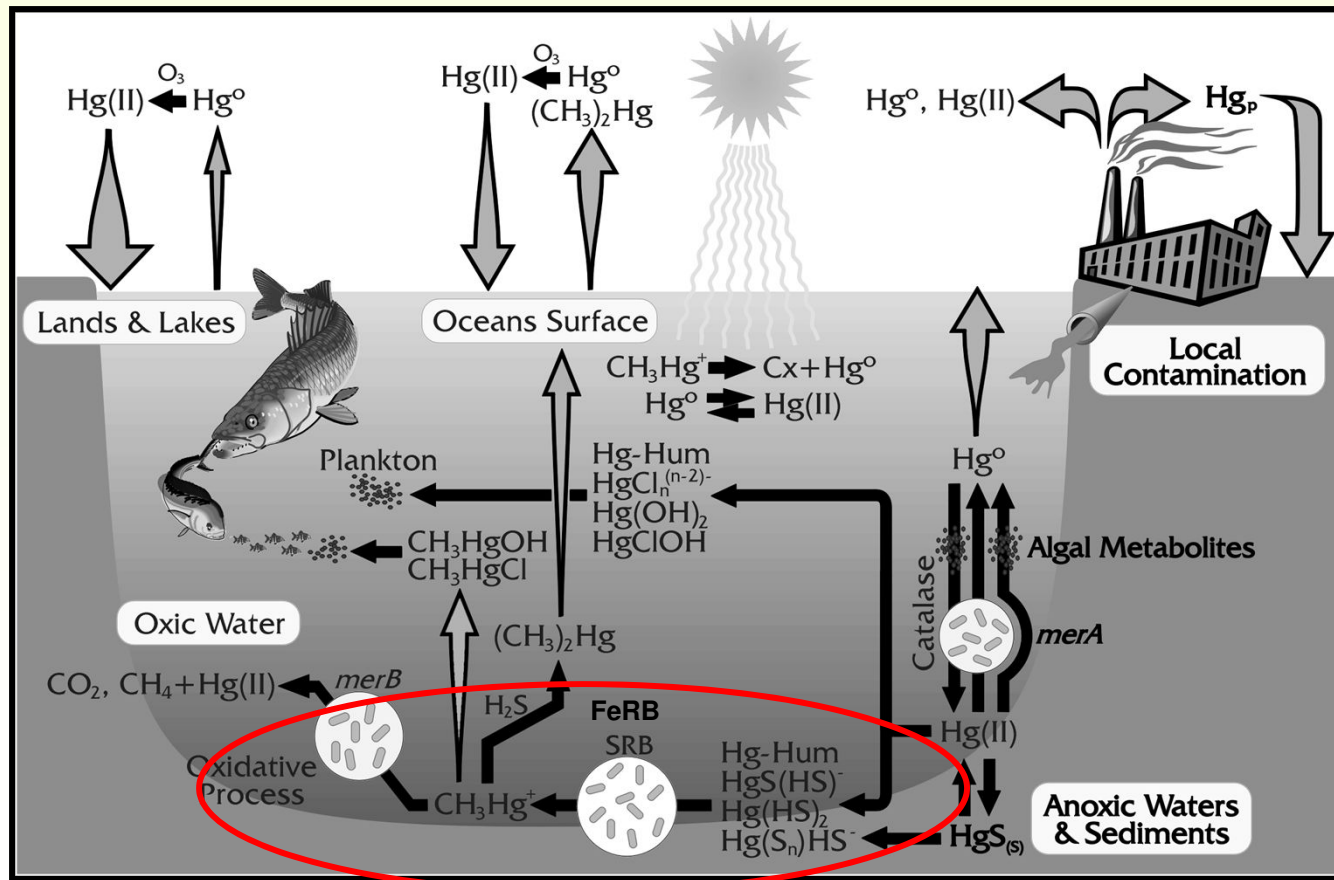


The microbiology of methylmercury production in South River sediments: Initial results

Tamar Barkay, Riqing Yu, Ralph
Turner, J.R. Flanders, and Erin Mack

Why is our study important ...



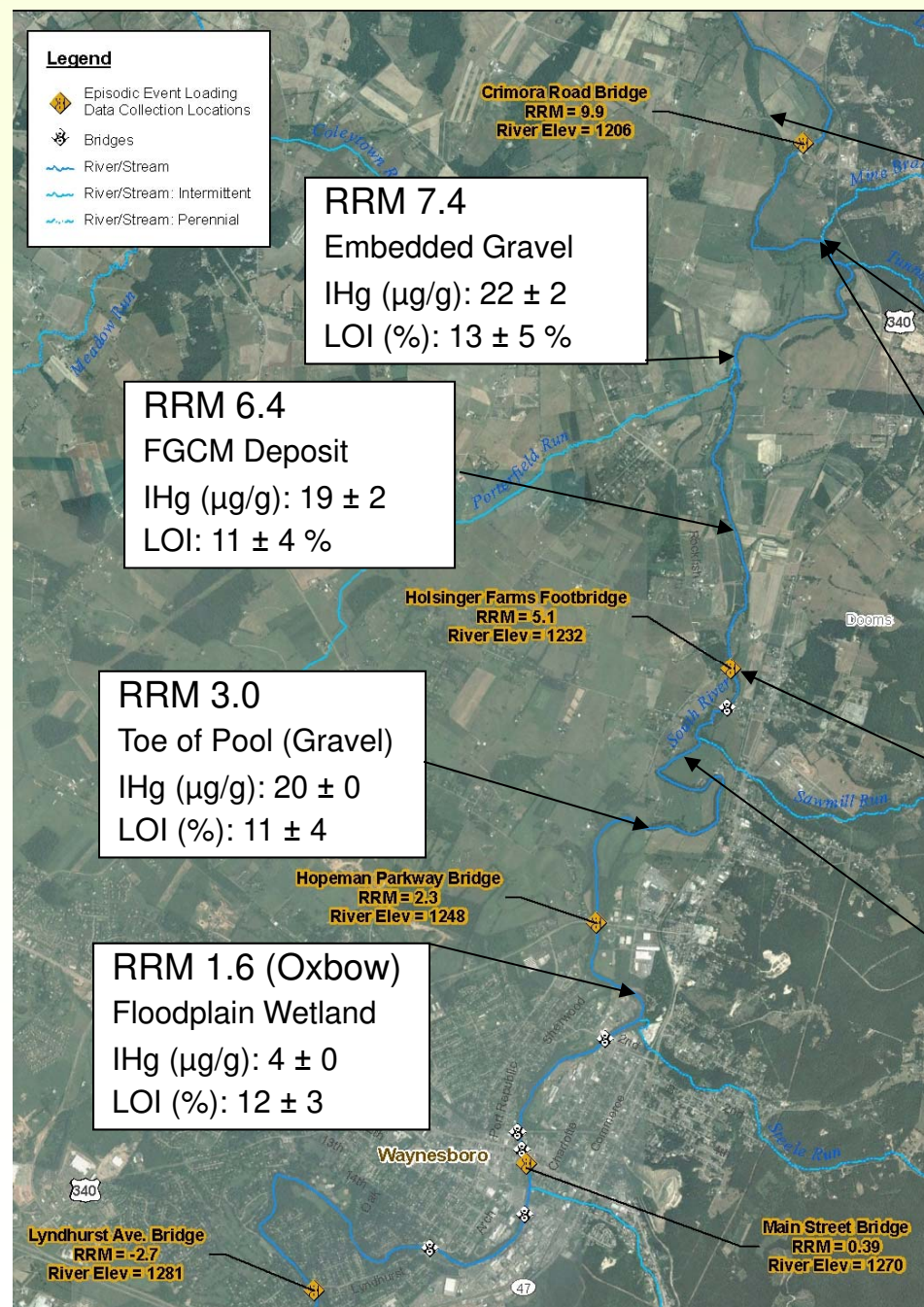
Three critical questions:

