In Situ Control of Methylmercury Production in Sediments by Redox-Buffering Mineral Amendments

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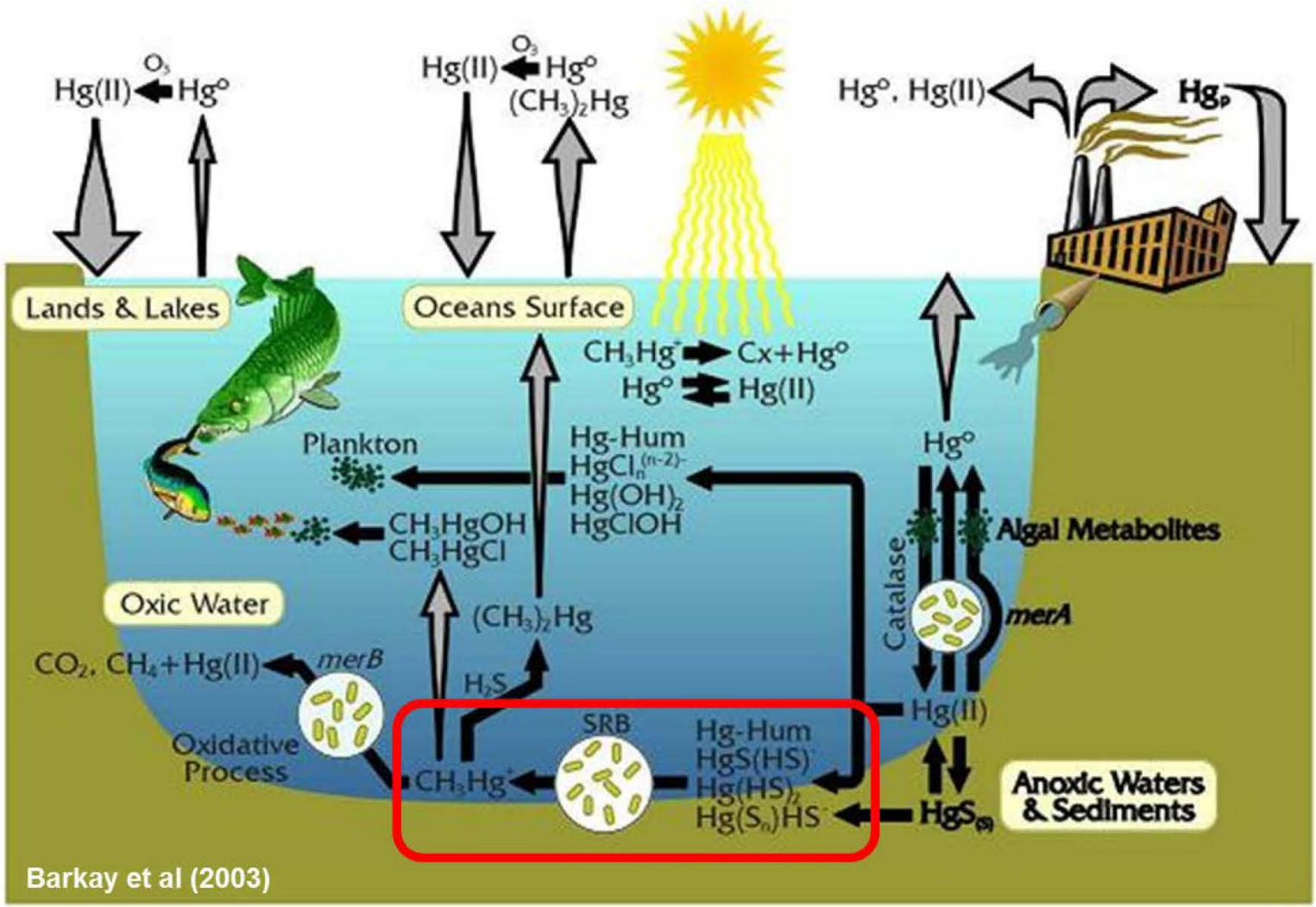
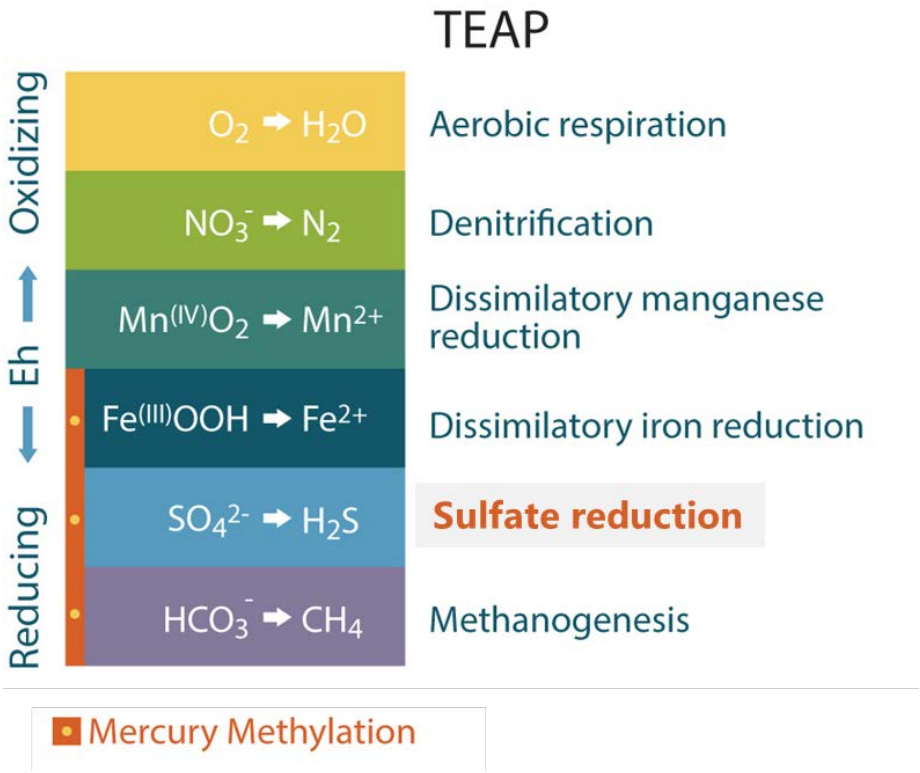
Hg Biogeochemical Cycle



