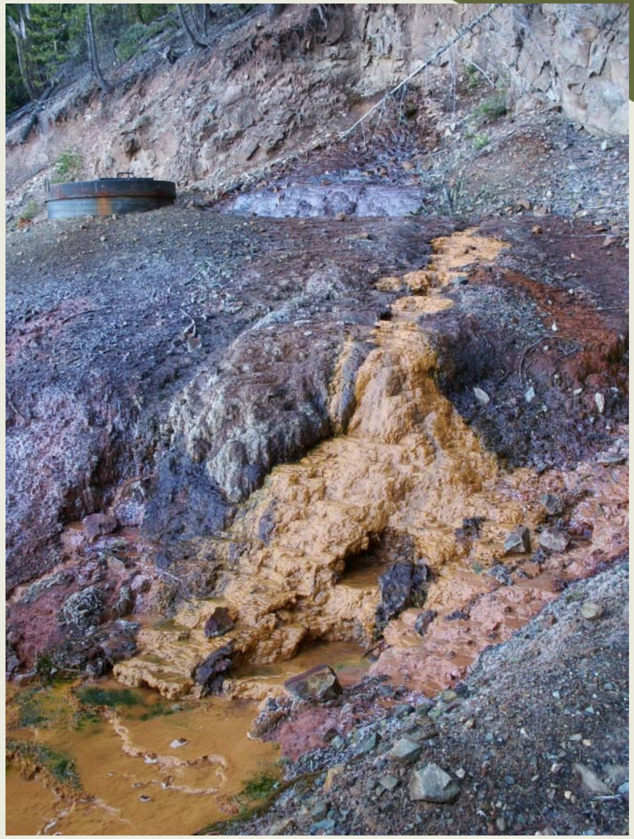
Formosa & Black Butte Mine Superfund Site

Methylation of Mercury at Mining Sites

March 29, 2016



Mine Locations

Black Butte Mine Site Characteristics

Deposit: primarily cinnabar

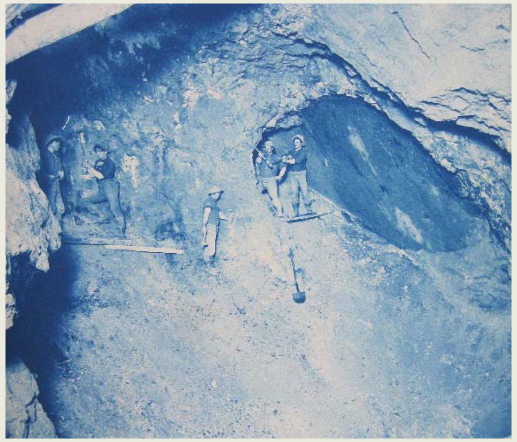
Operation timeframe: 1890 to late 1960s

Mine: underground mine; surface waste rock & tailings

Ore Processing: elemental mercury was produced on the site by heating crushed ore in a furnace.

Production: ~635,000 kg of Hg

Environmental Issues: High Hg content tailings located in and near stream channels. Elevated methylmercury (MeHg) levels in fish in downstream reservoir.

Formosa Mine Site Characteristics

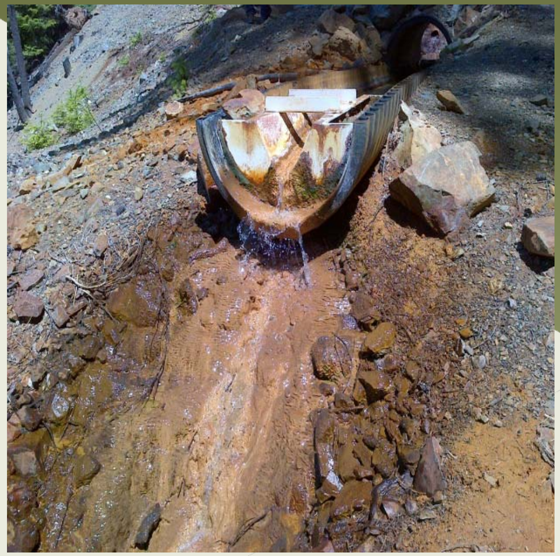
Mine type: Copper & Zinc

Operation timeframe: 1910 to1993

Mine: underground mine; surface waste rock & tailings

Environmental Issues:

- Release ~19,000 m^3/y of acid mine drainage to area streams, which contains up to 15 tons of dissolved copper, zinc, and other heavy metals
- Streambed sediment and precipitate

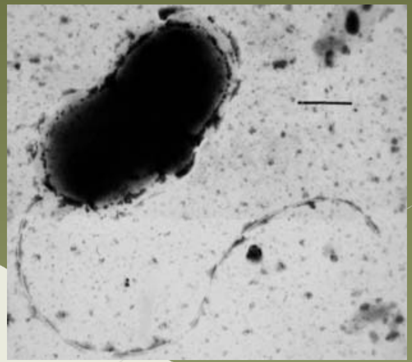


Introduction to Mercury Methylation

Methylmercury is of concern due to its increased toxicity and ability to bioaccumulate

Mercury is methylated by some anaerobic bacteria

Main Factors Necessary for Methylmercury Production:



1) Source of bioavailable inorganic mercury
2) Microbial activity:
- **Anoxic conditions**
- **Electron donors: organic carbon**
- **Electron acceptors: sulfate, ferric iron, etc**

Site Aqueous Mercury Concentrations

Formosa Mine

Adit Water:

Low THg: 3.0± 0.7 ng/L
41 ± 11% dissolved-phase
Low MeHg: <0.03 ng/L
High Sulfate: 2,245 ± 500 mg/L
Low pH: 2-3 s.u.
Low organic carbon: 2.1 ± 1.1

Black Butte Mine

Furnace Creek Water:

High THg: 32,000 ± 36,000 ng/L
(Max: 93,000 ng/L during storm events)
17 ± 11% dissolved
Low MeHg: <0.001% MeHg
Low Sulfate: 3.1 ± 0.9 mg/L
Neutral pH: 6.8
Low organic carbon: 3.0 ± 1.4

Site Aqueous Mercury Concentrations

Formosa Mine

Adit Water:

Low THg: 3.0± 0.7 ng/L

Black Butte Mine

Furnace Creek Water:

High THg: 32,000 ± 36,000 ng/L

For comparison: USGS Mercury Streams Study (Scudder et al, 2009_

Parameter	Site grouping	Mean	Median	Std Dev	Min	Max	n	Units	Comparison
Methylmercury	All sites	0.19	0.11	0.35	<0.010	4.11	337	ng/L	No significant difference
	Sites in unmined basins	0.20	0.11	0.37	<0.010	4.11	257		
	Sites in mined basins	0.18	0.10	0.31	<0.010	2.02	80		
Total mercury	All sites	8.22	2.09	32.8	0.27	446	336	ng/L	Mined > Unmined (p<0.0001)
	Sites in unmined basins	2.96	1.90	5.29	0.27	75.1	250		
	Sites in mined basins	23.5	3.79	62.1	0.48	446	86		
Methyl/Total mercury	All sites	7.08	4.60	8.18	0.02	81.5	328	Percent	Unmined > Mined (p<0.0001)
	Sites in unmined basins	7.46	5.35	6.72	0.19	46.8	249		
	Sites in mined basins	5.87	2.37	11.6	0.02	81.5	79		

Downstream conditions

Formosa Mine

Relatively steep gradient stream systems

Well oxygenated; low potential for methylation

Black Butte Mine

Reservoir downstream of mine with wetlands

Conditions conducive to MeHg production

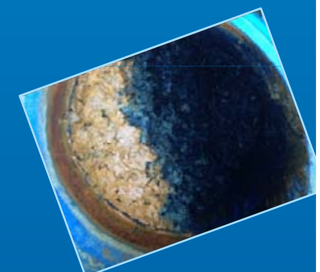
AN EVALUATION OF MERCURY FATE AND TRANSPORT IN MINING-INFLUENCED WATER TREATED WITH ENHANCED SULFATE REDUCTION BIOCHEMICAL REACTORS

Stephen Dent, Ph.D.

Coauthors: Nick Anton, Dave Reisman (CDM Smith), Chris Cora, Chris Eckley, Souhail Al-Abed, Kira Lynch (USEPA)

Clu-In Webinar

March 29, 2016



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

CDM Smith®

Clu-In Topic: Identifying the Potential for Methylation of Mercury at Mine Sites

Presentation Objectives

- Background: Mercury in the Environment
  - Mercury Advisories
  - Food-Web Interactions
  - Trace Mercury Assessments
- Biochemical Reactors – Mining Impacted Water
  - Formosa Treatability Study
    - Treatment Configuration and Setup
    - Mercury Assessment Results
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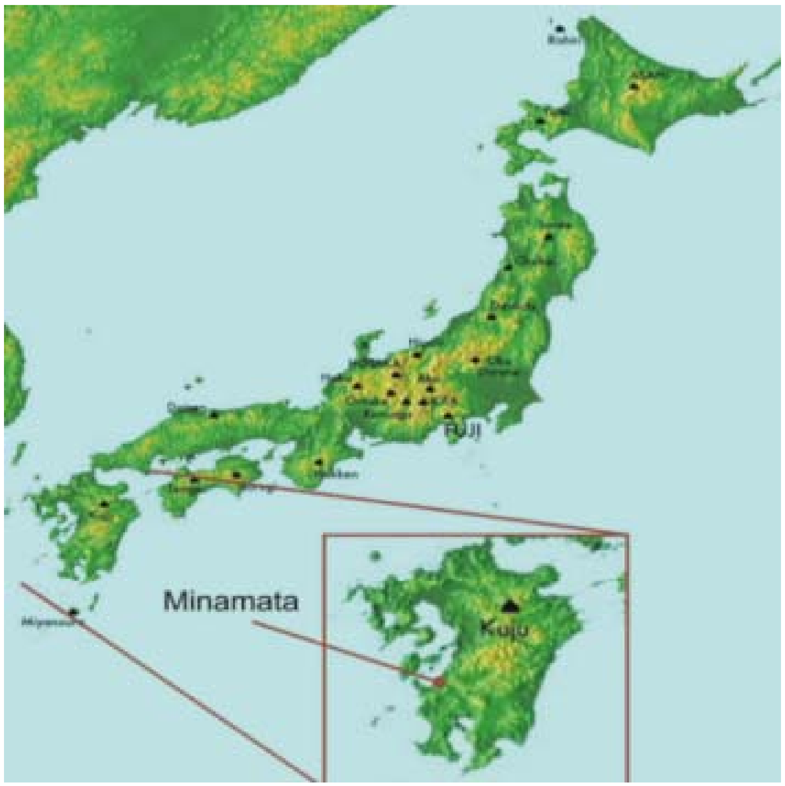
Anthropogenic Point Source Impacts

Minamata Bay



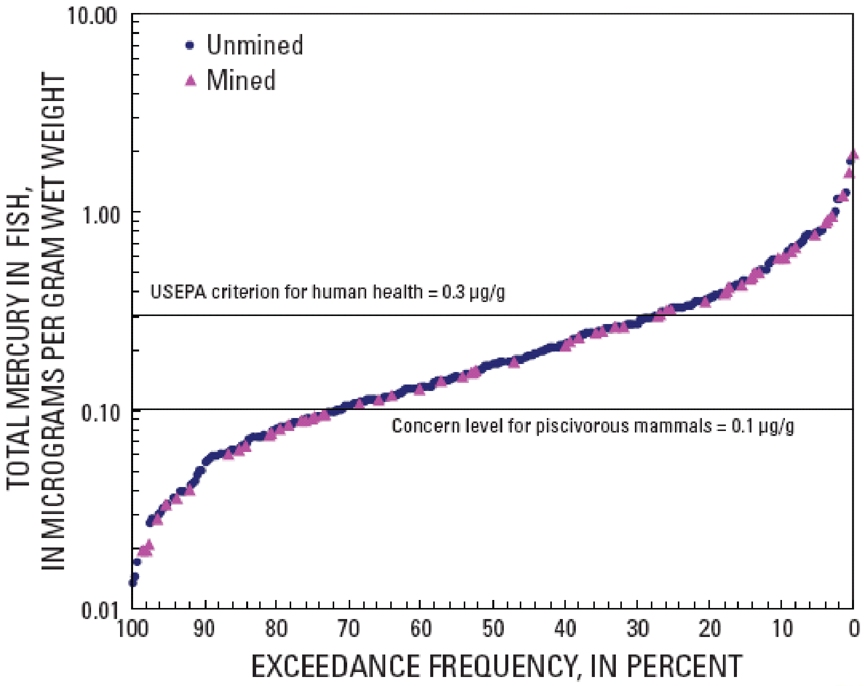
- Acetaldehyde Production 1932 -1968
- 27 Tons Methylmercury Dumped Into the Bay
- First Case: 1956
- 900 Killed
- 2 Million w/ Severe Health Effects

