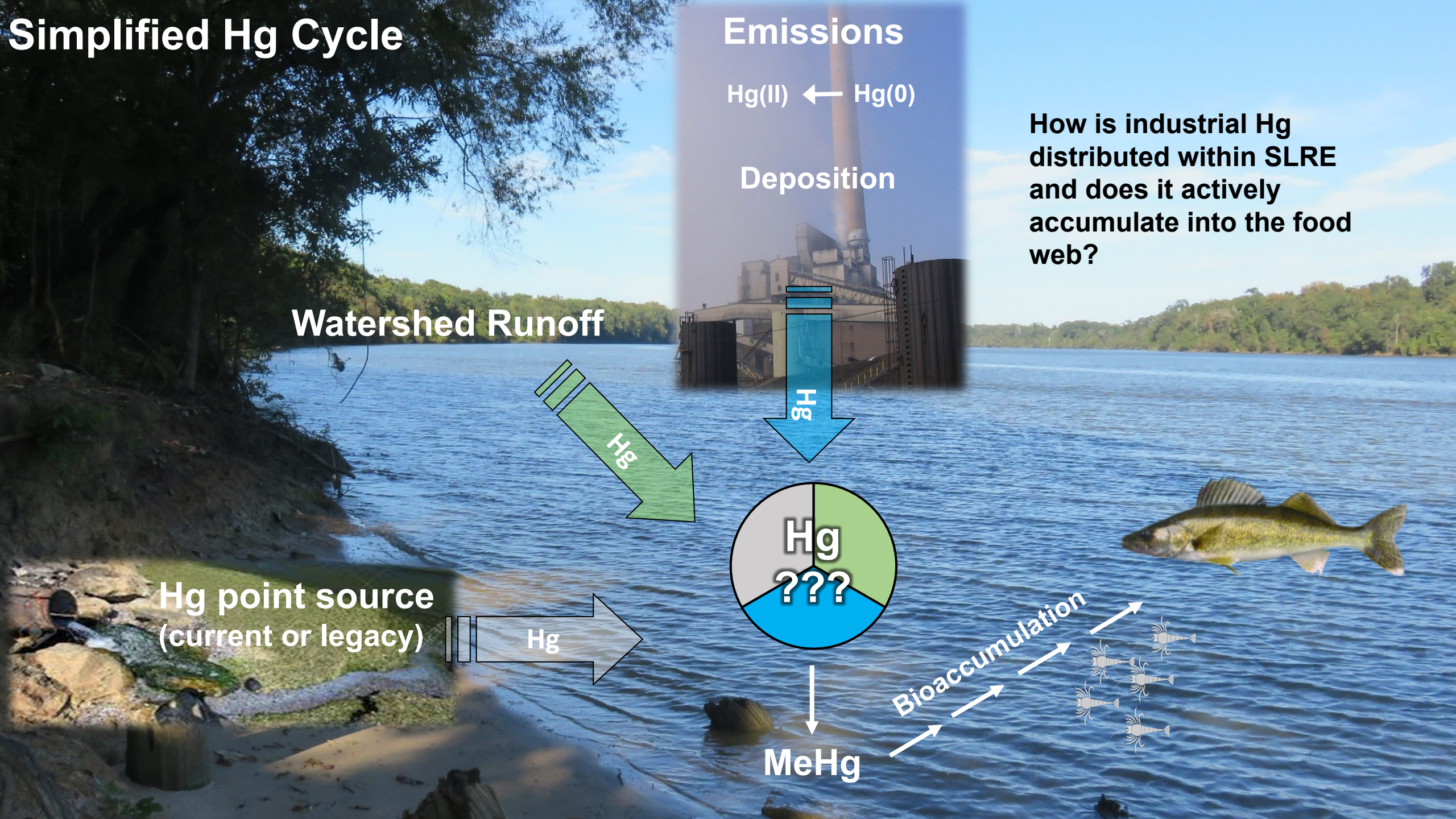
Hg

???

