Mercury Modeling Case Studies in NY/NJ Harbor

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Contaminant Assessment and Reduction Program

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CARP Project Modeling Team

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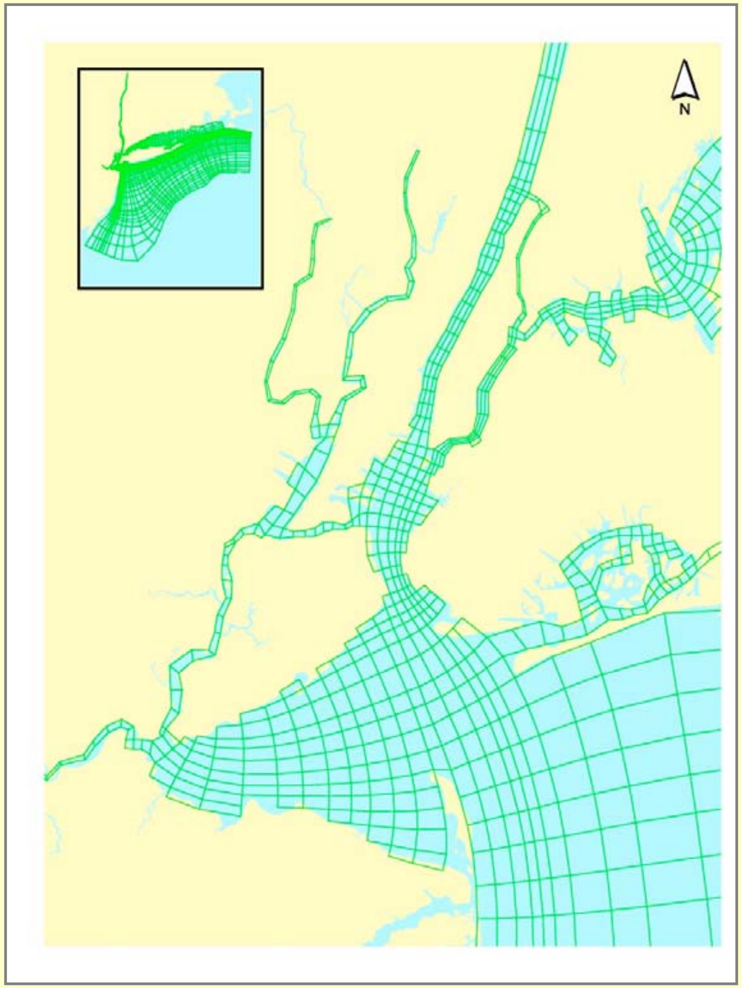
- Subir Saha
- Aaron Redman
- Robert Santore

Water Quality Modeling Framework

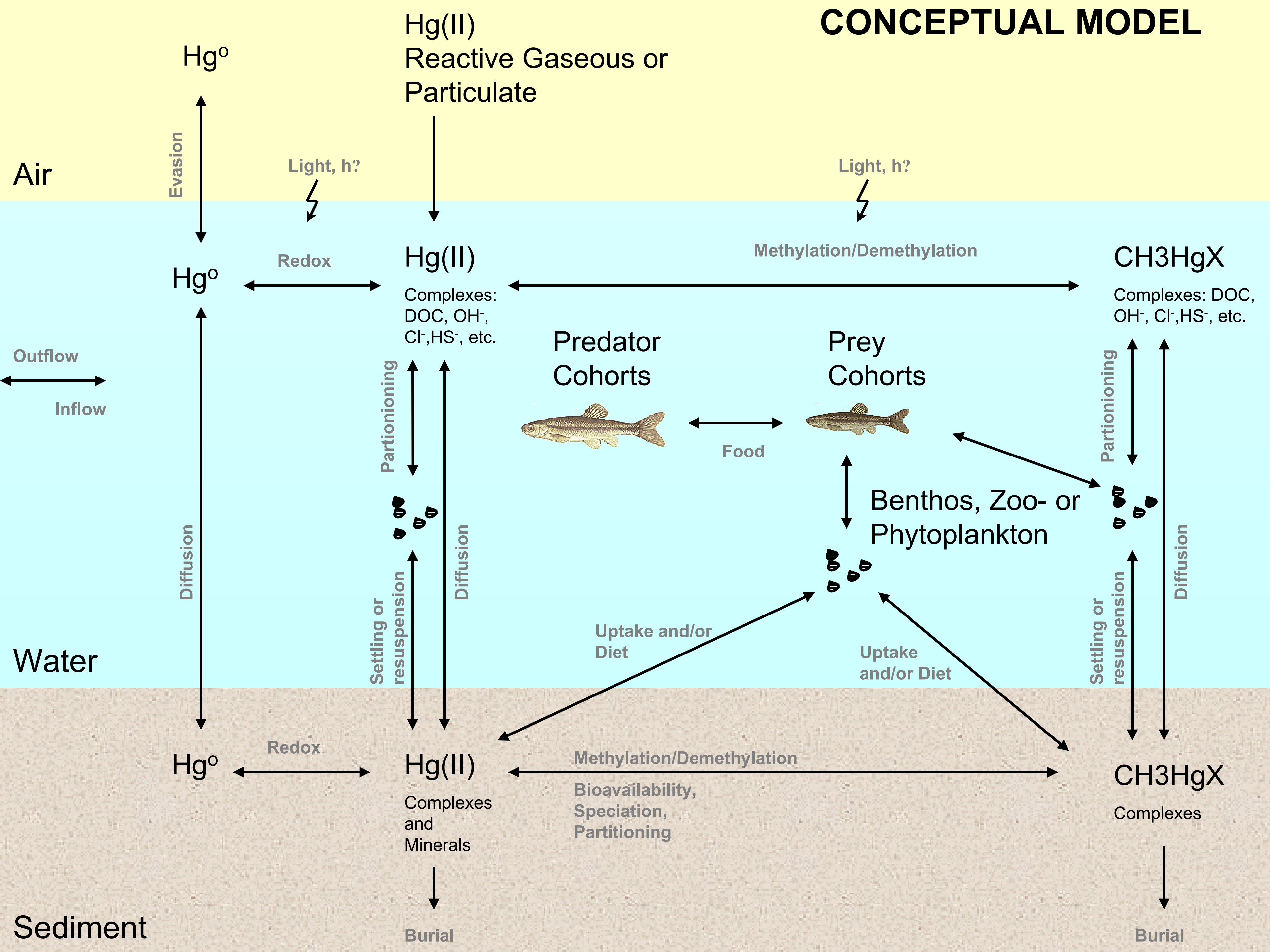
- System-Wide Eutrophication Model (SWEM) results available for use prior to mercury model development
- SWEM Model Was Developed by NYCDEP during 1994 to 1998
- Model Is State-of-the-Science, Well-Calibrated and Peer Reviewed
- Includes hydrodynamics, eutrophication, sediment dynamics



SWEM Model Grid

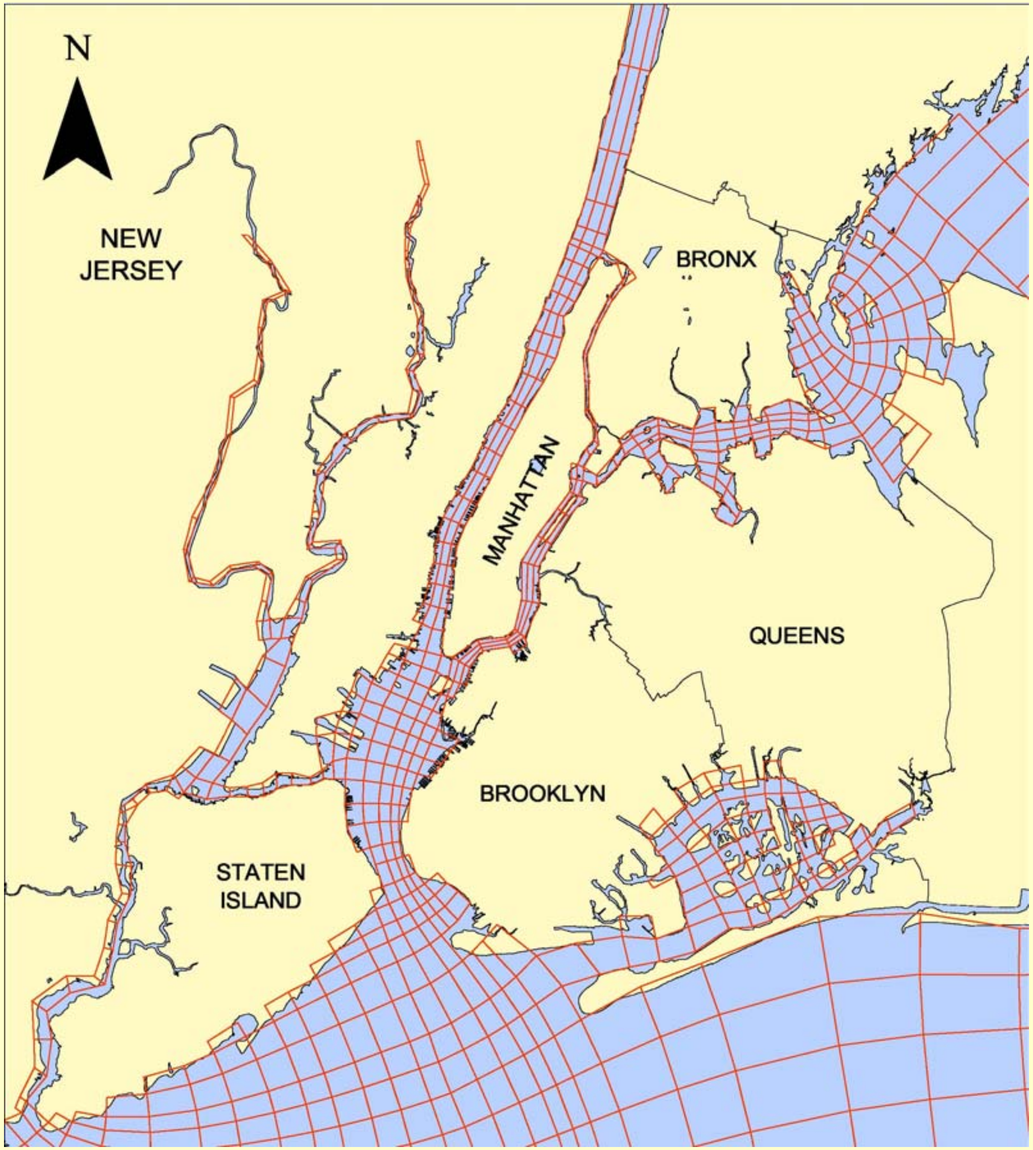
CARP Modeling Project

- Goals include projection of future water quality due to various management and remediation options
- Requires mechanistic approach for meaningful projections of Hg and meHg concentrations in water, sediment, and fish tissue
- Difficulties:
  - Large model domain covering diverse environments, systems, flow regimes
  - Sophisticated model needed due to the complexity of Hg cycling
  - Limited data available and no opportunity to collect process-level measurements (such as methylation rates)
- Modeling Strategies:
  - Avoid variation in calibration parameters across domain
  - Make use of case studies in peer-review and other literature