Mercury Advisories in US

Source: USEPA, 2008

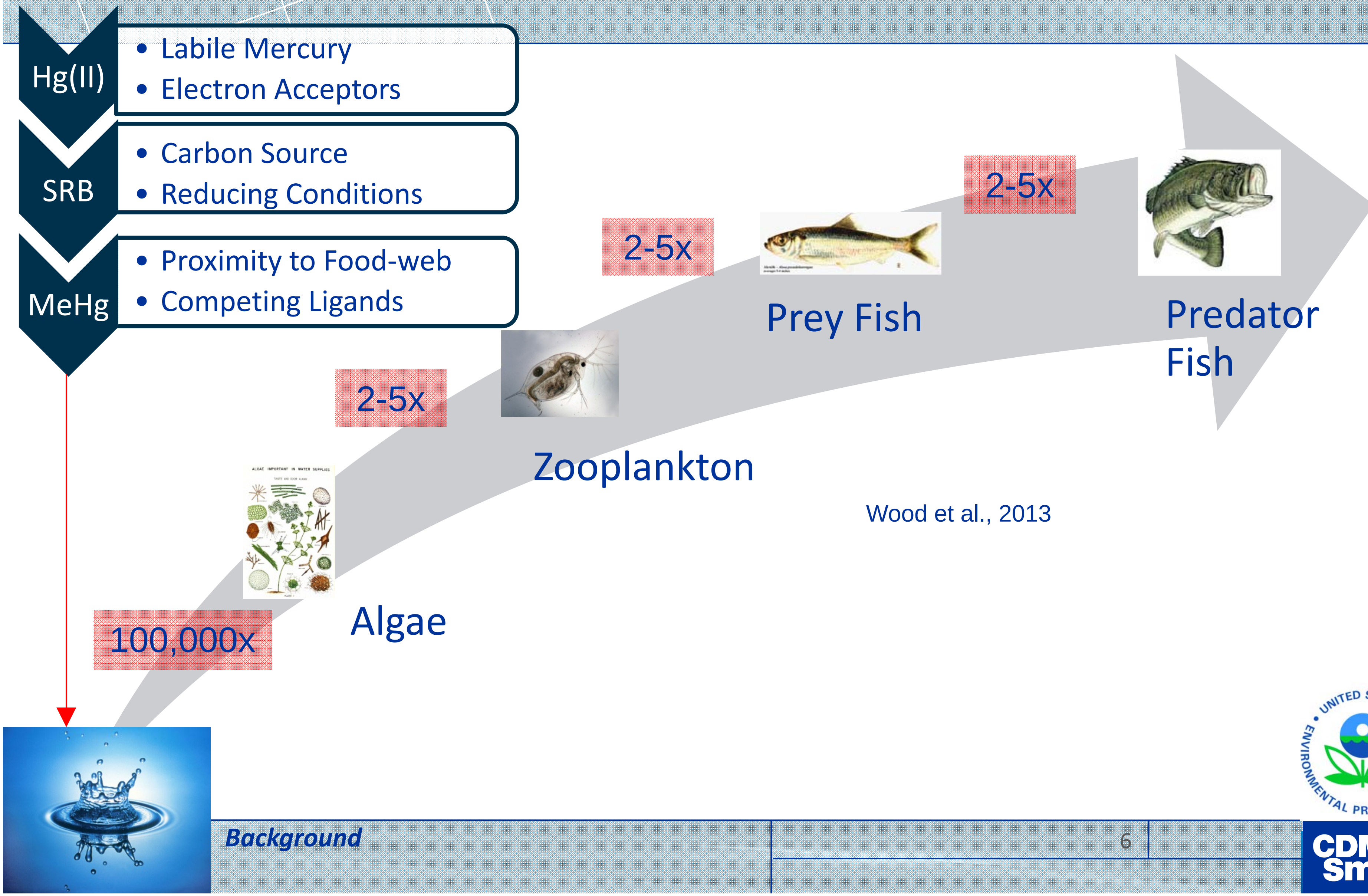
Non-Point Source Impact

- 367 Stream Sites Sampled Across United States
- Sites with Fish Greater than 0.3 µg/g or mg/kg or ppm
  - 25% Exceedances
- Sites with Fish Greater than 0.6 µg/g or mg/kg or ppm
  - 10% Exceedances



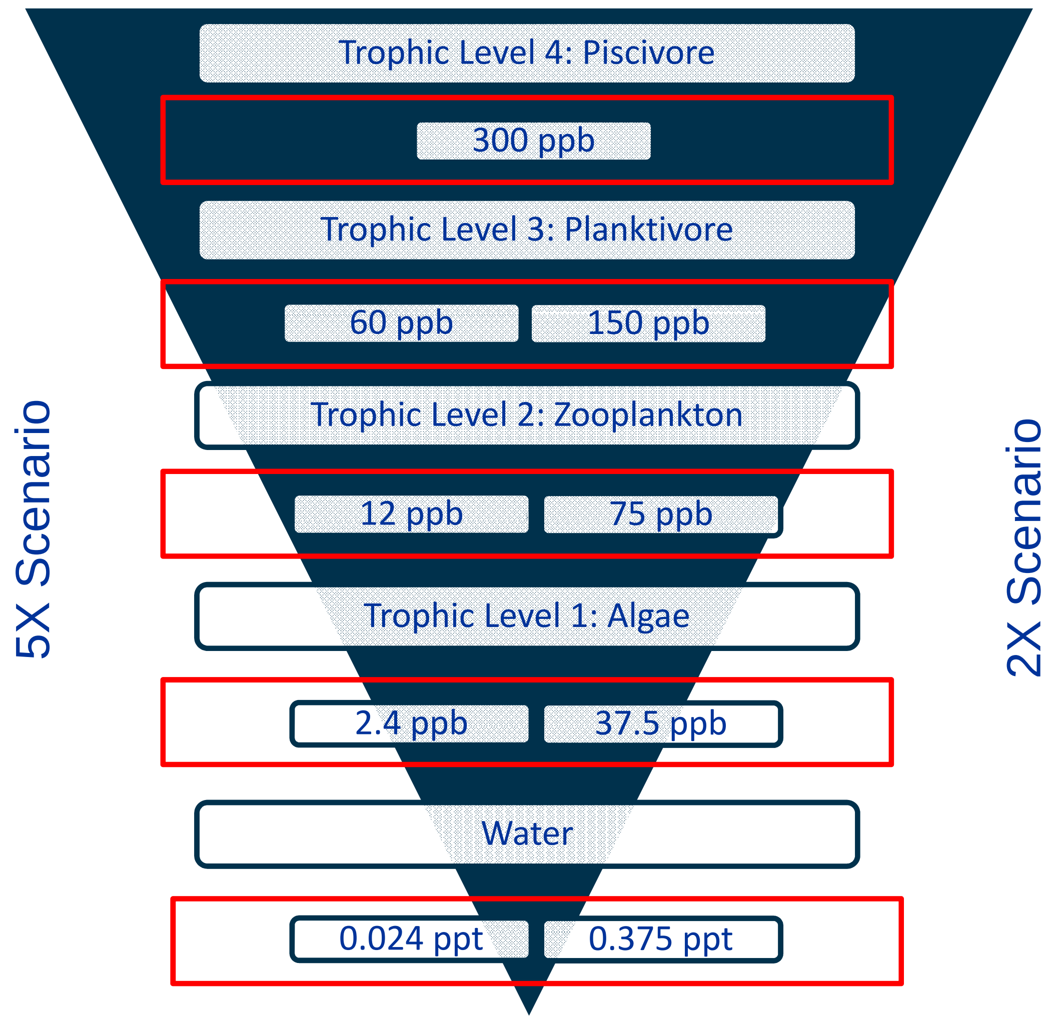
Scudder et al., 2009

Mercury Methylation to Bioaccumulation

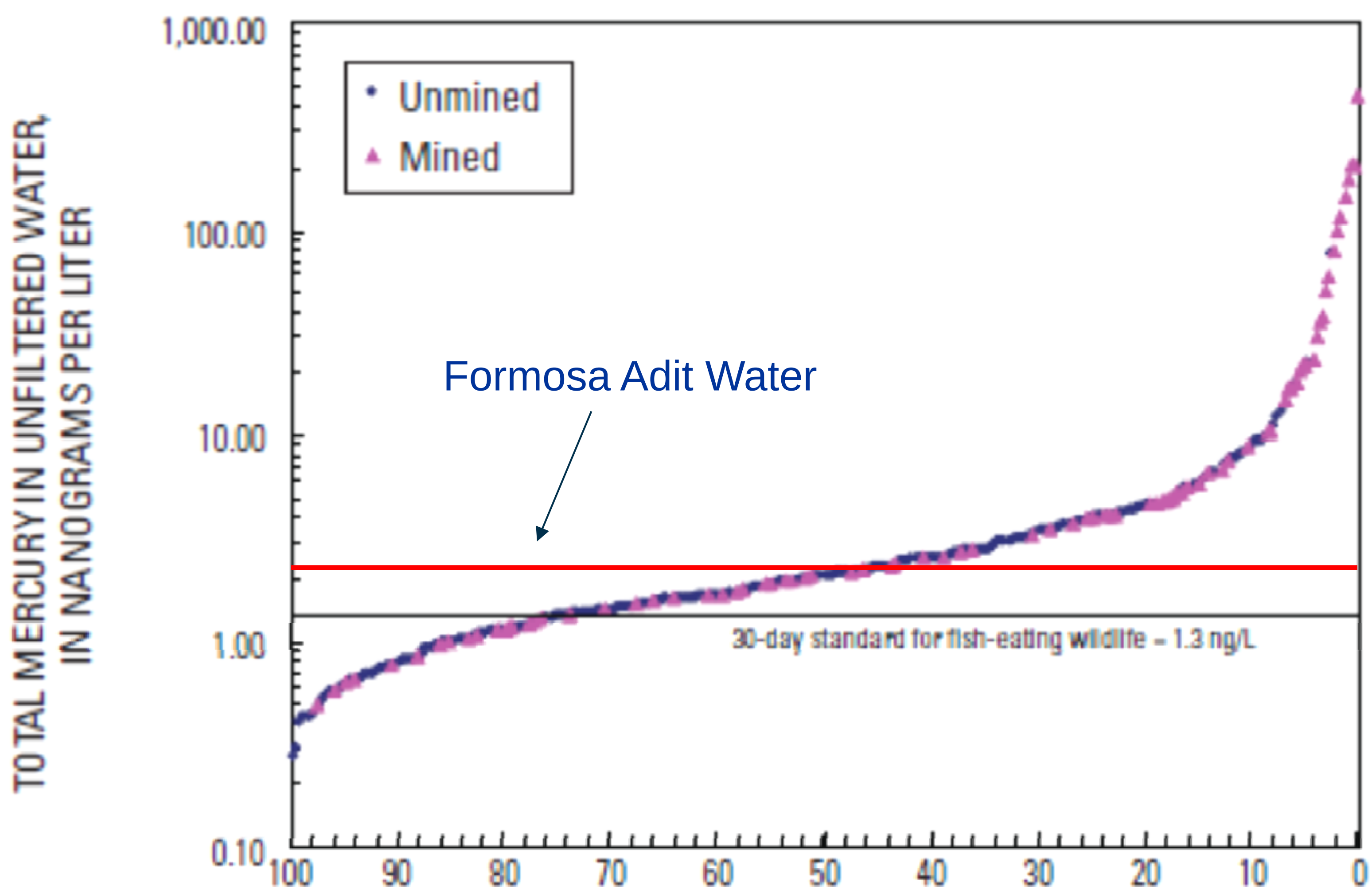


Wood et al., 2013

Working the Problem Backwards (MeHg)

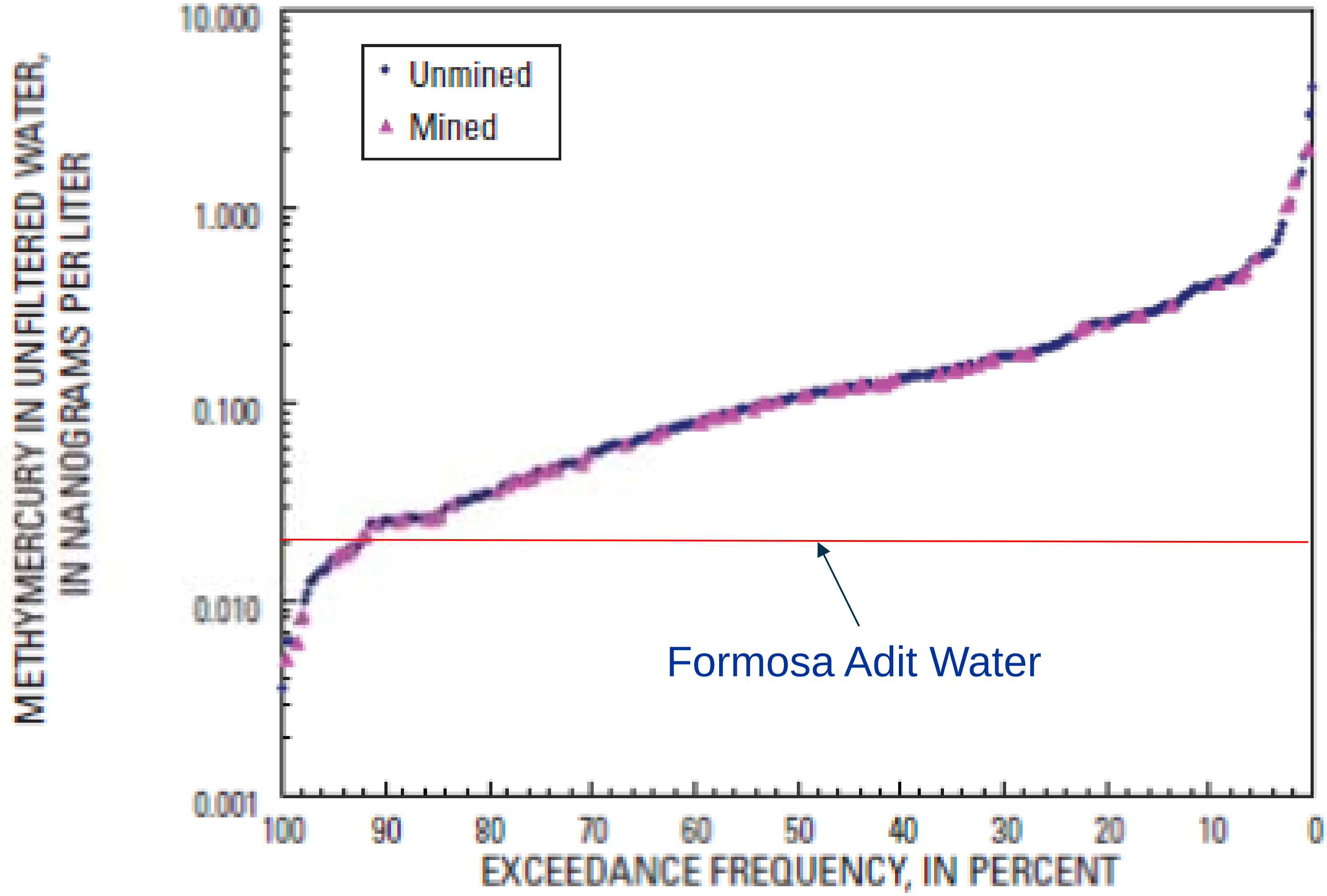


Total Mercury in Mined vs. Unmined Streams



Scudder et al., 2009

Methylmercury in Mined vs. Unmined Streams



Scudder et al., 2009

Method 1630 Trace Methylmercury & 1631 Trace Total Mercury

Battelle Marine Science Laboratory

Detection Limits (Brooks Rand Instruments)

- THg: <0.03 ng/L
- MeHg: <0.002 ng/L

Presentation Objectives

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- Biochemical Reactors (BCRs)– Mining Impacted Water
  - Formosa Treatability Study
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Formosa Mine Impacted Water

Select Metals	Average 2009 -2012 (µg/L)
Cadmium	286
Chromium III	9
Copper	17,436
Iron	167,286
Lead	49
Manganese	2,106
Mercury	0.003
Nickel	66
Silver	1
Zinc	82,700