- Where along the South River is there a potential for Hg production?
- What microorganisms dominate and are active in river sediments with a high potential for Hg methylation?
- What fraction of Hg in the environment is available for methylation?

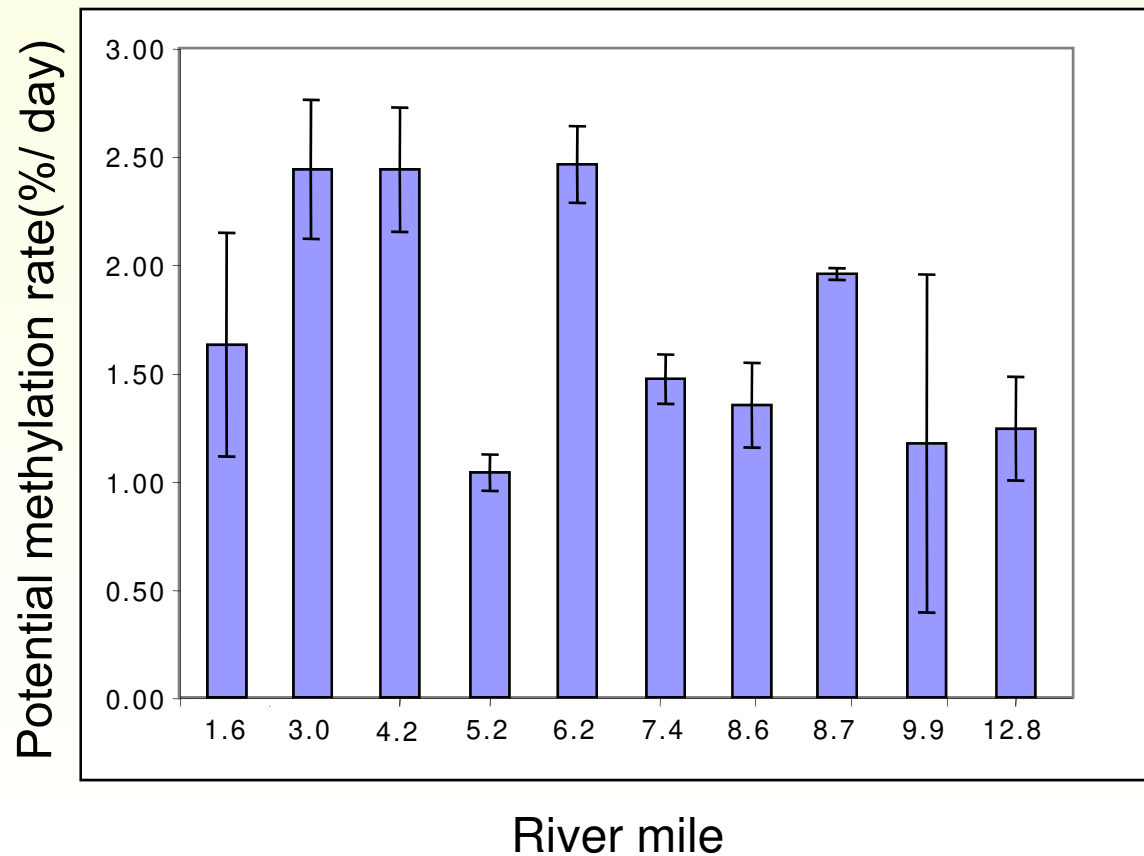
The potential for MeHg production - methodology

- Set up incubations of sediment slurries with:
 - ✓ $^{203}\text{HgCl}_2$ for the determination of potential rate of methylation
 - ✓ ^{14}C -MeHg for the determination of the potential rate of MeHg degradation
 - ✓ Samples collected along the South River (RRM1.6 to RRM12.8) in May and Aug. 2008
- Calculate percent methylation/demethylation rates per day
- Samples for which potential methylation relative to potential demethylation rates are high are likely places where MeHg is produced

Sediment Samples: Locations and Characteristics



Potential methylation (May 08)