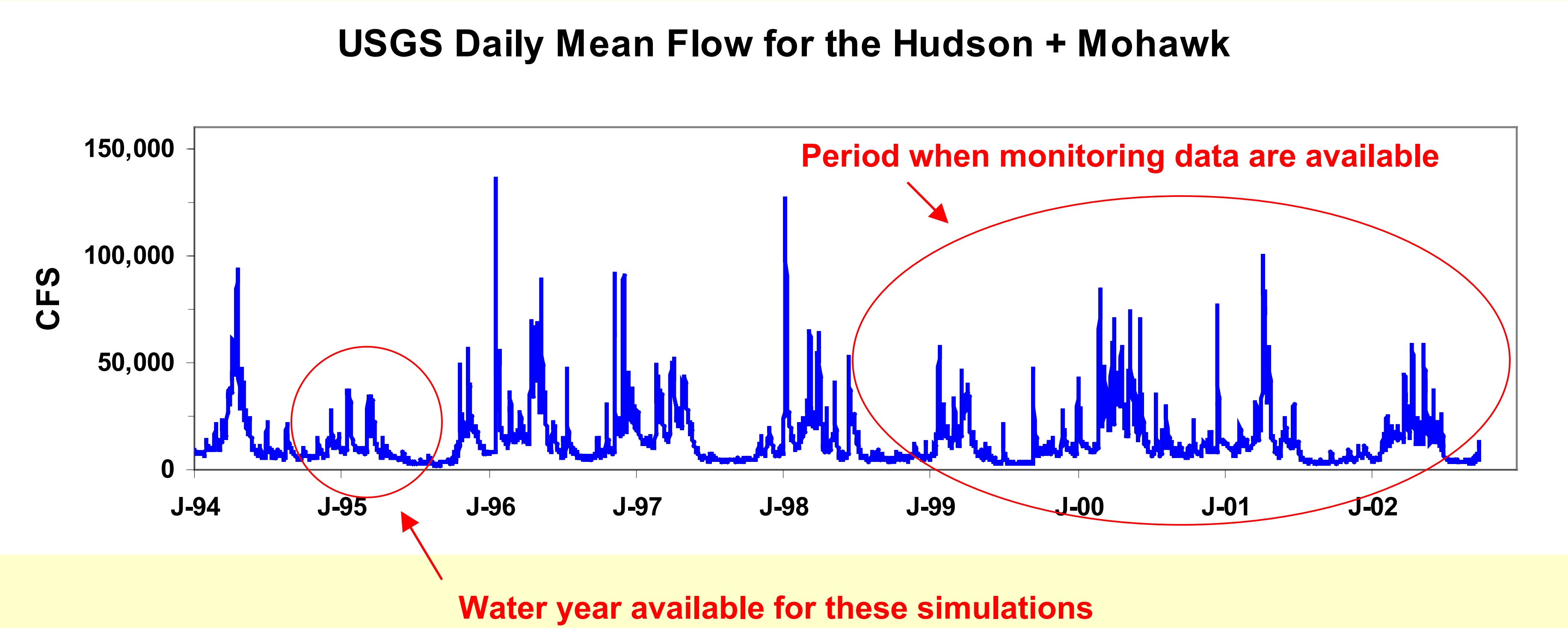
CONCEPTUAL MODEL
Air
Water
Sediment
Hg°
Hg(II)
Reactive Gaseous or Particulate
Evasion
Light, h?
Light, h?
Hg°
Redox
Hg(II)
Complexes: DOC, OH-, Cl-,HS-, etc.
Methylation/Demethylation
CH3HgX
Complexes: DOC, OH-, Cl-,HS-, etc.
Outflow
Inflow
Predator Cohorts
Prey Cohorts
Food
Partionioning
Partionioning
Benthos, Zoo- or Phytoplankton
Diffusion
Diffusion
Diffusion
Settling or resuspension
Settling or resuspension
Uptake and/or Diet
Uptake and/or Diet
Hg°
Redox
Hg(II)
Complexes and Minerals
Methylation/Demethylation
Bioavailability, Speciation, Partitioning
CH3HgX
Complexes
Burial
Burial

Model Domain NY/NJ Harbor

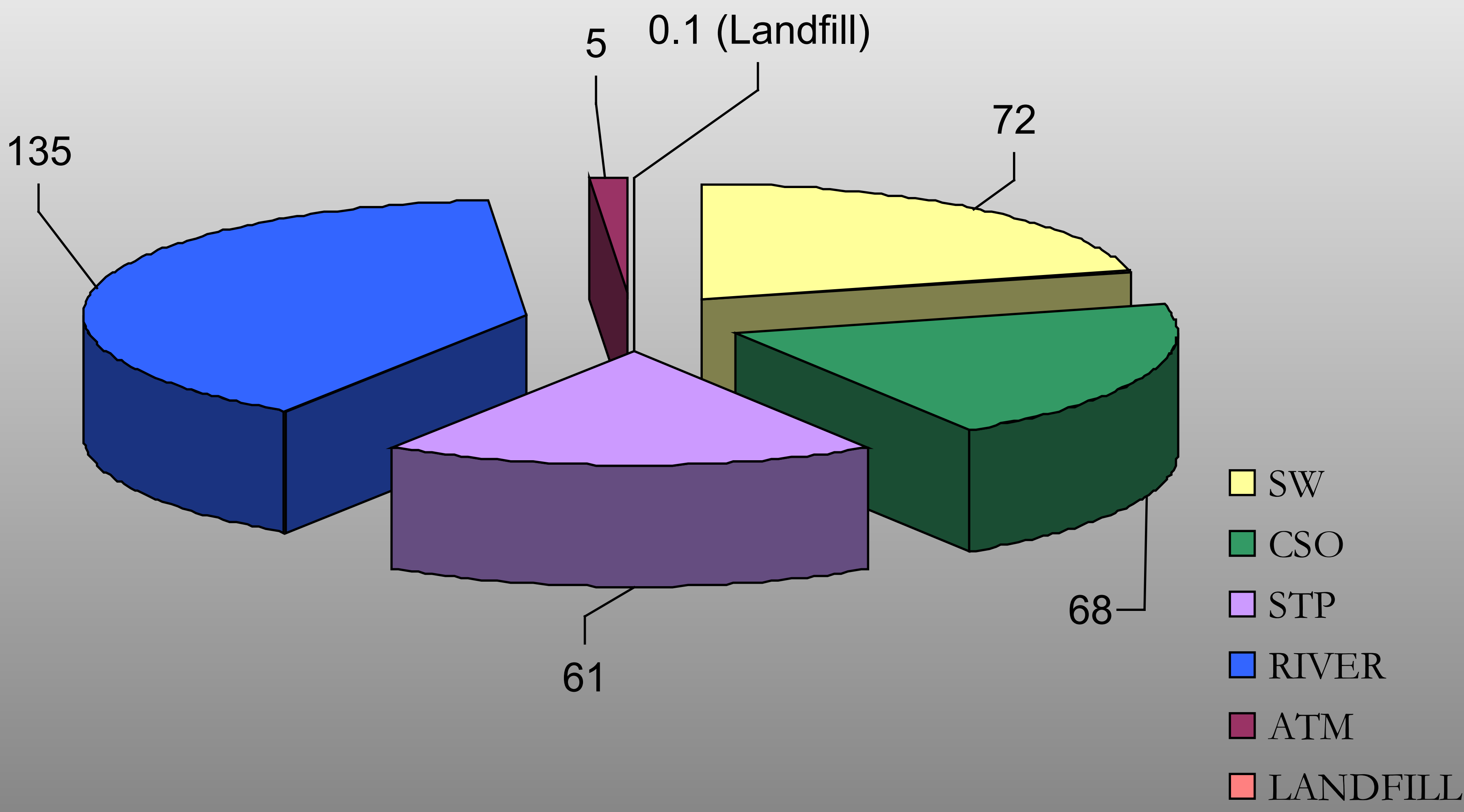


Available Hydrology for Loadings

Current simulations use flows from a relatively dry year and do not match the time period when monitoring data were collected.



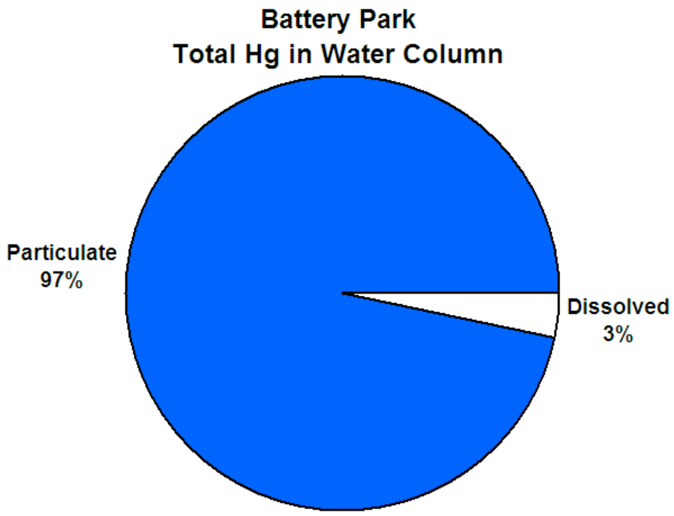
Total Mercury Loads (kg/year) Distribution Under 1998-99 Flow Conditions - 340 Kg/year

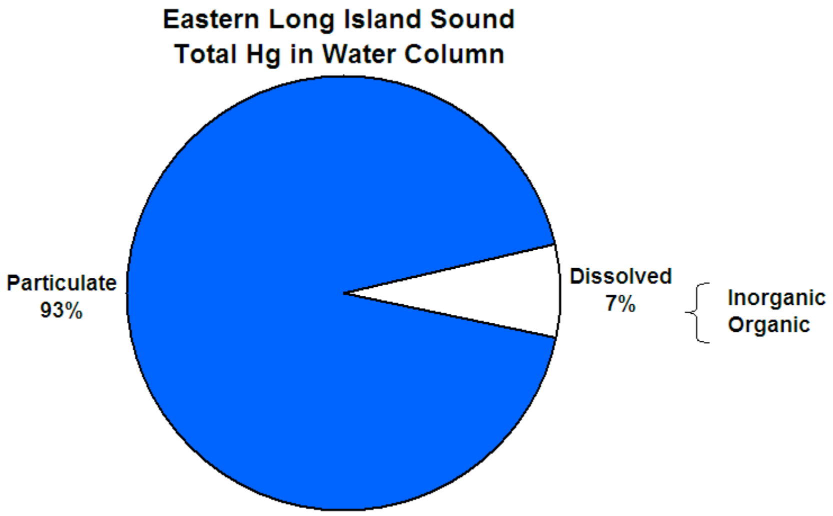


Summary of metal complexation reactions:

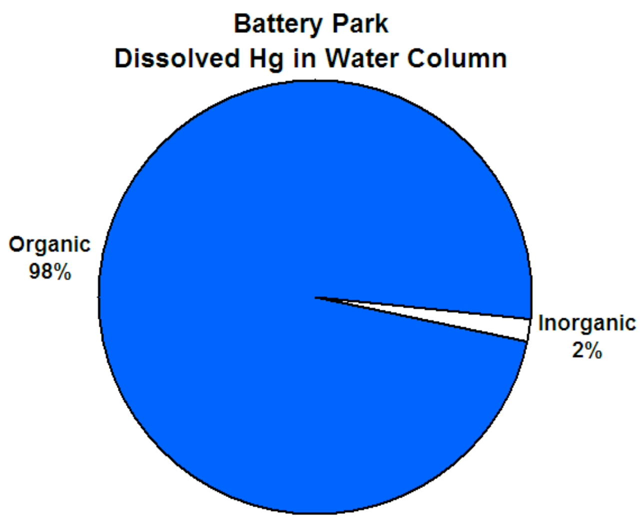
- Mercury:
  - Hg Sulfides including AVS – Benoit et al 1999 EST, and NIST Database of Critical Stability Constants
  - HgPOM – Calibration to H&F 2004
  - HgDOM – Calibration to observed data in NY/NJ Harbor
- Methylmercury:
  - MeHg Inorganics and sulfides – NIST
  - MeHgPOM – Calibration to H&F 2004
  - MeHgDOM – Calibration to observed data in NY/NJ Harbor

