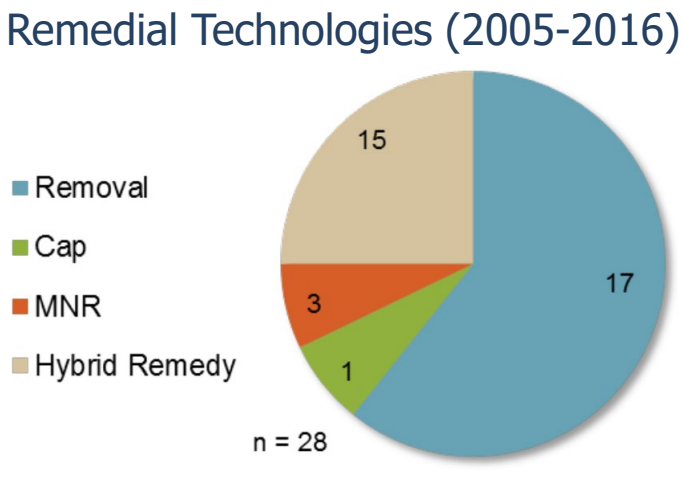
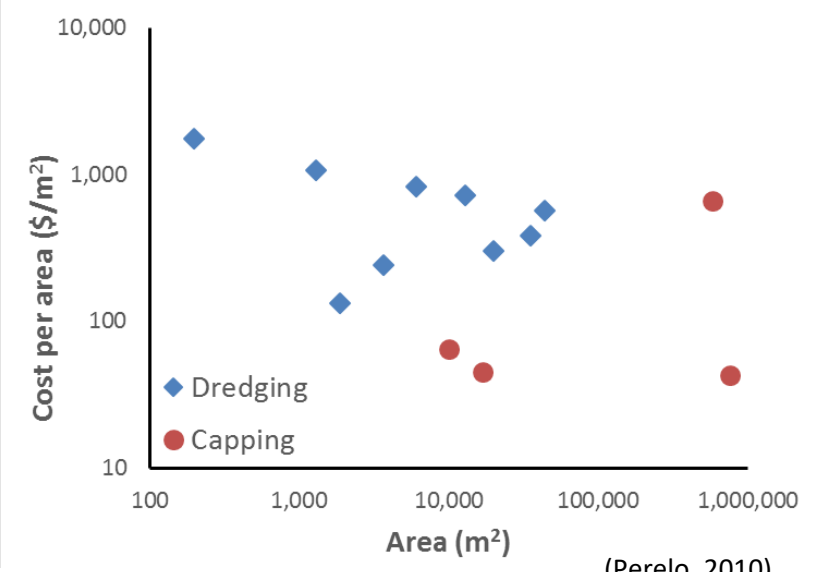
CapSim 4 – An Innovative Model for Remedial Design of Contaminated Sediments

Reible Research Group

Sediment Remediation

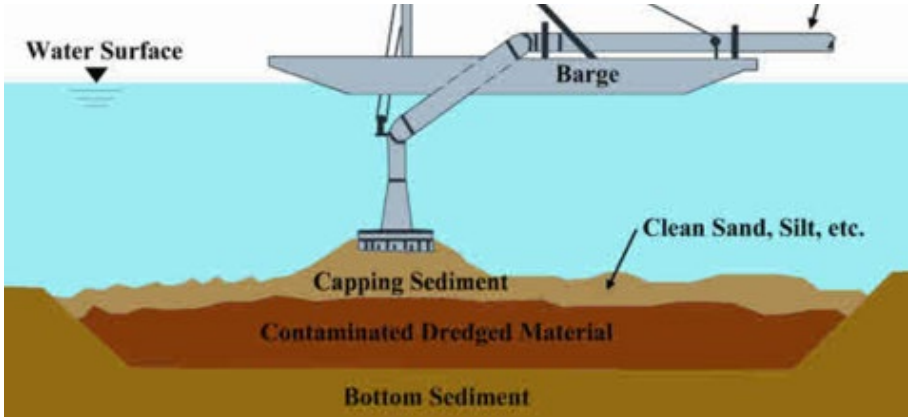


(Mohan, 2016)



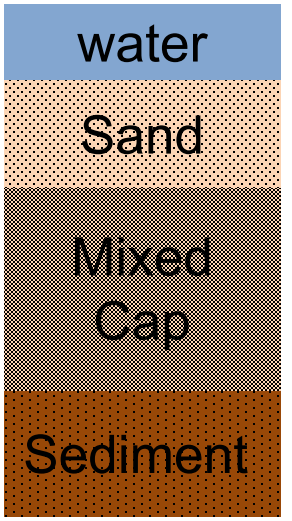
(Perelo, 2010)

- **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

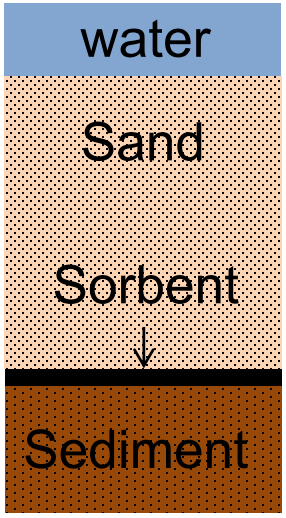


Model for Remedial Design

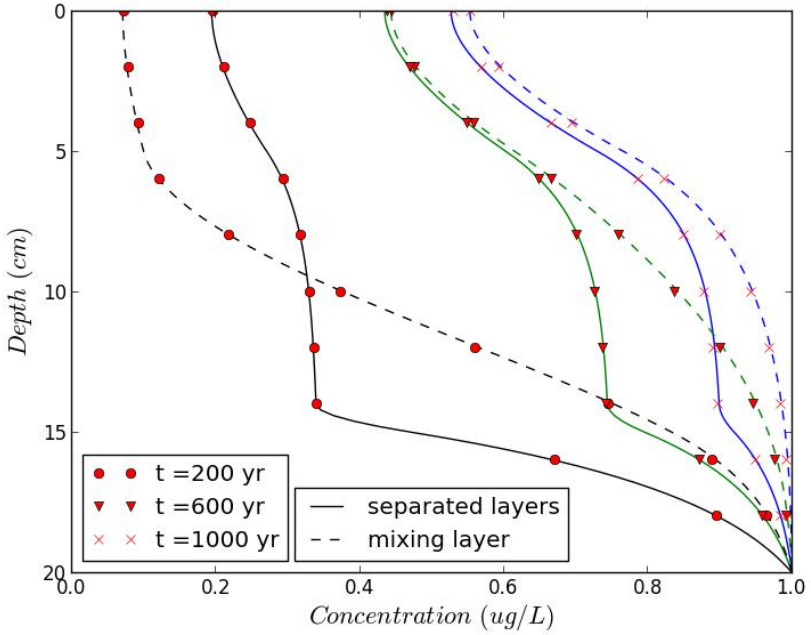
- **In-situ remedial design - model prediction**
- **1-D multi-layered porous media model**
  - Porewater/Solid matrix/Dissolved organic carbon (DOC)
  - Sorption/Diffusion/Dispersion/Advection/Reaction
  - Bioturbation/Consolidation/Deposition/Erosion/Hyporheic exchange



Mixed ✓



Separated



1-D Fate and Transport Model

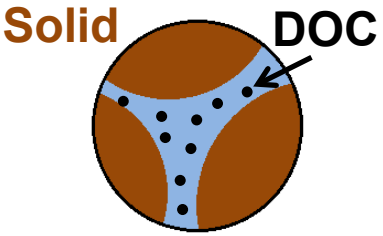
$$\frac{\partial q_{n,i}}{\partial t} = -\frac{\partial F_{n,i}}{\partial z} + \sum_l a_{l,n} rxn_{l,i}$$

