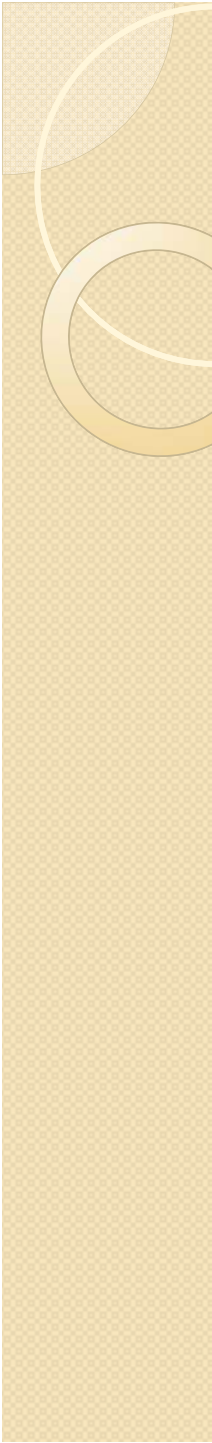




Development of Diffusive Gradient in Thin Film Probes for the Measurement of Hg/MeHg

Danny Reible, Tim Chess, YS Hong, Nate Johnson
University of Texas at Austin



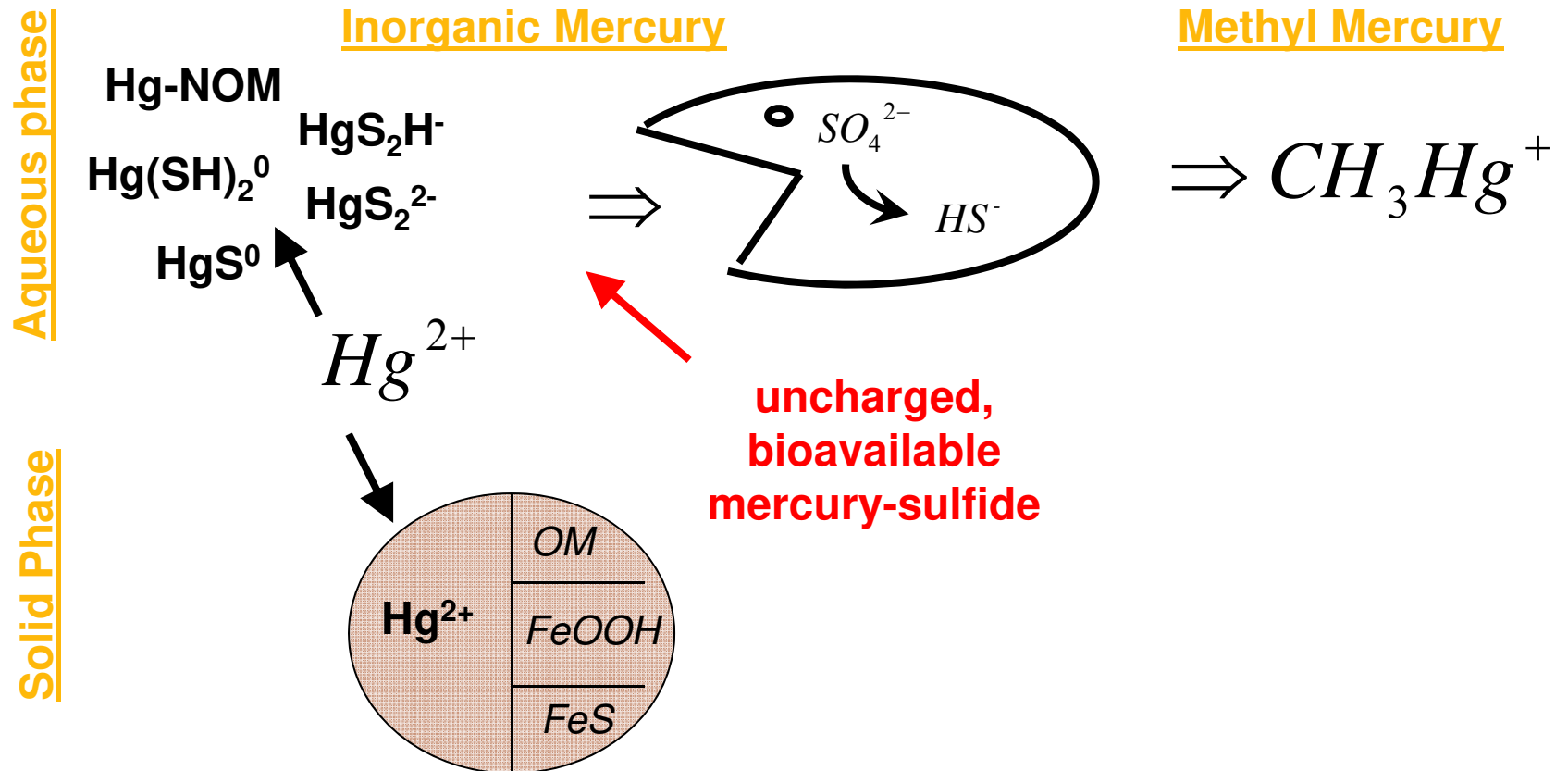
Outline

- Motivation- Mercury processes
- Porewater Sampling Techniques
- Background and Theory
- General DGT fabrication
- Laboratory Experiments
 - Resin performance
 - Measurement of Hg/MeHg
- Future Work

Background

methyl mercury

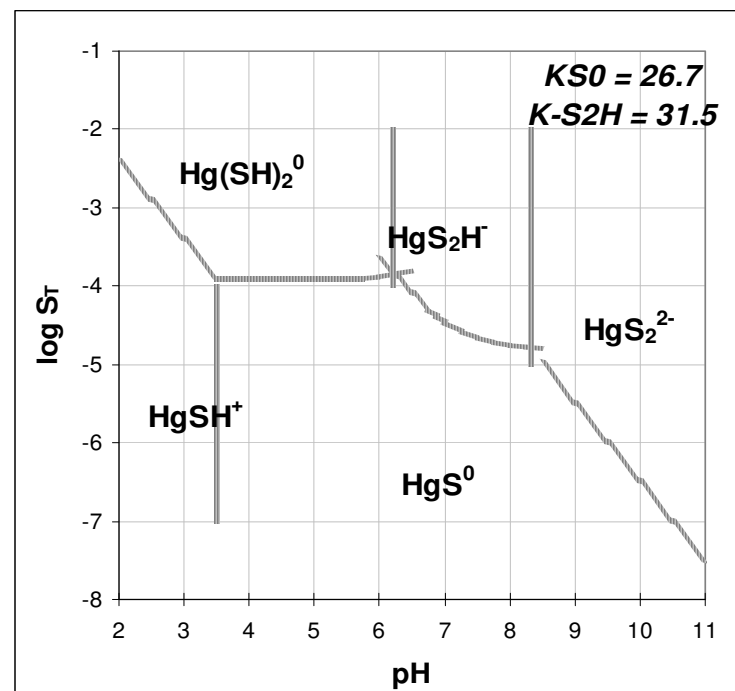
- Mercury vs. methyl mercury (MeHg)
 - Methylation is a byproduct of microbial activity sulfate reducing bacteria



