

**Project Update:  
Review of Conceptual Site  
Model of Mercury Cycling in  
South River**

**Aaron Redman, Ed Garland,  
Cristhian Mancilla, Bob Santore**

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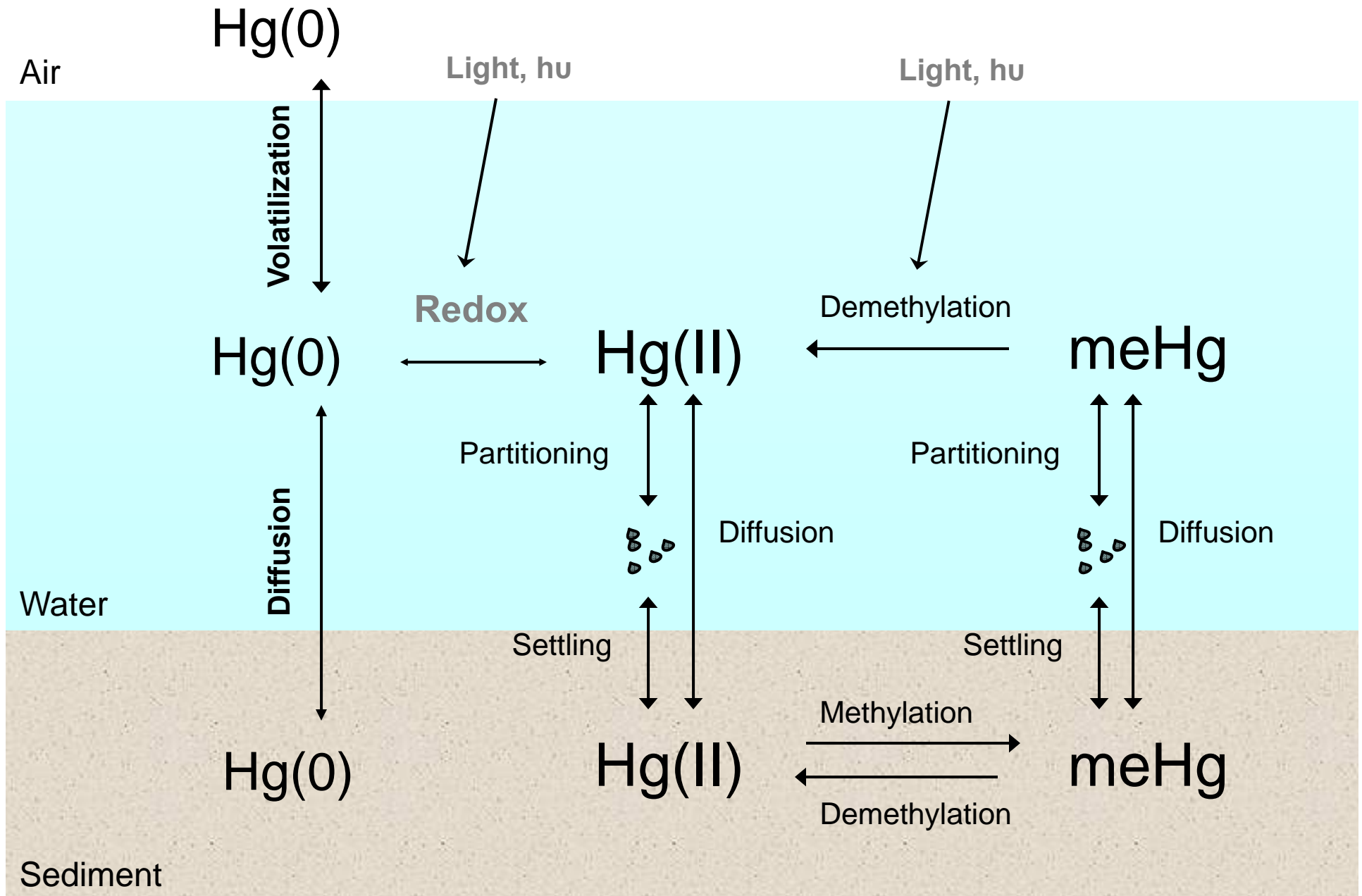


# Goals and Objectives

A semi-quantitative approach is used to:

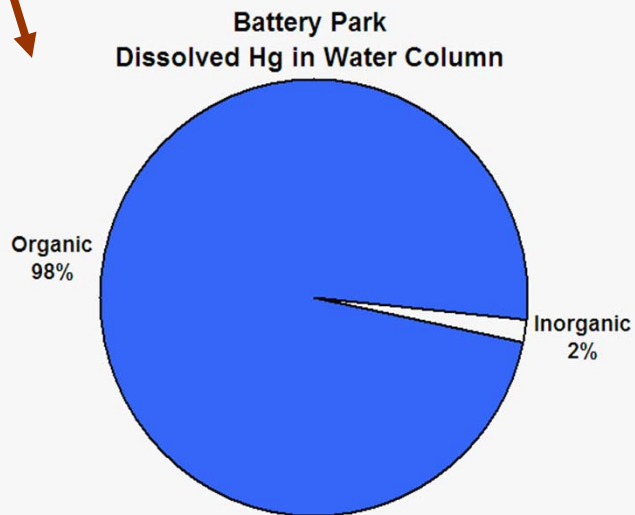
- Identify potential sources of mercury and methylmercury to the South River
- Identify important processes for migration and exposure pathways
- Identify data needs for further refinement of the CSM
- Recommend new or improved methodologies for collecting data to meet needs
  - See last slide for citations on conceptual model for Hg bioavailability