Biochemical Reactors

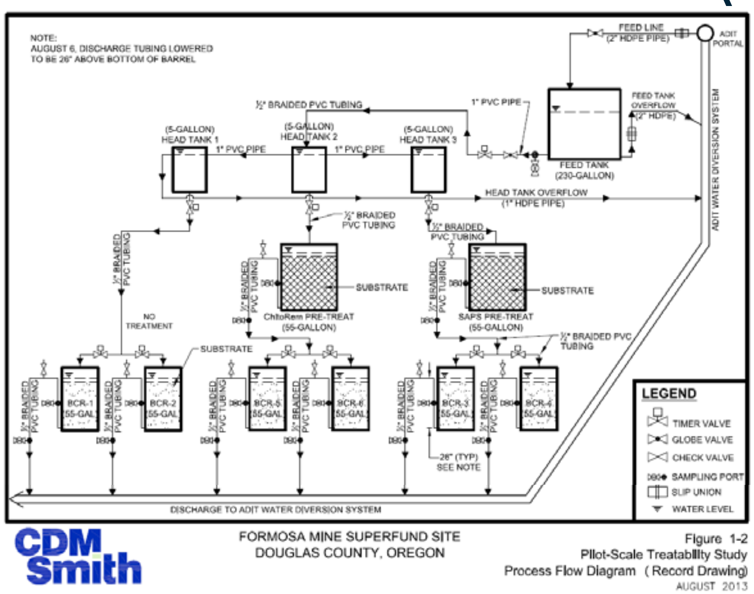
- BCRs are engineered systems that use an organic substrate (electron donor) to drive microbial (sulfate reducing bacteria (SRBs)) and chemical reactions to reduce concentrations of metals, acidity, and sulfate in MIW.
  - Reactors for this Study:
    - Successive Alkalinity Producing System (SAPS) ***Pre-Treatment Only***
    - ChitoRem® Mix: SC-20/Sand/Gravel
      - SC-20 a blend of calcium carbonate, protein, and processed crab shells
    - Woody Substrate/Manure Including Limestone

BCR Chemistry (Also Ideal for Hg(II) formation)

- $SO_4^{-2} + 2\ CH_2O \rightarrow HS^- + 2\ HCO_3^- + H^+$
- $S^{2-} + Me^{2+} \rightarrow MeS(s)$ and $HS^- + Me^{2+} \rightarrow MeS(s) + H^+$

Treatability Configuration

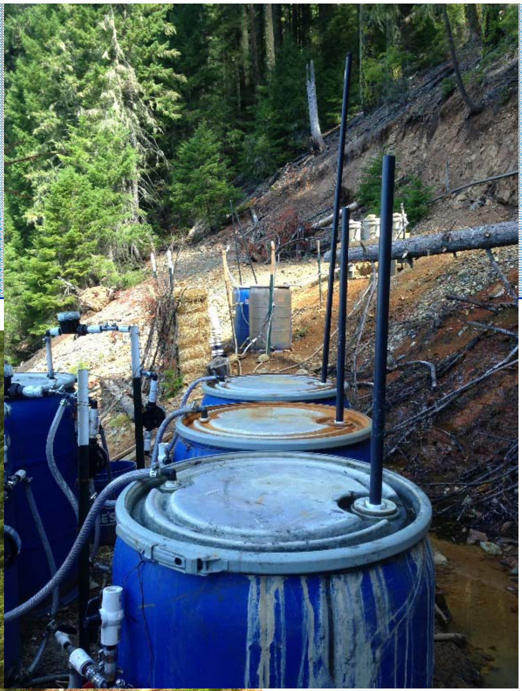
- Adit MIW
  - Wood/Manure
  - SC-20/Sand
  - Pre-Treatment: SAPS
    - Wood/Manure
    - SC-20/Sand
  - Pre-Treatment: SC-20/Sand
    - Wood/Manure
    - SC-20/Sand



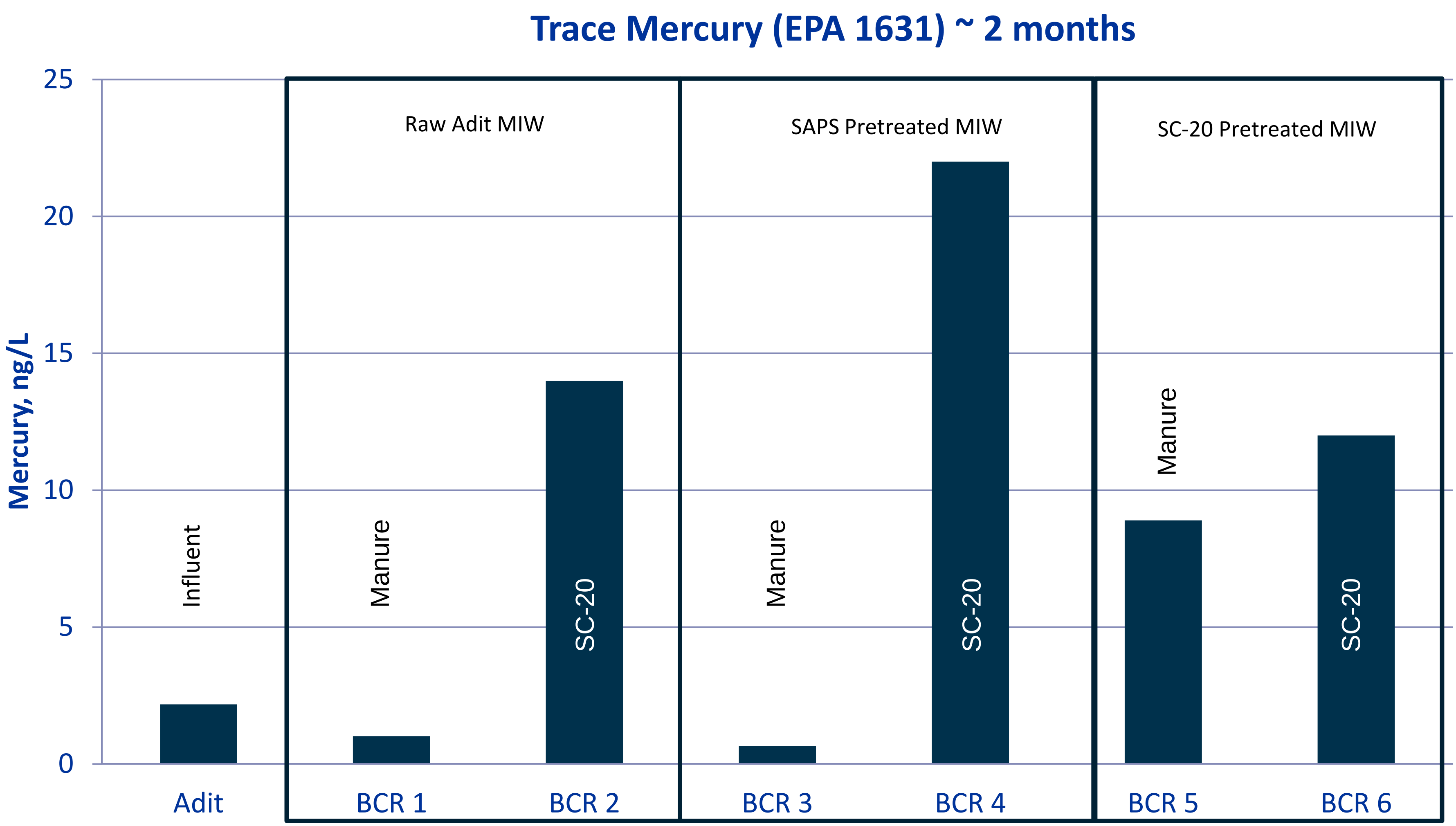
Mercury Assessment on BCR Evaluation

- Checklist for Mercury Methylation
  - Anoxic conditions: ☑
  - E-Donors (organic carbon): ☑
  - E-Acceptors (sulfate/iron): ☑
- Question: Considering inorganic mercury is methylated by sulfate reducing bacteria, could the environment inside a BCR contribute to MeHg in the effluent stream?

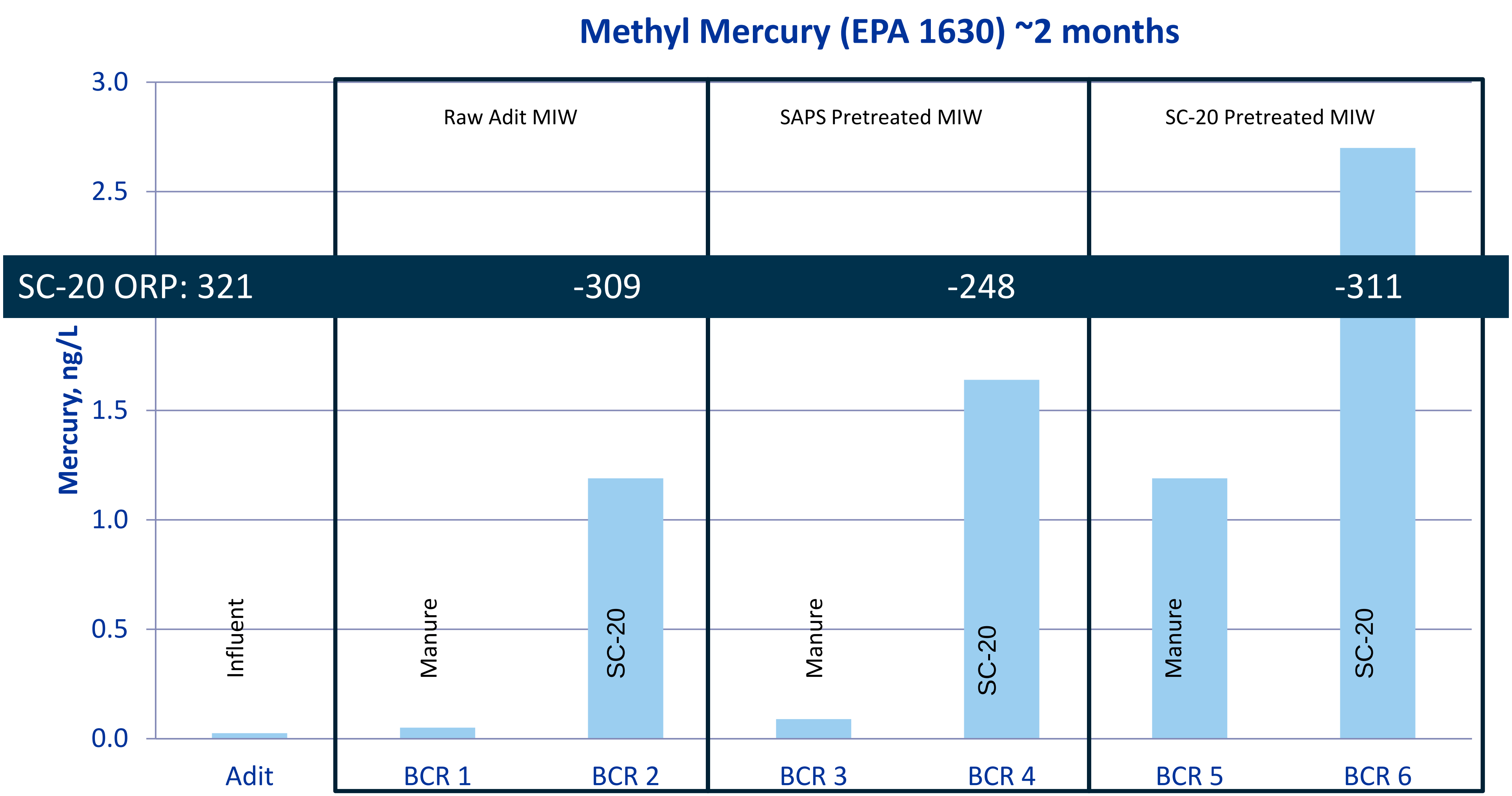
BCR Setup Below Adit



Mercury Results



Mercury Results (Continued)



Formosa Mercury Evaluation Summary

- All Manure BCRs Decreased THg
  - Slight increases in MeHg
- All SC-20 BCRs Increased THg and MeHg
  - THg Increased 10 to 20 ng/L
  - MeHg Increased 1 to 2.7 ng/L
- Release of Hg from BCR
  - SC-20 – ground crab shell and tissue: Crab Hg body burden ~ 0.16 mg/kg
  - Sand/Gravel
- Release or Generation of MeHg
  - Potential Resident Source:
    - MeHg effluent higher than THg influent
    - Aquatic organisms typically enriched in MeHg
  - Potential MeHg Generation
    - Evidence of SRB activity
      - ORP and Sulfide
      - Hg(II) sourced from influent and media
      - Slight MeHg increase in manure BCRs

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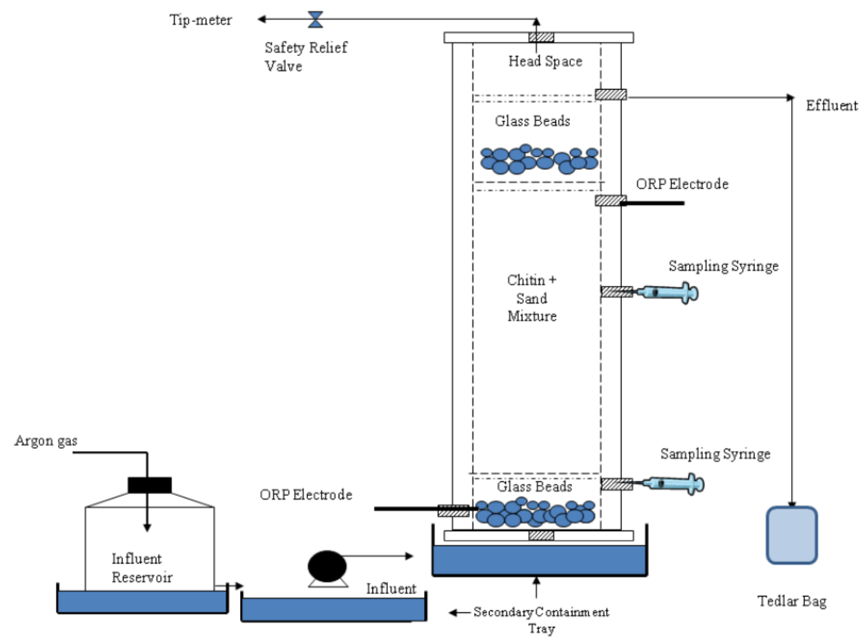
ORD Bench Top Study