Research Approach

Aqueous speciation modeling

Equilibrium Reaction	LogK
$\text{Hg}^{2+} + 2\text{HS}^- = \text{Hg}(\text{SH})_2^0$	37.7
$\text{Hg}^{2+} + 2\text{HS}^- = \text{HgS}_2\text{H}^- + \text{H}^+$	31.5
$\text{Hg}^{2+} + 2\text{HS}^- = \text{HgS}_2^{2-} + 2\text{H}^+$	23.2
$\text{Hg}^{2+} + \text{HS}^- = \text{HgSH}^+$	30.2
$\text{Hg}^{2+} + \text{HS}^- + \text{H}_2\text{O} = \text{HOHgSH}^0 + \text{H}^+$	26.7
$\text{Hg}^{2+} + \text{RS}^- = \text{HgRS}^-$	22.4-23.8*



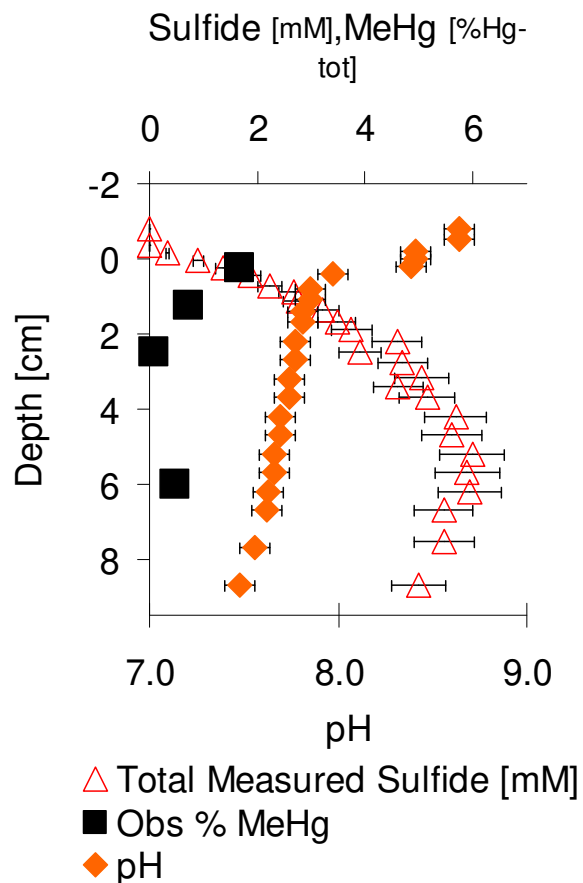
- Equilibrium modeling for aqueous speciation based on sulfide and DOM complexes
- Bioavailable complexes at ~20-100uM HS^- neutral pH

Results

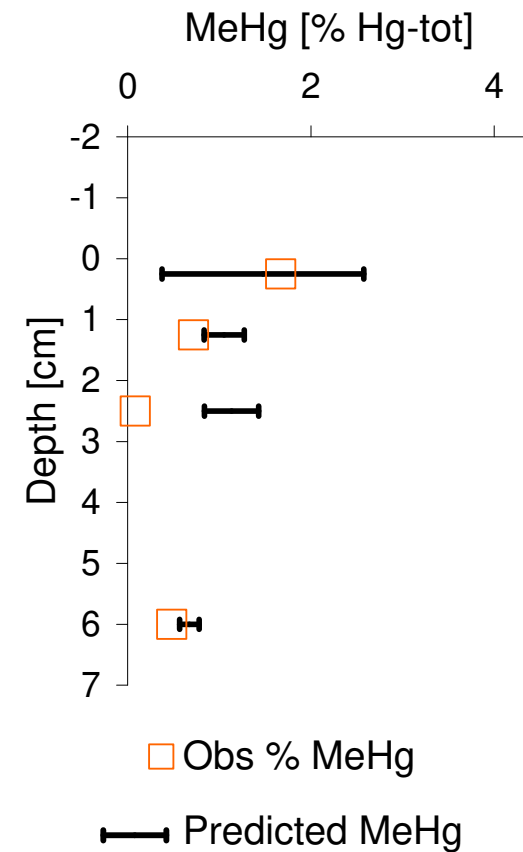
in-situ model application

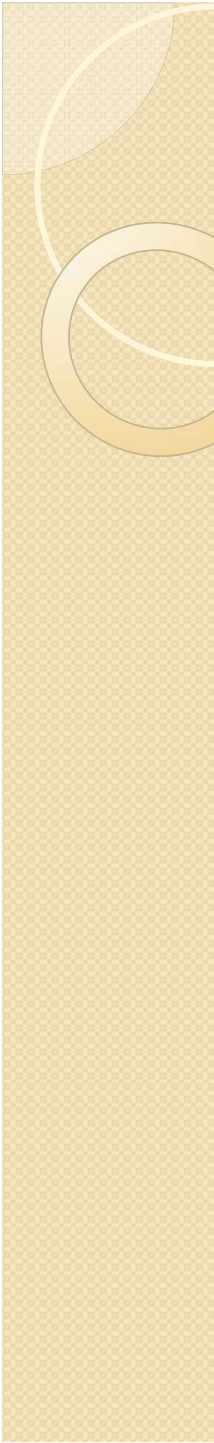
model results & sensitivity analysis

In-situ BGC observations



Methyl mercury model predictions

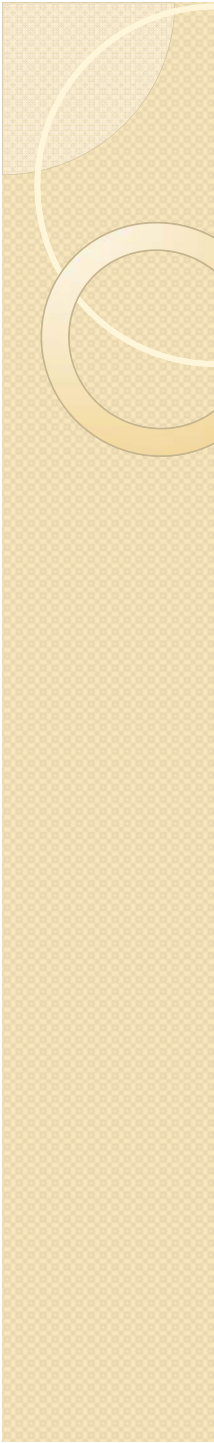




Selected Characteristics South River

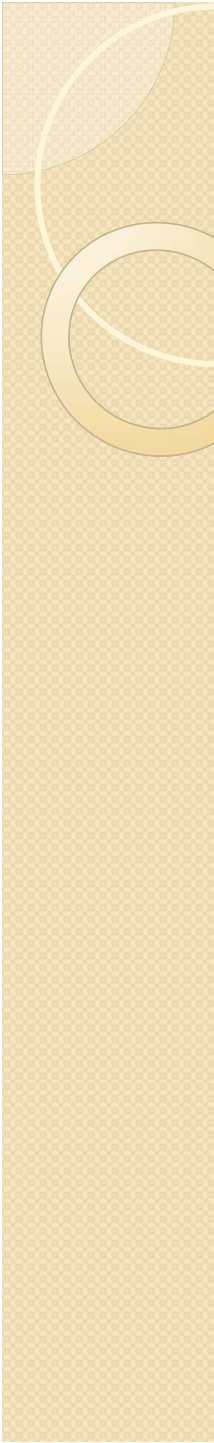
Fine Bank Deposit Sample

- Sediment
 - Hg 9.7 ± 1 mg/kg
 - AVS – 8.85 μ mole/g
 - OM – 9.2 ± 0.7
- Porewater
 - pH – 6.97
 - Hg – 106 ± 7.9 ng/L
 - aqueous equilibrium
 - filtered



