Mechanistic Studies and Tool Development

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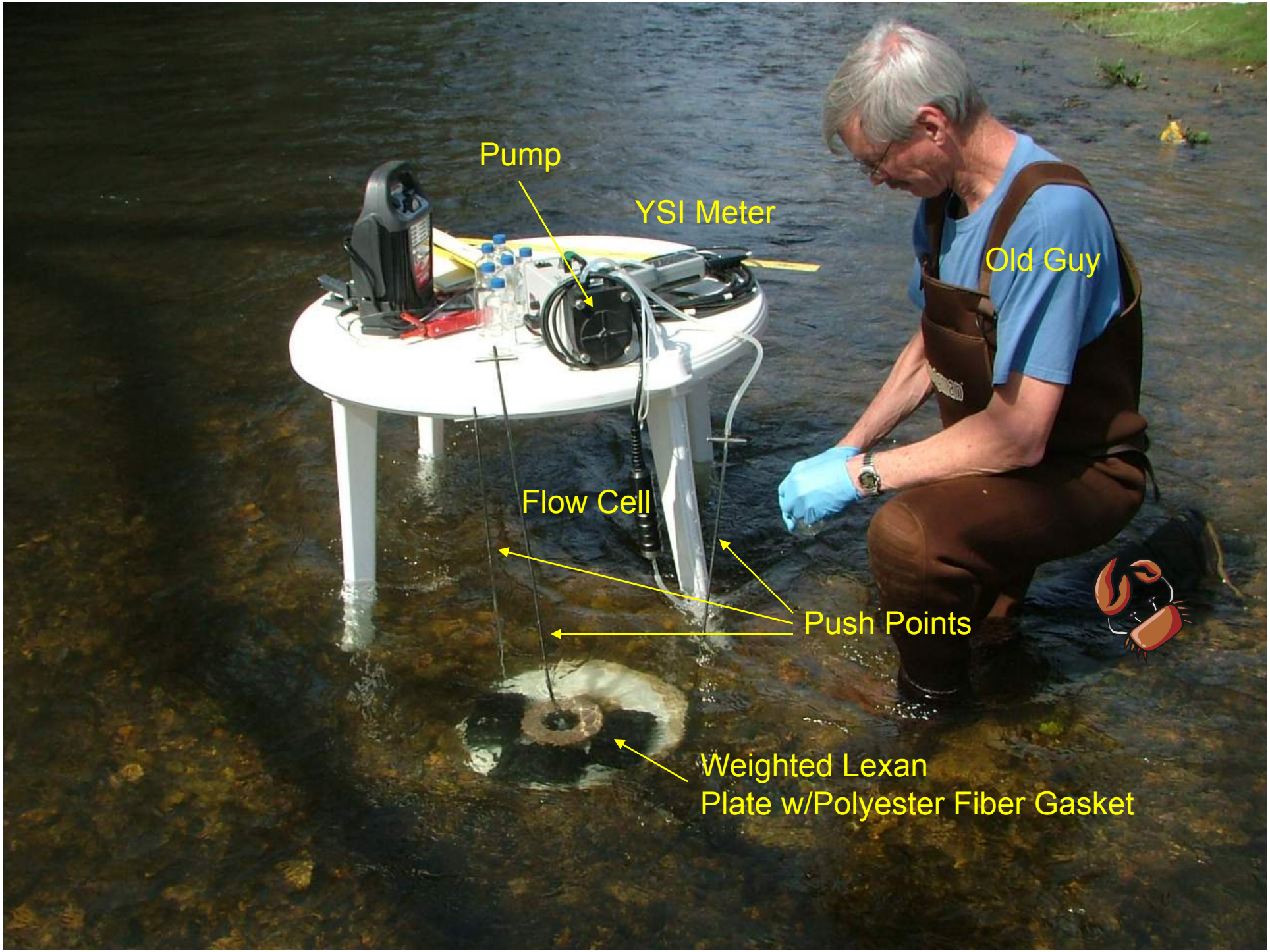
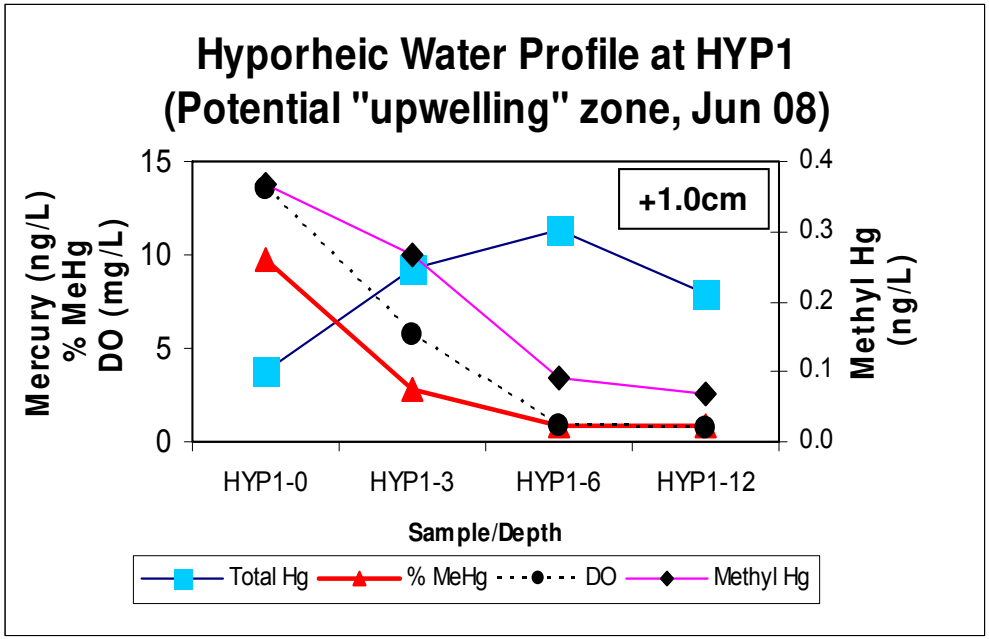
2008 Focus Areas

