Mercury Isotopes: A New Tool for Understand Mercury Sources and Cycling

USGS Mercury Research Lab

Upper Midwest Water Science Center

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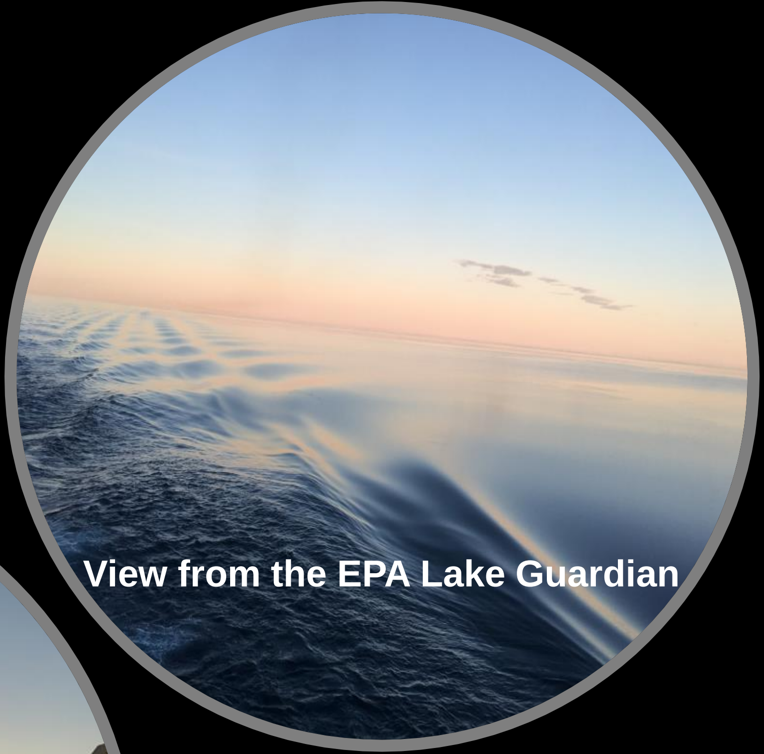


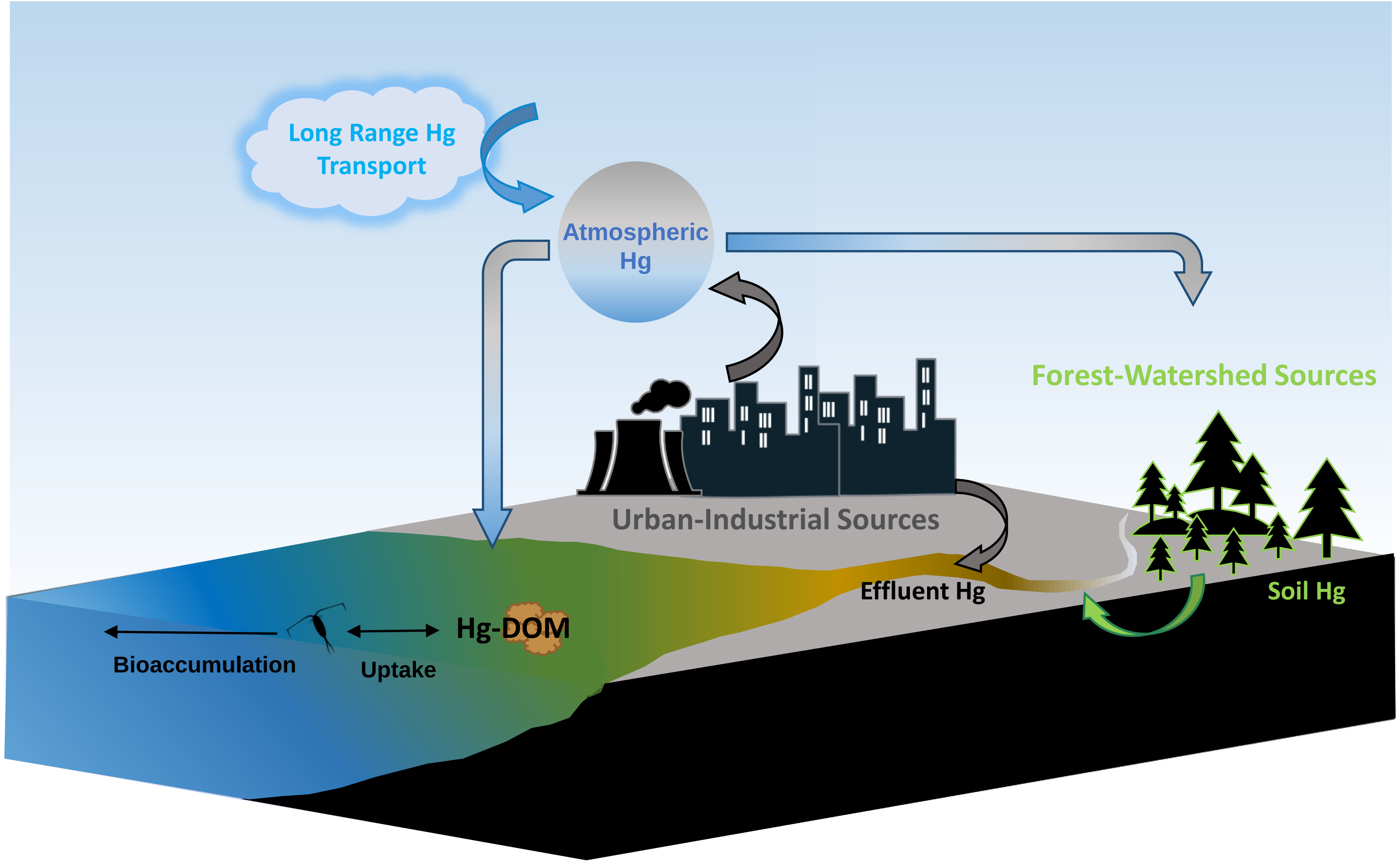
USGS science for a changing world

Great Lakes RESTORATION

wq-iw4-02j7

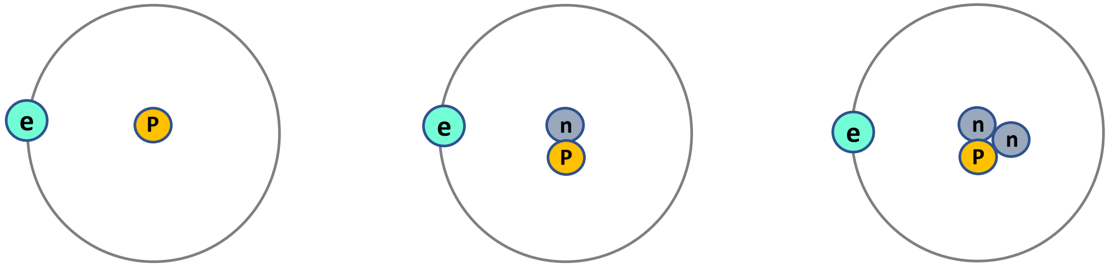
Mercury Sources in the Environment

Hg can enter the environment through multiple sources and in many cases, it is unclear which source is entering the food web



Using Isotopes to Resolve Sources

Hydrogen System



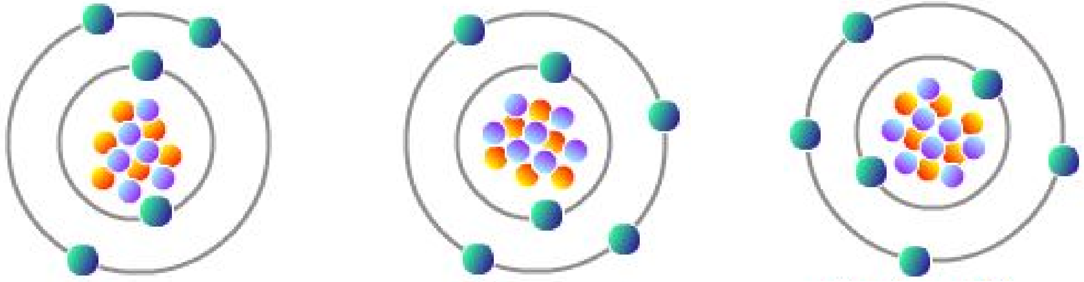
$^{1}_{1}H$ **Hydrogen** $^{2}_{1}H$ **Deuterium** — **Stable Isotopes**

$^{3}_{1}H$ **Tritium**

Unstable Isotope (half-life 12.3 years)

Same element, but different number of neutrons leading to a different atomic mass

Carbon System



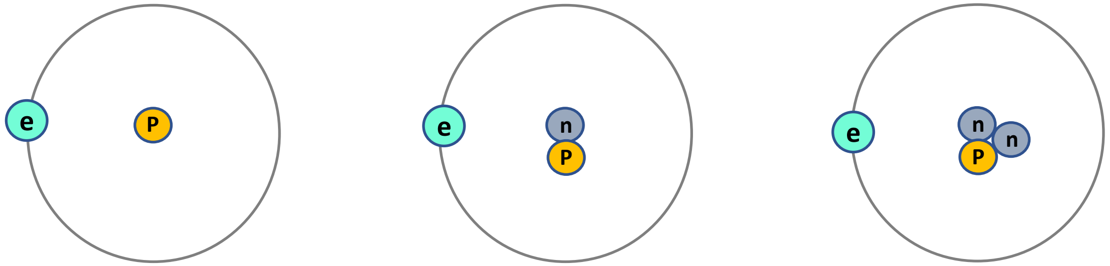
$^{12}_{6}C$ **Carbon-12** $^{13}_{6}H$ **Carbon-13** — **Stable Isotopes**

$^{14}_{6}H$ **Carbon-14**

Unstable Isotope (half-life 5,730 years)

Using Isotopes to Resolve Sources

Hydrogen System

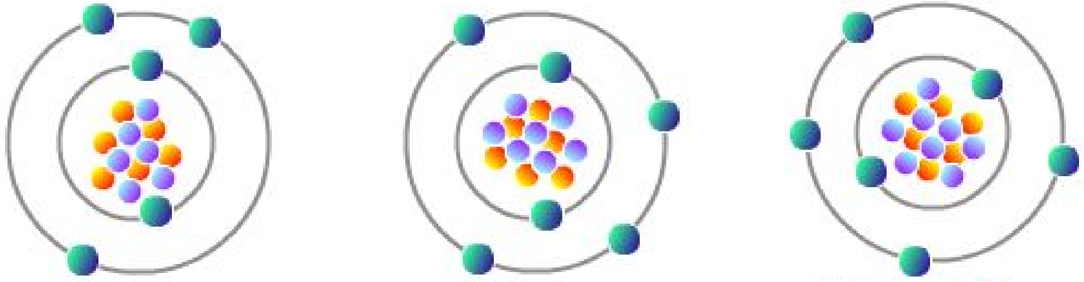


$^{1}_{1}H$ **Hydrogen** $^{2}_{1}H$ **Deuterium** $^{3}_{1}H$ **Tritium**

Stable Isotopes

Unstable Isotope (half-life 12.3 years)

Carbon System



$^{12}_{6}C$ **Carbon-12** $^{13}_{6}H$ **Carbon-13** $^{14}_{6}H$ **Carbon-14**

Stable Isotopes

Unstable Isotope (half-life 5,730 years)

