Mechanistic Source Studies Update

Turner/Jensen

July 2007

General Objectives

- Resolve/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)

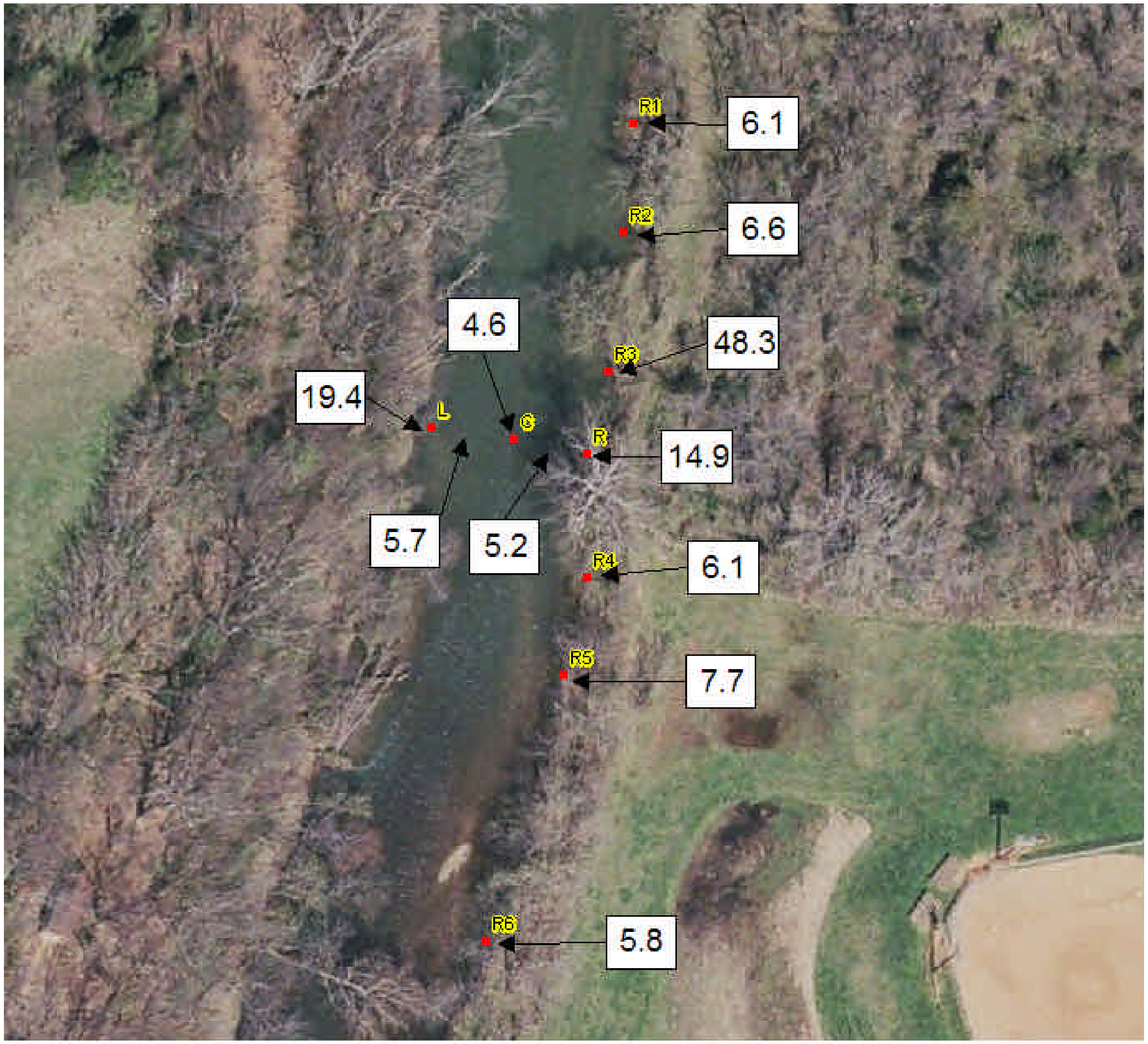
Basic Park

Reasons for Study Site Selection

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

May 2006 SW Results

Confirmation of THg-DIS Inputs



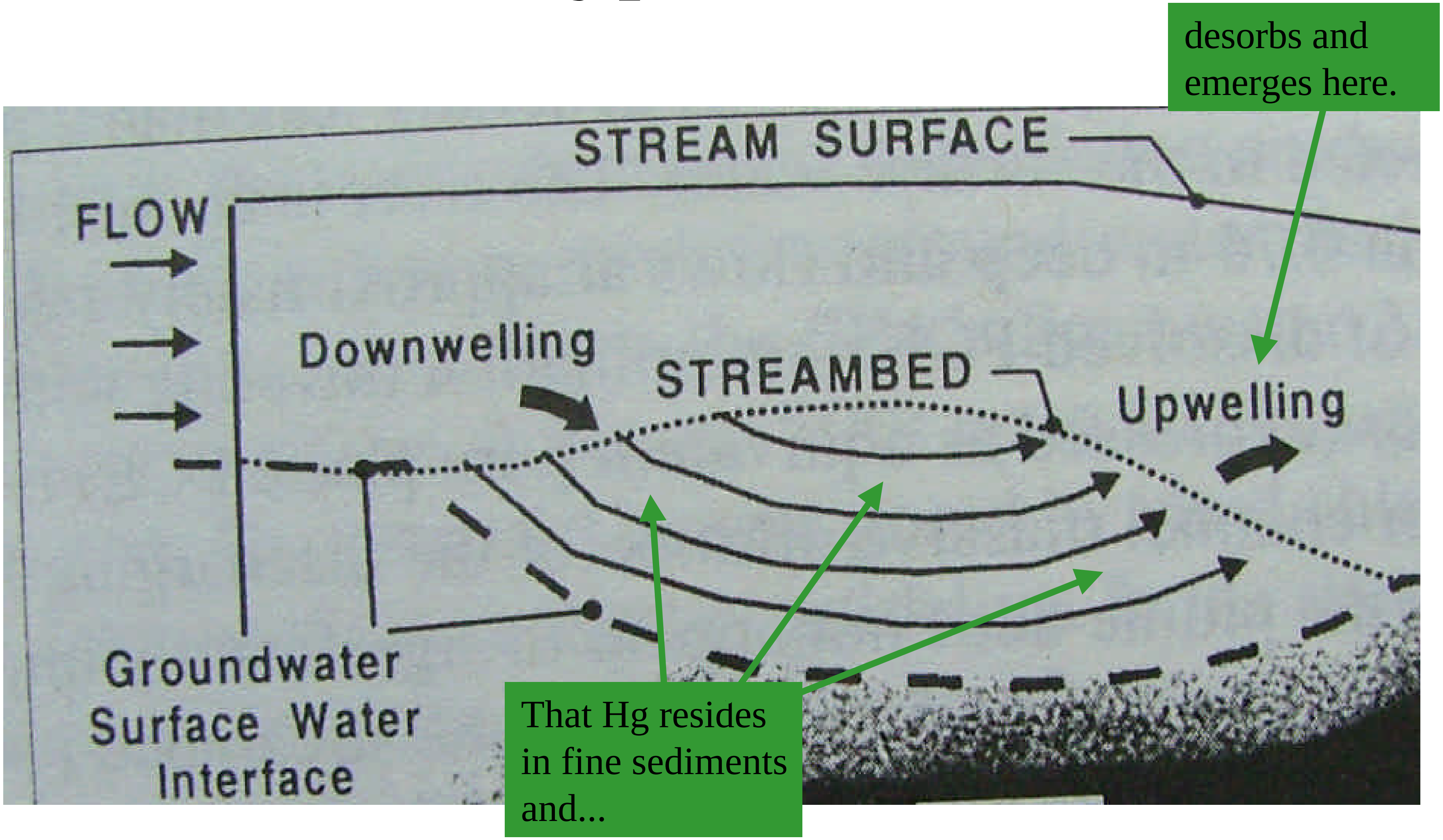
1st Half Year Indications

- Confirmed dissolved loading inputs
- Large point-point variations in SW, seds, pore water, flux. Some correlation.
- Very large extract concentrations
- Muddy areas under-contributing
- Groundwater likely 1-10% contribution
- Gravel beds (and other) may be larger contributor of dissolved loading input

2nd Half Year Goals

- Further characterize gravel beds as source
  - longitudinal arrays of sample points
- Additional extractions, soft sediment pore waters, centrifuge, ultra-filter
- Additional shallow well installation and sampling
- Refine indications

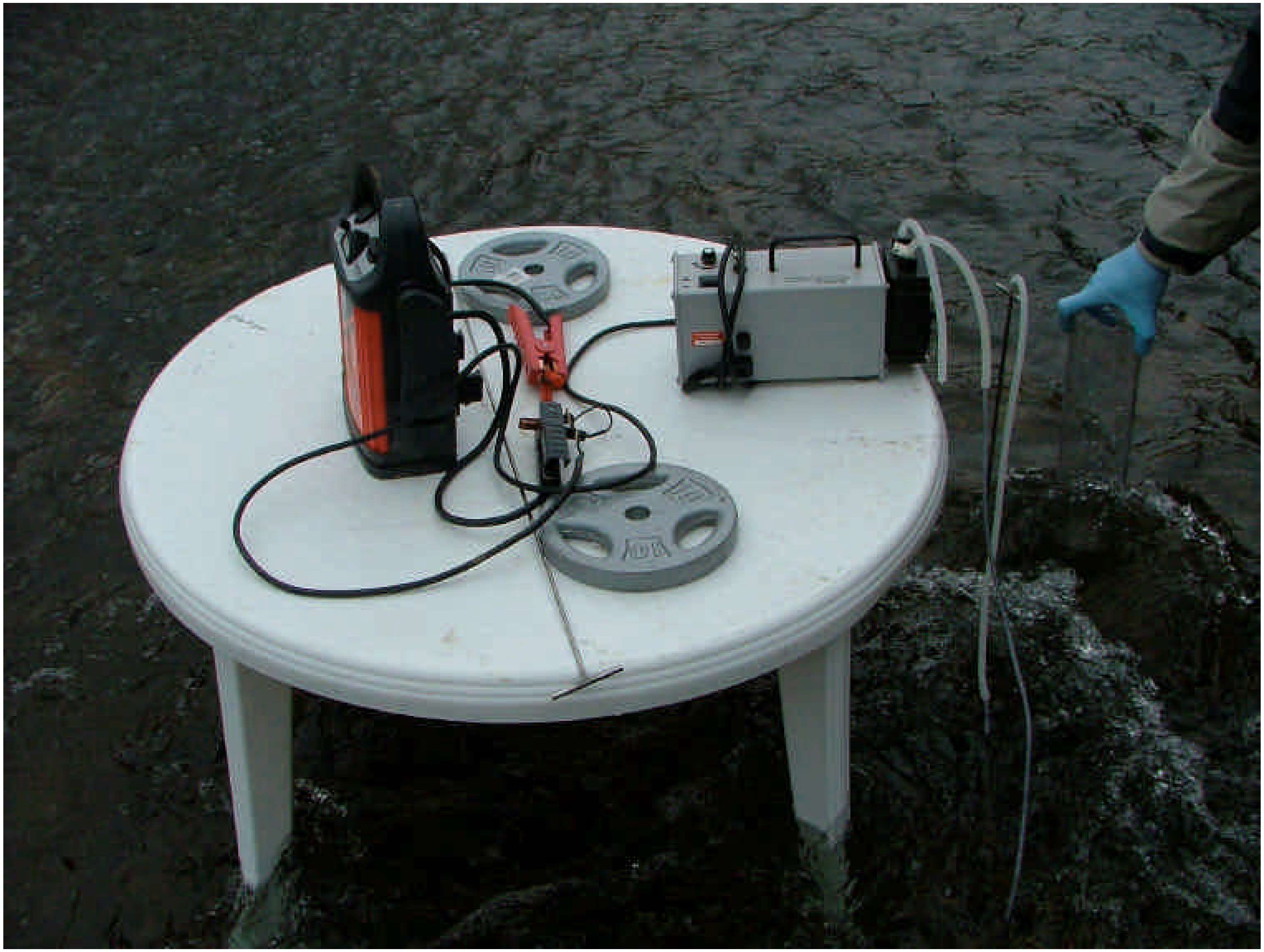
Hypothesis


desorbs and emerges here.
STREAM SURFACE
FLOW
Downwelling
STREAMBED
Upwelling
Groundwater Surface Water Interface
That Hg resides in fine sediments and...

