



Field Testing of Diffusive Gradient in Thin Film Probes for the Measurement of Hg/MeHg

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DGT Research for Hg in South River

- DGT Development 2009-2010
- Field deployment June 2010





Goal

- **Primary Goal**
 - Insitu measurement of porewater concentrations
 - Indicator of available mercury
- **Secondary Goal (largely future work)**
 - Couple available Hg with other indicators
 - Methyl mercury
 - Extraction efficiency
 - Redox state
 - Incorporate into conceptual site model to support remedy development



Porewater Sampling Techniques

- Active sampling techniques
 - Centrifugation and Filtration
 - Displacement
 - Direct water sampling (Henry's sampler)
- Passive sampling techniques
 - Diffusive gradient in thin films (**DGT**)
 - Advantages
 - Minimal disturbance
 - Suspension of particles
 - Redox conditions
 - Flexible
 - Vertical profiling possible

DGT Piston and Probe Samplers

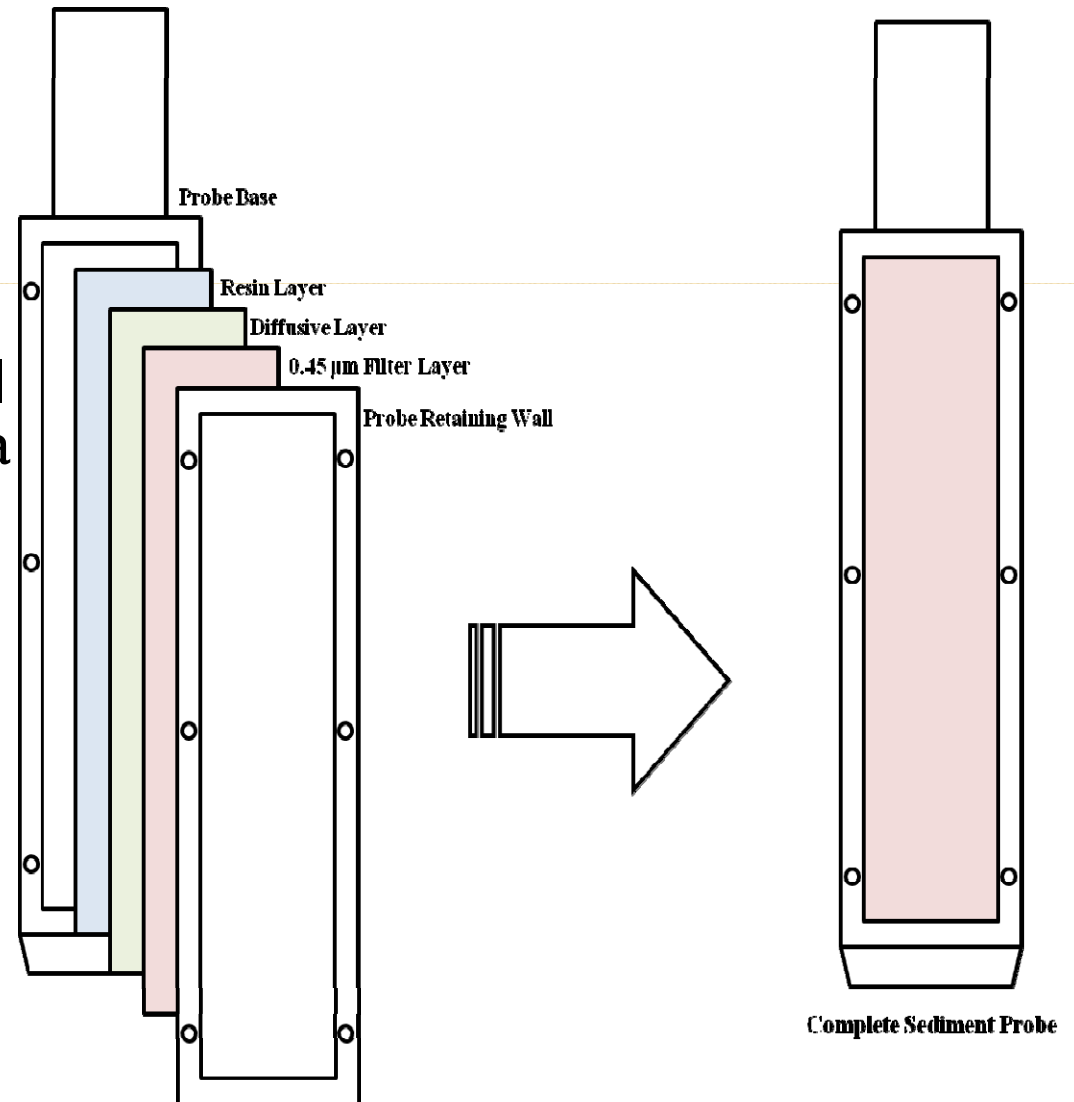


DGT Piston and Probe Samplers



Diffusion Gel Thin Film Device

- Resin – Chelex 100
 - Hg, MeHg – thiol (3-mercaptopropyl functionalized silica gel resin) 3MFSG
 - Acrylamide gel base
- Diffusion layer
 - Agarose gel

