## Mercury Sources and Loads: Connecting Terrestrial Mercury Fluxes to Lake Superior

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View from the EPA Lake Guardian

Plankton Sampling Great Lakes



St Louis River, MN

### **Presentation Outline**

- Overview on Hg Cycling
- The Big Picture: Examining Hg Loads and Sources to Lake Superior
- What Controls Hg Release: Assessing SLR Peatlands
- Next Steps



### **Mercury Cycling in the Great Lakes**



- Hg bioaccumulation is highly efficient in the Great Lakes and surrounding regions!
- Lake Superior has some of the lowest water concentrations of Hg in the world but one of the highest biomagnification rates

Adapted from Ogorek et al. 2021 ES&T, https://doi.org/10.1021/acs.est.1c02319

### **Mercury Burdens in Fish Tissue**



Lake Trout and Walleye\*



- In Minnesota and across the Great Lakes there are waterbody specific and statewide safe-eating guidelines and consumption advisories for Hg in fish
- There are many chemical, physical, and biological factors that dictate Hg burdens in fish making it a complicated contaminant to study
- The extreme sensitivity that Lakes Superior and Huron exhibit on one hand are problematic, but on the other are advantageous when considering their potential applicability as good indicator sites for Minamata Effectiveness Evaluation

## **How are Mercury Delivery and Cycling Changing?**



### How are Mercury Delivery and Cycling Changing?

What are the sources of Hg to food webs within and surrounding Lake Superior?

Are those Hg source inventories changing due to regulatory shifts, climate change, and other cooccurring stressors?

### Approach:

- Conduct a lakewide assessment of Hg loads and sources within Lake Superior
- Examine site specific sources and controls on Hg cycling within the St. Louis River



## **Assessment of Lake Superior (includes Hg isotopes!)**



### **Tributary Samples**

- 18 US tributaries sampled monthly
- 10 Northshore tributaries sampled 3x per year
- 9 tributaries sampled 2x a year in Pukaskwa National Park





### **Atmospheric Samples**

4 gaseous elemental Hg sites and 2 rainfall sites collected monthly







This design combines the Lake Superior effort with the Great Lakes Sediment Surveillance Program (GLSSP)!

## **Examining Hg Concentrations Across Tributaries**



High Hg concentrations were observed during spring runoff (the highest flow event for the region)

These concentrations have not decreased since the 1990s

We also observed that certain regions are more sensitive to high Hg concentrations during runoff (MN Northshore) as well as summertime upticks in Hg methylation (Eastern UP Michigan)

## **Examining Hg Yields Across Tributaries**



Different watersheds produced different Hg yields (e.g., amount of Hg coming off the watershed as a function of size)



Once again the Northshore sites had some of the highest Hg yields including the Baptism and Knife Rivers

## What Controls Hg Release in Tributaries?



Total Hg in the filtered phase was controlled by **organic carbon** across all tributaries

Methylmercury in the filtered phase was controlled by total Hg, organic carbon, and wetland coverage across all tributaries



### What is the Upstream Source of Mercury?

We have previously defined sources in the St. Louis River using isotope tracers!

### **2017-Main Channel Sediments** Site Description St. Louis Bay Remediation or restoration complete, Lake Superior monitoring underway or complete Restoration site underway or planned 20 Remedial action proposed Source Attribution Industrial/Legacy Source Watershed Source Precipitation Source Superior Bay **Boyscout Spirit Lake Allouez Bay**

Industrial sources were prominent in the lower St. Louis River Bay and Superior Bay regions

# \*

Watershed sources dominated (>40%) sediments near Boyscout Landing, behind Clough Island, Pokegama Bay, and Allouez Bay

•••

Precipitation (direct atmospheric input) were also more prominent in nearshore areas in comparison to main channel sediments

## What is the Upstream Source of Mercury?



We scaled this up in Lake Superior and found that watershed sources make a big impact in the nearshore zone of the lake

### **Summary of Lake Superior Work**

- 1. Total mercury concentrations in Lake Superior U.S. tributaries have not revealed notable declines in the past 25 years
- 2. There are spatial and temporal "hotspots" for Hg runoff and MeHg production
- 3. Across all streams organic matter is a driving factor for Hg and MeHg concentrations and loads
- 4. Watershed sources, runoff Hg derived from legacy accumulation in soils, is the main contributor to tributary Hg loads and the nearshore of Lake Superior; whereas wet deposition is the primary source to the offshore parts of the lake
- 5. In the coming months/year, the US needs to develop the the details for its version of a Minamata Effectiveness Evaluation plan. The lake's extremely high biomagnification rates and now good data base to establish where the air (not shown today) precipitation, surface water, sediment, and food web condition currently sit provide compelling case.



### How are Mercury Delivery and Cycling Changing?

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## **Upstream Sources: Examining Peatland Systems**

Peatland systems are great sinks for Hg deposition, but also perfect environments for Hg methylation



Upstream peatlands, wetlands, and forest soils in SLR are the source of "watershed" Hg in the lower estuary

## **How Does Peatland Restoration Impact Hg Release**



- Unfiltered water samples collected 2019-2021
- Filtered water samples, 2022



## **How Does Peatland Restoration Impact Hg Release**



While total Hg is generally consistent between peatland sites, MeHg concentrations increase in highly ditched and restored peatlands

Total Hg and MeHg concentrations are also higher in restored peatland drainages in comparison to main river sites

Unfiltered water samples

### **How Does Peatland Restoration Impact Hg Release**

### High levels of MeHg correspond to:



Sampling Site: CR 7N

### **Conceptual model for how SLR hydrology drives production**



## **Summary of SLR Peatland Work**

This preliminary data provides important insight regarding the complex Hg cycling and transport from restored peatland regions, but questions still exist regarding:

**Response Time**: how will Hg and MeHg concentrations respond (magnitude and timing) to restoration actions?

Water Quality and Water Management: how will MeHg and Hg concentrations change in relation to wetting/drying cycles and possible changes to sulfate/DOC inputs?

**Spatial Diversity**: are the patterns observed here specific to peatlands near Sax, MN or will other sites respond similarly?



### **Next Steps and Products**

**Other Ongoing and Related MN Mercury Projects:** 

- Conducting follow up work on the SLR Peatlands starting in Spring 2024, examining sources and methylation potential within restored peatlands (*with UMN*)
- > Completion and interpretive write-up of the St. Louis River AOC Hg study (*with EPA ORD*)
- Completion of inland lake study examining changes in Hg cycling due to invasive mussels (with UMN)

### **Data Products**

- Lake Superior Data Release (<u>https://doi.org/10.5066/P9W6I5EK</u>)
- St Louis River AOC Data (<u>https://doi.org/10.5066/P96HIBA4</u> & <u>https://doi.org/10.5066/P9EOTIR3</u>)
- St. Louis River Peatlands dataset available through NWIS (<u>https://waterdata.usgs.gov/nwis</u>)



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