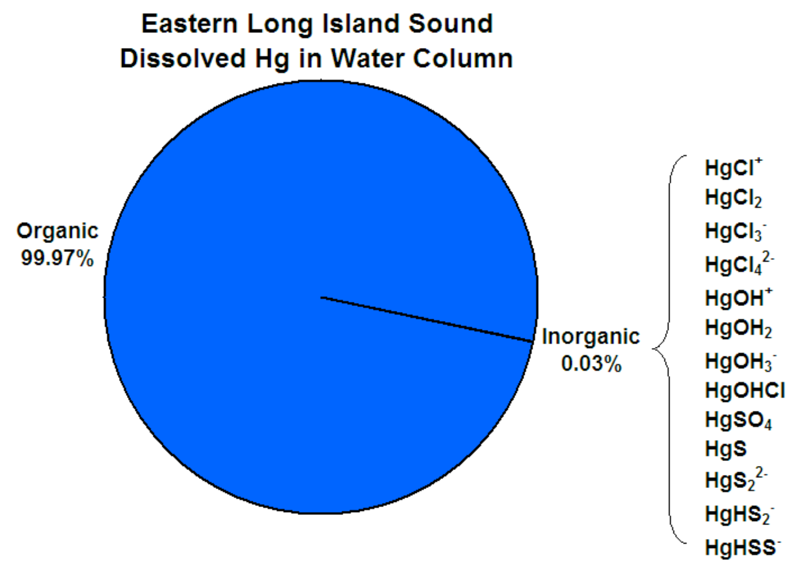
Water Column Total Hg Distribution



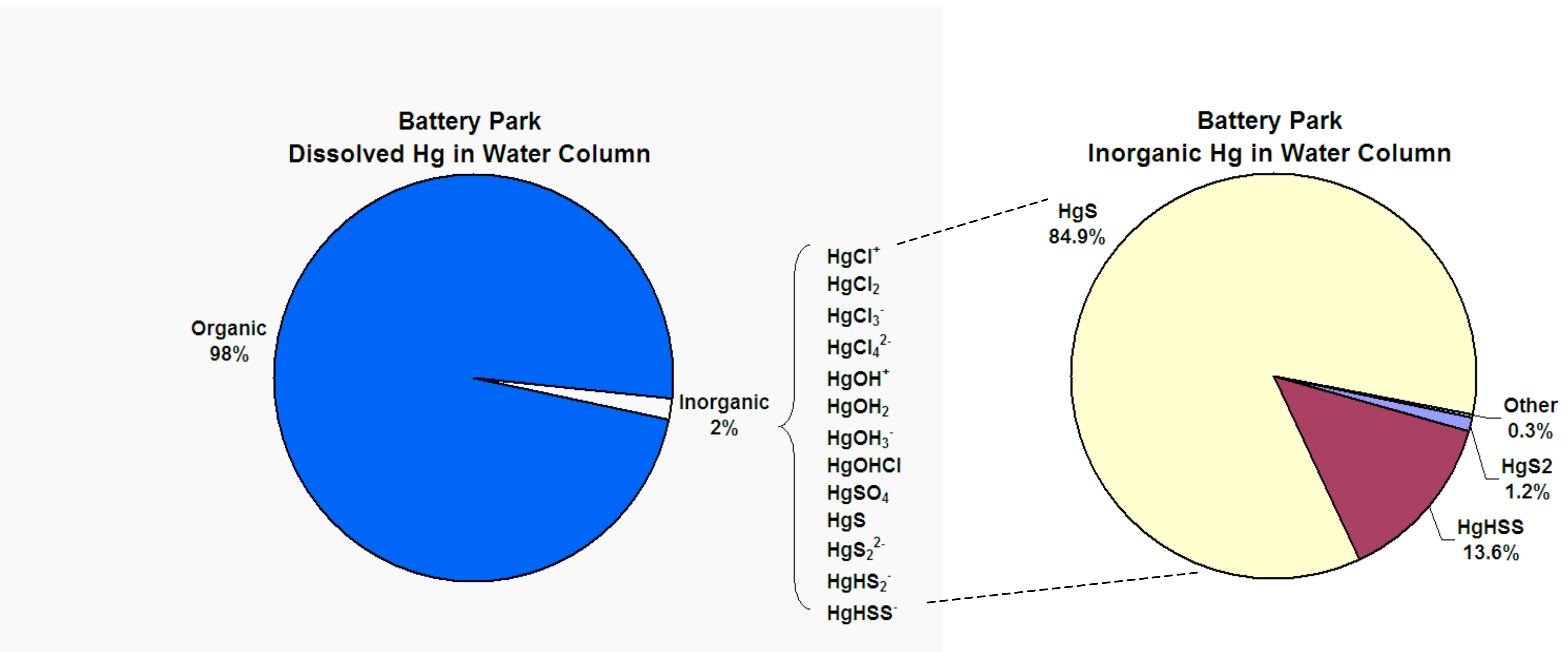


Water Column Dissolved Hg Distribution

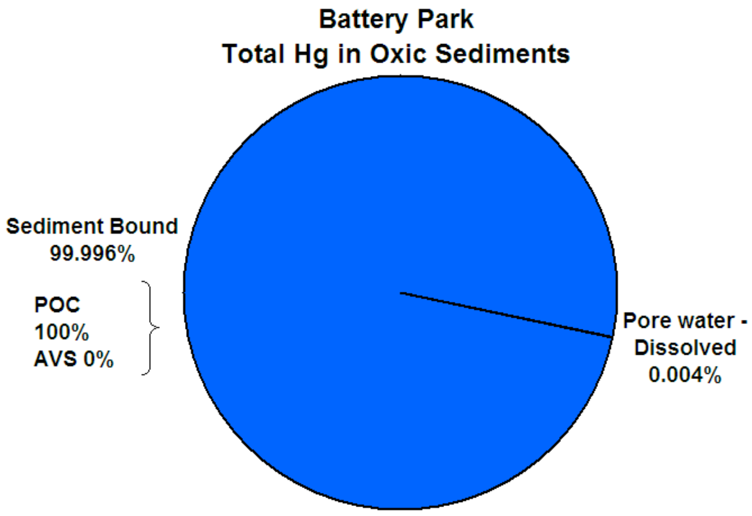


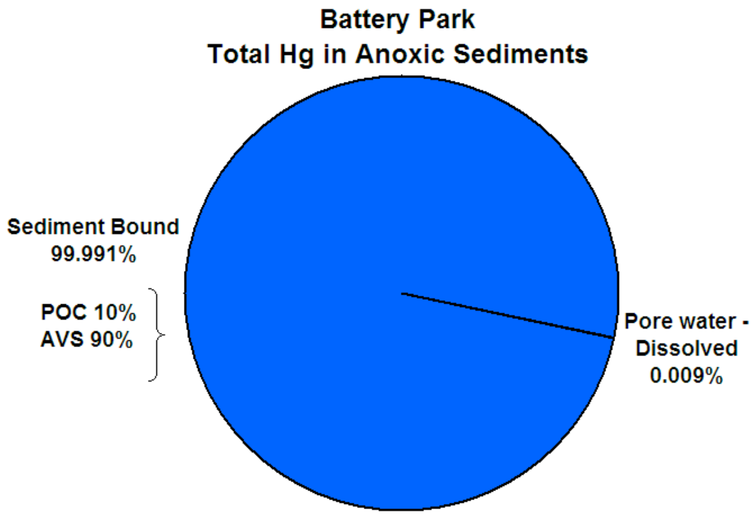


Water Column Inorganic Hg Distribution

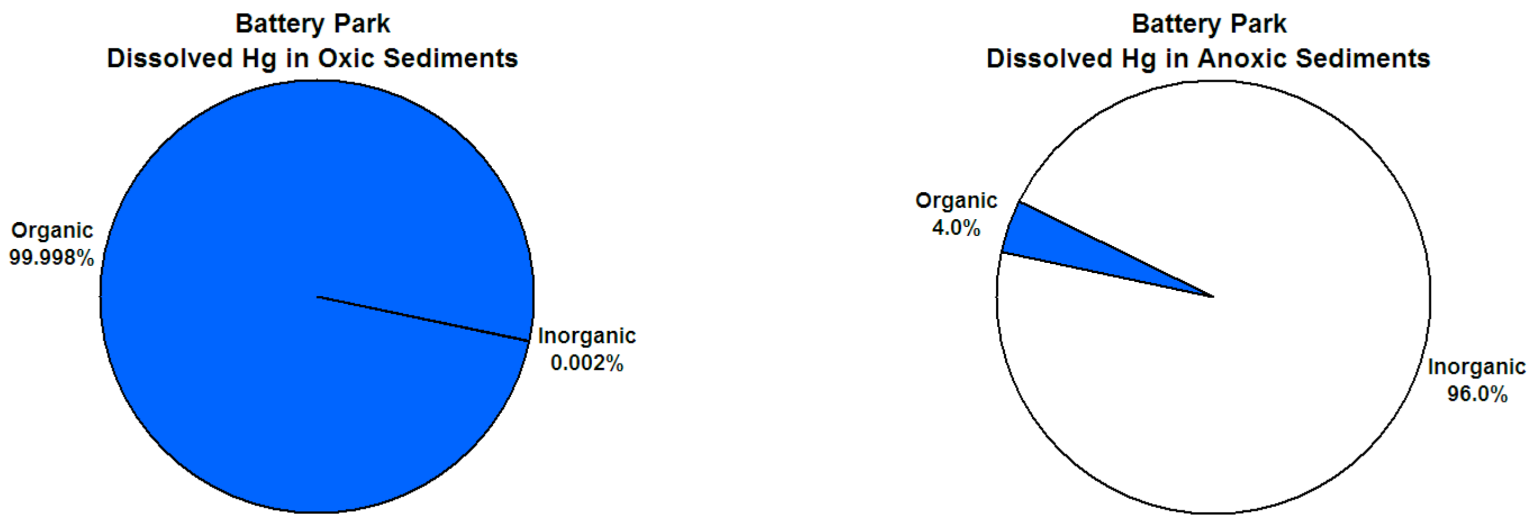


Sediment Total Hg Distribution





Sediment Dissolved Hg Distribution



Two film model formulation

Flux = K_{LA} * (C_w – C_a / K_{AW})

K_{LA} = f(MW, temperature, wind speed)

K_{AW} = Henry's Constant / (8.314 * T)

