Density-dependent Transport and Sequential Biotransformation of Trichloroethylene in a Variably Saturated Zone

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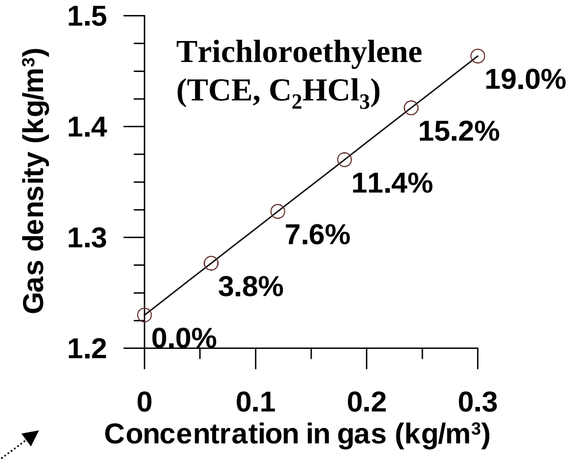
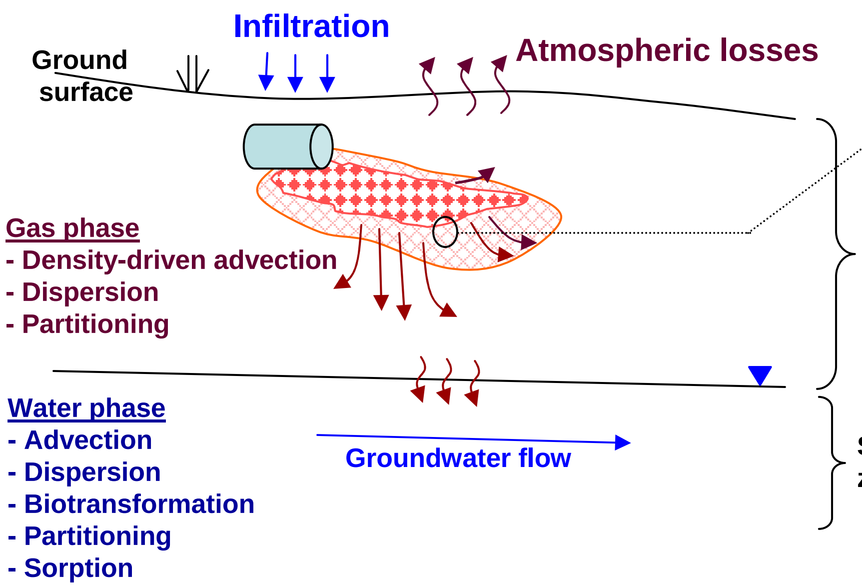
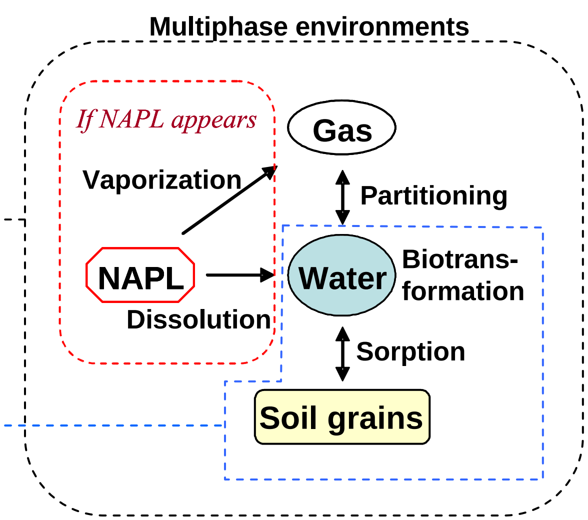
Introduction

- **Density-driven advection of gas phase**
  - Is generated by density-gradient within gas phase.
  - Occurs near contaminant source zones.



$\rho_g = f(P_g, C_g)$





NAPL = Non-Aqueous Phase Liquid

Study objectives

- **Objective is:**
  - To investigate density-driven transport of multi-species with biological reactions in a variably saturated subsurface.