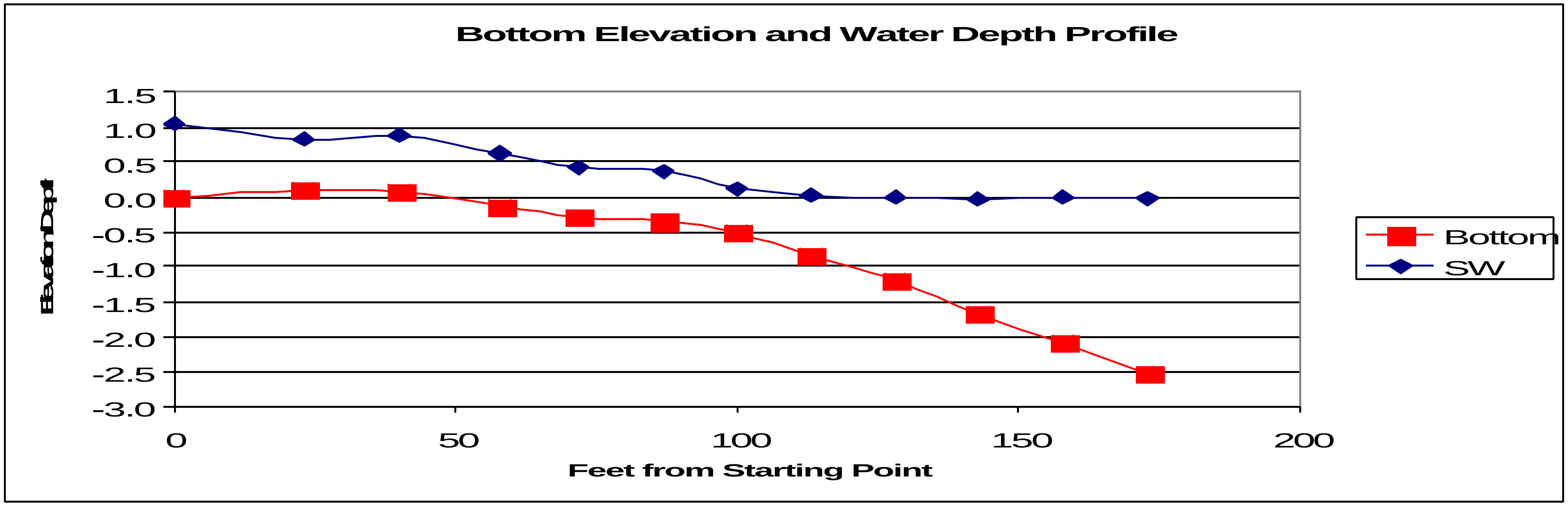
Longitudinal Gravel Series (2+)

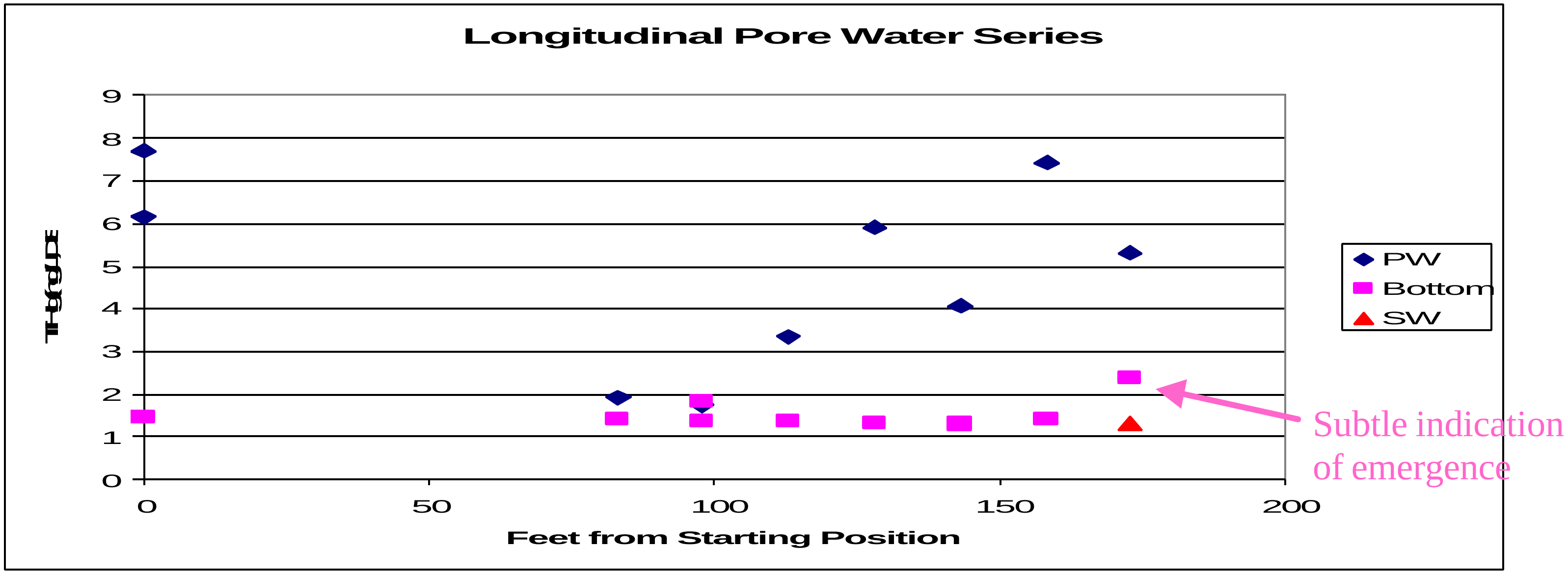
- Pore waters at 6-8 or 12 inches depth
- Near bottom surface waters
  - Probe tip placed on gravel bottom surface
- Thalweg surface water
- All filtered
- Field readings with YSI meter
- Bottom and SW elevations