C_w = Dissolved Gaseous Mercury = 0.1 * Diss Hg

- Calibration, Tseng et al 2004

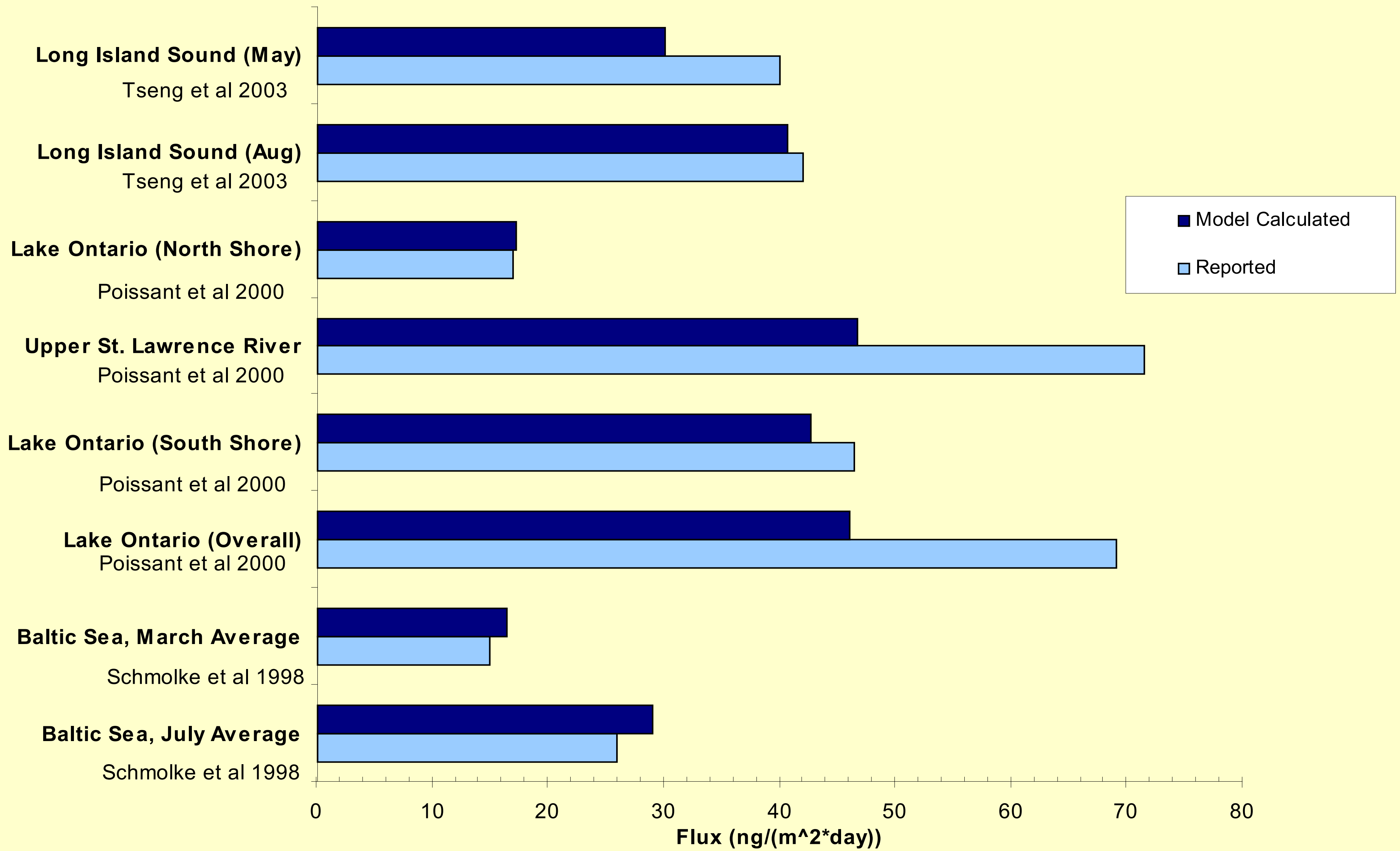
C_a = Airborne Gaseous Mercury = 3 ng/m^3

- Gao 2001, Rolfhus and Fitzgerald 2001, Tseng et al 2003

Henry's Constant = 729 Pa-m^3/mol

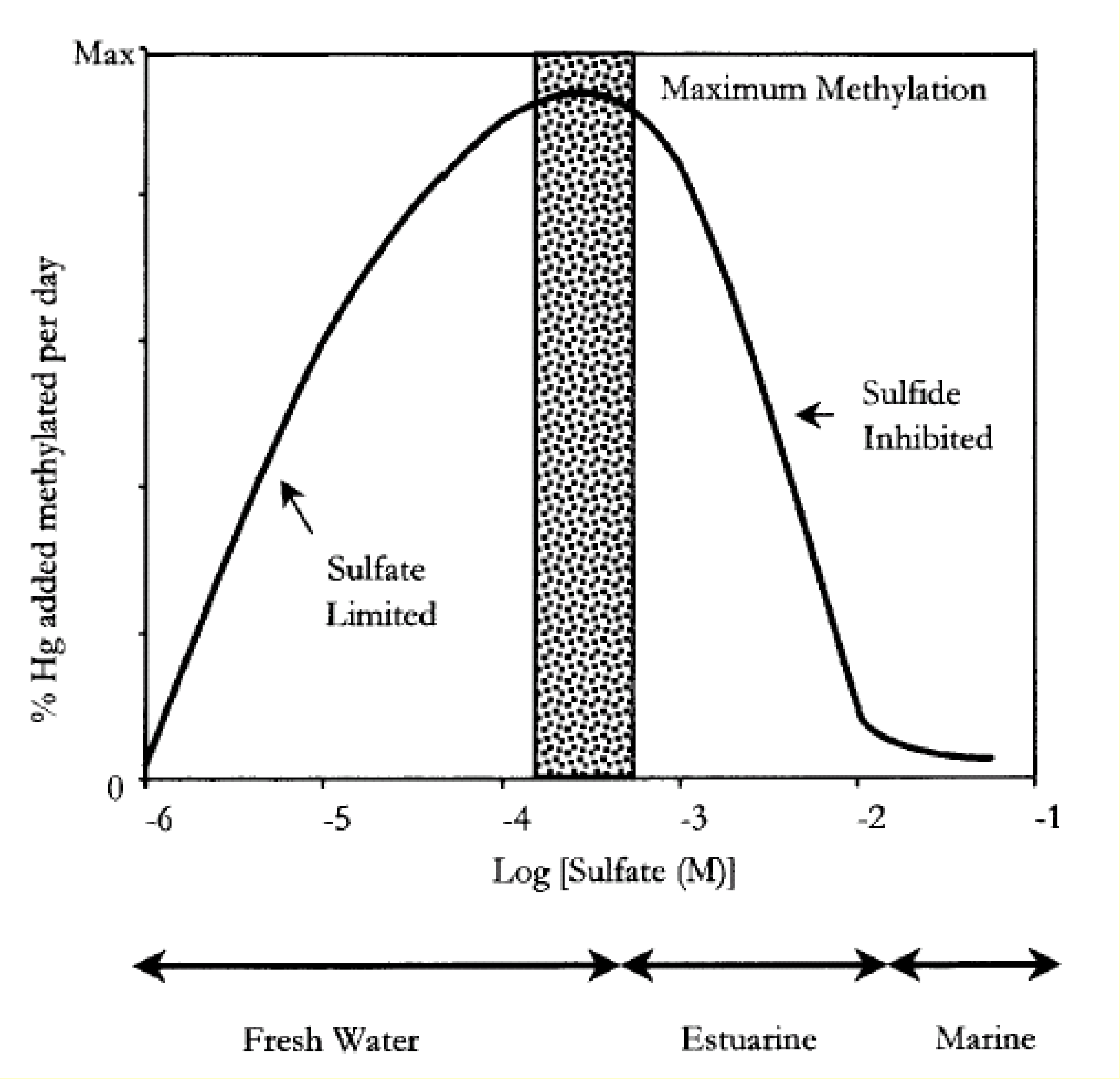
- Poissant et al 2000

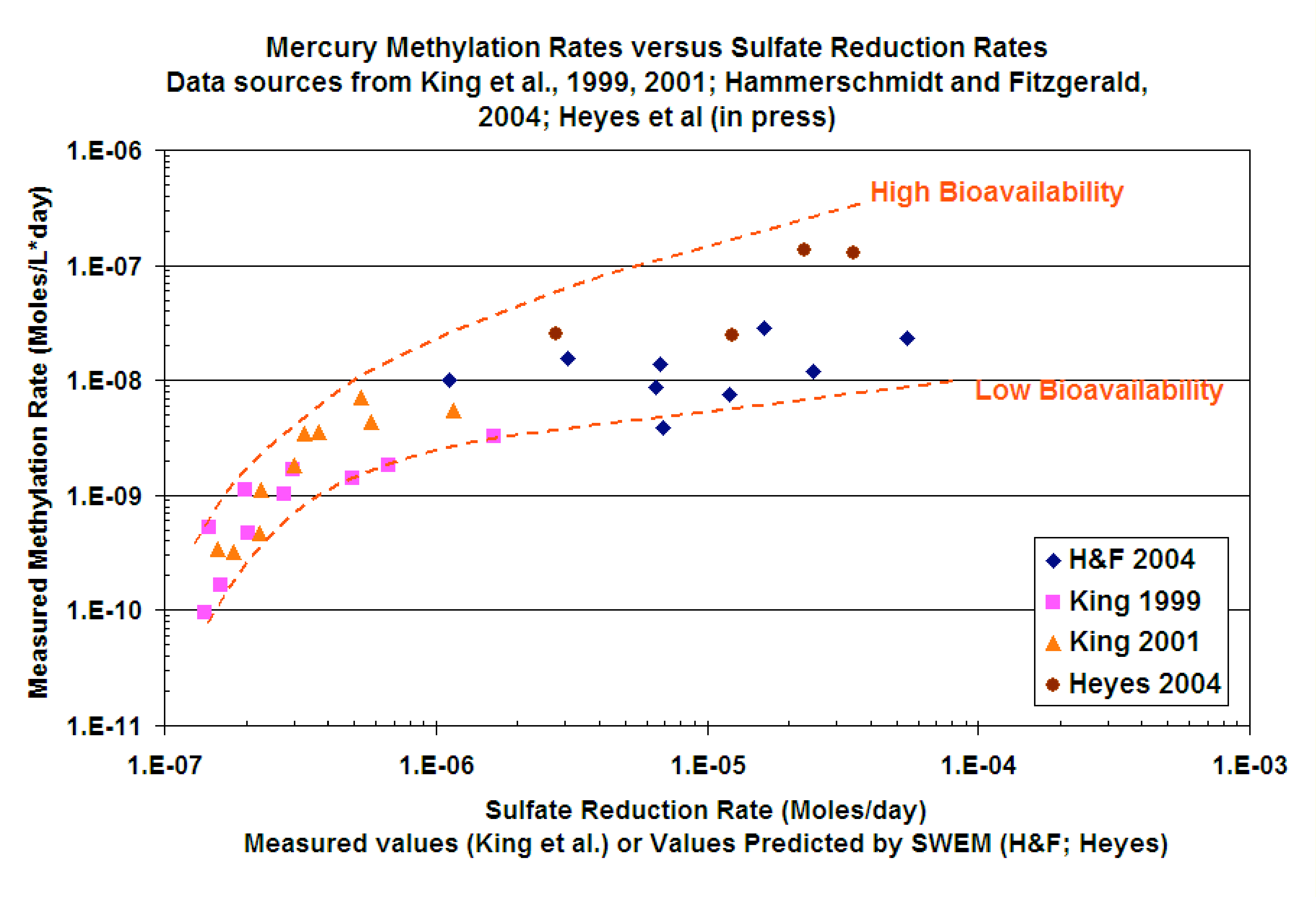
Volatilization:
Reported and Modeled Hg Flux (Two-Layer)



Conceptual model of Mercury Methylation

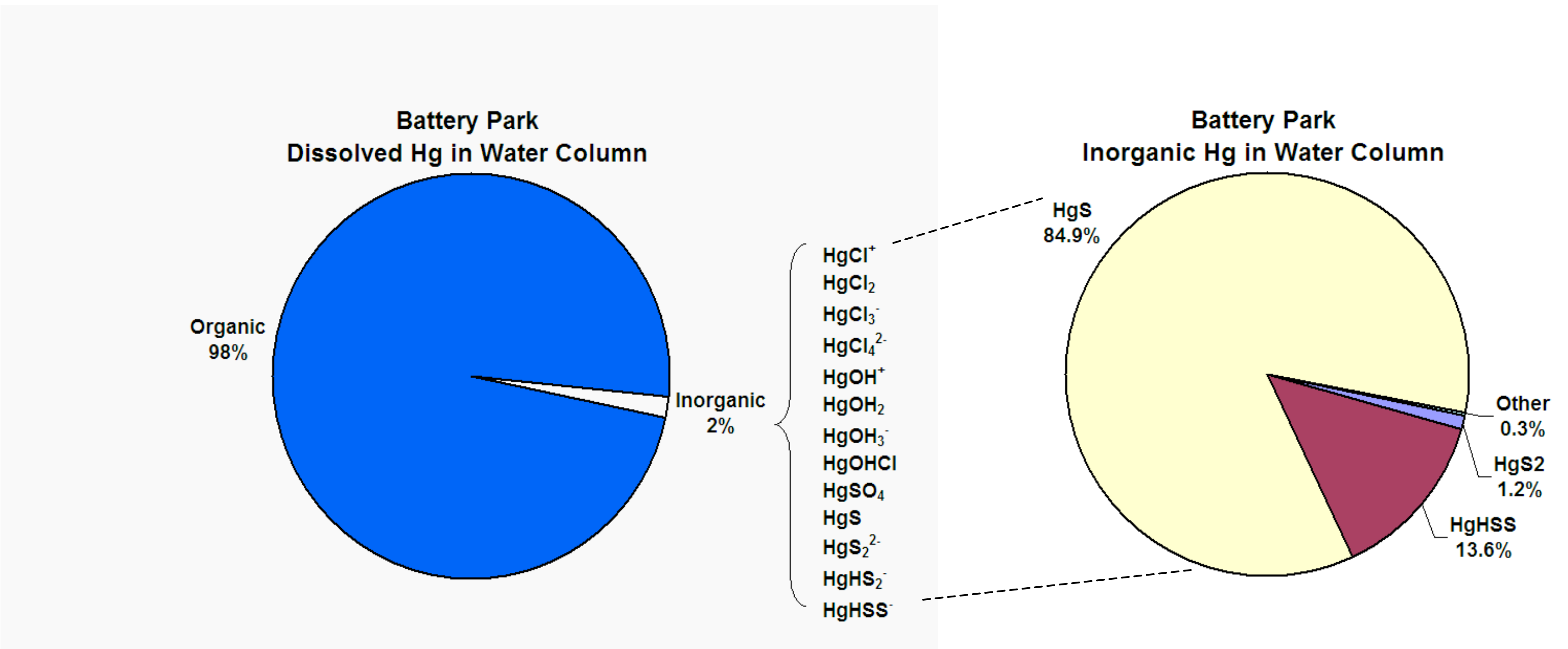
(Gilmour and Henry 1991 as redrawn by Langer et al 2001)

