

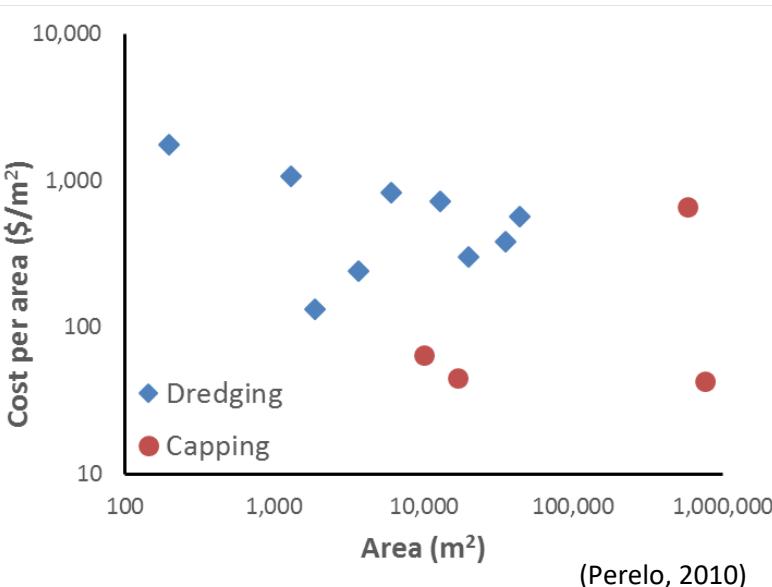
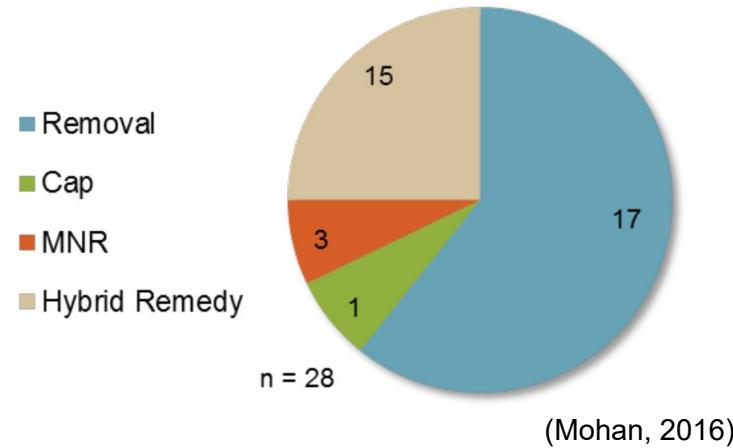


CapSim 4 – An Innovative Model for Remedial Design of Contaminated Sediments

Reible Research Group

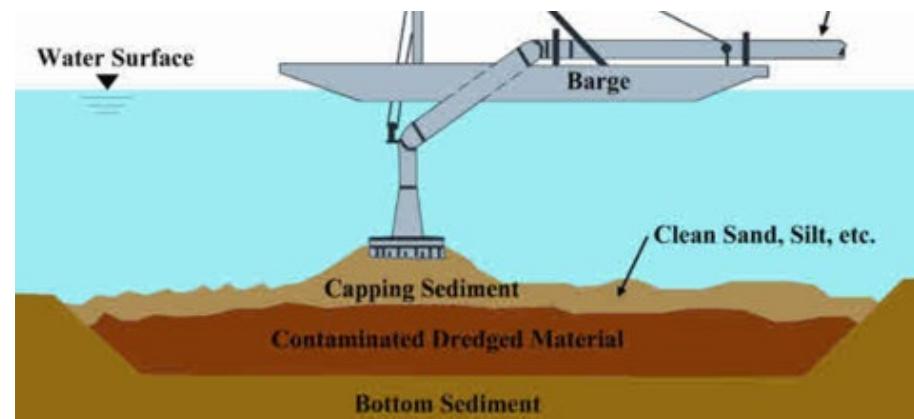
Sediment Remediation

Remedial Technologies (2005-2016)



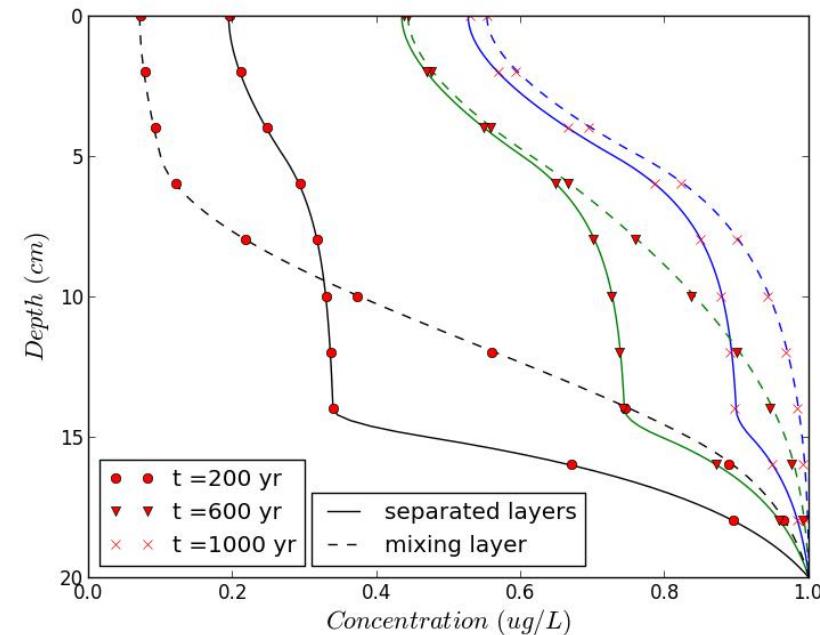
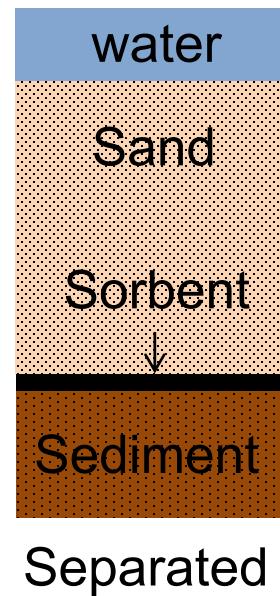
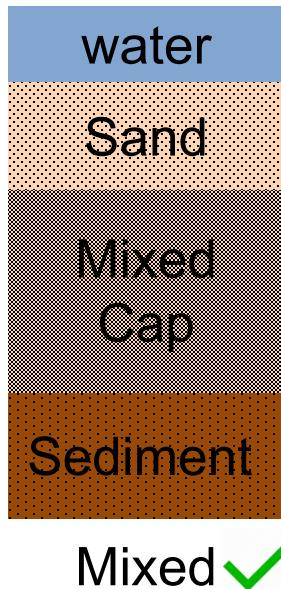
- **Sediment contamination**
 - Porous media/high carbon content
 - From sink to source
 - Large volume (10% of total)

- **Remediation approach**
 - Dredging
 - Monitored natural recovery
 - Capping and in-situ treatment



Model for Remedial Design

- In-situ remedial design - model prediction
- 1-D multi-layered porous media model
 - Porewater/Solid matrix/Dissolved organic carbon (DOC)
 - Sorption/Diffusion/Dispersion/Advection/Reaction
 - Bioturbation/Consolidation/Deposition/Erosion/Hyporheic exchange





1-D Fate and Transport Model

$$\frac{\partial q_{n,i}}{\partial t} = -\frac{\partial F_{n,i}}{\partial z} + \sum_l a_{l,n} rxn_{l,i}$$

i : Layer number
 n : Chemical number
 m : Solid matrix number
 l : Reaction number

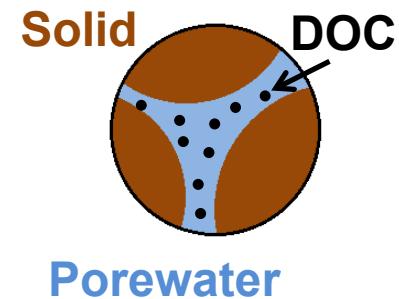
Accumulation

$$q_{n,i} = \sum_m (\varepsilon_m \phi_m C_n + \varepsilon_m \phi_m \rho_{DOC,i} q_{DOC,n} + \rho_{b,m} \phi_m q_{m,n})$$

Porewater

DOC

Sorption in solid matrix



Transport

$$F_{n,i} = -D_{n,i} \frac{\partial C_n}{\partial z} - E_i \frac{\partial (C_n + \rho_{DOC,i} q_{DOC,n})}{\partial z} + U(C_n + \rho_{DOC,i} q_{DOC,n}) + F_{hyp,n} + F_{bio,n}$$

Diffusion

Dispersion

Advection

Hyporheic

Bioturbation

Porewater and DOC



Porewater/DOC/Solid

Key transport process in diagenetic model



Numerical Solution

- **Finite difference method with nonlinear solver**
 - 1-D mass conservation at boundaries
 - Implicit upwind scheme
 - Global implicit calculation
 - Newton's method
- **Optimization in CapSim 4**
 - Process all calculations in 1-D vector form
 - Reshape 1-D vectors to 2-D matrices

Sum of 100×100 identity matrix

```
for i in range(100):  
    A[i,i] += B[i,i]           A = A + B
```

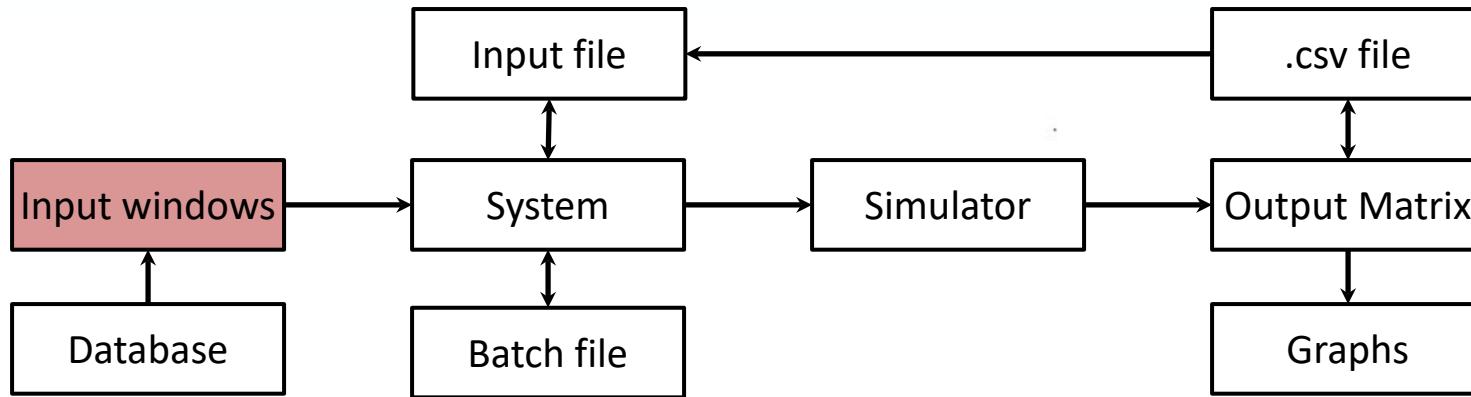
$t_1 \quad \gg \quad t_2$

$$\begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix}$$

identity matrix



CapSim – Graphic User Interface



CapSim 4.0

Please provide the following chemical properties:

Chemical name	Formula	Molecular Weight	Phase	Dissipativity in water cm/s	OC partition coefficient log(L/kg)	DOC partition coefficient log(L/kg)	Reference
DDx		331	Solute	5.15e-6	5.71	5.13	CapSimAvg
Dieldrin		381	Solute	6.01e-6	6.67	5.11	ATSDR
HPAHs		245	Solute	6.54e-6	5.49	5.44	CapSimAvg
LPAHs		157	Solute	7.58e-6	3.56	3.15	CapSimAvg
PCBs		326	Solute	5.23e-6	5.44	4.02	CapSimAvg
TCDD		322	Solute	6.76e-6	6.81	5.71	MOE2015

Add new chemicals
Import from database
Import from files
OK

Chemical

CapSim 4.0

Please select the potential layer materials and provide the following properties:

Matrix	Porosity	Bulk density g/cm³	Particle size mm	Organic carbon fraction
Activated Carbon	0.6	0.4	0.5	1.0
Sand	0.5	1.25	0.2	0.001
Sediment	0.69	0.797	0.06	0.051
SED 0-0.5	0.59	1.128	0.06	0.0352
SED 0.5-2.5	0.59	1.128	0.06	0.0396
SED-10%GAC	0.592	0.9543	0.165	0.1317

Load materials
Load commercial products
Add materials
Create mixtures
OK

Solid matrix

CapSim 4.0

Please input the sorption isotherms and corresponding coefficients for chemicals in each layer:

Matrix	Chemical	Sorption Isotherm	Isotherm coefficients	Kinetic options
Activated Carbon	DDx	Linear-Kd specified	$K_d = 1.02e+5 \text{ L/kg}$	$k_{desp} = 365 \text{ yr}^{-1}$ Equilibrium
	Dieldrin	Linear-Kd specified	$K_d = 3.55e+4 \text{ L/kg}$	Equilibrium
	HPAHs	Linear-Kd specified	$K_d = 4.27e+5 \text{ L/kg}$	Equilibrium
	LPAHs	Linear-Kd specified	$K_d = 3.39e+6 \text{ L/kg}$	Equilibrium
PCBs	Linear-Kd specified	$K_d = 3.8e+5 \text{ L/kg}$	Equilibrium	
TCDD	Linear-Kd specified	$K_d = 1.1e+4 \text{ L/kg}$	Equilibrium	

