

Mercury Source Tracing and Mechanistic Source Studies

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October 2007

General Objectives

- Identify/rank contributions of Hg sources at Basic Park study reach (RRM2)
- Define mechanism(s) by which Hg in bioavailable form is released from floodplain soils and bed sediment.
- Expand/refine understanding of Hg source(s) at Plant reach (RRM<0.5)

Rationale for Selecting Basic Park Reach

- NRDC Ecostudy location
- LIDAR bank erosion study site
- Presence of near-bank elevations in THg and MeHg in surface water
- Ease of access/publicly owned
- Within river continuum of max rate of increase in “dissolved” Hg

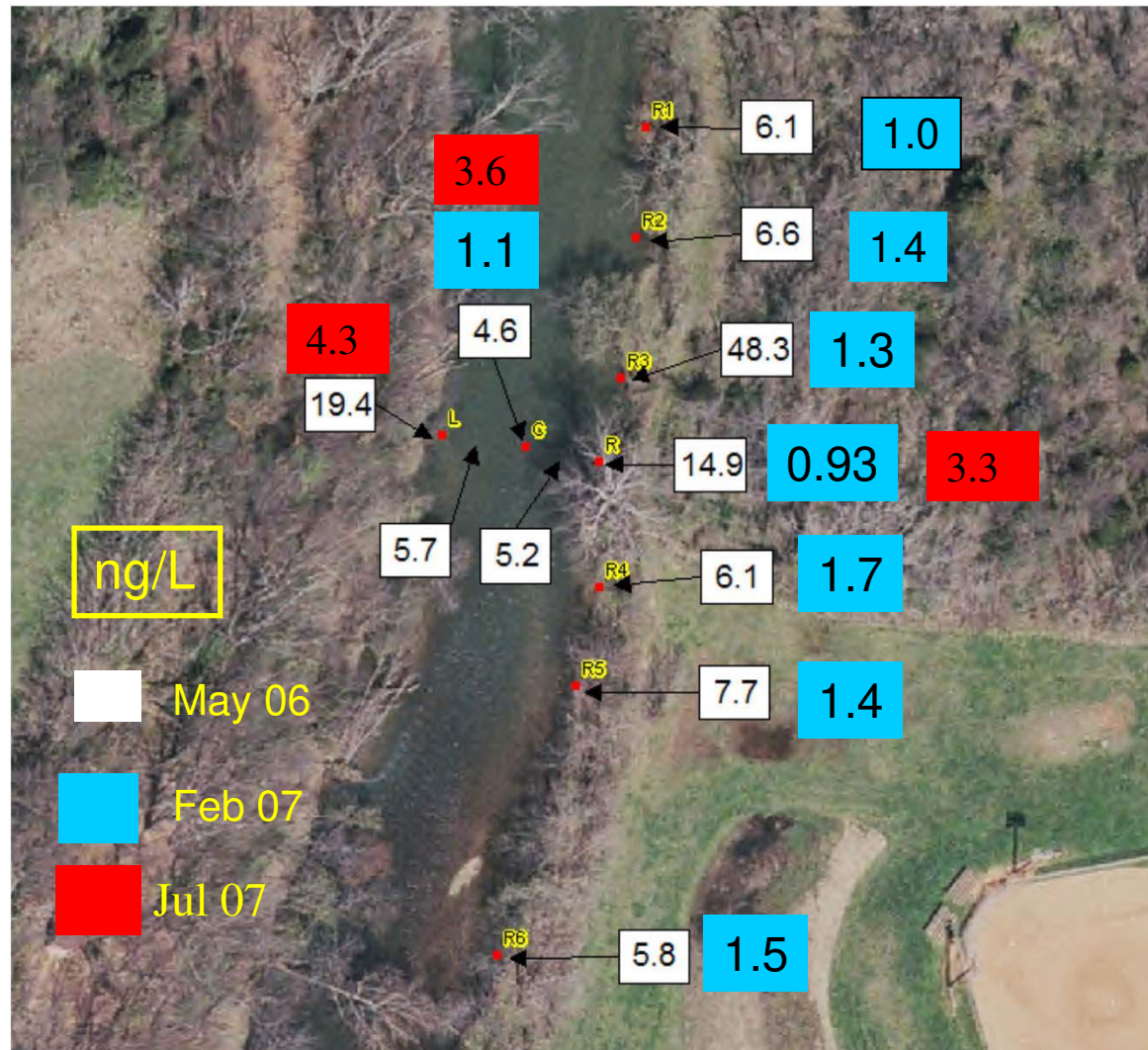
- Potential Hg sources at Basic Park
 - Eroding bank/floodplain soils
 - Fine-grained near-bank sediments/porewater
 - Gravel bar sediments/hyporheic water
 - Alluvial groundwater

Basic Park Activities

- Close-interval sfc water, sediment and soil sampling.
- Close-interval porewater (muds) and hyporheic (gravel/sands) water sampling.
- Laboratory extractions of soils and sediment for speciation.
- Benthic flux measurements and amended flux measurements.
- Alluvial groundwater investigation.

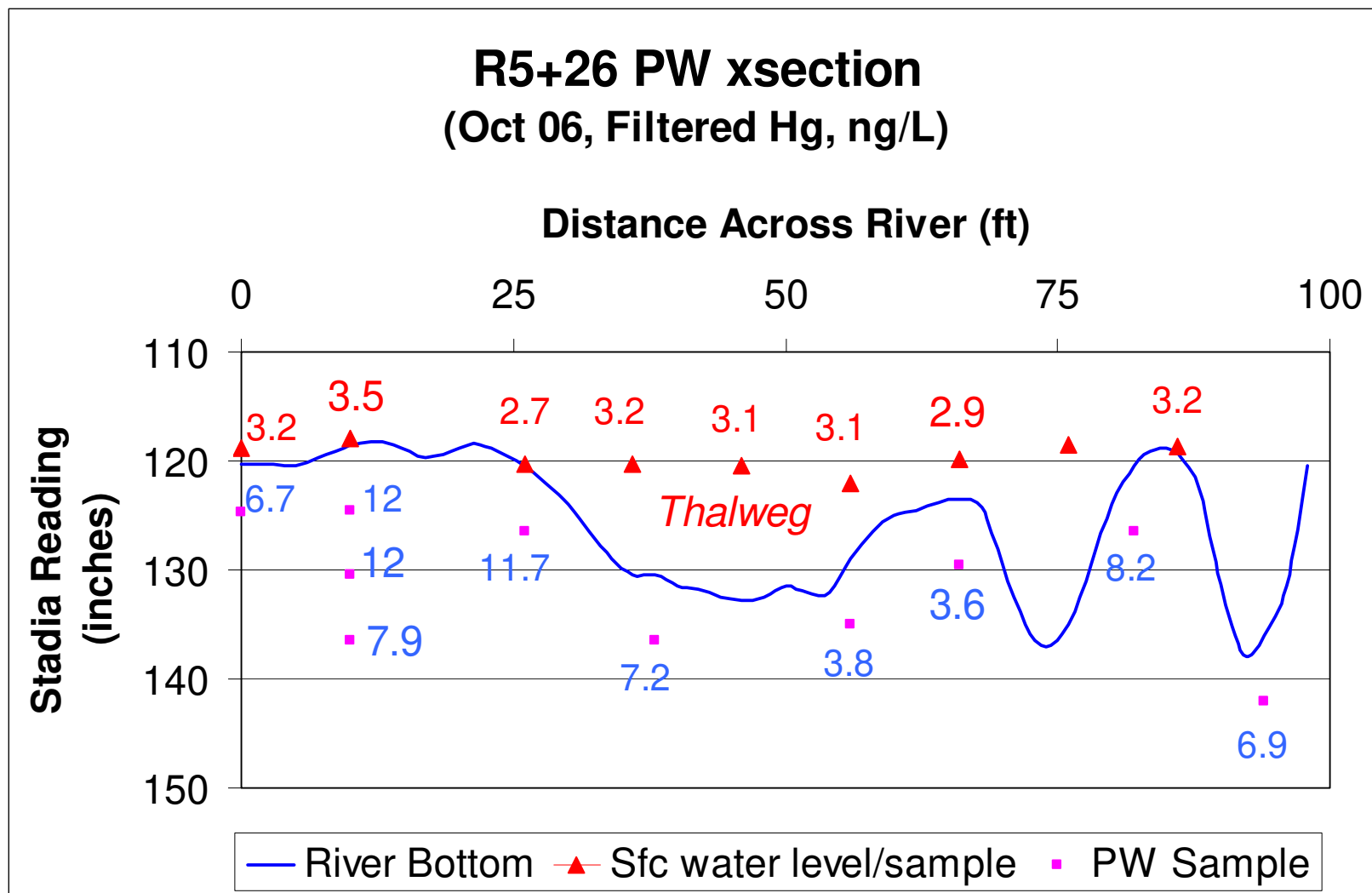
Close-Interval Sfc Water Results

Near-Bank “Anomaly” Seasonal or Loss of LWD?