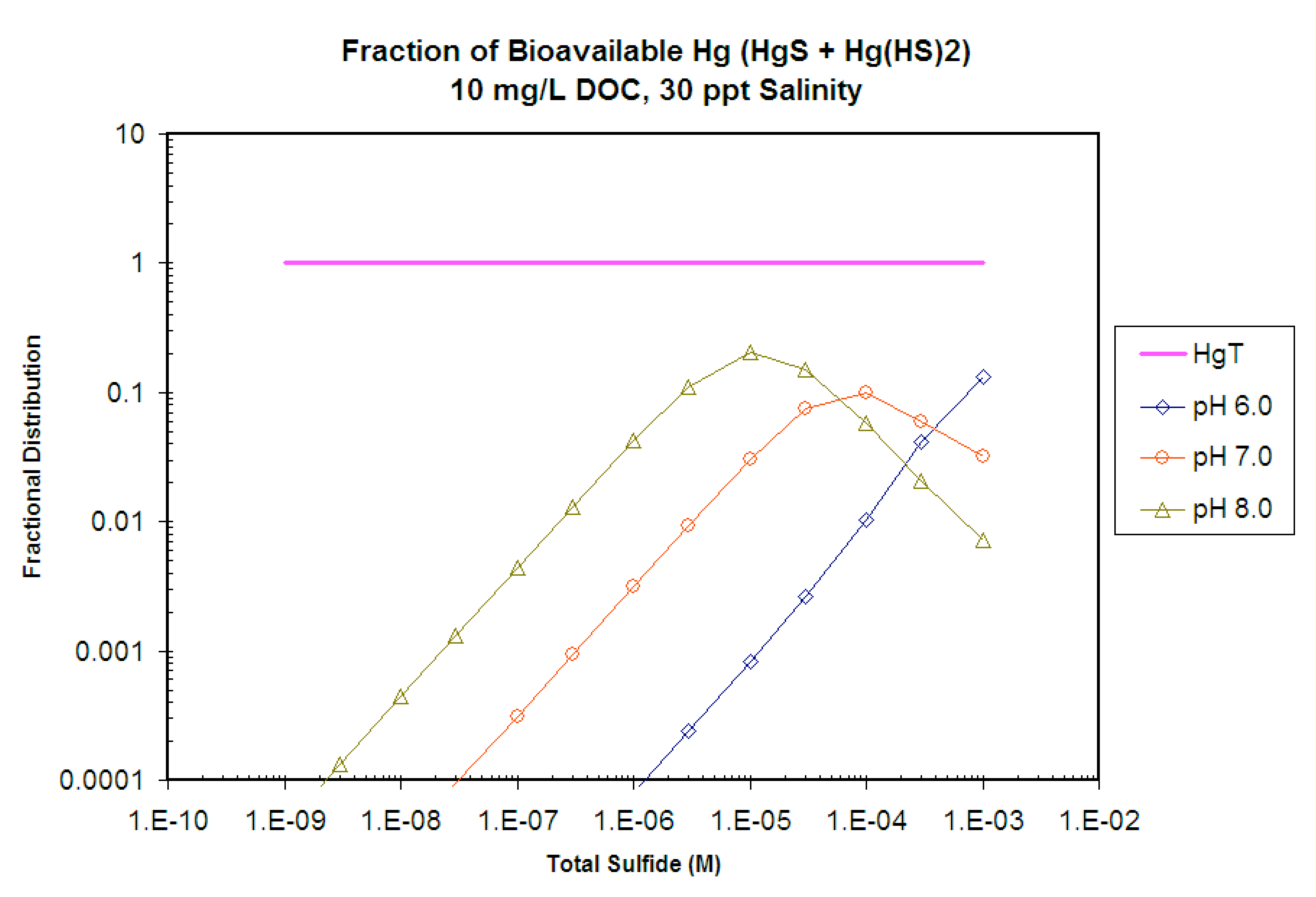




Mercury Methylation Rates versus Sulfate Reduction Rates
Data sources from King et al., 1999, 2001; Hammerschmidt and Fitzgerald, 2004; Heyes et al (in press)
High Bioavailability
Low Bioavailability
Measured Methylation Rate (Moles/L*day)
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
H&F 2004
King 1999
King 2001
Heyes 2004
Sulfate Reduction Rate (Moles/day)
Measured values (King et al.) or Values Predicted by SWEM (H&F; Heyes)

Water Column Inorganic Hg Distribution





Fraction of Bioavailable Hg (HgS + Hg(HS)2)
10 mg/L DOC, 30 ppt Salinity
Fractional Distribution
10
1
0.1
0.01
0.001
0.0001
1.E-10
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
Total Sulfide (M)
HgT
pH 6.0
pH 7.0
pH 8.0

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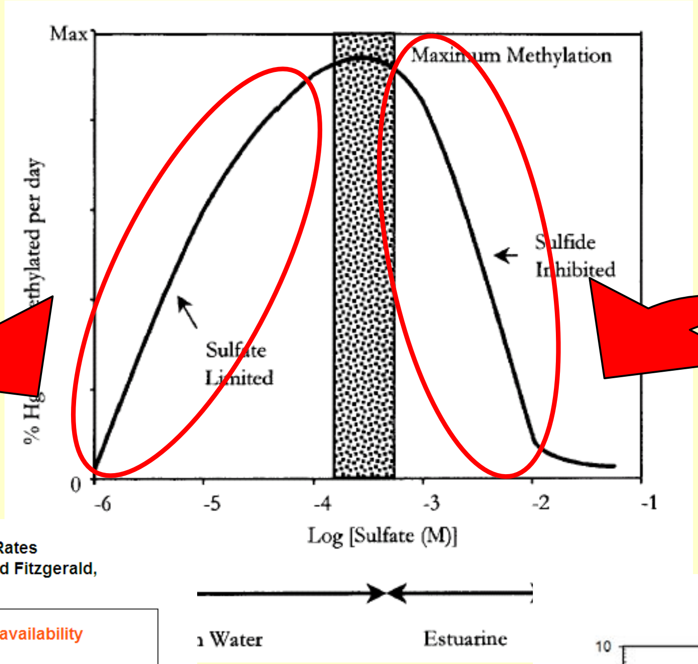
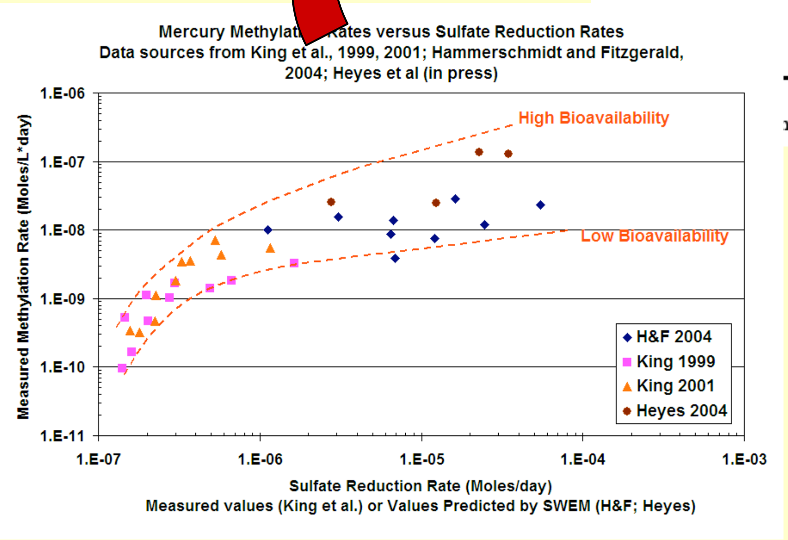
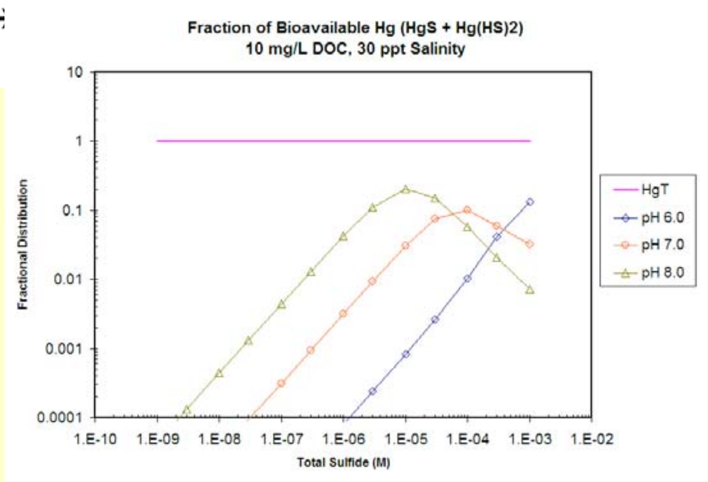