OK

Sorption

CapSim 4.0

Starting with the layer nearest the overlying water, please provide the following information for each layer:

Name	Material	Tortuosity Correction	Thickness cm	Hydrodynamic Dispersion cm	Dissolved organic matter concentration mg/L
Deposition	Sediment	Boudreau	0.59/yr	1.0	43.0
Layer 1	Sand	Millington & Quirk	15.24	1.0	43.0
Layer 2	SED-10%GAC	Boudreau	15.24	1.5	43.0
Layer 3	SED 0.5-2.5	Boudreau	60.96	6.1	43.0

Add layers
OK

Layers

CapSim 4.0

Please provide the information of the following system properties:

Upwelling groundwater flow Darcy velocity	Steady flow cm/s
None	—
None	—
None	—
Uniform	—
15.0	cm
10.0	cm ² /yr
100.0	cm ² /yr
Consolidation	—
6.0	cm
0.3	yr
None	—
Threshold concentration	—

OK

Process

CapSim 4.0

Please edit the initial concentration profiles:

Chemical	Layer	Solid matrix	Porewater concentration µg/L	Solid concentration µg/kg
DDx	Layer 1	Edit	Amer-SED	0
	Layer 2	Edit	Sand-1%GAC	0
	Layer 3	Edit	ULSediment	0.0136
927				

OK

BC & IC

CapSim 4.0

Please specify the simulation options for the system:

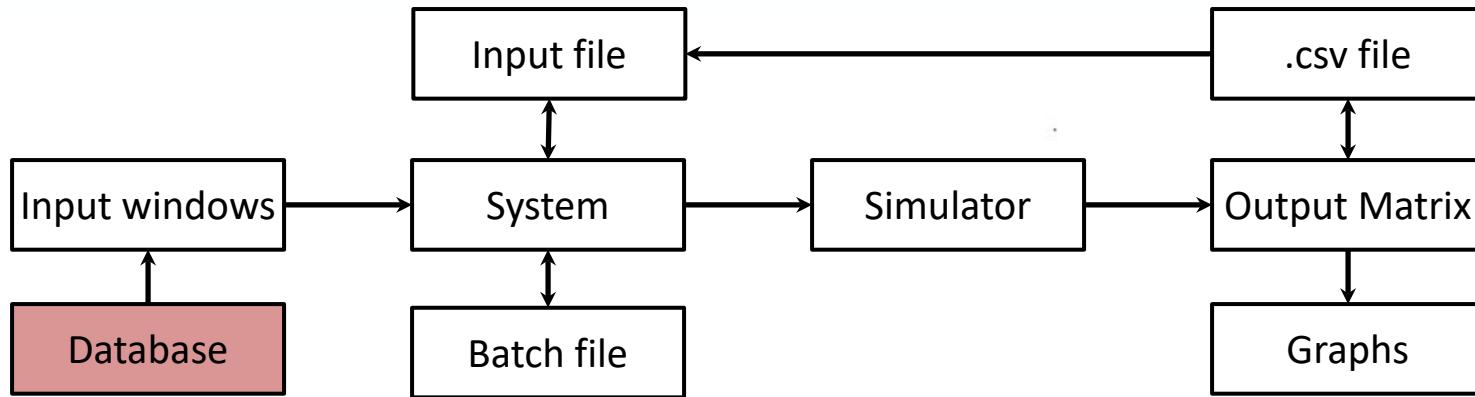
Simulation duration (yr)	250
Steps in output files:	250
Usage of CPU cores (Max 3):	1
Time step options:	Implicit
Mass balance options:	Track
Discretization options:	Specify manually
Number of grid points:	60
Time step (yr):	1.0
Steps in deposition grid:	1

OK

Solver



CapSim - Database



CapSim 4.0

Please provide the following fundamental properties for the chemicals:

	Chemical name	Formula	Type	Temperature °C	Diffusivity cm ² /s	OC partition coefficient log(L/kg)	DOC partition coefficient log(L/kg)	Reference
Add	Edit	Delete	Acenaphthene	C ₁₀ H ₈	Solute 20.0 —	7.69e-6	3.75	3.34
Add	Edit	Delete	Acenaphthylene	C ₉ H ₈	Solute 20.0 —	7.06e-6	3.54	3.09
Add	Edit	Delete	Anthracene	C ₁₄ H ₁₀	Solute 20.0 —	7.74e-6	3.93	3.56
Add	Edit	Delete	Benz(a)anthracene	C ₁₉ H ₁₂	Solute 20.0 —	9e-6	5.09	4.95
Add	Edit	Delete	Benz(a)pyrene	C ₂₁ H ₁₂	Solute 20.0 —	9e-6	5.67	5.65
Add	Edit	Delete	Benzofluoranthene	C ₁₉ H ₁₂	Solute 20.0 —	5.56e-6	5.67	5.65
Add	Edit	Delete	Benz(e)pyrene	C ₂₀ H ₁₂	Solute 20.0 —	5.49e-6	6.25	6.35
Add	Edit	Delete	Benz(g,h,i)perylene	C ₂₂ H ₁₂	Solute 20.0 —	5.65e-6	6.25	6.35
Add	Edit	Delete	Benz(j)fluoranthene	C ₂₀ H ₁₂	Solute 20.0 —	5.48e-6	5.67	5.65
Add	Edit	Delete	Benz(k)fluoranthene	C ₂₀ H ₁₂	Solute 20.0 —	5.56e-6	5.67	5.65
Add	Edit	Delete	CO ₃ ²⁻	CO ₃ ²⁻	Solute 0.0 —	1e-5	0.0	0.0
Add	Edit	Delete	Ca	Ca ²⁺	Solute 0.0 —	1e-5	0.0	0.0
Add	Edit	Delete	Chrysene	C ₁₆ H ₁₂	Solute 20.0 —	6.21e-6	5.09	4.95
Add	Edit	Delete	Dibenzo(a,e)pyrene	C ₂₂ H ₁₄	Solute 20.0 —	5.06e-6	7.37	7.7
Add	Edit	Delete	Dibenzo(a,h)anthracene	C ₂₁ H ₁₄	Solute 20.0 —	5.18e-6	6.25	6.35
Add	Edit	Delete	Dibenzo(a,h)pyrene	C ₂₁ H ₁₄	Solute 20.0 —	5.07e-6	7.33	7.66
Add	Edit	Delete	Dibenzo(a,i)pyrene	C ₂₃ H ₁₄	Solute 20.0 —	5.07e-6	7.33	7.66
Add	Edit	Delete	Fe(OH) ⁻	Fe(OH) ⁻	Solute 0.0 —	1.15e-9	0.0	0.0

CapSim 4.0

Please select the chemical you would like to add to the database

Search:

Original Name	Imported Name
Acenaphthene	Acenaphthene
Acenaphthylene	Acenaphthylene
Anthracene	Anthracene
Benz(a)anthracene	Benz(a)anthracene
Benz(a)pyrene	Benz(a)pyrene
Benz(b)fluoranthene	Benz(b)fluoranthene
Benz(e)pyrene	Benz(e)pyrene
Benz(g,h,i)perylene	Benz(g,h,i)perylene
Benz(j)fluoranthene	Benz(j)fluoranthene
Benz(k)fluoranthene	Benz(k)fluoranthene
Chrysene	Chrysene
Dibenzo(a,e)pyrene	Dibenzo(a,e)pyrene
Dibenzo(h)anthracene	Dibenzo(h)anthracene
Dibenzo(h)pyrene	Dibenzo(h)pyrene
Dibenzo(j)pyrene	Dibenzo(j)pyrene
Fluoranthene	Fluoranthene
Fluorene	Fluorene
Indeno(1,2,3-c,d)pyrene	Indeno(1,2,3-c,d)pyrene
Naphthalene	Naphthalene
Phenanthrene	Phenanthrene
Pyrene	Pyrene

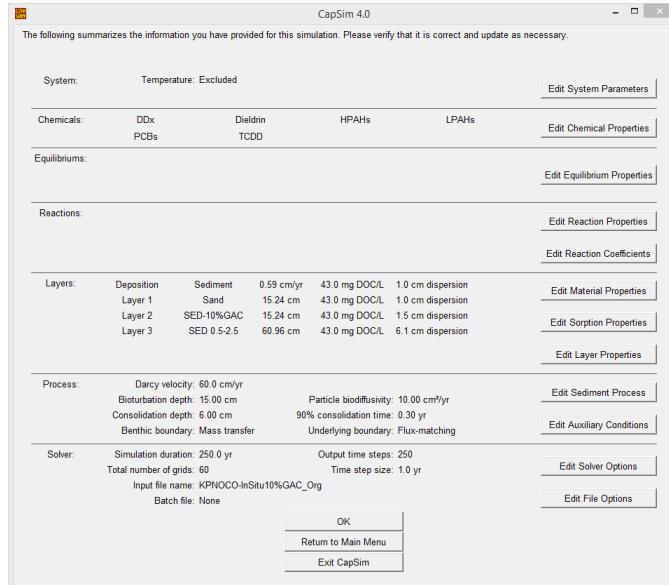
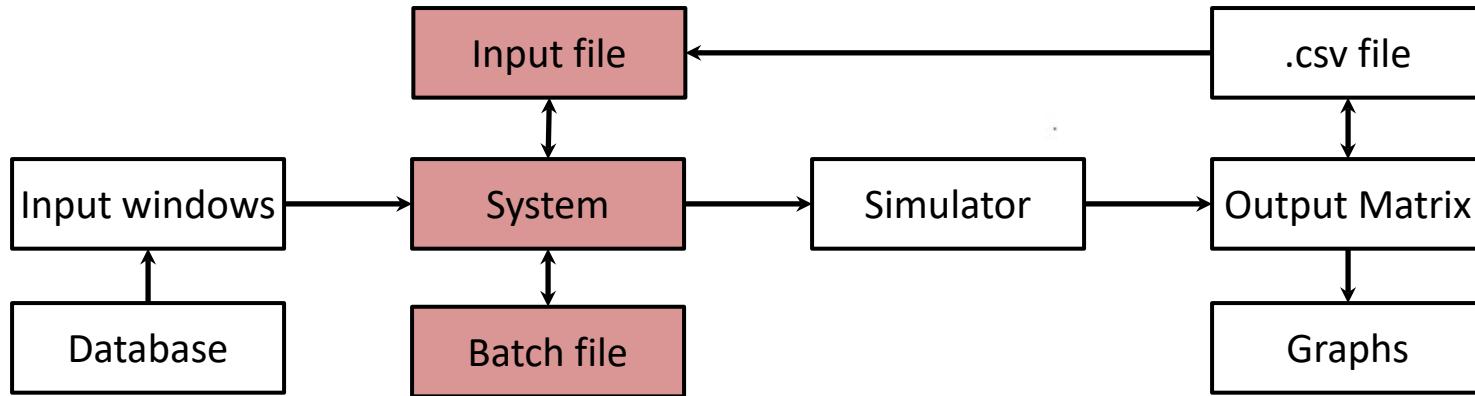
PAHs

PCBs

Pesticides

Heavy metals

CapSim – Input/Batch Function



Summary of system



.cpsi input file

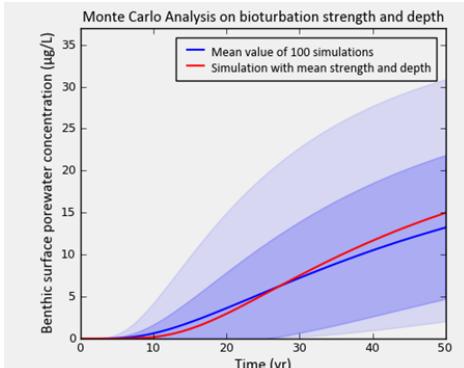
KPNOCO-InSitu1
0%GAC_Org_test.
cpsi

```

30PD-4I_new - Notepad
File Edit Format View Help
# CapSim 3.8

# Batch simulation
# 1. Define the type of batch function (self.type)
#     1) 'Multiple Scenarios': generates multiple output files for each scenario
#     2) 'Monte Carlo Simulation' generates one output file with the mean values for all scenarios.
# 2. Determine the number of scenarios (l_num) in the batch function
# 3. Define the output files in the batch function
#     1) 'Multiple Scenarios': the number of names in the vector (self.filenames) should be the same as l_num
#     2) 'Monte Carlo Simulation': the number of names in (self.filenames) should be 1
# 4. Assign the given values to the target parameter in each scenario
#     1) Assign the vector with the same number of desired values
#     2) Assign those values to the parameter
# 5. Assign random values to the target parameter in each scenario
#     1) use the function random() to generate a random number between
  