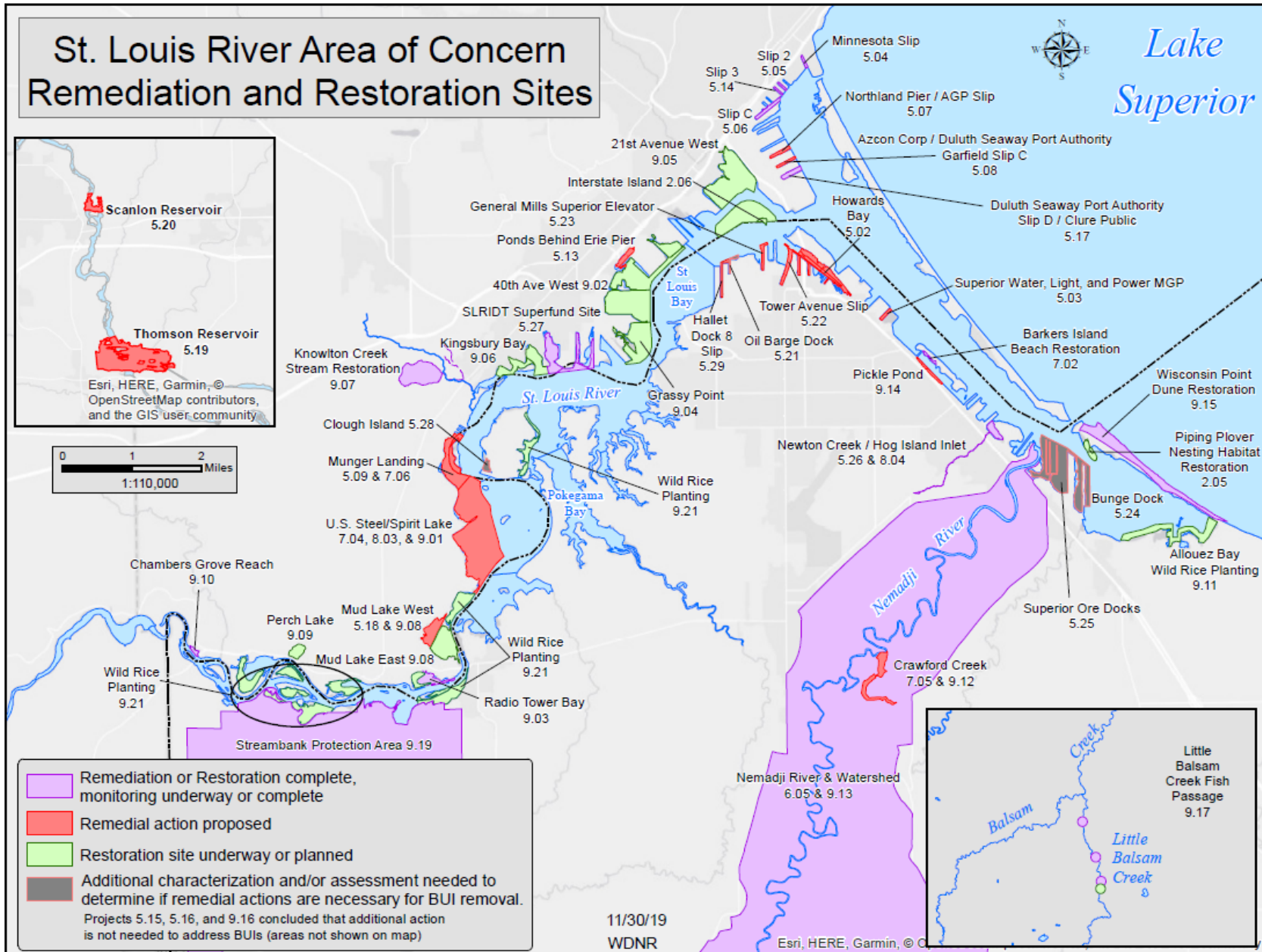
MeHg

Bioaccumulation

How is industrial Hg distributed within SLRE and does it actively accumulate into the food web?

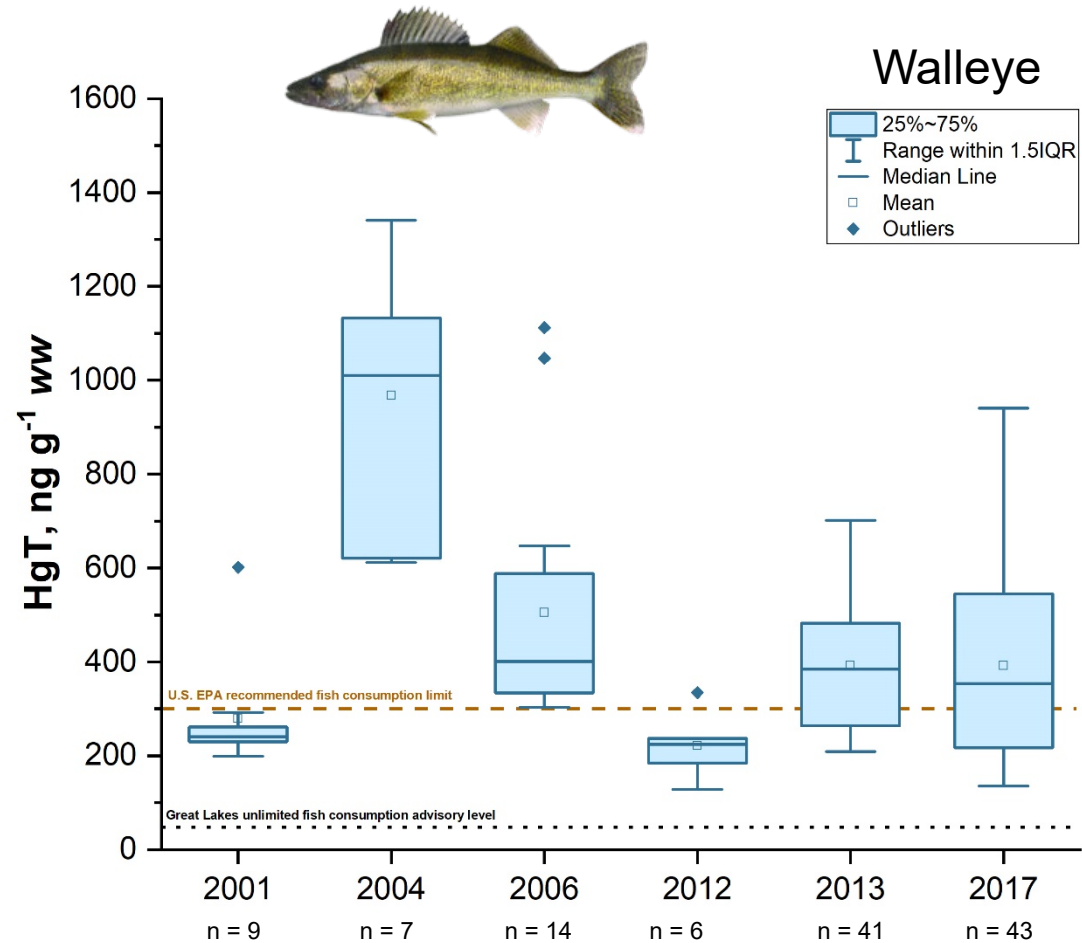


The St Louis River, MN Area of Concern

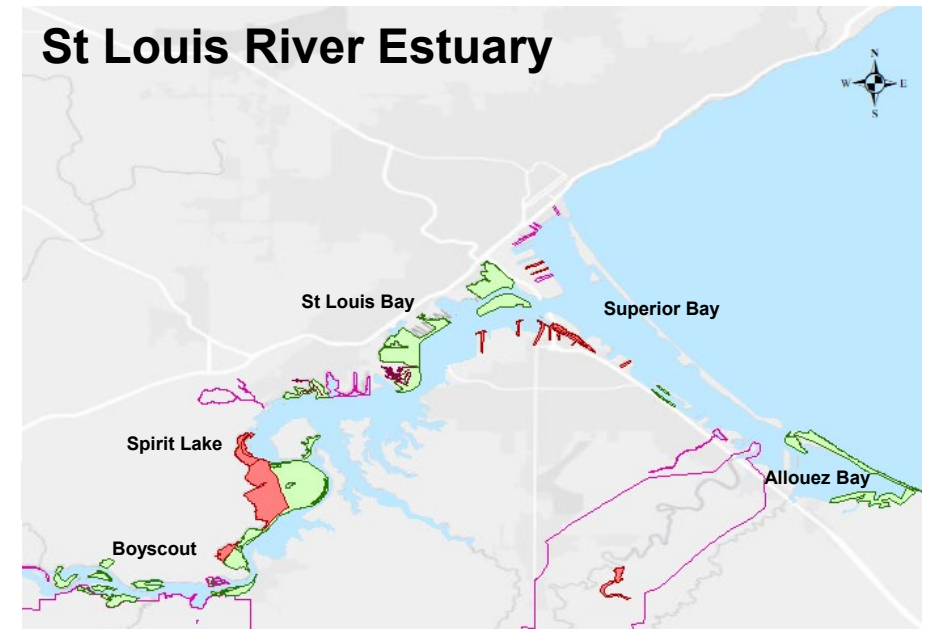


- Areas of concern (AOC) are regions within the Great Lakes that have significant impairment of beneficial uses due to the result of human activities at the local level
- 39 miles of the lower St. Louis River estuary (SLRE) is designated in the AOC as well as two upstream reservoirs
- Historic contamination from point sources, superfund sites, landfill discharge, and wastewater discharge
- Hosts mercury (Hg), PCBs, dioxin, and PAHs