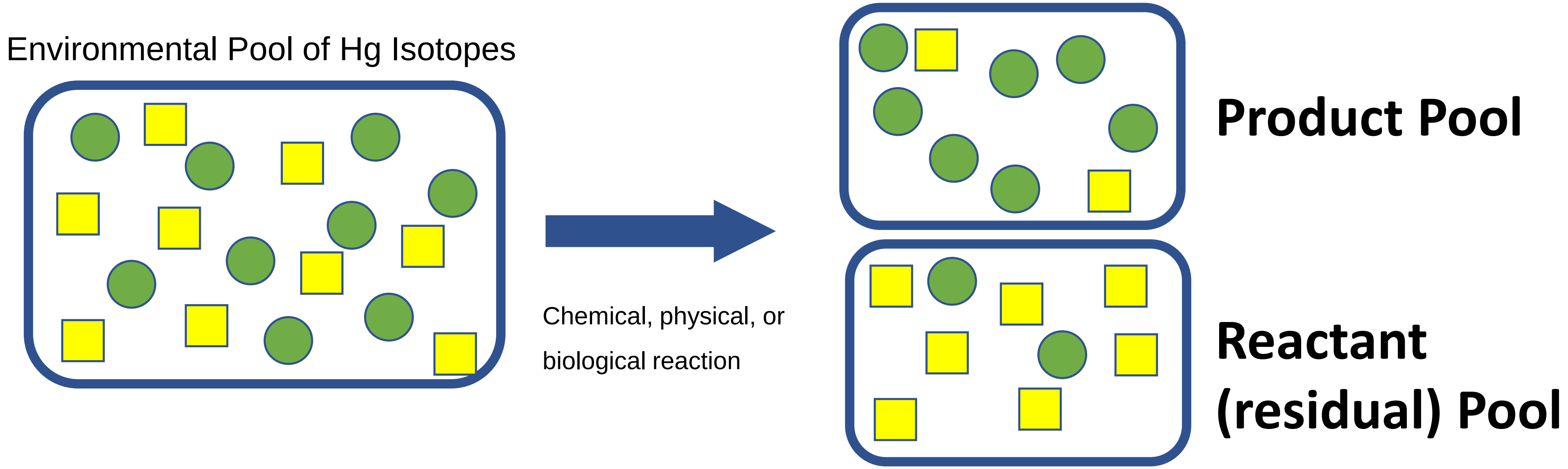
Mercury System

Hg Stable Isotopes	Abundances
^{196}Hg	0.16%
^{198}Hg	10.0%
^{199}Hg	16.9%
^{200}Hg	23.1%
^{201}Hg	13.2%
^{202}Hg	29.7%
^{204}Hg	6.8%

https://ciaaw.org/mercury.htm

Using Isotopes to Resolve Sources

Isotope fractionation: the process leading to a change in the abundance of individual isotopes (before and after a reaction, phase change, etc.…)



Mercury exhibits two types of fractionation:

- Mass-dependent fractionation (MDF)
- Mass-independent fractionation (MIF)

Using Isotopes to Resolve Sources

Hg Stable Isotopes	Abundances
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^{204}Hg	6.8%

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

Common Applications of Different Hg Isotopes

$\delta^{202}Hg$ → Source tracking

$\Delta^{199}Hg$, $\Delta^{201}Hg$ → Photochemistry

$\Delta^{200}Hg$, $\Delta^{204}Hg$ → Atmospheric Deposition

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

m = mass scaling factor

Using Isotopes to Resolve Sources

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

m = mass scaling factor

A multi-Hg isotope approach allows for different sources to be fingerprinted

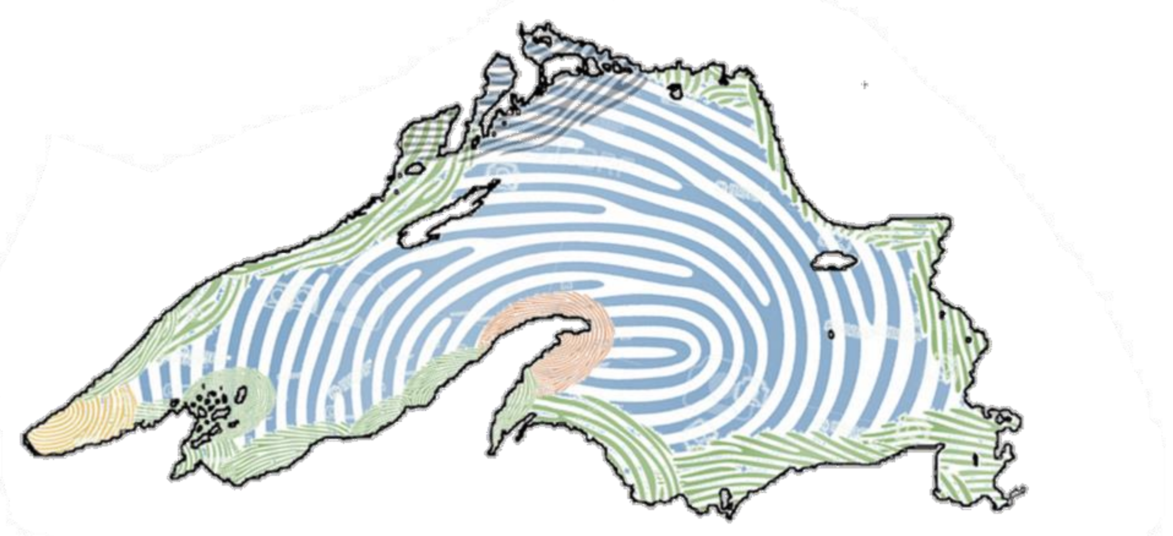
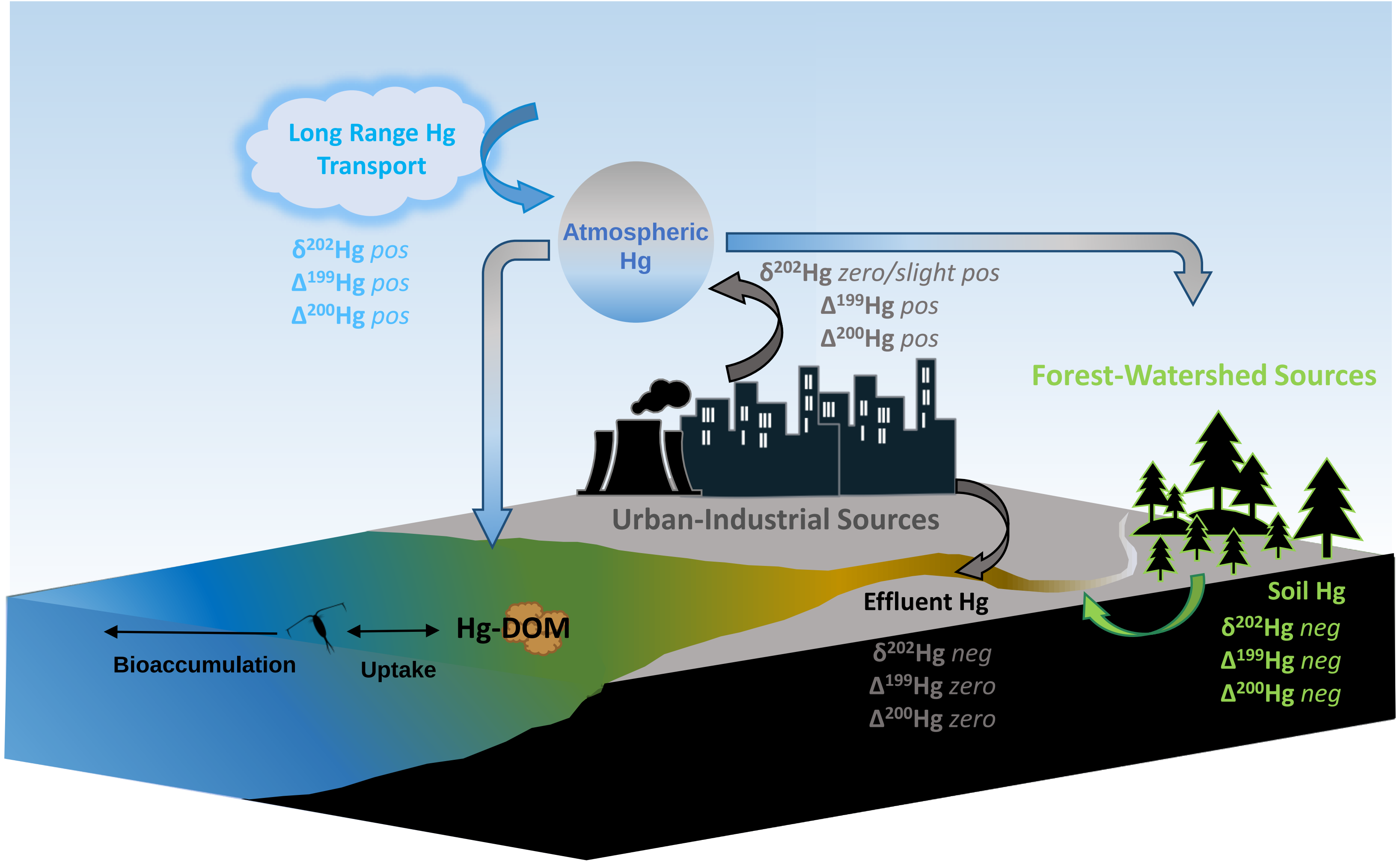


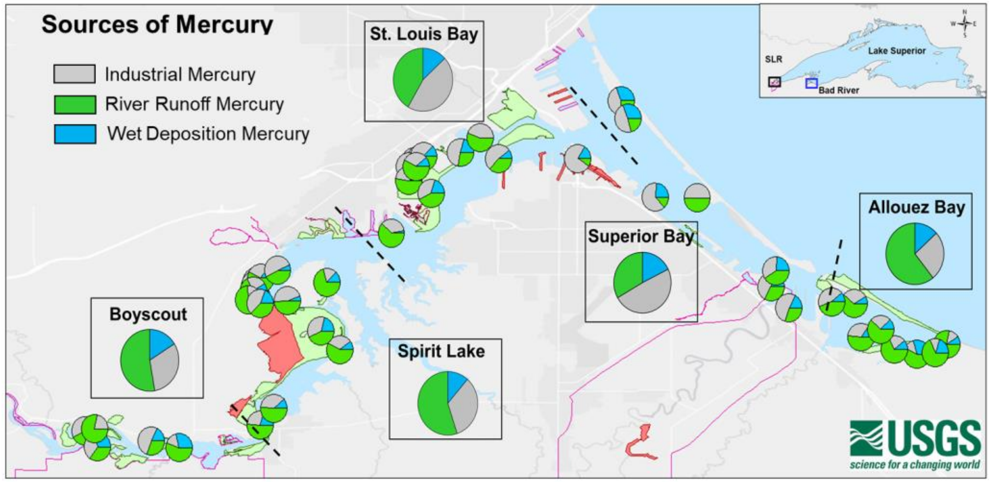
Image from Ryan Lepak (EPA)

Mercury Sources in the Environment

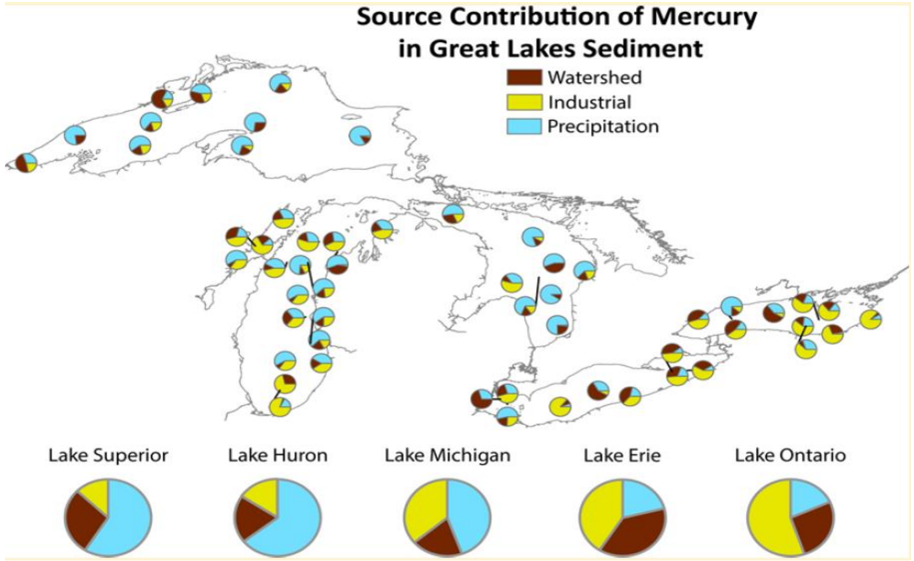
Hg can enter the environment through multiple sources and in many cases, it is unclear which source is entering the food web