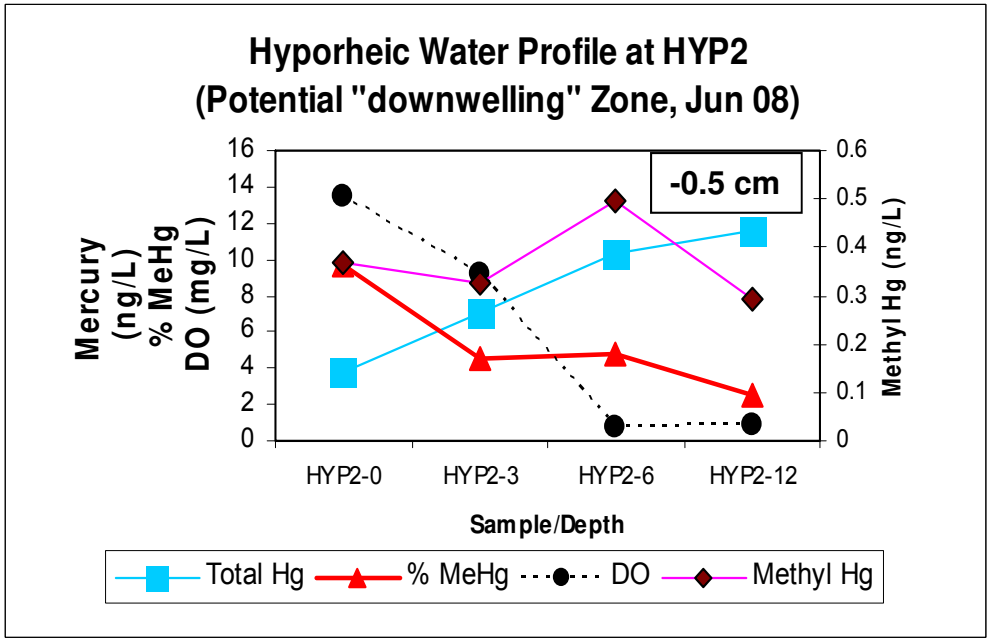
- Gravel Bar Hyporheic Zone Characterization
- Characterization of “reactive Hg” [Hg(II)] in surface water and outfalls.
- Methyl Hg Desorption Kinetics

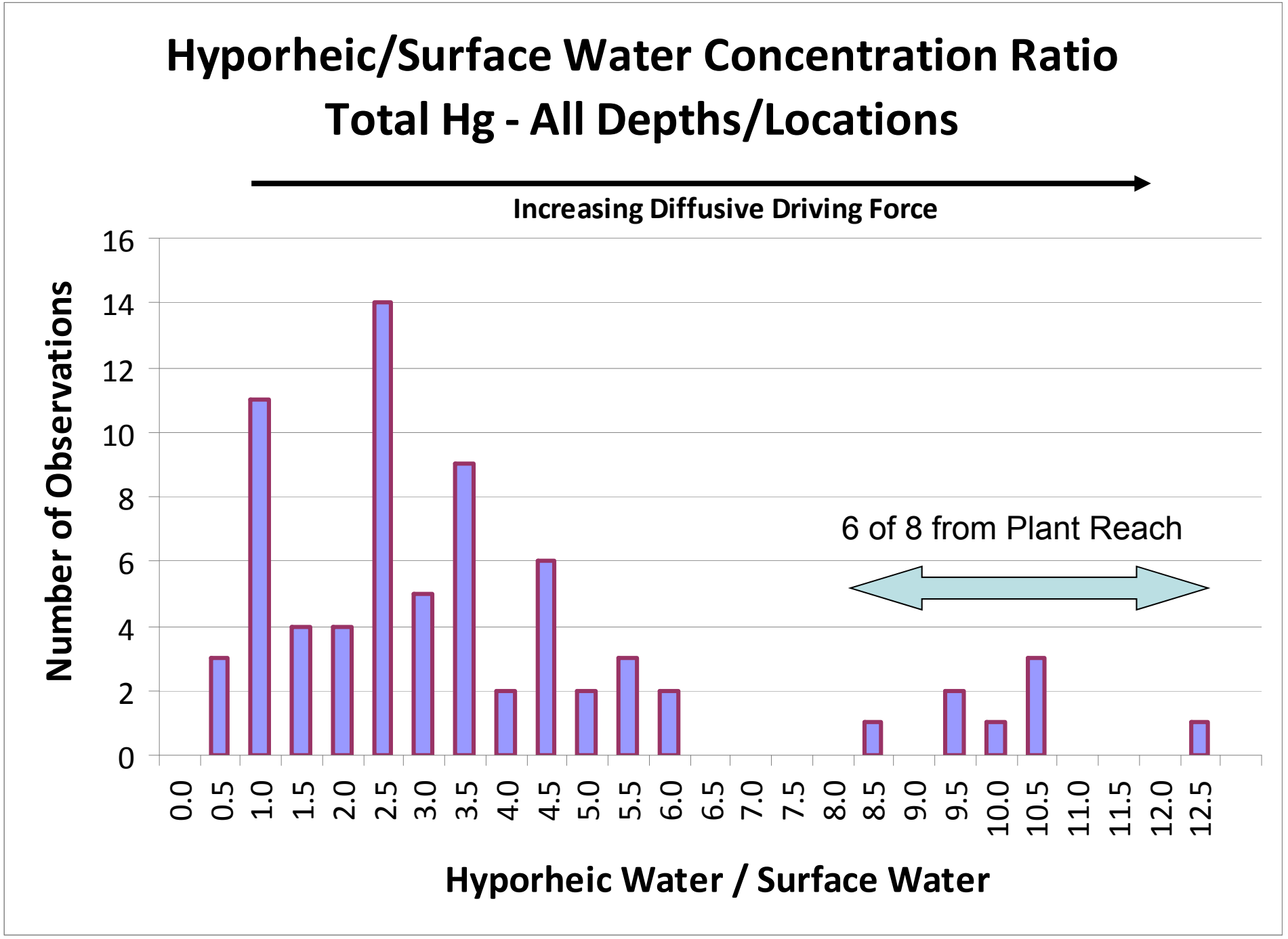
Hyporheic Sampling at Basic Park Gravel Bar

