Remediating mercury-contaminated sediment sites

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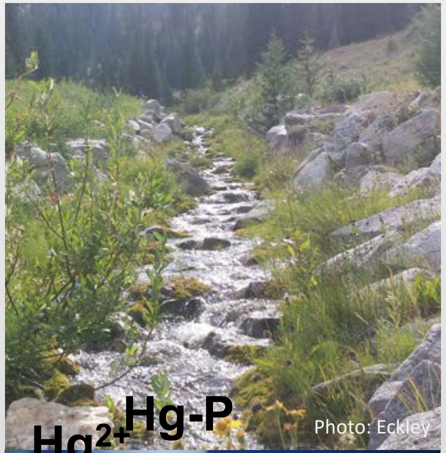
Introduction: Mercury Pollution

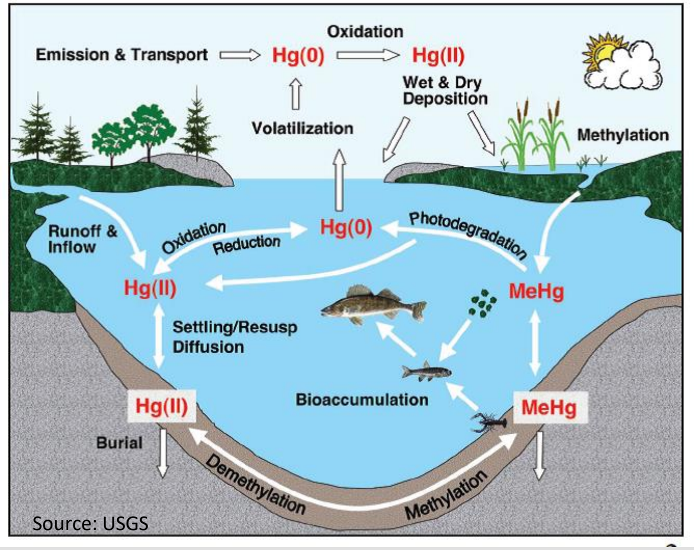
Mercury Releases



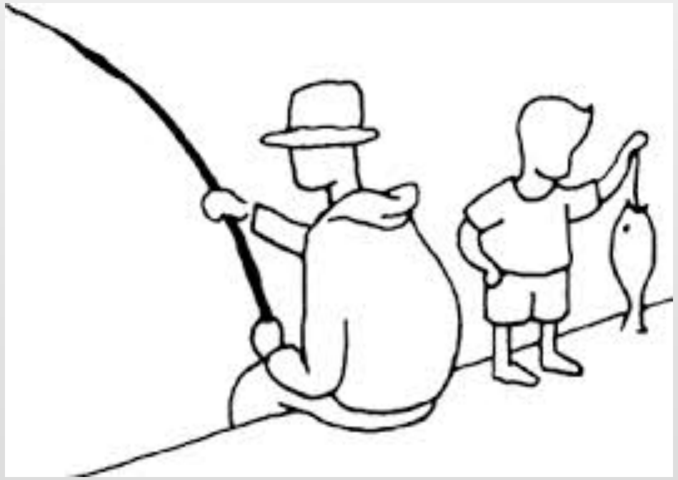
Hg-P
Hg^{2+}
Hg^{0}

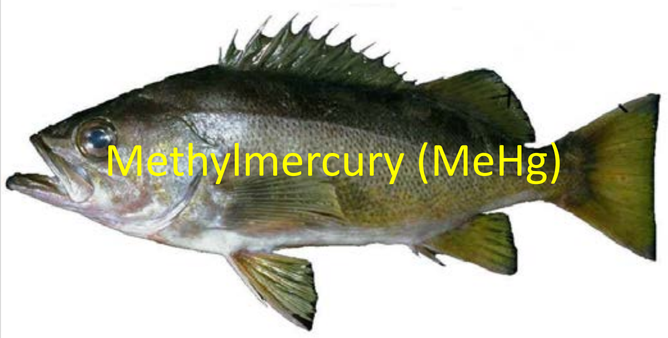
Mercury in the Environment

Transport, Methylation, Bioaccumulation

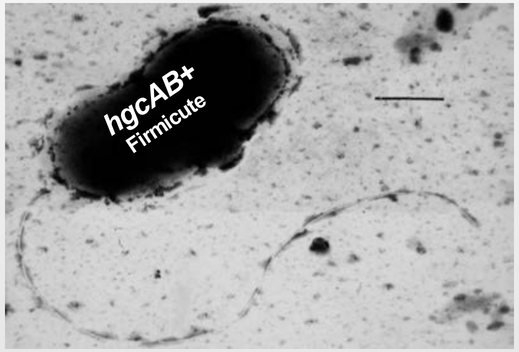


Mercury Exposure





Introduction: Methylmercury (MeHg)



How is Hg methylated? **Methylation is a microbial process**

- Many Sulfate Reducing Bacteria
- Some Iron Reducing Bacteria
- Some Methanogens

Where is Hg methylated? **Occurs under anoxic conditions**

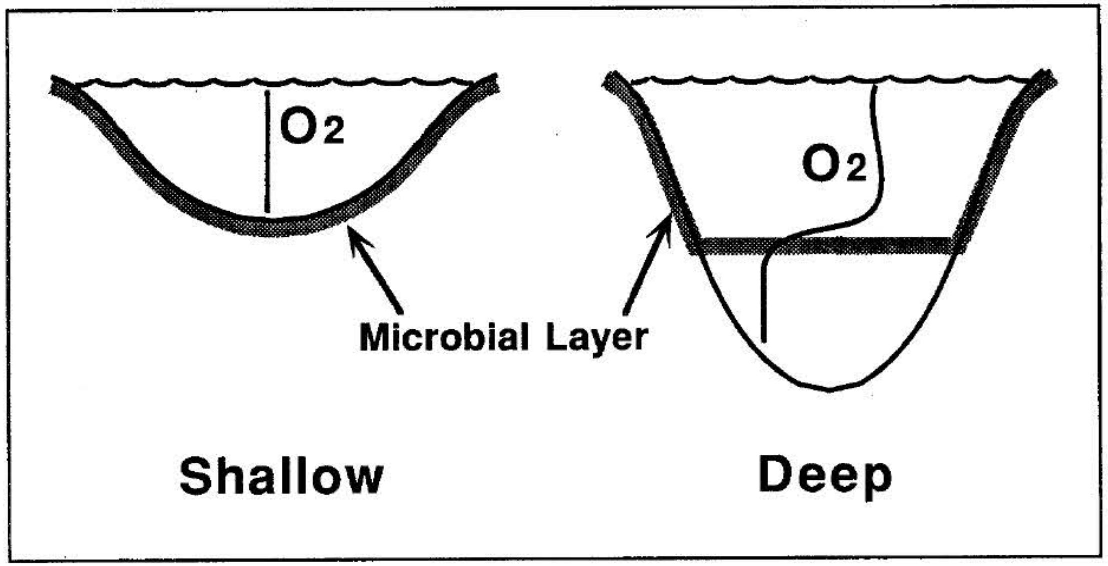
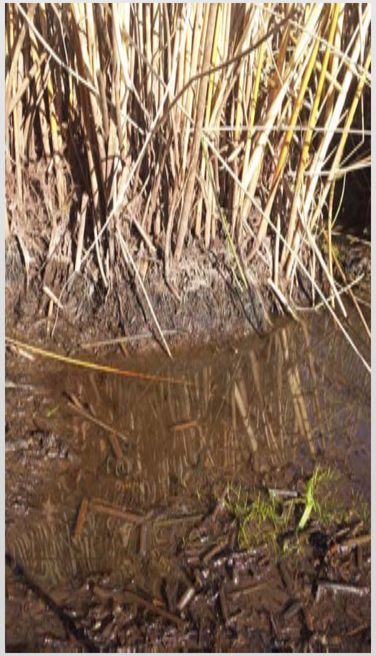


Fig. 4. Location of biogeochemically active microbial layer in shallow, well-mixed and deep, stratified lakes.