# Conceptual Mercury Model

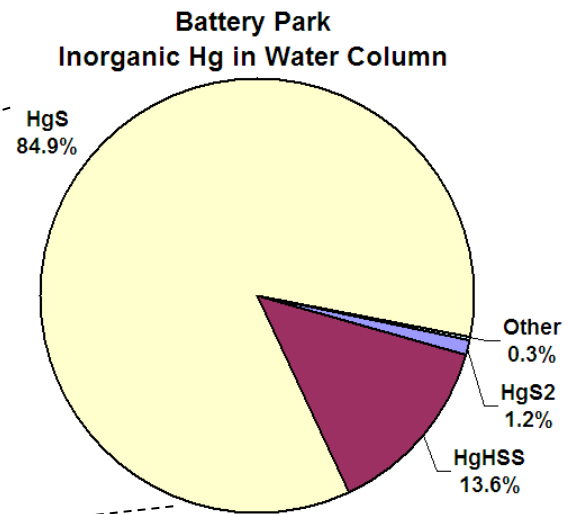


# Water Column Inorganic Hg Distribution – NY/NJ Harbor

- Inputs: DOC, POC, Sulfide, pH and more

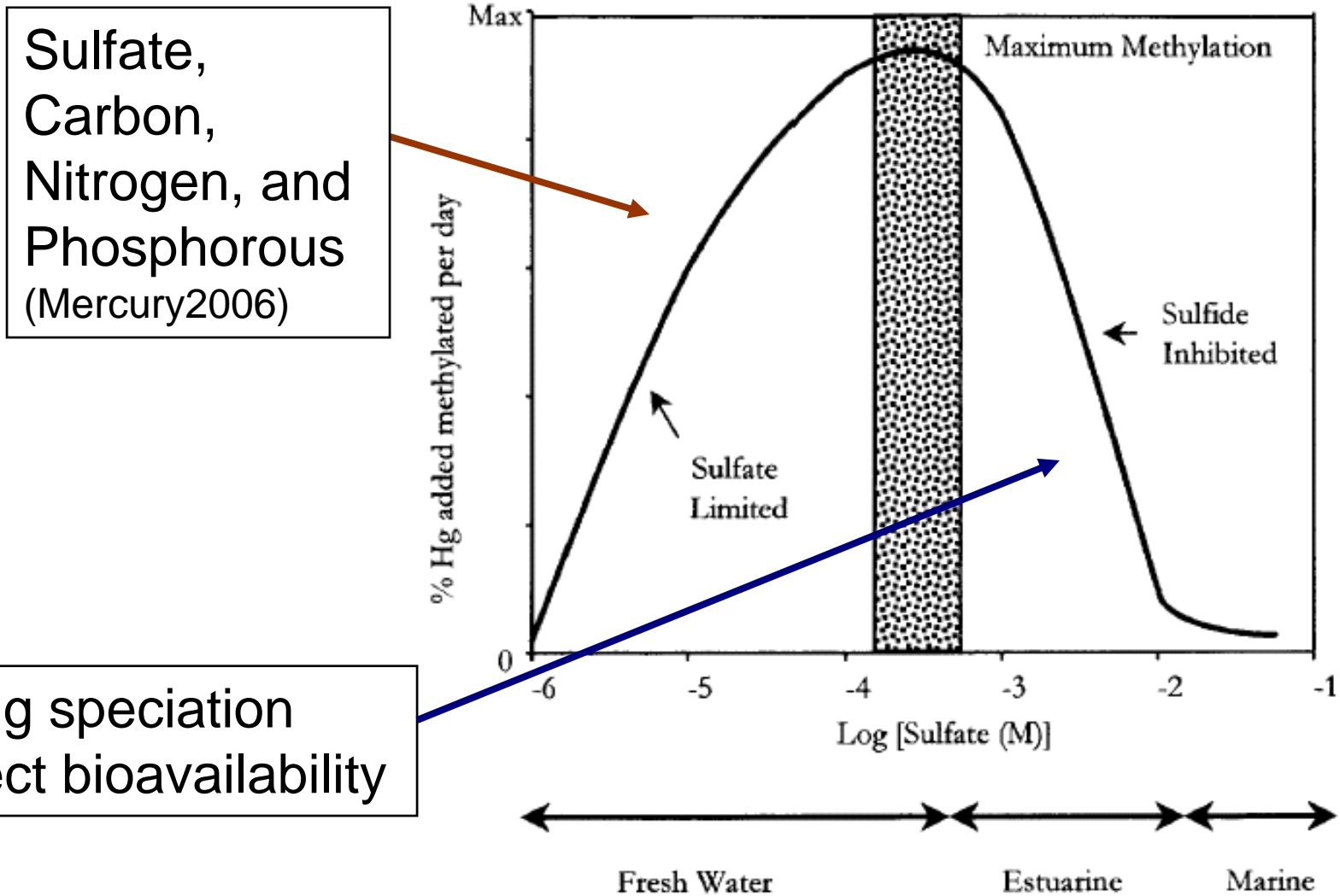


$\text{HgCl}^+$   
 $\text{HgCl}_2$   
 $\text{HgCl}_3^-$   
 $\text{HgCl}_4^{2-}$   
 $\text{HgOH}^+$   
 $\text{HgOH}_2$   
 $\text{HgOH}_3^-$   
 $\text{HgOHCl}$   
 $\text{HgSO}_4$   
 $\text{HgS}$   
 $\text{HgS}_2^{2-}$   
 $\text{HgHS}_2^-$   
 $\text{HgHSS}^-$



# The Evolving Conceptual Model of Microbial Mercury Methylation

(Gilmour and Henry 1991 as redrawn by Langer et al 2001)