Transverse Close Interval

October 2006



Porewater/Sediment Extractions

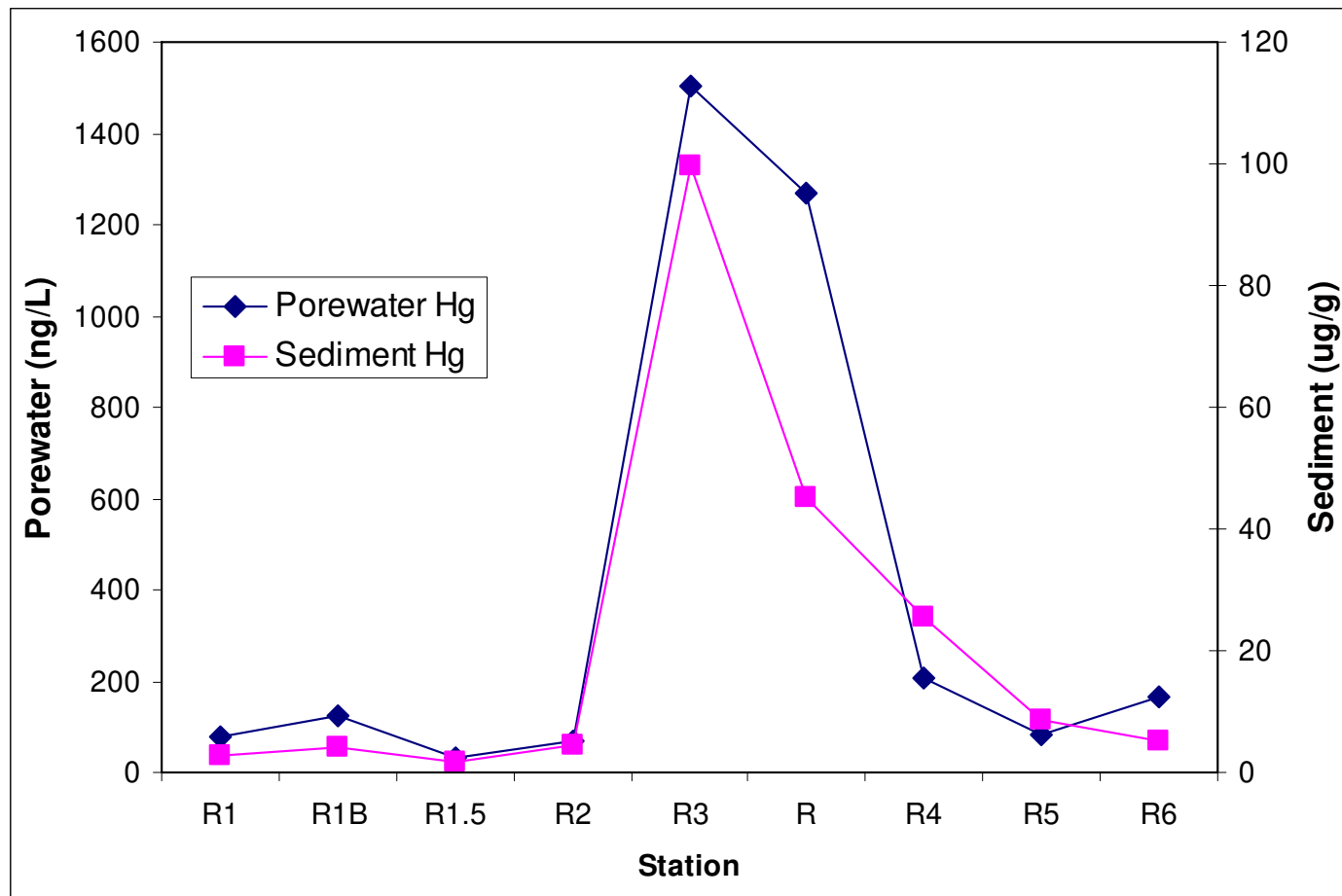
Centrifuged Porewaters and Sediments

February 2007



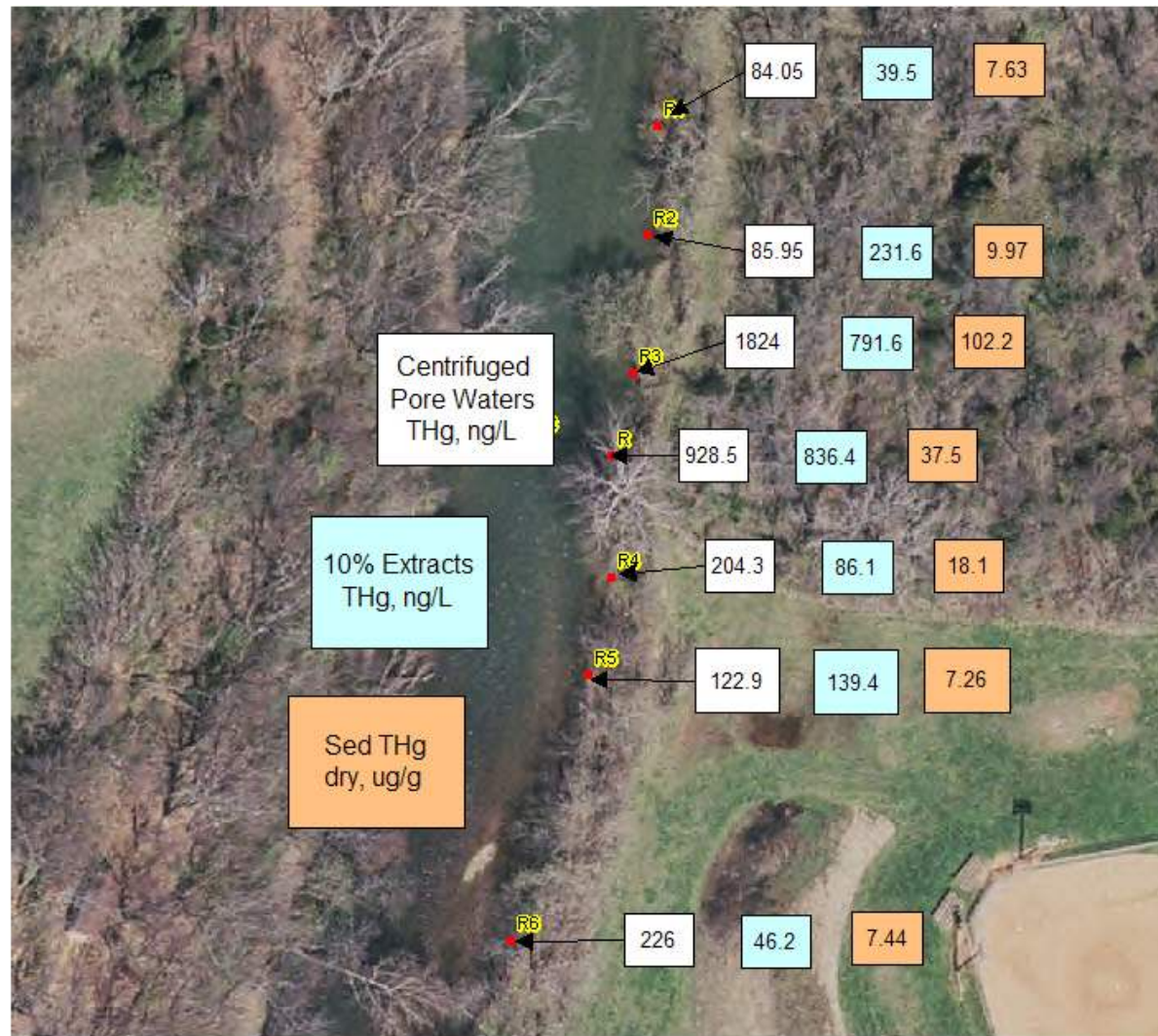
Centrifuged Porewaters and Sediments

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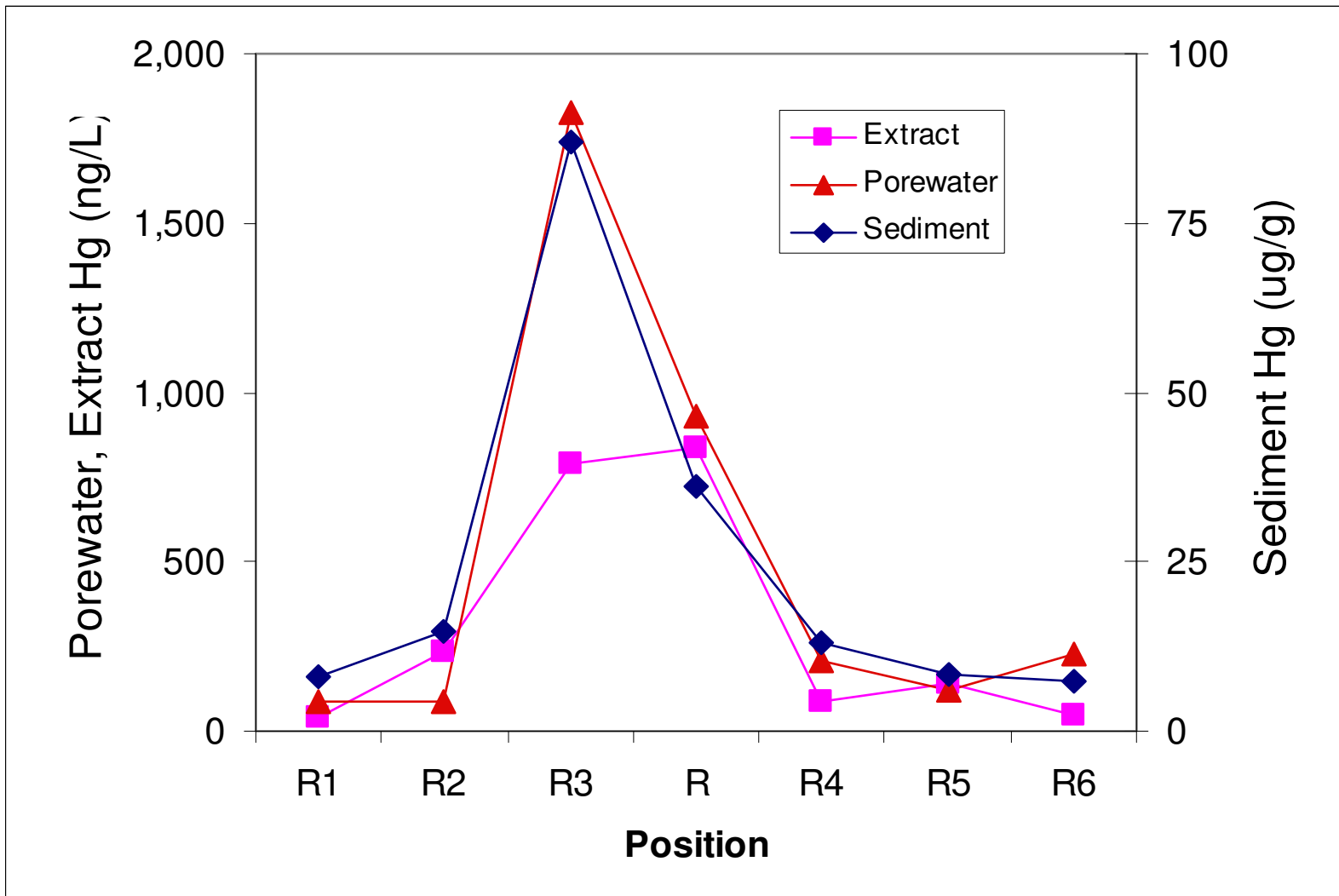
Centrifuged Porewater, Sediment and 10% Extract

April 2007



Centrifuged Porewater, Sediment and 10% Extract

April 2007



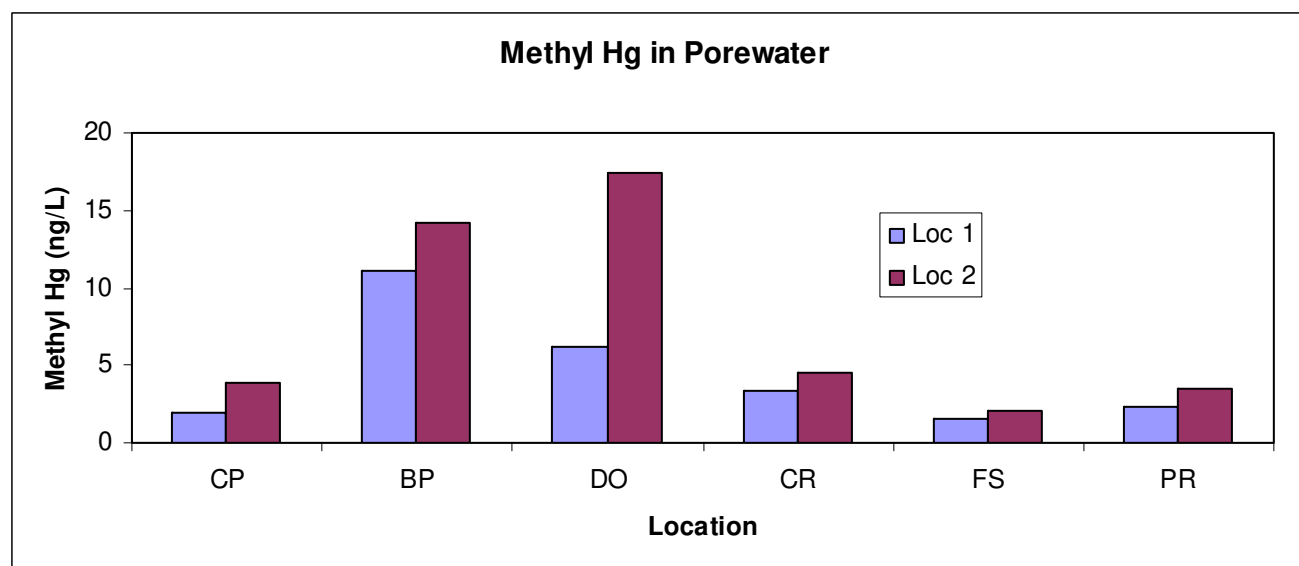
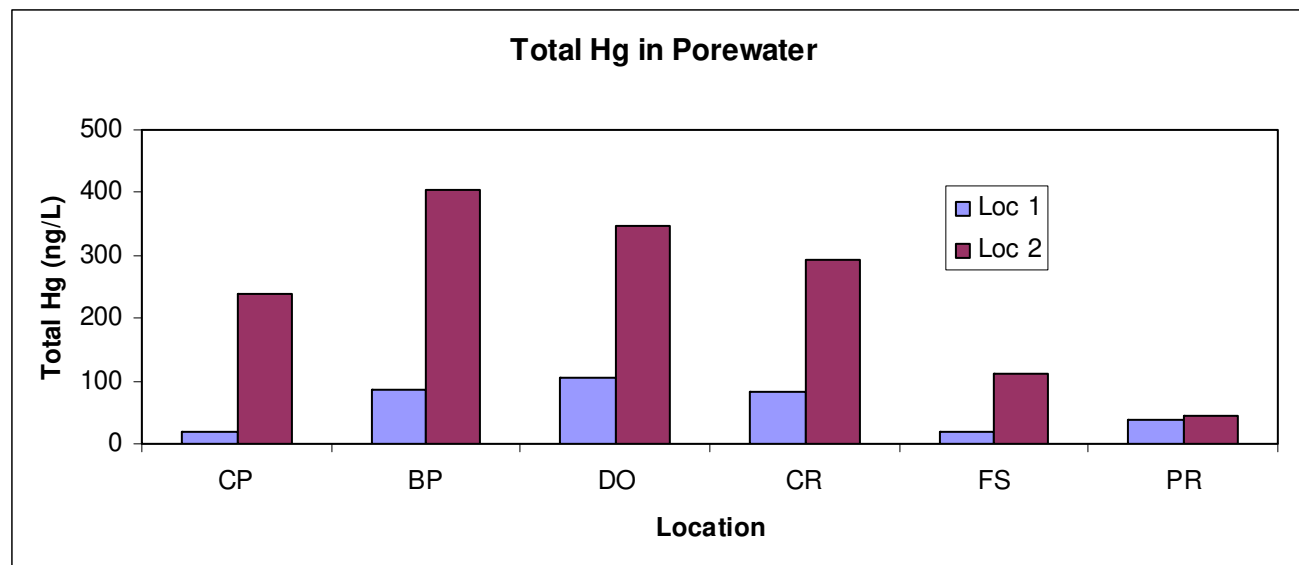
Porewater Beyond Basic Park