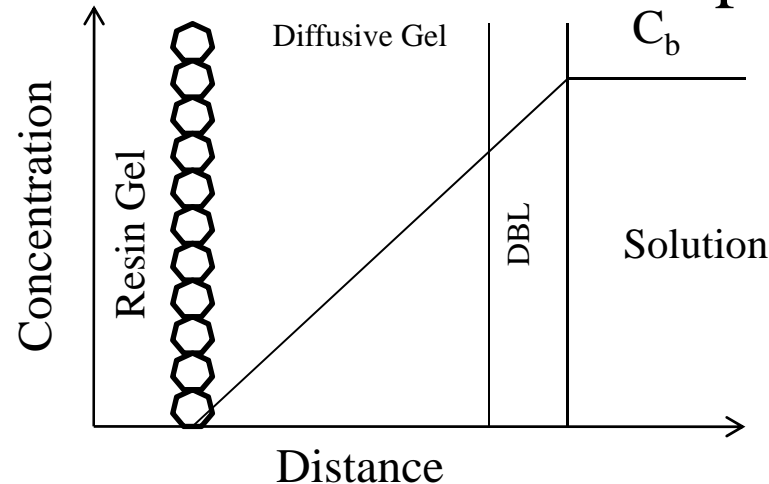


Background and Theory

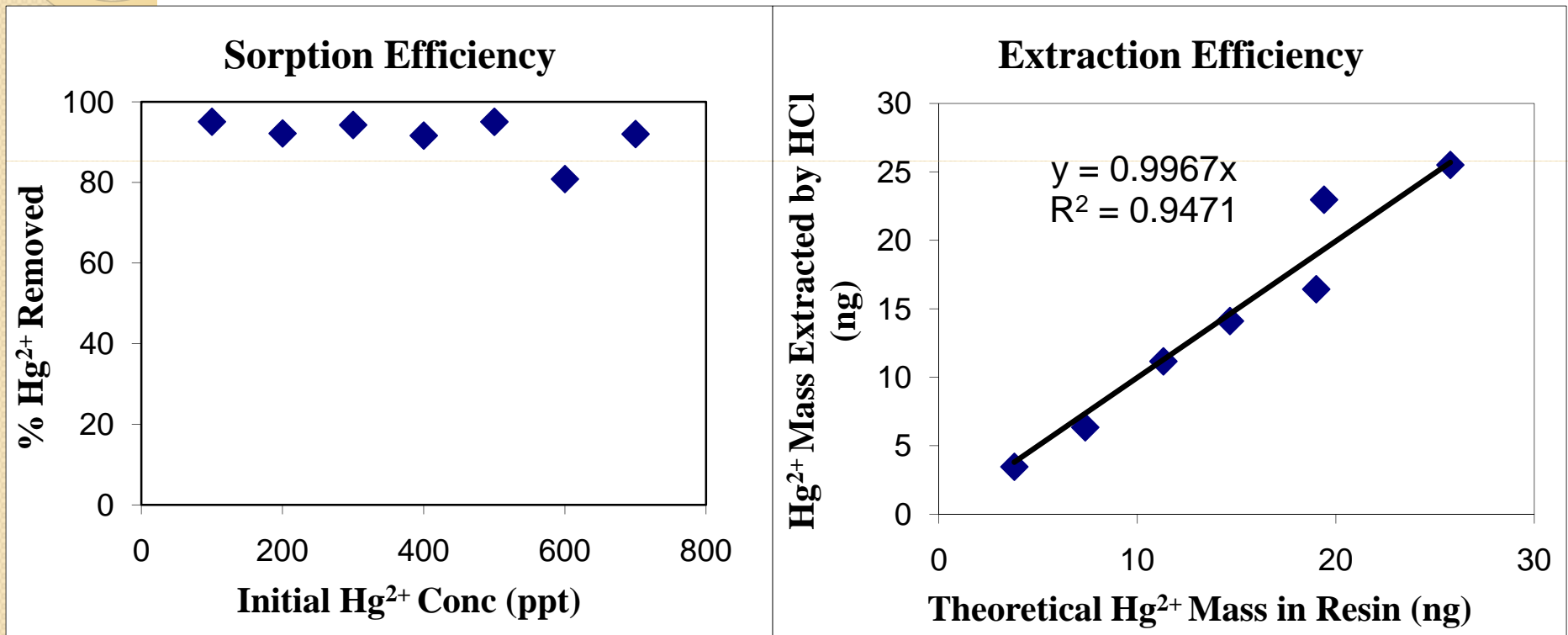
- Davison & Zhang – Lancaster, UK
- Based on Fick's 1st Law of Diffusion
 - Measures flux, not an equilibrium device

$$J = -D \frac{\partial \phi}{\partial x} \quad \longrightarrow \quad J = \frac{DC_b}{\Delta g} \quad \longrightarrow \quad C_b = \frac{M\Delta g}{DtA}$$

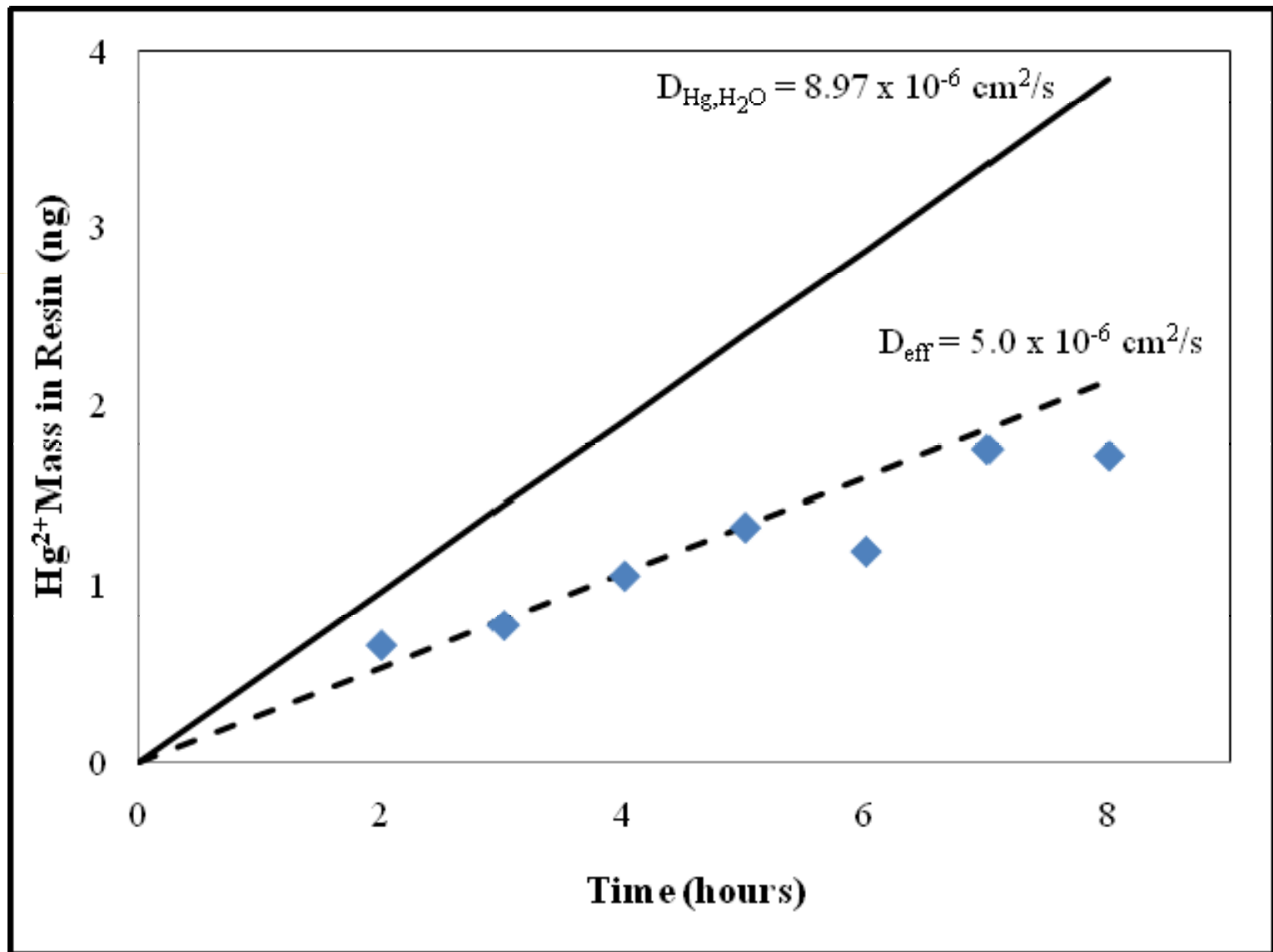
- Diffusion of metal = to that in pure water



Laboratory Experiments (3-M)