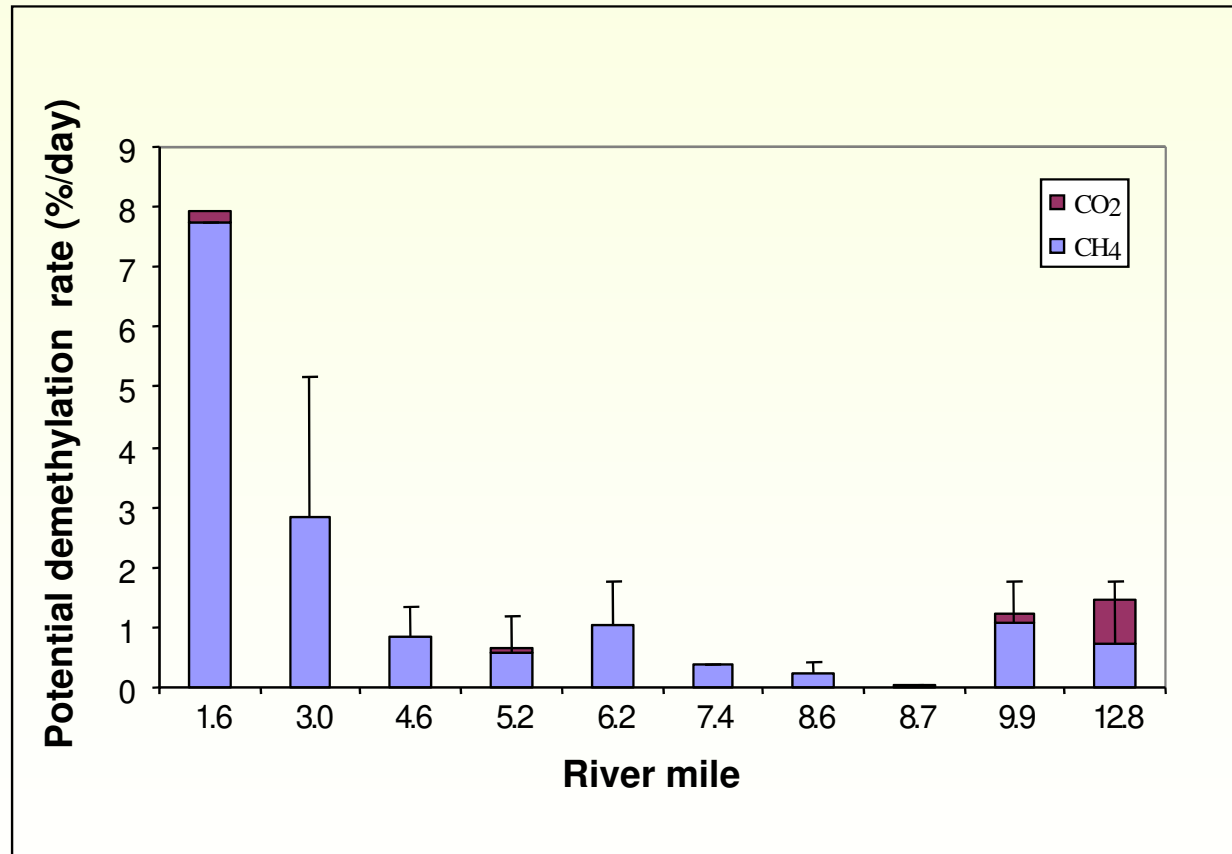


Range: 1.04 ± 0.08 (RRM 3.0) to 2.46 ± 0.18 (RRM 6.2) %/day

In comparison:

- Adirondack wetland - 0.1 ± 0.04 to 1.2 ± 0.14 %/day (Yu et al, in preparation)
- Gulf of Trieste - 0.5 to 1.5 %/day (Hines et al., Env. Res. 83:129, 2000)
- Valdeazogues River sediments (Almadén, Spain) - 0.38 to 13 %/day (Gray et al., ES&T 38:4285, 2004)

Potential demethylation (May 08)