Equipment



January 07 Results



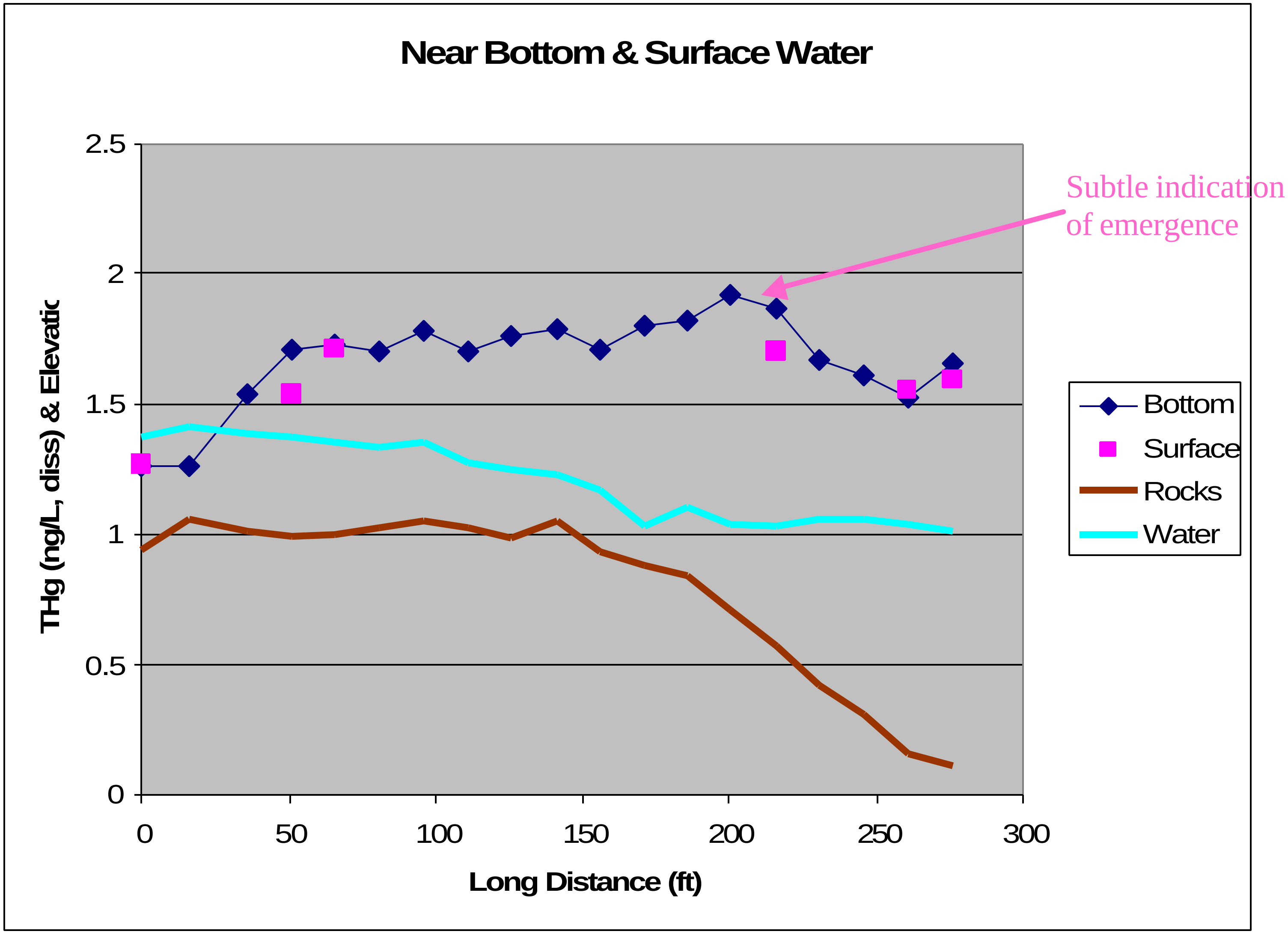


Extended Locations

January 07

April 07

Longitudinal Results April



Island Channel

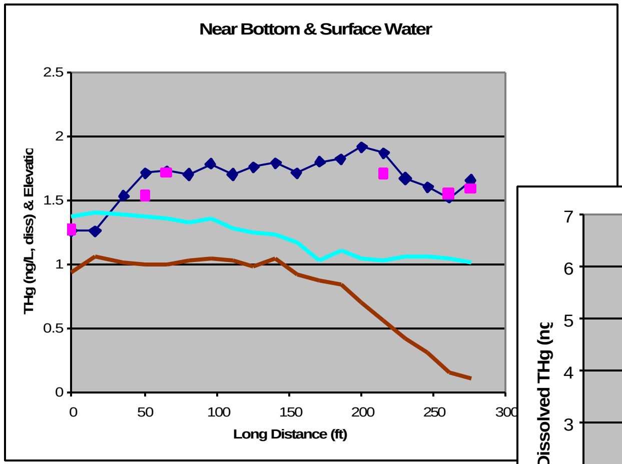
Upstream Entry

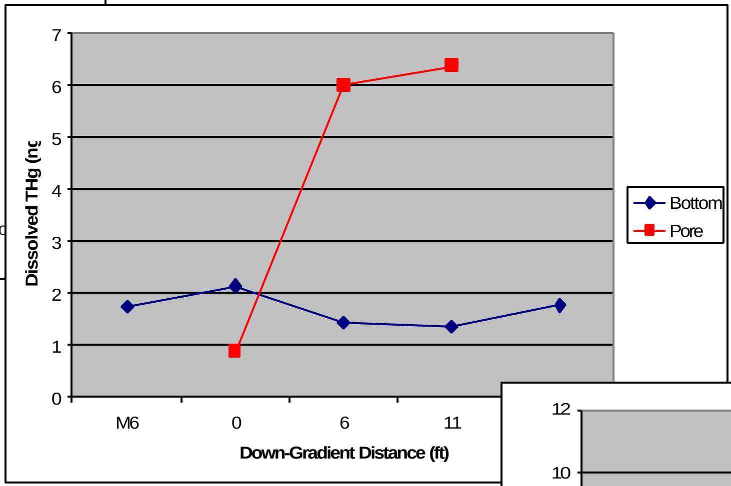
Island Channel

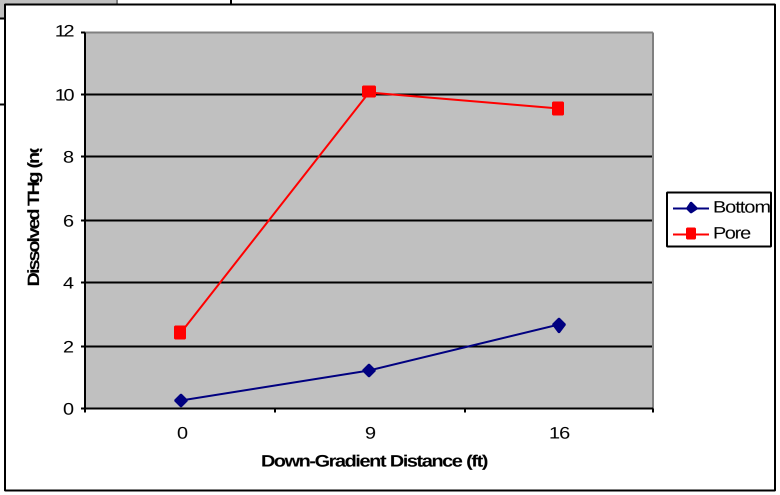
Downstream Exit

Additional Transects April

Concentration Perspective



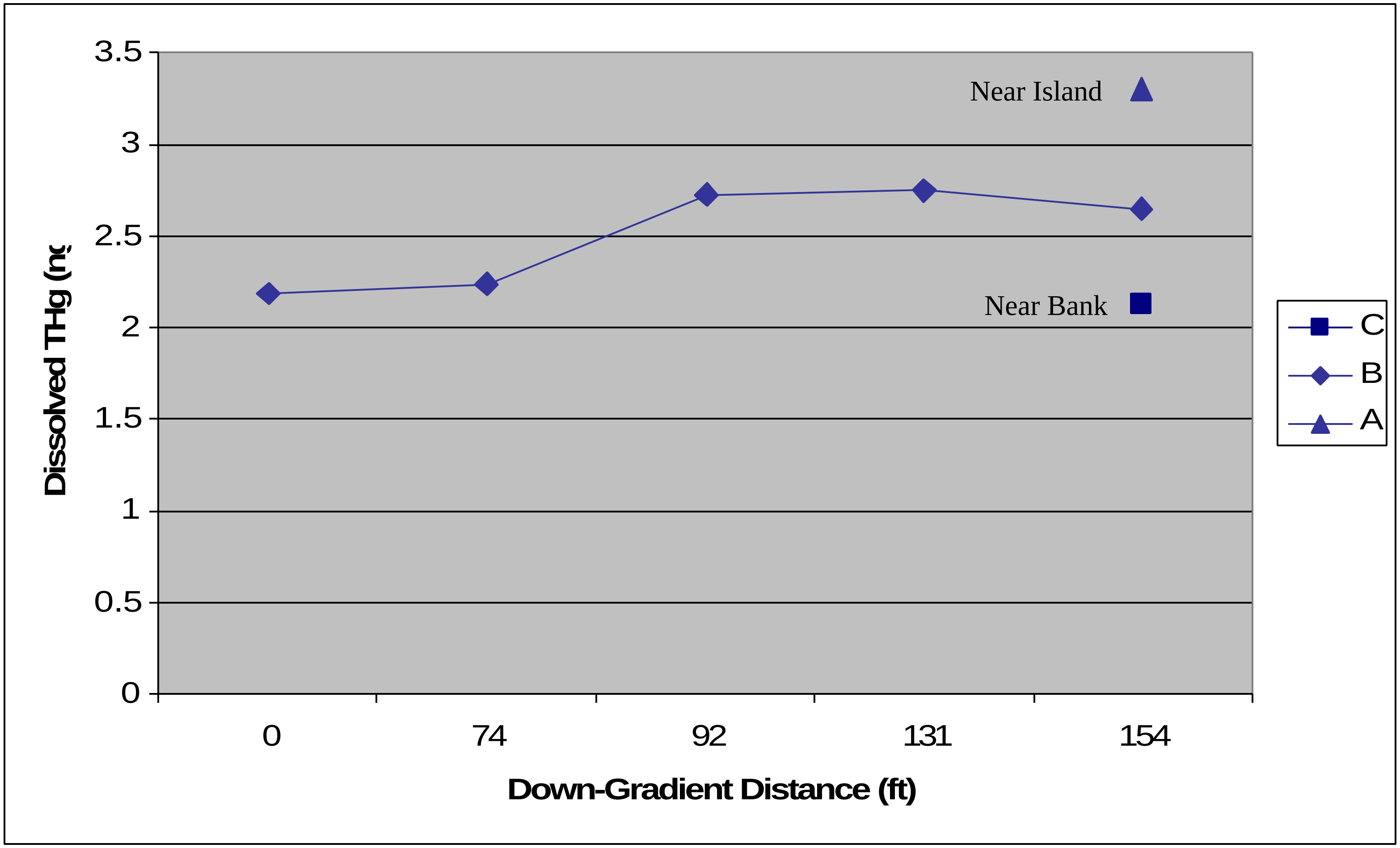




Longitudinal Channel Set

Longitudinal Channel Results

All Near Bottom



Gravel Bar Indications

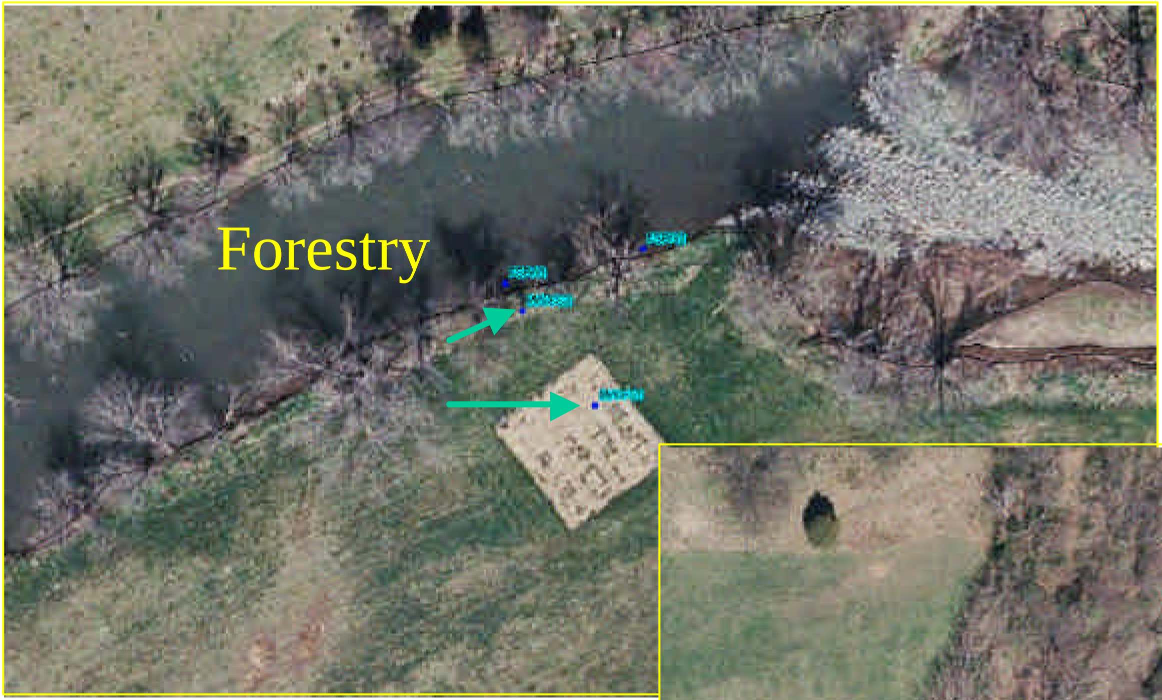
- Important area of THg-DIS input
  - Wide variations in water concentrations
- Surface water < Near Bottom < Sub-gravel
  - Indicates driving force for THg transfer
- Subtle indications of flow through gravel, driven by head differences
- Subtle indications of elevated THg emergence from gravel bar downstream

