# Dynamic Fugacity Approach in Modeling Contaminant Fate and Transport in Rivers

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# Objective

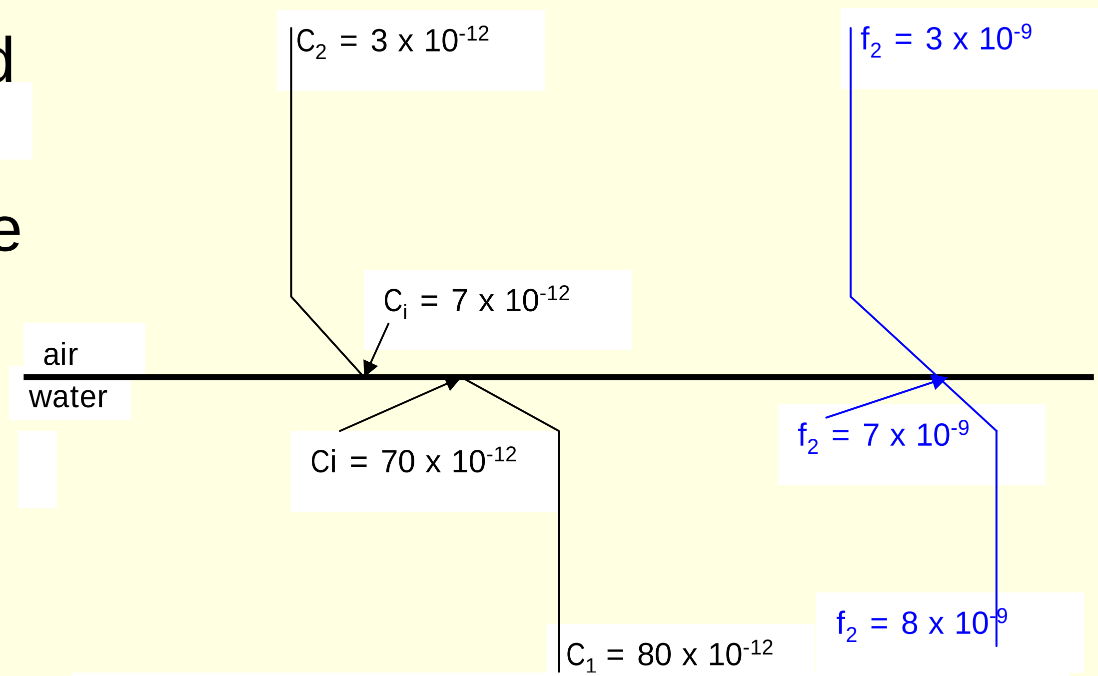
Development of a dynamic fugacity-based model to simulate concentration distribution of a contaminant in the water column as well as sediments of a river reach.

# Outline

- Why Fugacity?
- Hydrodynamic model
- Contaminant Transport
- Solution of Governing Equations
  - Hydrodynamics
  - Contaminant Transport
- Application
- Future work

# Why Fugacity?

- Linear relationship between concentration and fugacity C = F Z
- Continuous profile among different phases
- Decreases the number of coefficients used




*Source: Mackay, 1980*

# Hydrodynamics of Rivers

- Characteristics of Channel Flow
  - Free surface
  - Gravity is the driving force
  - Always unsteady
- Development of unsteady flow equations for open channels
  - First published in 1871 by Saint Venant
  - Still used

# Derivation of Saint-Venant Equations for River Hydrodynamics

- Conservation of mass

$$\frac{\partial A}{\partial t}+\frac{\partial Q}{\partial x}=0$$

A – cross-sectional area ($L^2$)
Q – volumetric flowrate ($L^3/T$)
t – time (T)
X – distance along the river (L)

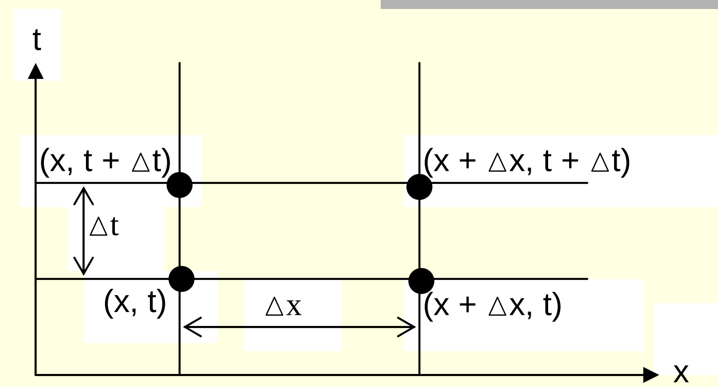
- Conservation of momentum

$$\frac{\partial Q}{\partial t}+\frac{\partial (Qu)}{\partial x}=-gA\frac{\partial h}{\partial x}+gA(S_o-S_f)$$