Biogeochemical Redox Ladder and Hg Methylation

- Ability of microorganisms to methylate Hg linked to possession of *hgc*AB gene cluster
- Present in sulfate-reducing bacteria, as well as some iron-reducing and methanogenic bacteria
- To date *hgc*AB gene <u>not</u> found in any manganese-reducers, denitrifiers or aerobic bacteria

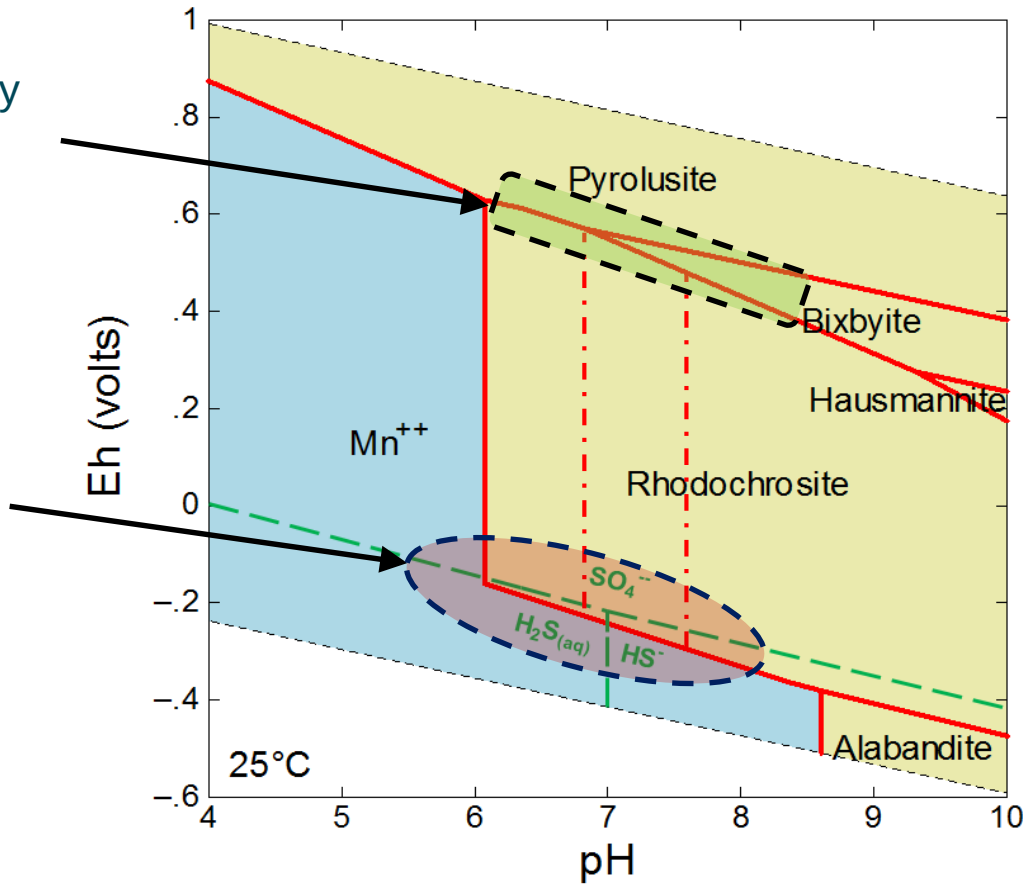


[Gilmour et al (2013) Mercury methylation by novel microorganisms from new environments. Environ Sci Technol. 47(20): 11810-20].

Can Sediment Redox Buffering by Manganese Oxides Suppress MeHg Production?

Redox buffered by Mn(IV)/Mn(III) oxides and Mn(II)

Conditions favoring MeHg formation



Pyrolusite
$Mn^{(IV)}O_2$

Bixbyite
$Mn^{(III)}OOH$

Hausmannite
$Mn^{(III/II)}{}_3O_4$

Rhodochrosite
$Mn^{(II)}CO_3$

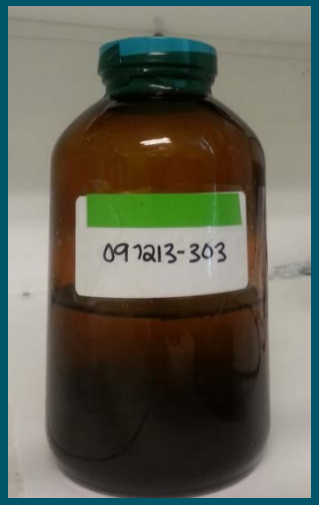
Alabandite
MnS

Sediment-Water Slurry Tests

- Investigate effect of MnO_2 on MeHg production in sediment following addition of:
  - labile DOC (acetate, 40 mg/L C)
  - available Hg ($HgCl_2$, 25 mg/kg)
- Triplicate sediment (150g) + water (500 mL) slurries:
  - control (sediment only)
  - amended (+MnO_2)
- Incubated under N_2 atmosphere in the dark, sampled for THg, MeHg, solution chemistry
- Microbial activity/structure examined by respirometry and qPCR

Sediment

Analyte	Result (n=3)	SD
Total Mercury (mg/kg)	94.8	8.9
TOC (%)	8.52	0.08
Iron (mg/kg)	36,600	1,800
Manganese (mg/kg)	12,700	924
Sulfide (mg/kg)	1.7	0.07
Total Solids (%)	30.0	0.2