```

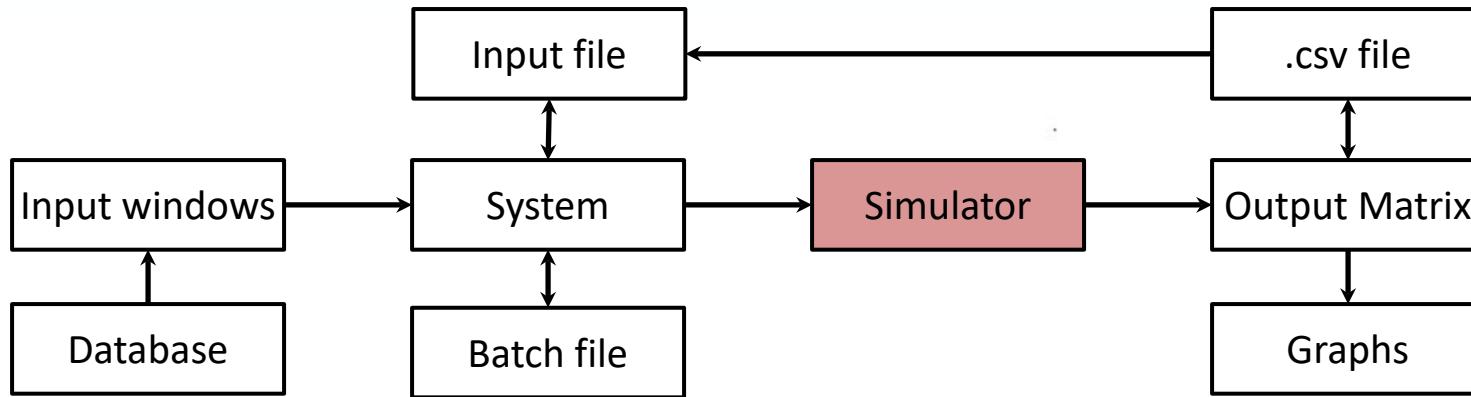
txt batch file



Monte Carlo simulation



CapSim – Solver



NumPy

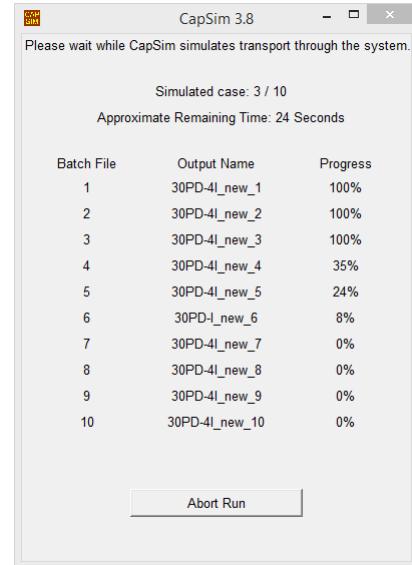
Numpy

L A P A C K
L -A P -A C -K
L A P A -C -K
L -A P -A -C K
L A -P -A C K
L -A -P A C -K

Lapack

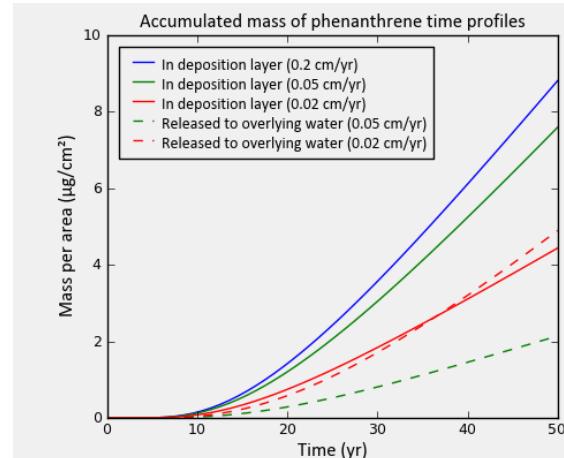
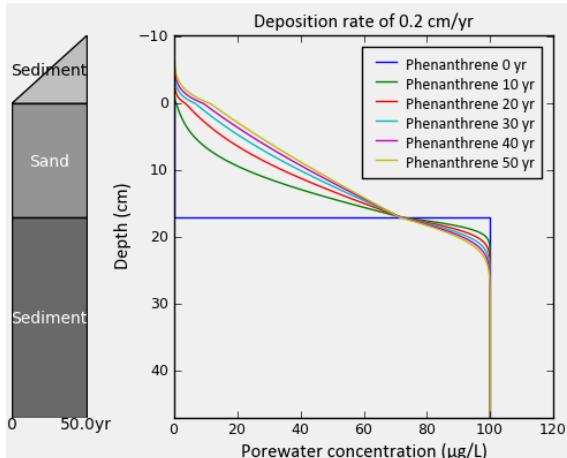
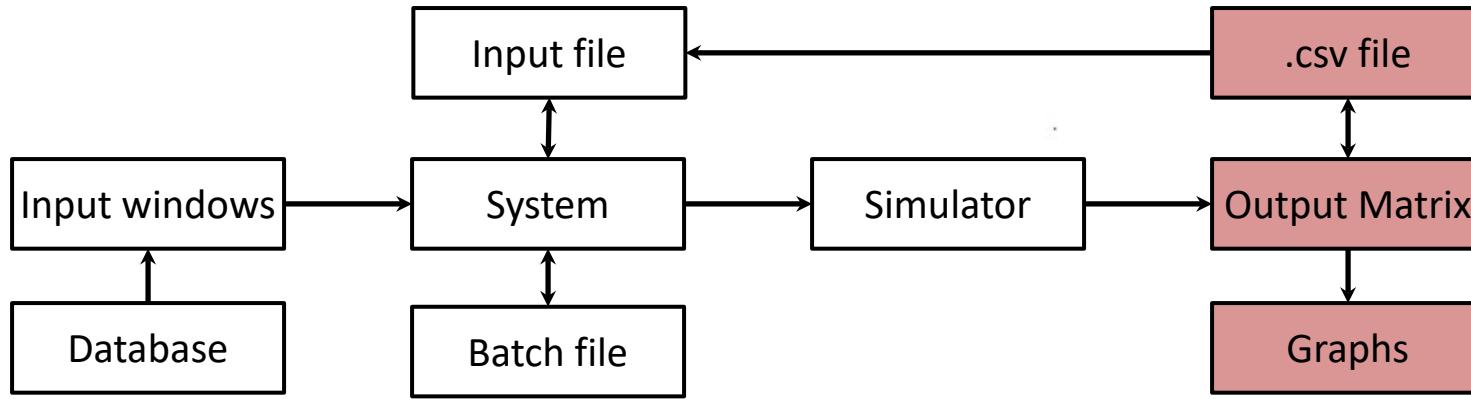


Input case processing



Batch multi-core processing

CapSim – Output



TCDD_4%_kinetic_sorption - Microsoft Excel

	A	B	C	D	E	F	G	H	I	J
1	CapSim	3.8								
2										
3	Output ty	Regular								
4										
5	System Units									
6	Length:	cm								
7	Concentr:	ug/L								
8	Time:	yr								
9	Diffusivity:	cm ² /s								
10										
11	Chemicals	1								
12	Name	TCDD	Formula	MW	Temperat	Dw	cm ² *log[Koc]/log[Kow]	Reference		
13										
14										
15	Matrices	11								
16	Name		Compon	Porosity	Bulk dens	foc				
17	Activated	1	0.6	0.4	1					
18	Sand	1	0.5	1.25	0.001					
19	Sediment	1	0.5	1.25	0.051					
20	Organocla	1	0.5	1	0.2					
21	Sed 0-2 ft	1	0.5	1.25	0.072					
22	Topsoil	1	0.5	1.25	0.05					
23	SED 0-0.5	1	0.5	1.25	0.071					
24	SED 0.5-2	1	0.5	1.25	0.073					
25	Sand-1%G	2	0.5	1.224	0.011					
26	Sand-2%G	2	0.51	1.199	0.021					

Temporal profiles

.csv output file

Example 1 - Chemical & Solid Matrix



- Design a capping layer for contaminated sediment

Chemical properties

CAP SIM CapSim 4.0

Please provide the following chemical properties:

Name:	DDx
Formula:	DDx
Molecular weight:	330.85
Reference:	AvgCapSim
Type:	Solute
Diffusivity in water:	5.19e-6 cm ² /s
OC partition coefficient:	6.2 log(L/kg)
DOC partition coefficient:	5.12 log(L/kg)

Solid matrix properties

CAP SIM CapSim 4.0

Please provides the following information about the mixture:

Name	Properties	Porosity	Bulk density g/cm ³	Particle size mm	Permeability cm ²	Organic carbon fraction
Sand-1%GAC	Linear sums	0.408	1.544	0.2116	1e-7	0.01099
Component	Weight fraction					
Delete	Activated Carbon	0.01	0.6	0.4	0.5	1e-7
Delete	Sand	0.99	0.4	1.59	0.2	1e-7
	Load components					
	Add components					
	OK					
	Cancel					

Bioturbation

Hyporheic exchange

Groundwater upwelling



Example 1 – Sorption & Layer

Sorption
– partitioning of chemicals in matrices

CAP SIM CapSim 4.0

Please provide the following sorption properties:

Matrix: UL Sediment

Chemical: DDX

Sorption isotherm: Linear-Kocfoc

Sorption kinetics: Equilibrium

Isotherm equation: $q = K_{oc}f_{oc}C$

Organic carbon partition coefficient K_{oc} : 6.2 log(L/kg)

Organic carbon fraction f_{oc} : 0.043

OK Cancel

Layer properties
- tortuosity/dispersivity/DOC

CAP SIM CapSim 4.0

Please input the following information about the layer properties:

Layer: Layer 2

Material: Sand-1%GAC

Tortuosity correction: Millington & Quirk

Thickness defined by: Activated Carbon loading

Dispersivity type: Length

Thickness: 25.9 cm

Hydrodynamic dispersivity: 1.0 cm

DOC concentration: 46.0 mg/L

Matrix component Loading (g/cm²)

Activated Carbon 0.4

Sand 39.6

OK Cancel



Example 1 – Solver Parameters

Multi-layered system

CAP SIM CapSim 4.0

Starting with the layer nearest the overlying water, please provide the following information for each layer:

	Name	Material	Tortuosity Correction	Thickness	Hydrodynamic Dispersivity	Dissolved organic matter concentration
Edit	Layer 1	Armor-SED	Millington & Quirk	15.24	1.0	46.0
Edit	Layer 2	Sand-1%GAC	Millington & Quirk	7.62	1.0	46.0
Edit	Layer 3	ULSediment	Boudreau	60.96	1.0	46.0

Add layers
OK

Discretization option

CAP SIM CapSim 4.0

Please specify the grid and time step options for the system:

Grid option:	User-defined	Total number of grids:	110		
Time step option:	User-defined	Time step size (yr):	0.1		
Layer	Thickness cm	Number of grids	Grid size cm	Max Pecllet number	CFL Time Step yr
Layer 1	15.24	20	0.762	0.72	0.576
Layer 2	7.62	10	0.762	0.72	35.721
Layer 3	60.96	80	0.762	0.71	1.64

Update
OK
Cancel

CAP SIM CapSim 4.0

Please specify the simulation options for the system:

Simulation duration (yr):	250.0
Steps in output files:	250
Usage of CPU cores (Max 32):	1
Time step options:	Implicit
Track mass options:	Track
Discretization options:	Specify manually
Number of grid points:	70
Time step (yr):	0.1
Error tolerance(%):	0.001

OK



Example 1 – Auxiliary Conditions

Boundary conditions

- Concentration/Flux/Mass transfer

CapSim 4.0

Please select the benthic boundary condition type:

Type: Mass transfer

Water DOC: 0.0 mg/L

Deposition settling velocity: 0.0 cm/yr

Chemical	Water concentration µg/L	Mass transfer coefficient cm/yr
<input checked="" type="checkbox"/> DDX	0.0	14600.0
<input checked="" type="checkbox"/> Dieldrin	0.0	17400.0
<input checked="" type="checkbox"/> HPAH	0.0	12700.0
<input type="checkbox"/> LPAH	N/A	N/A
<input type="checkbox"/> PCB	N/A	N/A
<input checked="" type="checkbox"/> TCDD	0.0	18900.0

Estimate coefficient

Select All

Unselect All

OK

Cancel

Initial conditions

- Uniform/Depth-dependent

CapSim 4.0

Please input the initial information for the compound:

Layer: Layer 1

Thickness(cm): 30.0

Profile: Linear

Input option: Equilibrium

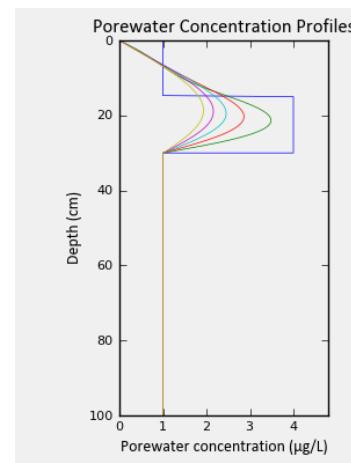
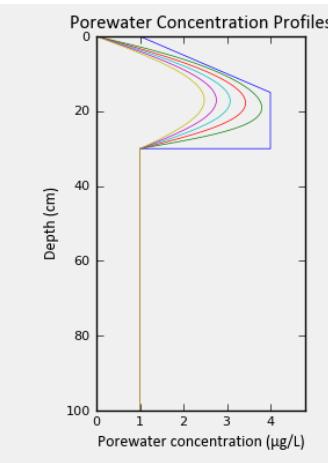
Initial concentrations of Benzo(a)pyrene in porewater (µg/L) and solid components (µg/kg)

Depth (cm)	Input phase	Porewater	Sand
0.0	Sand	1.0	10.0
15.0	Sand	1.0	10.0
15.0	Porewater	4.0	40.0
30.0	Porewater	4.0	40.0

Add depth

OK

Cancel





Example 1 – Sediment Processes

CapSim 4.0

Please provide the information of the following system properties:

Upwelling groundwater flow: Steady flow

Darcy velocity: 940 cm/yr

Modeling hyporheic exchange: Depth-dependent

Friction velocity: 0 m/s

Modeling erosion: Constant erosion rate

Erosion rate: 0 cm/yr

Modeling bioturbation: Depth-dependent

Particle size impact:

Gaussian model coefficient: 0 cm

Particle biodiffusion coefficient: 0 cm²/yr

Pore water biodiffusion coefficient: 0 cm²/yr

Modeling consolidation: Consolidation

Maximum consolidation depth: 0 cm

Time to 90% consolidation: 0 yr

Modeling ionic activity: None

Biotic reaction model: Threshold concentration

OK

Groundwater upwelling

Darcy's Law

CapSim 4.0

Calculate the Darcy velocity:

Darcy's law: $U = -k \Delta h g / v / (z_2 - z_1)$

Darcy's velocity (U): 0.0 cm/yr

Kinematic viscosity (v): 1e-6 m²/s

Depth 1 (z₁): 0.0 cm

Depth 2 (z₂): 100.0 cm

Water head drop (Δh): 0.0 cm

Layer	Permeability (k)	Thickness
	cm ²	cm
Layer 1	1e-7	30.0
Layer 2	1e-7	15.0
Layer 3	1e-7	55.0

Calculate velocity

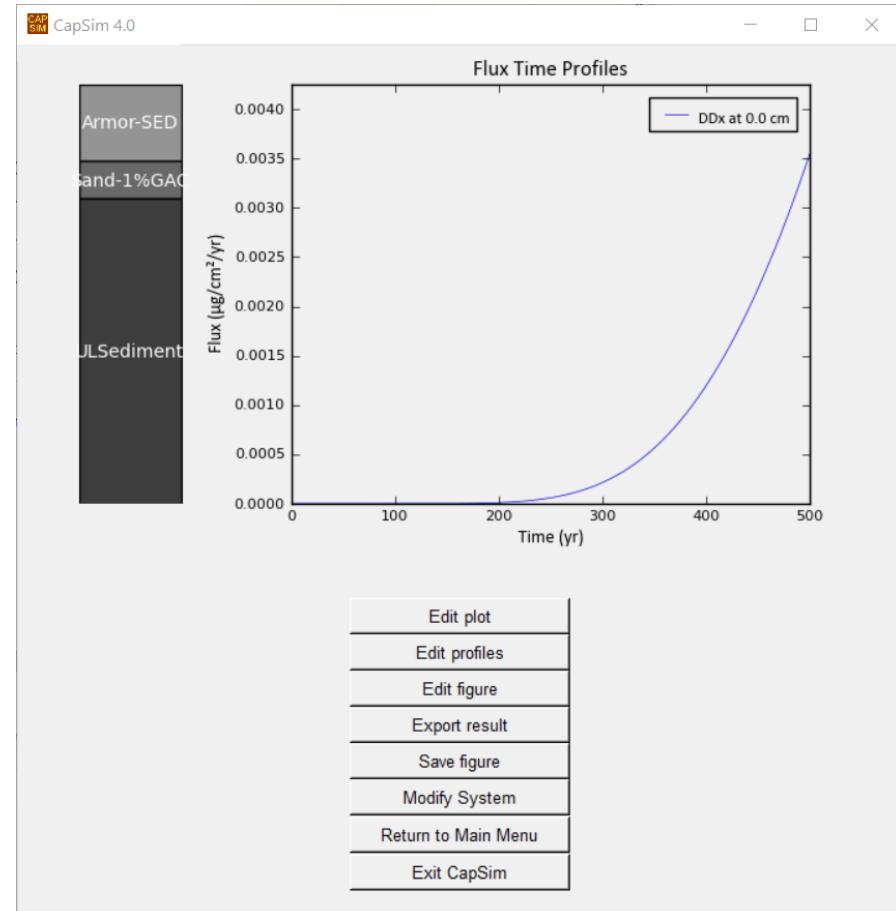
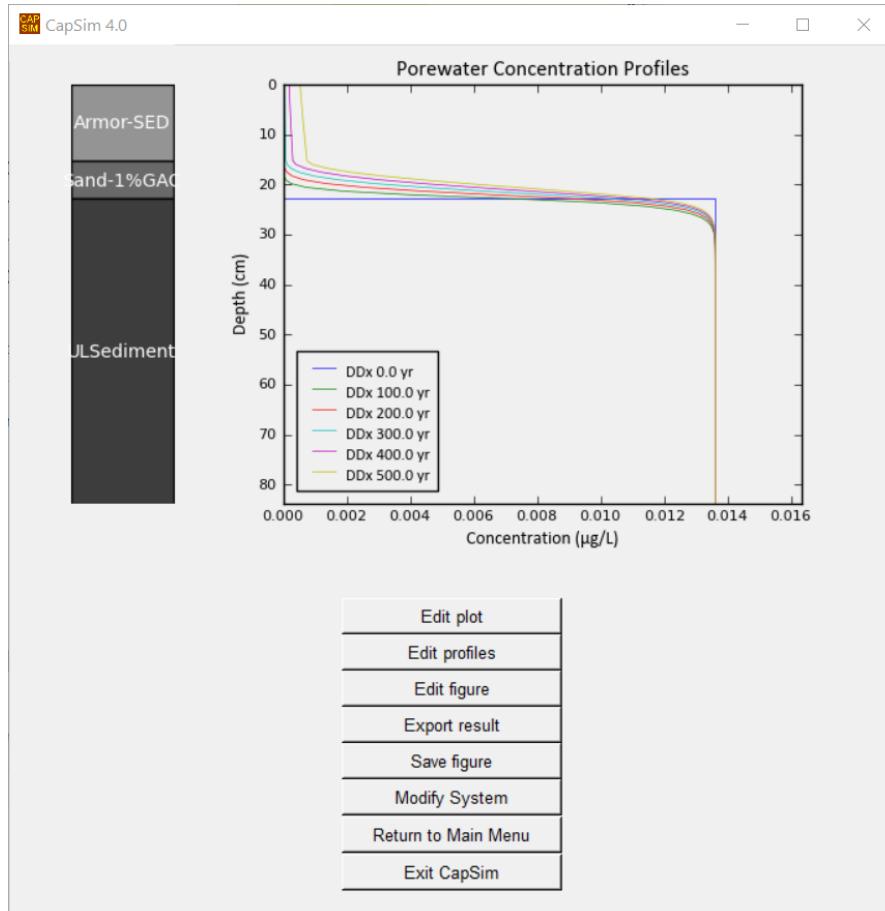
OK

Cancel



Example 1 – Baseline Results

3-layer system – DDx contaminated sediment remediated by 1% GAC



Hyporheic Exchange

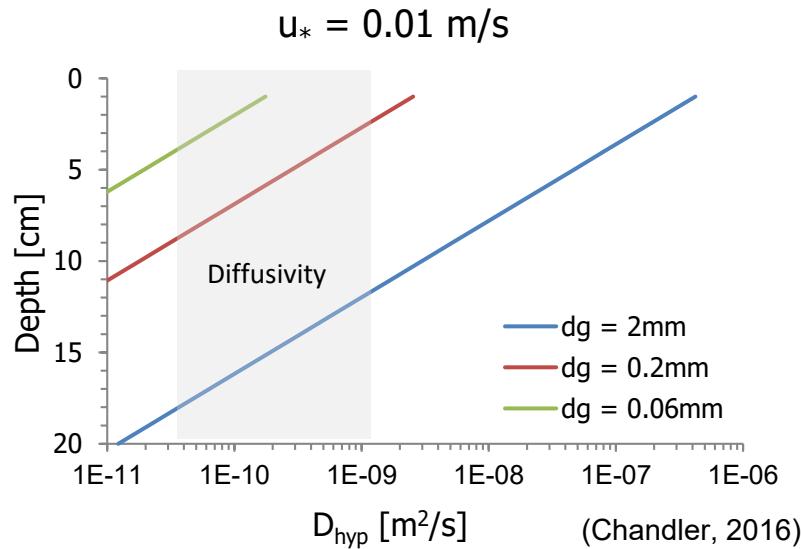
- 1-D Hyporheic exchange

$$F_{hyp,n} = -D_{hyp} \frac{\partial(C_n + \rho_{DOC,i} q_{DOC,n})}{\partial z}$$

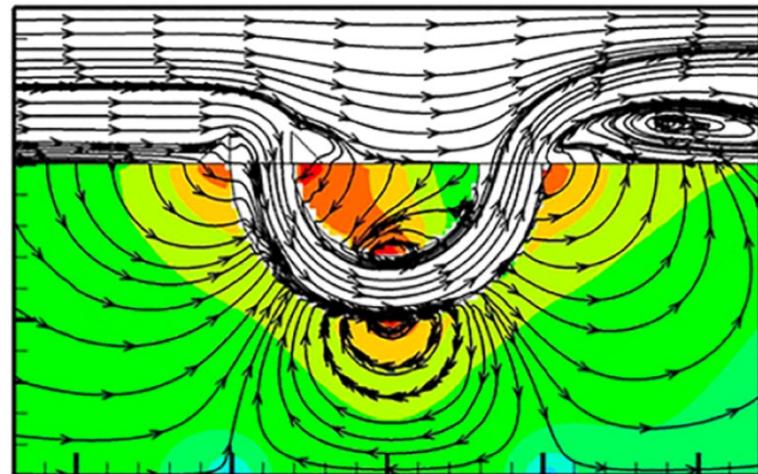
$$D_{hyp} = 1.19 * 10^{-6} d_g^{2.22} u_*^{3.11} e^{-55y}$$

y : Depth [m] d_g : Particle size [m]

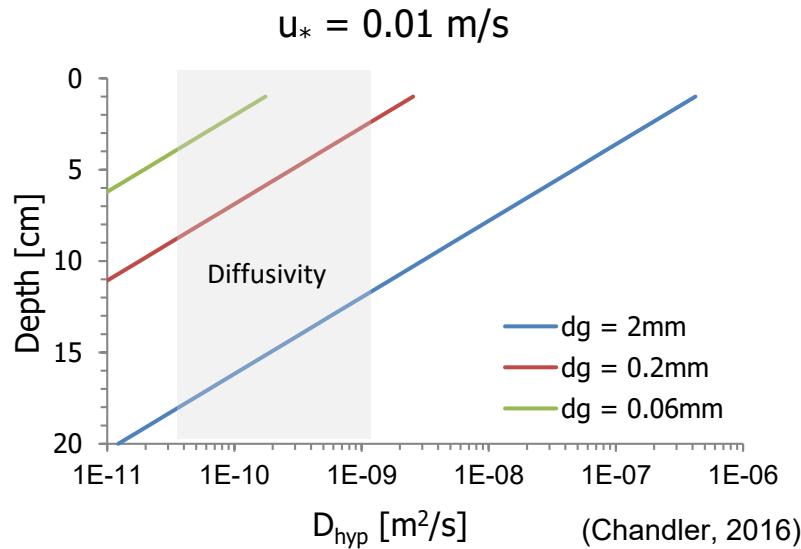
u_* : Friction velocity [m/s]



(Chandler, 2016)



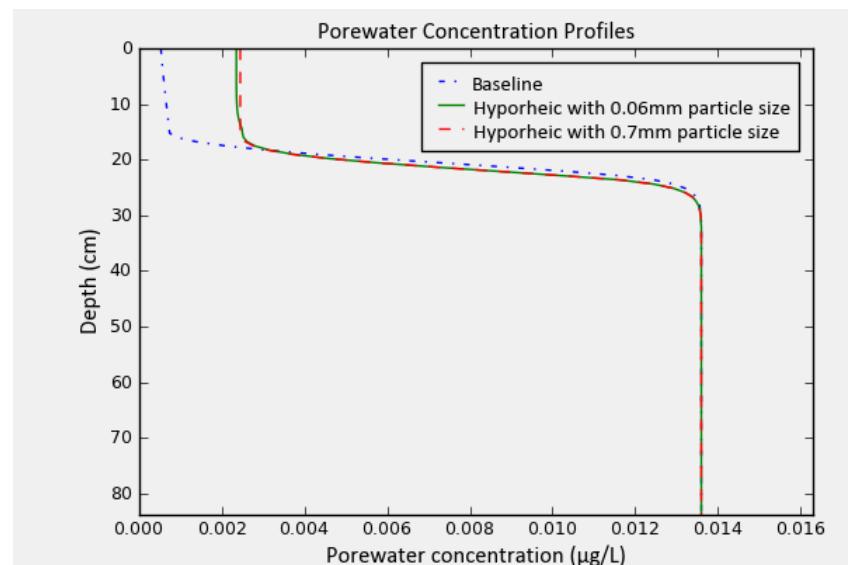
(Liu, 2019)



$u_* = 0.01 \text{ m/s}$

Diffusivity

- $d_g = 2\text{mm}$
- $d_g = 0.2\text{mm}$
- $d_g = 0.06\text{mm}$



Bioturbation

- Mixing particles and porewater**

$$F_{bio,n} = -D_{bio,p} \sum_m \rho_{b,m} \frac{\partial \phi_m q_{m,n}}{\partial z} - D_{bio,pw} \frac{\partial (c_n + \rho_{DOC,i} q_{DOC,n})}{\partial z}$$

