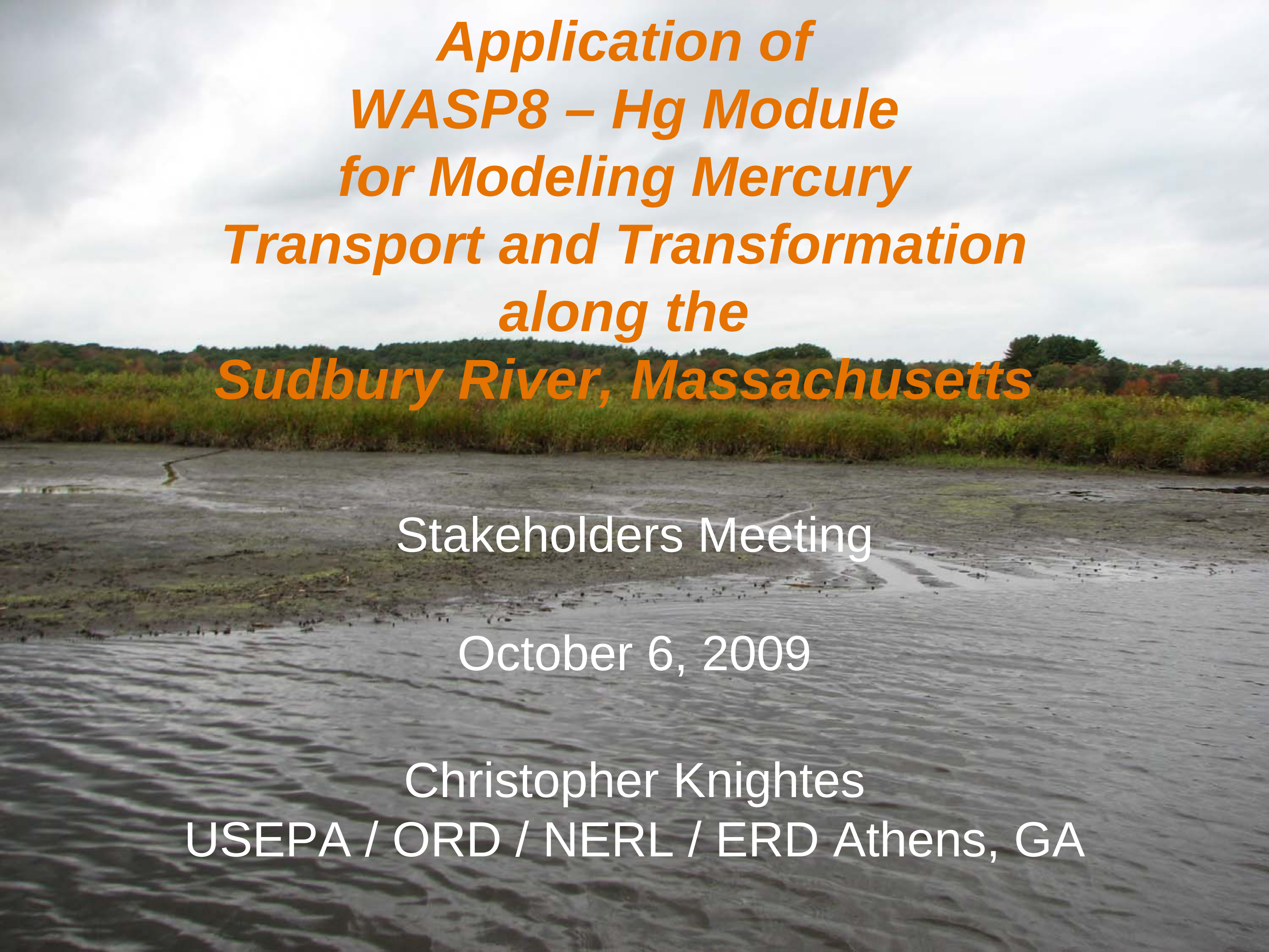


Application of WASP8 – Hg Module for Modeling Mercury Transport and Transformation along the Sudbury River, Massachusetts

Stakeholders Meeting

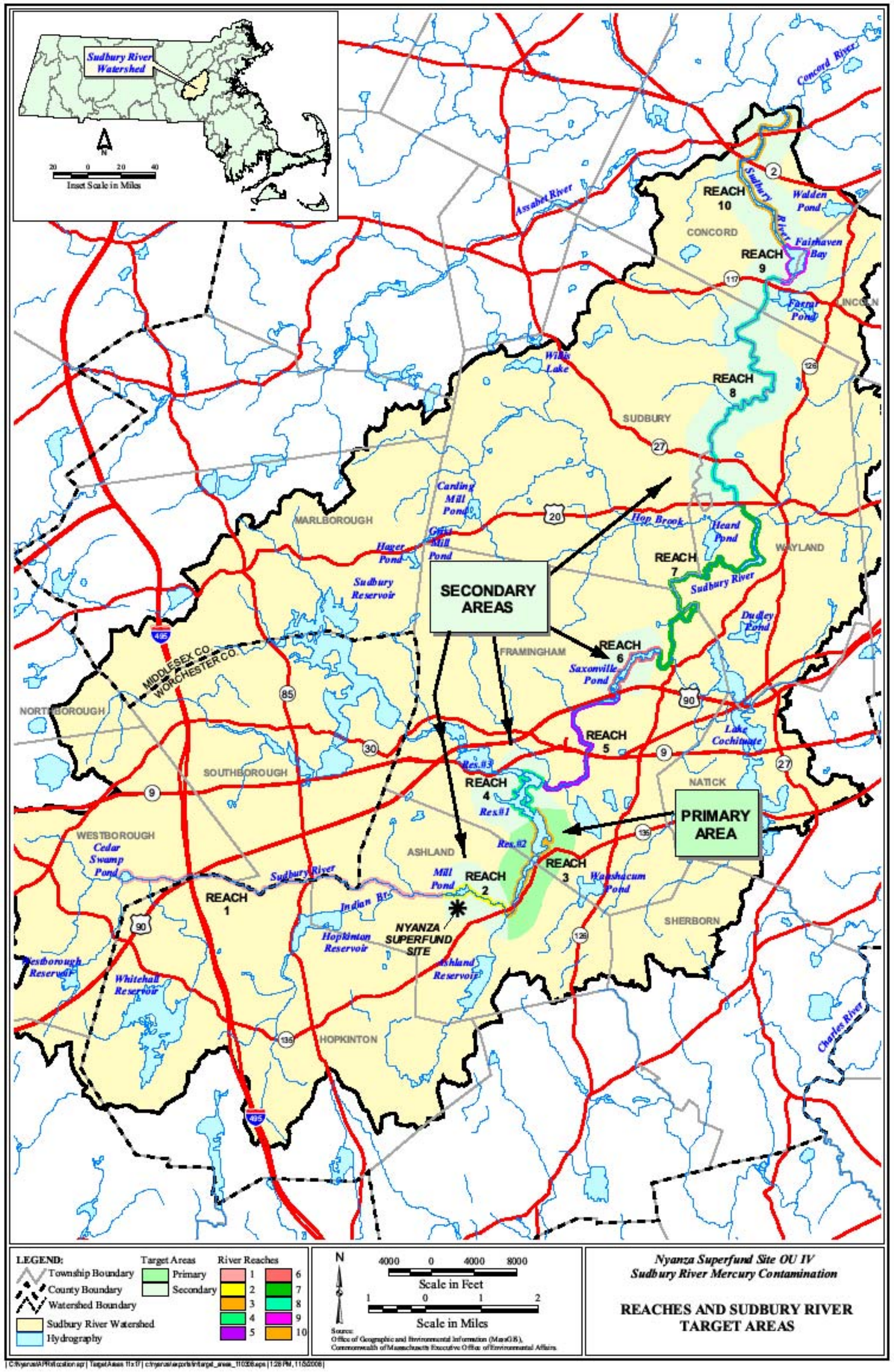
October 6, 2009

Christopher Knightes
USEPA / ORD / NERL / ERD Athens, GA

Talk Outline

- Brief Background on Site
- Questions to be Addressed
- WASP Model
- WASP Sudbury River Application
- Results