Transient Hg Uptake from Water



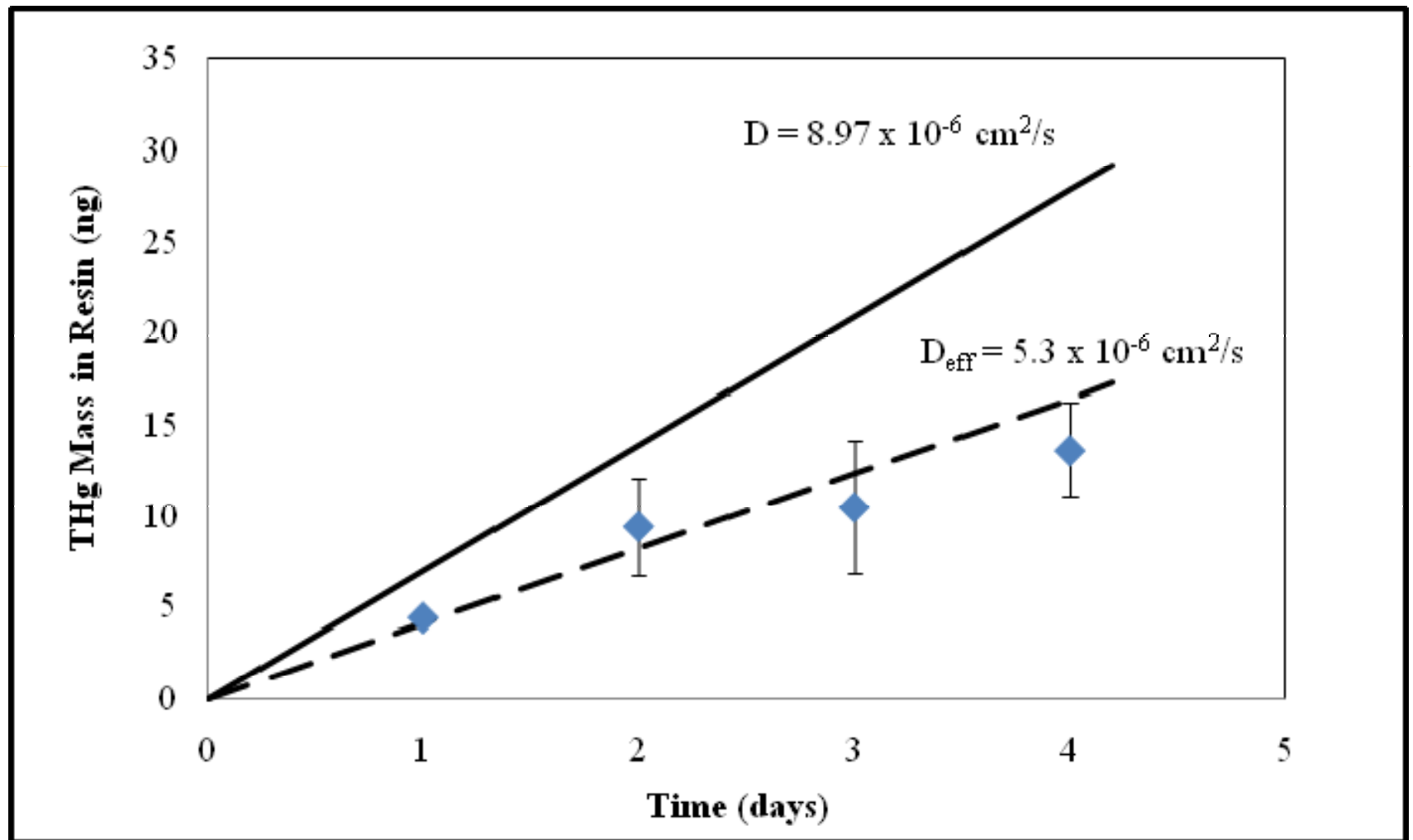


Selected Characteristics South River Fine Bank Deposit Sample

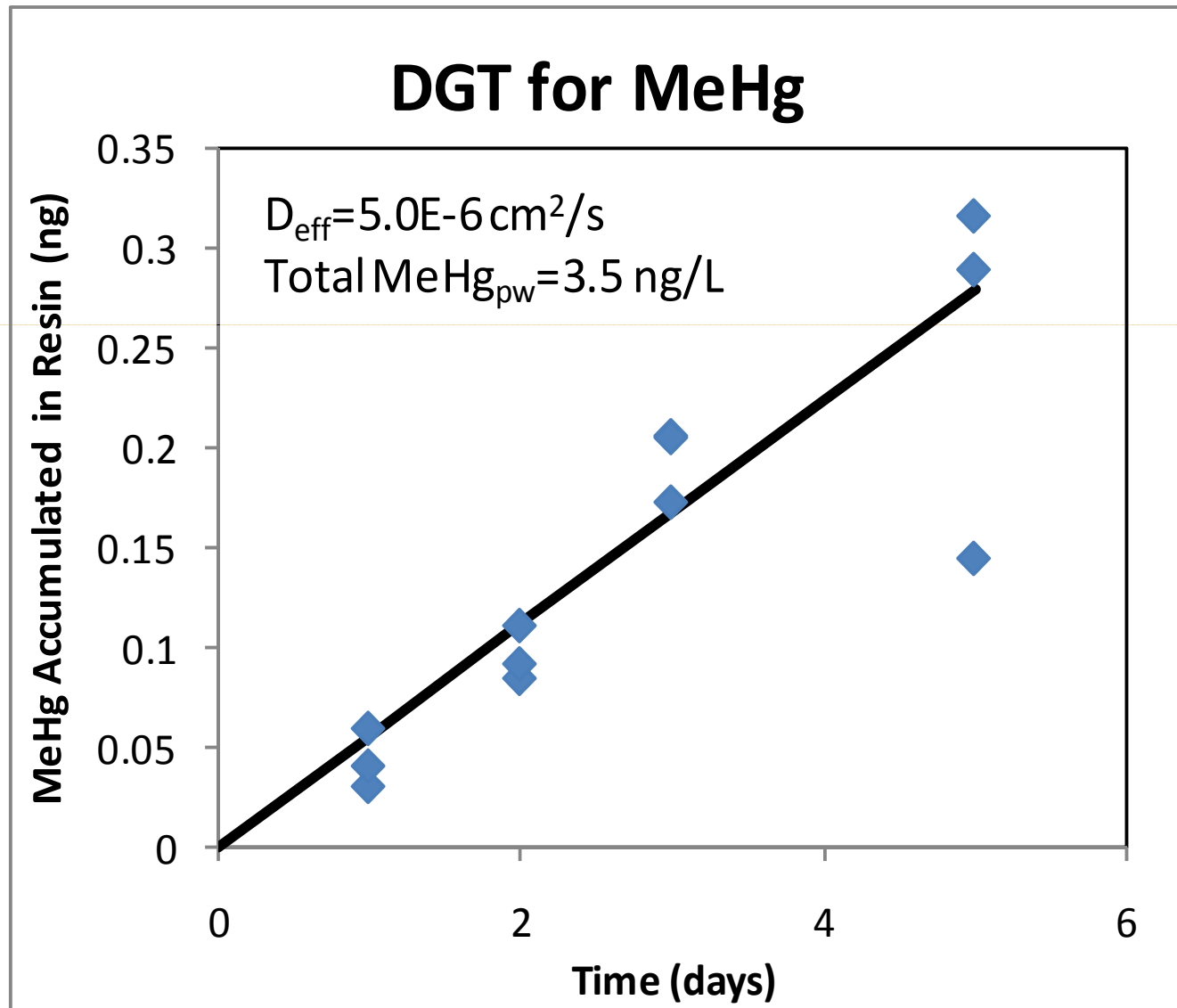
- Sediment
 - Hg 9.7 ± 1 mg/kg
 - AVS – 8.85 μ mole/g
 - OM – 9.2 ± 0.7
- Porewater
 - pH – 6.97
 - Hg – 243 ± 96 ng/L
 - Centrifugation
 - Filtered
 - DOC – 16.1 mg/L

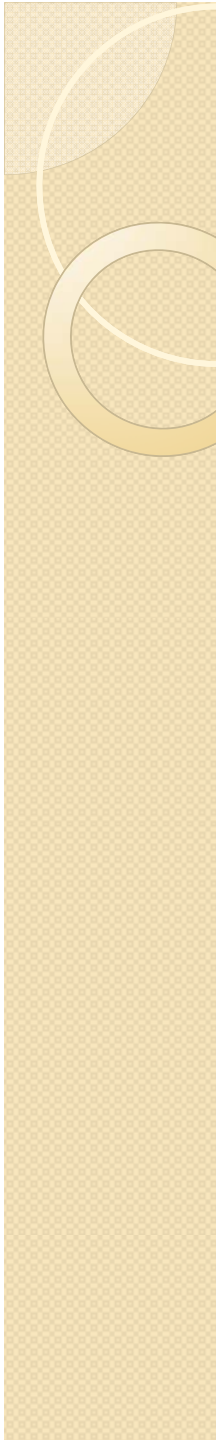
Transient Hg Uptake from sediment

- Water = sediment \Leftrightarrow DGT controlled



Methyl Mercury





Site 3 (RRM 11.6):
5' offshore: Sediment 3, 4
Piston 12
10' offshore: Sediment 5, 6
Piston 11
15' offshore: Sediment 7
Piston 9, 10