- **Model development activities:**
  - Develop a three-dimensional numerical model
  - Verify and validate the model using analytical solutions, experimental data, and numerical results available in literature

- **Assumptions:**
  - First-order relations
    : Biotransformation, sorption, and partitioning
  - Gas phase: $\rho = f(P,C)$ and $\mu = f(C)$
  - Water phase: Constant properties
  - NAPL: Immobile residuals

Flow equations

- From mass conservation and continuity equations

$$\frac{\partial(\phi s_f \rho_f)}{\partial t} - \nabla \cdot \{\rho_f \underbrace{\frac{\mathbf{k}_m k_{rf}}{\mu_f} \cdot [\nabla(\psi_f \rho_w g) - \rho_f \mathbf{g}]}_{q_f\text{, Darcy velocity}} \} = I_f + \rho_f^* Q_f$$

Subscript f = fluid phases (water and gas)
ψ_f = Pressure head (primary variable)
s_f = Saturation
k_{rf} = Relative permeability
ρ_f = Density

- Gas density

$$\rho_g(P_g, C) = \rho_{air} + \gamma_g P_g + \sum_{i=1}^{N} C_g^i \left(1 - \frac{\rho_{air}}{\rho_v^i}\right)$$

i = contaminants
N= total number of contaminants

(Thomson et al., 1997)

- Relative permeability = f (effective saturation)
  - Water phase $k_{rw} = s_{we}^{1/2}\left\{1 - \left[1 - s_{we}^{1/m}\right]^m\right\}^2$ *(van Genuchten, 1980)*
  - Gas phase $k_{rg} = s_{ge}^{1/2}\left[1 - (1 - s_{ge})^{1/m}\right]^{2m}$ *(Parker et al., 1987)*
- Effective saturation

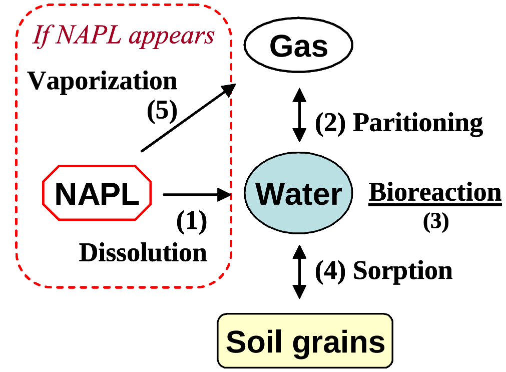
$$s_{we} = \left[1 + (\alpha_{gw}\psi_{gw})^n\right]^{-m}$$

$$s_{ge} = 1 - s_{we} - s_{ne}$$

α_{gw} , n= experimental coefficient
m = 1-1/n

- Gas viscosity = f (concentration) as gas mixture *(Wilke equation, Reid et al., 1987)*

Contaminant Transport Equations



- Multi-species in water and gas phases

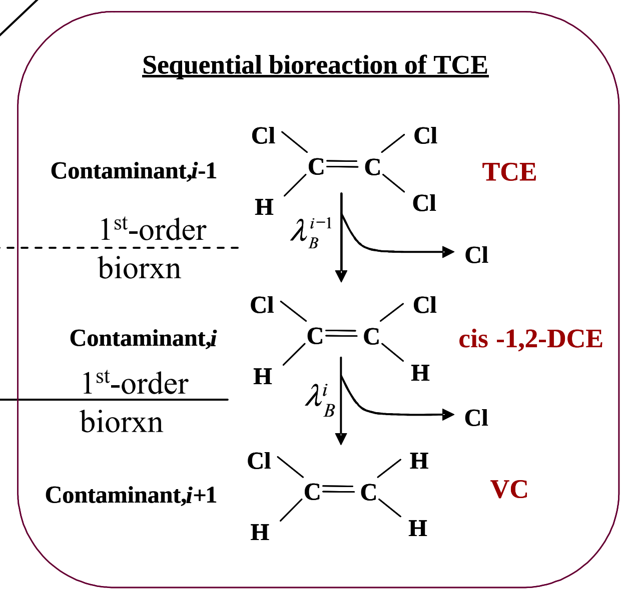
$$\frac{\partial(\phi s_f C_f^i)}{\partial t} = \underbrace{\nabla(\phi s_f D_f^i \nabla C_f^i)}_{\text{Dispersion}} - \underbrace{\nabla(q_f C_f^i)}_{\text{Advection}} + \underbrace{I_f^i}_{\text{Mass transfer / Bioreaction}} + \underbrace{Q_f C_f^{*i}}_{\text{Pumping, Injection}}$$