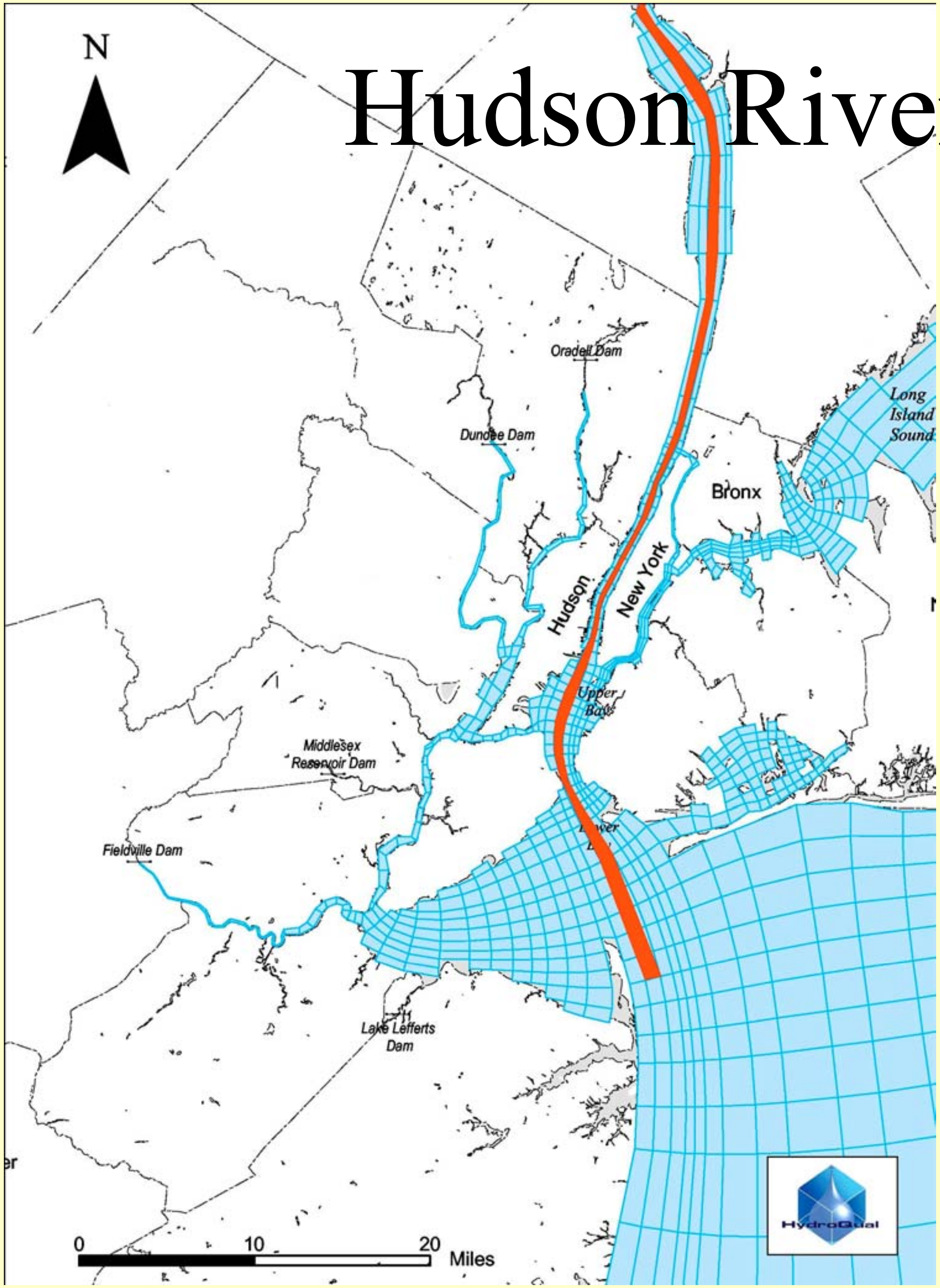




Net Mercury Methylation

- Net Methylation = MMR – DR
  - Mercury Methylation Rate
    - King et al 1999 and 2001
    - Hammerschmidt and Fitzgerald 2004
    - SRR and Sulfide from SWEM
  - Demethylation Rate
    - Marvin-DiPasquale ACME dataset

Hudson River Transect



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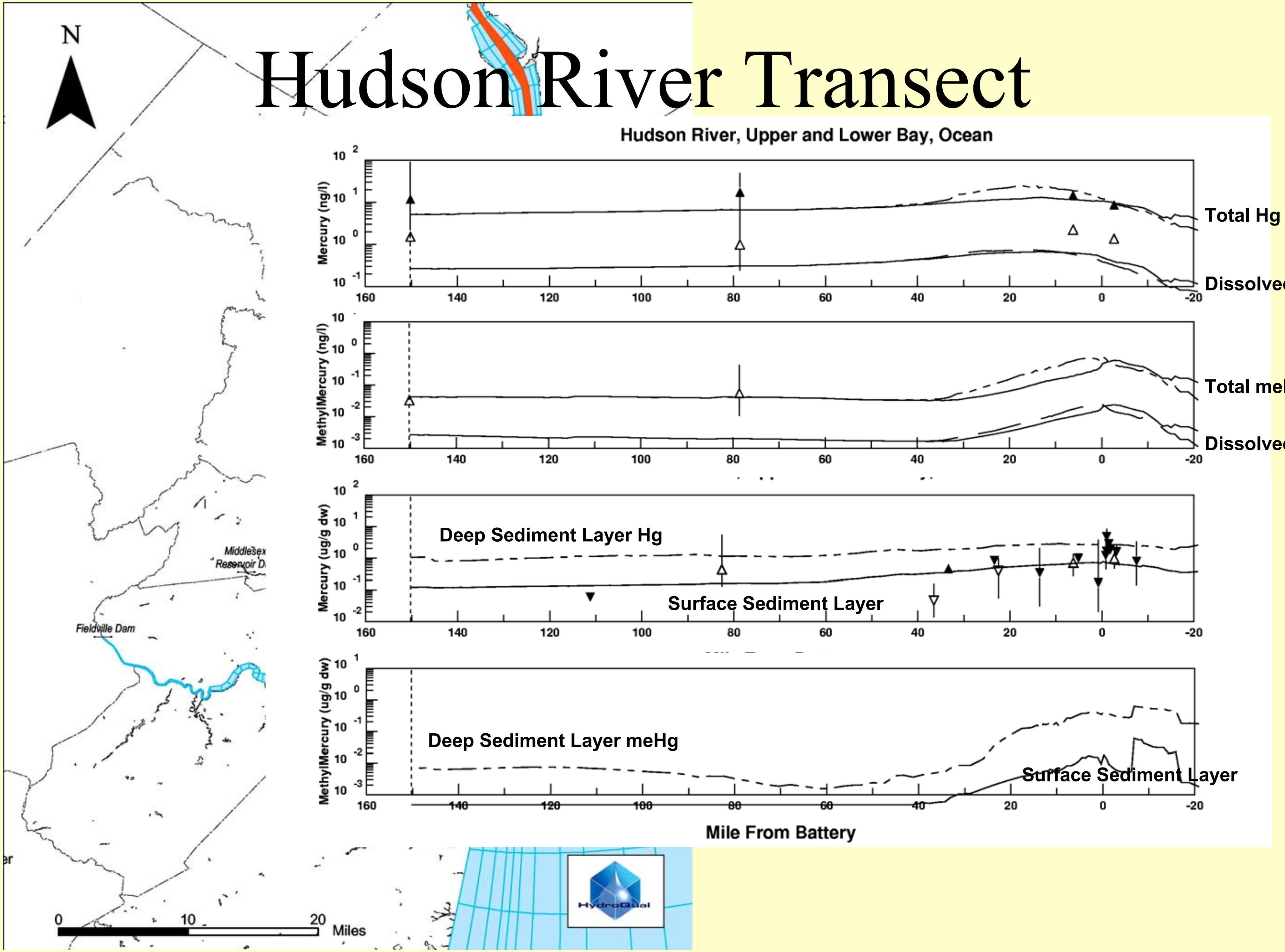