RRM 0 - 24

Locales

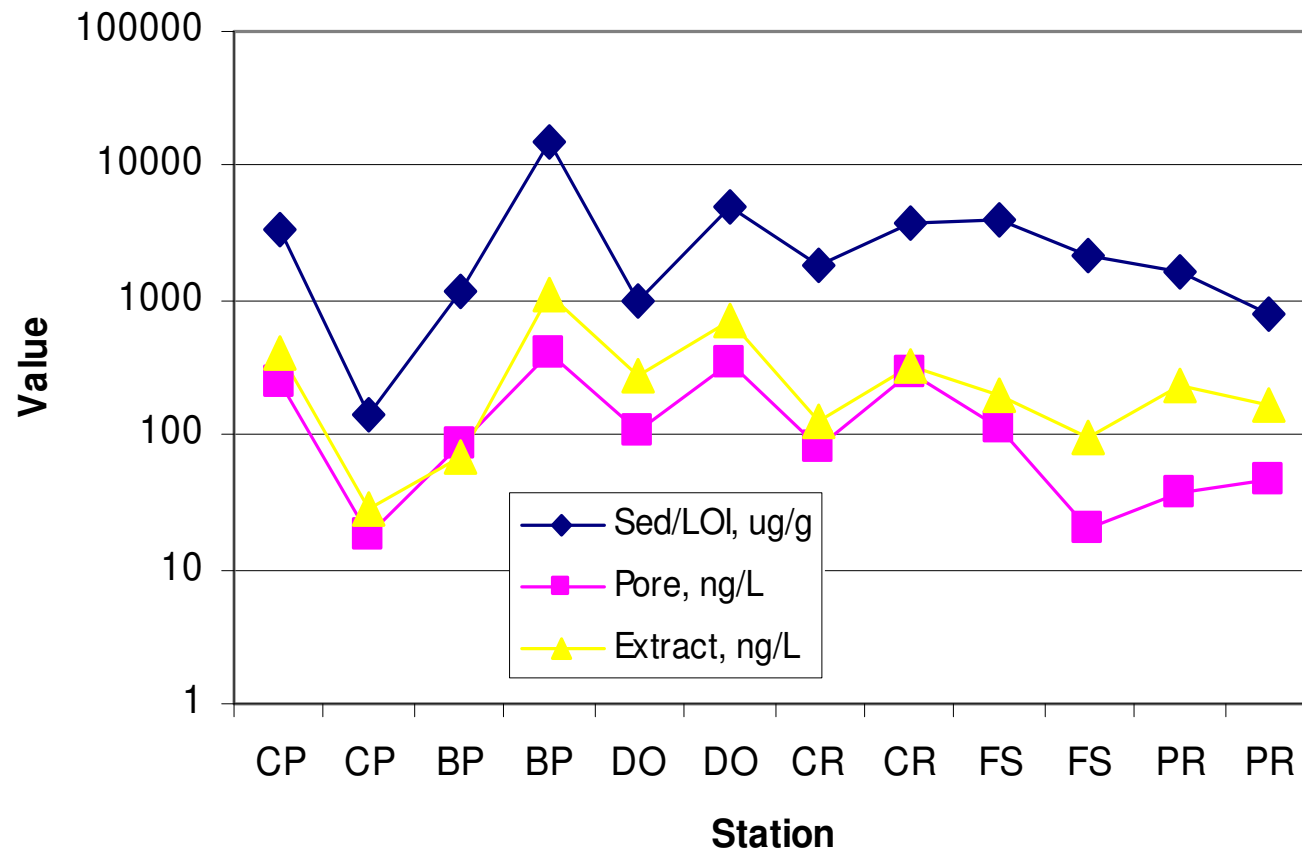
2 Sample Points Each - Top 2 CM

- Constitution Park (CP)
- Basic Park (BP)
- Dooms - Holsinger Farm (DO)
- Crimora (CR)
- Forestry (FS)
- Port Republic (PR)



Porewater, Sediment and 10% Extract

July 2007



Porewater and 10% Extractions

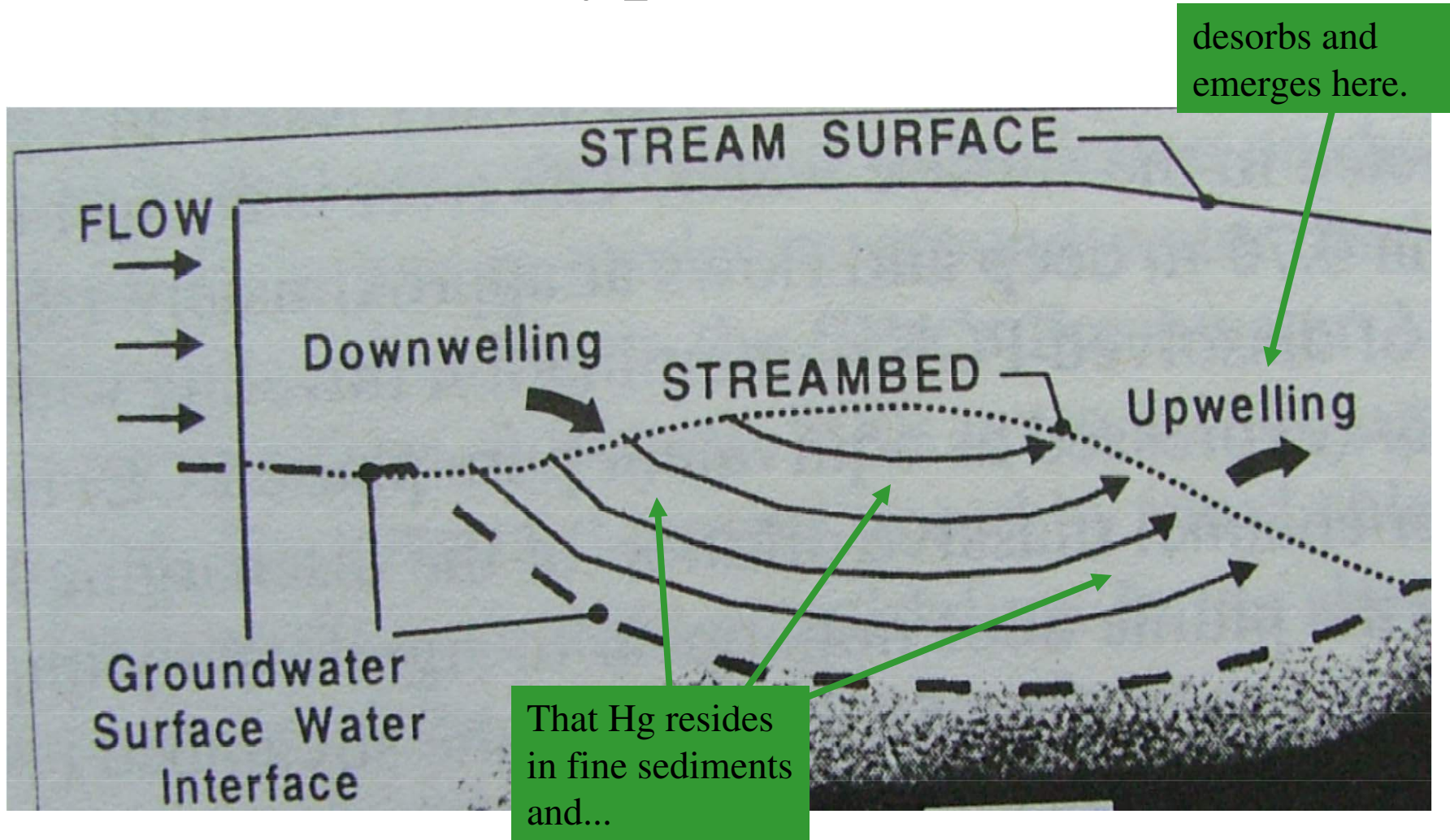
Whole River Indications

- Wide variations within each river mile locale
- Downstream declines in THg and MHg more dramatic in pore waters than in surface waters
- Extractions and pore waters track each other well
- LOI-adjusted sediment THg may be a good surrogate for porewater THg?

Gravel Bars

- Prominent feature of many reaches
 - Small submerged “bumps”
 - Mid-channel islands
 - Terminus of some pools (riffle)
- Well-developed example at Basic Park
- Elevation changes over short lengths foster hyporheic exchange with surface water.

Hypothesis



Sampling Locations



January 07

April 07



Additional Transects April



MeHg Survey in May/June 07

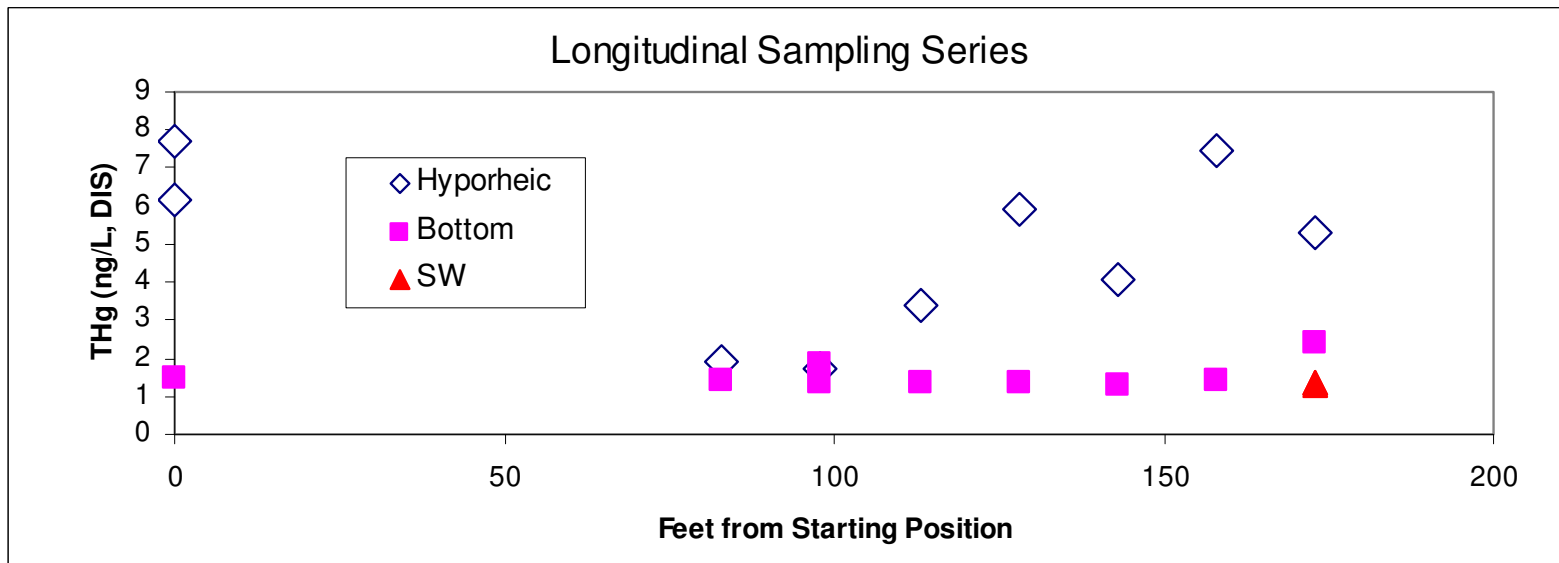
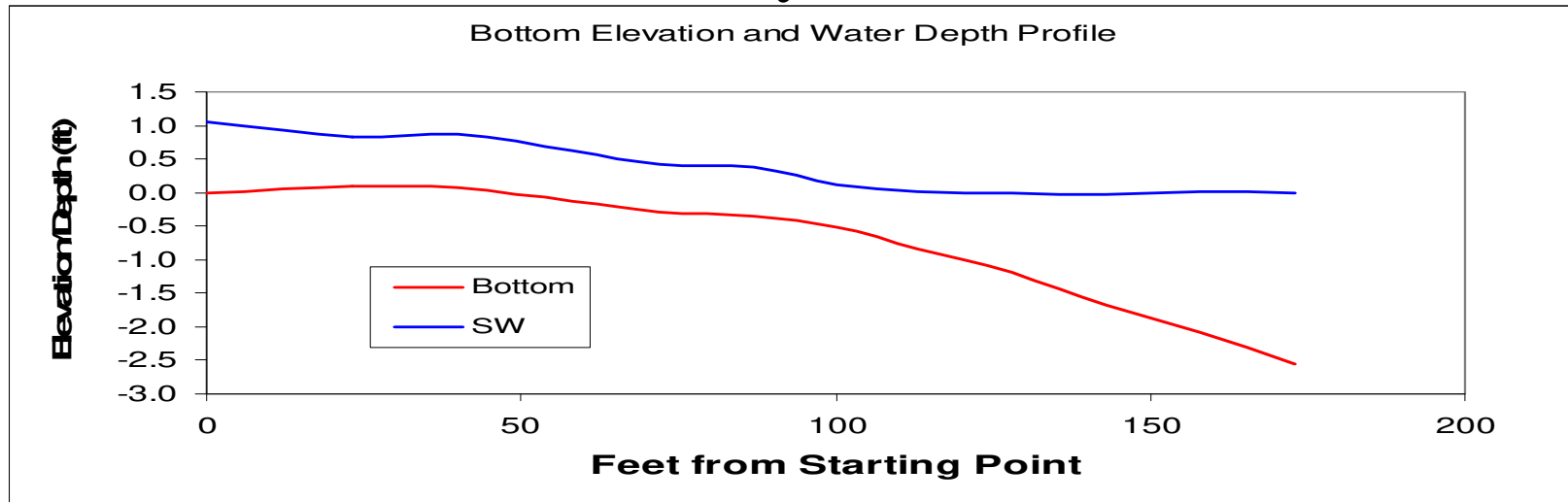