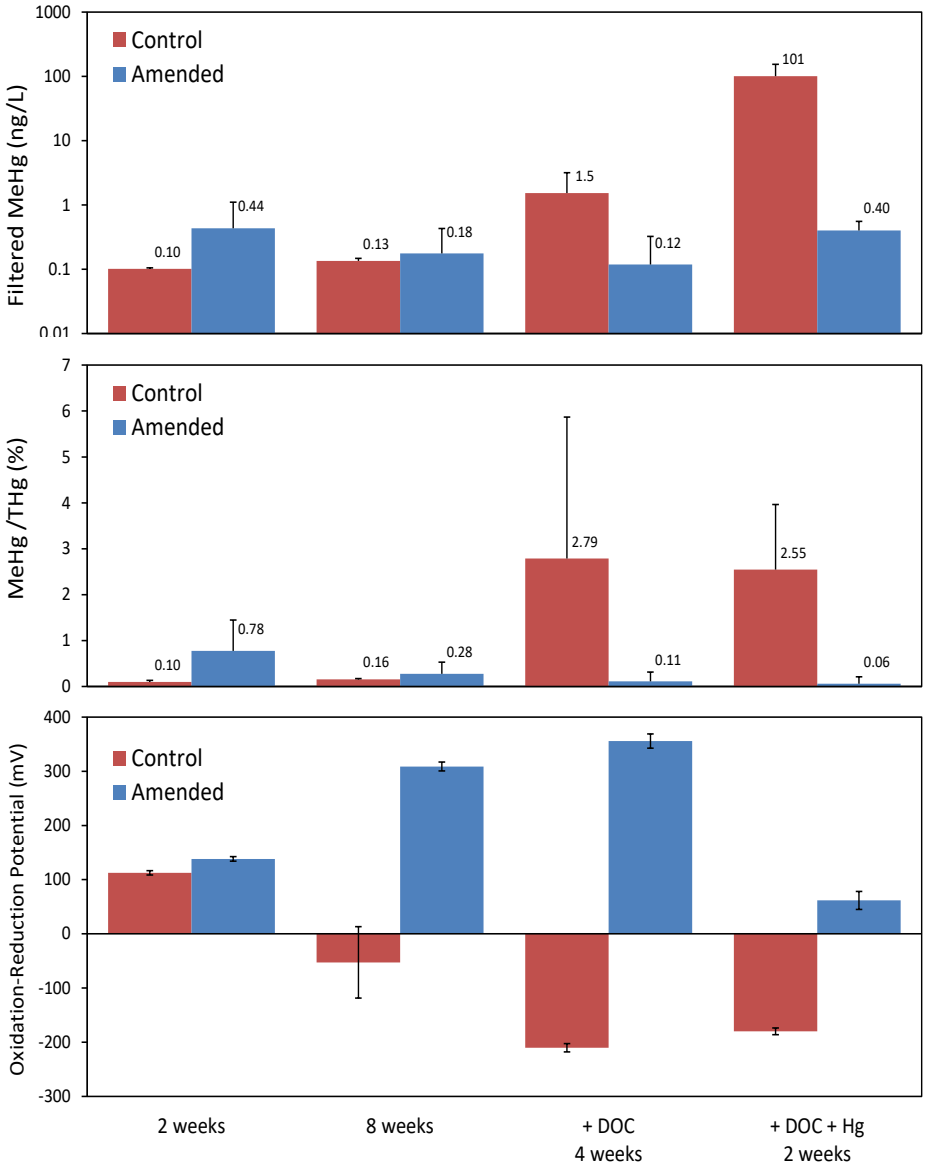


Porewater

Analyte	Result
FTHg (ng/L)	22,900
FMeHg (ng/L)	5.86
Calcium (mg/L)	106
Magnesium (mg/L)	171
Potassium (mg/L)	57.7
Sodium (mg/L)	1,420
Chloride (mg/L)	2,870
Sulfate (mg/L)	355
Alkalinity (mg/L)	126
Nitrate-N (mg/L)	1.69
Manganese (mg/L)	0.017
Iron (mg/L)	<0.02
Sulfide (mg/L)	0.04
DOC (mg/L)	6.2

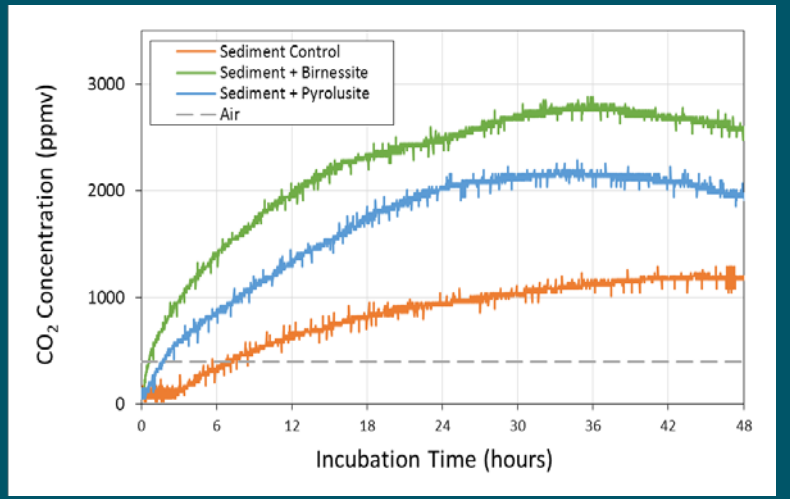
Slurry Test Results

- MeHg in MnO_2-amended microcosms lower than controls by 92 to >99%
- MnO_2 reduced net methylation (%MeHg/THg) by 1-2 orders of magnitude relative to controls
- Redox poising by MnO_2 suppresses MeHg production under conditions otherwise favorable for methylation (sulfate, labile organic matter, available Hg)



Respirometry

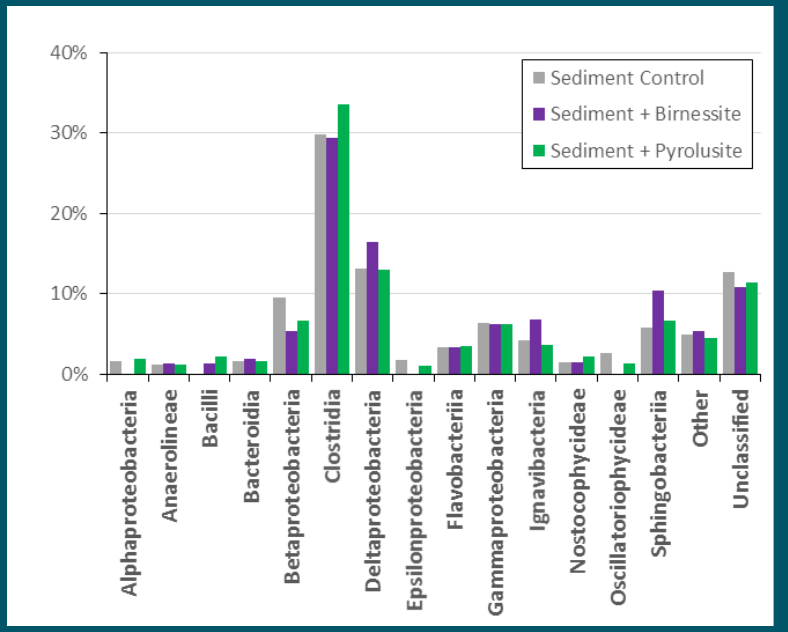
- Sediment ± MnO_2 (pyrolusite or birnessite) microcosms inoculated with culture medium (peptone-yeast-acetate), incubated under N_2 in the dark
- Continuous monitoring of CO_2 concentration in chamber headspace
- All microcosms showed significant CO_2 production due to microbial activity
- Higher CO_2 production in MnO_2-amended microcosms
- MnO_2 amendment of sediment **stimulated** microbial activity while reducing MeHg production