Gravel
with
organic
fine
deposits

Site 2 (RRM 3.5):
3' offshore: Sediment 1
Piston 4, 7
6' offshore: Piston 6
9' offshore: Sediment 2
Piston 5, 8

Gravel
with fine
deposits

Site 1(RRM 0.1):
2' offshore: Piston 2, 3
8' offshore: Piston 1

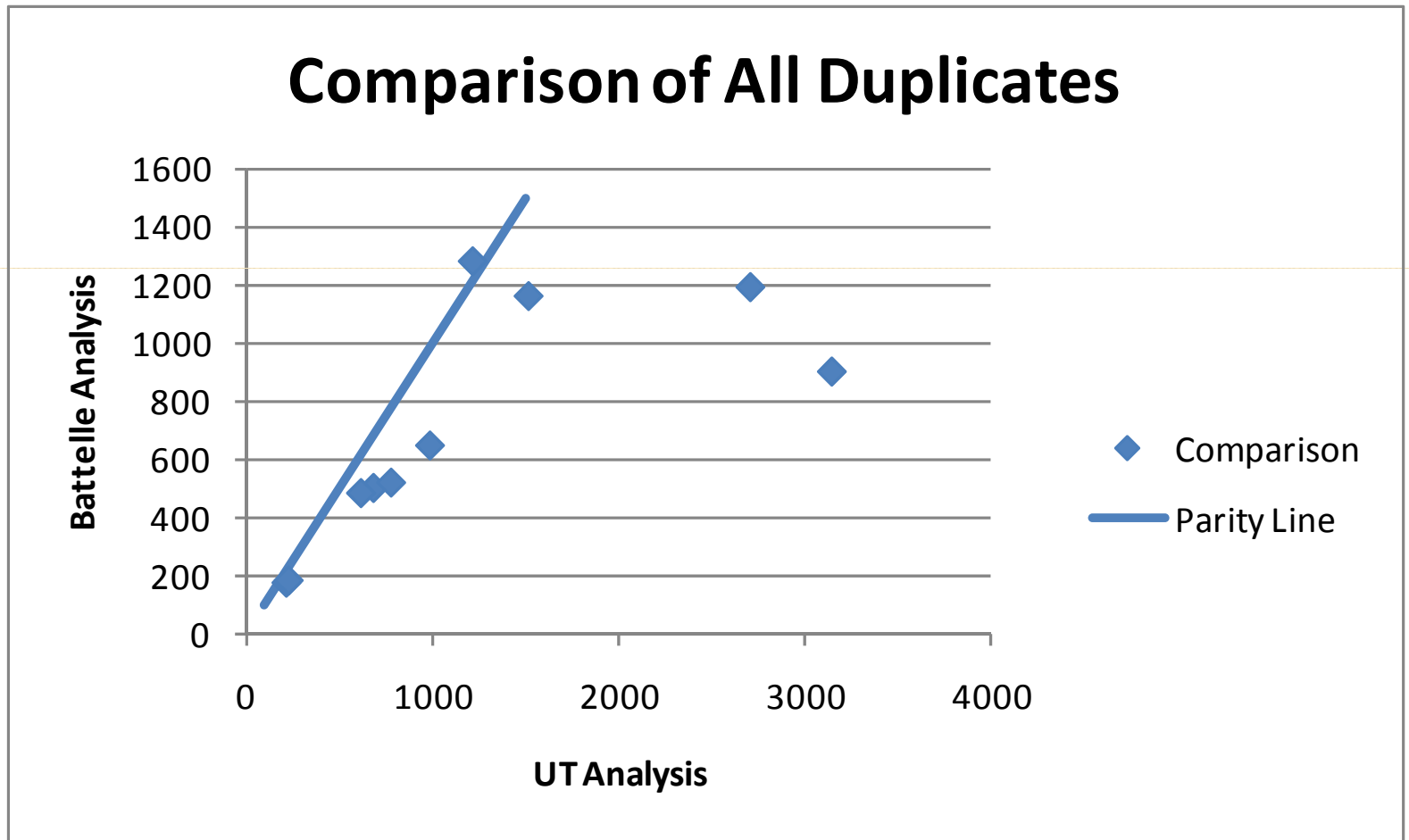
Sandy
depositional
area

Former DuPont
Manufacturing Facility

Chemical Analysis

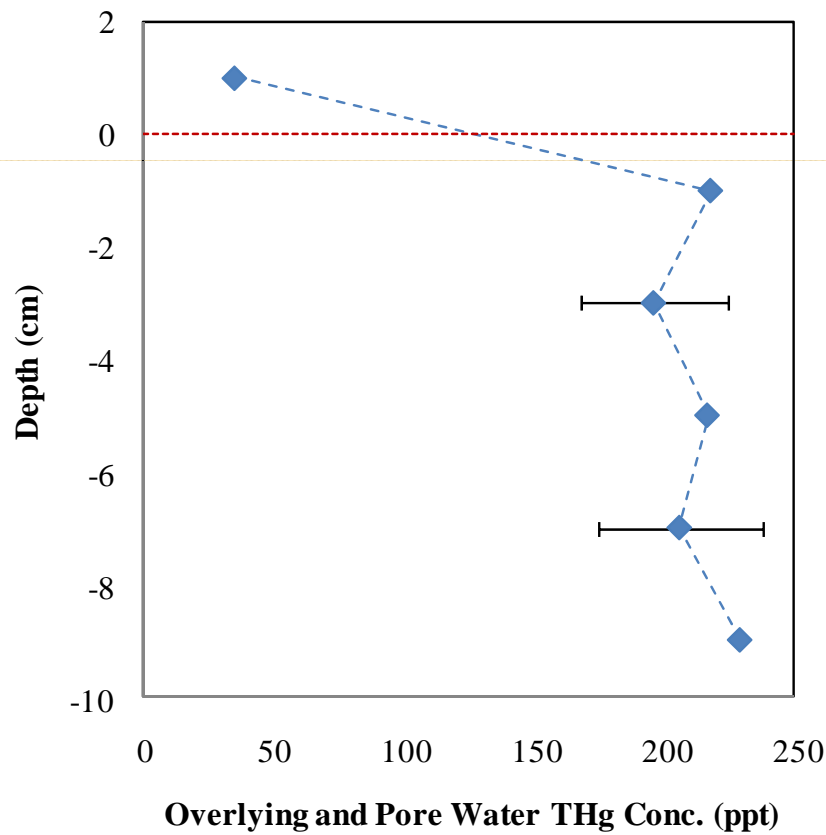
- Bulk of Hg samples analyzed at UT
 - 2 cm sections of resin
 - EPA Method 1631
 - Filtration with polyethersulfone membranes, digestion for 1 day in 2% BrCl, stannous chloride reduction
 - Cold vapor atomic fluorescence spectrophotometry (CVAFS) TekranModel 2600
 - Field blank ~ 20 ng/L
- Battelle Pacific Northwest Laboratory
 - 10 duplicates (split sections)
 - 1 Hg/MHg probe at each site