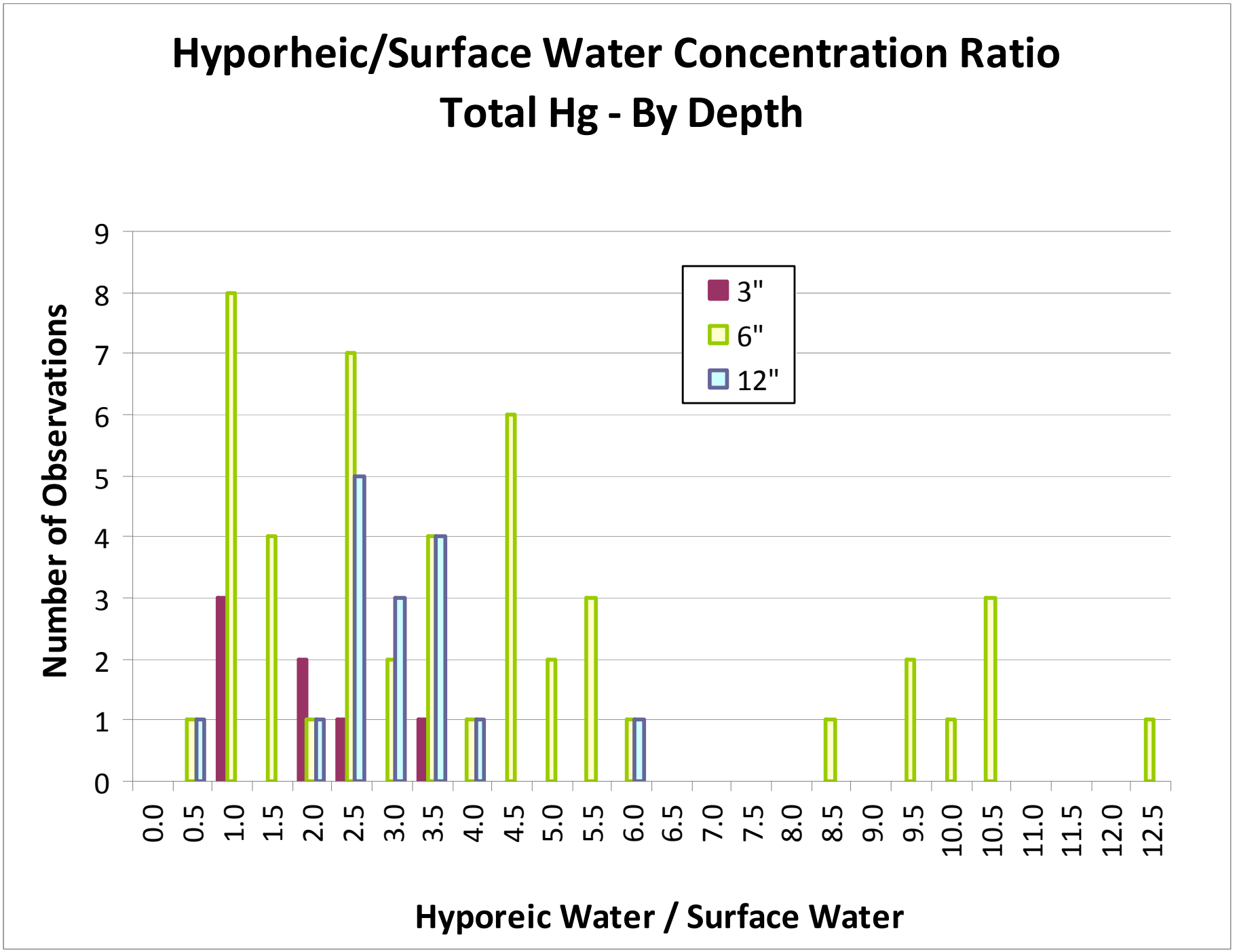
- Objective was to retrieve water and sediment samples at increasing depths in the bed
  - Reduce/eliminate influence of river flow on near-interface water samples using a “gasket”
  - Sediment collected by “sequential excavation” and “micro-guzzling” (April and June only)
  - Water collected April, June and September.
  - Measured hydraulic gradients manometrically
- Persistent Question Addressed: Are Embedded Gravels Zones of MeHg Production/Release?


Pump
YSI Meter
Old Guy
Flow Cell
Push Points
Weighted Lexan
Plate w/Polyester Fiber Gasket


Hyporheic Water Profile at HYP1
(Potential "upwelling" zone, Jun 08)
+1.0cm
Mercury (ng/L)
% MeHg
DO (mg/L)
Methyl Hg (ng/L)
15
10
5
0
0.4
0.3
0.2
0.1
0.0
HYP1-0
HYP1-3
HYP1-6
HYP1-12
Sample/Depth
Total Hg
% MeHg
DO
Methyl Hg


Hyporheic Water Profile at HYP2
(Potential "downwelling" Zone, Jun 08)
-0.5 cm
Mercury (ng/L)
% MeHg
DO (mg/L)
Methyl Hg (ng/L)
16
14
12
10
8
6
4
2
0
0.6
0.5
0.4
0.3
0.2
0.1
0
HYP2-0
HYP2-3
HYP2-6
HYP2-12
Sample/Depth
Total Hg
% MeHg
DO
Methyl Hg


Hyporheic/Surface Water Concentration Ratio
Total Hg - All Depths/Locations
Increasing Diffusive Driving Force
Number of Observations
16
14
12
10
8
6
4
2
0
6 of 8 from Plant Reach
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
Hyporheic Water / Surface Water


Hyporheic/Surface Water Concentration Ratio
Total Hg - By Depth
Number of Observations
0
1
2
3
4
5
6
7
8
9
3"
6"
12"
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
Hyporeic Water / Surface Water

Stratified Guzzling Layer Prep

Sediment Profiles at Hyporheic Stations

Station	Depth (Inches)	Total Hg (ng/g)	Methyl Hg (ng/g)	%Methyl Hg	%LOI	MeHg-LOI (ng/g)
HYP2	1 to 3	9764	13.86	0.14	19.0	73.0
	3 to 6	14381	5.60	0.04	13.4	41.8
	6 to 9	13119	2.68	0.02	7.87	34.1
HYP3	1 to 3	8432	6.90	0.08	8.40	82.1
	3 to 6	7248	5.83	0.08	10.0	58.4
	6 to 9	12104	4.24	0.04	11.6	36.6

