Simulating Mercury Transport and Transformation along the Sudbury River, MA

Christopher D. Knightes, Bart Hoskins, and Daniel Keefe

Public Meeting

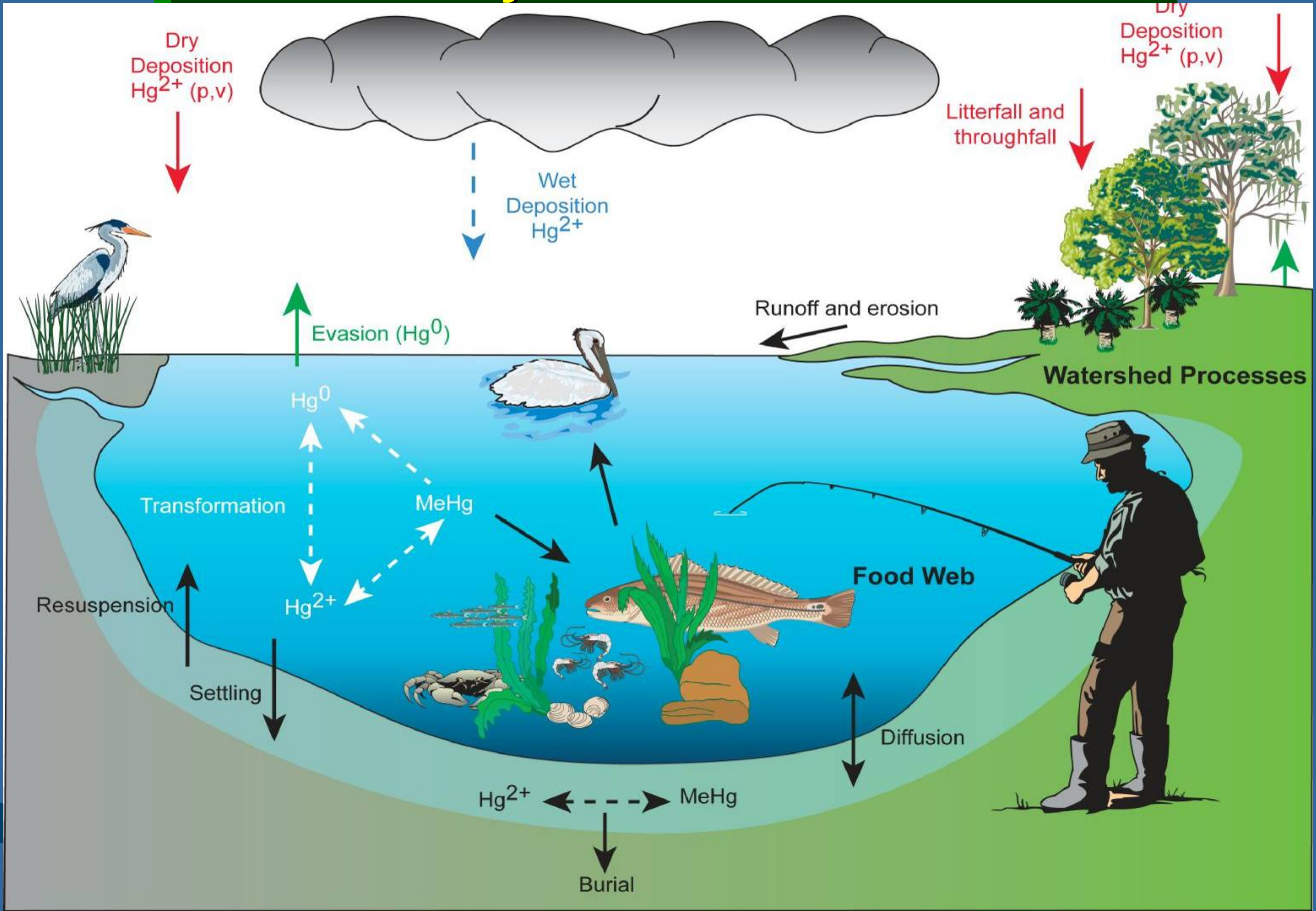
USEPA - Region 1

June 24, 2010

Outline of Presentation

- Mercury in the Environment
- Fate and Transport Modeling
- The WASP Model
- Nyanza Superfund Site (Sudbury River, MA)
- Setting up WASP Model for the Sudbury River
- Final Model Results for Current Conditions
- Sensitivity and Uncertainty
- Remedial Alternative Modeling

Mercury in the Environment



Fate and Transport Environmental Modeling

• To effectively manage and reduce risks due to contamination, we must understand the ***processes*** that brought about those risks.

- past and ongoing sources
- transport of chemicals
- changes in chemicals

• Process-based numerical models can be the most useful mathematical models for contaminated sediments.

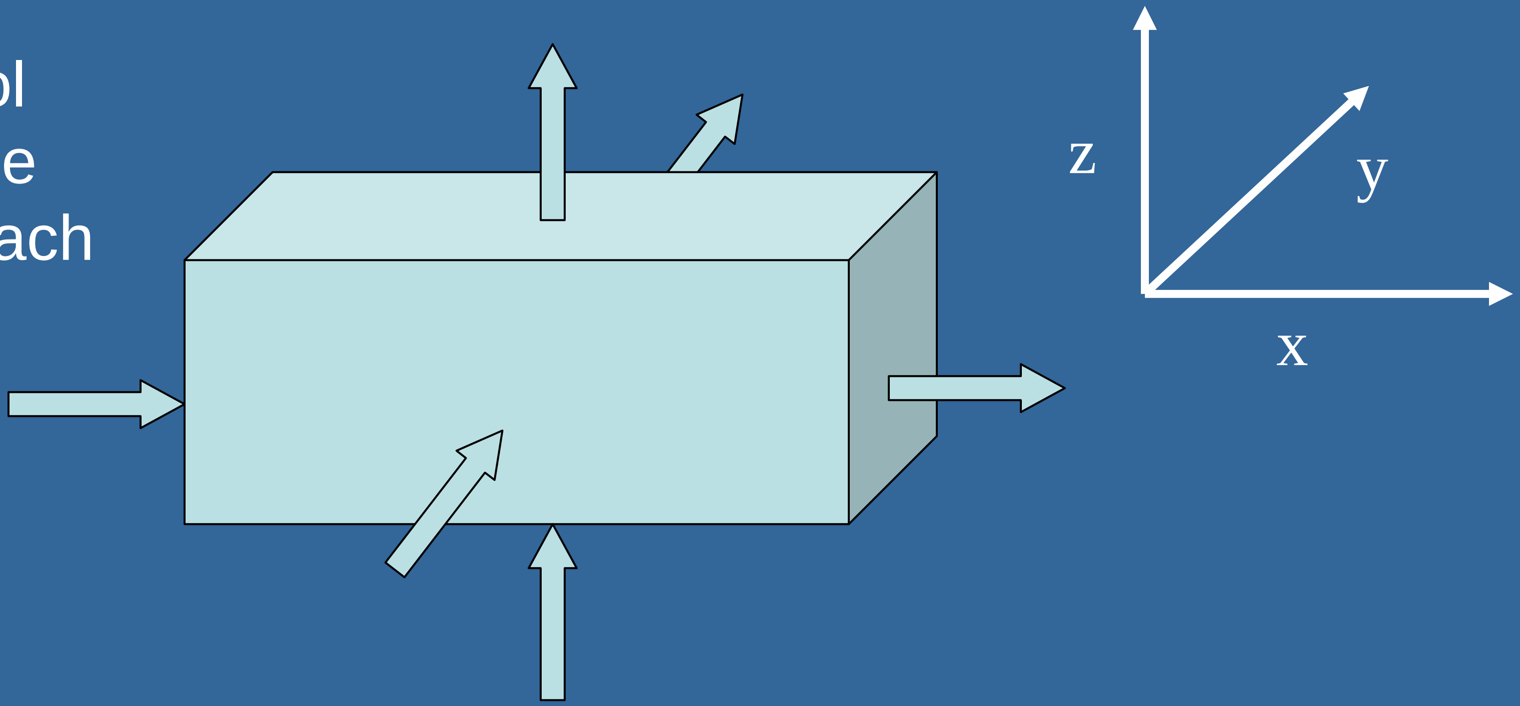
from "Understanding the Use of Models in Predicting Risk Reduction of Proposed Remedial Actions at Superfund Sediment Sites. Draft 2009. Office of Superfund Remediation and Technology Innovation.

Basic Principles of Mass Balance Models

- Mass Balance Model:
  - Applies Law of Conservation of Mass to analyze physical systems
- Law of Conservation of Mass
  - Mass cannot be gained or destroyed
  - Account for any change by simply keeping track of all governing processes that change total mass
- Differential Mass Balance
  - Generates differential equations to be solved to model the system