Q – flowrate, L3/T
u – velocity, L/T
t – time, T
A – area, L2
x – distance along the river, L
h – water surface elevation, L
g – gravitational accelaration,$L/T^2$
$S_o$ – bed slope, L/L
$S_f$ – friction slope L/L

# Solution of Saint-Venant Equations

- Coupled, non-linear, first order partial differential equations
- No analytical solution, so require numerical solution
- Numerical technique used in this study:
  - Preissmann Weighted Four-Point Method
    - Implicit scheme
    - Flexible time steps and distance
    - Unconditionally stable




$$\frac{\partial \phi}{\partial x} = \frac{(1-\theta)\left(\phi^{t}_{x+\Delta x} - \phi^{t}_{x}\right) + \theta\left(\phi^{t+\Delta t}_{x+\Delta x} - \phi^{t+\Delta t}_{x}\right)}{\Delta x}$$

$$\frac{\partial \phi}{\partial t} = \frac{\left(\dfrac{\phi^{t+\Delta t}_{x} + \phi^{t+\Delta t}_{x+\Delta x}}{2} - \dfrac{\phi^{t}_{x} + \phi^{t}_{x+\Delta x}}{2}\right)}{\Delta t}$$

$$\phi = (1-\theta)\left(\frac{\phi^{t}_{x+\Delta x} + \phi^{t}_{x}}{2}\right) + \theta\left(\frac{\phi^{t+\Delta t}_{x+\Delta x} + \phi^{t+\Delta t}_{x}}{2}\right)$$

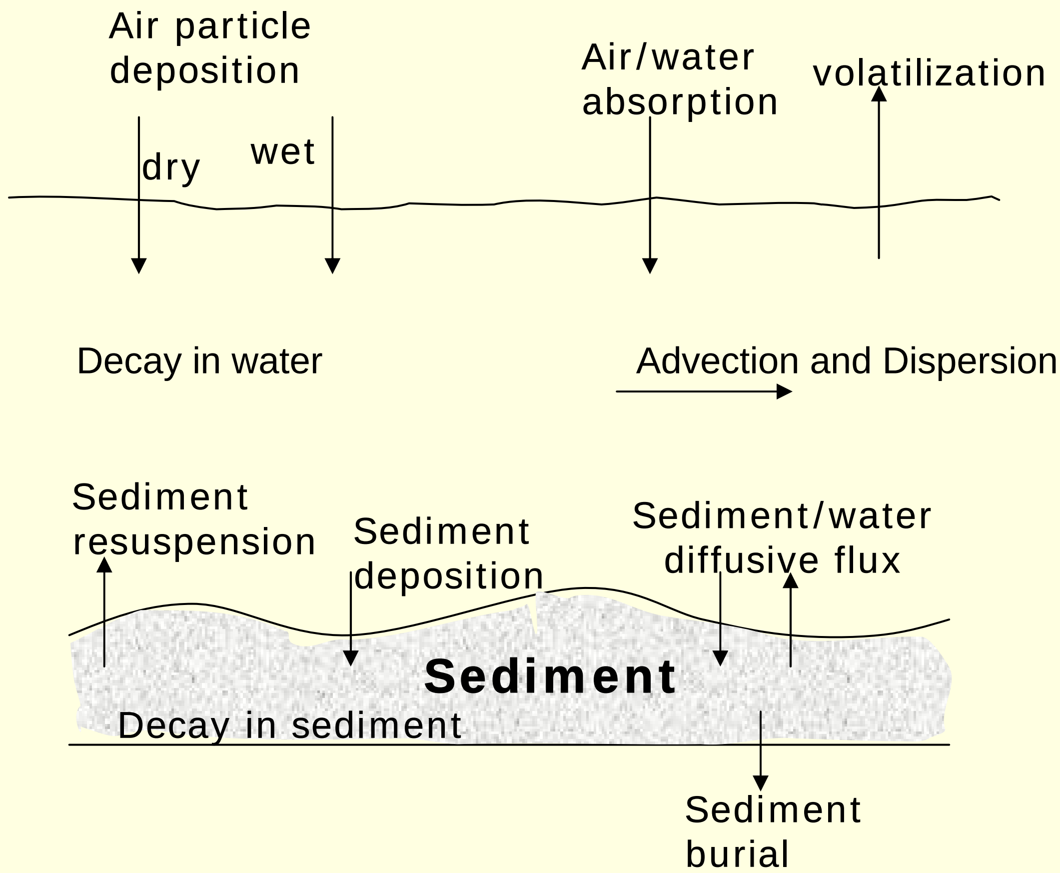
# Contaminant Transport:

- Advection Dispersion Equation is used

$$\boxed{\frac{\partial C}{\partial t}+\frac{\partial (Cu_x)}{\partial x}-\frac{\partial}{\partial x}\left(D_{Hx}\frac{\partial C}{\partial x}\right)=\sum \text{Reaction}}$$

- Reactions include:
  - Volatilization
  - Diffusion between air/water and water/sediment
  - Deposition/resuspension of suspended particles
  - Wet and dry deposition of aerosols from atmosphere
  - Decay of the chemical in water column and sediments

# Natural Processes in a River Reach



# Contaminant Transport

- Contaminants are distributed among all media in the vicinity of water column
- Sediments and air are also considered as a compartment in the contaminant transport model
- Sediments are immobile
- Air concentration is assumed to be constant

$$\boxed{\frac{\partial(F_{water} Z_{bw})}{\partial t} + \frac{\partial(F_{water} Z_{bw} u_x)}{\partial x} - \frac{\partial}{\partial x}\left( D_{Hx} \frac{\partial F_{water} Z_{bw}}{\partial x} \right) = \sum \mathrm{Reactions}}$$

Water Phase

$$\boxed{\frac{\partial\left(F_{sed} Z_{sw}\right)}{\partial t} = \sum (\mathrm{Reactions} + \mathrm{interactions\ with\ water})}$$

Sediment Phase

# Water Phase Fugacity Model:

Resuspension Diffusion

$$V_w Z_{Bw}\frac{\partial f_w}{\partial t} = V_w Z_{Bw} D_H \frac{\partial^2 f_w}{\partial x^2} - V_w Z_{Bw} U \frac{\partial f_w}{\partial x} + f_s\left( M\left(\frac{\tau_b}{\tau_c} - 1\right)\frac{K_p\rho_s}{H} + \frac{A_w}{H\left(\frac{1}{K_w} + \frac{1}{K_s K_p \rho_s}\right)} \right)$$

Dispersion Advection

Decay Settling

Volatilization

Diffusion

$$+ f_a\left(\frac{HA_w}{K_{aw}} + u_D\frac{A_w}{RT} + u_R\frac{QA_w}{RT}\right) - f_w\left(\frac{HA_w}{K_{aw}} + V_w\frac{k_w}{H} + \frac{gd^2}{18}\left(\frac{\rho_s - \rho}{\mu}\right)\frac{K_p\rho_s}{H} + \frac{A_w}{H\left(\frac{1}{K_w} + \frac{1}{K_s K_p \rho_s}\right)}\right)$$

Diffusion Dry and wet deposition

$$\boxed{\frac{\partial f_w}{\partial t} = \frac{\partial}{\partial x}\left(D_H \frac{\partial f_w}{\partial x}\right) - \frac{\partial (u f_w)}{\partial x} + S_3 f_s + S_4 f_a - f_w S_5}$$

# Sediment Phase Fugacity Model:

Settling

Diffusion

$$V_s Z_{Bs} \frac{\partial f_s}{\partial t} = f_w \left( \frac{gd^2}{18} \left( \frac{\rho_s - \rho}{\mu} \right) \frac{K_p \rho_s}{H} + \frac{A_w}{H \left( \frac{1}{K_w} + \frac{1}{K_s K_p \rho_s} \right)} \right)$$

Resuspension

Diffusion

$$- f_s \left( M \left( \frac{\tau_b}{\tau_c} - 1 \right) \frac{K_p \rho_s}{H} + \frac{A_w}{H \left( \frac{1}{K_w} + \frac{1}{K_s K_p \rho_s} \right)} + V_{burial} \frac{K_p \rho_s}{H} + V_s \frac{k_s K_p \rho_s}{H} \right)$$

Burial

Decay

$$\boxed{\frac{\partial f_s}{\partial t} = S_6 f_w - S_7 f_s}$$

# Contaminant Transport Model:

- The final aqueous fugacity balance:

$$\frac{\partial f_w}{\partial t} = \frac{\partial}{\partial x}\left( D_H \frac{\partial f_w}{\partial x} \right) - \frac{\partial (U f_w)}{\partial x} + S_3 f_s + S_4 f_a - f_w S_5$$

$$\frac{\partial f_w}{\partial t} = D_H \frac{\partial^2 f_w}{\partial x^2} + \frac{\partial D_H}{\partial x}\frac{\partial f_w}{\partial x} - U \frac{\partial f_w}{\partial x} - f_w \frac{\partial U}{\partial x} + S_3 f_s + S_4 f_a - f_w S_5$$

