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

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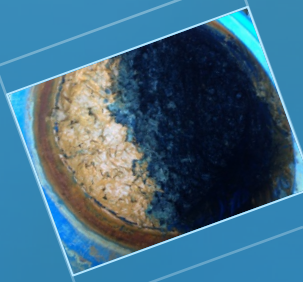
Clu-In Webinar

March 29, 2016



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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
  - ORD Bench Top Study
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- General Conclusions
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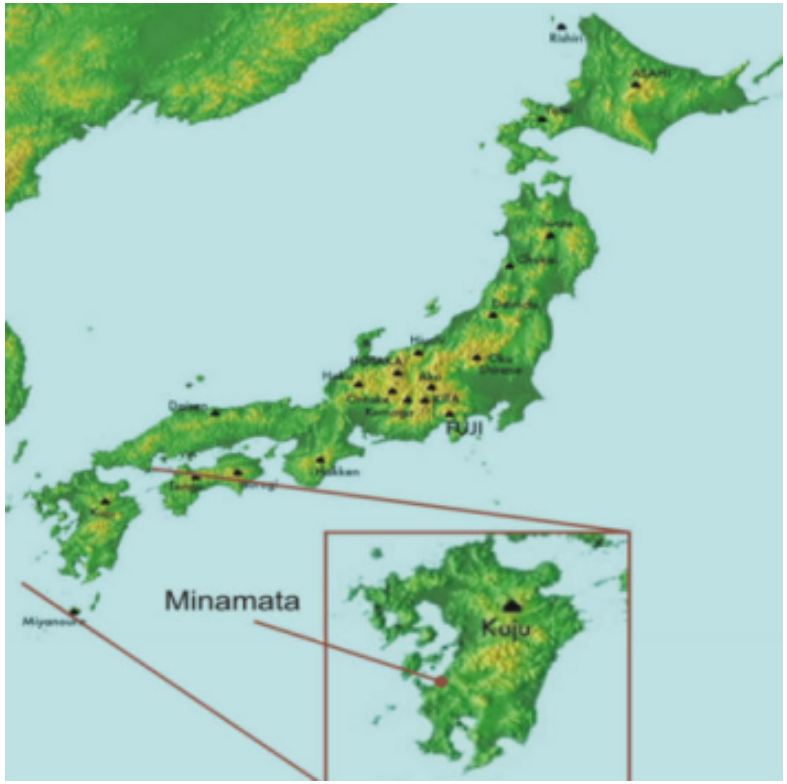
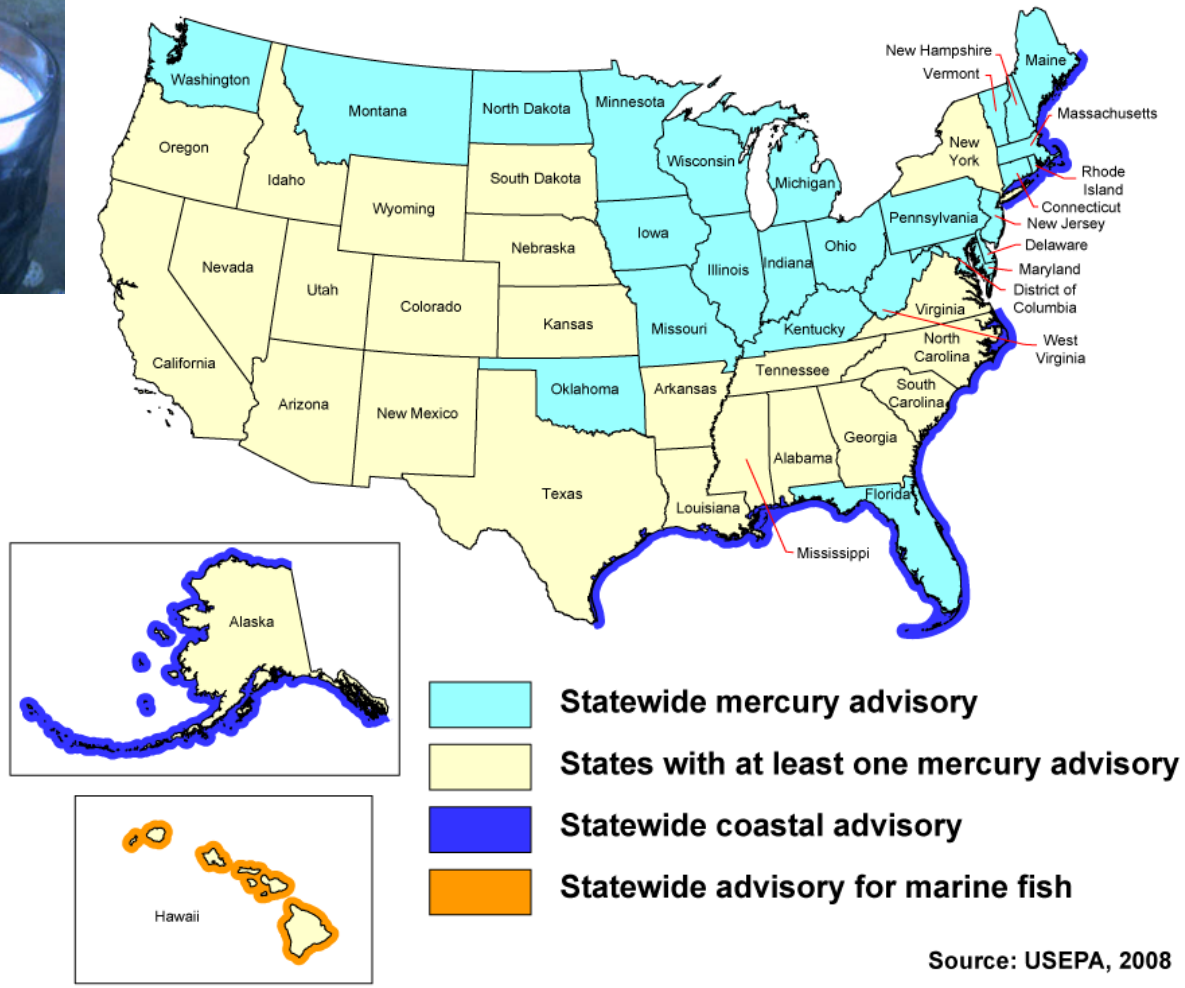
Anthropogenic Point Source Impacts

