The Influence of Reservoir Water Level Fluctuations on Methylmercury Production: Black Butte Mine Case Study

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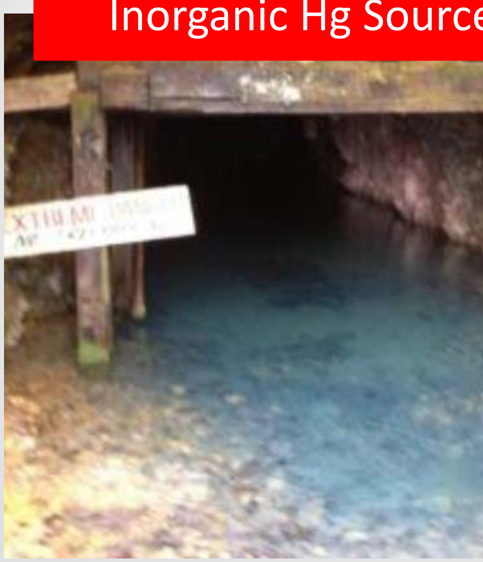
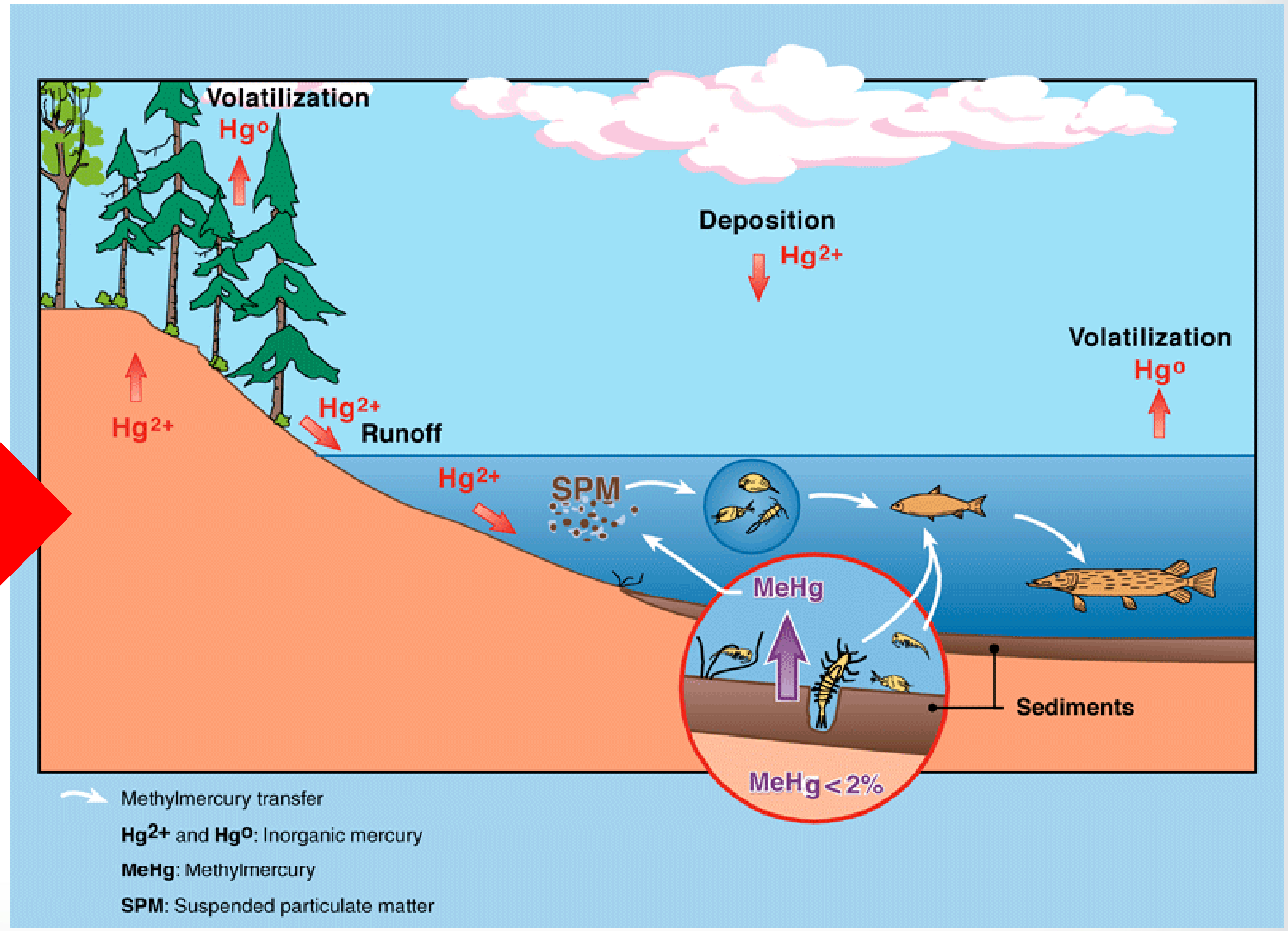
Presentation Outline

- **Introduction to Methylmercury**
- **Black Butte Mine Superfund Site**
- **Black Butte Mine: Cottage Grove Reservoir Study**
  - Reservoir Management
  - Water Column Methylmercury
  - Sediment Methylmercury
  - Wetland Contributions
- **General Conclusions and Lessons Learned**

Introduction to Methylmercury

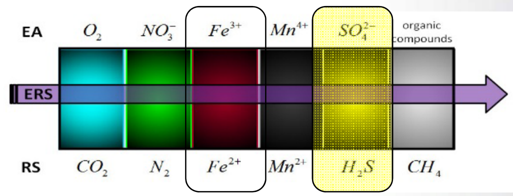


Inorganic Hg Source

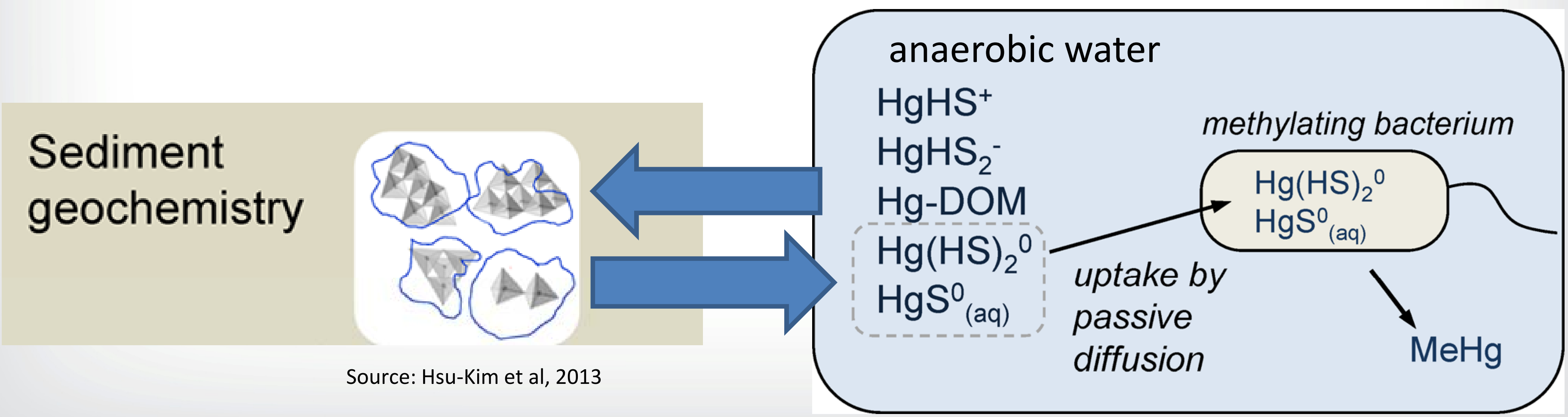


Introduction to Methylmercury

1) **Microbial Activity**: Hg is methylated by anaerobic bacteria—mostly sulfate reducers (some iron reducers)