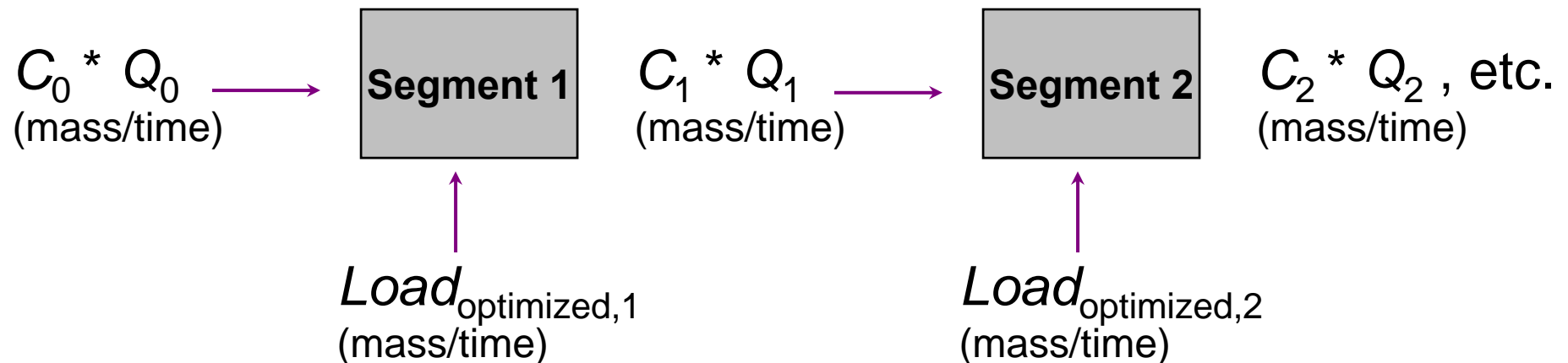




# Evaluating Potential Sources

## Loading Model

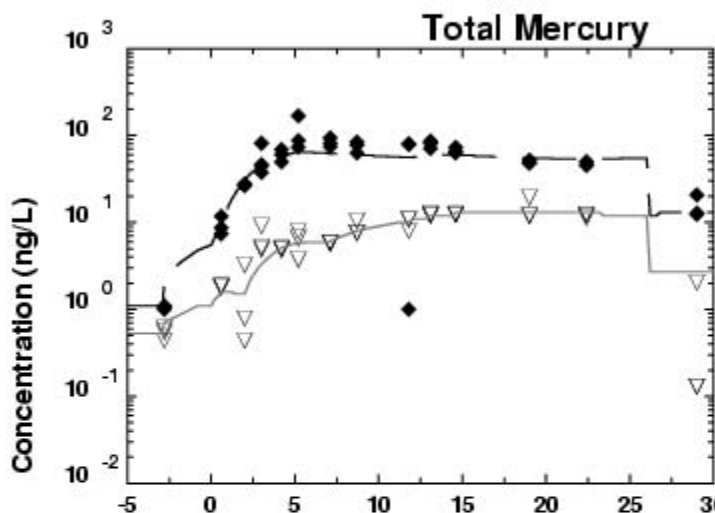
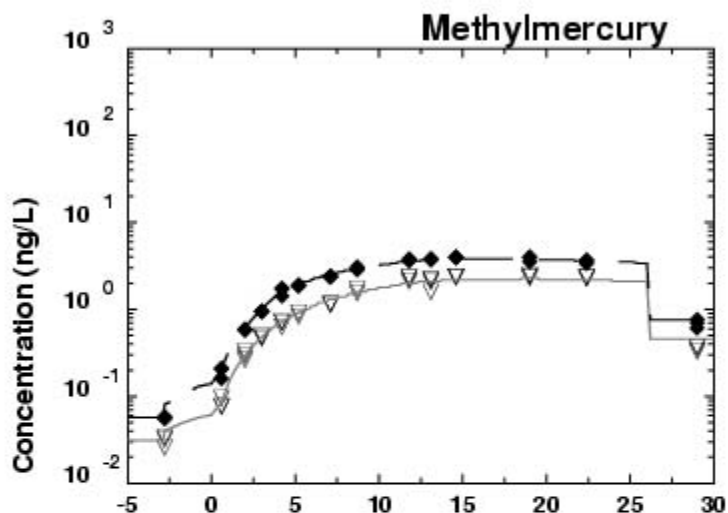
- Empirical loading model fitted to data (least squares) to identify regions of differential Hg/meHg inputs
- Also, areas of differential partitioning are identified
- Results related to physical and biogeochemical parameters that can affect fate of Hg and meHg
- Framework applied to filtered and unfiltered Hg, meHg measurements:



- 0.2 mile increments, RRM -2.8 to 30, assuming linearly increasing flow

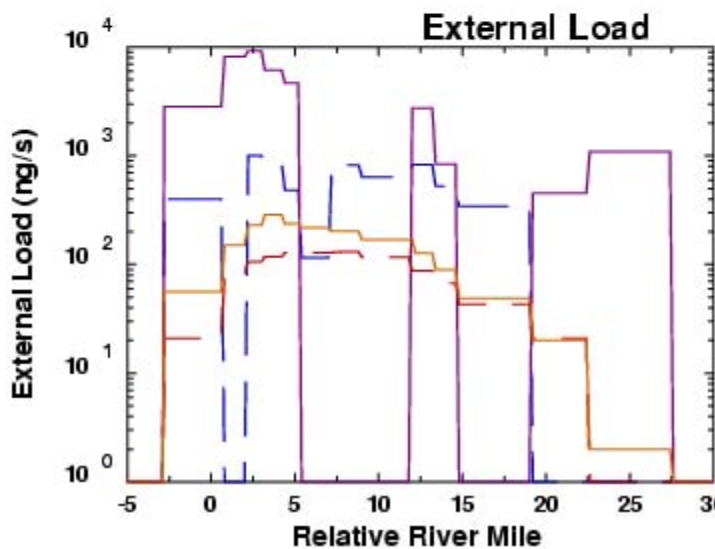
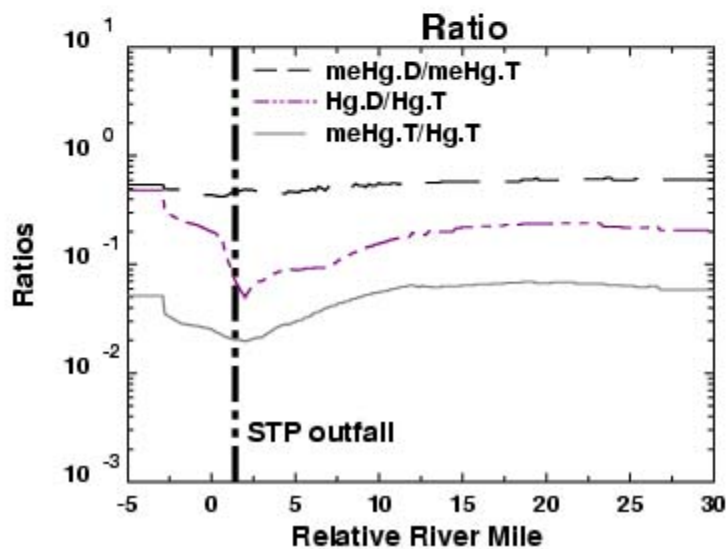
# Transect of Water Column Dissolved and Total Concentrations along the South River

Assuming flow increases linearly and WC constituents behave conservatively



◆ WC Total  
 ▼ WC Dissolved  
 - - - Pred. Tot.  
 — Pred. Dis.