MHg Survey in May/June 07

Monitoring Wells

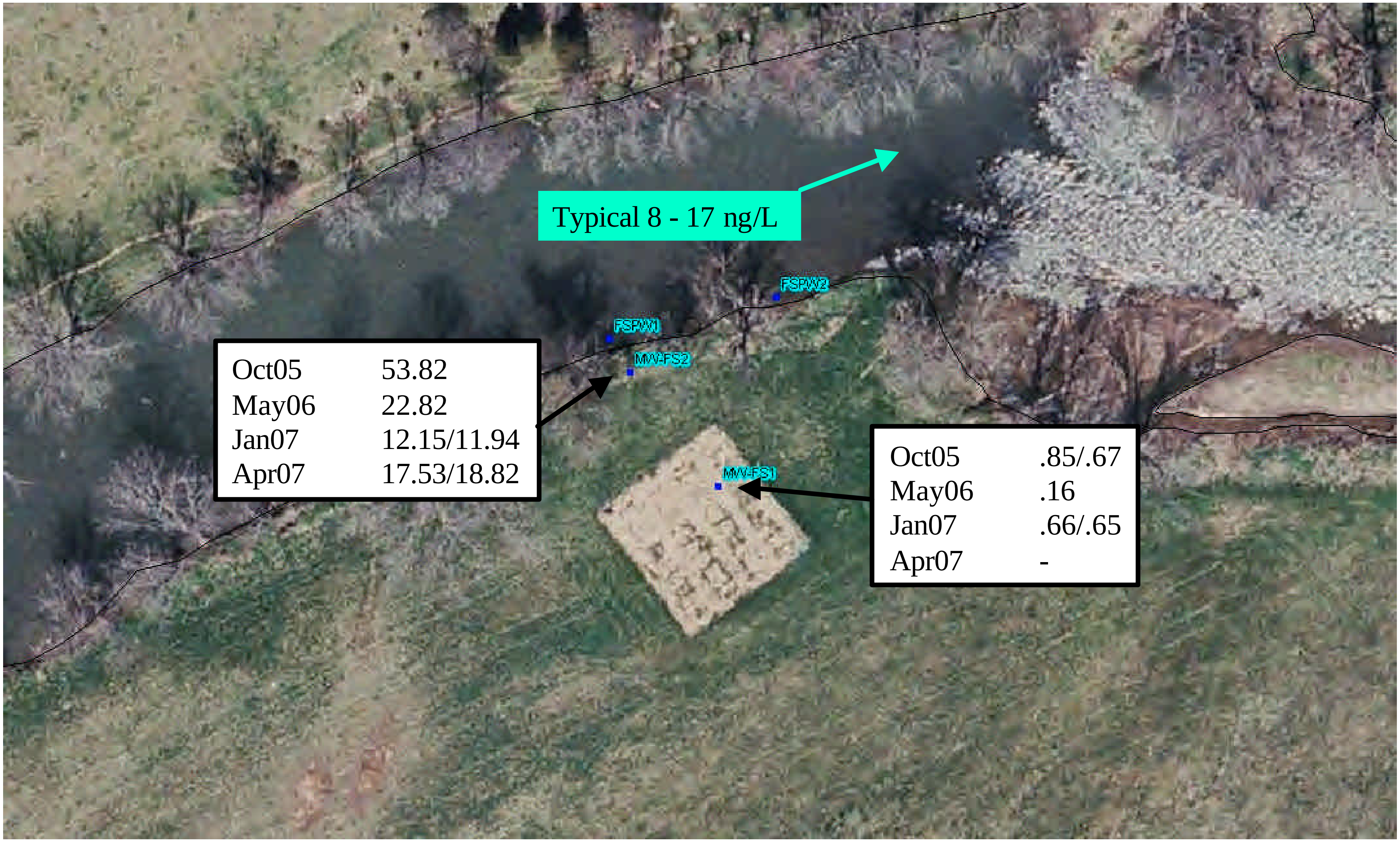
Forestry and Basic Park

Well Locations



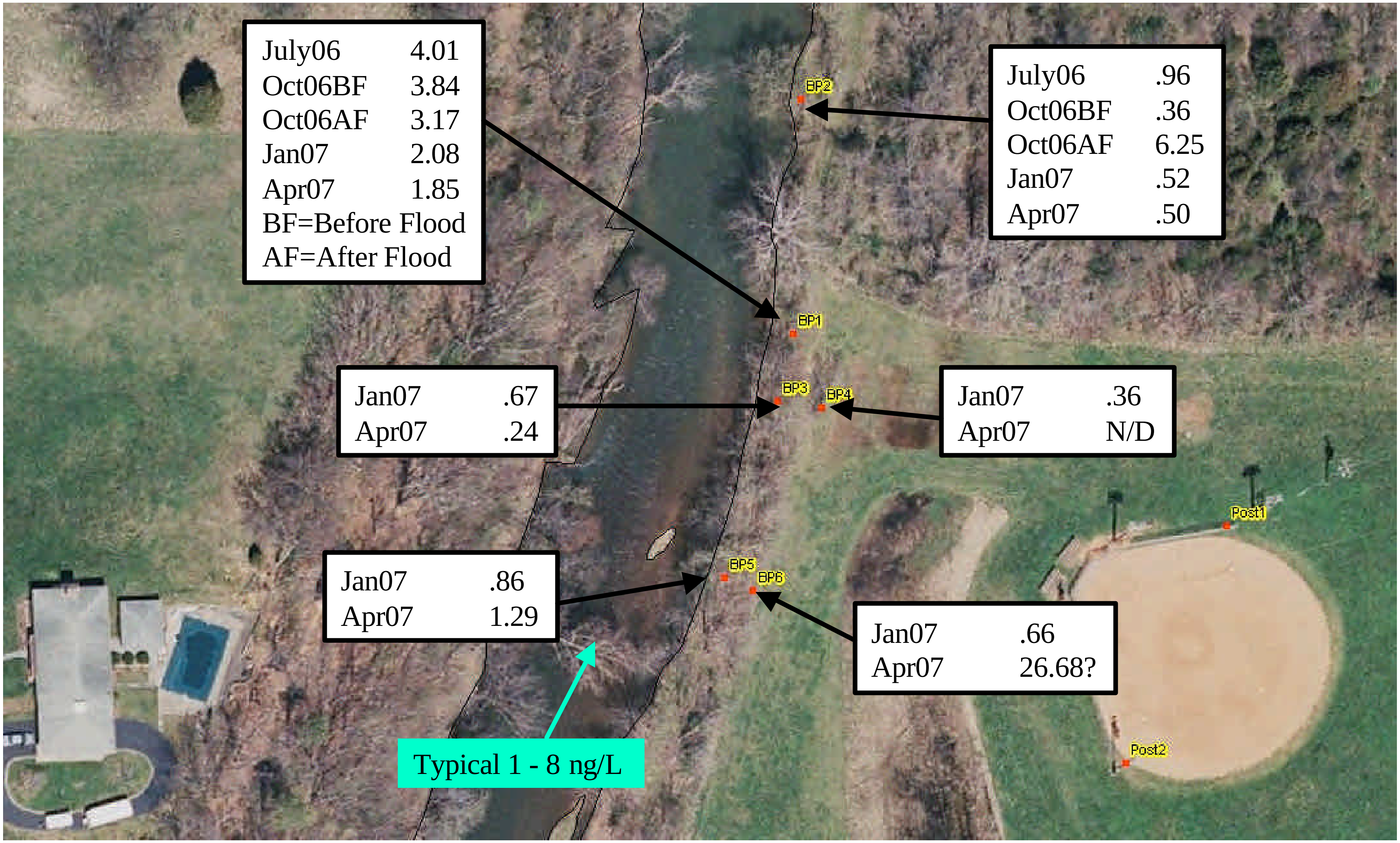
Forestry Well Results

Dissolved, ng/L



Basic Park Well Results

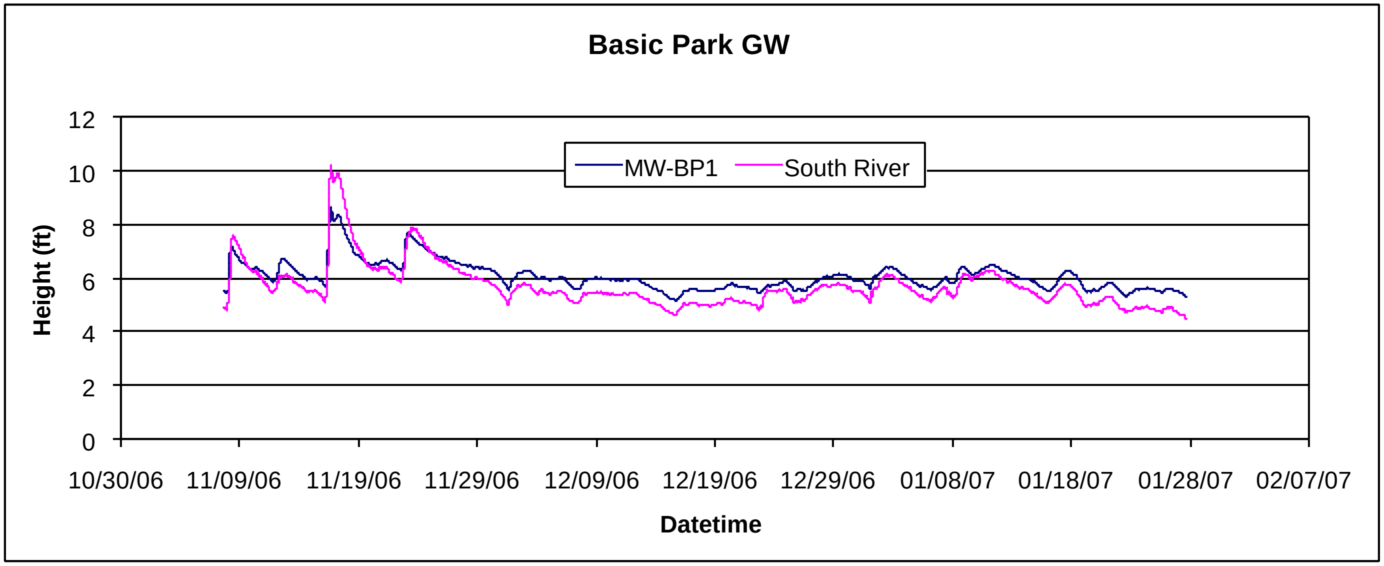
Dissolved, ng/L

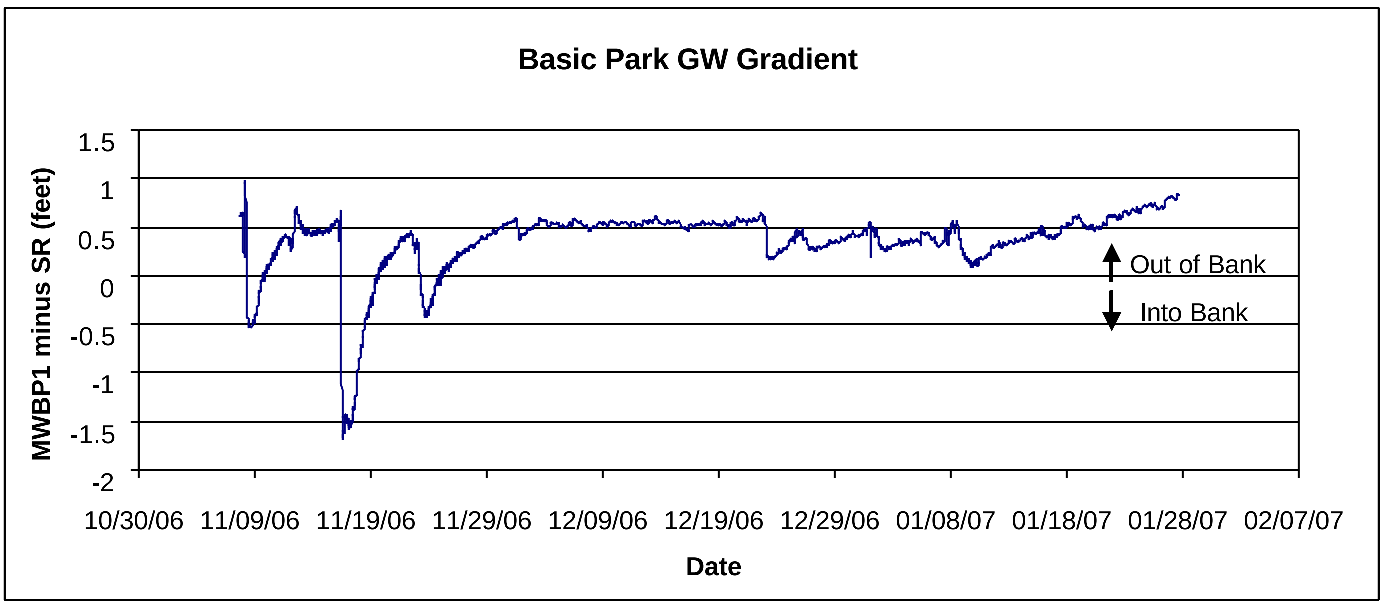


Example Calculation

5/25/05

- 15 CFS estimated (linear) discharge increase, SR01 to Dooms (Tribs decrease GW share).
- THg-DIS increase of 1.17 g/day.
- 32 ng/L GW needed to totally account for Hg input.
- Average of all (believed) GW results: 1.62 ng/L or 5.1% share for GW.
- Max value of 6.25 ng/L would be ~20%.
- Minimum (detected) value of 0.24 would be <1%.
- Median value of 0.86 would be ~2.7%.


Basic Park GW
Height (ft)
12
10
8
6
4
2
0
MW-BP1
South River
10/30/06
11/09/06
11/19/06
11/29/06
12/09/06
12/19/06
12/29/06
01/08/07
01/18/07
01/28/07
02/07/07
Datetime


Basic Park GW Gradient
MWBP1 minus SR (feet)
1.5
1
0.5
0
-0.5
-1
-1.5
-2
Out of Bank
Into Bank
10/30/06
11/09/06
11/19/06
11/29/06
12/09/06
12/19/06
12/29/06
01/08/07
01/18/07
01/28/07
02/07/07
Date

Groundwater Indications

Shallow/Local/ Basic Park

- Water level tests have shown measurable gradient at BP. (None measurable at Forestry, but that's where highest THg!)
- Groundwater should not be discounted.
- Groundwater probably not the major source, but it might be #2 in importance.
- Groundwater should be more broadly characterized.
- If Basic Park is "representative", groundwater THg-DIS share for whole river might be between 1% and 10% on average.
- Forestry (and any similar) situations require additional scrutiny. FSMW2 = 54 ng/L in Oct 05. Always somewhat elevated. Is this a "pore water" as opposed to a Mr. Coffee? Will a more thorough GW survey find other such examples?