- The final sediment fugacity balance:

$$\frac{\partial f_s}{\partial t} = S_6 f_w - S_7 f_s$$

# Numerical Solution:

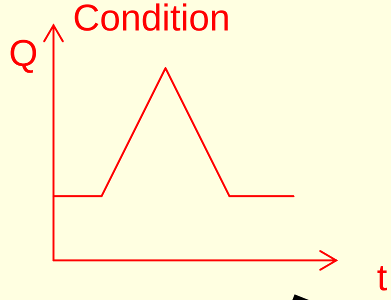
- Only water phase is mobile
- Sediment phase is immobile
- Air is assumed to be semi infinite (constant air concentration)
- Velocity input comes from hydrodynamics
- Dispersion coefficient calculated using velocity

$$\frac{df_w}{dt} = \frac{f_{w_i}^{k+1} - f_{w_i}^{k}}{\Delta t}$$

$$\frac{df_w}{dx} = \frac{f_{w_{i+1}}^{k} - f_{w_{i-1}}^{k}}{2\Delta x}$$

$$\frac{d^2 f_w}{dx^2} = \frac{1}{2}\left[\frac{f_{w_{i+1}}^{k+1} - 2 f_{w_i}^{k+1} + f_{w_{i-1}}^{k+1}}{(\Delta x)^2} + \frac{f_{w_{i+1}}^{k} - 2 f_{w_i}^{k} + f_{w_{i-1}}^{k}}{(\Delta x)^2}\right]$$