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

Accumulation

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

Porewater | DOC | Sorption in solid matrix



Transport

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

Diffusion | Dispersion | Advection | Hyporheic | Bioturbation

Diffusion, Dispersion, Advection, Hyporheic: Porewater and DOC

Bioturbation: 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]
```

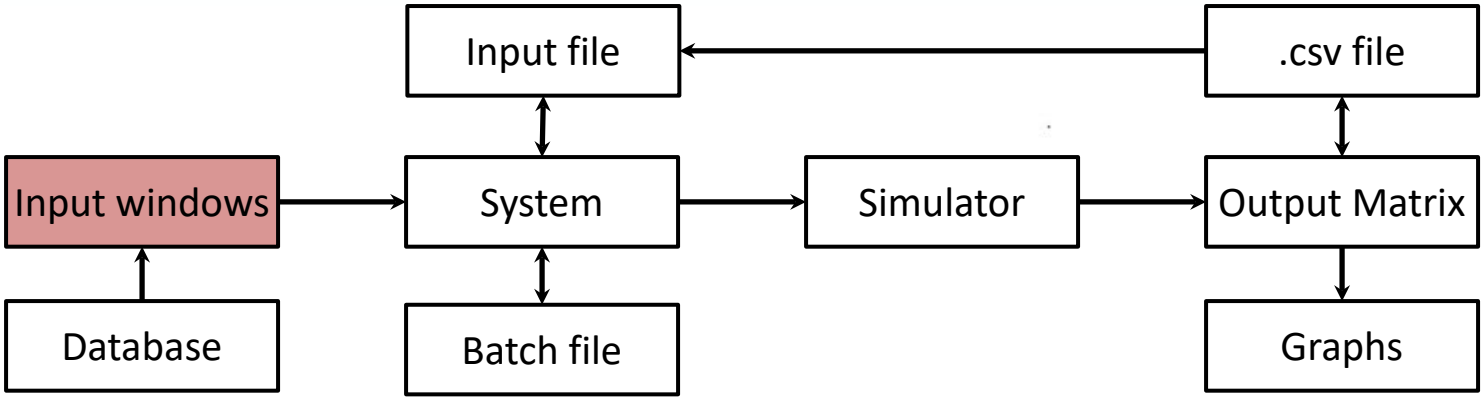
```
A = A + B
```

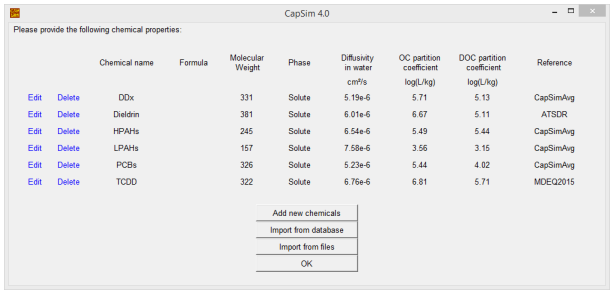
$t_1 \gg t_2$

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

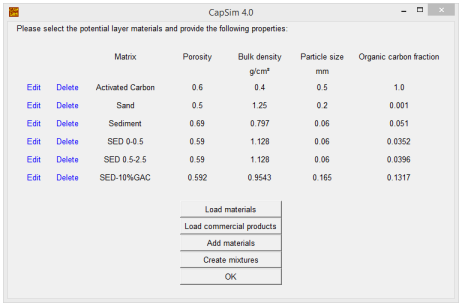
identity matrix

CapSim – Graphic User Interface

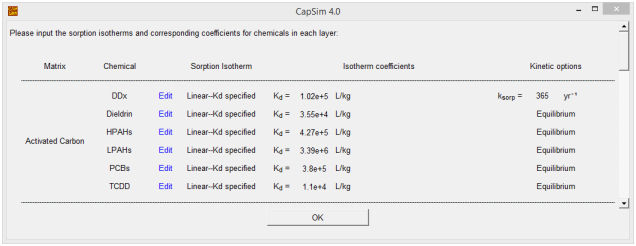




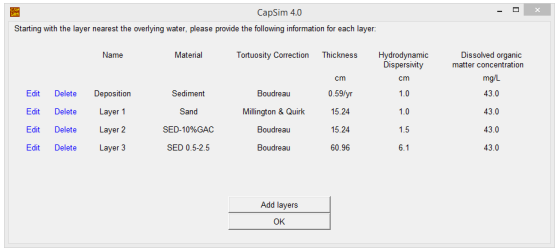
Chemical



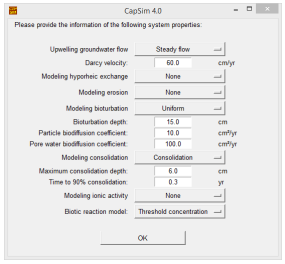
Solid matrix



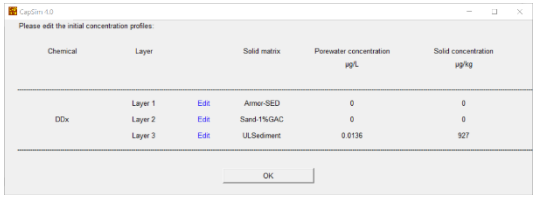
Sorption



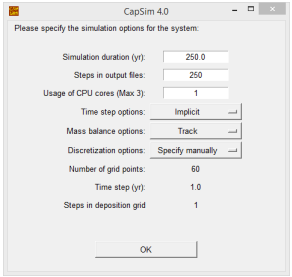
Layers



Process

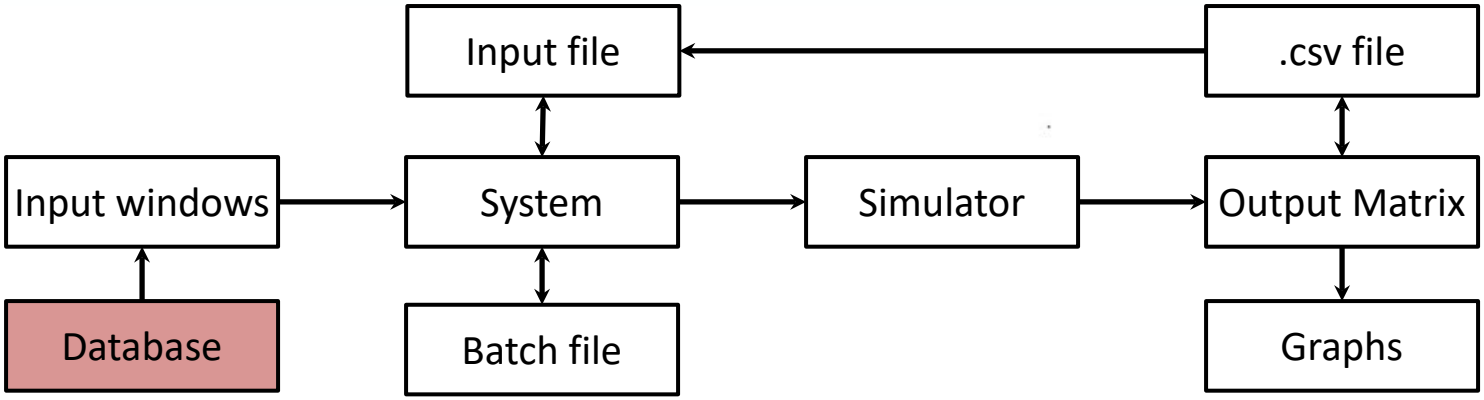


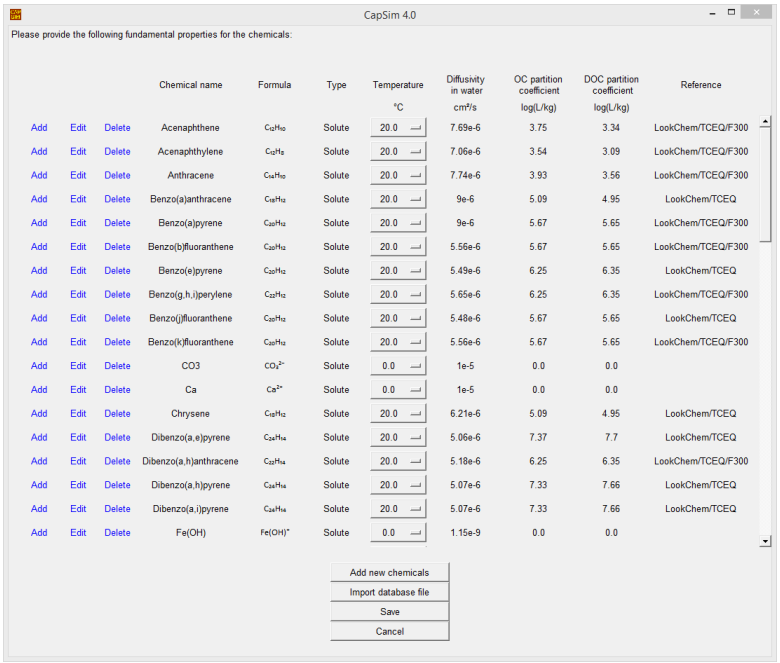
BC & IC

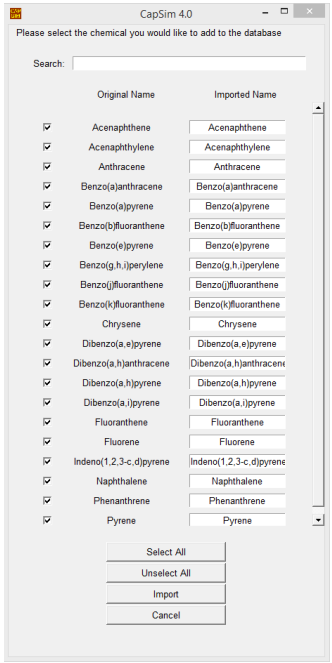


Solver

CapSim - Database







PAHs

PCBs

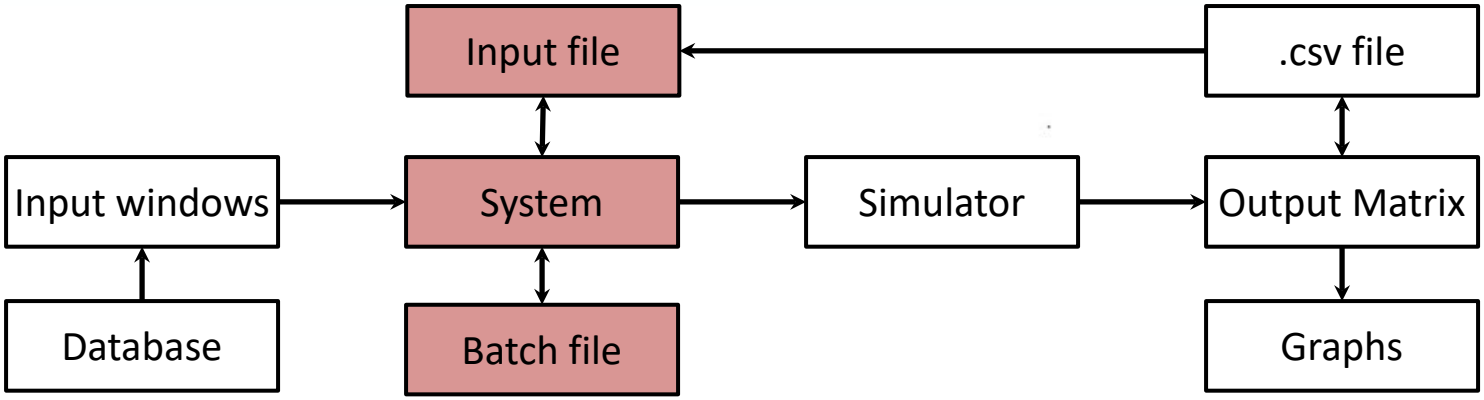
Pesticides

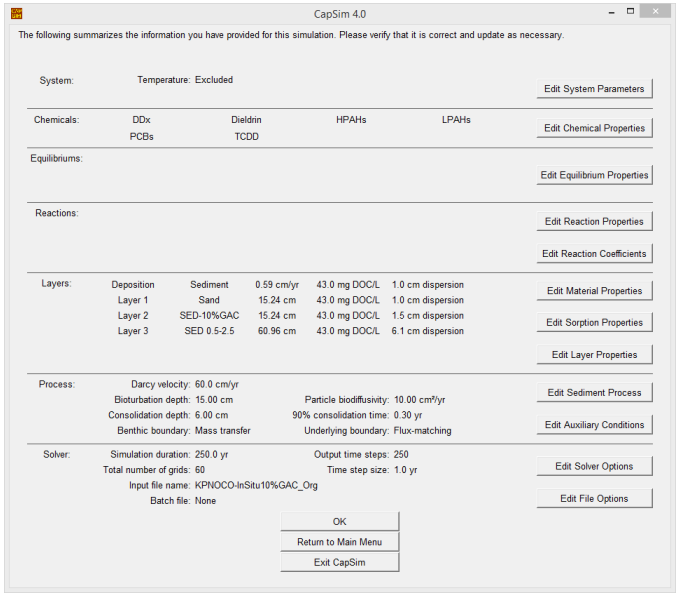
Heavy metals

sparc
SPARC Performs Automated Reasoning in Chemistry