Source: Watras et al, 1995



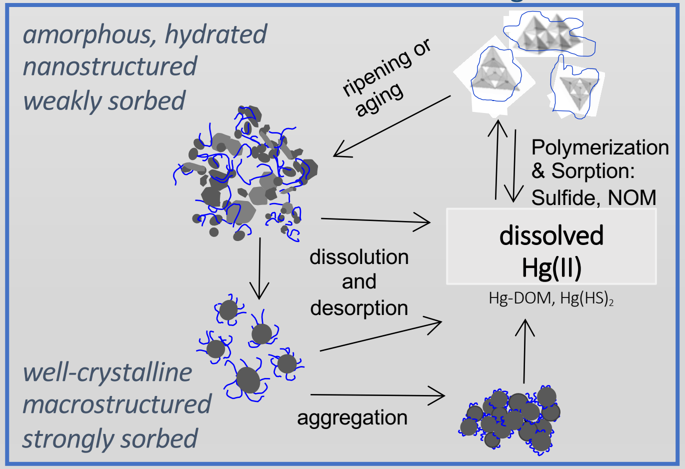
Sediment processes are important—they are often the primary zones of MeHg production

Introduction: MeHg production in sediment

Hg Inputs
Sulfate (Sulfide)
Organic carbon

Carbon substrates
Electron acceptors
Nutrients

Bioavailable Inorganic Hg



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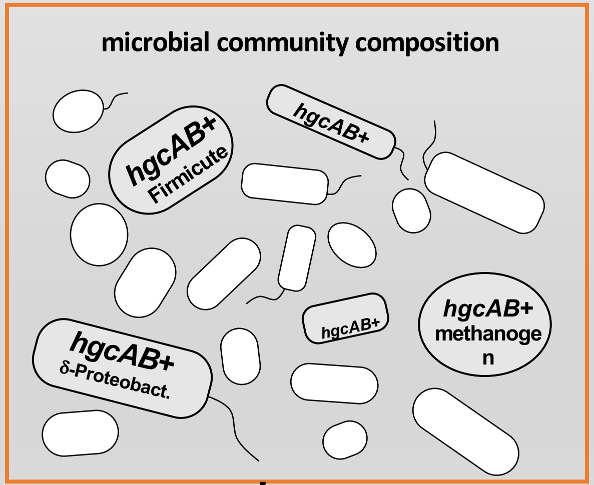
Anaerobic Microbiome



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MeHg

Release to Ecosystem:
Biomagnification
Transport
Exposure

Biogenic sulfide,
organic carbon,
redox gradients

Adapted from: Hsu-Kim et al, 2018

Interactive Content idea

Select 4 parameters below that most likely identify areas of elevated methylmercury (MeHg) concentrations:

1) Elevated bulk sediment total mercury
2) Elevated sediment porewater total mercury
3) Sediment with a positive redox potential (oxic conditions)
4) Sediment with a negative redox potential (anoxic conditions)
5) Low organic matter sediment
6) High organic matter sediment
7) Low sulfate concentrations
8) Moderate sulfate concentrations
9) High sulfate concentrations and buildup of sulfide

Answer: 2, 4, 6, 8

Remediation of Mercury Contaminated Sediments

Commonly remediation options:

- Reduce loading to the sediment
- Sediment excavation/dredging
- Sediment containment/capping

Optimized by focusing on areas:

- Elevated Hg—specifically bioavailable Hg
- Higher MeHg production
- Preferential uptake into foodweb


Photo: EPA/CDM


Photo: EPA/CDM


Photo: Dune Technologies

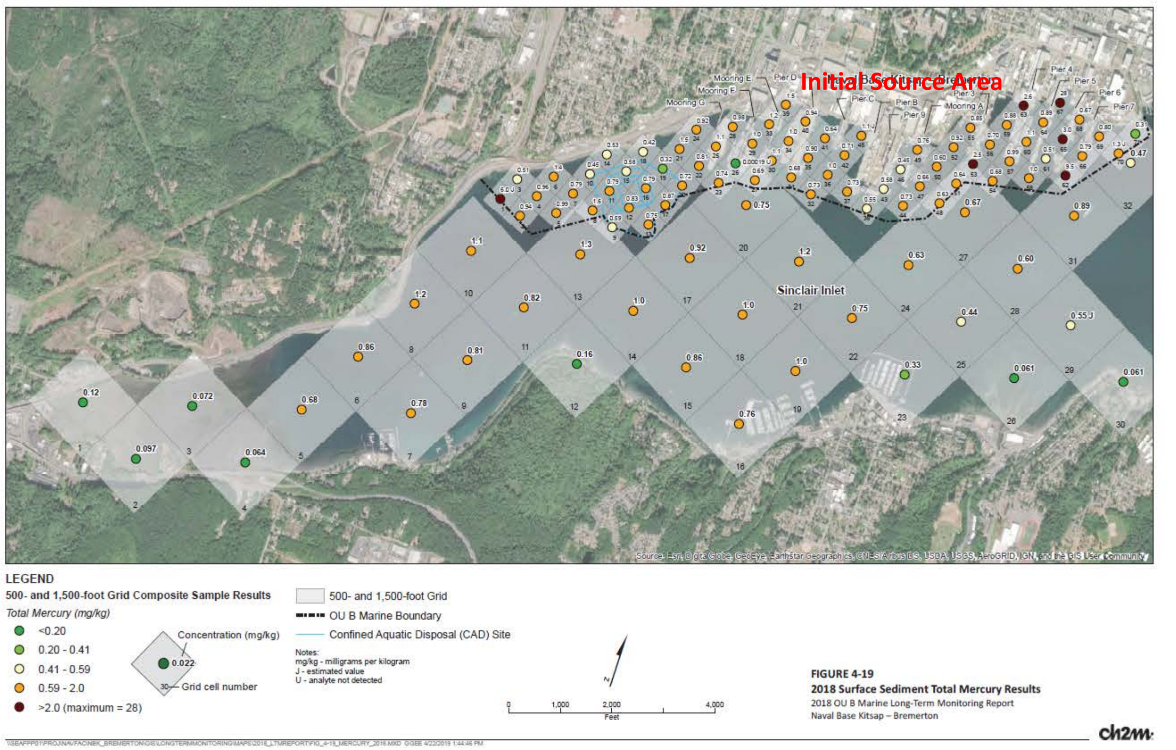
Addressing Spatial Variability of Hg Pollution

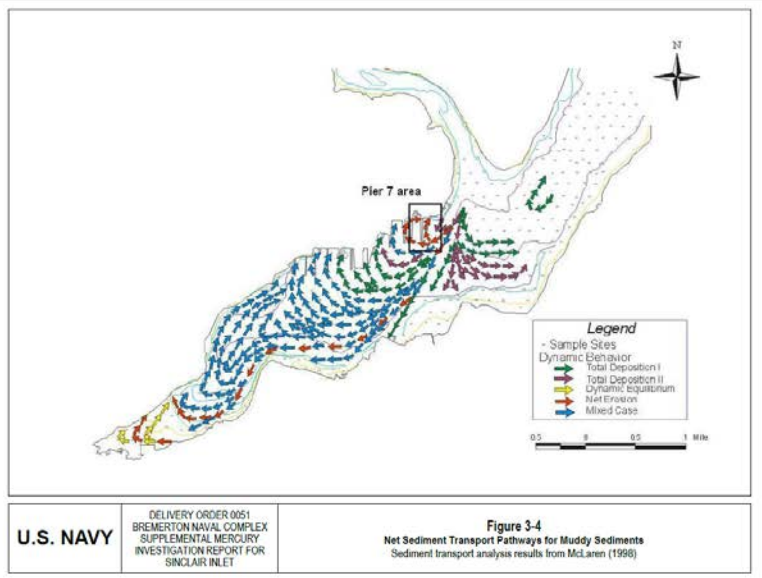
Identify spatial distribution of Hg contamination