Site Background

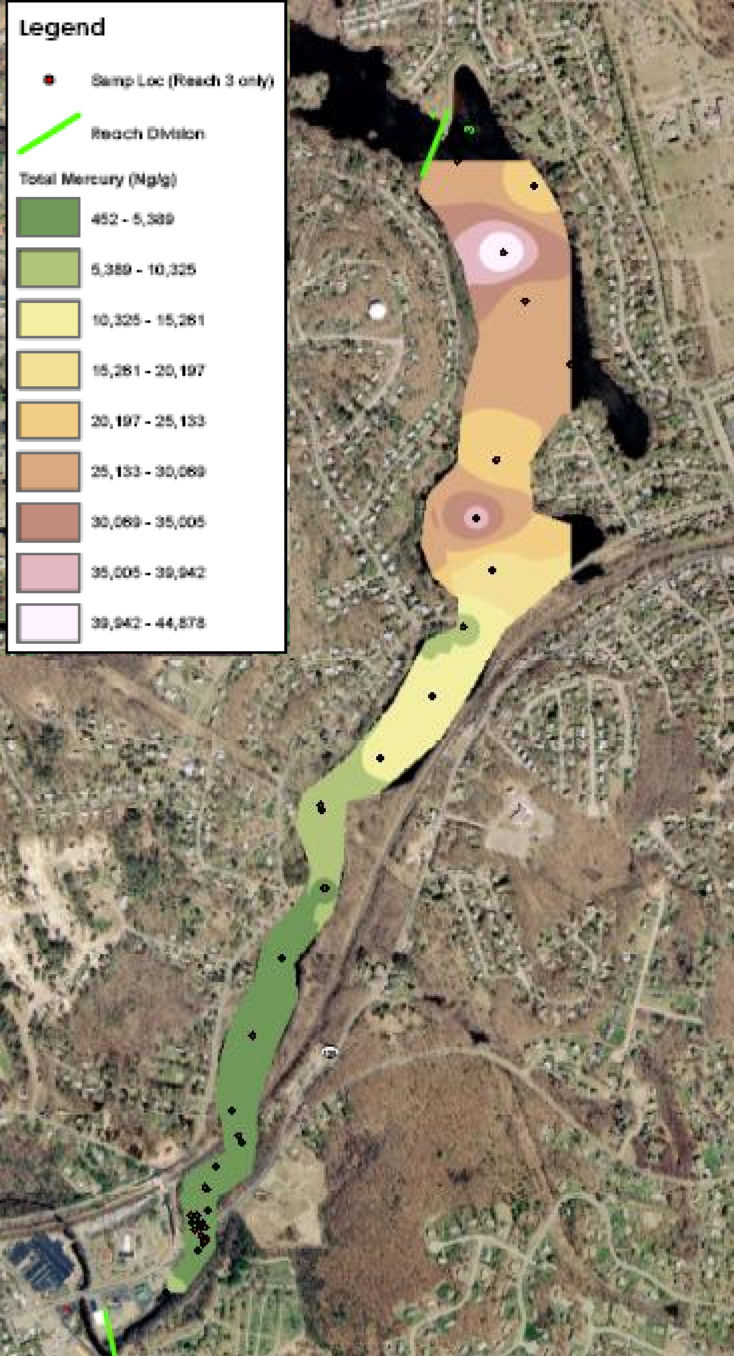


Nyanza – Sudbury River

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

What level of risk reduction would occur with different levels of site remediation ?



Surface Area	47 ha
Watershed Area	116 km^2
Mean Depth	4.4 m
Percent Watershed: Impervious	10%
Percent Watershed: Wetland	5%
Percent Watershed: Riparian	10%
Percent Watershed: Upland	75%
Hydraulic Residence Time	0.5 yr
pH	6.9-7.0
TSS	5.5 – 10.5 mg/L
DOC	5 – 6 mg/L
Sulfate	10.7 mg/L
Inflow from Sudbury River	
Unfiltered HgT	16 ng/L (Range 5.2 – 92 ng/L)
Unfiltered MeHg	0.2 ng/L (Range 0.23 – 0.45 ng/L
Filtered HgT	1.5 ng/L (Range 0.85 – 2.2 ng/L)
Filtered MeHg	16 ng/L (Range 0.21 – 0.42 ng/L)
Sediment HgT	17 ug/g dw (± 3.0 ug/g)
Sedimentation Rate	~5mm/yr

Questions to be Addressed

Correlation of Hg with $\ln(Hg_{fish}/\text{fish length})$

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.

ERASC Request #10: The Posed Problem

Question:

How can we develop a remediation goal for mercury in sediment when the concentration of mercury in sediment may be a poor predictor of mercury exposure to biota?

WASP8 / Hg Module

Mercury Species

- Elemental: Hg^0 (Hg0)
  - Pure metal
  - Major form in atmosphere (95-95%)
  - Can travel long distances from source
  - Oxidized to form Hg^{2+}: $Hg^0 \rightarrow Hg^{2+} + 2e^-$
- Divalent: Hg^{2+}
  - Inorganic (HgII)
    - Reactive Gaseous Mercury
    - HgII can form inorganic or organic bonds
    - Readily deposited from the air to land or water
    - Major form in water, sediments, and soils
  - Organic (MeHg)
    - Methyl Mercury
    - Microorganisms methylate inorganic mercury
    - Readily bioaccumulates in food web
    - Piscivorous fish, birds, and wildlife have mercury conc. 10,000 to 1,000,000 (10^4 – 10^6) times that of aqueous MeHg conc.

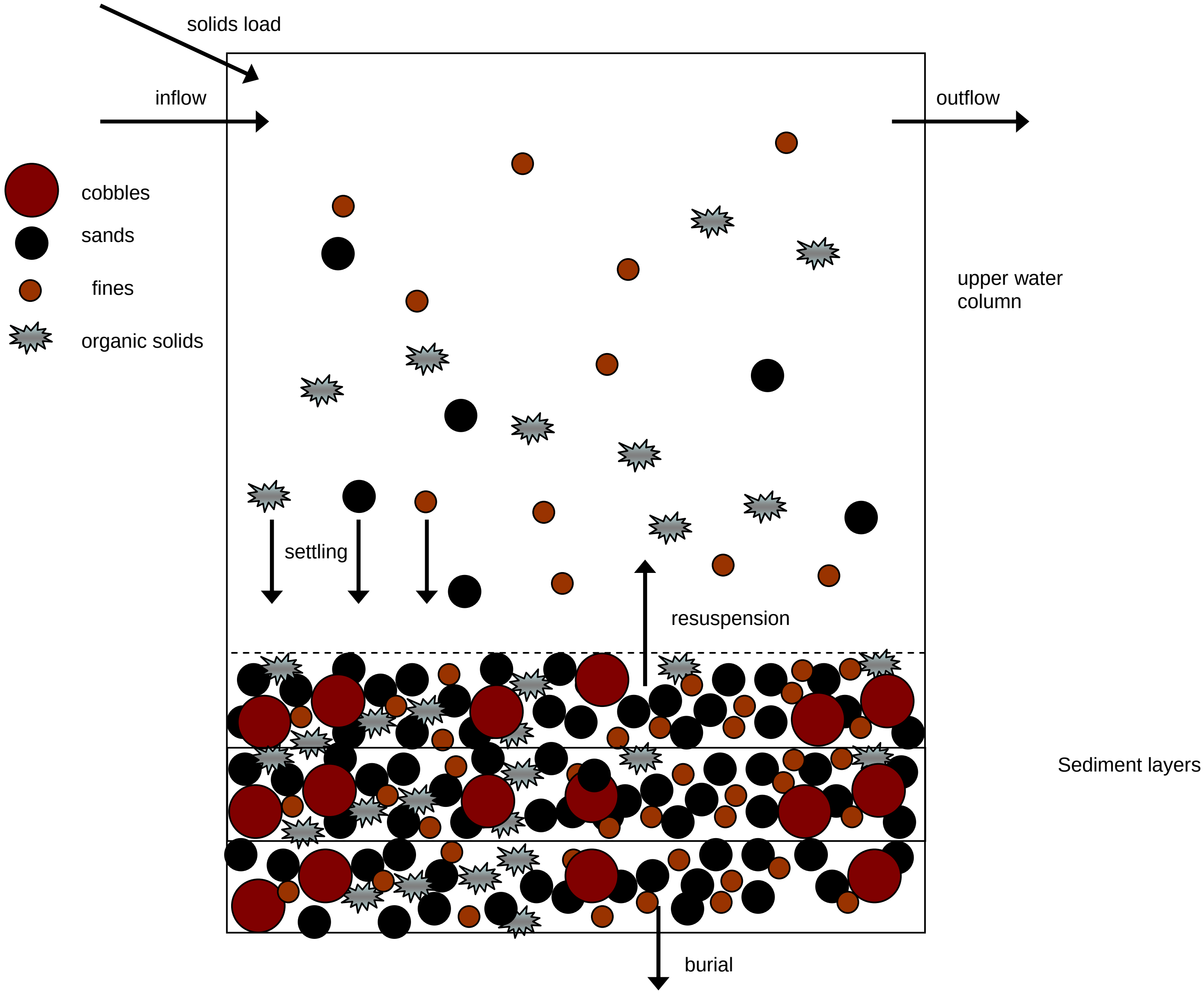
Mercury in Different Water Bodies

- Different water bodies have different governing processes for Methyl Mercury
- General Rule, % MeHg:

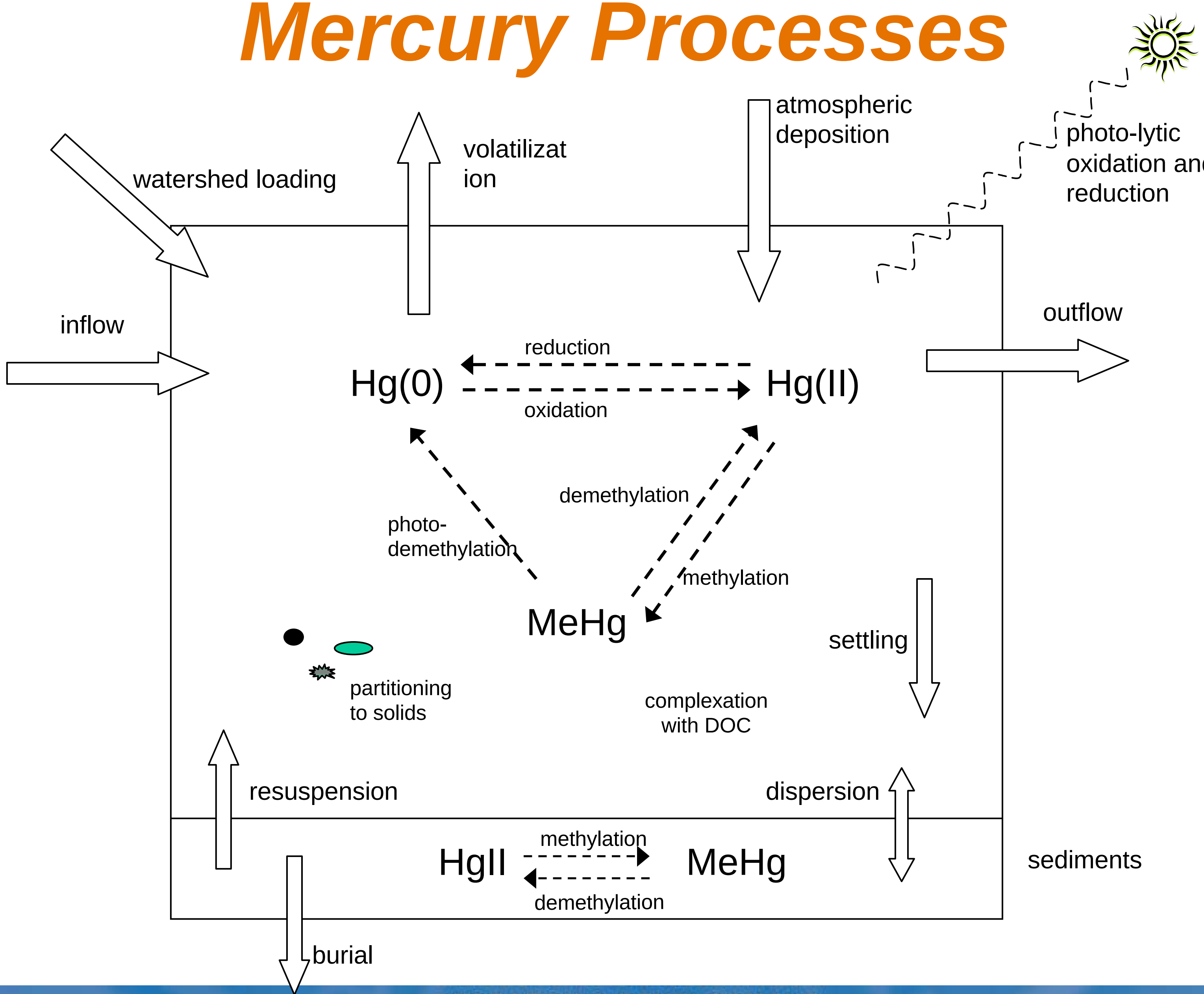
Water Body	Range of MeHg/HgT
River	4% - 6%
Lake	8% - 10%
Wetland	15% - 20%
Flooded areas	30+%

Krabbenhoft, et al., 1999; Kelley, et al., 1995.

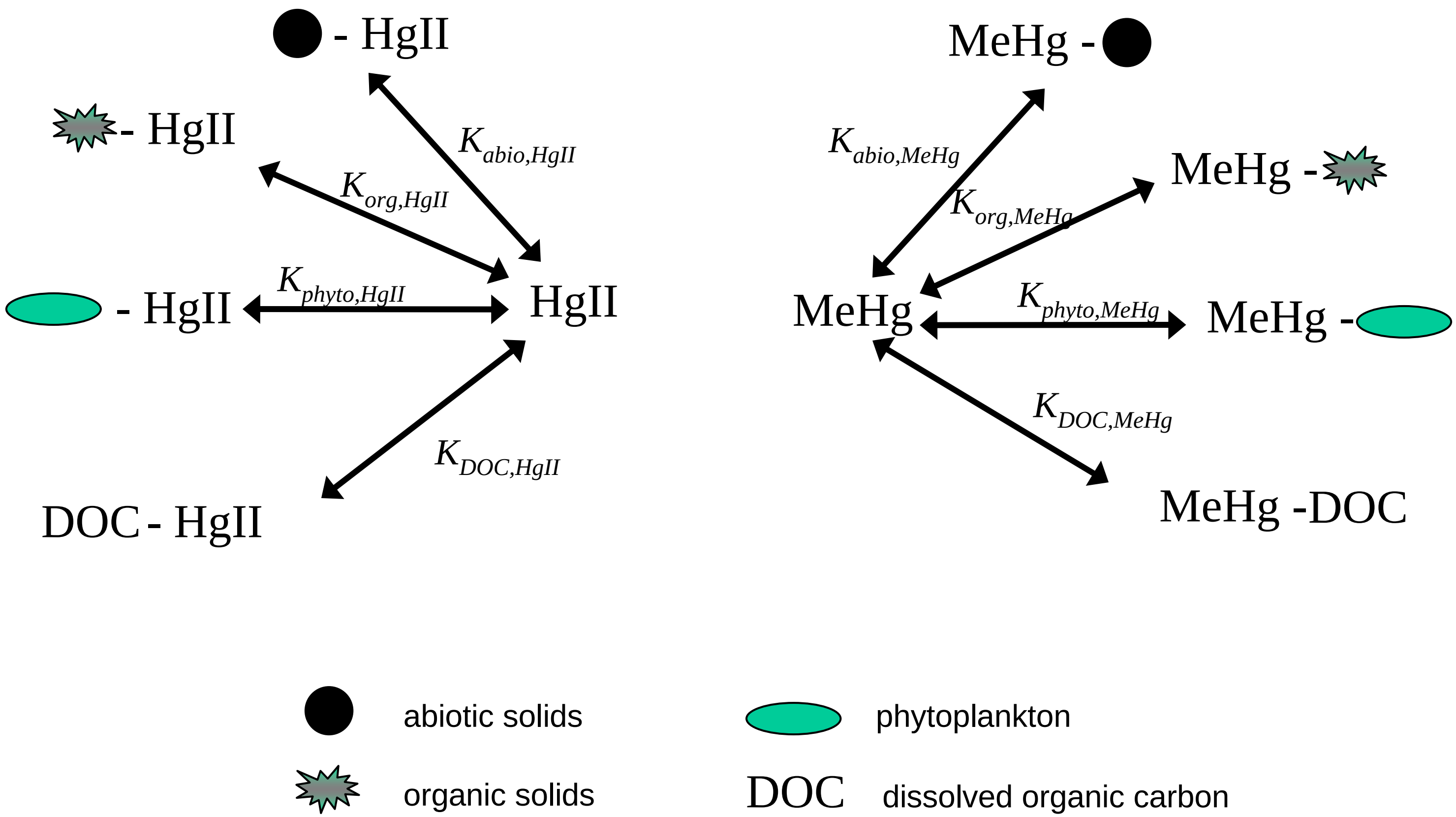
Solids Processes



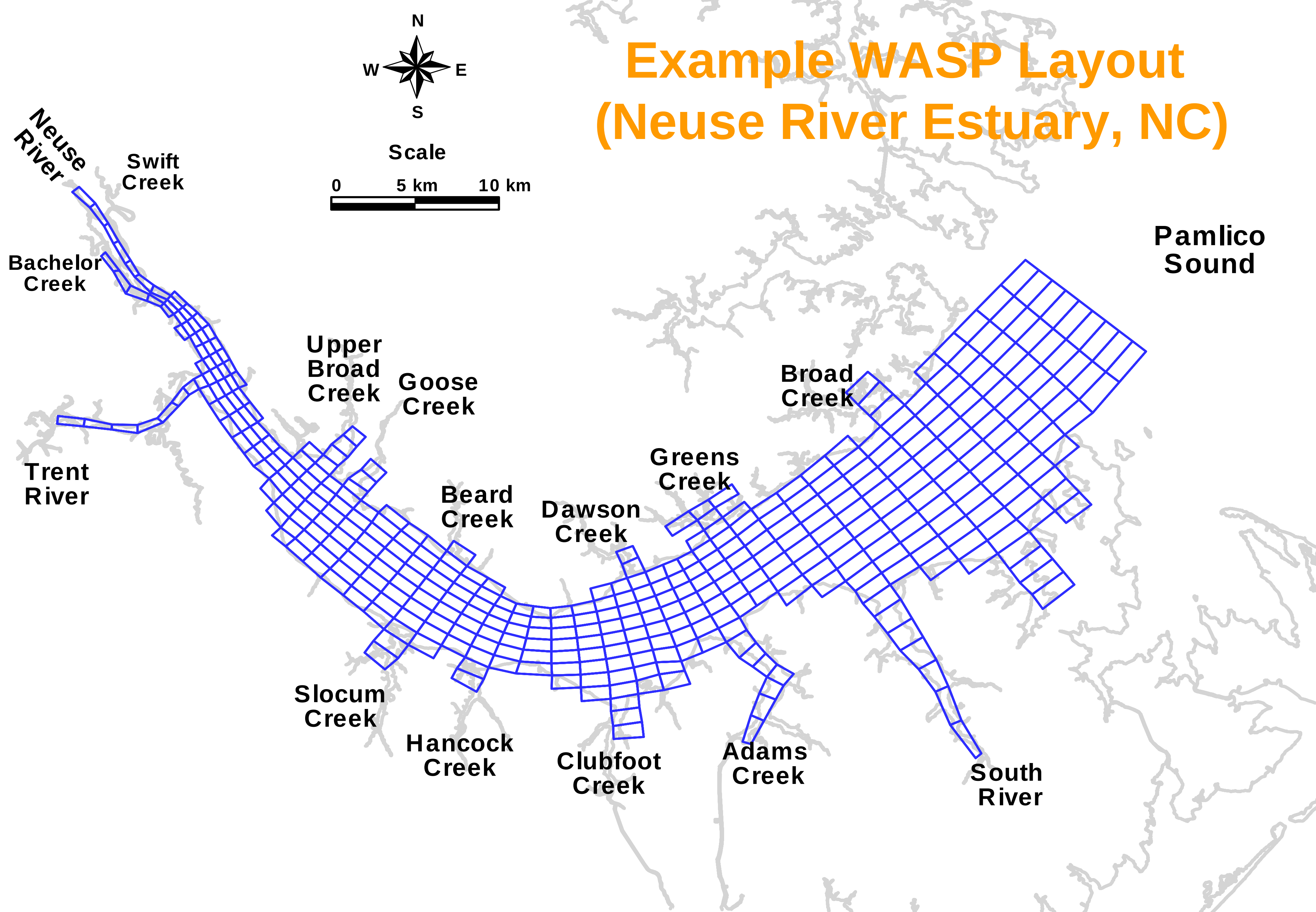
Mercury Processes



Equilibrium Partitioning



Example WASP Layout (Neuse River Estuary, NC)