Mercury Isotope Applications

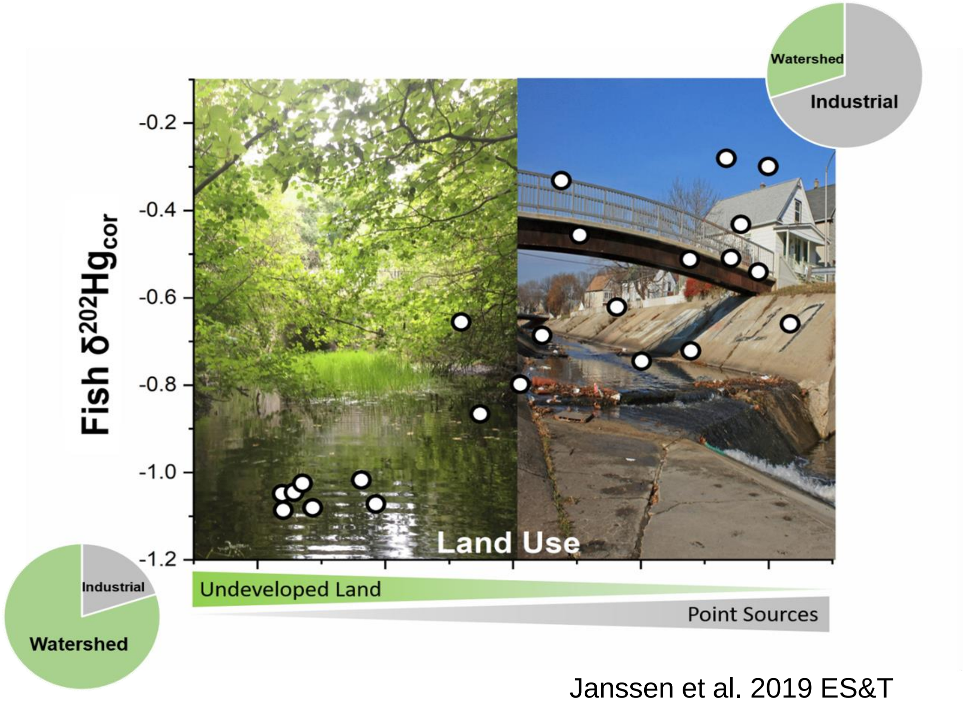


Janssen et al. 2021 STOTEN



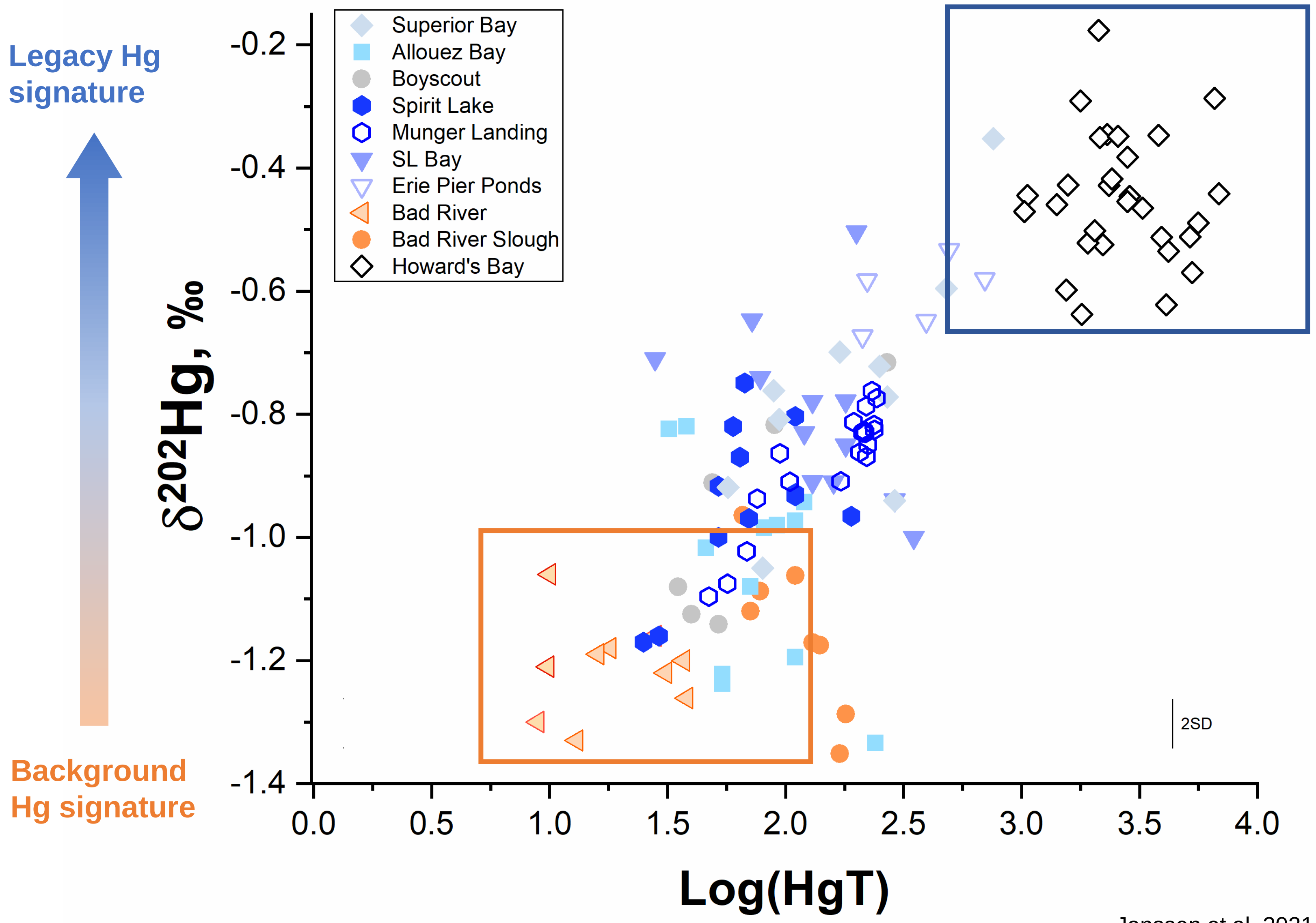
Lepak et al. 2015 ES&T Letters

These isotope tools have been used in regional and large-scale application within the Great Lakes to assess sources in sediments as well as in other parts of the nation to examine biological sources of Hg



Janssen et al. 2019 ES&T

Mercury Isotope Applications



Source attribution is obtained from examining the isotope gradient between sources

Two distinct mercury-source site conditions were identified with Hg isotopes in the St. Louis River:

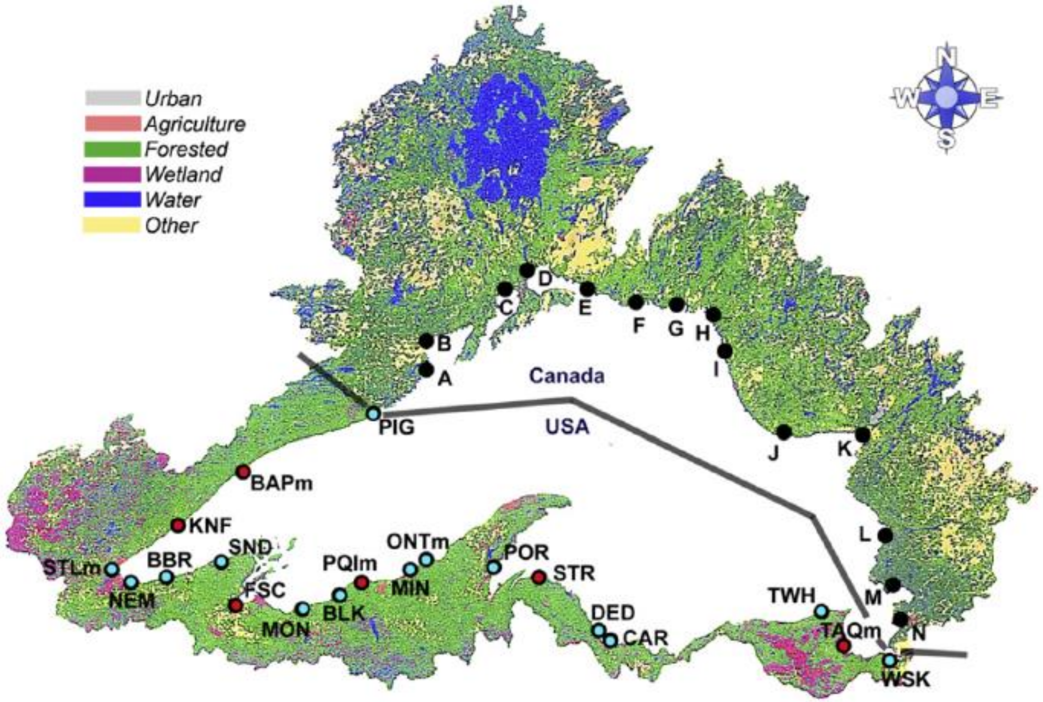
1. Legacy hotspots
2. Watershed run-off originating from atmospheric Hg deposition

Janssen et al. 2021 STOTEN

Sources of Mercury to Lake Superior

Hypothesis: Mercury sources from tributaries and atmospheric sources will differ, allowing for source attribution of Hg loads entering Lake Superior

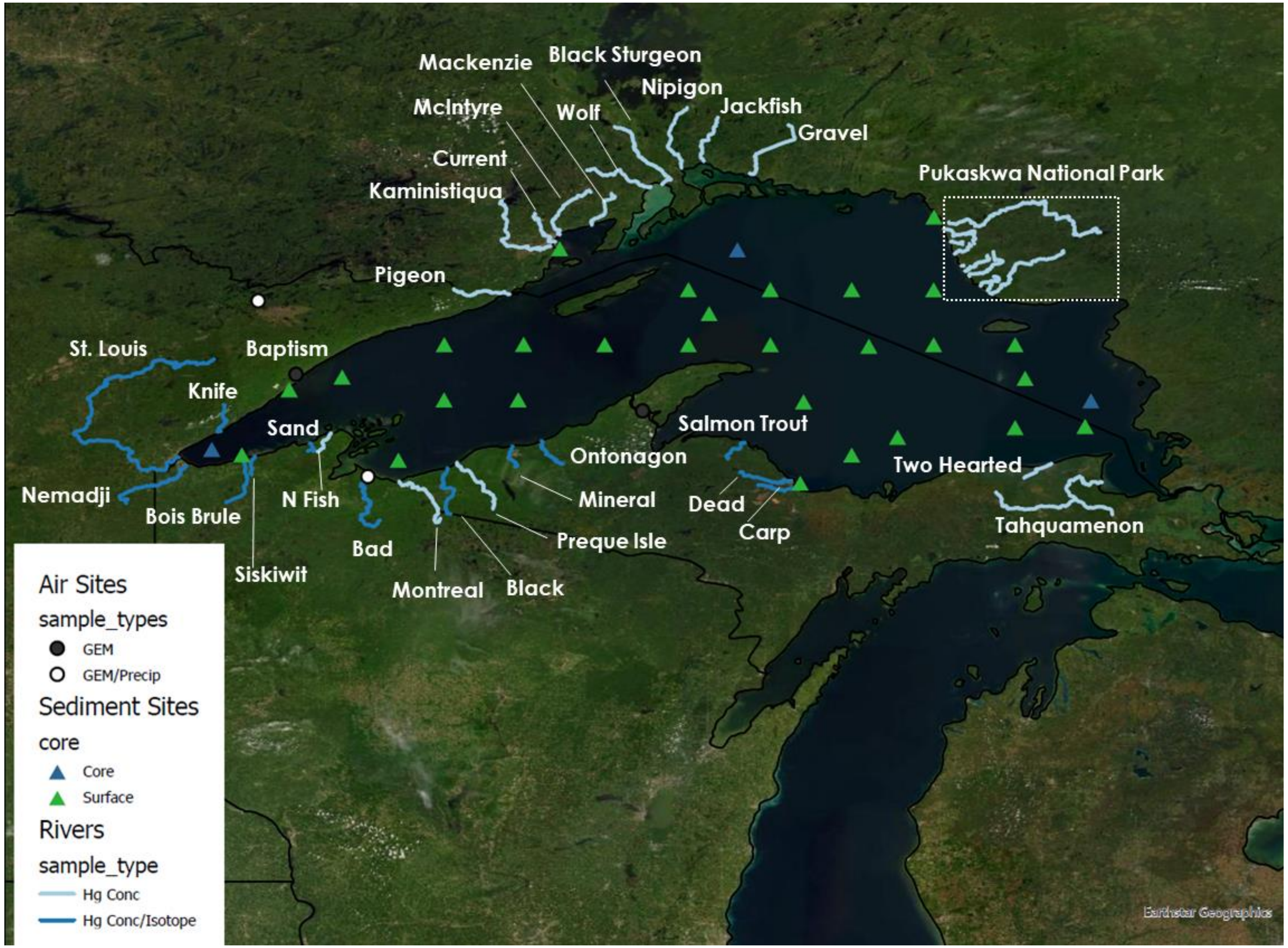
- Utilize Hg isotopes to identify source fingerprints in water, air, litterfall/soils, and sediments to assess the prominent sources of Hg to the lake