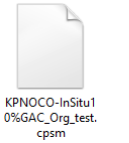
TCEQ

CapSim – Input/Batch Function

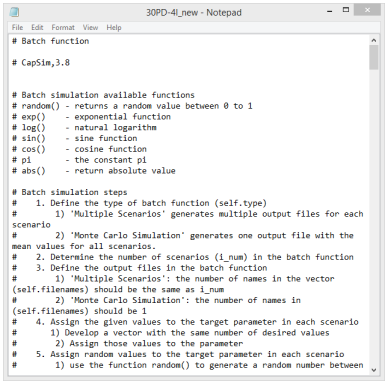




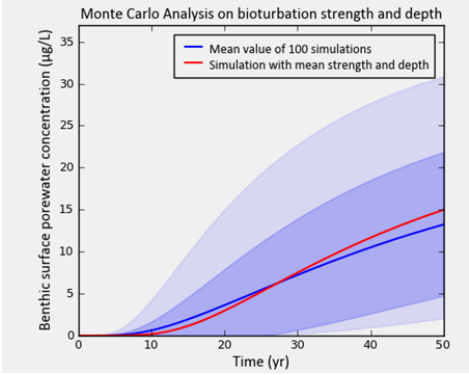
Summary of system



.cpsm input file

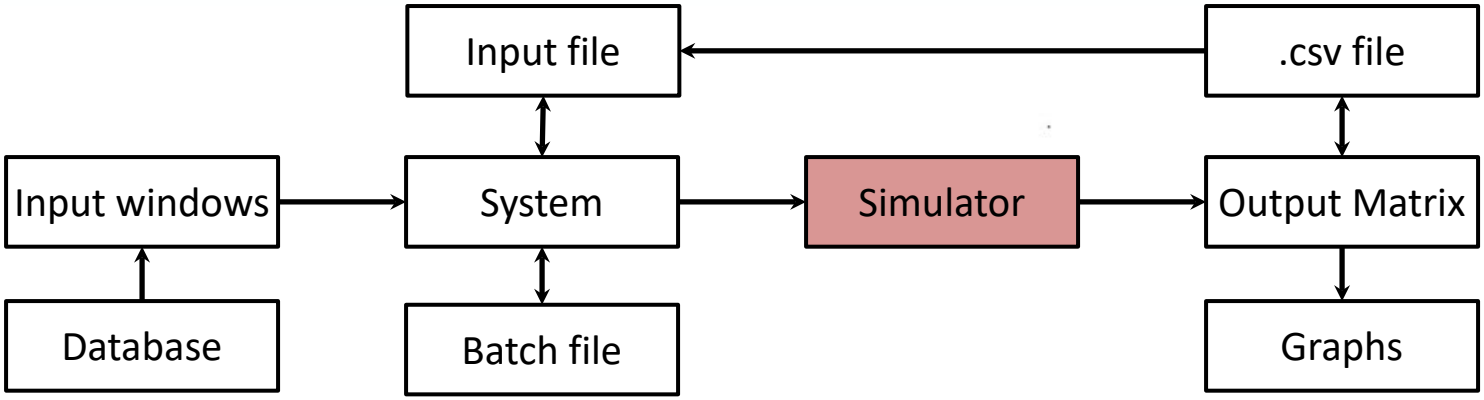


.txt batch file



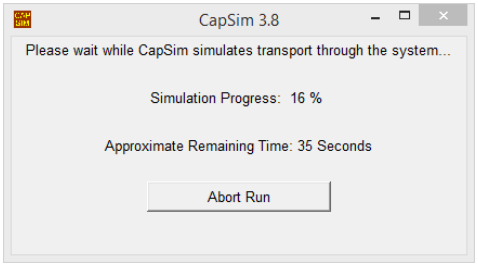
Monte Carlo simulation

CapSim – Solver

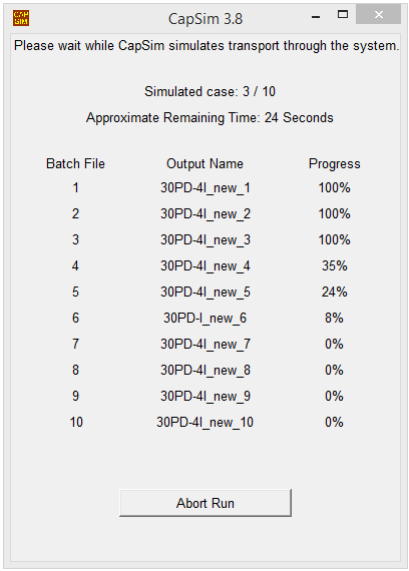


Numpy

Lapack

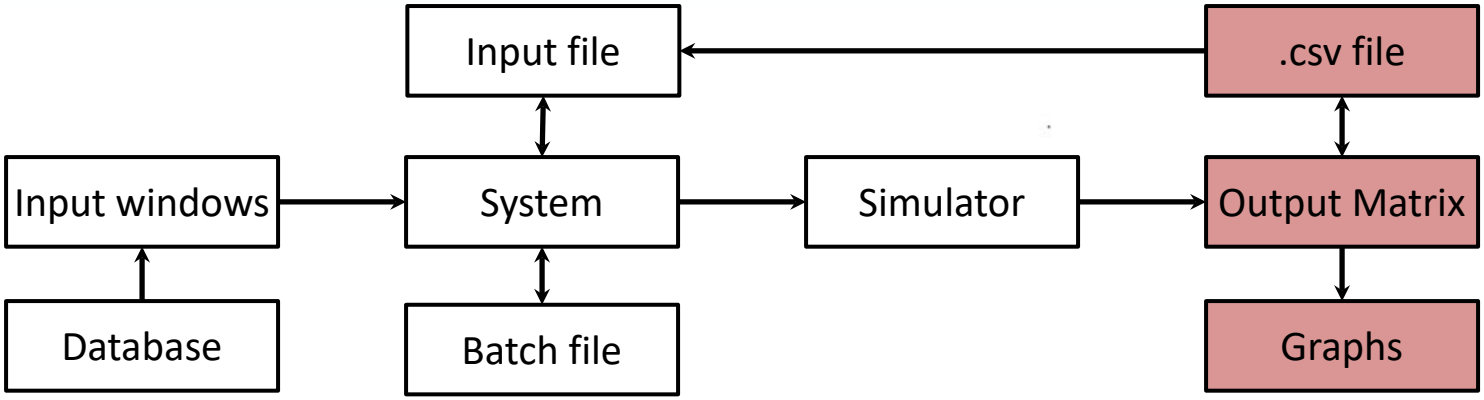


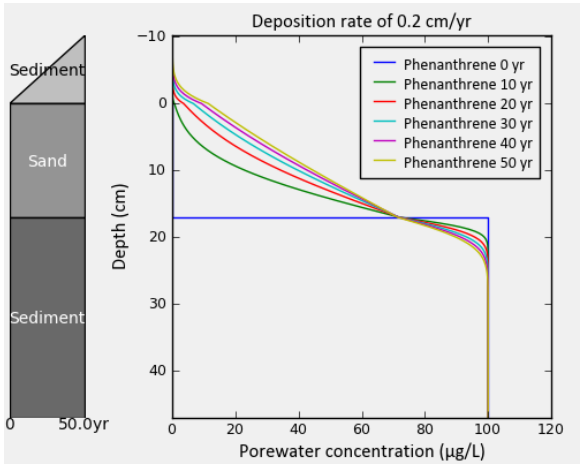
Input case processing



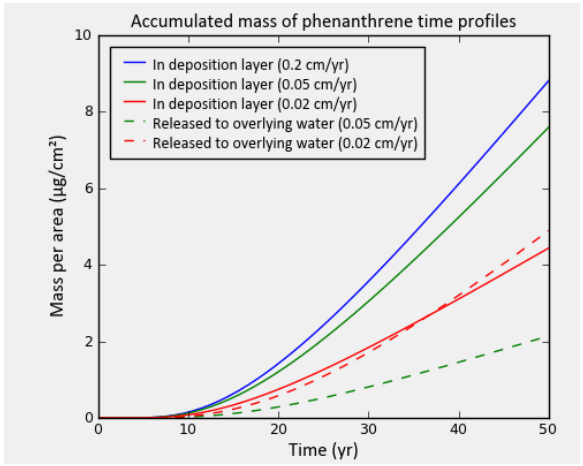
Batch multi-core processing

CapSim – Output

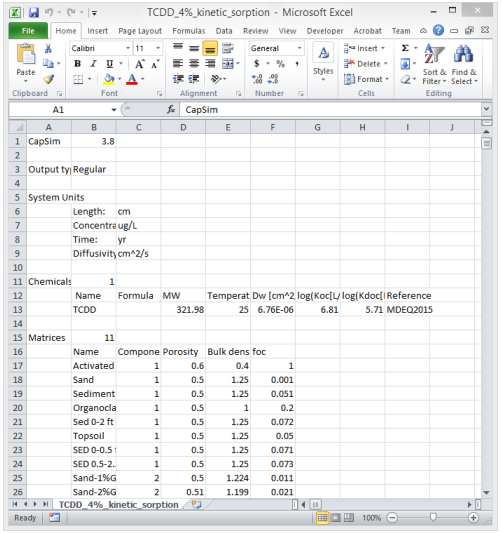




Spatial profiles



Temporal profiles

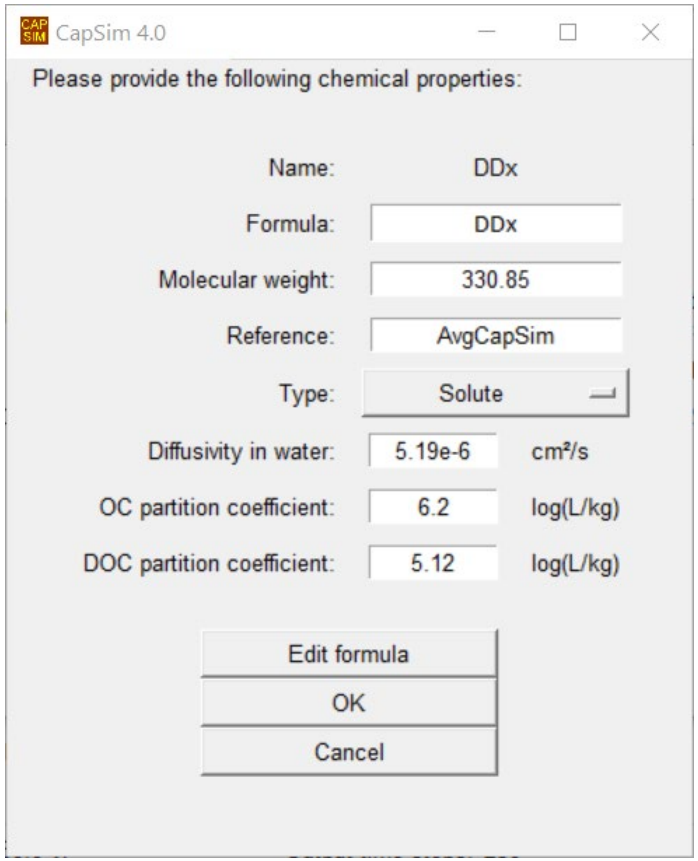


.csv output file

Example 1 - Chemical & Solid Matrix

- **Design a capping layer for contaminated sediment**

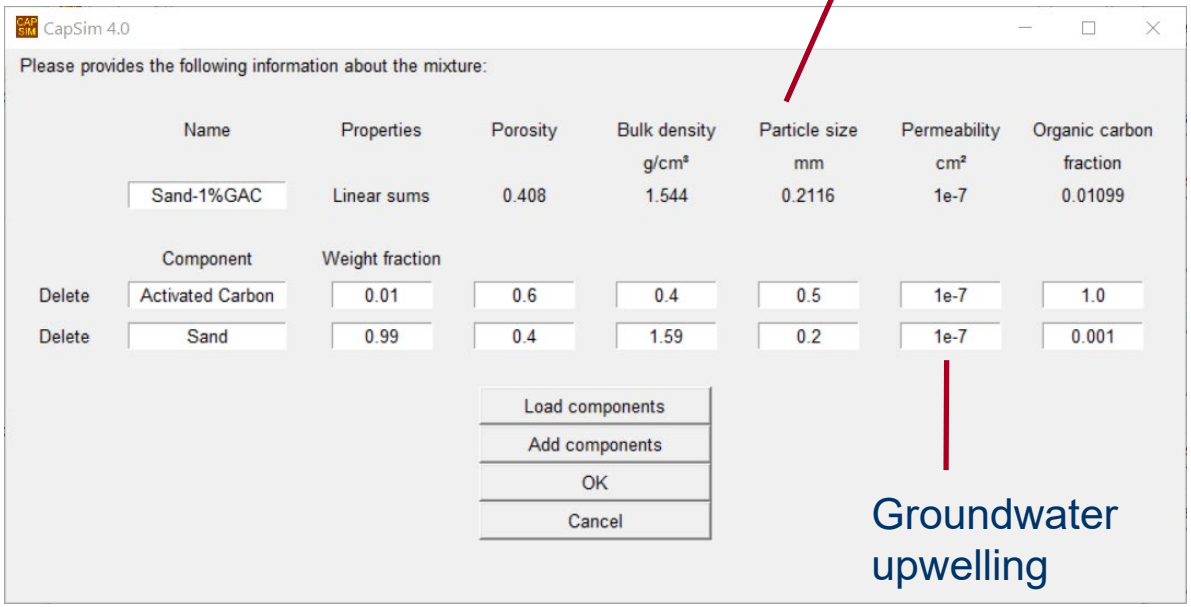
Chemical properties



Solid matrix properties

Bioturbation

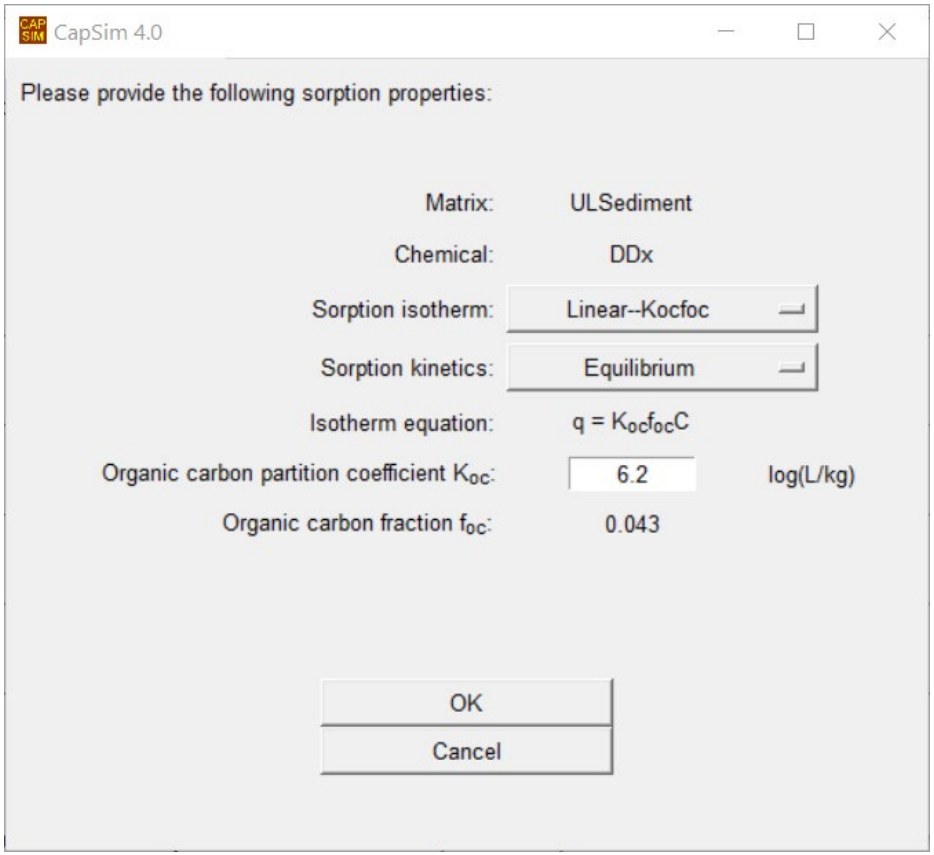
Hyporheic exchange



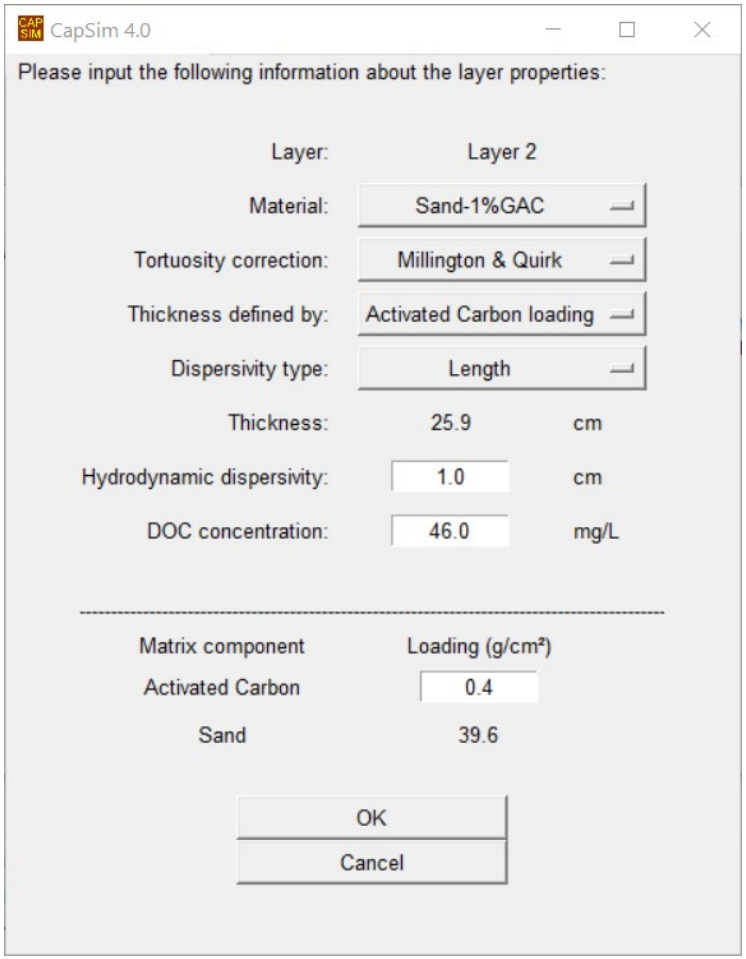
Groundwater upwelling

Example 1 – Sorption & Layer

Sorption
– partitioning of chemicals in matrices

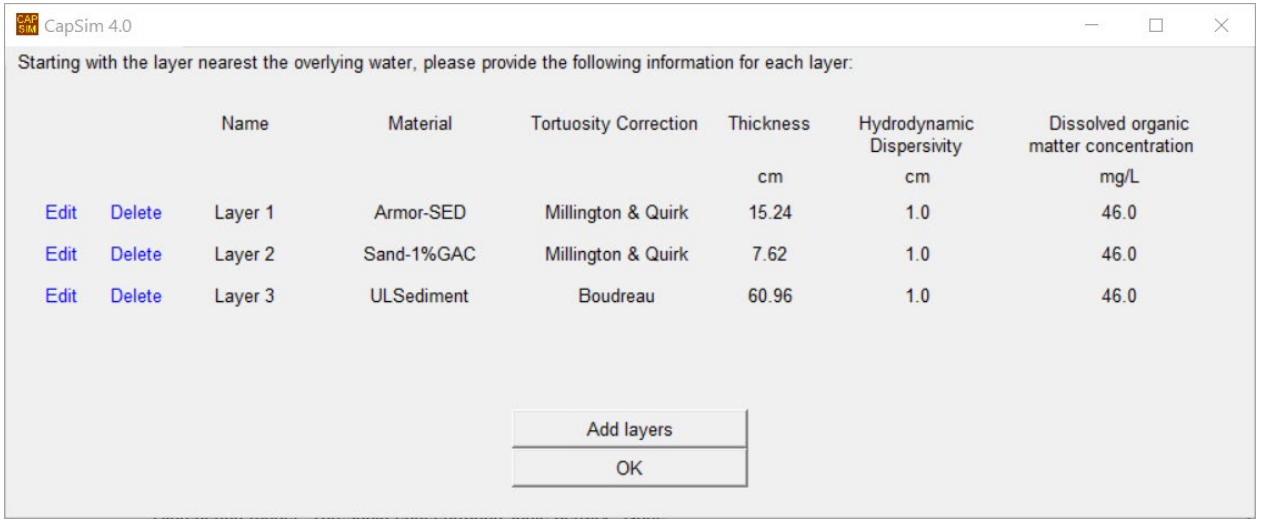


Layer properties
- tortuosity/dispersivity/DOC

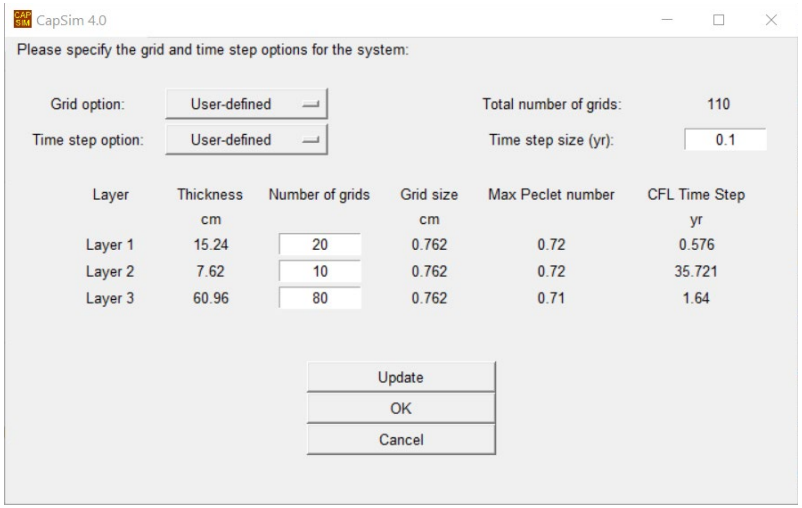


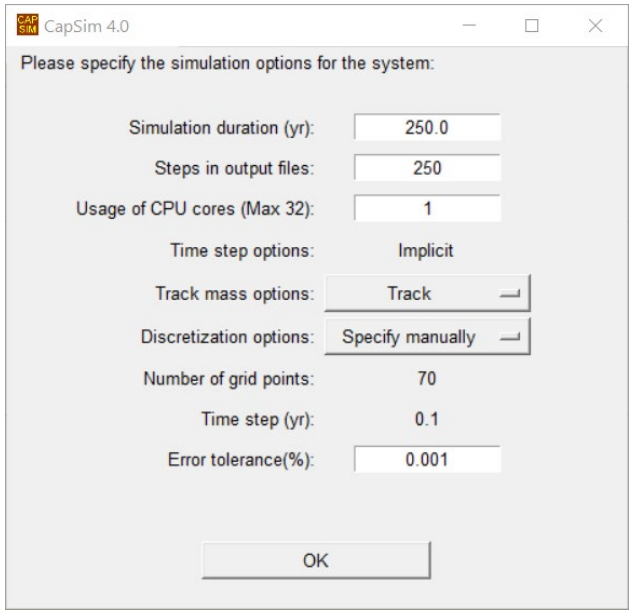
Example 1 – Solver Parameters