Goal

- Primary Goal
 - Insitu measurement of porewater concentrations
 - Mercury 10-100 ng/L
 - Methyl mercury 0.1-10 ng/L
- Secondary Goal
 - Couple with direct or indirect biogeochemical measures
 - Sulfate reduction rate
 - Sulfide concentrations

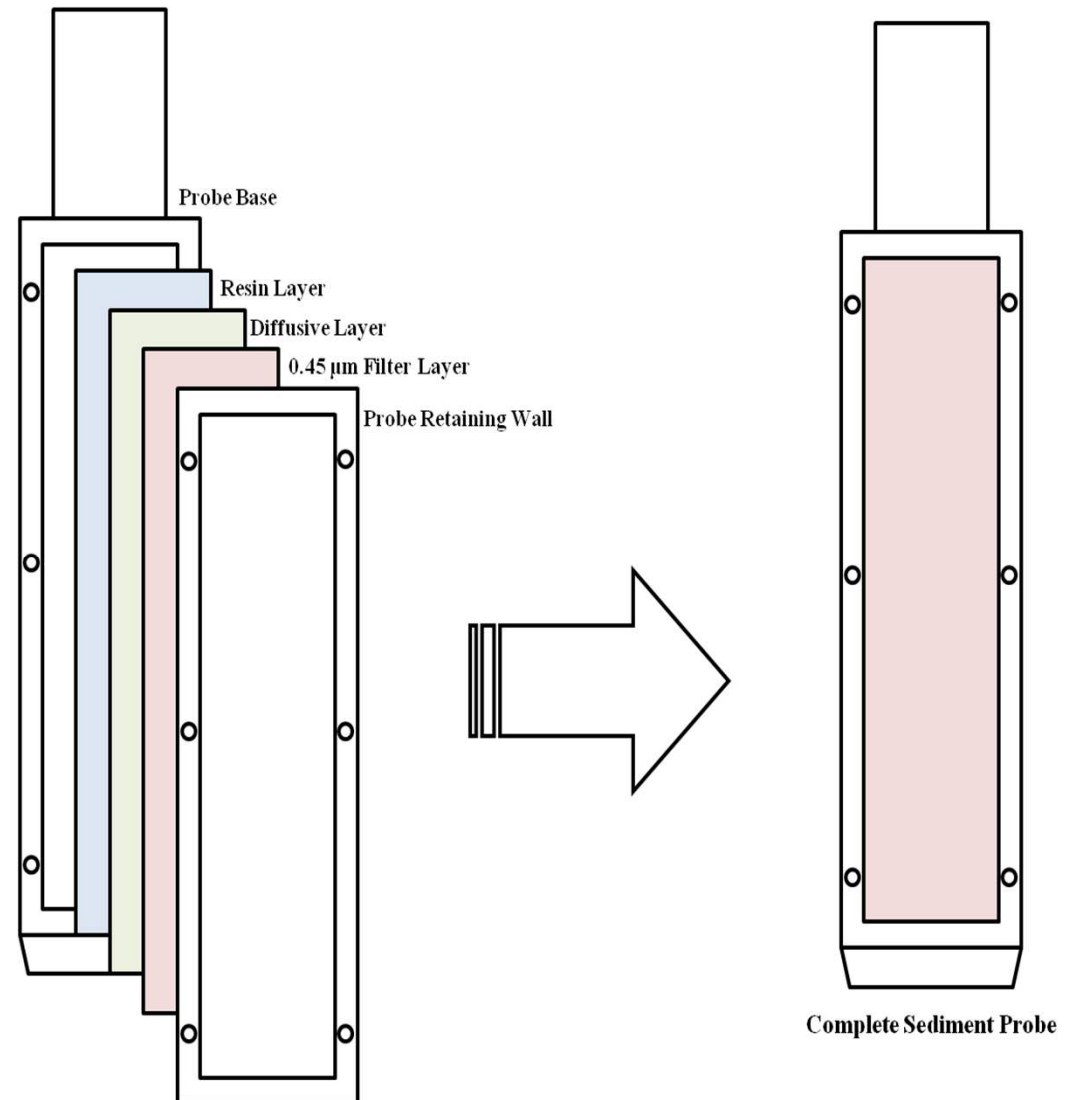


Porewater Sampling Techniques

- 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 Resolution

Diffusion Gel Thin Film Device

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

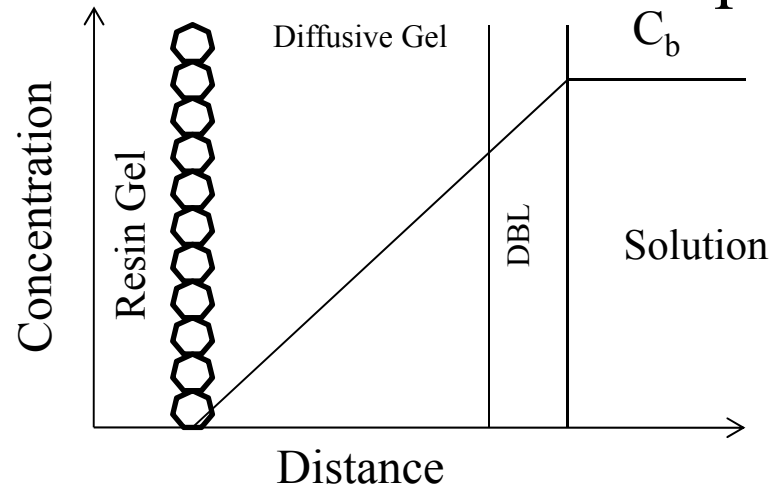


Background and Theory

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

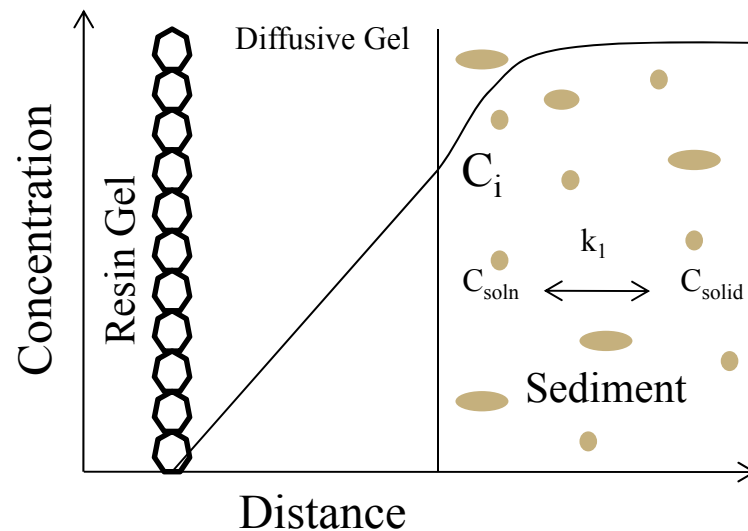
$$J = -D \frac{\partial \phi}{\partial x} \quad \longrightarrow \quad J = \frac{DC_b}{\Delta g} \quad \longrightarrow \quad C_b = \frac{M\Delta g}{DtA}$$