# Application:



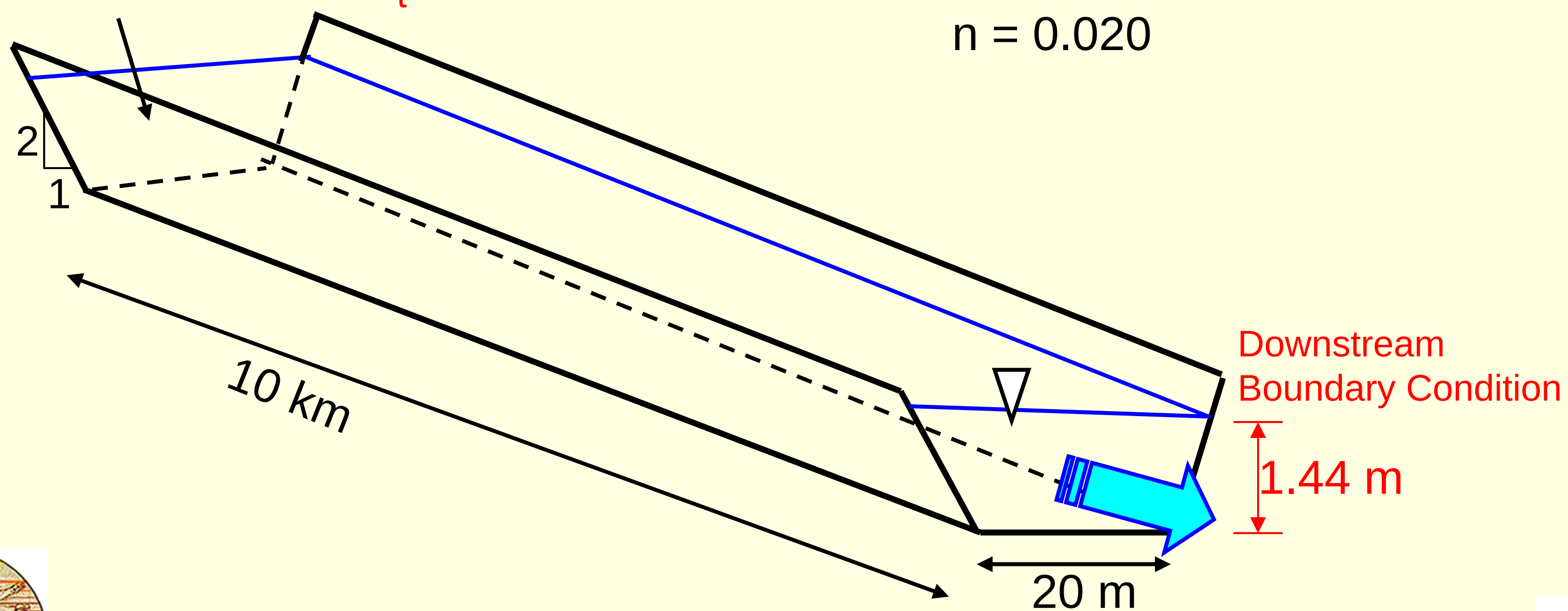

Total simulation time = 1 week

Number of nodes = 101

$\triangle x$ = 100 m

S0 = 0.001 m/m

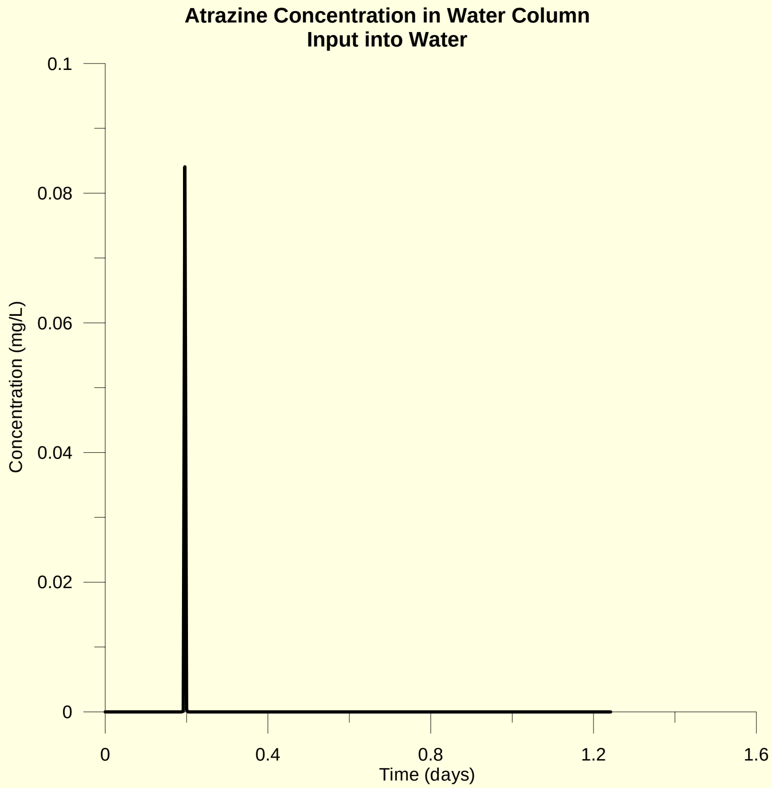
n = 0.020

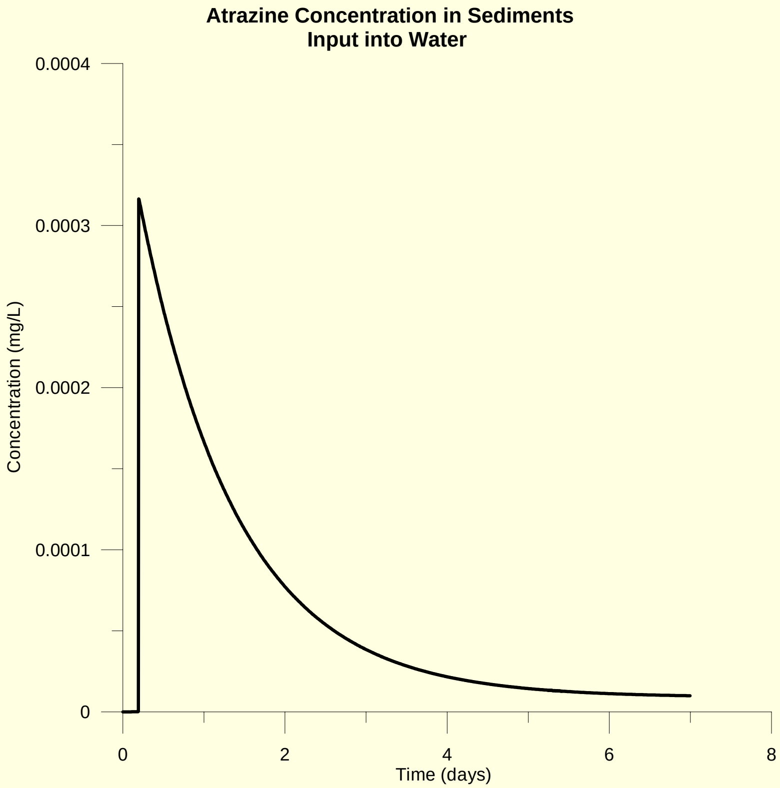


# Application:

- Two application cases:
  - Case 1 : Instantaneous spill of atrazine into water column ($C_0$ = 0.1 mg/L)
    - Atrazine is the most commonly used agricultural herbicide
  - Case 2: Sediment release of PCB as a result of dredging ($C_0$ = 0.1 mg/L)
    - Although abandoned, PCBs are still existent in large amounts in the sediments of rivers

