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ECOSYSTEMS SERVICES RESEARCH PROGRAM
BUILDING A SCIENTIFIC FOUNDATION FOR SOUND ENVIRONMENTAL DECISIONS

Simulating Mercury Transport and Transformation along the Sudbury River, MA

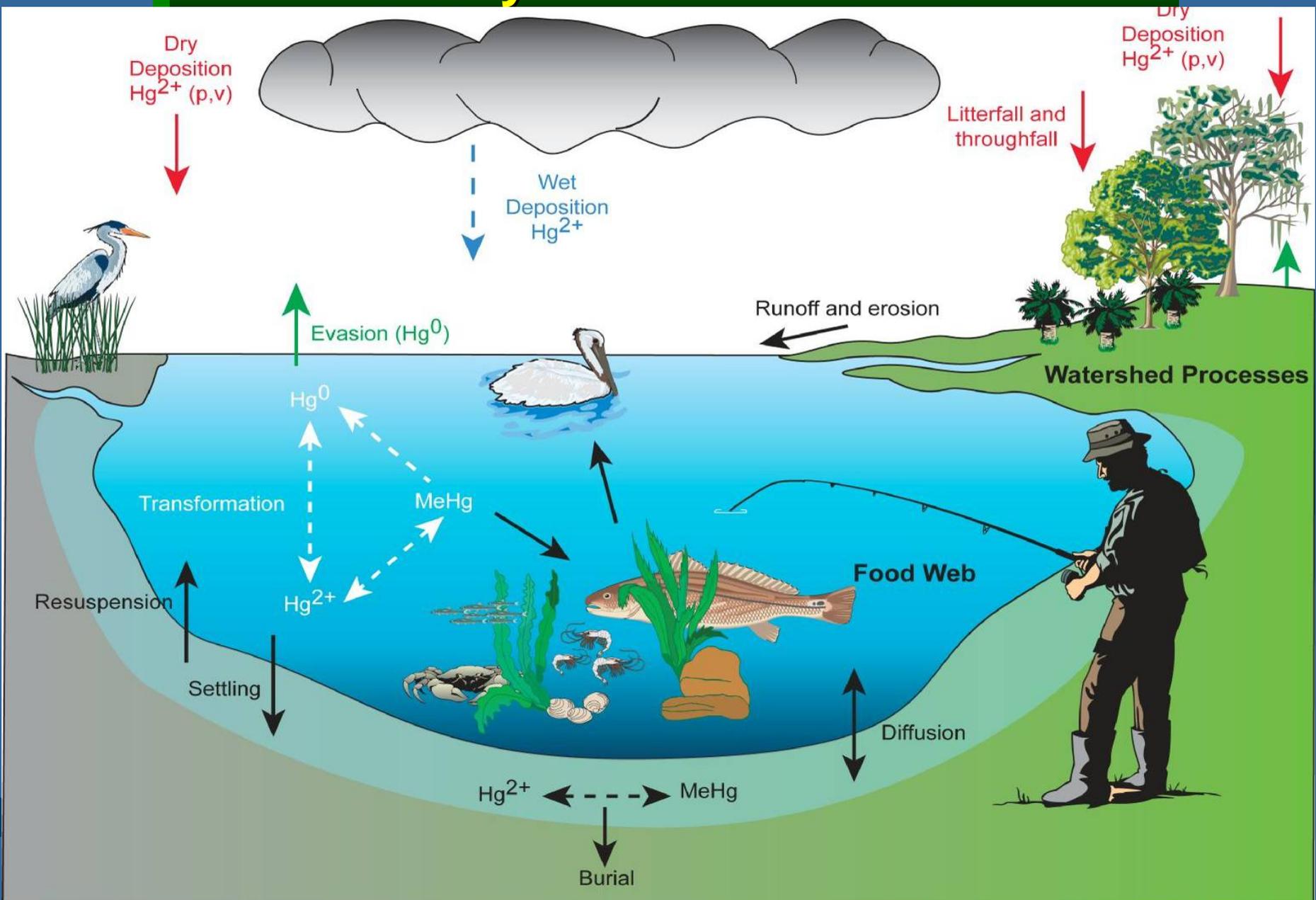
Christopher D. Knightes, Bart Hoskins, and Daniel Keefe

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.

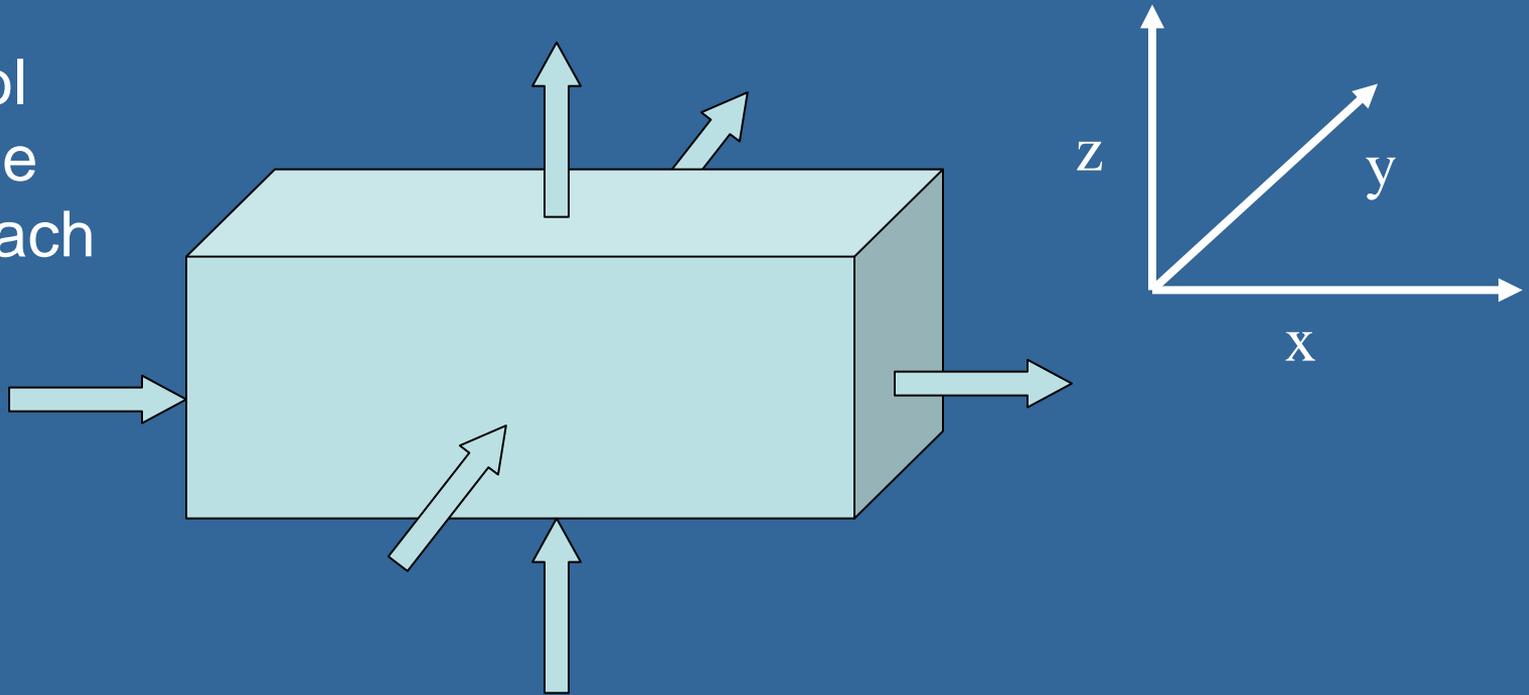
from “Understanding the Use of Models in Predicting Risk Reduction of Proposed Remedial Actions at Superfund Sediment Sites. Draft 2009. Office of Superfund Remediation and Technology Innovation.

