Reactive Capping Assessment South River, VA

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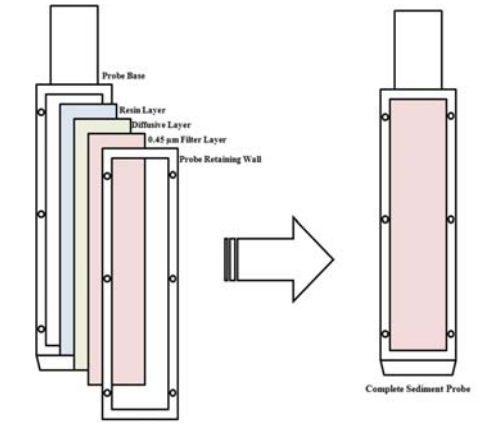
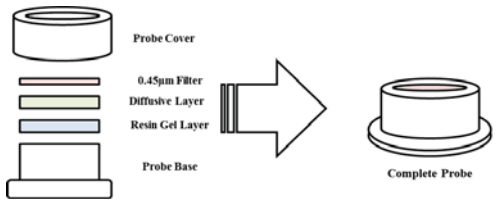
Reactive Capping Assessment- Outline

- Short summary of river/bank study results
  - To define what would need to be managed
- Baseline studies
  - Mesocosm studies from RRM 11.8
    - Redox profiles and THg and MeHg concentrations
    - Benthic bioaccumulation and relationship to DGTs
  - Mesocosm studies from RRM 3.5 ongoing
    - Baseline THg and MeHg concentrations
- Effects of various sediment caps (RRM 3.5)
  - Cap amendments
    - Screening performance tests
    - Site specific influences on performance
  - Mesocosm testing
  - Timeline (completion of initial mesocosm studies Dec 2014)

Why DGTs?

- Resin
  - 3-mercaptylpropyl functionalized silica gel resin
  - Acrylamide or agarose gel base
- Diffusion layer
  - Agarose gel
- 0.45 µm polysulfone filter





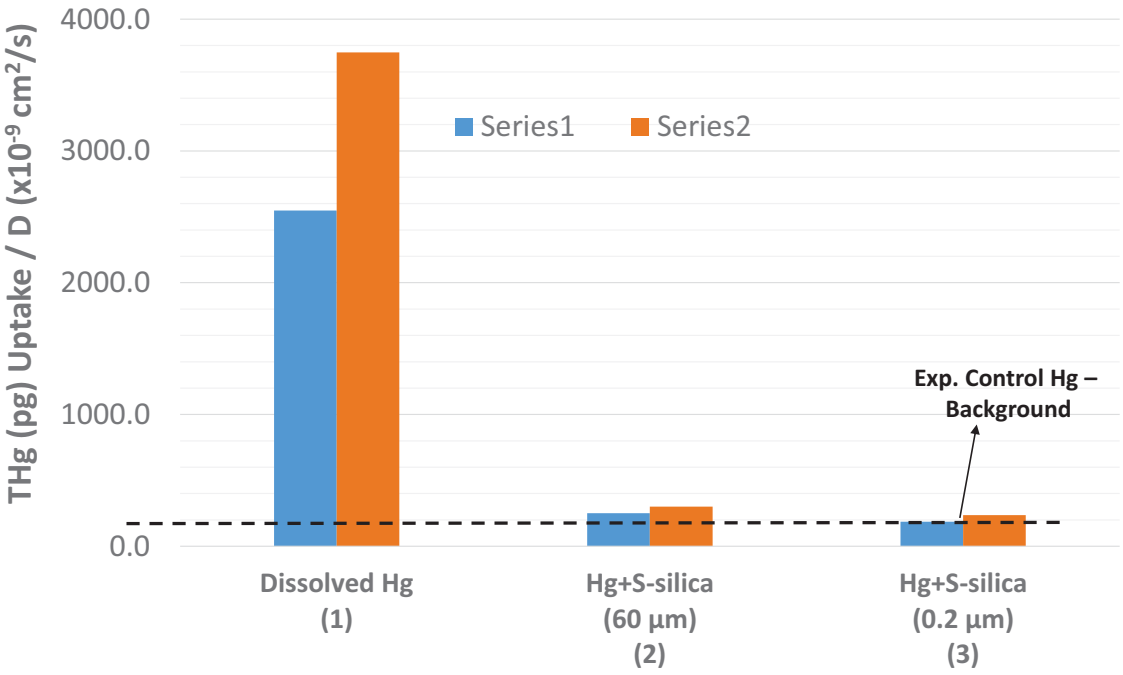
DGT uptake of Hg+Thiolated-Silica particles

