# Mercury Source Tracing and Mechanistic Studies

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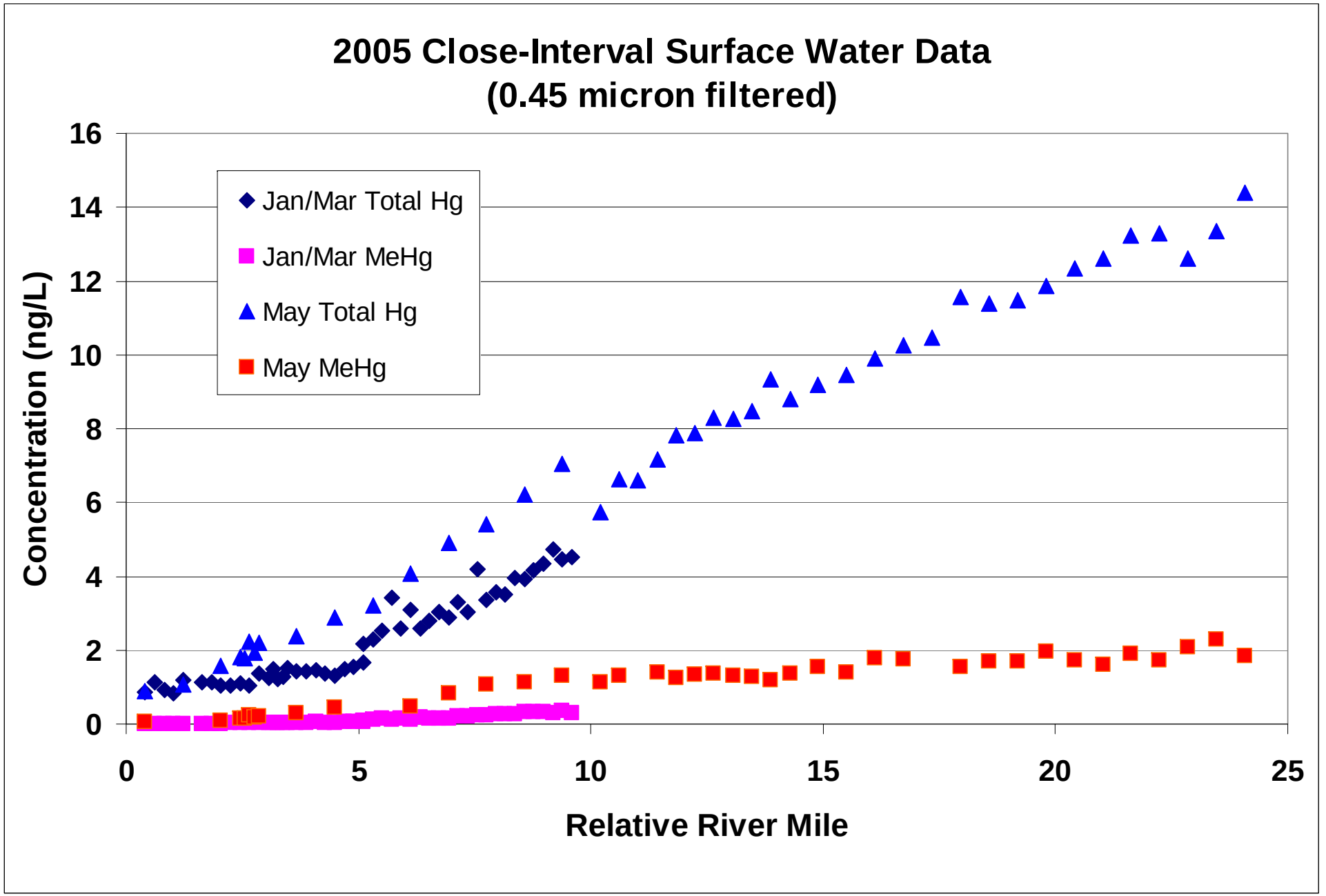
# Synopsis