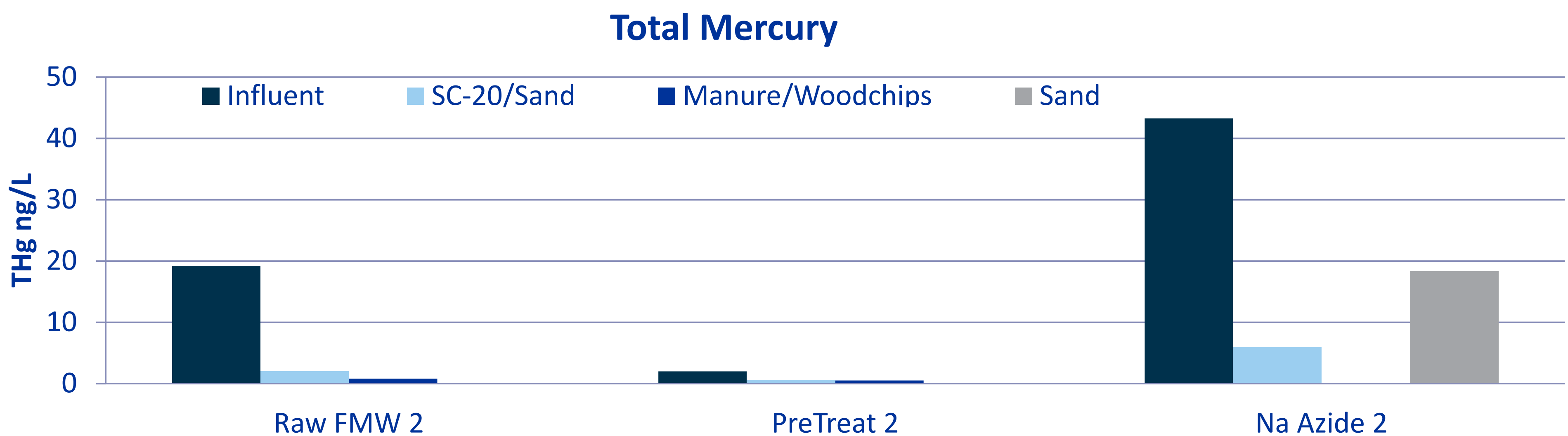
Influent and Column Specifics

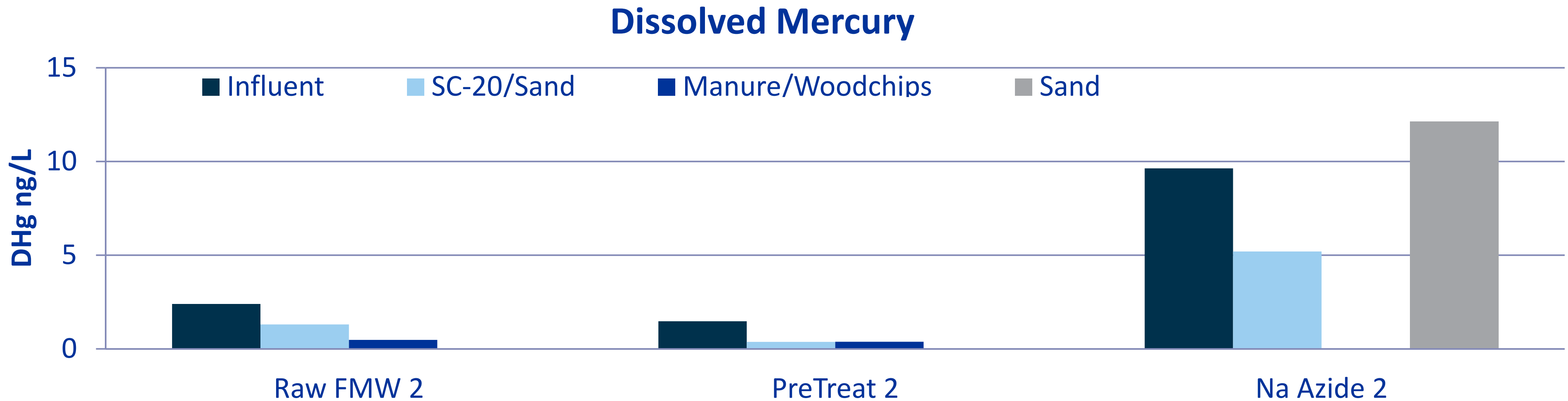
24 hr Hydraulic Residence Time

- Column 1: SC-20 + Sand – Pretreat MIW
- Column 2: Wood Chips + Manure – PreTreat MIW
- Column 3: SC-20 + Sand – Raw MIW
- Column 4: Wood Chips + Hay + Manure – Raw MIW
- Column 5: SC-20 + Sand – Na Azide Raw MIW (abiotic)
- Column 6: Sand – Na Azide Raw MIW (abiotic)

Total Mercury: 34 Weeks into Test

Data Provided by EPA ORD Laboratory

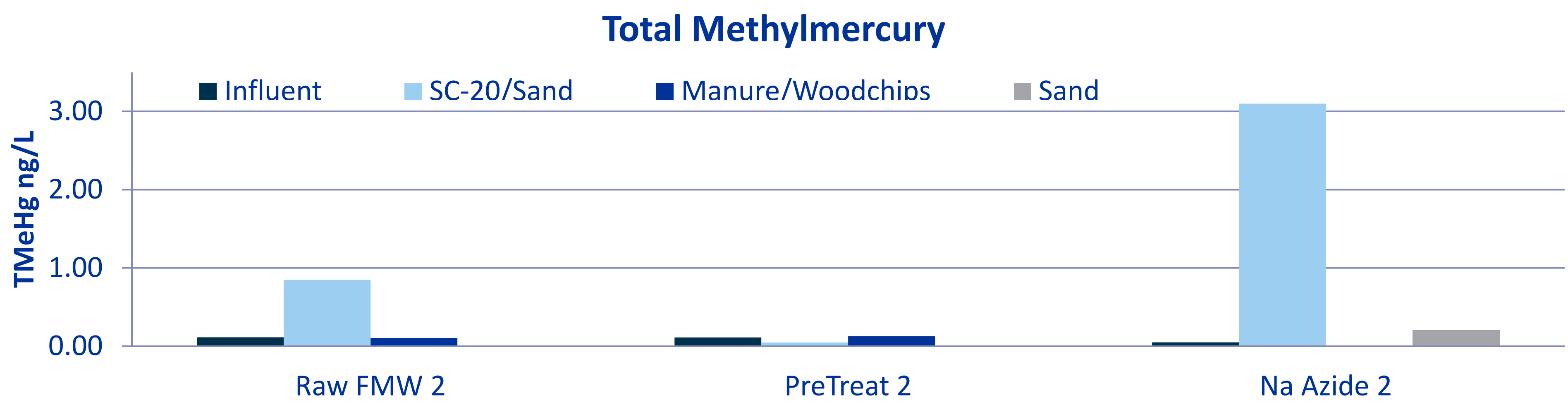


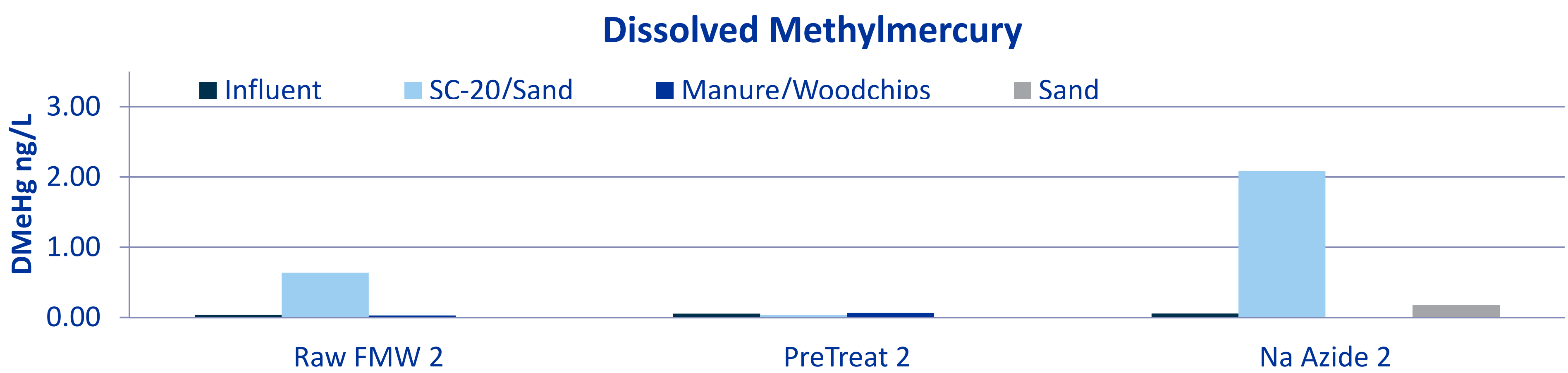


Total Mercury 34 Weeks into Test

- Wood/Manure BCRs
  - Buffer capacity gone after 34 weeks
  - Pre-Treat BCR has no sign of SRB activity
  - Raw BCR has diminished sign of SRB activity
  - BCRs a sink for THg
- SC-20/Sand BCRs
  - Buffer capacity maintained
  - Both Pre-Treat and Raw BCR have continued sign of SRB activity (low ORP, reduced sulfate, increased sulfide)
  - BCRs a sink for THg
    - ***In contrast with Formosa Treatability Study***

Methylmercury 34 Weeks into Test





Methylmercury 34 Weeks into Test

- Wood/Manure BCRs
  - No real change between influent and effluent
- SC-20/Sand BCRs
  - Raw BCR contributing MeHg to effluent
  - PreTreat BCR has no real change between influent and effluent
  - Abiotic BCR contributing up to 3 ng/L MeHg.
    - Most likely sourced from media

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Key Difference Between Treatability and Bench Top Study

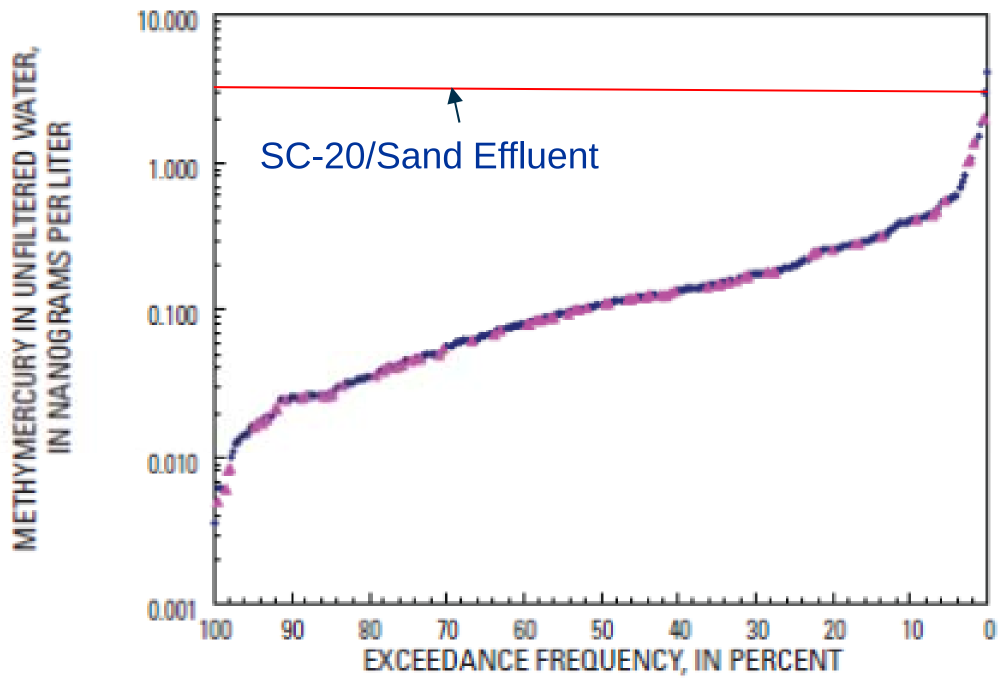
- Duration and Flow Consistency:
  - Treatability Study ran for 8 weeks
  - Treatability Study flow gravity fed and slowed over time
  - Bench top study ran for 34 weeks
  - Bench top flow consistent over time
- Total Mercury Source from SC-20/Sand Media
  - THg source in Treatability Study after 8 weeks
  - No THg source observed in Bench Top Study after 34 weeks
- Methylmercury Source from SC-20/Sand Media
  - MeHg effluent greater than THg influent during Treatability Study
  - MeHg effluent increased in abiotic BCR during Bench Top Study

Conclusions

- Wood/Manure BCRs chemical reduction and buffer capacity diminished over the study period, however, they remained mercury sinks throughout study
- Inorganic mercury appeared to flush from SC-20/Sand media following 34 weeks of continuous flow
- SC-20/sand media likely a source of MeHg and remained so after 34 weeks of continuous flow
  - MeHg in effluent greater in abiotic Bench Top BCR than all Treatability Study effluents

Conclusions (Cont.)

- Concentrations in effluent considerably elevated in MeHg relative to mercury impacted basins in United States



Recommendations

- Quantify mercury load in all material, with speciation.
- Perform mass balance to determine how long it would take to flush MeHg associated with media
- MeHg load from media prevented effective analysis of Hg(II) methylation potential in BCRs
  - Repeat study with fully flushed media
- Wood/Manure BCRs may be a good polishing step for SC-20 Applications

Acknowledgements

- Formosa Treatability Study:
  - Performed by CDM Smith Federal Programs: Task Order 047 for Architectural and Engineering Services (AES10) Contract Number 68-S7-03-04
- ORD Bench Top Study:
  - Mercury Component Funded by the Superfund and Technology Liaison Extramural Funding (2013); Project Code TEC-961J,L,M
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Questions?