Expt. Conditions

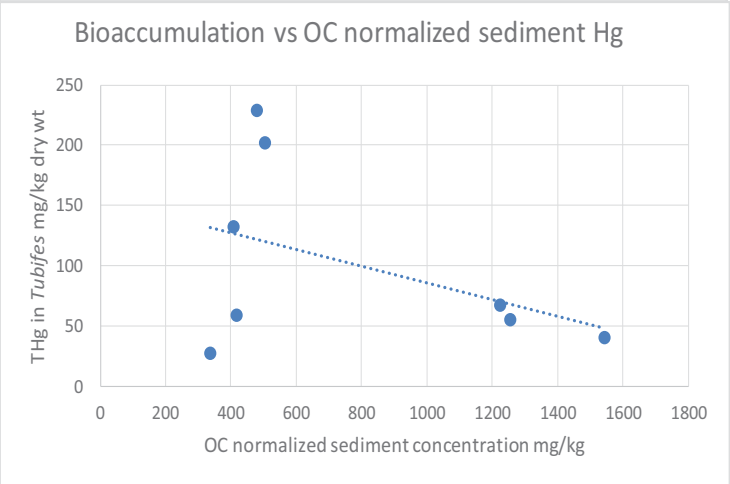
- Total uptake time ~ 6h
- Initial THg in sol. = 1ppb
- Temp. = 22.6 ^{o}C

Results

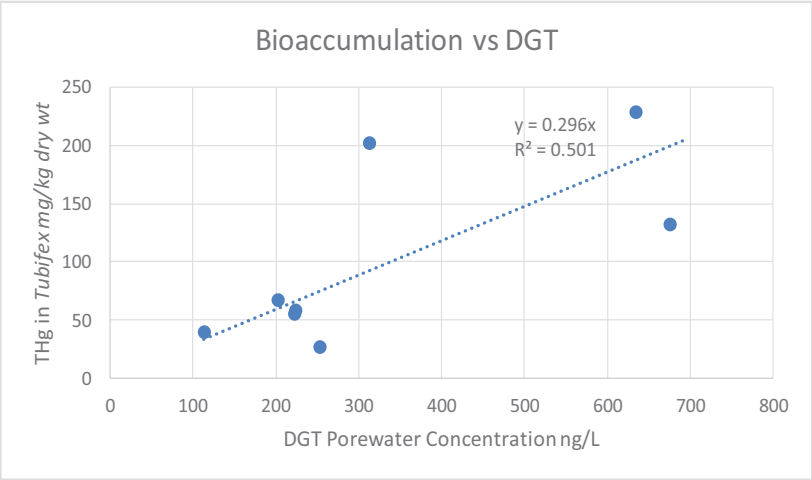
- Hg associated with 60 µm particles do not pass through DGT
- Hg associated with 0.2 µm do not pass through DGT
  - Complicated by potential particle aggregation of 0.2 µm Silica particles



DGT and bioaccumulation
(Baseline cap experiments)



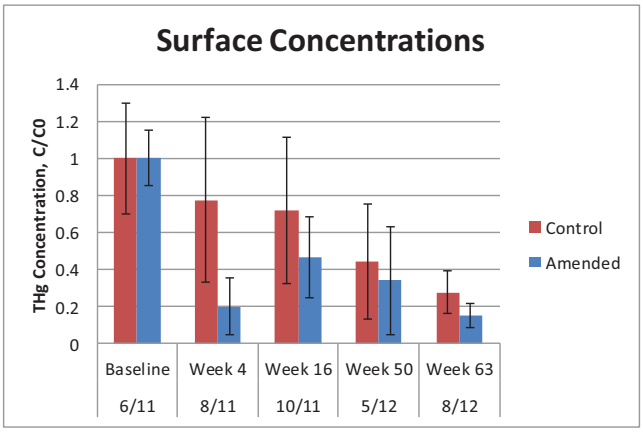
No Correlation

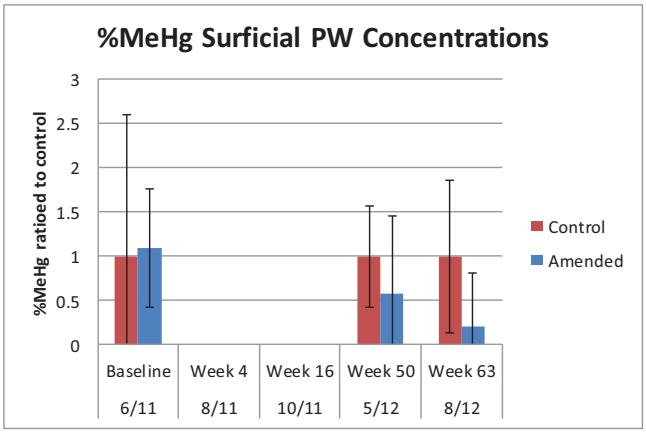


Correlation

Wertman Pond Pilot

- Biochar reduced THg and MeHg relative to control area as indicated by DGTs (MeHg variable)
  - We have shown biochar enhancing methylation in carbon-limited environments offsetting somewhat positive benefits of sorption (not South River)
- Lower Hg levels also reflected in Planorbidae and Caenis
  - Chironimids no trend
    - deeper than biochar?