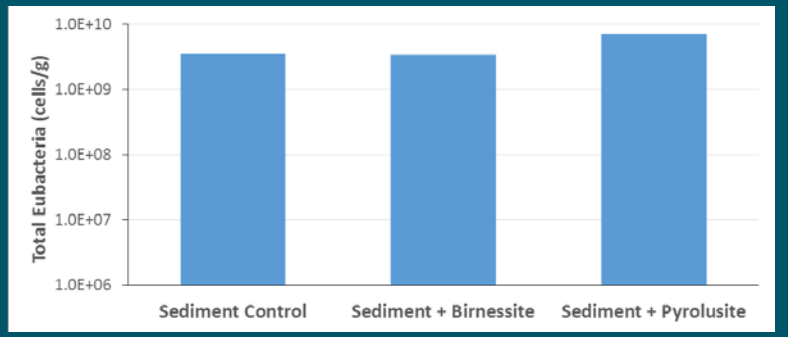


Microbial Community Census

- PCR and DNA sequencing -- phylogenetic composition and major genera present
- Treated and untreated microcosms had similar total eubacterial counts and community composition at the Class level
- Mix of soil and marine bacteria ranging from aerobic to methanogenic
- Dominated by fermentative and anaerobic bacteria
- Iron and manganese reducers present in both control and amended sediment

Phylogenetic Class Distribution





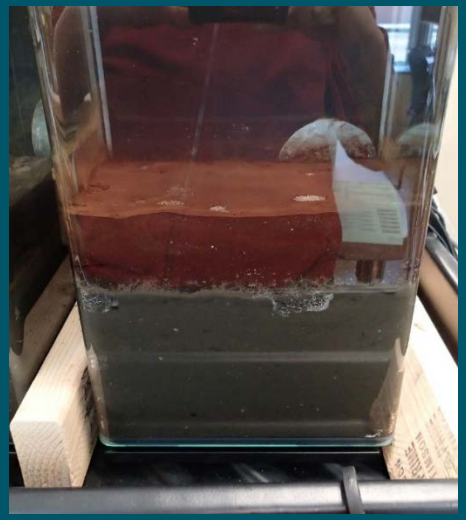
Aquarium Mesocosms

- Are MnO_2 amendments effective at suppressing MeHg under more realistic application conditions?
- How long are amendments likely to be effective?

- Aquarium mesocosm tests:
  - Aerated water column
  - 20 cm sediment column
  - MnO_2 added directly to upper sediment layer or applied on top of sediment in a thin layer reactive cover
  - Controls: sediment only and thin layer sand without amendments

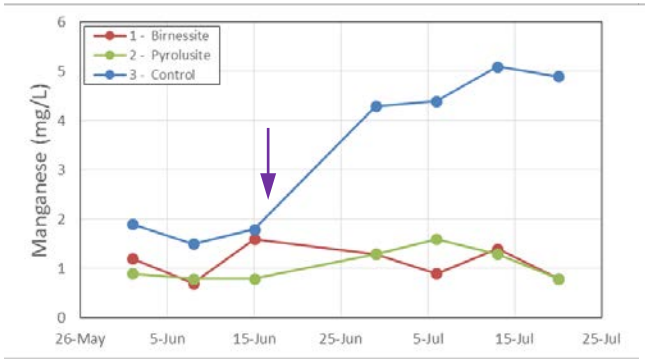
Aquarium Microcosm Setup

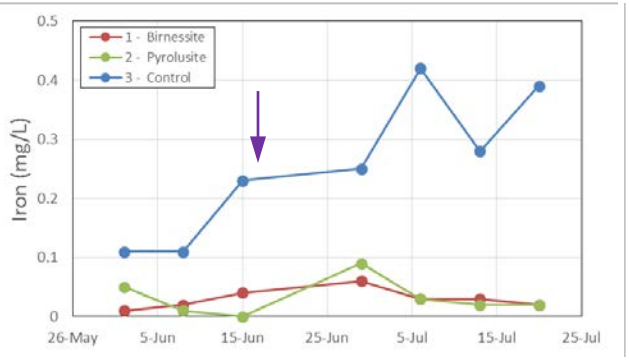
- Two MnO_2 amendments tested:
  - Pyrolusite (granular, mined)
  - Birnessite (powder, synthesized)
- Two configurations:
  - Direct addition to upper 5 cm of sediment (5 wt%)
  - Mixed in thin layer sand (5 cm, 5 wt%)
- Total of six mesocosms
- Measurements:
  - Overlying water monitored for pH, ORP, SC, Fe, Mn, SO_4, H_2S
  - Porewater and overlying water sampled for MeHg and THg (in replicate)
  - Sediment redox profiles by voltammetry
  - MnO_2 transformation over time (XANES)