2) Mercury Concentration & Bioavailability: Only a small fraction of Hg is bio-available for methylation



Source: Hsu-Kim et al, 2013

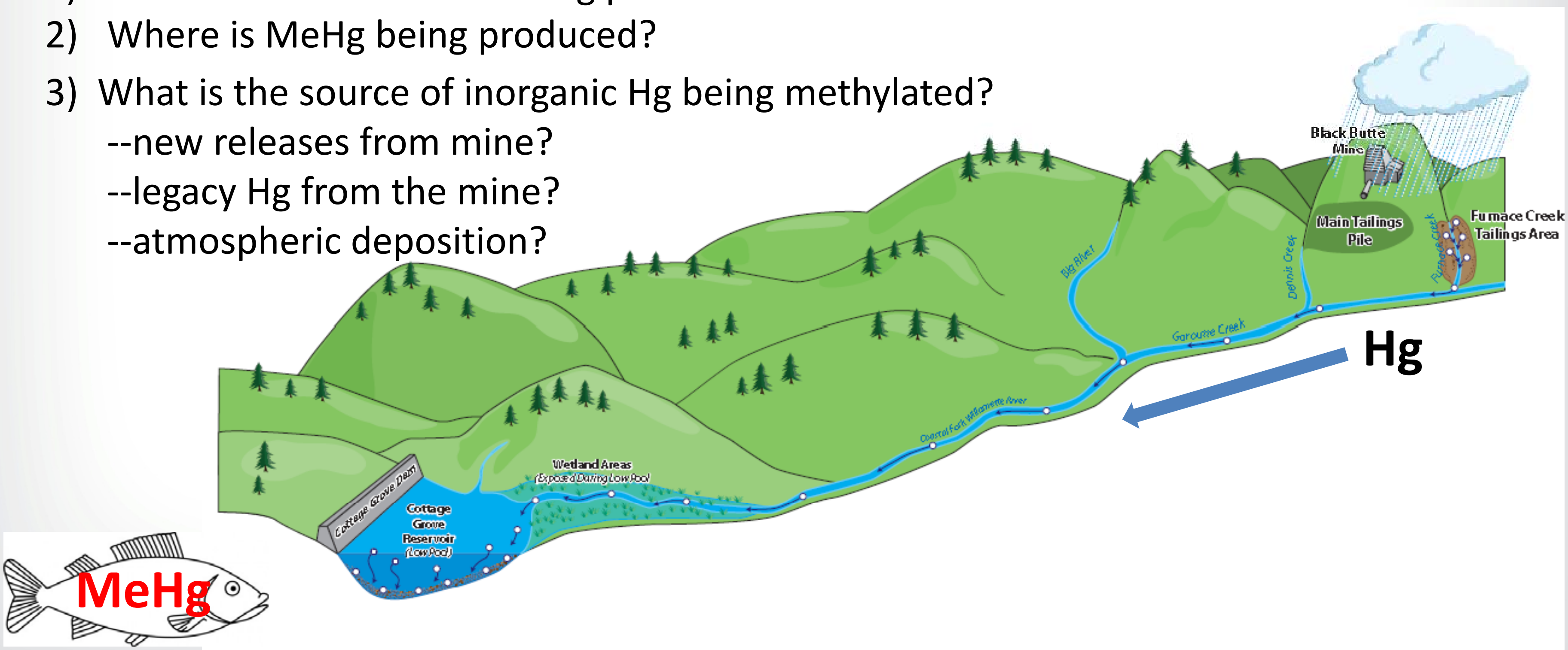
Black Butte Superfund Site: Cottage Grove Reservoir

Inorganic Hg exported from the mine site

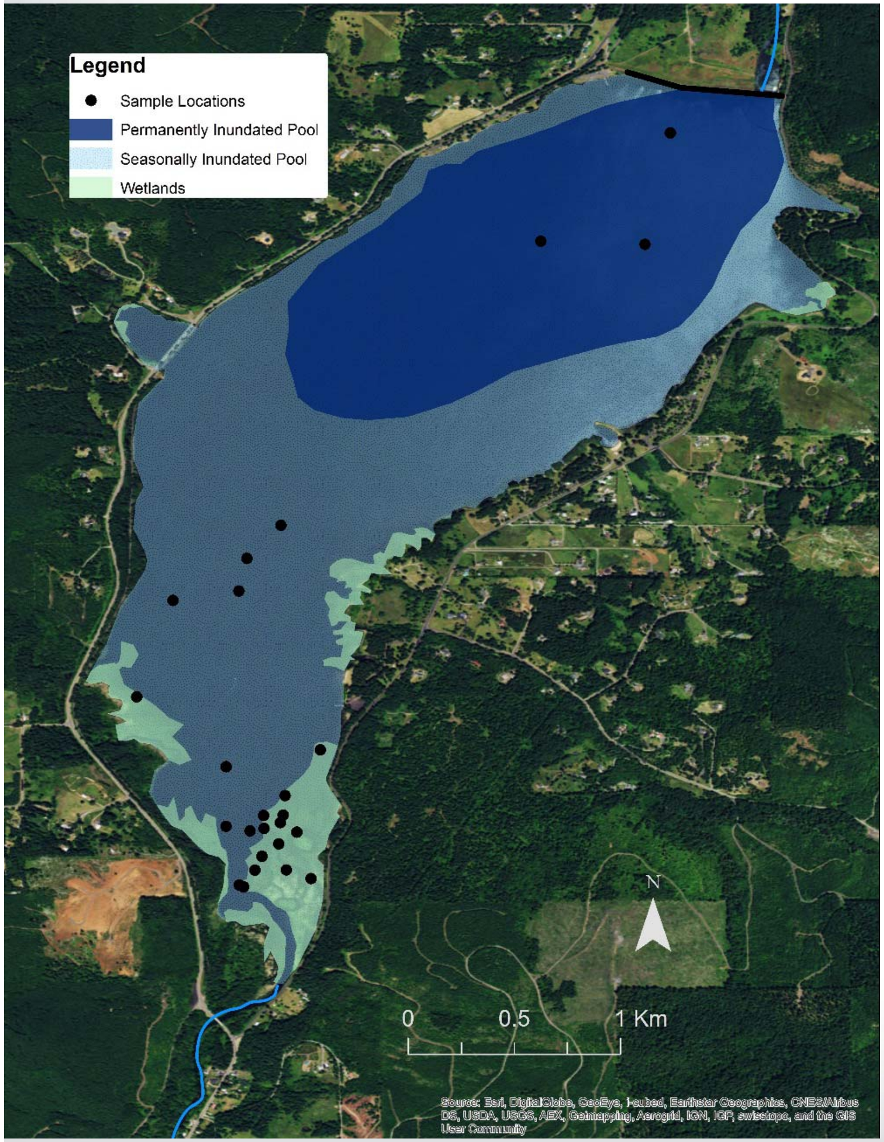
Methylmercury (MeHg) accumulating in Reservoir fish

Need to understand connection between inorganic Hg & MeHg

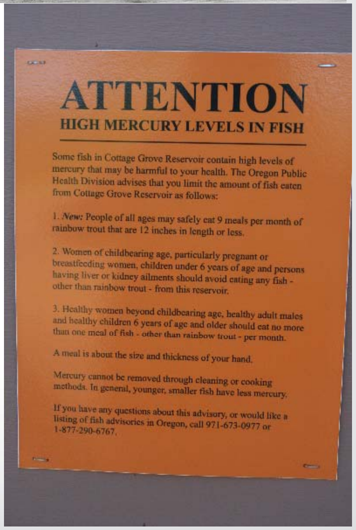
1) What variables control MeHg production?
2) Where is MeHg being produced?
3) What is the source of inorganic Hg being methylated?
   --new releases from mine?
   --legacy Hg from the mine?
   --atmospheric deposition?