- Diffusion of metal = to that in pure water

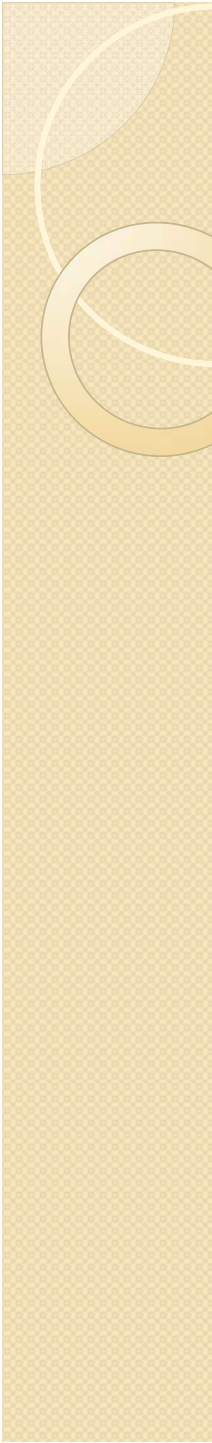


Background and Theory

- DGT theory also applicable to sediments
 - Difference is solid phase influence



- *Pseudo* steady state achieved in $\sim$ day deployments times

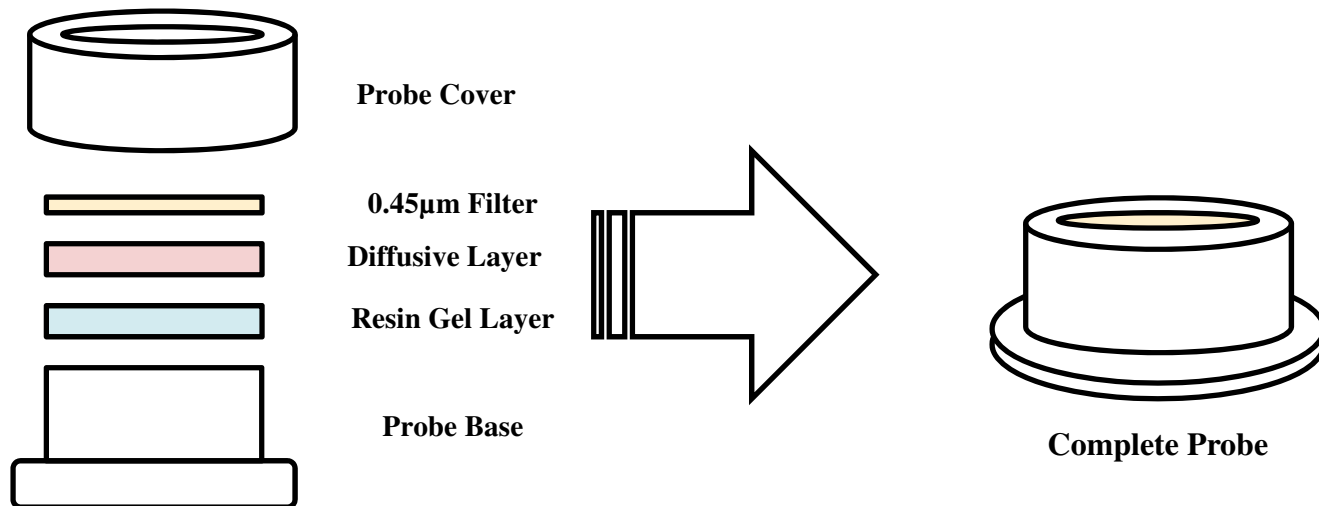
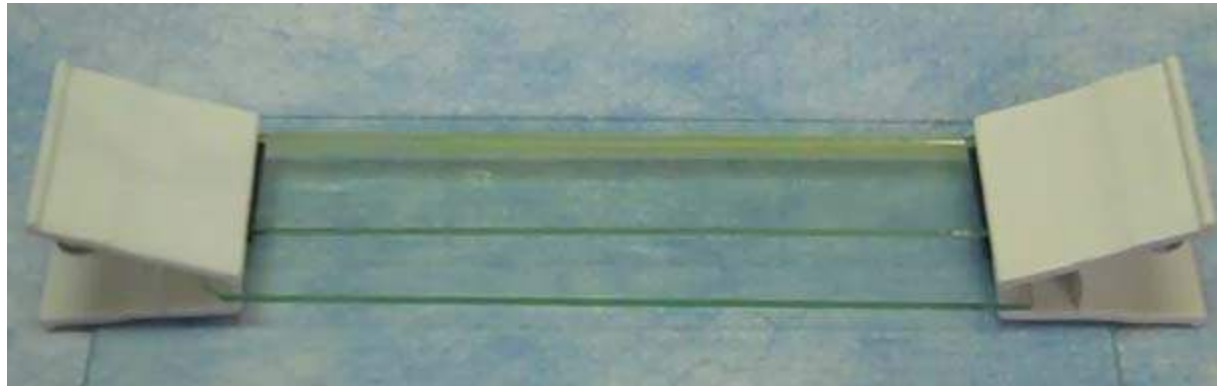


Background and Theory

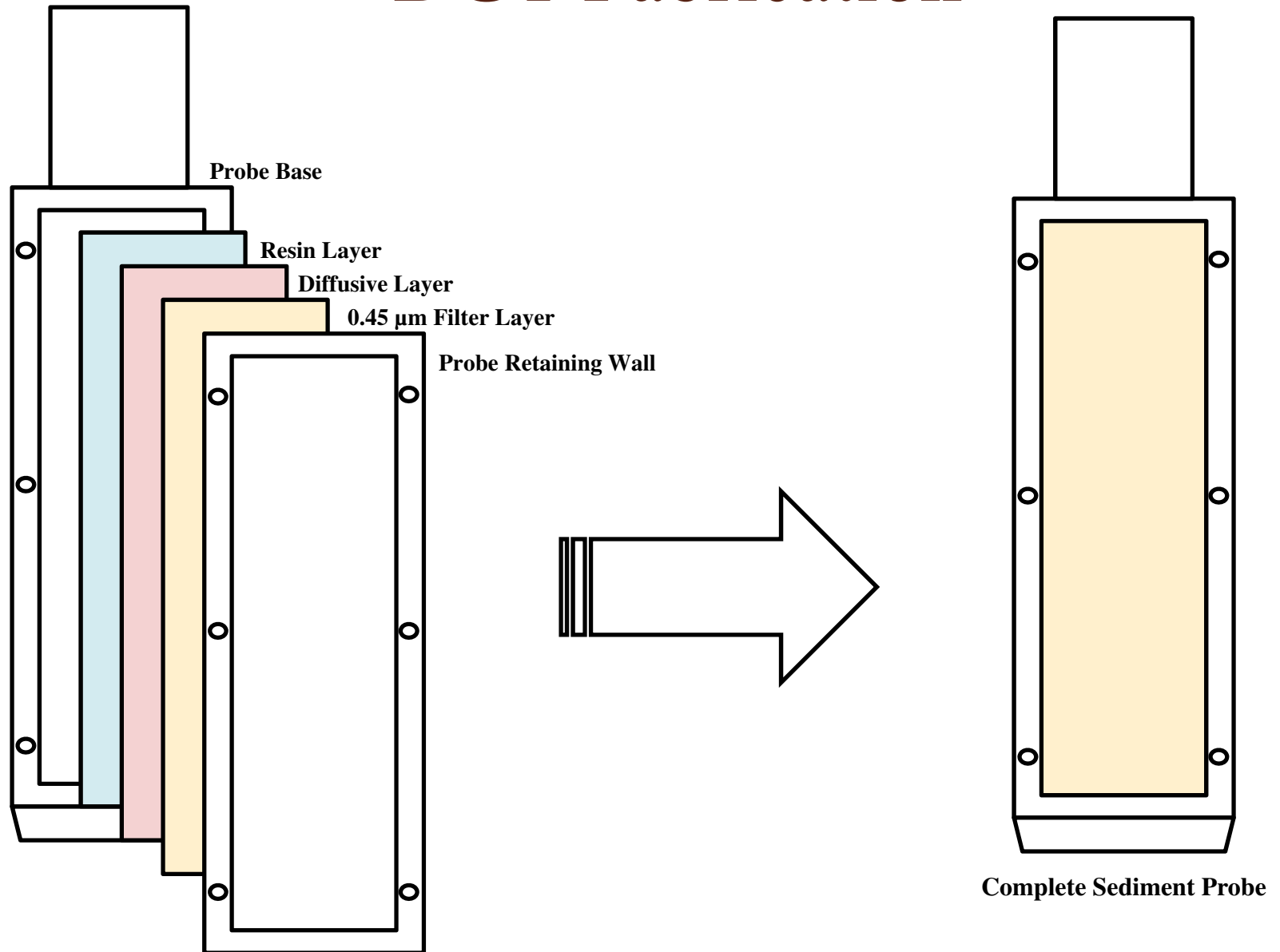
- Current Field Applications
 - Bulk water, Sediment, and Soil
 - Mn, Zn, Cu, Cd, Ni, Fe, Pb, Al, etc. (Chelex-100)
- Developing Applications
 - Hg & Me Hg
 - Requires
 - Different sorbing resin
 - Strong and complete sorption of mercury species
 - Complete extraction of mercury species during analysis

