Review of Recent Advances in Mercury Research: Assessment and remediation of mercury contaminated sites.

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Assessment

Remediation

Introduction

ICMGP Special Issue:
Reviews of Recent Advances in Mercury Research and Understanding the Biogeochemical Cycle

List of papers:

1. The mercury science-policy interface: history, evolution and progress (Bank)
2. Introduction to the biogeochemical cycle of Hg in light of recent advances in knowledge (Gustin)
3. An Updated Review of Atmospheric Mercury (Lyman et al.,)
4. Recent advances in understanding and measurement of Hg in the environment: Surface-atmosphere exchange of gaseous elemental mercury (Sommar et al.,)
5. Mercury in soil in the context of Minamata Convention (Horvat)
6. Recent advances in understanding & measurement of mercury in the environment: Terrestrial Hg cycling (Bishop et al.,)
7. What measurements are important for understanding freshwater Hg cycling (Branfireun)
8. Recent advances in understanding of factors controlling Hg methylation (Zhong et al.,)
9. Methylmercury and the microbiome: A review of exploratory bioinformatics tools (Rothenberg et al.,)
10. Methylmercury exposure in wildlife: a review of the ecological and physiological processes affecting contaminant concentrations and their interpretation (Chetelat et al.,)
11. Recent advances in understanding Hg in the environment: Stable Hg isotopes & their ecological applications (Tsui et al.,)
12. **The assessment and remediation of mercury contaminated sites: a review of current approaches (Eckley et al.,)**
13. Environmental archives of atmospheric Hg deposition – A review (Cooke et al.,)
14. New insight into factors controlling ocean mercury cycling (Bowman et al.,)
15. How do these advances impact our understanding of the Hg biogeochemical cycle and modeling efforts? (Bieser)

Introduction: Contaminated Sites

Examples of common industrial-scale Hg contaminated sites:

Hg Mines


Photo: Eckley


Photo: Marcia Wright

Gold & Silver Mines


Photo: NDEP


Photo: Eckley

Hg Recycling Facilities


Photo: EPA

Chemical Production

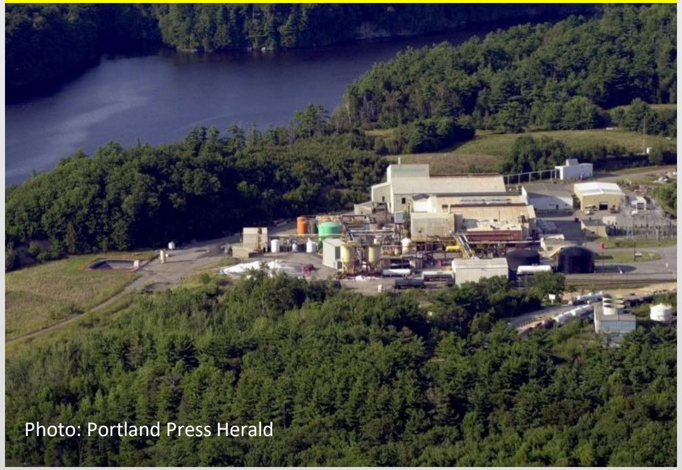


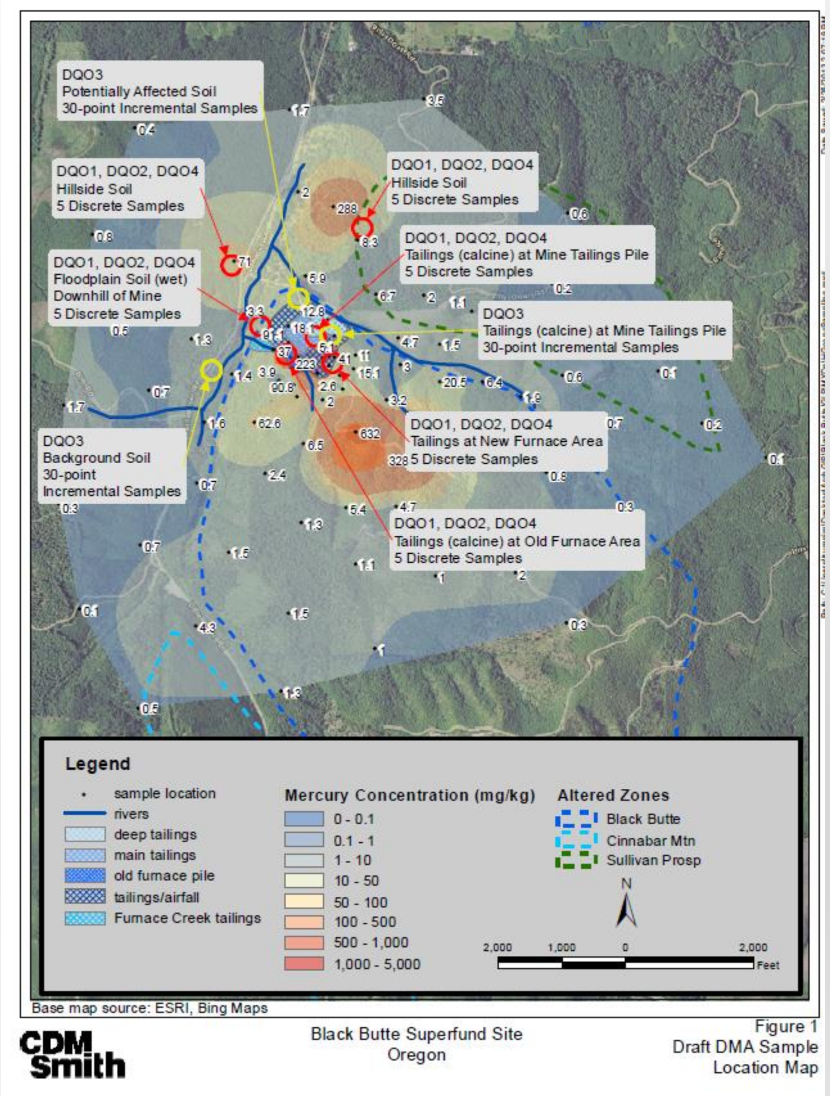
Photo: Portland Press Herald

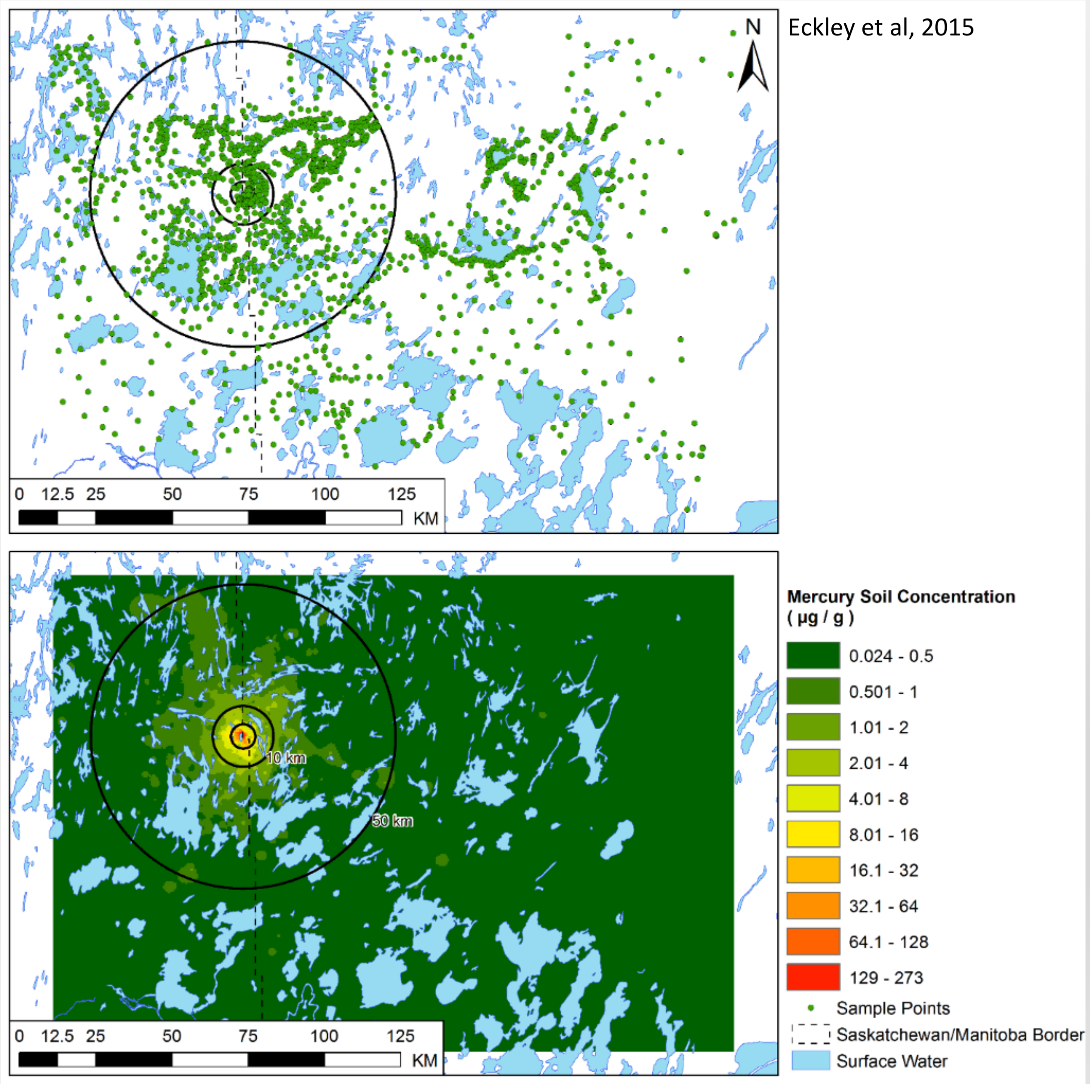
Other Historical Hg Use


Photo: Eckley

Site Assessment: Spatial Variability

Identifying source areas and geographic extent of contamination

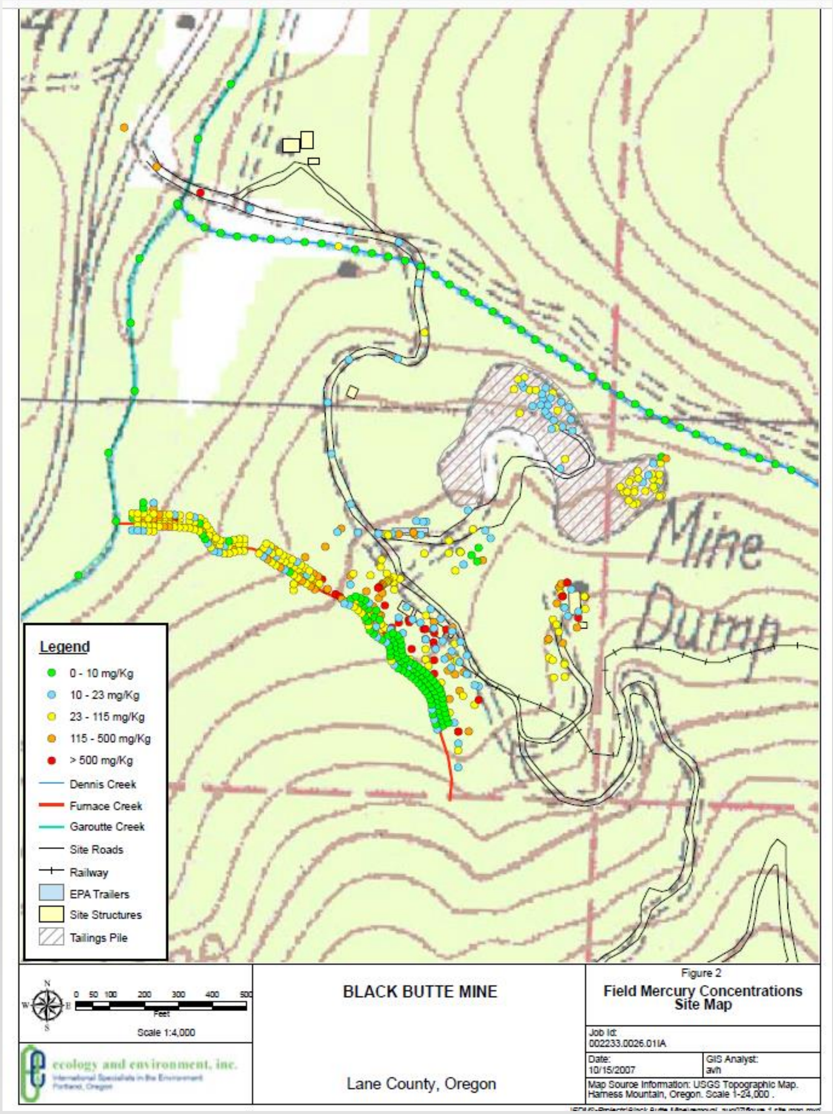




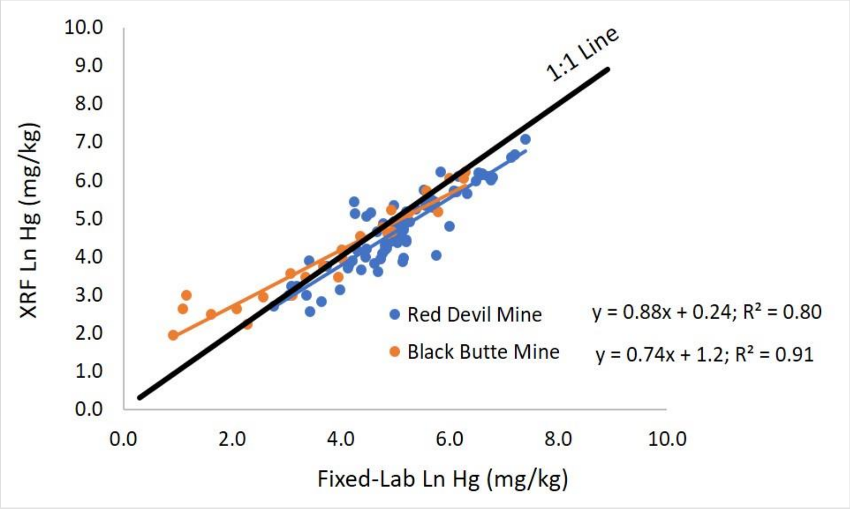
Eckley et al, 2015

Site Assessment: Spatial Variability

Handheld X-Ray Fluorescence Spectrometers (XRF)

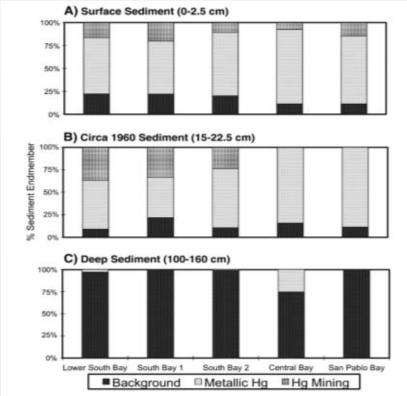


- Field portable; measurements within seconds/minutes
- High density of data: reduced uncertainty & increased representativeness
- Facilitates adaptive investigations and remedial strategies
- Most useful at highly contaminated sites (>20 mg/kg)
- Hg^0 in soils creates disagreements between lab and XRF data

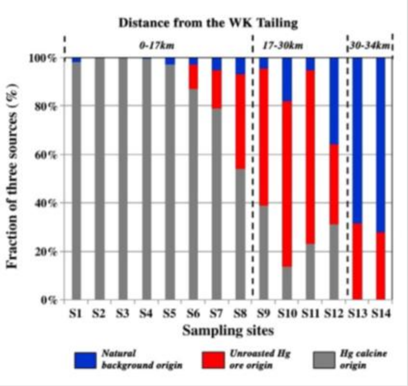


Site Assessment: Source attribution using stable isotopes

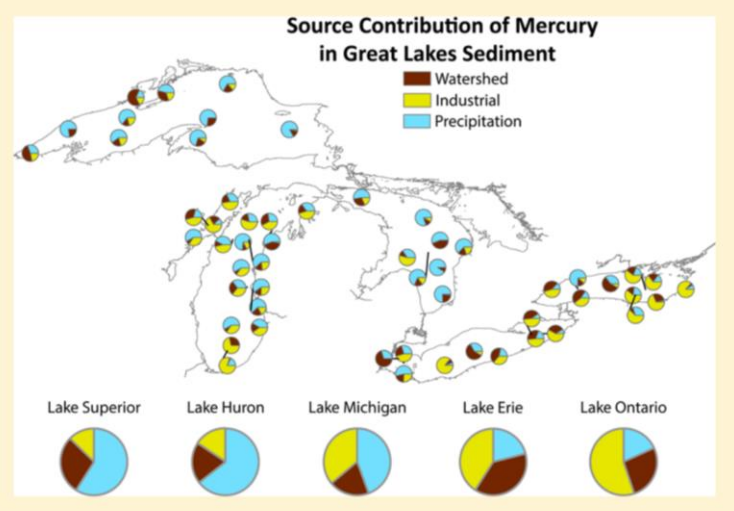
- Downstream/wind of contaminated sites the source of Hg pollution can be more difficult to discern, especially when there are multiple potential sources
- Hg stable isotope analysis has provided insights into different environmental pools of Hg as well as the transformations (requires unique end-members)