Equipment



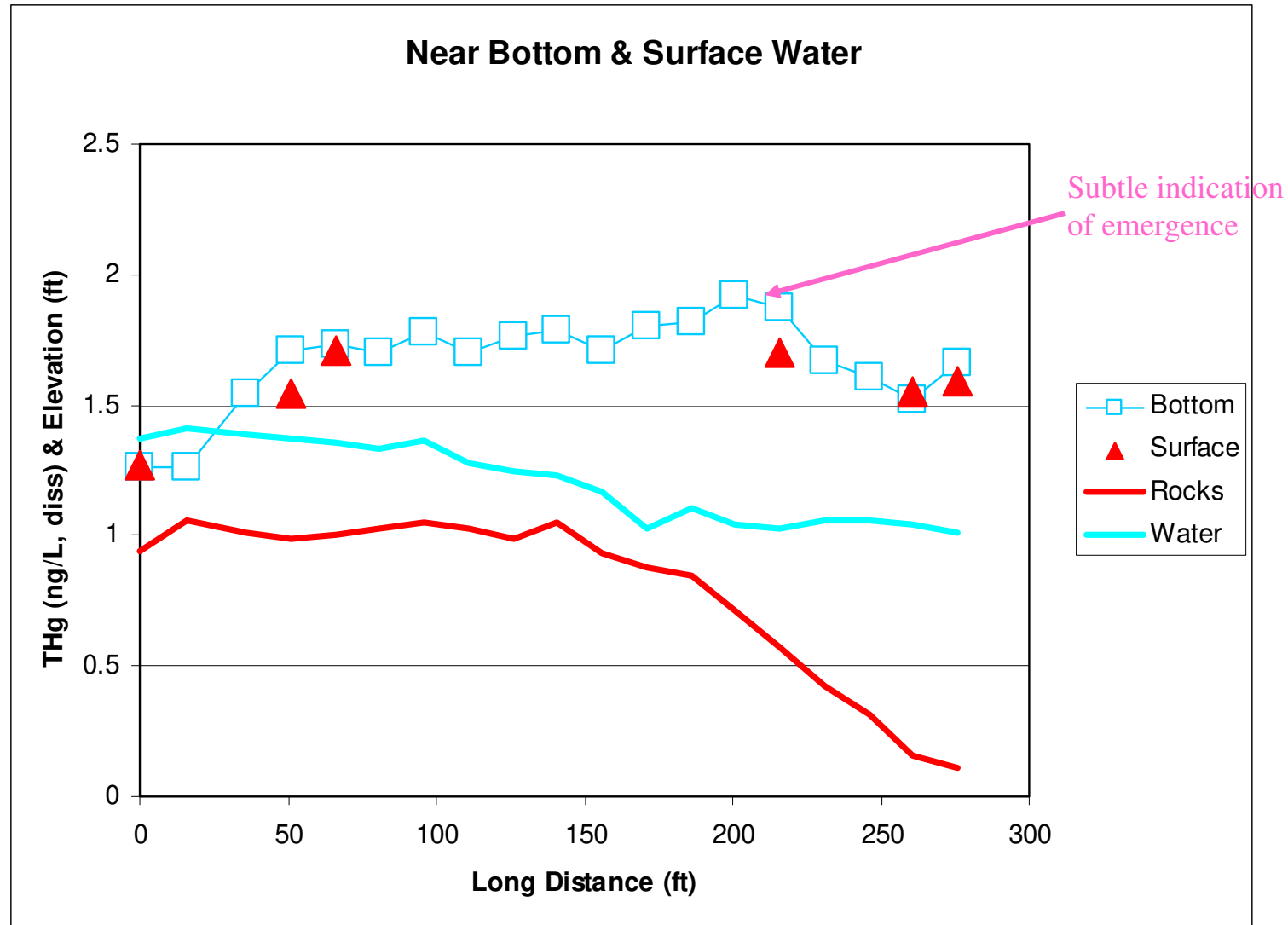
Basic Park Gravel Bar

January 07



Longitudinal Results April 07

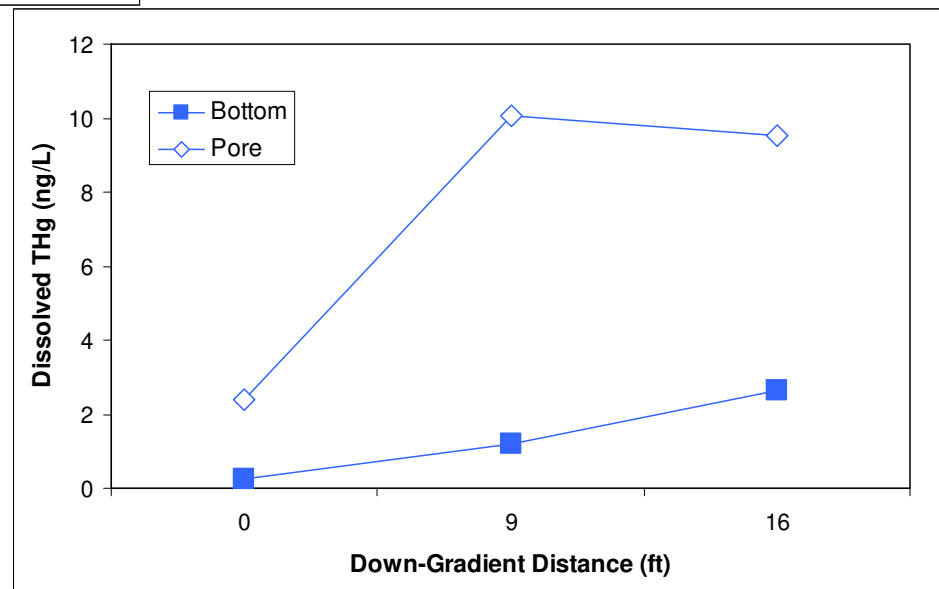
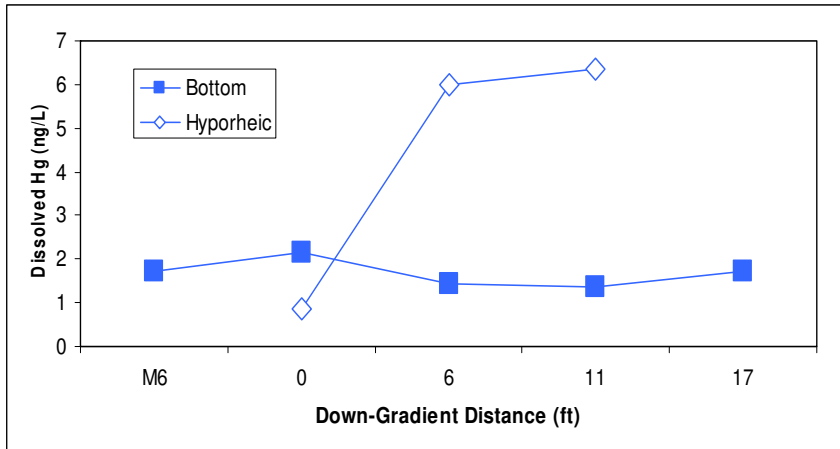
(No Hyporheic Sampling)



April 2007

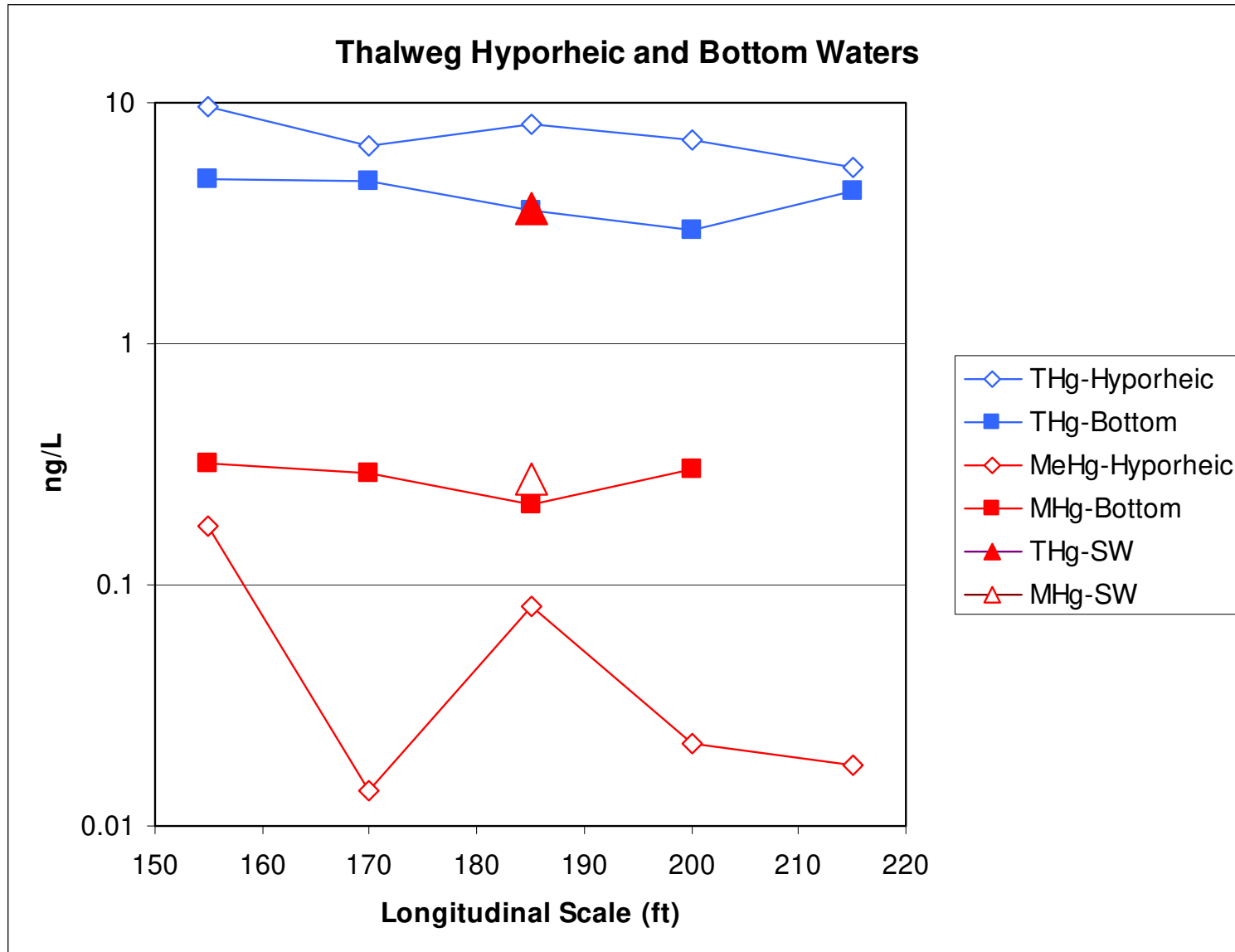


Side Channel Bars



Basic Park Gravel Bar

May 2007



Sub-Gravel Hyporheic Waters

- Sub-gravel total Hg all higher than co-located near-bottom water total Hg.
- MeHg results exactly inverted!! All sub-gravel MeHg values were lower than co-located near-bottom water MeHg
- At 6 inches below gravel surface, did we sample beneath any methylation zones?

Basic Park Side Channel

(Like Crimora and Mill Races??)