- Contaminant (ith) in water phase

$$I_w^i = \underbrace{\phi s_w \lambda_D^i (C_{we}^i - C_w^i)}_{\text{(1) Dissolution}} + \underbrace{\phi s_g \lambda_H^i (C_g^i - H^i C_w^i)}_{\text{(2) Partitioning : water-gas phase}} + \underbrace{\phi s_w \lambda_B^{i-1} Y_{i-1/i} C_w^{i-1}}_{\text{(3) Generation by biodegradation of parent contaminant, } i\text{-1}} - \underbrace{\phi s_w \lambda_B^i C_w^i}_{\text{(3) Biodegrdation of contaminant, } i} - \underbrace{\rho_b K_D^i \frac{\partial C_w^i}{\partial t}}_{\text{(4) Sorption : water-soil}}$$

- Contaminant (ith) in gas phase

$$I_g^i = \underbrace{\phi s_g \lambda_V^i (C_{ge}^i - C_g^i)}_{\text{(5) Vaporization from NAPL}} - \underbrace{\phi s_g \lambda_H^i (C_g^i - H^i C_w^i)}_{\text{(2) Partitioning : water-gas}}$$



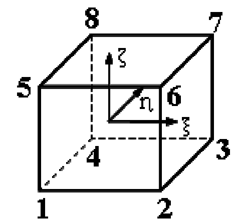
- **NAPL saturation**

$$\frac{\partial}{\partial t}(\rho_n \phi s_n) = \underbrace{-\phi s_w \lambda_D (C_{we} - C_w)}_{\text{(1) Dissolution}} \underbrace{-\phi s_g \lambda_V (C_{ge} - C_g)}_{\text{(5) Vaporization}}$$

- First-order relation coefficients : λ_D, λ_H, λ_B, λ_V
- Yield coefficient = DCE mw / TCE mw

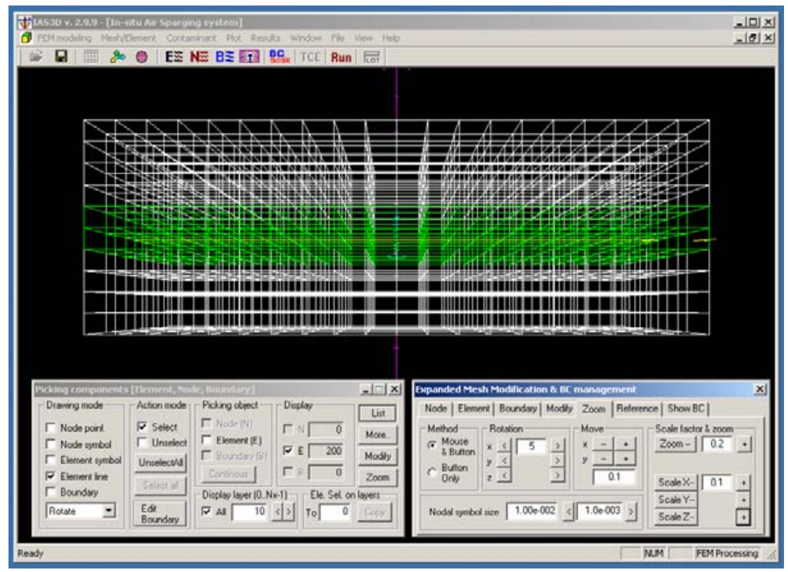
Numerical method

- **Galerkin Finite Element Method** (FEM)
  - Modified Picard method
  - Element of domain
    - Rectangular prism
    - 8 nodes each element
  - Three-dimensional mesh generator



Element with eight nodes

- **Material balance calculation**
  - Accuracy and error checking
- **Numerical codes** **(TechFlow^{MP})**
  - Program language
    - C, C++, and Visual C++
  - Support platform
    - Linux
    - Unix (High Performance Computating)
    - Microsoft Window



TechFlow^{MP}
Graphical user interface and 3D mesh generator

Model verification

1. Density-driven transport in the unsaturated zone

- Numerical results published by Mendoza and Frind (1990)
- Density-driven gas flow and contaminant transport