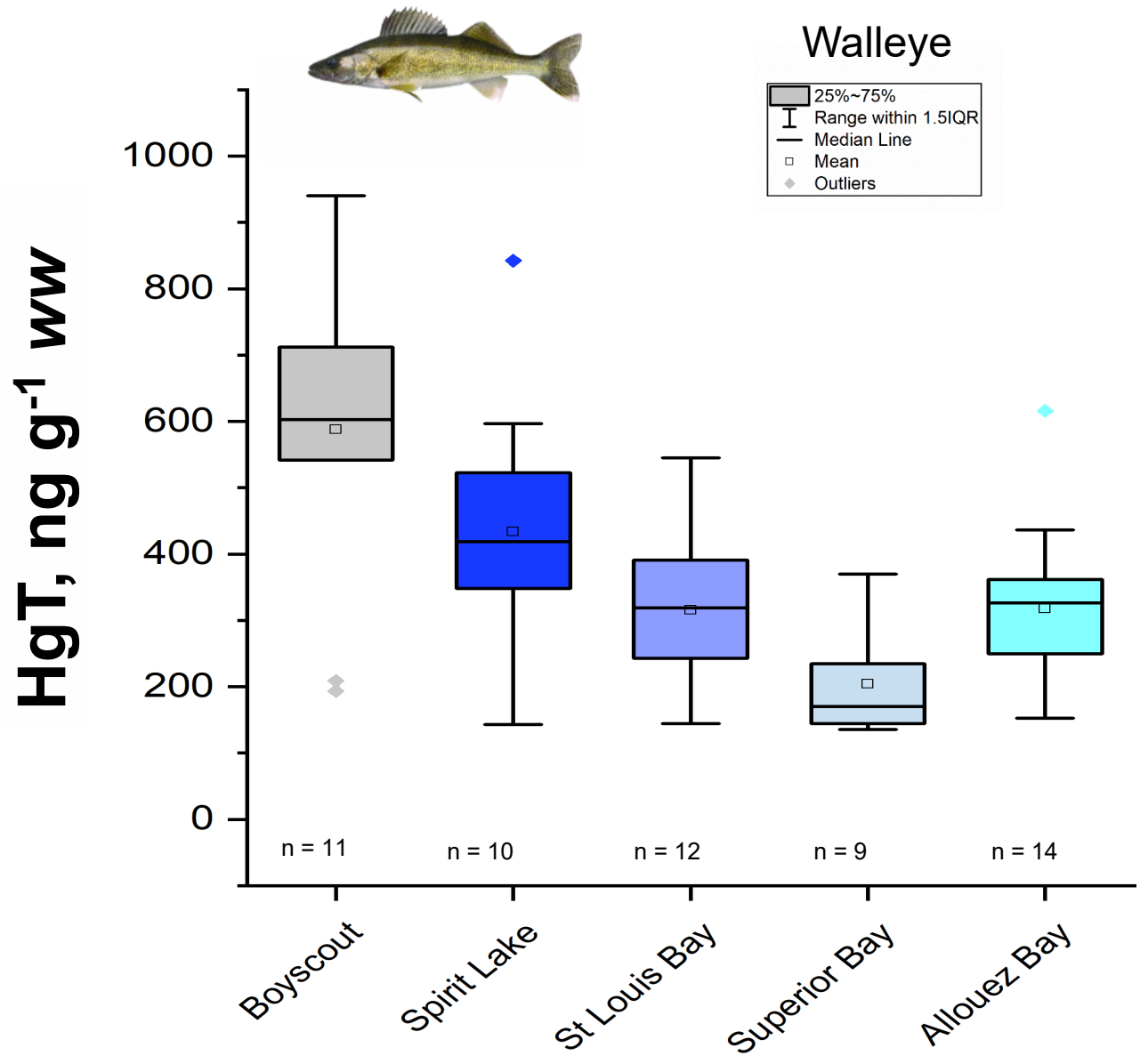
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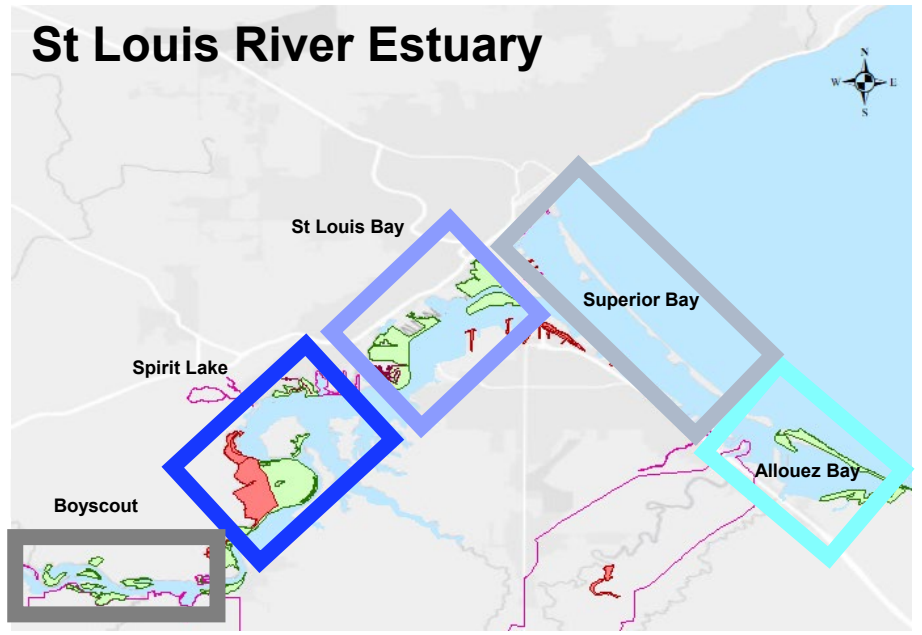
Walleye from the lower estuary have variable Hg concentration, which show no temporal changes



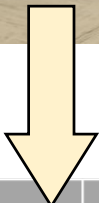
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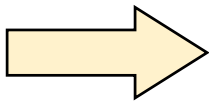
Concentrations in walleye are highly variable within and across sites in the system, often showing a decreasing concentrations towards St Louis Bay and Superior Bay



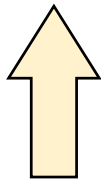
Hg Stable Isotope Primer



Hg Stable Isotopes	Abundances
¹⁹⁶Hg	0.16% Too low
¹⁹⁸ Hg	10.0%
¹⁹⁹ Hg	16.9%
²⁰⁰ Hg	23.1%
²⁰¹ Hg	13.2%
²⁰² Hg	29.7%
²⁰⁴ Hg	6.8%