Duplicate comparison

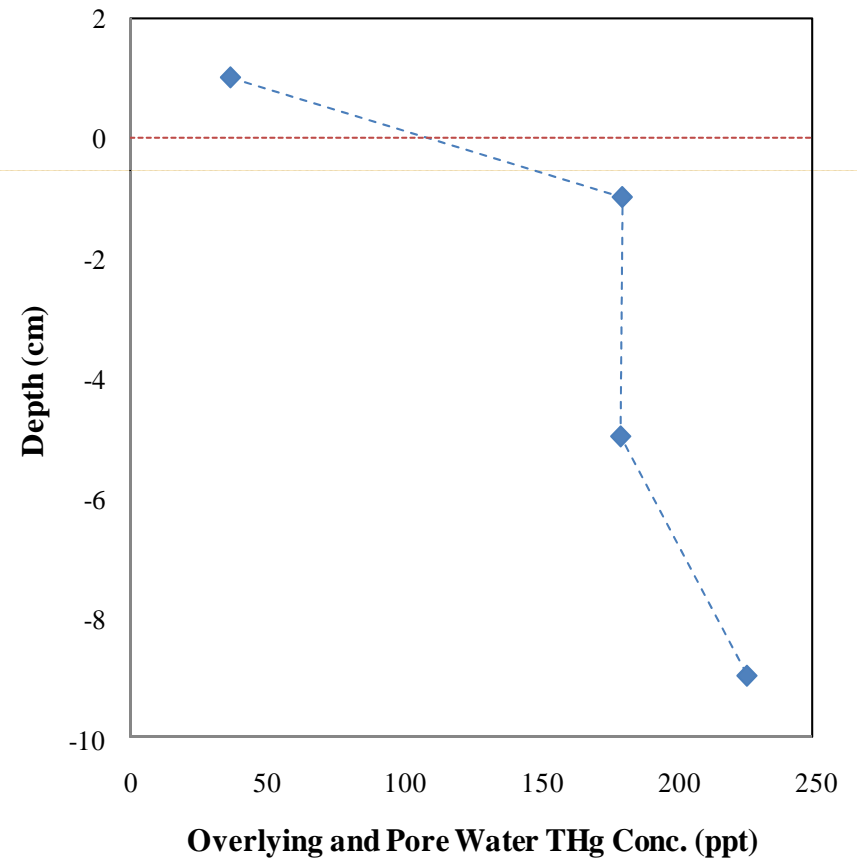


Site I (RRM 0.1) Probe Results

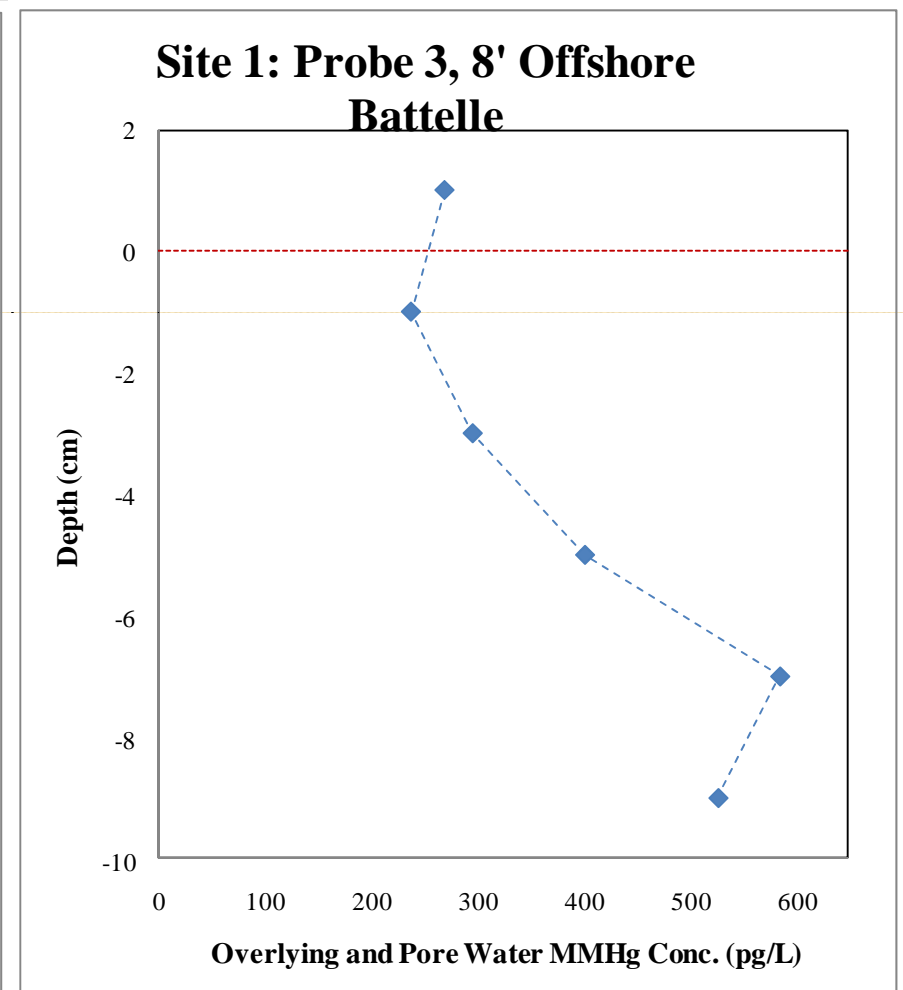
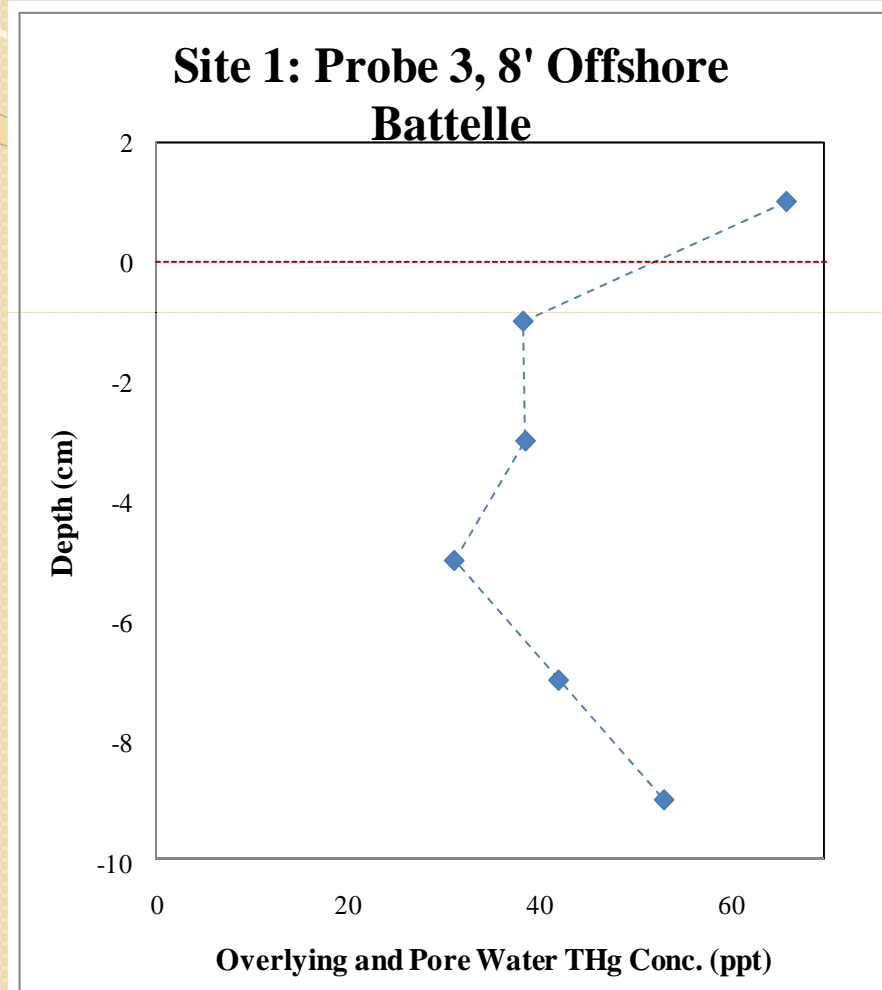
Site 1: Probe 1, 4' Offshore