Three Dimensional Transport Equation

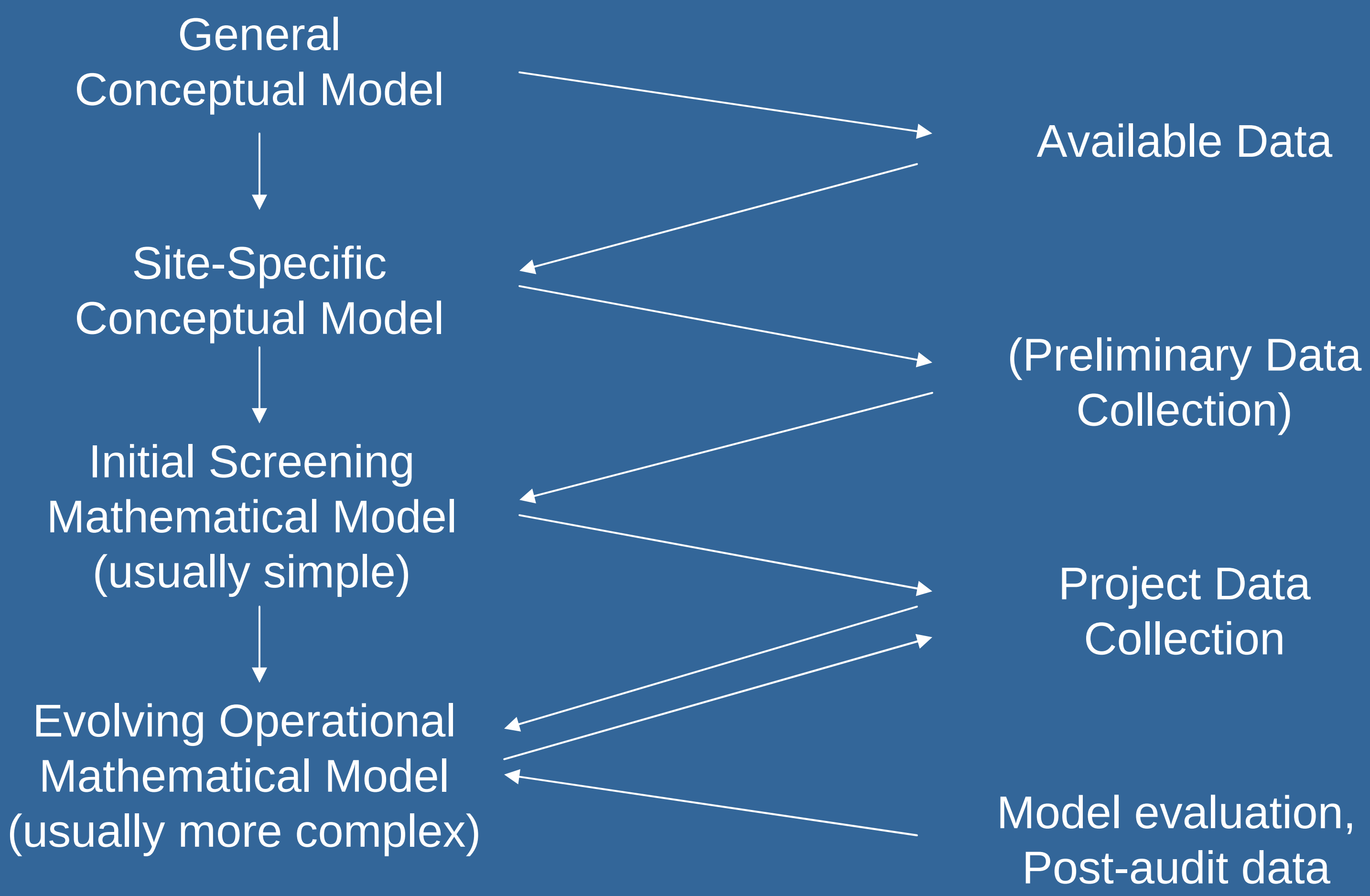
Control Volume Approach



Accumulation = Input – Output ± Reactions

$$\frac{\Delta(VC)}{\Delta t} = Q_{in}C_{in} - Q_{out}C_{out} \pm rV$$

Iterative Model Development Process



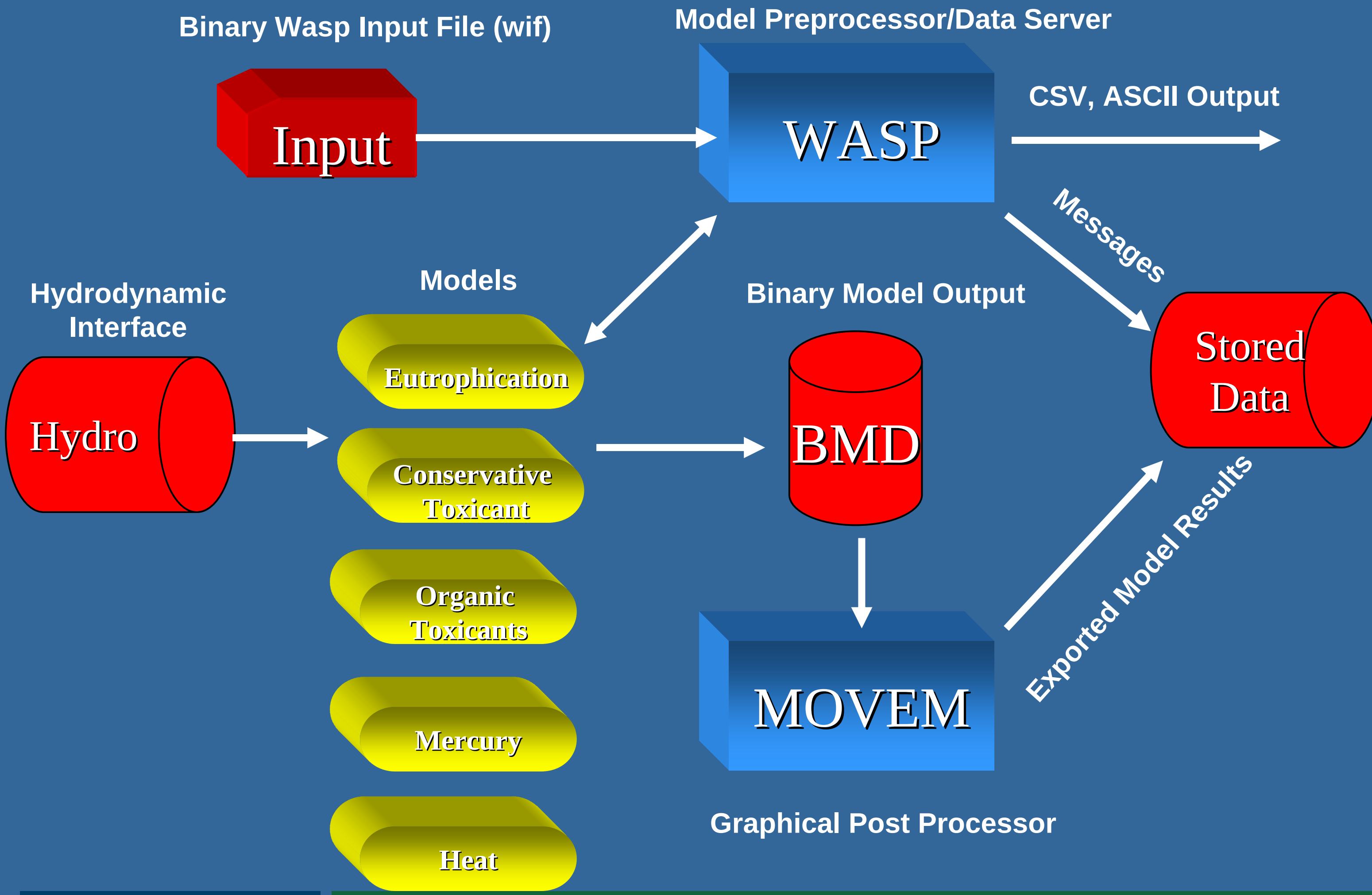
Appropriate Level of Complexity

- Proper model complexity is driven by:
  - Complexity of the environmental system
  - Complexity of pollutants of interest
  - Management questions
- Consequences of an overly simple model
  - Miss key processes and extrapolate inaccurately
  - May not address relevant management questions
  - May not be defensible
  - Insufficient adaptability to changing management requirements
- Consequences for overly complex model
  - More data collection
  - Increased computational burden
  - Increased uncertainty

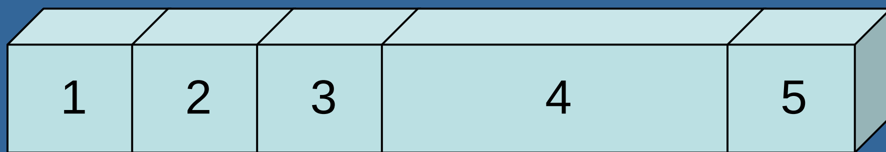
WASP:
Water Quality Analysis Simulation Program

- Dynamic Differential Mass Balance Surface Water Model
- General Surface Water w/ Underlying Sediments
  - Flexible network: 0D (lakes, ponds), 1D (lakes, streams), 2D (rivers), 3D (large lakes, estuaries)
- Different Water Quality Problems
  - Conventional Water Quality: DO, nutrients, eutrophication, algae, heat
  - Toxicants: organics, pesticides, metals, Hg-specific module
  - Solids balance (sands, fines, biotic solids, cobbles)
  - Three chemicals (Hg(0), Hg(II), MeHg)
- Separation of Processes
  - Transport (Advection, Exchange/Dispersion, Solids)
  - Kinetics (e.g., methylation, demethylation, oxidation, reduction)
- Simple hydrodynamic modeling approaches for water routing
  - Dams and impoundments
  - Tidal influence and reverse flows

WASP Modeling Framework



WASP Terminology

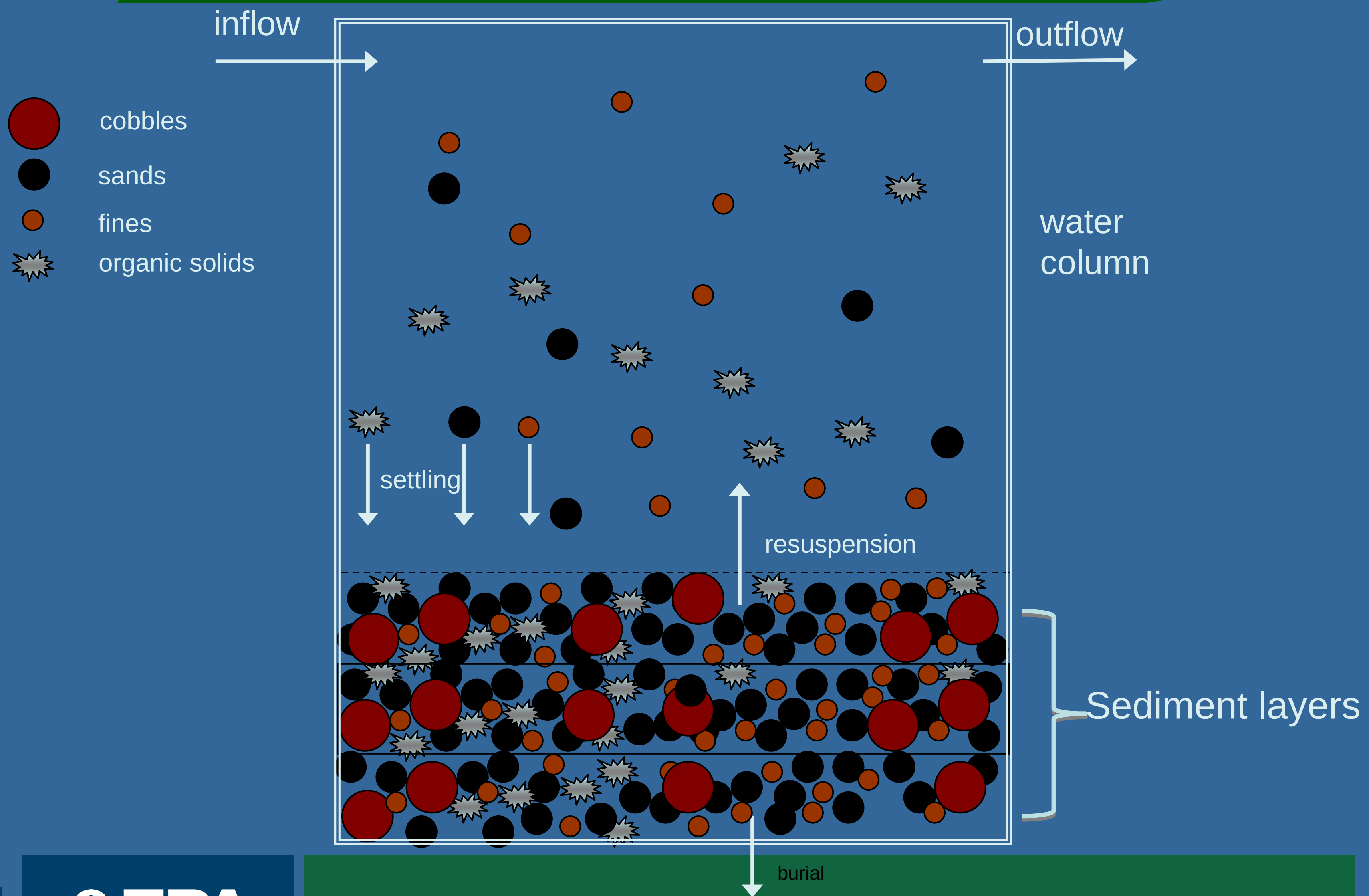


WASP Segments

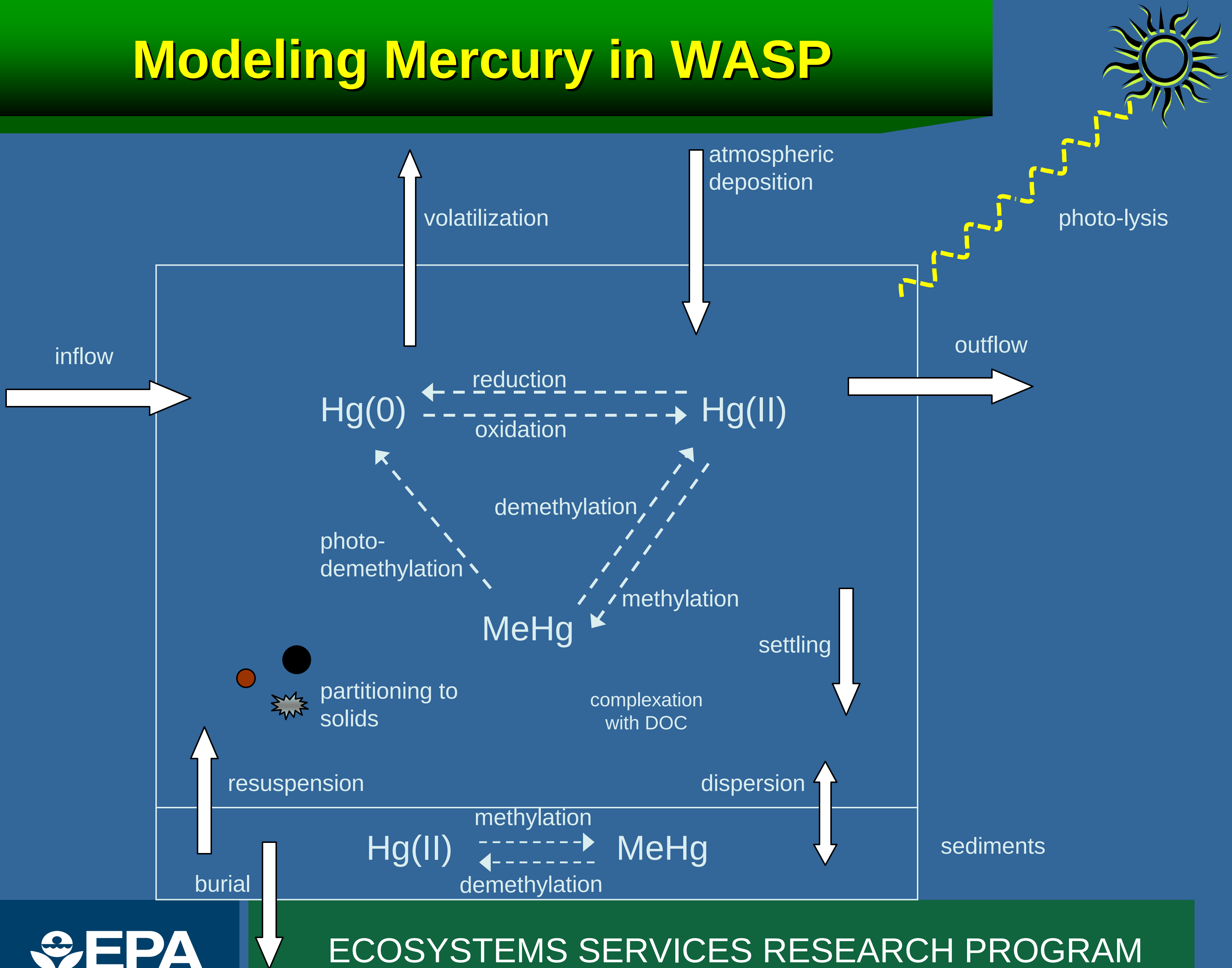
Silts
Sands
Particulate Organic Matter
Hg(II)
Hg(0)
MeHg