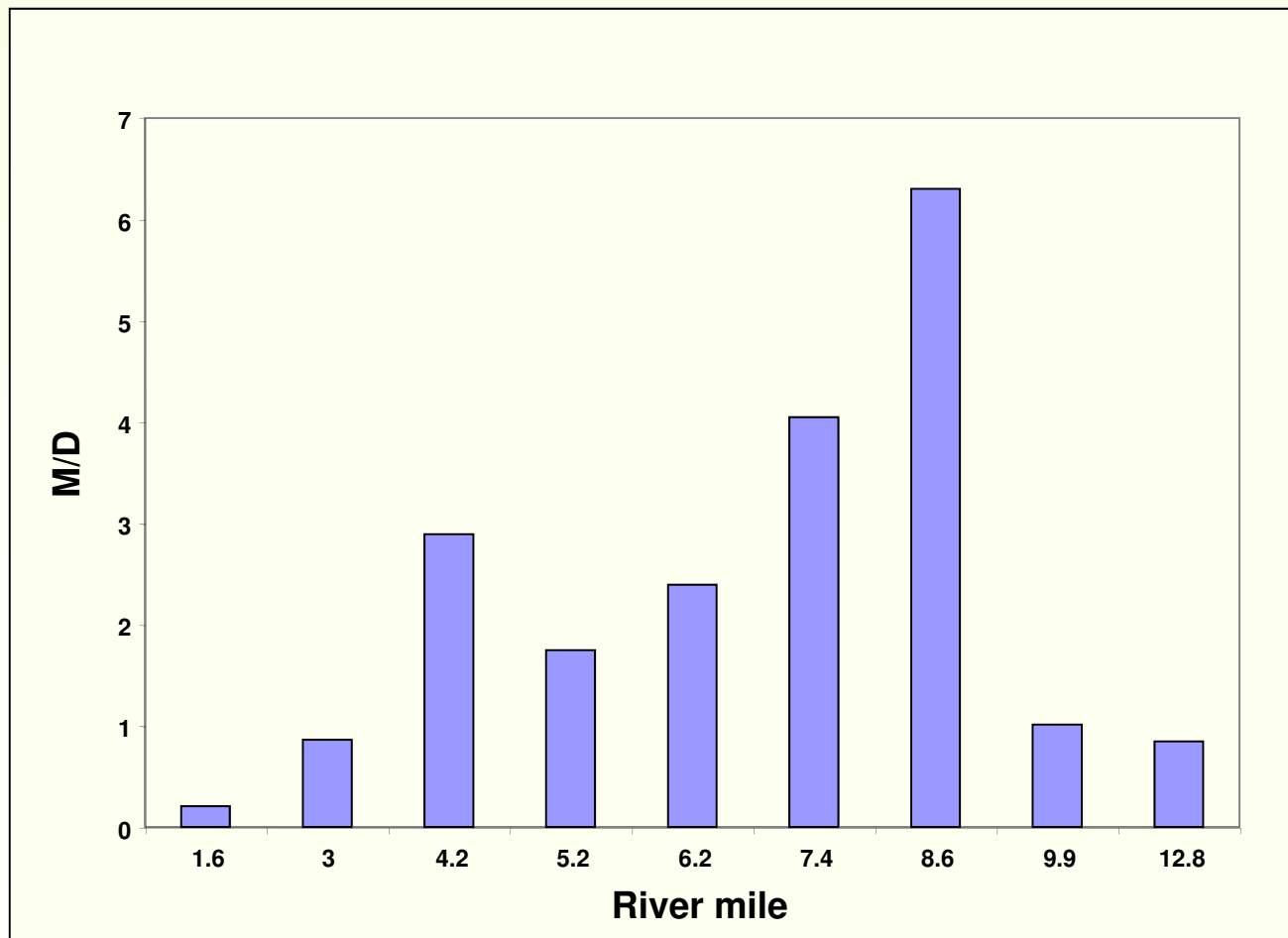


Range: 7.94 (RRM 1.6) to 0.05±0.04 (RRM 8.7) %/day

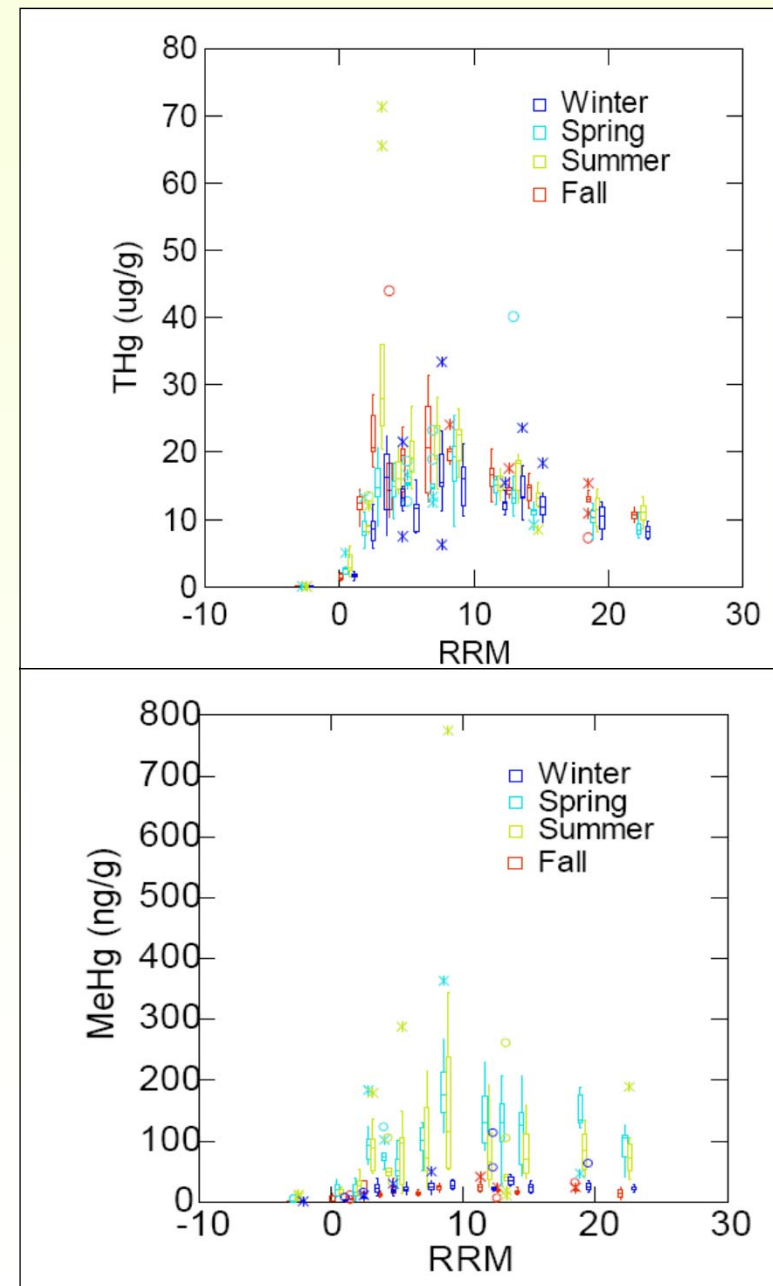
In comparison:

- Gulf of Trieste - 6 to 8 %/day and all CO₂ (Hines et al., Env. Res. 83:129, 2000)
- Valdezogues River sediments (Almadén, Spain) - 0.04 to 17 %/day and both CO₂ and CH₄ (Gray et al., ES&T 38:4285, 2004)

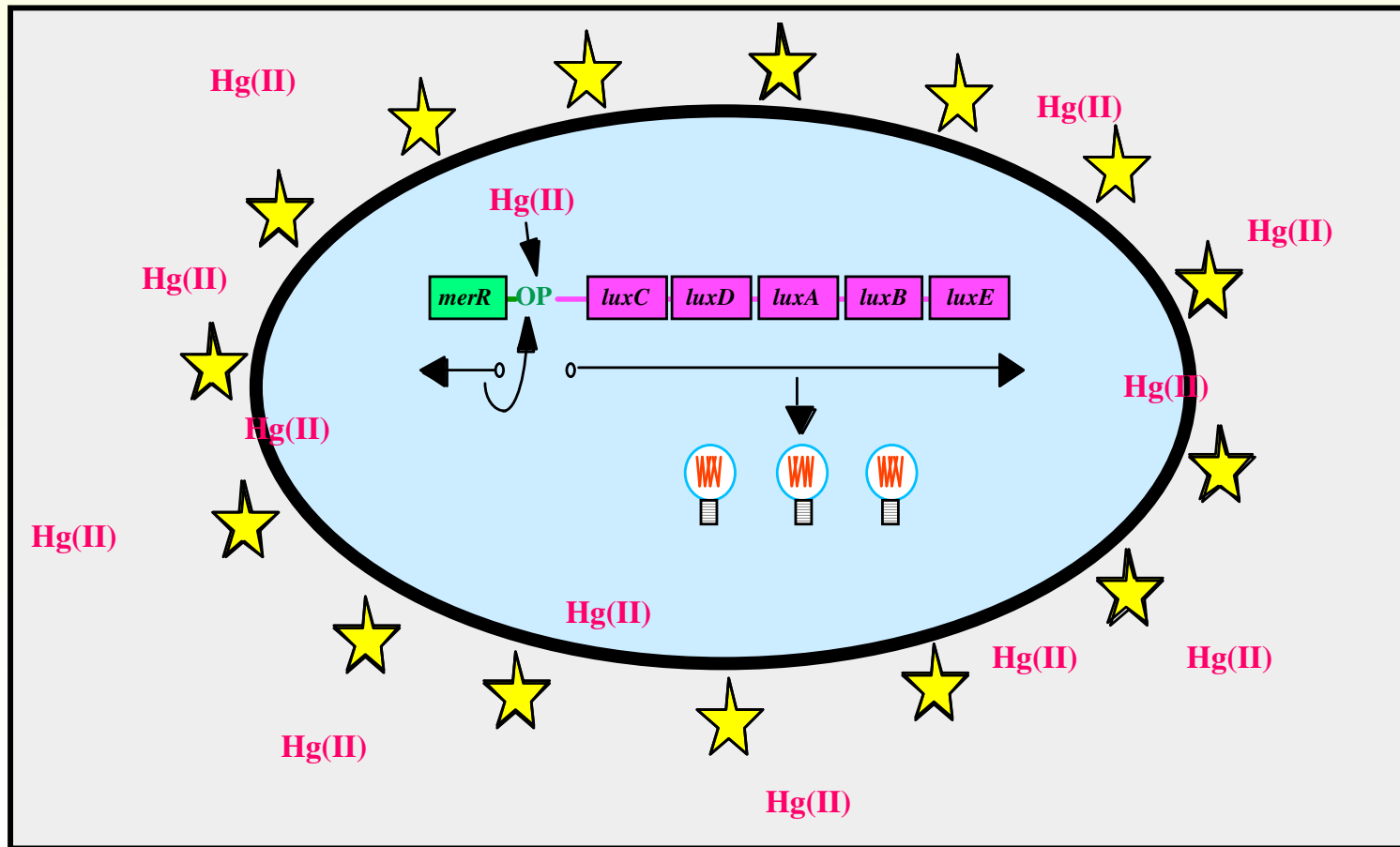
Net potential for MeHg formation (M/D)