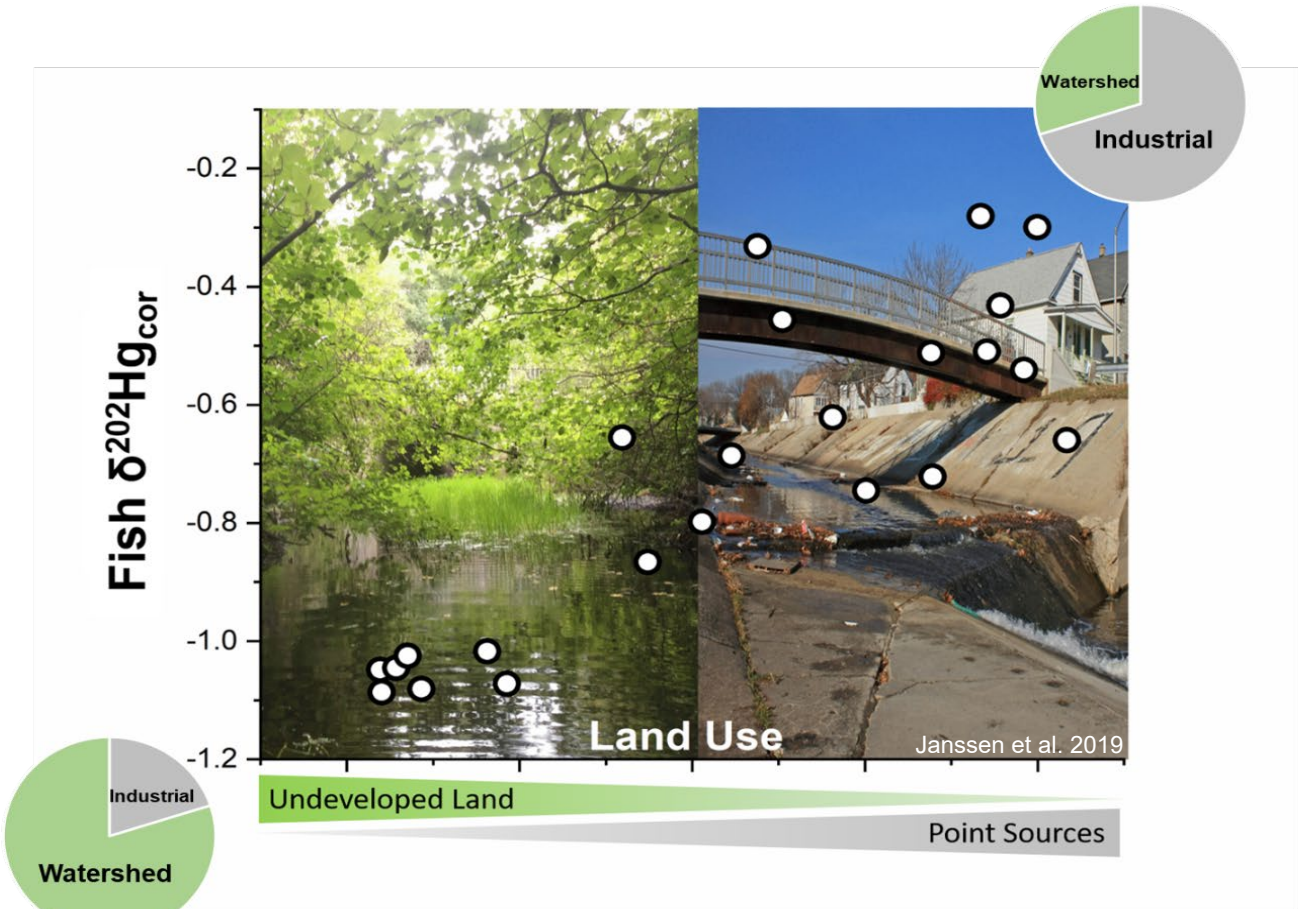


$$\delta^{xxx}\text{Hg} = \left(\frac{\left(\frac{^{xxx}\text{Hg}}{^{198}\text{Hg}} \right)_{\text{sample}}}{\left(\frac{^{xxx}\text{Hg}}{^{198}\text{Hg}} \right)_{\text{SRM3133}}} - 1 \right) \times 1000\text{‰}$$



$$\Delta^{xxx}\text{Hg} = \delta^{xxx}\text{Hg} - (\delta^{202}\text{Hg} \times m)$$

m = mass scaling factor



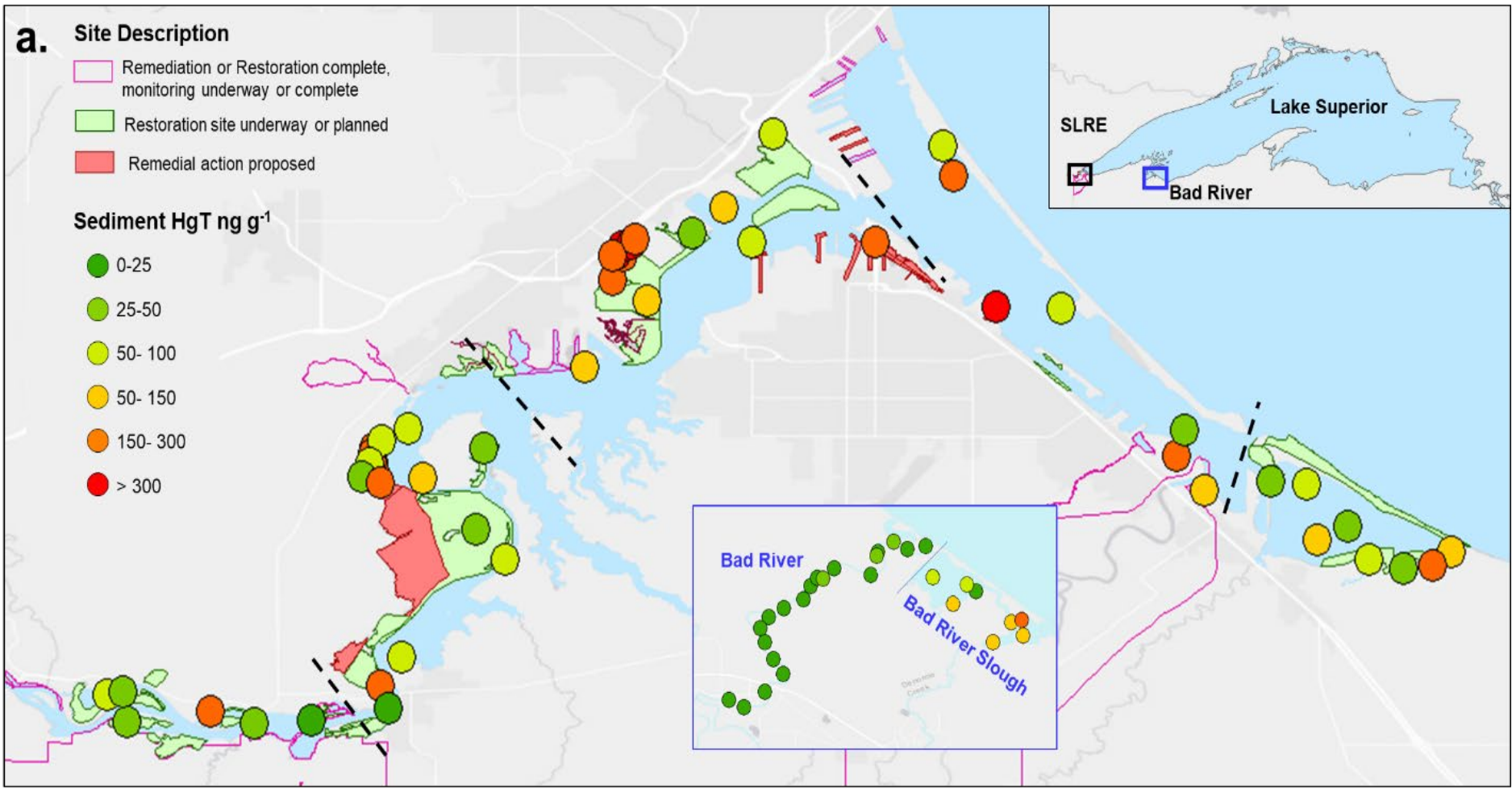
Hg Isotope Application to the St Louis River AOC