Site 1: Probe 2, 8' Offshore

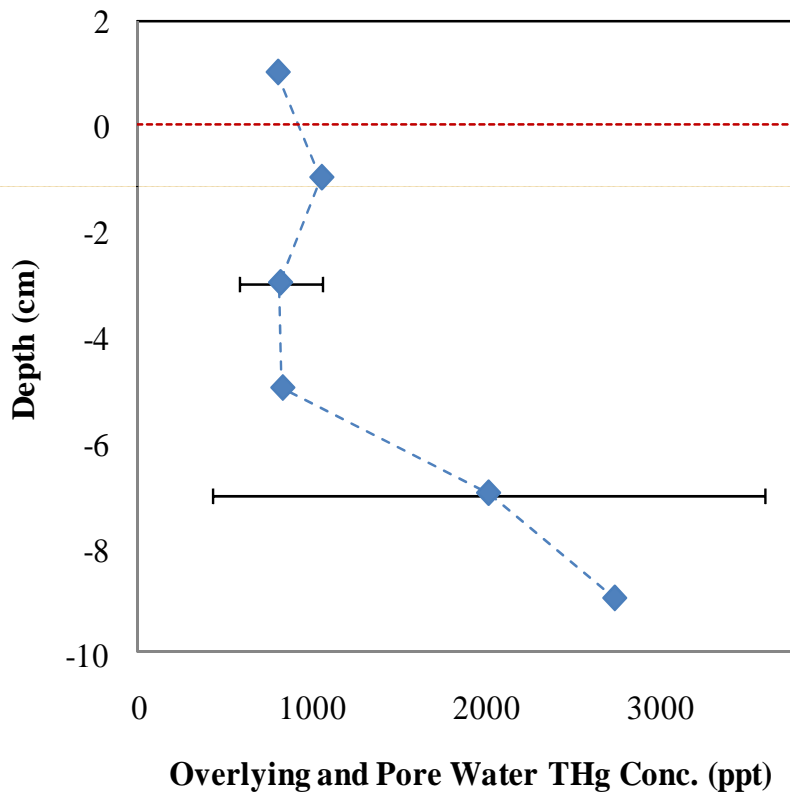


Site 1 (RRM 0.1) Thg/MHg

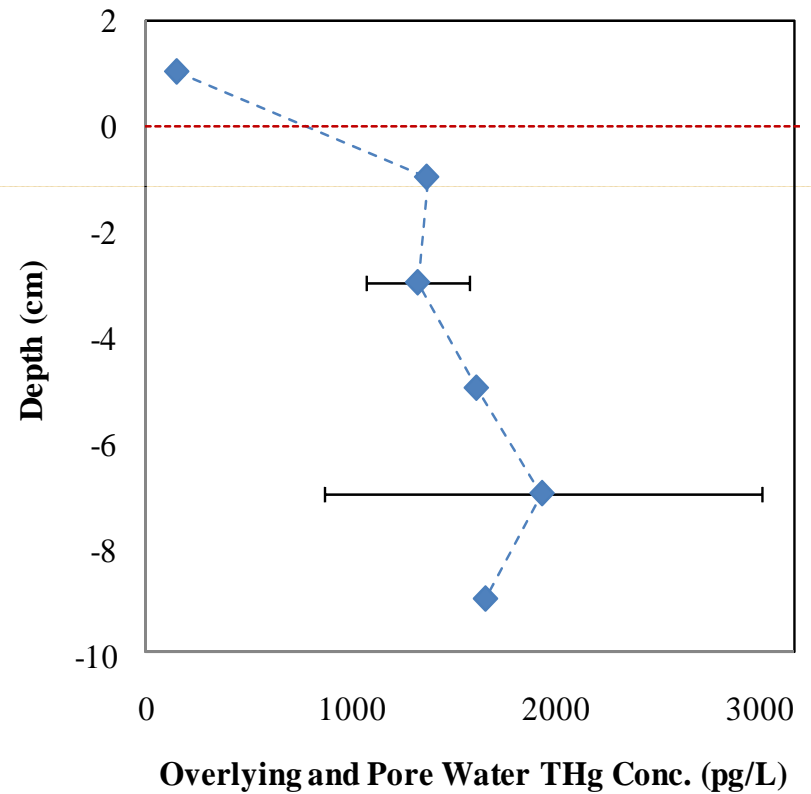


Site 2 (RRM 3.5) Probe Results

Site 2: Probe 5, 3' Offshore

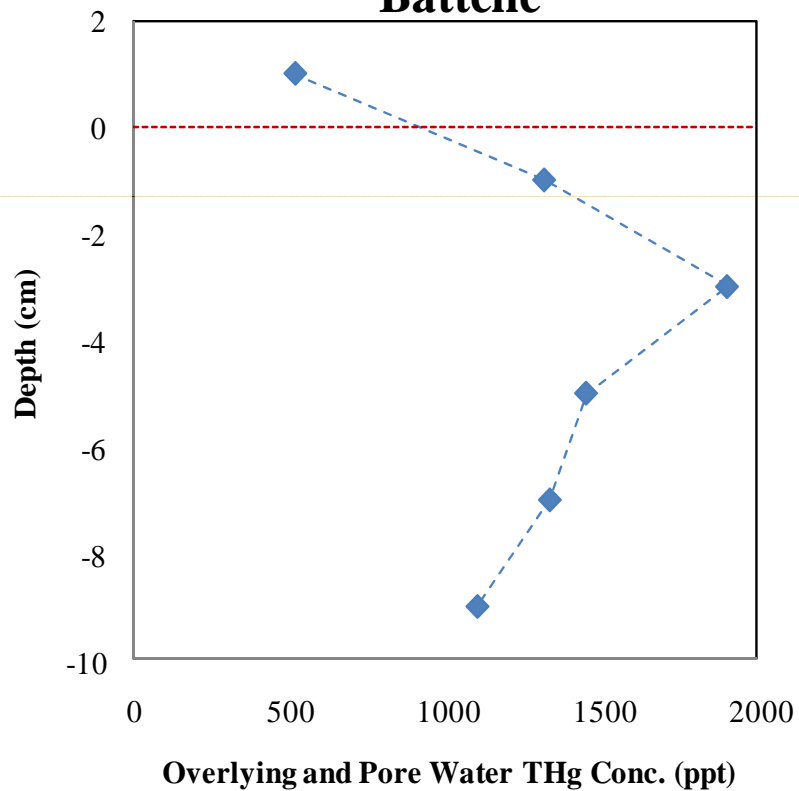