Black Butte Mine Superfund Site: Cottage Grove Reservoir



- Flood Control Reservoir
- Most fish >0.3 µg/g; some fish up to 2.5 µg/g
- Reservoir popular recreational fishery
- Actively stocked

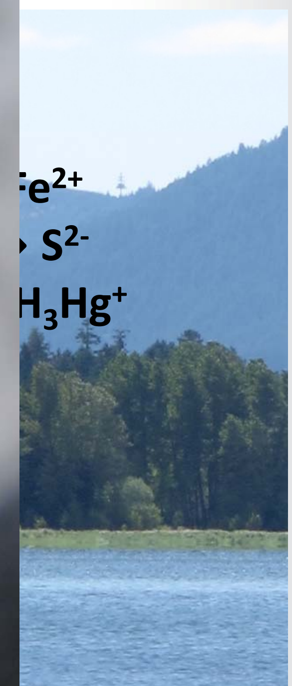


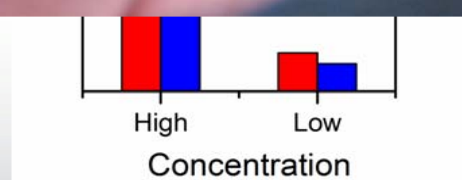
Black Butte Superfund Site: Cottage Grove Reservoir