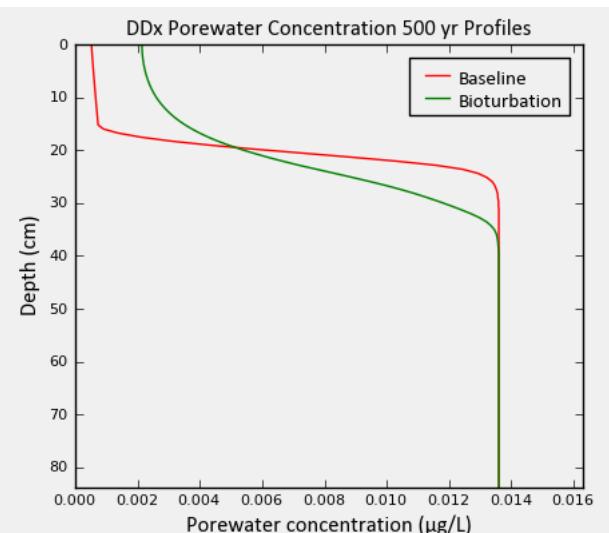
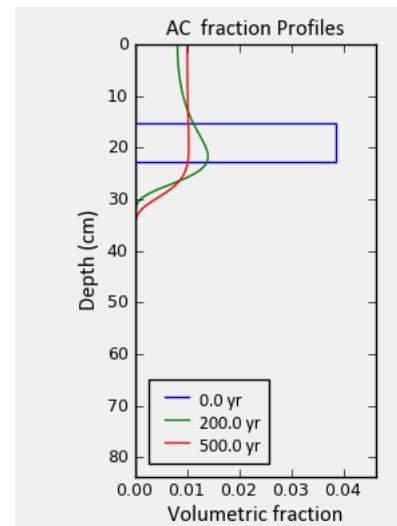
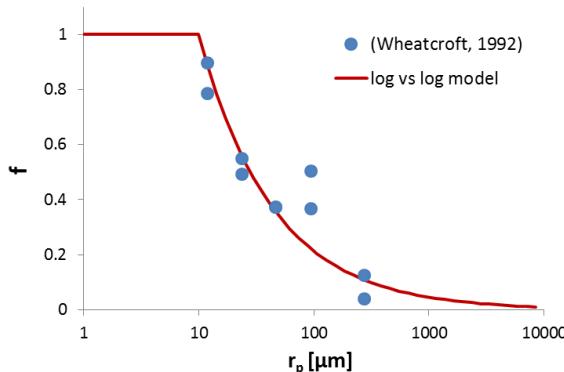
- Factors on biodiffusion coefficient**

- Depth from benthic surface (z)

$$D_{bio,p} = D_{bio,p,0} * \exp\left(-\frac{z^2}{2\sigma^2}\right)$$

$$D_{bio,p,0} = 1 \text{ cm}^2/\text{yr} \quad \sigma = 10 \text{ cm}$$

- Particle size (r_p)

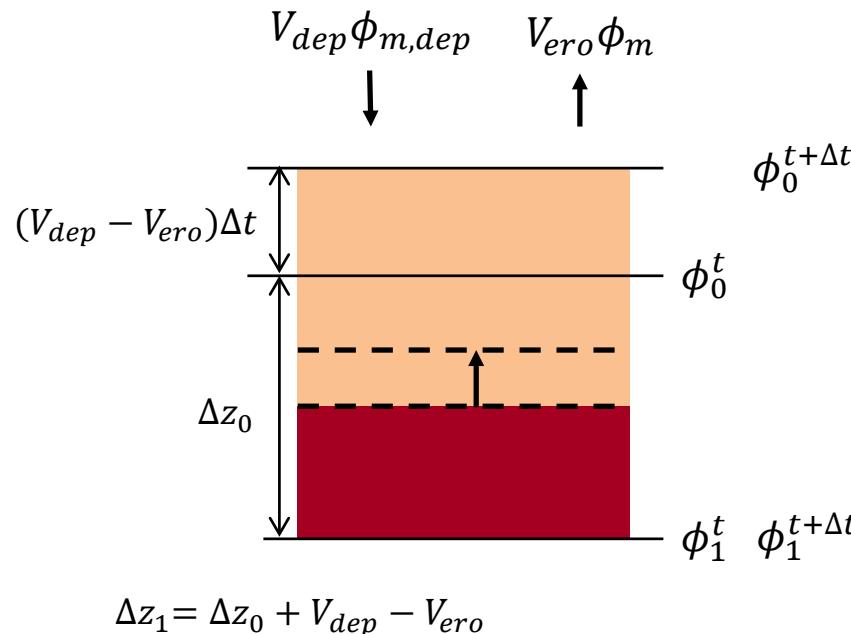




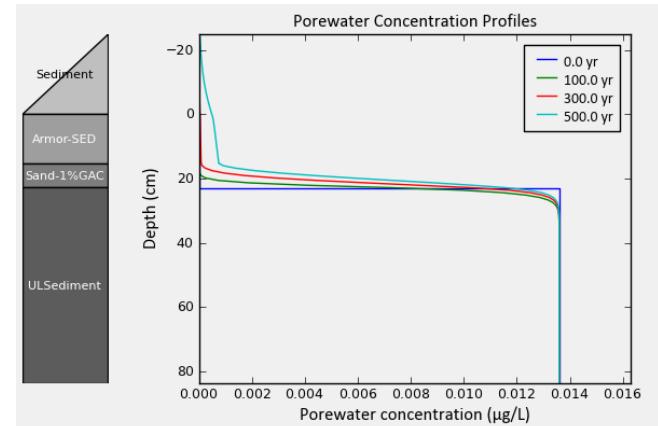
Deposition and Erosion

- 1-D mass conservation at benthic boundary

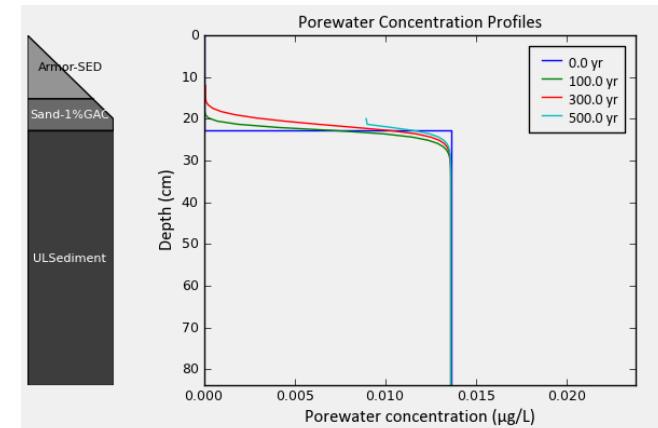
$$\frac{\Delta z_1 \phi_0^{t+\Delta t} - \Delta z_0 \phi_0^t}{2\Delta t} = V_{dep} \phi_{m,dep} - V_{ero} \phi_m^t - D_{bio,p} \frac{\phi_1^{t+\Delta t} - \phi_0^{t+\Delta t}}{\Delta z_1} - \frac{V_{dep} - V_{ero}}{2} \phi_0^{t+\Delta t}$$



0.04 cm/yr
deposition



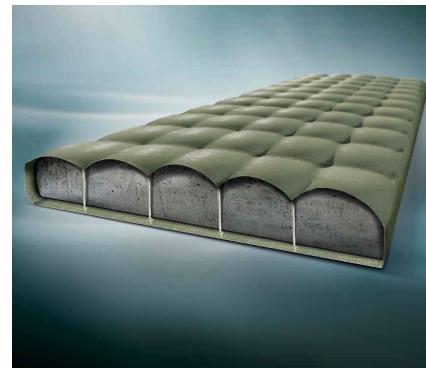
0.04 cm/yr
erosion





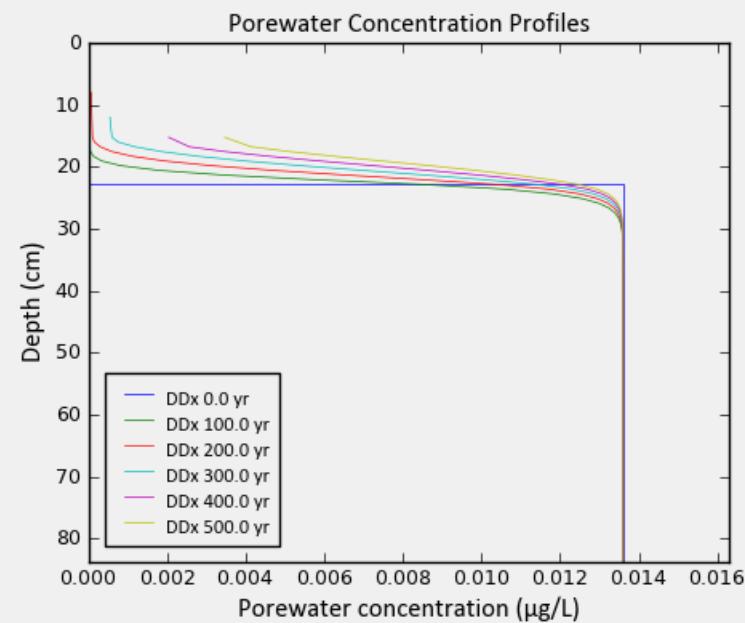
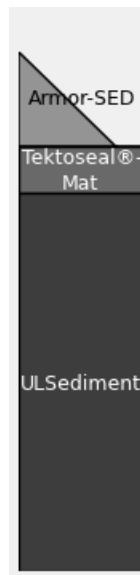
Commercial Sorbents

Matrix	Porosity	Bulk density g/cm ³	Particle size mm	Permeability cm ²	Organic carbon fraction
Aquagate®	0.526	1.031	0.2773	1e-7	0.1009
RCM®-AC	0.538	0.7692	12.5	2.241e-7	0.2
RCM®-OC	0.5	1.0	13.82	2.639e-7	0.062
Sedimite®	0.576	0.6061	0.4273	1e-7	0.5005
Tektoseal®-AC	0.549	0.7042	10.39	1.839e-7	0.28
Tektoseal®-OC	0.5	1.0	12.22	2.217e-7	0.078
Tektoseal®-Mat	0.5	1.0	18.01	5.263e-7	0.001



Tektoseal® Active Mattress

Mat-like sorbents are not impacted by bioturbation and erosion





Example 2 – Naphthalene NAPL

■ Non-aqueous phase liquid (NAPL)

- Immobile stock of organic contaminants
- Modeled using precipitation/dissolution
- Keep pw concentration at solubility until the depletion of NAPL

Please provide the following chemical properties:							
	Chemical name	Formula	Molecular Weight	Phase	Diffusivity in water cm²/s	OC partition coefficient log(L/kg)	DOC partition coefficient log(L/kg)
Edit	Delete	Naphthalene	Nap	128	Solute	7.5e-6	2.79
Edit	Delete	Nap_NAPL	Nap_NAPL	128	Solid	Not applicable	Not applicable
<input type="button" value="Add new chemicals"/> <input type="button" value="Import from database"/> <input type="button" value="Import from files"/> <input type="button" value="OK"/>							

Log molar Solubility

Please input the kinetic processes in the system:					
	Number	Name	Type	Chemical equation	Rate equation
Edit	Delete	1	Nap_precipitation	Precipitation	$\text{Nap} \Rightarrow \text{Nap_NAPL}$
Edit	Delete	2	NAPL_dissolution	Dissolution	$\text{Nap_NAPL} \Rightarrow \text{Nap}$
<input type="button" value="Add reactions"/> <input type="button" value="OK"/>					

Please input the models and coefficients of each chemical in the reaction					
Chemical	Formula	Model	Rate index	Equi index	
Naphthalene	Nap	Power	0.0	1.0	
Nap_NAPL	Nap_NAPL	Excluded			
<input type="button" value="OK"/>					

Log K: -0.993

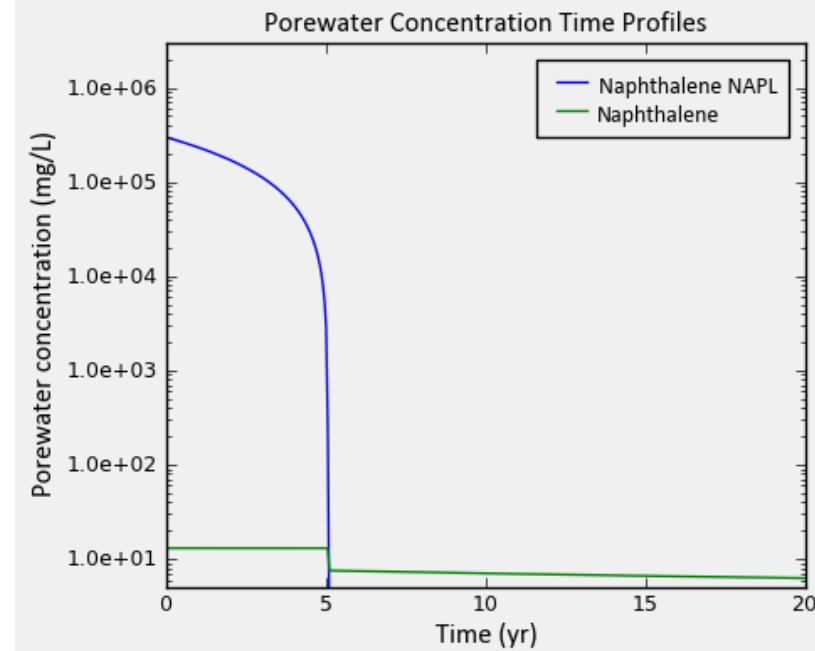
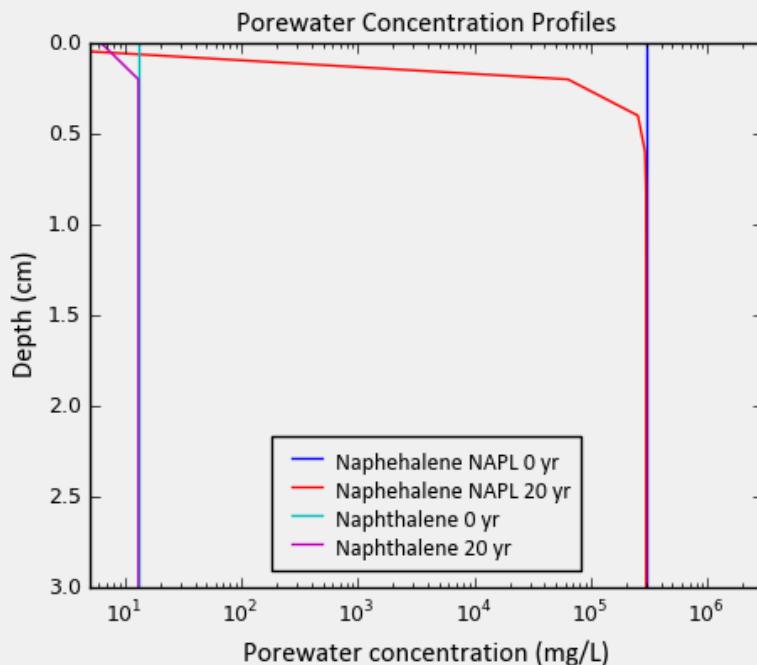