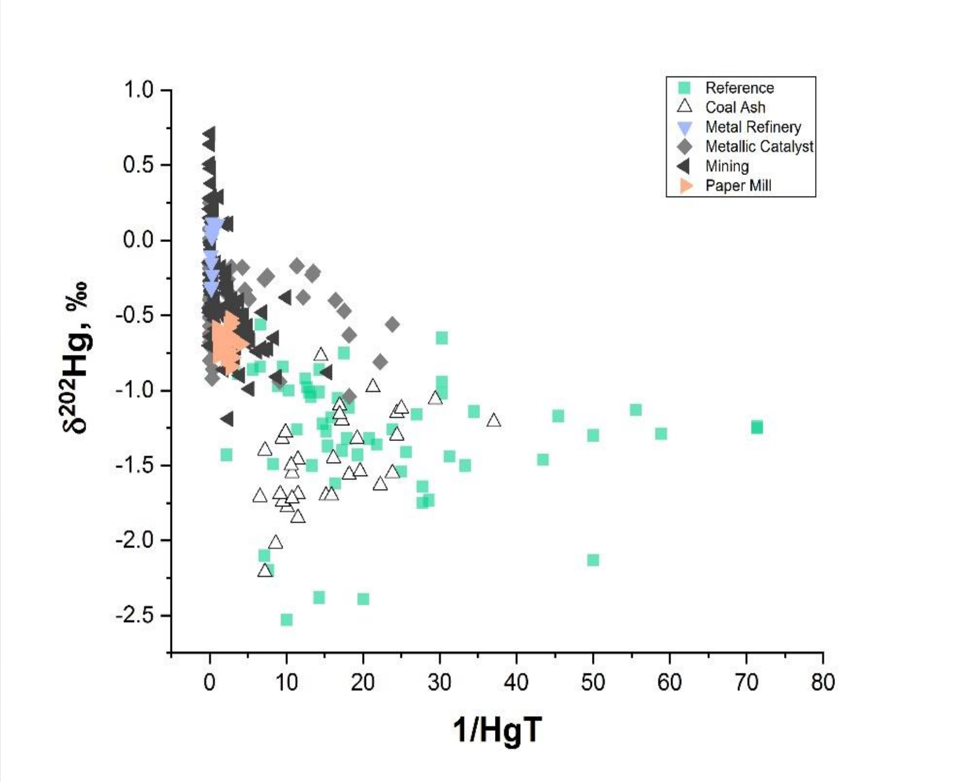
Donovan et al, 2013



Yin et al, 2013



Lepak et al, 2015



Data sources: mining (Donovan et al., 2013; Foucher et al., 2009; Gehrke et al., 2011a; Yin et al., 2013b), coal ash (Bartov et al., 2012), metallic Hg usage (Feng et al., 2010; Grigg et al., 2018; Mil-Homens et al., 2013; Perrot et al., 2010; Washburn et al., 2018), metal refinery (Sonke et al., 2010), and paper mills (Yin et al., 2016)

Site Assessment: Hg speciation, fractions and bioavailability

- Many regulatory criteria are based on total-Hg (THg) concentrations.
- Hg speciation impacts its mobility, toxicity and availability for methylation.

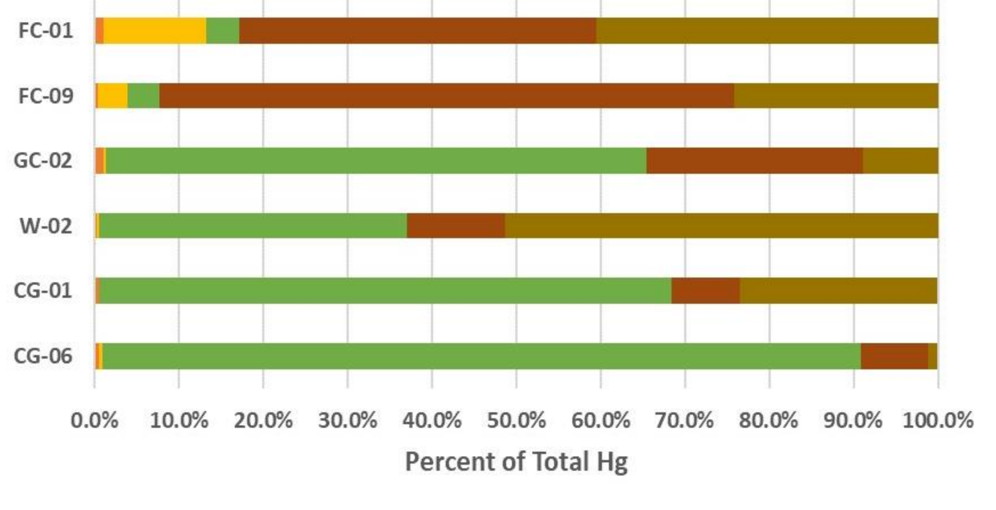
Types of speciation/fractions measurements:

- X-ray absorption fine structure (XAFS) spectroscopy provides direct measure of Hg speciation
  - Requires relatively high Hg concentrations (typically > 1 mg/kg)

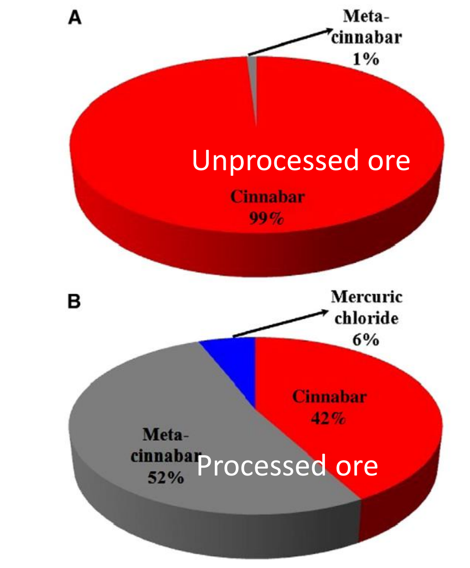
- Chemical extractions (SPLP, TCLP, IVBA, HgR, SSE)

	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



Cleveland, 2018

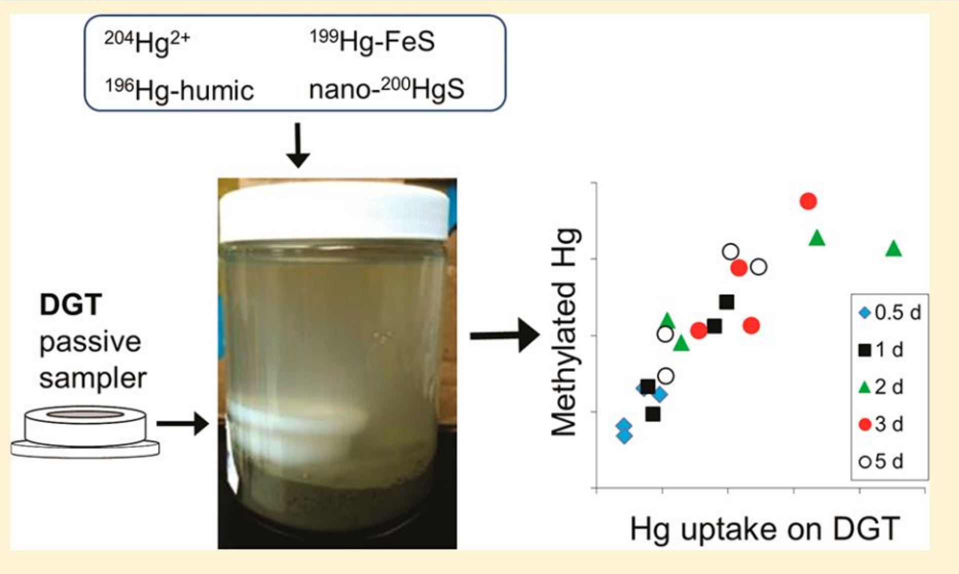


Yin et al, 2016

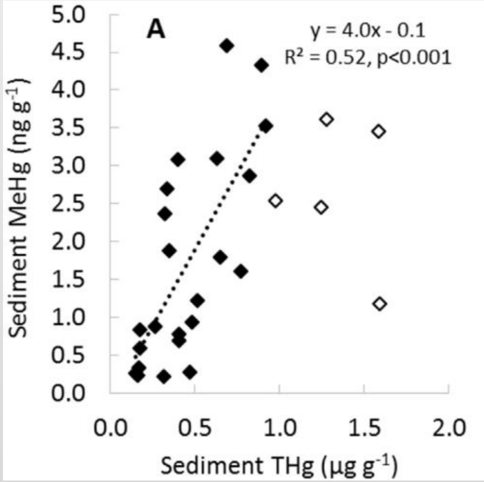
Site Assessment: Bioavailability & Methylation

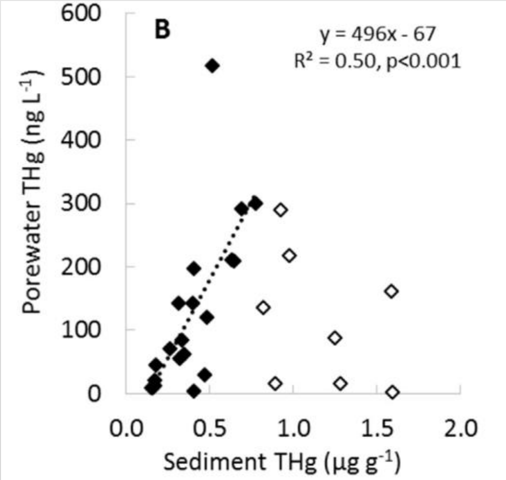
- Porewater & diffuse gradient in thin film (DGT) samplers:

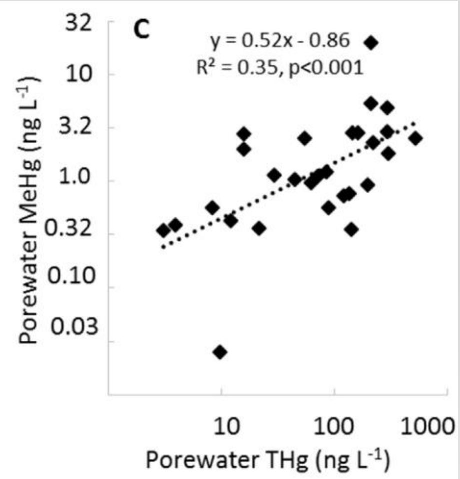
The fraction Hg in the sediment that is more available for methylation



Ndu et al, 2018



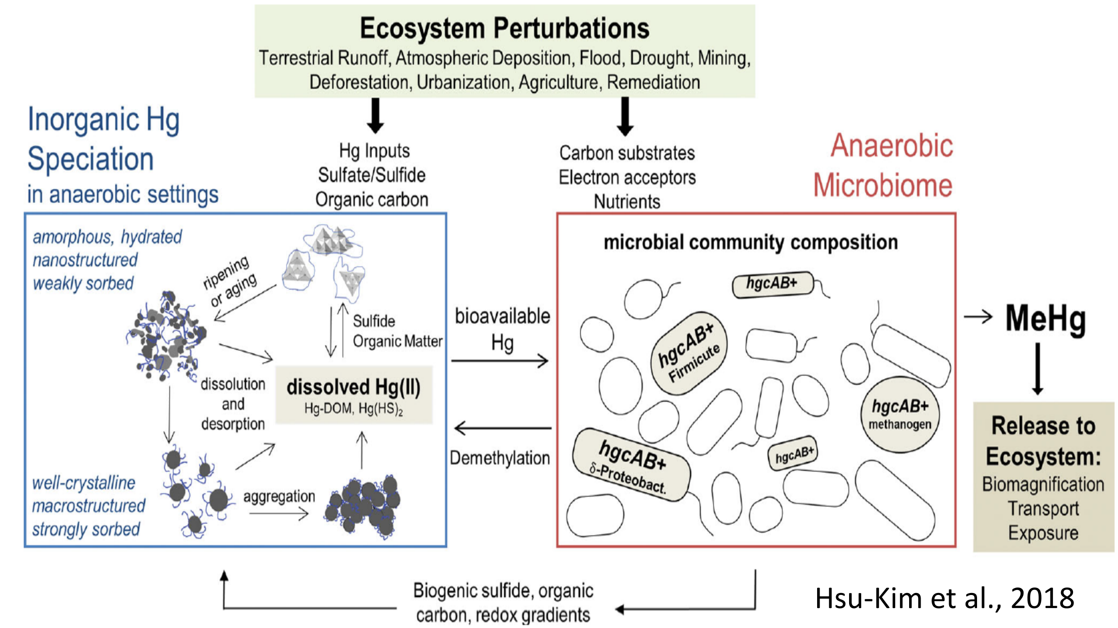




Eckley et al, 2017

Site Assessment: Bioavailability & Methylation

- MeHg production impacted by: bioavailability of Hg + microbial community/activity
- Effective management actions should consider the variables limiting/controlling MeHg production



Hsu-Kim et al., 2018

Factorial incubation experiments:

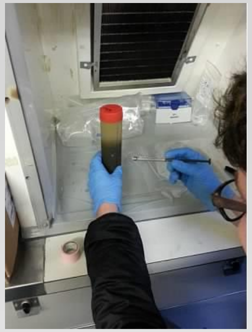
- Varying sulfate, DOC, etc
- Varying redox conditions
- Inhibiting microbial populations

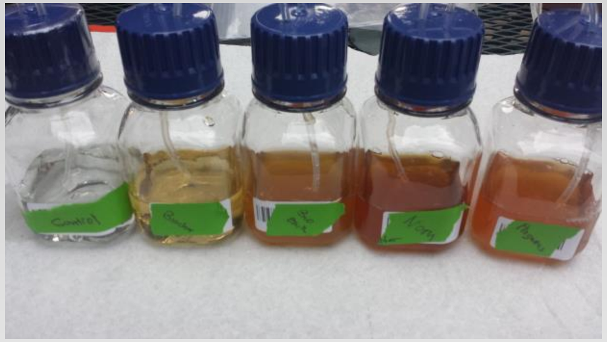
Table 1
Controlled factorial addition experimental design

	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

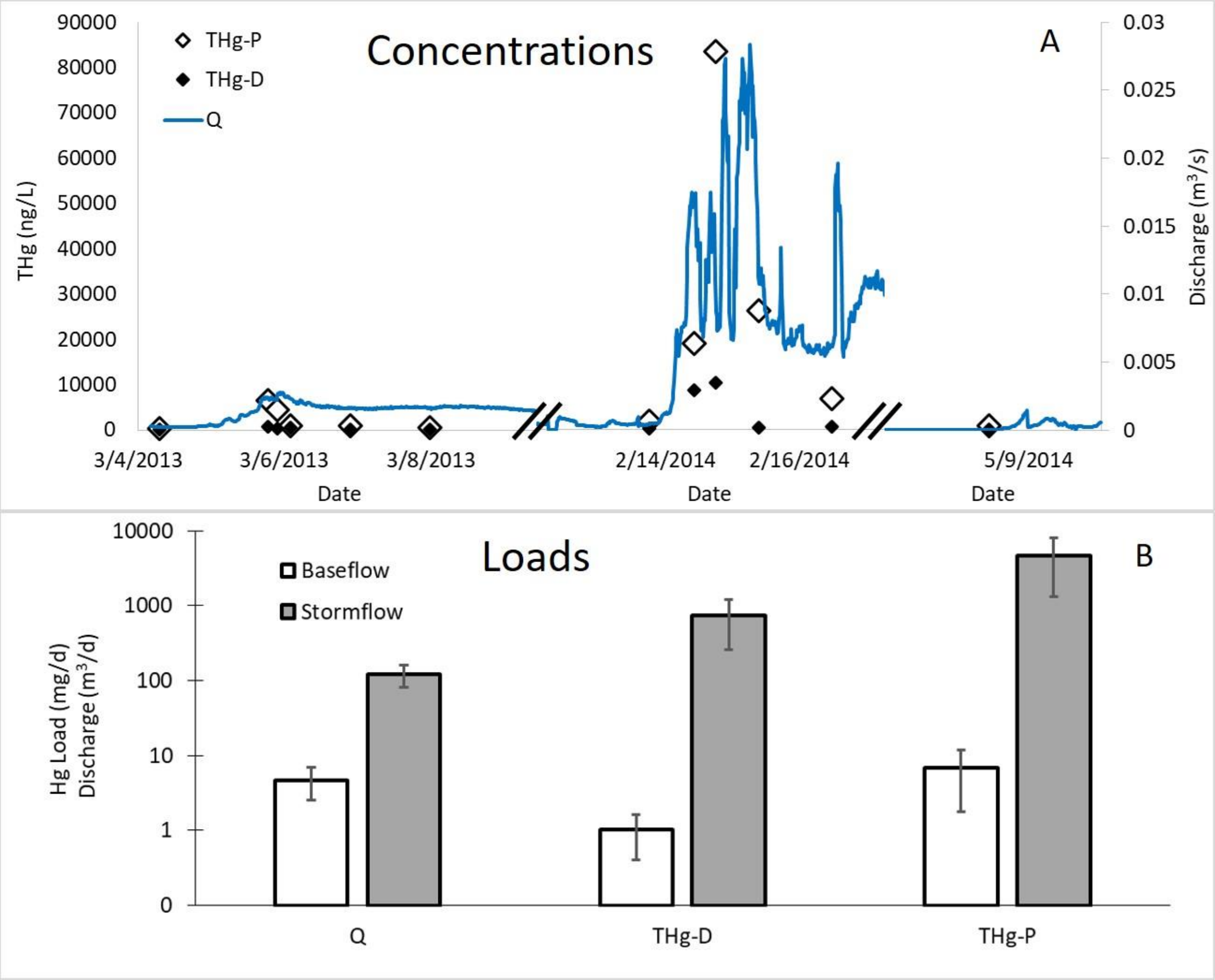




Site Assessment: Pathways of release—flux to water

Releases are a concern due to the potential for downstream methylation & bioaccumulation.