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

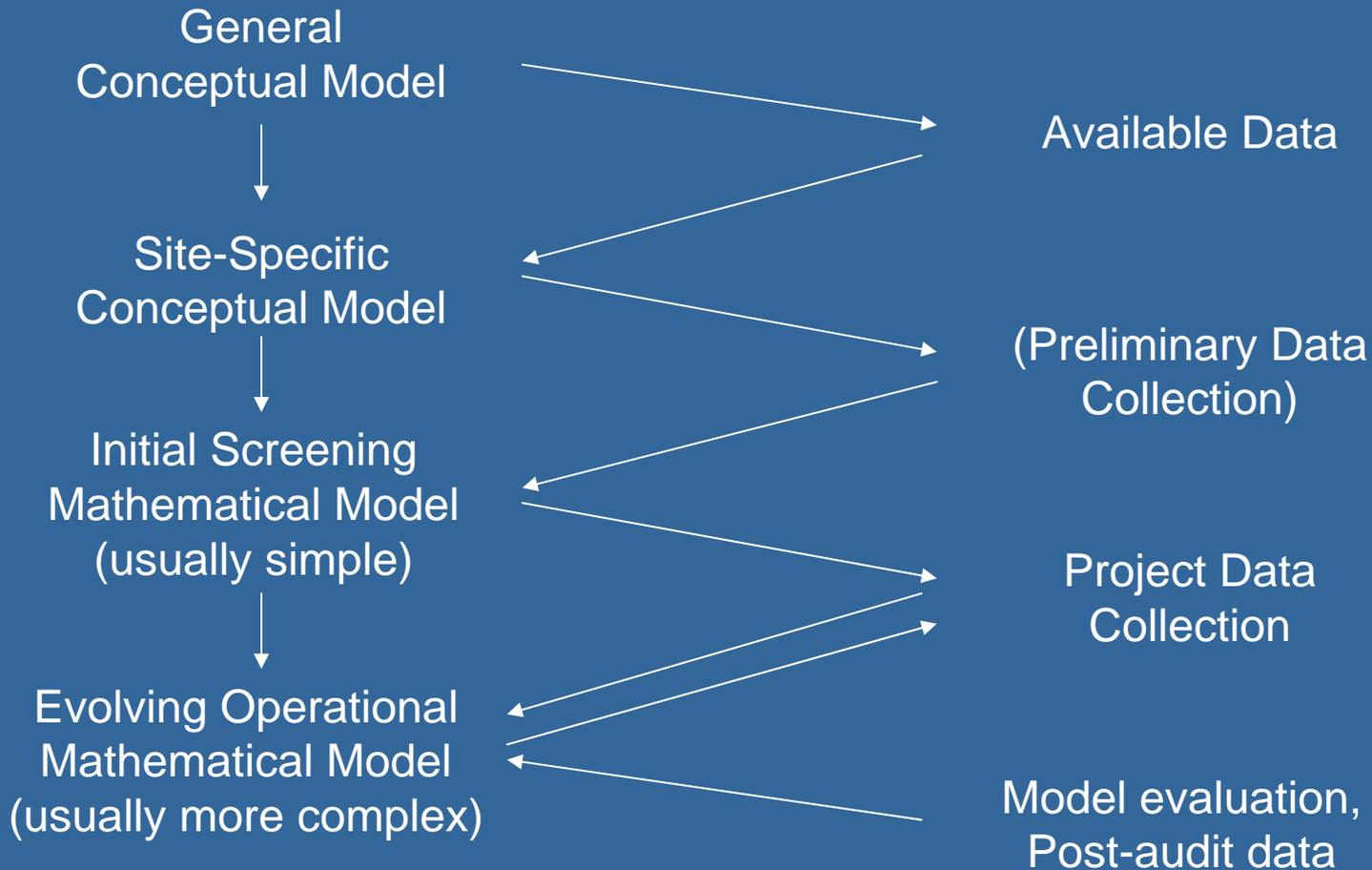
Control
Volume
Approach



Accumulation = Input – Output ± Reactions

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

Iterative Model Development Process



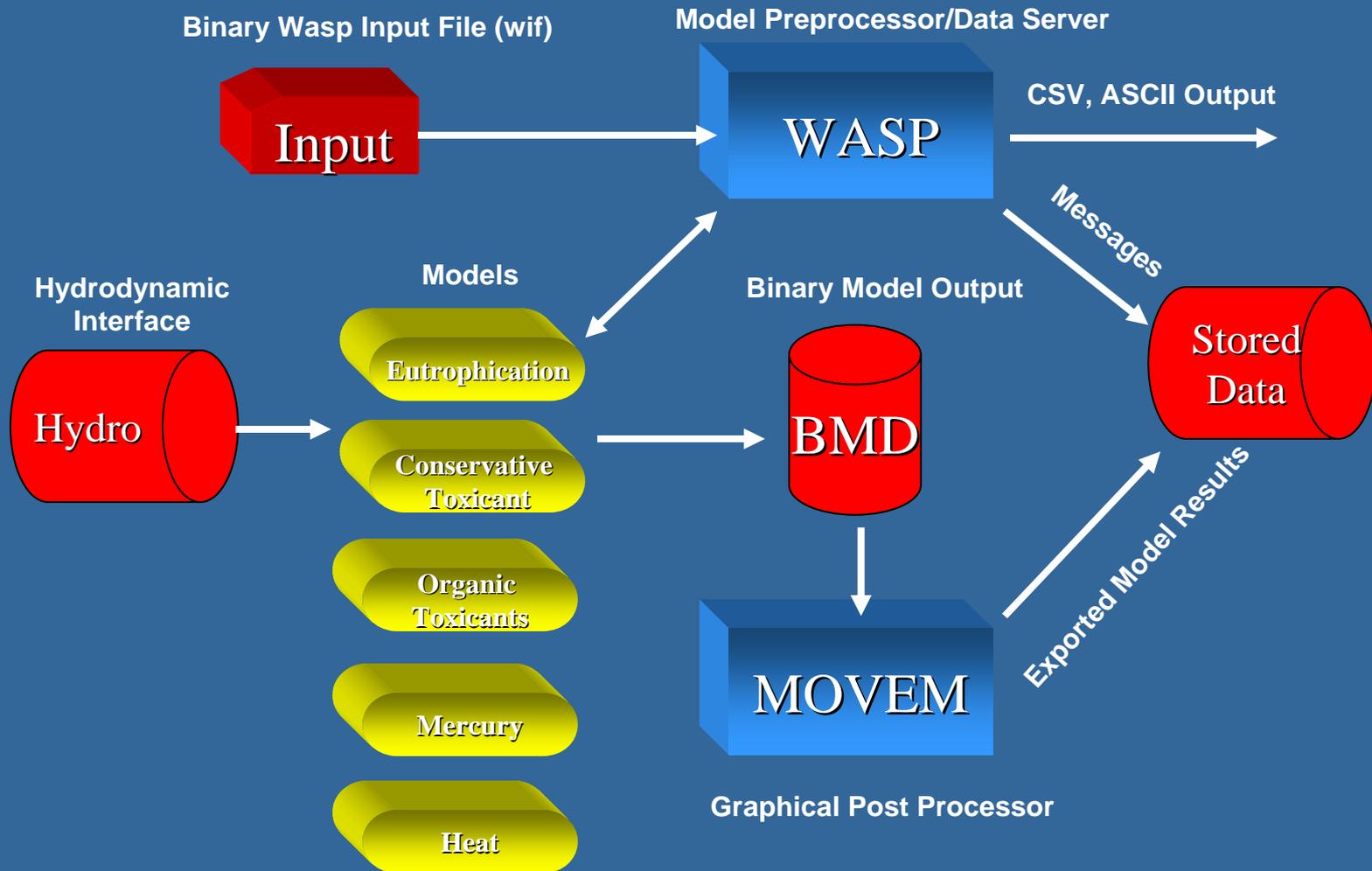
Appropriate Level of Complexity

- 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

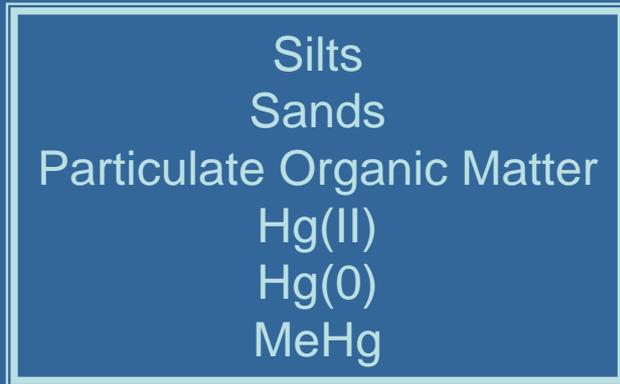
WASP Modeling Framework



WASP Terminology

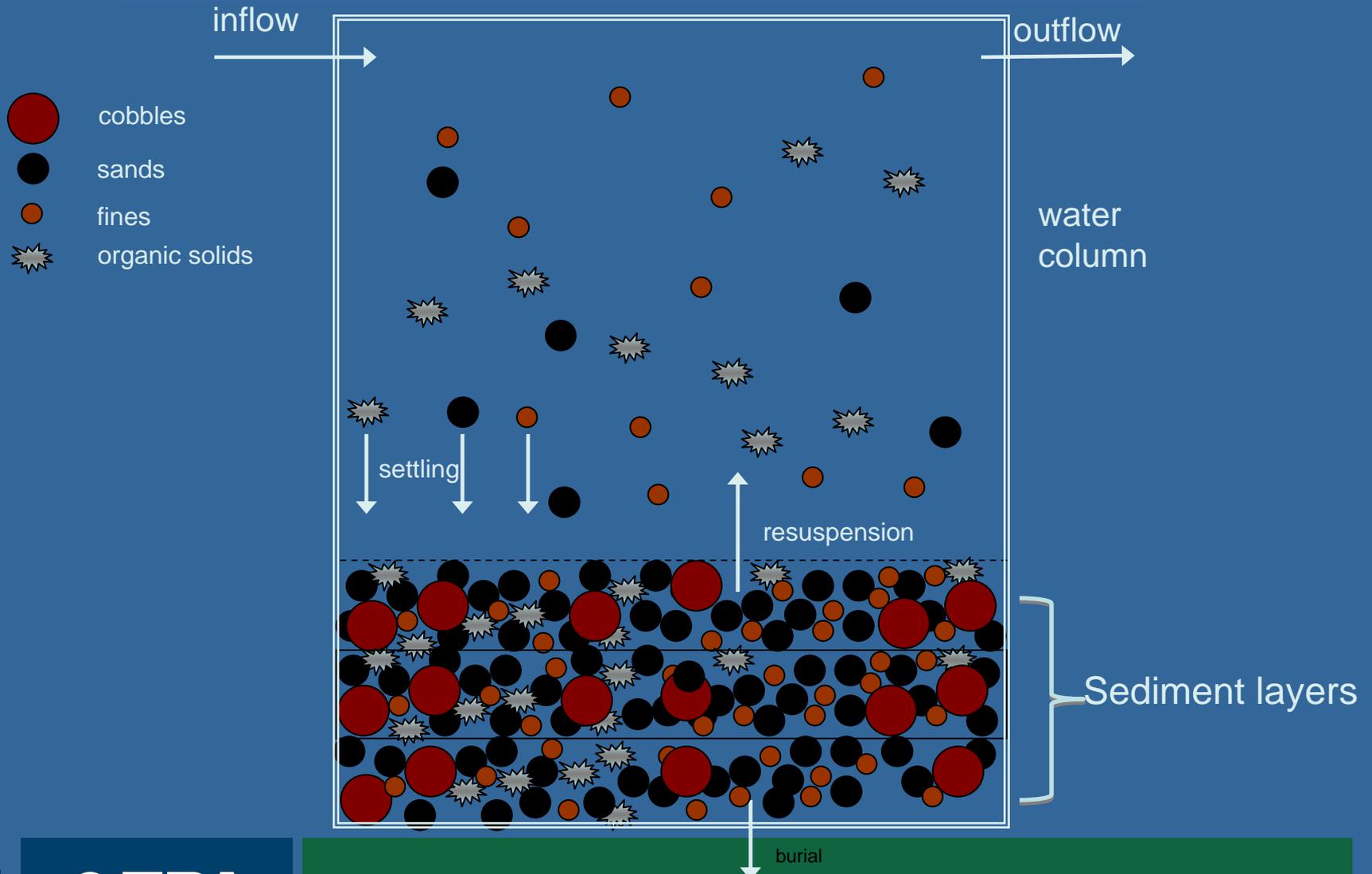