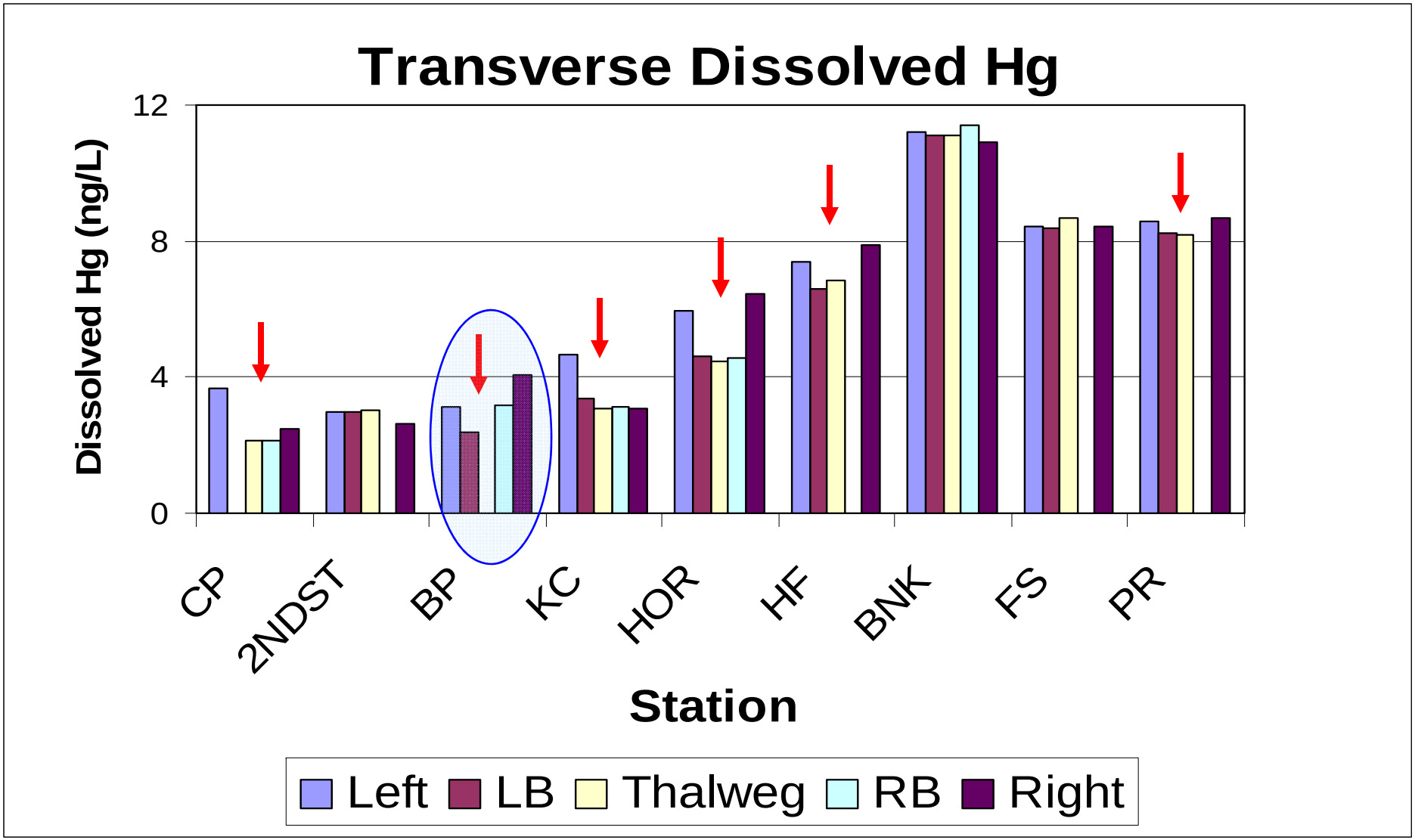
- Getting closer to answering the question “How is Hg getting into the South River in bioavailable form?”
  - Very likely not from point source(s)
  - Likely related to presence of Hg in floodplain/bank/bed solids in form(s) that can be released continuously into surface water
  - Role of shallow alluvial groundwater still being quantified

# General Objectives

- Identify in-stream Hg source(s) within Plant reach (RRM-0.7 to 0.3).
  - Bank or bed source(s)
- Determine origin of higher dissolved Hg concentration near banks (@RRM2.2) relative to thalweg.
  - Desorption from bank/bed solids
  - Shallow groundwater
- Develop tools and procedures applicable elsewhere on the river.


2005 Close-Interval Surface Water Data
(0.45 micron filtered)
Concentration (ng/L)
16
14
12
10
8
6
4
2
0
Jan/Mar Total Hg
Jan/Mar MeHg
May Total Hg
May MeHg
0
5
10
15
20
25
Relative River Mile

# Near-Bank Study Background



# Special Clarification

- Elevated dissolved Hg results for near-bank SW samples **do not** rule out possible additional center stream inputs/fluxes.
- They **are** a strong indicator that a reach is an active input location for SW.
- They **are** a strong indicator that the near-bank locations are active input locations to SW.