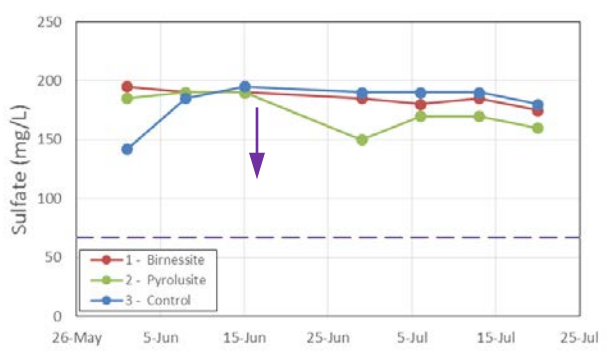


Overlying Water Quality Monitoring

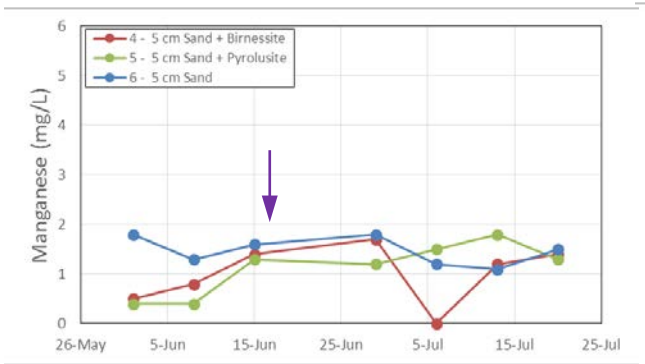
Direct MnO_2 Addition to Sediment

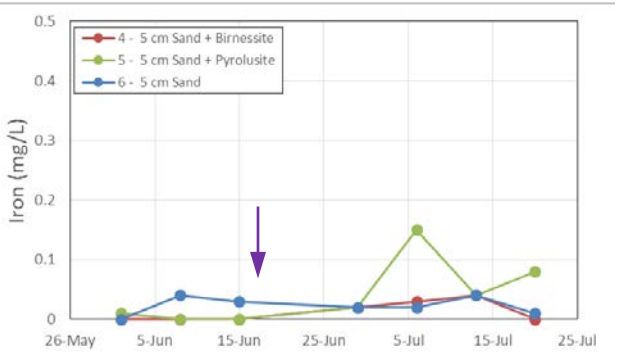


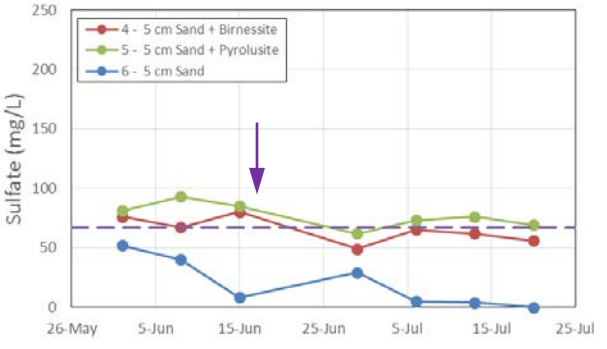




Thin Layer Cover Over Sediment





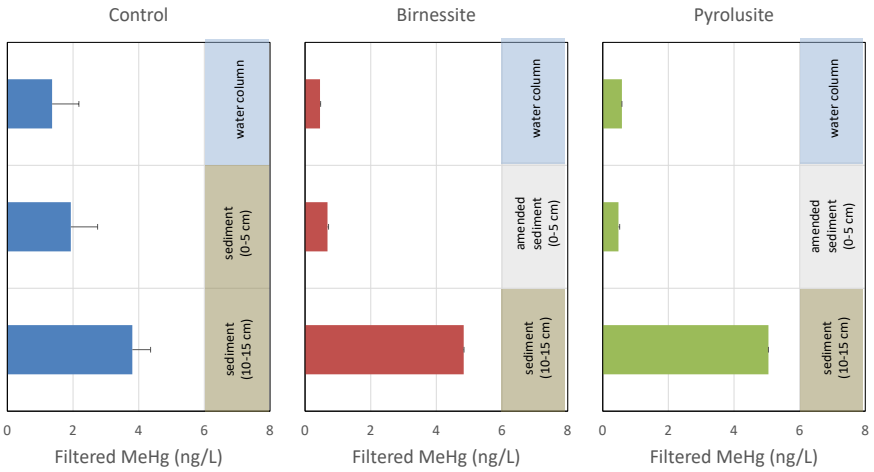


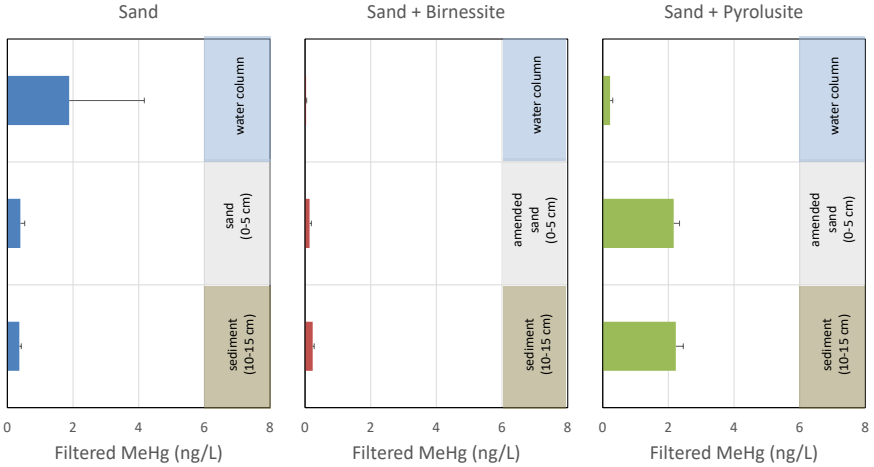
Arrow indicates date of sampling of porewater for THg/MeHg and voltammetry profiling
Horizontal dashed line indicates concentration in site water

MeHg in Mesocosm Porewater and Overlying Water

- Control tank shows diffusion-reaction depth profile for MeHg
- Birnessite and pyrolusite treatments show reduced MeHg in amended sediment porewater (0-5 cm) and overlying water; ~90% lower than underlying sediment porewater (10-15 cm)
- Sand had lower porewater MeHg concentrations than control, suggests reduced MeHg production, likely due to depletion of sulfate over time
- Birnessite and pyrolusite amended sand reduced both MeHg and THg in overlying water, mixed results for amended sediment porewater 0-5 cm porewater

