DGT as a Field Sampling Tool for Porewater Mercury and Methylmercury

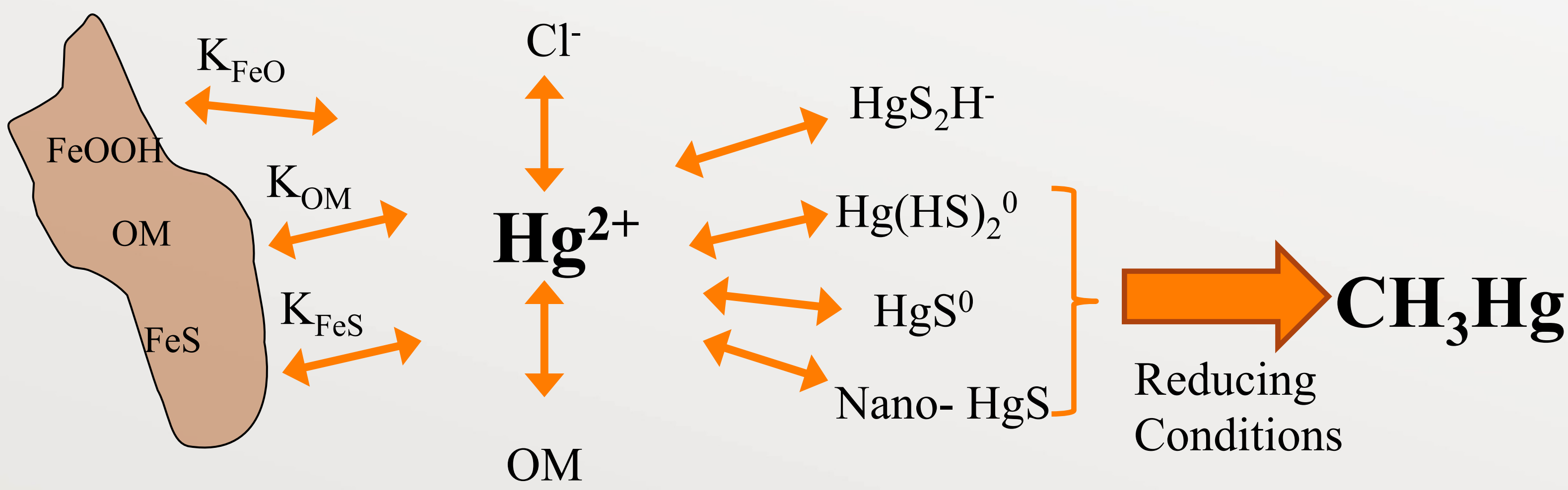
Paul Bireta
University of Texas at Austin
Danny Reible, Ariette Schierz
Texas Tech University
Rich Landis
Dupont

Outline

- Porewater sampling techniques
- DGT Theory and Background
- DGT Field Applications
  - Time-Integrated Sampling
  - Measuring Remedy Effectiveness
  - Mercury Behavior in River Banks and Sediments

Mercury Conceptual Model

- Dissolved mercury is available to microbes for methylation
- Bulk solid mercury is not a good measure for methylation potential of the system
- To reduce methylation, control solid phase sorption or aqueous speciation



Solid phase sorption **Aqueous Speciation**

Porewater Sampling Techniques

- Active sampling techniques
  - Centrifugation and Filtration
  - Displacement
  - Direct water sampling (Henry sampler)
- Passive sampling techniques
  - Diffusive gradient in thin films (DGT)
  - Advantages
    - Minimal disturbance
      - No suspension of particles
      - Maintain redox conditions
    - Flexible Placement
    - Vertical Resolution

Henry Sampler Porewater

- Henry Sampler- Conventional porewater sampler

Location	THg Unfiltered (ng/L)	THg Filtered (ng/L)
A	2300	1
B	310,000	301
C	72,000	2.5

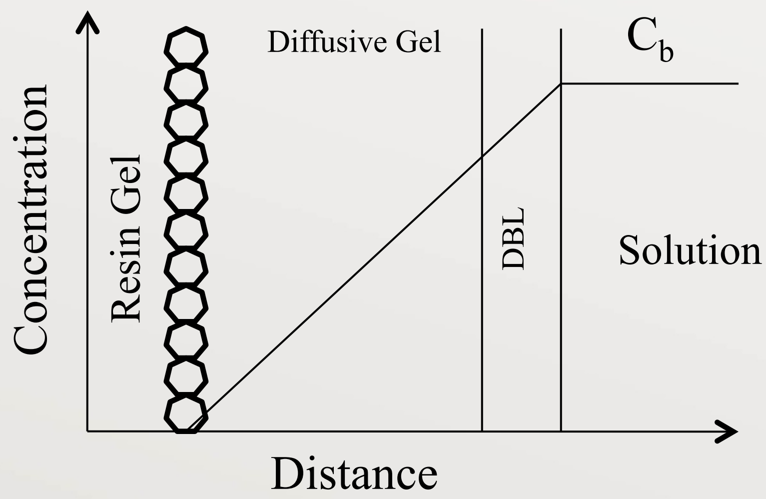
- Conventional porewater samples filtered <0.1% of unfiltered
  - Compared to 10-60% in surface water