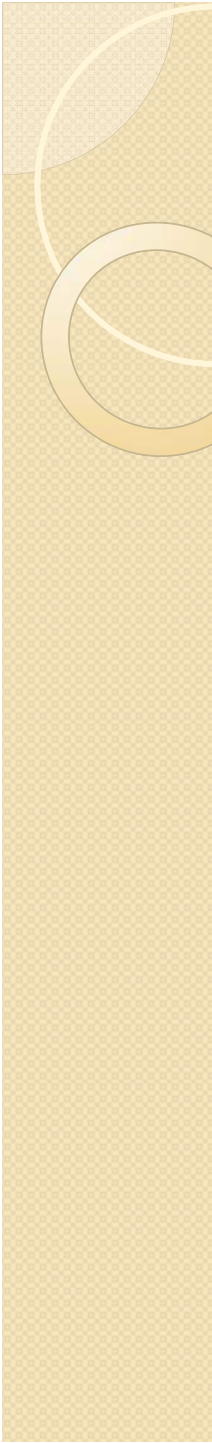
DGT Fabrication

- Both diffusive and resin gel thickness controlled by glass plates/spacers



DGT Fabrication

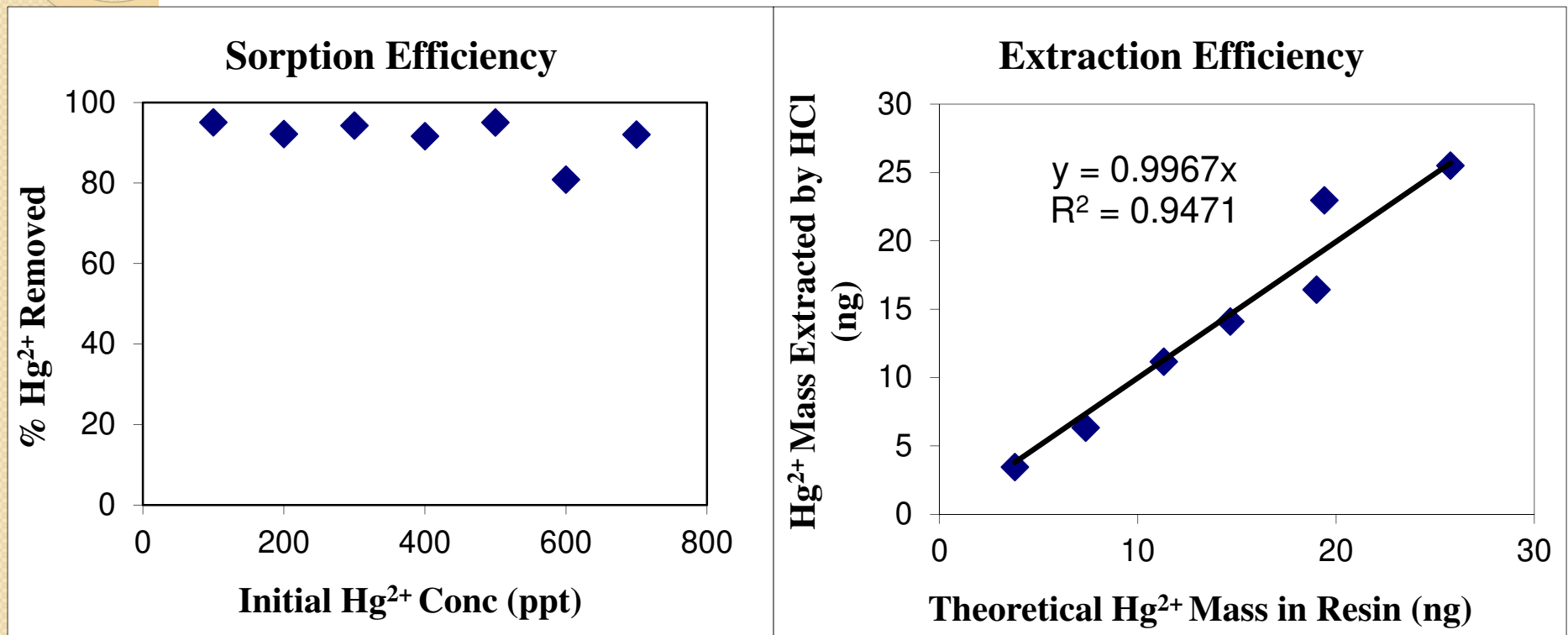


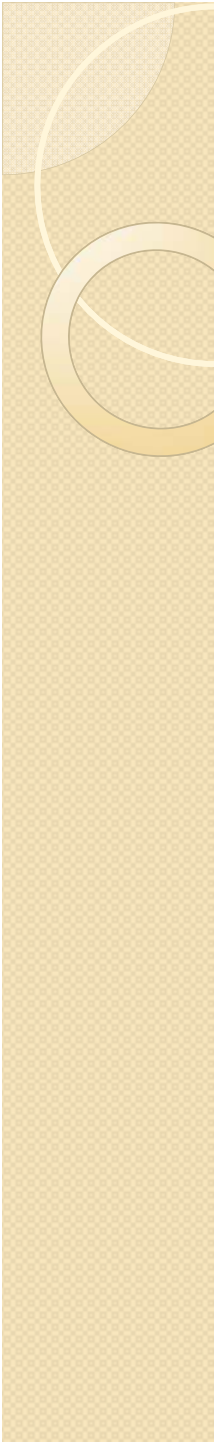


Laboratory Experiments (3-M)

- Sorption and Extraction Efficiency Experiments
 - Evaluated after 24 hr equilibrium while in end-over-end tumbler (CVAFS)
 - 100 ppt to 700 ppt Hg^{2+} concentrations
 - 92% average Hg sorption
 - 96.5% average Hg extraction efficiency w/ HCl
 - Demonstrates potential of resin for *in-situ* Hg detection

Laboratory Experiments (3-M)





Laboratory Experiments (3-M)