- Typically, flux to surface water > groundwater
- Stormflow flux >>> baseflow flux
- Annual loads dominated by a few large events
- Mobilization from erosion of particles/sediment entrainment

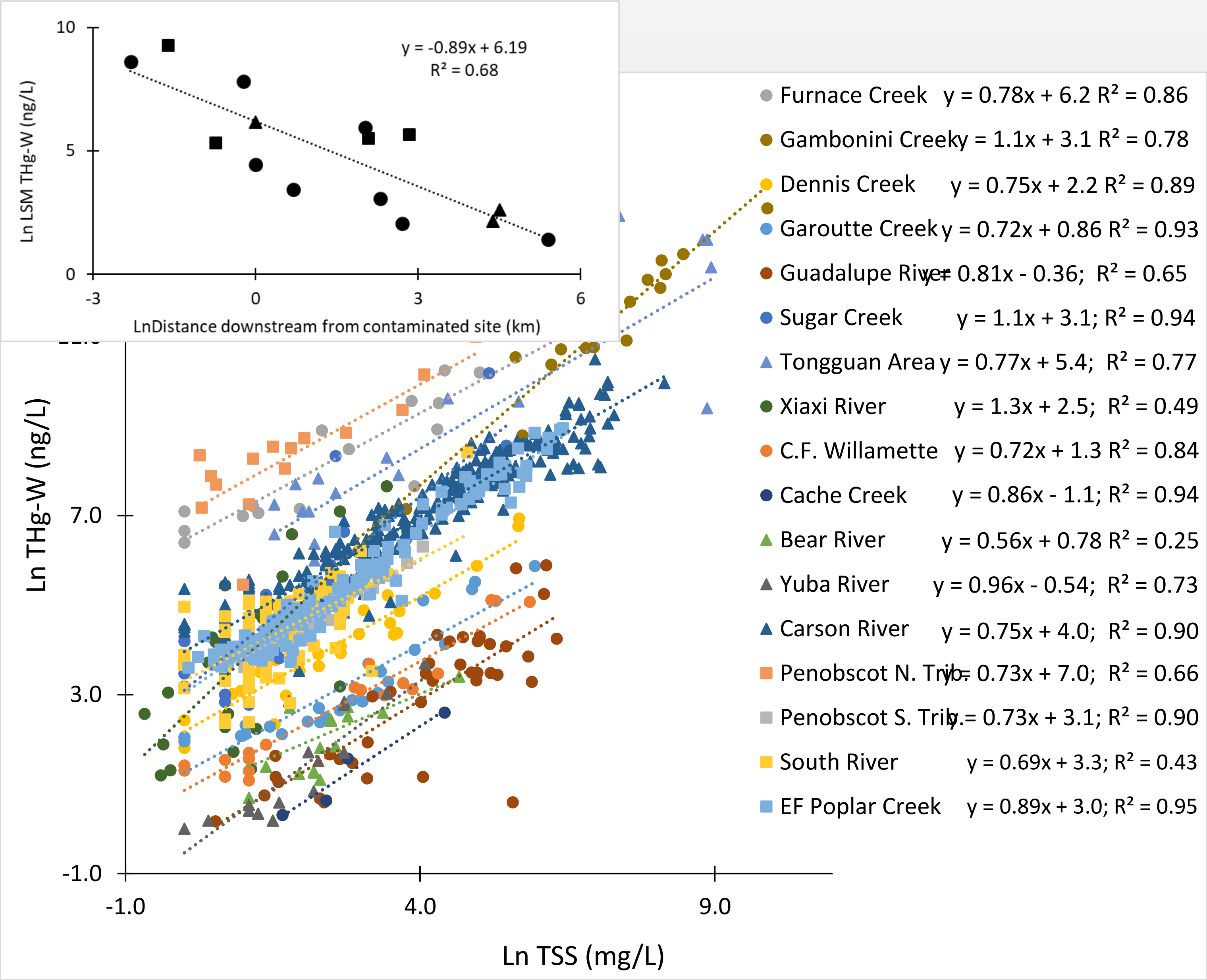


Source: CDM/EPA Black Butte Mine

Site Assessment: Pathways of release—flux to water

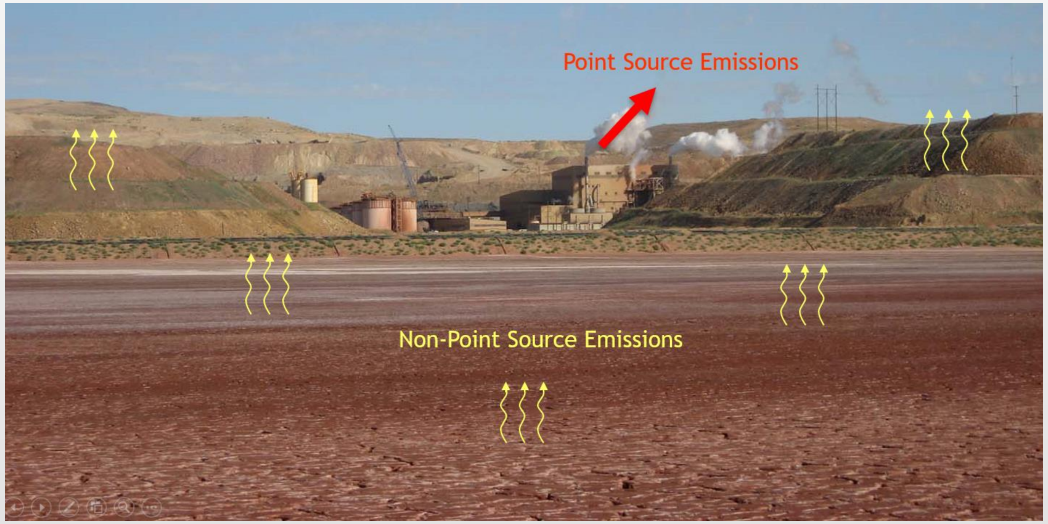
- Positive relationship between THg and total suspended solids (TSS).
- Most regression slopes not significantly different

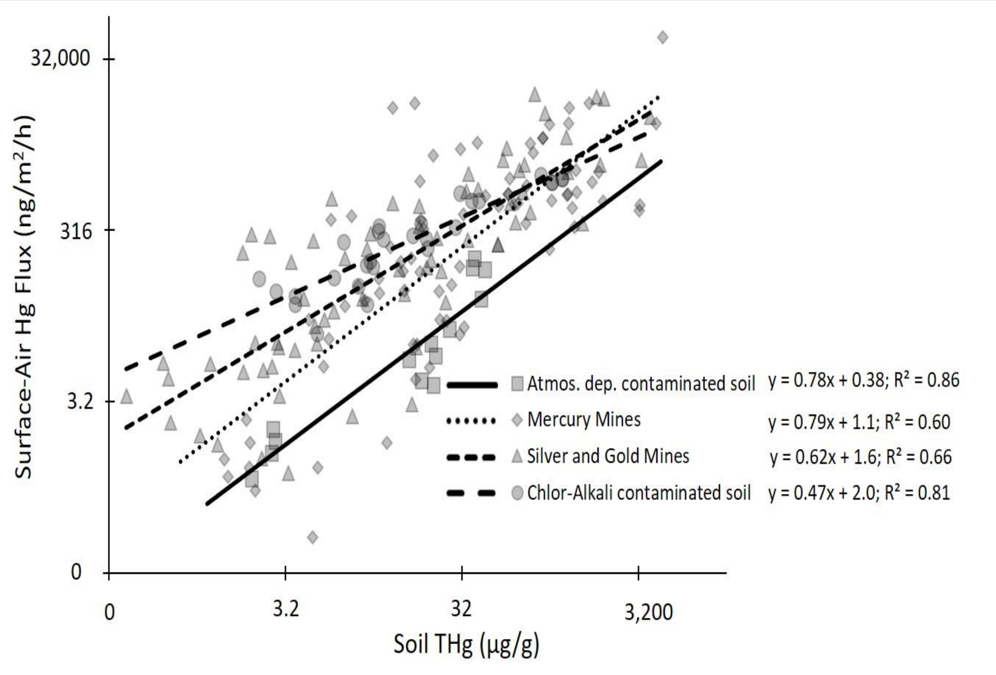
- Most intercepts were significantly different and were correlated with the distance downstream from the contaminated source area.