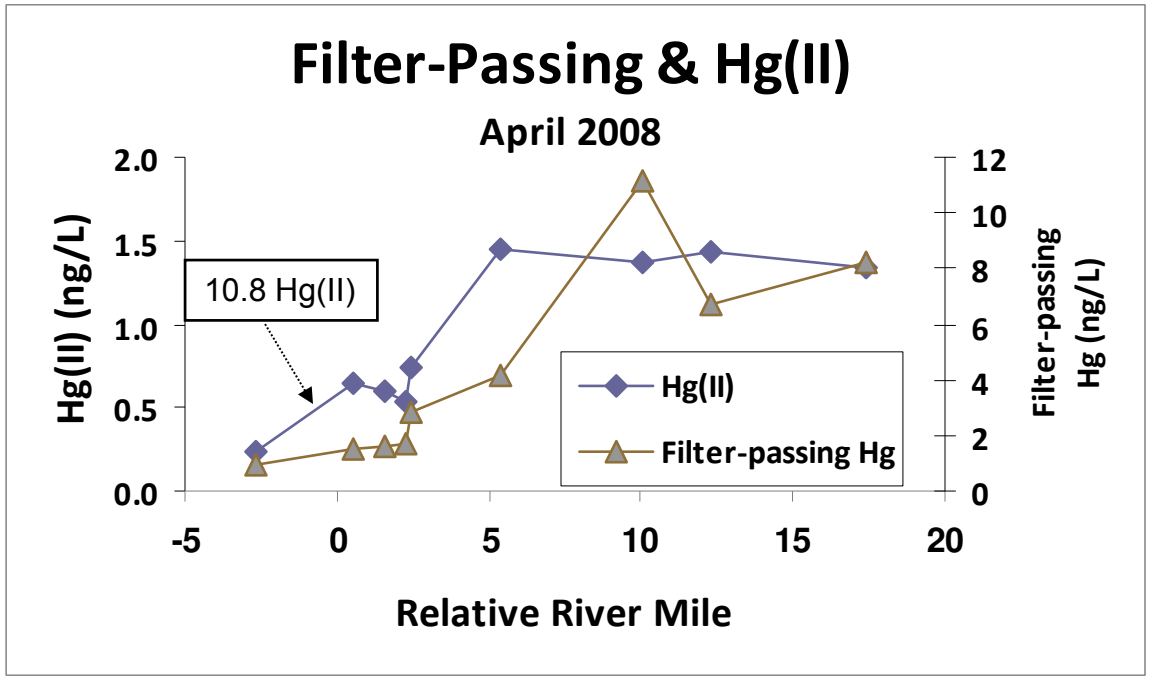
- THg increases (slightly) with depth
- MeHg, MeHg-LOI and %MeHg decrease with depth
- MeHg atypically low (too early in spring??)

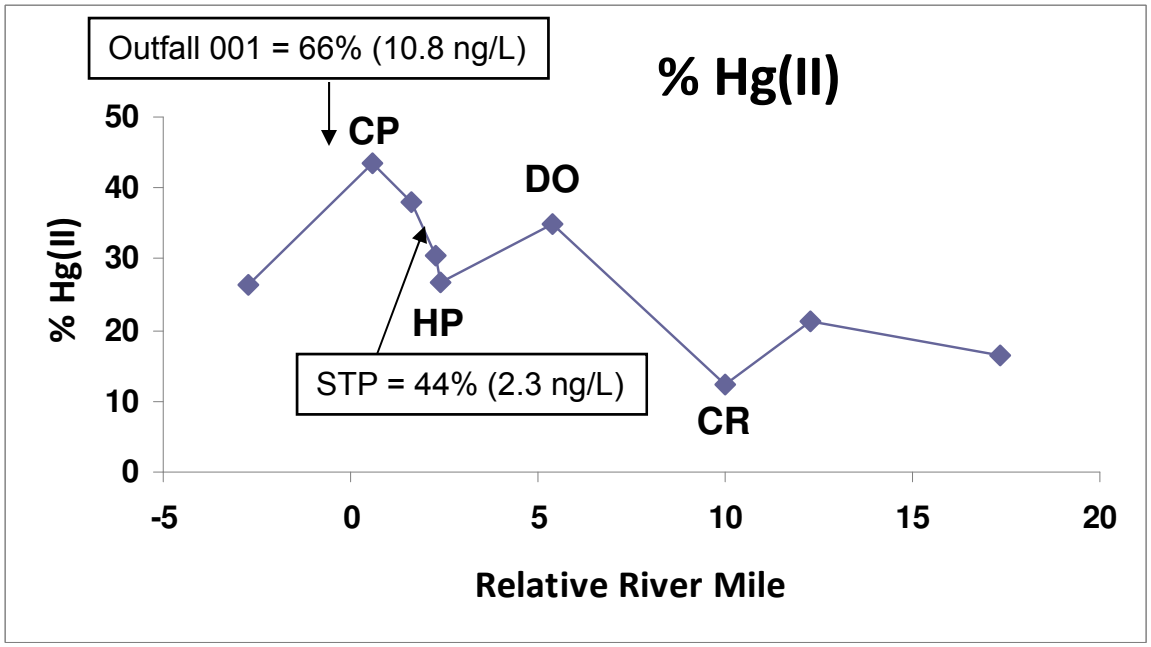
Stratified Hyporheic Indications

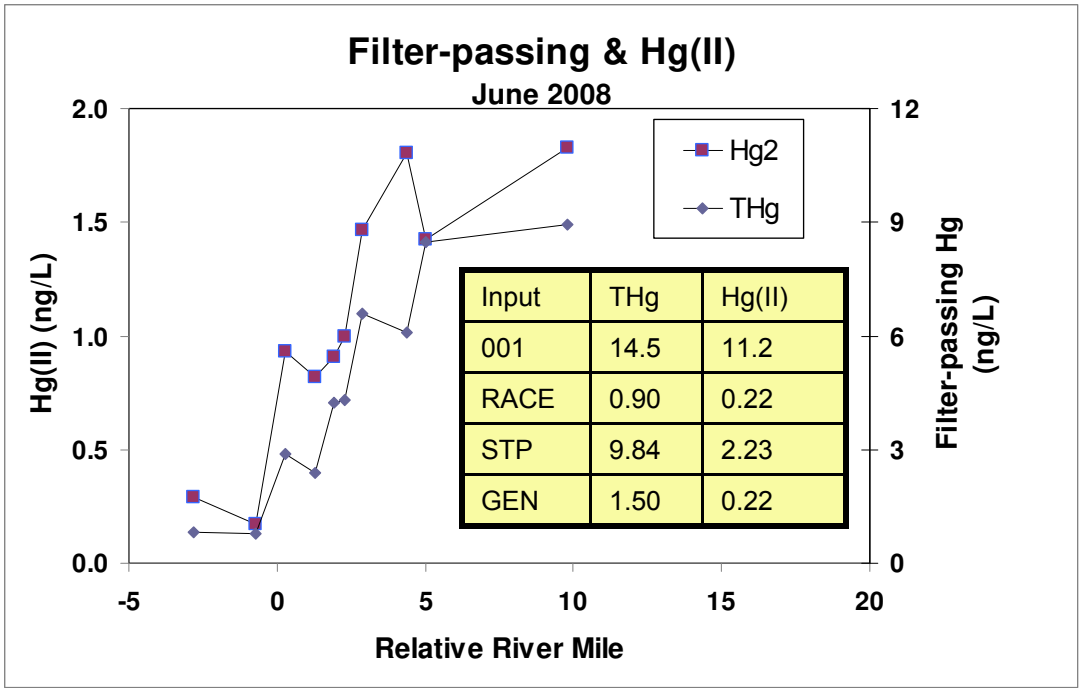
- THg & MHg behaviors opposite
  - THg peak deeper
  - MHg peak shallower
  - Both for sediment and pore water
- Pattern suggests local MHg production near interface, vs arrival sorbed to same solids, but….*higher [MHg] is not where dissolved oxygen lowest*