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

Presenter: Todd Luxton, EPA Office of Research and Development

Project Collaborators: Chris Eckley[1] and John McKernan[2]

[1]EPA Region 10

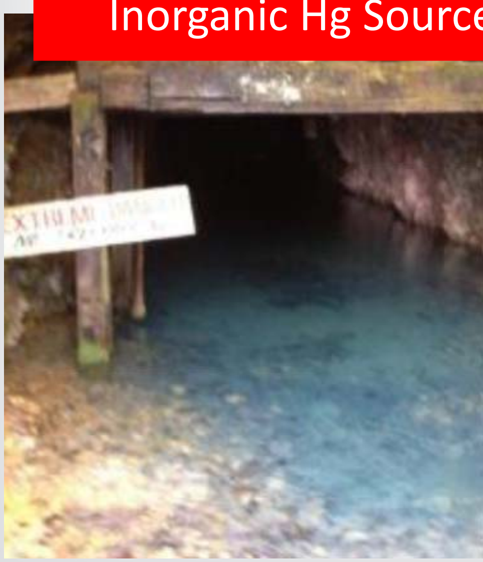
[2]EPA Office of Research and Development

Tuesday March 29th, 2016

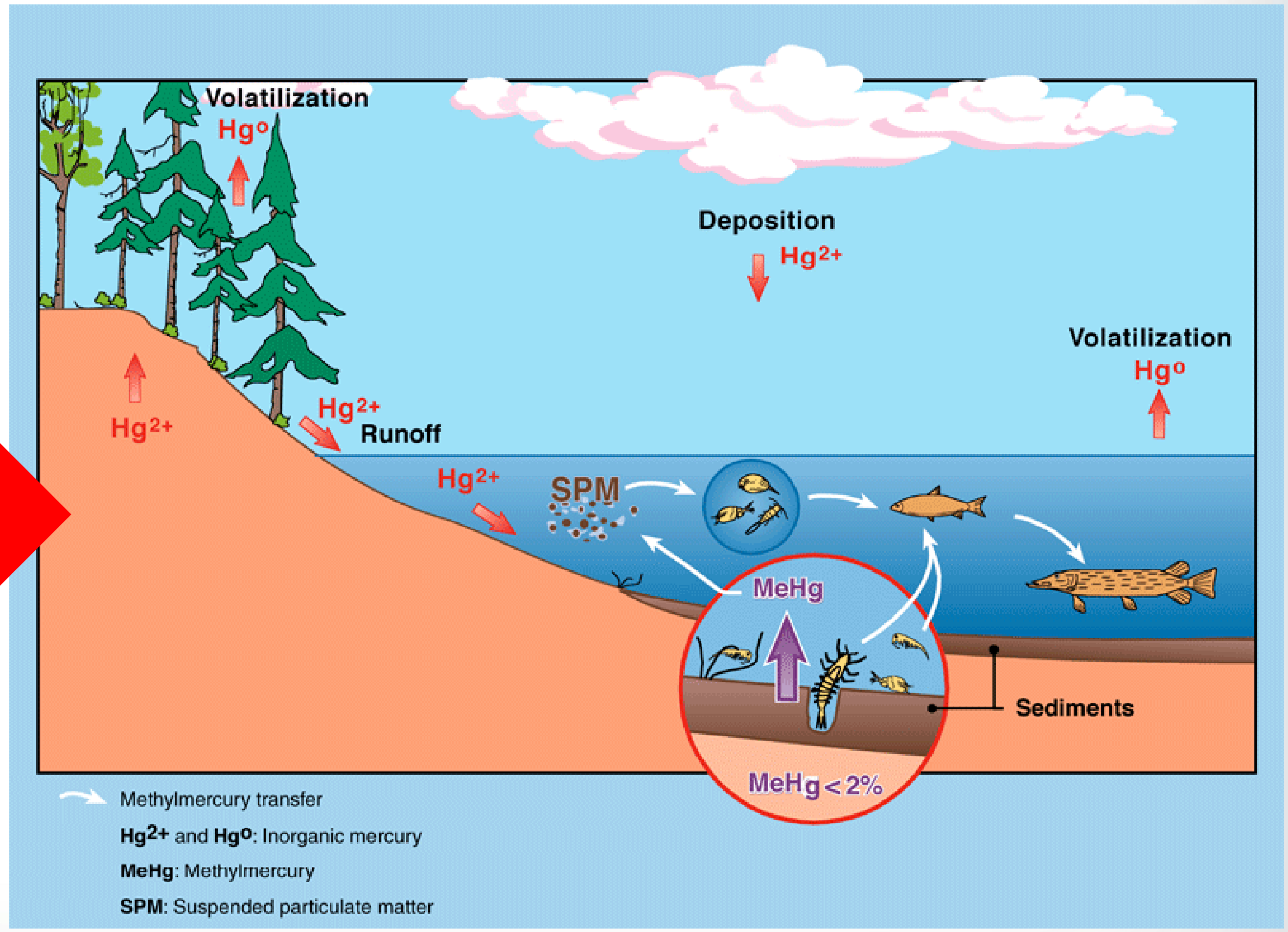
Presentation Outline

- **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

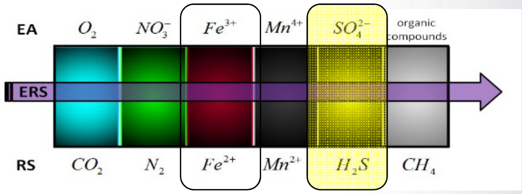


Inorganic Hg Source

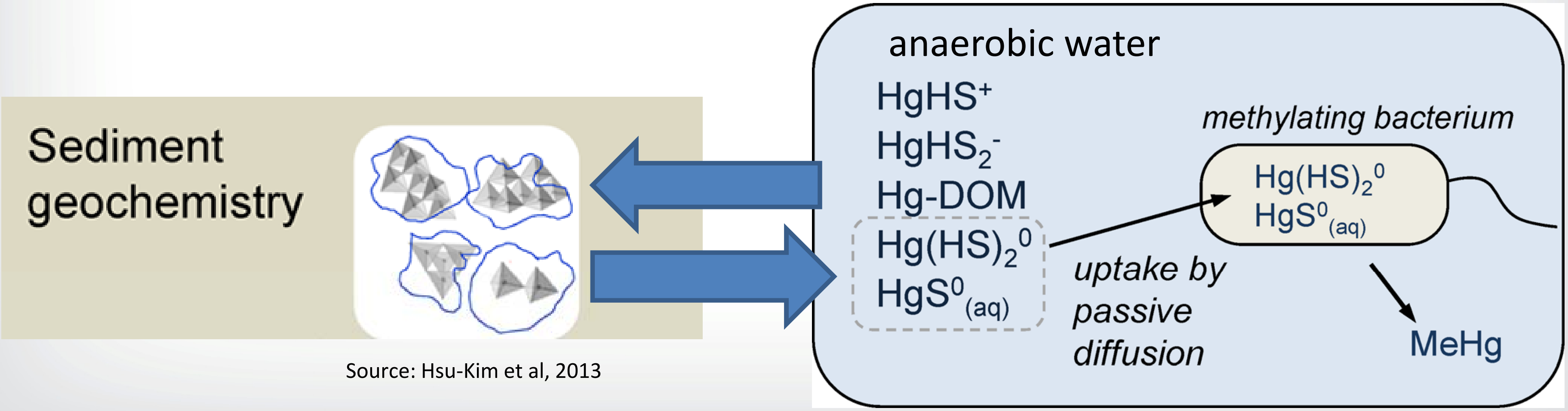


Introduction to Methylmercury

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

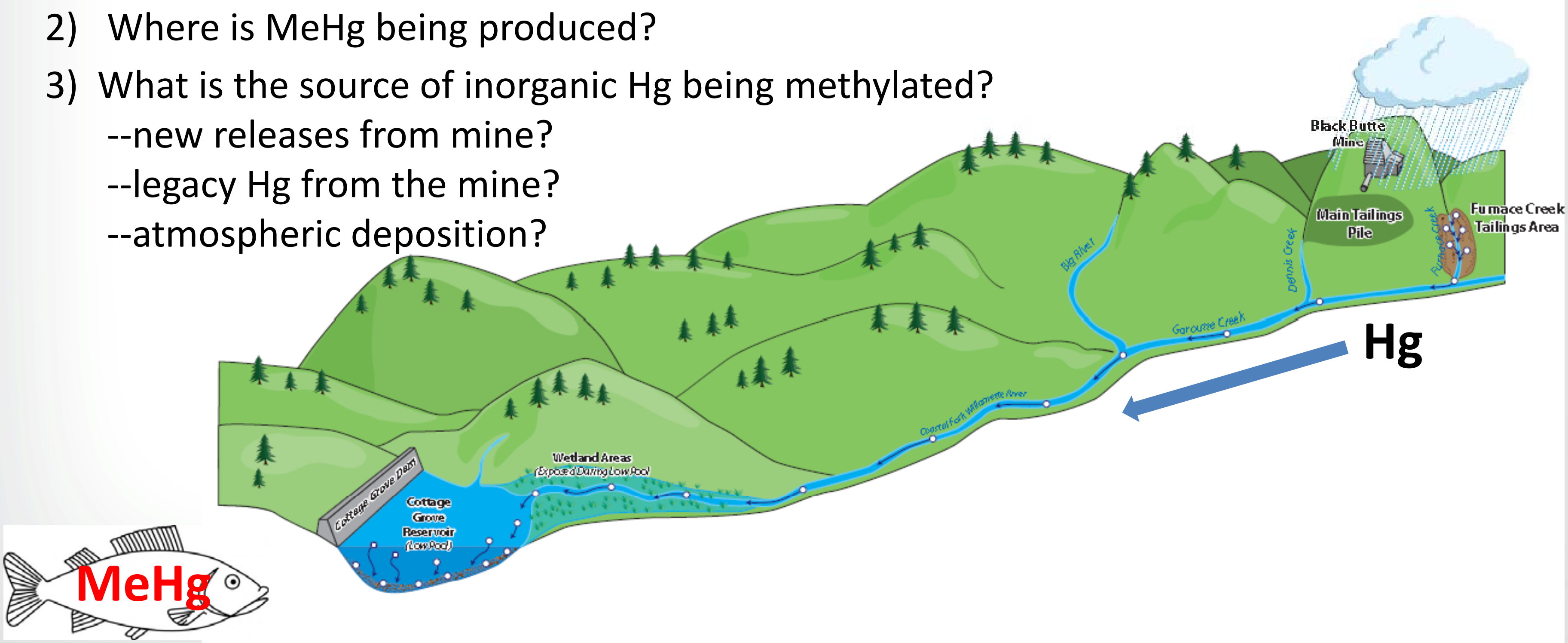
Black Butte Superfund Site: Cottage Grove Reservoir

Inorganic Hg exported from the mine site

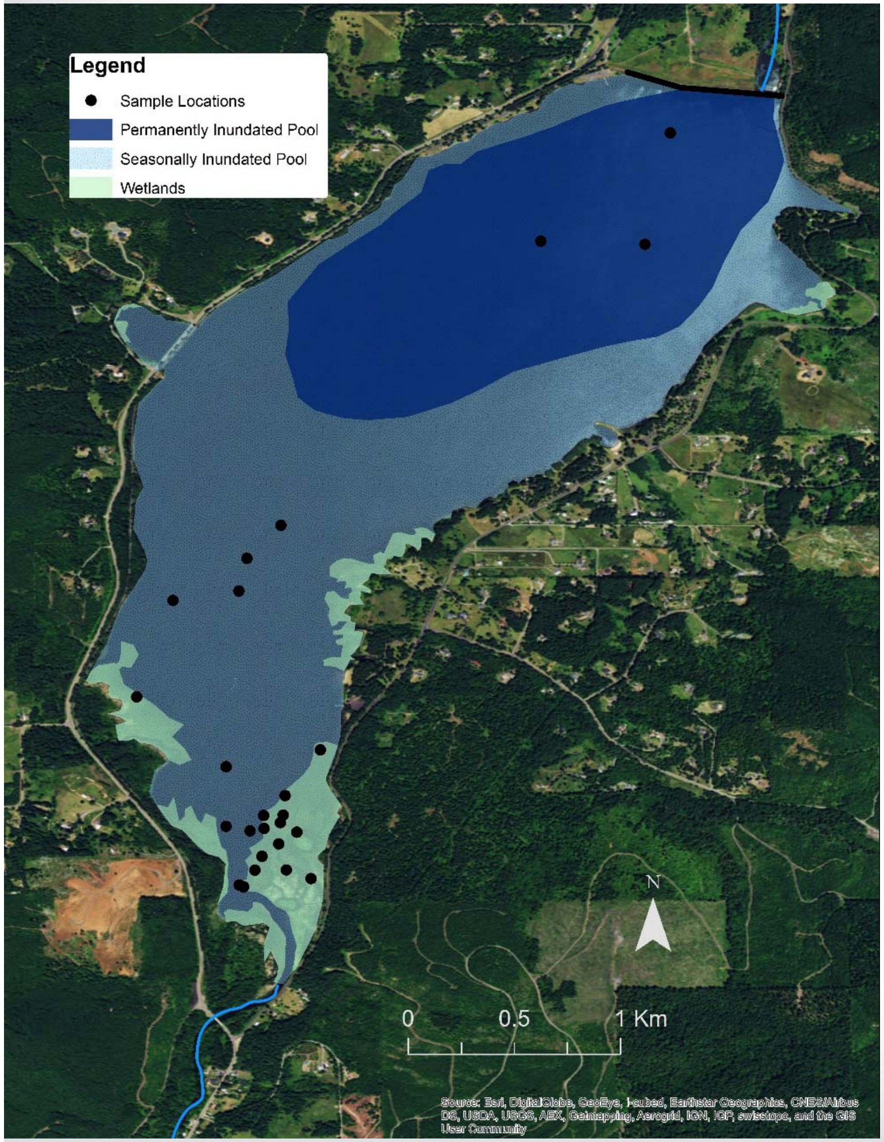
Methylmercury (MeHg) accumulating in Reservoir fish

Need to understand connection between inorganic Hg & MeHg

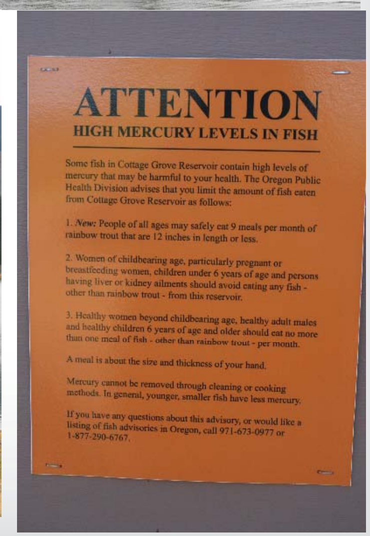
1) What variables control MeHg production?
2) Where is MeHg being produced?
3) What is the source of inorganic Hg being methylated?
   --new releases from mine?
   --legacy Hg from the mine?
   --atmospheric deposition?