Reducing Conditions

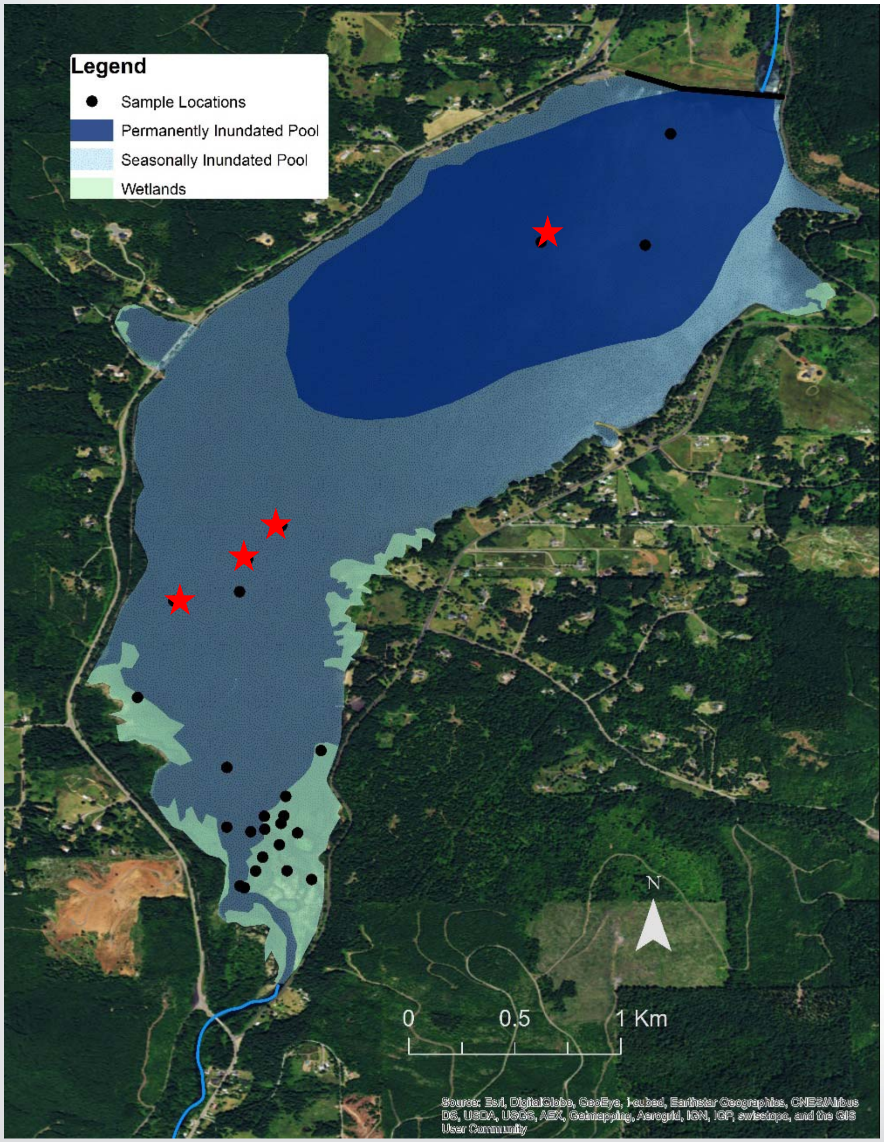
Fall and Win

Summer

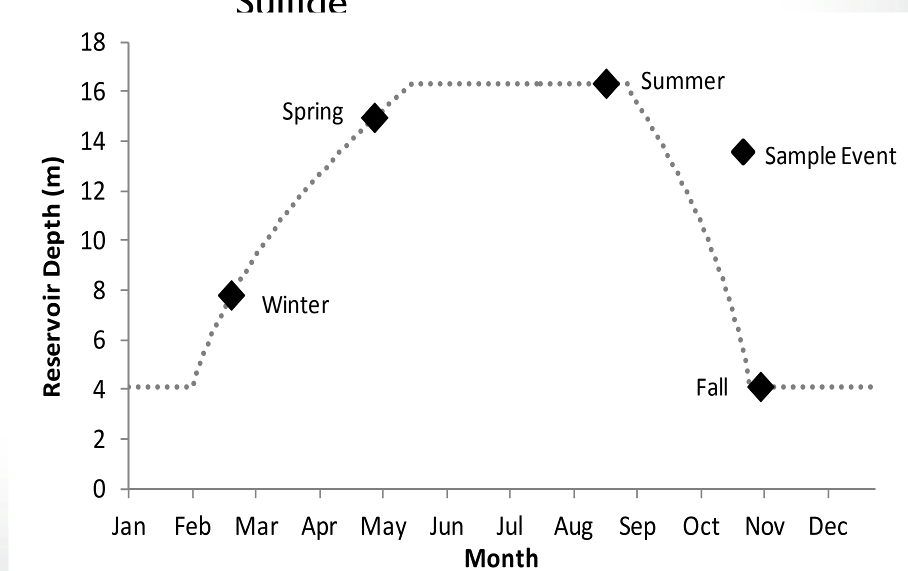




Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 1

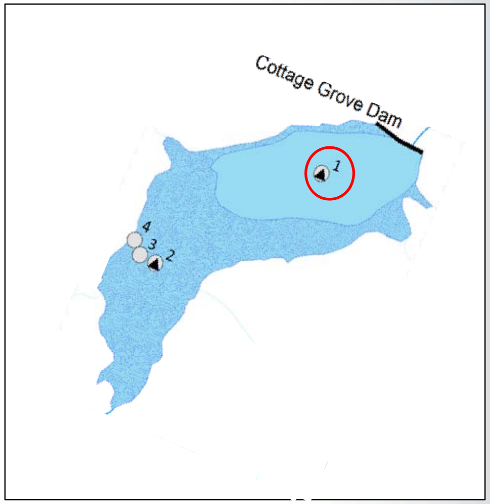


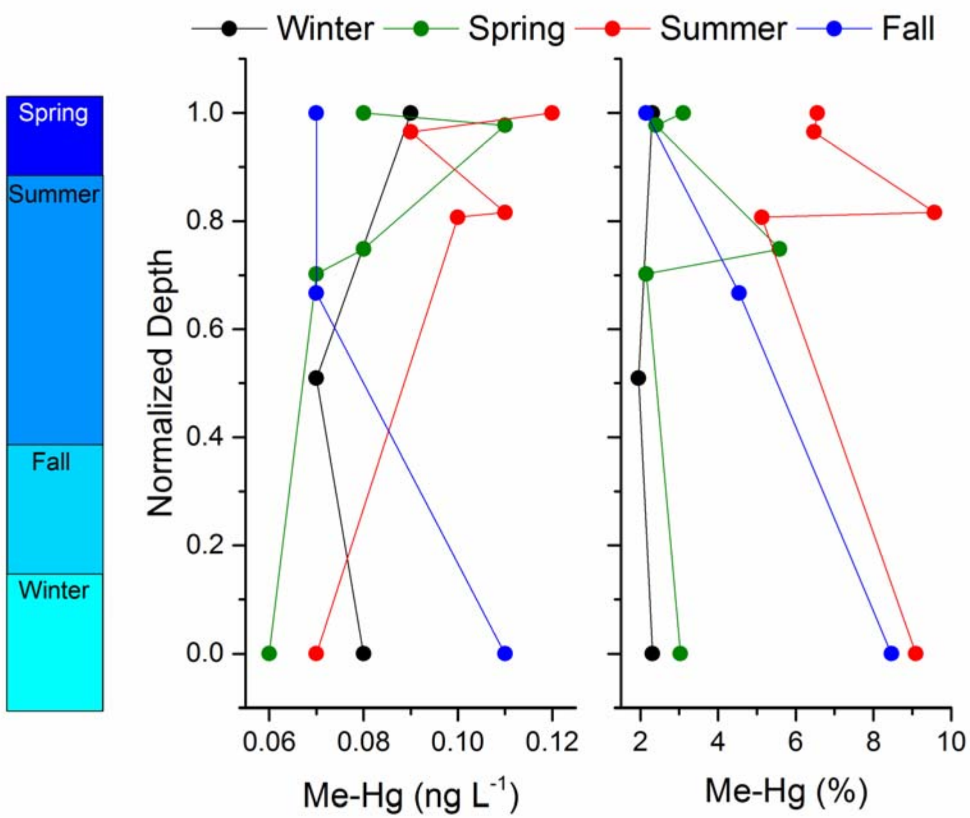
- **Do seasonal changes in water level increase Mercury Methylation?**
  - 4 sample Locations
  - 4 sampling Events
  - Measurements
    - <u>Surface Water:</u> T-Hg, Me-Hg, DOC, Sulfate, Sulfide, TSS, pH
    - <u>Sediment:</u> T-Hg, Me-Hg, Organic Carbon, Sulfide



Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 1, Water Column

- Highest Total-Hg concentration at permanently inundated location
- Highest methylation potential at the seasonally inundated locations

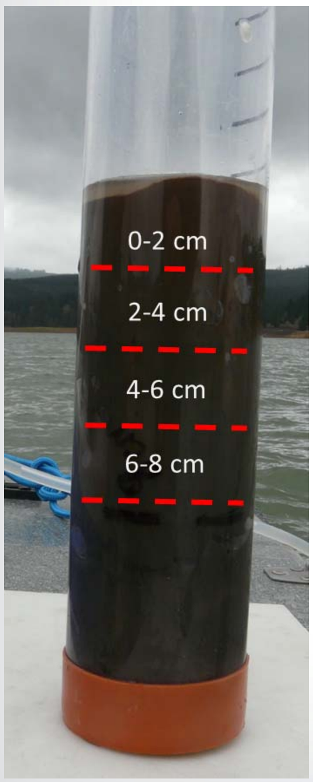


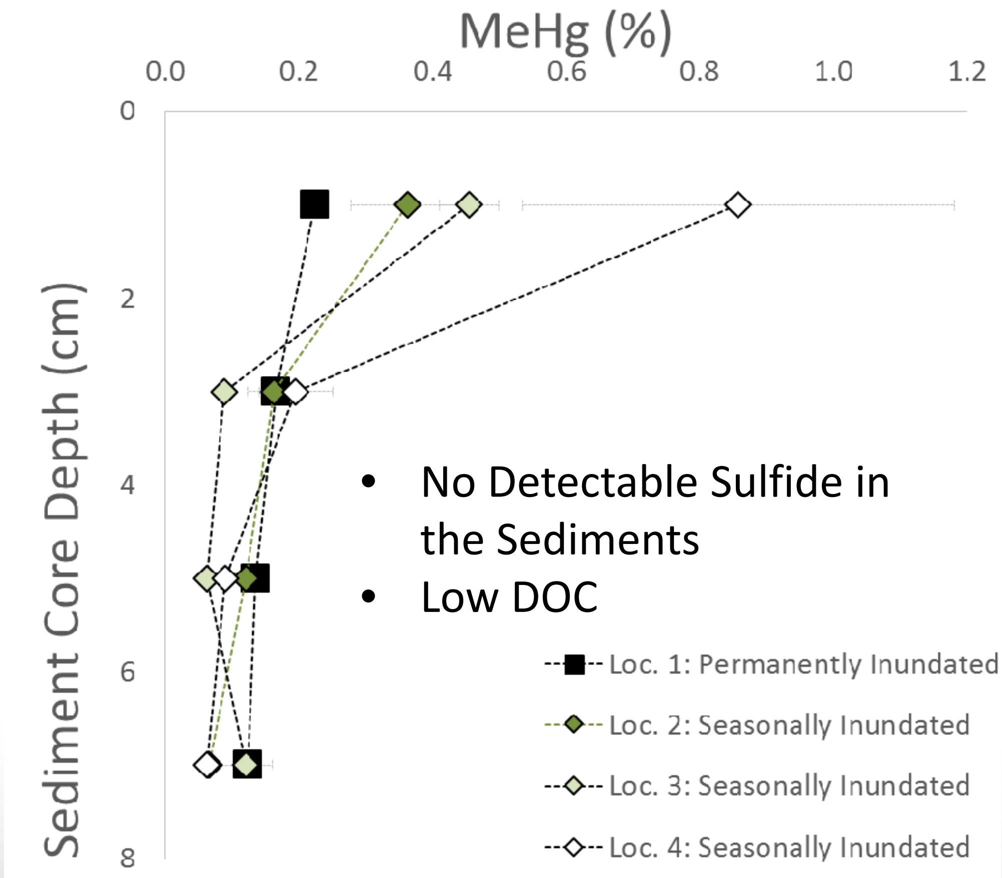


- Oxic Water Year Round
- No Detectable Sulfide
- Very Low Fe^{2+}
- Very Low DOC

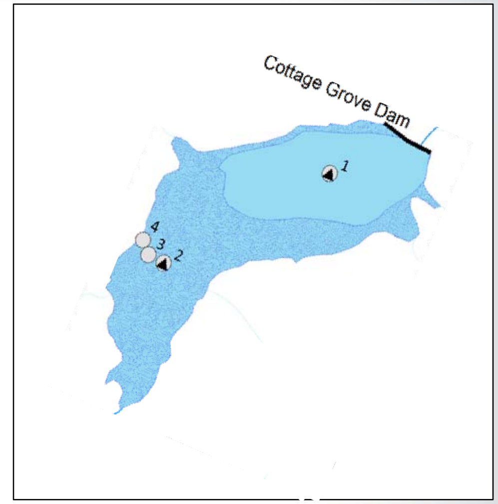
Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 1, Sediment

- Highest Total-Hg concentration at permanently inundated location
- Highest methylation potential at the seasonally inundated locations