Minamata Bay



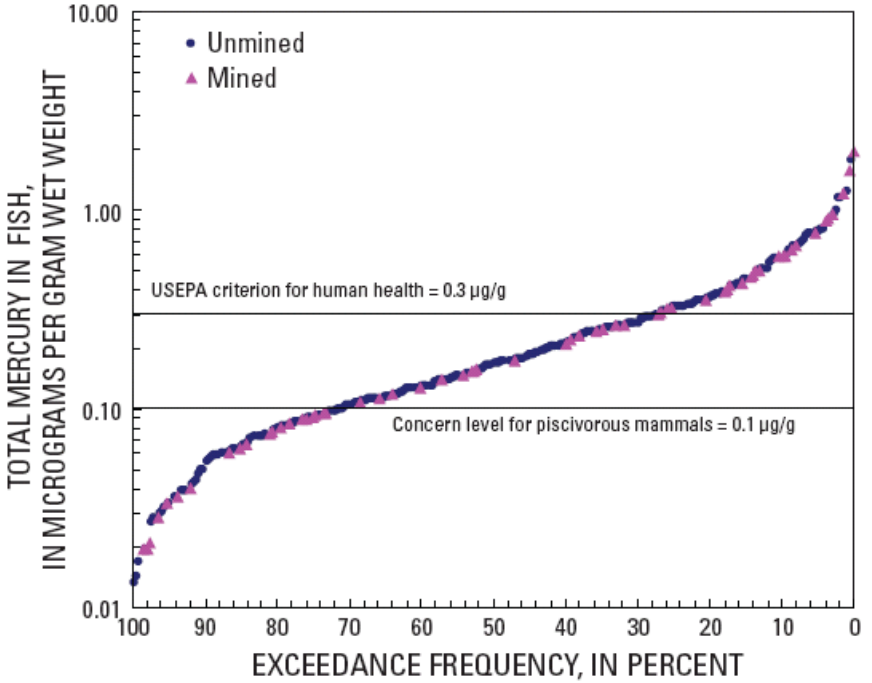
- Acetaldehyde Production 1932 -1968
- 27 Tons Methylmercury Dumped Into the Bay
- First Case: 1956
- 900 Killed
- 2 Million w/ Severe Health Effects