Sudbury River
Model Application

Model Development and Application

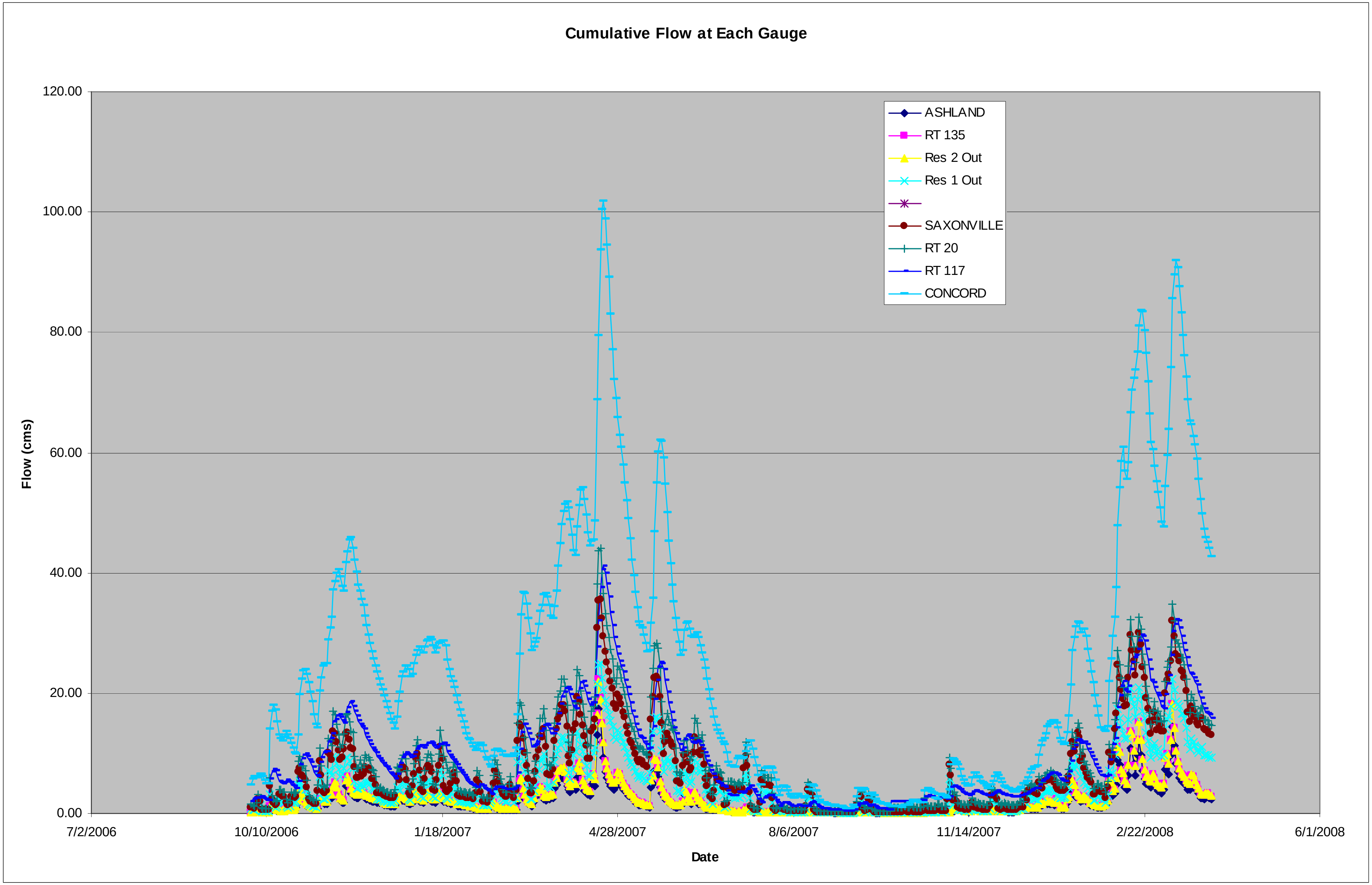
- Model System
- Flow Hydrology
- Solids loading and parameterization
- Boundary Conditions
- Initial Conditions
- Mercury Chemistry and parameterization

Model System

- 33 surface water segments
- 34 water segments
- 1-D water system except
  - Reservoir 2 has one deep segment
- 84 sediment segments
  - 33 surface sediments and sub-surface sediments
  - Additional 2 layers of sediment in Res 1 and 2
- Physical characteristics (length, mean depth, slope) taken from National Hydrology Dataset
- Manning's bottom roughness coefficient determined based on tables

Flow Hydrology

- Flows based on gage data and USGS extrapolations for
  - Ashland Gage
  - Route 135
  - Reservoir 2 outflow
  - Reservoir 2 outflow
  - Saxonville Gage
  - Route 20
  - Route 117



Cumulative Flow at Each Gauge
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Flow (cms)
7/2/2006
10/10/2006
1/18/2007
4/28/2007
8/6/2007
11/14/2007
2/22/2008
6/1/2008
Date
ASHLAND
RT 135
Res 2 Out
Res 1 Out
SAXONVILLE
RT 20
RT 117
CONCORD

Solids: Settling, Resuspension, and Burial

- Used observed TSS, TOC and DOC concentrations to set boundary conditions for sands, fines, POM
- DOC is constant per segment
- Erosion parameterization based on US ACoE sediment tests (2001) (sediment shear stress tests)
- Observed particle size distribution used to represent mean particle diameters of fines and sands
- Reported % solids and particle distribution used for sediment initial conditions (SBERA)
- Model system was run for 100 yrs with no mercury chemistry to state allow solids concentrations in sediment to approach pseudo-steady

Initial Conditions

- Initial mercury concentrations in the sediment layers were incorporated by using composite samples, cores, and historic data
- For samples with multiple measurements, averages were used
- Interpolation was used for segments with no observations

Boundary Conditions

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

Inflow Hg Concentrations

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

Partitioning

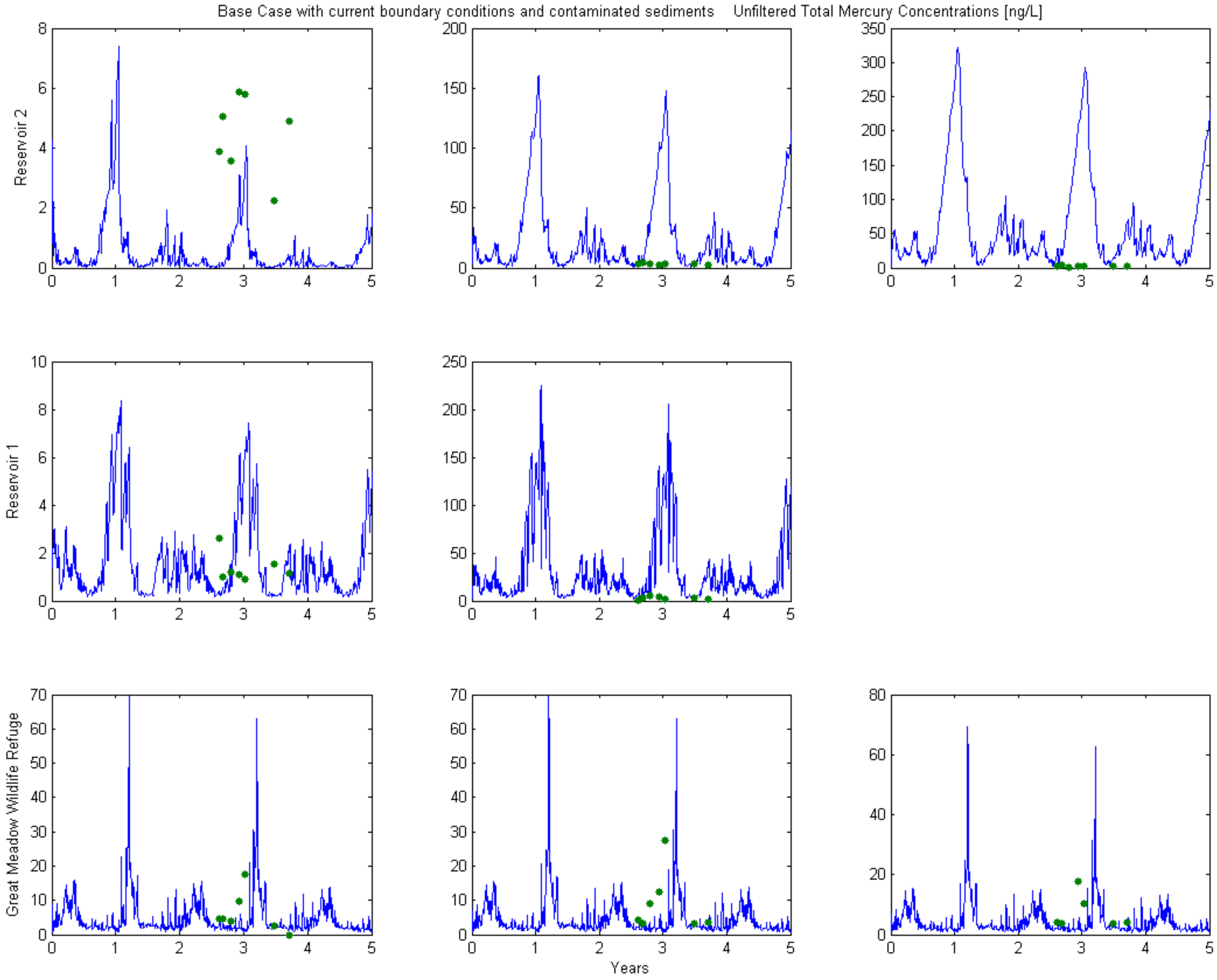
Parameter	sorbant	Hg(0)	Hg(II)	MeHg
K_{silts}	Silts and Clays	0	$1.3\text{x}10^6$	$2.31\ \text{x}10^5$
K_{sand}	Sands	0	$1\ \text{x}10^3$	$1\ \text{x}10^2$
K_{org}	Particulate Organic Matter (POM)	0	$4\ \text{x}10^5$	$5\ \text{x}10^5$
K_{DOC}	Dissolved Organic Carbon (DOC)	0	$2\ \text{x}10^5$	$1\ \text{x}10^5$