DGT Background

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

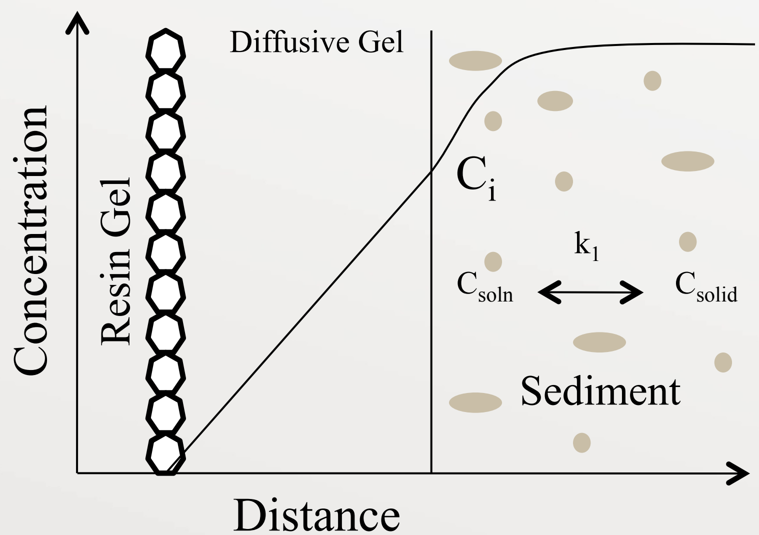
$$J = -D\frac{\partial \varphi}{\partial x} \Rightarrow J = \frac{DC_b}{\Delta g} \Rightarrow C_b = \frac{M\Delta g}{DtA}$$

- Diffusion of metal = to that in pure water



DGT in sediments

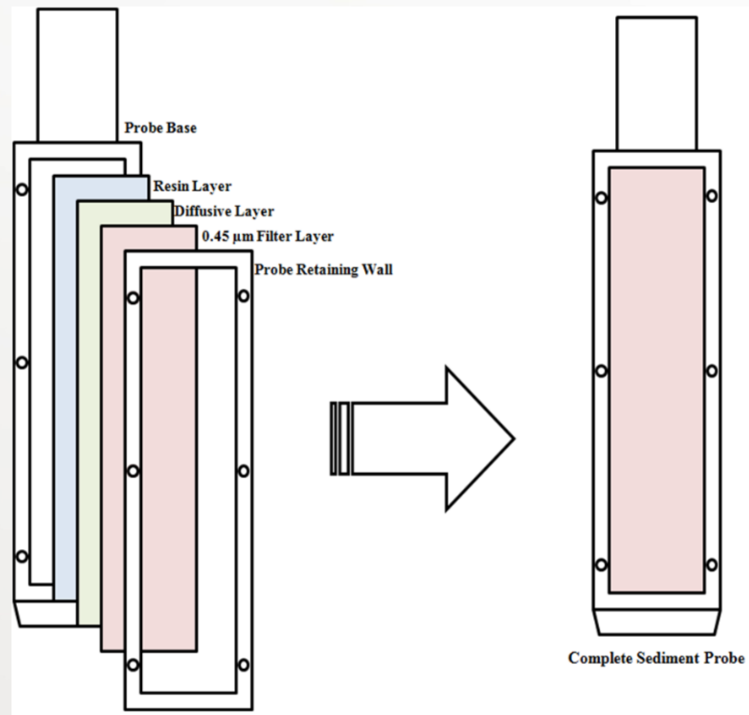
- DGT theory also applicable to sediments
  - Difference is solid phase influence

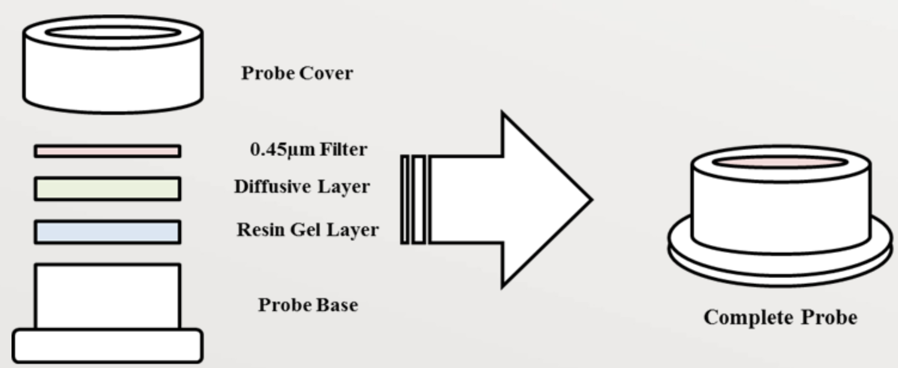


- *Pseudo* steady state achieved in ~ day deployments times

DGT for Hg/MeHg Measurement

- Resin
  - 3-mercaptylpropyl funtionalized silica gel resin
  - Acrylamide gel base
- Diffusion layer
  - Agarose gel
- Filter Layer
  - 0.45 μm polysulfone





DGT Fabrication Procedure

- DGT are fabricated at Texas Tech
- Deployed in sediment/water for ~2days
- Analysis performed at Texas Tech
  - Depth profilers sectioned at 1-2cm intervals
  - Resin split for TotHg/MeHg
  - TotHg resin is eluted in HCl and analyzed by EPA 1631
  - MeHg resin is eluted in HCl/Thioreau and analyzed by EPA 1630