→ **WASP Segments**



→ **State Variables**

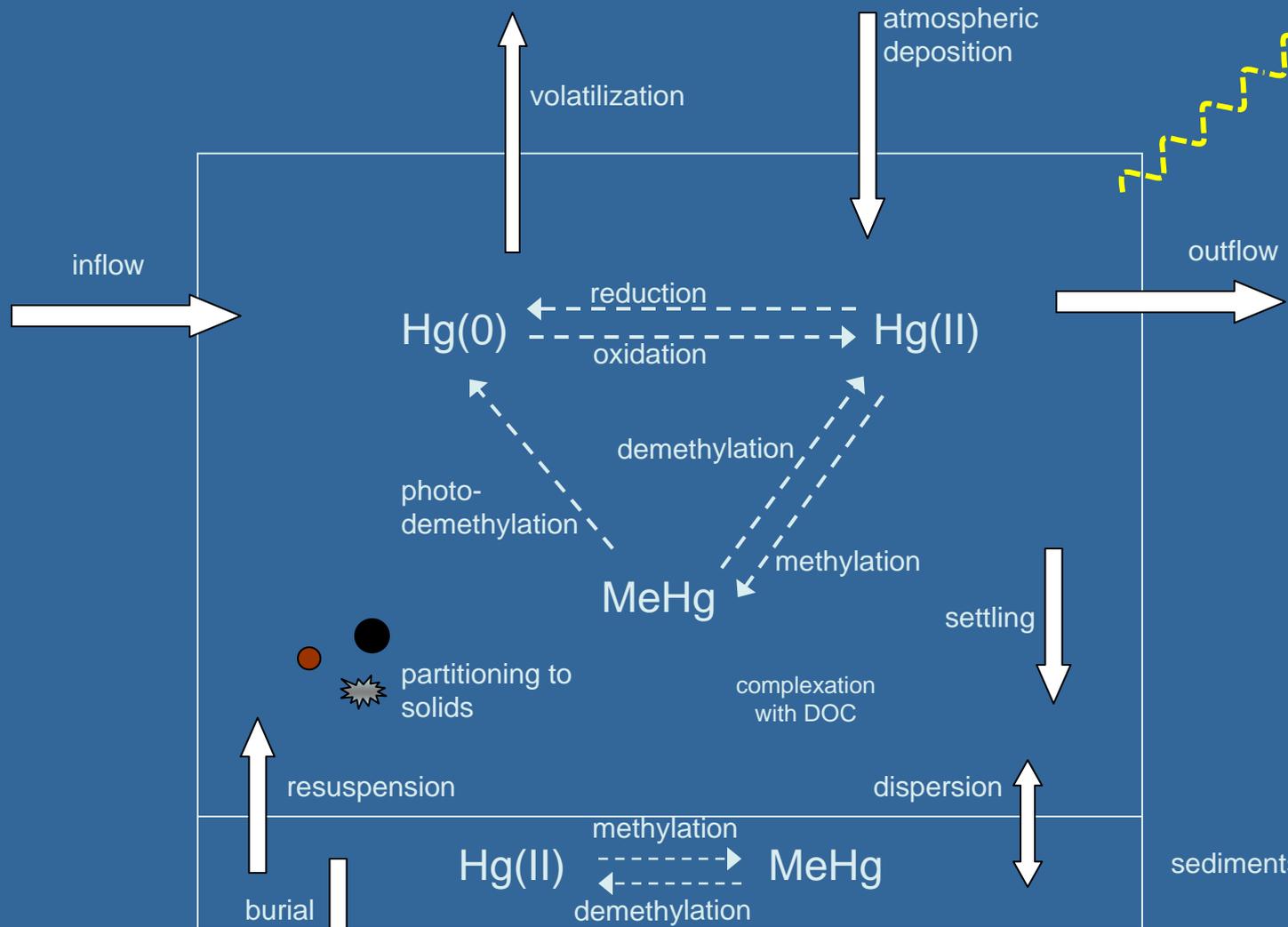
Modeling Solids in WASP



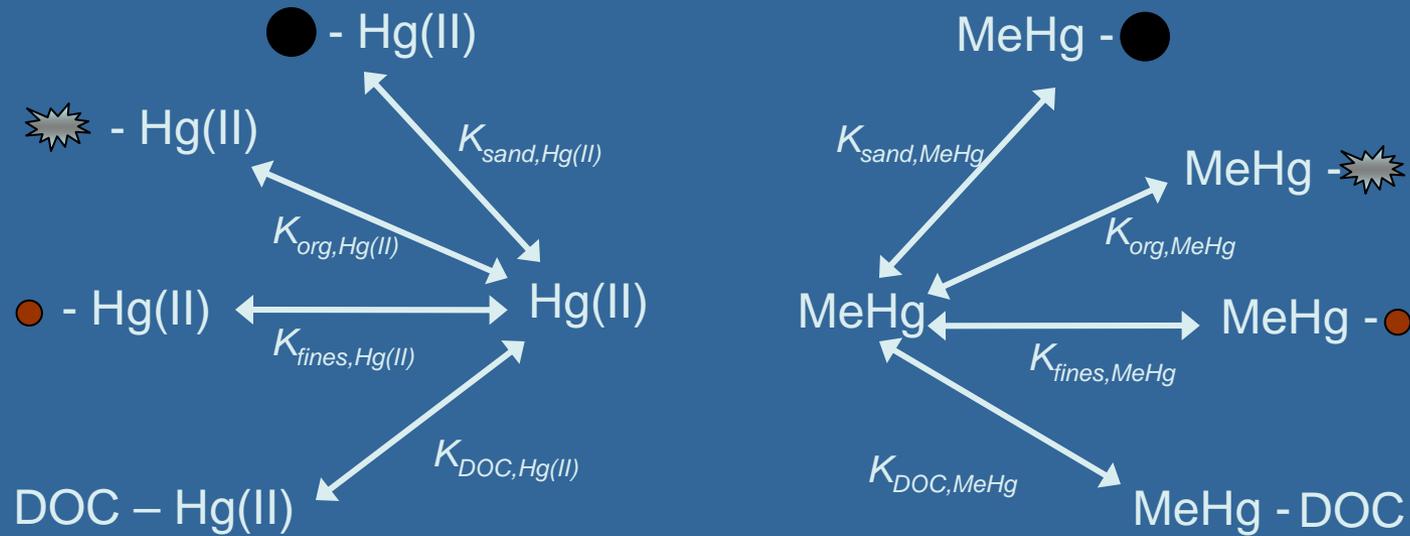
Modeling Mercury in WASP



photo-lysis



Modeling Partitioning in WASP



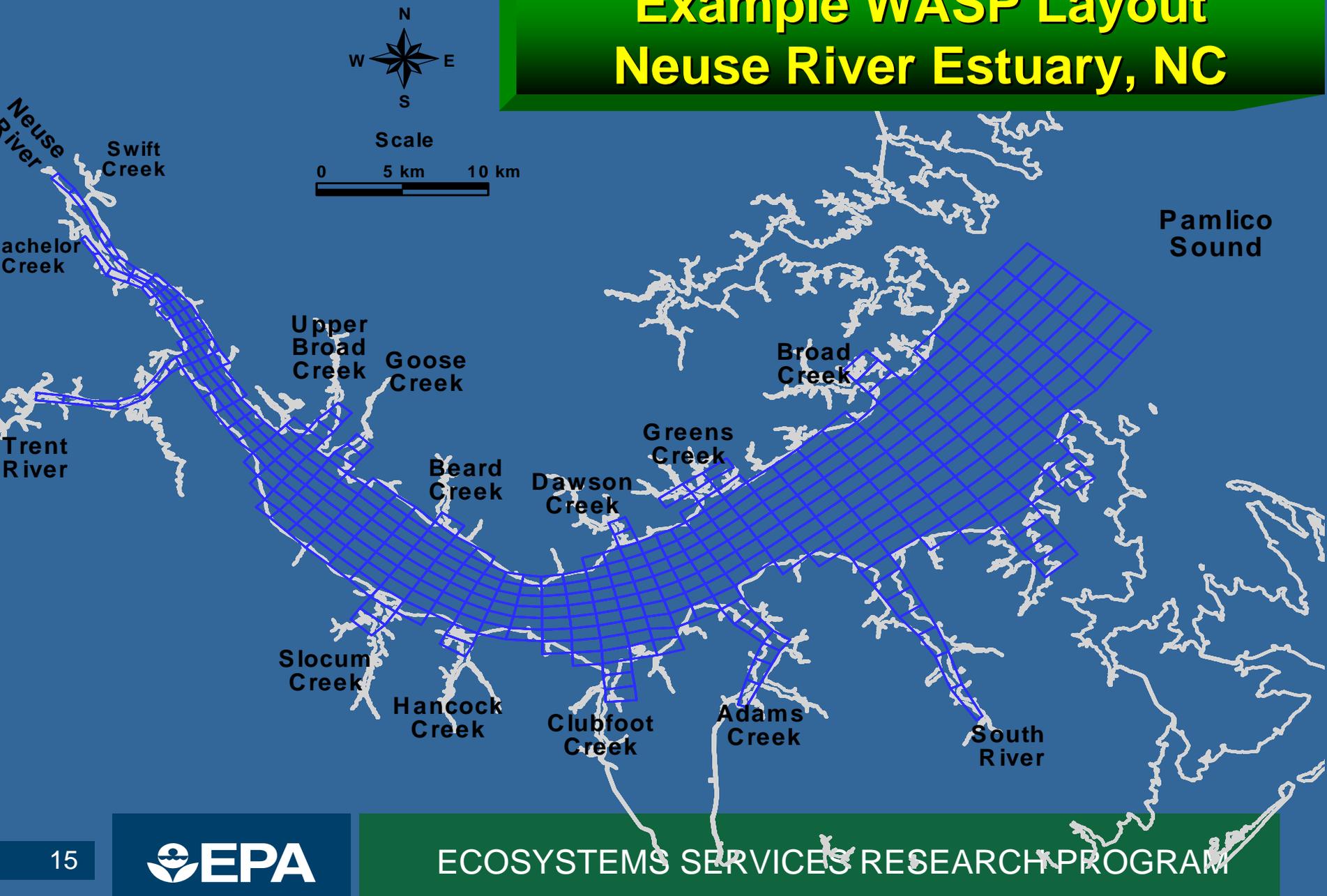
● abiotic solids

● phytoplankton

☀ organic solids

DOC dissolved organic carbon

Example WASP Layout Neuse River Estuary, NC



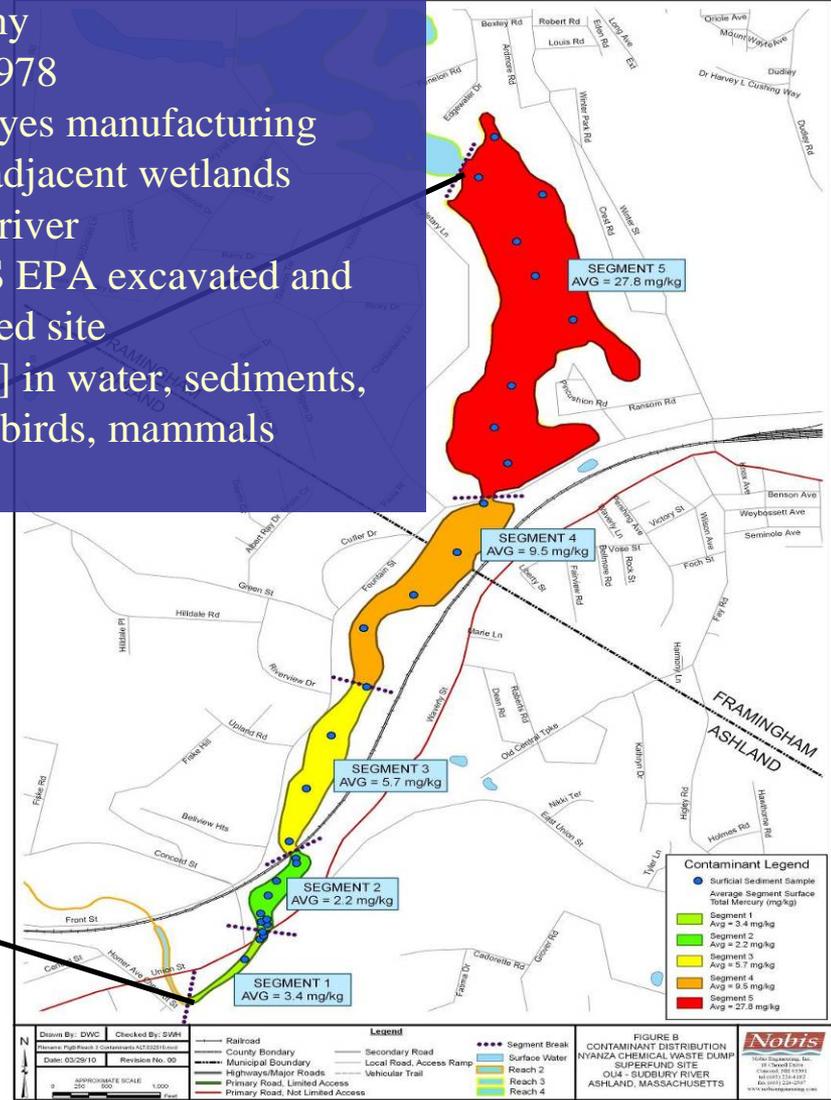
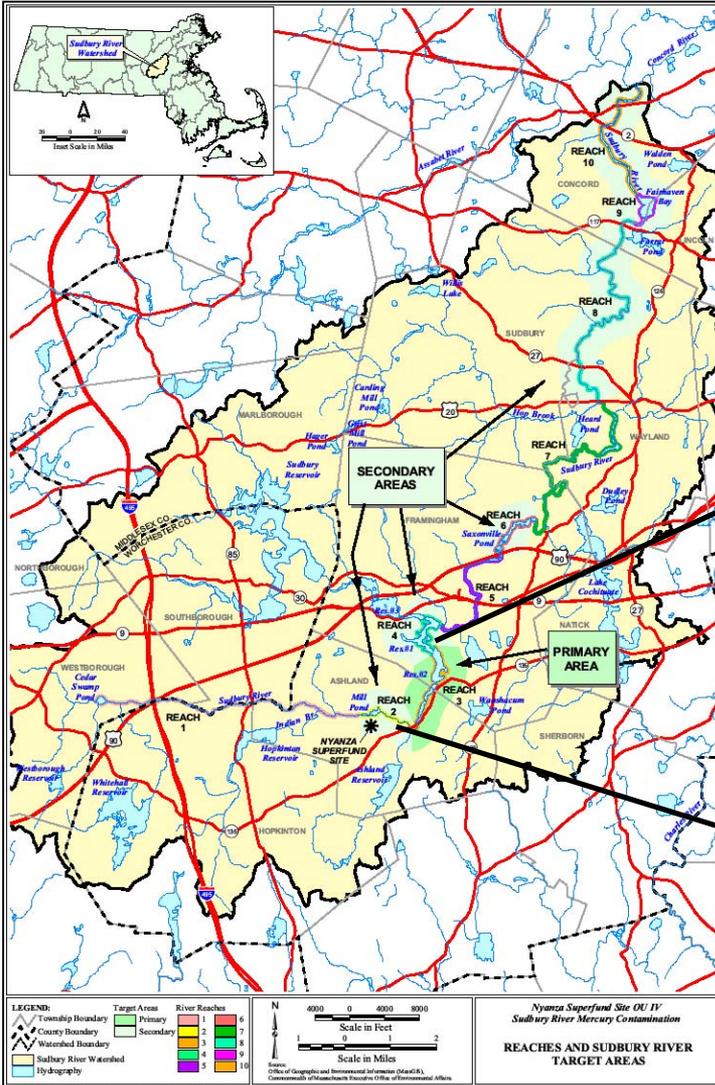
Nyanza Superfund Site (Sudbury River, MA):