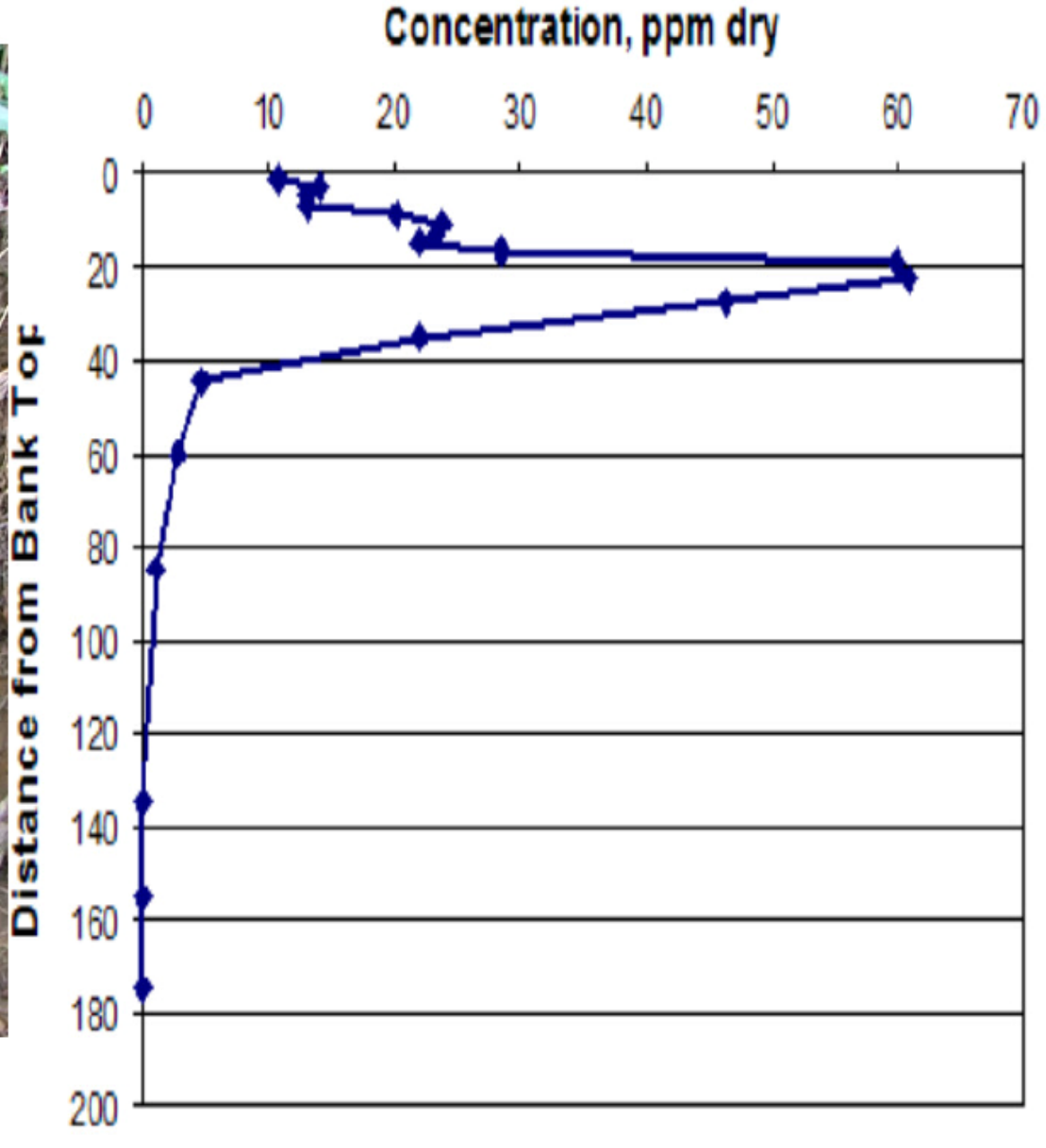
# Basic Park Study

*Objectives:* Confirm near-bank elevations of Hg and quantify/partition source between desorption from solids and alluvial groundwater.

# Near-Bank Study

## Investigative Approaches in Phase I

- Chose location coincident with ecostudy
- Synoptic measurement of
  - Surface water Hg, transverse and longitudinal in study area, to verify elevated near-banks and provide baseline.
  - Near-bank sediment Hg
  - Pore water/groundwater Hg
  - “Exhaustive” extraction of near-bank sediments and nearby “parent” bank soils.