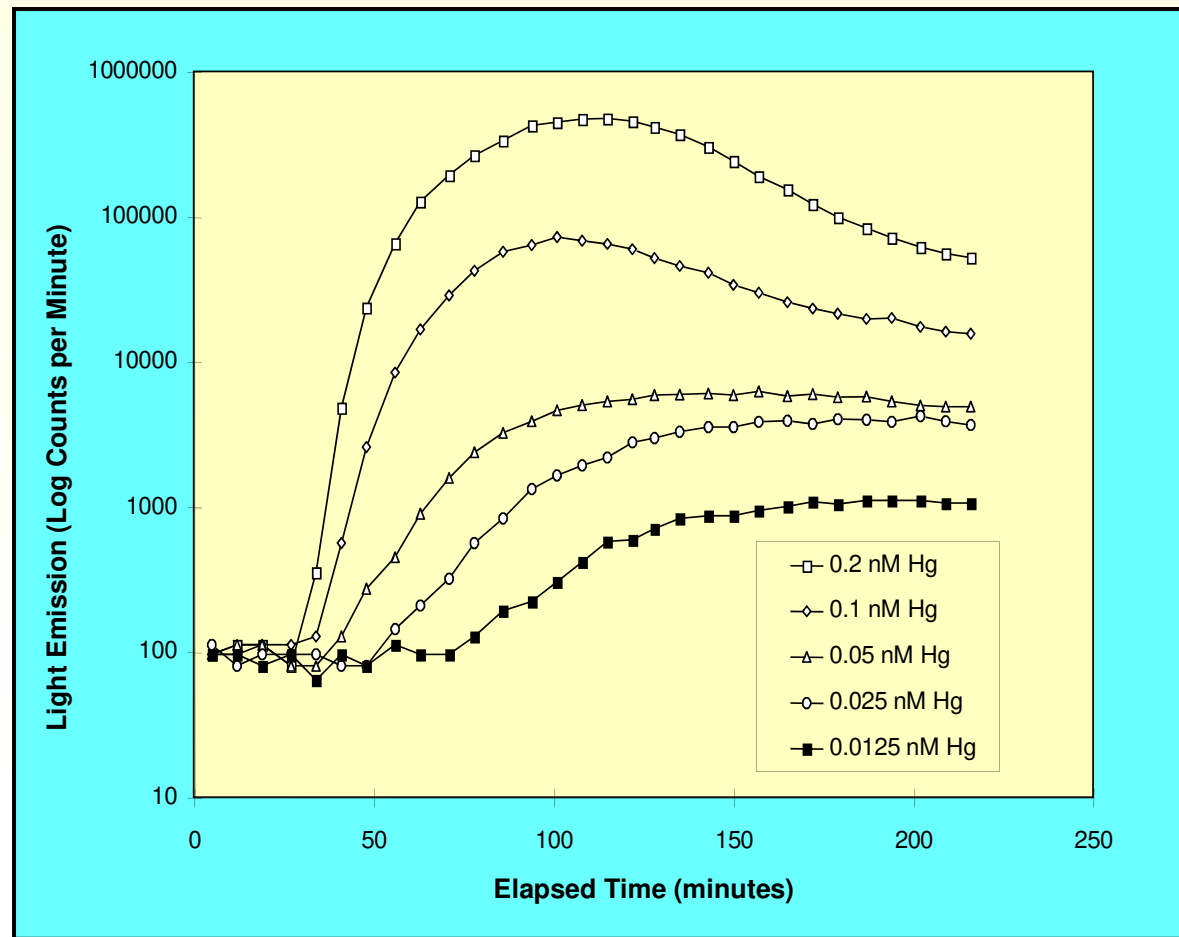
- Pattern of M/D ratio with RRM resembles that of THg and MeHg in sediment from Eco Study sampling
- Potential artifacts include
 - ✓ Different habitat types
 - ✓ Varying parameters (THg, LOI, pH, etc) in sediment
- Confirmation - Analyses of samples collected in Aug. 2008 in progress