Execute a scientific assessment that informs consumable fish mercury levels and sources in the St Louis River estuary (SLRE) AOC:

- **Assess the distribution of legacy (industrial) Hg contamination within SLR in comparison to a reference location (Bad River, WI)**
- **Apply Hg stable isotopes to the SLRE food web to assess the relative contributions of legacy mercury pollution (retained in sediments) versus new mercury in sport fish from the system**



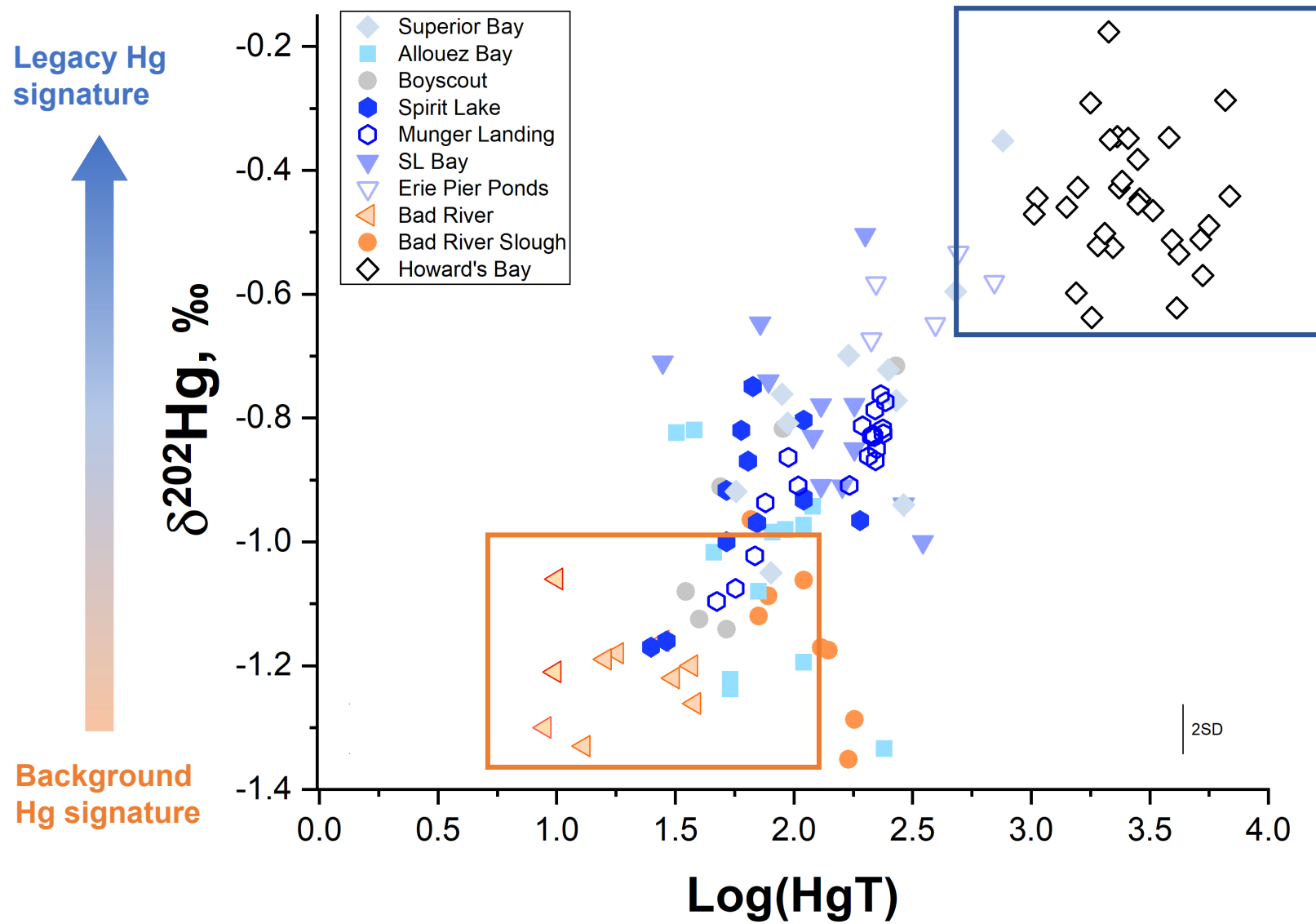
Mercury Concentrations in SLRE AOC Sediments



Hg was heterogeneously distributed in SLRE sediments and were higher than the reference location within the Bad River

Concentrations are not indicative of just industrial contamination, as depicted in regions of the Bad River slough and Allouez Bay