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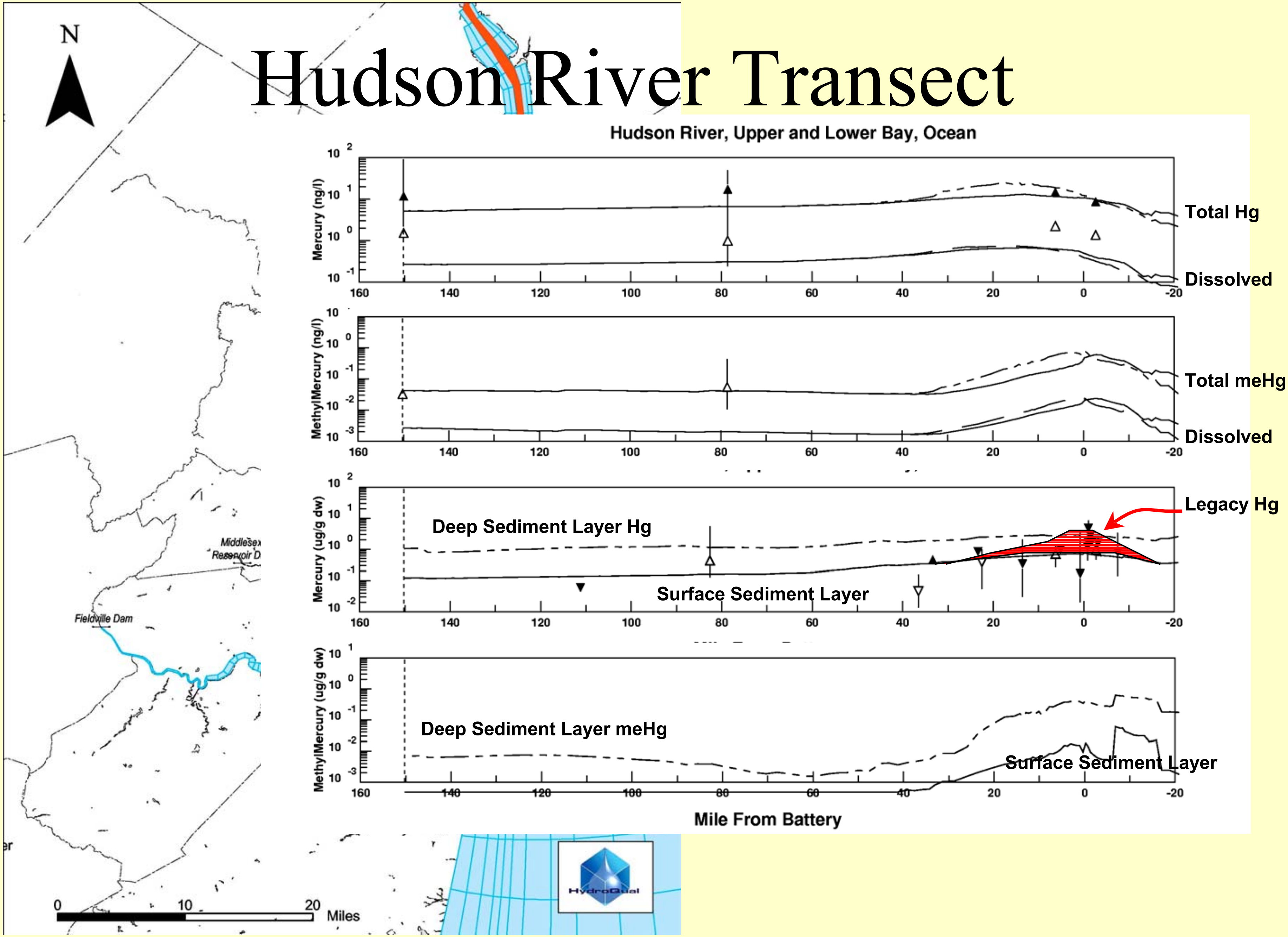
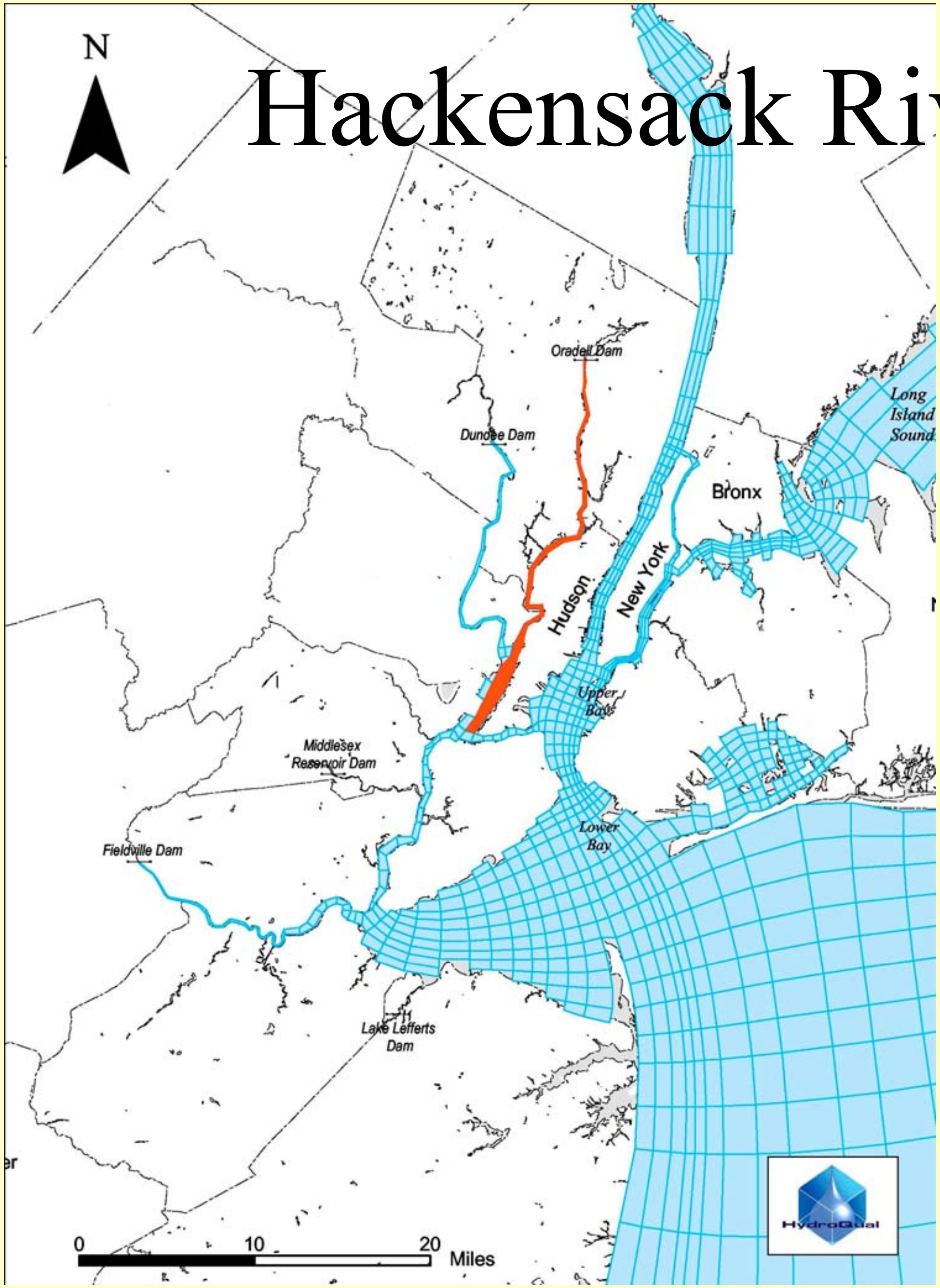
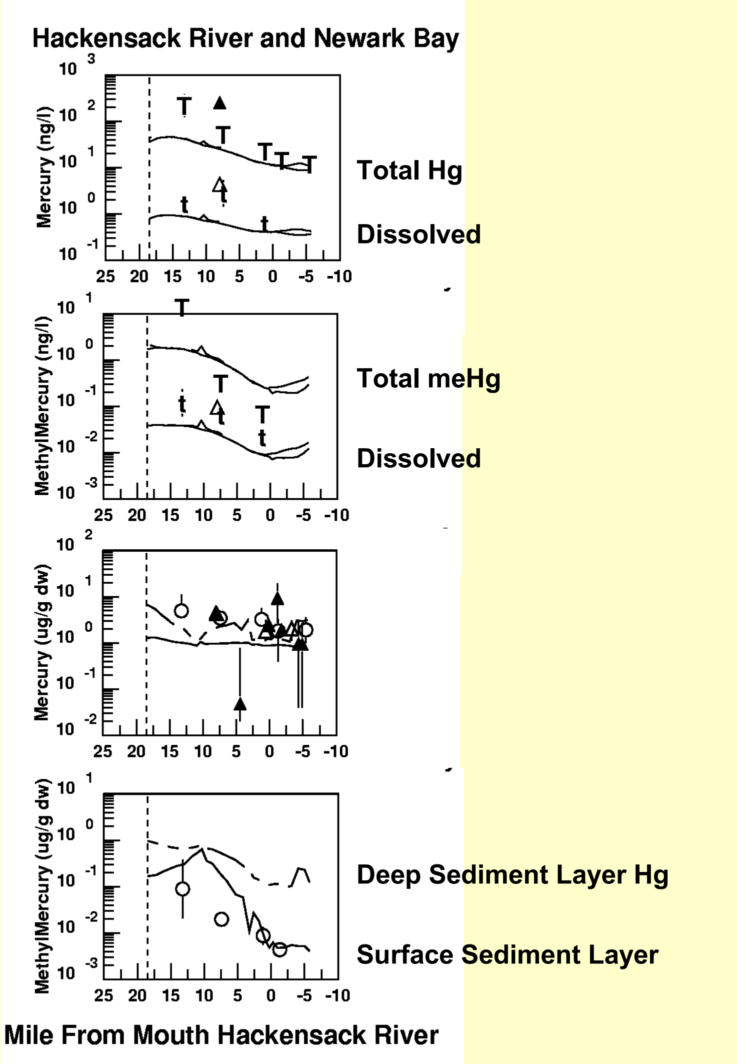
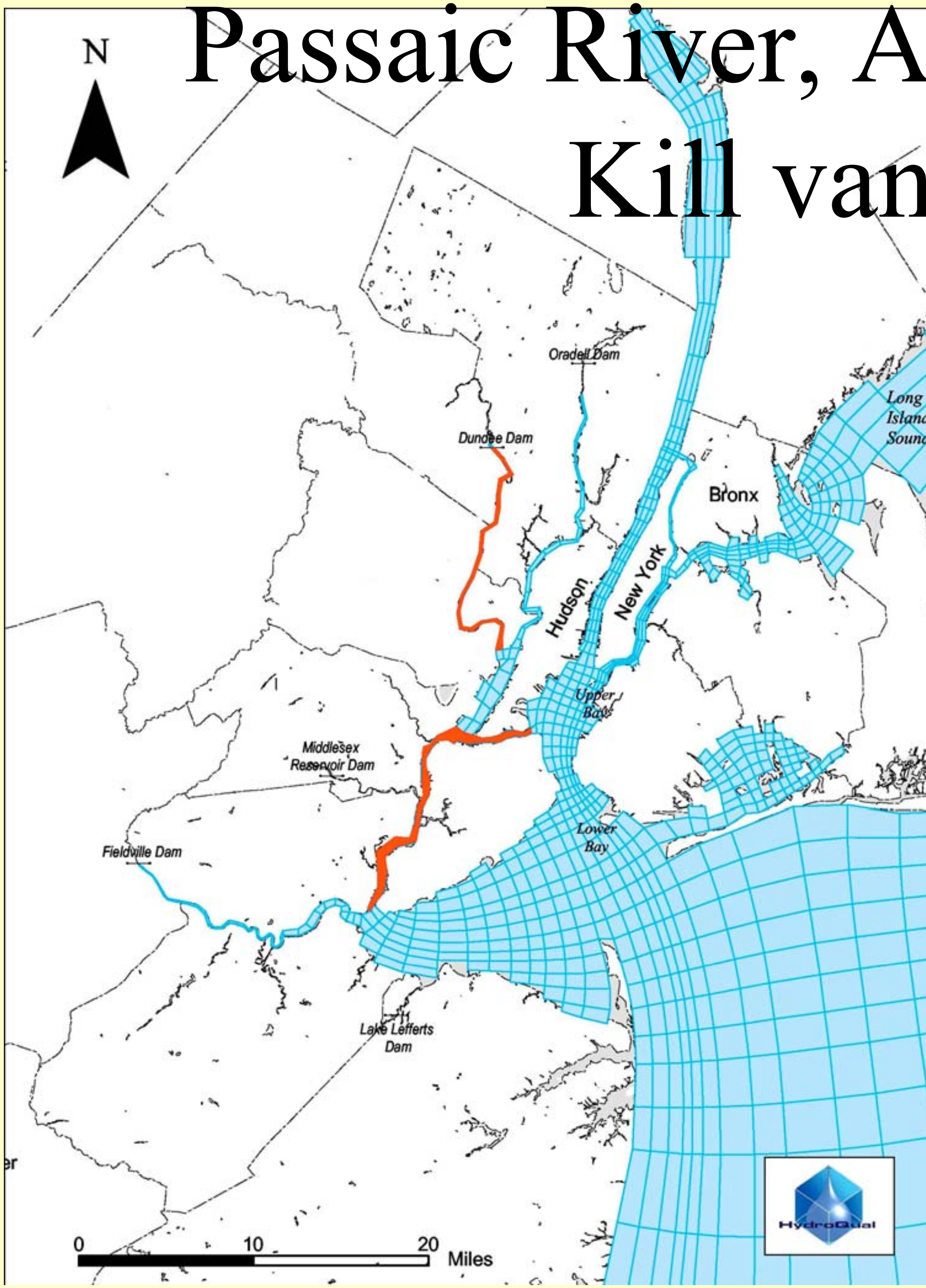