Basin	Area (km²)	Percent Land Use					Percent Soil Type				
		Forest	Farm	Wetland	Urban	Other	Sand	Clay	Peat	Loam	Other
USA	43,994	74.1	6.4	14.9	1.2	3.5	63.5	23.6	6.8	4.3	1.8
Canada	94,587	86.3	0.7	1.1	0.01	11.9	53.2	25.0	0.01	14.8	7.0
Sum/Ave	**138,581**	**82.4**	**2.5**	**5.5**	**0.4**	**9.2**	**56.5**	**24.5**	**2.2**	**11.4**	**5.4**

Babiarz et al. 2012 Environmental Pollution

Sources of Mercury to Lake Superior



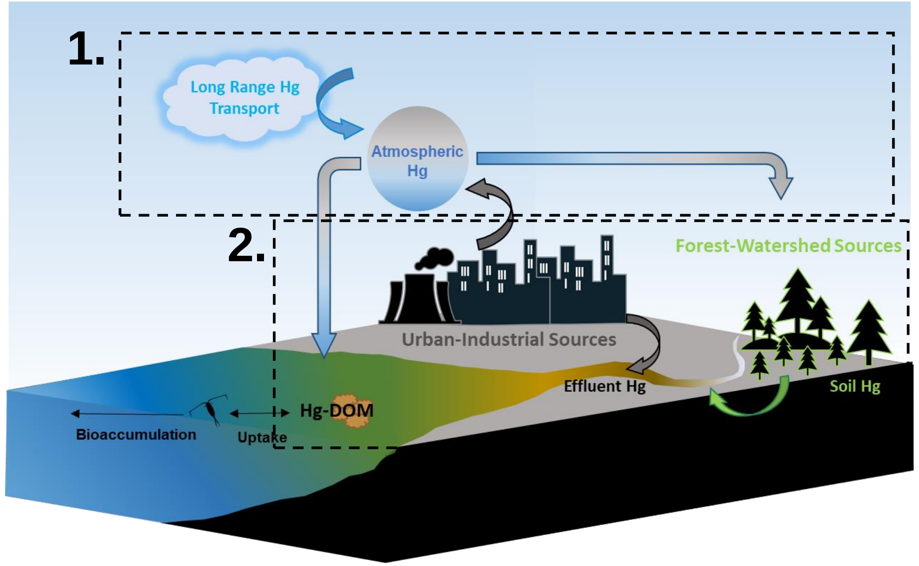
- 29 Tributaries sampled monthly for concentrations (USGS, Lakehead University, Lakehead region Conservation Authority)
- 10 Tributaries sampled twice in Pukaskwa National Park for concentrations (Parks Canada)
- 26 coring locations within Lake Superior
- Two Hg isotope intensives at 12 tributary sites
- 4 gaseous elemental Hg sites and 2 rainfall sites collected monthly

Sources of Mercury to Lake Superior

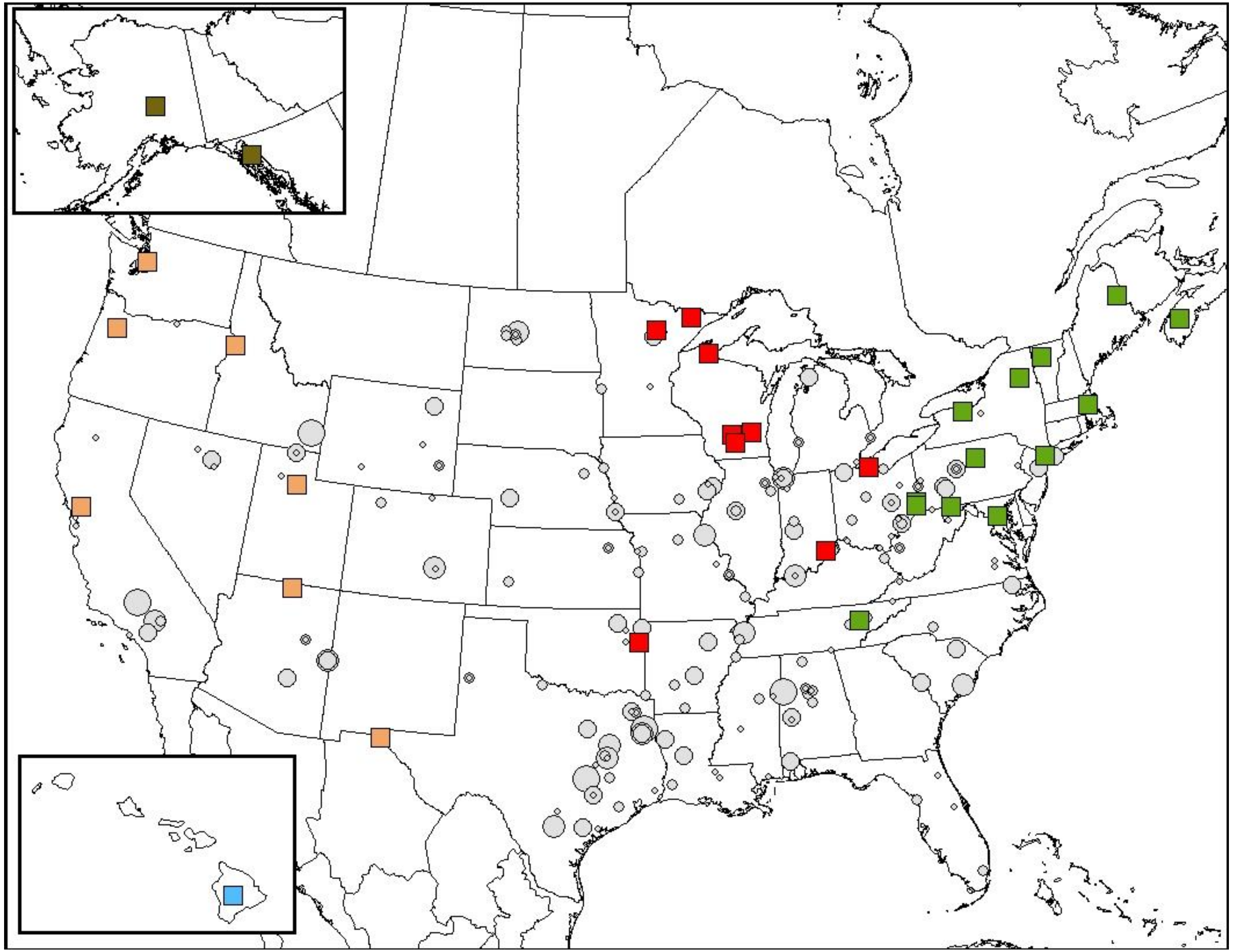
Source Identification in Lake Superior

1. **Assess Hg fingerprints in atmospheric endmembers of precipitation and gaseous elemental Hg**
   - Overview of National Survey and how Lake Superior data will be integrated

2. **Measure tributary water to differentiate urban/industrial, watershed, and atmospheric sources**
   - Preliminary tributary data from May 2021



What Can Air Hg Isotopes Tell Us?



Network of 32 sites across the U.S. sampled from May 2016-May 2018

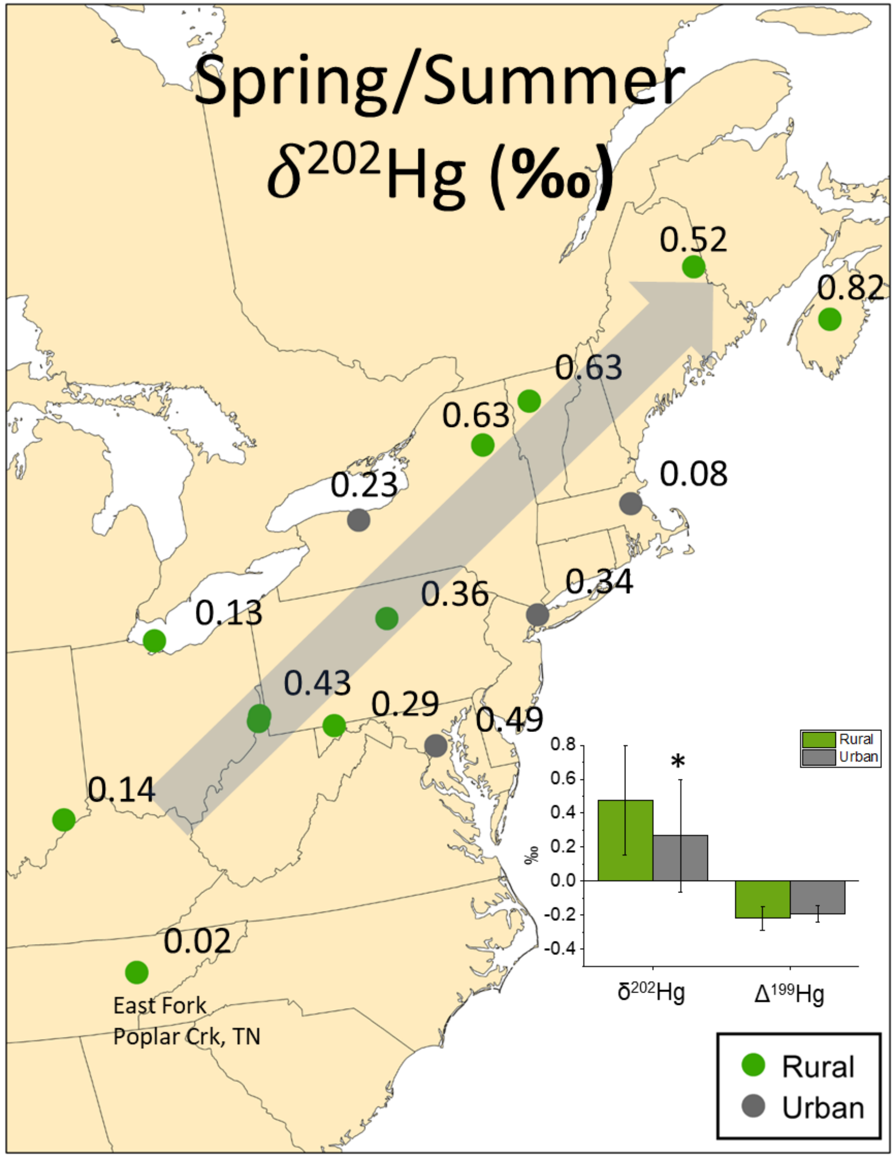
Targeting sites near regional emissions and sites removed from local/regional emissions

Legend

- NEI Emitters (scaled by size)
- Eastern Sites
- Midwest Sites
- Western Sites
- Alaska Sites
- Hawaii Site

National Emissions Inventory (NEI) :https://www.epa.gov/air-emissions-inventories/2017-national-emissions-inventory-nei-data

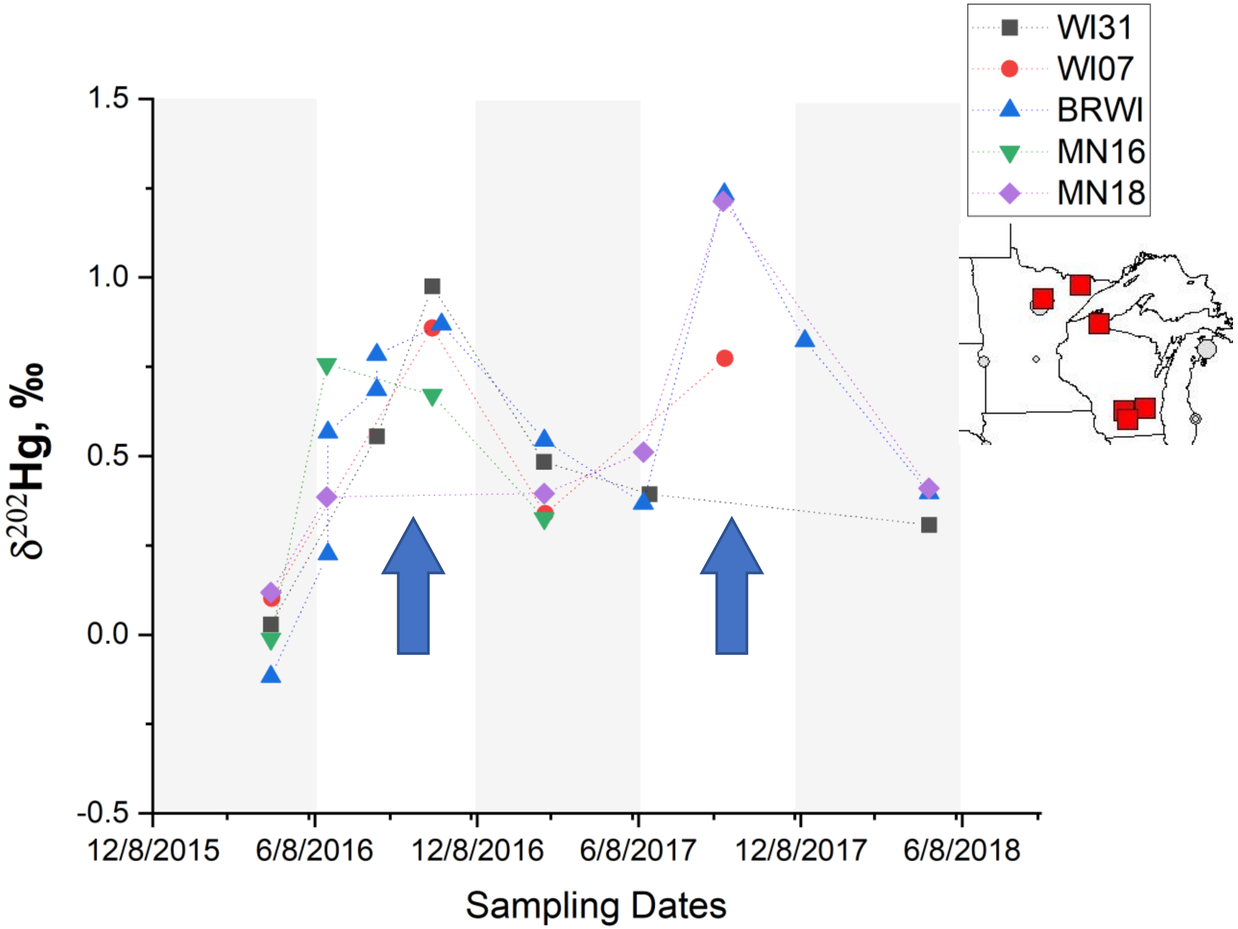
What Can Air Hg Isotopes Tell Us?