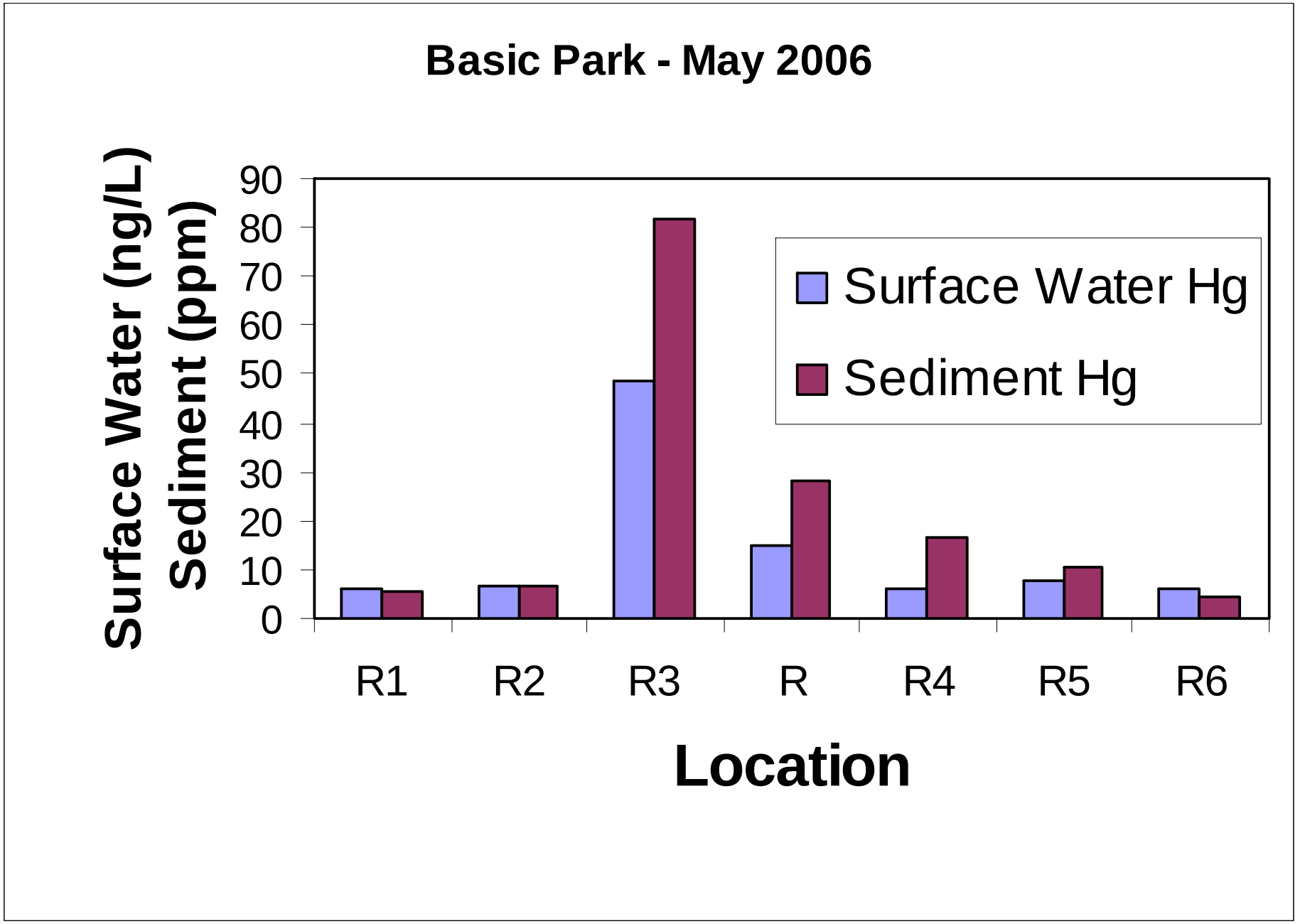

Sampled by University of Delaware-2005

# Surface Water Pattern

## Filtered THg (ng/L), May 2006

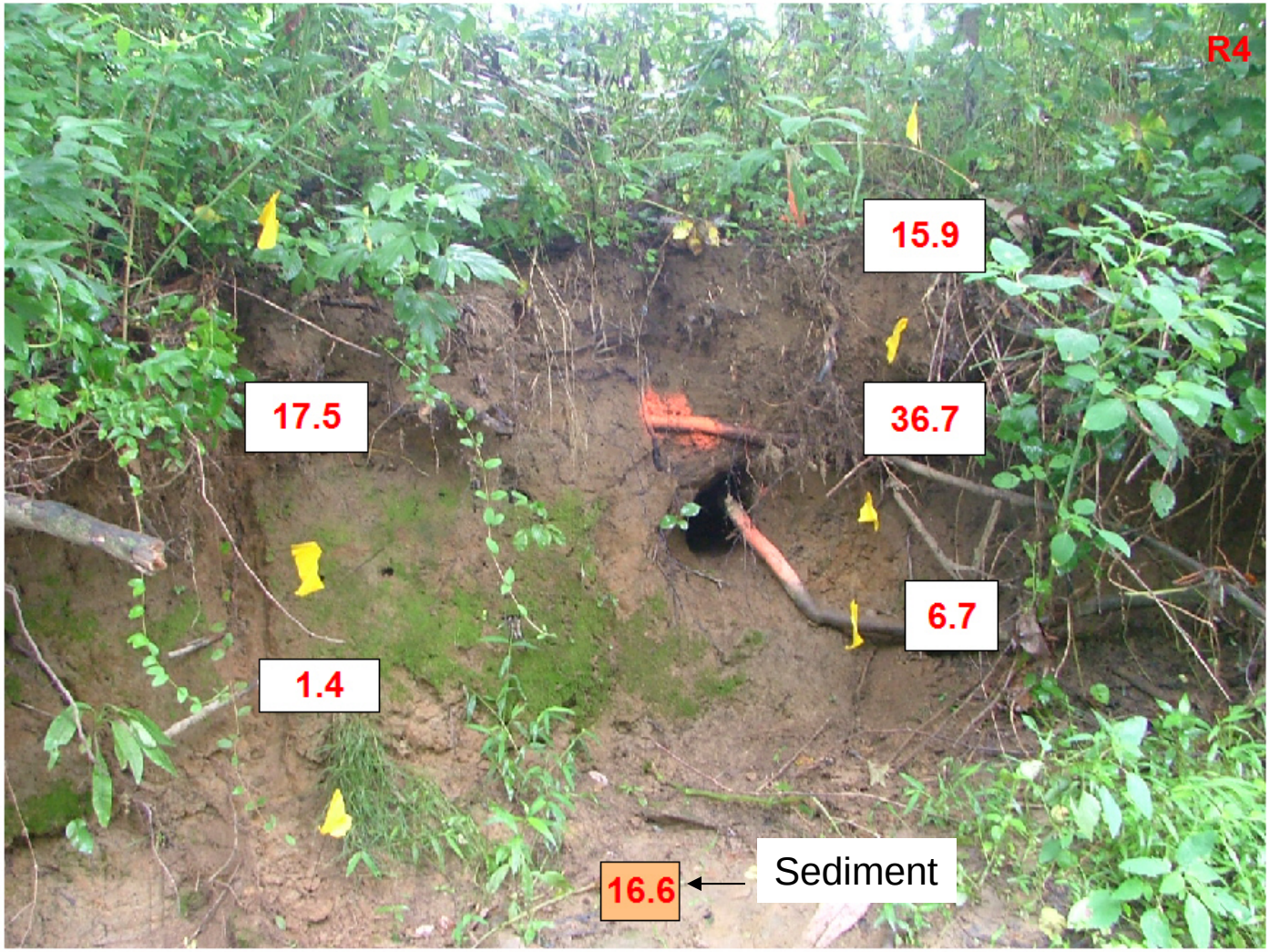
# Shallow Sediment Pattern

## THg (μg/g), MHg (ng/g)


Basic Park - May 2006
Surface Water (ng/L)
Sediment (ppm)
90
80
70
60
50
40
30
20
10
0
Surface Water Hg
Sediment Hg
R1
R2
R3
R
R4
R5
R6
Location