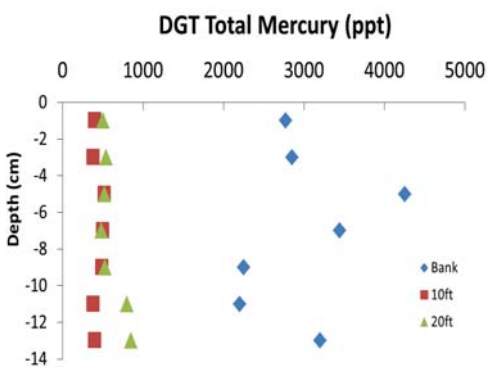
Conclusions of "what does the DGT measure?"

- DGT is measuring dissolved Hg, Hg associated with molecular size complexes and small DOM associated Hg
- DGT does not measure particulate and large colloidal Hg
- Pore size of agarose gel of order of 50-100 nm with smaller pores at surface excluding Hg associated with colloidal matter that is not biologically relevant
- DGT appears (with limited data) to better relate to bioaccumulation of Hg- more biologically relevant?

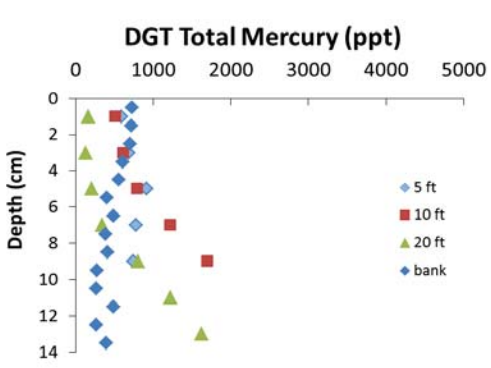
Baseline data

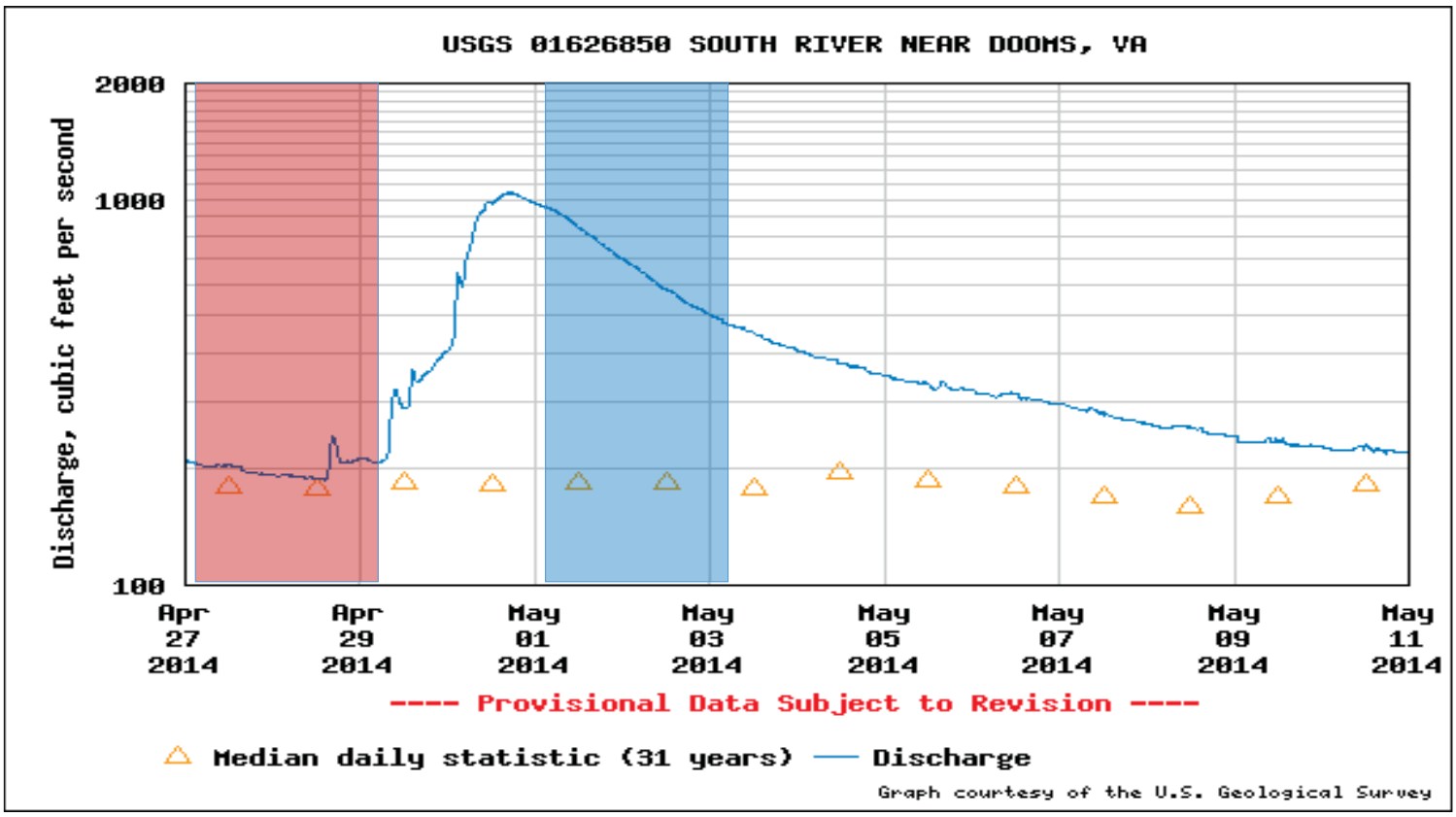
- DGT Field Sampling Conducted 2010-2014
- Three areas sampled
  - Source area (RRM 3.5), downstream (RRM 11.8), upstream (RRM 0.1)
- Consistent results 2010-2012
  - Low-water sampling