State Variables

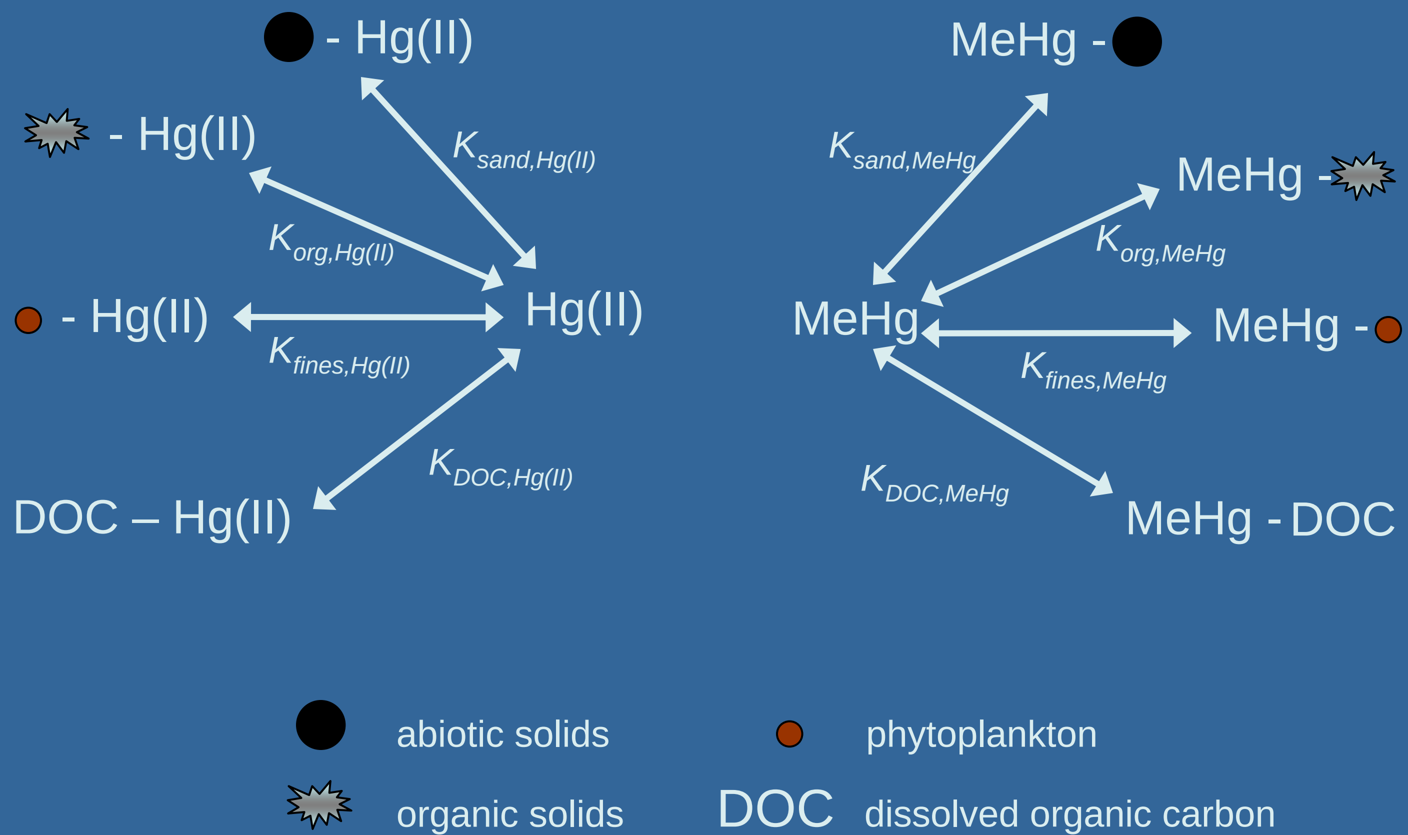
Modeling Solids in WASP



Modeling Mercury in WASP



Modeling Partitioning in WASP

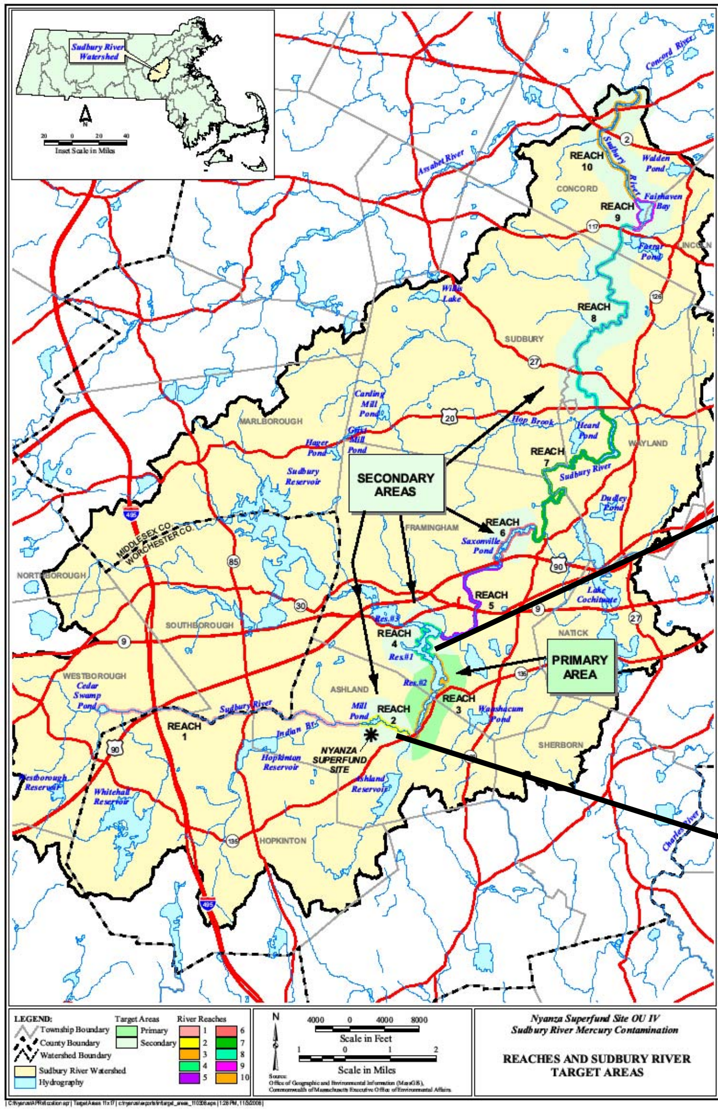


Example WASP Layout
Neuse River Estuary, NC

ECOSYSTEMS SERVICES RESEARCH PROGRAM

Nyanza Superfund Site (Sudbury River, MA):

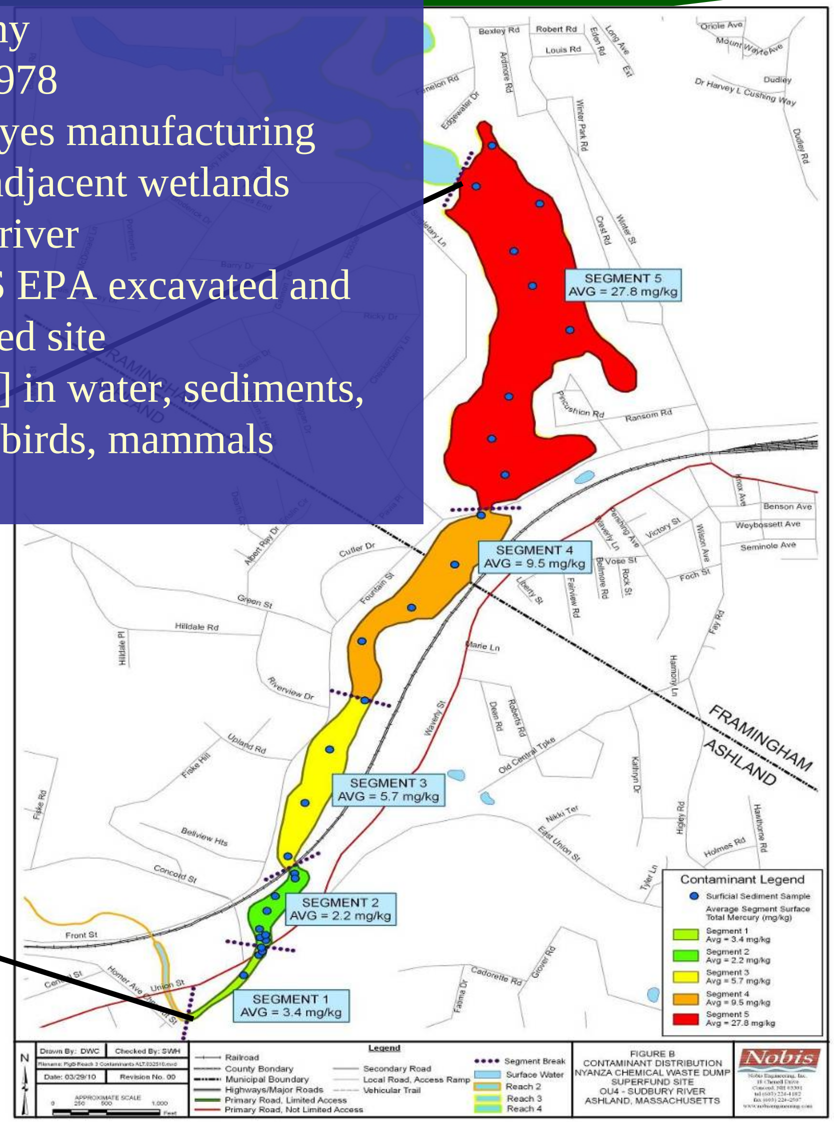
1917 – 1978
Textile dyes manufacturing



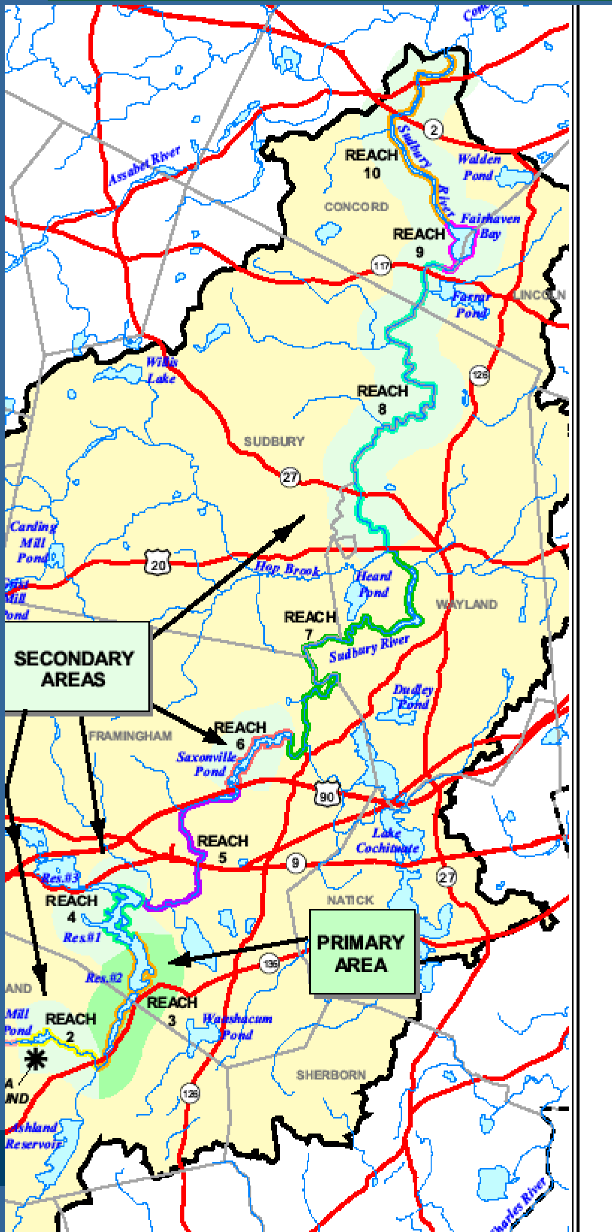
Nyanza Company

- 1917 – 1978
- Textile dyes manufacturing
- Hg into adjacent wetlands and river
- 1991, US EPA excavated and capped site
- high [Hg] in water, sediments, fish, birds, mammals