South River Background

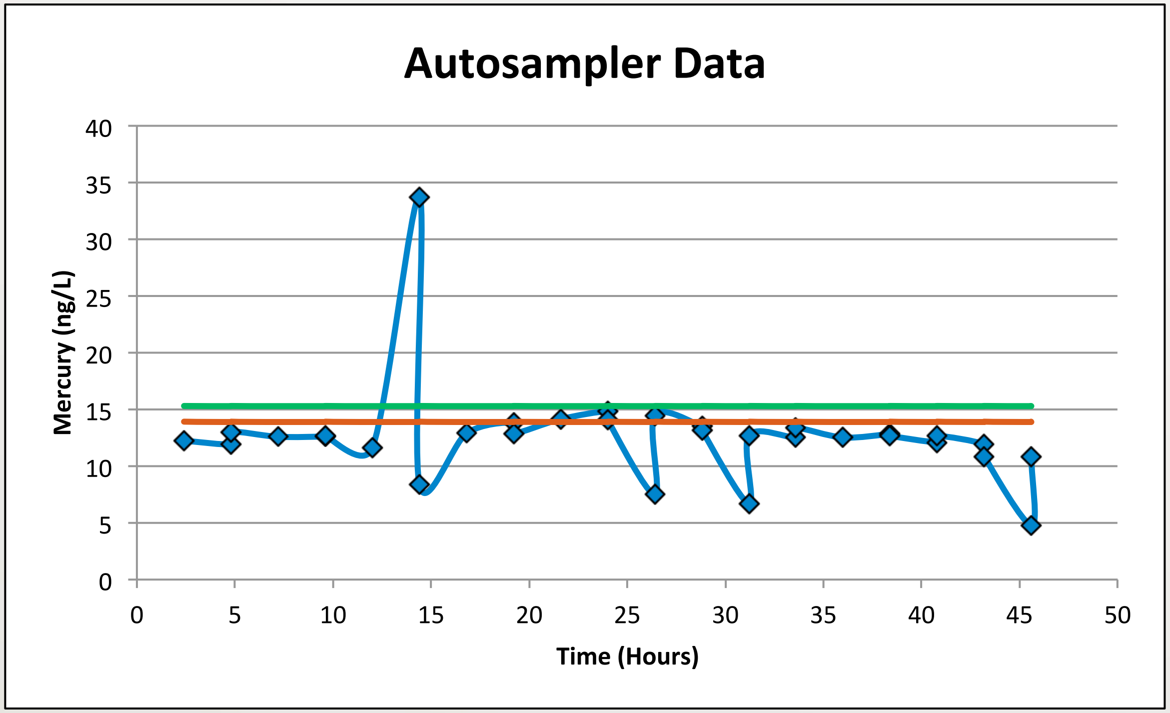
- Legacy mercury contamination from industrial source
- Large amount of traditional sampling
  - Biota, sediments, soils, surface water, groundwater
- Goal was to use diffuse gradient in gel-thin film (DGT) samplers to measure surface water and in-situ porewater mercury and methylmercury

Time Integrated Sampling

- Concentration calculated is an average over the deployment time
  - Can capture variations over sampling interval

Water Column Sampling

- Autosampler and DGT deployed in a river for 48 hours
- Autosampler measured an average concentration of 13.9 ng/L
- DGT Measured an average concentration of 15.3 ng/L



DGT

Autosampler Average

Measuring Remedy Effectiveness

- Goal of remediation is to lower mercury levels in biota
- Sediment amendment does this by lowering the amount of available mercury through sorption

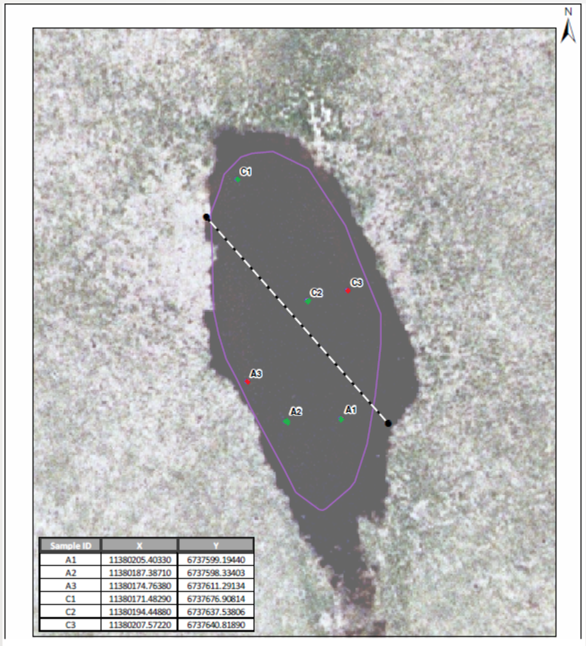
- DGT allow for a chemical measurement of remedy effect instead of just endpoints

Biochar Sediment Amendment

- Pilot site was a 2-year floodplain pond, adjacent to the South River, Virginia, USA
- Pond was divided and Biochar amendment was applied to one side

Sampling

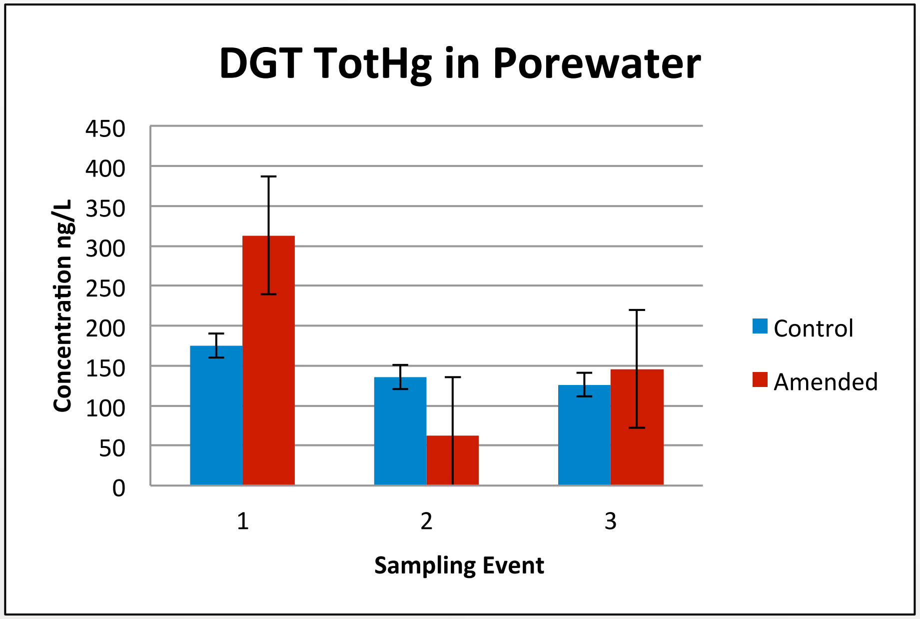
- DGT sampling was conducted at 0, 4, 16 weeks and ~10 months
  - 3 amended and 3 control locations
  - 18 samples from each sampling event
- Conventional Sampling performed in parallel
  - Included surface water, sediment porewater (Henry samplers), bulk sediment and biota
  - Analyzed for TotHg and MeHg