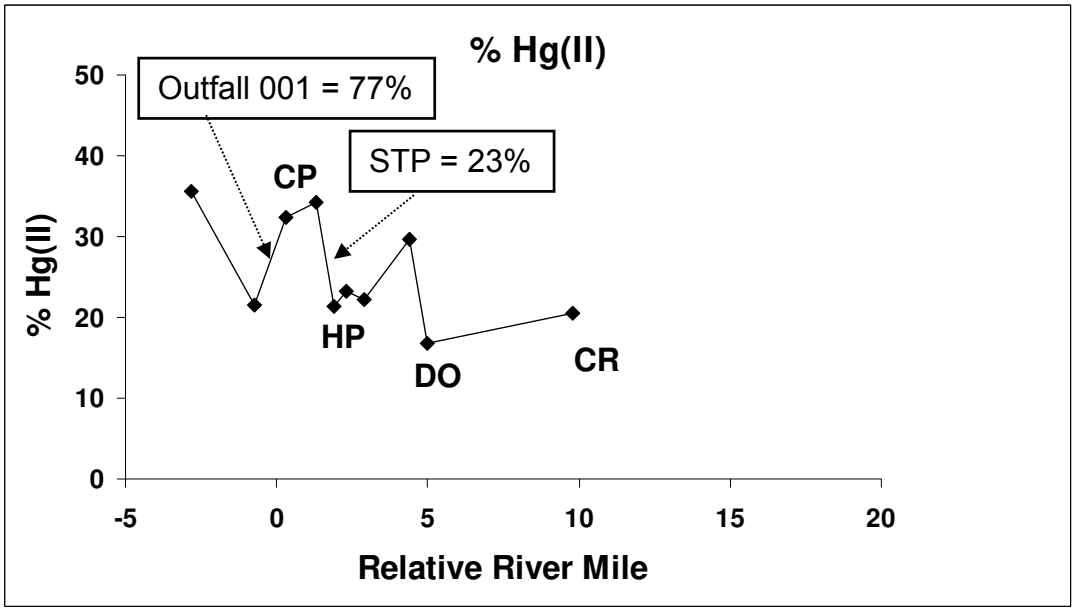
Reactive Mercury [Hg(II)]

- Potential as surrogate for “bioavailable”
  - May be “pathfinder” for inputs of “new” Hg
- Reactive=Easily reducible to Hg(0)
  - Likely inorganically complexed Hg(II), incl Hg^{2+}
  - Highly bioavailable (but some debate)
- Can we use the Lumex to measure in “field”, i.e., “close interval sampling”?
  - Trial setup in Waynesboro office on April 5
- Trial surveys from SR01 to Harriston on April 8, and SR01 to Crimora on June 24
- Hg(II) samples sent to Studio Geochimica.


Filter-Passing & Hg(II)
April 2008
Hg(II) (ng/L)
Filter-passing Hg (ng/L)
10.8 Hg(II)
Hg(II)
Filter-passing Hg
Relative River Mile


Outfall 001 = 66% (10.8 ng/L)
% Hg(II)
CP
DO
HP
CR
STP = 44% (2.3 ng/L)
% Hg(II)
Relative River Mile


Filter-passing & Hg(II)
June 2008
Hg(II) (ng/L)
Filter-passing Hg (ng/L)
Relative River Mile
Hg2
THg
Input | THg | Hg(II)
001 | 14.5 | 11.2
RACE | 0.90 | 0.22
STP | 9.84 | 2.23
GEN | 1.50 | 0.22