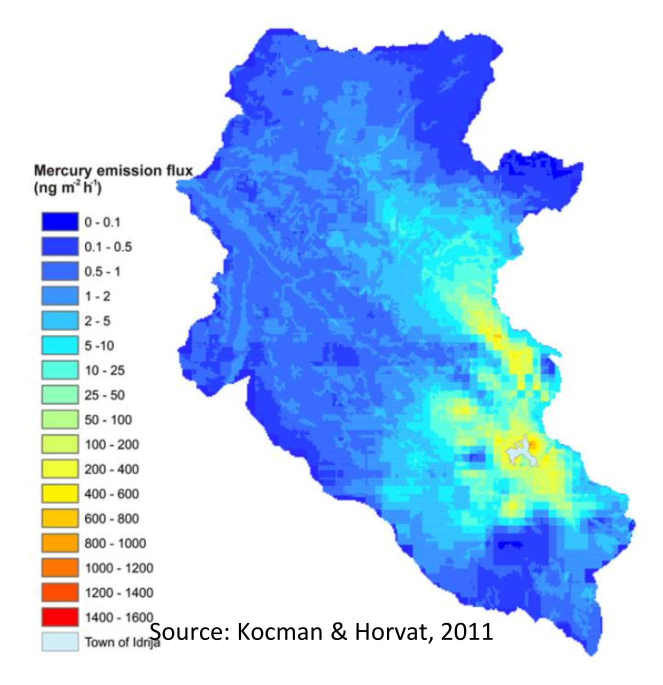


Site Assessment: Pathways of release—flux to air

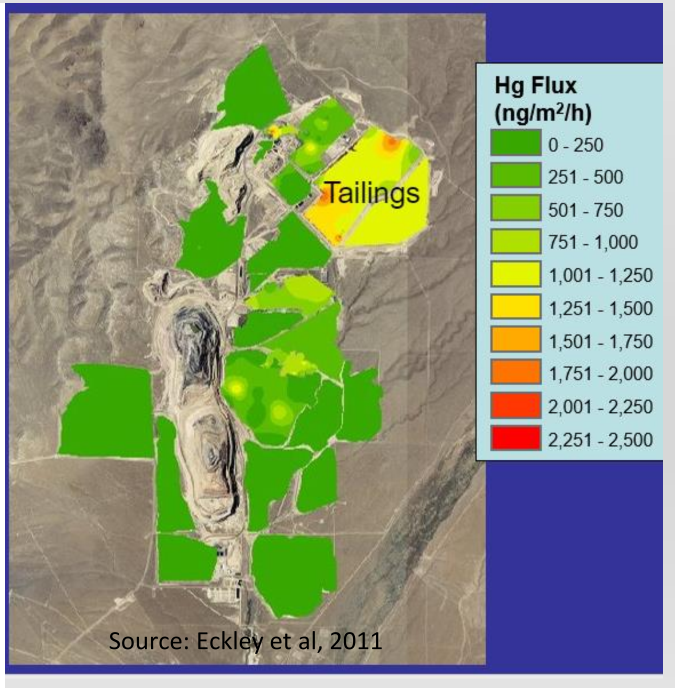
- Relative magnitude of surface-air versus water flux depends on hydrological/meteorological conditions.
- Annual fluxes to the air can be 50-100 kg/year from some contaminated sites.
- Soil Hg speciation (along with several environmental parameters) affect surface-air fluxes.







Source: Kocman & Horvat, 2011

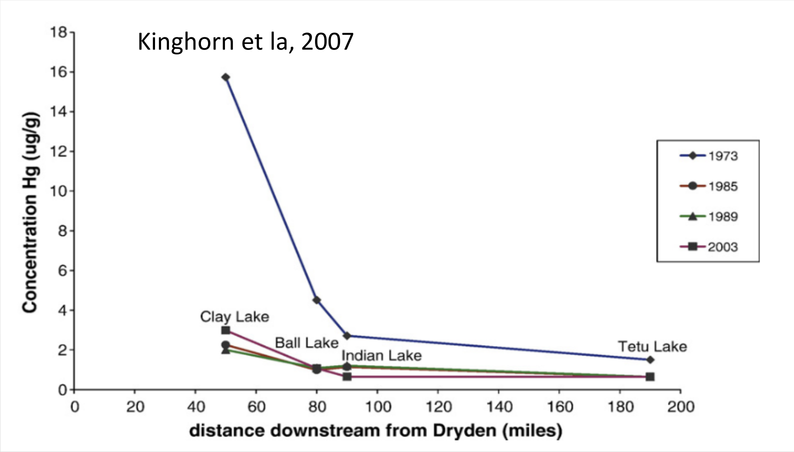


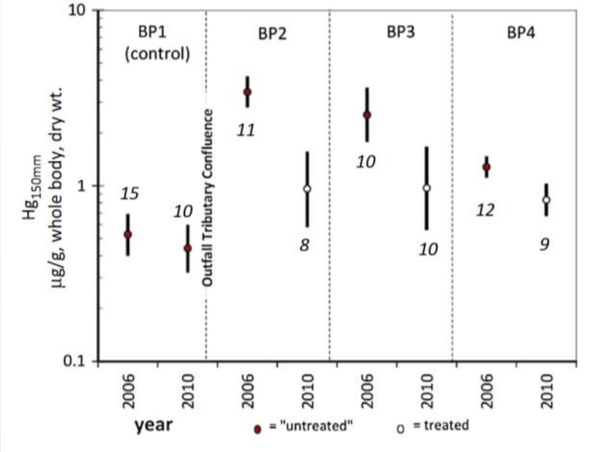
Source: Eckley et al, 2011

Site Remediation:

Site Remediation: Source Reductions

- Some studies have shown THg source reductions can result in reduced MeHg in biota





Mathews et al., 2015

- Other studies have shown MeHg remains elevated after THg source reductions

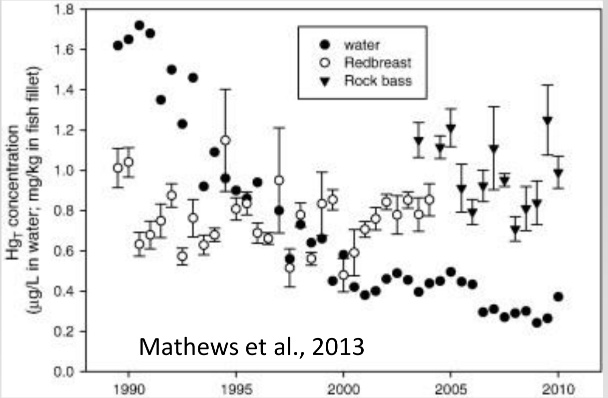


Table 2. Low-level Mercury Results

Date	Site ID	Depth m	T-Hg ng/L	Dissolved Hg ng/L	Methyl Hg ng/L	T-Hg ng/g	Methyl Hg ng/g
			water			sediment	
6/27/2012	PBL-A	10	9.72	6.59	2.05	229	5.16
		2	5.41	5.26	0.097		
	PBL-B	8	8.43	7.29	1.82	239	6.78
		2	5.60	3.91	0.077		
	PBL-C	2	6.32	3.84	0.175	146	3.66
damp	W wash local					79.4	
dry	S wash local					48.3	
[illegible]/2012	PBL-A	10	18.2	7.36	5.00	136	3.68
		1.7	2.72	1.78	0.361		
	PBL-B	8	19.2	3.97	6.42	79.5	2.20
		1.7	2.74	1.85	0.253		
	PBL-C	1.5	2.04	2.07	0.250	87.4	0.885
wet	Main wash S trib					279	
wet	Main wash W trib					163	

Curiel, 2013

Site Remediation: Reducing THg

Soils:

Commonly applied options:

- Excavation & removal
- Containment in-place

Other options:

- Soil-washing
- Solidification/stabilization
- Thermal treatment
- Electrochemical/kinetic recovery
- Bioremediation/biotreatment
- Phytoremediation/stabilization
- Chelating agents

Groundwater, surface water, or sediment:

Commonly applied options:

- Sediment excavation/dredging
- Sediment containment
- Hydraulic groundwater containment
- Pump and treat
- Permeable reactive barriers


Photo: EQM


Photo: CDM/EPA


Photo: Dune Technologies

Most effective when the sites are:

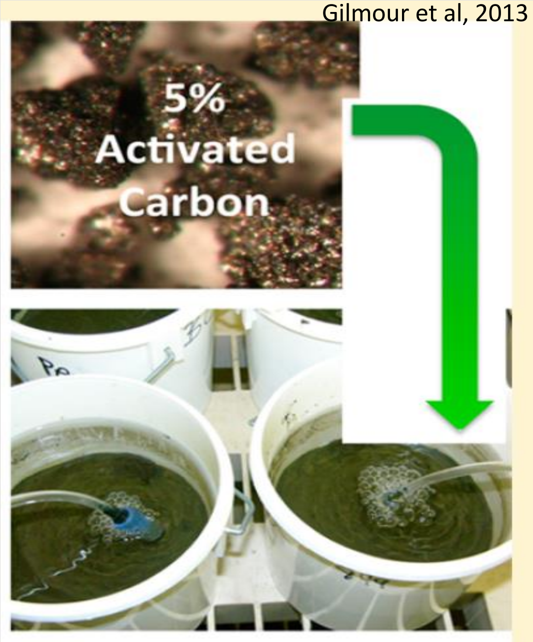
- highly contaminated
- cover relatively small area
- easily accessible
- large remediation budgets