July 19, 2007, no estimate of flow

SR thalweg: THg = 2.44 ng/L, MeHg = 0.159 ng/L

Inlet: THg = 2.46 ng/L, MeHg = 0.227 ng/L

Outlet: THg = 3.22 ng/L, MeHg = 0.716 ng/L

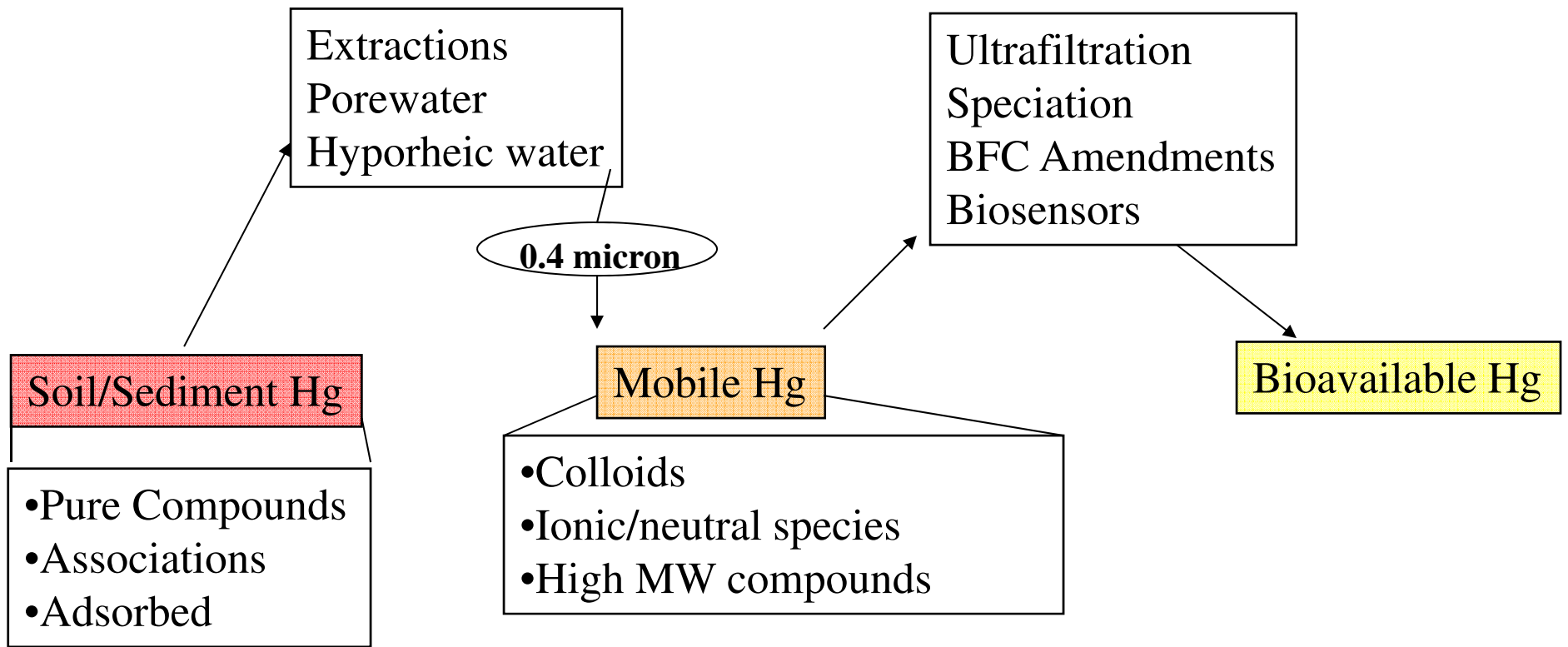
% Change: THg = +131%, MeHg = +315%



Special Extraction, Ultrafiltration and Speciation Studies

Objectives

- Determine extent and nature of desorption of Hg from bank soil and bed sediments.
- Measure or estimate speciation of desorbed forms (molecular weight, gaseous, reactive).
- *Determine if bank soil extracts stimulate methylation (using BFC as in situ lab)*



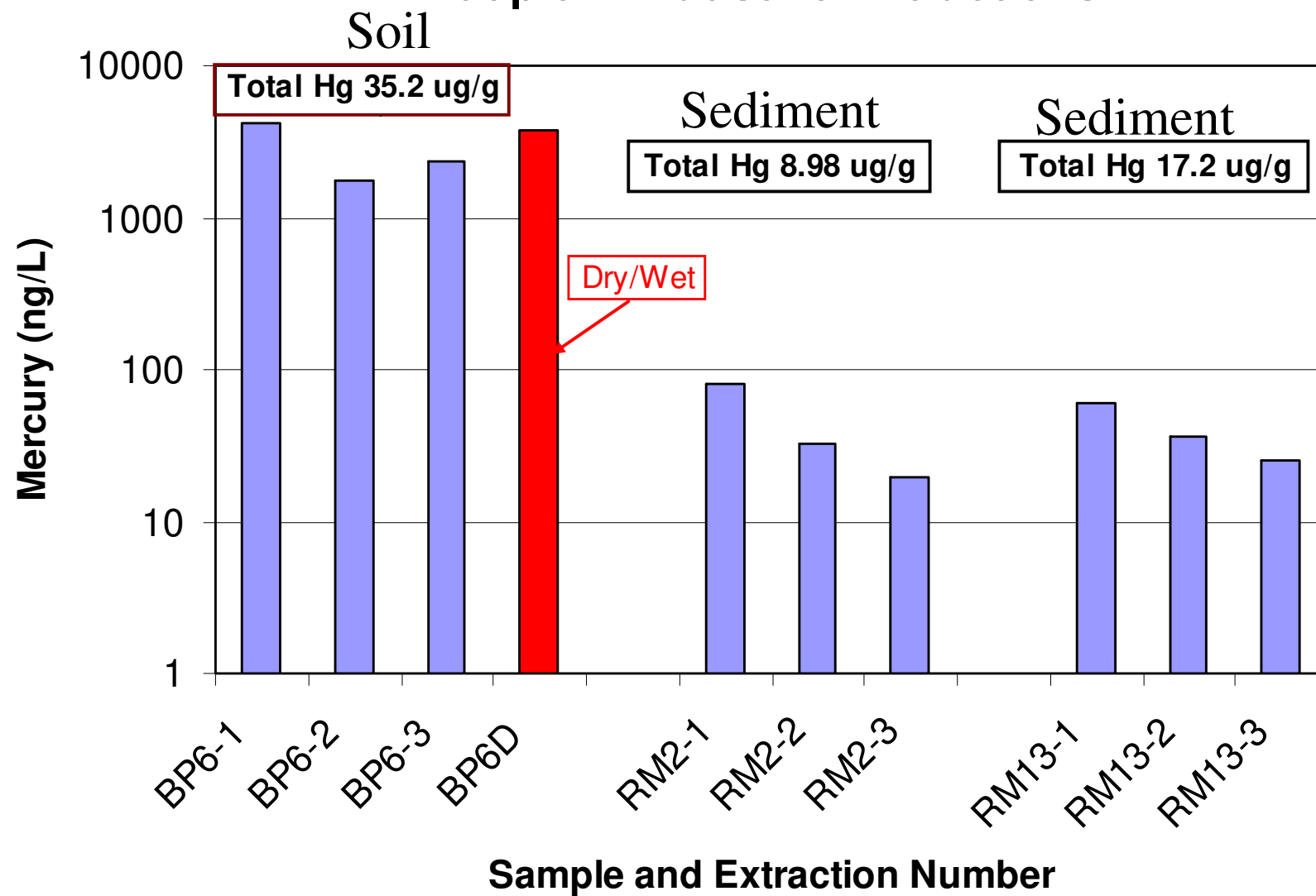
Exhaustive Extractions and Speciation

- 4 grams of soil/sediment in 40 mL of SR01 water (<1 ng Hg/L, SC 150-200 μ S/cm).
- Mix by rotation (30 rpm) for 4 hrs.
- Filtration w/0.4 micron pore size filter.
- Repeat “x” times using same sample.
- Measure DGM, “reactive” and <5000 MWCO fractions.

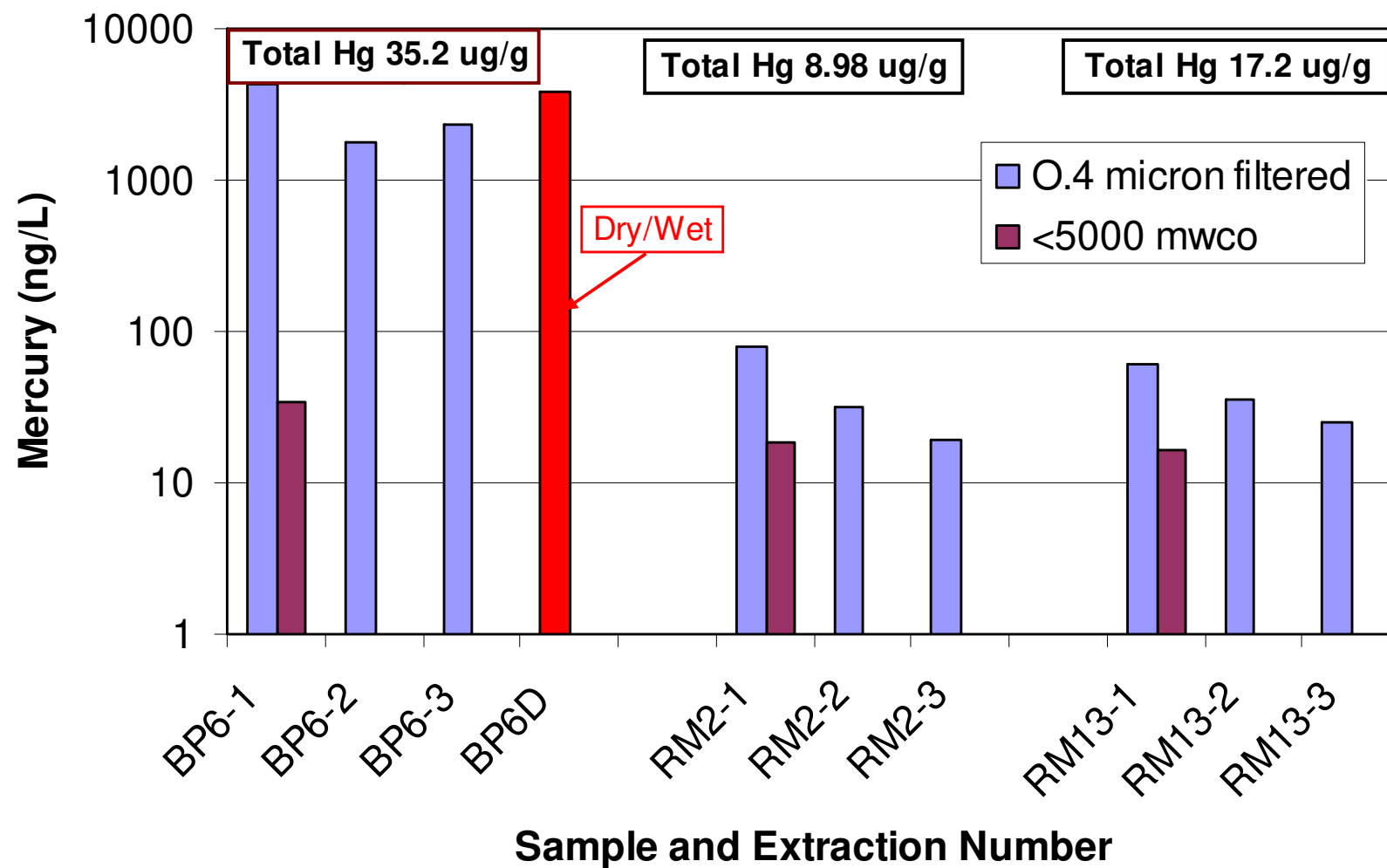
Speciation

- DGM=Dissolved Gaseous Hg,
 - Likely Hg(0)
 - Not bioavailable but easily oxidized to Hg(II)
- Reactive=Easily reducible to Hg(0) with tin
 - Likely inorganically complexed Hg(II), incl Hg²⁺
 - Highly bioavailable (but some debate)
- <5000 MWCO=Low MW compounds
 - Likely inorganically complexed Hg(II) and simple organic Hg complexes, e.g., acetate
 - Bioavailability undetermined

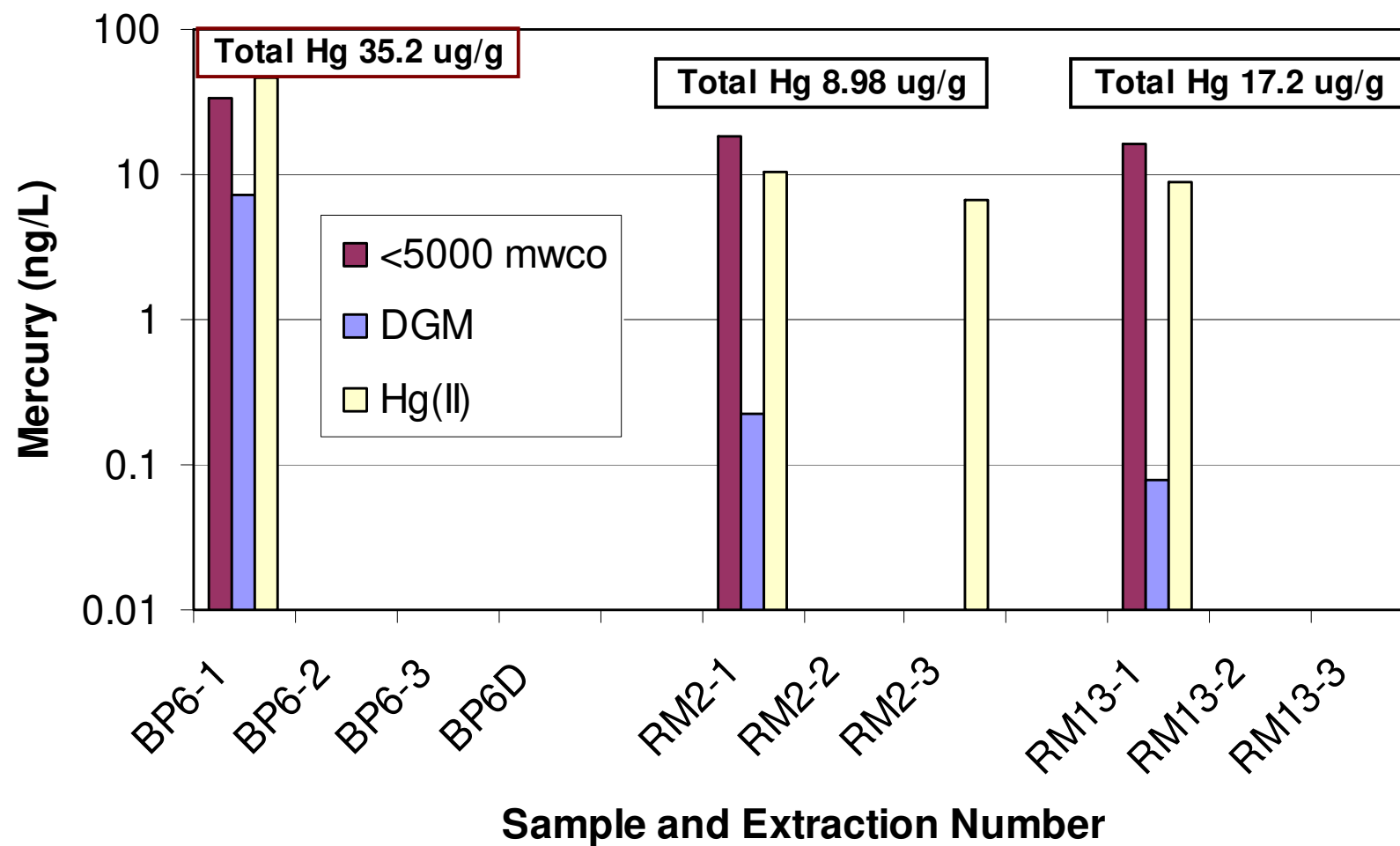
Multiple Exhaustive Extractions



Multiple Extractions and Ultrafiltration



Multiple Extractions, Ultrafiltration and Speciation



Indications (so far)