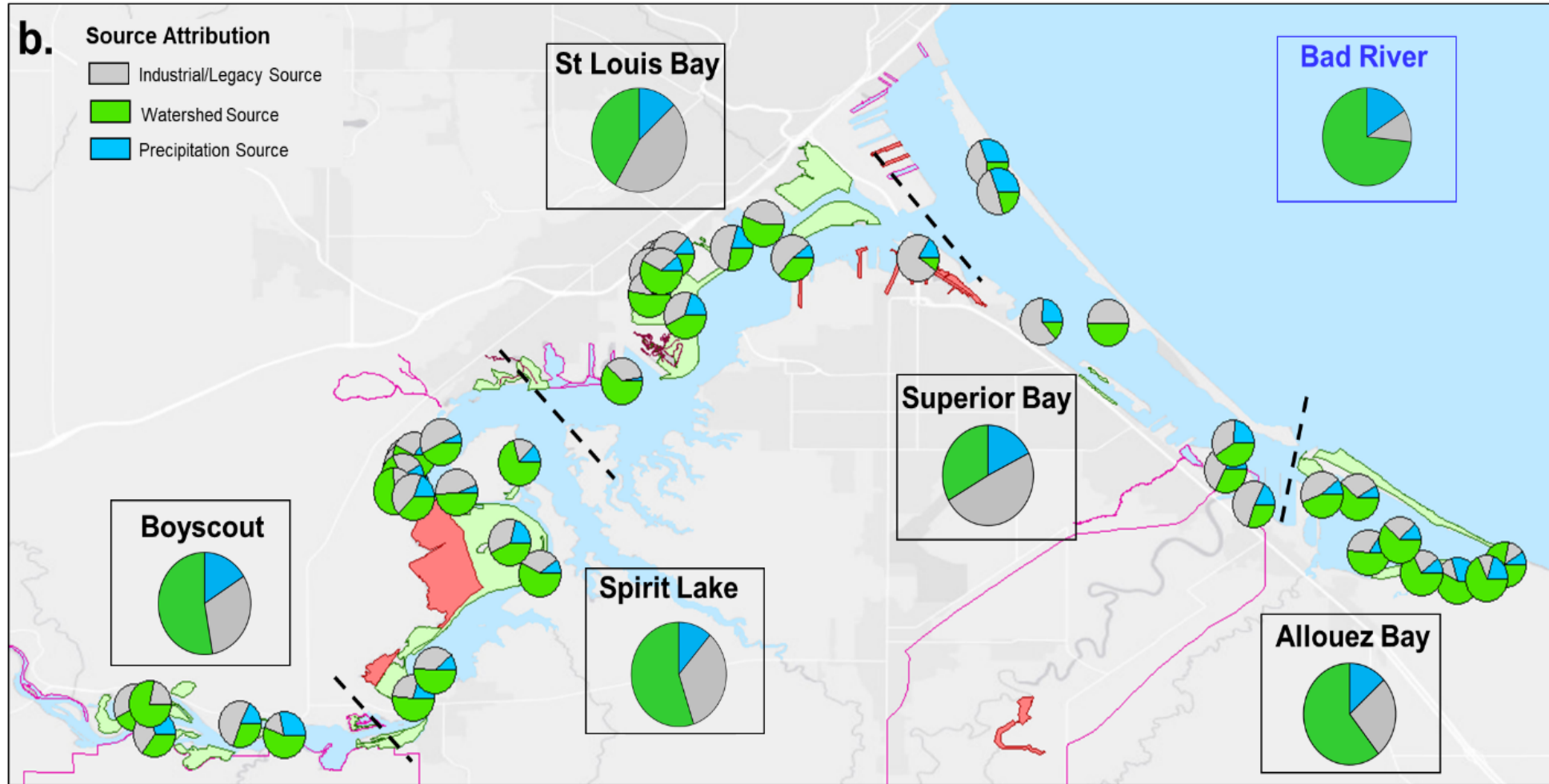
Are Concentration and Mercury Source Related?



Two distinct mercury-source site conditions were identified with Hg isotopes:

- 1. Legacy hotspots
- 2. Watershed run-off originating from atmospheric Hg deposition

What is the Source Distribution of Hg within Sediments?



Results from binary and tertiary mixing models suggest that industrial Hg is widespread within SLR even outside regions of remedial activity