Direct MnO_2 Addition to Sediment

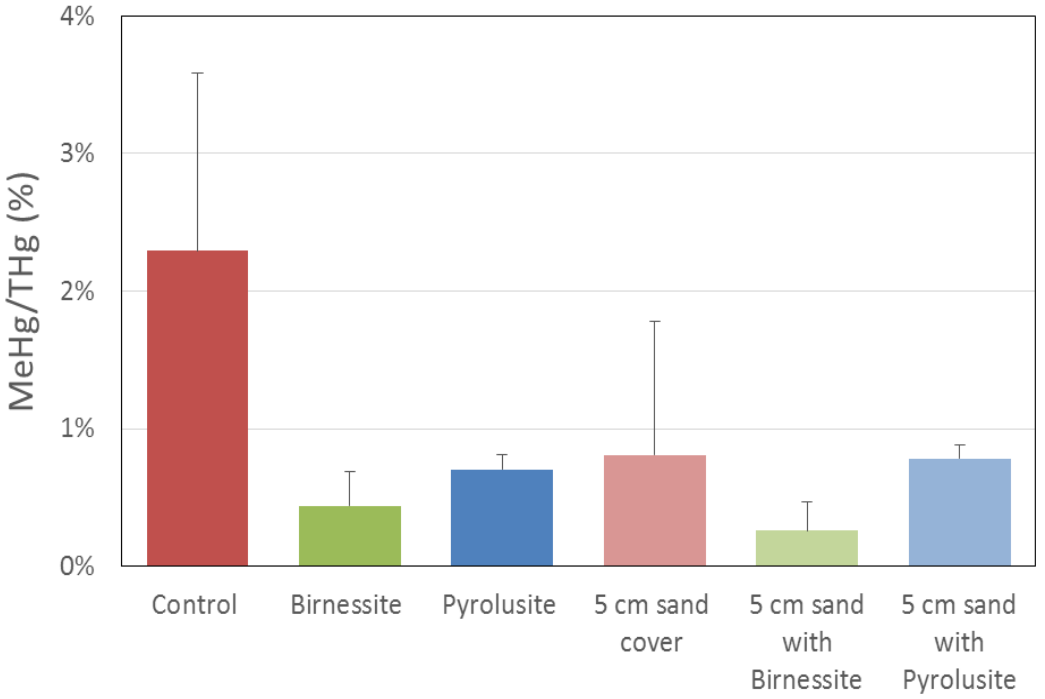




Thin Layer Cover Over Sediment

Effect of MnO_2 on Net MeHg Production

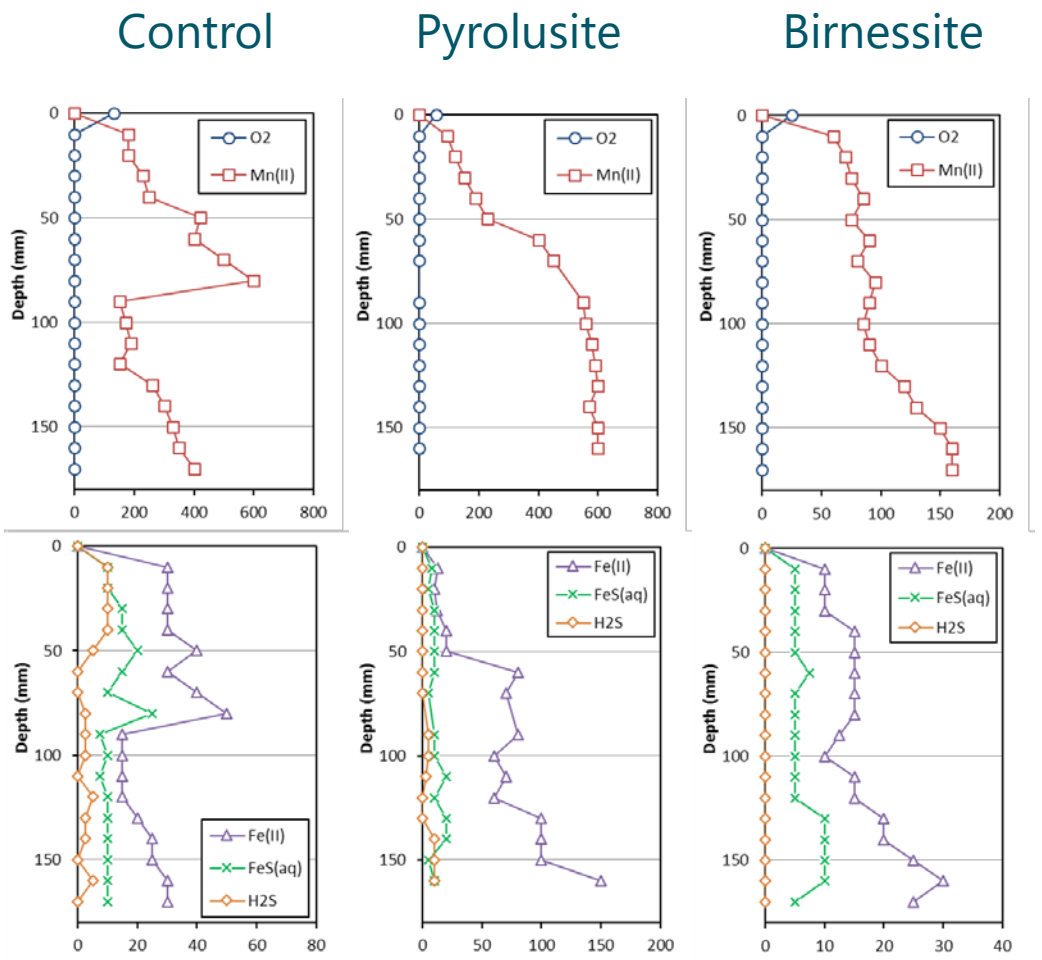
- Reduction in net methylation (as indicated by %MeHg/THg) measured in 0-5 cm porewater relative to control microcosm at 4 months:



	Pyrolusite	Birnessite	Sand Only
Direct Addition	69%	81%	-
Thin Layer Cover	66%	89%	65%

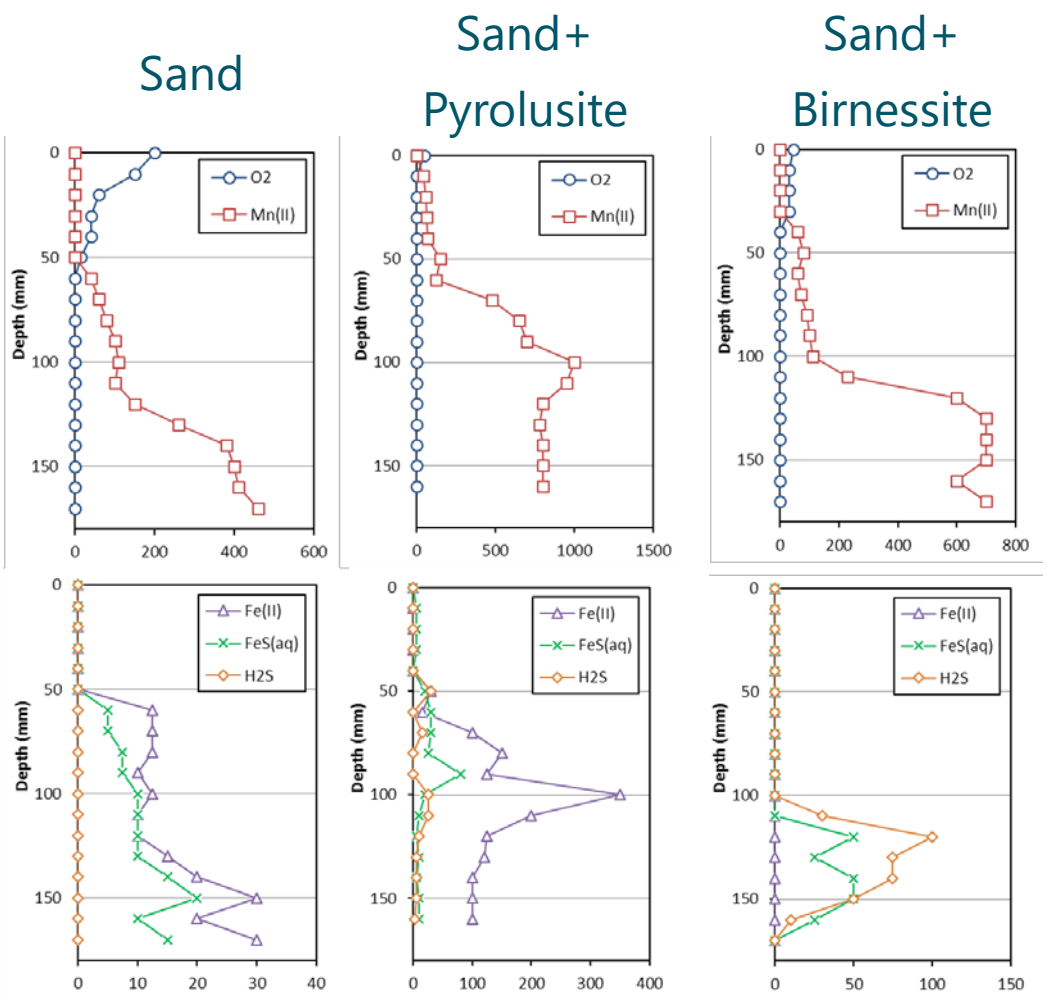
Insights from Redox Profiles (Voltammetry) Direct MnO_2 Addition