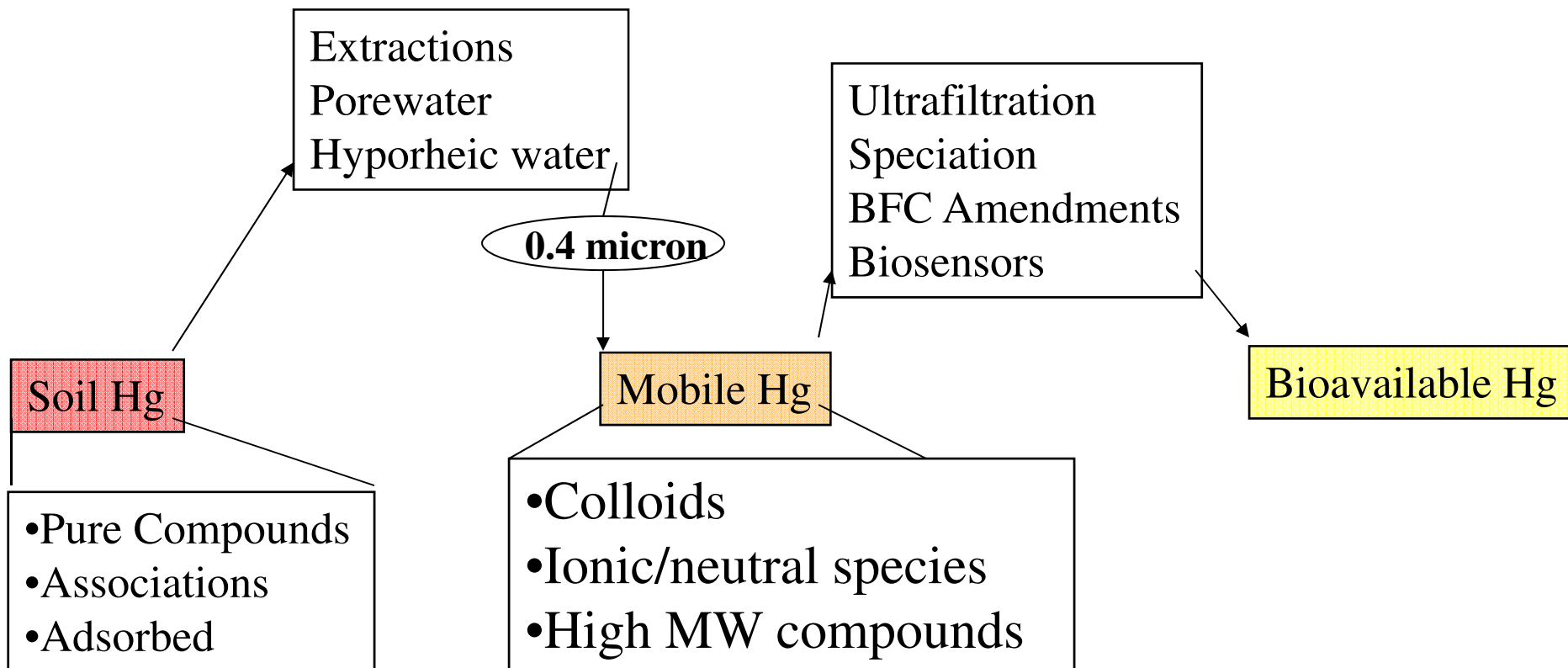
- Release patterns from both soil and sediments suggest “exchange” reaction, dissolution of sparingly soluble compound or presence of “colloid-associated” Hg.
- Much of the Hg extracted from soil and sediment appears to be “high molecular weight” (>5000 MWCO).
- DGM [Hg(0)] detectable but very small fraction.
- Hg(II) “similar” to <5000 MWCO, as might be expected.
- Hg(II) in <5000 MWCO fraction increases with successive extractions (removal of DOC??).

Future Work

- Use Rutgers microbial biosensor to evaluate “bioavailability” of Hg in soil/sediment extracts.
- Using soil extracts and soil slurries to amend BFCs.

Amended Flux Chambers

1st Chemical Amendment Experiment Attempted on SR



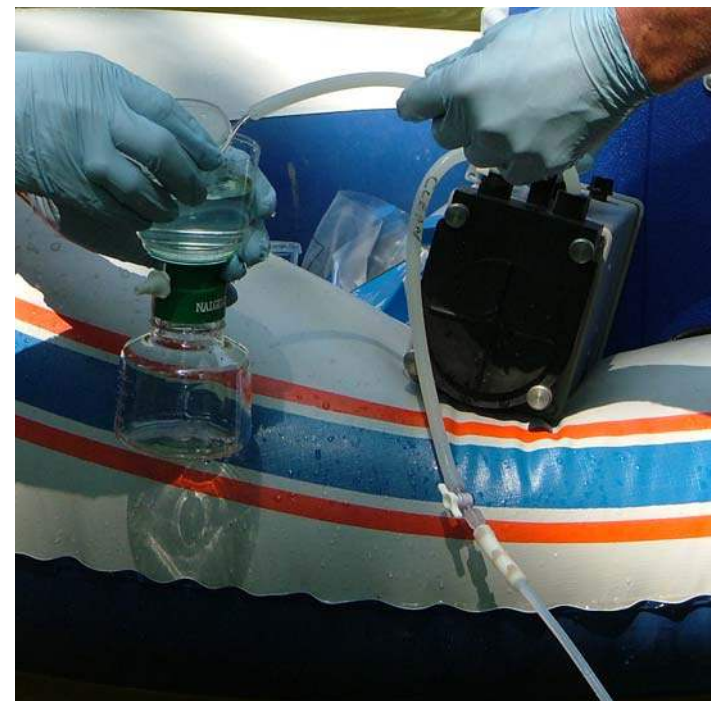
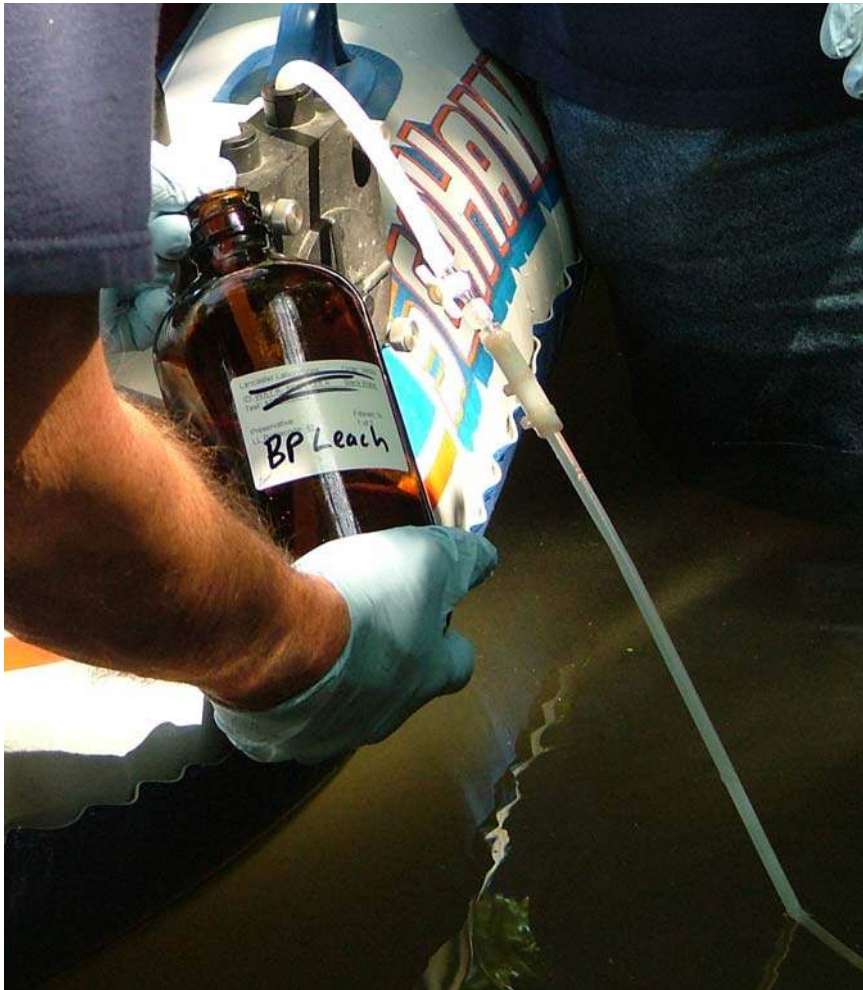
Purpose of Experiments

- Hypothesis: A step increase in dissolved THg (or in sediment THg) in a MHg production locale will result in a measurable step increase in MHg production within 4 to 24 hours. And the converse.



Multi-Use Pump

- Amendment Injection
- Sampling
- Filtering



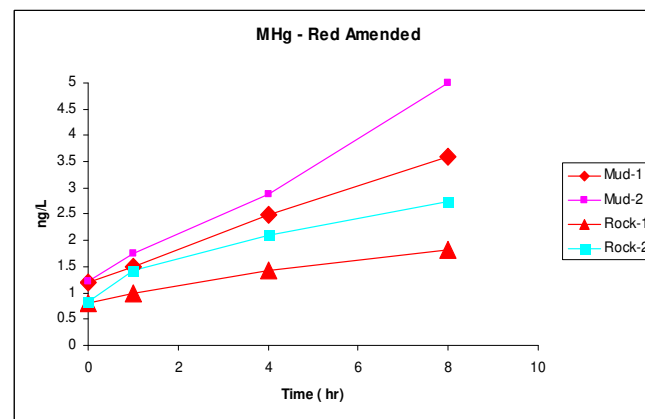
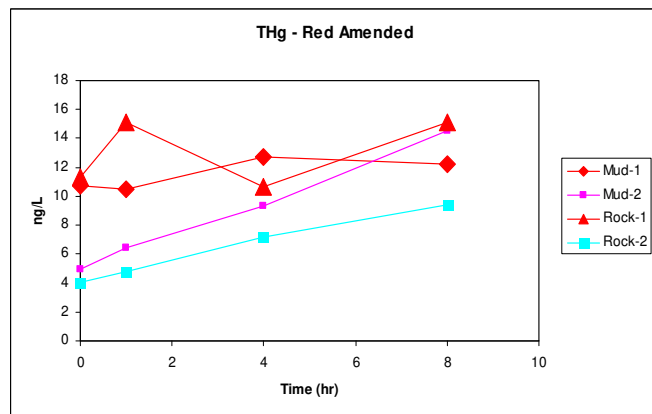
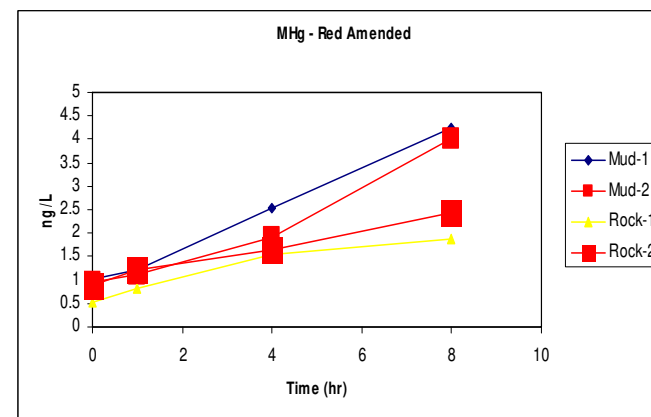
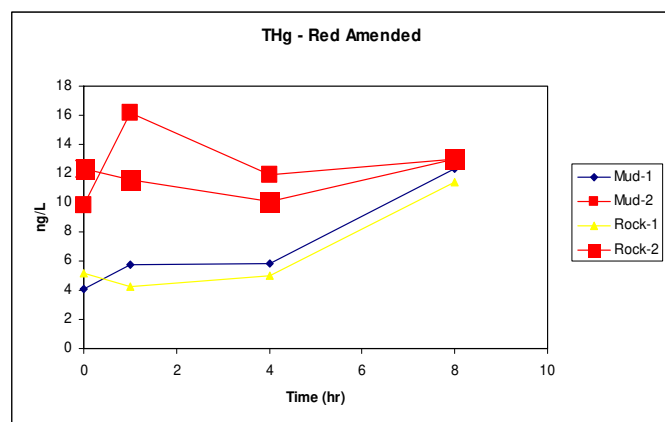
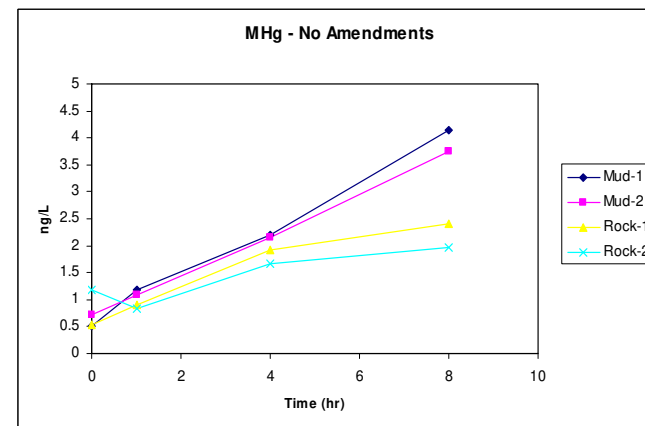
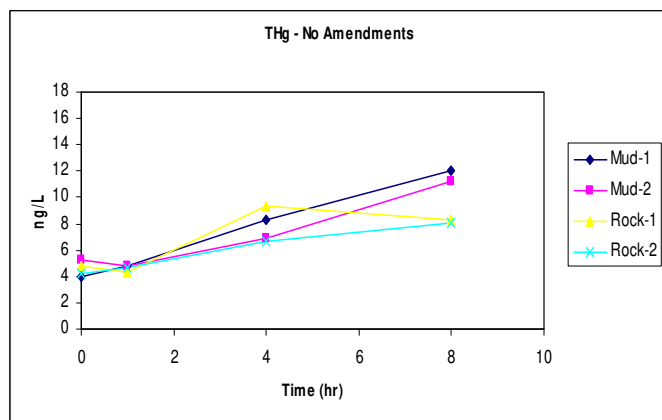
Experimental Design