Sample ID	X	Y
A1	11380205.40330	6737599.19440
A2	11380187.38710	6737598.33403
A3	11380174.76380	6737611.29134
C1	11380171.48290	6737676.90814
C2	11380194.44880	6737637.53806
C3	11380207.57220	6737640.81890

DGT Sampling

- Data from sediment porewater 0-4 cm
- Higher concentrations in area to be amended initially
- Decrease at surface over time in amended
- Control approximately constant

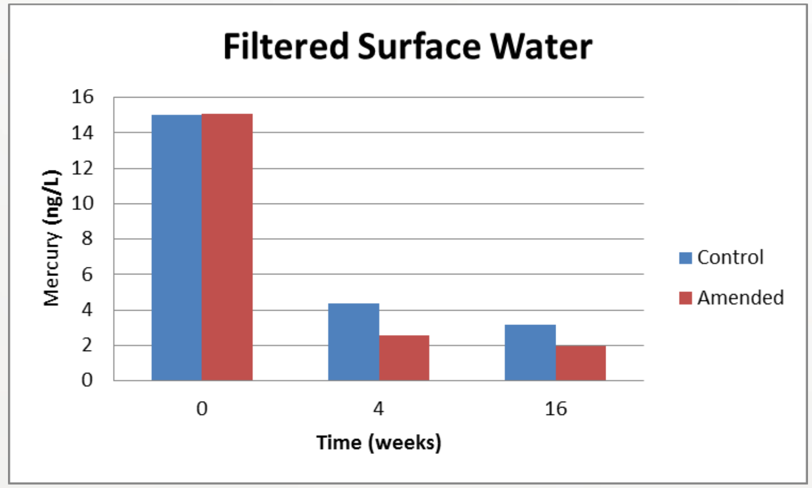


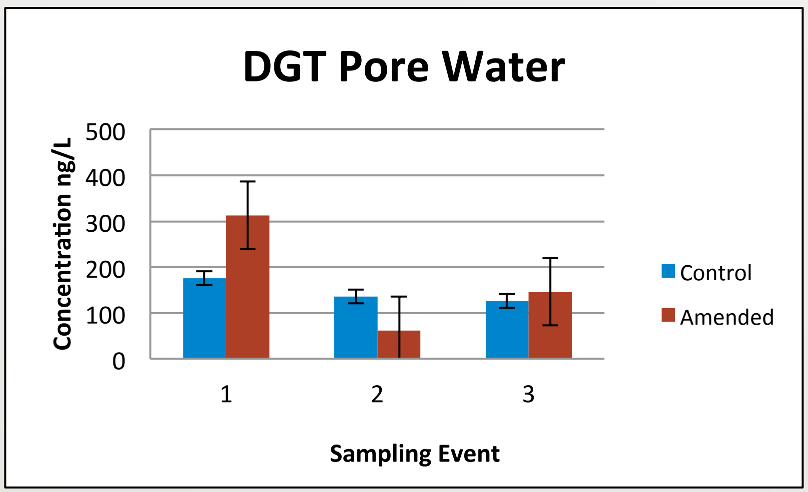
% Reduction in Total Mercury

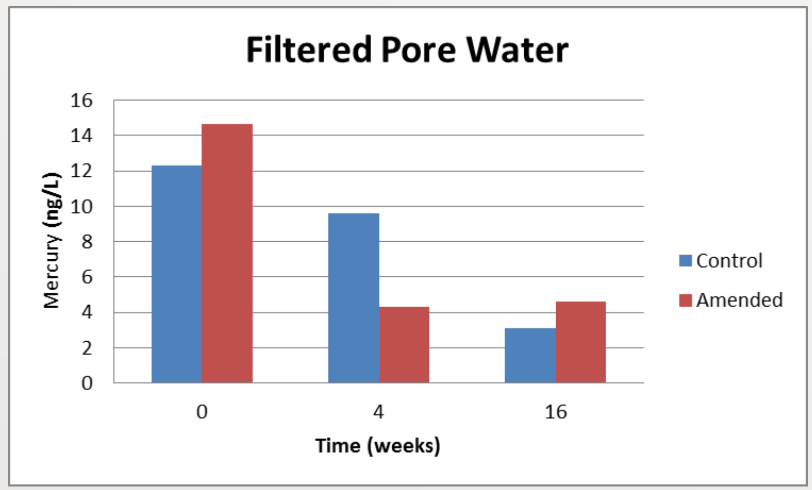
Treatment	SE1	SE2	SE3
Control	-	.23	.28
Amended	-	.80	.53

Conventional Sampling

- Filtered porewater data is significantly lower than DGT
  - Very close to filtered surface water
- Porewater collected with Henry samplers
  - Dilution of porewater samples?