- Little penetration of O_2 in sediment (<1 cm)
- Control microcosm showed development of Fe(II) and H_2S (indicators of iron and sulfate reduction) very close to surface (~ 1 cm)
- Both pyrolusite and birnessite inhibited sulfate reduction (no H_2S detected within treatment zone)



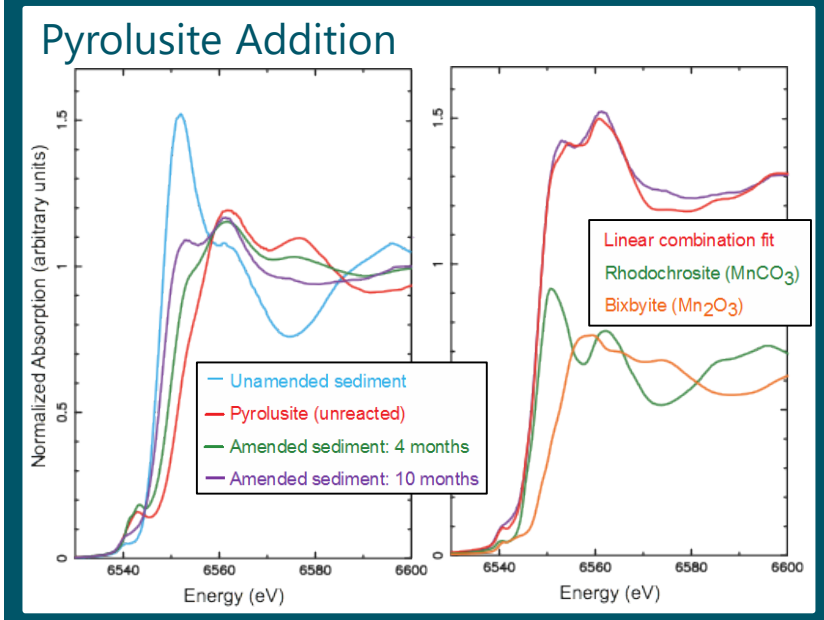
Insights from Redox Profiles (Voltammetry) Thin Layer Cover

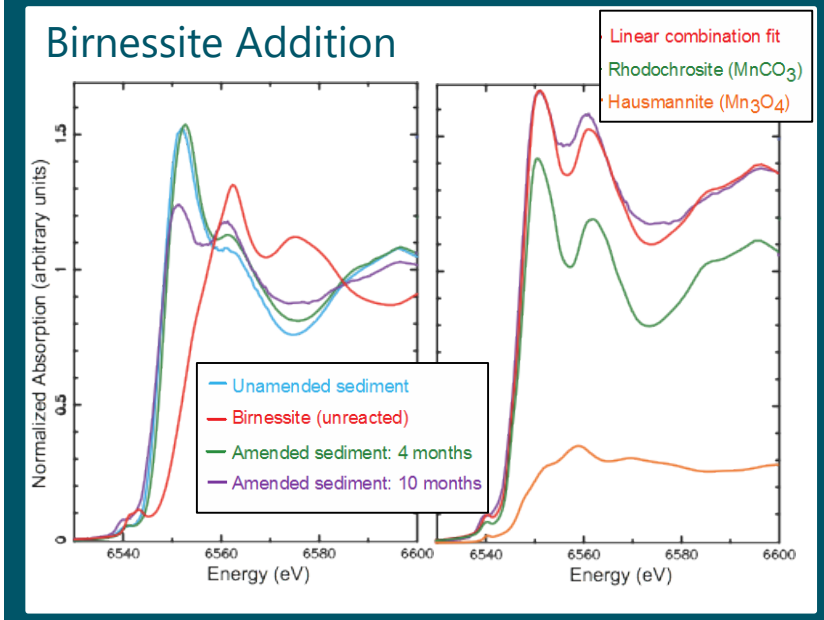
- O_2 penetration to base of sand layer (low O_2 demand)
- Less O_2 penetration in MnO_2-amended sand
- No H_2S detected within sand layer in all 3 microcosms
- Birnessite seems to have a greater depth of influence on redox than pyrolusite



Transformation of MnO_2 Amendments with Time

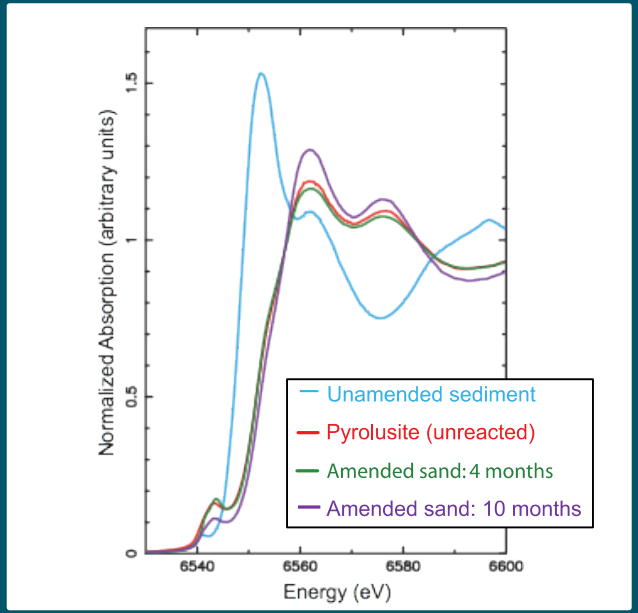
- Mn K-edge XANES used to monitor changes in solid phase manganese speciation over time
- Mn speciation in unamended sediment is predominantly Mn(II), present as rhodochrosite and/or adsorbed species
- In direct addition microcosms, changes in Mn XANES spectra over time indicate partial conversion of original pyrolusite and birnessite to Mn(III) and mixed Mn(II/III) oxides and rhodochrosite