% Hg(II)
Outfall 001 = 77%
STP = 23%
CP
HP
DO
CR
% Hg(II)
Relative River Mile

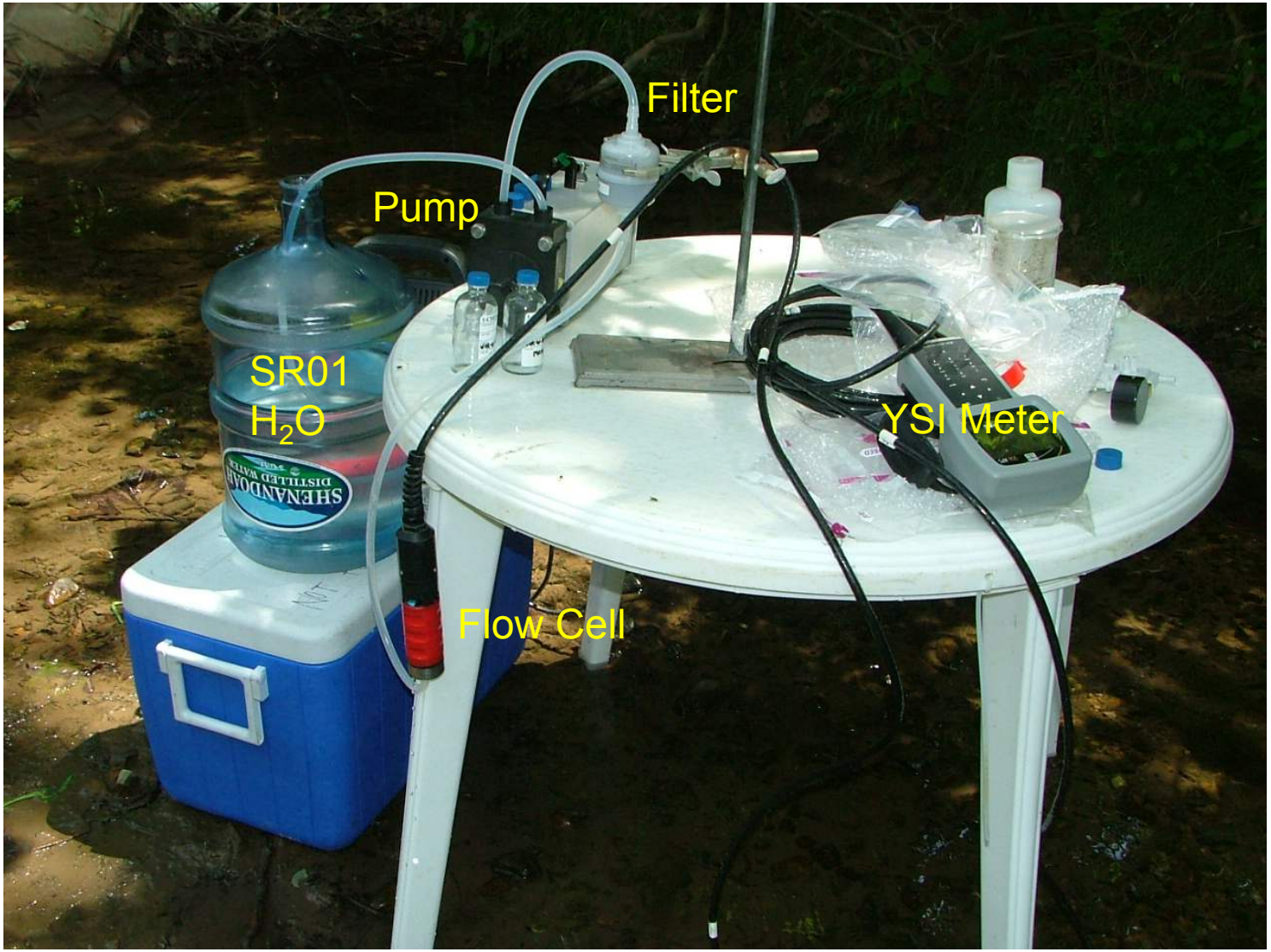
Hg(II) Indications

- [Hg(II)] generally tracks filter-passing Hg and increases downstream.
- % Hg(II) generally decreases downstream.
- Unlikely to be very useful as an input pathfinder: *Inputs not significantly "enriched" in Hg(II) compared with river surface water.*