July 2007

	Mud-1	Mud-2	Rock-1	Rock-2
Day-1	Natural	Natural	Natural	Natural
Day-2	Natural	Amended	Natural	Amended
Day-3	Amended	Natural	Amended	Natural
		Time = 0		
		1 hr		
		2 hrs		
		4 hrs		
		8 hrs		

Amendment

- Soil from elevated (Hg) layer of R4 bank
- Filtered water from SR-01 (Lyndhurst Ave bridge)
- 10% slurry shaken for ~ 2hrs
- Centrifuged and decanted
- Filtered at 0.45 micron
- Submitted to lab for THg/MHg
- Result: ~ 680 ng/L THg & ~ 0.46 ng/L MHg
 - May 06, Ecostudy, RRM2.0, dissolved: ~ 2.5 & 0.2
- Injected 375 ml into 8000 ml chamber, should have produced a ~ 32 ng/L increase in THg in chamber



Amended Flux Indications

- Results regular and “well-behaved”
- Much of amendment “disappeared” quickly
- Amended THg remained constant - reason?
- No significant effect on MHg flux
 - within 8 hr time frame
- No effects transferred from day to day
 - returned to normal overnight

Amended Flux Questions

- Induction period > 8 hrs?
- Would more/higher amendments give higher THg, or is sediment controlling?
- Is THg quickly attaching to sediment and walls?
- Is dissolved THg in SW not controlling MeHg production?
- Is porewater THg controlling MeHg pproduction?

September 07 Experiments

- Repeated base cases - 2 mud chambers
- Doubled (at least) the amendment of THg
- Amended with large volume of Lyndhurst water (low Hg)
- Amended with slurry of elevated bank soil from Basic Park R-4
- Ran all cases for 24-25 hours, overnight
- Tracked DO

Alluvial Groundwater

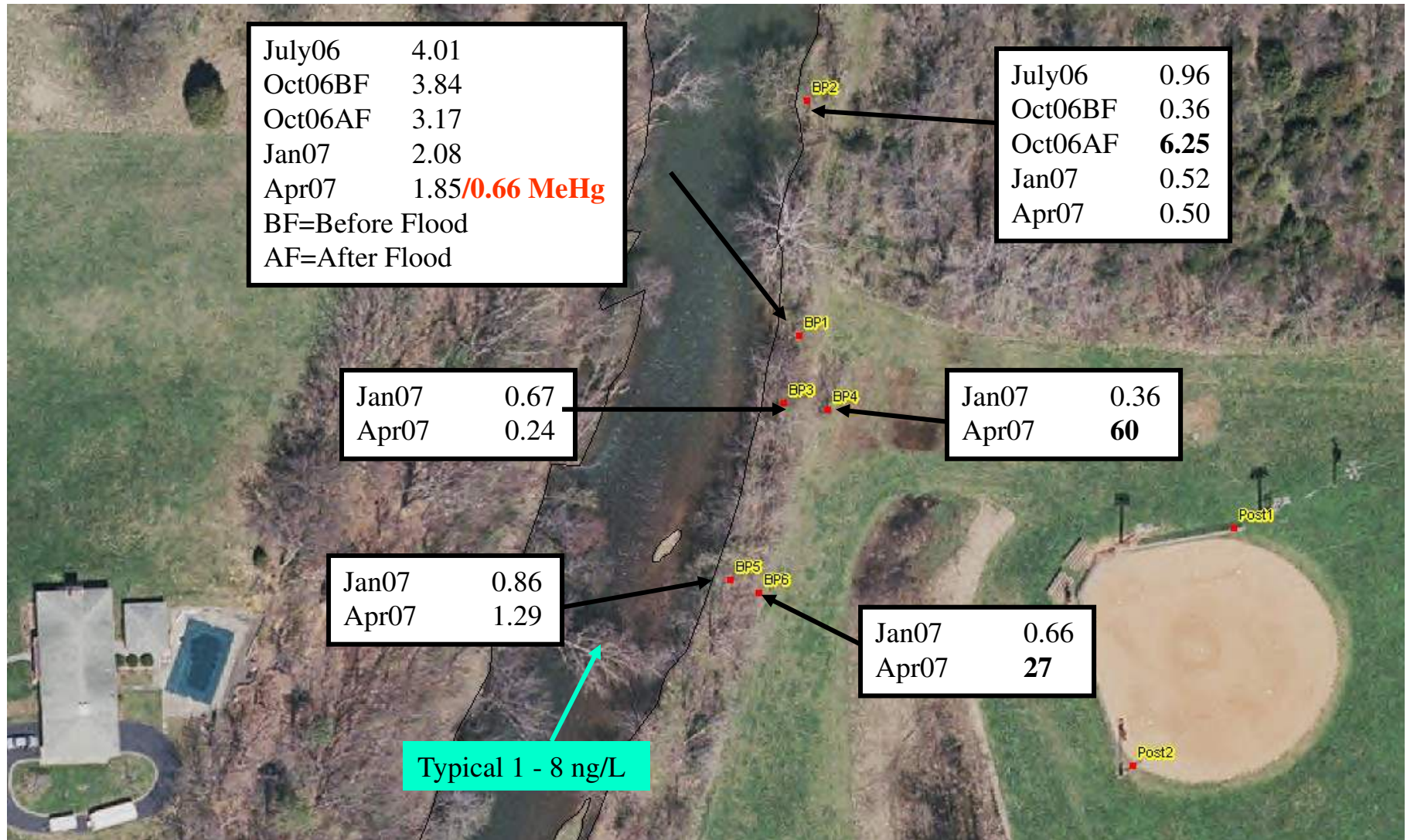
Basic Park

Well Locations



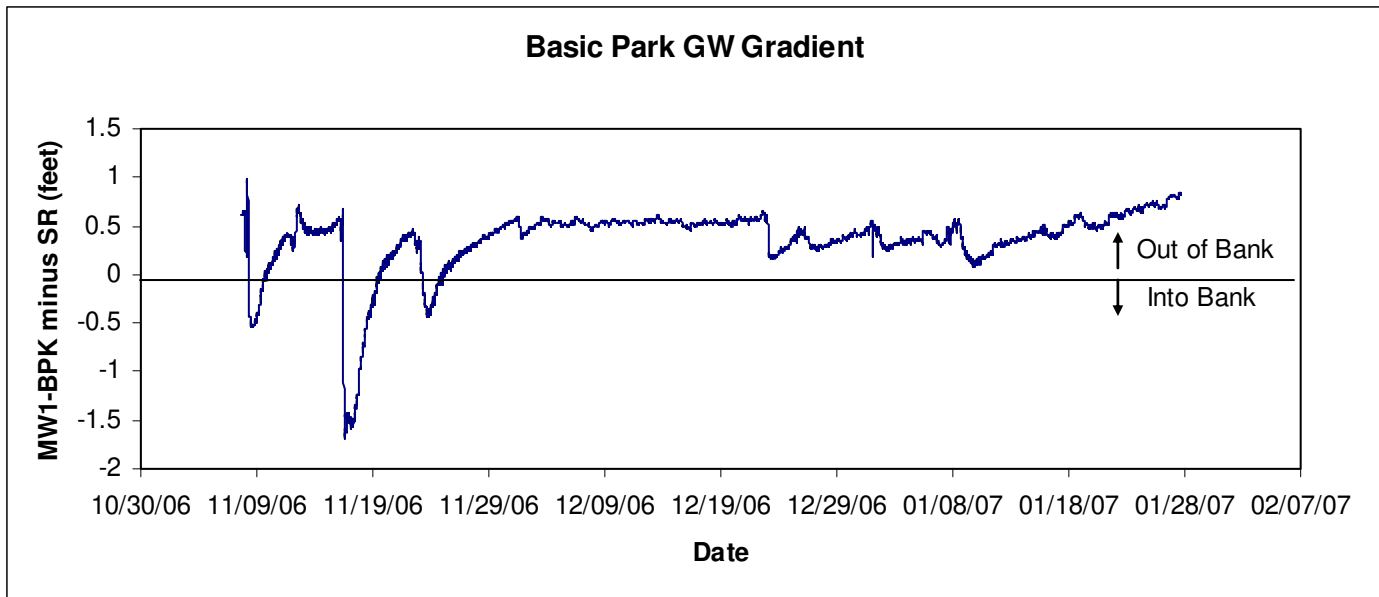
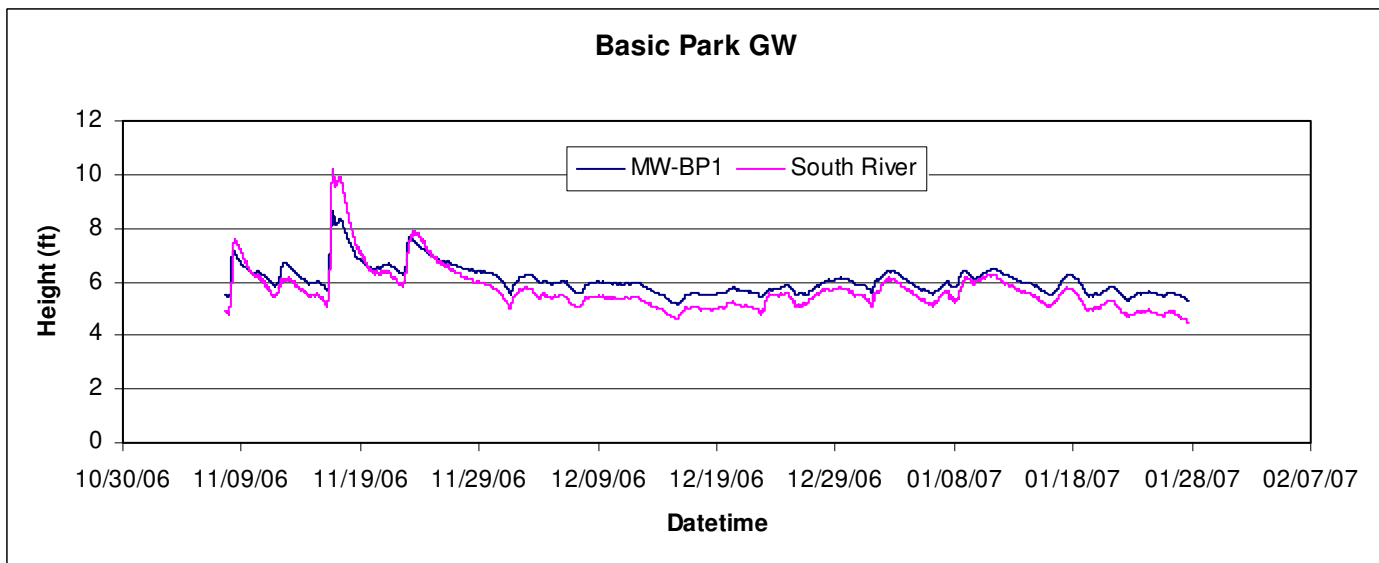
Basic Park Well Results