RRM 3.5



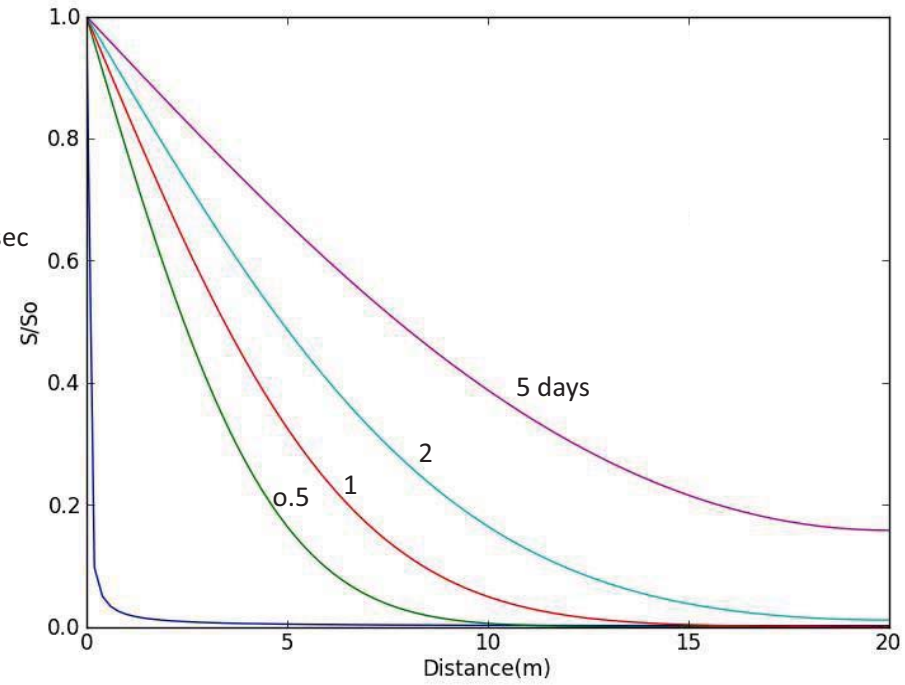
RRM 11.8





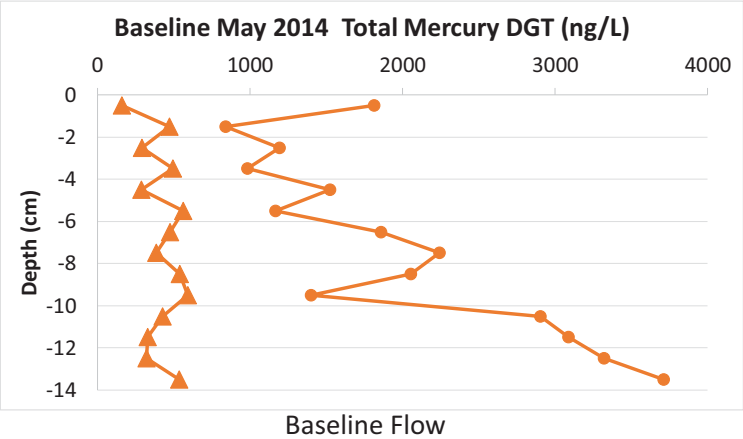
Seepage into the bank

S_y =0.1
K=0.001 cm/sec
(2.8 ft/day)
Δh=1.5 m

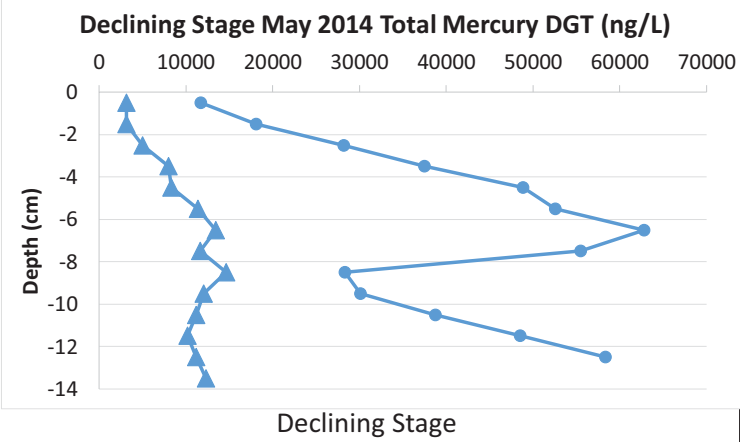


May 2014 THg

Baseline Flow

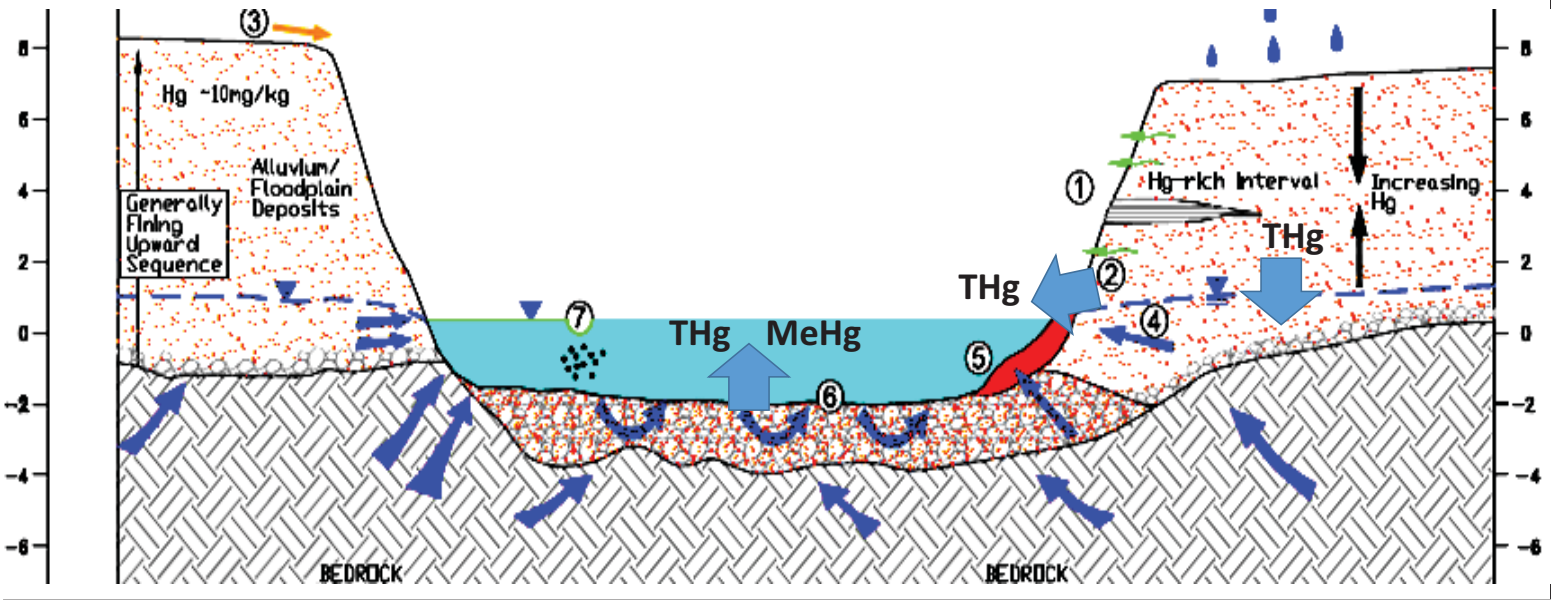


Declining Stage



Data shown are two different DGT profilers in different bank locations under each condition
Order of magnitude increase during declining stage although not as high as May 2013
Maximum river stage approximately half that of May 2013 (less bank inundation)

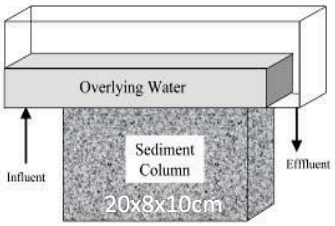
In-Situ Management



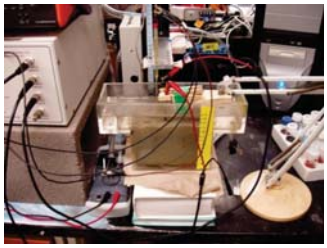
Laboratory Evaluation of Reactive Capping

Porewater Measurements ~ Biological Structure

Geochemical observations-
Voltammetry:
Redox profile, pH



DGT- porewater analysis:
MeHg and THg



- Periodic, non-destructive measurements made with microelectrodes at mm-scale depth resolution
- Byproducts of microbial metabolism (Fe^{2+}, Mn^{2+}, HS^-) measured in sediment porewater

- DGT-depth profiler (Diffusive gradient in thin films)
- Practical method quantification limits of 10 ng/L for THg,
  0.1 ng/L for MeHg

Baseline Studies

RRM 11.8- with benthic organisms
Organisms – tubificids , active burrowing deposit feeders. Not common in South River but used as a active sediment burrower, deposit feeder to indicate potential bioaccumulation
Analysis by voltammetry, DGT, post-experiment coring completed
RRM 3.5
Pre capping equilibration completed

Sample	Treatments
11.8 Bank	Control (no organisms) and populated mesocosms
11.8 FGCMD	Control, autoclave control and duplicated populated mesocosms
11.8 Gravel	Control, control with potting soil, populated with potting soil
3.5 Bank	Control with GAC, biochar, bank soils, sand
3.5 Gravel	Control with biochar, bank soils