Mercury Advisories in US



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

Hg(II)
- Labile Mercury
- Electron Acceptors

SRB
- Carbon Source
- Reducing Conditions

MeHg
- Proximity to Food-web
- Competing Ligands

100,000x

Algae

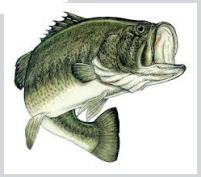
2-5x

Zooplankton

2-5x

Prey Fish

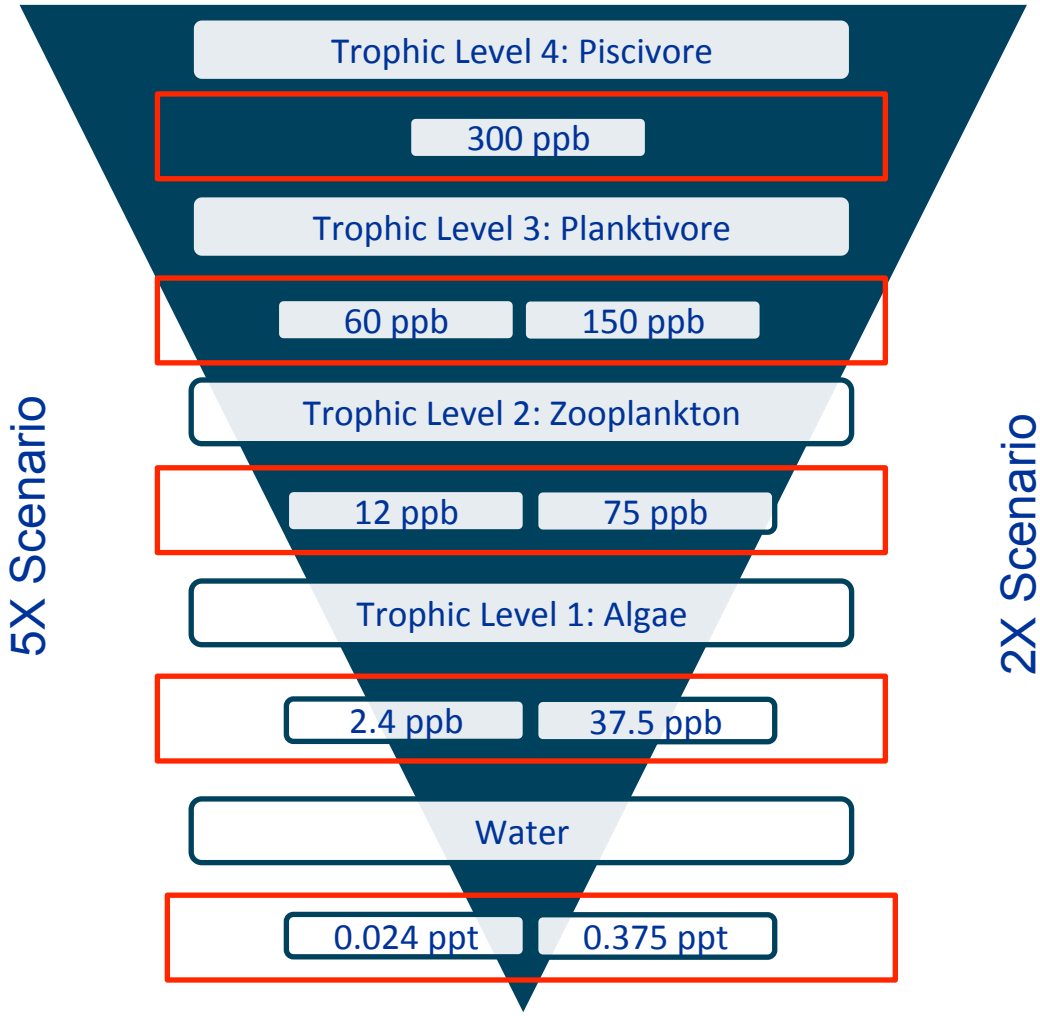
2-5x



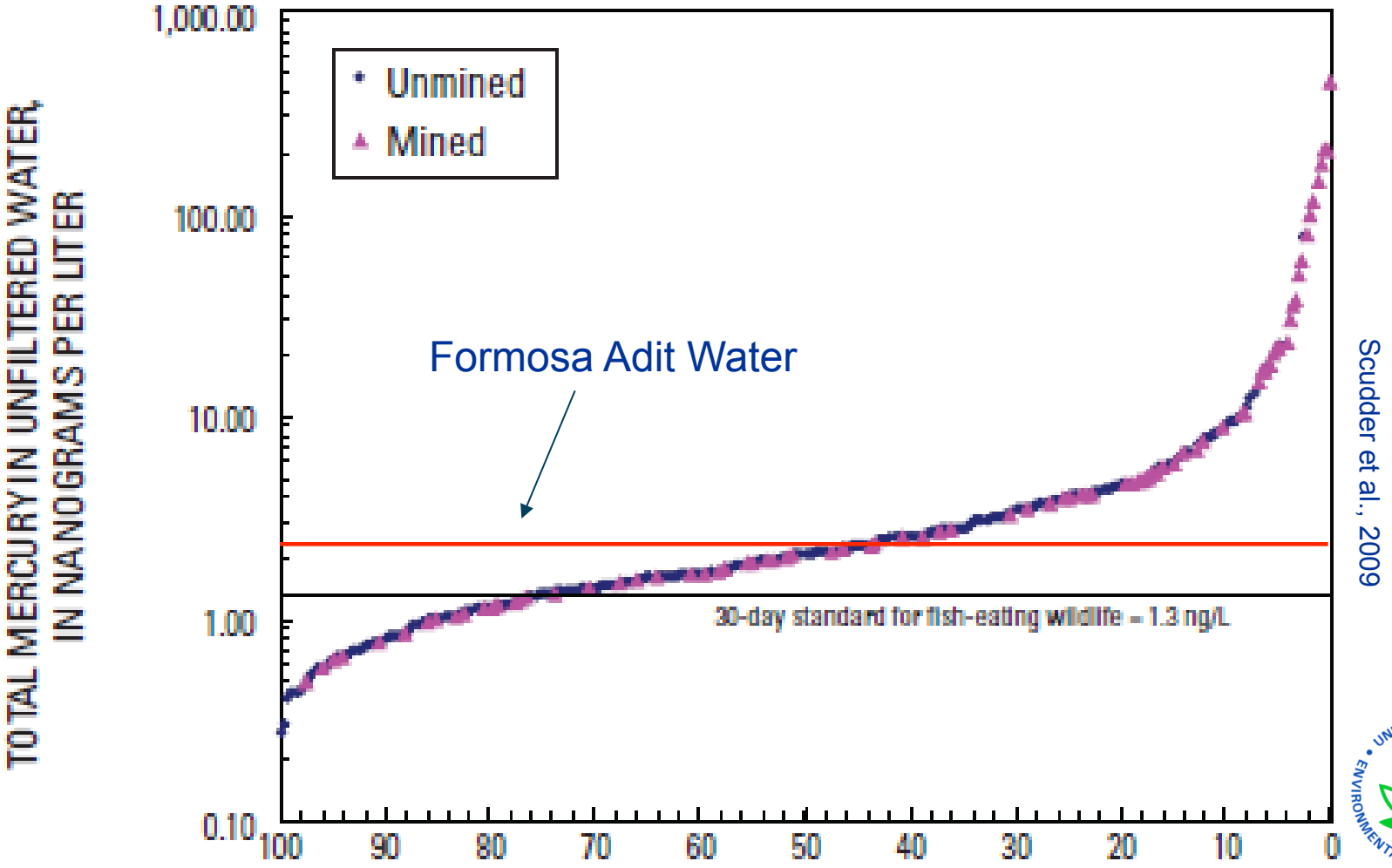
Predator Fish

Wood et al., 2013

Working the Problem Backwards (MeHg)