Site 2: Probe 9, 9' Offshore

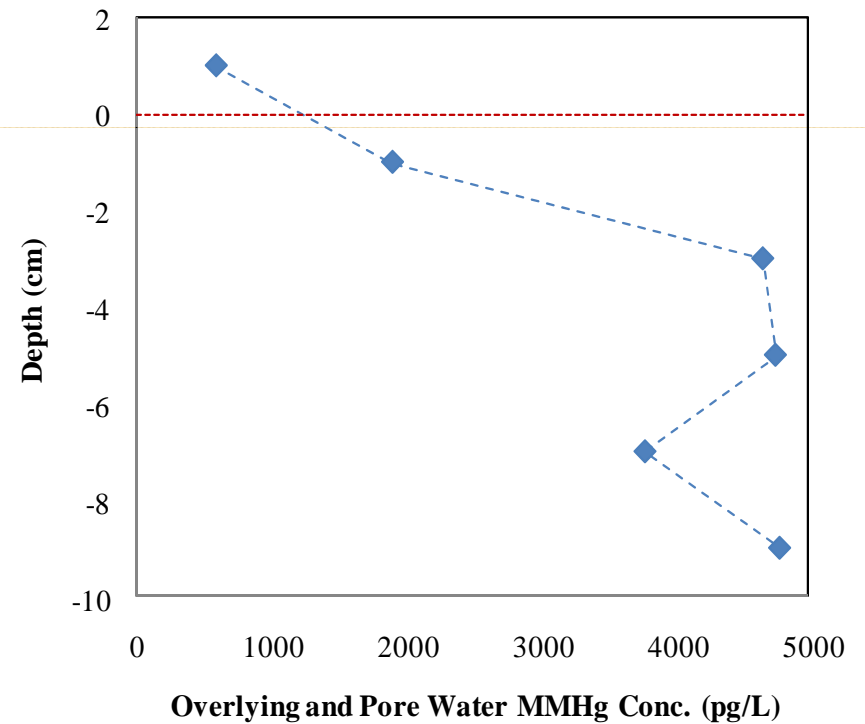


Site 2 (RRM 3.5) THg/MHg

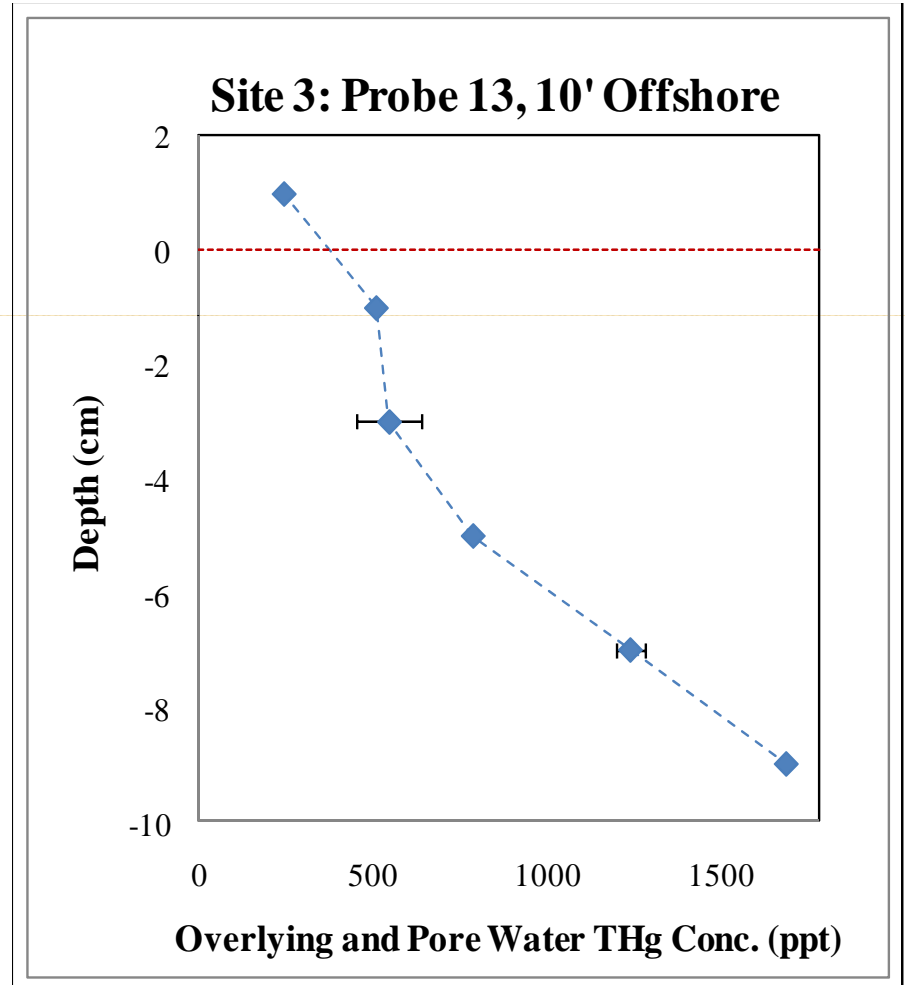
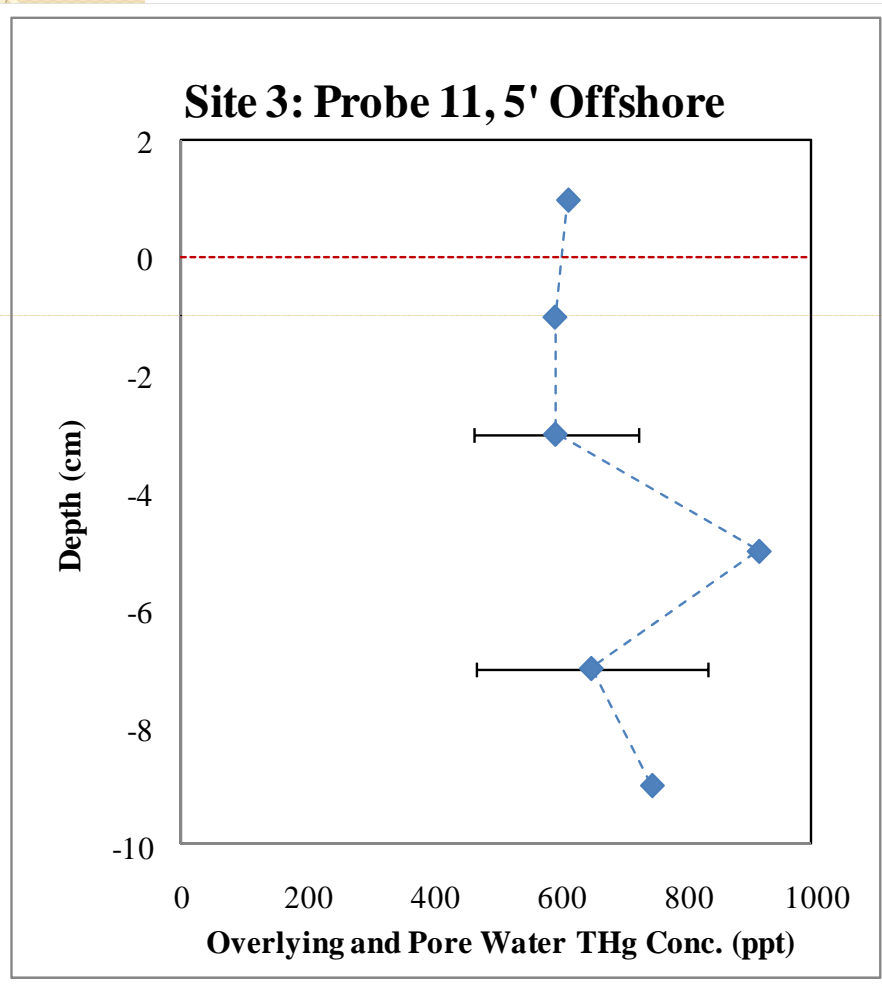
Site 2: Probe 7, 6' Offshore
Battelle