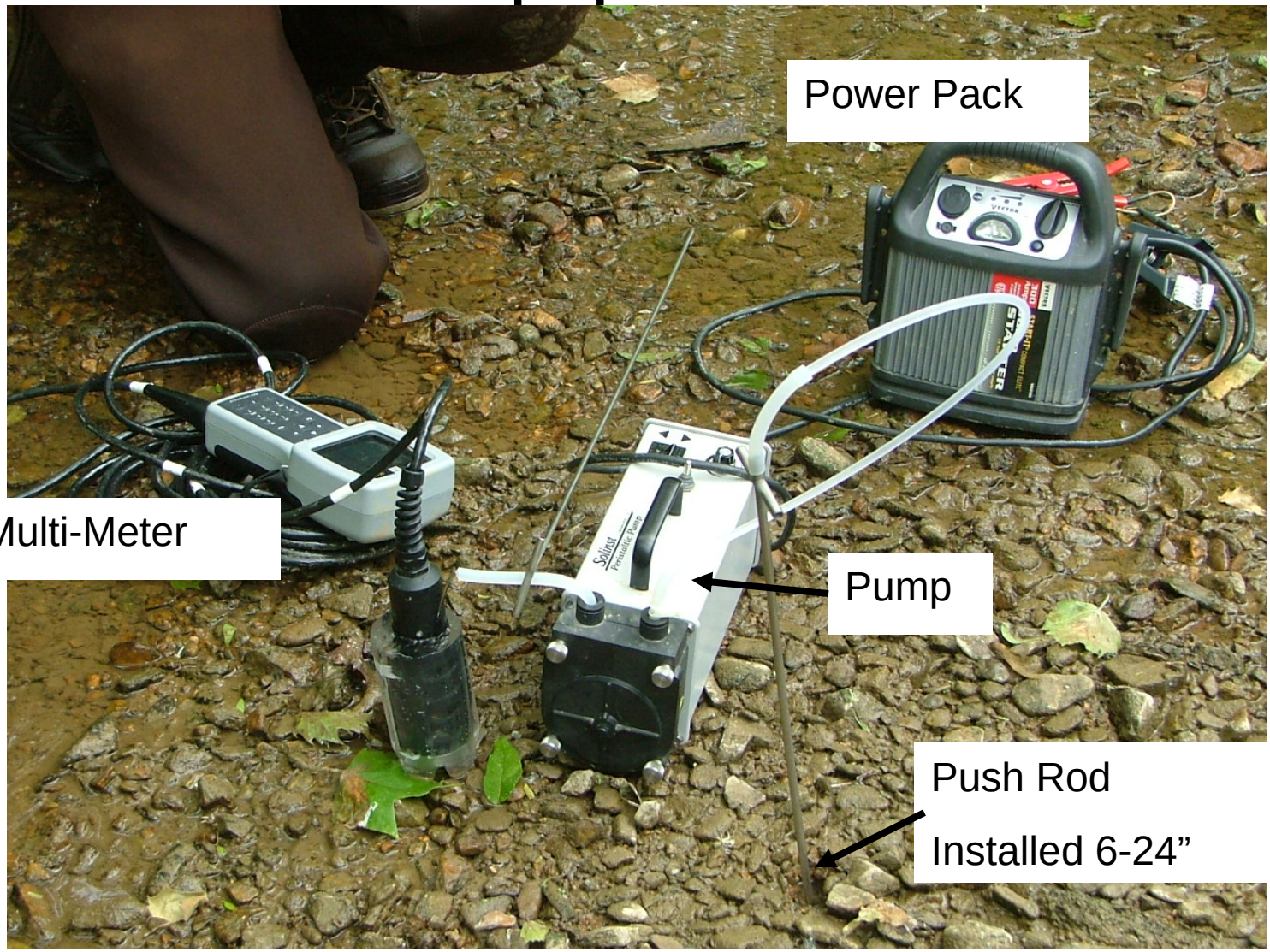
# Bank Soil Characterization, R4

vertical channels between flags in ppm




Enough Hg in bank soil to account for Hg in sediment beneath bank

# Pore/Hyporheic Water Sampling Equipment

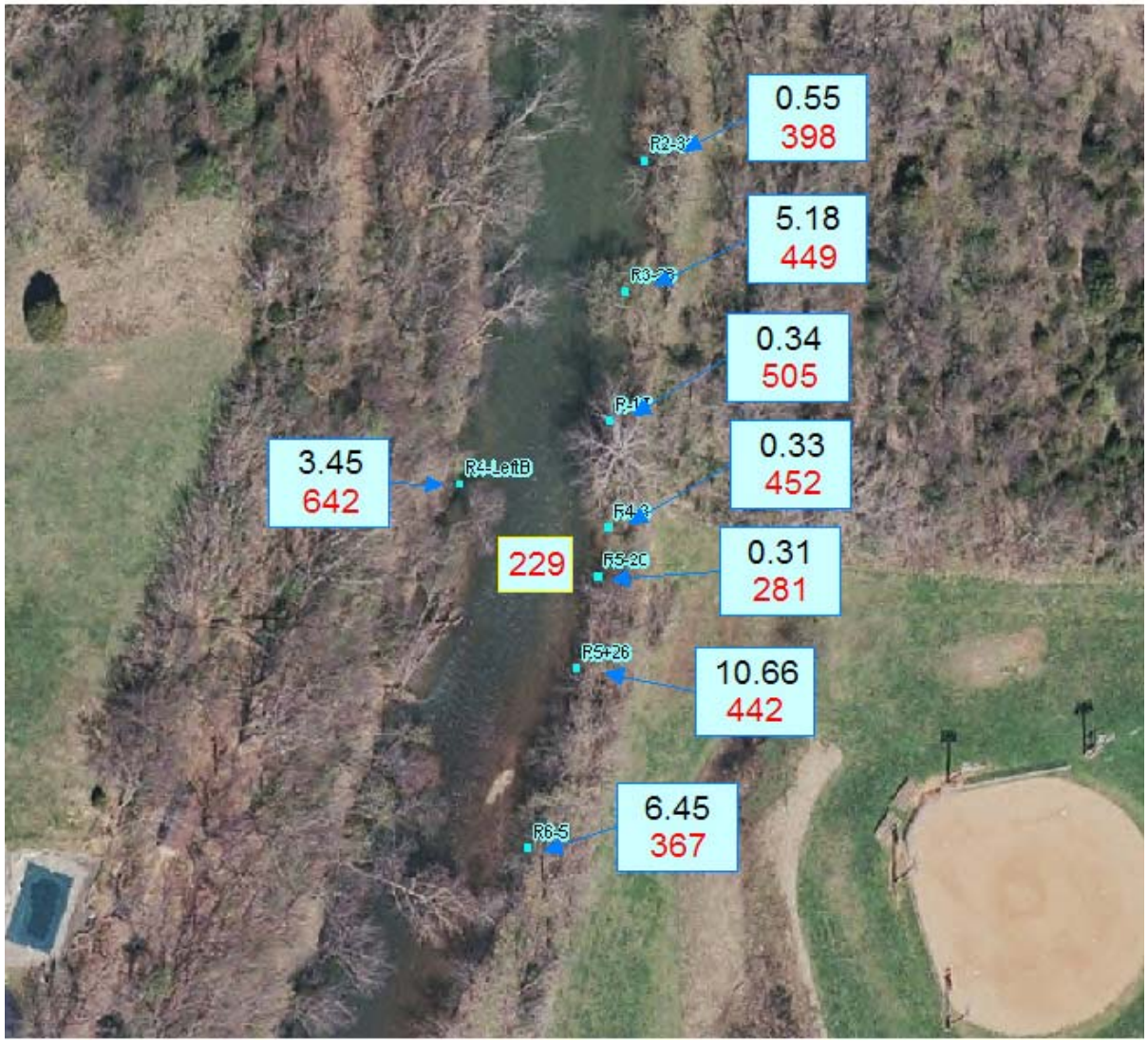



Also measure water level in manometer relative to river water level

# Porewater (GW) Pattern at Bank

## Dissolved (ng/L); Spec Cond (μS/cm)

## May 2006



# Hyporheic Water Pattern

## July 2006, Including one SW

# Hyporheic Water Transect

## Dissolved THg (ng/L)-July 2006


[Hg] in streambed hyporheic zone generally 2x to 3x surface water (SW) value

# Diffusion Buckets

Intended as a device to isolate a section of near-bank sediment from continuous “flushing” by upstream surface water, i.e., a simplified benthic flux chamber