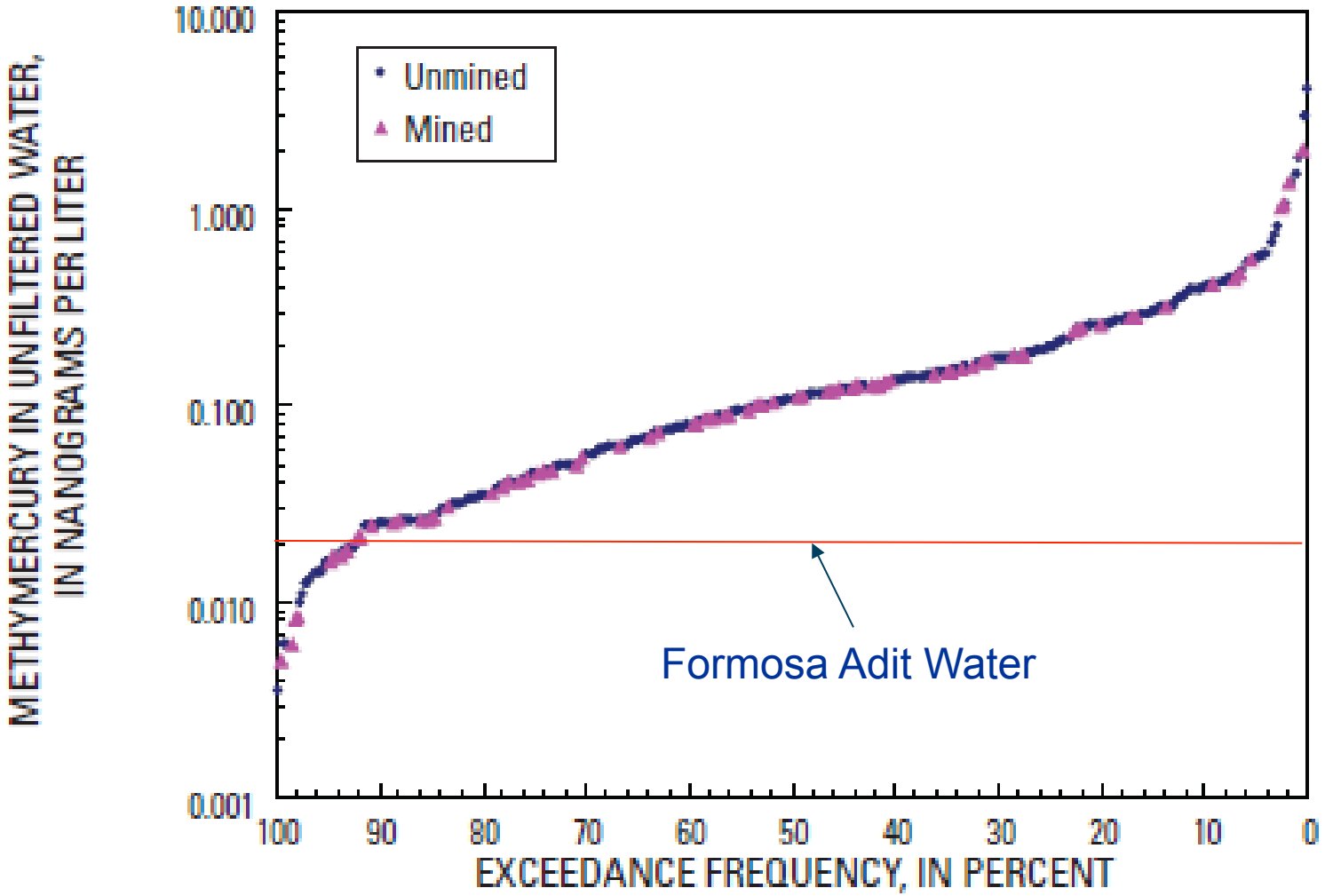


Total Mercury in Mined vs. Unmined Streams



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

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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- Biochemical Reactors (BCRs)– Mining Impacted Water
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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

CDM Smith 2014

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

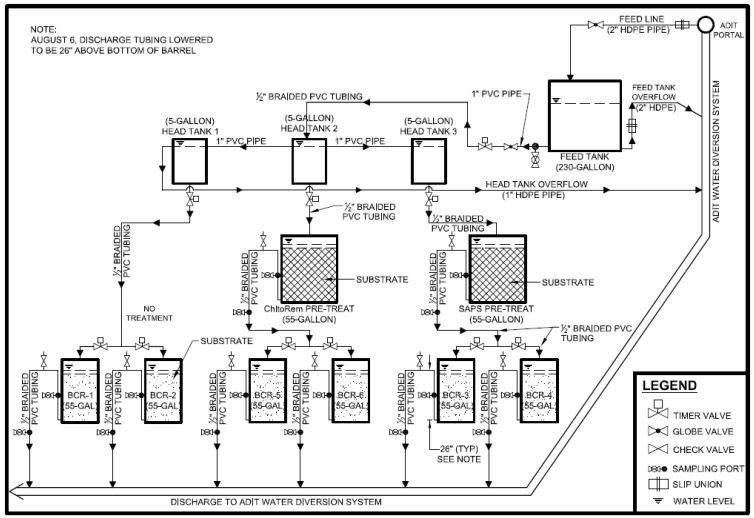
BCR Chemistry (Also Ideal for Hg(II) formation)