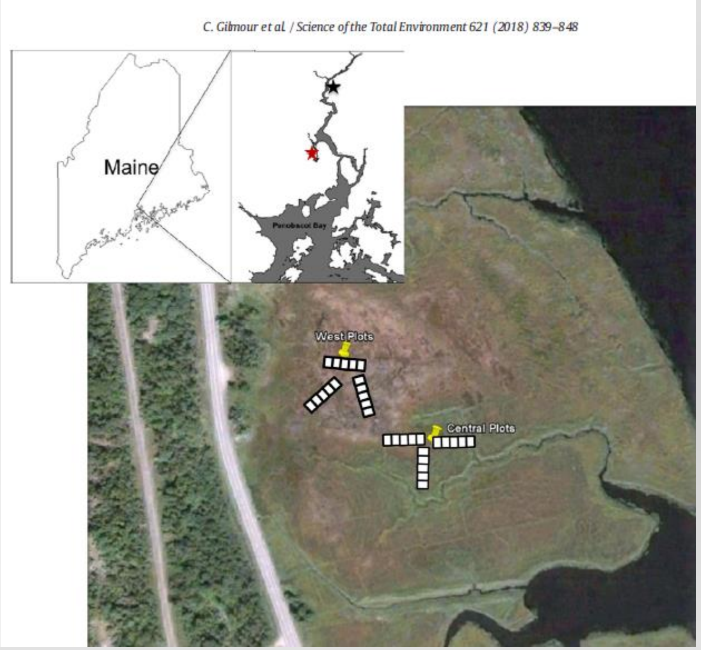
Alternative options needed when:

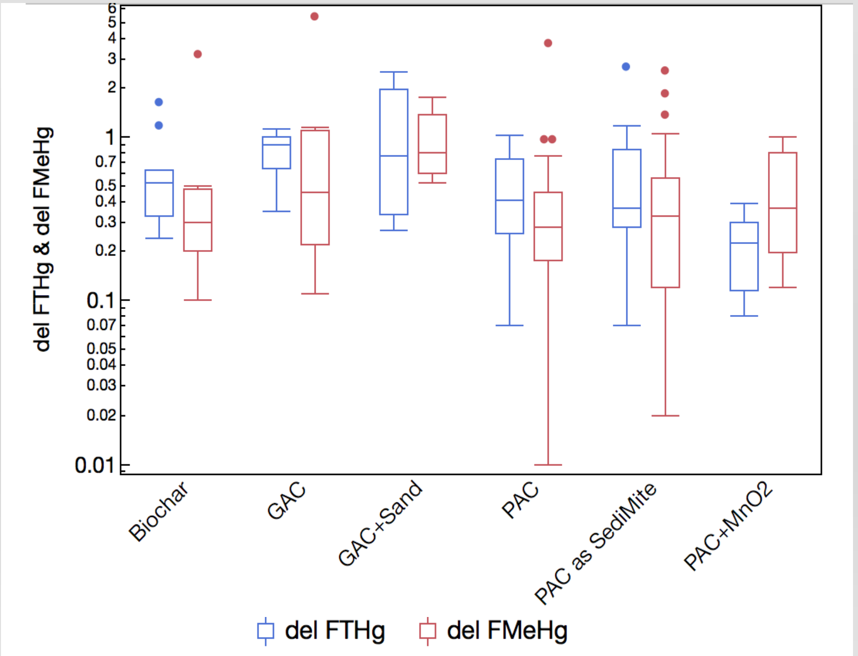
- Widely dispersed contamination
- Remote area/difficult access
- Limited funding

Site Remediation: *In situ* amendments

- *In situ* amendments to sediments/soils to compete for Hg or MeHg against natural sorbents.
- Common types: biochar, activated carbon (AC), material modified with S ligands, Fe.
- Lab and field tests have shown reductions in porewater THg & MeHg from amendments
- However, amendments may be less effective in reducing MeHg production and may accumulate MeHg in the solid-phase.
- Effectiveness impacted by type of amendment and soil/sediment properties, and DOM



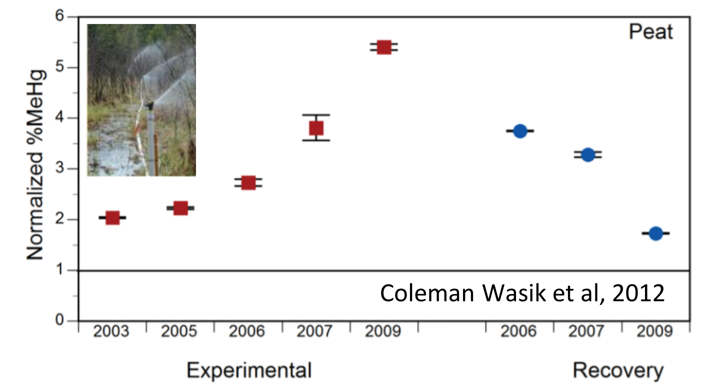


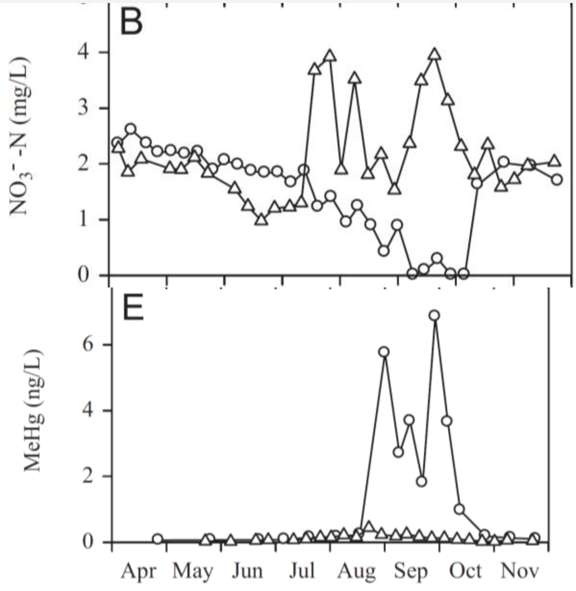


Site Remediation: Reducing MeHg

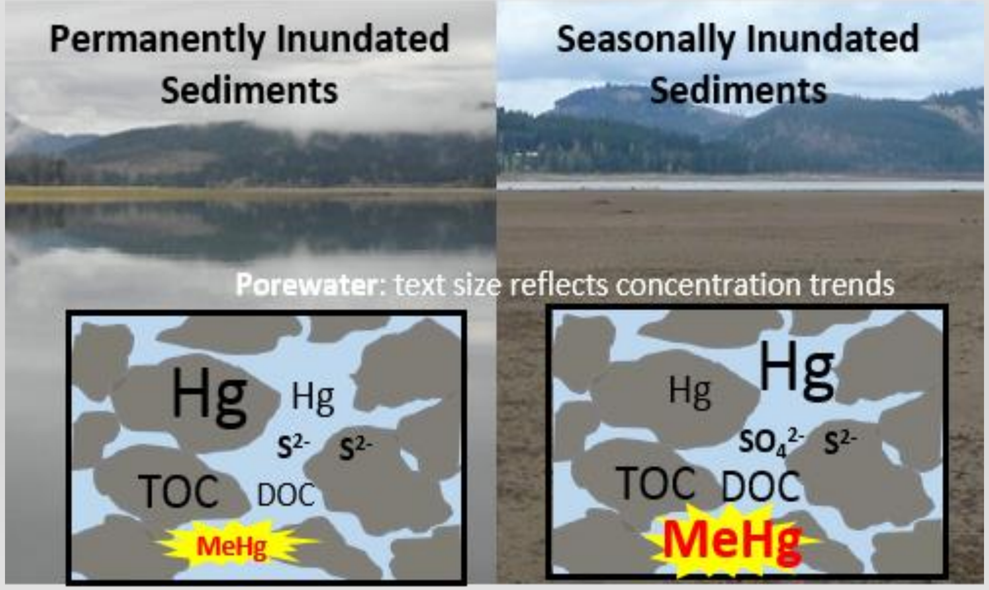
Reducing MeHg production within lakes:

- Redox poising: O_2, NO_3^-, Mn additions
- Sulfate reductions
- Carbon reductions
- Hydrological alterations