1917 – 1978

Textile dyes manufacturing

Nyanza Company

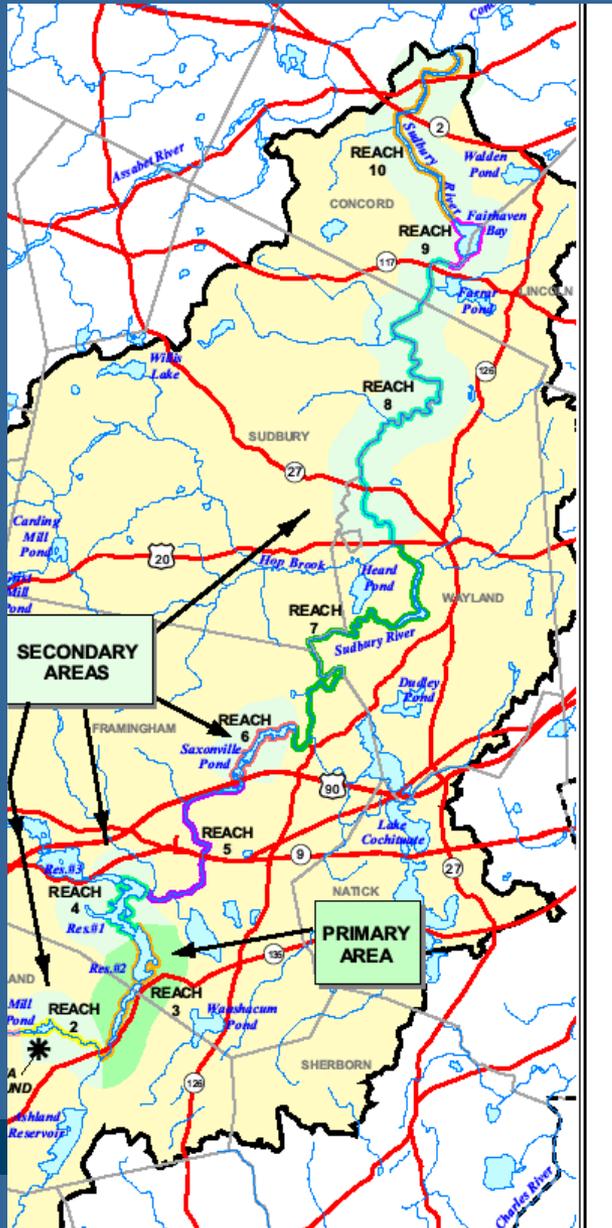
- 1917 – 1978
- Textile dyes manufacturing
- Hg into adjacent wetlands and river
- 1991, US EPA excavated and capped site
- high [Hg] in water, sediments, fish, birds, mammals



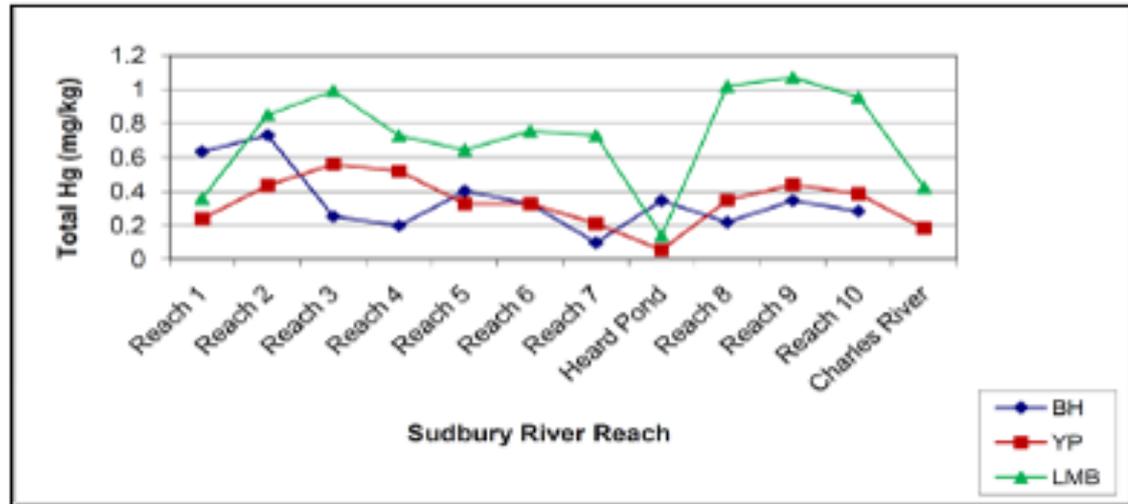
SYSTEMS SE



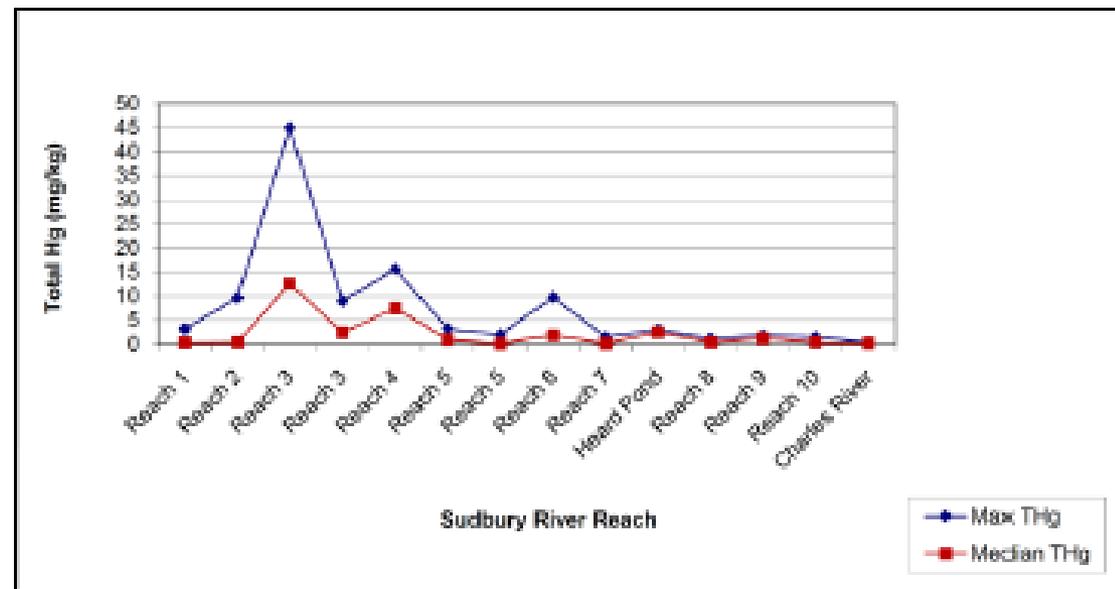
Nyanza Extent of Mercury Concentrations



Fish



Sediment



COS

Correlation to $\ln(\text{Hg}_{\text{fish}}/\text{fish length})$

Parameter	All Fish	Largemouth Bass
$\ln(\text{MeHg}_{\text{water}})$	$R = 0.623, p < 0.001$	$R = 0.712, p < 0.001$
MeHg_{sed}	$R = 0.332, p < 0.001$	$R = 0.596, p < 0.001$
$\ln(\text{HgT}_{\text{water}})$	$R = 0.227, p < 0.01$	$R = 0.453, p < 0.01$
$\ln(\text{HgT}_{\text{sed}})$	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*