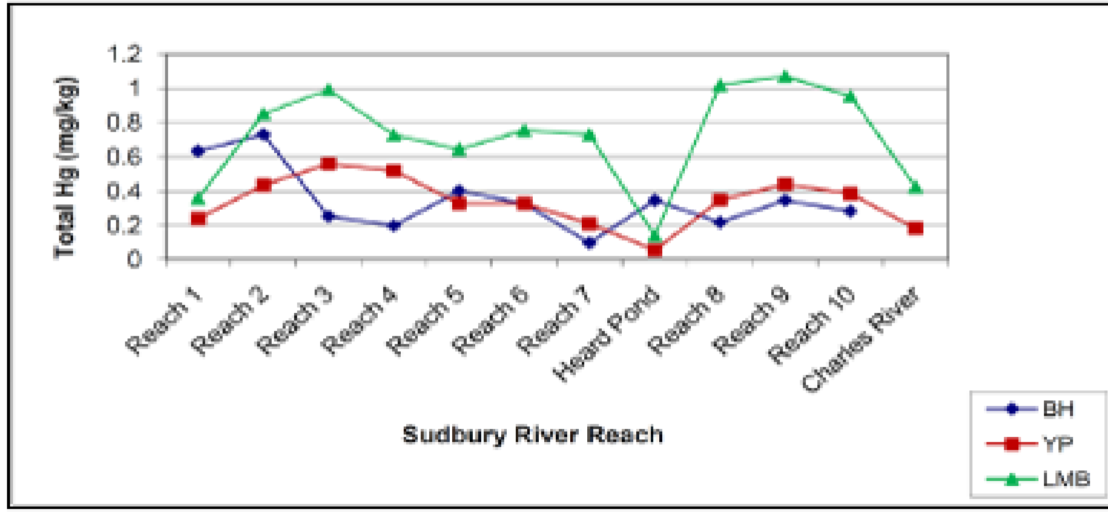
YSTEMS SE



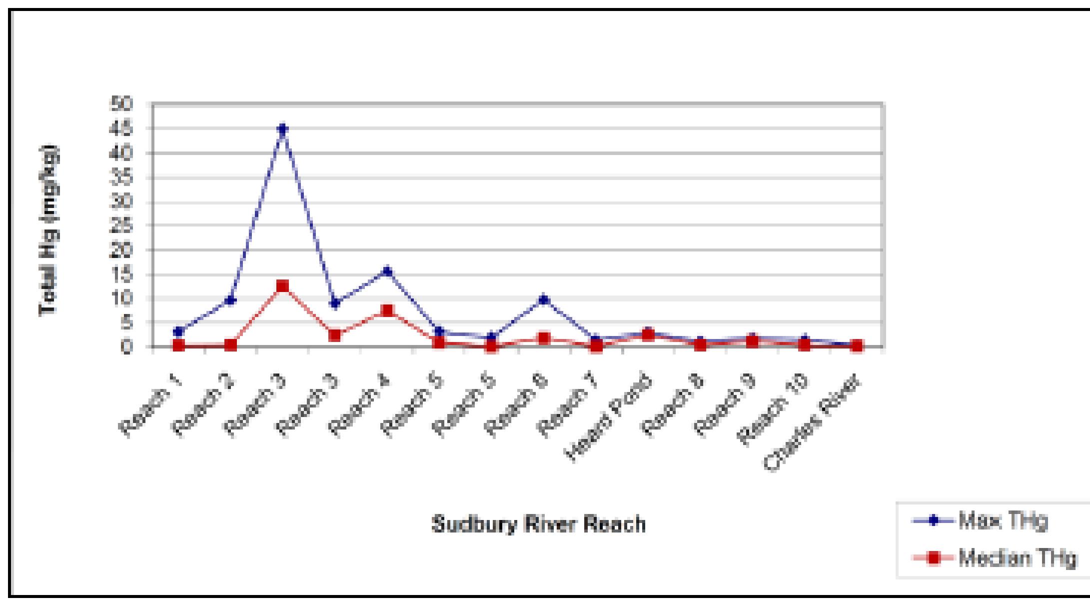
Nyanza Extent of Mercury Concentrations



Fish



Sediment



Correlation to ln(Hg_{fish}/fish length)

Parameter	All Fish	Largemouth Bass
ln($MeHg_{water}$)	$R = 0.623$, $p<0.001$	$R = 0.712$, $p<0.001$
$MeHg_{sed}$	$R = 0.332$, $p<0.001$	$R = 0.596$, $p<0.001$
ln(HgT_{water})	$R = 0.227$, $p<0.01$	$R = 0.453$, $p<0.01$
ln(HgT_{sed})	n.s.($p>0.05$)	n.s. ($p>0.05$)

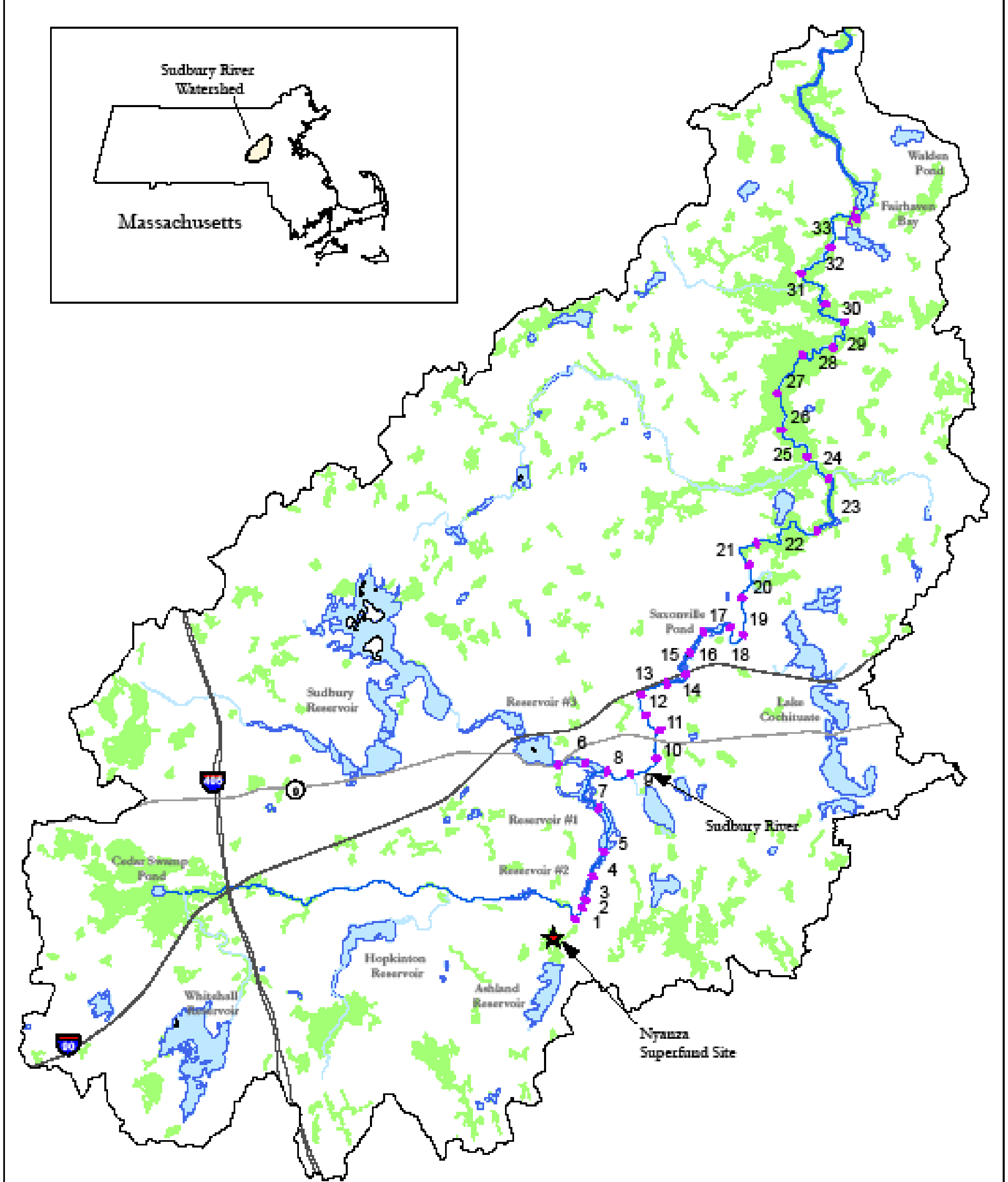
Brumbaugh et al., 2001.

The Problem

- *Mercury accumulates in sediments*
- *Sediment mercury may act as a long-term source*
- *Mercury clean-up strategies target HgT, but exposure risk is from ingestion of MeHg in fish*
- *MeHg in fish tissue correlated with MeHg in water column, but poorly correlated with HgT in sediments or water column.*
- *Atmospheric deposition is an additional source to aquatic ecosystems*

Nyanza WASP Model Setup

1. Delineation of Model System using WASP segments
2. Flow: Movement of water (Hydrology)
3. Solids: Sediment layers and Movement of solids
4. Boundary Conditions
5. Determination of Partitioning Coefficients
6. Mercury Cycle Rate Constants and Parameters
7. Mechanistic Evaluation of System
8. Comparison of Model Results to Observed



1. WASP Delineation

The Sudbury River (Reaches 3 – 8) is first separated into 33 WASP segments.

RCH PROGRAM

Delineation of WASP Segmentation: Reach 3 (Reservoir 2)

upstream boundary →

Segment 1	Segment 2	Segment 3	Segment 4	Segment 5	
Segment 34	Segment 35	Segment 36	Segment 37	Segment 38	Segment 100
Segment 67	Segment 68	Segment 69	Segment 70	Segment 71	Segment 101
Segment 105	Segment 106	Segment 107	Segment 108	Segment 109	Segment 102
Segment 112	Segment 113	Segment 114	Segment 115	Segment 116	Segment 103
					Segment 104

→ to segment 7

- Surface Water
- Surface Sediments
- Subsurface Sediments
- Subsurface Sediment
- Bottom Sediment

- Each reach is divided into a number of small pieces as WASP segments.
- For each surface water segment, there are underlying sediment layers.
- Res 2 and 1 have 4 underlying sediment layers, the rest have 2.