Organism: Deposit Feeding Oligochaete

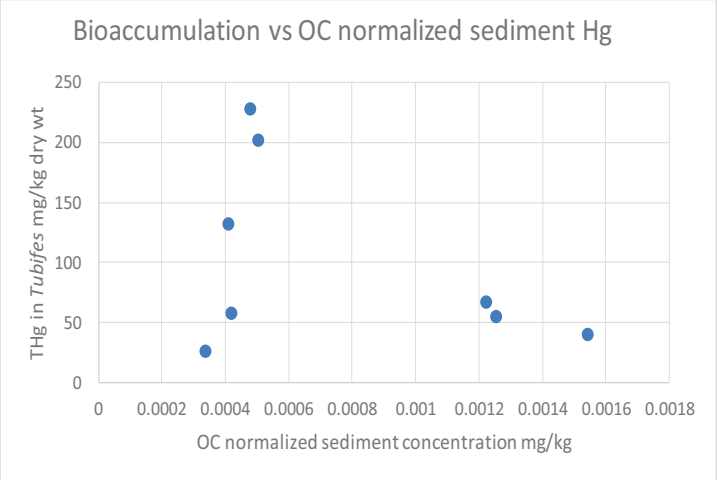
- *Tubifex tubifex (T.tubifex)* selected as test organism
  - Subsurface-deposit feeders
  - Process 10-20x weight each day, and thus overcome mass transfer limitations
  - Tolerant of many physical and chemical conditions
  - Preferentially consumes organic particles in 0.5-10 µm size range
- 28-day bioaccumulation test
  - Exposure, depuration, analysis
- Higher bioaccumulation of THg than might be expected based upon bulk solids (feeding on fine particles?)
- Bulk of bioaccumulation – THg 90+%

Muller, O.F. (1774). *Tubifex tubifex*. BioLib Retrieved from wwww.biolib.cz (bottom)

Depth of Bioaccumulation and Bioturbation

- There is visible evidence of bioturbation in the 28 days
- Extends to a maximum depth of 4 cm

DGT and bioaccumulation
(Baseline cap experiments)



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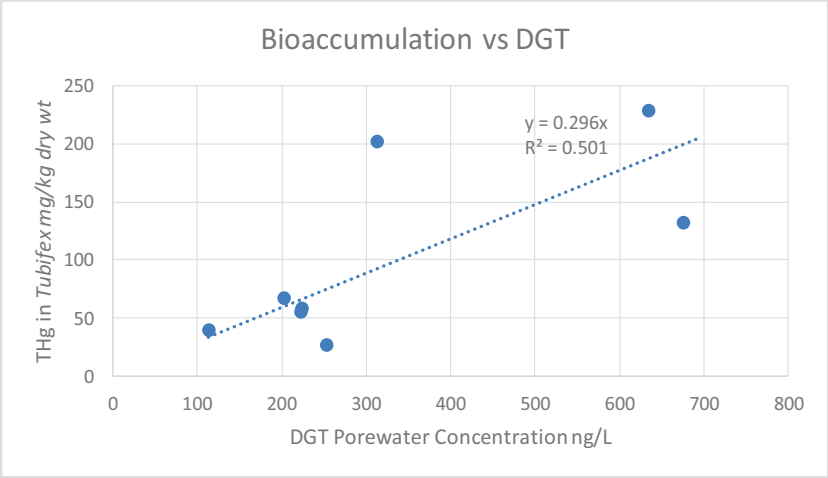
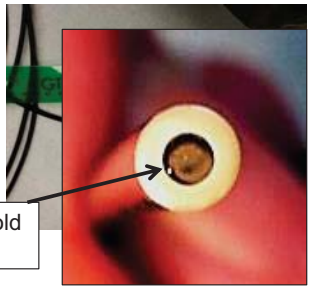
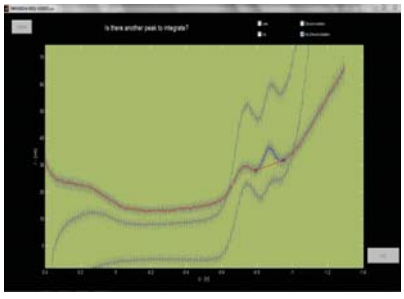


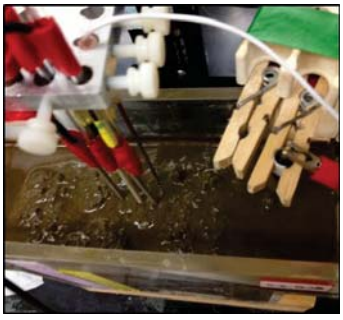
Correlation

Cyclic voltammetry

- Passive sampling technique for measurement of dissolved redox sensitive species in porewater
  - Mn^{2+}, Fe^{2+}, HS^-, Fe^{3+}, dissolved oxygen
  - 0.5 cm depth resolution
- Detection limits range from 0.1-10 µM
- Able to quantify redox zones in-situ