Multi-layered system



Discretization option





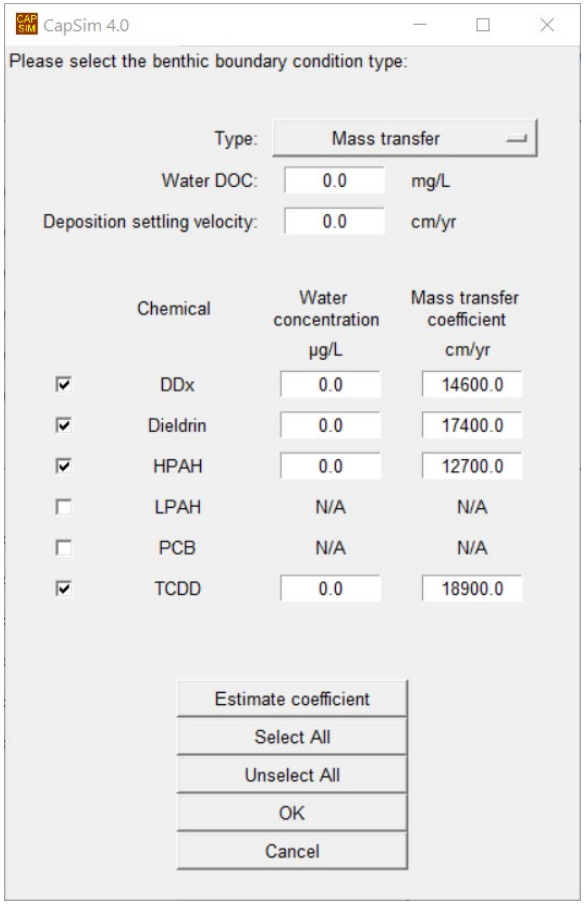
Example 1 – Auxiliary Conditions

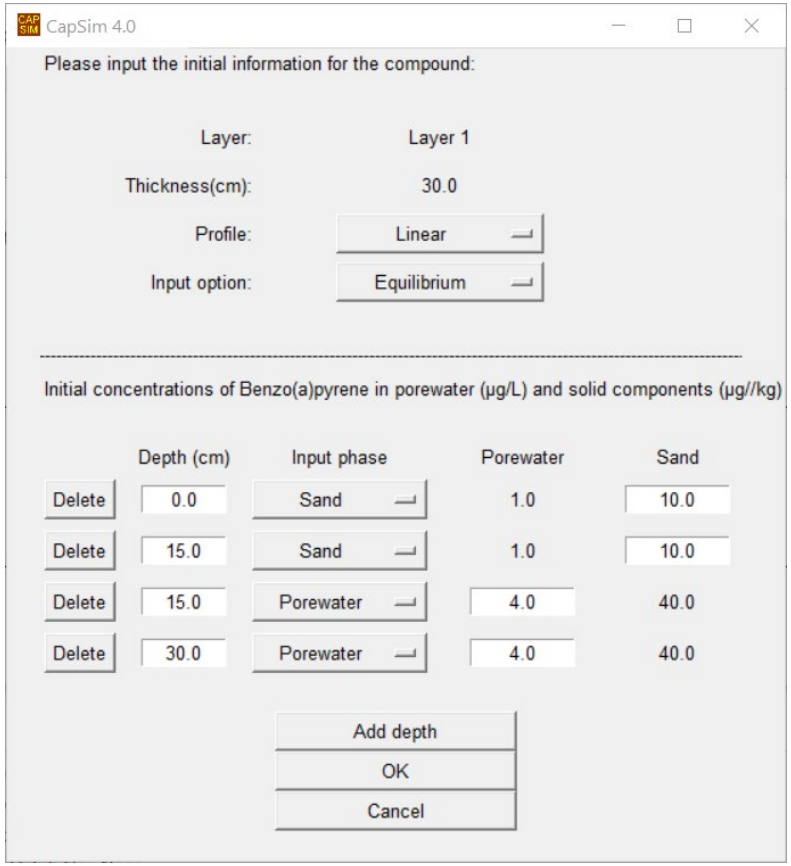
Boundary conditions

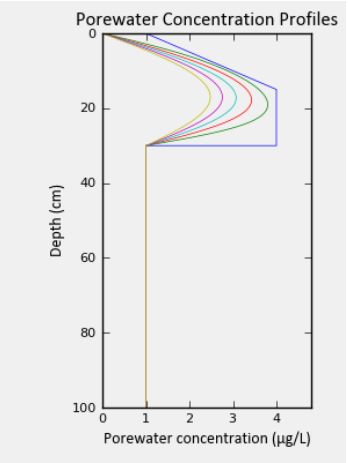
- Concentration/Flux/Mass transfer

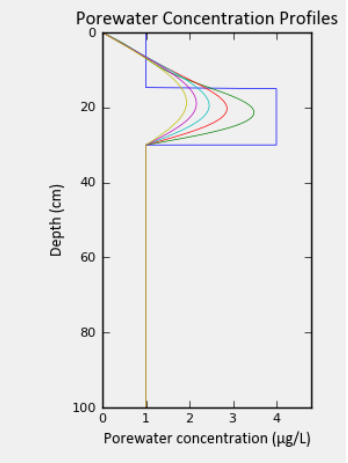
Initial conditions

- Uniform/Depth-dependent

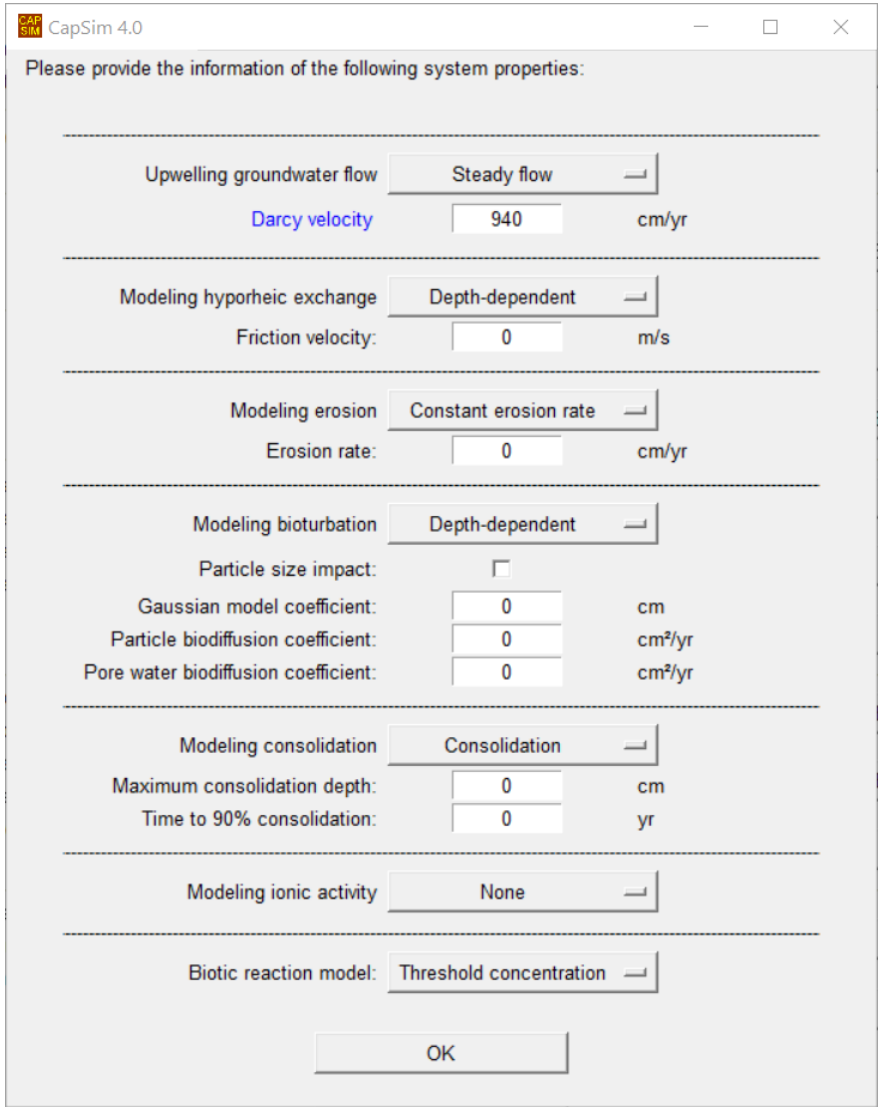






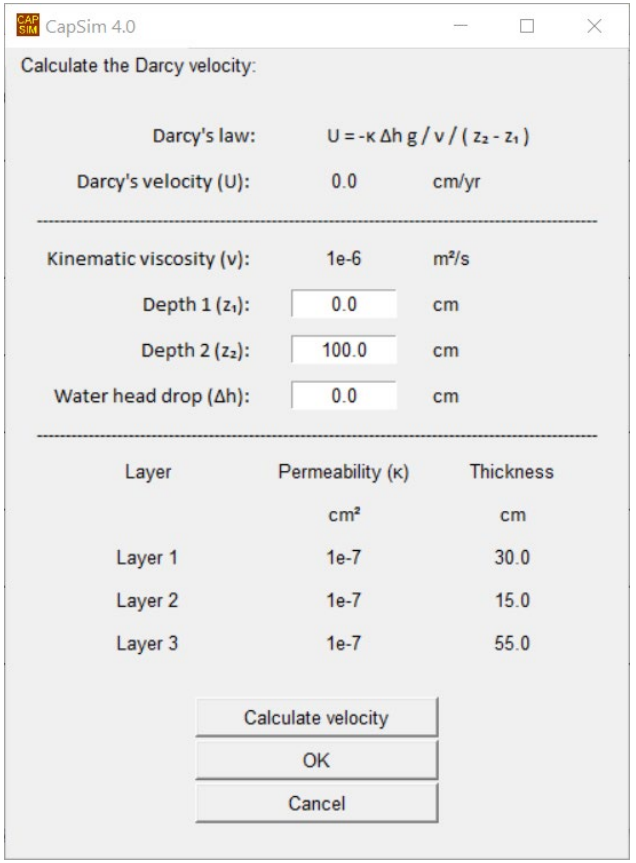


Example 1 – Sediment Processes



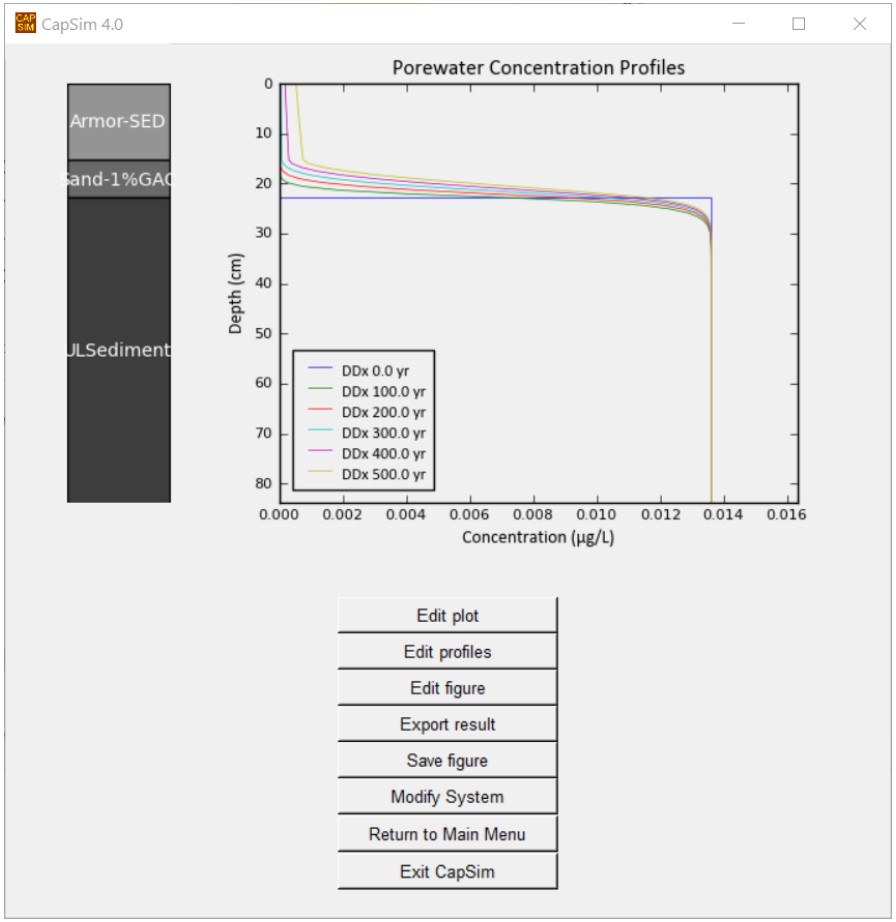
Groundwater upwelling

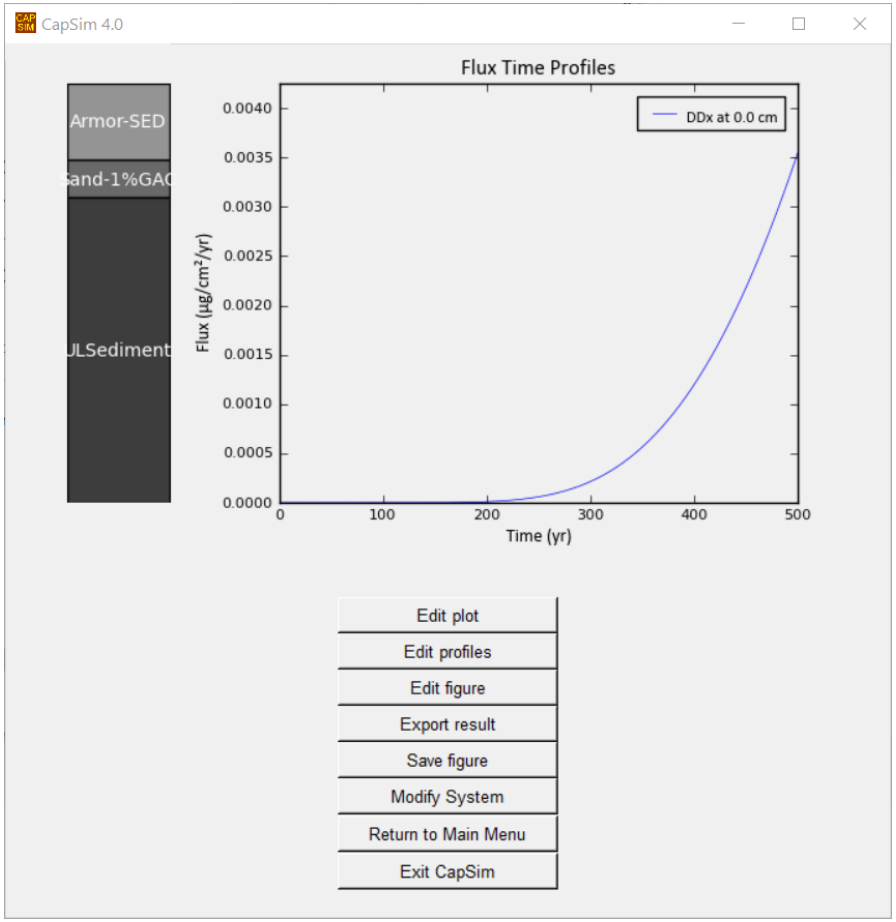
Darcy's Law



Example 1 – Baseline Results

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





Hyporheic Exchange

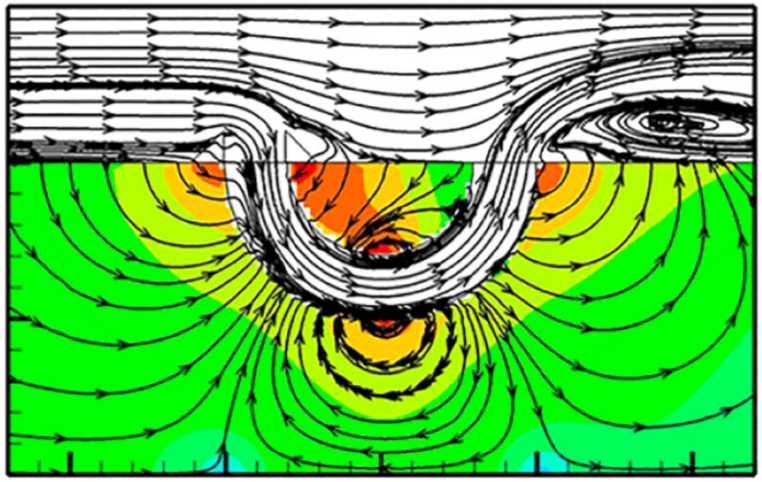
- **1-D Hyporheic exchange**

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

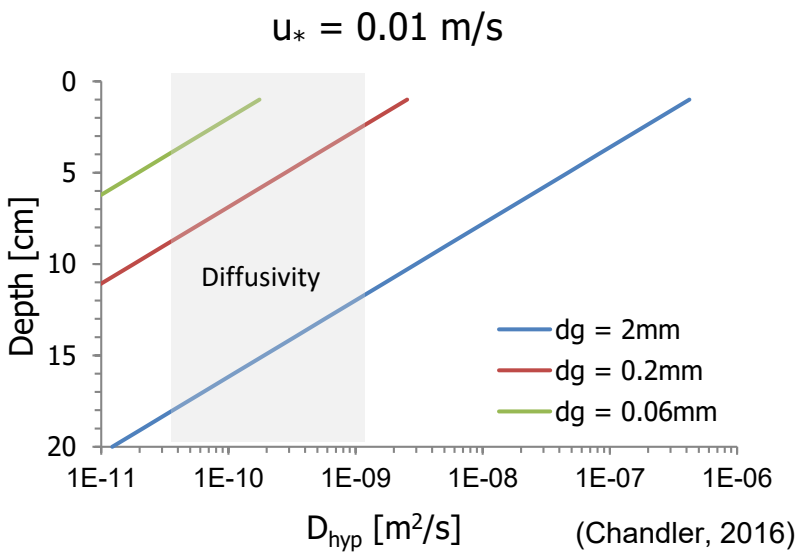
$$D_{hyp} = 1.19 * 10^{-6} {d_g}^{2.22} {u_*}^{3.11} e^{-55y}$$

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

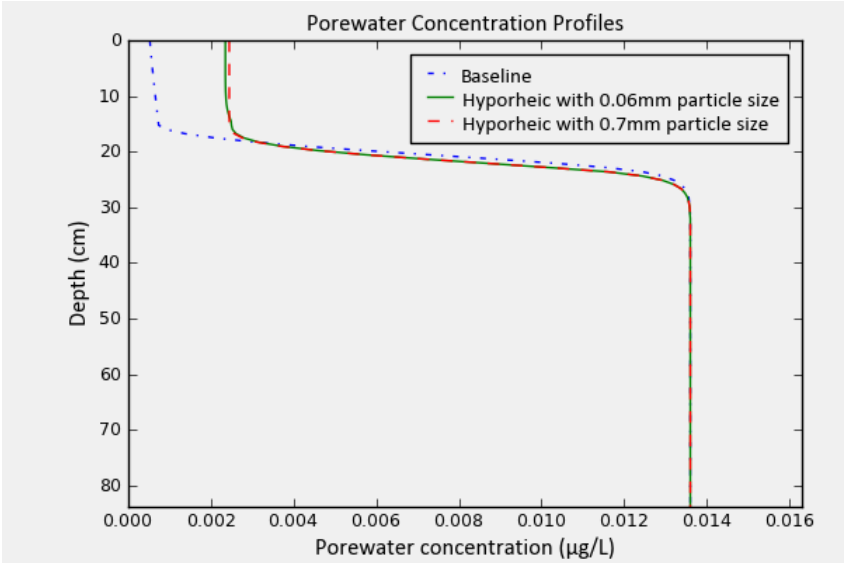
u_*: Friction velocity [m/s]



(Liu, 2019)



(Chandler, 2016)



Bioturbation

- **Mixing particles and porewater**

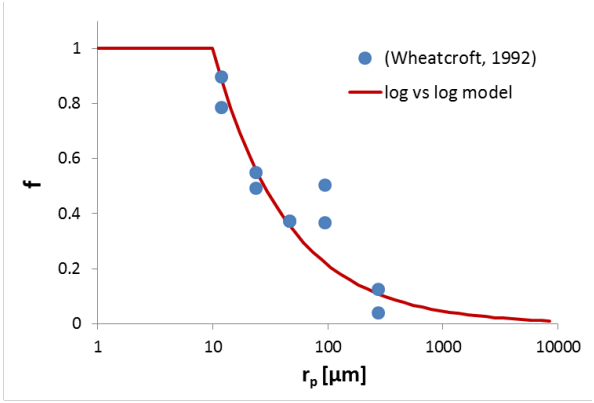
$$F_{bio,n} = -D_{bio,p} \sum_m \rho_{b,m} \frac{\partial \phi_m q_{m,n}}{\partial z} - D_{bio,pw} \frac{\partial (C_n + \rho_{DOC,i} q_{DOC,n})}{\partial z}$$