- Previous atmospheric Hg isotope work has demonstrated that background Hg can be distinguished from regional or local sources in the Northeastern US

- Rural and urban areas are shown to be significantly different in Hg source

What Can Air Hg Isotopes Tell Us?

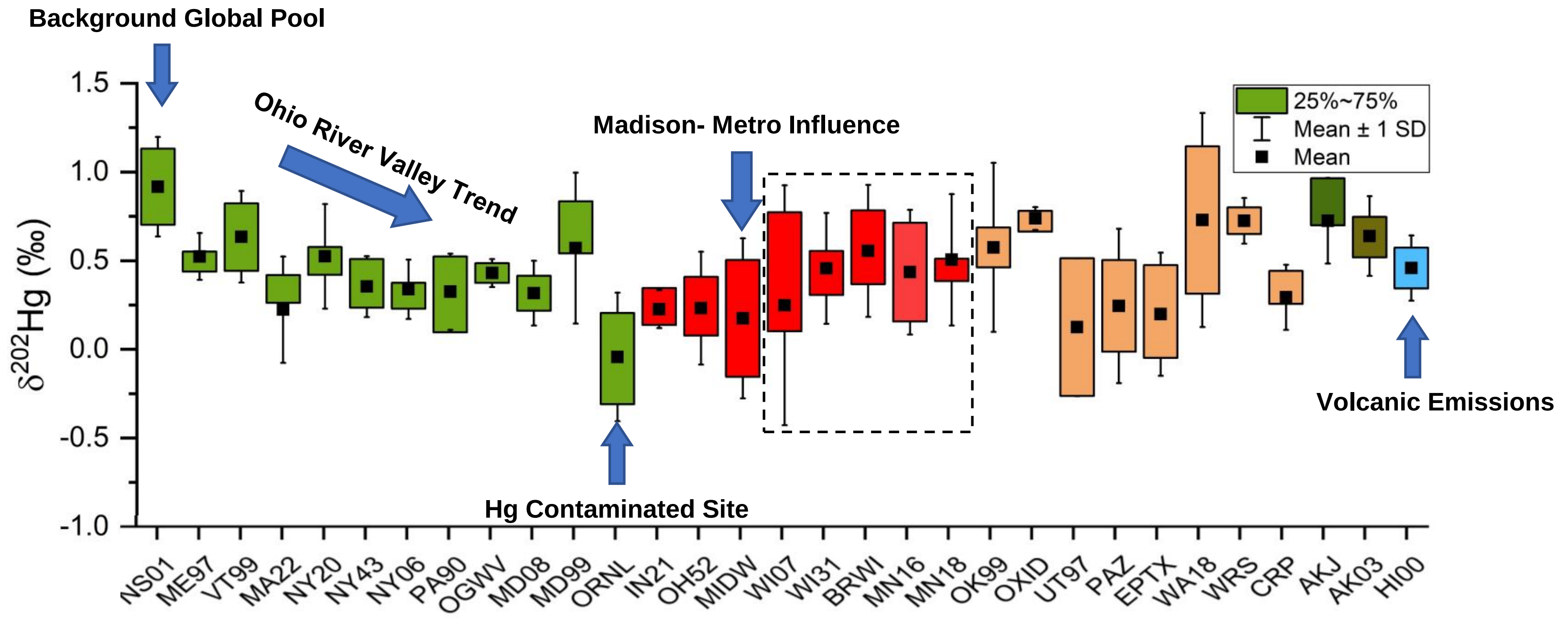


- Atmospheric sources are variable, the isotope fingerprint of gaseous elemental Hg can change over the course of the season

- This counters the idea of a universal source pool in the atmosphere, and suggest regional sources including regional emissions or even soil remissions can play a role

- There can also be repeating trends in the data (arrows on graph)

What Can Air Hg Isotopes Tell Us?



- The overarching trends develop when examining data on a national scale
- Sites near urban, industrial, or geologic sources tended to have lower isotope values
- Sampling near Nova Scotia showed the highest value, and was originally selected to be a “global” atmospheric source site

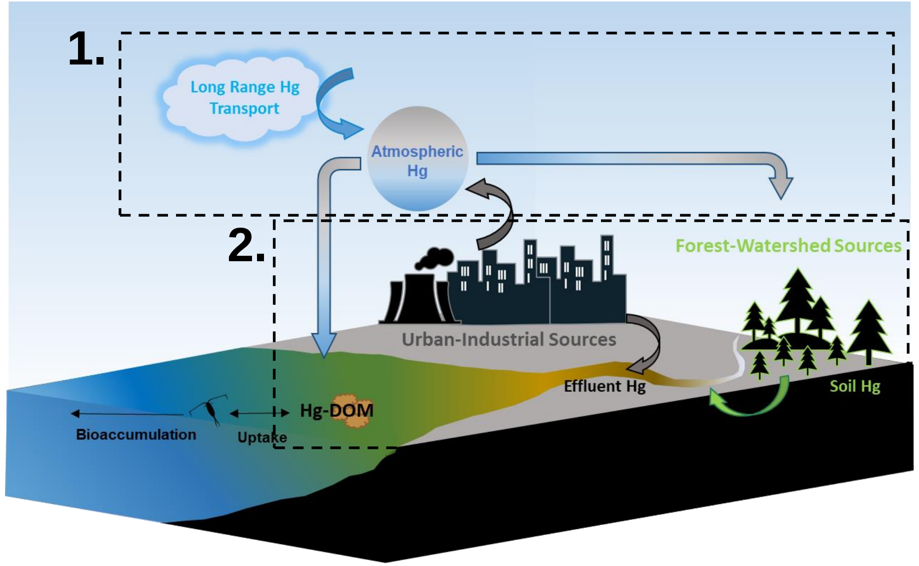
Sources of Mercury to Lake Superior

Source Identification in Lake Superior

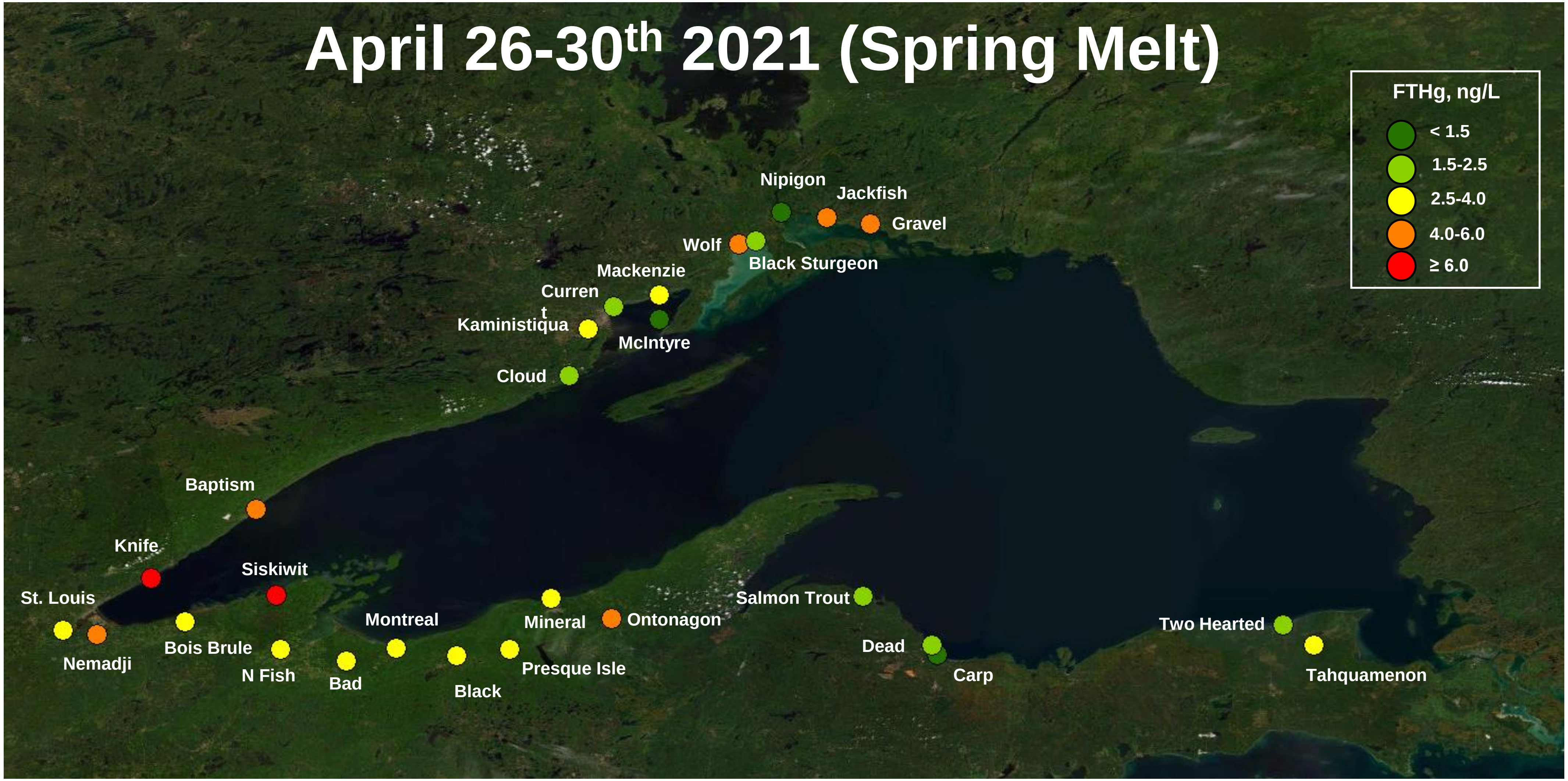
1. **Assess Hg fingerprints in atmospheric endmembers of precipitation and gaseous elemental Hg**

- Previous atmospheric Hg isotope work has demonstrated that background Hg can be distinguished from regional or local sources in the Northeastern US
- Atmospheric sources of Hg shift seasonally, already observed in the Lake Superior airshed
- There are overarching national trends in Hg atmospheric sources that will allow us to put new air and precipitation data into context

2. **Measure tributary water to differentiate urban/industrial, watershed, and atmospheric sources**