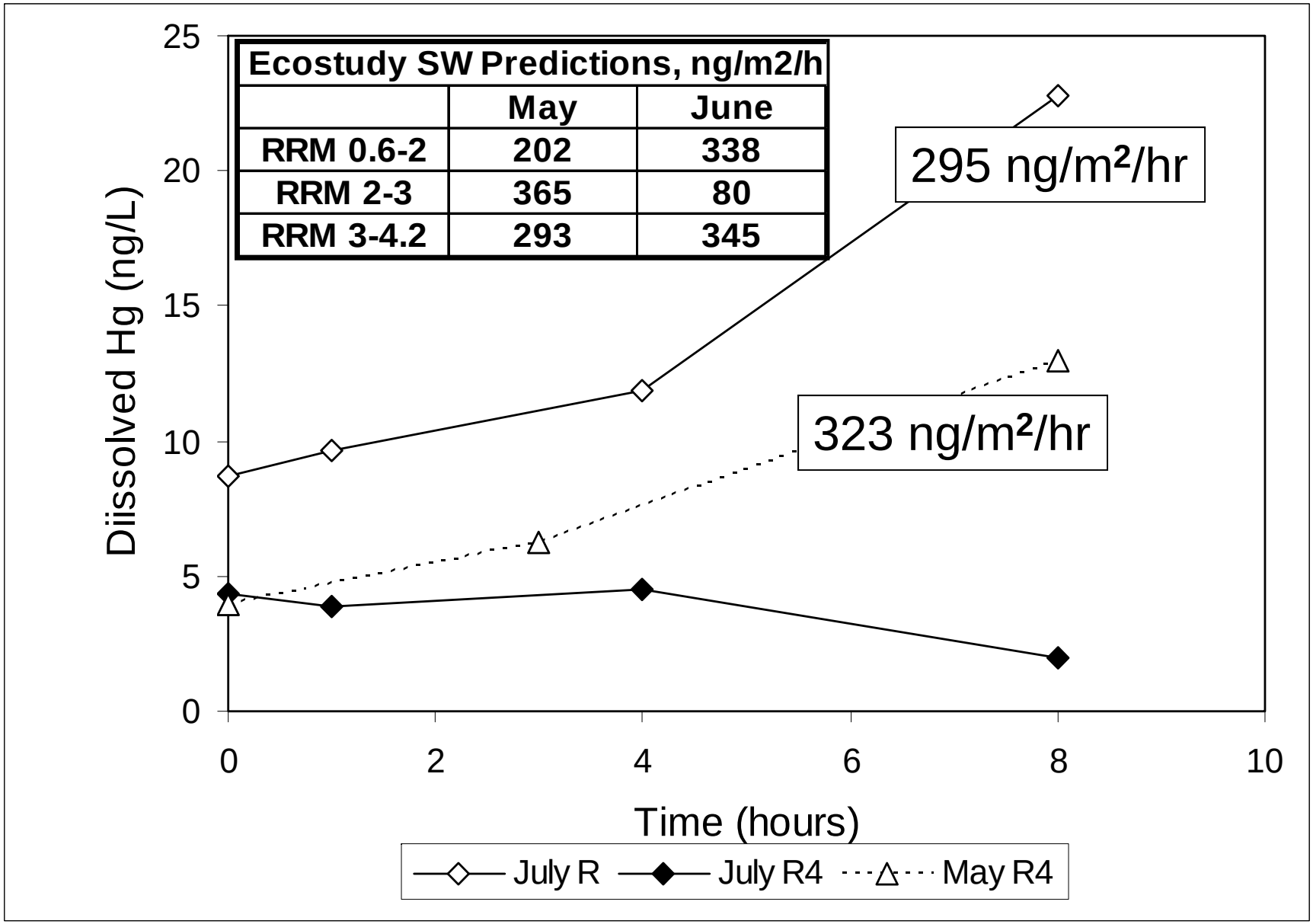
# Diffusion Buckets - July 06

R-4

RV Sea Hawk 200

R

# Diffusion Bucket Results



- Additional diffusion bucket data pending from 5 locations monitored for up to 23 hours in Sept 2006

# Near Bank Results - May/July 06

- Strong SW “signal” at near-bank Basic Park location
- SW results seem to “follow” sediments
- Sediments perhaps more “localized” than previously expected?
- Sufficient bank soil Hg to account for sediments
- Shallow groundwater at base of bank relatively clean in most locations (i.e., lower than SW)
  - Pore water elevations do not “follow” SW or seds
- Near-bank sediments appear to release Hg at rates comparable to apparent “whole” river releases

# Soil/Sediment Leaching Study

Objective: Determine whether Hg release from bank soils and near-bank sediments follows a “simple” desorption equilibrium.

# Experimental Approach

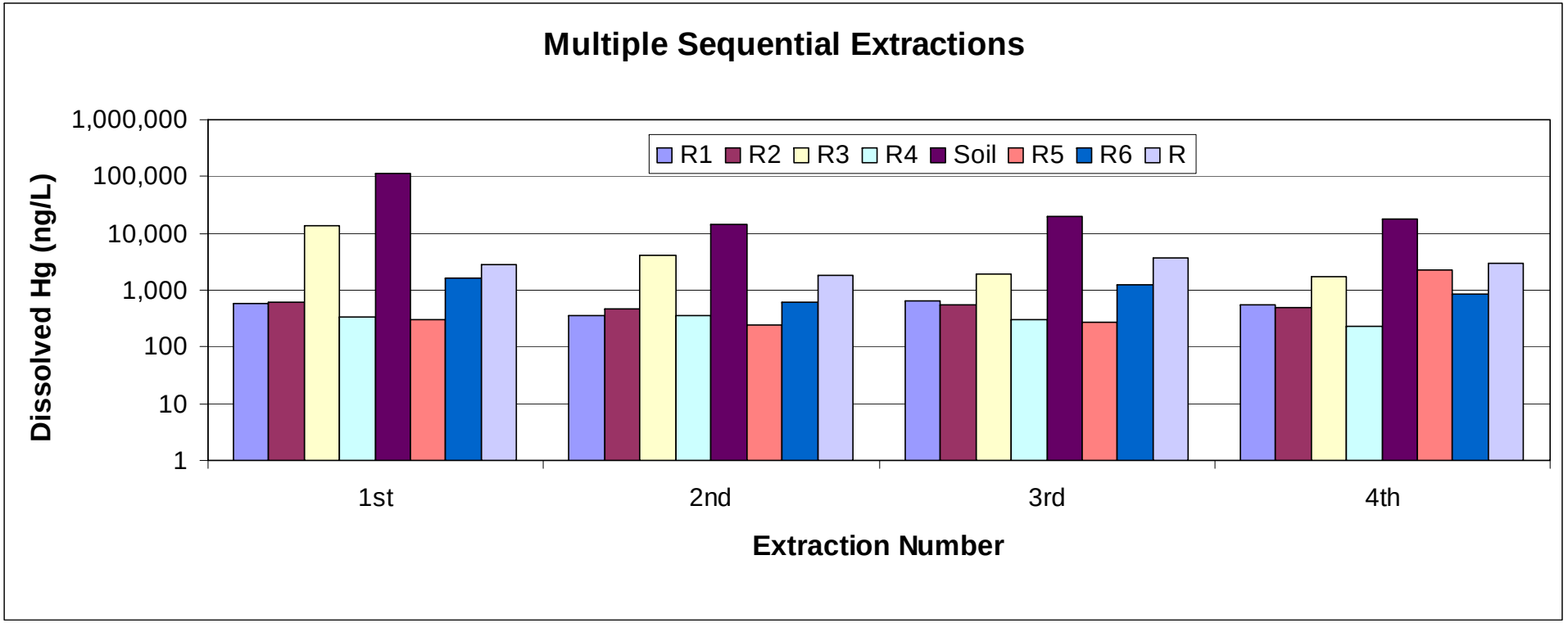
- Collect representative soil and sediments from study area at Basic Park.
- Perform four (4) successive extractions of each sample with DI water at solution/solid=10 (40 mL/4g)
- Analyze extracts for filtered (0.4 micron) mercury.
- Compare leaching patterns.