# Results – Case 1 (Atrazine Spill into Water Column)



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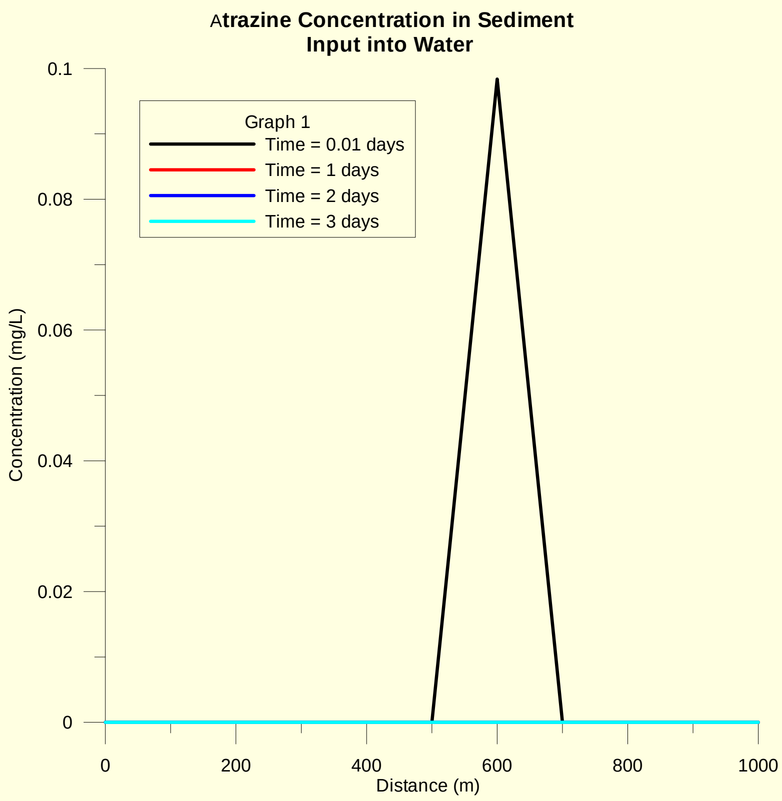