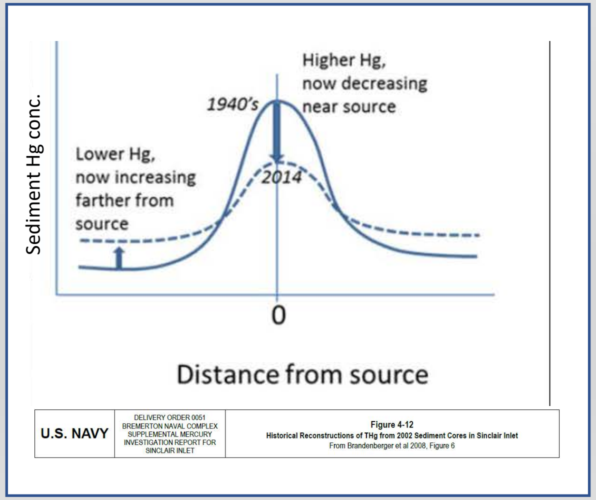
Opportunities for optimization:

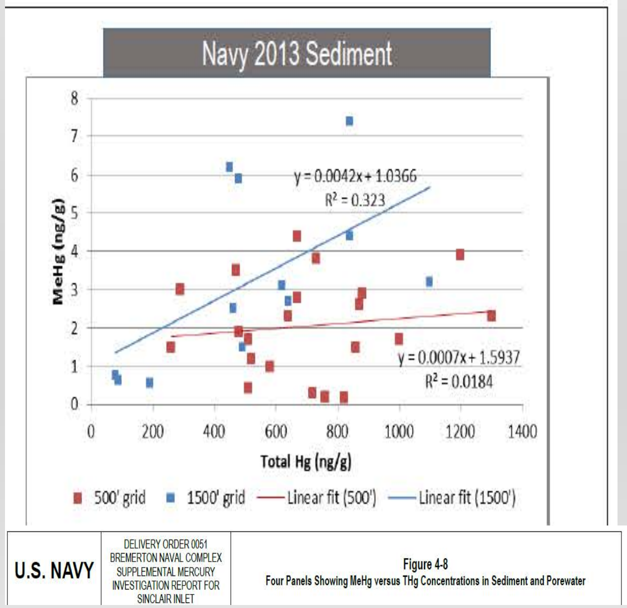
- Identifying erosion/ deposition zones
- Areas of MeHg production

Example from Puget Sound Naval Shipyard, WA:



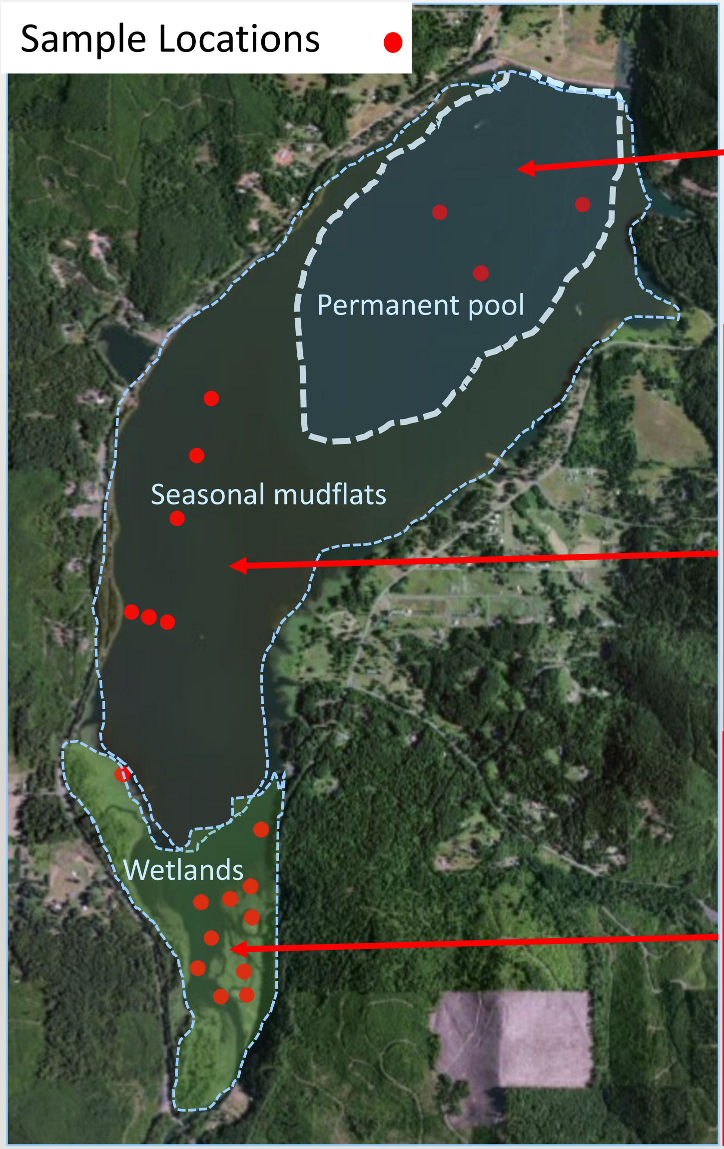


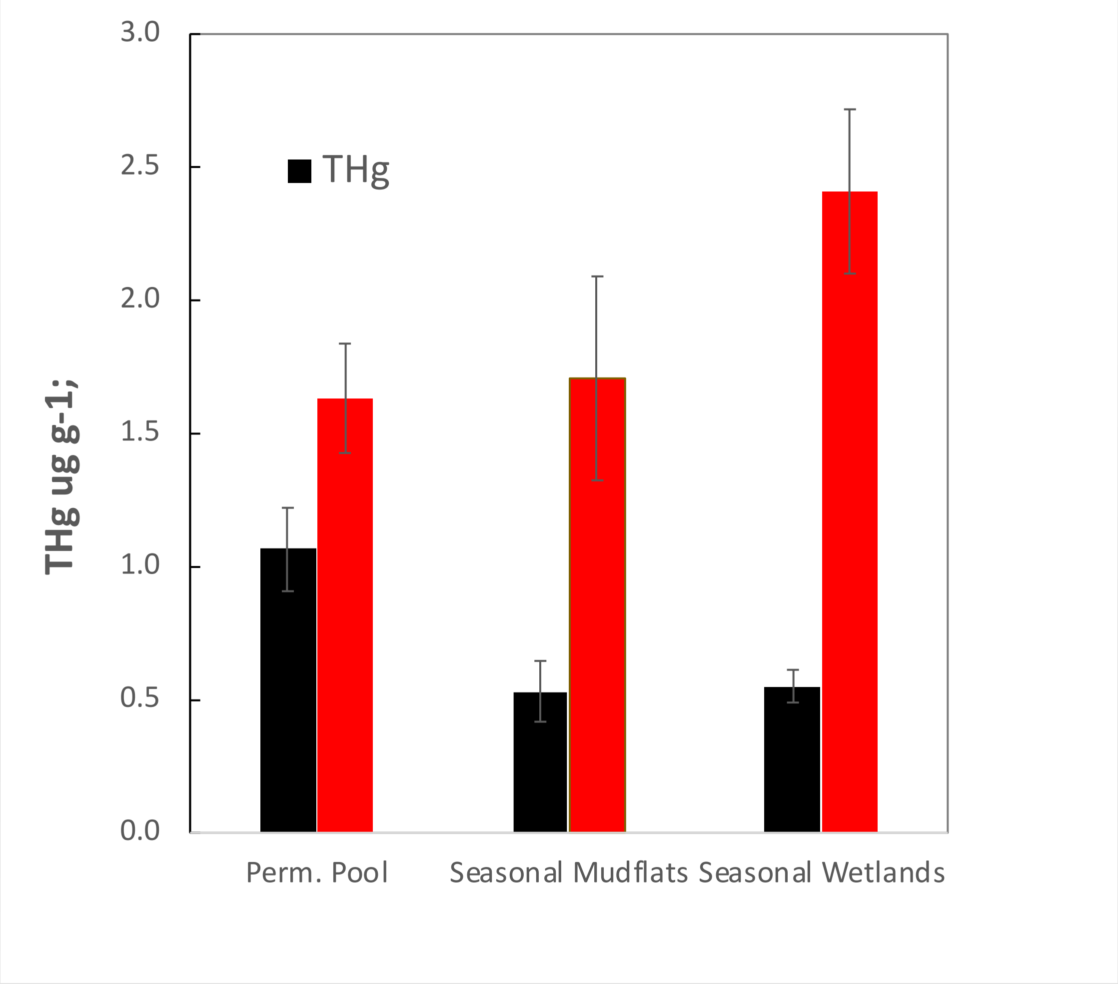




Addressing Spatial Variability of Hg Pollution

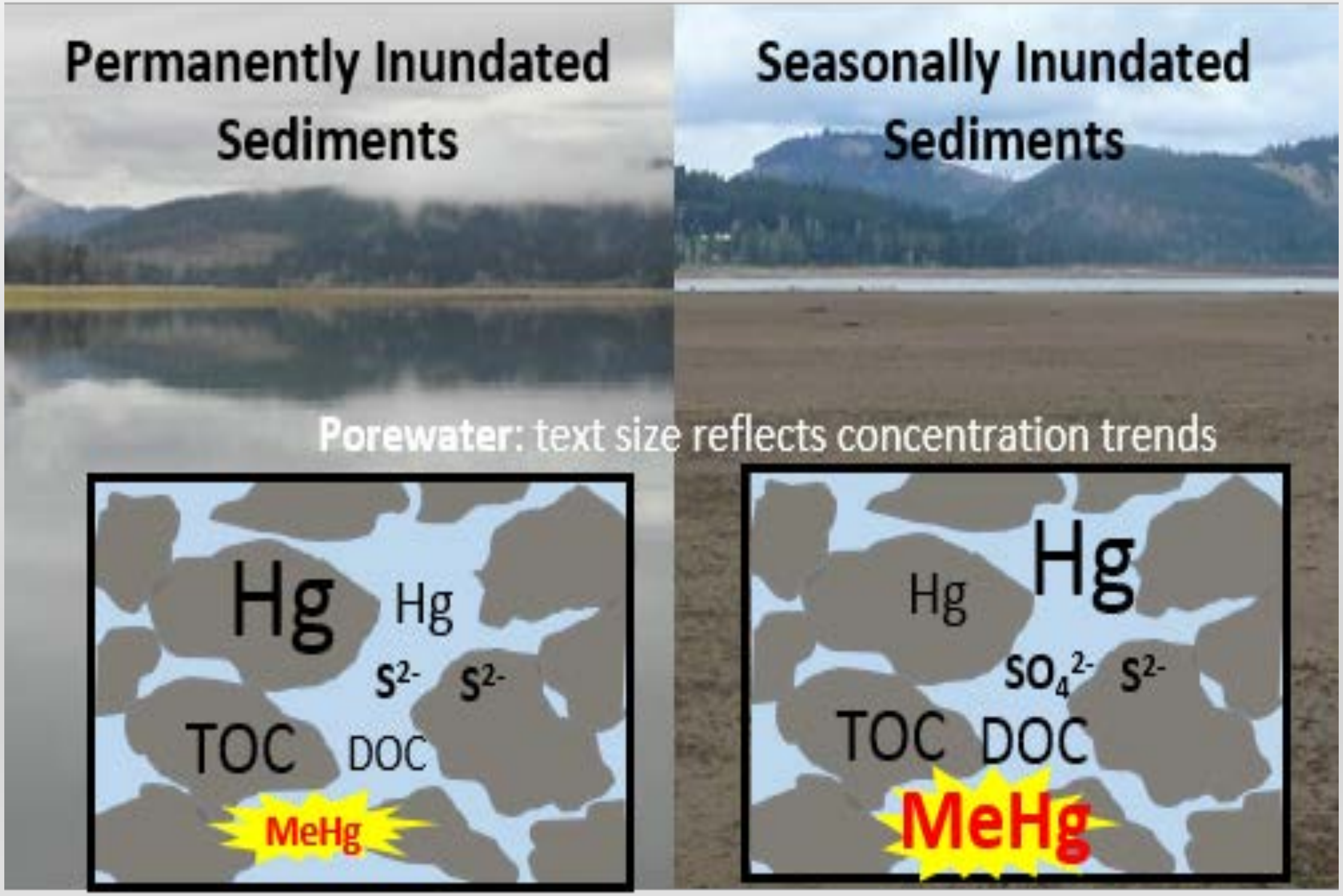
Optimization potential: targeted remediation on area of high MeHg production





Factors Controlling Methylmercury Production

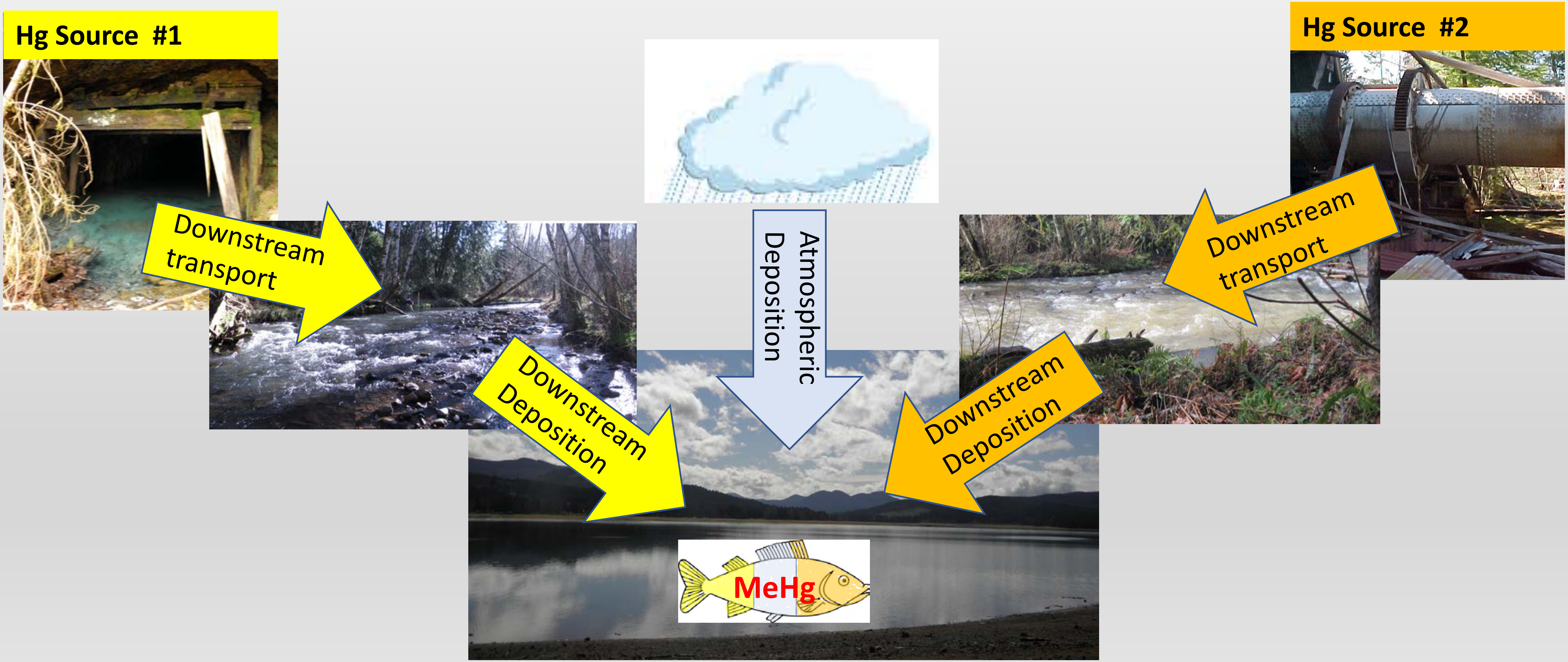
Remediation options may include controlling variables other than total-Hg