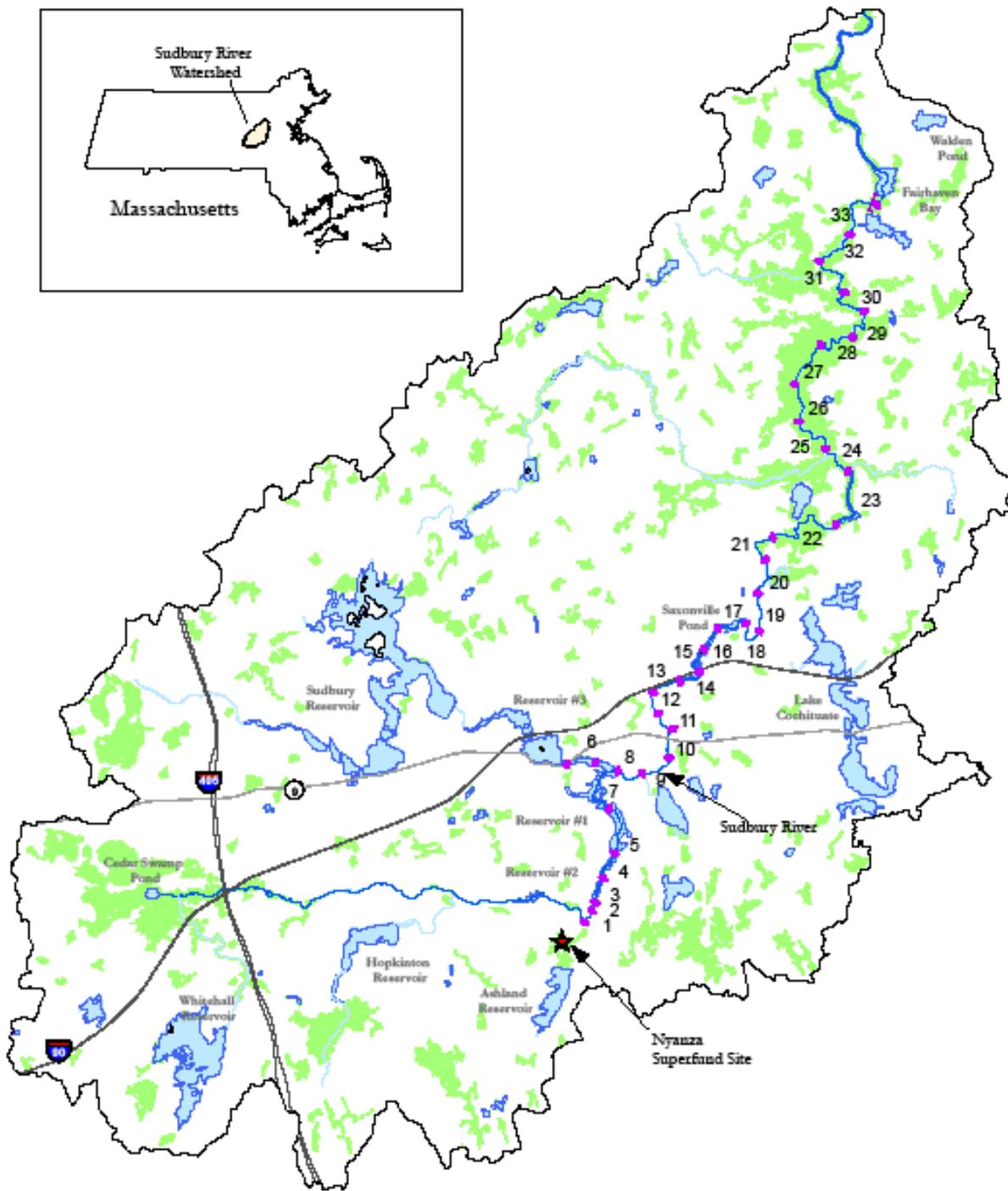
Nyanza WASP Model Setup

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)



Surface Water

Surface Sediments

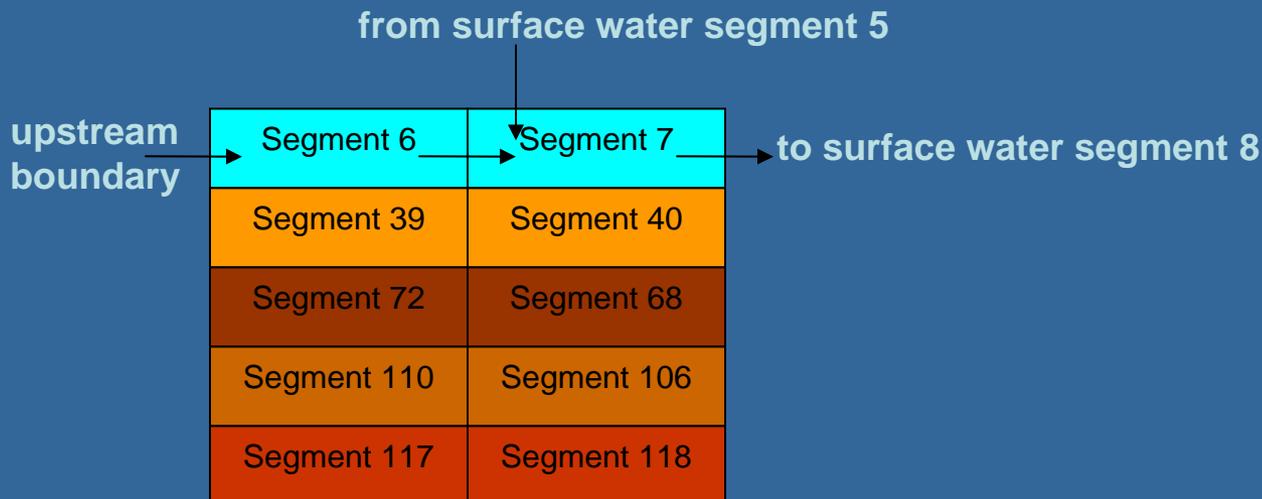
Subsurface
Sediments

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.

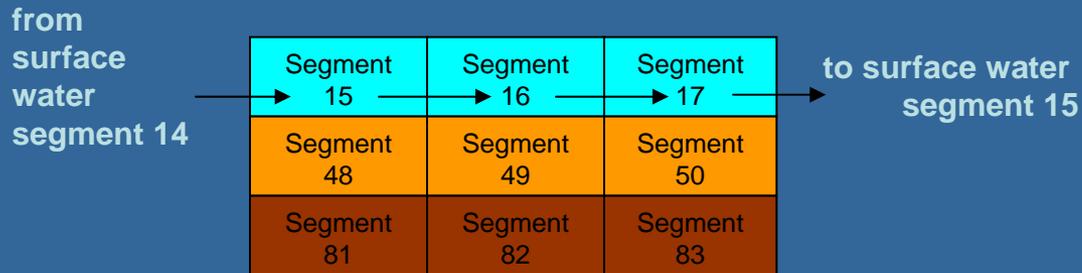
Delineation of WASP Segmentation: Reach 4 (Reservoir 1)



Delineation of WASP Segmentation: Reach 5



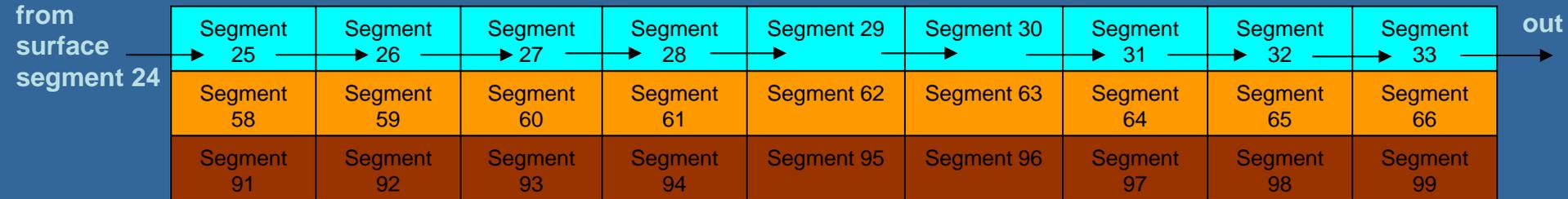
Delineation of WASP Segmentation: Reach 6



Delineation of WASP Segmentation: Reach 7



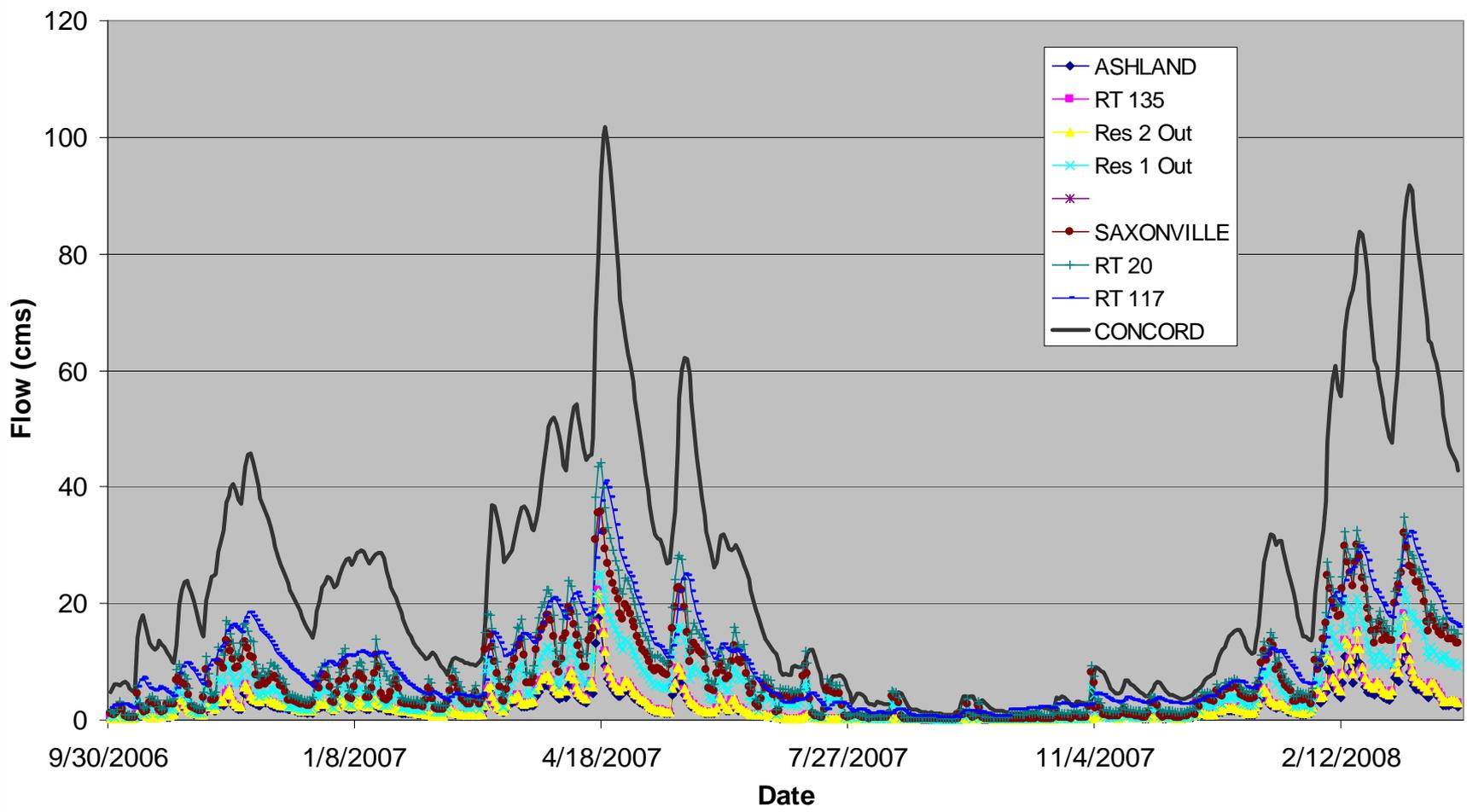
Delineation of WASP Segmentation: Reach 8 (Great Meadows National Wildlife Refuge)