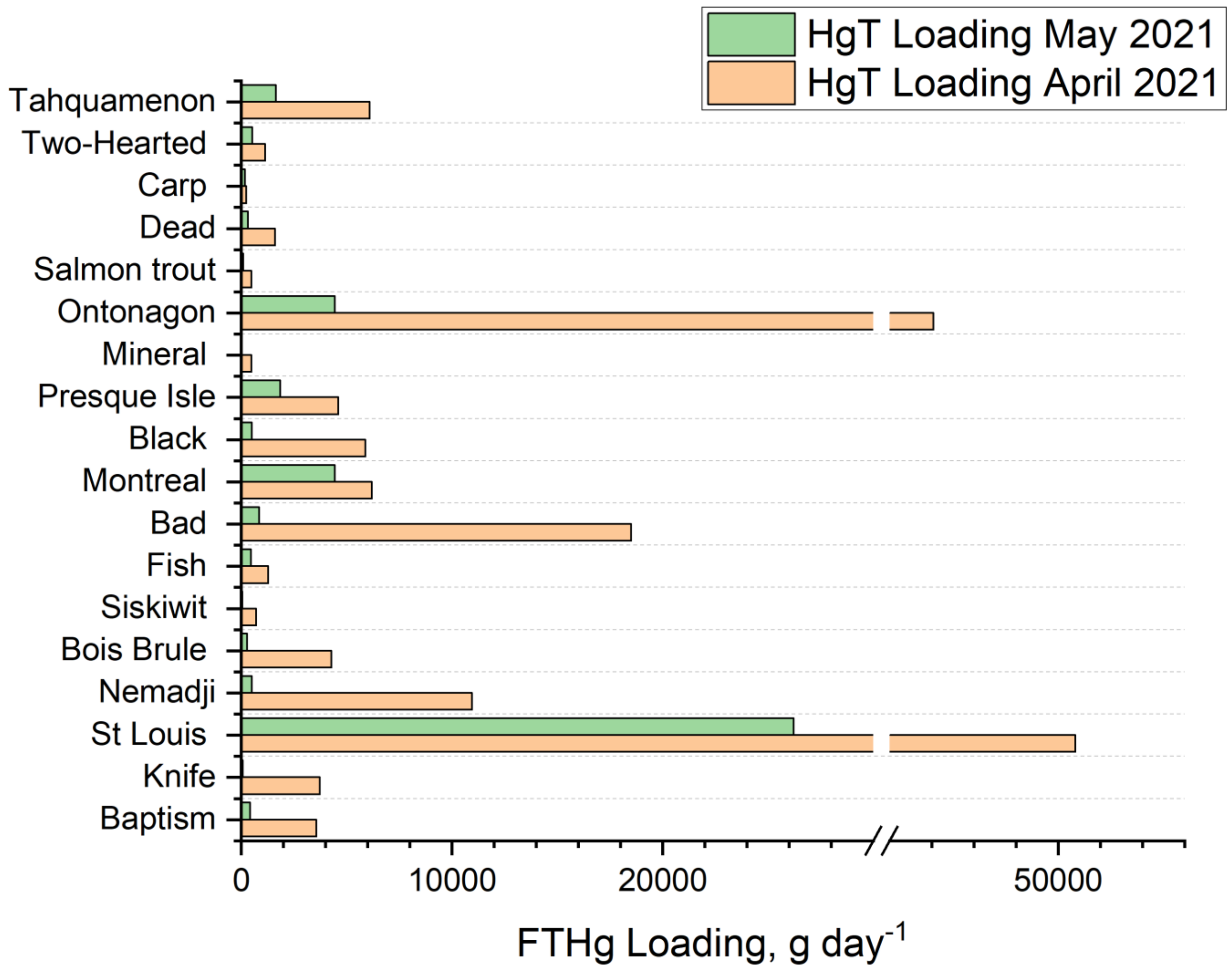


Tracking Sources in Tributaries



Preliminary Information-Subject to Revision. Not for Citation or Distribution.

Tracking Sources in Tributaries



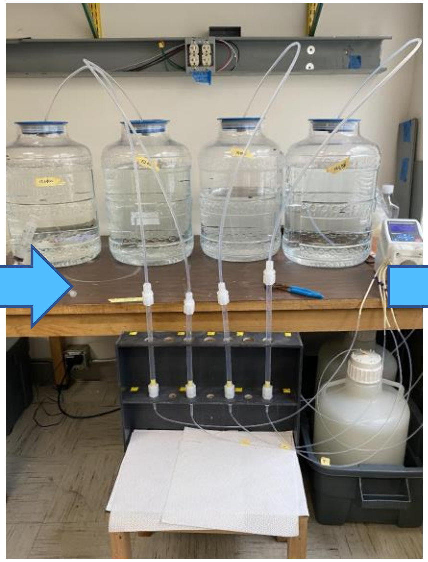
- Loads of Hg entering Lake Superior vary monthly
- Spring melt brings large amounts of Hg from upstream regions usually tied to dissolved organic carbon
- We are unsure if these sources are related to overland runoff or direct atmospheric sources such as more recent snow and rainfall

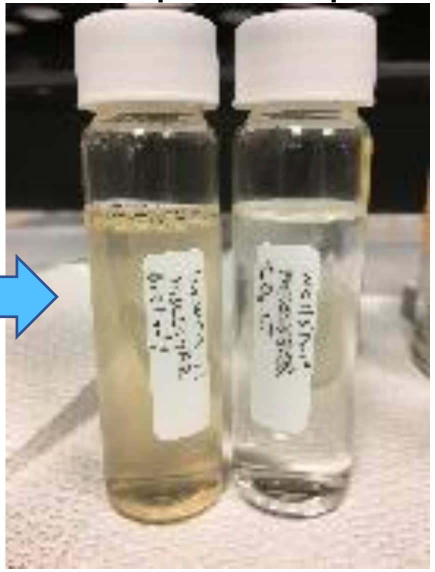
What Can Source Tracking in Water Tell Us?

Waters are a new and challenging frontier for Hg isotopes!

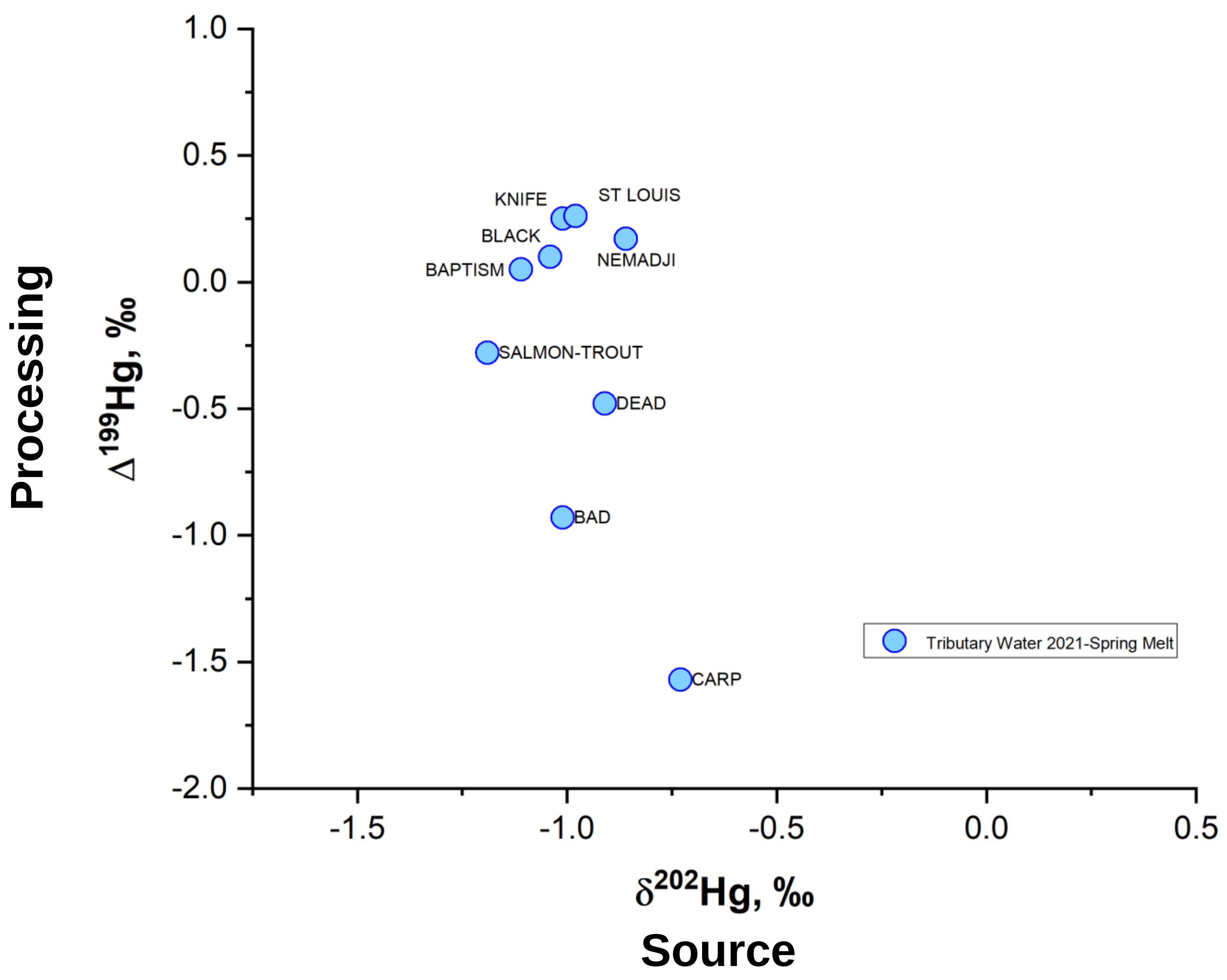
This gives us the ability to look at sources actively being delivered to Lake Superior rather than just the past accumulation (e.g., sediments)

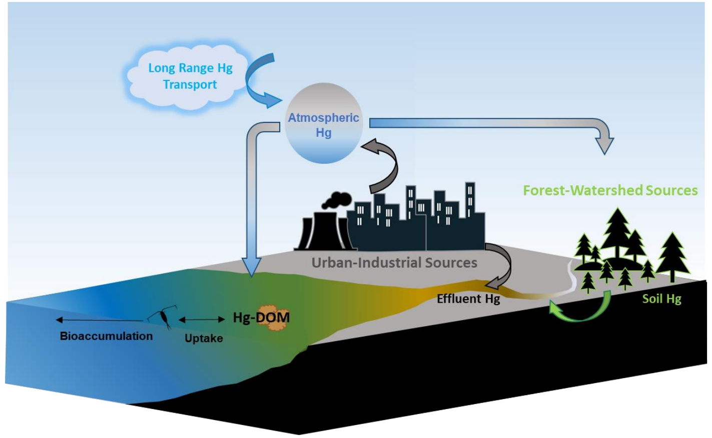
20 L per sample → 10 mL per sample





What Can Source Tracking in Water Tell Us?