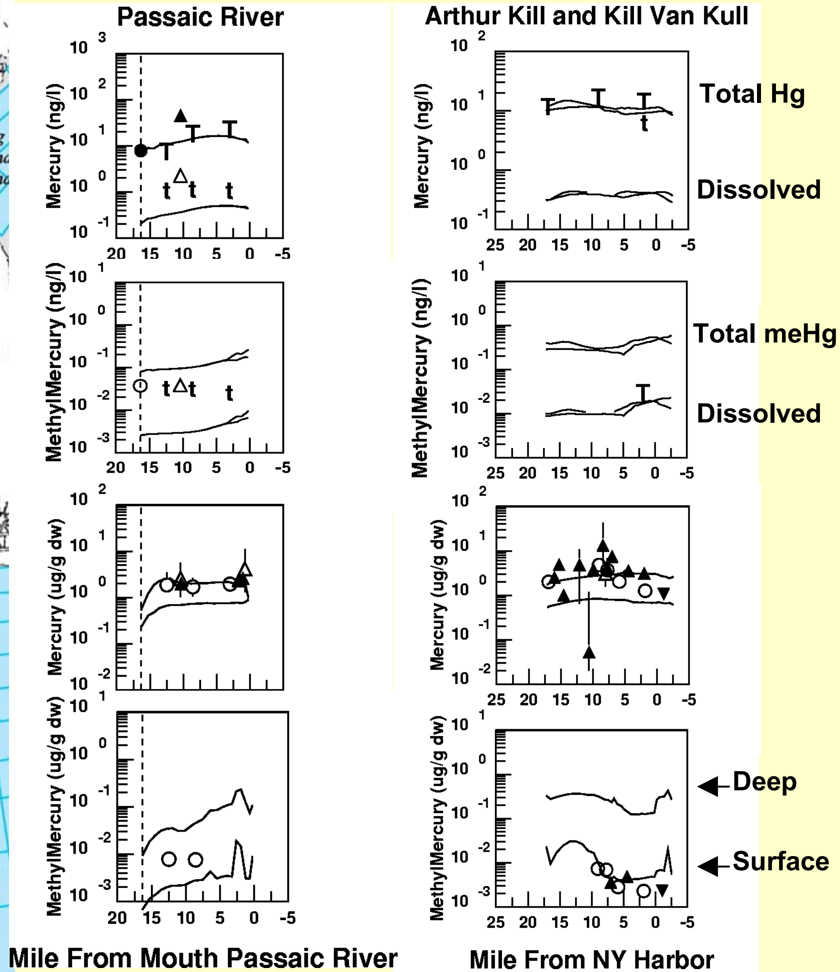
Hackensack River Transect





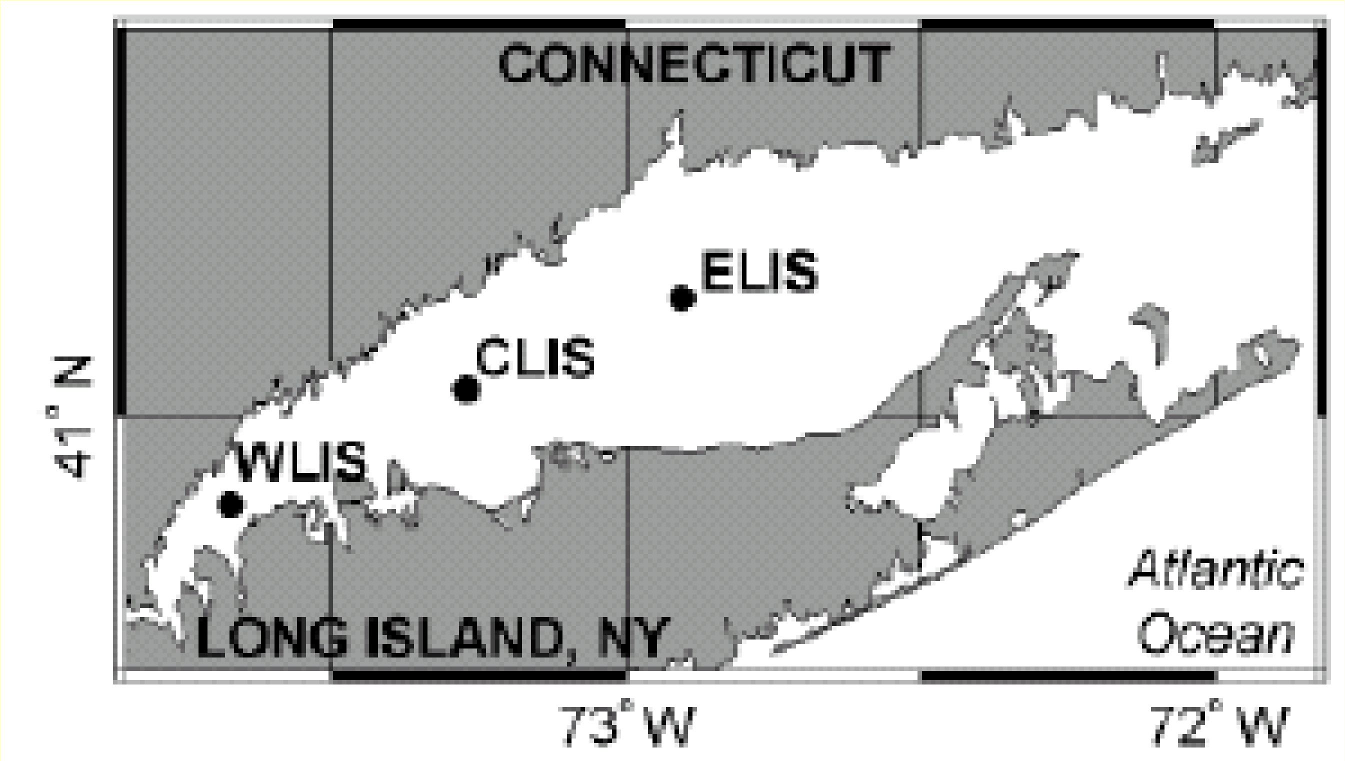
Passaic River, Arthur Kill and Kill van Kull

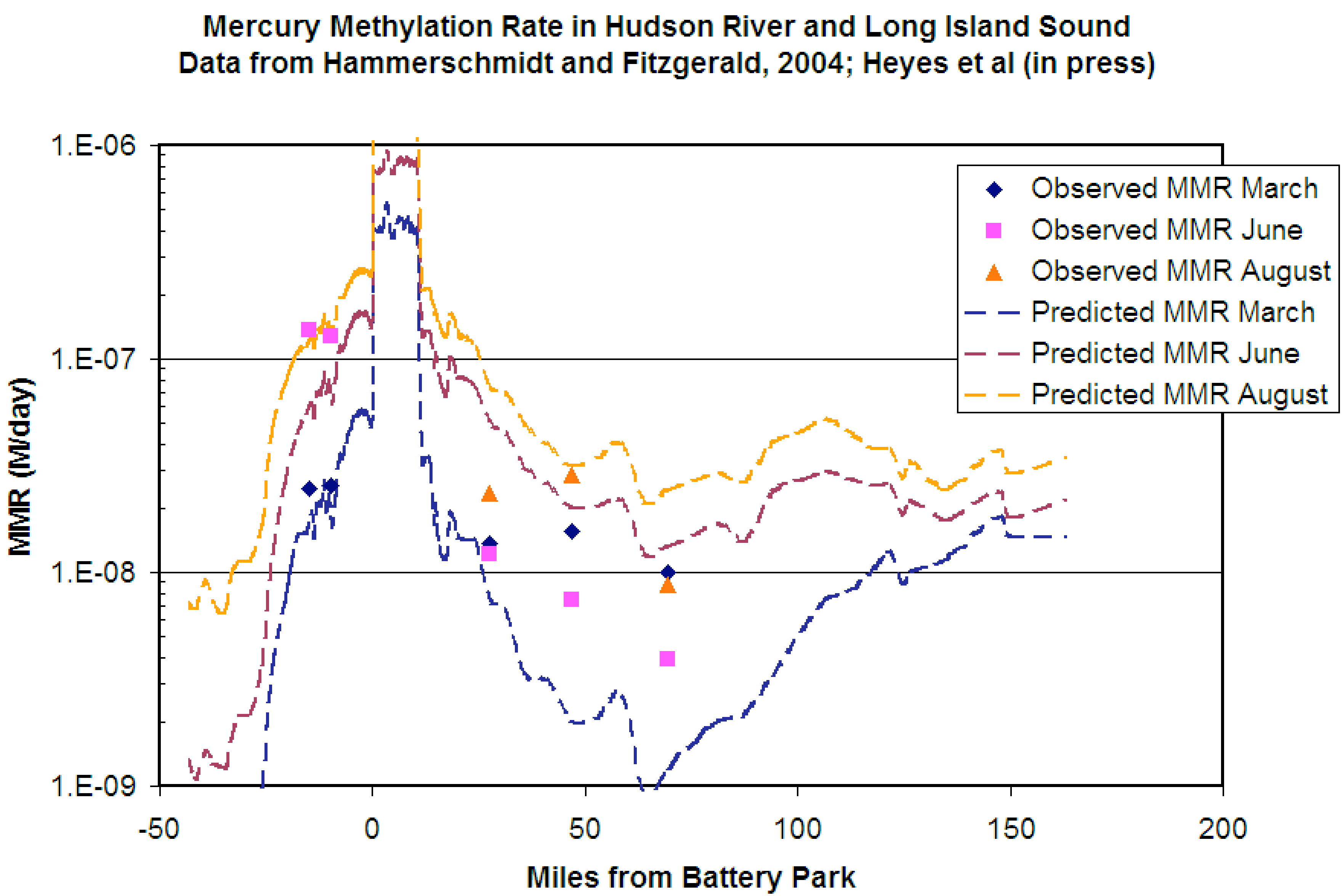




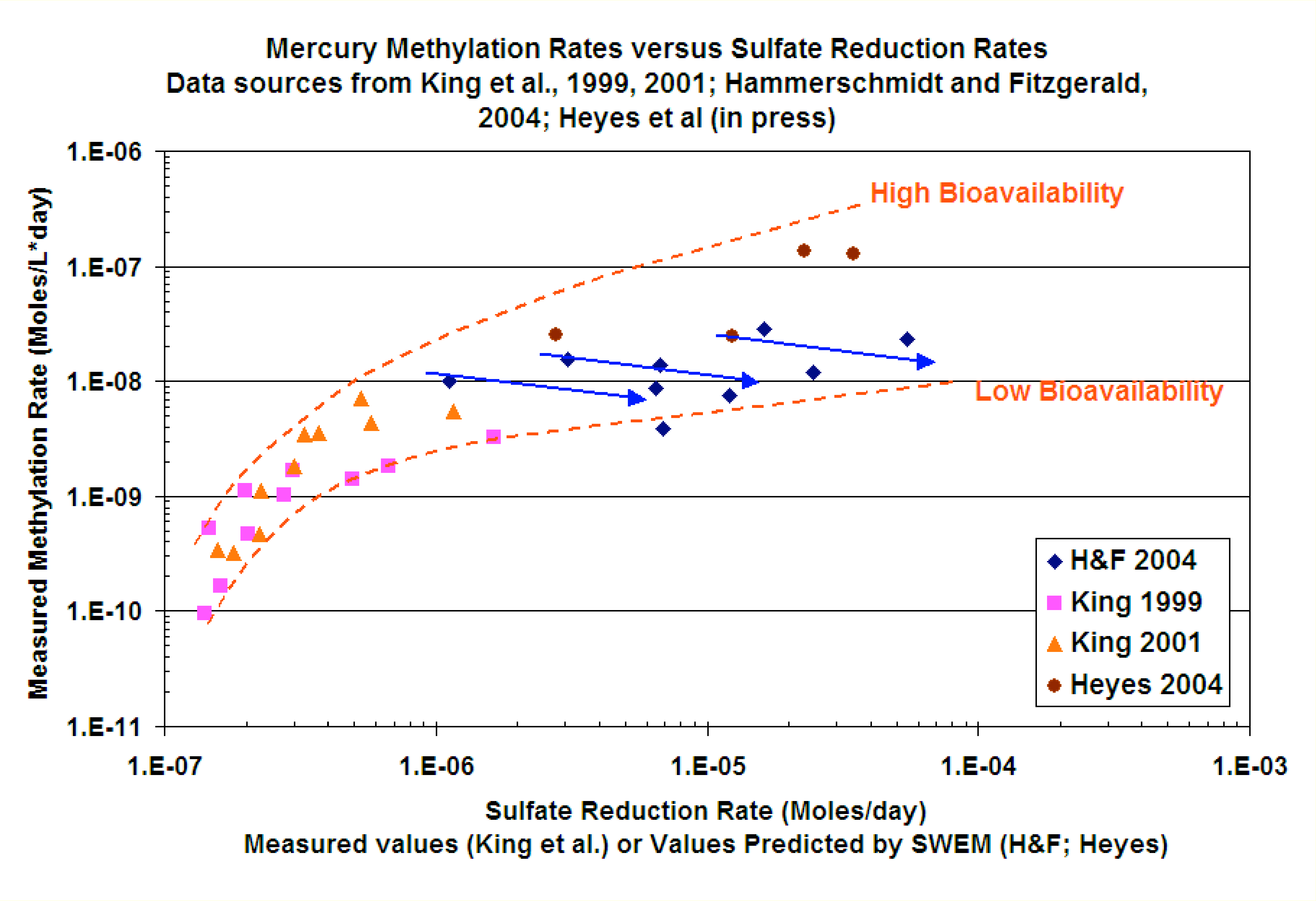
Locations of Sampling Stations in Long Island Sound

(Hammerschmidt and Fitzgerald 2004)





Mercury Methylation Rate in Hudson River and Long Island Sound
Data from Hammerschmidt and Fitzgerald, 2004; Heyes et al (in press)
MMR (M/day)
1.E-06
1.E-07
1.E-08
1.E-09
-50
0
50
100
150
200
Miles from Battery Park
Observed MMR March
Observed MMR June
Observed MMR August
Predicted MMR March
Predicted MMR June
Predicted MMR August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High Bioavailability
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Measured Methylation Rate (Moles/L*day)
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
Sulfate Reduction Rate (Moles/day)
Measured values (King et al.) or Values Predicted by SWEM (H&F; Heyes)

Summary

- Current mercury model can reproduce the major trends observed for mercury and methylmercury in a large model domain covering riverine, estuarine, and marine environments
- Methylmercury production successfully based on detailed chemical speciation and sediment microbial activity
- A single set of parameters can be used over this large system, possibly due to mechanistic approach

Current Development Efforts

- Recently completed hydrology and hydrodynamics simulations for more recent water years
- Bioaccumulation and food-web interactions to predict fish methylmercury concentrations

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