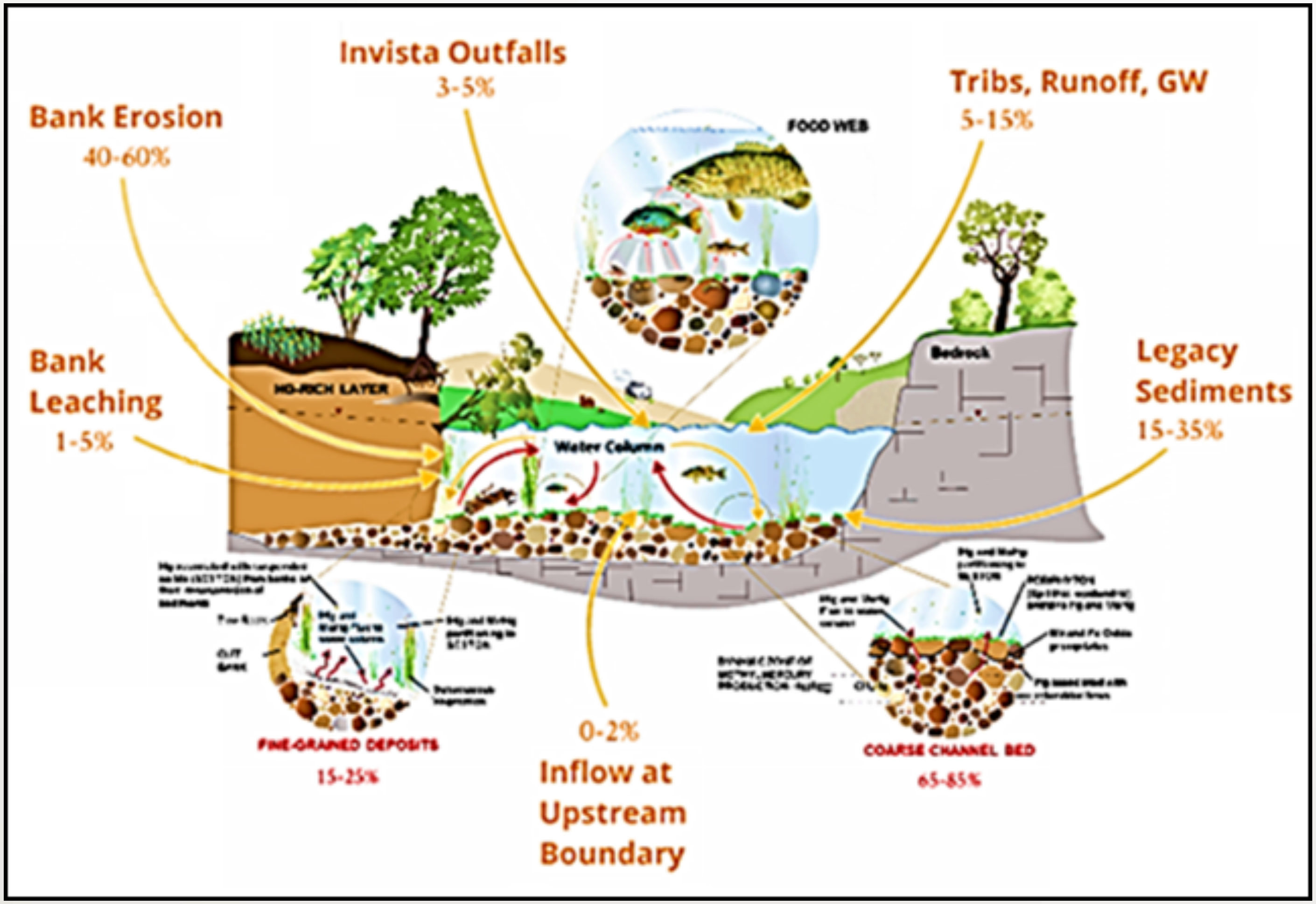




Mercury Behavior in River Banks and Sediments

- Terrestrial soil is a major source of mercury to the river
  - River banks are interface
- More accurate measurements in channel and bank sediments
  - Improve understanding of how banks and sediments influence mercury cycling in the river

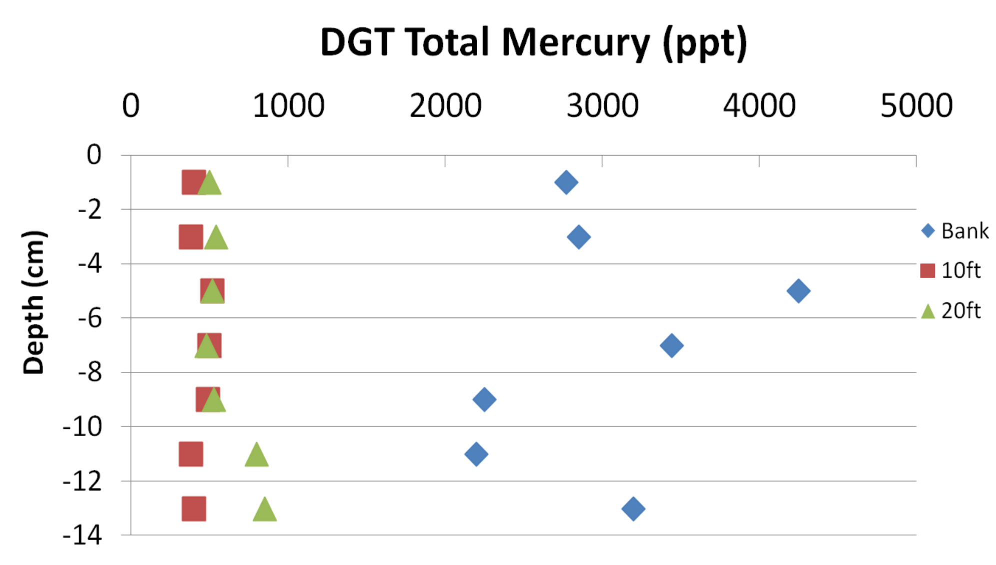
Site Conceptual Model



Brent, R. N. (2013). *Conceptual Model of the South River, VA*.
James Madison University.