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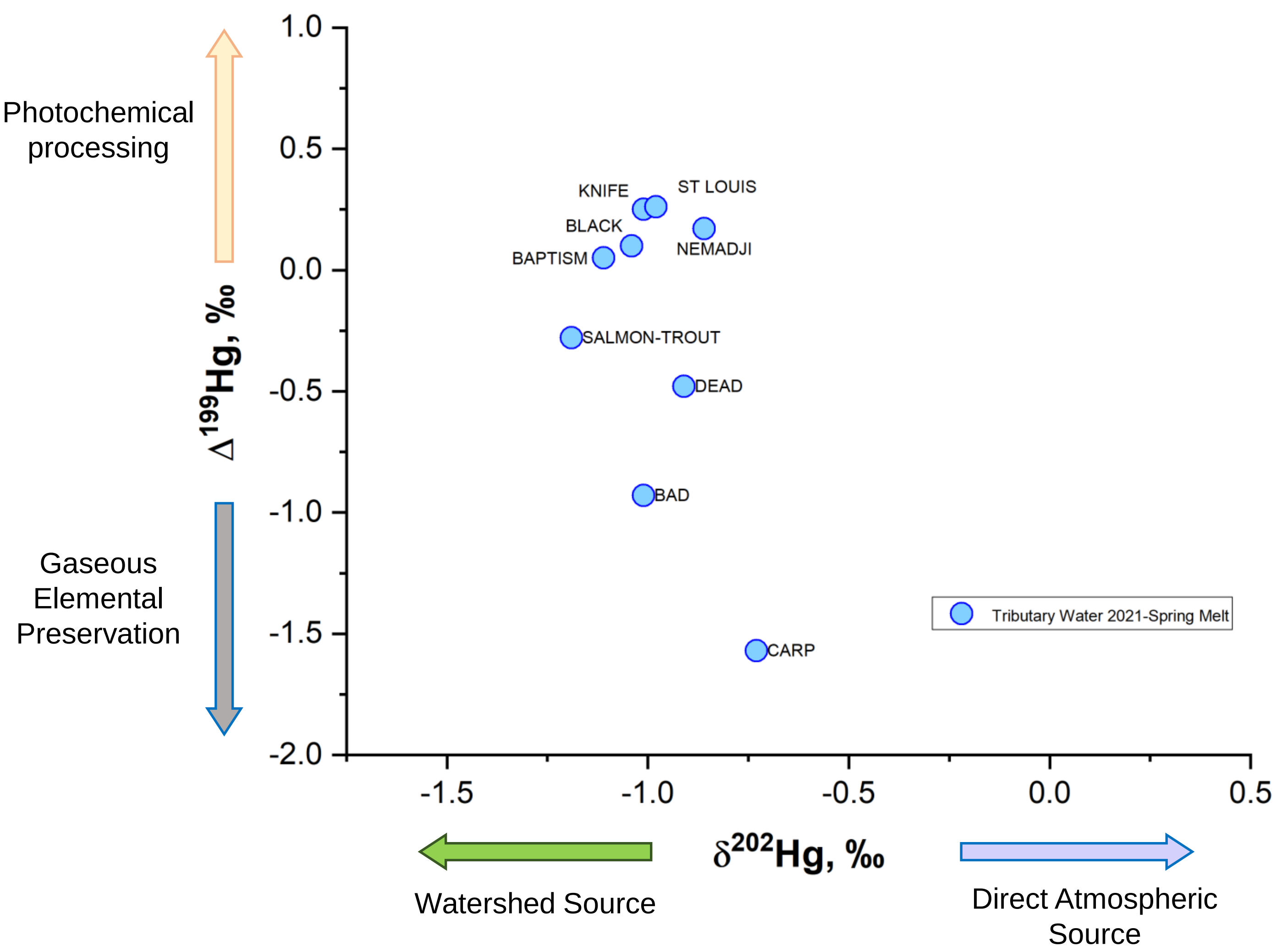
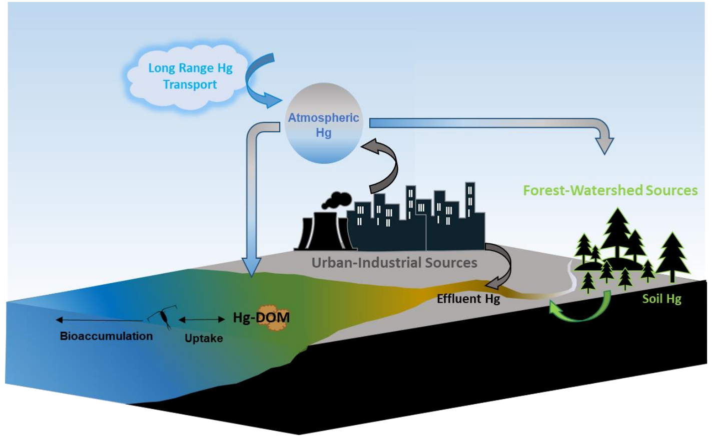
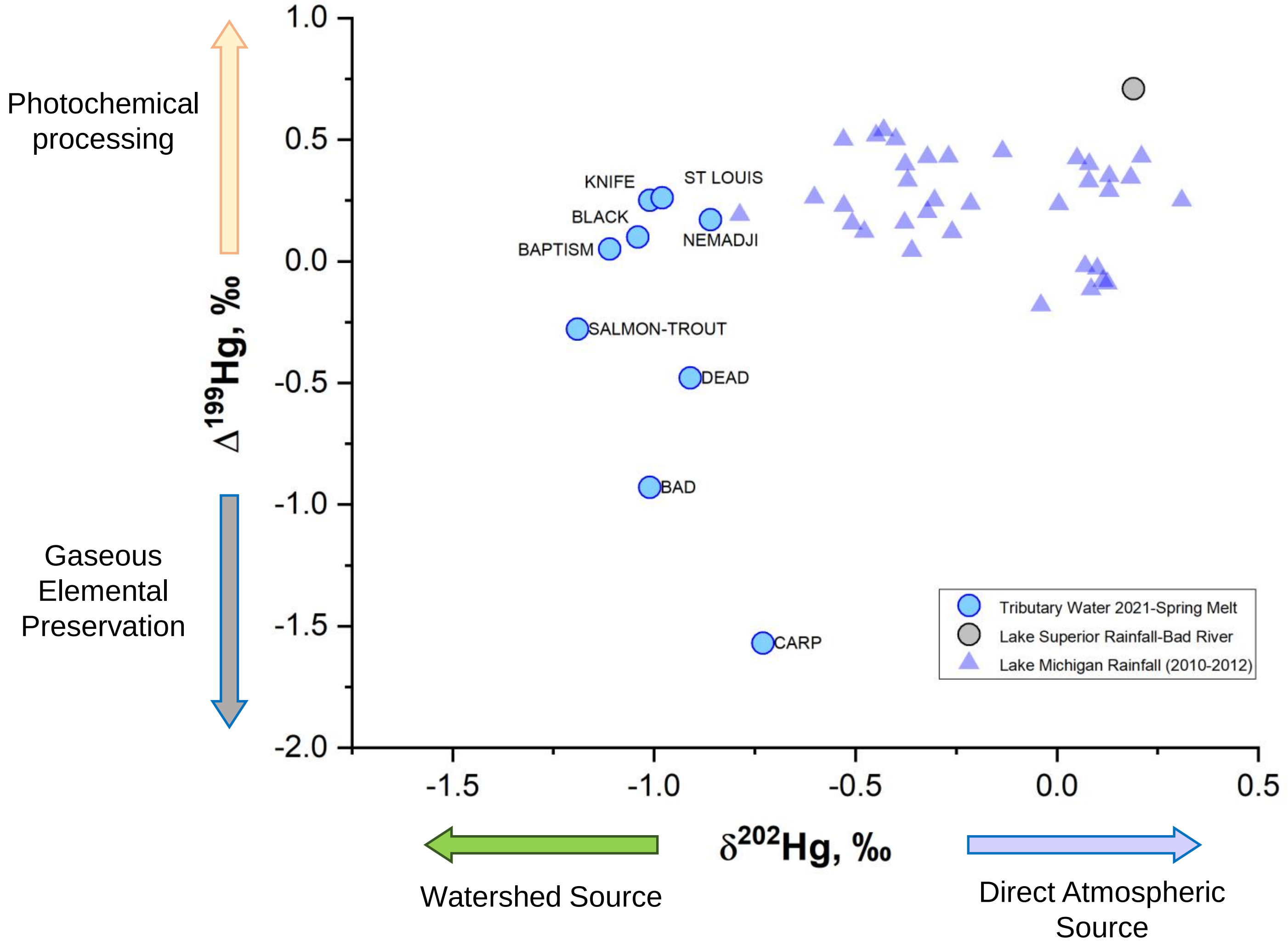
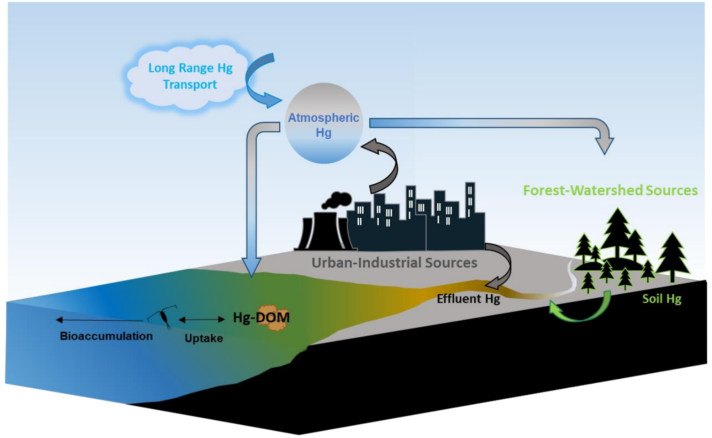




Samples show a similar source, but a different amount of “processing”, which may be related to site specific conditions or age of the Hg source

What Can Source Tracking in Water Tell Us?





Initial isotope analysis of waters indicate “new” Hg sourced from precipitation does not overlap with surface water values

Precipitation Data:
Sherman et al. 2012
Gratz et al. 2010

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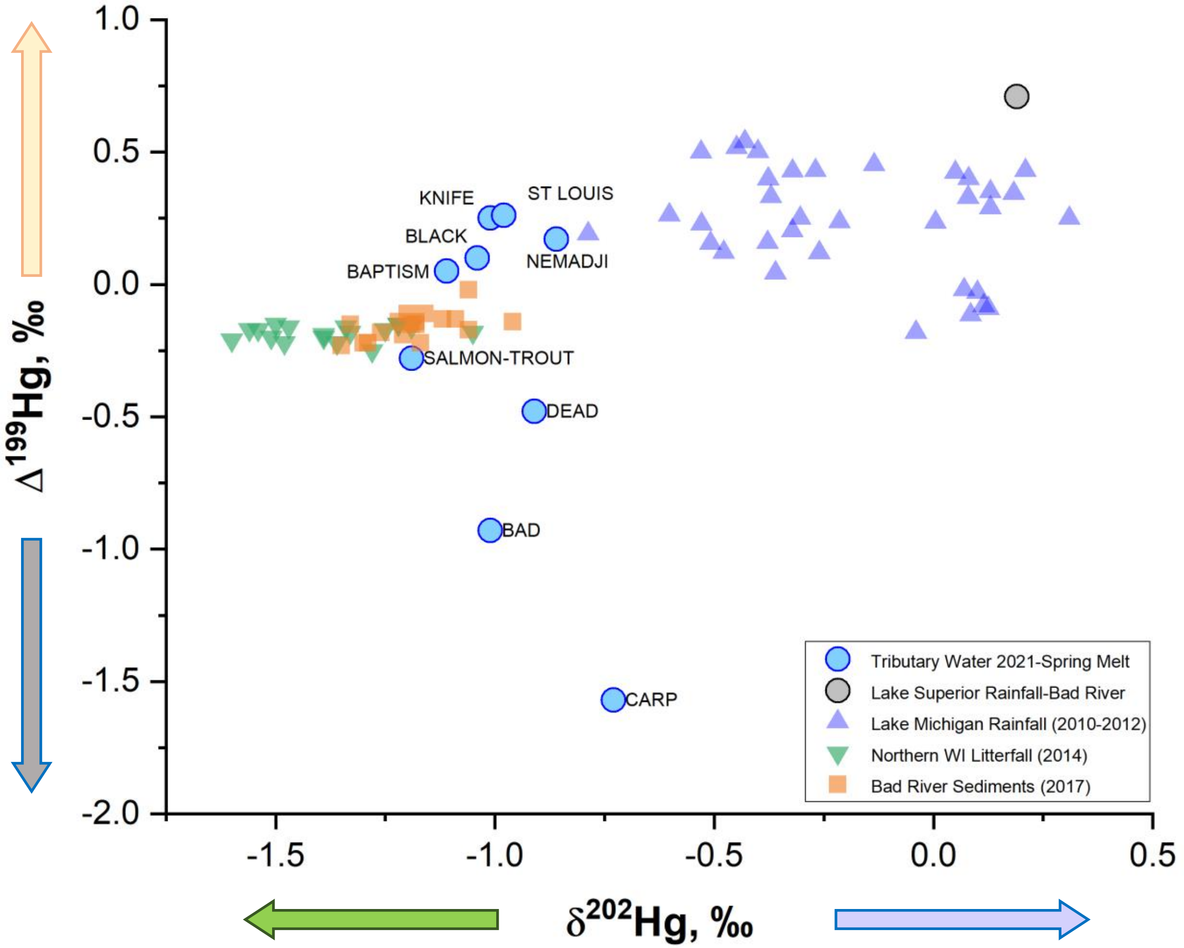
What Can Source Tracking in Water Tell Us?