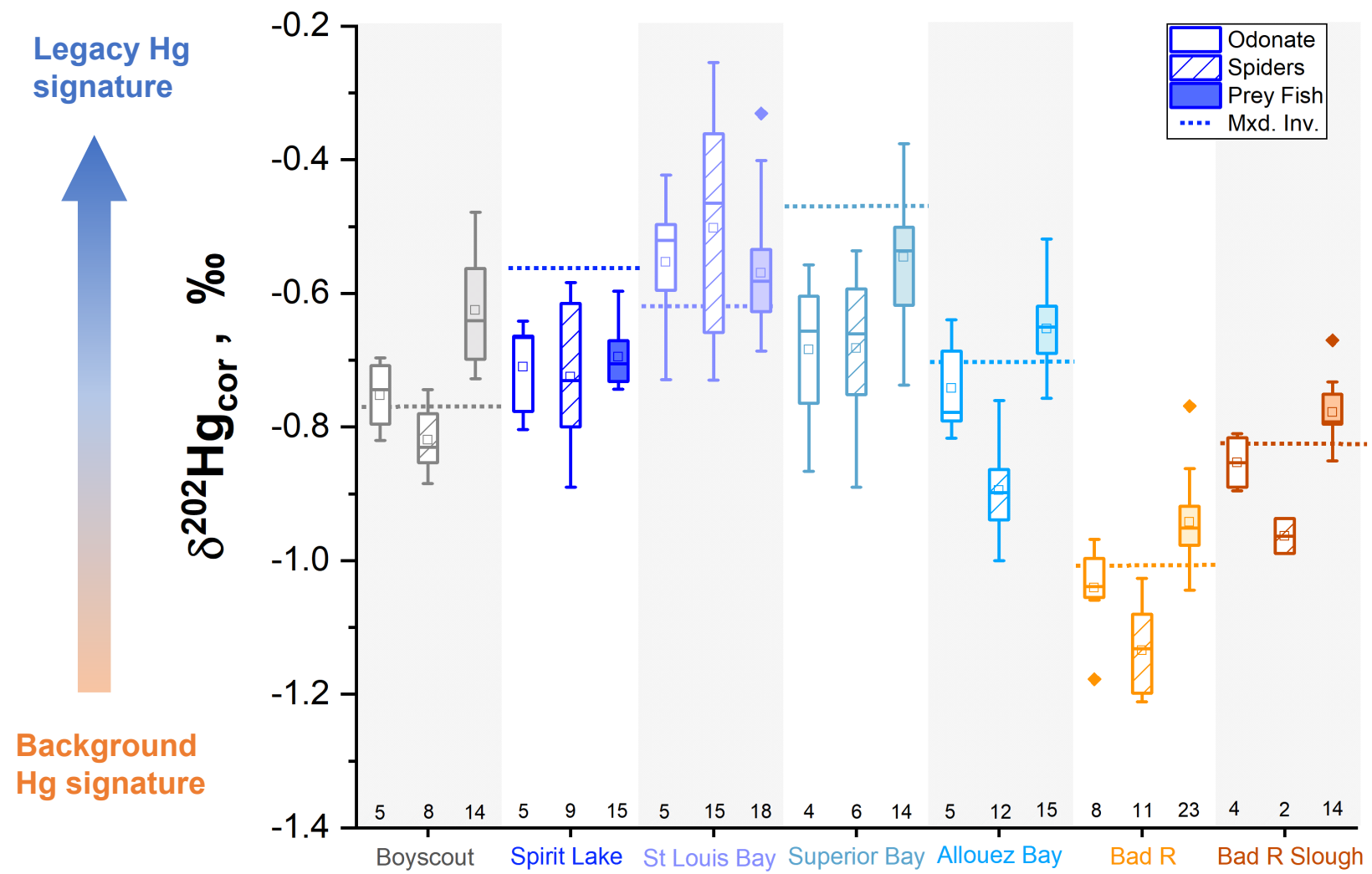
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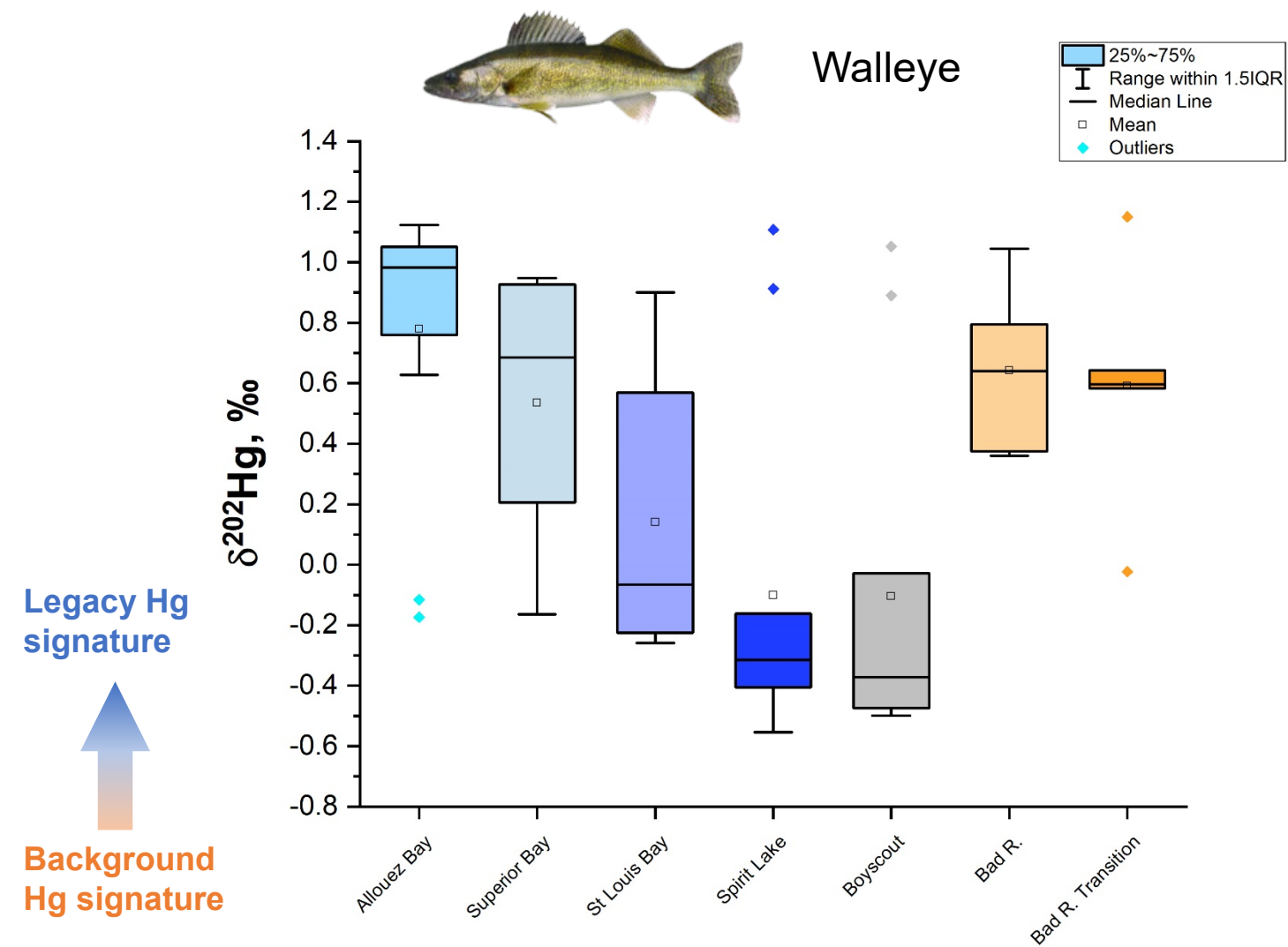
Sources of Hg to the SLRE and Bad River Food Webs



The isotope distinction seen in sediments between legacy Hg and watershed Hg is also reflected in the lower food web

Prey fish and benthic invertebrates suggest the accumulation of legacy Hg within SLRE