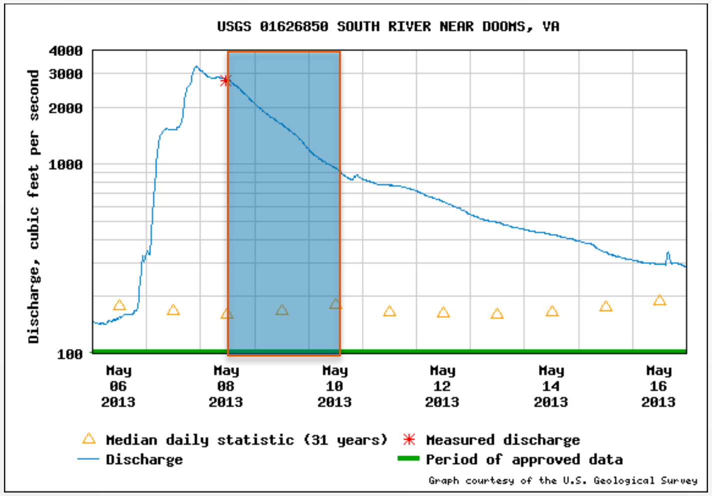
Baseline Data

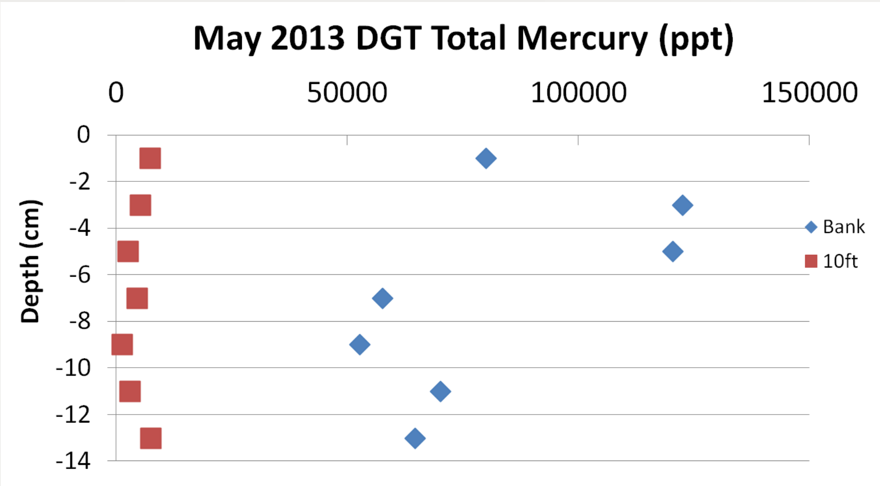
- DGT Field Sampling Conducted 2010-2014
- Three areas of the river were sampled
  - Source area, upstream, downstream
- Consistent results 2010-2012
  - Always sampled at baseline flow



May 2013 Flood Event

- Sampling event occurred during a high flow event (~3000 cfs)
- DGTs deployed just after the high flow crested
  - Measured mercury behavior in banks during declining stage





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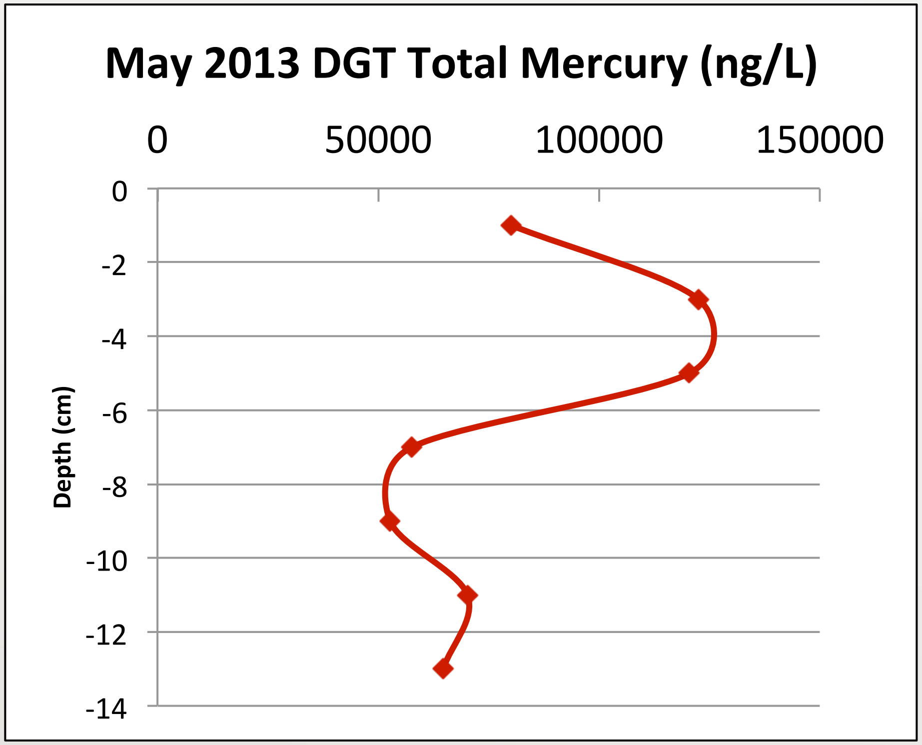
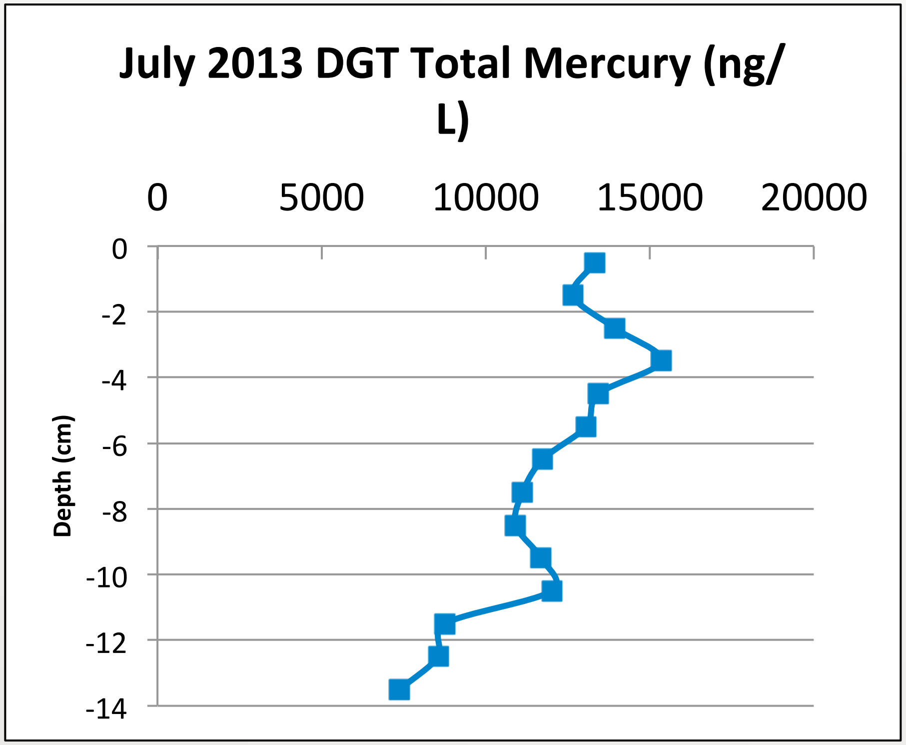
WHAT STARTS HERE CHANGES THE WORLD