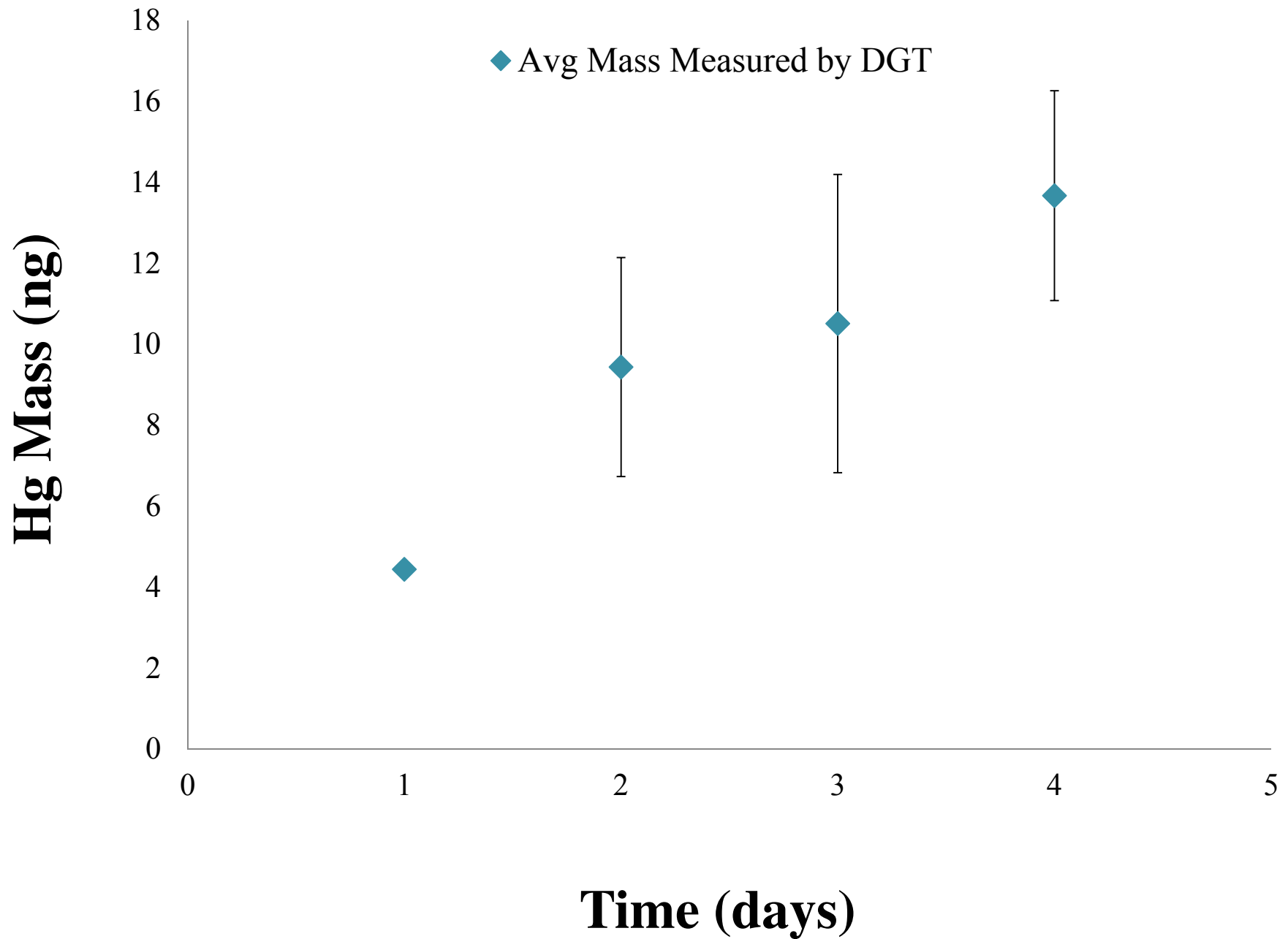
- Time dependent sediment experiment
 - Purpose: optimize specific resin for particular site and validate use in sediments
 - South River, VA site sediment
 - 3 probes per 24 hour interval for 4 days
 - Each probe elution measured twice

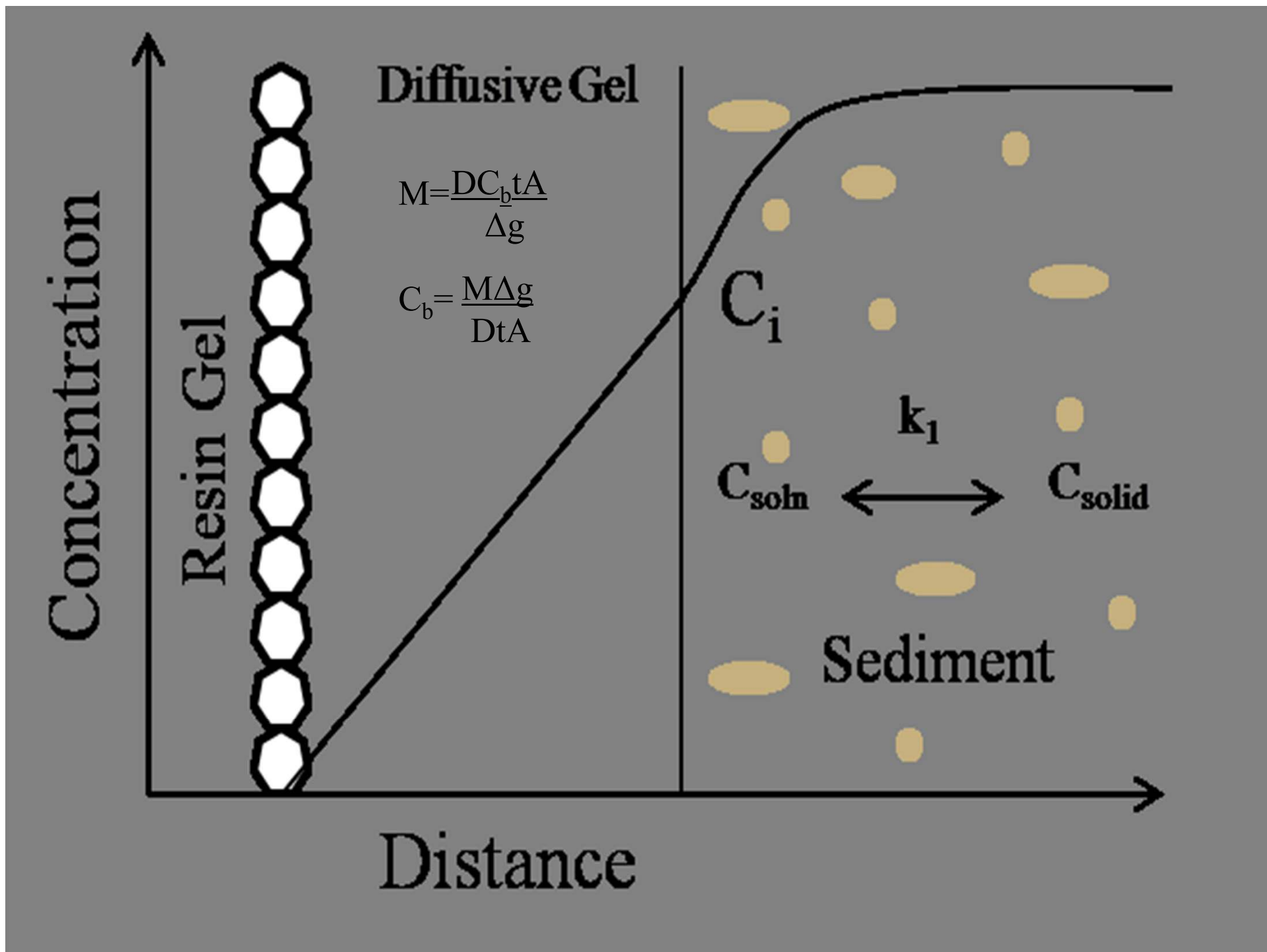
Laboratory Experiments (3-M)