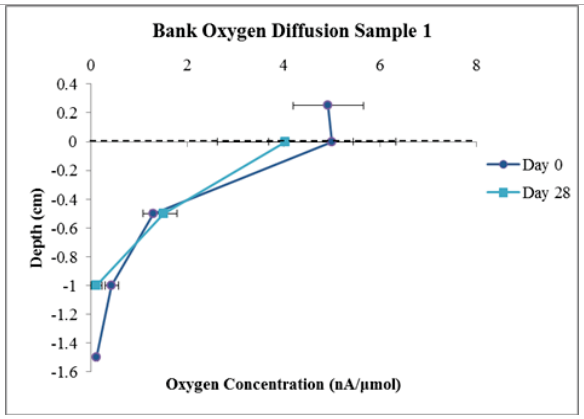


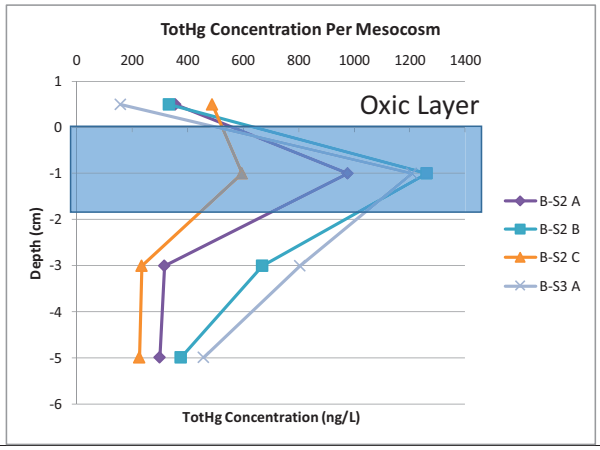




Effect on THg in porewater

- Porewater Hg highest in oxic layer
- Available Hg in oxic conditions >> available Hg in reduced conditions
  - Reduced conditions Hg associated with sulfides or other reduced phases
  - Oxic conditions encourages DOM release
- Highly localized elevated concentration at sediment-water interface