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



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:
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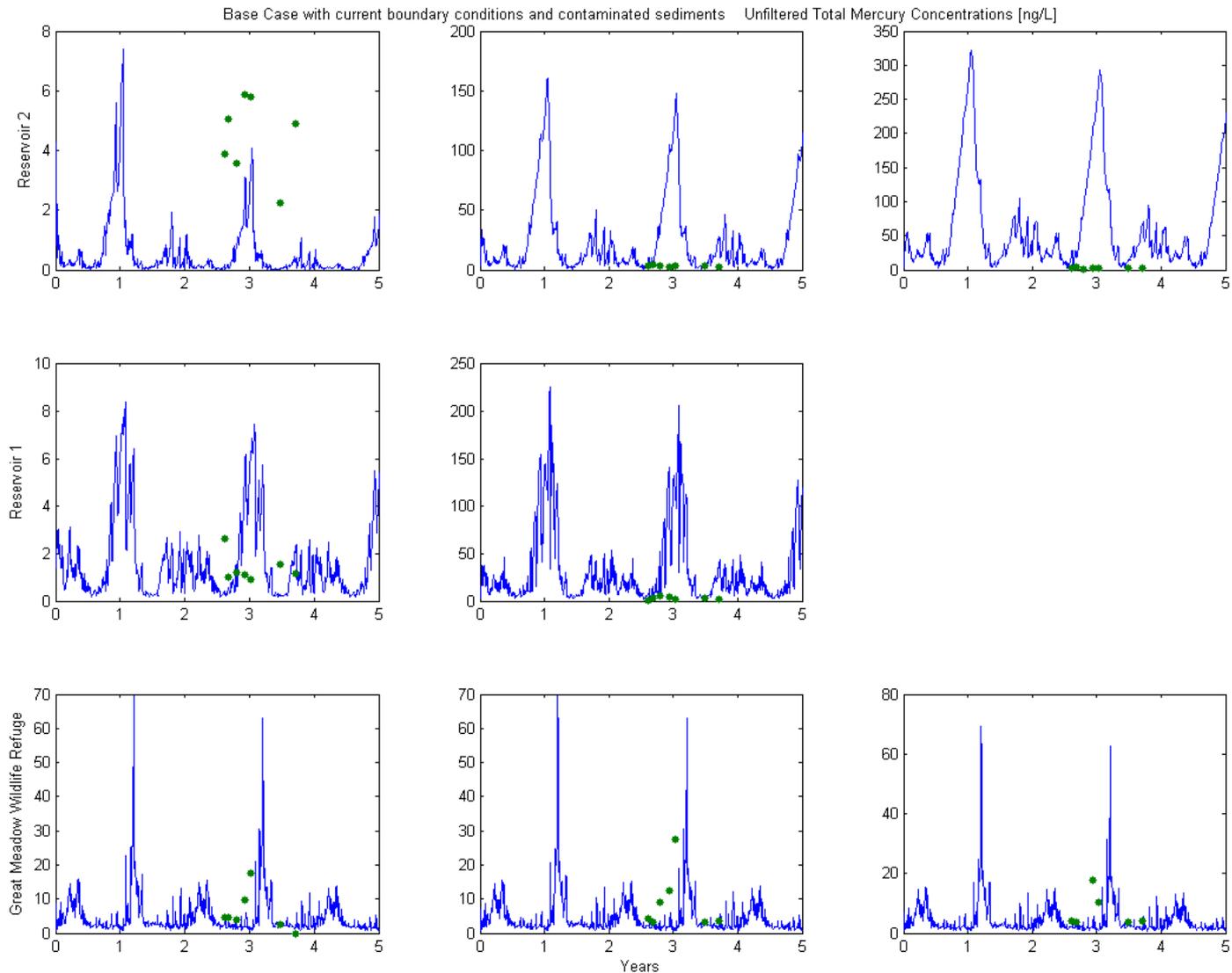
Mercury Cycle Rate Constants and Parameters

Transformation Process (rate)	Reaction	Water Column	Water: Deep Reservoir	Reservoir Sediments	Main River Sediments	GMNWR Sediments
Methylation (d^{-1}) ^{a,b}	$Hg(II) \rightarrow MeHg$	0^a	0.0^a	0.02^b	0.02^b	0.02^b
Demethylation (d^{-1}) ^{b,c}	$MeHg \rightarrow Hg(II)$	0.04^c	0.04^c	0.5^b	0.7^b	0.25^b
Methylation/ Demethylation (%MeHg)		0	25%	4%	3%	8%
Dark Oxidation ^d	$Hg(0) \rightarrow Hg(II)$	1.6^d	1.6^d	0	0	0
Surface Photo-Oxidation (d^{-1}) ^e	$Hg(0) \rightarrow Hg(II)$	6^e	0	0	0	0
Surface Photo-Reduction (d^{-1}) ^f	$Hg(II) \rightarrow Hg(0)$	14^f	0	0	0	0
Surface Photo-Demethylation (d^{-1}) ^g	$MeHg \rightarrow Hg(0)$	0.2^g	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	1.6x10 ⁻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	6x10 ⁻⁶ cm ² /s ^f
Pore Water Dispersion between sediment layer and surface water	5x10 ⁻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

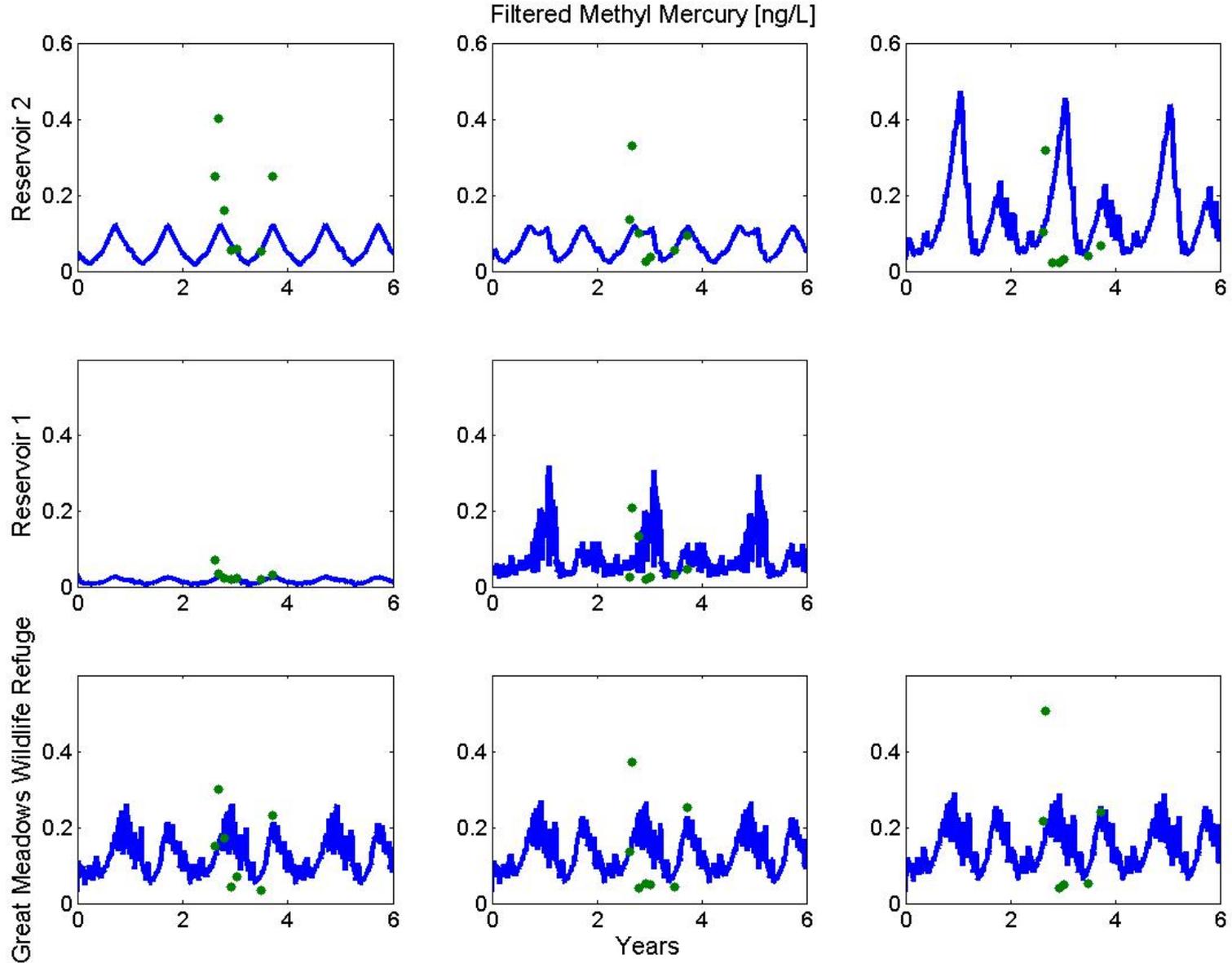
- Clean Sediment case uses original parameterization
- Contaminated Sediment case

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

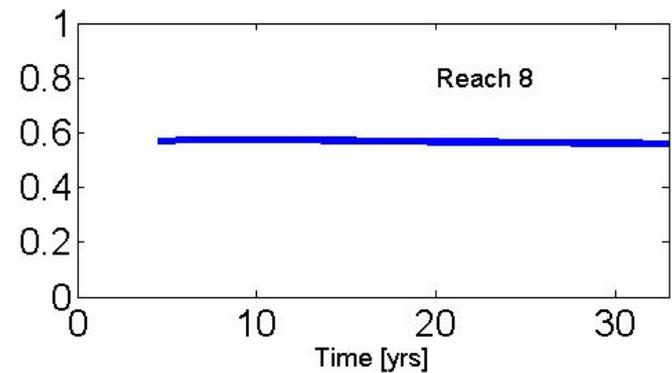
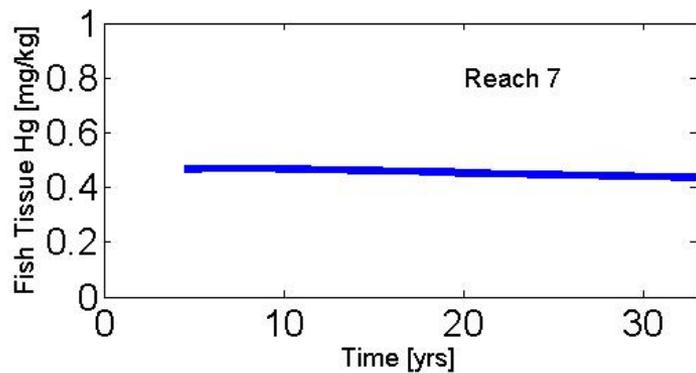
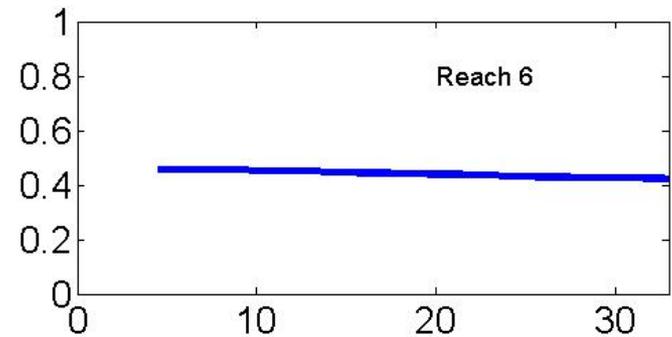
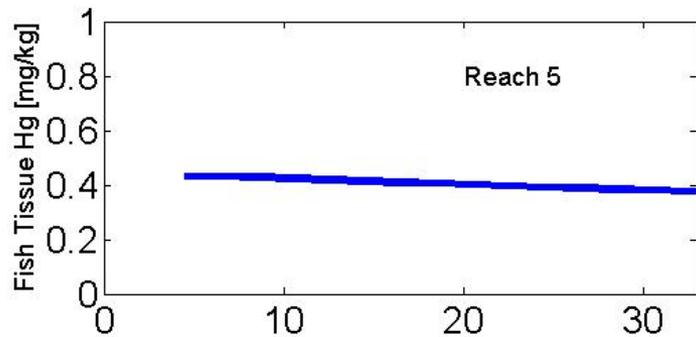
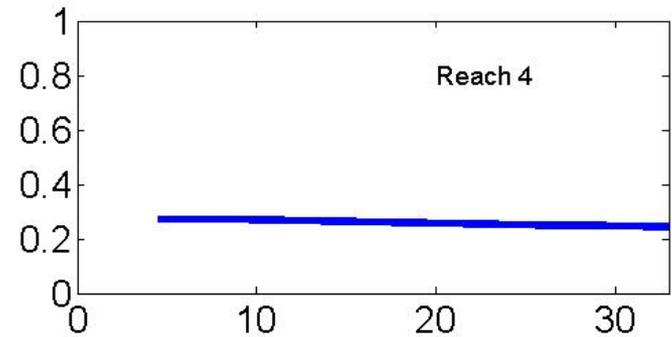
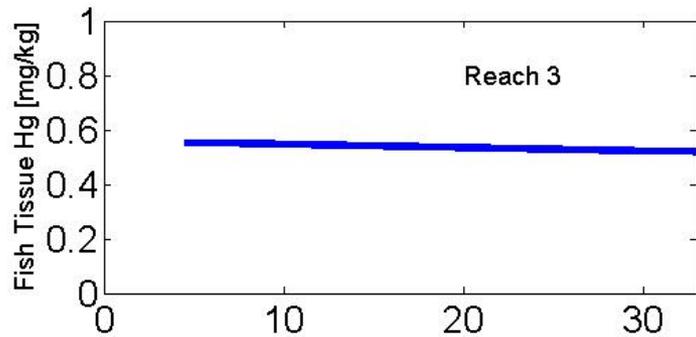
Mechanistic Evaluation of System