- Experiment Set-up

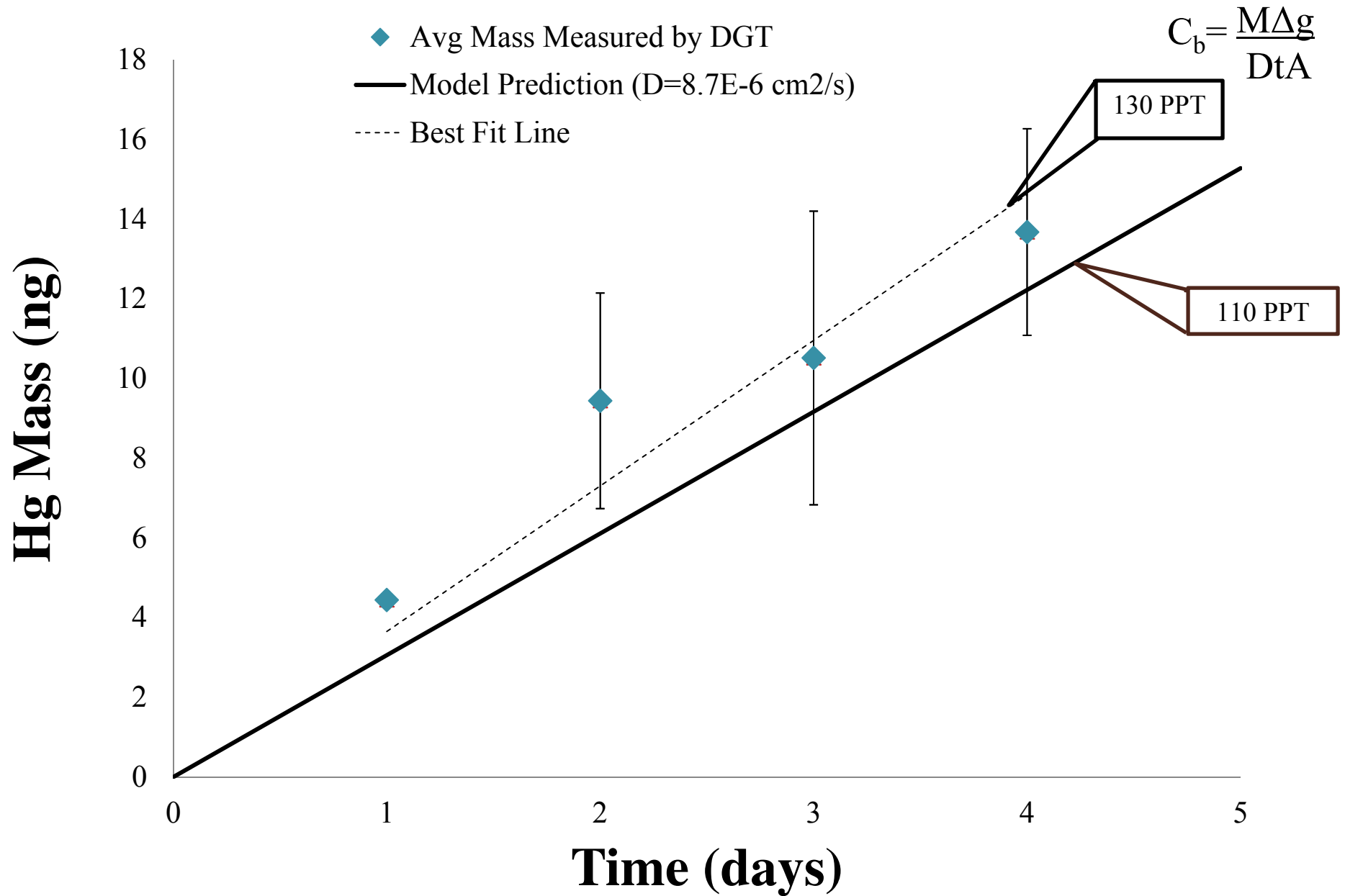


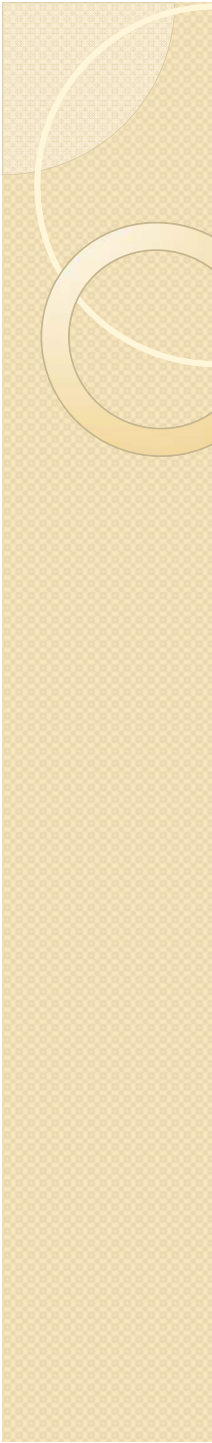
Time Dependent Sorption in Site Sediment