The Hg²⁺ bioreporter

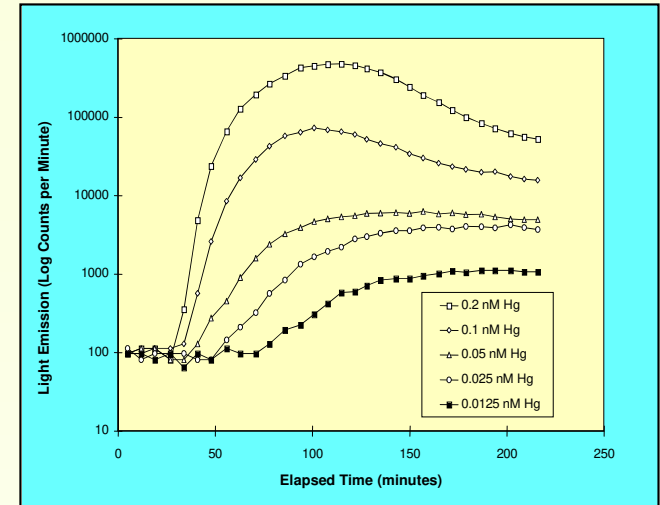


**The response of the bioreporter is
quantitative - 10^5 cells/ml**

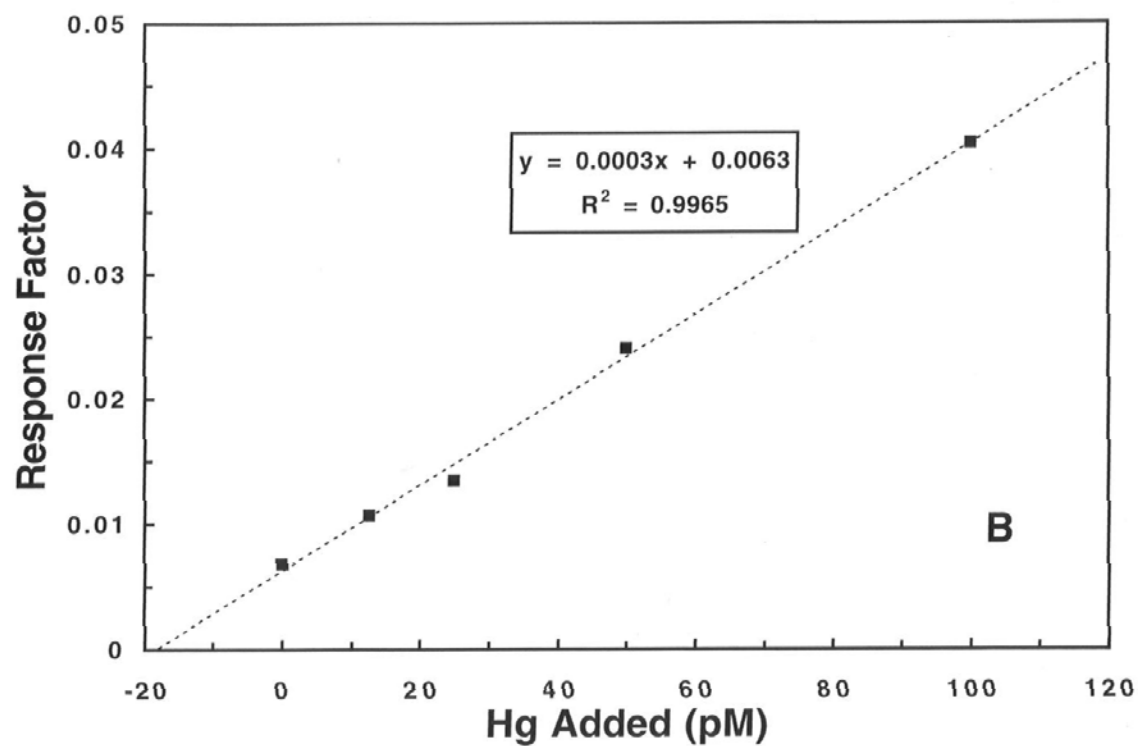


Bioreporter data processing

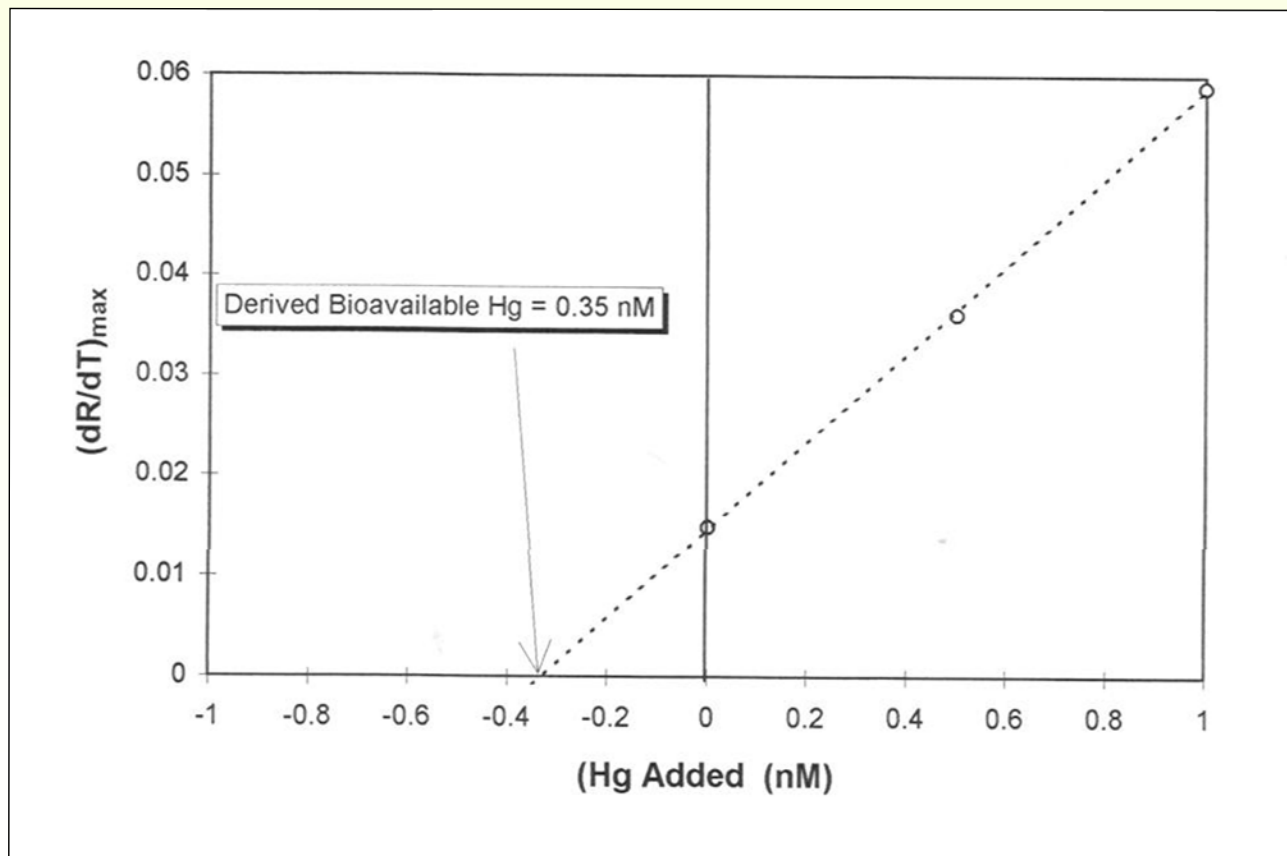
- Possible Figures of Merit for Calibration
 - ✓ Peak light value (RLU)
 - ✓ Integrated light production (Σ RLU)
 - ✓ Lag Time (minutes)
 - ✓ **Maximum rate of light production ($dRLU/dT_{max}$)**
a.k.a. “Response Factor”
- Applications (quantitative) in natural water require calibration of Response Factor to reagent Hg in distilled or site water