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



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FORMOSA MINE SUPERFUND SITE
DOUGLAS COUNTY, OREGON

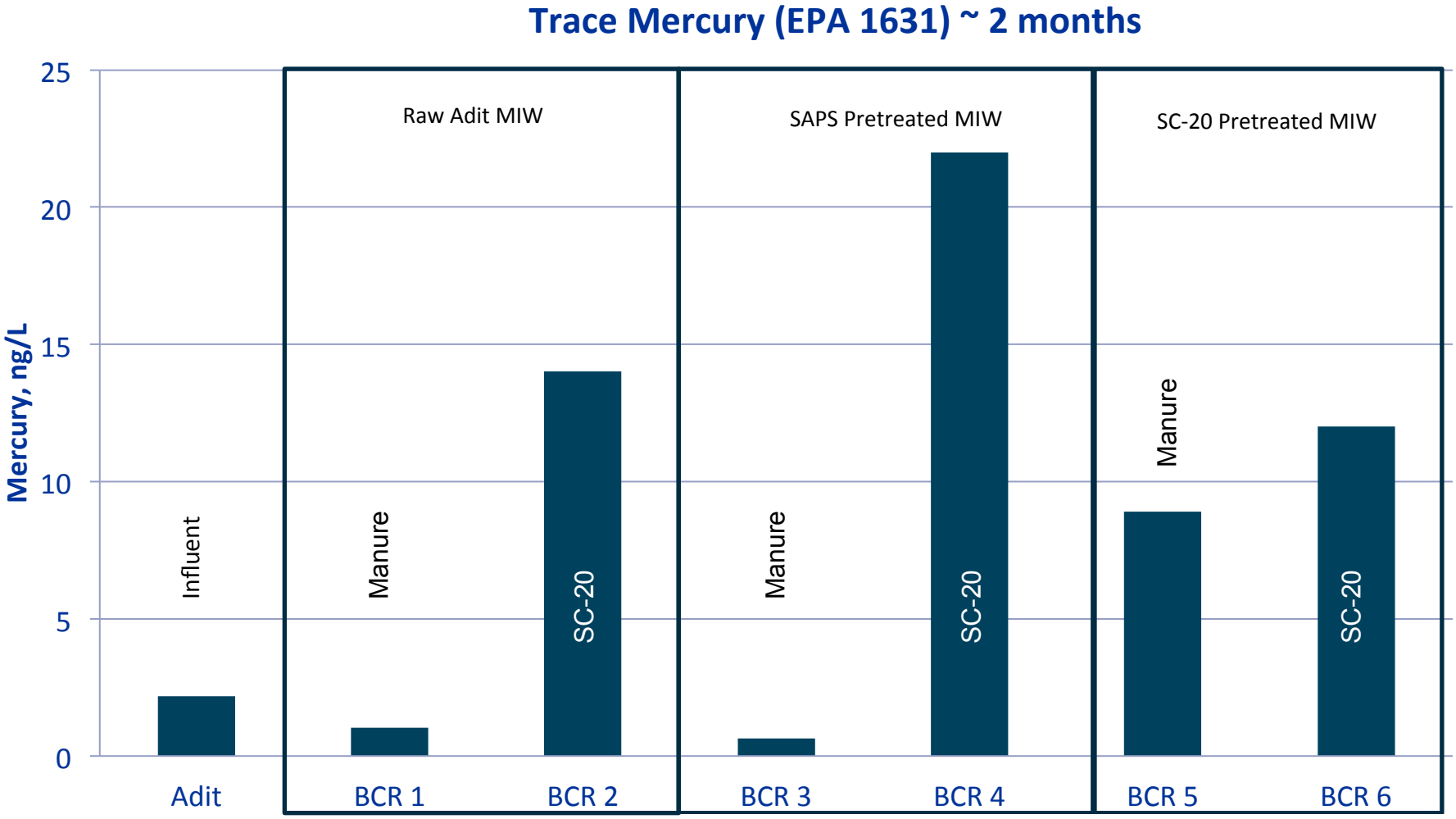
Figure 1-2
Pilot-Scale Treatability Study
Process Flow Diagram (Record Drawing)
AUGUST 2013