2. Biotransformation of contaminant in the saturated zone

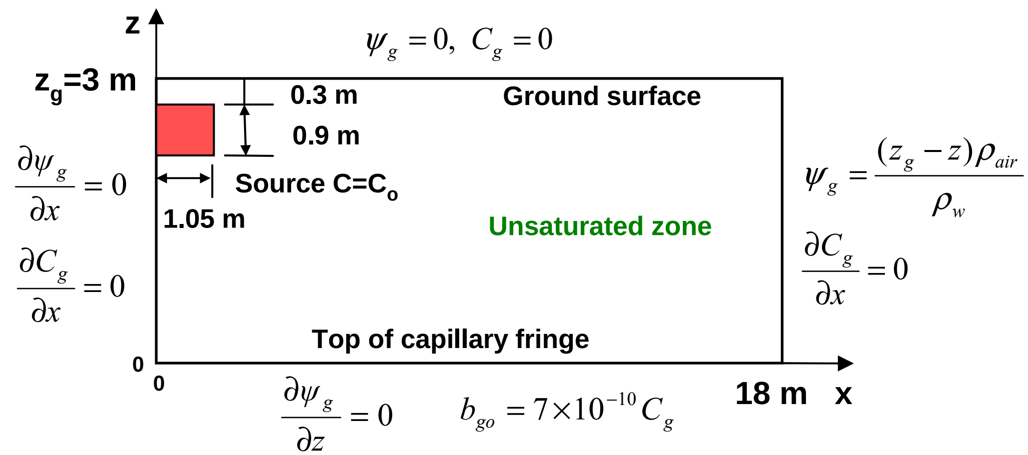
- Analytical solutions in a three-dimensional domain
- Transport of three contaminants

Model verification: 1. Density-driven transport

▪ Gas flow and transport in the unsaturated zone (2D)

Mendoza and Frind (1990)

- Simulation : density-driven transport of generic volatile organic compound (VOC).
- No advective flow of gas phase in the unsaturated zone at t=0 (no pressure gradient at gas phase)
- No reaction except equilibrium between water and gas phases
- Constant concentration at source zone

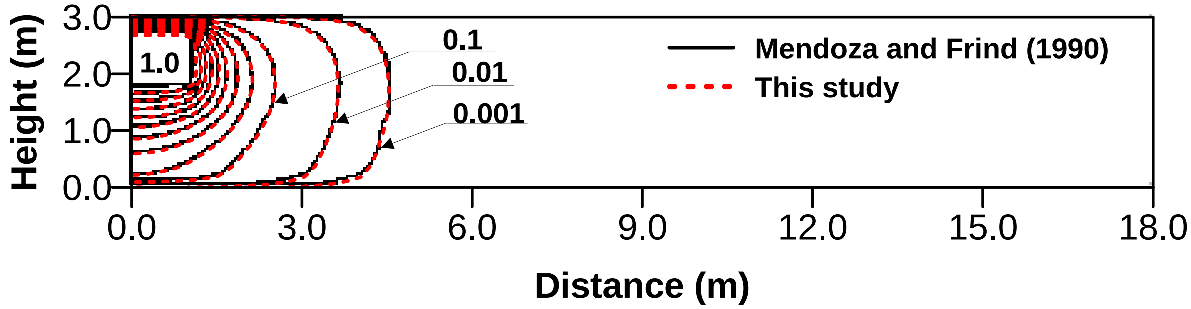


Soil medium	Permeability, k	1.0×10^{-10} m^2
	Porosity, ϕ	40 %
	Water saturation, s_w	20 %
	Residual water saturation, s_m	20 %
	Pore-size index, λ	1.65 g/cm^3
	Longitudinal dispersivity, α_L	0.15 m
	Transverse dispersivity, α_T	0.0075 m
	Temperature, T	20 °C
Generic VOC	Molecular weight, M_C	100.625 g/mol
	Molecular diffusion coefficient, D^*	9.0×10^{-6} m^2/s
	Vapor viscosity, μ_C	1.0×10^{-5} Pa s
	Henry's constant, H	0.17