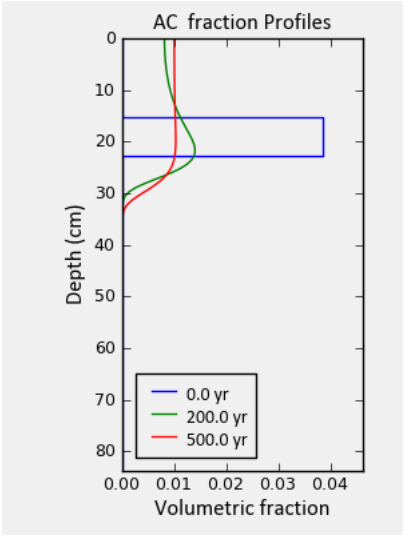
- **Factors on biodiffusion coefficient**
  - Depth from benthic surface (z)

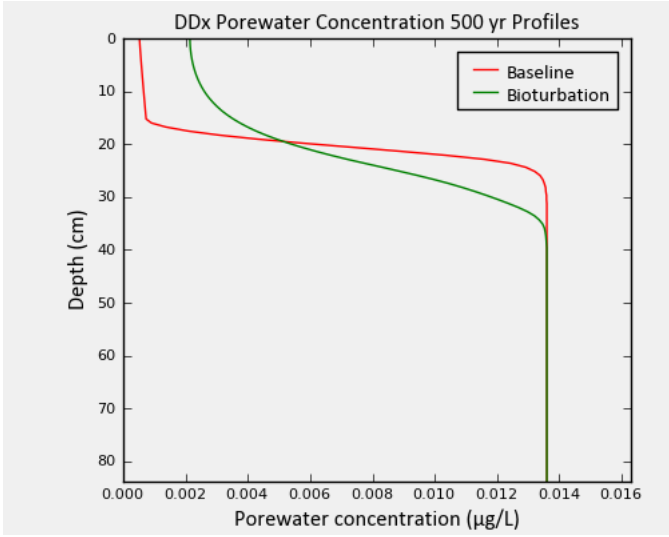
$$D_{bio,p} = D_{bio,p,0} * exp\left(-\frac{z^2}{2\sigma^2}\right)$$

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

  - Particle size (r_p)



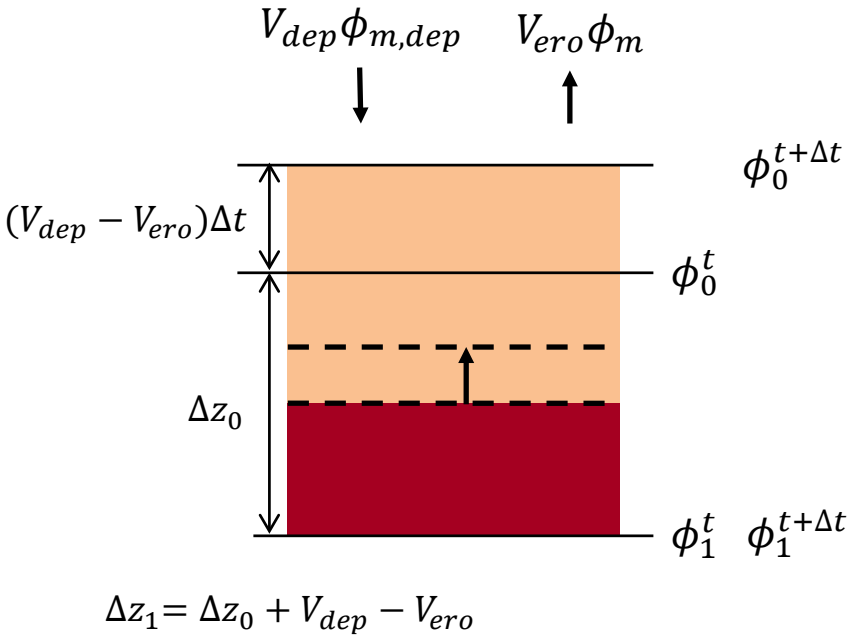




Deposition and Erosion

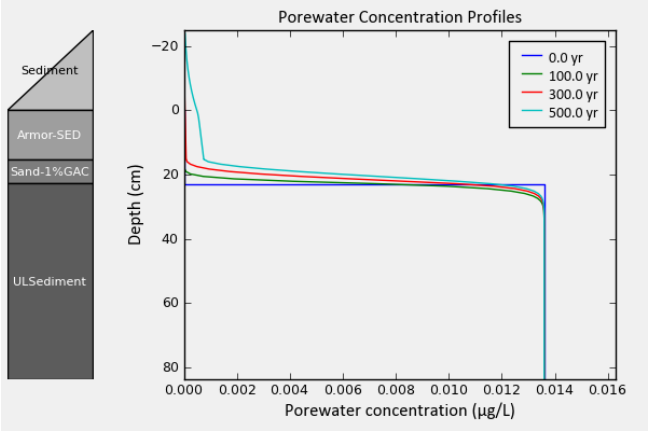
- **1-D mass conservation at benthic boundary**

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

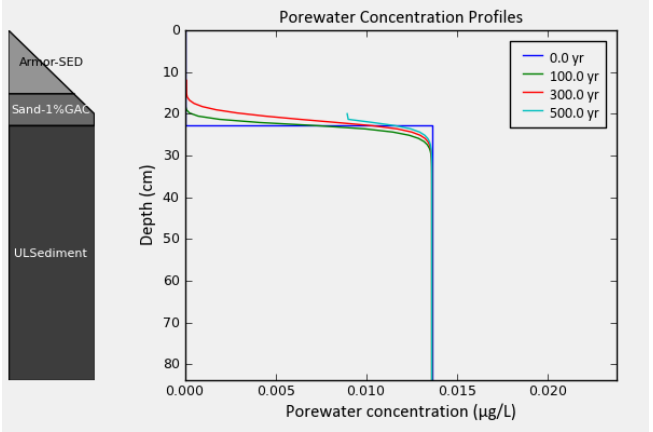


$$\Delta z_1 = \Delta z_0 + V_{dep} - V_{ero}$$

0.04 cm/yr deposition

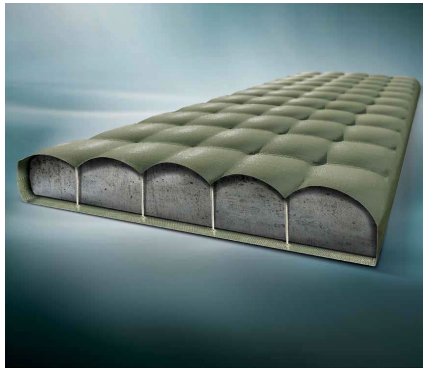


0.04 cm/yr erosion



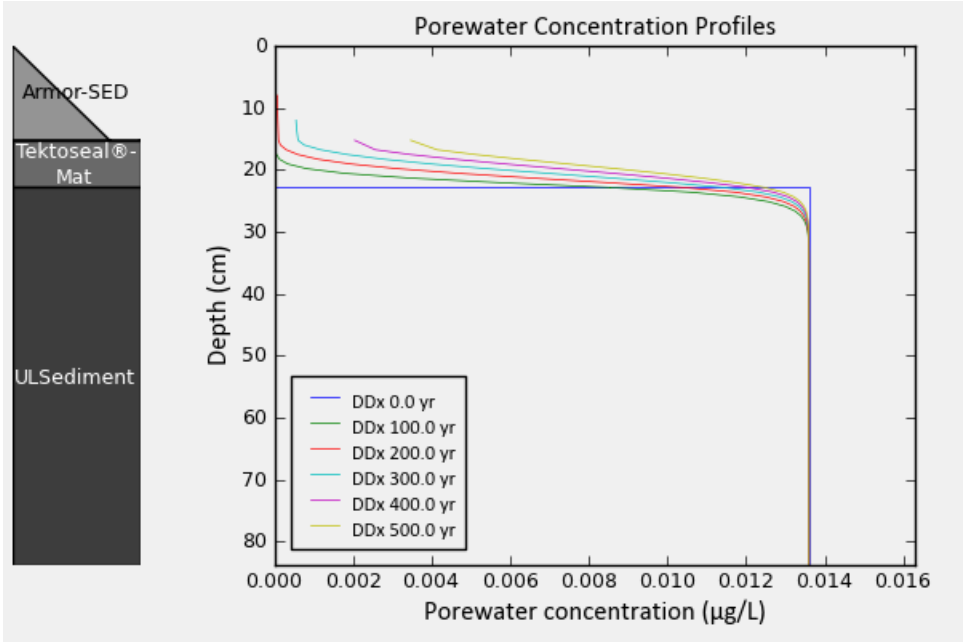
Commercial Sorbents

Matrix	Porosity	Bulk density g/cm³	Particle size mm	Permeability cm²	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



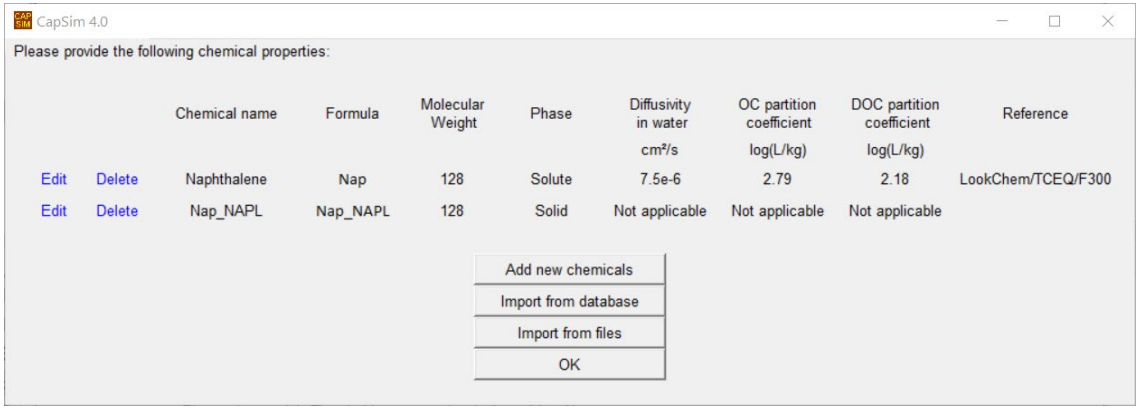
Tektoseal® Active Mattress

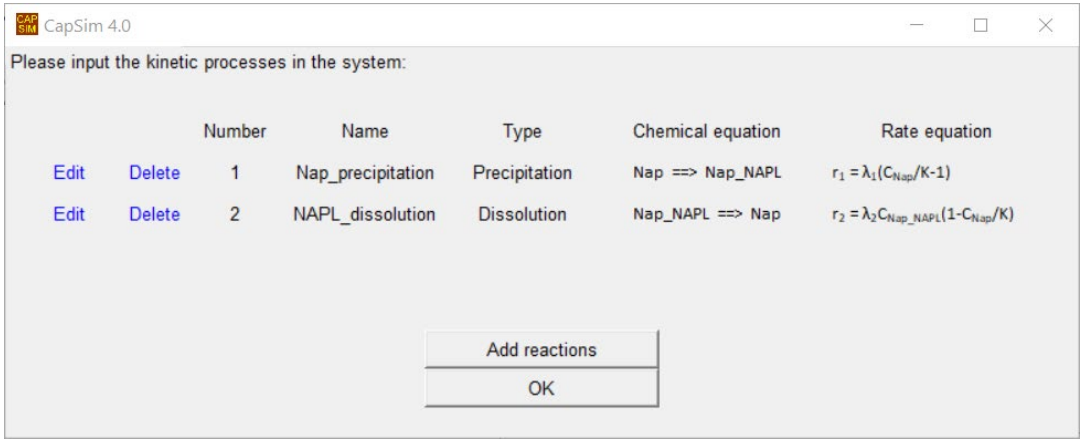
Mat-like sorbents are not impacted by bioturbation and erosion



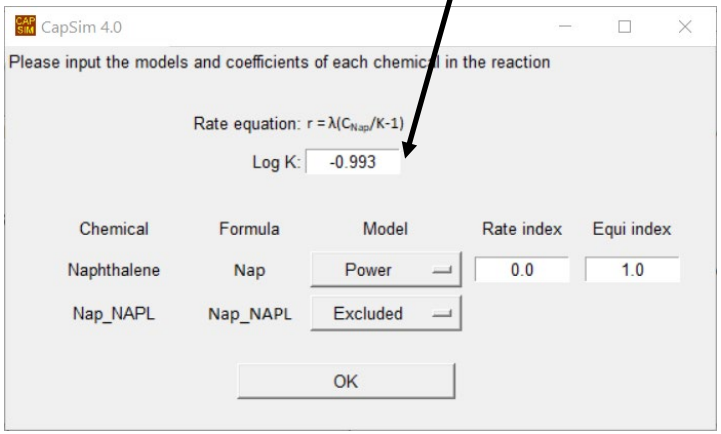
Example 2 – Naphthalene NAPL

- **Non-aqueous phase liquid (NAPL)**
  - Immobile stock of organic contaminants
  - Modeled using precipitation/dissolution