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

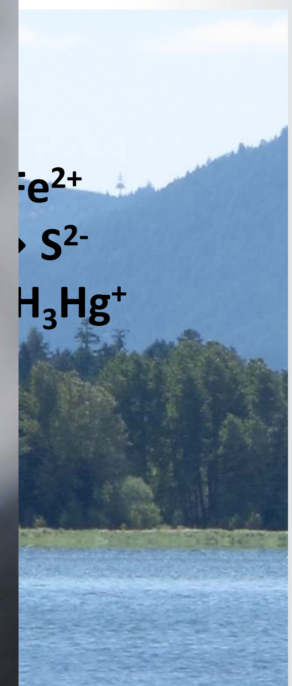


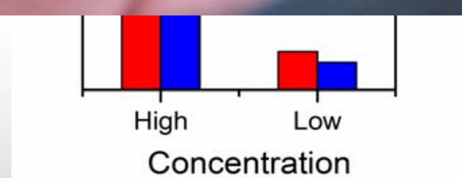
Black Butte Superfund Site: Cottage Grove Reservoir

Reducing Conditions

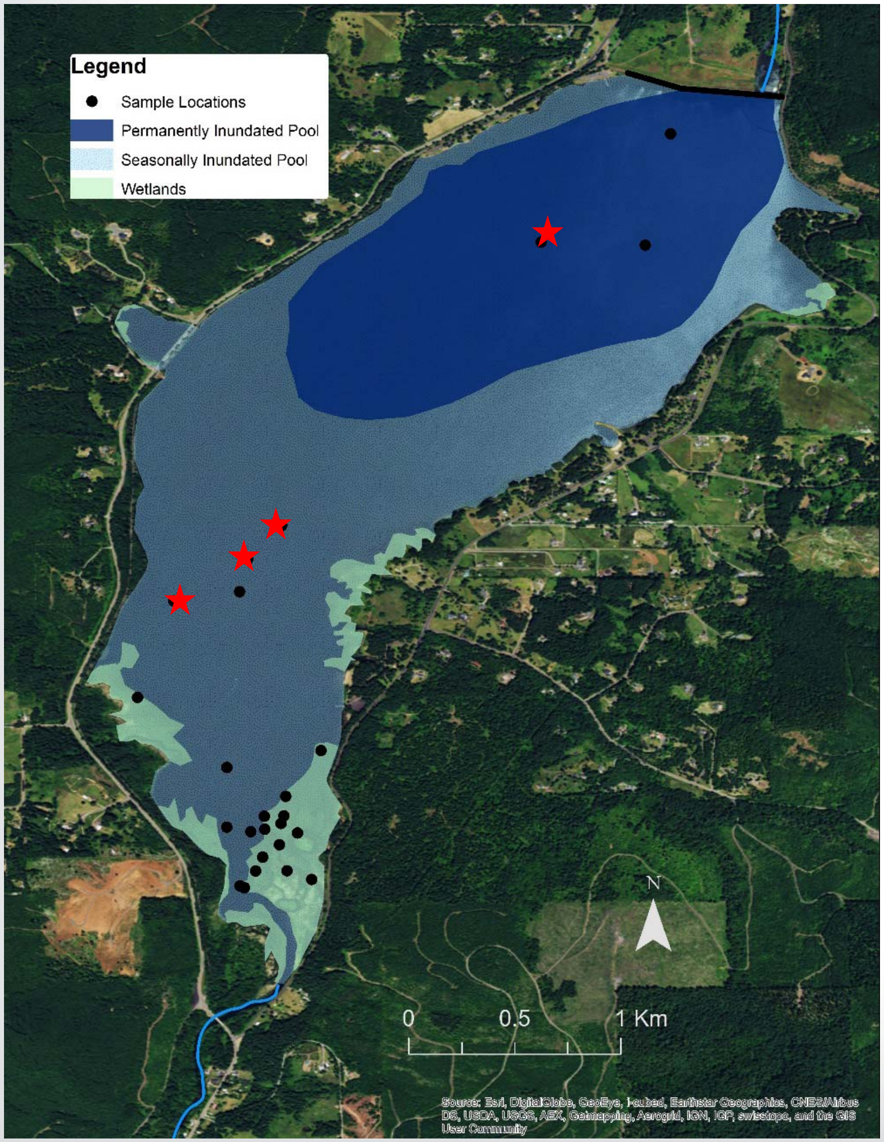
Fall and Win

Summer

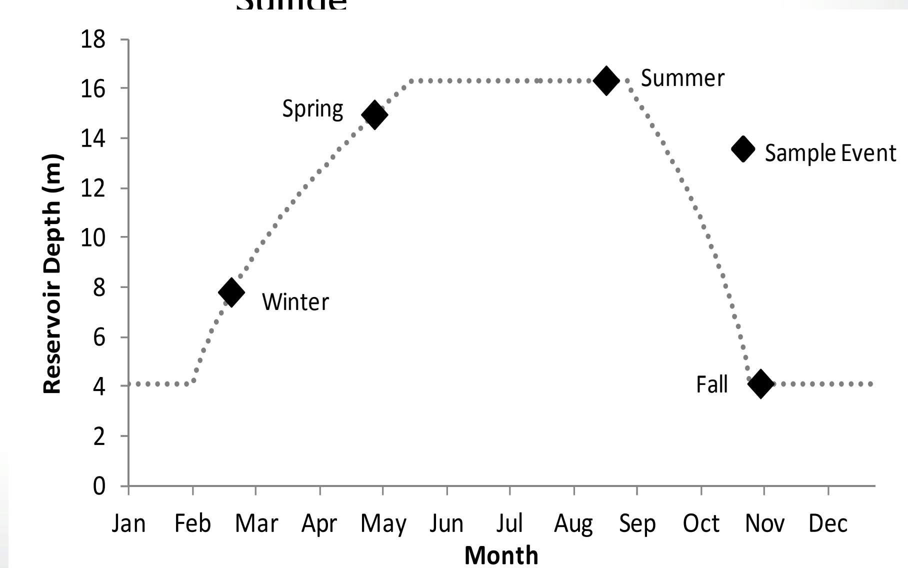




Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 1

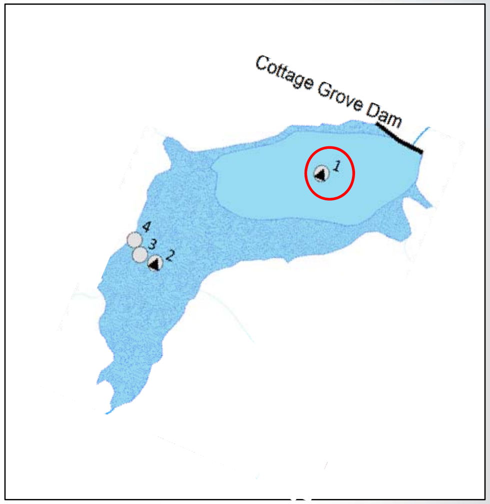


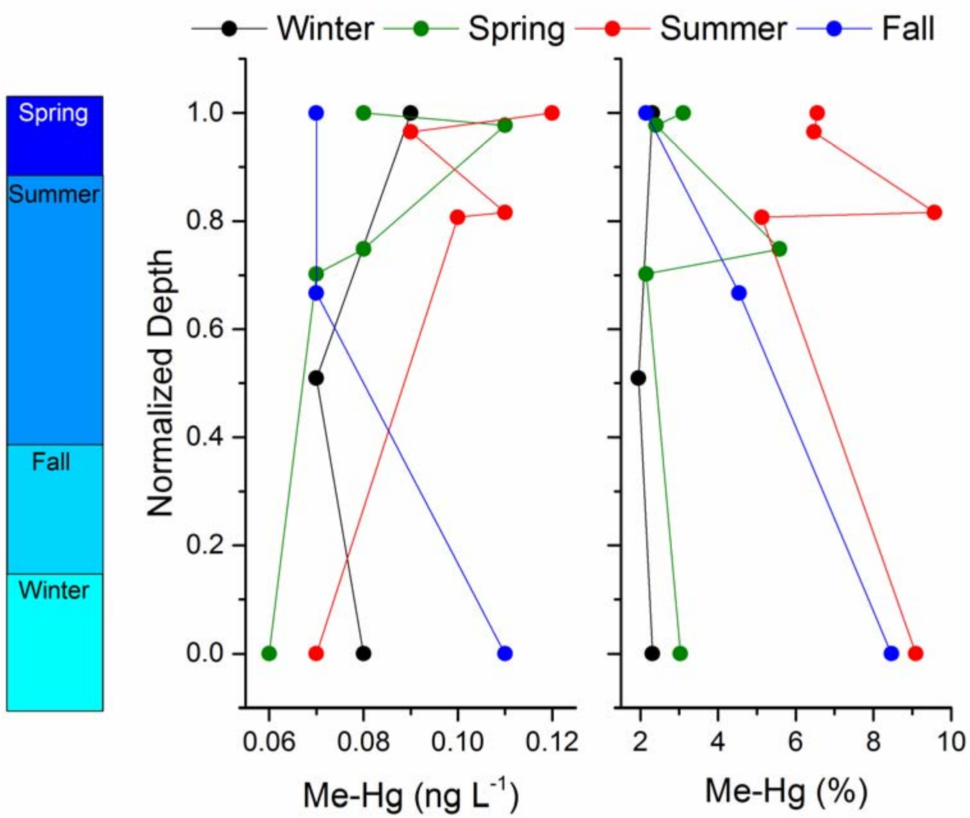
- **Do seasonal changes in water level increase Mercury Methylation?**
  - 4 sample Locations
  - 4 sampling Events
  - Measurements
    - Surface Water: T-Hg, Me-Hg, DOC, Sulfate, Sulfide, TSS, pH
    - Sediment: T-Hg, Me-Hg, Organic Carbon, Sulfide



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

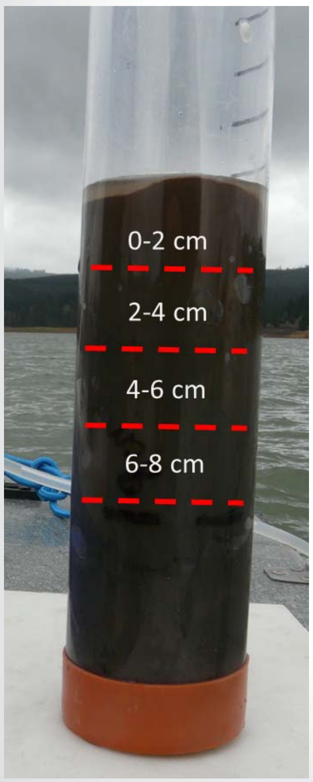


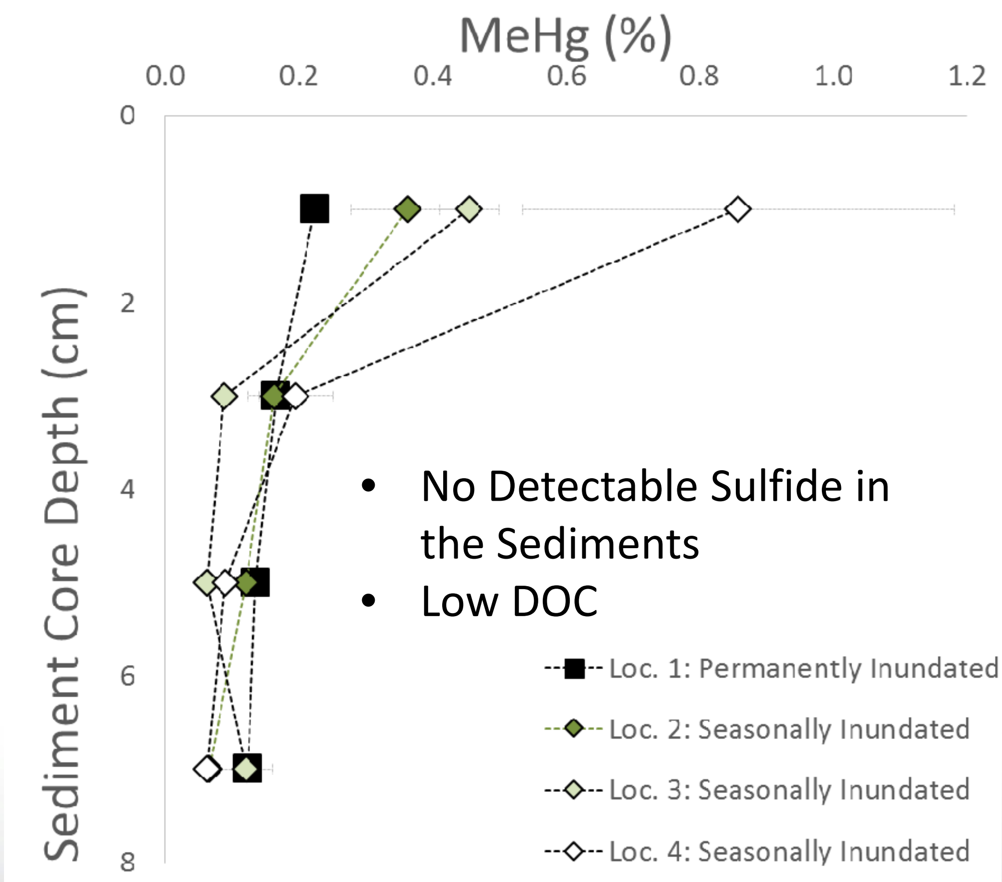


- Oxic Water Year Round
- No Detectable Sulfide
- Very Low Fe^{2+}
- Very Low DOC

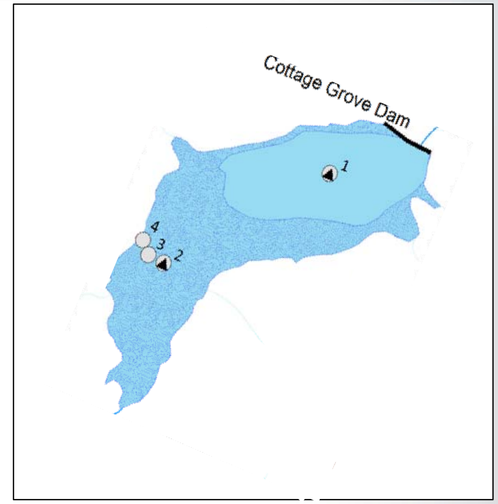
Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 1, Sediment