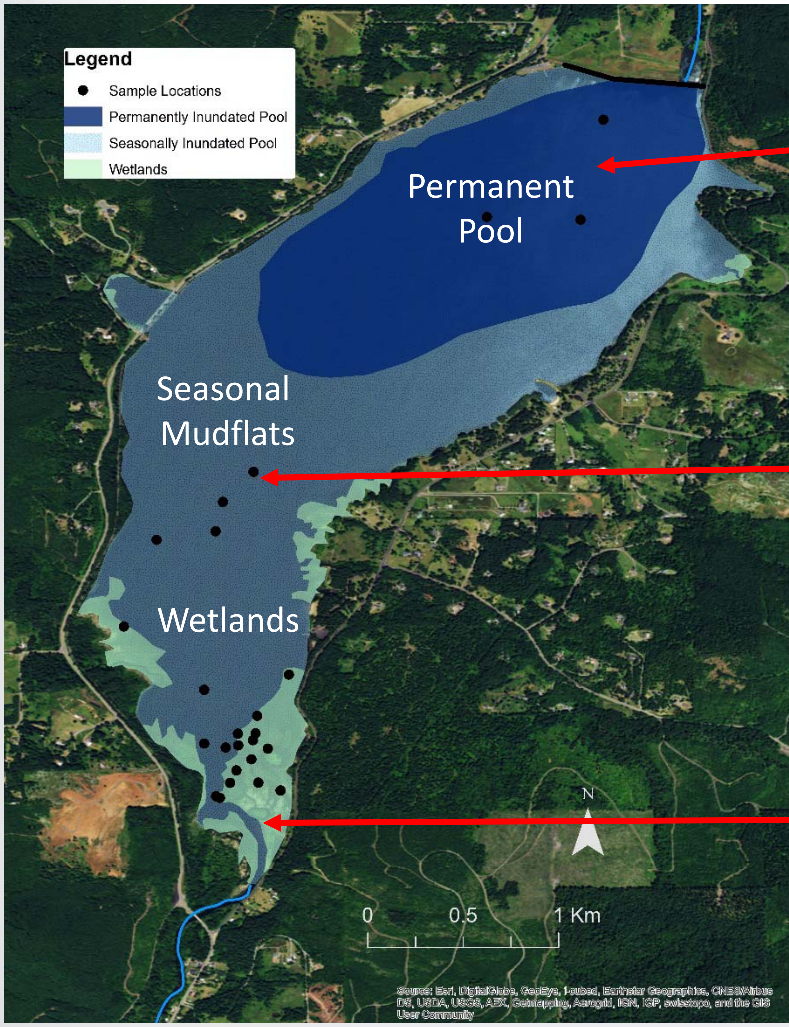
- No Detectable Sulfide in the Sediments
- Low DOC



Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 1

- **Conclusions**
  - Minimal methylation of mercury occurs in the water column
    - Oxic conditions persist through out the year
  - Majority of methylation occurring in the sediments
  - Sediments undergoing seasonal inundation result in increased Me-Hg compared to permanently inundated sediments
- **Remediation Implications**
  - Changes in reservoir management may reduce total methyl mercury concentration and production
  - Mostly "new" mercury being methylated, total concentration of methyl mercury in the reservoir may respond quickly to reductions in loading
- **Lingering Question: Where is the Majority of Methylmercury being produced?**

Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2



Where is Me-Hg being Produced?

- Additional sample Locations added in the wetlands
- 3 sampling Events: Winter, Late Spring, Late Summer
- Measurements
  - –Surface Water: T-Hg, Me-Hg, DOC, Sulfate, Sulfide, TSS, pH
  - –Sediment: T-Hg, Me-Hg, Organic Carbon, Sulfide
  - –Sediment Pore Water: T-Hg, Me-Hg, Organic Carbon, Sulfide

Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

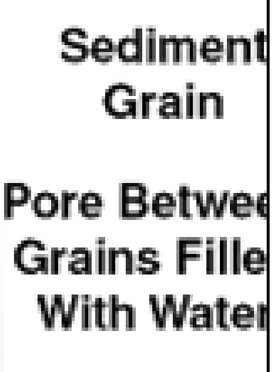
- **Rational for Porewater**
  - Porewater Hg is more bioavailable for methylation
  - Me-Hg/Hg tr nt trends
    - Isolating
  - Pore water M ptake
  - Porewater di

Core Squeezer: Grain Size, Porewater Flow Path, Oxidation

n Techniques
g (Peepers)