  - Keep pw concentration at solubility until the depletion of NAPL





Log molar Solubility

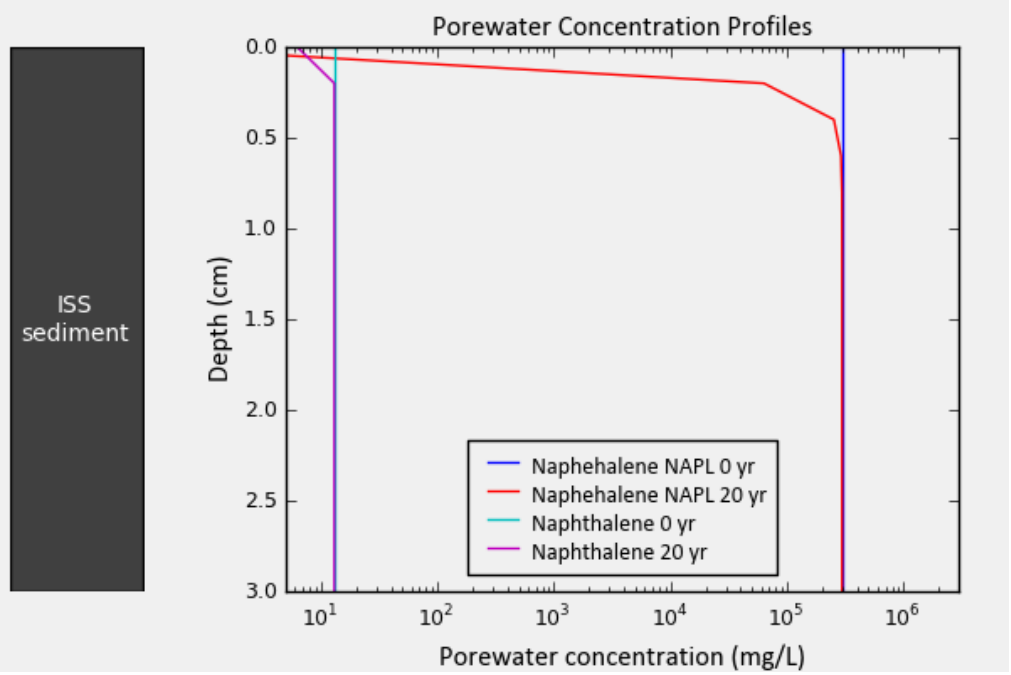


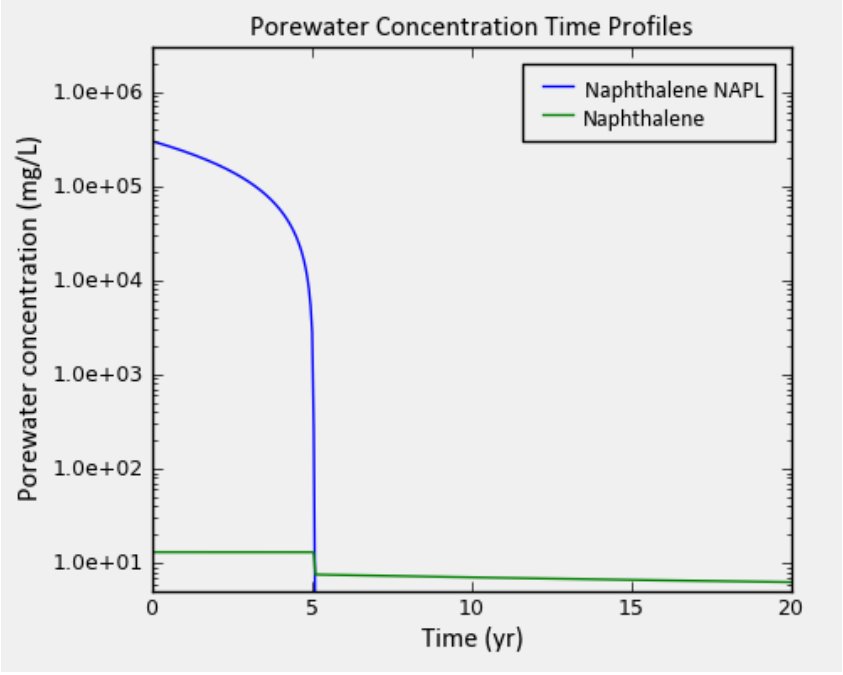
Example 2 – Naphthalene NAPL

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

Local equilibrium by fast precipitation/dissolution

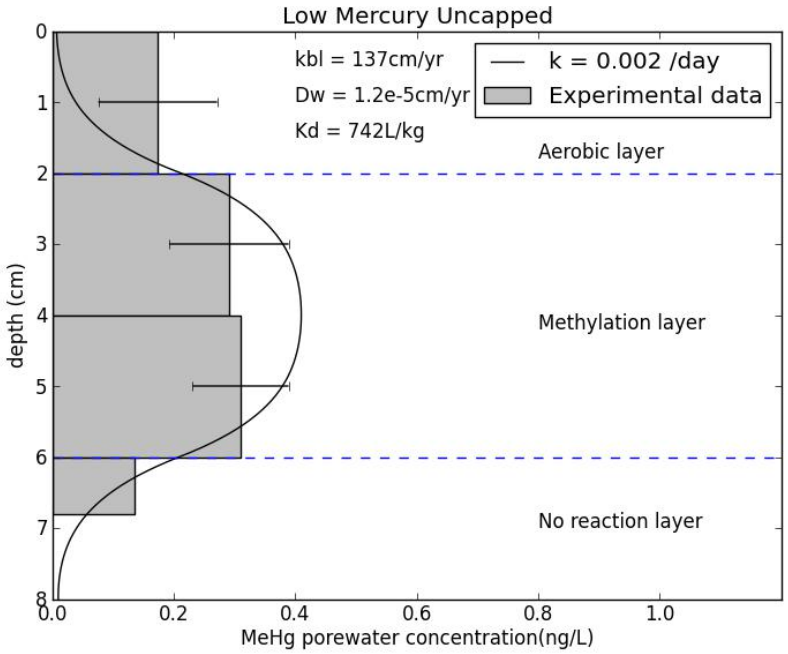
Solubility of Naphthalene: 13 mg/L

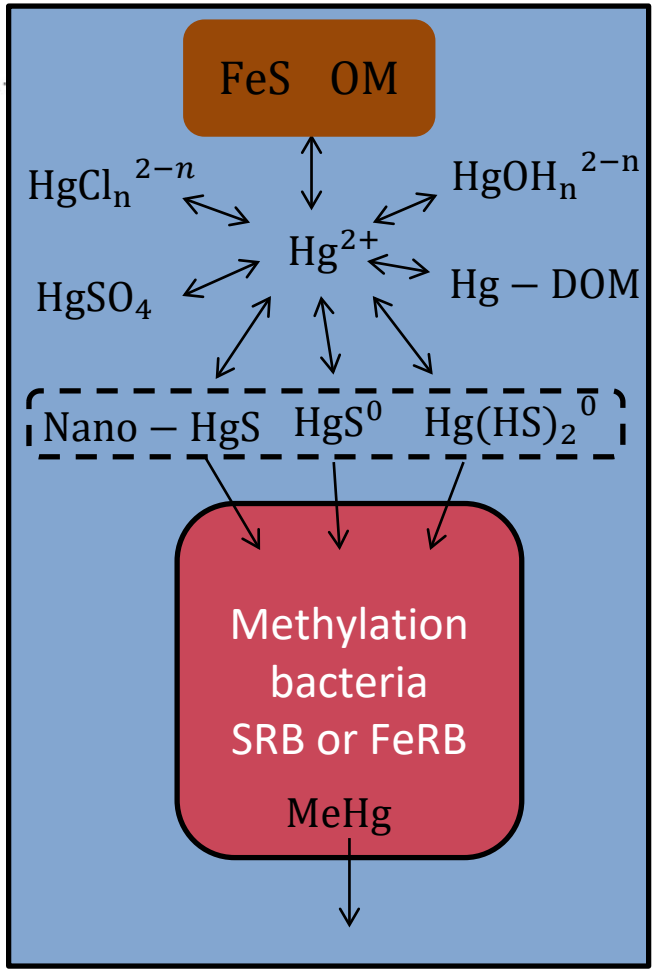




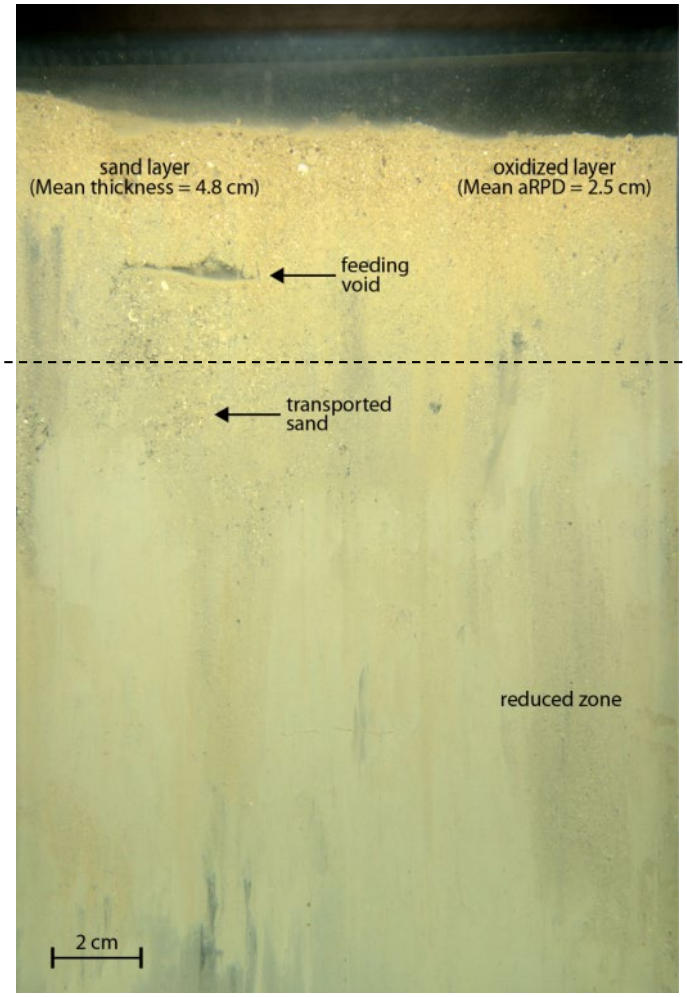
Example 3 – Hg Methylation

- **Methylmercury (MeHg)**
  - Toxic species of Hg
  - Byproduct of sulfate reduction/iron reduction
  - Primarily produced in anaerobic zones

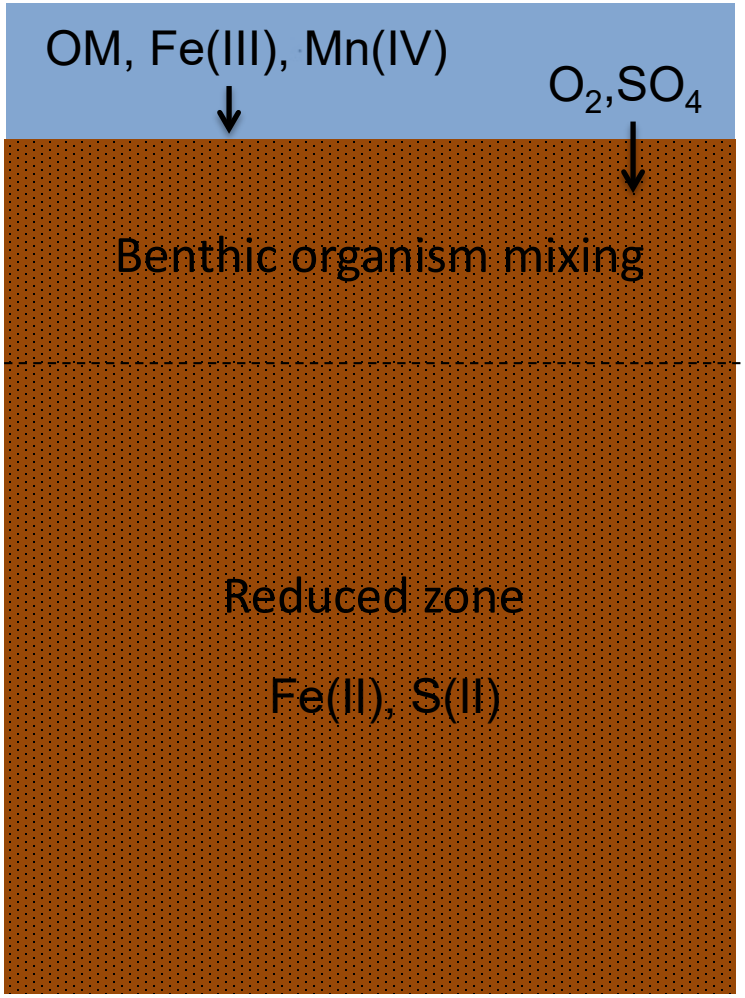




Redox Profile in Sediment

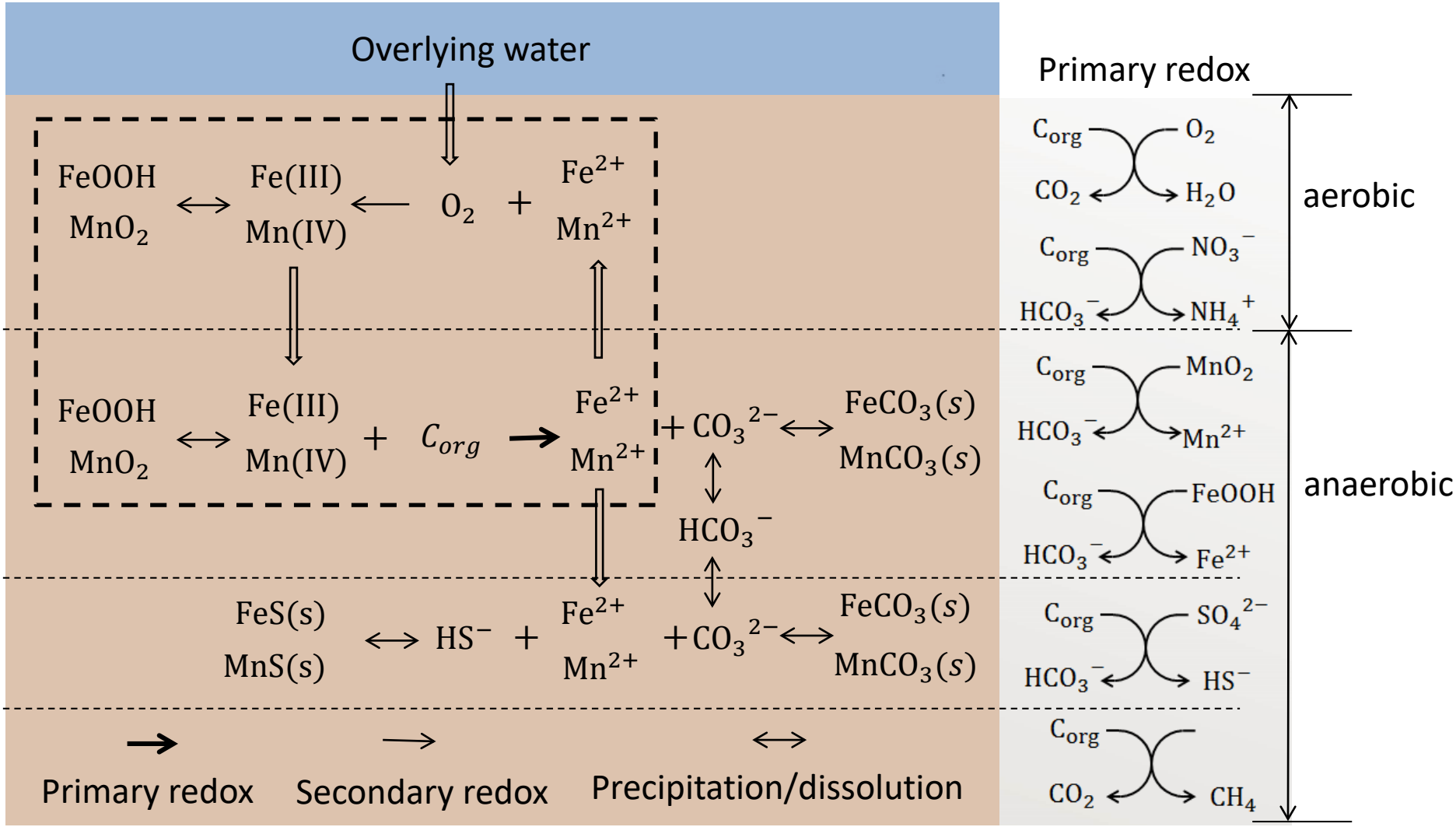


Sediment profile imaging (SPI)



Conceptual model

Biogeochemical Reaction Network



Secondary and Equilibrium Reactions

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

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

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

- **Secondary redox reactions**
  - Kinetic model

Second redox reaction	Reaction rate
$Mn^{2+} + 0.5O_2 + H_2O \rightarrow MnO_2(s) + 2H^+$	$r = k_{MnO} C_{Mn^{2+}} C_{O_2}$
$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3\,(s) + 2H^+$	$r = k_{FeO} C_{Fe^{2+}} C_{O_2}$