- 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

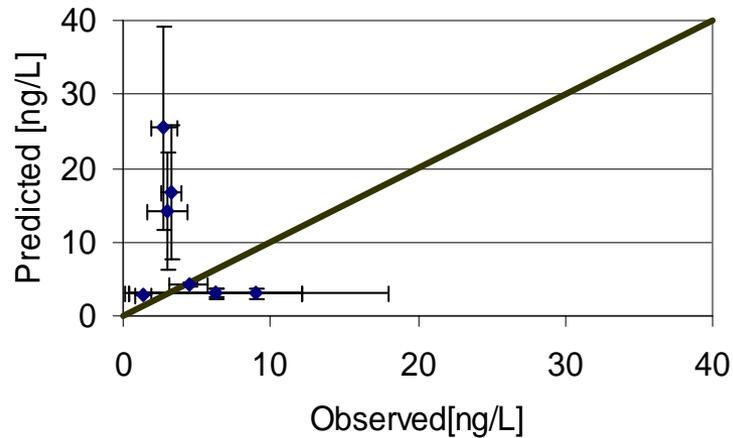


Fish Tissue MeHg Concentrations

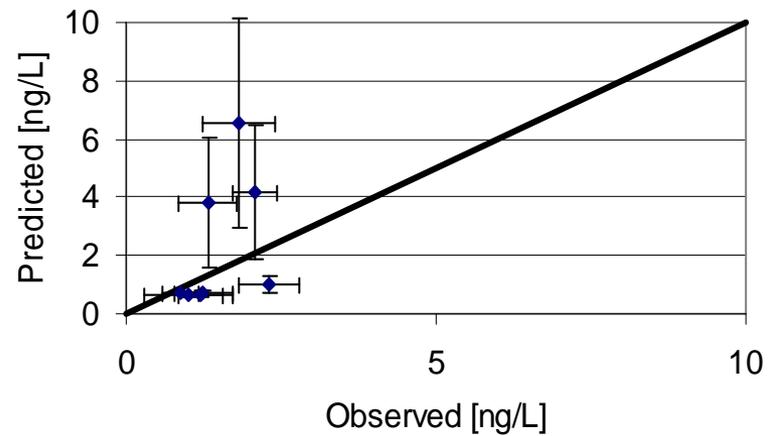


Comparison of Modeled vs. Predicted

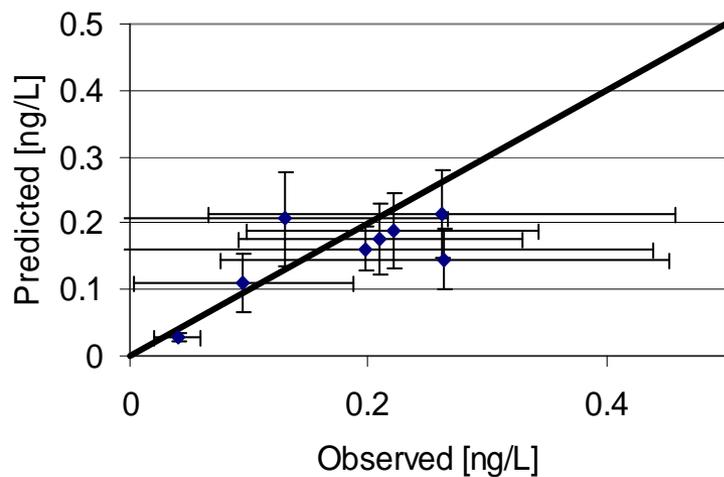
Unfiltered HgT



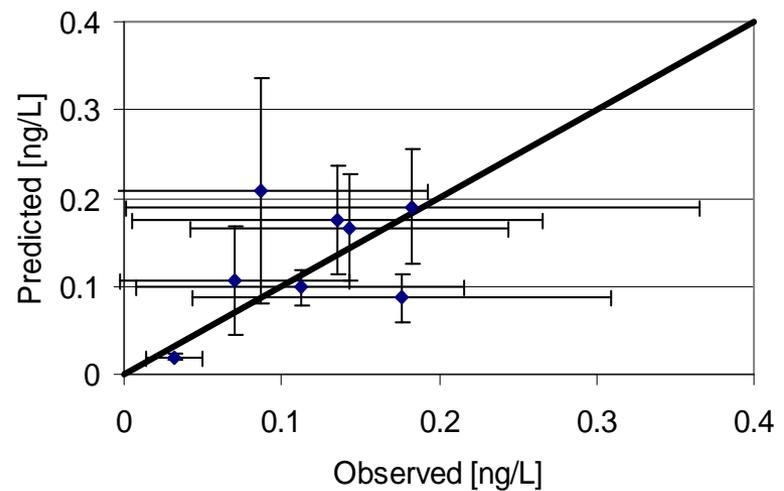
Filtered HgT



Unfiltered MeHg



Filtered MeHg



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).
 - Applicability 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
Alternative 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

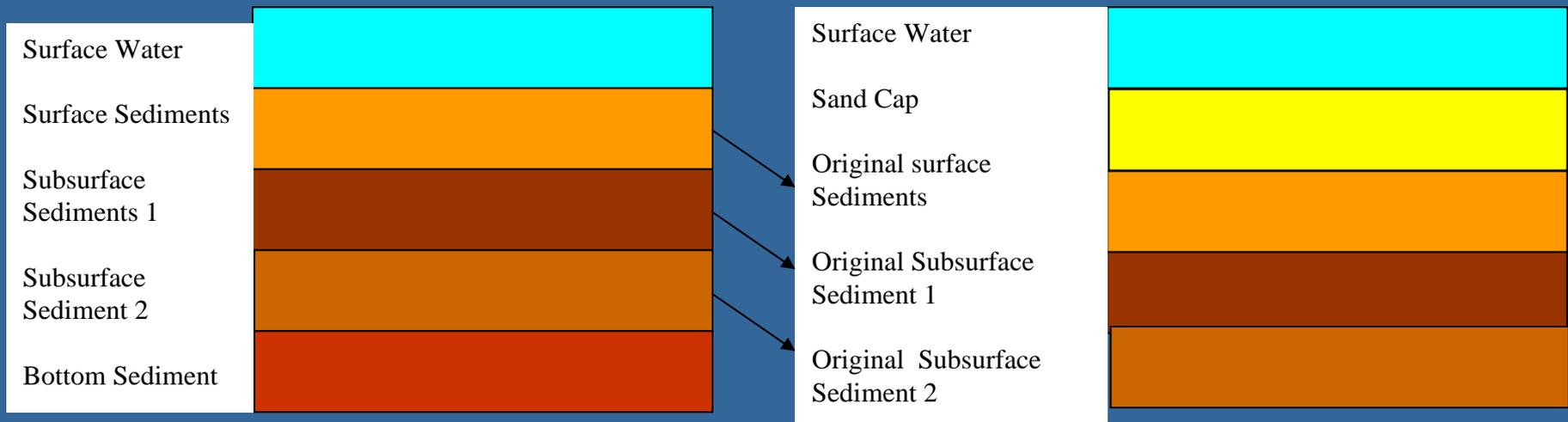
Notes:

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.

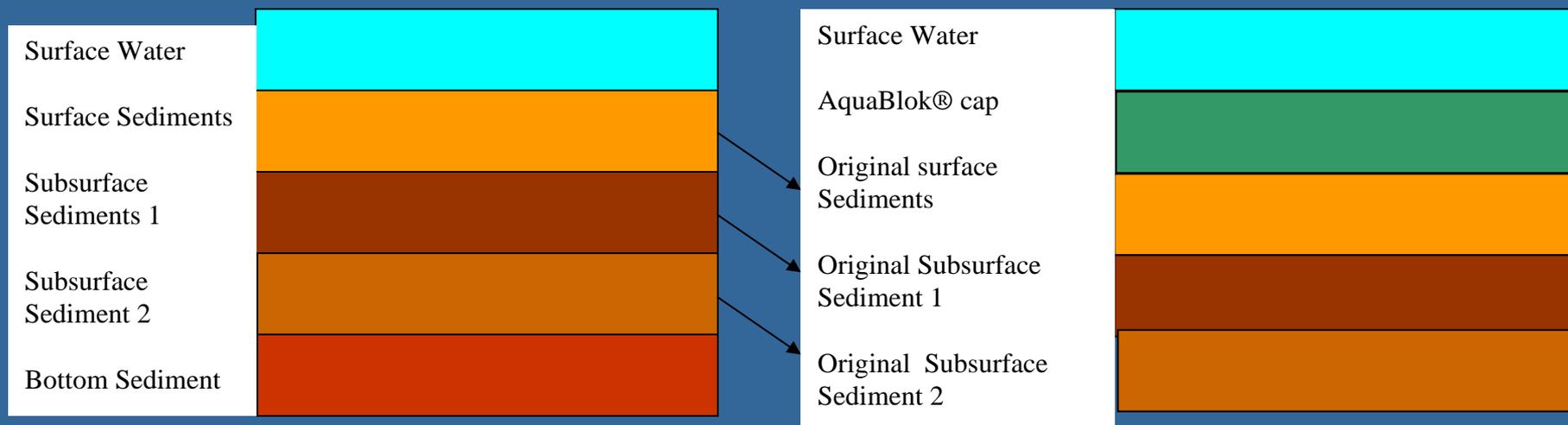
The added sand layer has no Hg and has is comprised of 100% sand
(0% silt, 0% organic matter, 0 Hg(II), 0 MeHg)