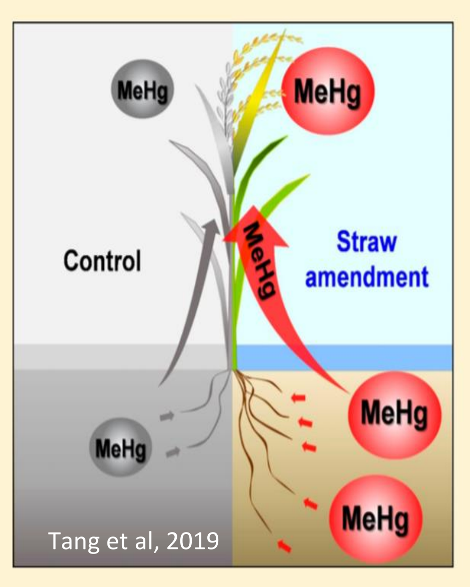




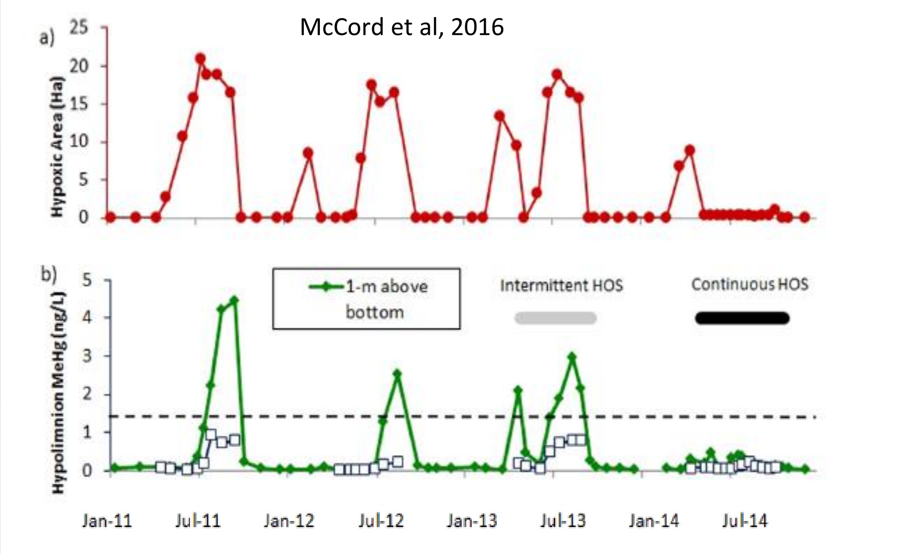
Mathews et al, 2013



Eckley et al., 2017



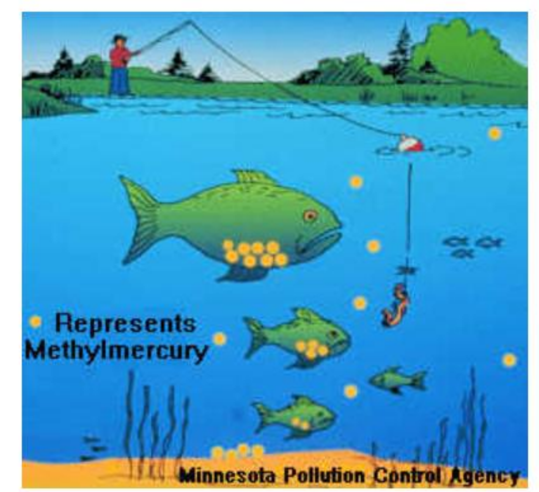
Tang et al, 2019

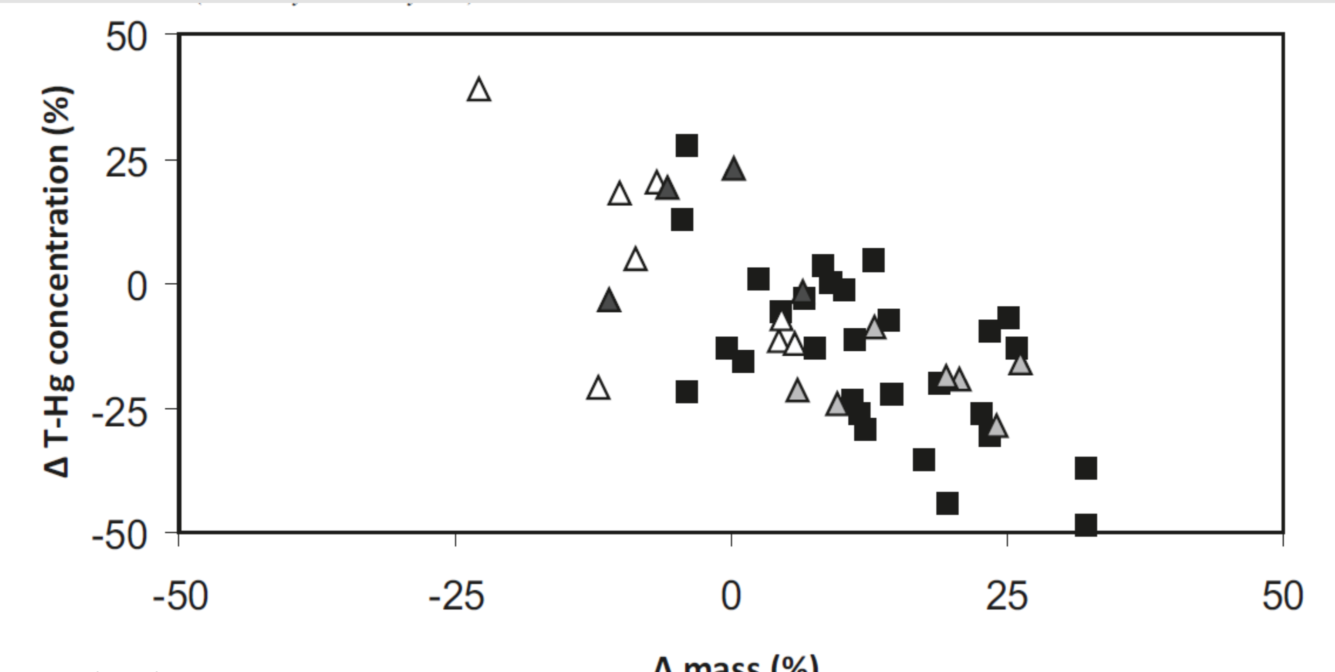


Site Remediation: Foodweb manipulation

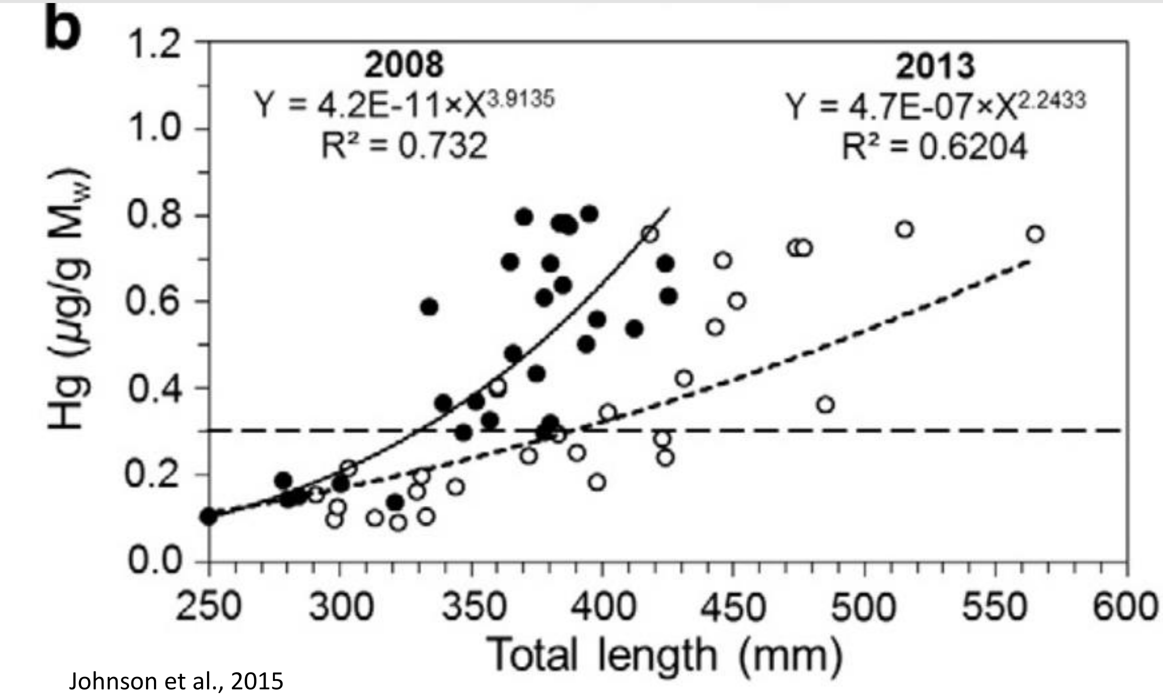
Reducing MeHg bioaccumulation:

- Foodweb and fish growth manipulations
  - ➢ Introduction of low Hg prey fish
- Only applicable to closed systems amenable to manipulations





Lepak et al, 2012



Johnson et al., 2015

Conclusions:

Recent Advances:

- **<u>THg concentrations</u>**: increased ability to measure Hg conc., forms/speciation, and potential sources.
- **<u>Methylation process</u>**: opportunities to reduce MeHg levels by targeting pools of more bioavailable Hg_i and/or other factors associated with the methylation process
- **<u>Bioaccumulation</u>**: foodweb manipulations

- Many novel approaches have not moved beyond lab/test plot scale and tested site-wide.
- Source reduction of THg has been shown to be effective at reducing MeHg in biota at some sites, but not at others.
- Successful remediation actions require a significant investment in research aimed at identifying the sources and mechanisms responsible for contamination.