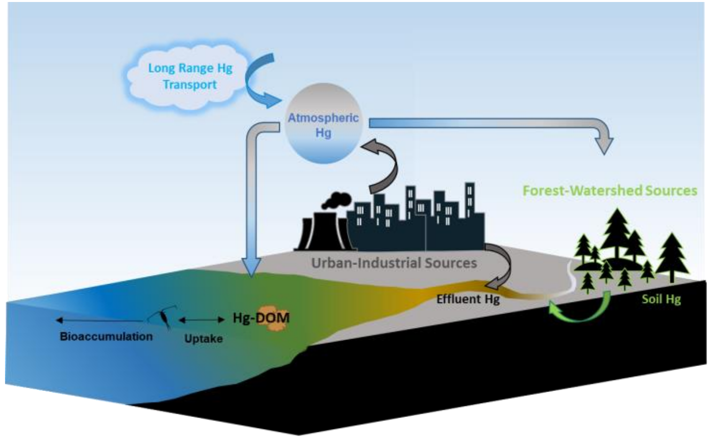
Photochemical processing

Gaseous Elemental Preservation



Watershed Source

Direct Atmospheric Source



Source indicators overlap with measurements of sediments from the Bad River (known to be watershed derived) and leaf litter samples from northern WI

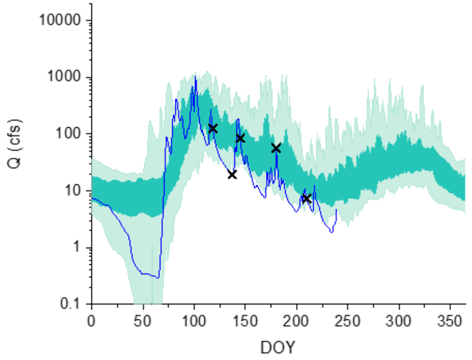
Precipitation Data:
Sherman et al. 2012
Gratz et al. 2010

Litterfall Data:
Demers et al. 2013

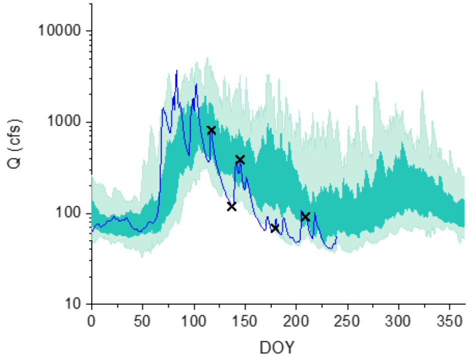
What Can Source Tracking in Water Tell Us?

When interpreting the data, we need to be mindful that this is not a typical flow year

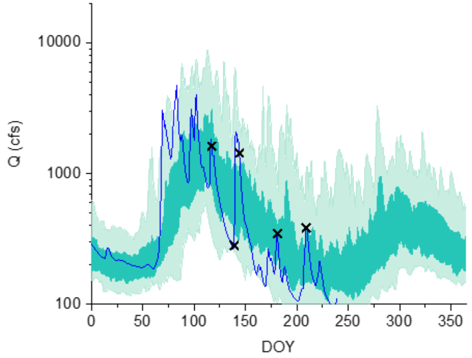
KNIFE RIVER NEAR TWO HARBORS, MN



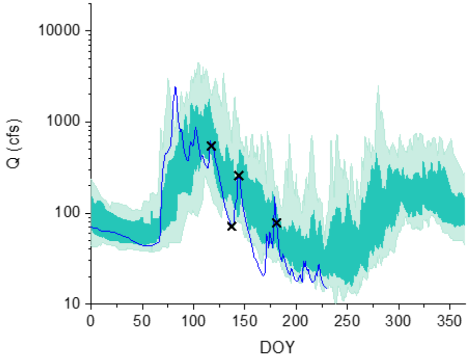
NEMADJI RIVER NEAR SOUTH SUPERIOR, WI



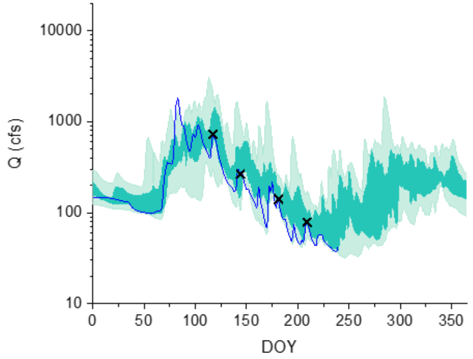
BAD RIVER NEAR ODANAH WI



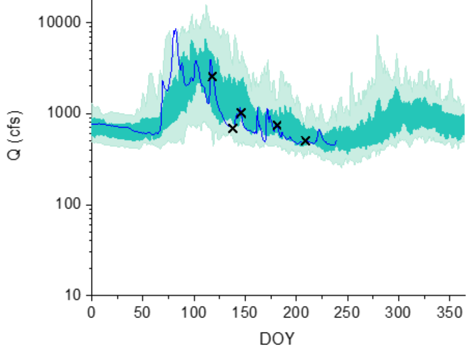
BLACK RIVER NEAR BESSEMER, MI



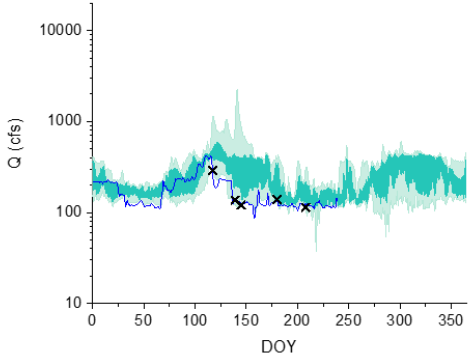
PRESQUE ISLE RIVER NEAR TULA MI



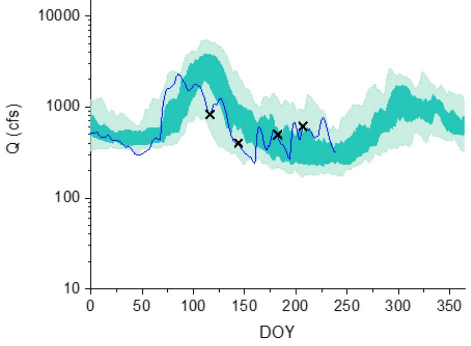
ONTONAGON RIVER NEAR ROCKLAND, MI



DEAD RIVER AT MARQUETTE, MI



TAHQUAMENON RIVER NEAR PARADISE, MI



Dark Blue Line- 2021 flows
Dark Teal Fill- 25th percentile of flow conditions for all measurements years
Light Teal Fill- 75th percentile of flow conditions for all measurement years

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Data adapted from USGS NWIS Realtime gage data : https://waterdata.usgs.gov/nwis/rt

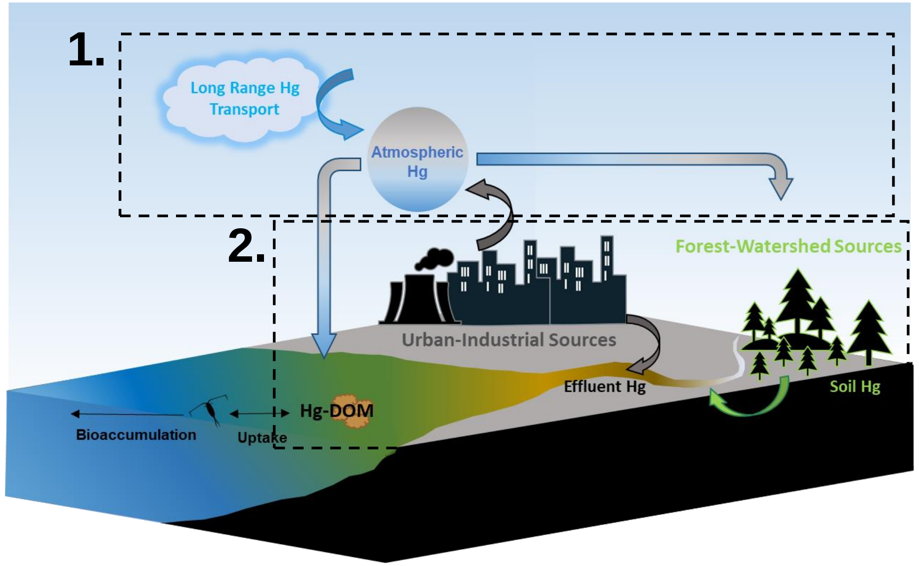
Sources of Mercury to Lake Superior

Source Identification in Lake Superior

1. **Assess Hg fingerprints in atmospheric endmembers of precipitation and gaseous elemental Hg**

2. **Measure tributary water to differentiate urban/industrial, watershed, and atmospheric sources**

- Hg loads to Lake Superior are highest during spring melt, these also show some high filtered water concentrations
- Preliminary Hg isotopes suggest tributary sources are driven by watershed Hg rather than newer atmospheric deposition, potential influence of Hg age or groundwater sources need to be further assessed.
- Due to the low rainfall and snowpack this year it is unclear if this source dominates Hg delivery in more typical flow years



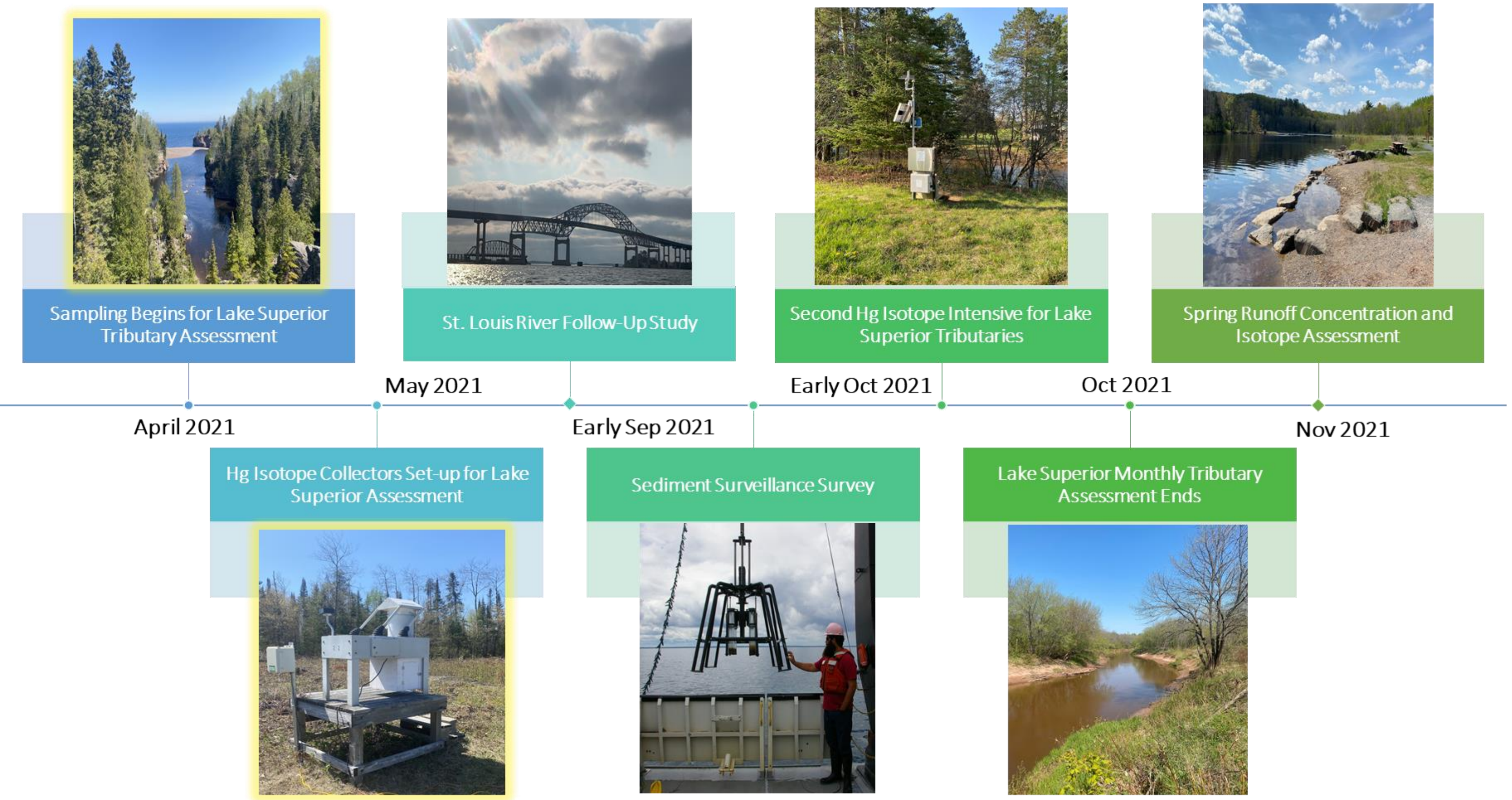
Conclusions

1. These Hg isotope tracers are proven tools for differentiating Hg sources in the environment and have been successfully applied to sediments and biota in the Great Lakes region

2. New applications for gaseous elemental Hg in the atmosphere demonstrate the ability to separate global background pools from mixed regional pools. These also show that source profiles can vary across seasons, indicating shifting sources

3. Analysis of Hg isotopes in waters from Lake Superior tributaries indicate that watershed sources dominate in spring runoff, follow up work is needed to fully characterize the source profile

Future Work and Acknowledgments



Great Lakes RESTORATION

Canada

Canada

LAKEHEAD REGION CONSERVATION AUTHORITY

Lakehead UNIVERSITY

FOREST SERVICE U S DEPARTMENT OF AGRICULTURE

References

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