Mercury Cycling

Transformation Process (rate)	Reaction	Water Column	Water: Deep Reservoir	Reservoir Sediments	Main River Sediments	GMNWR Sediments
Methylation (d^{-1})	Hg(II) → MeHg	0	0.01	0.02	0.02	0.02
Demethylation (d^{-1})	MeHg → Hg(II)	0.04	0.04	0.5	0.7	0.25
Methylation/ Demethylation	--	0	0.25	0.04	0.03	0.08
Dark Oxidation	Hg(0) → Hg(II)	1.6	1.6	0	0	0
Surface Photo-Oxidation (d^{-1})	Hg(0) → Hg(II)	6	0	0	0	0
Surface Photo-Reduction (d^{-1})	Hg(II) → Hg(0)	14	0	0	0	0
Surface Photo-Demethylation (d^{-1})	MeHg → Hg(0)	0.2	0	0	0	0

Results

Base Case


Base Case with current boundary conditions and contaminated sediments
Unfiltered Total Mercury Concentrations [ng/L]
Reservoir 2
Reservoir 1
Great Meadow Wildlife Refuge
Years

Results of Base Case

- Hg Concentrations much higher than observed in Res 2, Res 1, and GMNWR. GMNWR not as far off.
- This suggests that inflowing mercury may not act the same as historic mercury
- Organic contaminated sites have demonstrated kinetic sorption. Contaminants that have been around have time to penetrate into the deeper portions of particles, which limits interaction with the pore water.
- APPROACH: Separate the modeling into two, use higher Kd's for contaminated case.

1) Clean sediment case:

   Hg in inflow, no mercury in sediment

2) Contaminated sediment case:

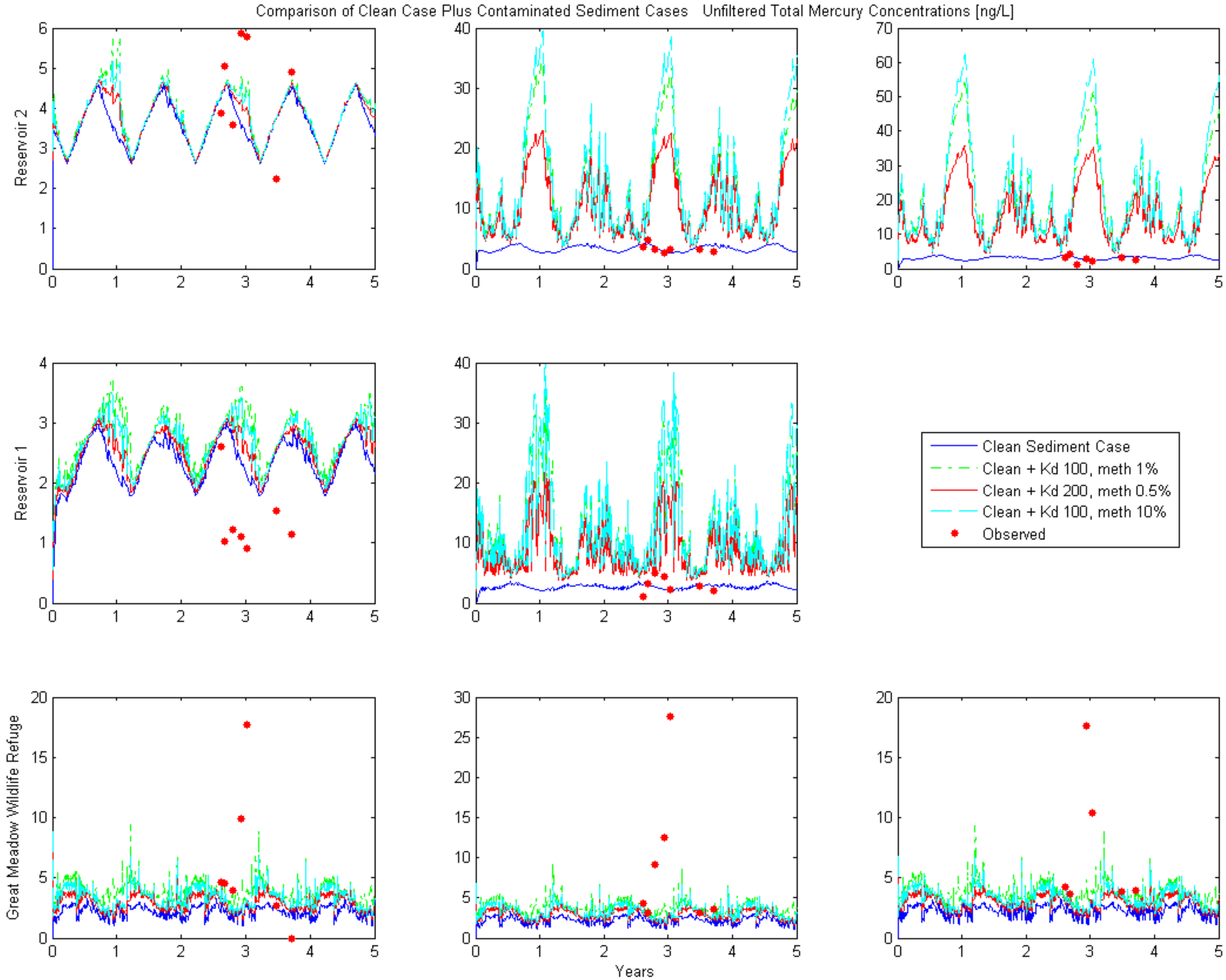
   No Hg in inflow, historic mercury in sediment,

Parameterizations for Two Cases

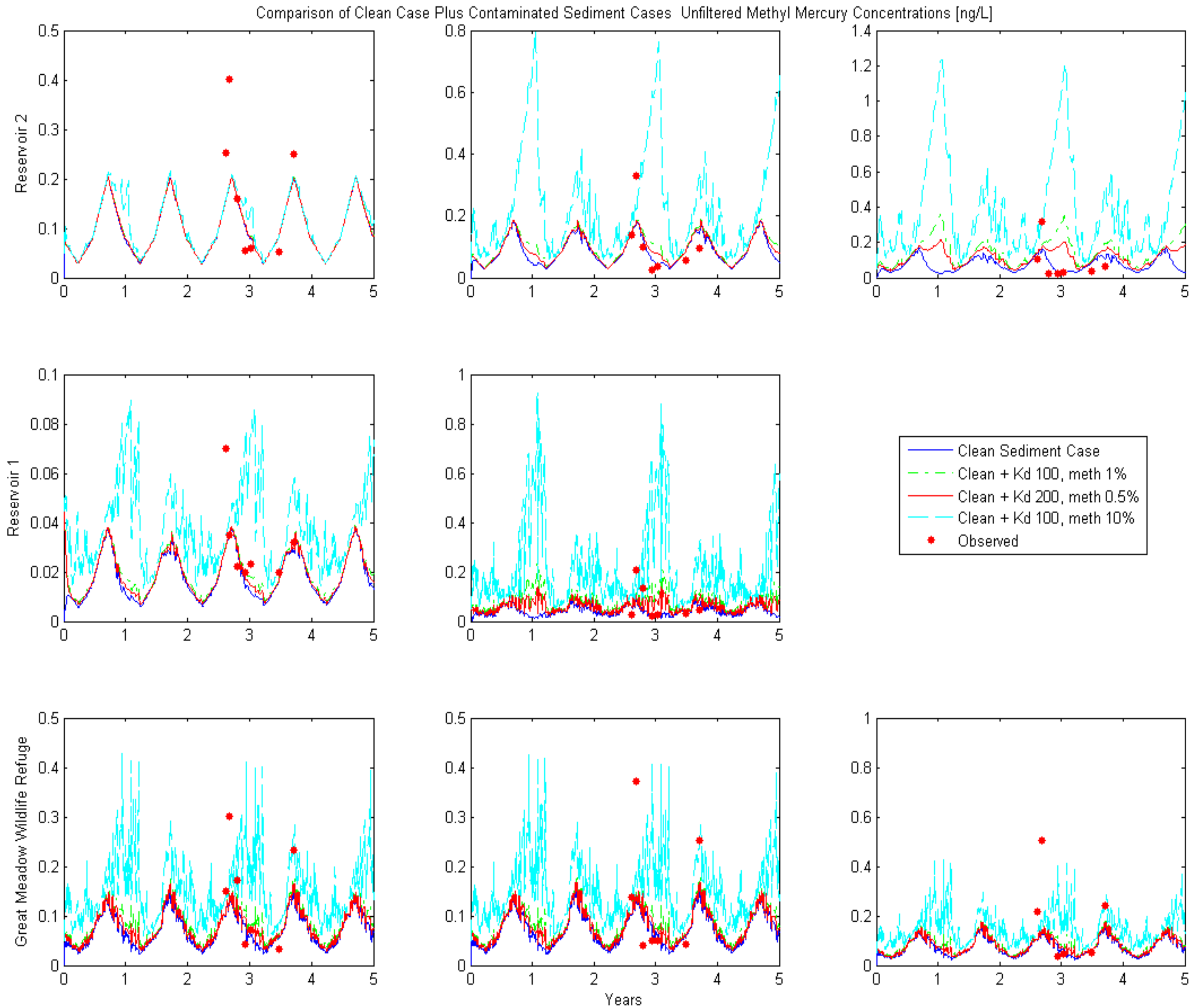
- Clean Sediment case uses original parameterization
- Contaminated Sediment case:

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

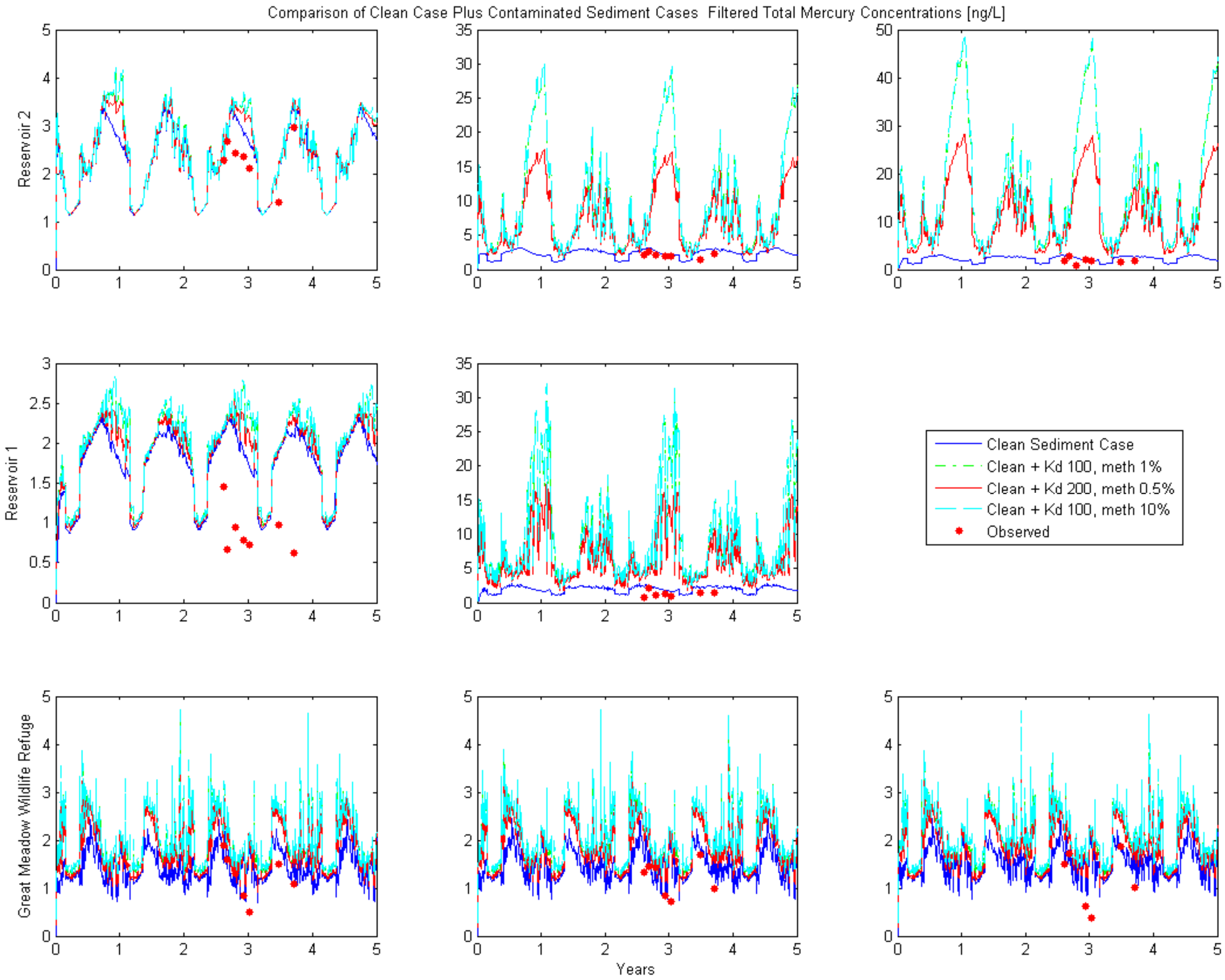
Unfiltered Total Hg



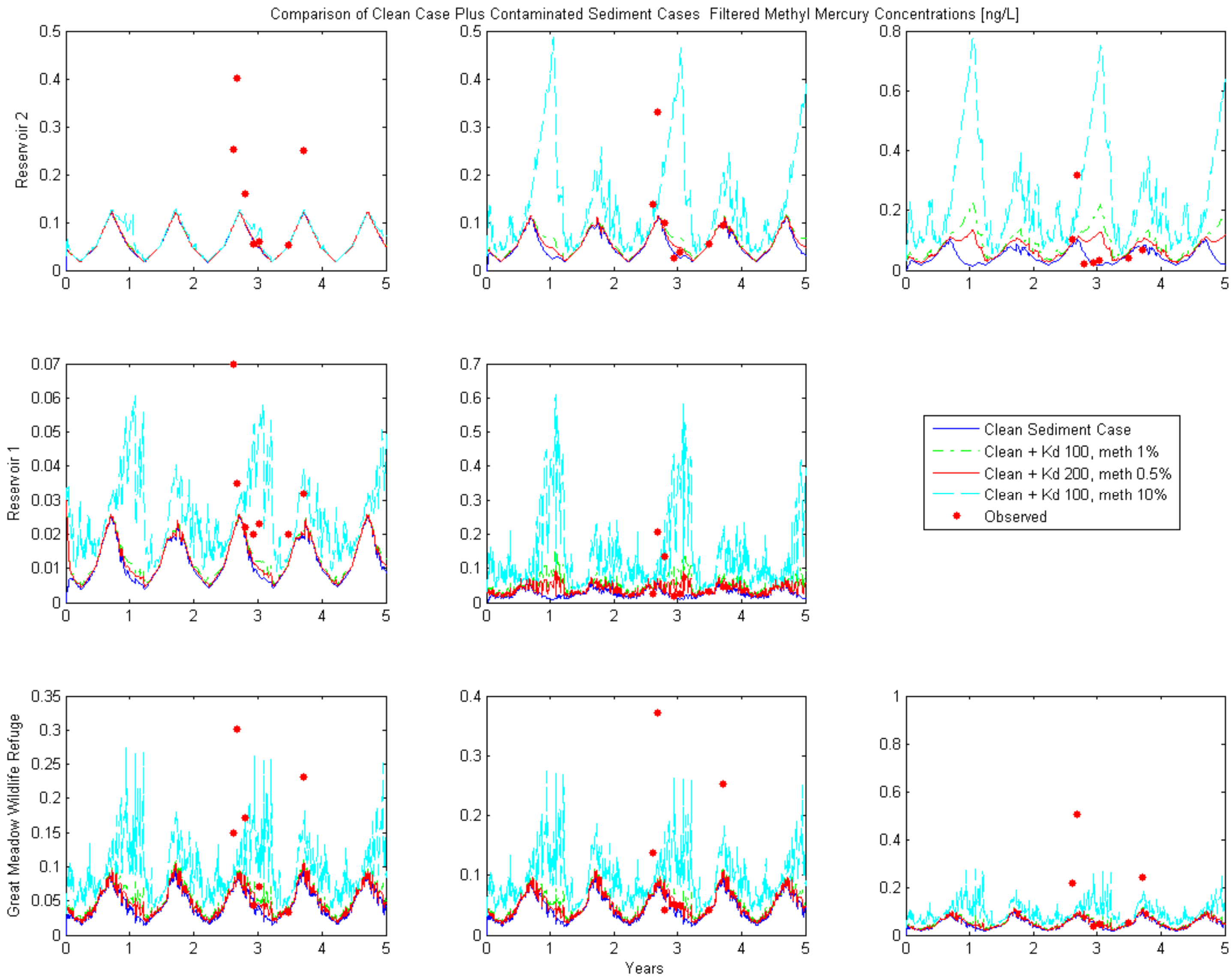
Unfiltered MeHg