May/July 2013 Data

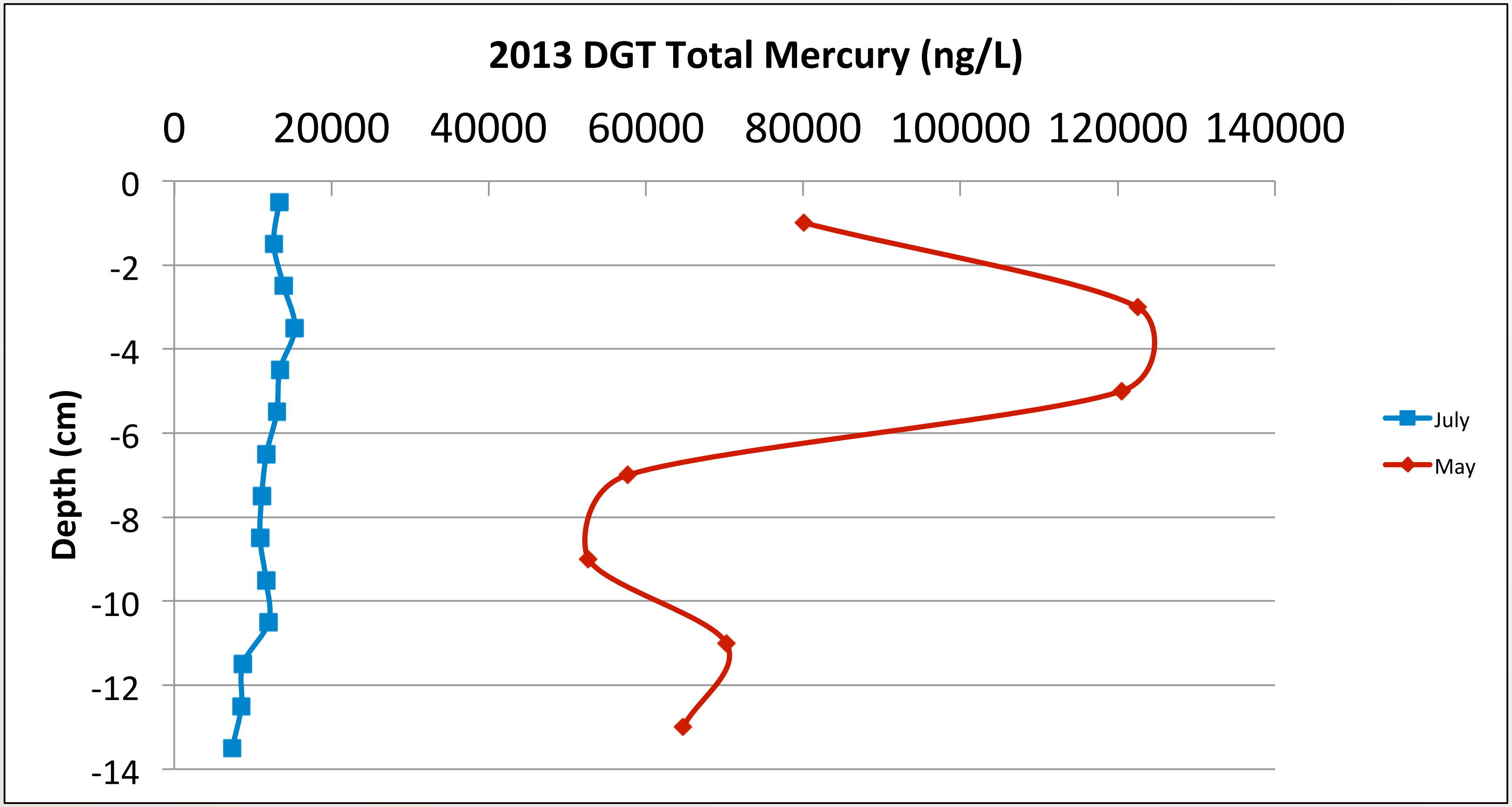
May 2013 – Declining Stage



July 2013 – Baseline Flow



May/July 2013 Data



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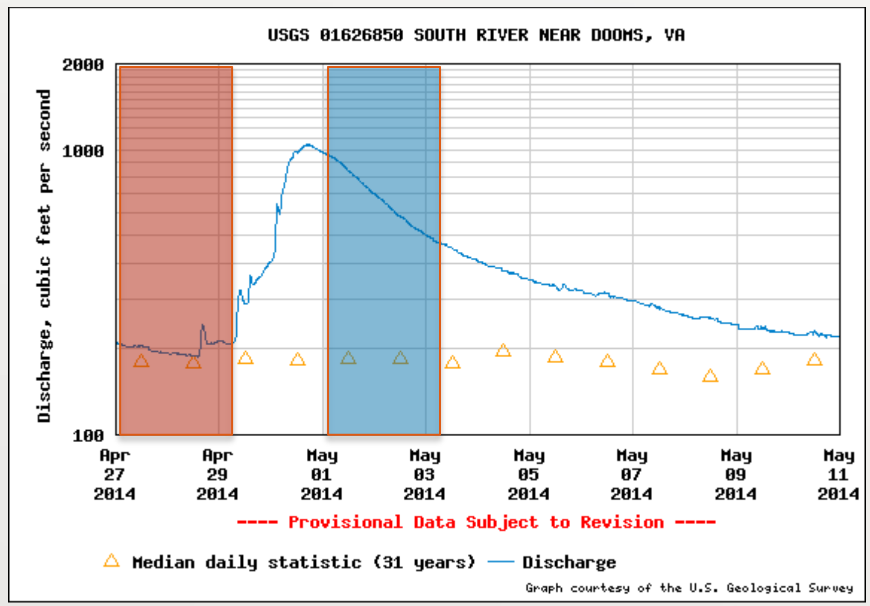
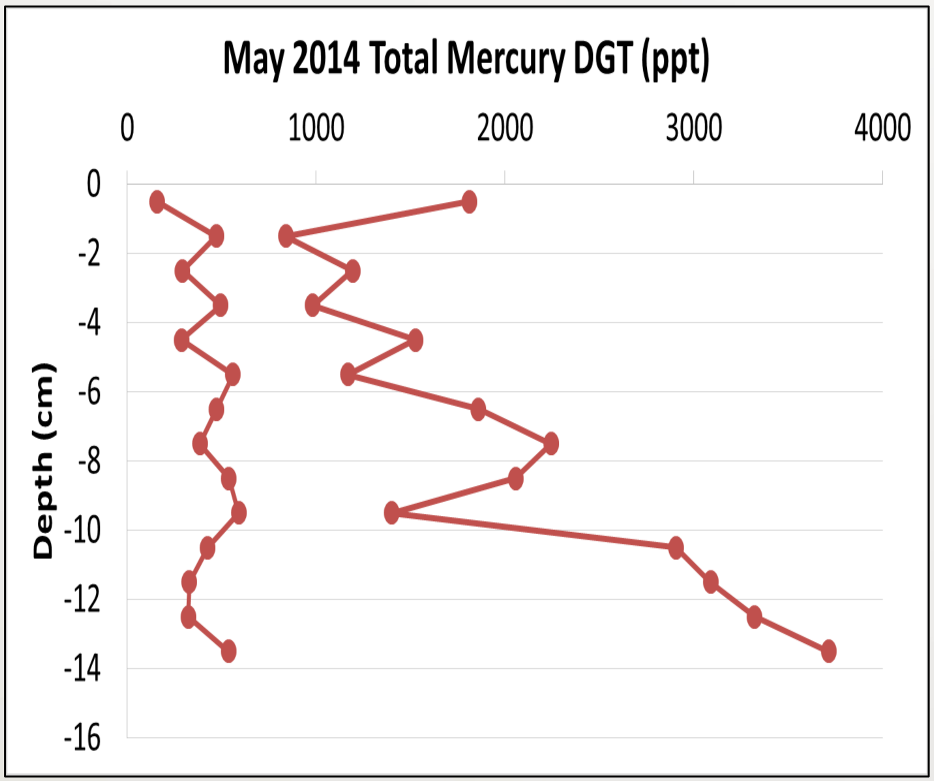
May 2014 Sampling

- Sampling conducted at baseline flow and declining stage, ~3 days apart
- Peak flow ~1000 cfs
- DGT samplers deployed during both flow regimes

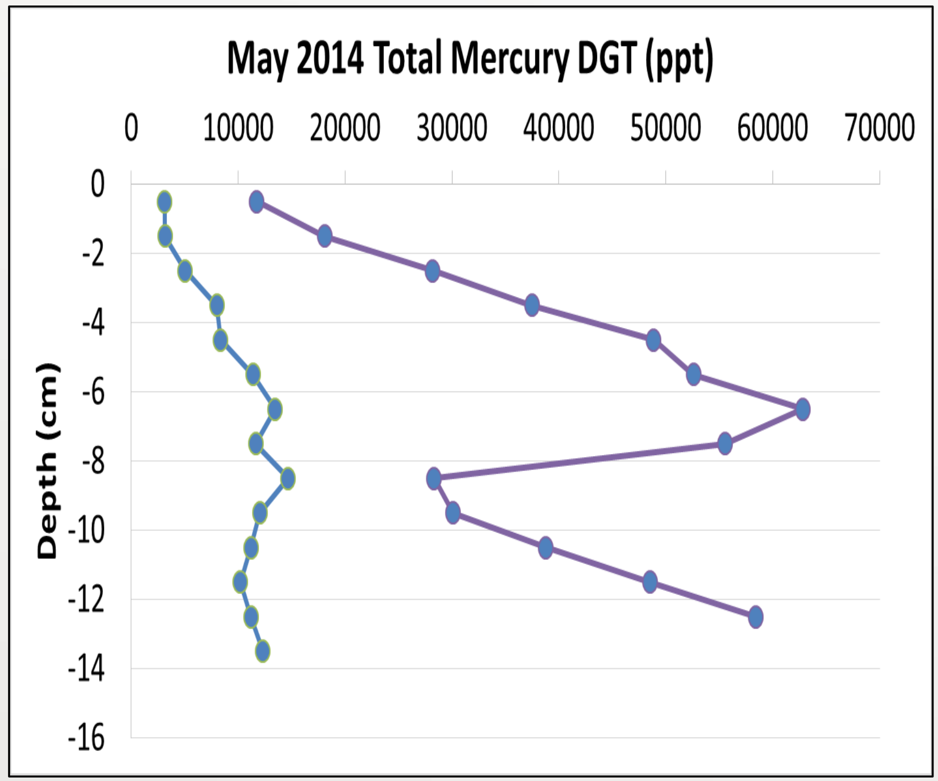


May 2014 Data

Baseline flow



Declining Stage



Mercury Behavior in River Banks and Sediments

- DGT able to capture major differences in mercury behavior
  - Large concentration range
- DGT able to give vertical resolution
  - Not bulk sample
- Small sampler size allow placement in difficult sampling environments

Conclusions

- DGT can effectively measure low and high level mercury concentrations
  - PDL: 10 ng/L, depending on sampling parameters
  - Wide range of concentrations can be measured with same samplers, but can tailored for specific ranges
- More direct chemical measurement that sampling biota
  - Important for understanding remediation mechanisms
- DGT samplers give flexibility in sampling
  - Vertical resolution in a narrow space
- Related Talk: *Validation of Diffusive Gradient in Thin-films Technique for Mercury and Methylmercury*
  - Thursday, 11am. Dr. Ariette Schierz

Acknowledgements

- DuPont
- South River Science Team
- The University of Texas at Austin
- Texas Tech University