Delineation of WASP Segmentation: Reach 4 (Reservoir 1)

from surface water segment 5

upstream boundary

Segment 6	Segment 7
Segment 39	Segment 40
Segment 72	Segment 68
Segment 110	Segment 106
Segment 117	Segment 118

to surface water segment 8

Delineation of WASP Segmentation: Reach 5

from surface segment 7

Segment 8	Segment 9	Segment 10	Segment 11	Segment 12	Segment 13	Segment 14
Segment 41	Segment 42	Segment 43	Segment 44	Segment 45	Segment 46	Segment 47
Segment 74	Segment 75	Segment 76	Segment 77	Segment 78	Segment 79	Segment 80

to surface water segment 15

Delineation of WASP Segmentation: Reach 6

from surface water segment 14 →

Segment 15	Segment 16	Segment 17
Segment 48	Segment 49	Segment 50
Segment 81	Segment 82	Segment 83

→ to surface water segment 15

Delineation of WASP Segmentation: Reach 7

from surface segment 17 →

Segment 18	Segment 19	Segment 20	Segment 21	Segment 22	Segment 23	Segment 24
Segment 51	Segment 52	Segment 53	Segment 54	Segment 55	Segment 56	Segment 57
Segment 84	Segment 85	Segment 86	Segment 87	Segment 88	Segment 89	Segment 90

→ to surface water segment 25

Delineation of WASP Segmentation: Reach 8 (Great Meadows National Wildlife Refuge)

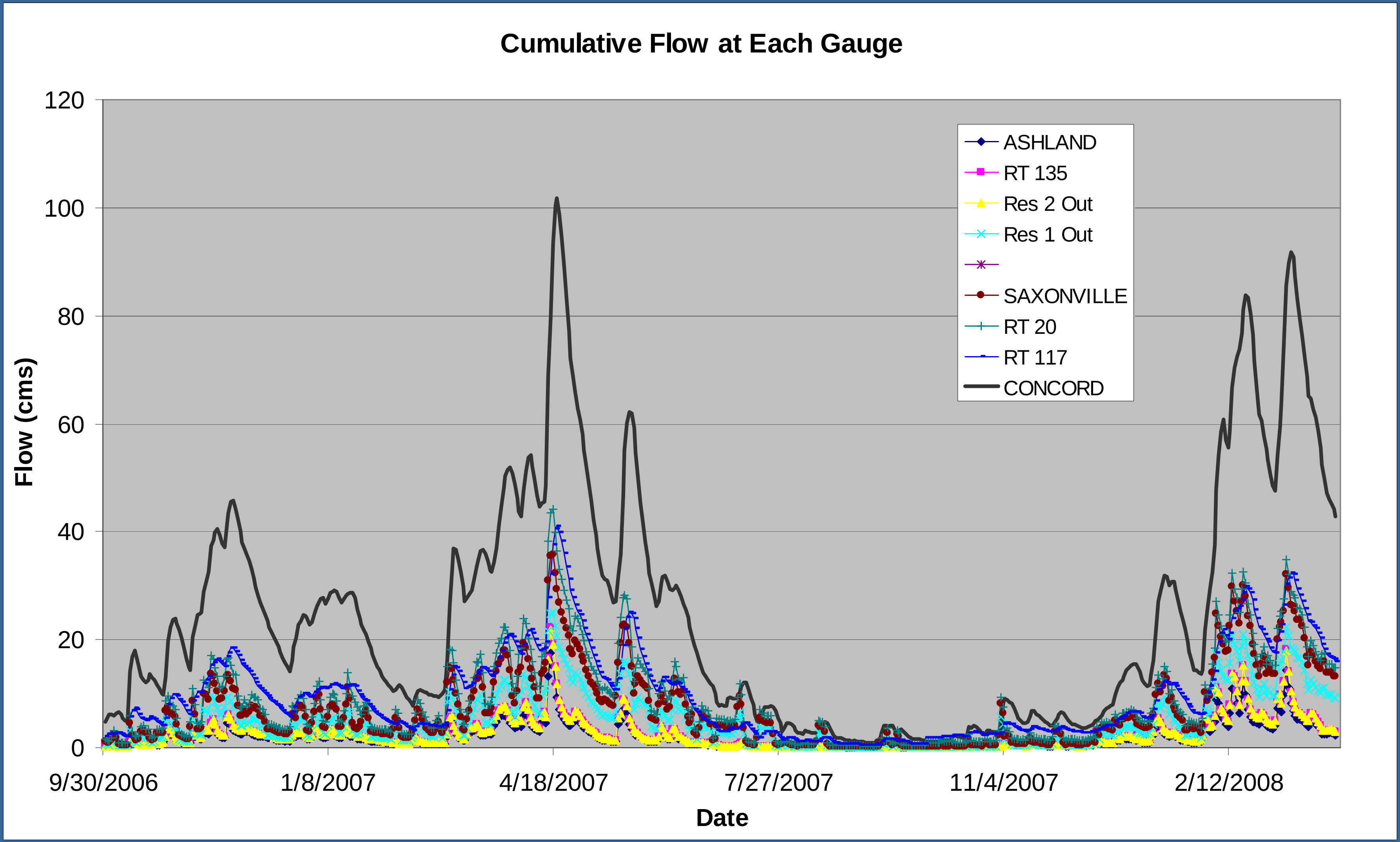
from surface segment 24

Segment 25	Segment 26	Segment 27	Segment 28	Segment 29	Segment 30	Segment 31	Segment 32	Segment 33
Segment 58	Segment 59	Segment 60	Segment 61	Segment 62	Segment 63	Segment 64	Segment 65	Segment 66
Segment 91	Segment 92	Segment 93	Segment 94	Segment 95	Segment 96	Segment 97	Segment 98	Segment 99

out

Flow: Movement of Water (Hydrology)

- USGS Stream Gages are used to determine incoming flow (cubic meters per second) for upstream boundaries and incoming streams
- A 2 year period of flow was used and repeated to extend into the future
- Manning's roughness coefficients and kinematic wave flow parameters were adjusted to calibrate flow and velocities


Cumulative Flow at Each Gauge
Flow (cms)
120
100
80
60
40
20
0
9/30/2006
1/8/2007
4/18/2007
7/27/2007
11/4/2007
2/12/2008
Date
ASHLAND
RT 135
Res 2 Out
Res 1 Out
SAXONVILLE
RT 20
RT 117
CONCORD

Solids: Sediment layers and Movement of solids

- Average measured total suspended solids used as incoming flow concentrations
- Initial sediment concentrations of solids were determined using observed fractions of sands, silts, and organic matter.
- With only water and solids in the model, system was run for 100 yrs until the sediment solids concentrations reached a pseudo-steady state
- Burial rates were compared to observed

Solids: Sediment layers and Movement of solids

- Dynamic erosion equations (Lick Equations) for settling and resuspension
- Base resuspension rate for bioturbation
- Lick Equations parameterized using observed data (based on ACoE 2001 sediment report)
- Results were compared and calibrated to match observed sediment compositions and burial rates
- Cobbles were added to WASP (non-erodable solids) to account for high level of scour in sediments after impoundments

Mercury Boundary Concentrations

- Mercury enters the Sudbury System via upstream inflow as well as from the historic contamination.
- Wet deposition : 8 – 12 ug/m2/yr
- Dry deposition : 6 – 14 ug/m2/yr
- Approximately 20% of deposition reaches surface water (Rudd, 1995)
- MeHg (% of HgT): 1% in winter, 2% in fall/spring, 4% summer

Date	Dry Deposition [ug/m^3/yr]	Wet Deposition [ug/m^3/yr]	Total Deposition [ug/m^3/yr]	Hg(II) [ng/L]	MeHg [ng/L]
9/23	10	10	20	3.76	0.08
12/23	6	8	14	2.74	0.028
3/20	10	10	20	3.76	0.08
6/20	14	8	22	4.68	0.208

Determination of Partitioning Coefficients

- Hg(II) and MeHg partition between different phases:
  - Aqueous, DOC complexed, sorbed to solids
- Using observed fractions of filtered and unfiltered Hg(II) and MeHg, DOC and solids, partition coefficients were modeled
- Partition coefficients for each observation location was determined
- Log-mean for all locations was used

Determination of Partitioning Coefficients

For Segment 2

Silts	1.78 mg/L
Particulate Organic Matter (POM)	0.48 mg/L
Dissolved Organic Carbon (DOC)	6.9 mg/L

Unfiltered Hg(II)	4.6 ng/L
Unfiltered MeHg	0.29 ng/L
Filtered Hg(II)	2.4 ng/L
Filtered MeHg	0.22 ng/L
Fraction dissolved Hg(II)	0.53
Fraction dissolved MeHg	0.76

	Hg(II)	MeHg
K_{silt}	1×10^6	2×10^5
K_{POM}	2×10^5	1×10^5
K_{DOC}	4×10^5	5×10^5

Mercury Cycle Rate Constants and Parameters

- Hg(II) and MeHg partition between different phases:
  - Aqueous, DOC complexed, sorbed to solids
- Using observed fractions of filtered and unfiltered Hg(II) and MeHg, DOC and solids, partition coefficients were modeled
- Partition coefficients for each observation location was determined
- Log-mean for all locations was used

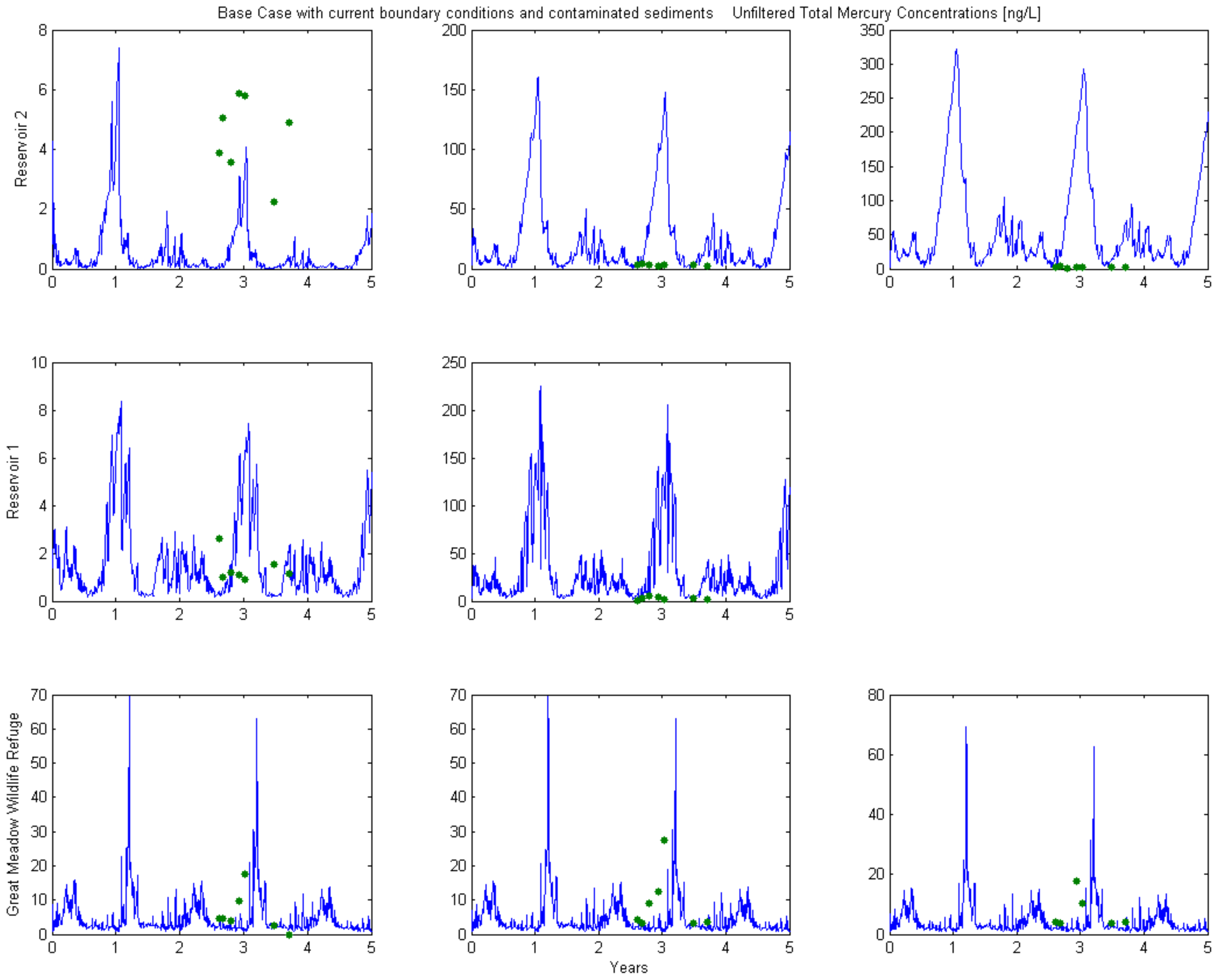
Mercury Cycle Rate Constants and Parameters