Time Dependent Sorption in Site Sediment



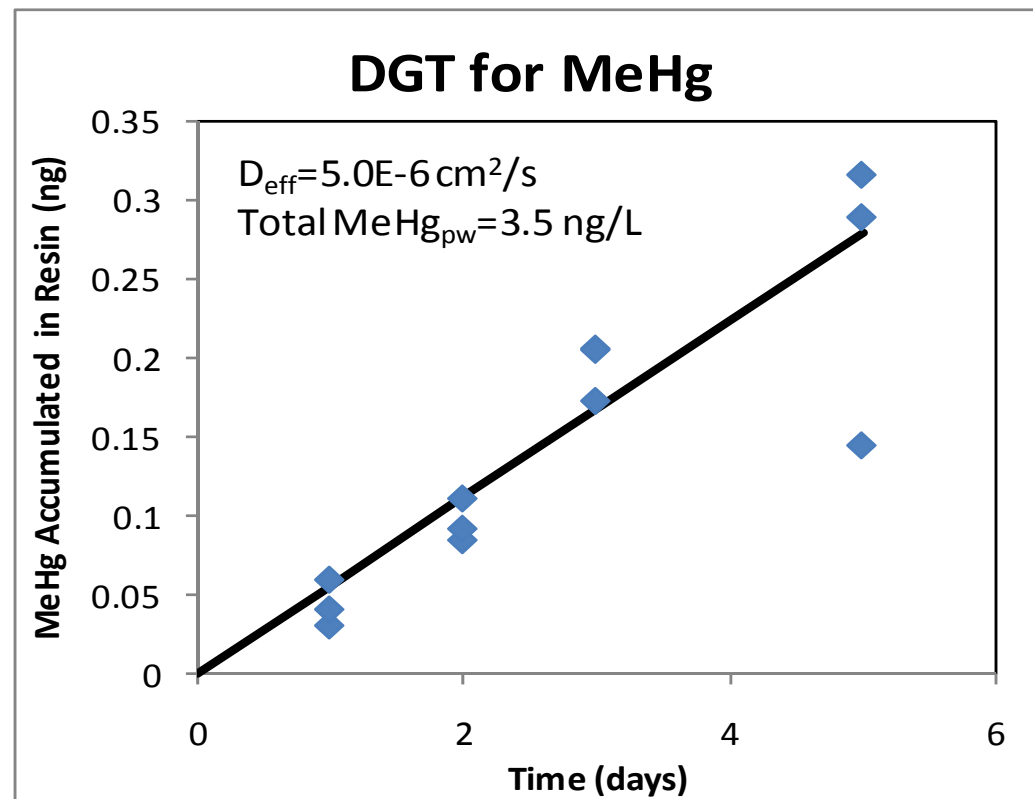


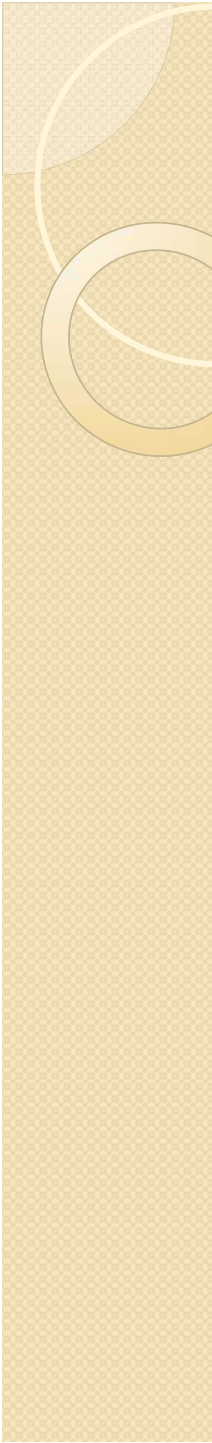
Laboratory Experiments (3-M)

- Time dependent sediment experiment
 - Data follows linear uptake
 - Data approx. fits model with diffusivity of Hg in water
 - 130 ppt (DGT Measured) vs. 110 ppt (Equilibrium Measured)

Laboratory Experiments (3-M)

- Methyl Mercury
 - Initial research shows promise for measuring porewater Me Hg





Laboratory Experiments (3-M)

- Conclusions

- 3-M demonstrates affinity for Hg and Me Hg, has a high extraction efficiency, and is compatible with the gel making process
- Method
 - Best results if you are able to utilize a site specific sediment D_{eff} for determining the pore water concentration
 - Even w/o calibration, the 3-M DGT provides good estimate of pore water concentration

Future Work- South River

- sediment experiments (sediment probe)
- Field deployment June 2010

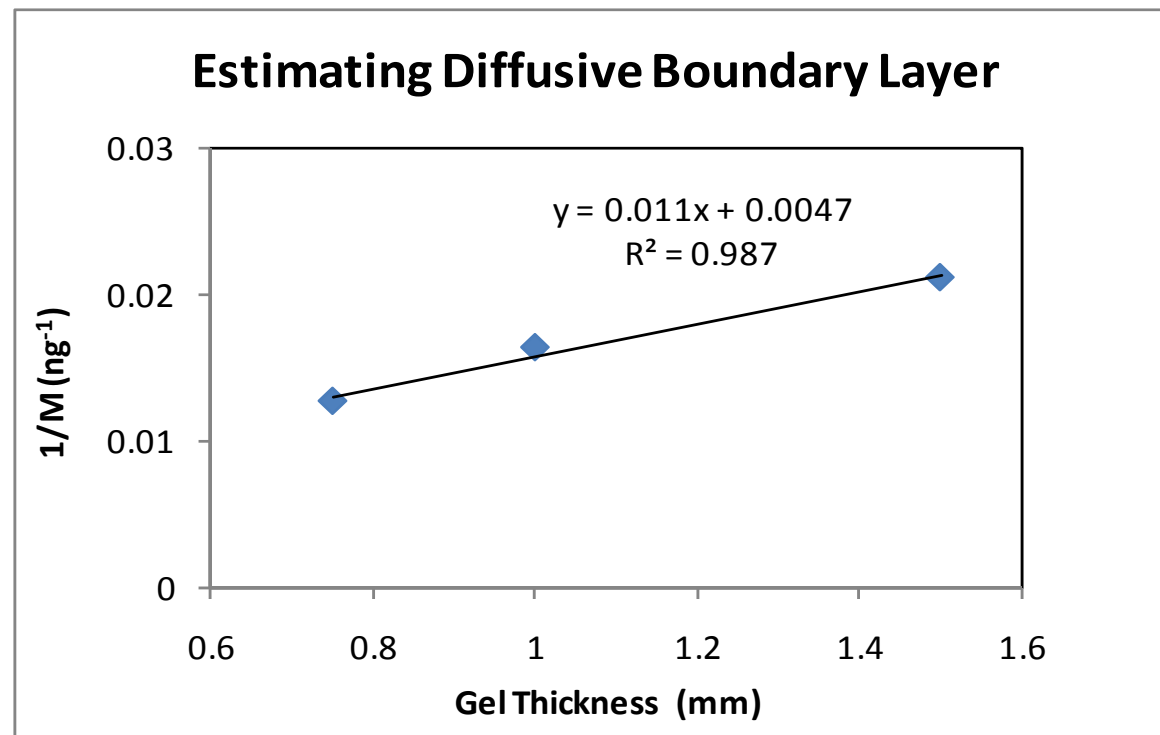


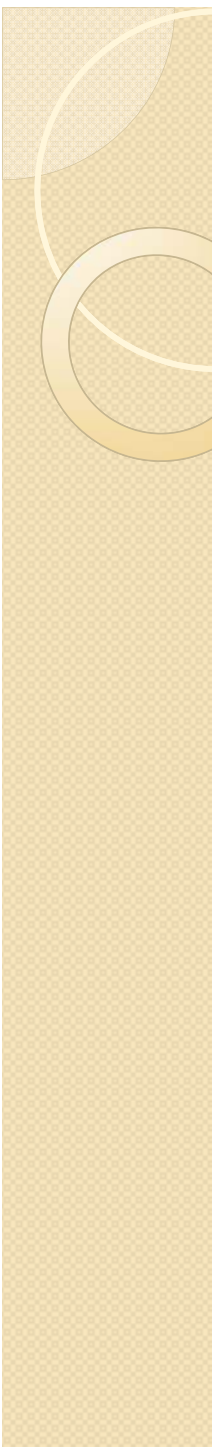
DBL

- Used equation proposed by Zhang and Davidson

$$\frac{1}{M} = \frac{\Delta g}{DC_b t A} + \frac{\delta}{DC_b t A}$$

- Different thicknesses deployed for 6 hrs
- Plot 1/M vs. gel thickness: DBL=intercept/slope $\approx$ 0.4mm





SOURCES

- www.dgtresearch.com
- Zhang, H., & Davison, W. (1995). Performance Characteristics of Diffusion Gradients in Thin Films for the In Situ Measurement of Trace Metals in Aqueous Solution. *Analytical Chemistry*, 67 (19), 3391-3400.
- Clarisse, O. & Hintelmann, H (2006). Measurements of Dissolved Methylmercury in Natural Waters Using Diffusive Gradients in Thin Film (DGT). *Journal of Environmental Monitoring*, 8, 1242-1247.
- Harper, M., Davison, W., Tych, W. (2000). DIFS – A Modeling and Simulation Tool for DGT Induced Trace Metal Remobilization in Sediments and Soils. *Environmental Modelling & Software*, 15, 55-66.