Site 2: Probe 7, 6' Offshore
Battelle

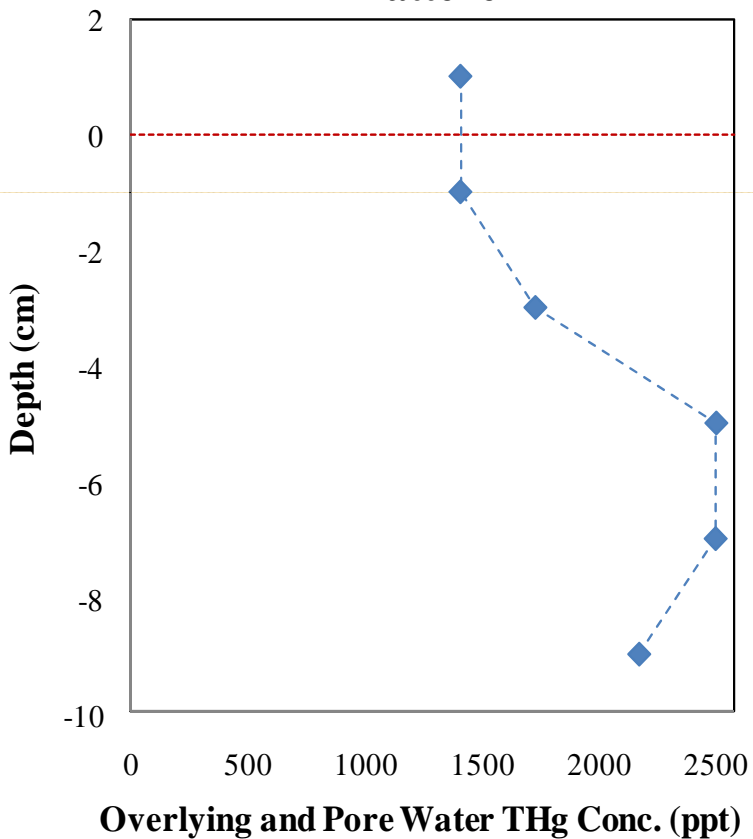


Site 3 (RRM 11.8) Probe Results

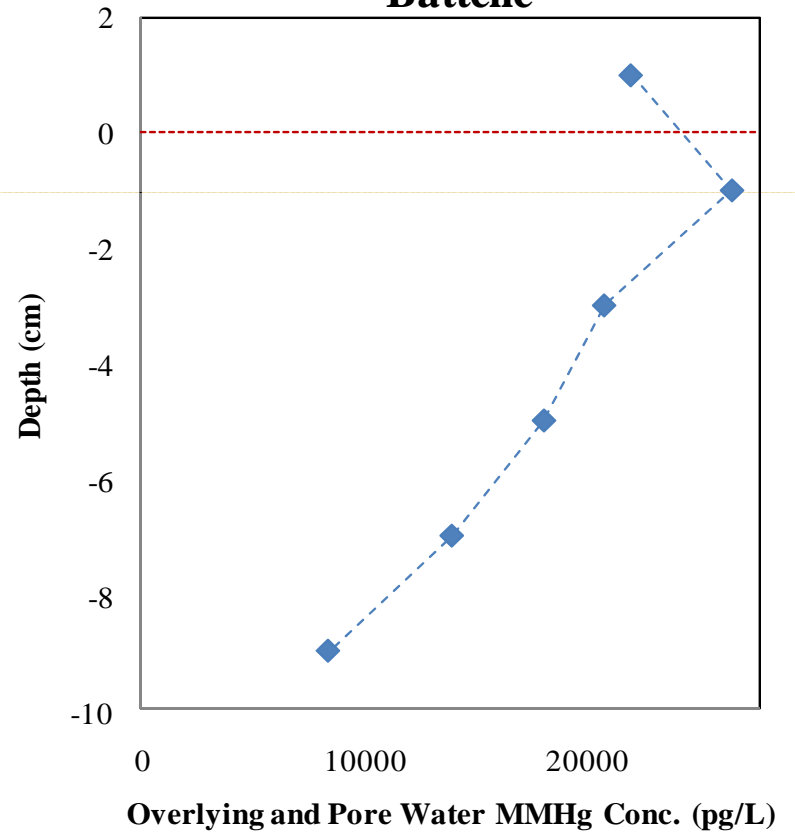


Site 3 (RRM 11.8) THg/MHg

Site 3: Probe 15, 15' Offshore
Battelle



Site 3: Probe 15, 15' Offshore
Battelle



Conclusions – THg/MHg data

- Generally good agreement PNL & UT
- Site 1 – 0.1 RRM
 - 50-250 ng/L THg, 600 pg/L MHg
 - No strong THg trends, MHg highest at 6-8 cm
- Site 2 – 3.5 RRM
 - 2-3 $\mu\text{g/L}$ THg, 5 ng/L MHg & vertically uniform except nearshore
- Site 3 – 11.8 RRM
 - Up to 2.5 $\mu\text{g/L}$ THg, 27 ng/L MHg offshore
 - Increase offshore and MHg highest near surface

Comparison data

- Sequential Extraction (depth averaged)

| THg ng/g | F1 | F2 | F3 | F4 | F5 |
|----------|----|-----|-----|------|-----|
| 0.1 RRM | 1 | 5.9 | 124 | 37.3 | 9.5 |

| | | | | | |
|---------|------|-----|-----|-----|------|
| 3.5 RRM | 79.2 | 3.1 | 749 | 790 | 2497 |
|---------|------|-----|-----|-----|------|

| | | | | | |
|----------|------|---|------|-----|-----|
| 11.8 RRM | 19.8 | 2 | 1265 | 386 | 521 |
|----------|------|---|------|-----|-----|

- THg by DGT follows trend of F1+F2+F3 fractions

Comparison Data

- Conventional Porewater Concentrations

| | Max THg, ng/L | | MHg |
|----------|---------------|----------|------|
| Location | Unfiltered | Filtered | ng/L |
| 0.1 RRM | 2,300 | 1 | 0.5 |
| 3.5 RRM | 310,000 | 301 | 5.7 |
| 11.8 RRM | 72,000 | 2.5 | 0.4 |

- DGT

- Unfiltered > THg > Filtered (But DGT filtered)
 - Conventional samples filtered < 0.1% of unfiltered
- Conventional MHg consistent with DGT except 11.8 RRM?

Comparison Data – Surface Water

| | Unfiltered | Filtered | |
|----------|------------|----------|-------|
| Location | ng/L | ng/L | % |
| 0.1 RRM | | | |
| • THg | 1.7 | 1 | 59 |
| • MHg | 0.3 | 0.2 | 67 |
| 3.5 RRM | | | |
| • THg | 22-719 | 5.9-9.1 | 1-27 |
| • MHg | 5.3-10.9 | 0.9 | 8-17 |
| 11.8 RRM | | | |
| • THg | 18-123 | 11.3 | 9-63 |
| • MHg | 3-15 | 1.3-1.6 | 11-43 |

Conclusions

- DGT
 - Should respond to dissolved & fine colloidal Hg
 - Results much higher than expected for THg
 - Conventional samplers generate more particulates?
 - Filtered THg typically 10-60% of unfiltered THg in surface water vs <0.1% in conventional porewater samples?
 - Conventional samplers introduce overlying water?
 - DGT responding to some particulate bound THg?
 - DGT values not representative or contaminated?
 - Generally consistent with observations of MHg
- Higher DGT THg values more consistent with observed fluxes to river



Future Plans

- QA check ongoing this week
 - Additional samplers placed with more field blanks and water column measurements for reference
- Some additional laboratory and field procedure fine tuning
 - More laboratory and field blanks to insure no contamination of samples
 - Refine placement approach in gravel beds
- Return to field with more samplers evaluating more areas