Transformation Process (rate)	Reaction	Water Column	Water: Deep Reservoir	Water: GMNWR	Reservoir Sediments	Main River Sediments	GMNWR Sediments
Methylation (d^{-1})[a,b]	Hg(II) → MeHg	**0**[a]	**0.01**[a]	**0.01**[a]	**0.02**[b]	**0.02**[b]	**0.02**[b]
Demethylation (d^{-1})[b,c]	MeHg → Hg(II)	**0.04**[c]	**0.1**[c]	**0.04**[c]	**0.5**[b]	**0.7**[b]	**0.25**[b]
Methylation/ Demethylation (%MeHg)		**0**	**10%**	**25%**	**4%**	**3%**	**8%**
Dark Oxidation[d]	Hg(0) → Hg(II)	**1.6**[d]	**1.6**[d]	**1.6**[d]	**0**	**0**	**0**
Surface Photo-Oxidation (d^{-1})[e]	Hg(0) → Hg(II)	**6**[e]	**0**	**0**	**0**	**0**	**0**
Surface Photo-Reduction (d^{-1})[f]	Hg(II) → Hg(0)	**14**[f]	**0**	**0**	**0**	**0**	**0**
Surface Photo-Demethylation (d^{-1})[g]	MeHg → Hg(0)	**0.2**[g]	**0**	**0**	**0**	**0**	**0**

Mercury Cycle Rate Constants and Parameters

Constant	Value
Light Extinction Coefficient	1.05 per m[a]
Wavelength of maximum absorption for photo-lytic processes	420 nm[b]
Temperature correction factor for biotic processes	2[c]
Hg(0) Volatilization Option	4: O'Connor Method [d]
Hg(0) Atmospheric Concentration	1.6×10^{-9} g/m^3 [d]
Hg(0) Henry's Law Constant	0.01 atm-m^3/mole[d]
Hg(0) Volatilization Temperature Correction, θ	1.04[d]
Macro-Dispersive Exchange for Deep Reservoir	0.00162 cm^2/s [e]
Pore Water Dispersion between sediment layers	6×10^{-6} cm^2/s [f]
Pore Water Dispersion between sediment layer and surface water	5×10^{-5} cm^2/s [e,g]

Mechanistic Evaluation of System



Mechanistic Evaluation of System

- Modeling of system greatly overpredicted all species of mercury (HgT, MeHg, filtered and unfiltered) in the 7 segments (3 reaches) where we had observed results
- Separated model into two parts:
  - Background levels of mercury due to atmospheric deposition, incoming streams, watershed sources
  - Nyanza-related mercury only
- Research has suggested that new mercury and old mercury may behave differently (Hintelmann, 2002; Harris et al., 2007)

Mechanistic Evaluation of System

- Separate the modeling into two
- Use higher partition coefficients (K_d's) for Nyanza case
- Add results of two cases

  1)Clean sediment case:

  Hg in inflow, no mercury in sediment

  2)Contaminated sediment case:

  No Hg in inflow, historic mercury in sediment
- Model sensitivity of Methylation Rates

  (x1 and x2 k_{meth})

Mechanistic Evaluation of System

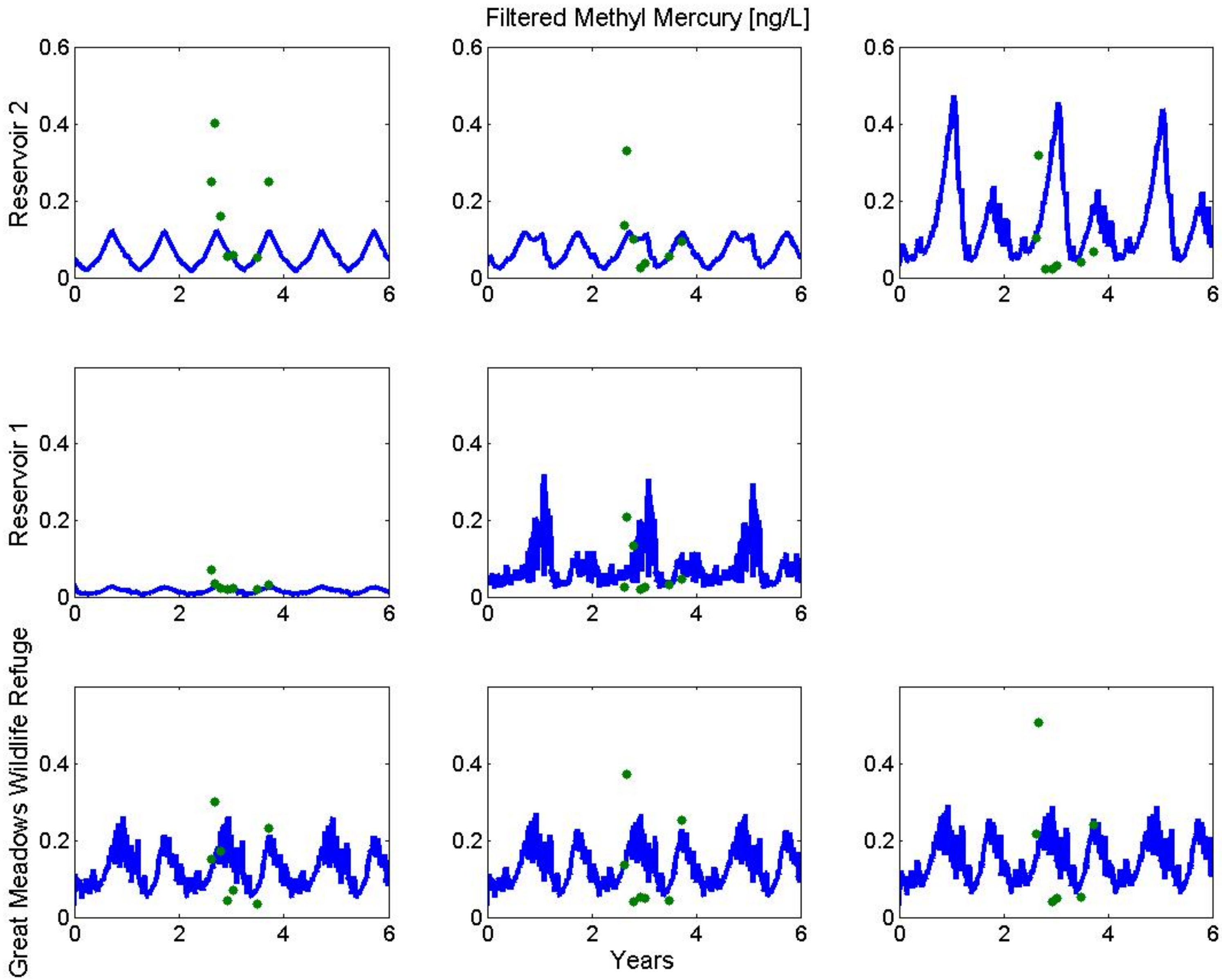
- Clean Sediment case uses original parameterization
- Contaminated Sediment case

Case	K_d (silt)	k_{meth}
Clean Case	1X	100%
A	100X	1%
B	200X	0.5%
C	100X	10%

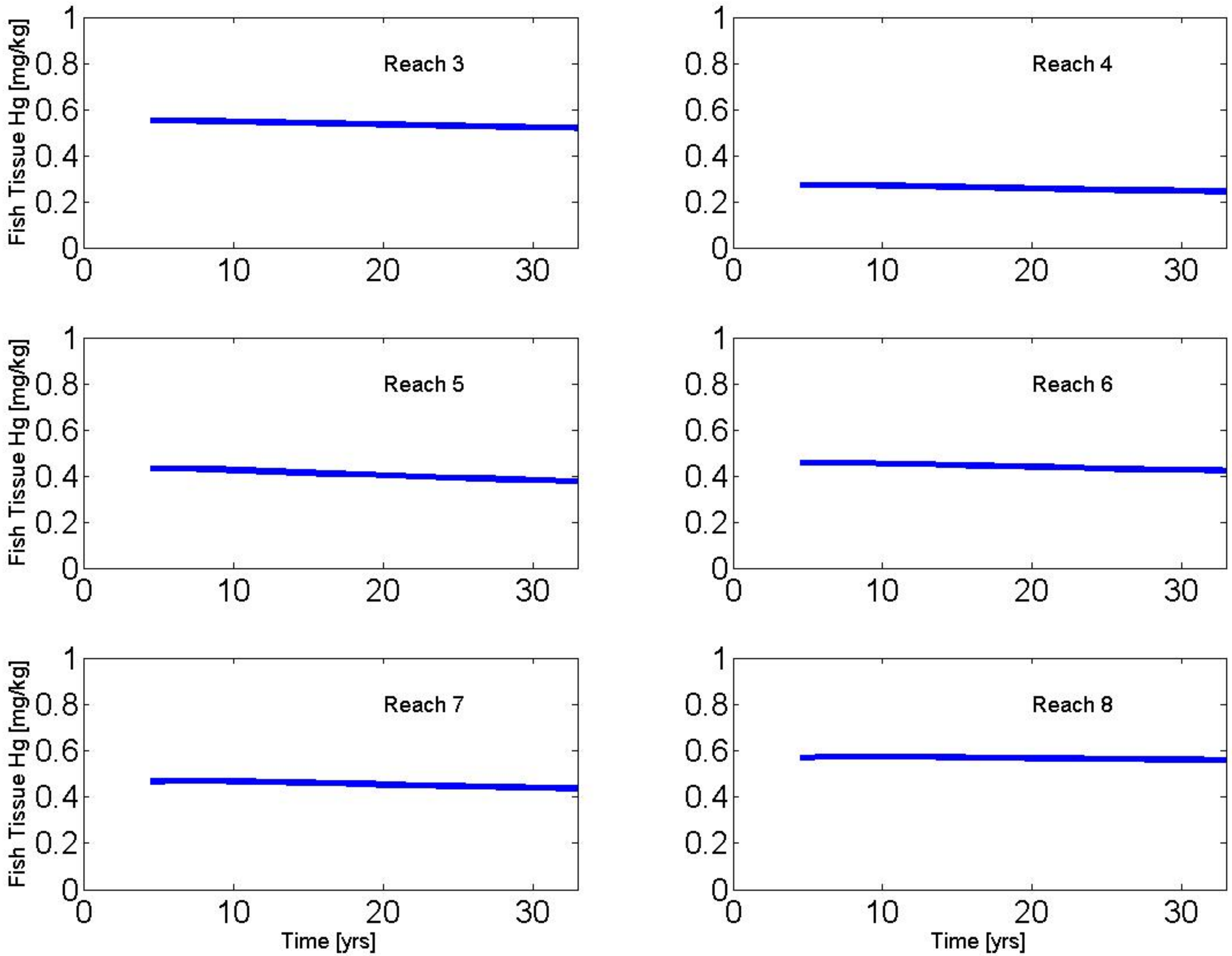
Mechanistic Evaluation of System

- Through mechanistic evaluation a final model was developed
  - Model split into two cases and then added together
  - Methylation rates kept the same for all regions except GMNWR, where methylation rates were doubled
  - Partition coefficients for Nyanza case “old mercury” were set to 100x that of the background case “new mercury”
  - 1% of sorbed old mercury was available for methylation