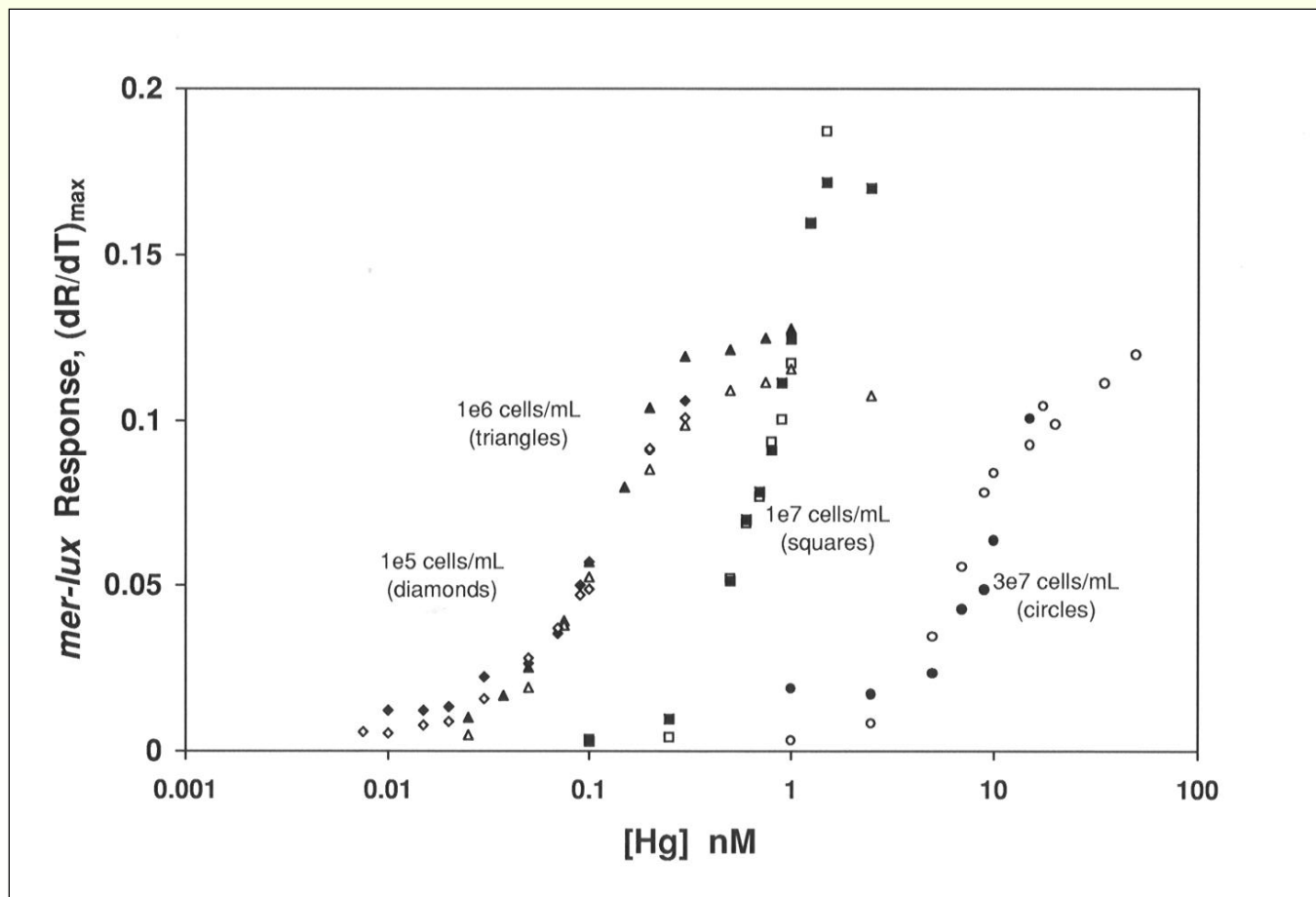
“Typical” linear calibration in distilled H₂O (from ORNL/EPA work)



Alternate calibration method (Natural Matrix Standard Additions)



The sensitivity range of the bioreporter is controlled by the number of bioreporter cells:



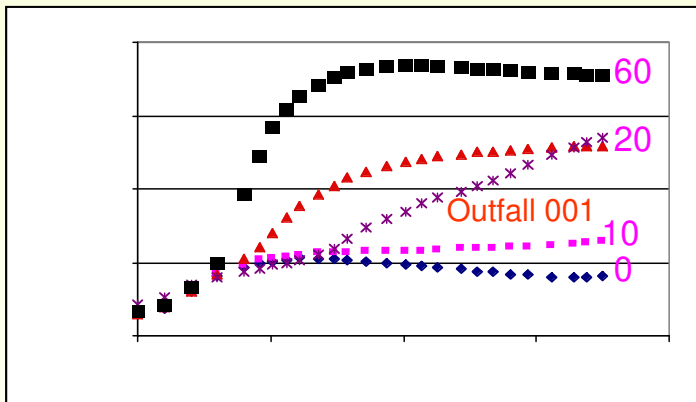
What has the Hg bioreporter been used for:

- Estimating “bioavailable” Hg in natural waters and soil extracts
- Assessing the impact of environmental factors on Hg bioavailability
- Studying transport of Hg through microbial cell walls

The South River:

- Use the bioreporter to compare the bioavailability of Hg in:
 - ✓ Water extracts of floodplain soils, near bank sediments,
 - ✓ and river bed deposits
 - ✓ Pore water of near-bank sediments
 - ✓ Hyporheic water from gravel bars
 - ✓ Outfalls
- Compare the bioreporter response to other methods for the assessment of bioavailable Hg (0.45 μm filter-passing, reactive and ultrafiltered [<5000 MWCO] Hg)
 - ✓ Can we find and validate a surrogate for the bioreporter that is easier to measure?