$HS^- + 2O_2 \rightarrow H^+ + SO_4^{2-}$	$r = k_{SO} C_{HS^-} C_{O_2}$
$MnO_2 + 2Fe^{2+} \rightarrow Mn^{2+} + 2Fe(OH)_3\,(s) + 2H^+$	$r = k_{SO} C_{HS^-} C_{O_2}$

- **Equilibrium reactions**
  - Water chemistry/Complexation
  - Precipitation/Dissolution

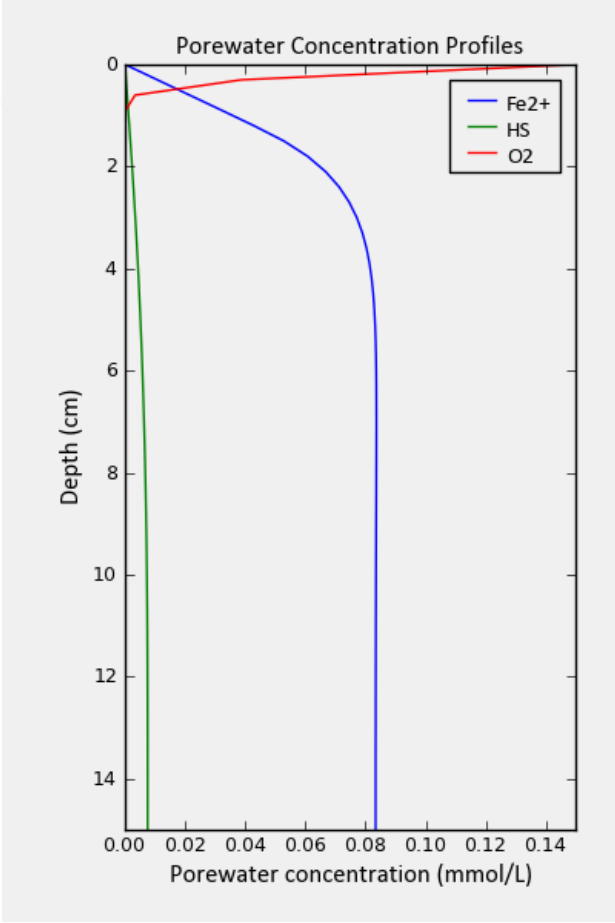
Precipitation/Dissolution	Reaction rate
$FeS + H^+ \rightarrow Fe^{2+} + HS^-$	$r = k_{FeSd}\, C_{FeS}(1 - (C_{Fe^{2+}} C_{H^+})/(K_{FeS} C_{FeS}))$
$Fe^{2+} + HS^- \rightarrow FeS + H^+$	$r = k_{FeSp}\,((C_{Fe^{2+}} C_{H^+})/(K_{FeS} C_{FeS}) - 1)$

Complexation reaction	Log K_L
$\{Fe^{2+}\} + \{OH^-\} = \{Fe(OH)^+\}$	4.5
{Fe2+} + 2{OH-} = {Fe(OH)2}	7.4
{Fe 2+} + 3{OH-} = {Fe(OH)3-}	11.0
{Fe 2+} + {SO42-} = {Fe(SO4)}	2.2

Biotic Reactions

Preference ↓

Primary redox reaction
$CH_2O + O_2 \rightarrow HCO_3^- + H^+$
$CH_2O + NO_3^- \rightarrow 0.5N_2 + HCO_3^- + H_2O$
$CH_2O + 2MnO_2(s) + H_2O \rightarrow 2Mn^{2+} + HCO_3^- + 3OH^-$
$CH_2O + 4Fe(OH)_3(s) \rightarrow 4Fe^{2+} + HCO_3^- + 7OH^- + 3H_2O$
$CH_2O + 0.5SO_4^{2-} \rightarrow 0.5HS^- + HCO_3^- + 0.5H^+$



- **Biotic reaction model**
  - Threshold concentration ($T_{EA,l}$)

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

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

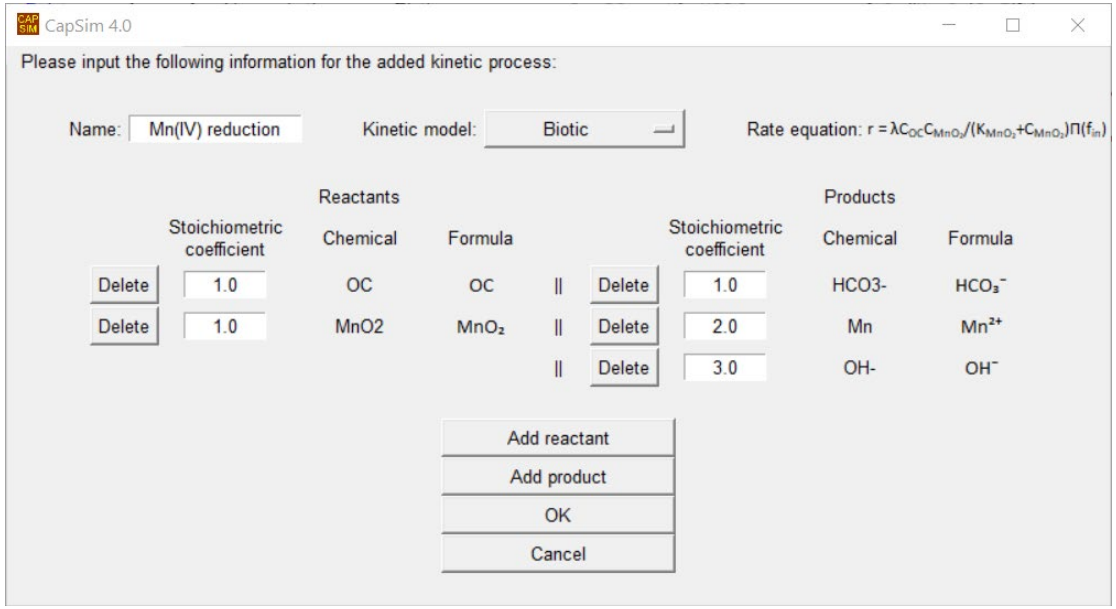
  - Inhibition constant