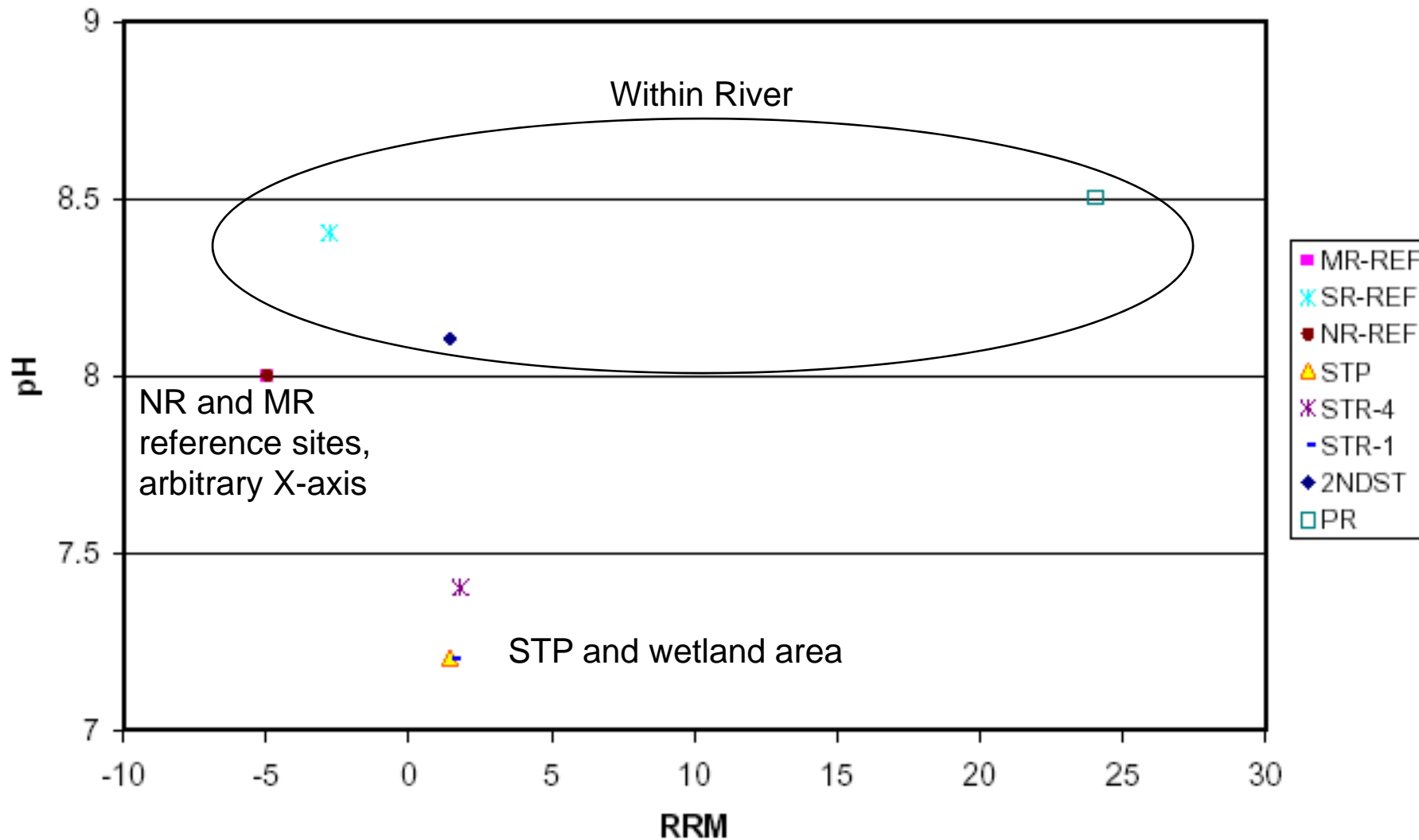
April 2006  
 Sampling  
 Campaign





# Surface Water pH in South River

March 12, 2005

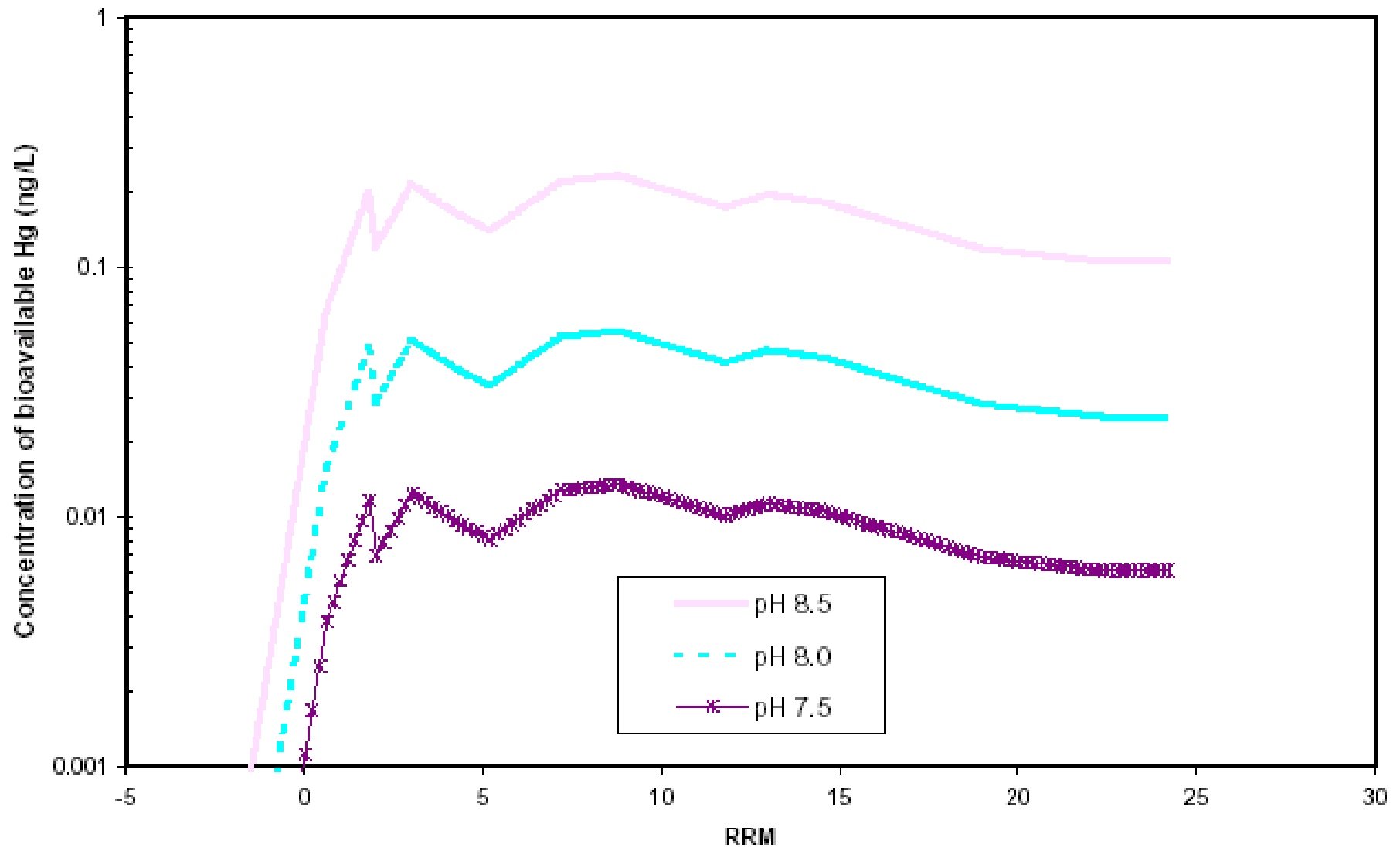




In sediments...