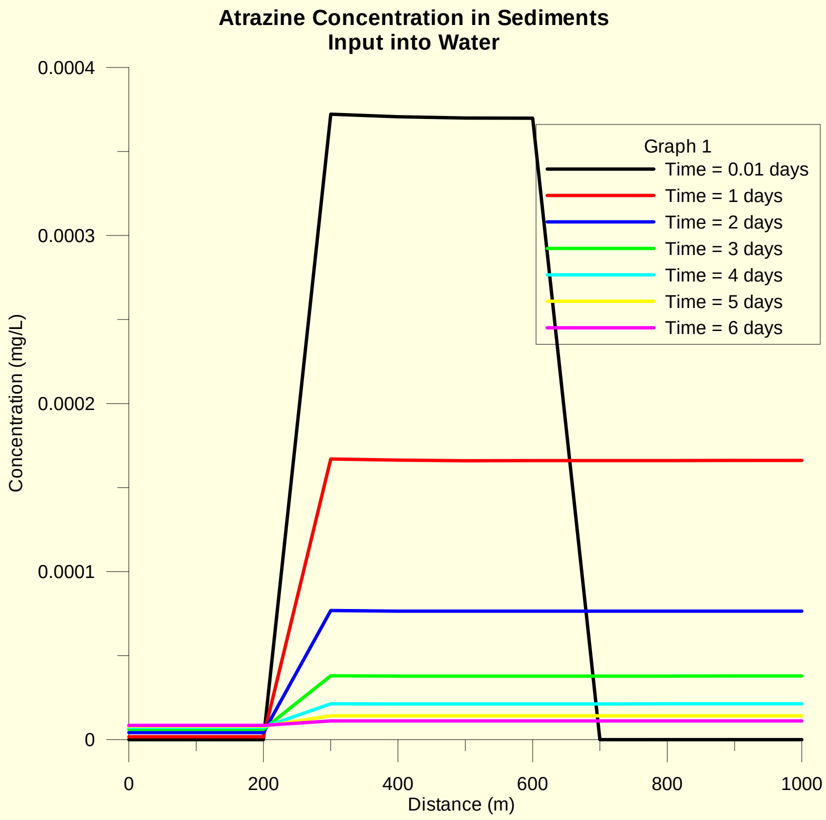
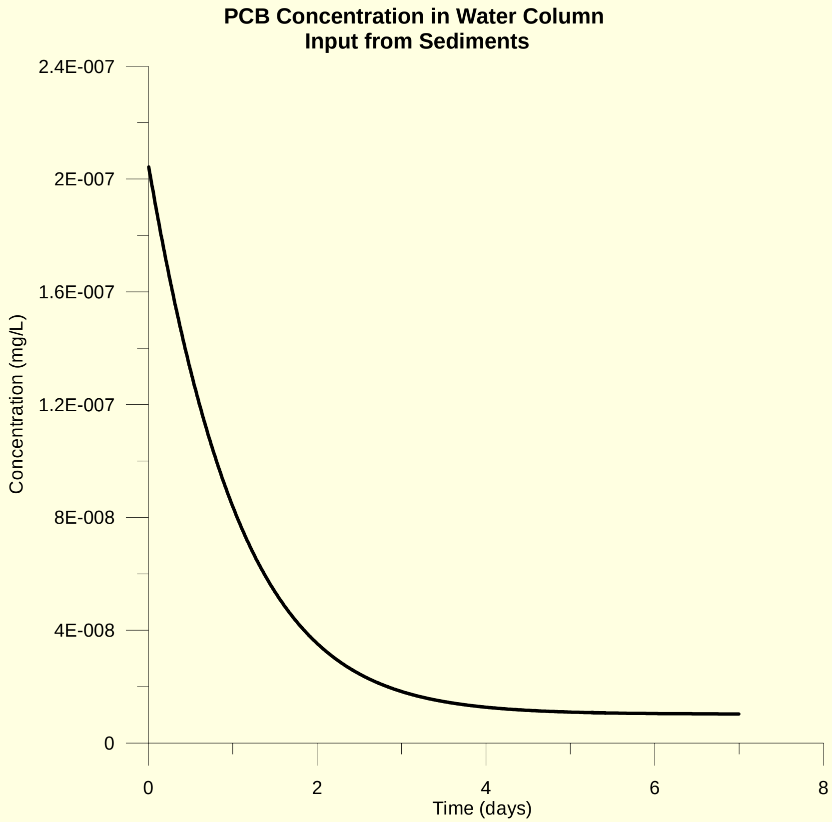
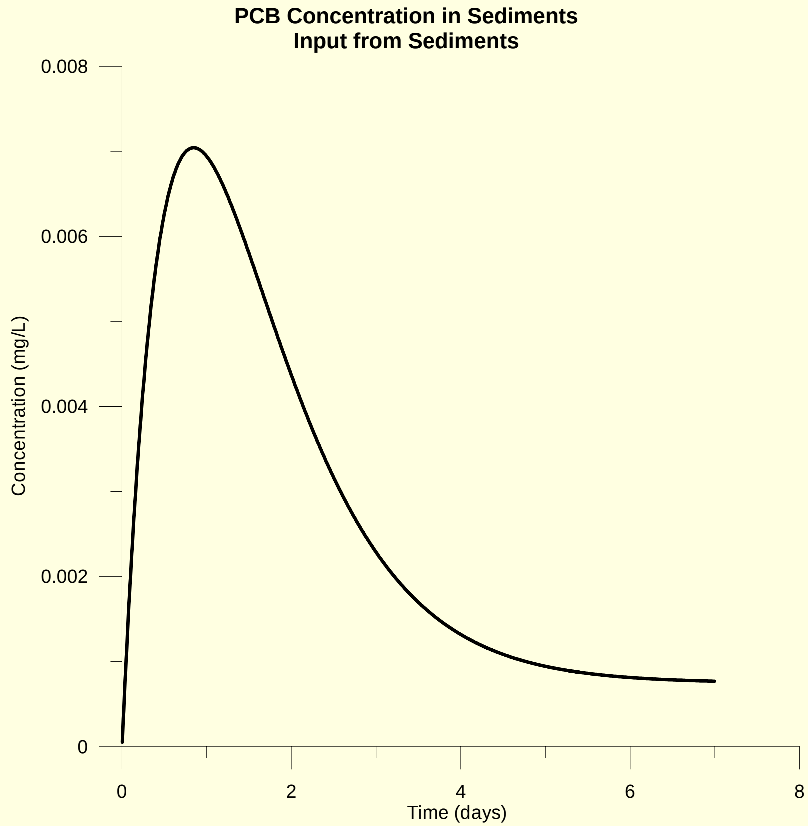