Example 2 – Naphthalene NAPL

Layer	Reaction	Chemical equation	Rate equation	Coefficient
Layer 1	Edit Delete Nap_precipitation	$C_{10}H_8 \rightleftharpoons \text{Chem 1}$	$r_{1,1} = \lambda_{1,1}$	$\lambda_{1,1} = 1e+4 \text{ (mmol/L)yr}^{-1}$
	Edit Delete NAPL_dissolution	$\text{Chem 1} \rightleftharpoons C_{10}H_8$	$r_{2,1} = \lambda_{2,1}C_{\text{Chem 1}}$	$\lambda_{2,1} = 1e+4 \text{ yr}^{-1}$

Local equilibrium by fast precipitation/dissolution

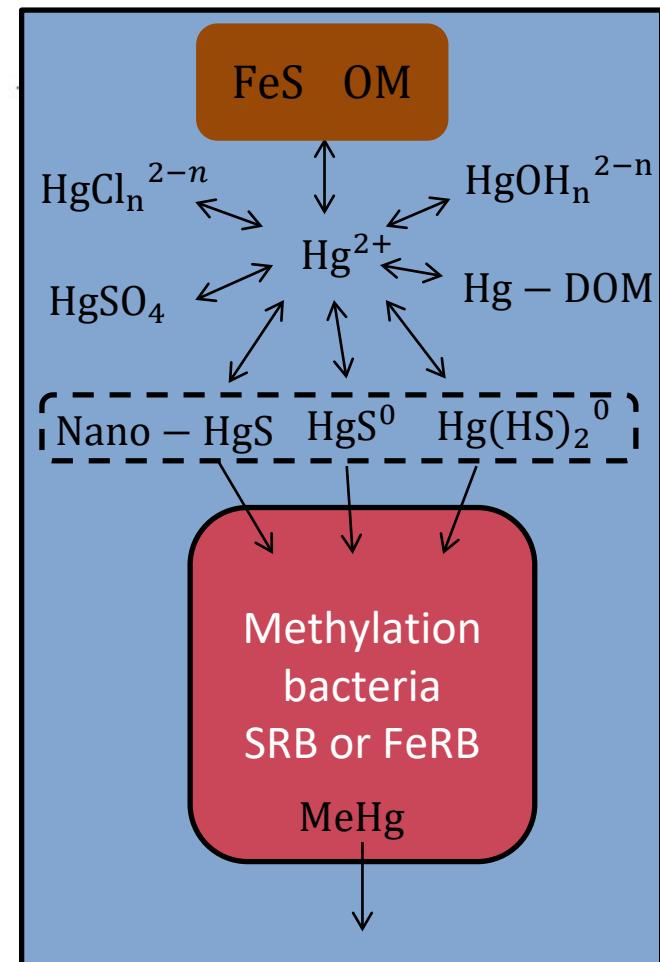
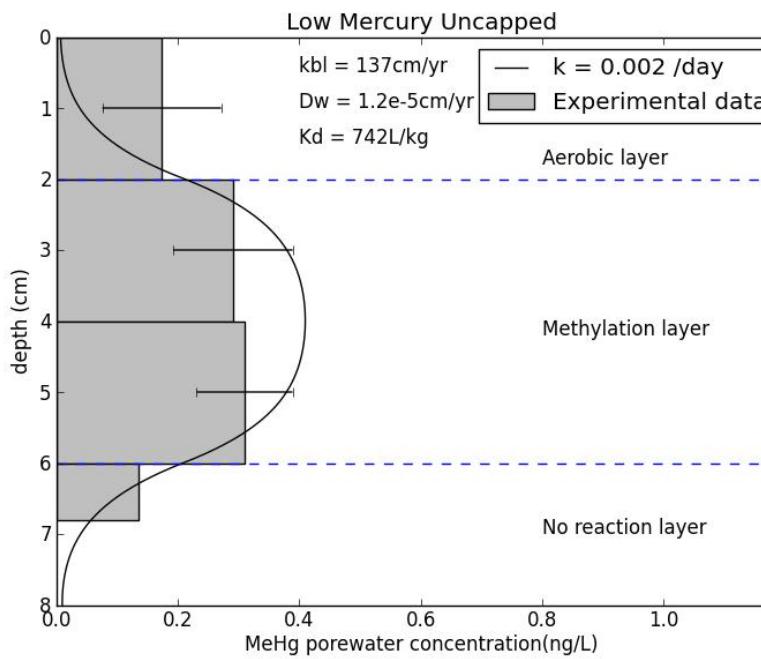
Solubility of Naphthalene: 13 mg/L



Example 3 – Hg Methylation

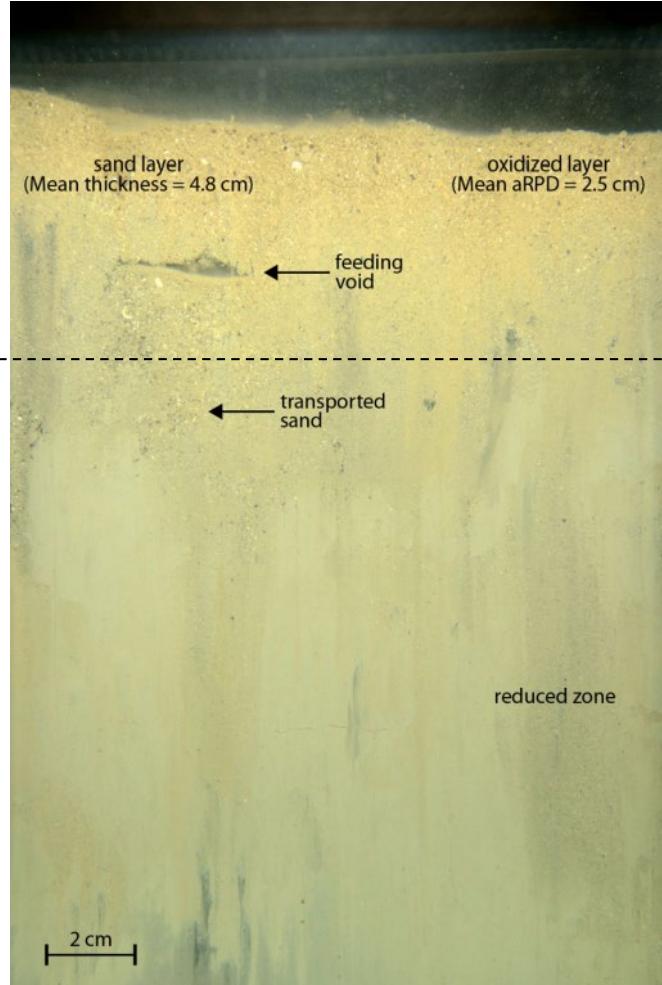
▪ Methylmercury (MeHg)

- Toxic species of Hg
- Byproduct of sulfate reduction/iron reduction
- Primarily produced in anaerobic zones

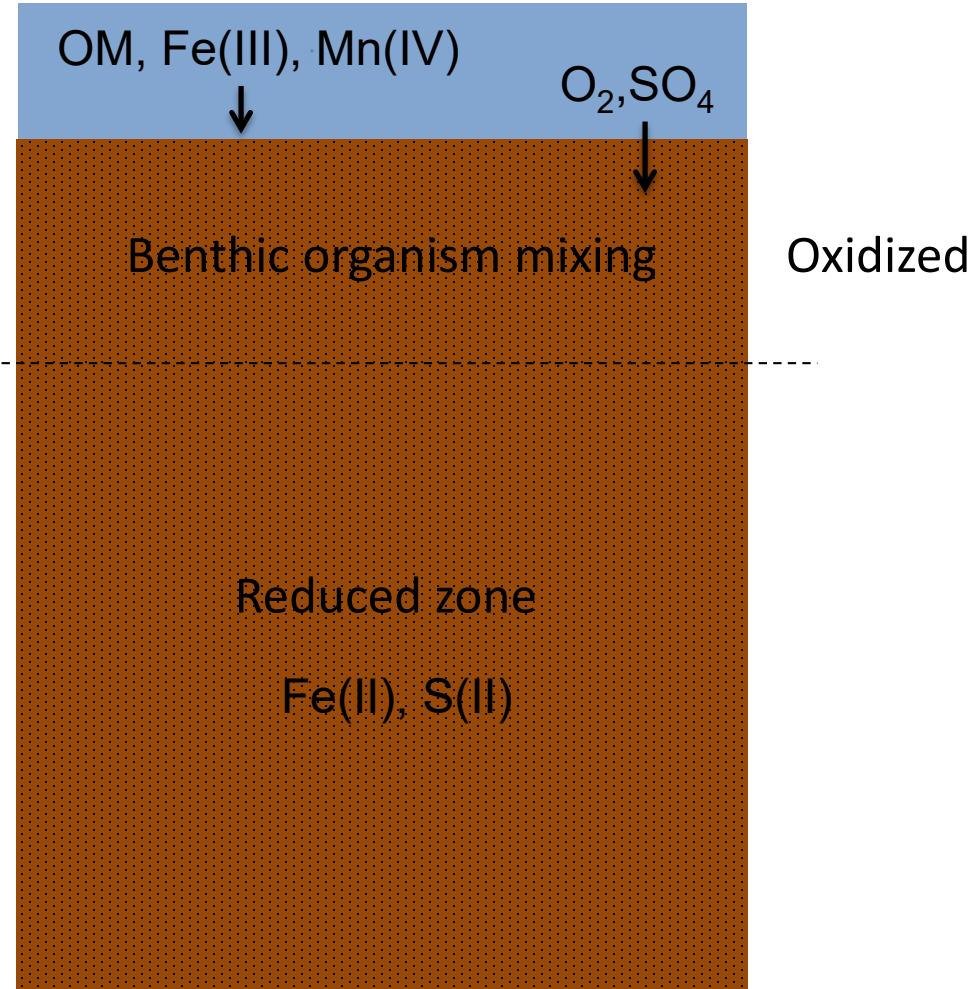




Redox Profile in Sediment



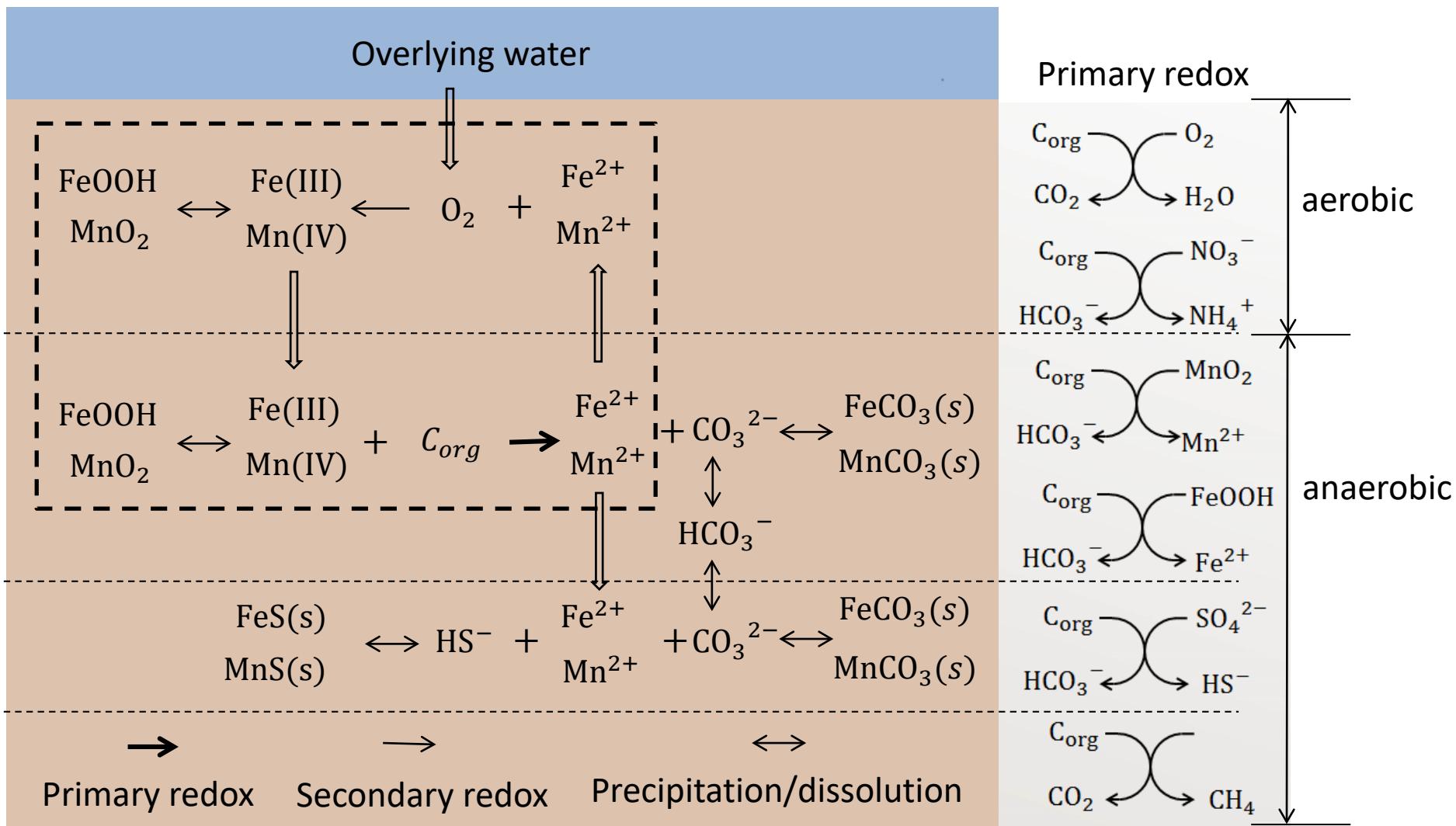
Sediment profile imaging (SPI)