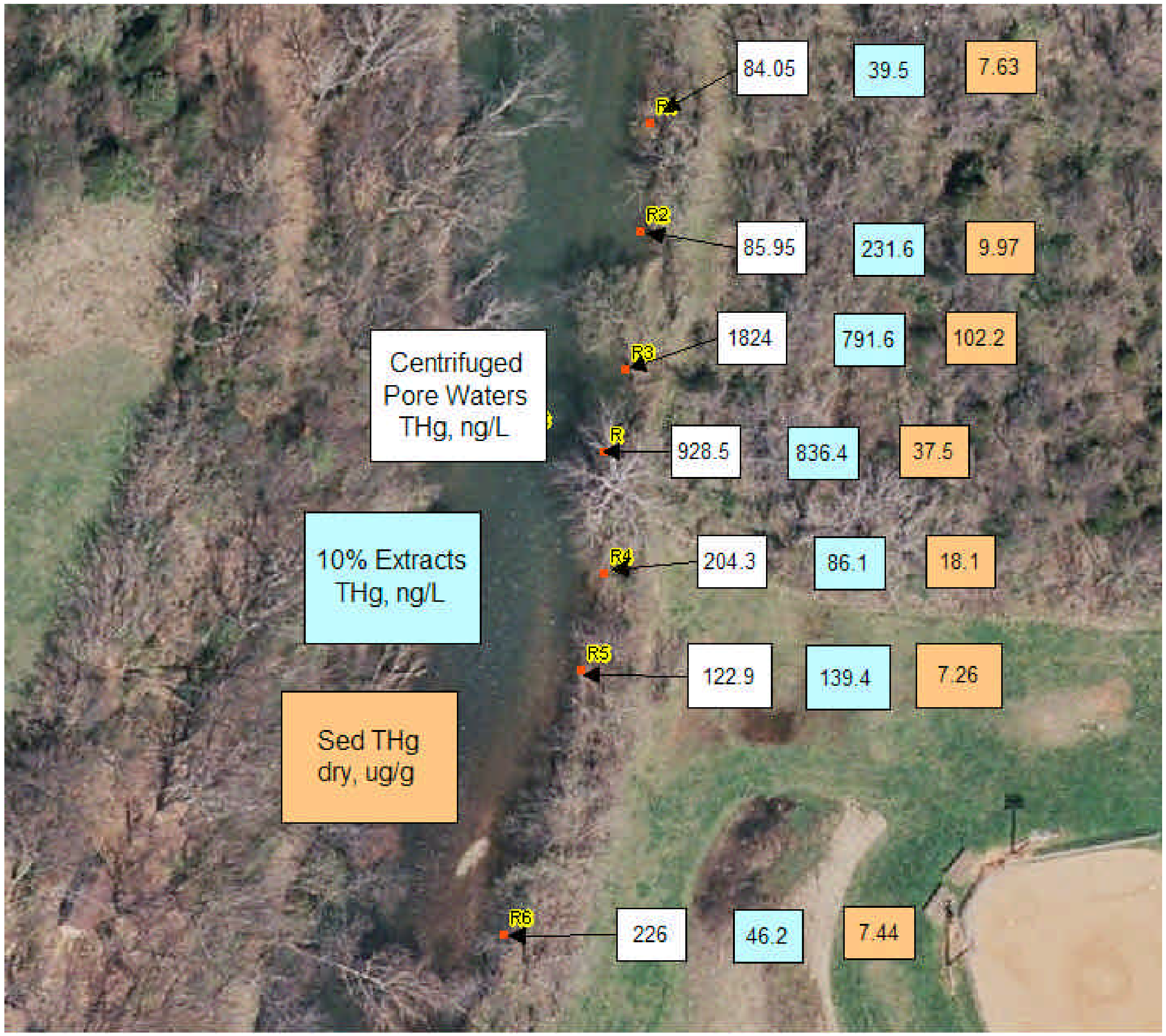
Pore Waters/Extractions

Centrifuged Pore Waters

Feb 07

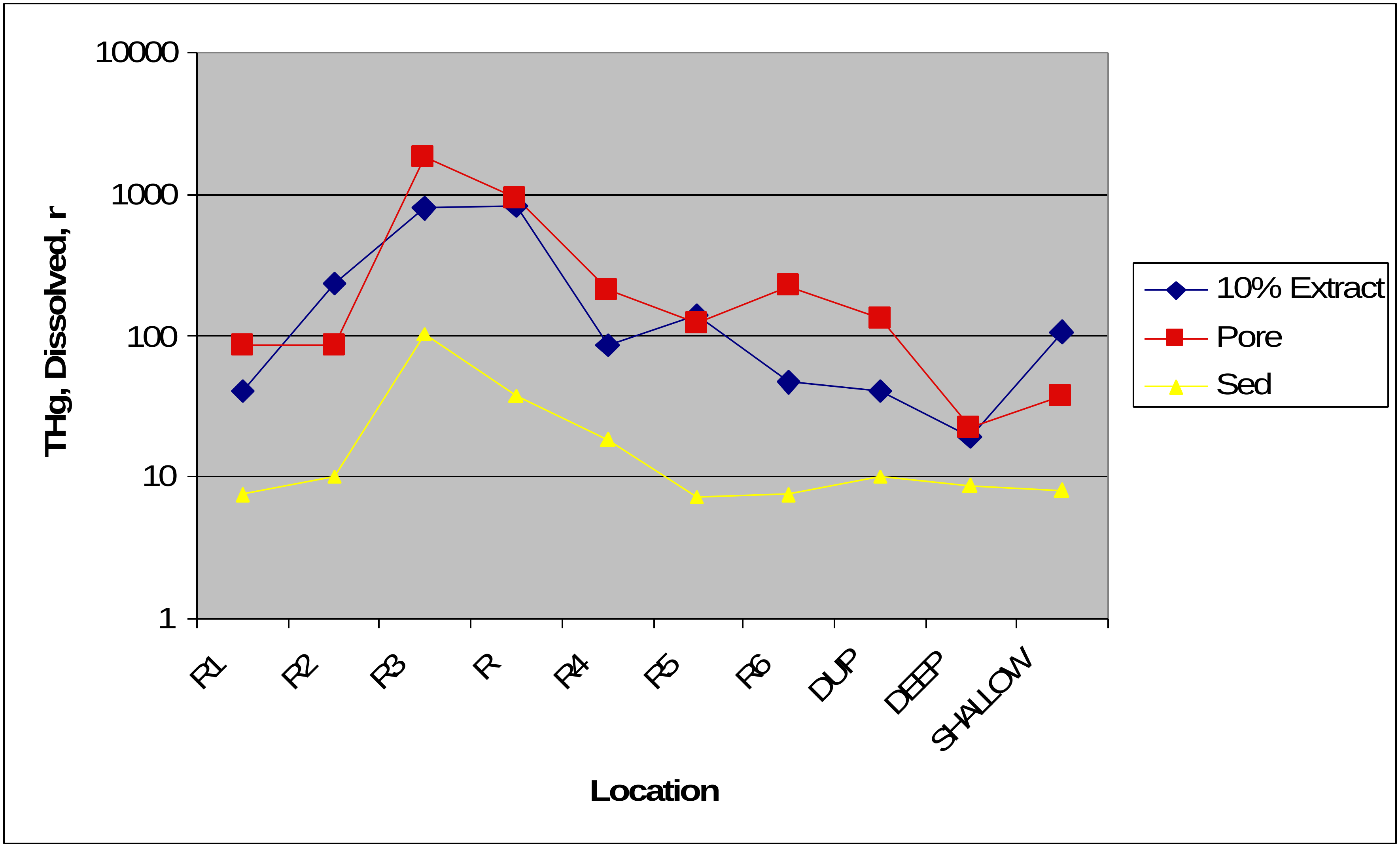
Sediment Pore/Extract

April 07

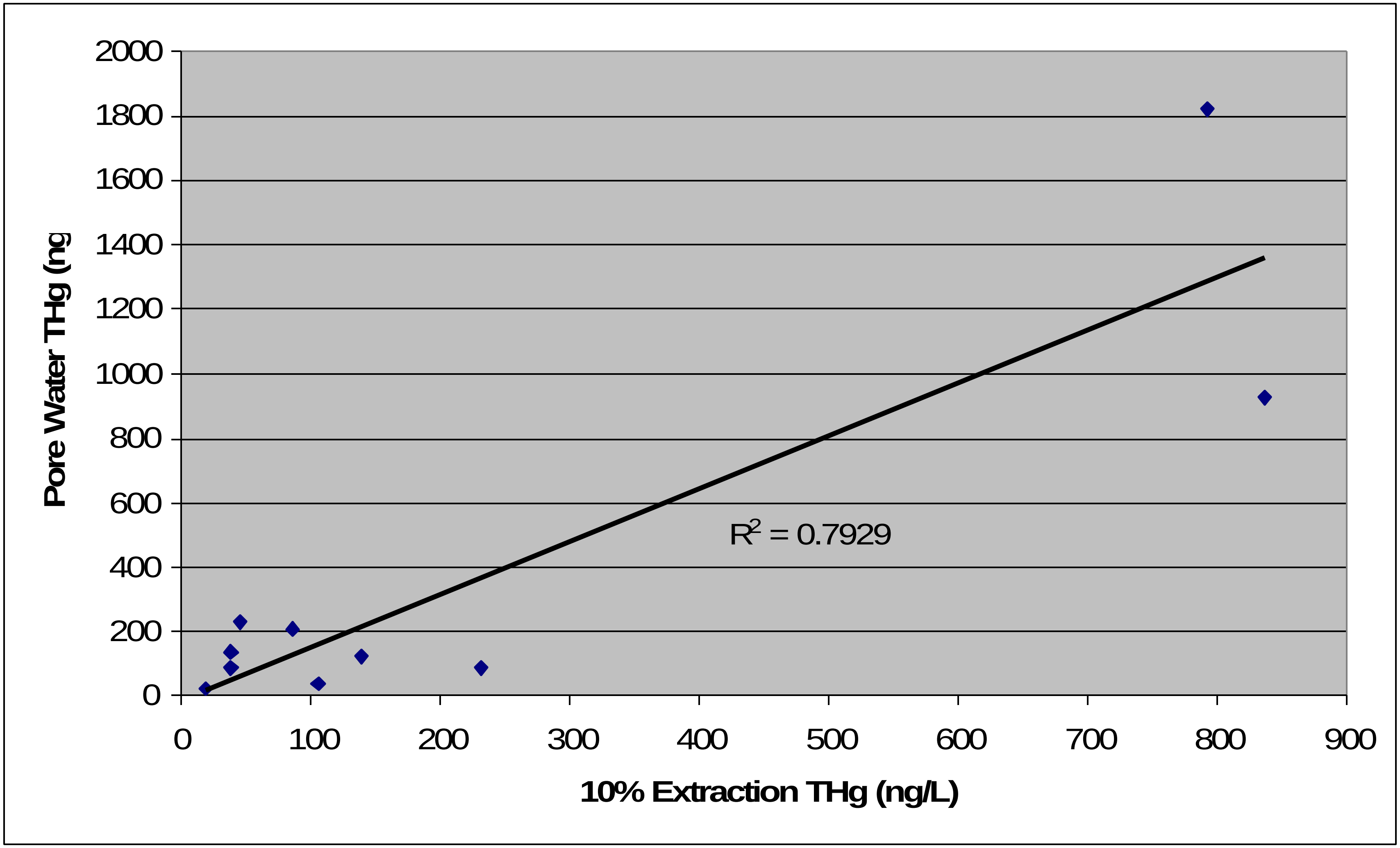


Extracts/Pores/Sediments

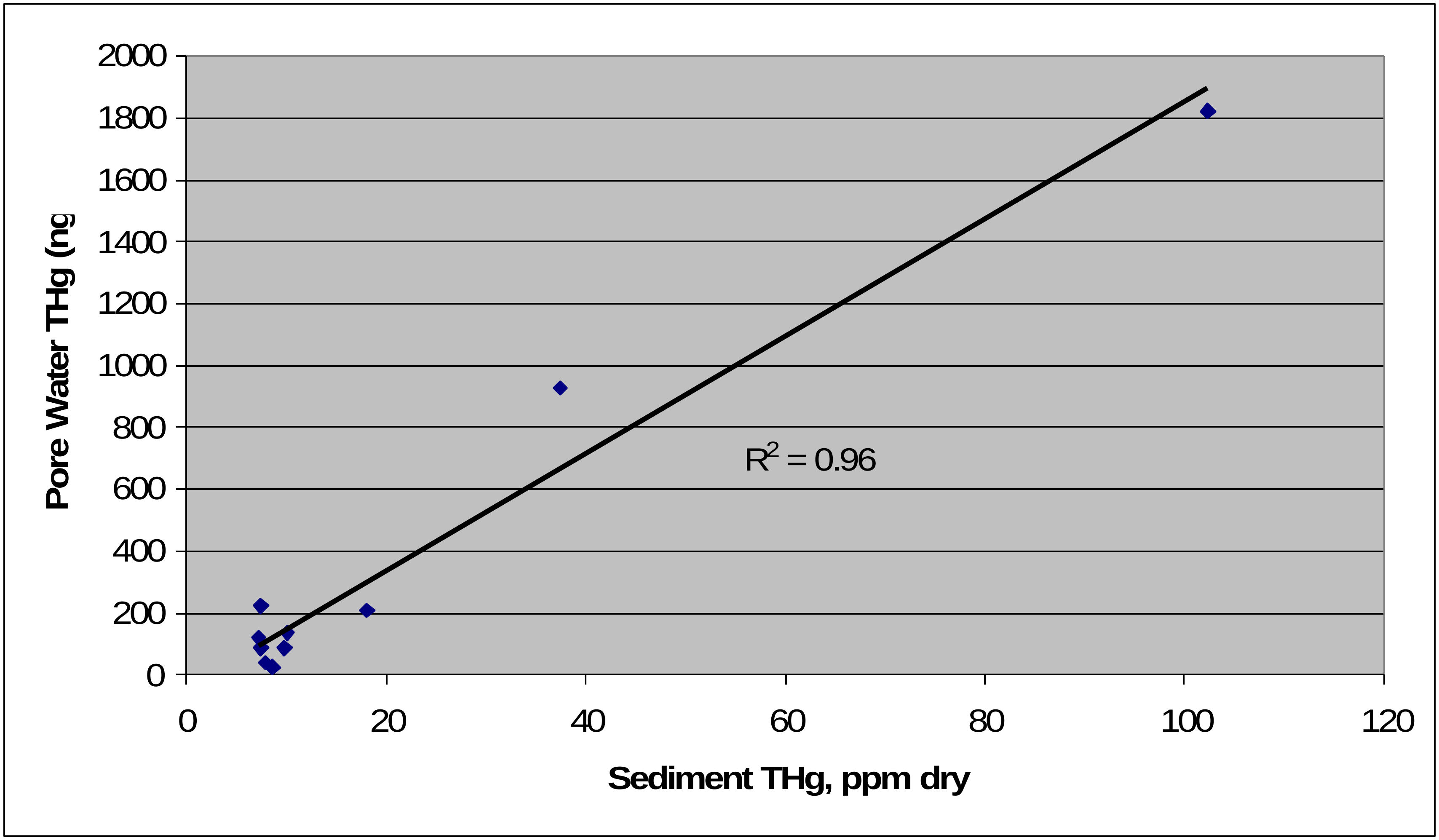
April 07



Extract Predicting Pore Water



Sediment Predicting Pore Water



Extract/Pore Water Indications

- Wide variability on short spatial interval
  - Can’t just go measure bank seds at RRM and be certain of anything
- “Hot Spot” sediments show themselves in various measures: THg, pores, extracts, fluxes… Surface water not good predictor. Eddy influence.
- But cannot suggest single measure as best surrogate, especially to predict lower end
- Bank soils can yield much higher THg extracts
- Results suggest river is way out of equilibrium for dissolved THg.

Way-Out-Of-Equilibrium

Implications