Sources of Hg to the SLRE and Bad River Game Fish

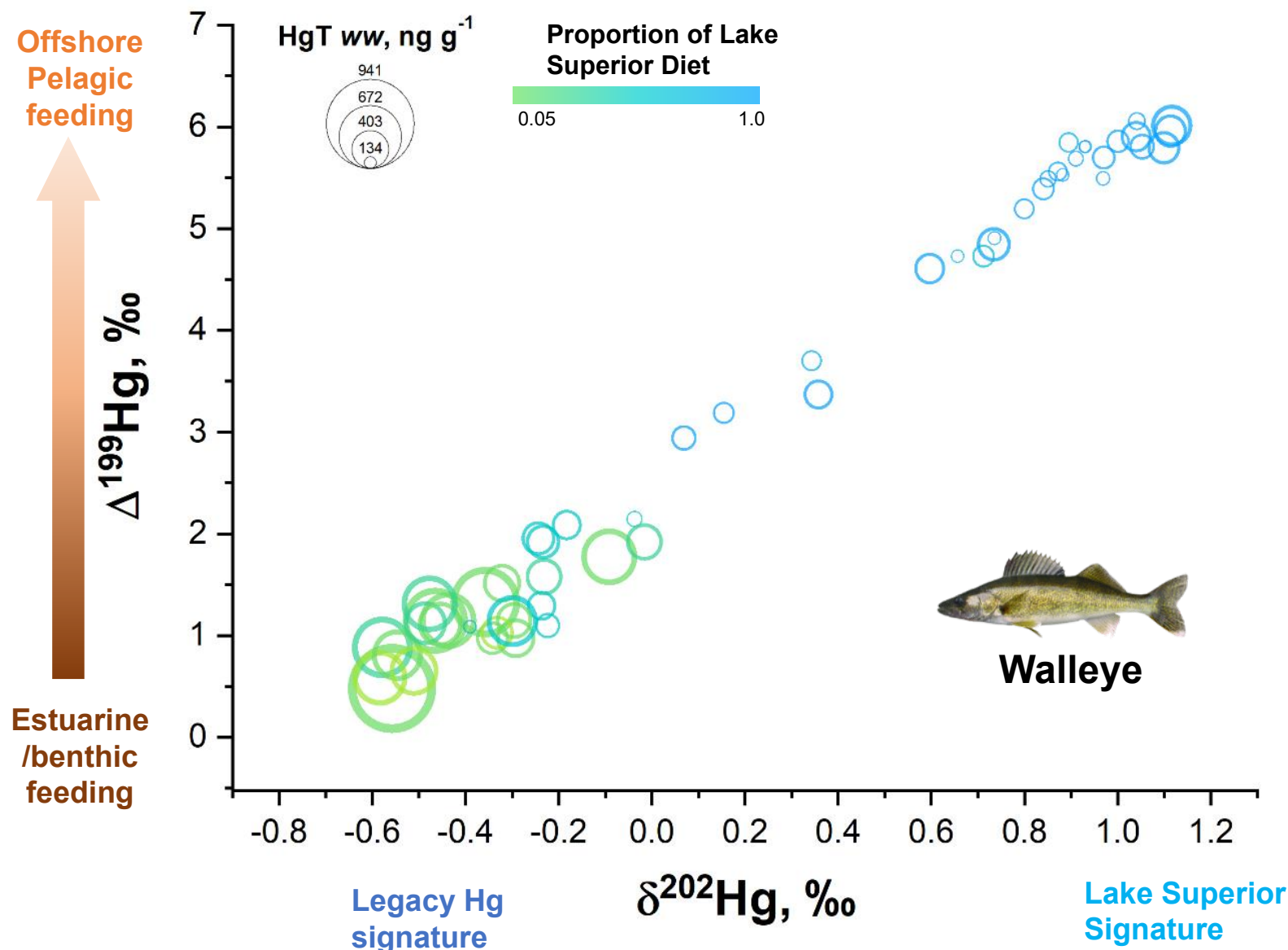


The Hg isotope range associated with walleye was much larger than compared to lower food web items

Significant overlap was observed in the Hg isotope profile in walleye from the Bad River and SLR

Migration patterns and larger home ranges had to be accounted for when assessing Hg sources in walleye

Mercury Isotopes in SLRE Game Fish

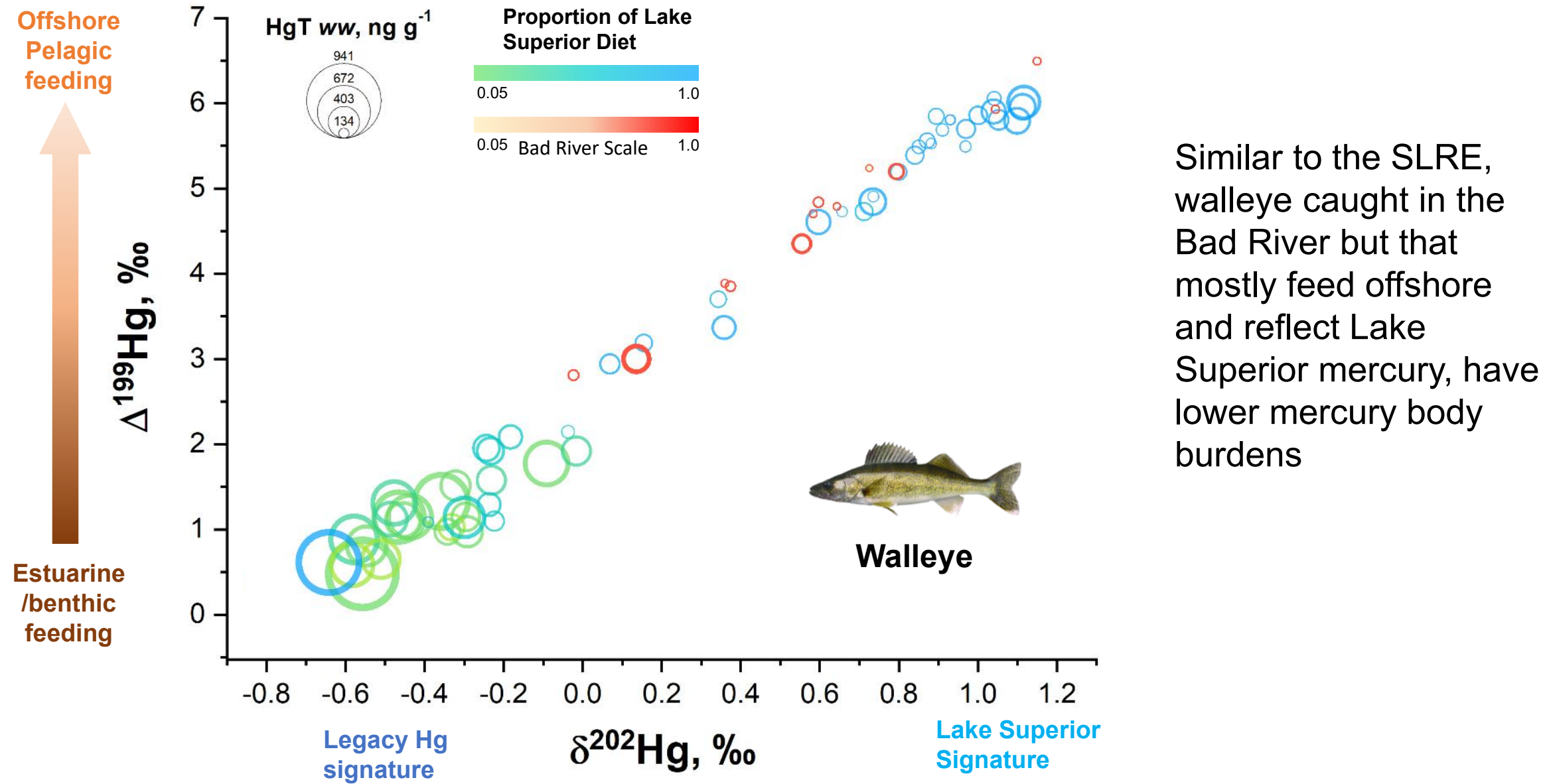


Mercury isotopes reveal that concentration trends observed in walleye are a function of source

A subset of fish captured in SLRE are actually feeding in Lake Superior (as denoted by C/N/Hg isotopes)

Walleye caught in the SLRE but from diet analysis mostly feed offshore in Lake Superior have lower mercury concentrations than those feeding in the estuary

Mercury Isotopes in SLRE and Bad River Game Fish



Conclusions for SLRE Hg Cycling

- Within the SLR AOC industrial Hg was found to be well distributed within estuary sediments and also was shown to be accumulating into prey fish of the system
- Hg concentration within game fish of the AOC were dependent on migration habits and Hg source
 - Walleye feeding offshore were picking up precipitation sources whereas residents were also accumulating legacy Hg sources similar to prey fish
- Offshore bioaccumulation and changes in Hg sources and dietary habits can be tracked using different Hg isotope tracers ($\Delta^{199}\text{Hg}$)

Special thanks to:



Minnesota Pollution
Control Agency



Bad River Tribe