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





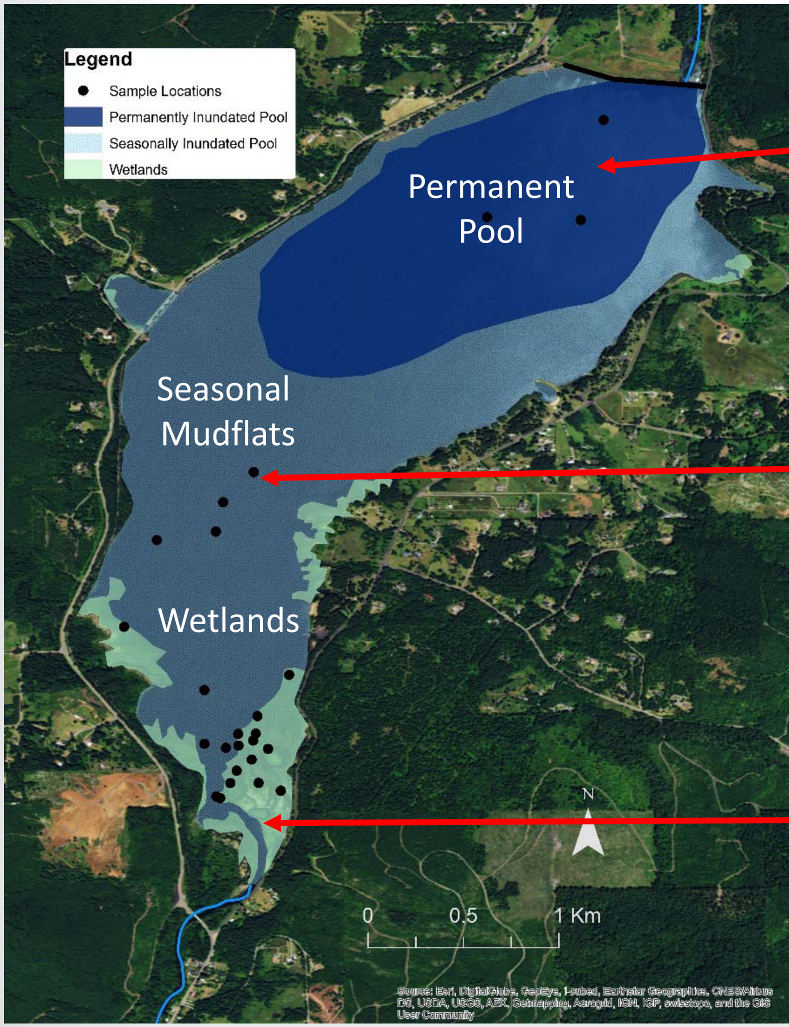
- No Detectable Sulfide in the Sediments
- Low DOC



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

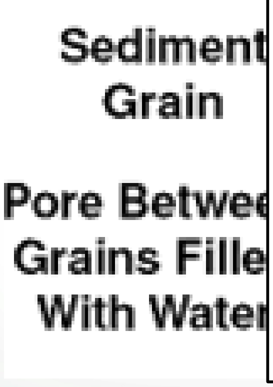


Where is Me-Hg being Produced?

- 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 …



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

Core Squeezer: Grain Size, Porewater Flow Path, Oxidation

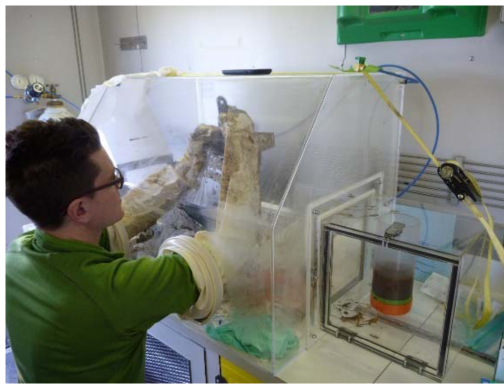
… n Techniques
… (Peepers)
… ery Sampler

- Centrifuge and Filter

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

Porewater Methodology—Centrifuge/Filtration

Step 1) Collect Cores



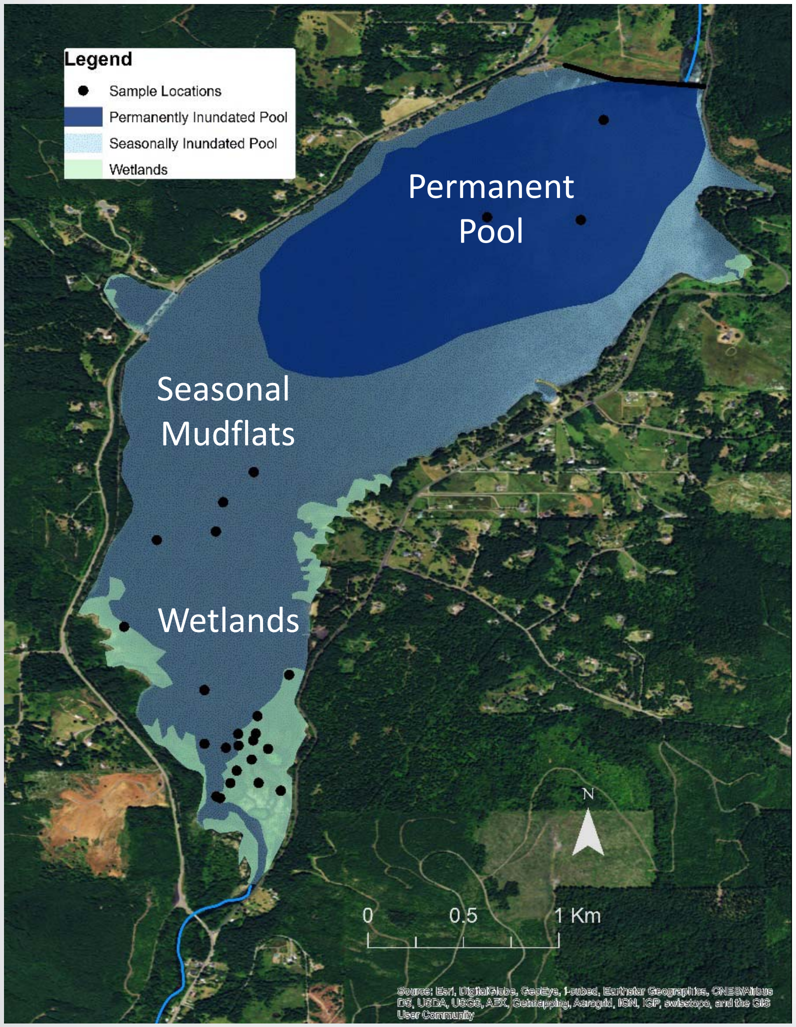
Step 2) Section cores

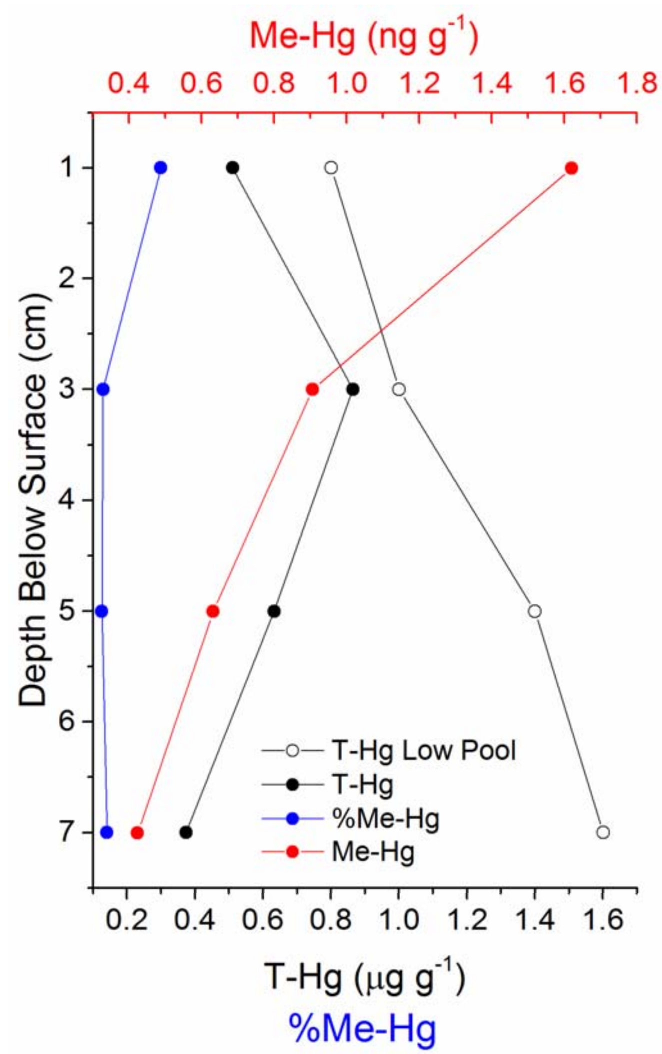
Step 3) Centrifuge

Step 4) Filter porewater

EPA Mobile Lab

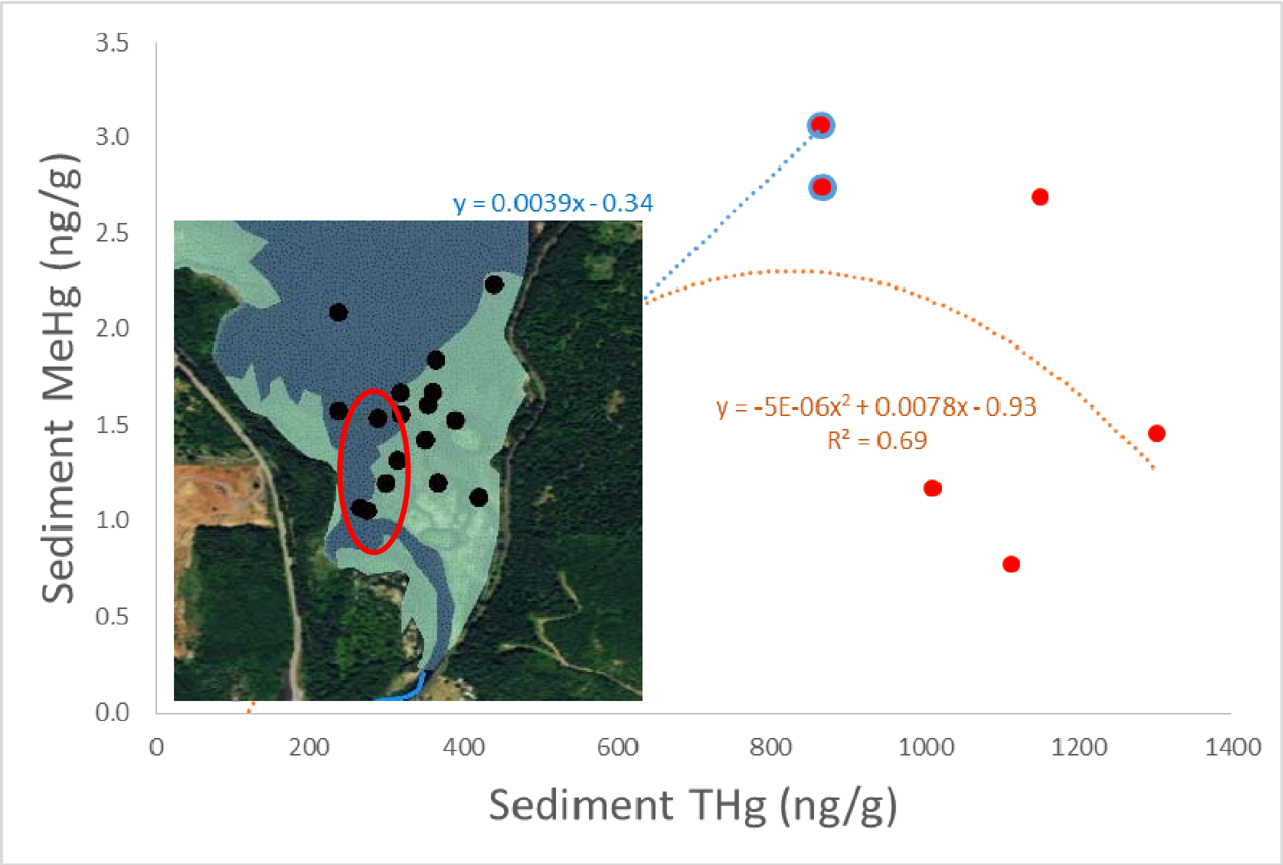
Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2





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

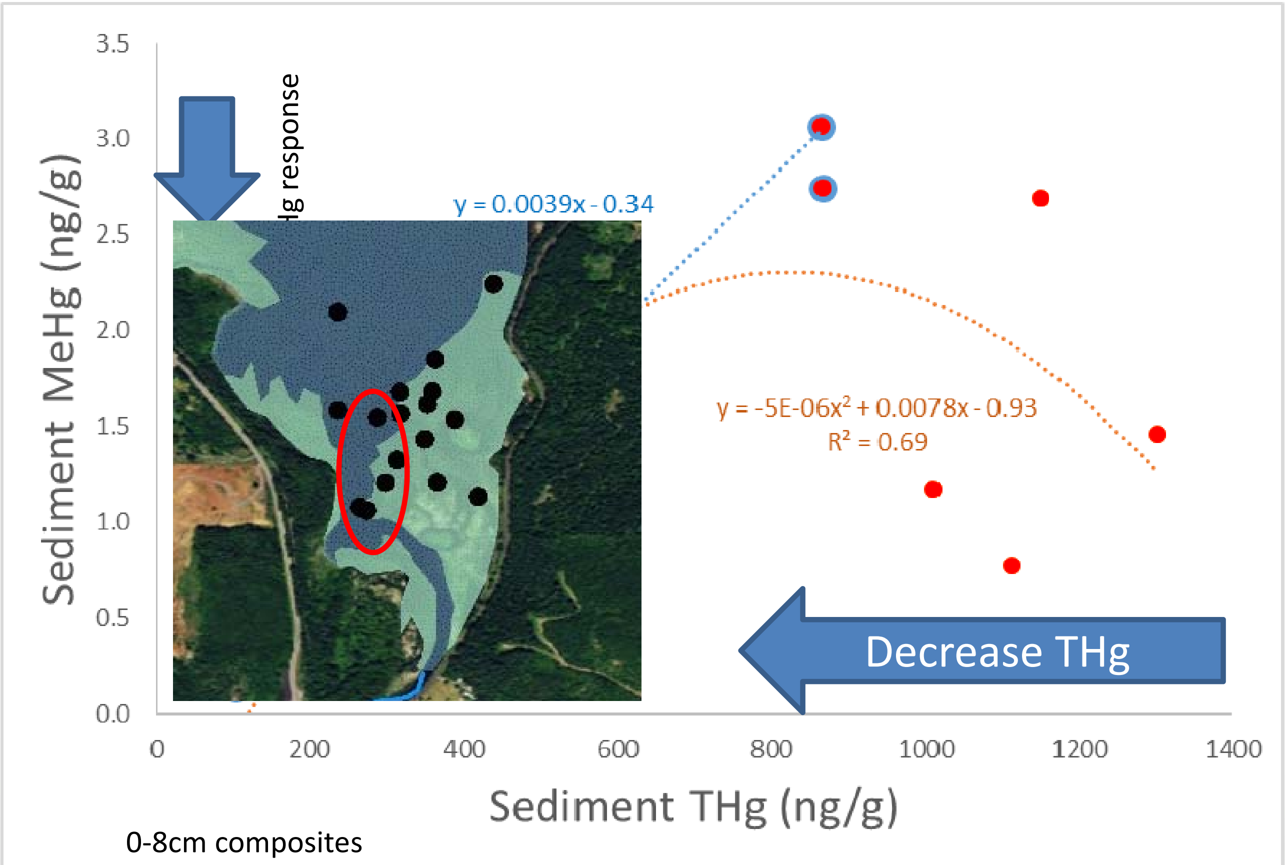


Data are provisional and subject to revision. Do not cite or distribute. 0-8cm composites