Mercury Assessment on BCR Evaluation

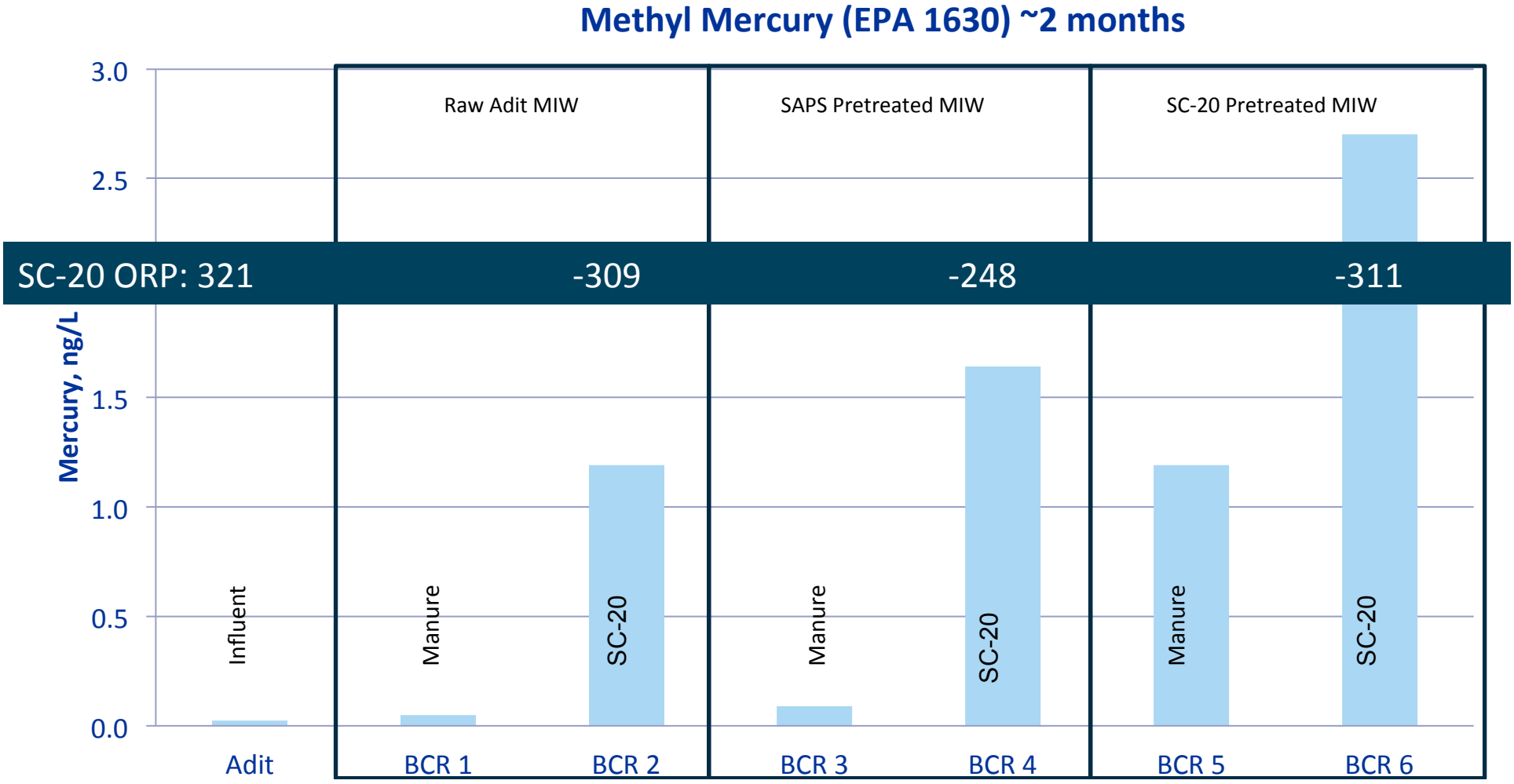
- Checklist for Mercury Methylation
  - Anoxic conditions: ☑
  - E-Donors (organic carbon): ☑
  - E-Acceptors (sulfate/iron): ☑
- Question: Considering inorganic mercury is methylated by sulfate reducing bacteria, could the environment inside a BCR contribute to MeHg in the effluent stream?

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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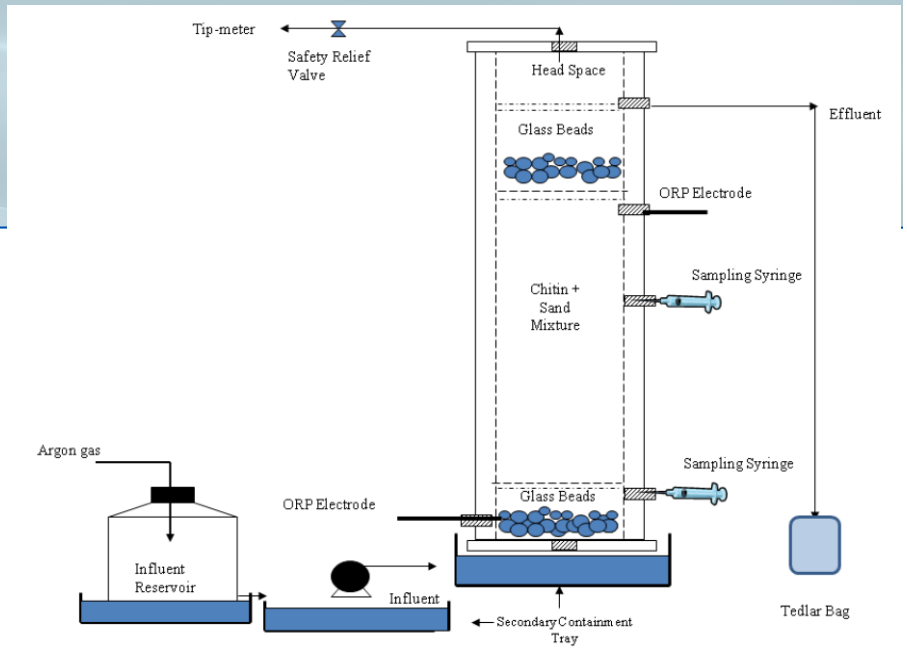
ORD Bench Top Study