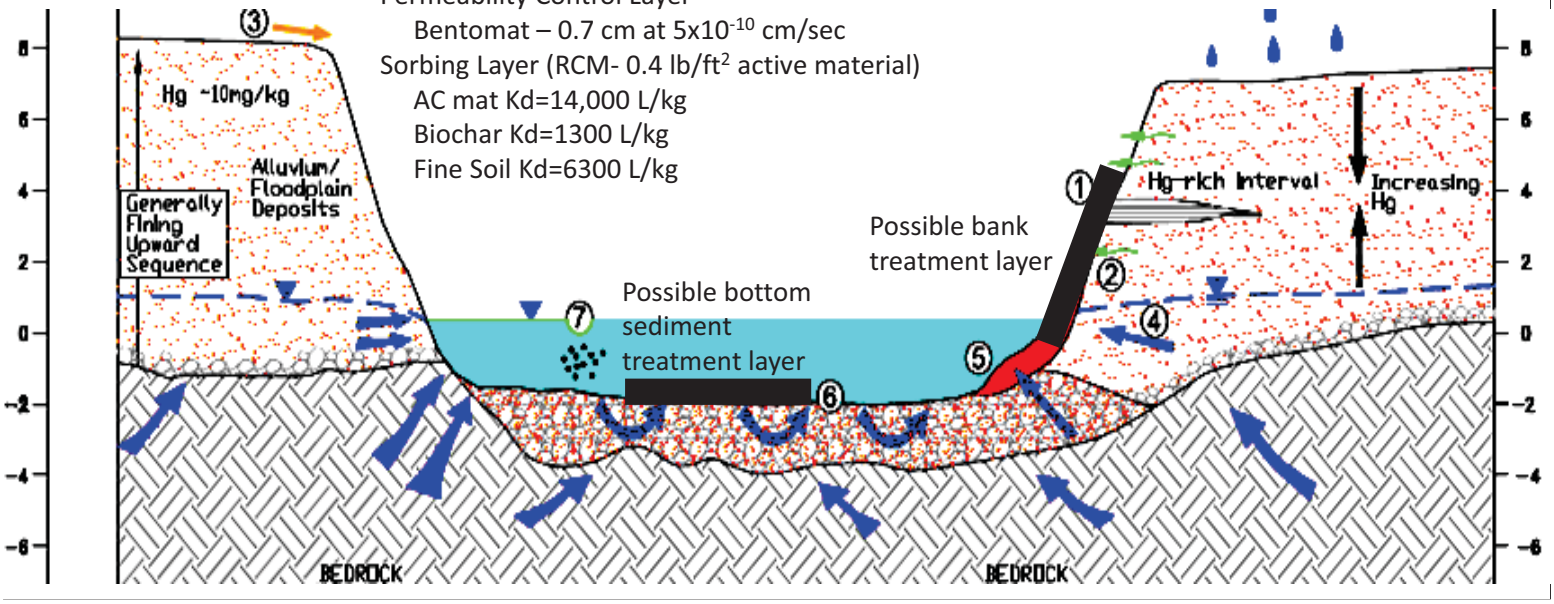




THg in porewater from baseline cap experiments

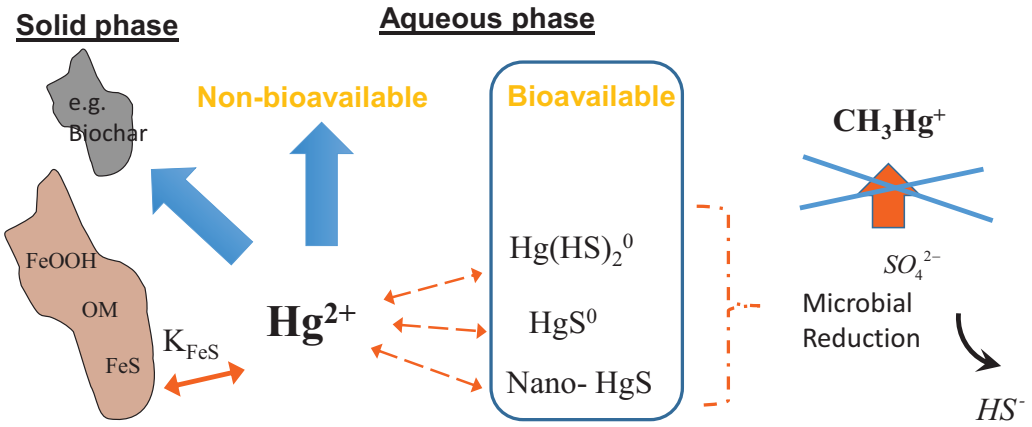
In-Situ Management

"Mat" layers? [redacted]
Permeability Control Layer
Bentomat – 0.7 cm at $5x10^{-10}$ cm/sec
Sorbing Layer (RCM- 0.4 lb/ft^2 active material)
AC mat Kd=14,000 L/kg
Biochar Kd=1300 L/kg
Fine Soil Kd=6300 L/kg



Hg Risk Management

- Goal of remediation is to lower mercury levels in biota
- Sediment amendment does this by lowering the amount of available mercury through sorption
- To reduce methylation, control aqueous (e.g. bioavailable HgS) or solid phase sorption of TotHg (sorbing amendments)



Screening of potential amendment materials – Freshwater sorption of THg

pore volumes sorbent can manage (pure amendment) ~ K_d

		Matrix
Material Type	Sorbent	Freshwater
		K_d [L/kg]
Carbon based material	GAC	14300*
	Biochar-wood	1310*
	Biochar-Rice Husk	190
organophilic clay based materials	PM199 granular	460
Natural materials	Kaolinite	1490
	Sand	6

*Does not include precipitation processes, e.g. cinnabar formation

Screening in laboratory waters, not site porewaters

Implications of estimated partition coefficients

- Surficial bank sediments effective K_d ~ 6,300 L/kg (3.1% TOC)
  - Approximately 20,000 L/kg in deeper sediments
- Biochar and activated carbon are similar in sorptive characteristics as the bank sediments for mercury (based upon preliminary screening data)
  - In situ treatment effectiveness requires $f_{amendment}$ K_d (amendment)>> $f_{sediment}$ Kd(sediment)

$$fractional\ reduction\ in\ porewater = 1 - \frac{1}{1 + \frac{f_{amendment} K_{d,amendment}}{f_{sediment} K_{d,sediment}}}$$

  - In situ treatment largely ineffective in bank sediments (sorbents can't out compete sediment)?
    - 5% activated carbon will reduce porewater Hg by 10%
    - 50% mix with clean bank soil will reduce porewater Hg by 50%
- As cap or containment layer
  - Effective pore volumes of order of K_d (1300 – biochar, 14000- activated carbon)
  - Clean organic-rich sediment could have similar retardation characteristics

Baseline Cap Studies Assessment RRM 3.5

- Mesocosms have been allowed to equilibrate and build a natural redox zonation
  - Characterization underway
- Candidate cap materials will be placed and capping studies evaluated
  - Evaluation of capping in channel and bank sediments
  - Sand, native soil and AC/organophilic clay and biochar
    - Final selection based upon screening studies in site waters
  - Operation in saturated mode but cyclic saturated/unsaturated mode planned
- Deliverable – screening assessment of effectiveness of cap materials for channel and bank deposits Hg control at RRM 3.5

Reactive Capping Assessment- Summary

- Potential Vectors to Manage
  - THg, MeHg from river bottom
  - Leaching of THg rom HRAD areas during drainage cycles
- Baseline studies
  - Mesocosm studies from RRM 11.8
    - Redox profiles and THg availability in aerobic zone
    - Benthic bioaccumulation and relationship to DGTs
  - Mesocosm studies from RRM 3.5 ongoing
    - Baseline THg and MeHg concentrations
- Effects of various sediment caps (RRM 3.5)
  - Cap amendments
    - Screening tests support activated carbon, biochar, permability control
    - Steady and dynamic testing needed
  - Completion of initial mesocosm studies (static release) Dec 2014