Eckley et al., 2017

Source Attribution Using Stable Isotopes

- Downstream/wind of contaminated sites the source of Hg pollution can be more difficult to discern, especially when there are multiple potential sources



Source attribution using Hg stable isotopes

What are stable isotopes?

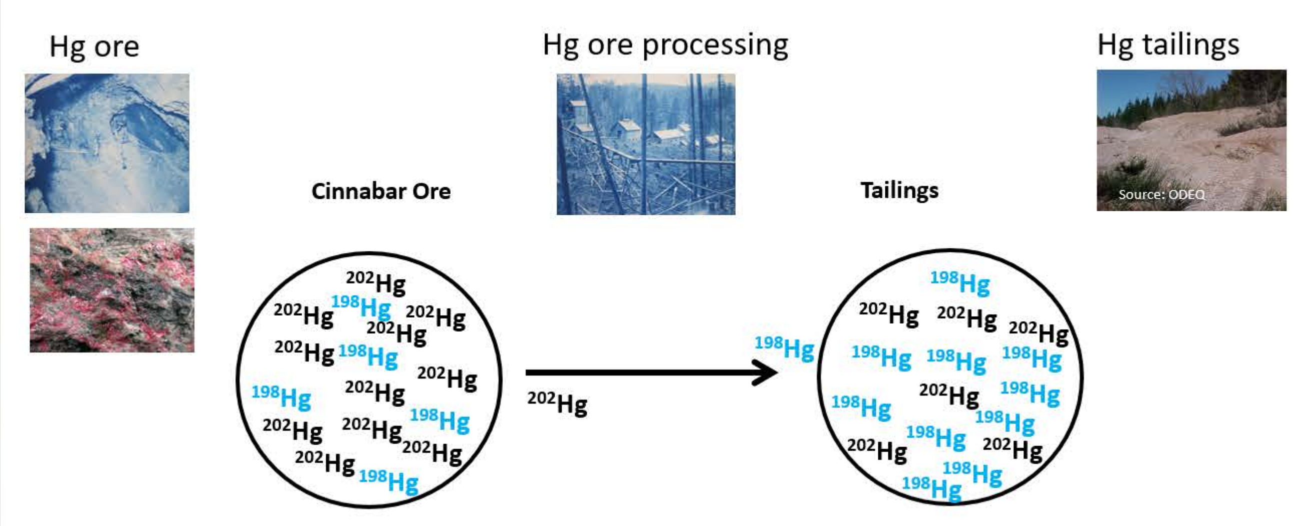
Forms of the same element that contain equal numbers of protons but different numbers of neutrons and as a result have different atomic masses

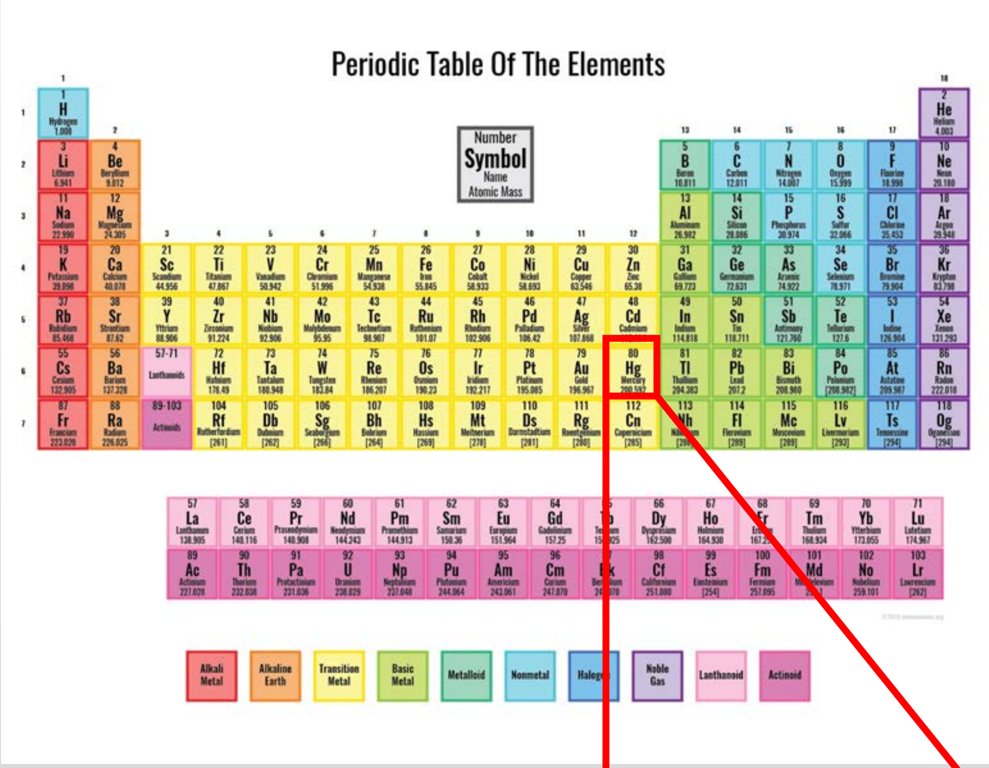
Mercury Isotopes:

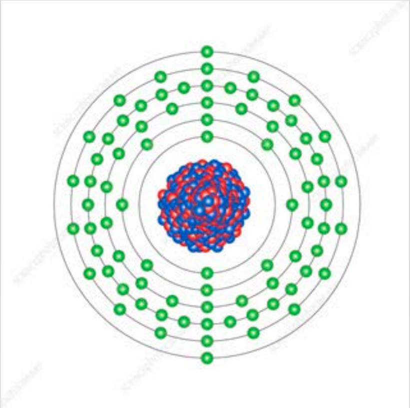
7 stable isotopes with range in mass from 196 to 204 amu

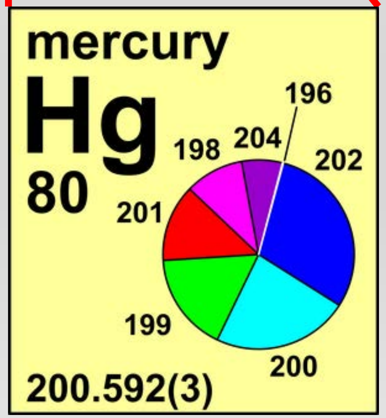
Mass dependent fractionation:

Lighter isotopes react faster and become enriched in the products



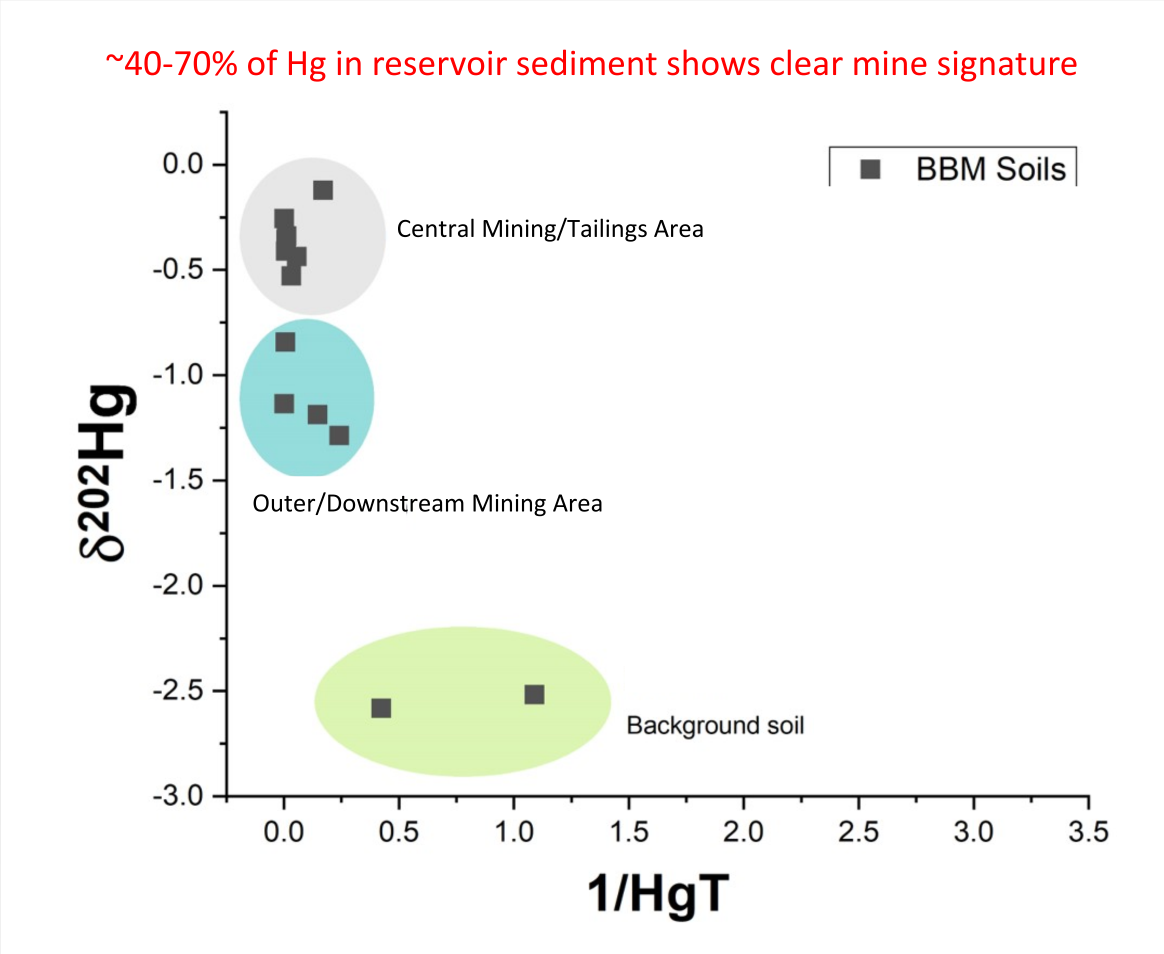




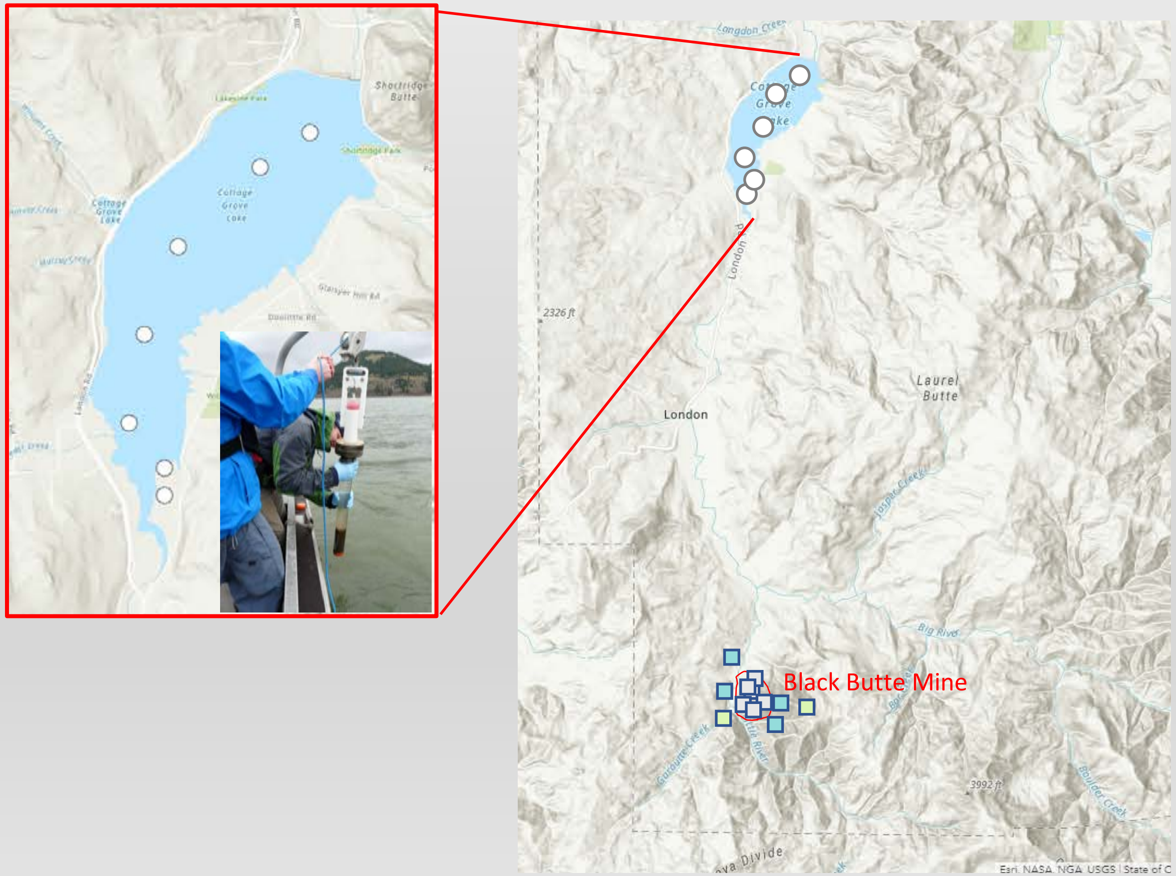


Source attribution using Hg stable isotopes

Remediations can be optimized by using stable isotopes to identify the portion of Hg in that originated from a contaminated site