Conceptual model



Biogeochemical Reaction Network





Secondary and Equilibrium Reactions

$$\frac{\partial q_{n,i}}{\partial t} = -\frac{\partial F_{n,i}}{\partial z} + \sum_l \alpha_{l,n} rxn_{l,i}$$

i : Layer number
 n : Chemical number
 m : Solid matrix number
 l : Reaction number

Reactions $\sum_l \alpha_{l,n} rxn_{l,i}$

■ Secondary redox reactions

- Kinetic model

■ Equilibrium reactions

- Water chemistry/Complexation
- Precipitation/Dissolution

Precipitation/Dissolution	Reaction rate
$\text{FeS} + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{HS}^-$	$r = k_{\text{FeSd}} C_{\text{FeS}} (1 - (C_{\text{Fe}^{2+}} C_{\text{H}^+}) / (K_{\text{FeS}} C_{\text{FeS}}))$
$\text{Fe}^{2+} + \text{HS}^- \rightarrow \text{FeS} + \text{H}^+$	$r = k_{\text{FeSp}} ((C_{\text{Fe}^{2+}} C_{\text{H}^+}) / (K_{\text{FeS}} C_{\text{FeS}}) - 1)$

Second redox reaction	Reaction rate
$\text{Mn}^{2+} + 0.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}^+$	$r = k_{\text{MnO}} C_{\text{Mn}^{2+}} C_{\text{O}_2}$
$\text{Fe}^{2+} + 0.25\text{O}_2 + 2.5\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(\text{s}) + 2\text{H}^+$	$r = k_{\text{FeO}} C_{\text{Fe}^{2+}} C_{\text{O}_2}$
$\text{HS}^- + 2\text{O}_2 \rightarrow \text{H}^+ + \text{SO}_4^{2-}$	$r = k_{\text{SO}} C_{\text{HS}^-} C_{\text{O}_2}$
$\text{MnO}_2 + 2\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 2\text{Fe(OH)}_3(\text{s}) + 2\text{H}^+$	$r = k_{\text{SO}} C_{\text{HS}^-} C_{\text{O}_2}$

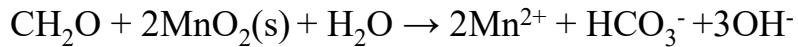
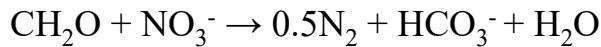
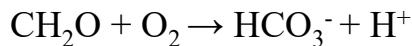
Complexation reaction	Log K _L
$\{\text{Fe}^{2+}\} + \{\text{OH}^-\} = \{\text{Fe(OH)}^+\}$	4.5
$\{\text{Fe}^{2+}\} + 2\{\text{OH}^-\} = \{\text{Fe(OH)}_2\}$	7.4
$\{\text{Fe}^{2+}\} + 3\{\text{OH}^-\} = \{\text{Fe(OH)}_3^-\}$	11.0
$\{\text{Fe}^{2+}\} + \{\text{SO}_4^{2-}\} = \{\text{Fe(SO}_4\}\}$	2.2



Biotic Reactions

Preference

Primary redox reaction



■ Biotic reaction model

– Threshold concentration ($T_{EA,l}$)

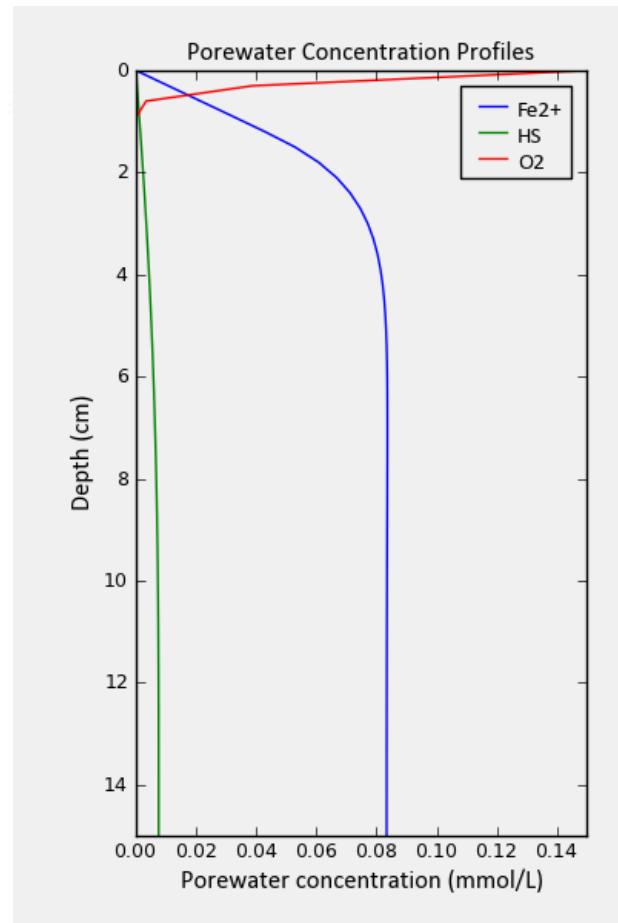
if $C_{EA,l-1} > T_{EA,l-1}$: $R_l = 0$

if $C_{EA,l-1} \leq T_{EA,l-1}$: $R_l = \lambda_l \frac{C_{OM}}{C_{OM} + K_{OM}} \frac{C_{EA,l}}{C_{EA,l} + K_{EA,l}}$

– Inhibition constant

$$R_L = \lambda_L C_{OM} \frac{C_{EA,L}}{C_{EA,L} + K_{EA,L}} \prod_{l=1}^{L-1} \frac{K_{in,l}}{C_{in,l} + K_{in,l}}$$

$$r_{IR} = \lambda_{OM} C_{OM} \frac{C_{\text{Fe(OH)}_3}}{K_{m,S} + C_{\text{Fe(OH)}_3}} \frac{K_{in,O_2}}{K_{in,O_2} + C_{O_2}} \frac{K_{in,NO_3}}{K_{in,NO_3} + C_{NO_3}}$$





Biotic Reactions

Reaction editor

CapSim 4.0

Please input the following information for the added kinetic process:

Name:	Mn(IV) reduction	Kinetic model:	Biotic	Rate equation: $r = \lambda C_{OC} C_{MnO_2} / (K_{MnO_2} + C_{MnO_2}) f_{in}$	
Reactants		Products			
Stoichiometric coefficient	Chemical	Formula	Stoichiometric coefficient	Chemical	Formula
<input type="button" value="Delete"/>	1.0	OC	1.0	HCO ₃ ⁻	HCO ₃ ⁻
<input type="button" value="Delete"/>	1.0	MnO ₂	2.0	Mn	Mn ²⁺
			3.0	OH-	OH ⁻
<input type="button" value="Delete"/>					
<input type="button" value="Add reactant"/> <input type="button" value="Add product"/> <input type="button" value="OK"/> <input type="button" value="Cancel"/>					

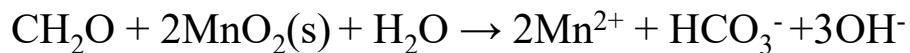
CapSim 4.0

Please input the following information

Electron donor:	OC			
Electron acceptor:	MnO ₂			
Favorable after:	O ₂			
Inhibition constant K:	1e-8 mol/L			
Rate equation: $r = \lambda C_{OC} C_{MnO_2} / (K_{MnO_2} + C_{MnO_2}) f_{O_2}$				
Chemical	Formula	Model	Coefficient	Unit
OC	OC	Power	1.0	
MnO ₂	MnO ₂	Monod	0.016	mol/L
<input type="button" value="OK"/>				

$K_{in,Mn(OH)_2}$

$K_{Mn(OH)_2}$



$$r = \lambda_{OM} C_{OM} \frac{C_{Mn(OH)_2}}{K_{Mn(OH)_2} + C_{Mn(OH)_2}} \frac{K_{in,O_2}}{K_{in,O_2} + C_{O_2}}$$



Example 3 – Hg Methylation

$$r = (k_{SR,\text{meth}} r_{SR} + k_{IR,\text{meth}} r_{IR}) C_{THg}$$

$$r_{IR} = k_{OM} C_{CH_2O} \frac{C_{Fe(OH)_3}}{K_{m,Fe} + C_{Fe(OH)_3}} \frac{K_{in,O_2}}{K_{in,O_2} + C_{O_2}} \frac{K_{in,Mn}}{K_{in,Mn} + C_{MnO_2}}$$

$$r_{SR} = k_{OM} C_{CH_2O} \frac{C_{SO_4}}{K_{m,S} + C_{SO_4}} \frac{K_{in,O_2}}{K_{in,O_2} + C_{O_2}} \frac{K_{in,Mn}}{K_{in,Mn} + C_{MnO_2}} \frac{K_{in,Fe}}{K_{in,Fe} + C_{Fe(OH)_3}}$$

Number	Name	Type	Chemical equation	Rate equation
1	Aerobic respiration	Biotic	$O_2 + OC \Rightarrow H^+ + HCO_3^-$	$r_1 = \lambda_1 C_{O_2} / (K_{O_2} + C_{O_2}) C_{OC} \Pi(f_{in})$
2	Mn(IV) reduction	Biotic	$OC + MnO_2 \Rightarrow HCO_3^- + 2Mn^{2+} + 3OH^-$	$r_2 = \lambda_2 C_{OC} C_{MnO_2} / (K_{MnO_2} + C_{MnO_2}) \Pi(f_{in})$
3	IR_methylation	Biotic	$0Fe(OH)_3 + OOC + IR + Hg^{2+} \Rightarrow HgCH_3$	$r_3 = \lambda_3 C_{Fe(OH)_3} / (K_{Fe(OH)_3} + C_{Fe(OH)_3}) C_{OOC} C_{Hg^{2+}} \Pi(f_{in})$
4	Fe(III) reduction	Biotic	$OC + 4Fe(OH)_3 \Rightarrow 4Fe^{2+} + HCO_3^- + 7OH^-$	$r_4 = \lambda_4 C_{OC} C_{Fe(OH)_3} / (K_{Fe(OH)_3} + C_{Fe(OH)_3}) \Pi(f_{in})$
5	SR_methylation	Biotic	$OSO_4^{2-} + OOC + SR + Hg^{2+} \Rightarrow HgCH_3$	$r_5 = \lambda_5 C_{SO_4^{2-}} / (K_{SO_4^{2-}} + C_{SO_4^{2-}}) C_{OC} C_{Hg^{2+}} \Pi(f_{in})$
6	S reduction	Biotic	$OC + 0.5SO_4^{2-} \Rightarrow 0.5H^+ + HCO_3^- + 0.5HS^-$	$r_6 = \lambda_6 C_{OC} C_{SO_4^{2-}} / (K_{SO_4^{2-}} + C_{SO_4^{2-}}) \Pi(f_{in})$
7	Mn oxidation	User-defined	$Mn^{2+} + 0.5O_2 \Rightarrow 2H^+ + MnO_2$	$r_7 = \lambda_7 C_{Mn^{2+}} C_{O_2}$
8	Fe oxidation	User-defined	$Fe^{2+} + 0.25O_2 \Rightarrow 2H^+ + Fe(OH)_3$	$r_8 = \lambda_8 C_{Fe^{2+}} C_{O_2}$
9	HS oxidation	User-defined	$HS^- + 2O_2 \Rightarrow H^+ + SO_4^{2-}$	$r_9 = \lambda_9 C_{HS^-} C_{O_2}$
10	S_Fe(III)_oxidation	User-defined	$HS^- + 2Fe(OH)_3 \Rightarrow 2Fe^{2+} + SO_4^{2-} + 5OH^-$	$r_{10} = \lambda_{10} C_{HS^-} C_{Fe(OH)_3}$
11	FeS precipitation	Precipitation	$Fe^{2+} + HS^- \Rightarrow H^+ + FeS$	$r_{11} = \lambda_{11} (C_{Fe^{2+}} C_{HS^-} / C_{H^+}^2 / K - 1)$
12	FeS dissolution	Dissolution	$H^+ + FeS \Rightarrow Fe^{2+} + HS^-$	$r_{12} = \lambda_{12} C_{FeS} (1 - C_{Fe^{2+}} C_{HS^-} / C_{H^+}^2 / K)$
13	Fe_Mn_oxidation	User-defined	$2Fe^{2+} + MnO_2 \Rightarrow Mn^{2+} + 2Fe(OH)_3 + 2H^+$	$r_{13} = \lambda_{13} C_{Fe^{2+}} C_{MnO_2}$
14	Demethylation	Fundamental	$HgCH_3 \Rightarrow Hg^{2+}$	$r_{14} = \lambda_{14} C_{HgCH_3}$