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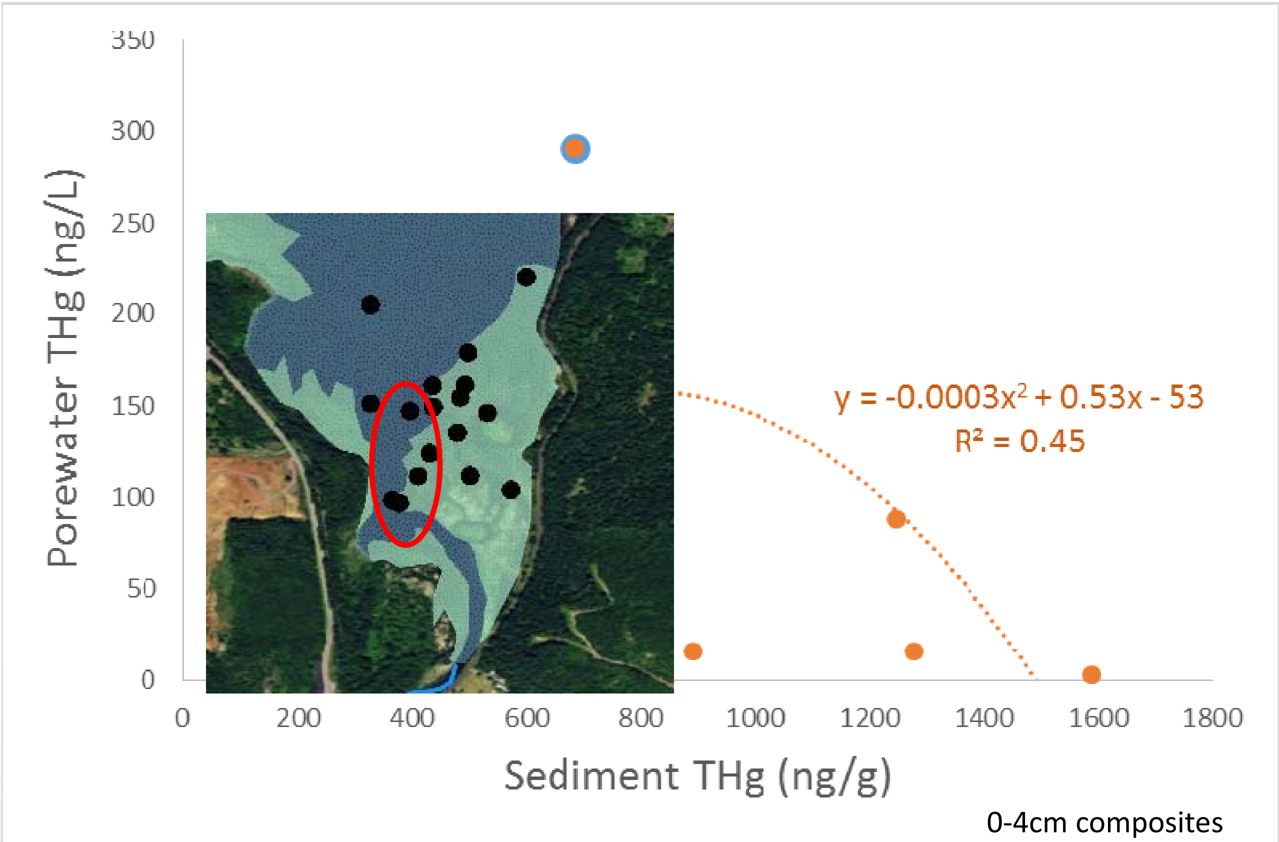
Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

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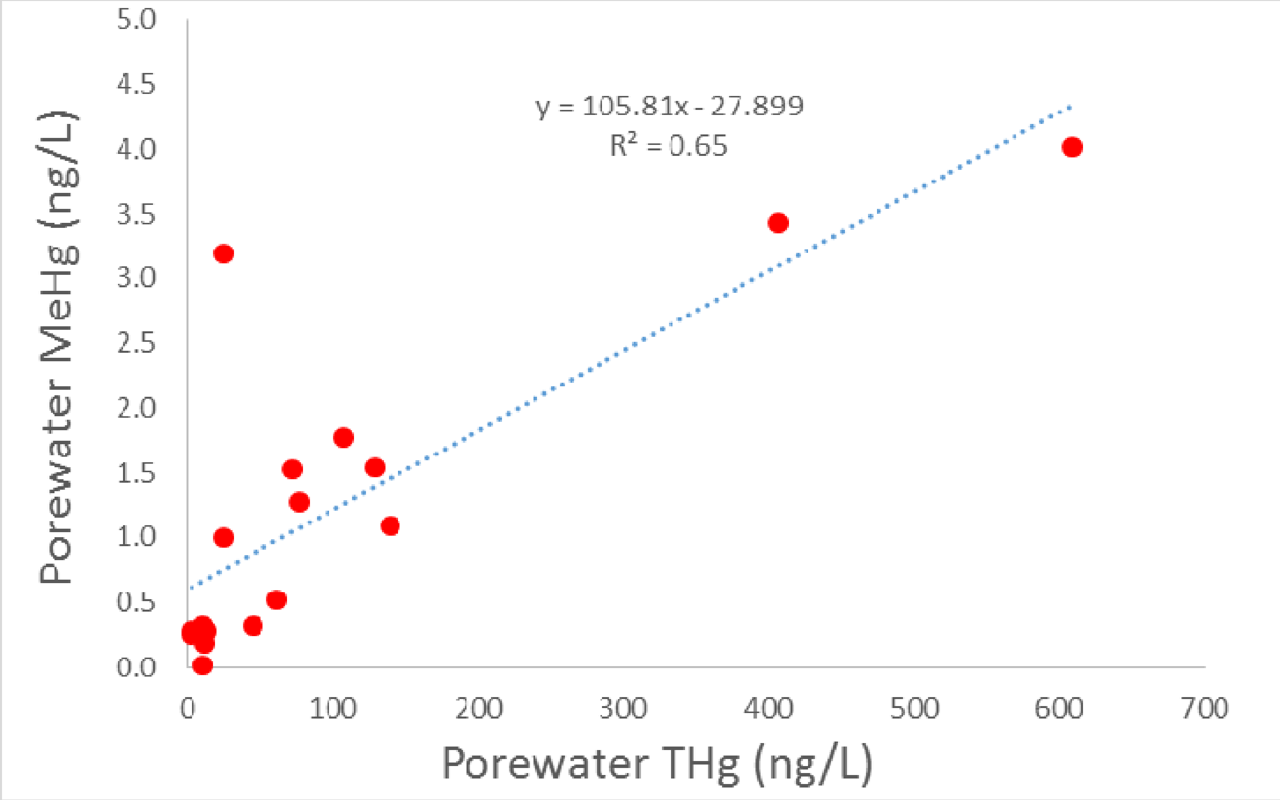
Black Butte Mine Superfund Site: Cottage Grove Reservoir, Year 2

- 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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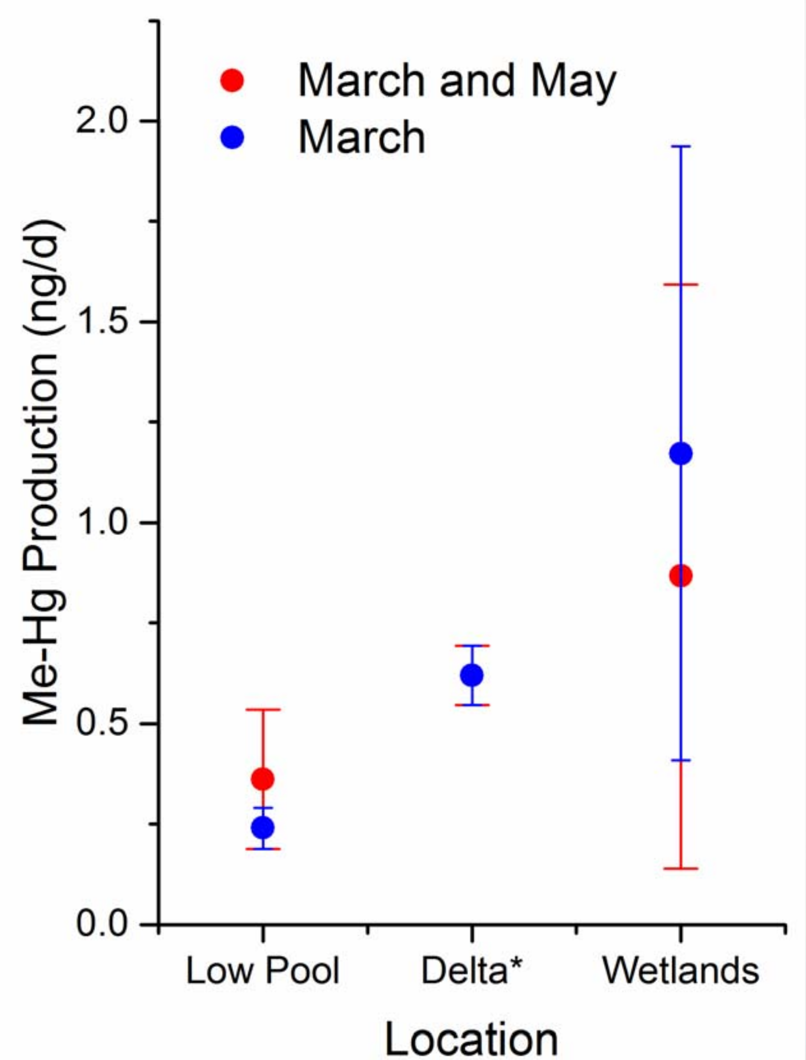
0-8cm composites

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

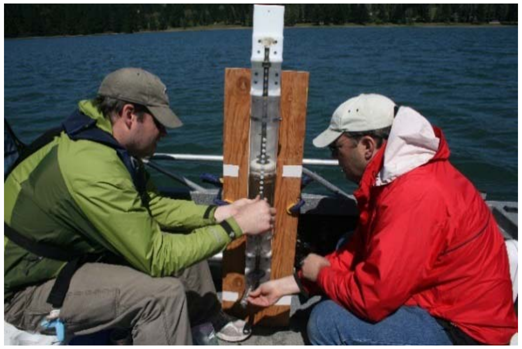
- Stable Isotope Additions Measuring Methylation Potential
  - Add available isotopically enriched source of Hg^{2+} (Hg^{198})
  - Measure amount of stable isotope methylated in a given time period
- Conditions in the Delta sediments are favorable for methylation
- Reason for decreased concentration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



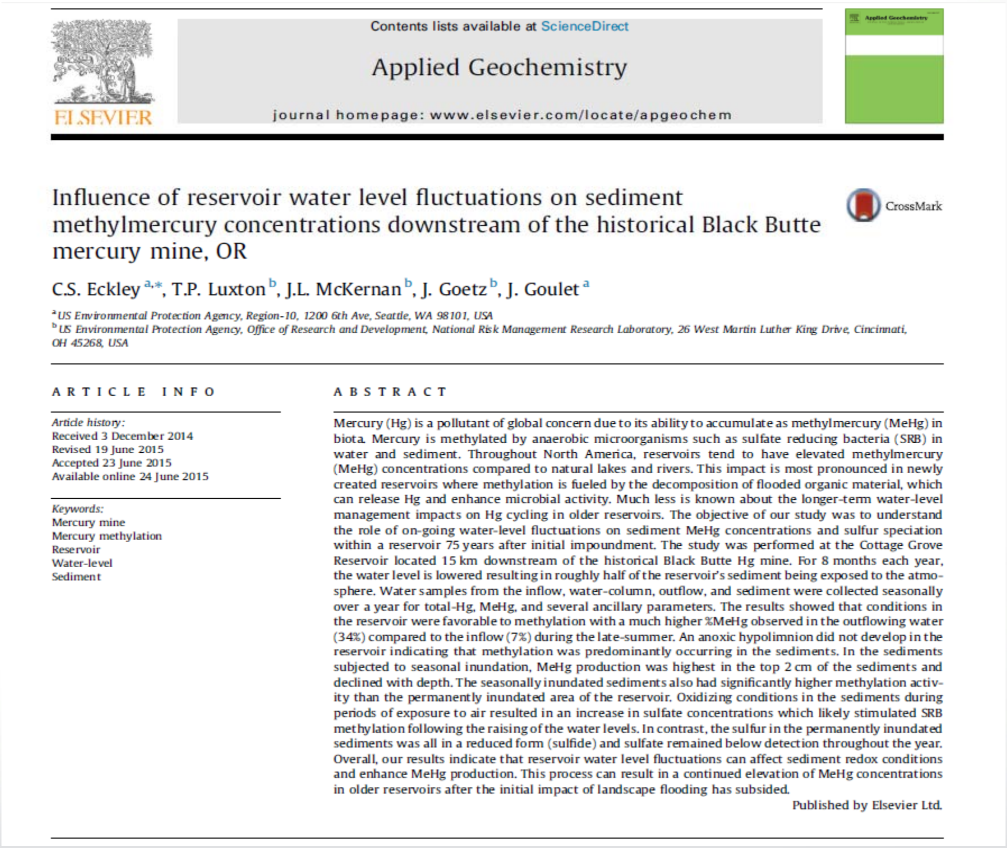
Data are provisional and subject to revision. Do not cite or distribute.

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



More information available!:



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Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

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

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ARTICLE INFO

Article history:
Received 3 December 2014
Revised 19 June 2015
Accepted 23 June 2015
Available online 24 June 2015

Keywords:
Mercury mine
Mercury methylation
Reservoir
Water-level
Sediment

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?