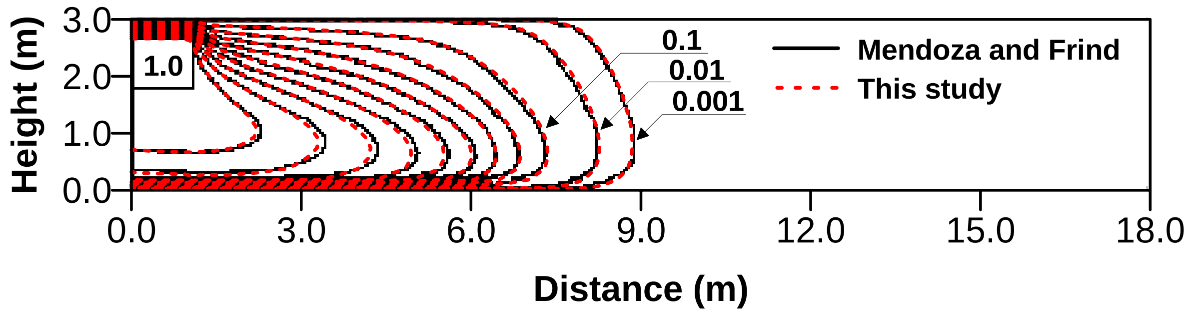
Model verification: 1. Density-driven transport (continued)

- **Contaminant transport in gas phase in the unsaturated zone at t=4days**

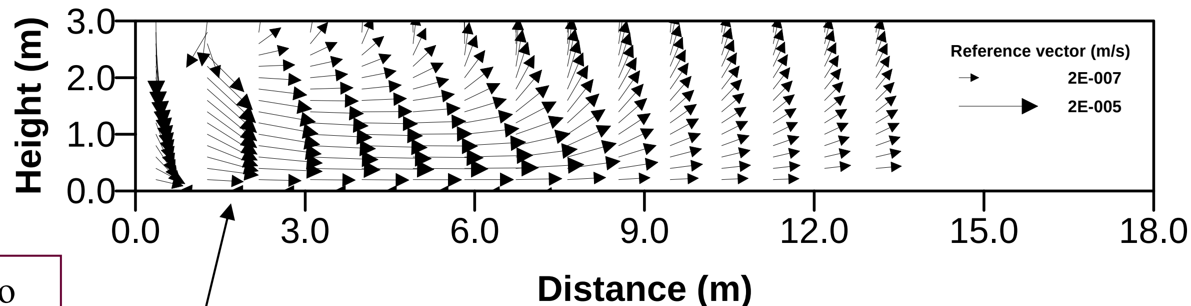
Molecular diffusion
(No advection)
Gas density = constant



Density-driven transport
(Advection + dispersion)
Gas density = *f* (concentration)



Darcy velocity of gas
Density-driven transport



Advection (gas flow) due to density gradient in gas phase

Model verification : 2. Biotransformation

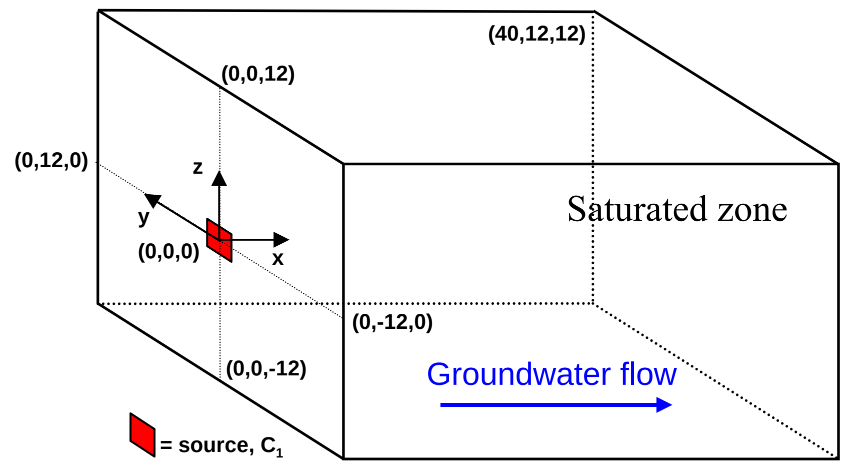
- **Transport of reactive contaminants in ground water flow (3D)**

$$TCE \xrightarrow{k_1} DCE \xrightarrow{k_2} VC \xrightarrow{k_3} ethene$$
$$C_1 \qquad C_2 \qquad C_3 \quad : \text{Concentration}$$

- Sequential biotransformation (First-order relations)
- Three contaminants
  - For example, TCE, DCE, and VC

- Initial condition
  - At source: $C_1 = 1$, Constant
  - C_2 and $C_3 = 0.$ in domain

- Simulation domain
  - Size = 40 m × 24 m × 24 m
  - dx, dy, dz =0.25 m~1.0 m



Parameters	Values
q_w, m/d	0.2
k_1, k_2, k_3, d^{-1}	0.05, 0.02, 0.01
D_x, D_y, D_z, m^2/d	0.3, 0.3, 0.1