BCs

$$O_2 = 0.025\text{mM}$$

$$SO_4 = 0.028\text{M}$$

Deposition

$$CH_2O = 0.04\text{M}$$

$$MnO_2 = 0.01\text{mM}$$

$$Fe(OH)_3 = 0.1\text{M}$$

Initial sediment

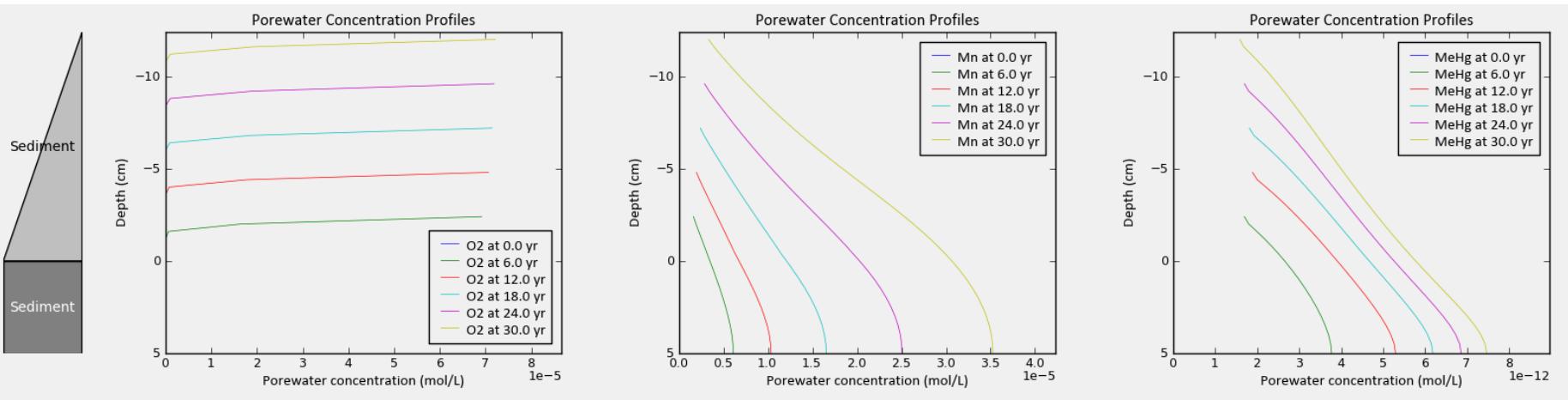
$$CH_2O = 0.04\text{M}$$

$$MnO_2 = 0.01\text{M}$$

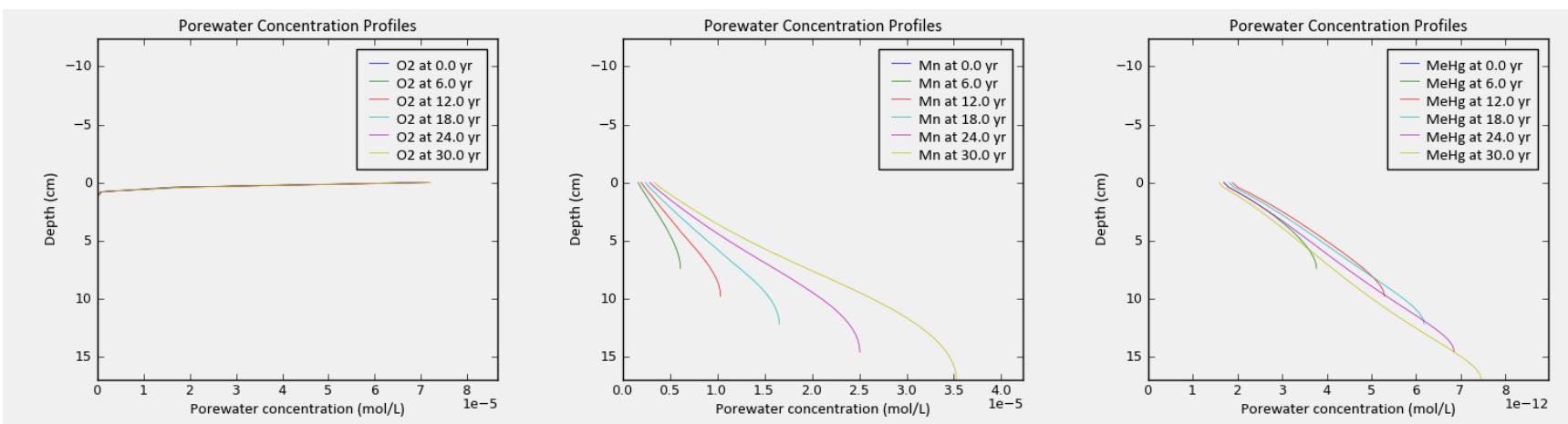
$$Fe(OH)_3 = 0.1\text{M}$$



Example 3 – CapSim Results



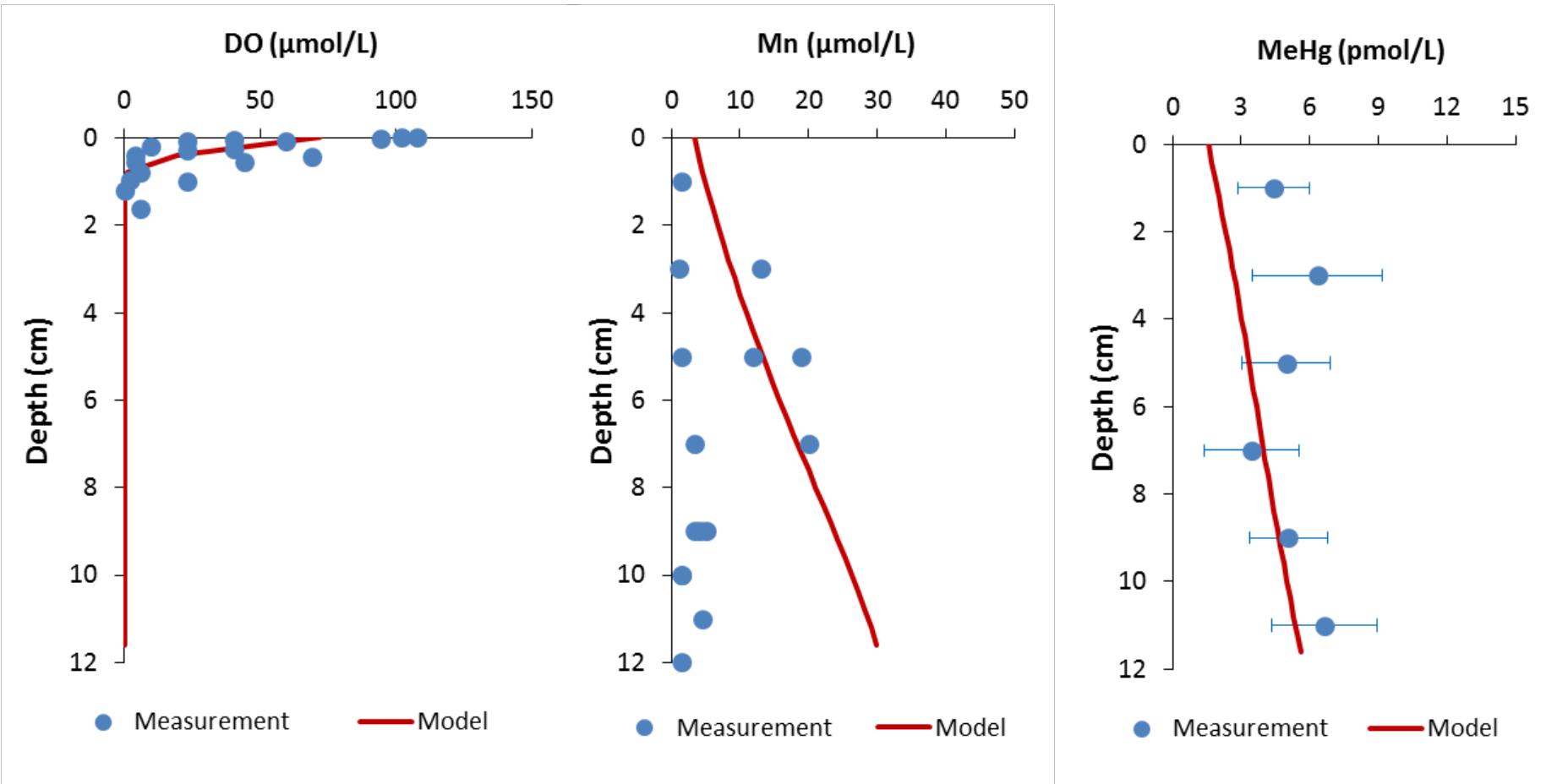
Original benthic surface



Updated benthic surface

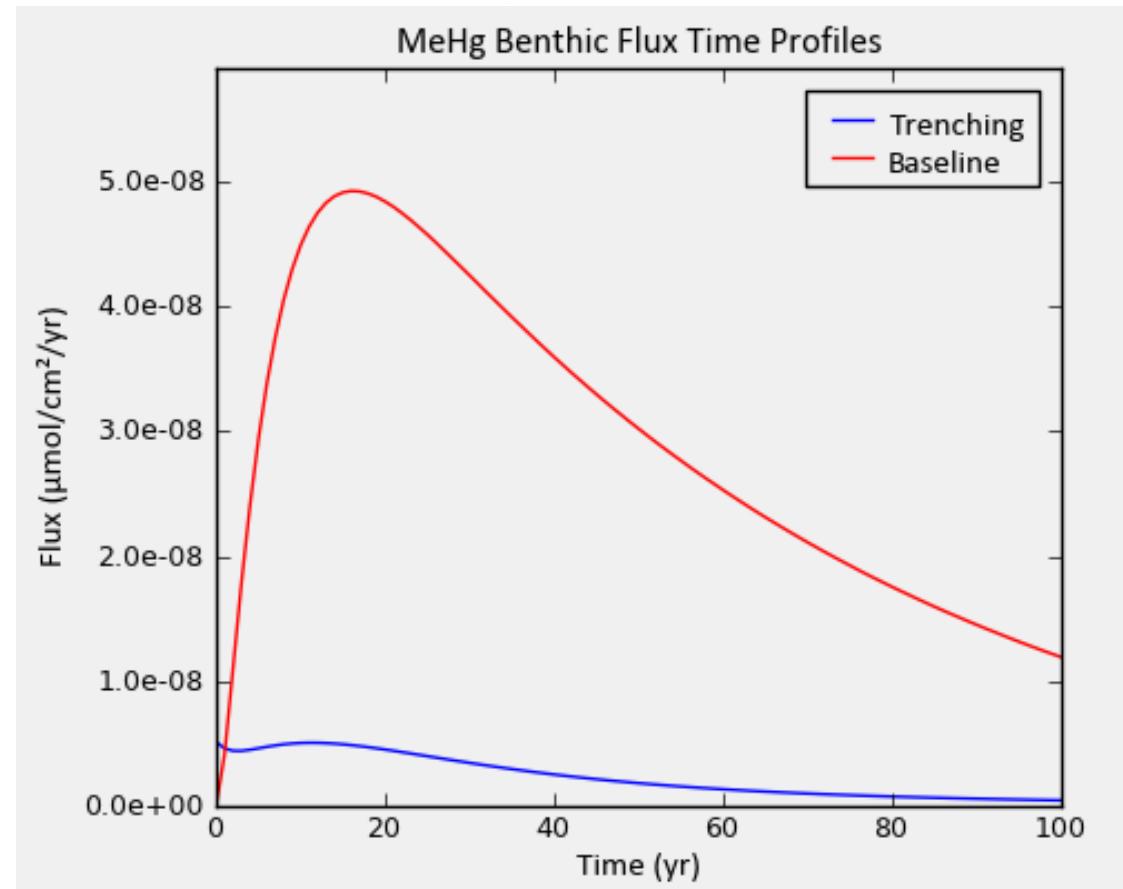
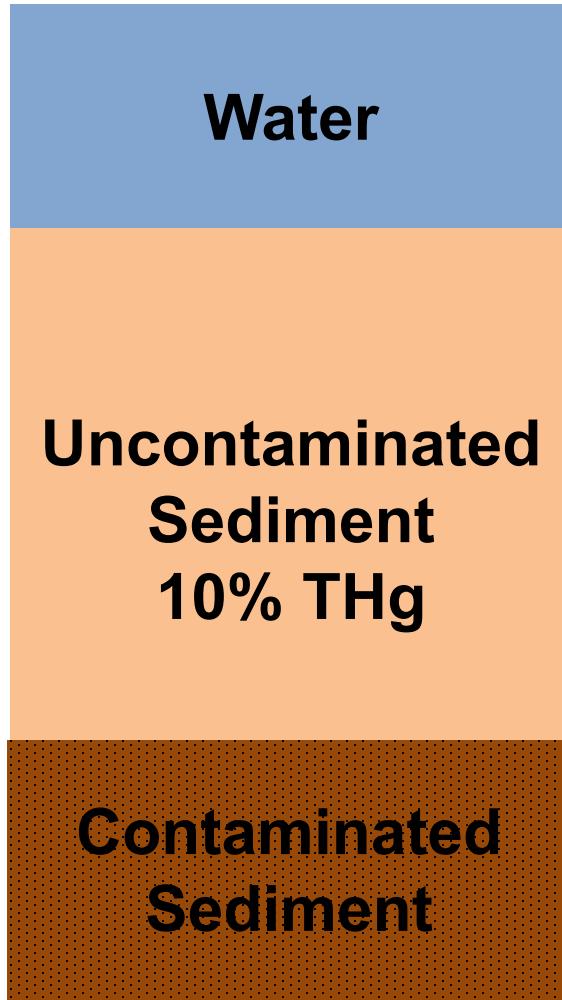


Example 3 – Hg Baseline



$$k_{\text{SR,meth}} \sim k_{\text{IR,meth}}$$

Example 3 – Trenching Remediation





Summary

■ CapSim 4

- Biogeochemical model for redox-sensitive contaminants
- Linked equilibrium and kinetic reactions
- Erosion and deposition
- Hyporheic exchange and bioturbation
- Commercial sorbents and materials
- Arbitrary initial profile specification in solids or porewater
- Improved simulation speed



Reference

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- Wheatcroft, R. A. (1992). Experimental tests for particle size-dependent bioturbation in the deep ocean. *Limnology and Oceanography*, 37(1), 90-104.



Thank you !