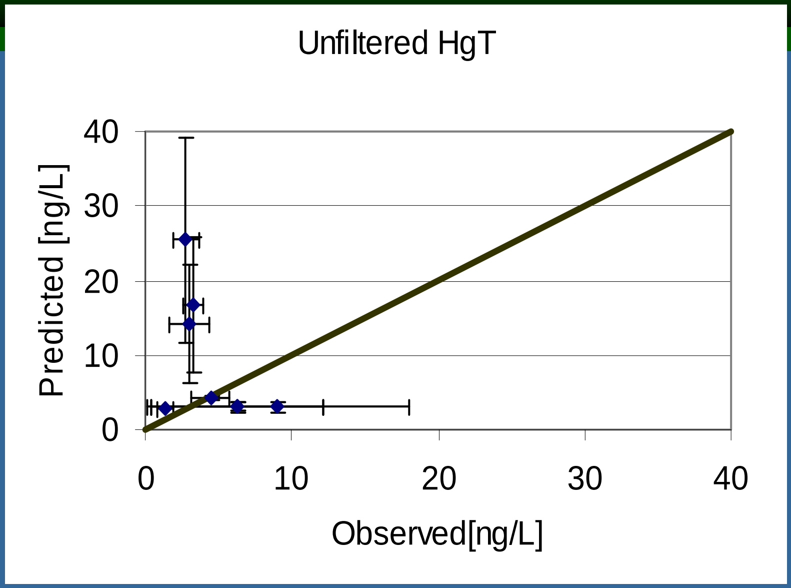
Simulated Dissolved MeHg Concentrations

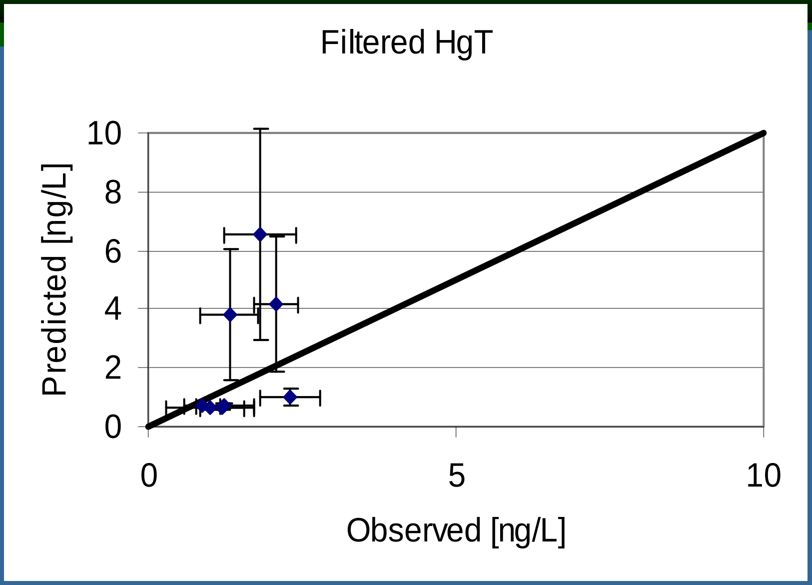


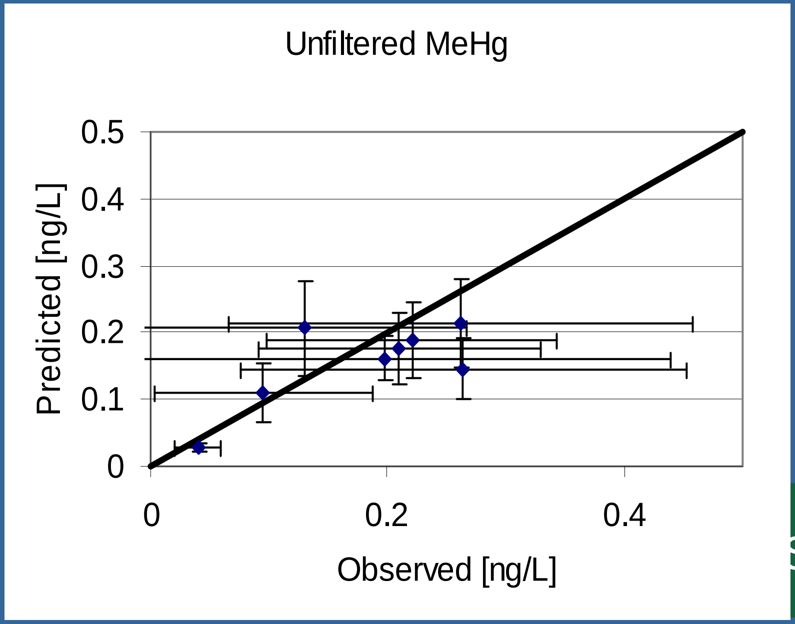
Fish Tissue MeHg Concentrations

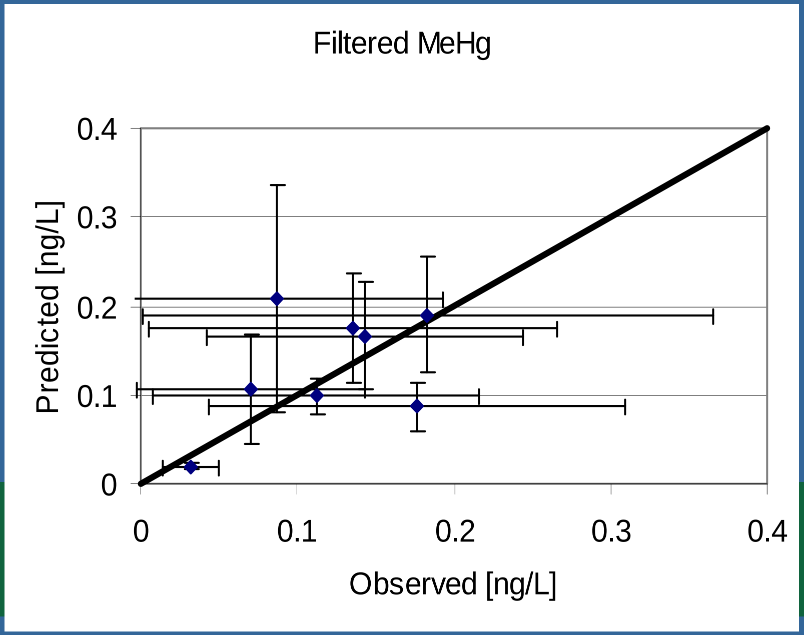


Comparison of Modeled vs. Predicted









Model Uncertainty

- As with all computer models, there is a level of uncertainty attributable to:
  - Values used as boundary conditions
  - Repeated 2-year hydrological cycle
  - Shape of the river over various reaches
  - Rate constants (such as partition coefficients, methylation rate, sedimentation rate).
  - Applicably of modeled results to non-modeled reaches

- Given this uncertainty, the modeling effort provides a reasonable basis to evaluate remedial alternatives

Summary of Remedial Alternatives

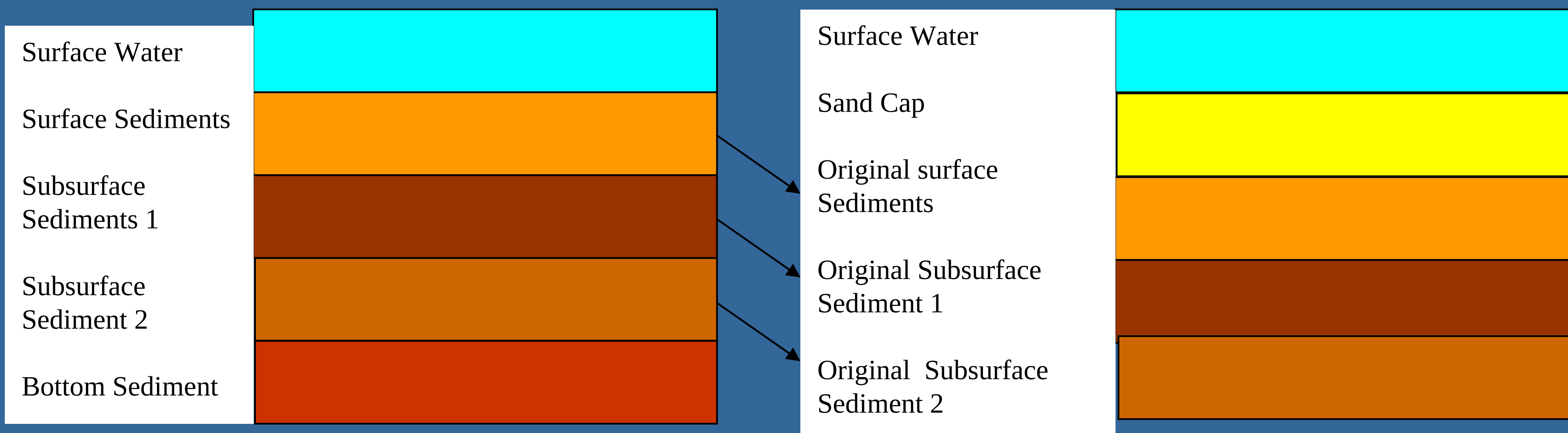
Table1
Remedial Alternatives Summary
Nyanza Chemical Waste Dump Superfund Site
Operable Unit 4 - Sudbury River
Ashland, Massachusetts

Alternatives	Remedial Action	2	3	4	6	8	9	10
Alternative 2	Limited Action (LA)	LA	LA	LA	LA	LA	LA	LA
Alternative 3A	Monitored Natural Recovery (MNR)	MNR	MNR	MNR	MNR	LA	MNR	MNR
Alternative 3B	Enhanced Natural Recovery	MNR	Thin Layer Placement	MNR	MNR	LA	MNR	MNR
Alternative 3C	Enhanced Natural Recovery	MNR	Thin Layer Placement	Thin Layer Placement	Thin Layer Placement	LA	MNR	MNR
Alternative 4A	In Situ Containment of Reach 3 Sediment Where Hg > 2 mg/kg	MNR	Capping	MNR	MNR	LA	MNR	MNR
Alternative 4B	In Situ Containment of Reaches 3, 4, and 6 Sediment Where Hg > 2 mg/kg	MNR	Capping	Capping	Capping	LA	MNR	MNR
Alternative 5B	Sediment Removal within Reach 3 Where Hg > 10 mg/kg and In Situ Containment in Reaches 3, 4, and 6 Where Hg > 2 mg/kg in Sediment	MNR	Partial Removal/ Capping	Capping	Capping	LA	MNR	MNR
Alernative 5A	Sediment Removal in Reach 3 Where Hg > 10 mg/kg	MNR	Partial Removal	MNR	MNR	LA	MNR	MNR
Alternative 5C	Sediment Removal in Reach 3 Where Hg > 2 mg/kg	MNR	Removal	MNR	MNR	LA	MNR	MNR
Alternative 5D	Sediment Removal in Reaches 3, 4, and 6 Where Hg > 2 mg/kg	MNR	Removal	Removal	Removal	LA	MNR	MNR

Notes:

Implementing Remedial Alternatives in WASP: Enhanced Natural Recovery

Enhanced Natural Recovery (Thin-layer Sand Capping)
A 6 inch layer of sand is laid on top of current top sediment layer.
The added sand layer has no Hg and has is comprised of 100% sand
(0% silt, 0% organic matter, 0 Hg(II), 0 MeHg)

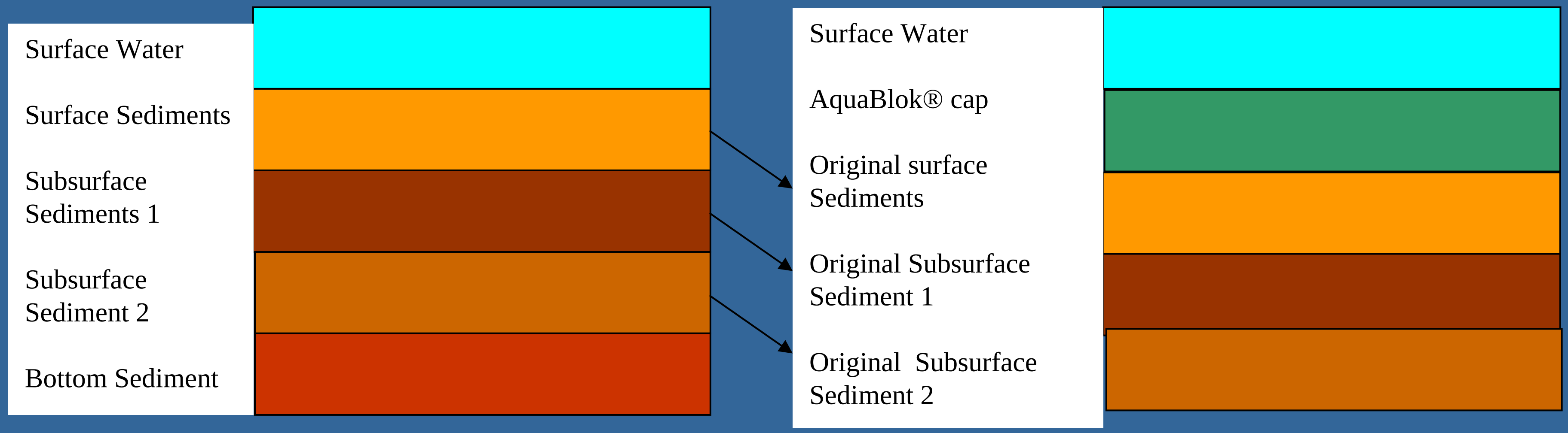


Implementing Remedial Alternatives in WASP: *In Situ* Containment

AquaBlok® Capping (*In Situ* Containment)