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/m³ as organic matter with no resuspension (0% silt, 0% sand, 0 Hg(II), 0 MeHg)

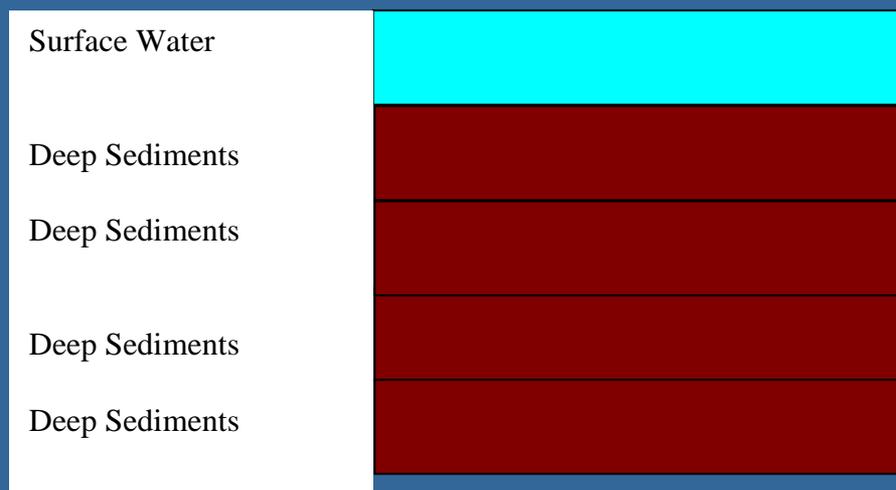
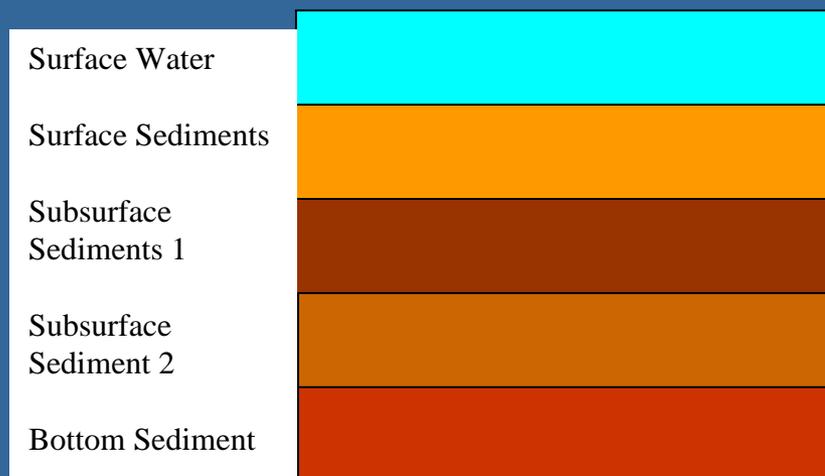


Implementing Remedial Alternatives in WASP: *Dredging*

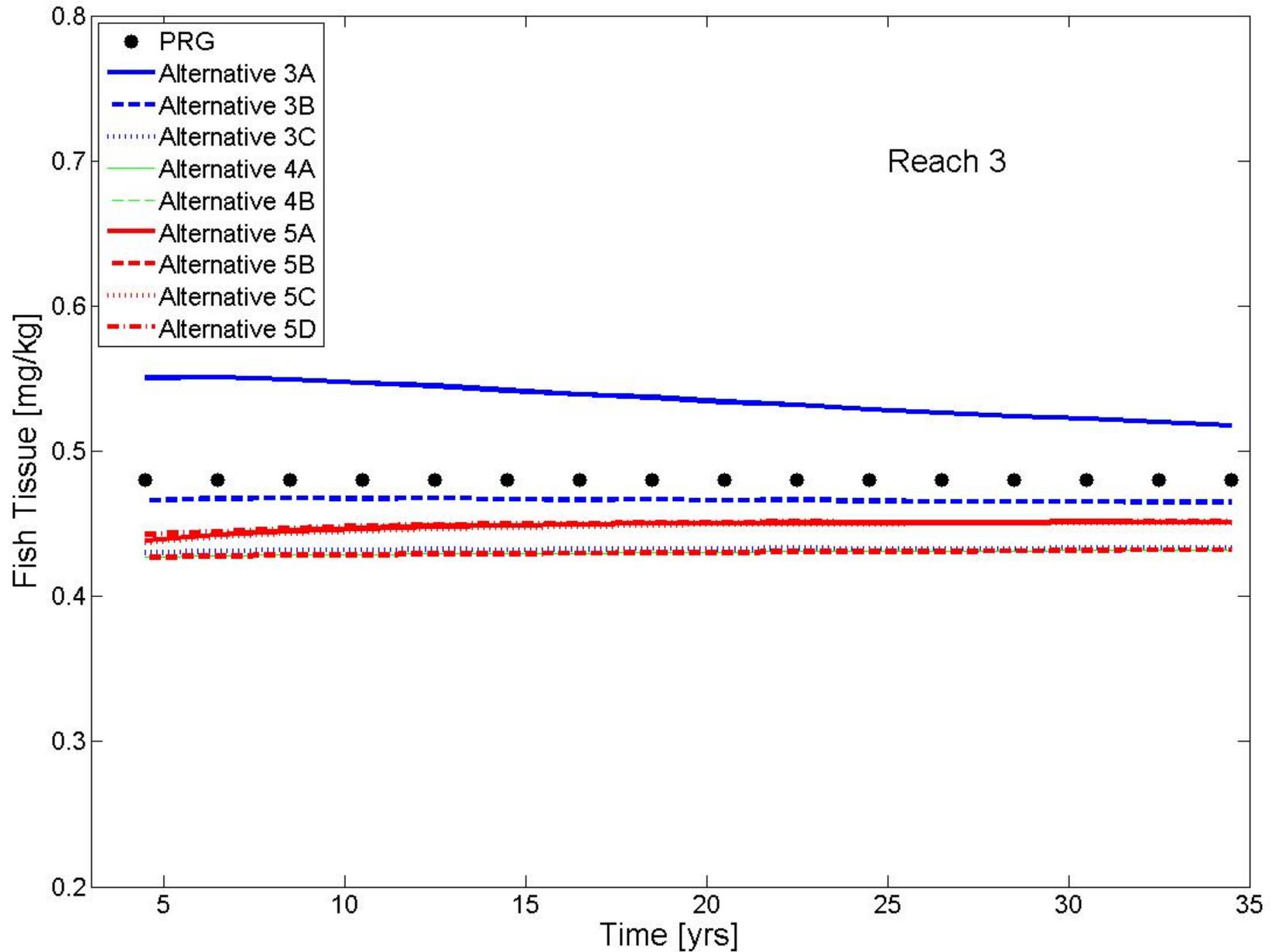
Dredging: Removal of sediment layers, with release back to water column.
New Sediment layers modeled with same solids composition as bottom segment, with Hg(II) = 1 mg/kg, MeHg = 1 ug/kg.

(except beneath segments 1, 6, 7, where Hg(II) = 3 mg/kg, MeHg = 2 ug/kg)

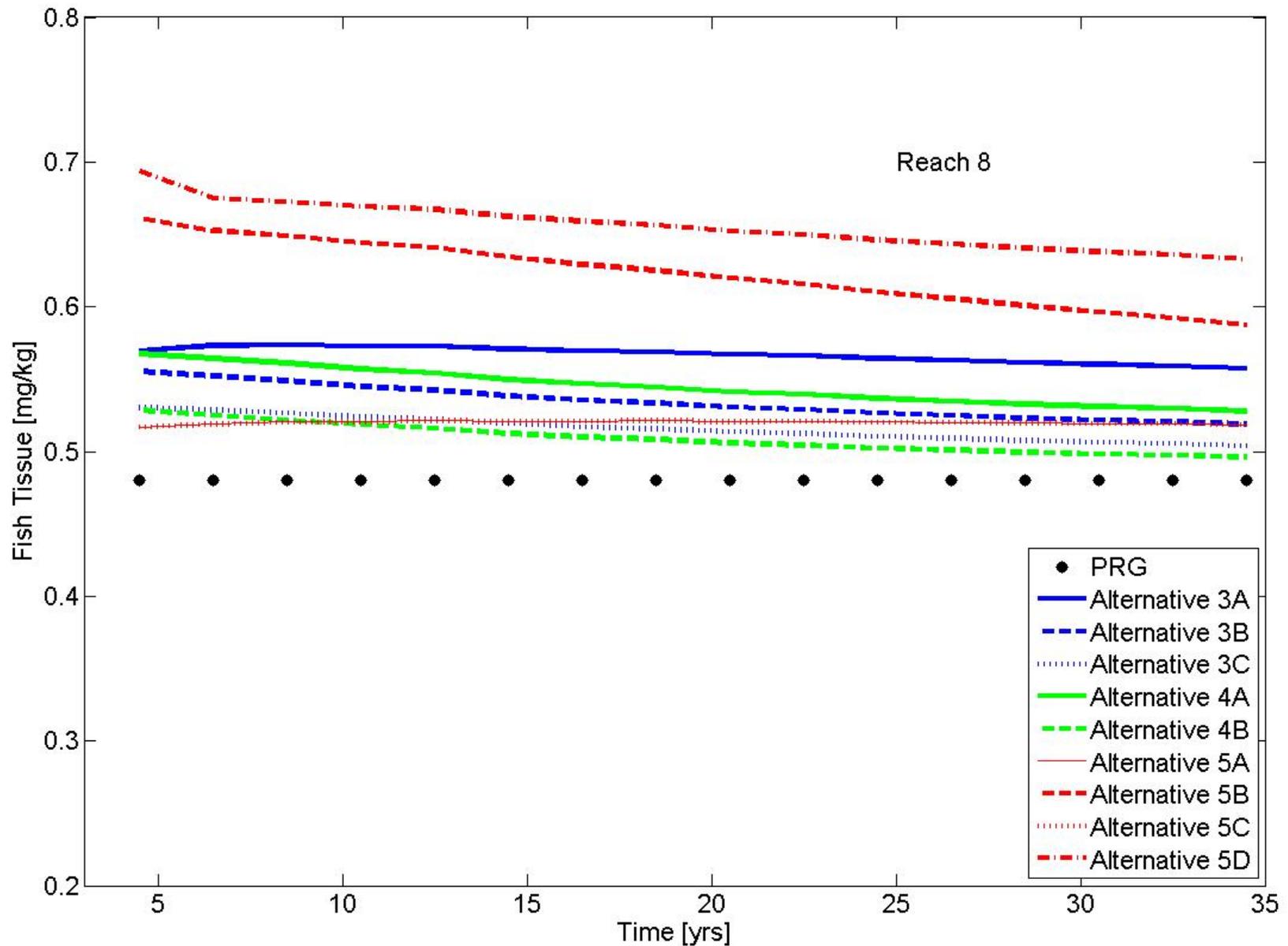
Dredging with Capping is a combination of previous methods.



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