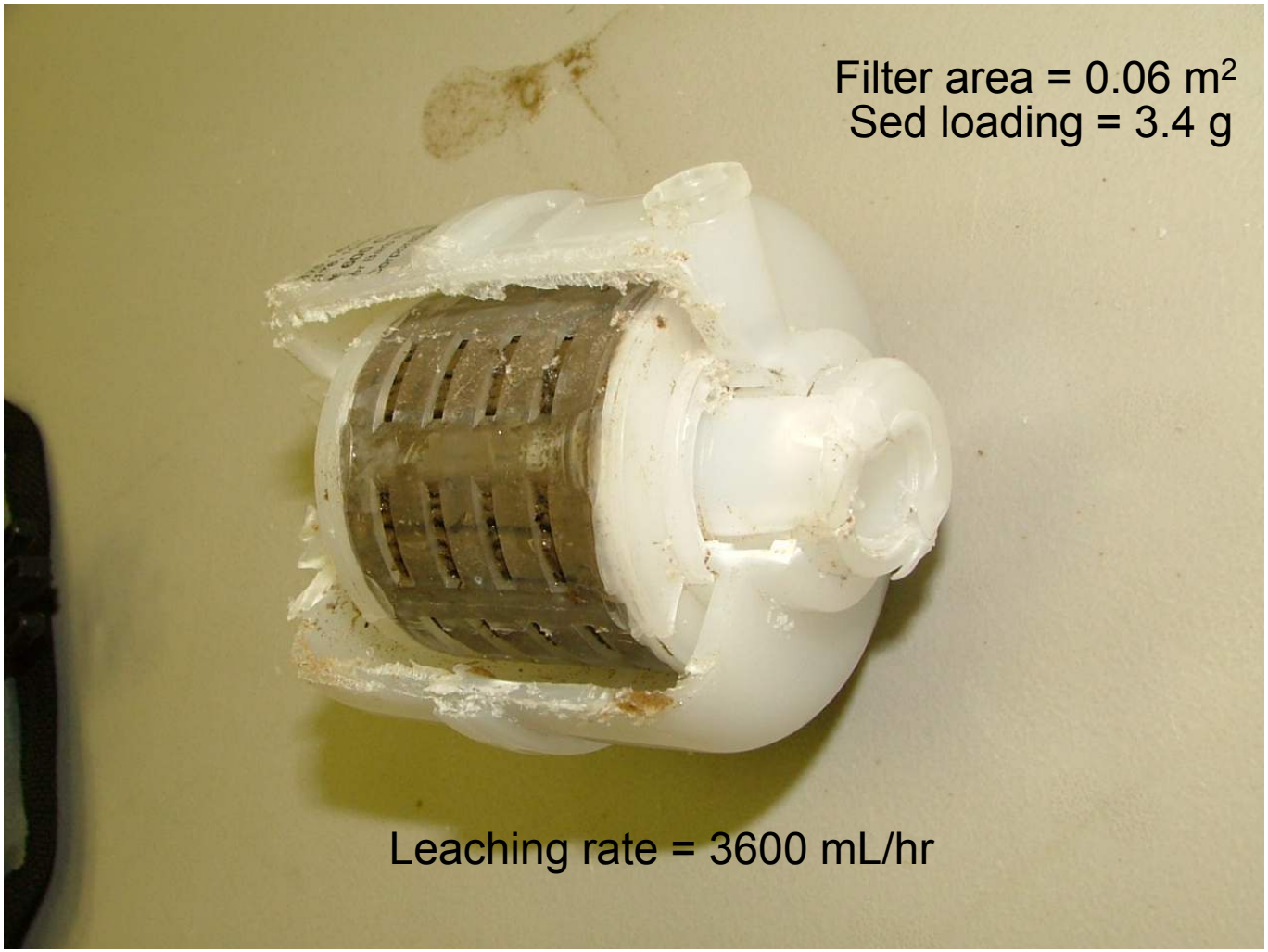
Methyl Hg Desorption

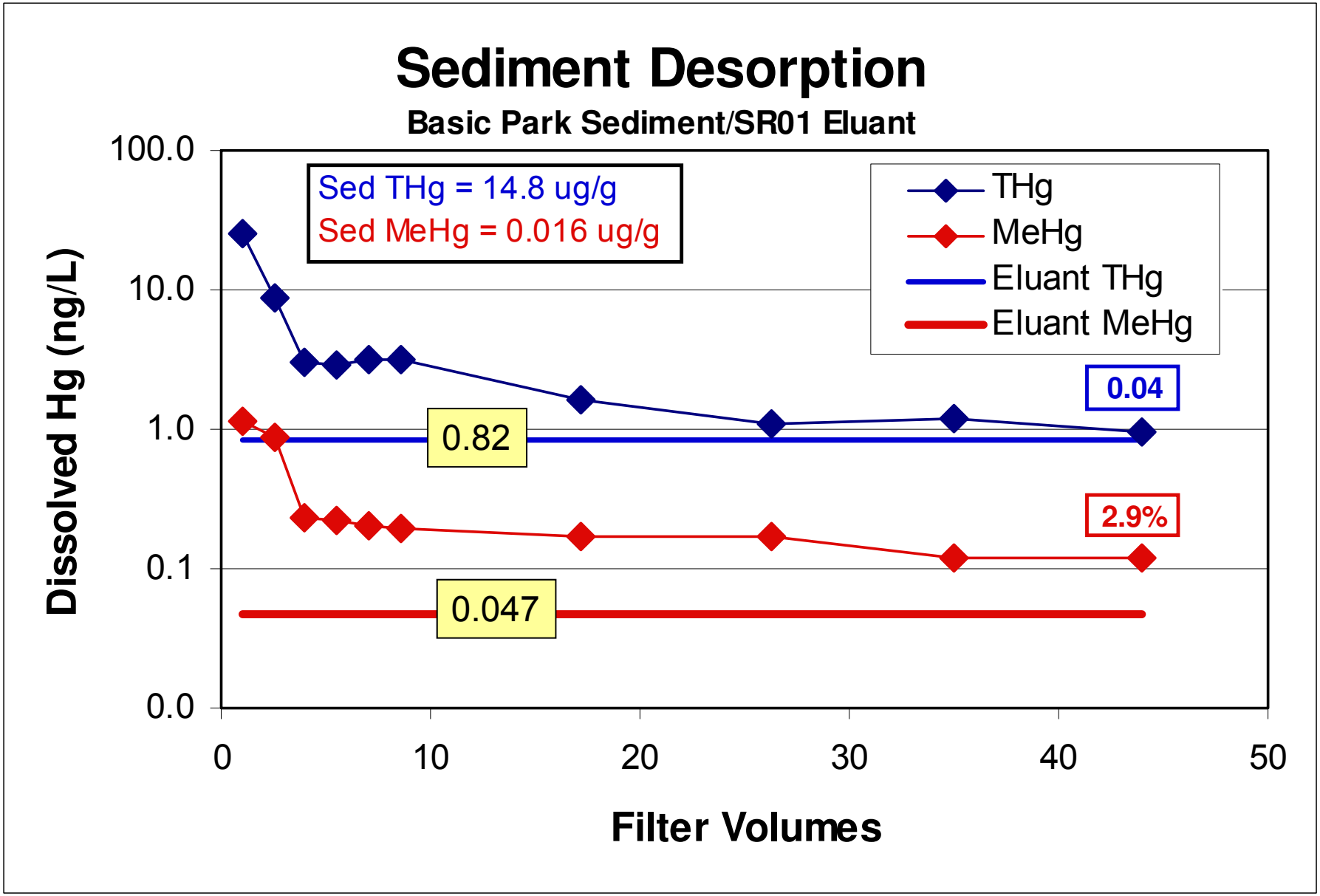
- What role does desorption of “pre-formed” MHg from sediments play in observed downstream increase in [MHg] in sfc water and rise in [MHg] in BFCs?
  - Partition coefficients for MHg lower than than for inorganic Hg but MHg still predominantly particle-associated.
  - Once formed could supply sfc water with filter-passing MHg even when favorable methylation conditions are absent.
  - Need to characterize kinetics of desorption vs methylation

MHg Filter Loading Extractions



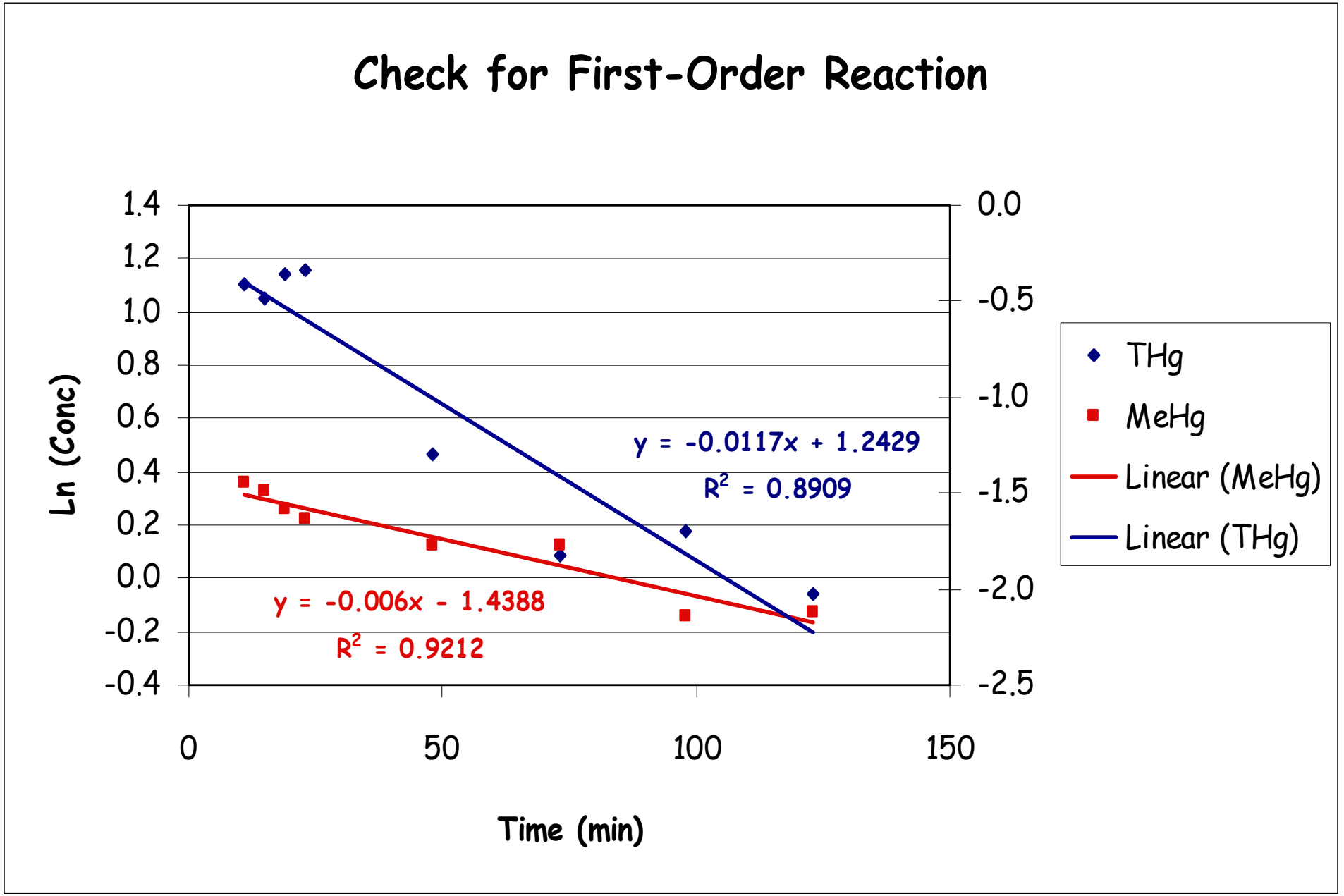
Filter Cut-away
Showing Sediment Layer




Sediment Desorption
Basic Park Sediment/SR01 Eluant
Sed THg = 14.8 ug/g
Sed MeHg = 0.016 ug/g
THg
MeHg
Eluant THg
Eluant MeHg
0.04
0.82
2.9%
0.047
Dissolved Hg (ng/L)
100.0
10.0
1.0
0.1
0.0
0
10
20
30
40
50
Filter Volumes