hery Sampler

- Centrifuge and Filter

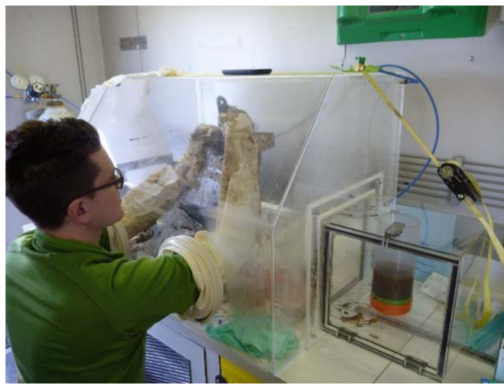


Curtesy of USGS: www.usgs.gov/definitions/porewater

Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

Porewater Methodology—Centrifuge/Filtration

Step 1) Collect Cores



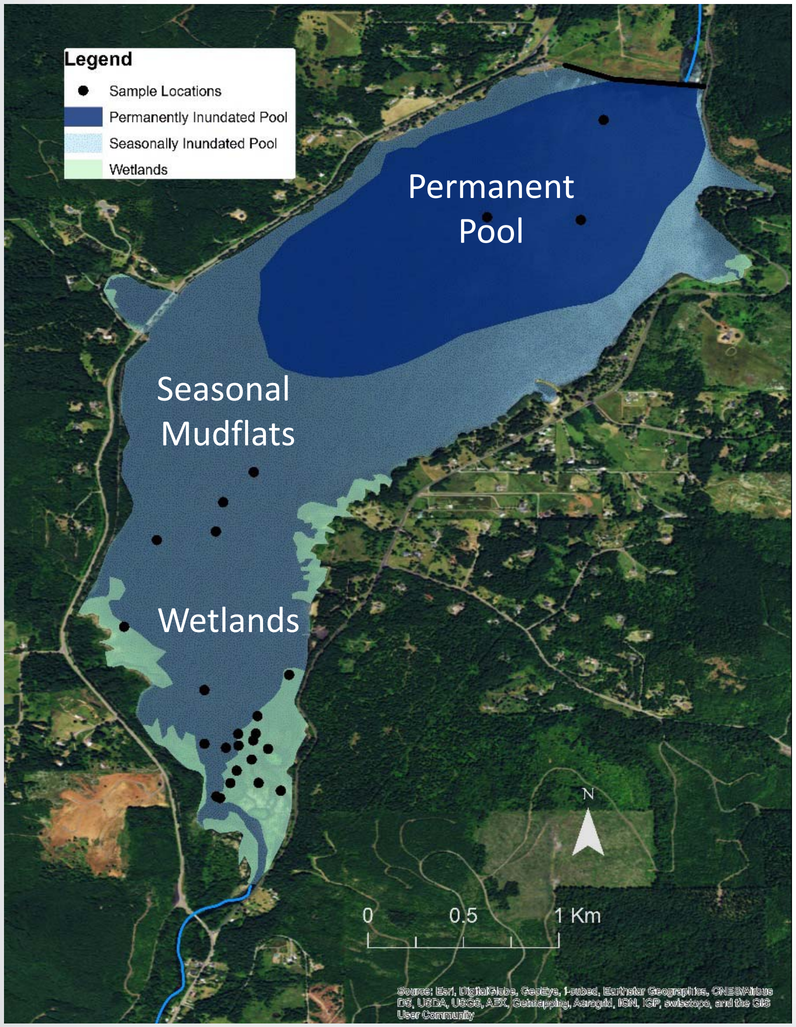
Step 2) Section cores

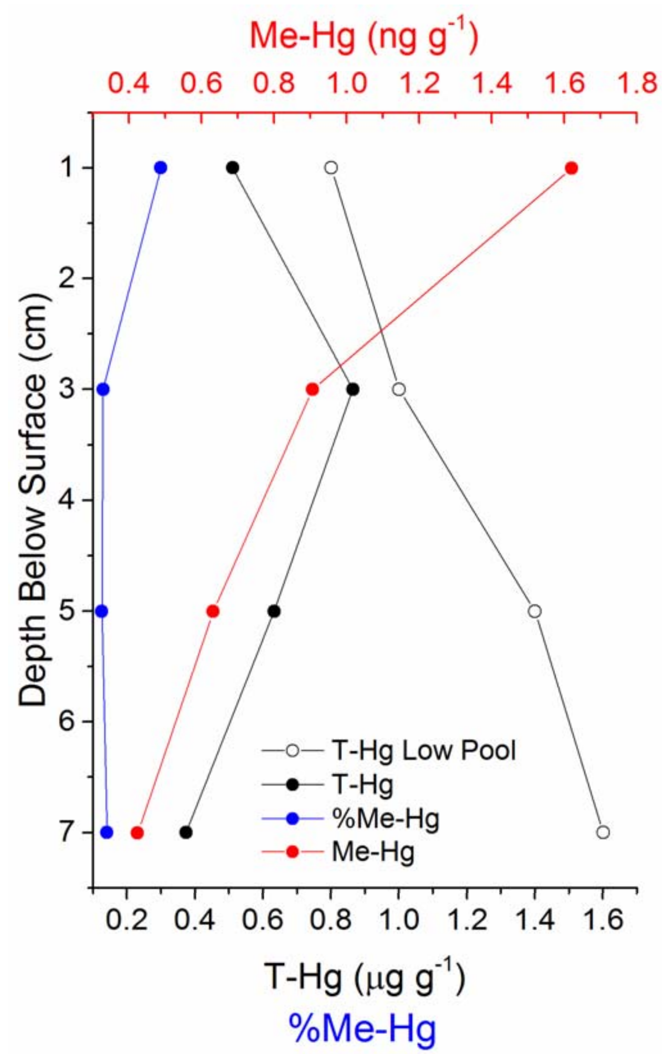
Step 3) Centrifuge

Step 4) Filter porewater

EPA Mobile Lab

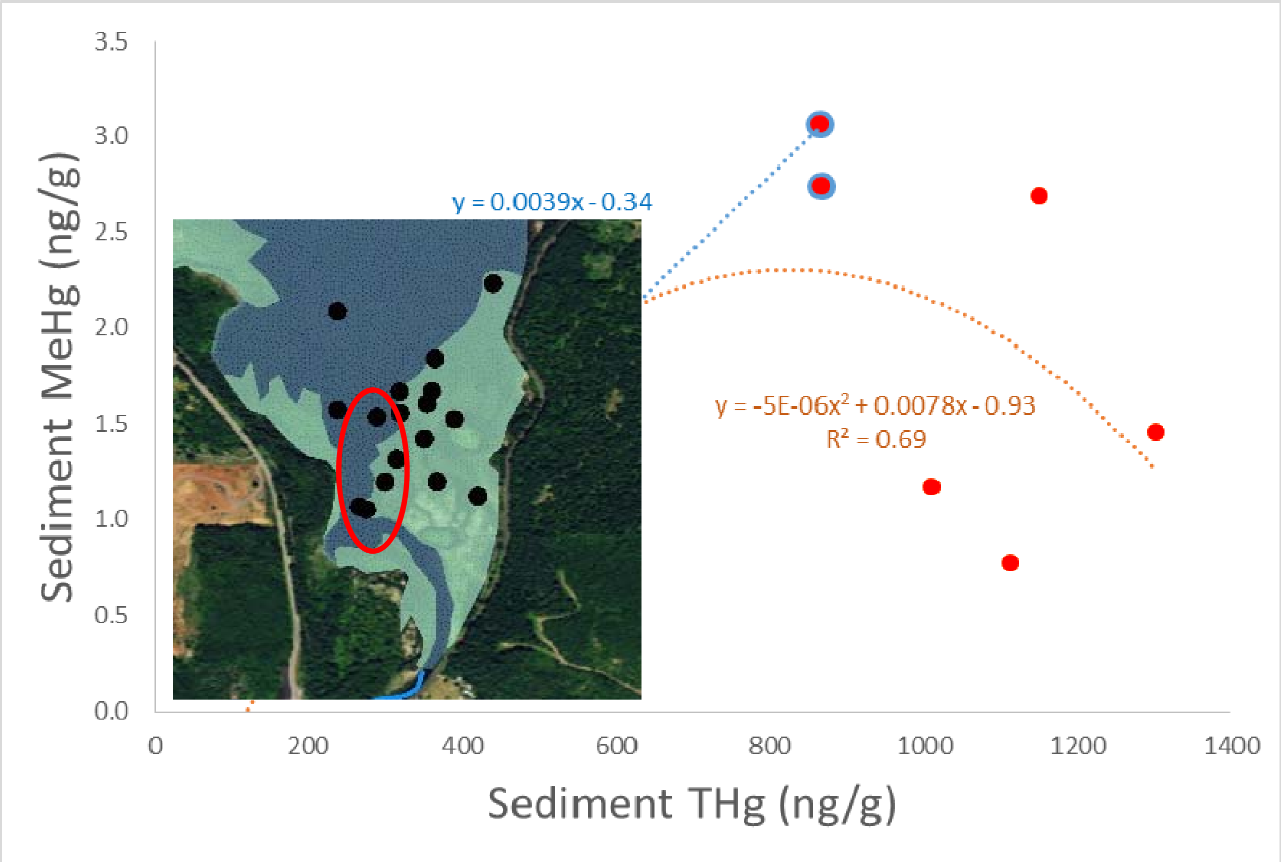
Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2





Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

- Sediment MeHg increases with Total-Hg at levels <1,000 ng/g Total-Hg
- Sediment Total-Hg bioavailability at higher concentrations may decrease