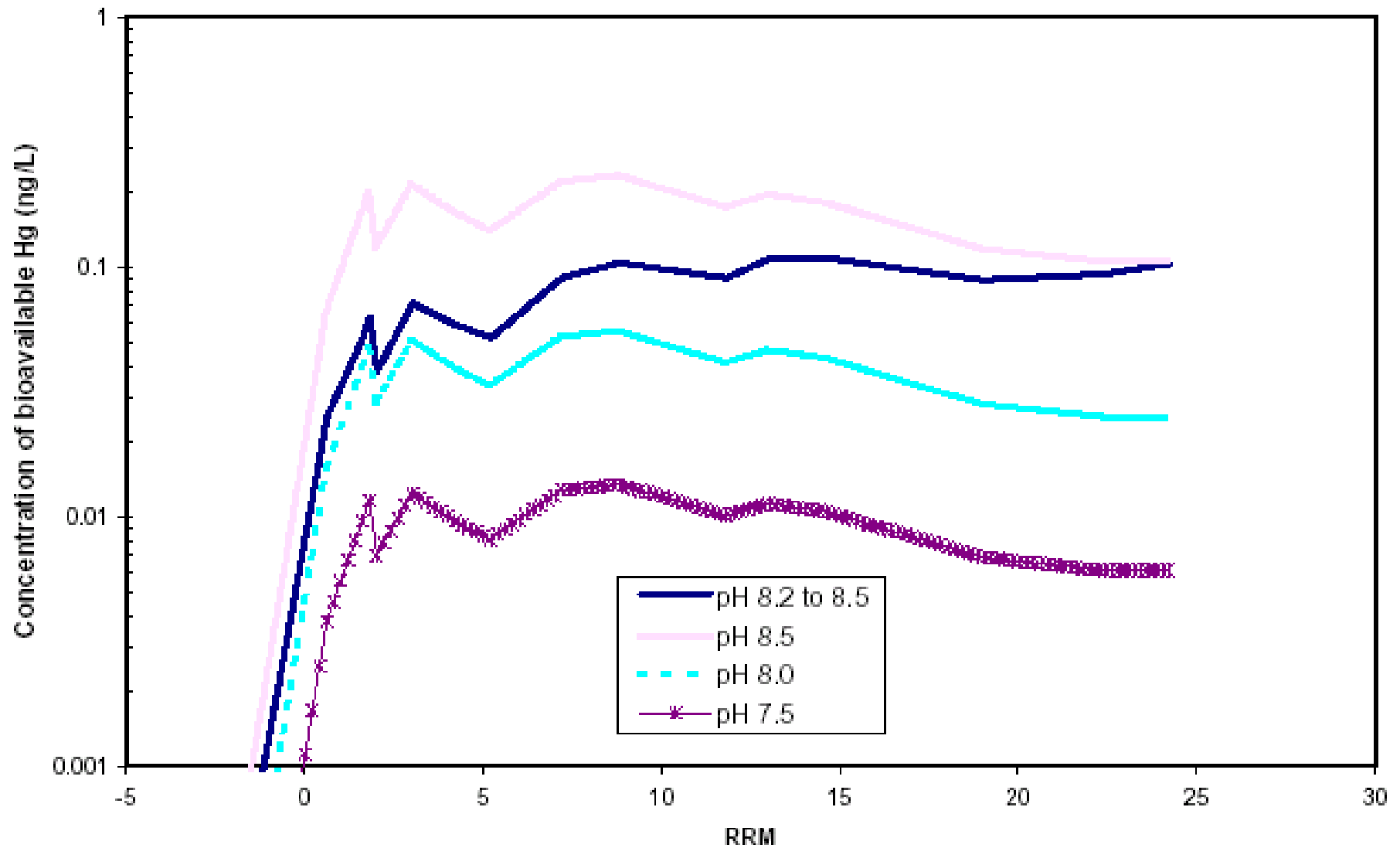
Role of pH on bioavailable Hg  
Assumed 0.1  $\mu\text{M}$  Sulfide (3.2 ppb)



In sediments...



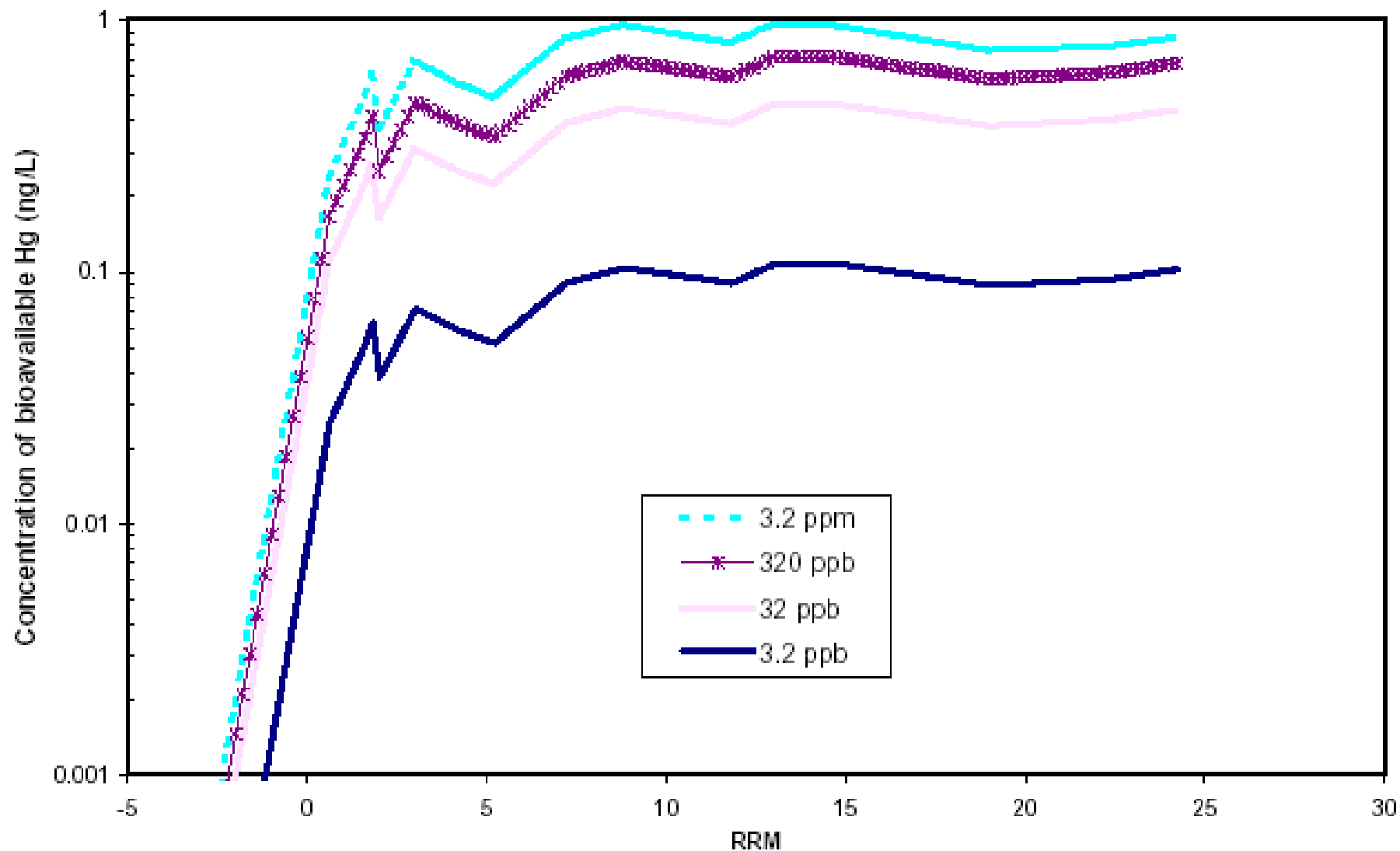
Role of pH on bioavailable Hg  
Assumed 0.1  $\mu\text{M}$  Sulfide (3.2 ppb)



In sediments...