Sediment Core Sample Locations

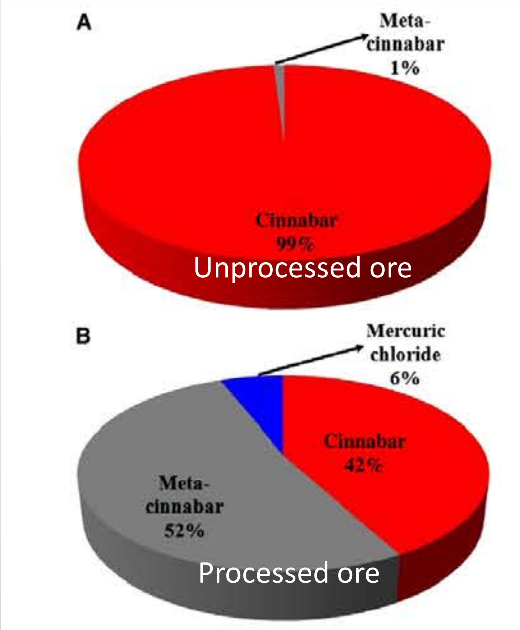


Mercury Speciation Measurements

Inorganic Hg speciation impacts its mobility, toxicity & availability for methylation

Types of factionation measurements:

- **X-ray absorption fine structure (XAFS) spectroscopy:** direct measure of Hg speciation
  - Requires relatively high Hg concentrations (typically > 1 mg/kg)
- **Chemical extractions:**
  - Environmental Mobility: SPLP, TCLP, SSE
  - Inorganic Hg bioavailability: IVBA (human ingestion); HgR (bacteria methylation)
- **Pyrolysis Method (thermal desorption monitored over a temperature range)**



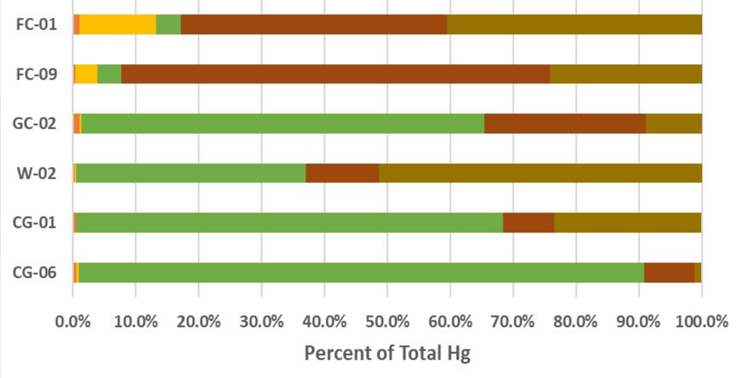
Yin et al, 2016

	Mercury Classification	Primary Compounds Extracted
F1	Water-soluble, i.e. salts	$HgCl_2$
F2	Weak acid-soluble/ "stomach acid" soluble	$HgSO_4$ HgO
F3	Organo-complexed	Hg-humics Hg_2Cl_2 CH_3Hg (MeHg)
F4	Strongly-complexed	mineral lattice bound Hg_2Cl_2 Hg^0 (liquid elemental)
F5	Mineral-bound	HgS (cinnabar) m-HgS (meta-cinnabar) HgSe (amalgam) HgAu (amalgam)

Brooks Applied Labs

Mine site

Downstream

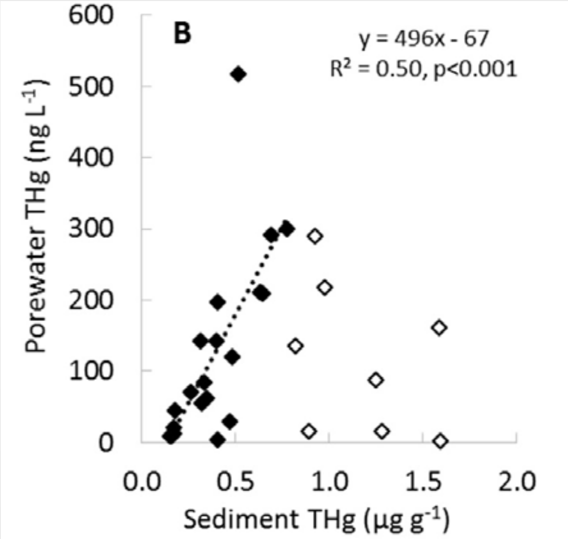


Cleveland, 2018

Mercury Speciation Measurements

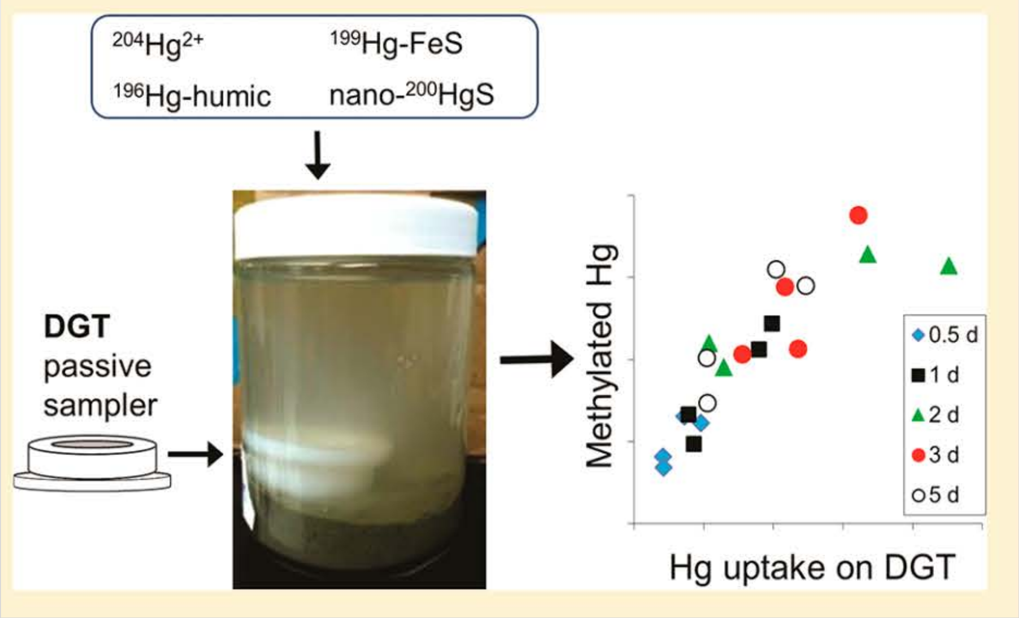
Remediation can be optimized by prioritizing areas where inorganic Hg is more mobile and/or bioavailable

Porewater Measurements



Eckley et al, 2017

Diffuse gradient in thin film (DGT) samplers



Ndu et al, 2018

Controlling Hg availability using *In Situ* Amendments

- *In situ* amendments to sediments compete for Hg or MeHg against natural sorbents
- Common types: biochar, activated carbon (AC), material modified with S ligands, Fe