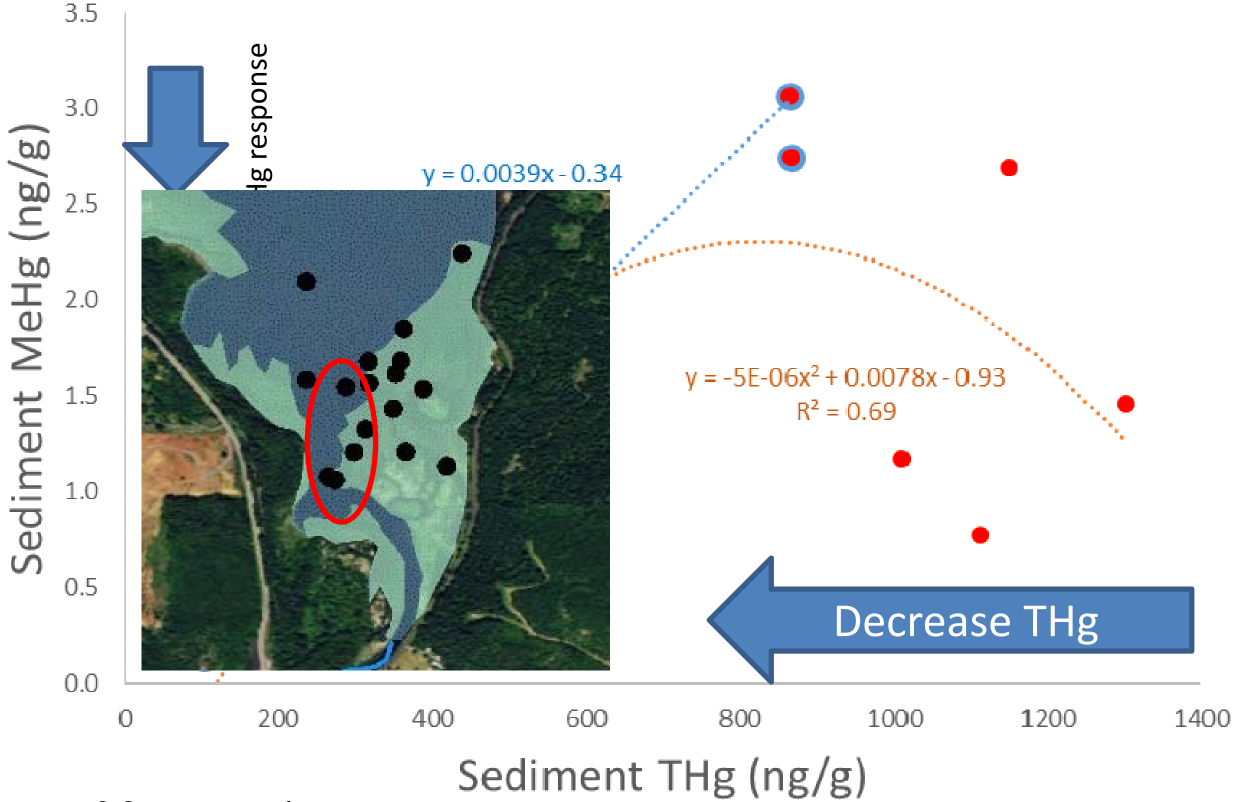


Data are provisional and subject to revision. Do not cite or distribute. 0-8cm composites

Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

Remediation implication:

Reductions in THg may not always result in 1:1 response in MeHg



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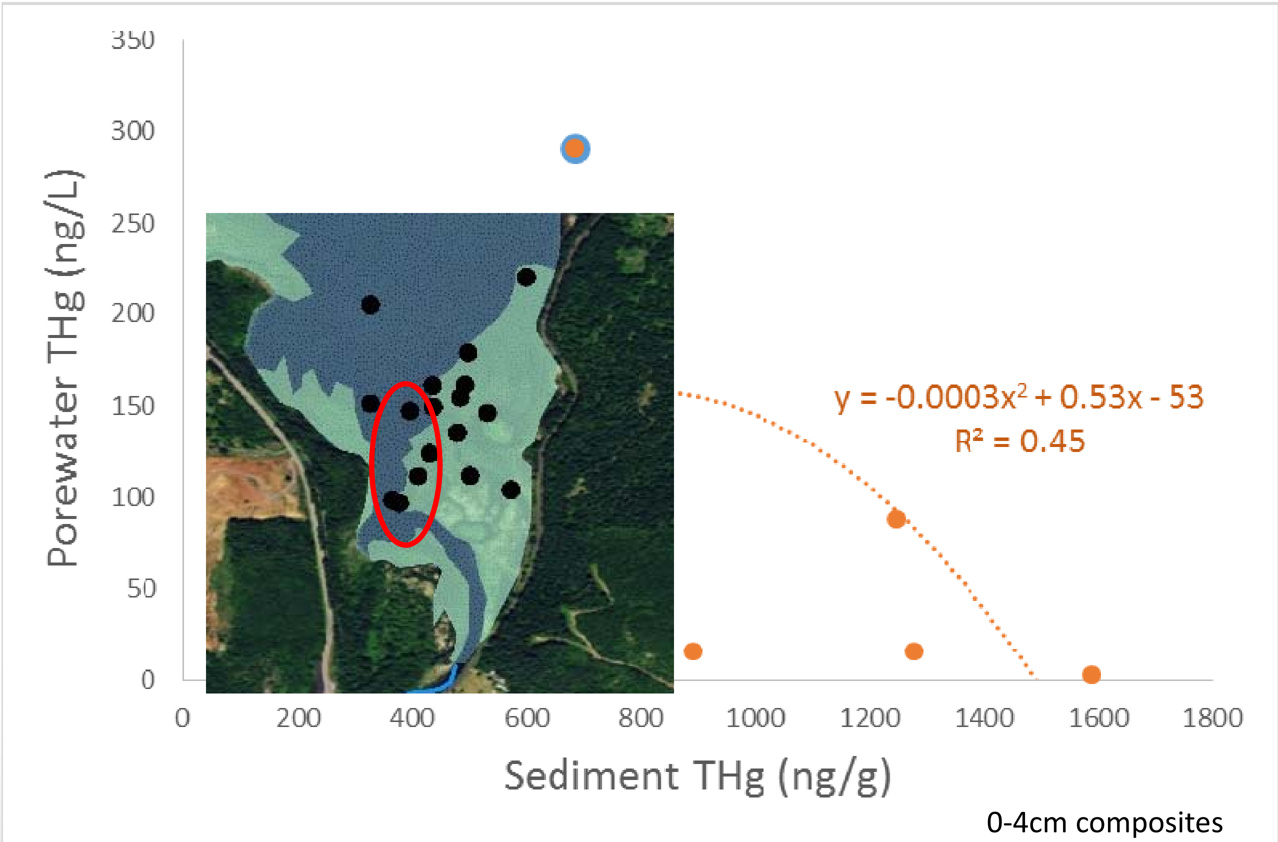
Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

- Porewater THg concentrations increase with sediment THg---except at locations with ~>1,000 ng/g
- THg in the most highly contaminated sediments shows low partitioning into porewater



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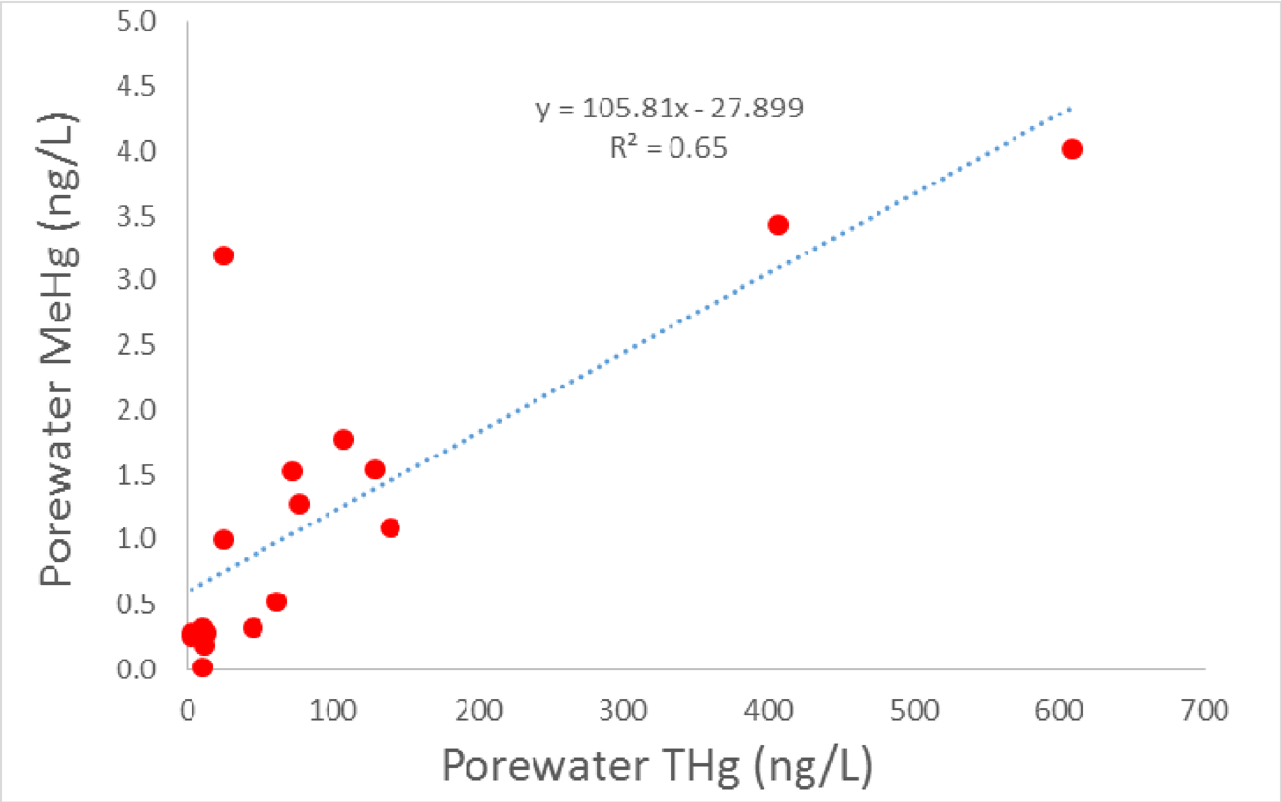
Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