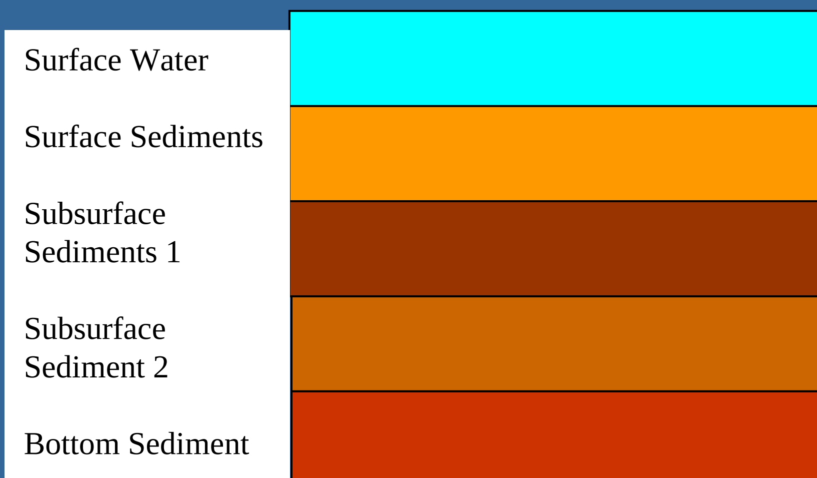
A 6 inch layer of AquaBlok ® is laid on top of current top sediment layer.

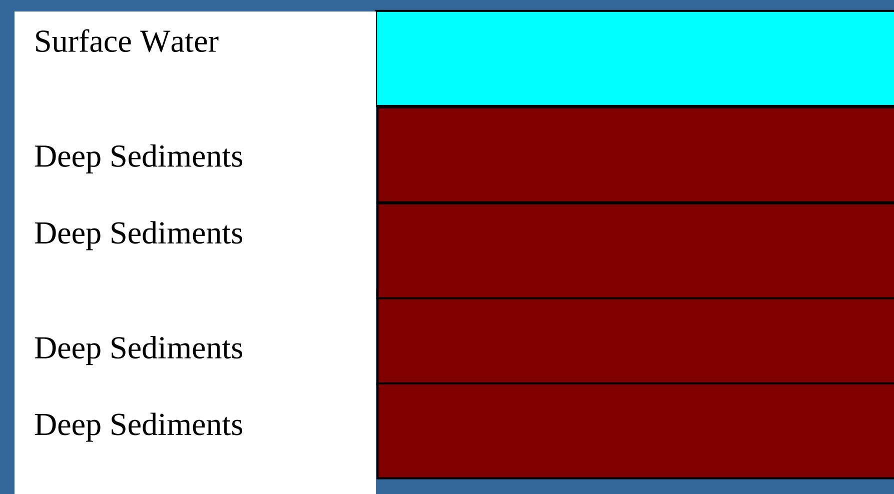
The added layer has no Hg and has is modeled as having a porosity of 0.62, and a concentration of 1.28×10^6 g/m^3 as organic matter with no resuspension (0% silt, 0% sand, 0 Hg(II), 0 MeHg)



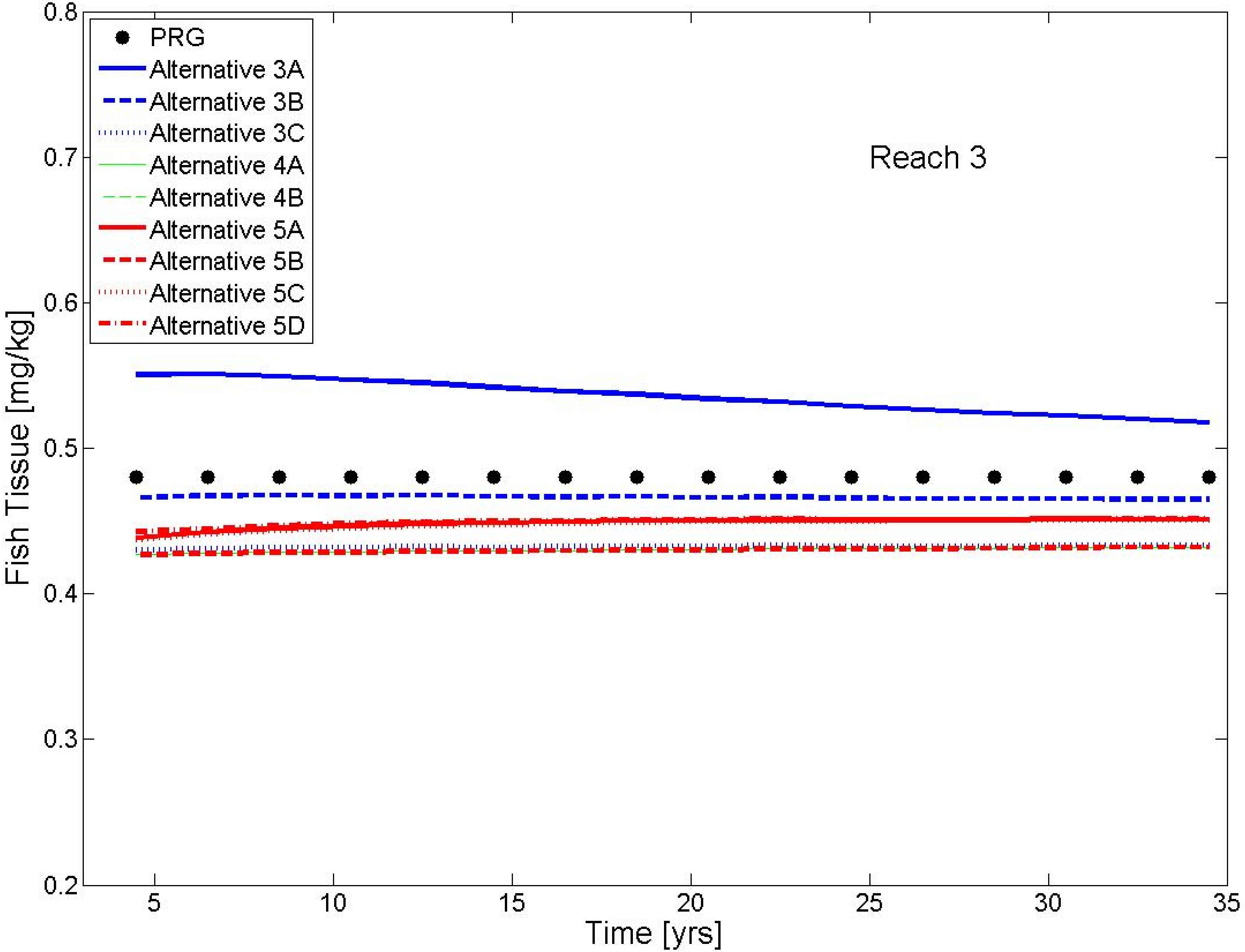
Implementing Remedial Alternatives in WASP: *Dredging*

Dredging: Removal of sediment layers, with release back to water column.
New Sediment layers modeled with same solids composition as bottom segment, with Hg(II) = 1 mg/kg, MeHg = 1 ug/kg.
(except beneath segments 1, 6, 7, where Hg(II) = 3 mg/kg, MeHg = 2 ug/kg)
Dredging with Capping is a combination of previous methods.

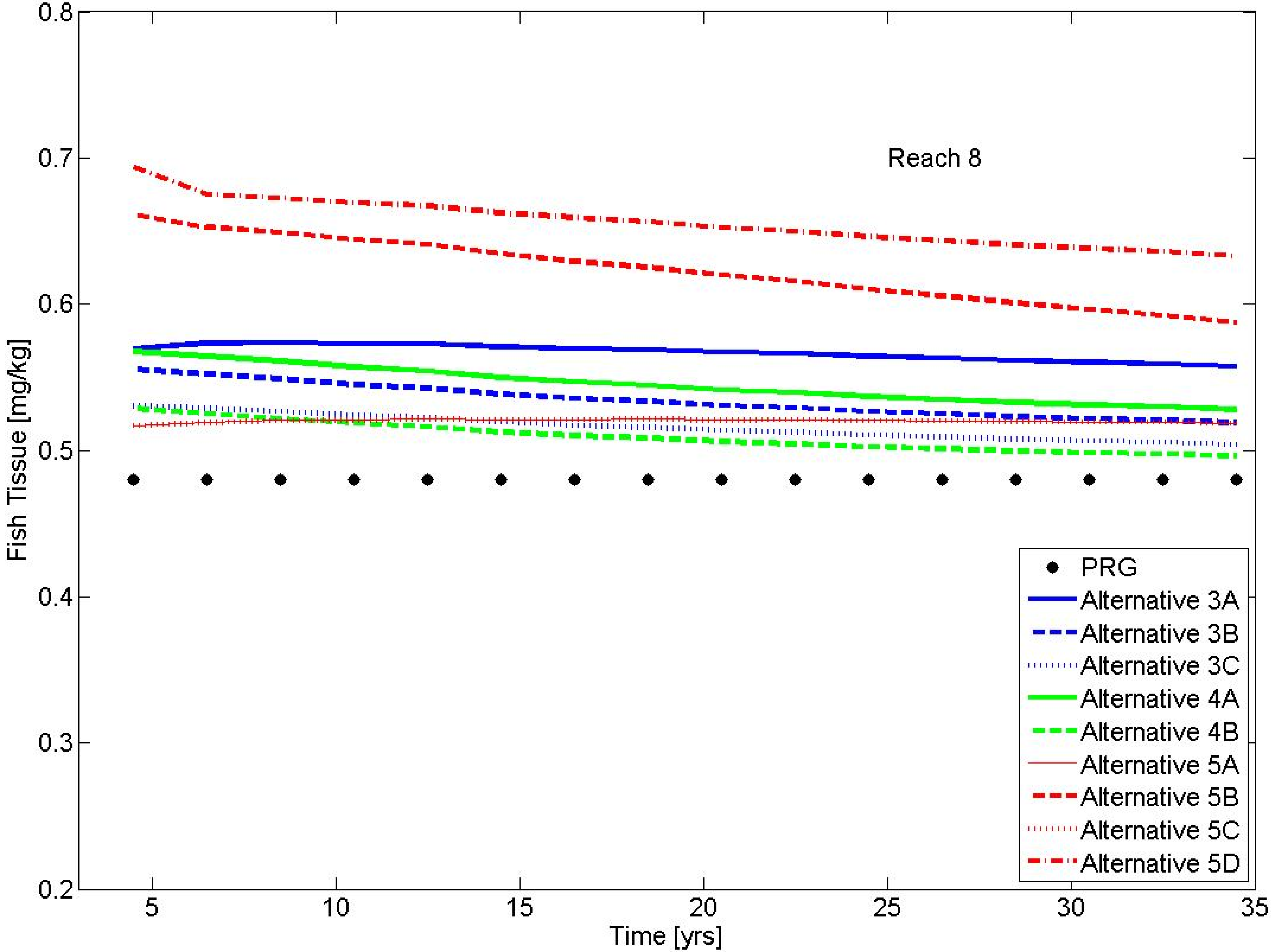




Simulated Fish Tissue Concentrations in Reach 3



Simulated Fish Tissue Concentrations in Reach 8



Model Reports

Modeling Mercury Transport and Transformation along the Sudbury River, with Implications for Regulatory Action (2010) – EPA/ORD/NERL/ERD (Athens)

- Volume 1: Mercury Fate and Transport

  (describes the "Base Case" also referred to Alternative 3A or MNR)

- Volume 2**:** Evaluating the Effectiveness of Different Remedial Alternatives to Reduce Mercury Concentrations in Fish