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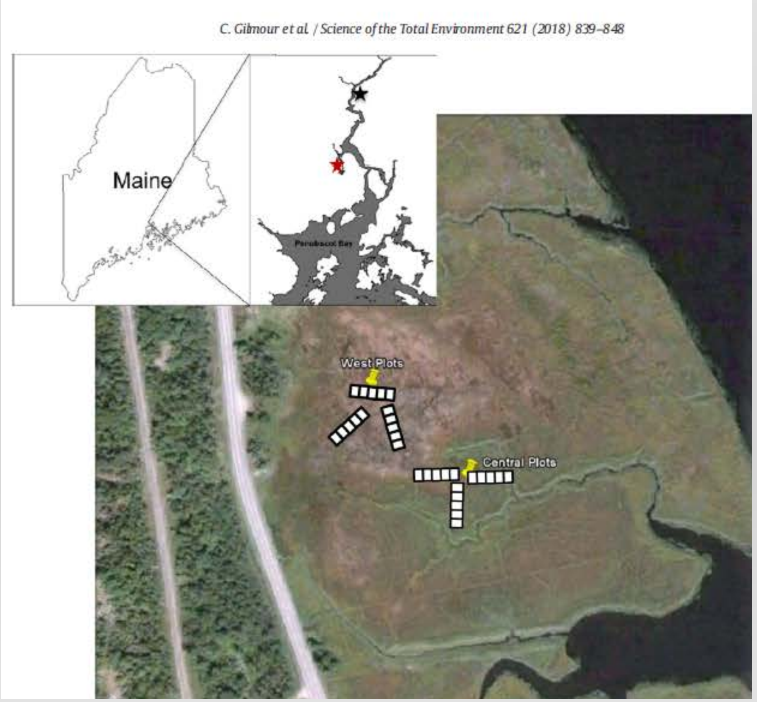
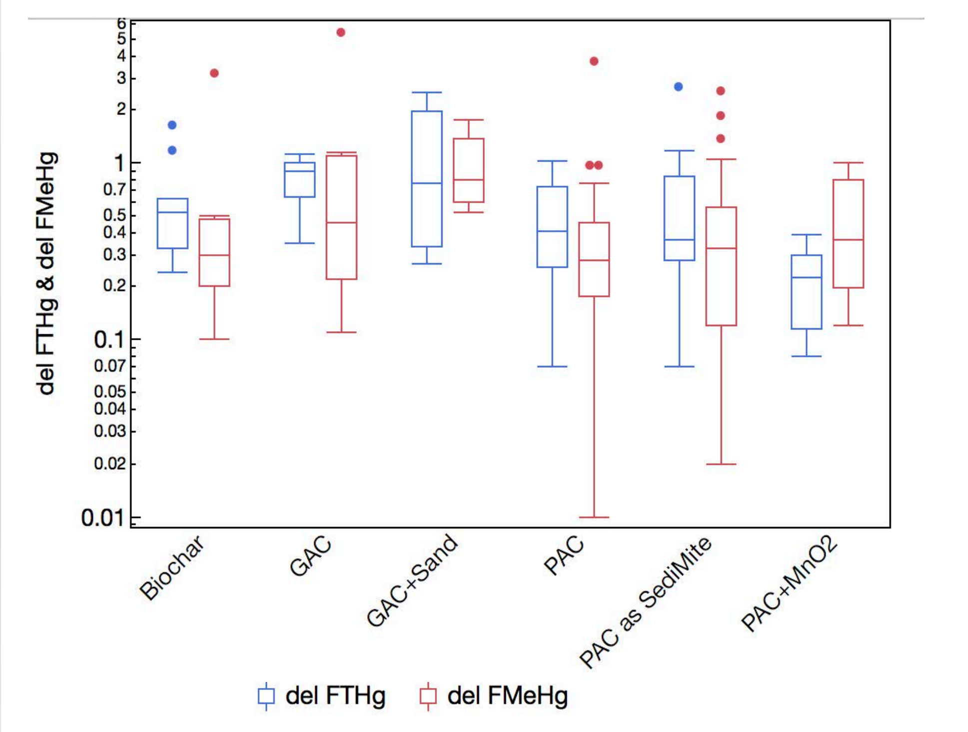
- **Lab and field tests with amendments**:
- Shown reductions in porewater THg & MeHg
- Effectiveness impacted by amendment type, sediment properties, and DOM

Gilmour et al, 2013





Variables Controlling Methylation

Remediation actions can focus on reducing variables enhancing MeHg production

Factorial incubation/mesocosm experiments:

Table 1
Controlled factorial addition experimental design

	No carbon	4X equiv.[a] acetate	10X equiv. acetate	4X equiv. lactate	10X equiv. lactate	4X equiv. glucose	10X equiv. glucose	Deciduous leachate	Coniferous leachate
No sulfate	4[b]	2	2	2	2	2	2	2	2
4X sulfate	2	2	n.i.[c]	2	n.i.	2	n.i.	2	2
10X sulfate	2	n.i.	2	n.i.	2	n.i.	2	2	2

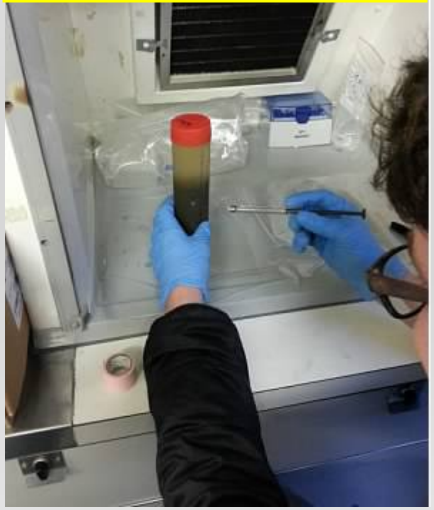
[a] Equiv. refers to an energetic-equivalent (same number of electrons) load.
[b] All numbers represent replicate experiments completed and reported in this paper.
[c] "n.i." indicates that experiments involving these combinations were not investigated.

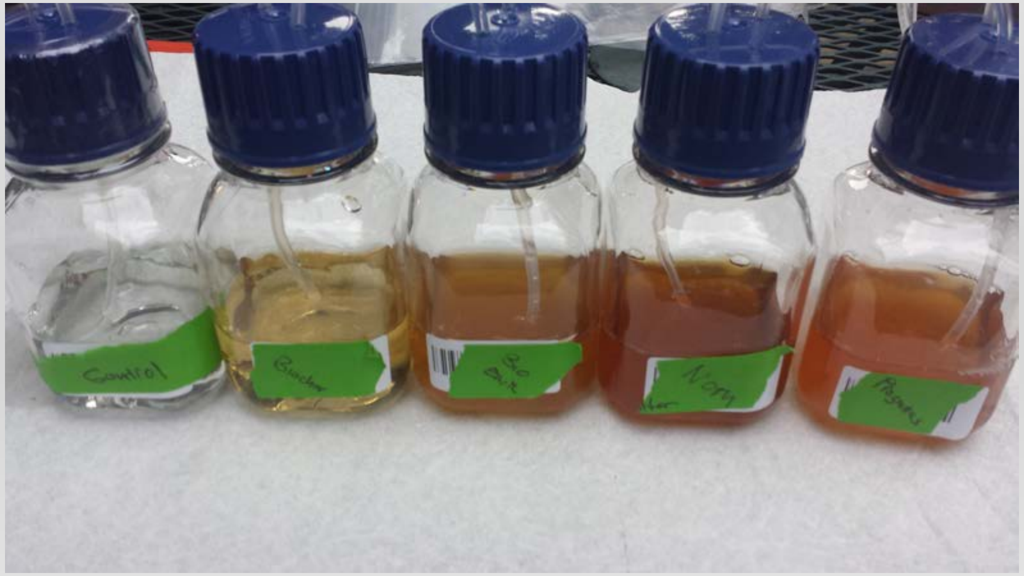
Mitchell et al, 2008

- Varying sulfate, DOC, Hg, etc
- Varying redox conditions
- Inhibiting microbial populations

Longer-term mesocosm plots

short-term isotope addition incubations





Conclusions:

Site assessments and remediation can be optimized by:

- Identify Hg forms/speciation that are mobile and available for methylation
- Using stable isotope fractionation to identify sources of contamination
- Identifying opportunities to reduce MeHg that may or may not require changes in THg

Requires significant investments in research aimed at understanding the system

Next Steps:

- Novel approaches to addressing contaminated sites have been identified at the laboratory and test plot scale;
- However, more examples of large-scale applications are needed to encourage broader adoption of these methods