# Possible Leaching Patterns

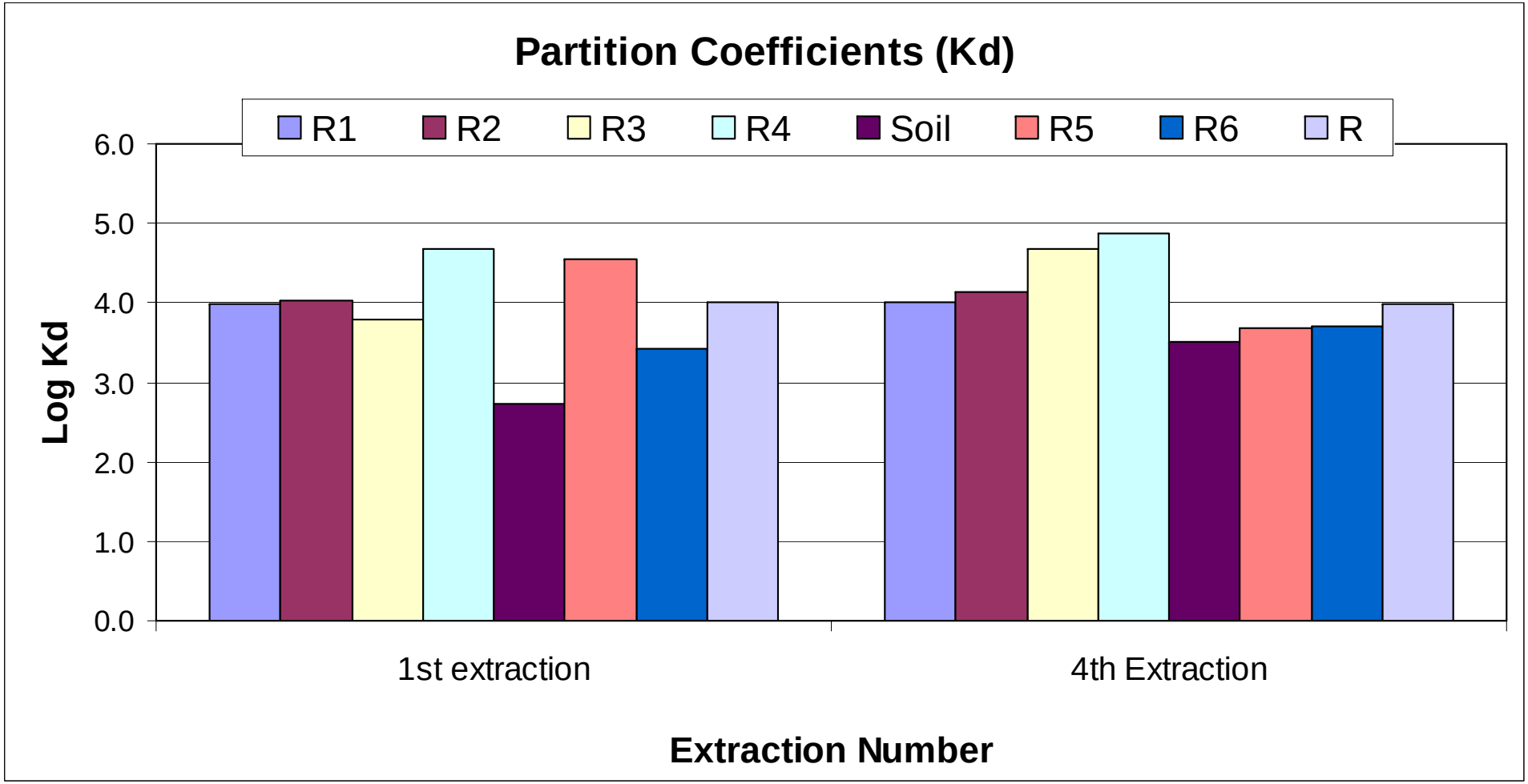
- Constant aqueous [Hg]
  - Suggests sorption/solubility “equilibrium” (infinite source)
- Decreasing aqueous [Hg]
  - Suggests “washout” of a highly soluble compound (e.g., HgO, $HgCl_2$)
- Increasing aqueous [Hg]
  - Suggests dissolution of an “occluding” compound or presence of a sparingly soluble compound (e.g., $Hg_2O_2$, $Hg_2Cl_2$, HgS) affected by redox reaction(s)

# Soil-Sediment Samples

| Sample ID | Total Hg (mg/kg dw) |
|---|---|
| R1 | 5.64 |
| R2 | 6.57 |
| R3 | 81.6 |
| R | 28.4 |
| R4 - Soil | 59.6 |
| R4 | 16.6 |
| R5 | 10.5 |
| R6 | 4.36 |




Similar aqueous [Hg] across all four extractions.
Bank soil produced highest aqueous [Hg]




Log Kds much lower than observed for  extractions run at higher solution/solid ratios.

Is this simply a “particle effect” due to overestimation of true aqueous [Hg] due to presence of colloidal Hg?

# Conclusions-Leaching Study

- Leaching patterns (constant [Hg]) suggest all samples have Hg in “exchange” positions.
- Bank soil produced the lowest partition coefficients (Kds) especially at the initial extraction.
- Release and diffusion of Hg from these materials could possibly account for longitudinal and transverse patterns in South River surface water Hg.
- Results from Rob Mason (shake & bake), and an earlier simulated TSS leaching, showed much lower releases but were conducted at much higher solution/solid ratios.

# Path Forward-Leaching Study

- Verify high aqueous [Hg] associated with the sediment samples by collecting “shallow” porewater samples from each location.
- Repeat extraction of one sample from set with filtered river water from SR-01 (Lyndhurst).
- Characterize the physical/chemical nature of Hg in these kinds of leachates (e.g., volatility, molecular weight, reactivity)