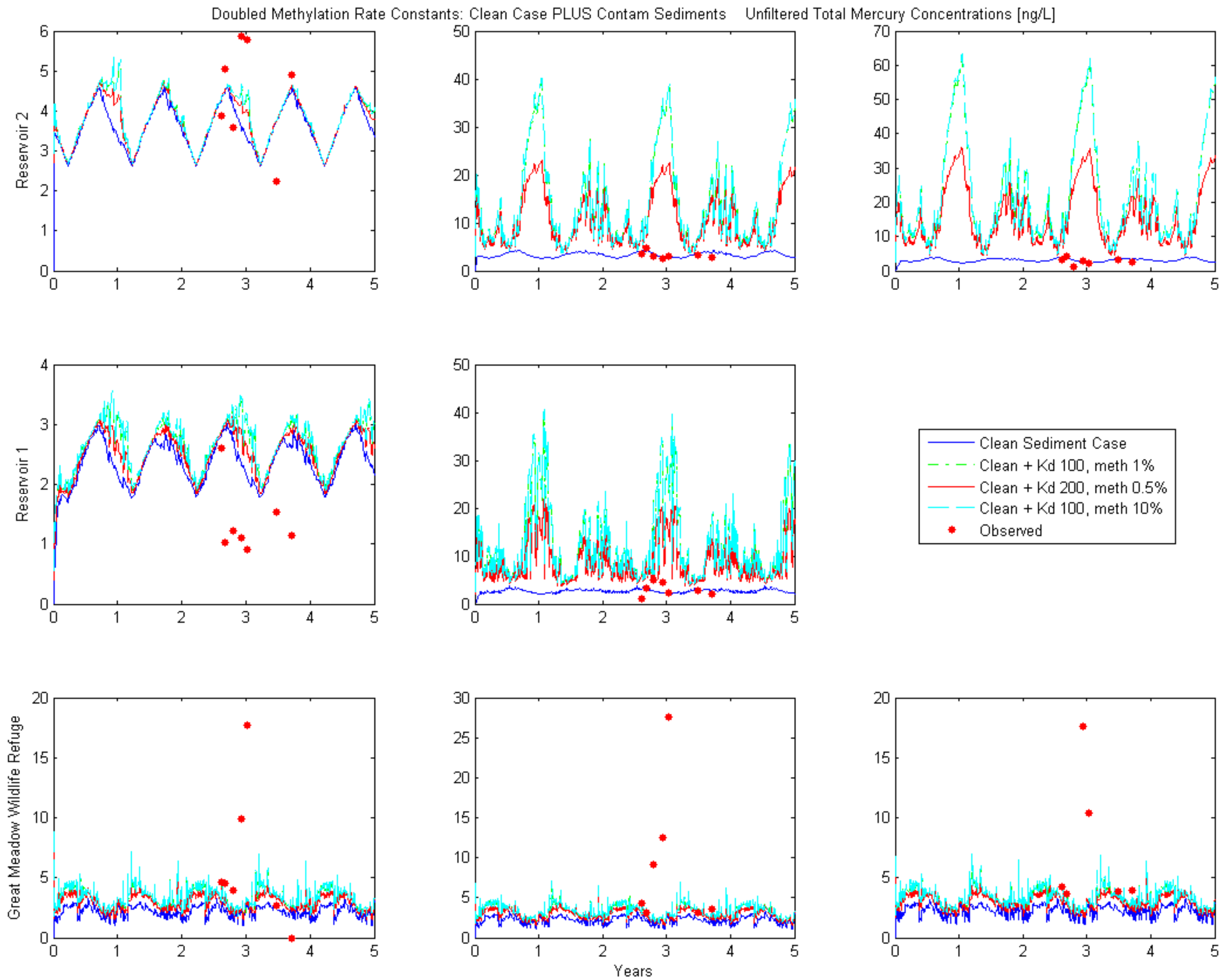
Filtered HgT



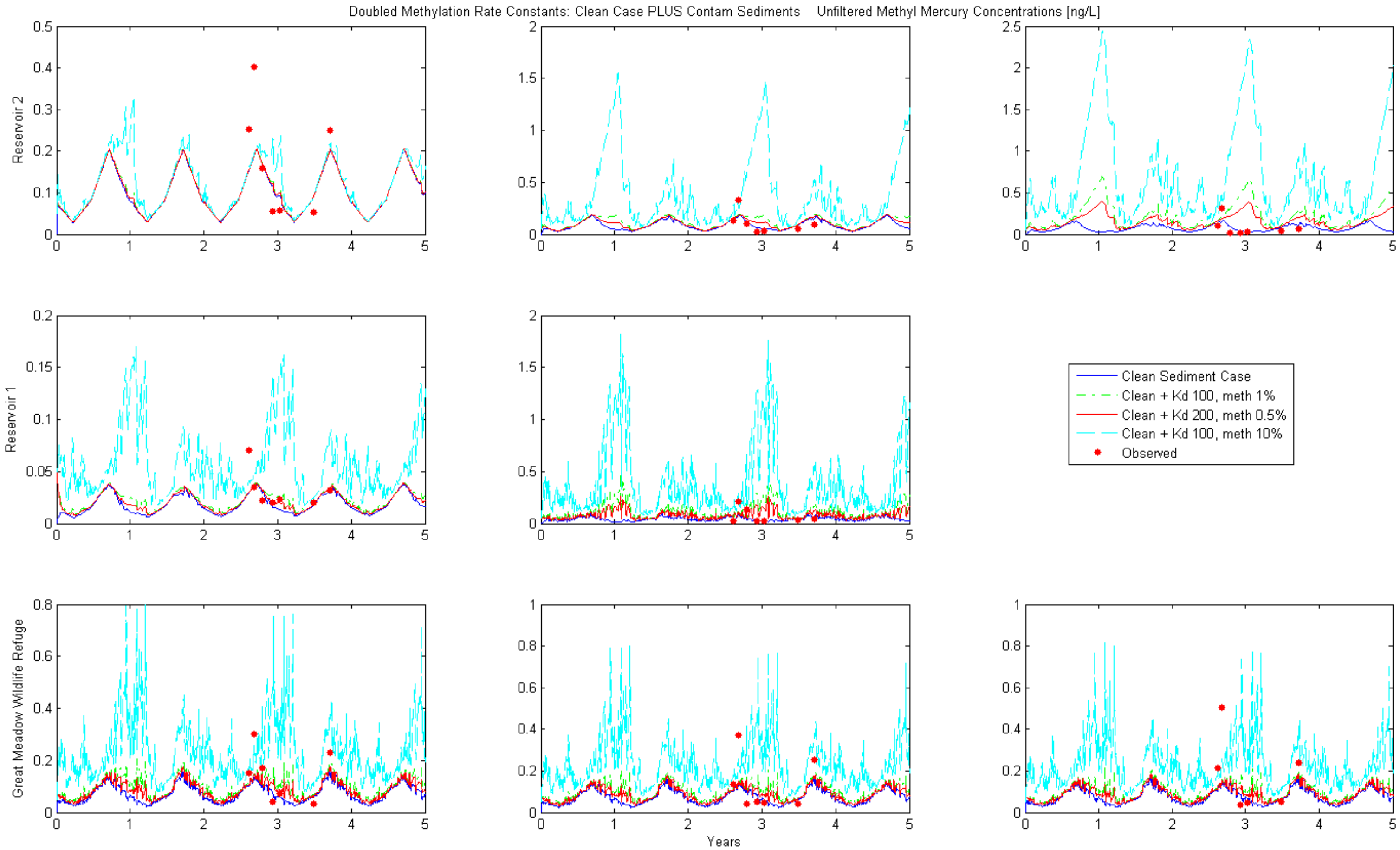
Filtered MeHg



Sensitivity Cases: Double Methylation Rates HgT (unfiltered)