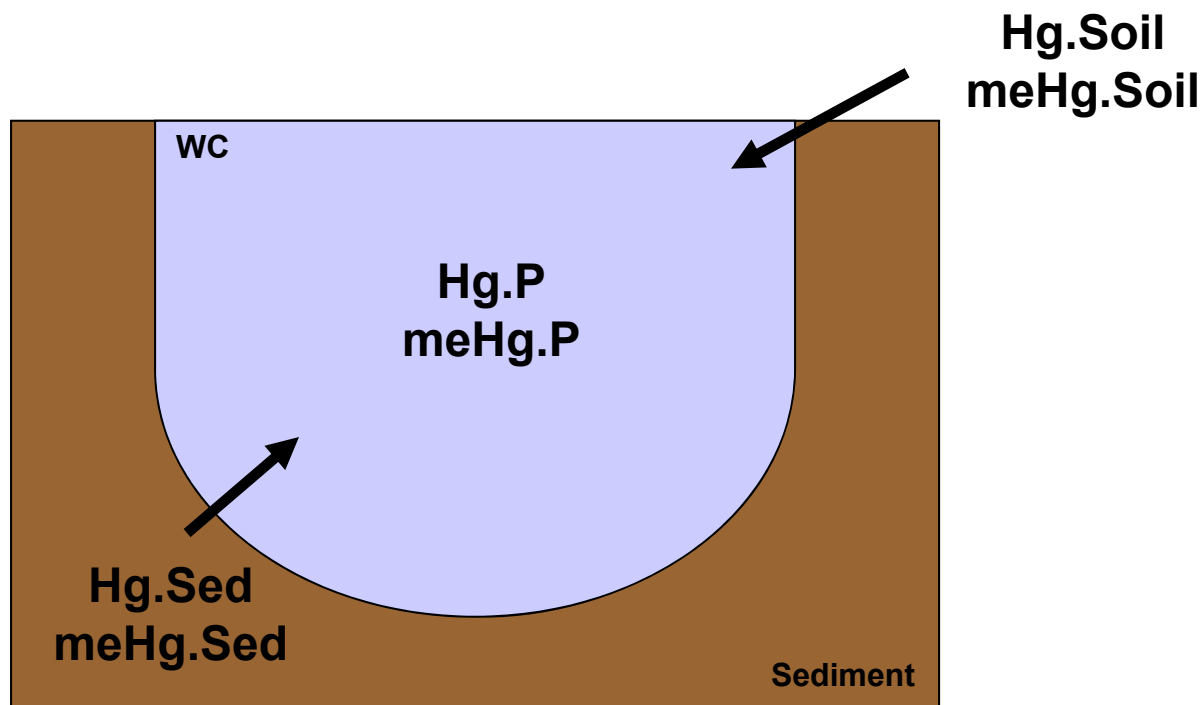


Role of Sulfide on bioavailable Hg, applied universally  
Interpolated pH varies from 8.2 to 8.5



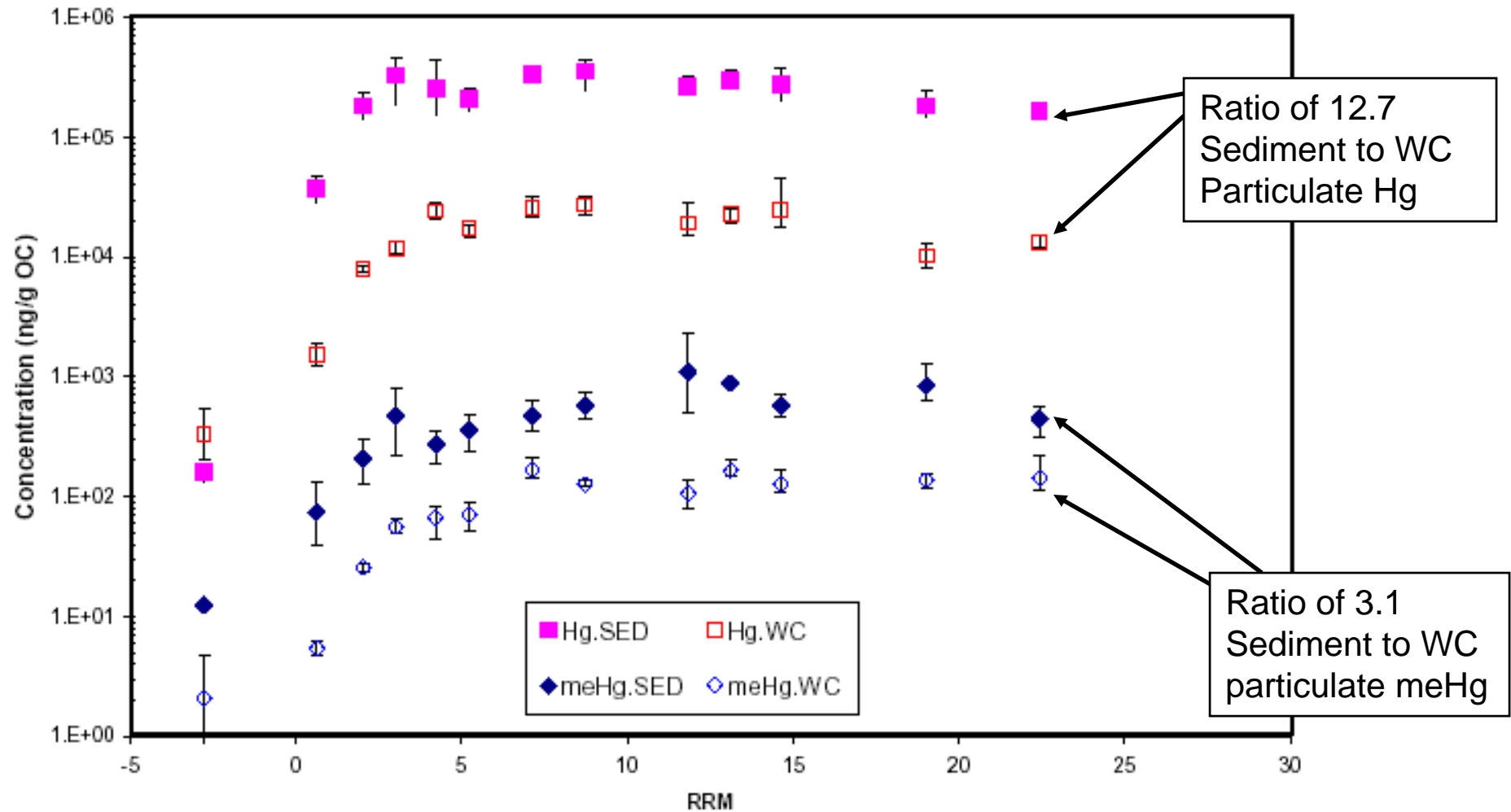
# Evaluating potential sources of Hg and meHg into South River