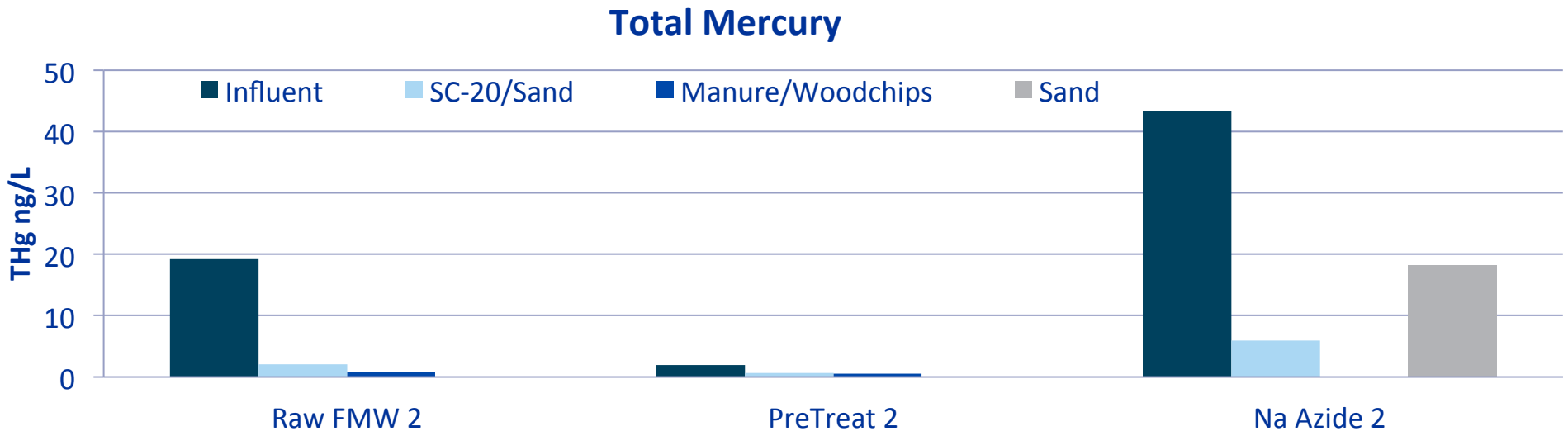
Influent and Column Specifics

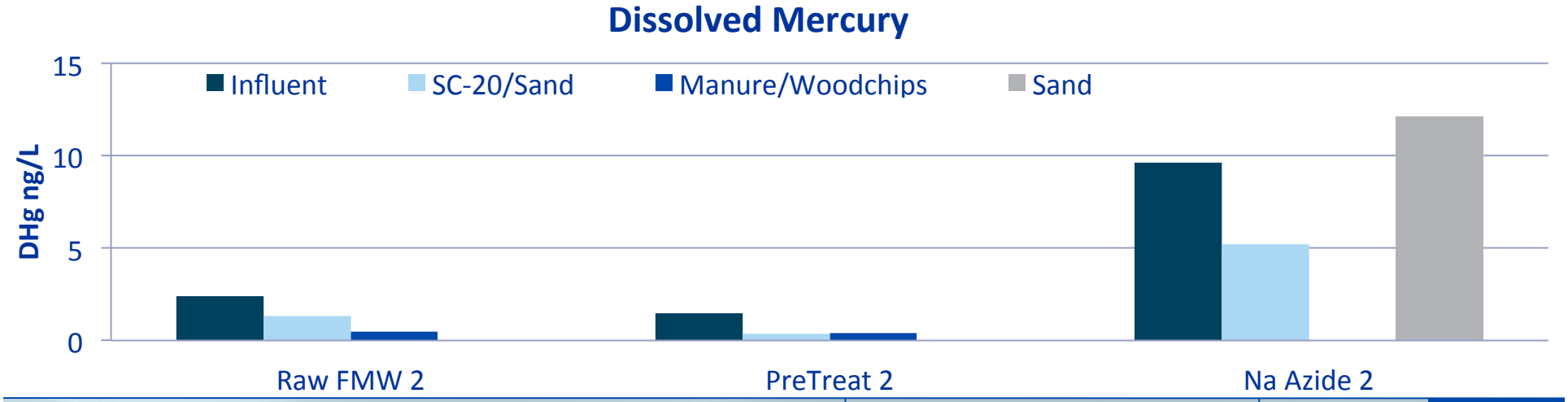
24 hr Hydraulic Residence Time

- 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

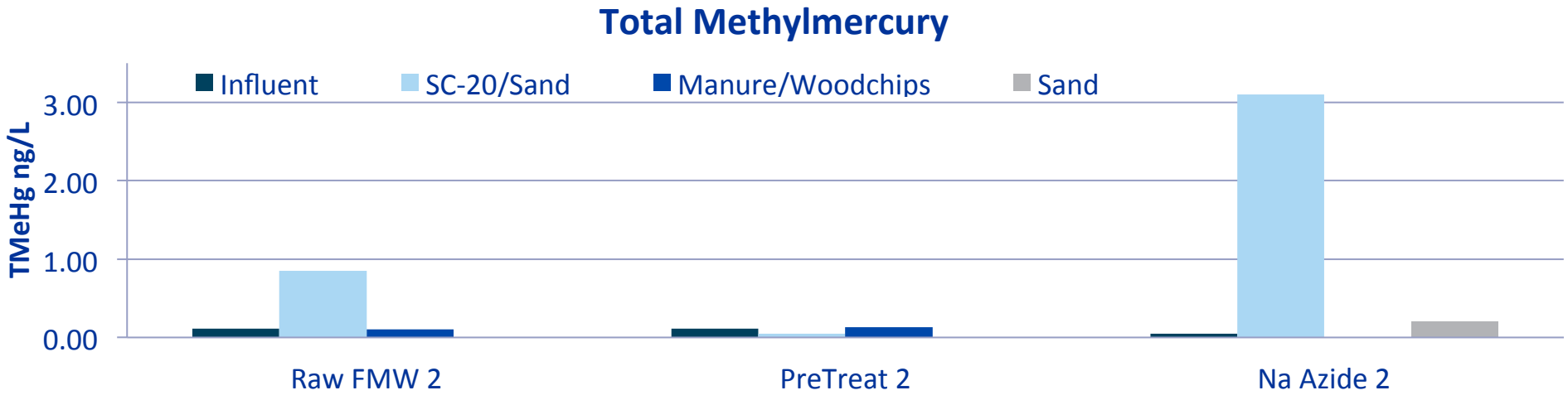


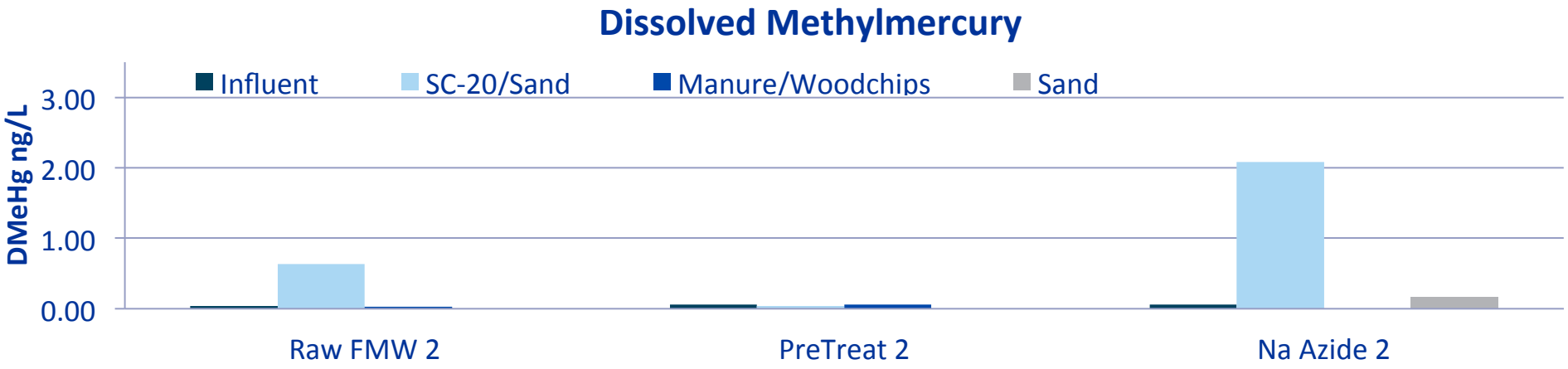


Total Mercury 34 Weeks into Test

- 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

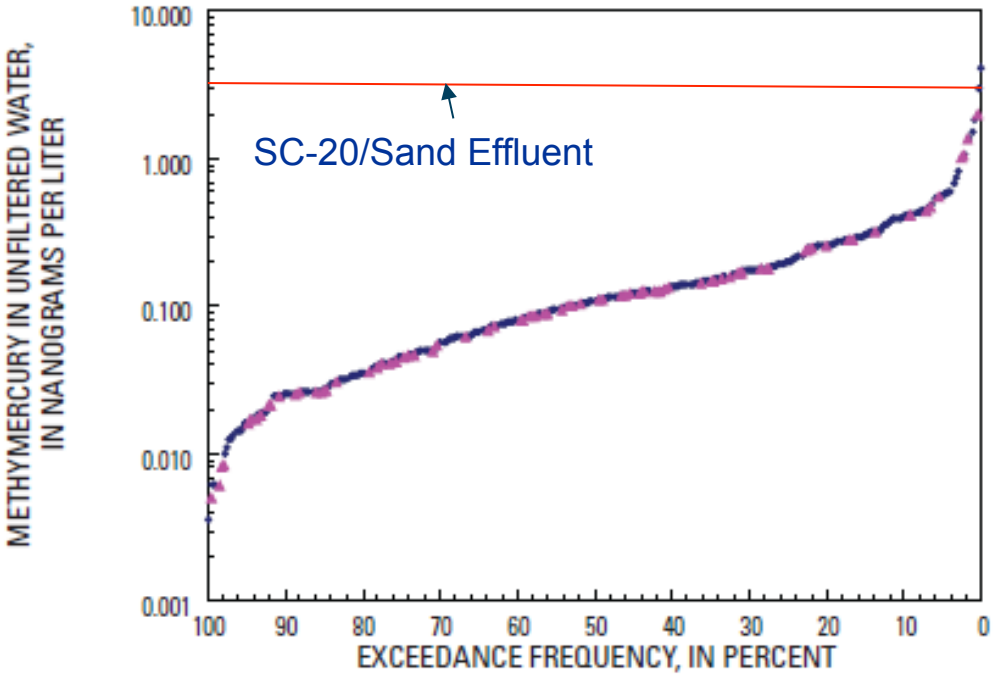
- Duration and Flow Consistency:
  - Treatability Study ran for 8 weeks
  - Treatability Study flow gravity fed and slowed over time
  - Bench top study ran for 34 weeks
  - Bench top flow consistent over time
- Total Mercury Source from SC-20/Sand Media
  - THg source in Treatability Study after 8 weeks
  - 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

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  - 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:
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Questions?

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