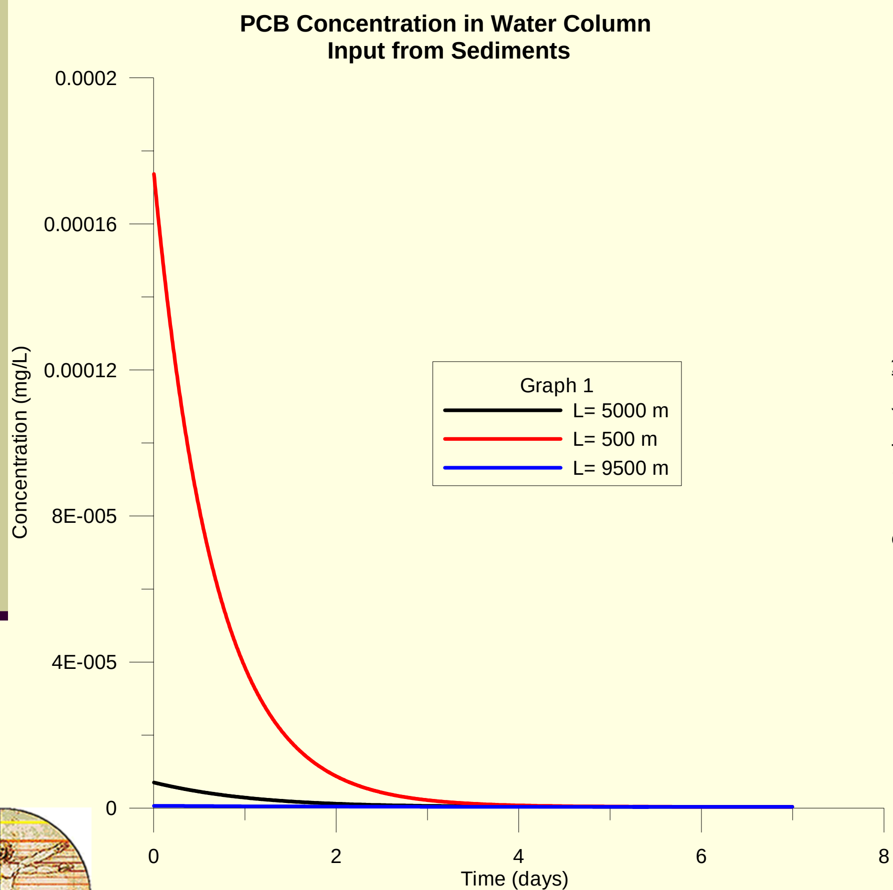



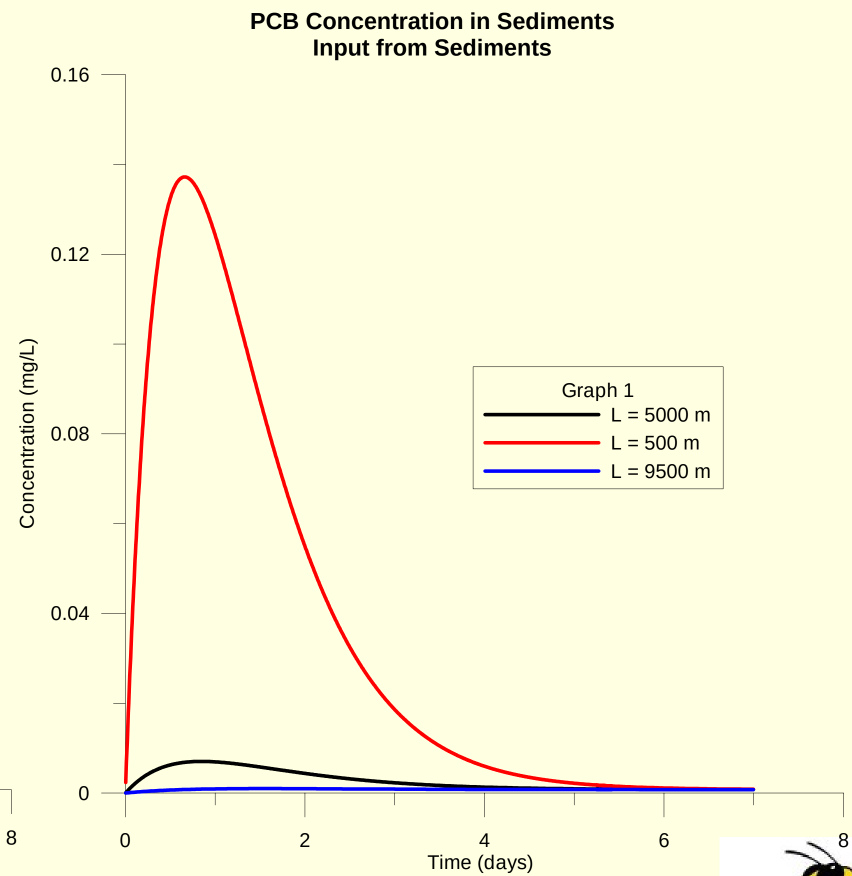
# Results – Case 2
# (PCB Release from Sediments)



# Results – Case 2 (PCB Release from Sediments)



# Future Work

- A real case application
- Altamaha River