- Hypothesis: Particulate Hg and meHg in WC are from resuspended sediments
  - Ratio of meHg/HgT in WC is proportional to sediment
  - Otherwise the ratio of meHg/HgT ???



# Comparing Particulate Data

March 2006 (median and range bars), Assuming TOC= 5%, POC = 2 ppm





<b>Parameters that are potentially useful for modeling mercury speciation and methylation</b>			
<b>Analytes</b>	<b>Reasoning</b>	<b>Analytes</b>	<b>Reasoning</b>
<i>Water column</i>		<i>Sediment</i>	
<u>Primary</u>		<u>Primary</u>	
DOC	speciation	Sulfide	speciation and bioavailability
POC	speciation	Sediment oxygen demand	microbial activity
pH	speciation	Methylation potential	calibration
Major Ions	ionic composition of water	pH	speciation and bioavailability
Temperature	chemical reactivity	POC	speciation and bioavailability
		DOC	speciation and bioavailability
<u>Secondary</u>		<u>Secondary</u>	
Nitrogen	nutrient levels	AVS	speciation and bioavailability
Phosphorous	nutrient levels	Temperature	chemical reactivity
		Total Hg, meHg	calibration
		Dissolved Hg, meHg	calibration
		<u>Secondary</u>	
		Dissolved Fe, Mn	redox state of sediments
		ORP	redox state of sediments
		Nitrogen	nutrient levels
		Phosphorous	nutrient levels



# Observations

- Widespread Hg input (RRM 0 to 10)
- Filtered meHg is 50-60% of meHg.T and generally constant throughout South River
- Filtered Hg is 6-21% of unfiltered Hg.T but variable and generally lower at RRM 0 to 10
- Difficult to identify point sources
  - Further analysis designed to test sensitivity of spatial sampling frequency and optimization methods is planned
- Sharper increase in Hg.T relative to meHg between RRM 0 to 10
  - A possible biogeochemical influence of the STP outfall or wetlands in area on Hg speciation and/or bioavailability?
  - Preliminary Hg bioavailability calculations in sediment were performed



# Pathforward

- Screening calculations of Hg and meHg bioaccumulation for fish and clam
  - In context of prey/predator relationships and Hg/meHg concentrations with recent and historic data
- Loading sensitivity analysis to identify optimal spatial sampling frequency and possible point sources
- Identify regions with physical or biogeochemical conditions in South River that could impact partitioning and methylation activity



# Citations on conceptual model of mercury bioavailability for methylation

- Benoit, J., Gilmour, C. and Mason, R., 2001a. Aspects of Bioavailability of Mercury for Methylation in Pure Cultures of *Desulfobulbus propionicus* (1pr3). *Applied and Environmental Microbiology*(51-58).
- Benoit, J., Gilmour, C. and Mason, R., 2001b. The Influence of Sulfide on Solid-Phase Mercury Bioavailability for Methylation by Pure Cultures of *Desulfobulbus propionicus* (1pr3). *Environmental Science and Technology*, 35: 127-132.
- Benoit, J., Gilmour, C., Mason, R. and Heyes, A., 1999a. Sulfide Controls on Mercury Speciation and Bioavailability to Methylating Bacteria in Sediment Pore Waters. *Environmental Science and Technology*, 33: 951-957.
- Benoit, J., Mason, R. and Gilmour, C., 1999b. Estimation of Mercury-Sulfide Speciation in Sediment Porewaters Using Octonal-Water Partitioning and Implications for Availability to Methylating Bacteria. *Environmental Toxicology and Chemistry*, 18(10): 2138-2141.
- Gilmour, C. and Henry, E., 1991. Mercury Methylation in Aquatic Systems Affected by Acid Deposition. *Environmental Pollution*, 71: 131-169.
- Langer, C., Fitzgerald, W., Visscher, P. and Vandal, G., 2001. Biogeochemical Cycling of Methylmercury at Barn Island Salt Marsh, Stonington, CT, USA. *Wetlands Ecology and Management*, 9: 295-310.
- [WWW.Mercry2006.com](http://WWW.Mercry2006.com)