Example Results and Calculations



Data Reduction

Sample	Exp Factor
Std 10, ng/L	9.37
Std 20, ng/L	428
Std 60, ng/L	10812
Outfall 001	258

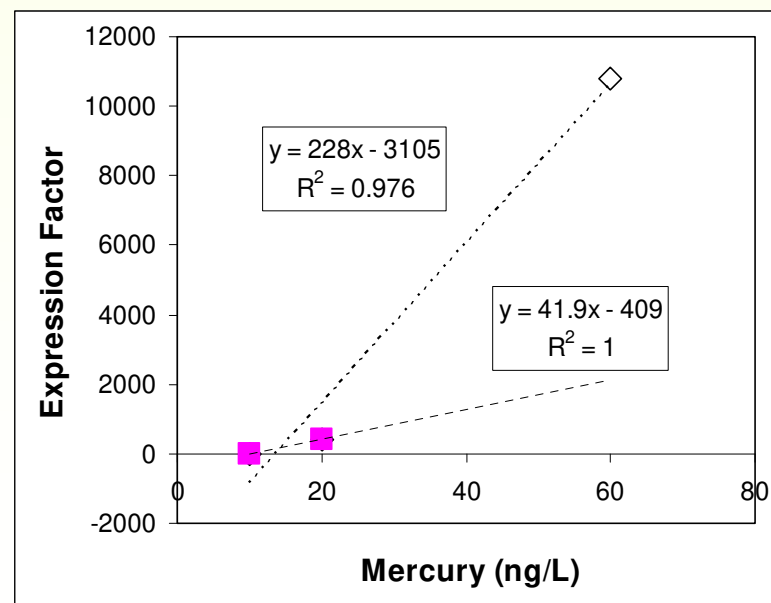
Analytical

Outfall 001, 9/23/2008
 $< 0.45 \mu\text{m} = 32 \text{ ng/L}$
 $\text{Hg(II)} = 29 \text{ ng/L}$

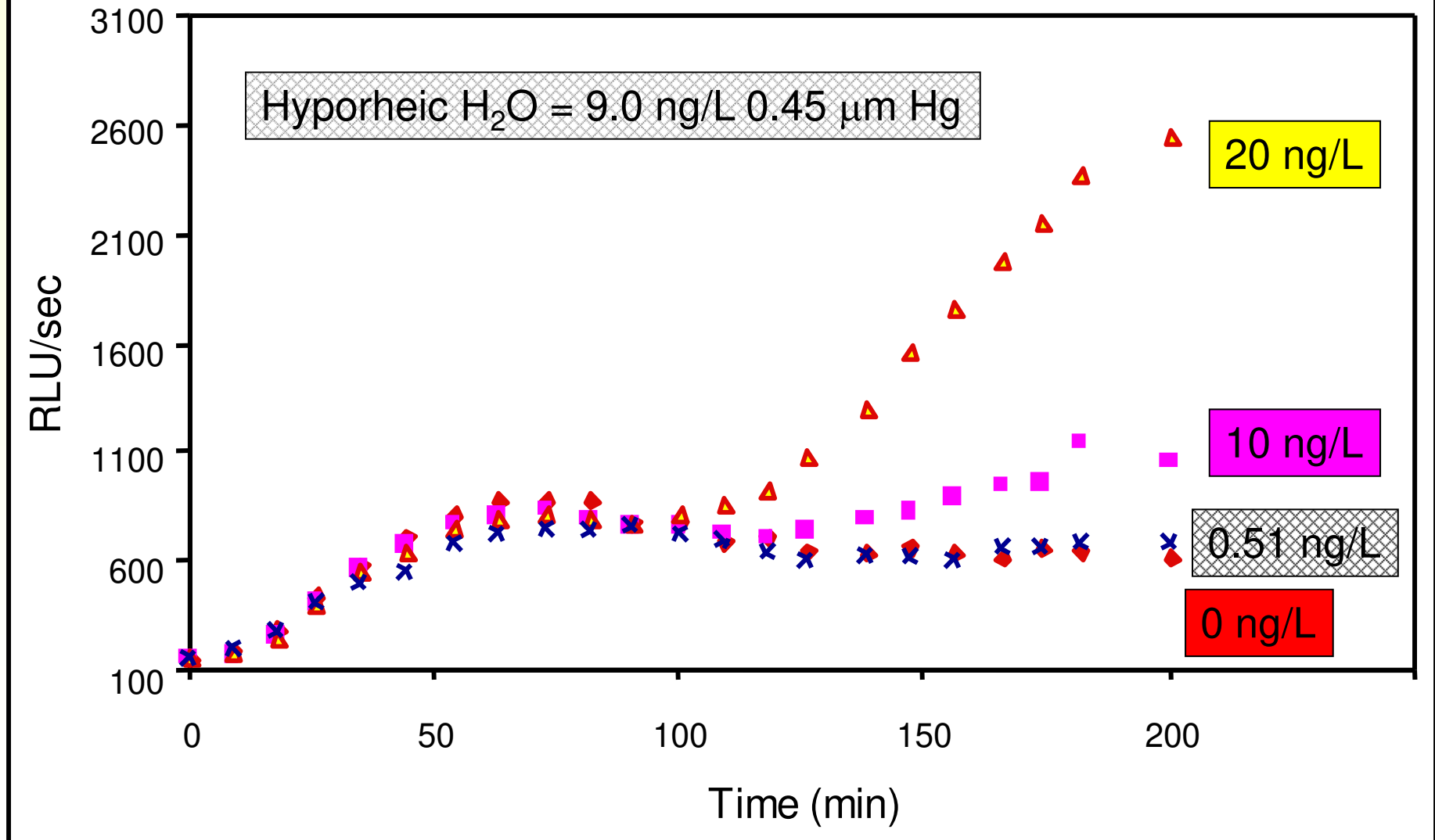
Bioreporter

Derived "BioHg", ng/L	
All Data	14.8
10 & 20 only	15.9

Calibration



10^6 cells/ml Calibration and Basic Park Hyporheic Water



Example of a case where using a lower cell density would have improved sensitivity of the assay

Summary - Bioreporter

- The bioreporter responds to Hg in SR samples!
- Further optimization of the bioreporter is needed for SR samples (calibration, cell density)