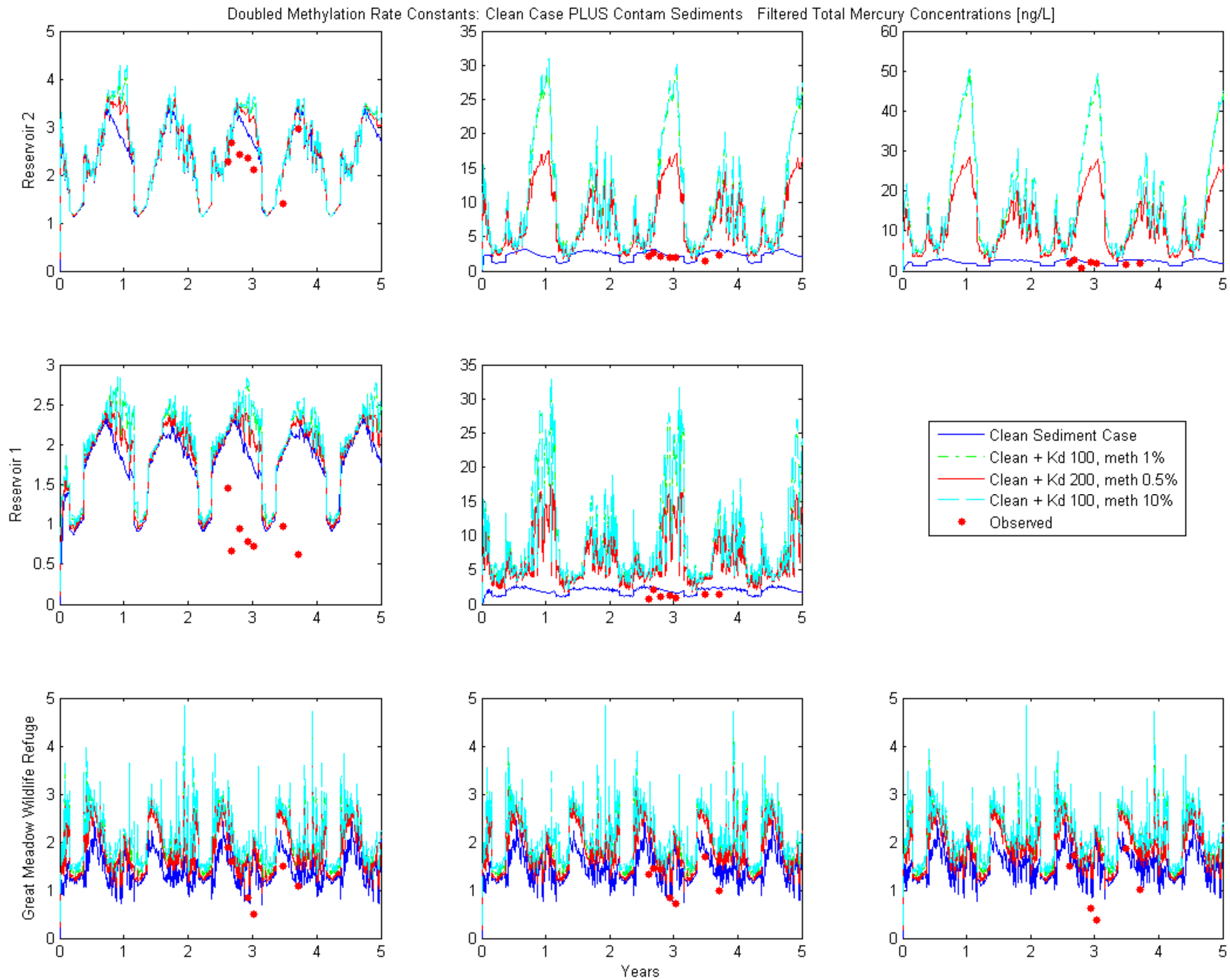


Sensitivity Cases: Double Methylation Rates HgT (unfiltered)

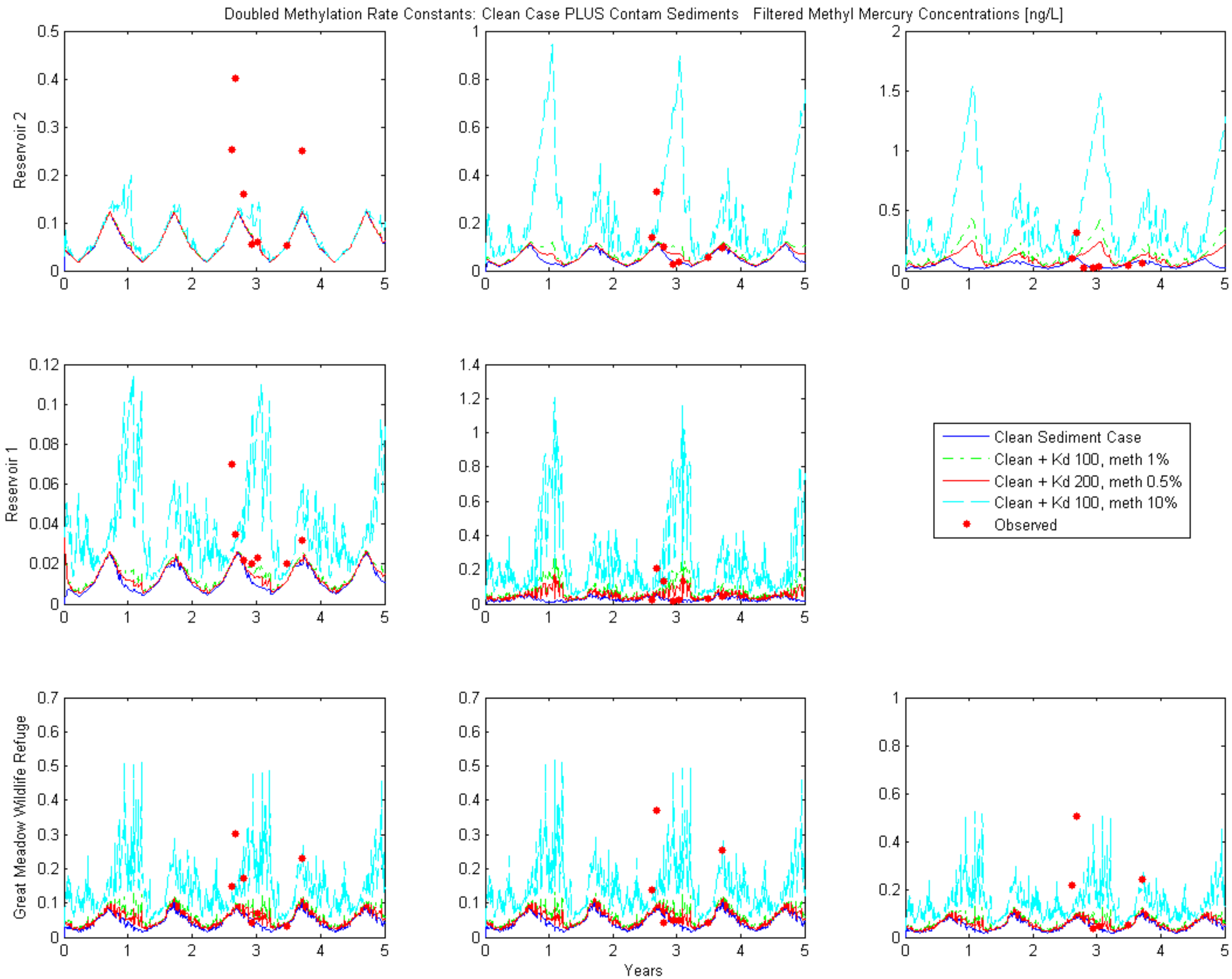


Sensitivity Cases: Double Methylation Rates

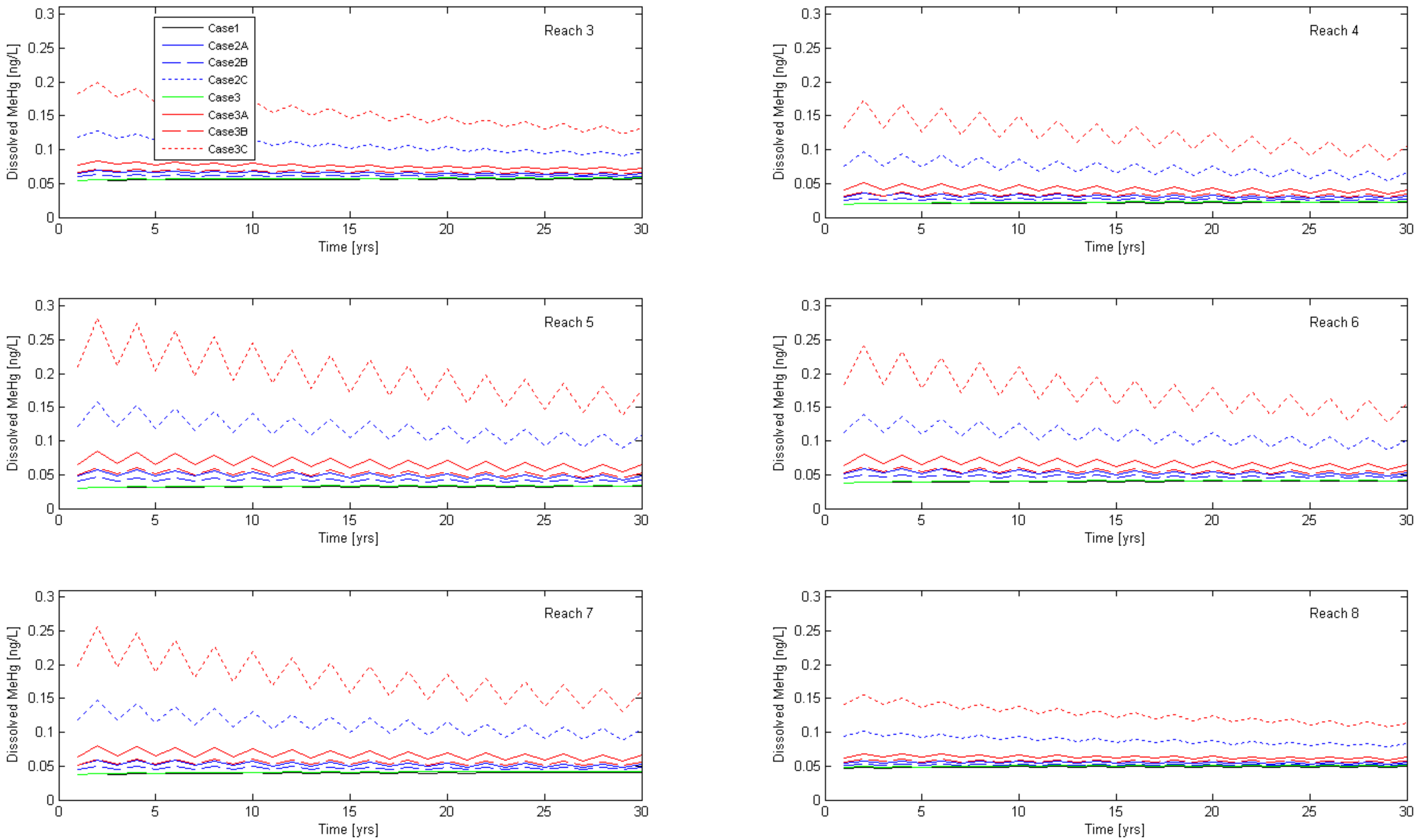
HgT (filtered)



Sensitivity Cases: Double Methylation Rates — MeHg (filtered)



Dissolved MeHg for 30 yrs



Fish Tissue for 30 yrs