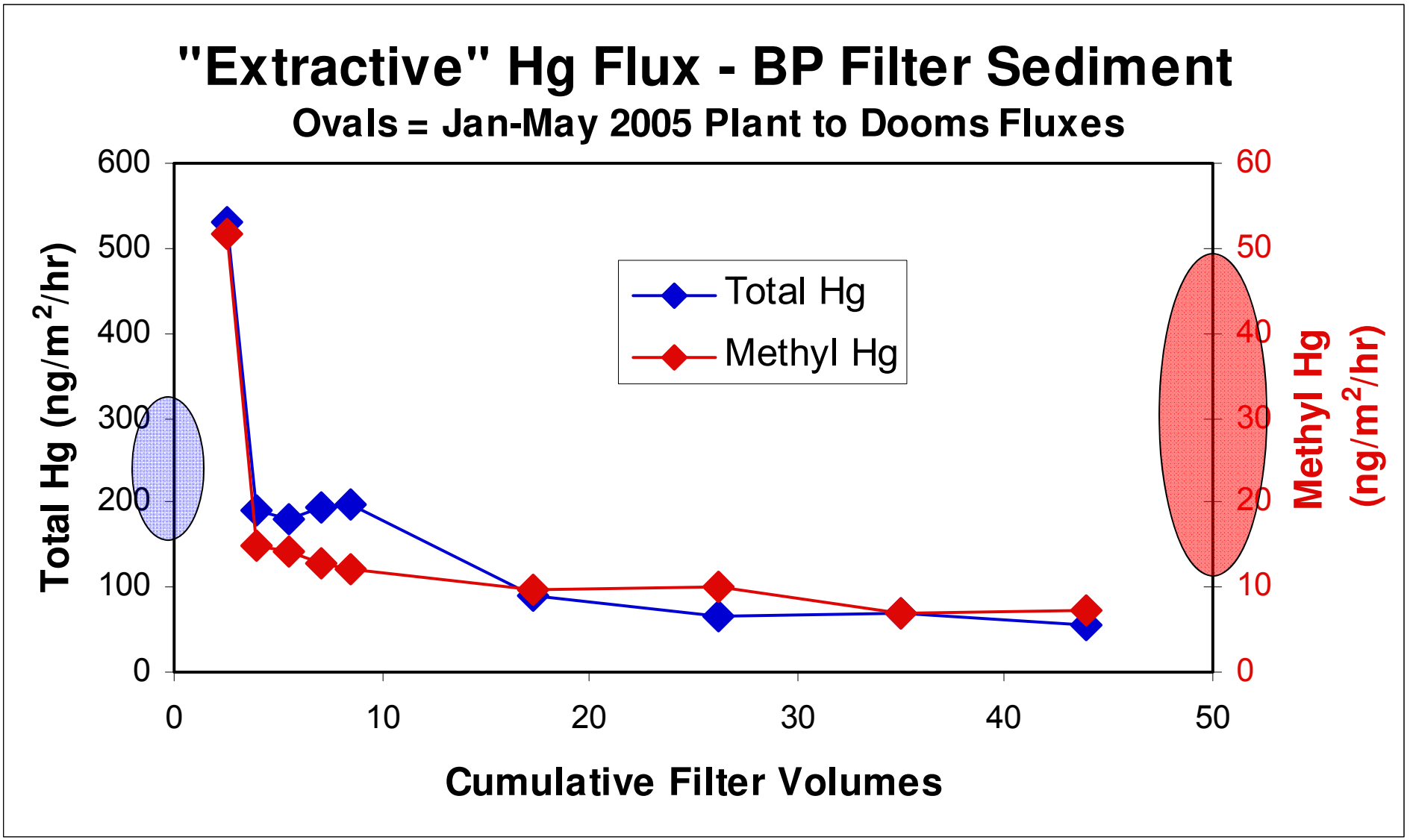
Methodology-Kinetic Analysis

- Consider both mechanistic and empirical kinetic models
  - mechanistic rate laws
    - zero-, first-, and second-order chemical kinetics
  - Parabolic diffusion equation
    - diffusion-controlled phenomena are rate limiting
  - Empirical equations
    - Elovich equation (heterogeneous chemisorption model)
    - Power function
- Only considered data for ≥ 4 filter volumes


Check for First-Order Reaction
Ln (Conc)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
0
50
100
150
Time (min)
y = -0.0117x + 1.2429
R2 = 0.8909
y = -0.006x - 1.4388
R2 = 0.9212
THg
MeHg
Linear (MeHg)
Linear (THg)

Conclusions

- First Order rate Model
  - k_1 = 0.0117 min^{-1} (16.9 d^{-1}) for FIHg
  - k_1 = 0.006 min^{-1} (8.6 d^{-1}) for FMHg
  - **$t_{1/2}$ = 1 hr for FIHg**
  - **$t_{1/2}$ = 2 hr for FMeHG**
  - Compare to typical methylation and demethylation rates
    - 1E-05 to 5E-02 d^{-1} in sediment and water column
  - These results suggest that desorption rates using background river water may be much faster than typical methylation and demethylation rates


"Extractive" Hg Flux - BP Filter Sediment
Ovals = Jan-May 2005 Plant to Dooms Fluxes
Total Hg (ng/m2/hr)
Methyl Hg (ng/m2/hr)
Total Hg
Methyl Hg
600
500
400
300
200
100
0
60
50
40
30
20
10
0
0
10
20
30
40
50
Cumulative Filter Volumes

Results Pending
(September 2008 studies)

- Repeated elution w/BPK sediment:
  - Free water removed from filter at start
  - First elution with BPK water then elution with SR01
  - Stop/start flow with both eluants
- Adsorption experiment with clean sediment and contaminated river water

Methyl Hg Desorption Indications (so far)

- Loaded filter – column leaching approach easy/fast to set up and operate
- Easy to impose “manipulations” like stopped flow, alternate eluants
- DO in freshly recovered slurries similar to in situ values (3-inch hyporheic)
- May be more a realistic “simulation” of river water flowing over sediment than at first glance
- Assumed to reflect predominantly desorption based on rates but this aspect needs further verification.