- Very large thermodynamic driving forces
- Areas of low flow (eddies, backwaters, gravel beds) can reach very high concentrations.
- Discrete dissolved inputs might persist along great lengths of river.

Special Extraction and Ultrafiltration Studies

Objectives

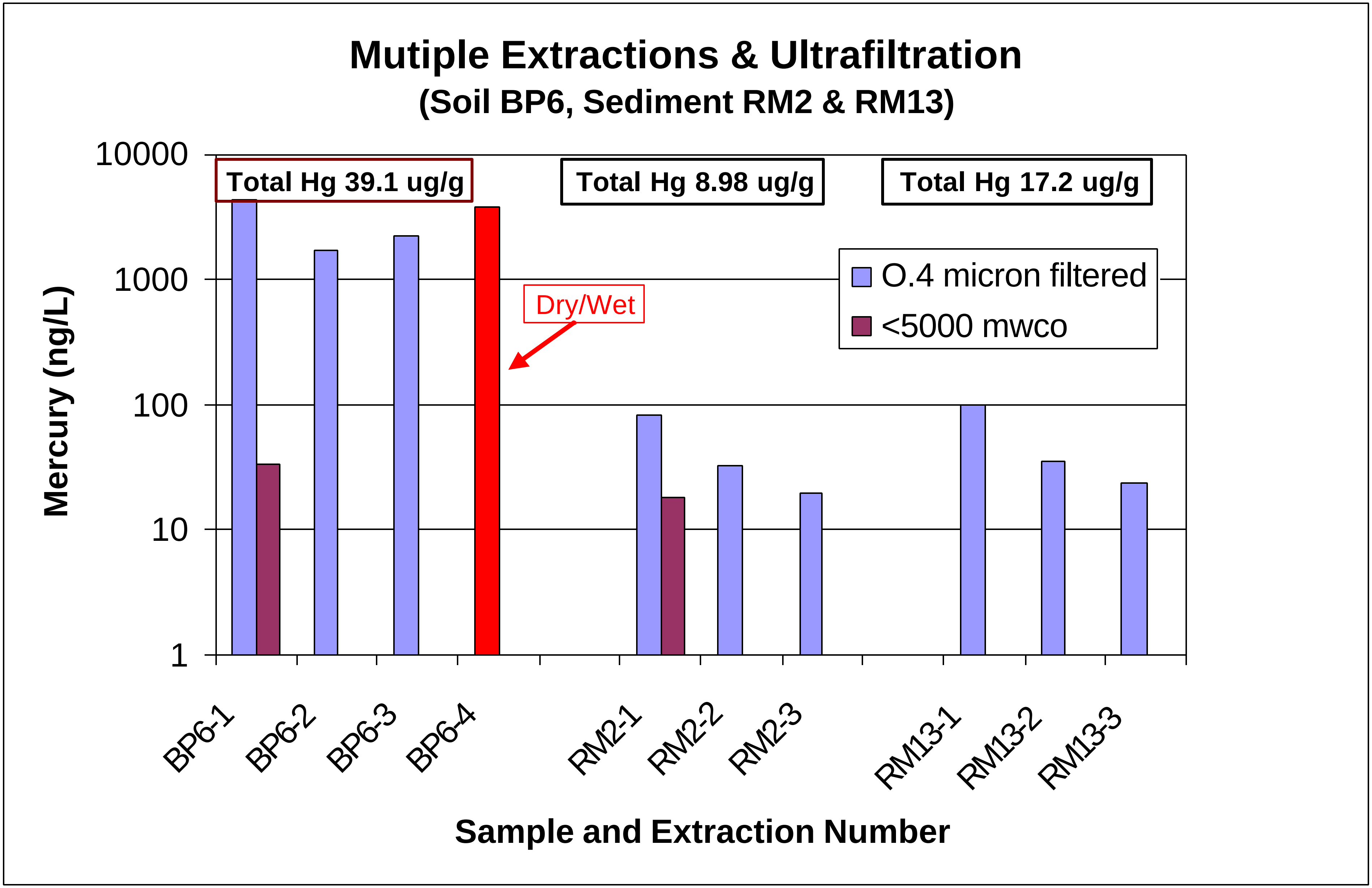
- Determine extent and nature of desorption of Hg from bank soil and bed sediments.
- Measure or estimate speciation of desorbed forms (molecular weight, gaseous, reactive).
- *Determine if bank soil extracts stimulate methylation (using BFC as in situ lab)*

Exhaustive Extractions and Speciation

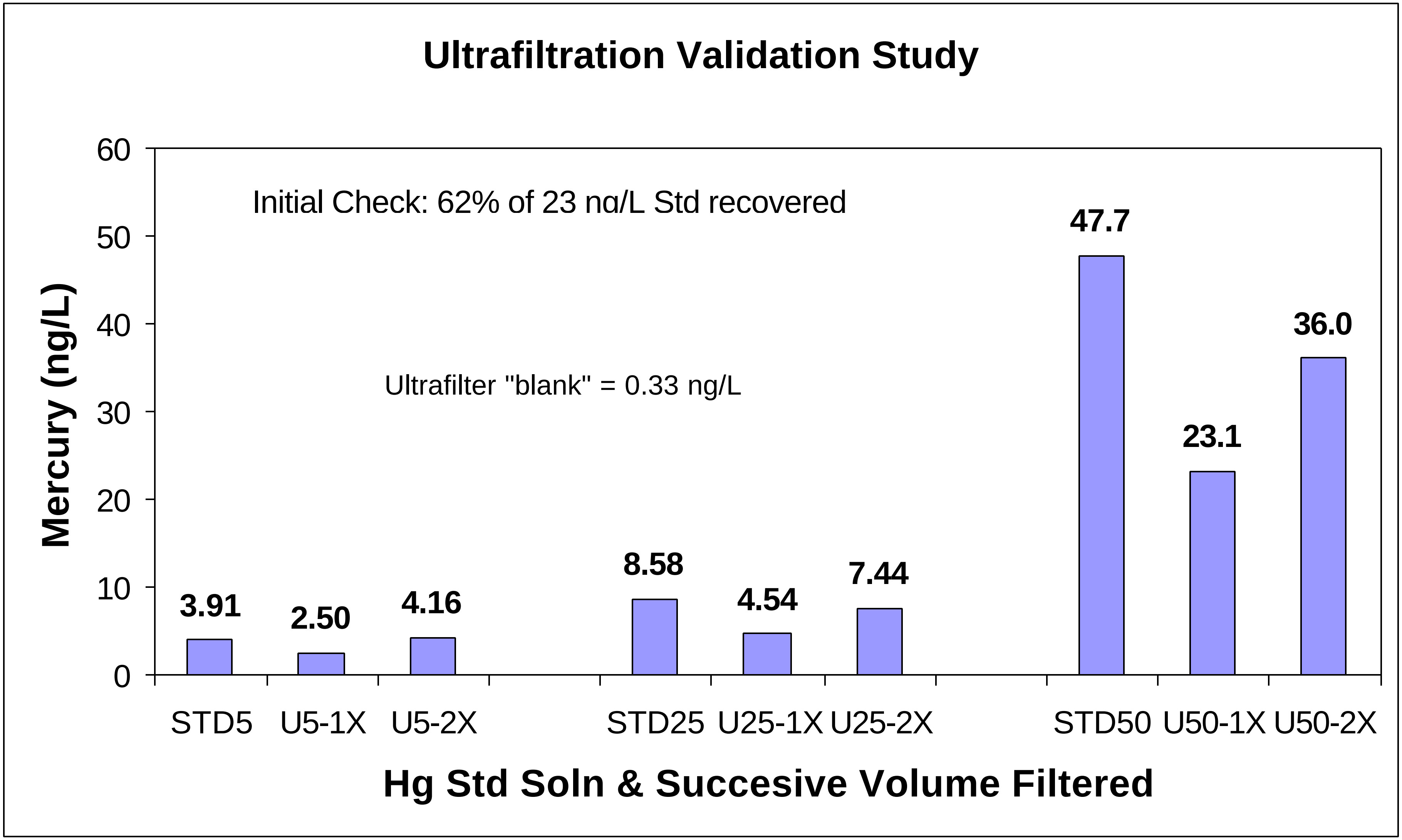
- 4 grams of soil/sediment in 40 mL of SR01 water (<1 ng Hg/L, SC 150-200 υS/cm).
- Mix by rotation (30 rpm) for 4 hrs.
- Filtration w/0.4 micron pore size filter.
- Repeat “x” times using same sample.
- Only 1st extraction used to measure DGM, “reactive” and <5000 MWCO fraction.