Dissolved, ng/L

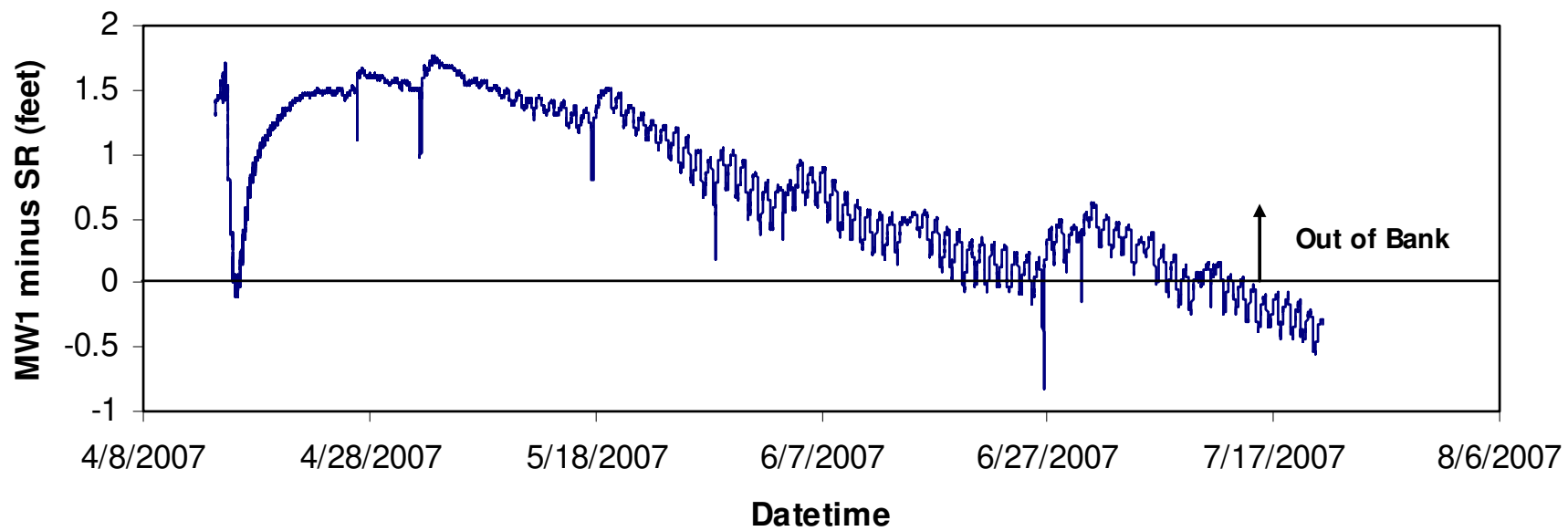


Example Calculation

- 15 CFS estimated (linear) discharge increase, SR01 to Dooms (Tribes decrease GW share).
- THg (dissolved) increase of 1.17 g/day (data for 5/25/2005).
- 32 ng/L GW needed to totally account for Hg input.
- Average of all BPK GW results: 9.24 ng/L or 29% share for GW.
- Max value of 60 ng/L would be ~194%.
- Minimum (detected) value of 0.24 would be <1%.
- Median value of 1.29 would be ~4.0%.



Basic Park GW Gradient



Alluvial Groundwater Indications

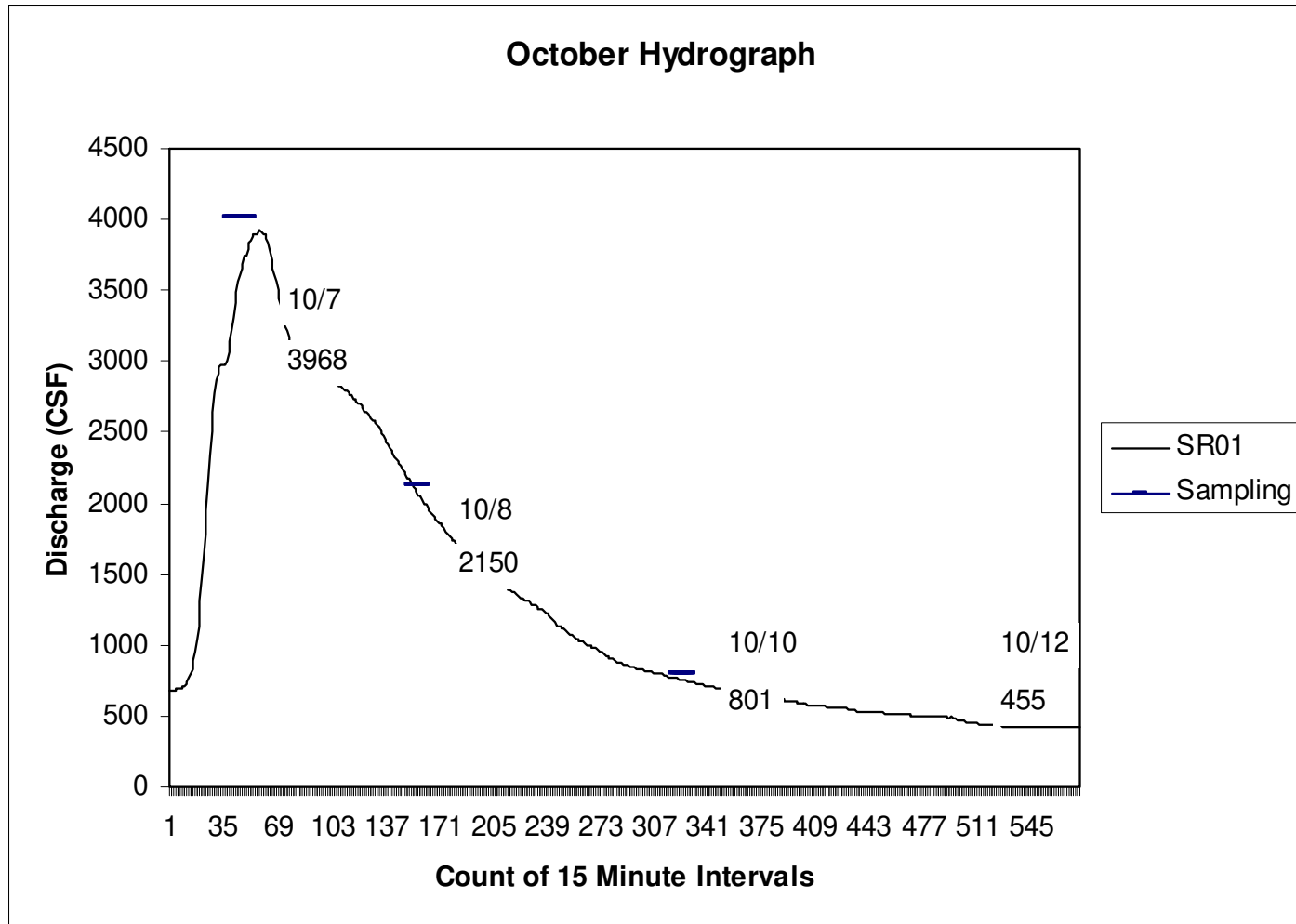
Basic Park

- Water level logging has shown measurable and seasonally variable gradients at BP. (*River may be recharging GW at highest and lowest stages*)
- Slug testing has shown very low K's (<0.5 ft/d)
- Groundwater should not be discounted as source of Hg.
- If mercury in Basic Park GW is “representative”, the GW loading “share” for whole river might be between 1% and 10% on average.
- Groundwater probably not a major source, but it might be #2 in importance.
- Groundwater should be more broadly characterized.

Plant Reach

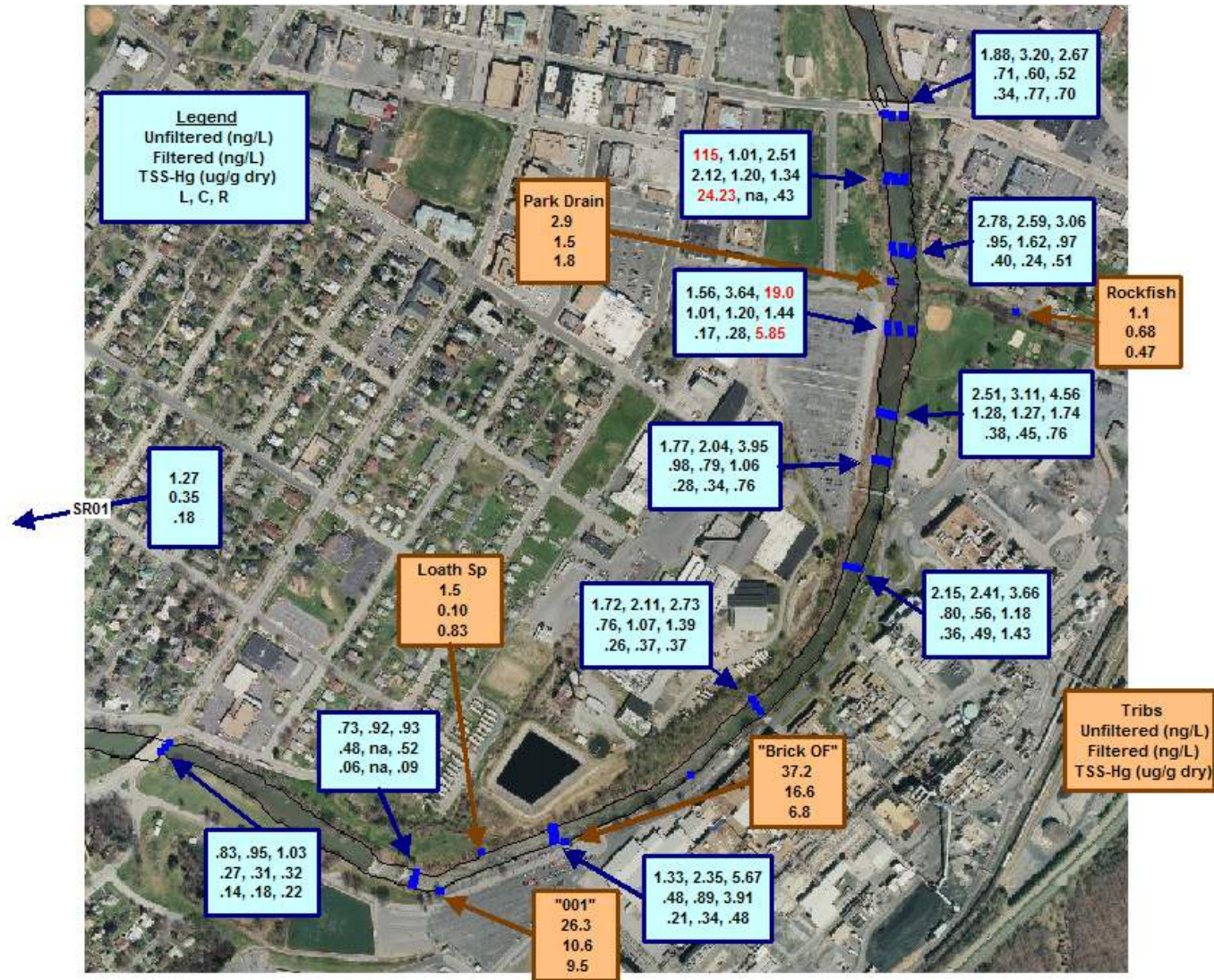
- Sampled major storm in Oct 2006
 - SR01, Wayne Ave, Footbridge, Main St
 - Days 1, 2, 3, 5
 - TSS, THg, DHg
- Very close interval sampling of SW, pore water, and sediments in plant reach.
- Sampled flowing tributaries and outfalls.

October Storm Hydrograph



Surface Water + Tribs

Feb 07 Base Flow



Plant Reach Indications

Loading Inputs

- At base flow, upper watershed, active plant reach, and downstream of footbridge all contributing importantly. (~ 1 g/d THg)
- Under flood conditions, upper watershed and downstream of footbridge most important. Active plant reach less important. (1000 g/d THg plus)
- Extreme importance of plant reach under flooding conditions now unlikely

Plant Reach Indications

Base Flow

- Influence of active plant (right) side (probably including 001) clearly visible in SW, but not in pore water or sediments much below footbridge.
- Eroding banks, downstream of footbridge, probably more important driver for sediments.
- Sediments a likely additional driver for SW, as seen in most porewaters.

Plant Reach Indications

Base Flow, Continued

- No evidence of an unusually large source beneath gravel in plant reach.
- Eroding banks downstream of footbridge probably a factor in base and flood flow.
- Tribs probably negligible.