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

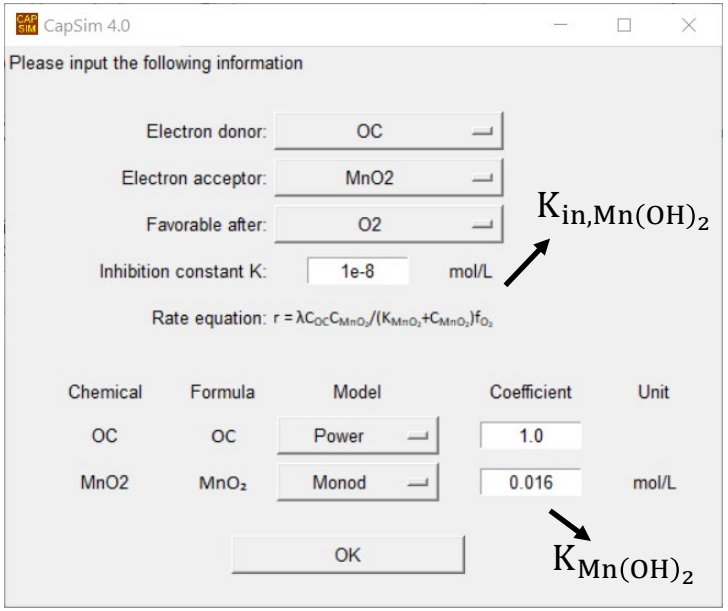
$$r_{IR} = \lambda_{OM} C_{OM} \frac{C_{Fe(OH)_3}}{K_{m,S}+C_{Fe(OH)_3}} \frac{K_{in,O_2}}{K_{in,O_2}+C_{O_2}} \frac{K_{in,NO_3}}{K_{in,NO_3}+C_{NO_3}}$$

Biotic Reactions

Reaction editor



Biotic model



$$CH_2O + 2MnO_2(s) + H_2O \rightarrow 2Mn^{2+} + HCO_3^- + 3OH^-$$

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

Example 3 – Hg Methylation

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

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

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

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

BCs

O_2= 0.025mM
SO_4 = 0.028M

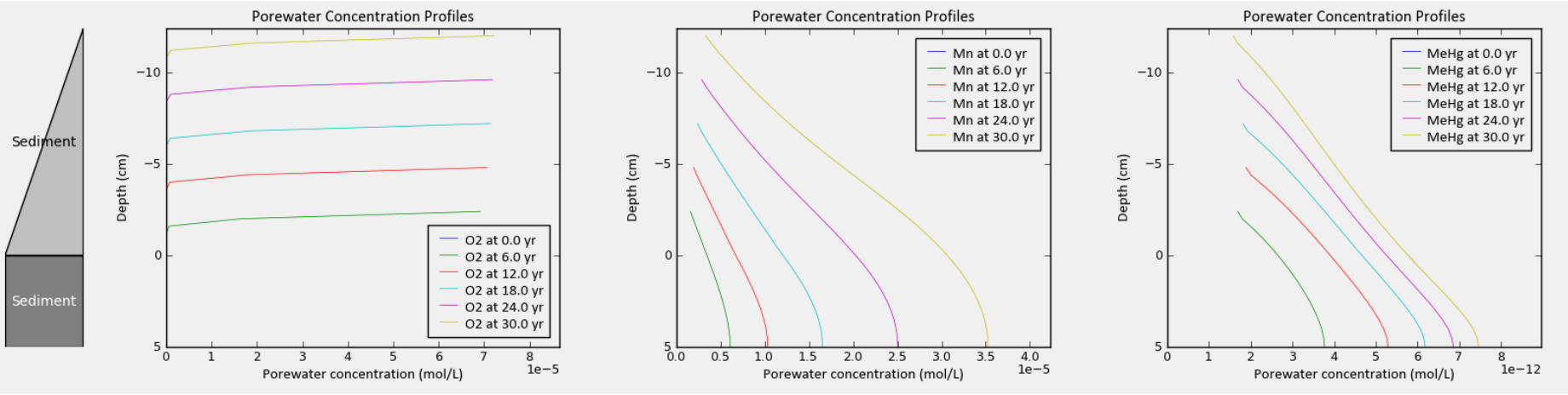
Deposition

CH_2O = 0.04M
MnO_2 = 0.01mM
$Fe(OH)_3$ = 0.1M

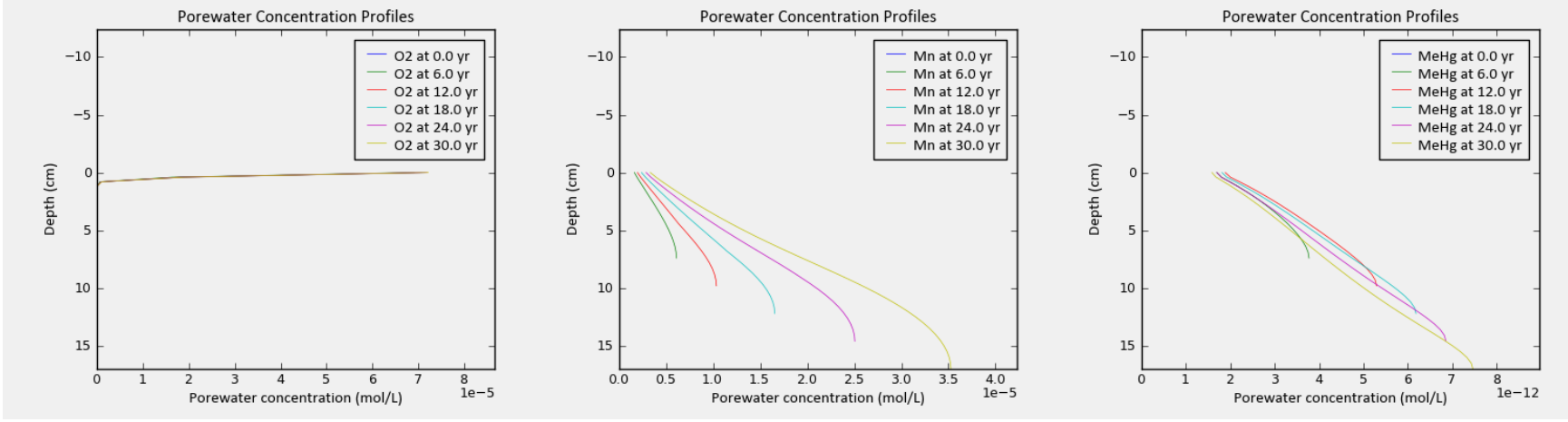
Initial sediment

CH_2O = 0.04M
MnO_2 = 0.01M
$Fe(OH)_3$ = 0.1M

Example 3 – CapSim Results

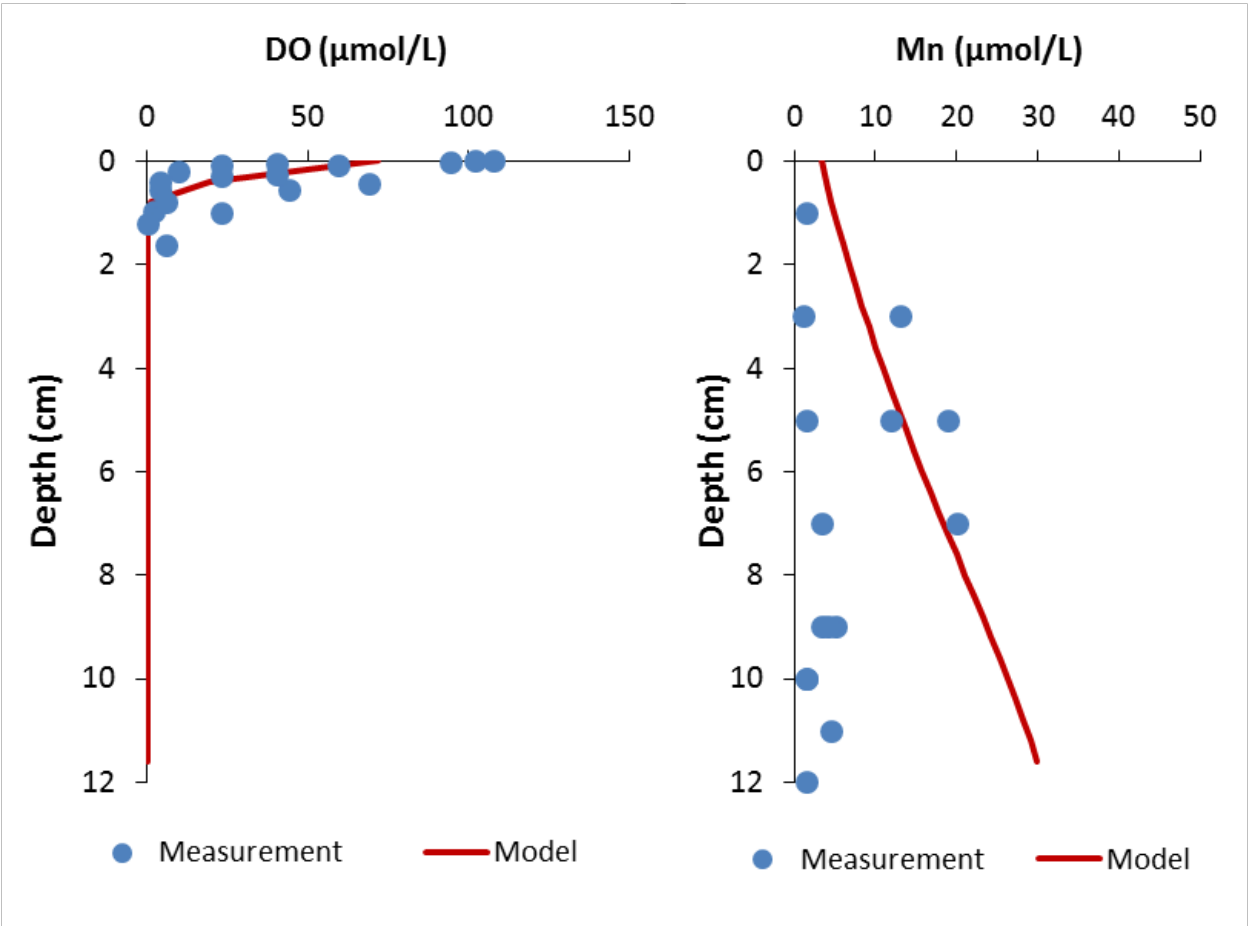


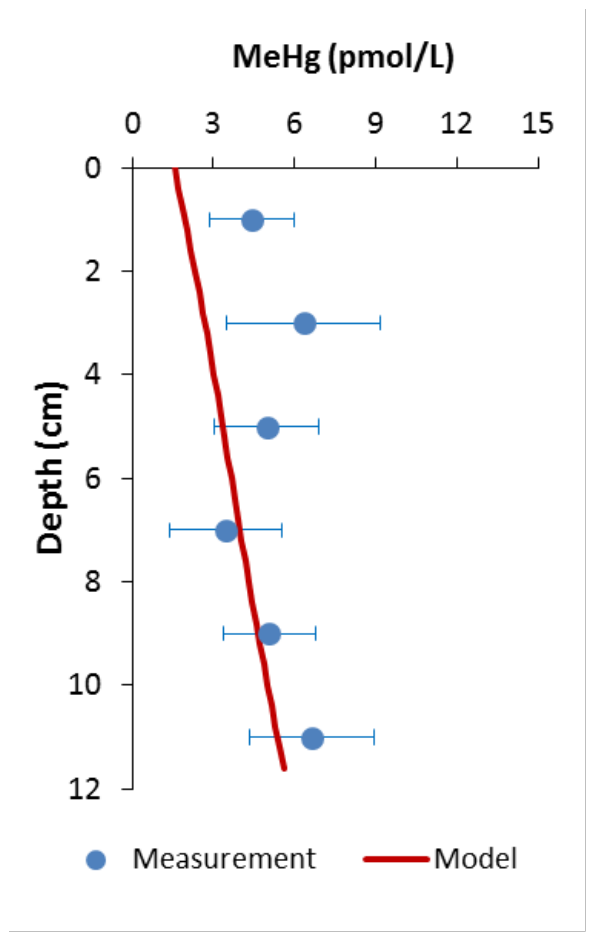
Original benthic surface



Updated benthic surface

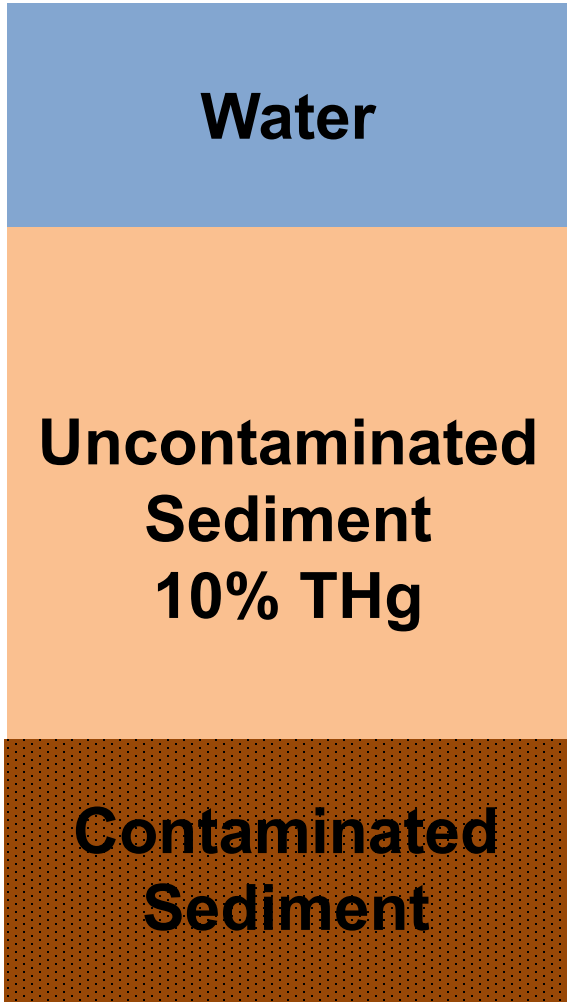
Example 3 – Hg Baseline

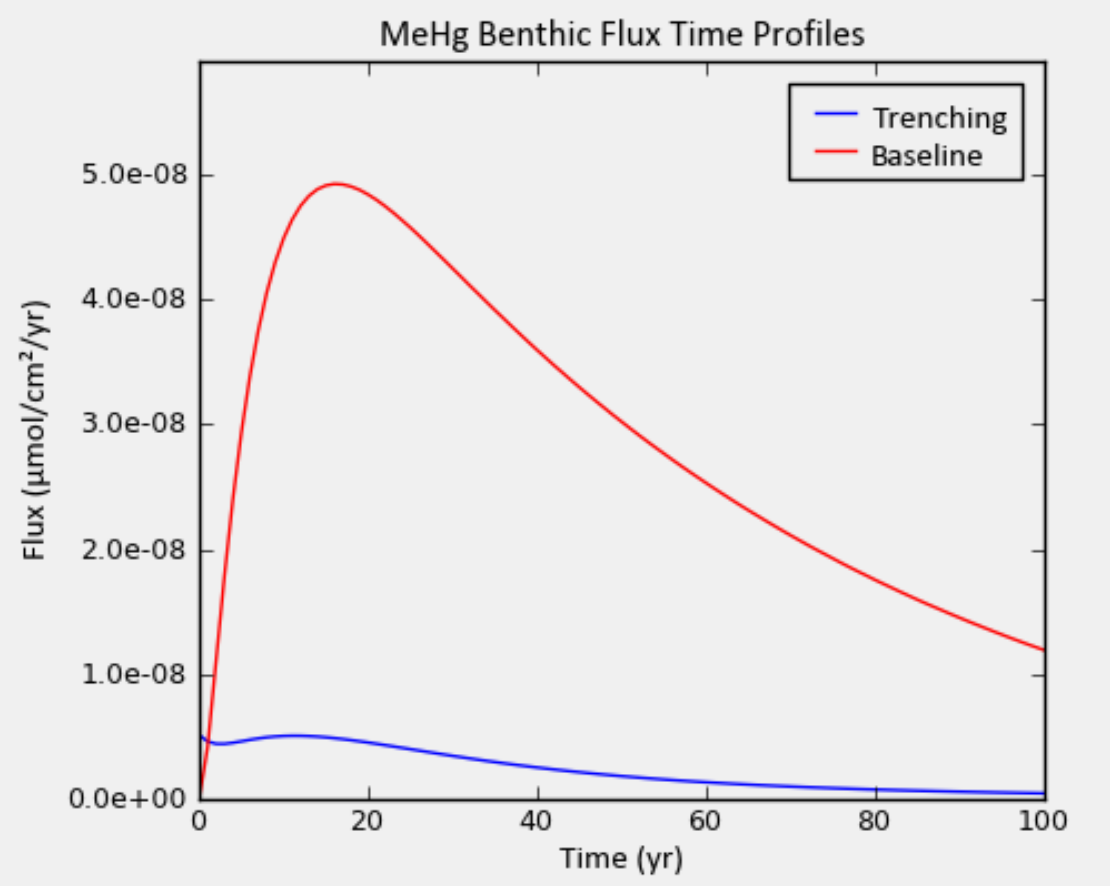




$k_{SR,meth} \sim k_{IR,meth}$

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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Thank you !