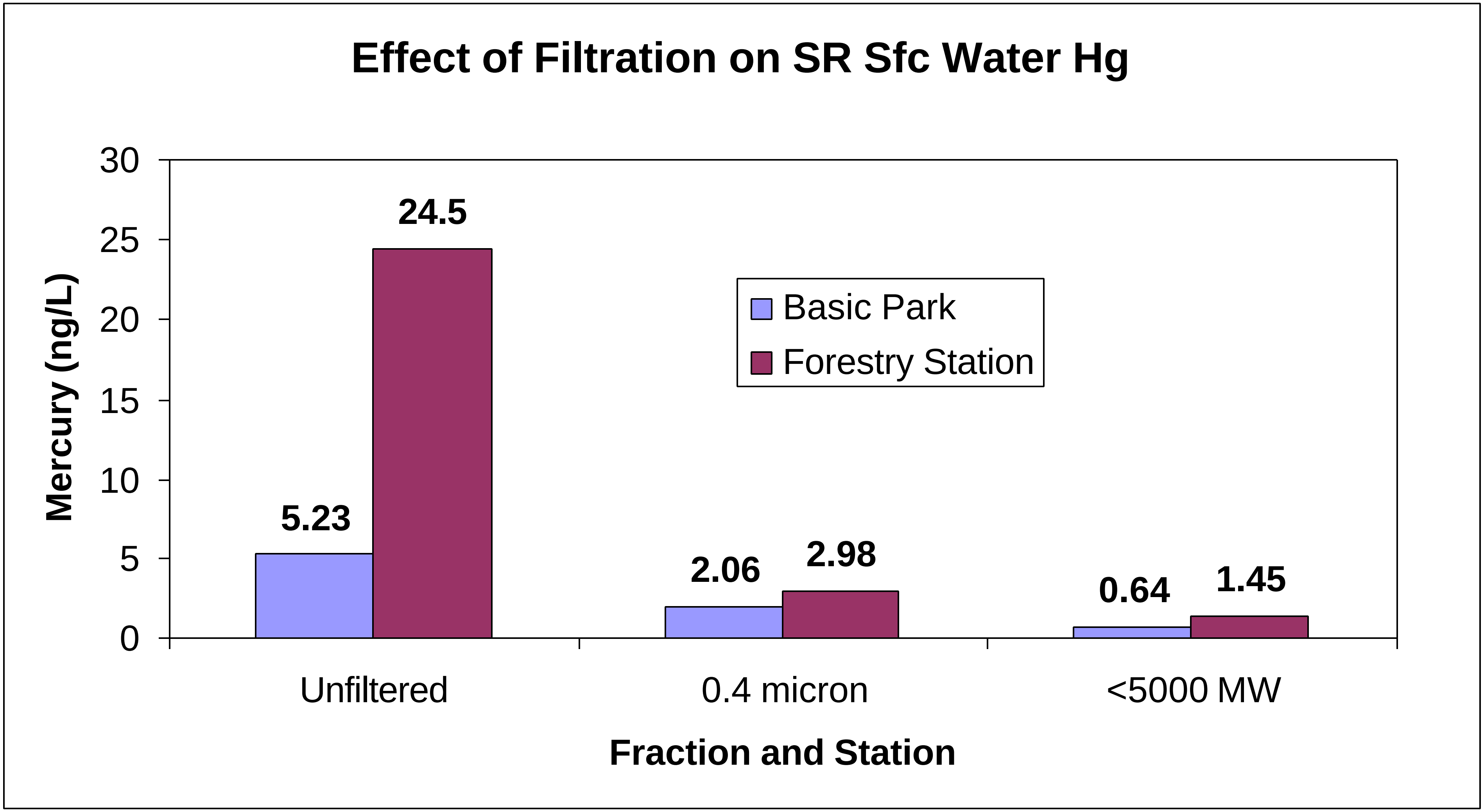
Speciation

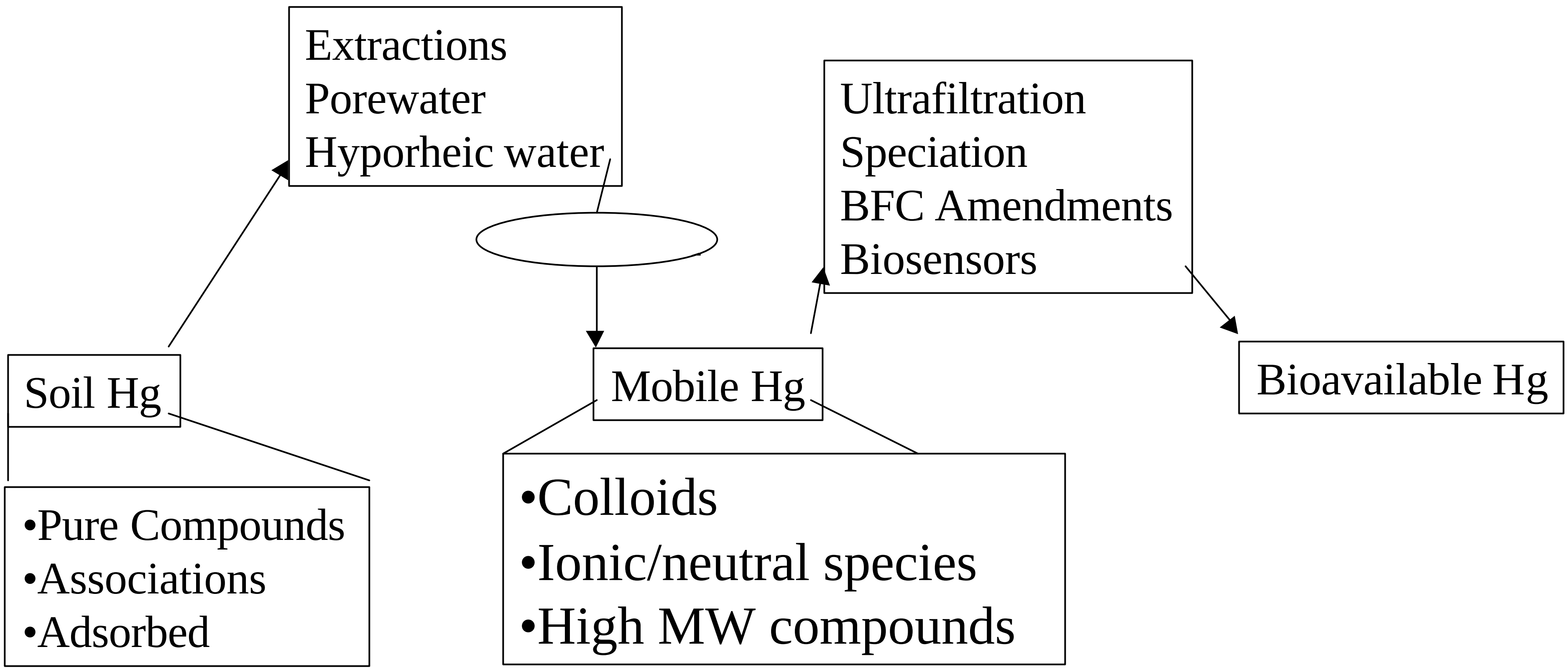
- DGM=Dissolved Gaseous Hg,
  - Likely Hg(0)
  - Not bioavailable but easily oxidized to Hg(II)
- Reactive=Easily reducible to Hg(0)
  - Likely inorganically complexed Hg(II), incl Hg^{2+}
  - Highly bioavailable (but some debate)
- <5000 MWCO=Low MW compounds
  - Likely inorganically complexed Hg(II) and simple organic Hg complexes, e.g. acetate
  - Bioavailability undetermined



Mutiple Extractions & Ultrafiltration
(Soil BP6, Sediment RM2 & RM13)
Mercury (ng/L)
10000
1000
100
10
1
Total Hg 39.1 ug/g
Total Hg 8.98 ug/g
Total Hg 17.2 ug/g
Dry/Wet
O.4 micron filtered
<5000 mwco
BP6-1
BP6-2
BP6-3
BP6-4
RM2-1
RM2-2
RM2-3
RM13-1
RM13-2
RM13-3
Sample and Extraction Number


Ultrafiltration Validation Study
Initial Check: 62% of 23 ng/L Std recovered
Ultrafilter "blank" = 0.33 ng/L
Mercury (ng/L)
60
50
40
30
20
10
0
3.91
2.50
4.16
8.58
4.54
7.44
47.7
23.1
36.0
STD5
U5-1X
U5-2X
STD25
U25-1X
U25-2X
STD50
U50-1X
U50-2X
Hg Std Soln & Succesive Volume Filtered


Effect of Filtration on SR Sfc Water Hg
Mercury (ng/L)
30
25
20
15
10
5
0
24.5
5.23
2.06
2.98
0.64
1.45
Basic Park
Forestry Station
Unfiltered
0.4 micron
<5000 MW
Fraction and Station



Extractions
Porewater
Hyporheic water
Ultrafiltration
Speciation
BFC Amendments
Biosensors
Soil Hg
Mobile Hg
Bioavailable Hg
•Pure Compounds
•Associations
•Adsorbed
•Colloids
•Ionic/neutral species
•High MW compounds

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) but…
- Ultrafilter medium binds significant fraction of inorganically complexed Hg, e.g., $Hg(OH)_2$
- DGM [Hg(0)] and reactive Hg [$Hg^{2+]}$ data pending.

Amended Flux Chambers

1st Chemical Amendment Experiment Attempted on SR

Purpose of Experiment

- Method development: To determine if a particular locale is a "factory" for MHg, or merely a transfer point.
- Hypotheses: A step increase in dissolved THg in a MHg production locale will result in a measurable step increase in MHg production within 4 to 8 hours. And the converse. And that this can be a useful tool.