- The fraction of sediment inorganic Hg that is available for methylation is in the porewater phase
- THg and MeHg in porewater are correlated over the full range of concentrations



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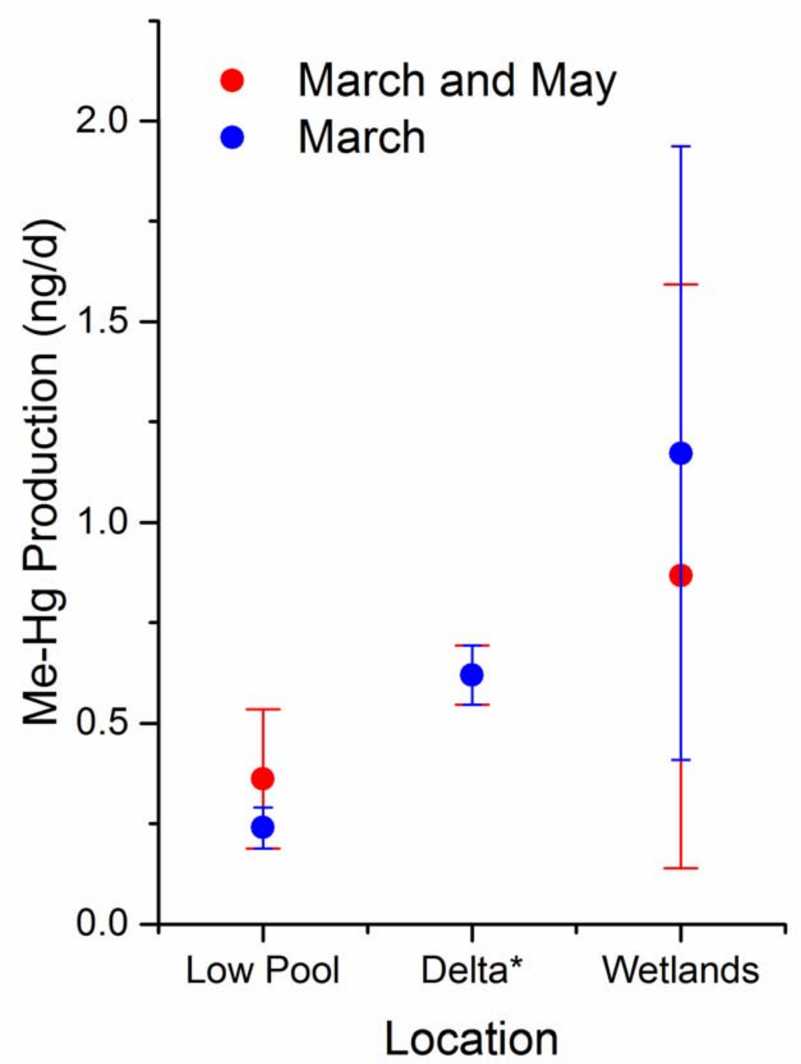
0-8cm composites

Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

- Stable Isotope Additions Measuring Methylation Potential
  - Add available isotopically enriched source of Hg^{2+} (Hg^{198})
  - Measure amount of stable isotope methylated in a given time period
- Conditions in the Delta sediments are favorable for methylation
- Reason for decreased concentration of Me-Hg may be related to the source/species of Hg present



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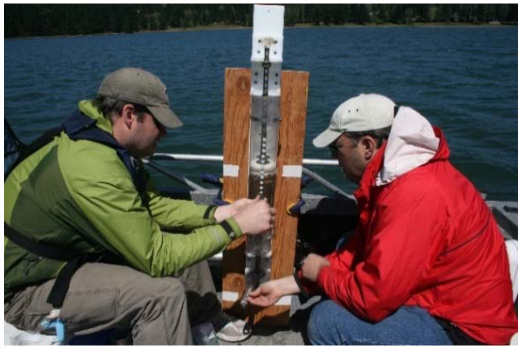
Conclusions

- Water-level fluctuations increase methylation–related to sulfate re-cycling
- Hg methylation has high spatial variability within a reservoir
- Inorganic Hg in the most highly contaminated sediments appears to be less available for methylation



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Influence of reservoir water level fluctuations on sediment methylmercury concentrations downstream of the historical Black Butte mercury mine, OR

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ABSTRACT

Mercury (Hg) is a pollutant of global concern due to its ability to accumulate as methylmercury (MeHg) in biota. Mercury is methylated by anaerobic microorganisms such as sulfate reducing bacteria (SRB) in water and sediment. Throughout North America, reservoirs tend to have elevated methylmercury (MeHg) concentrations compared to natural lakes and rivers. This impact is most pronounced in newly created reservoirs where methylation is fueled by the decomposition of flooded organic material, which can release Hg and enhance microbial activity. Much less is known about the longer-term water-level management impacts on Hg cycling in older reservoirs. The objective of our study was to understand the role of on-going water-level fluctuations on sediment MeHg concentrations and sulfur speciation within a reservoir 75 years after initial impoundment. The study was performed at the Cottage Grove Reservoir located 15 km downstream of the historical Black Butte Hg mine. For 8 months each year, the water level is lowered resulting in roughly half of the reservoir's sediment being exposed to the atmosphere. Water samples from the inflow, water-column, outflow, and sediment were collected seasonally over a year for total-Hg, MeHg, and several ancillary parameters. The results showed that conditions in the reservoir were favorable to methylation with a much higher %MeHg observed in the outflowing water (34%) compared to the inflow (7%) during the late-summer. An anoxic hypolimnion did not develop in the reservoir indicating that methylation was predominantly occurring in the sediments. In the sediments subjected to seasonal inundation, MeHg production was highest in the top 2 cm of the sediments and declined with depth. The seasonally inundated sediments also had significantly higher methylation activity than the permanently inundated area of the reservoir. Oxidizing conditions in the sediments during periods of exposure to air resulted in an increase in sulfate concentrations which likely stimulated SRB methylation following the raising of the water levels. In contrast, the sulfur in the permanently inundated sediments was all in a reduced form (sulfide) and sulfate remained below detection throughout the year. Overall, our results indicate that reservoir water level fluctuations can affect sediment redox conditions and enhance MeHg production. This process can result in a continued elevation of MeHg concentrations in older reservoirs after the initial impact of landscape flooding has subsided.


Questions?