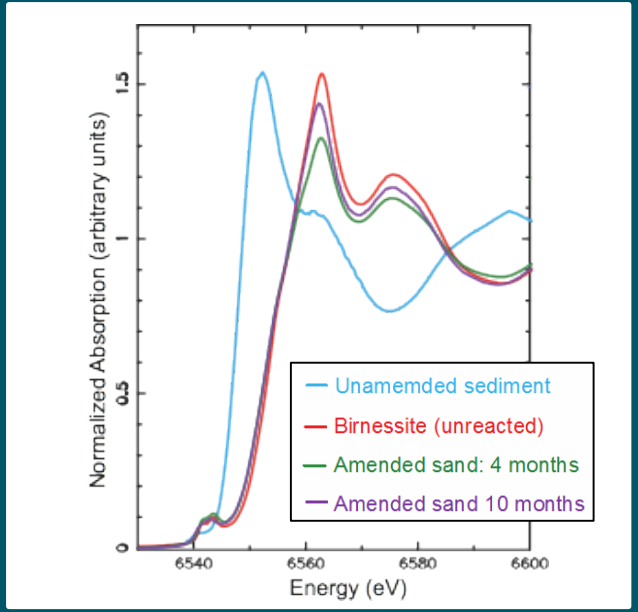




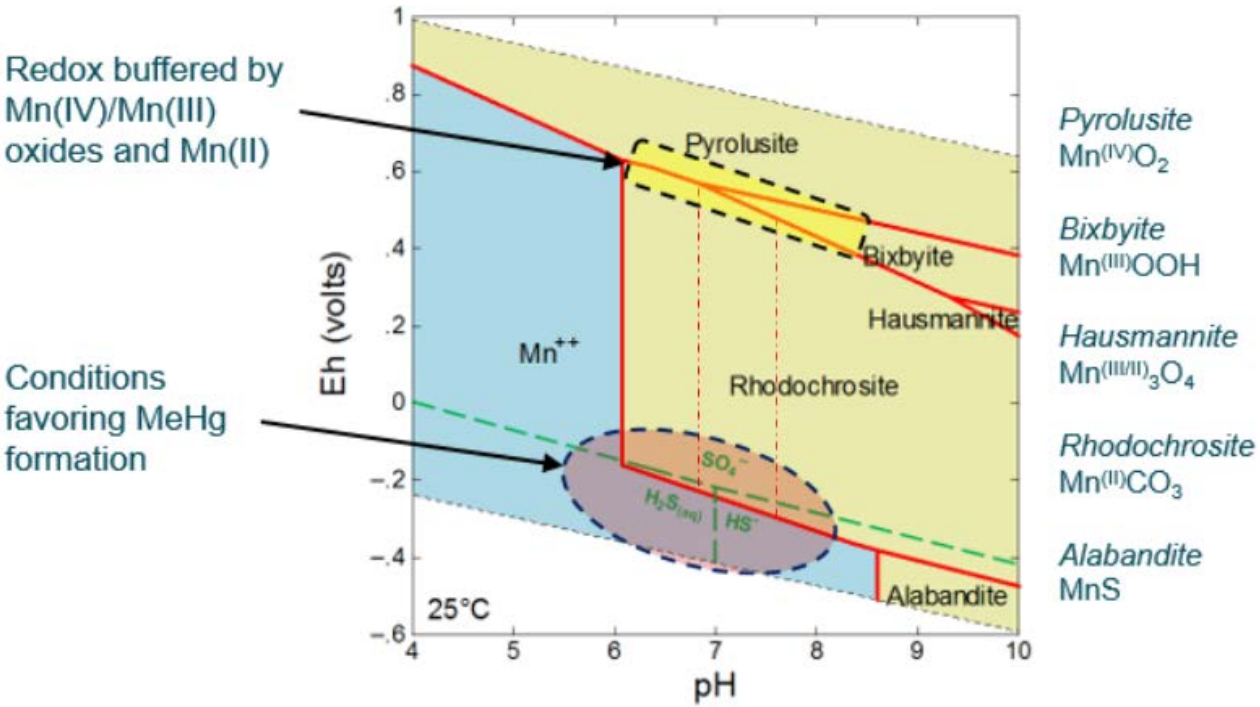
Transformation of MnO_2 Amendments with Time

- In thin layer cover application, Mn XANES spectra show that Mn mineralogy is largely unchanged from original pyrolusite or birnessite over 10 months of microcosm operation
- Contrast with underlying sediment in which Mn is predominantly present as rhodochrosite and/or adsorbed Mn(II)





Transformation of MnO_2 with Time



- MnO_2 converted to Mn(II/III) oxides and rhodochrosite over time
- Redox-buffering Mn phases persist for at least 10 months
- Bulk of added Mn retained in sediment in this system
- Potential for periodic (seasonal and/or tidal) regeneration of MnO_2 by rhodochrosite oxidation in field application

Summary and Conclusions

- Batch slurry experiments document effectiveness of MnO_2 amendments in suppressing net MeHg production in laboratory sediment microcosms
- MnO_2 amendments poise redox and shift predominant microbial activity from sulfate reduction to manganese reduction and suppressing Hg methylation
- In mesocosms, direct addition of MnO_2 amendment to sediment or in thin layer amended sand cover reduced net MeHg production by factor of 3 for pyrolusite and 4-5 for birnessite
- MnO_2 added to sediment was converted to Mn(II/III) oxides and Mn carbonate over time (months) but appears to be retained in solid phase – potential for in situ regeneration of MnO_2 through tidal and/or seasonal cycling in field application
- MnO_2 in thin layer sand application converted more slowly than when directly added to sediment – longer effective lifetime