Rock Plates


Mud

Multi-Use Pump

Amendment Injection

Sampling

Filtering

Experimental Design

	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

Plant Reach

1st Half Year Indications

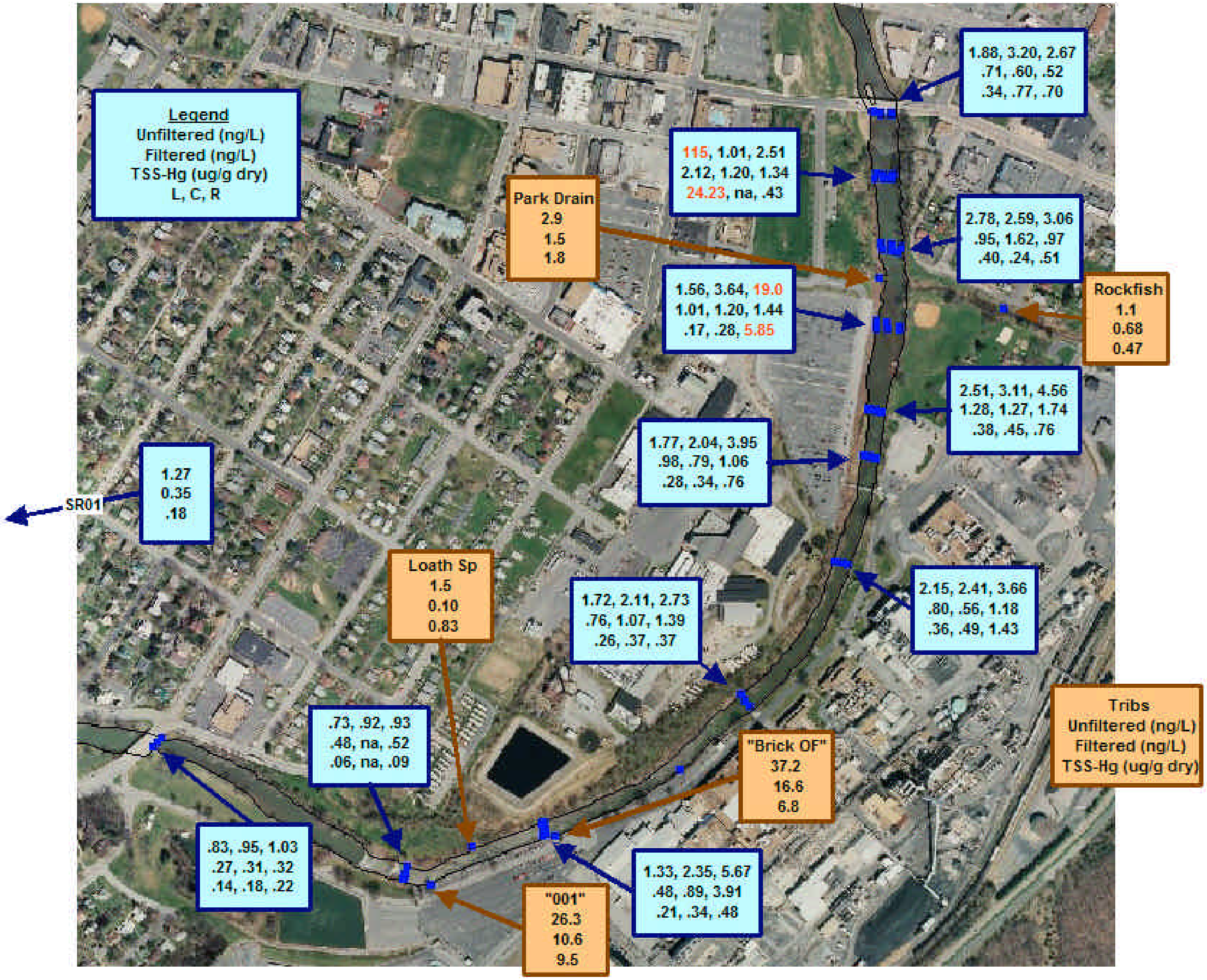
- Confirmed base flow loading of ~ 1 g/d THg.
- Flood flow loading > 1000 g/d instantaneous.
- Flood peak loading = split between upper watershed and below footbridge. ~5% plant.
- Day 9 after flood, ~46% load from plant. ~ 1.4 g/d.
- As flood subsides, active plant becomes more important, as fraction of total load.
- Significant THg inventory in eroding banks downstream of footbridge.

2nd Half Year Goals

- Very close interval sampling of SW, pore water, and sediments in plant reach.
- Sampling flowing tributaries and outfalls.
- Material balance across plant reach - eliminated from program.

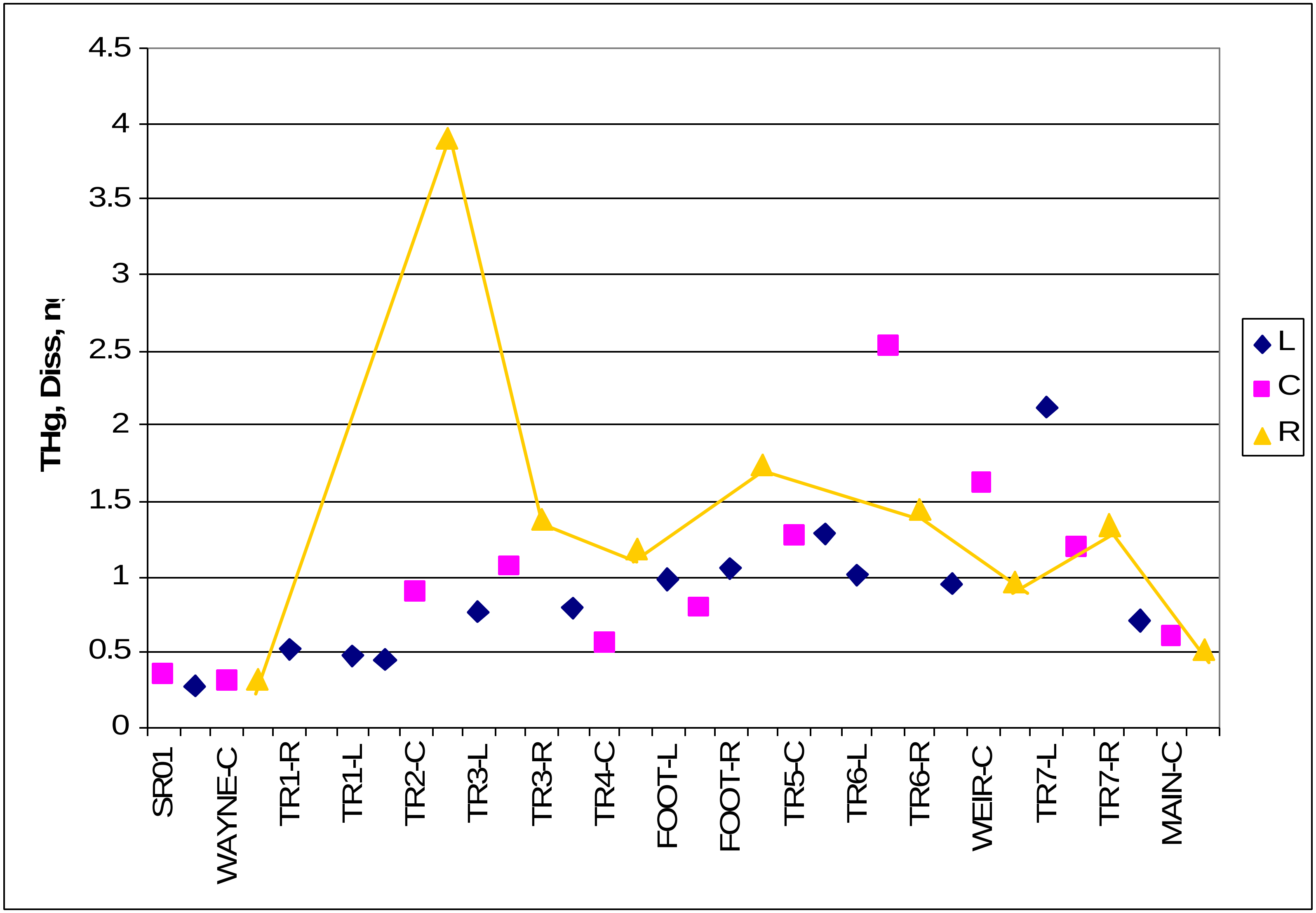
Surface Water + Tribs

Feb 07 Base Flow



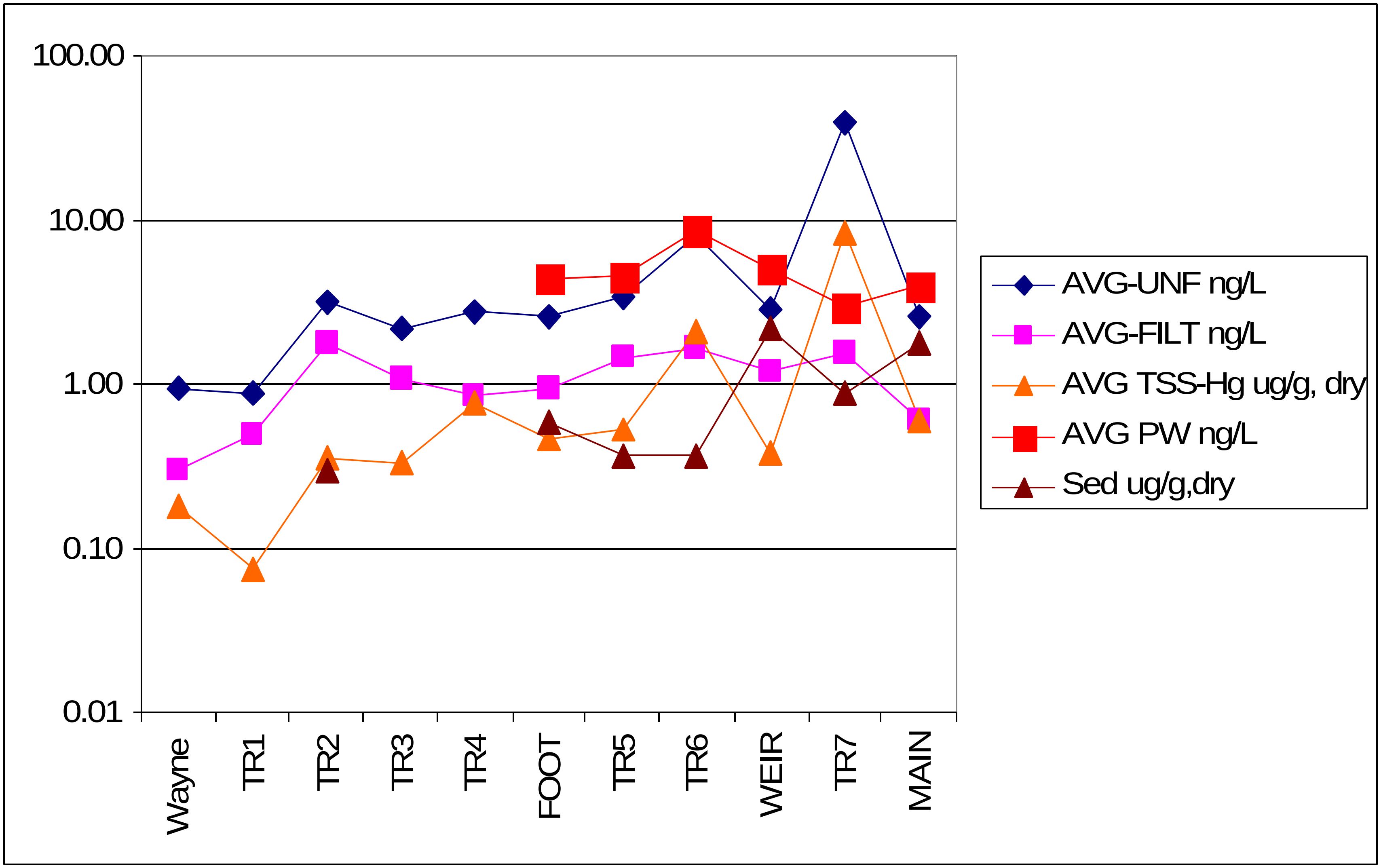
Right Bank Dominates SW

Dissolved THg (ng/L)



Average Close Interval Results

+ Sediments



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 pore waters.

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.