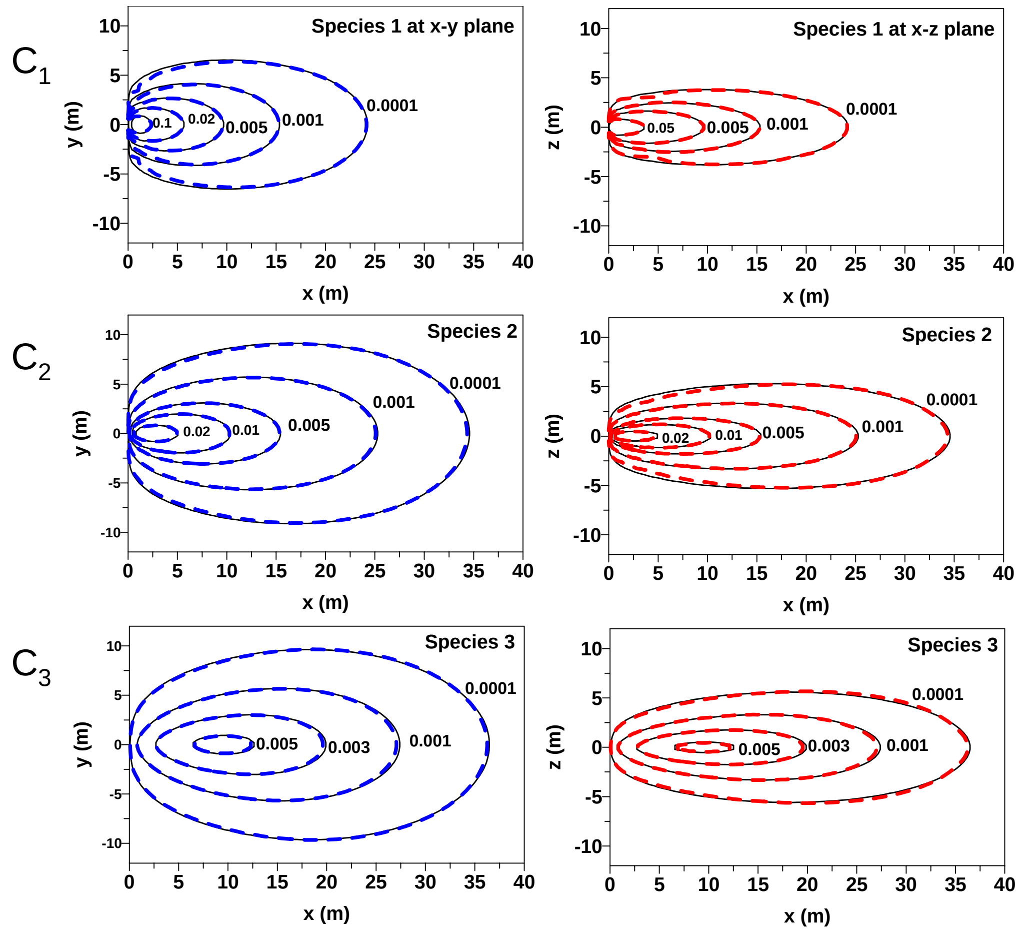
TCE: Trichloroethylene
cDCE: cis-Dichloroethylene
VC: Vinyl chloride

Model verification: 2. Biotransformation (continued)

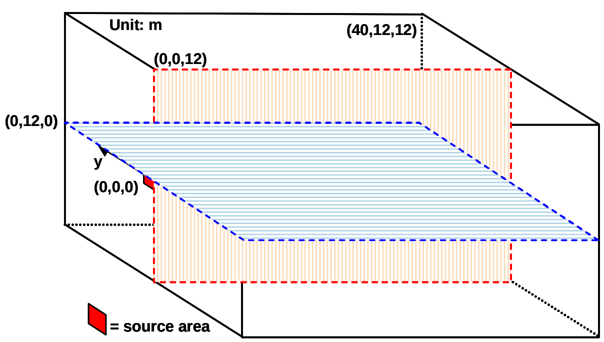
- **Results : Concentration of reactive contaminants**

t=100 days

- Results are compared with analytical solutions



Analytical solutions (Wexler, 1992)
This study at *x-y* planes ($z = 0$)
This study at *x-z* planes ($y = 0$)

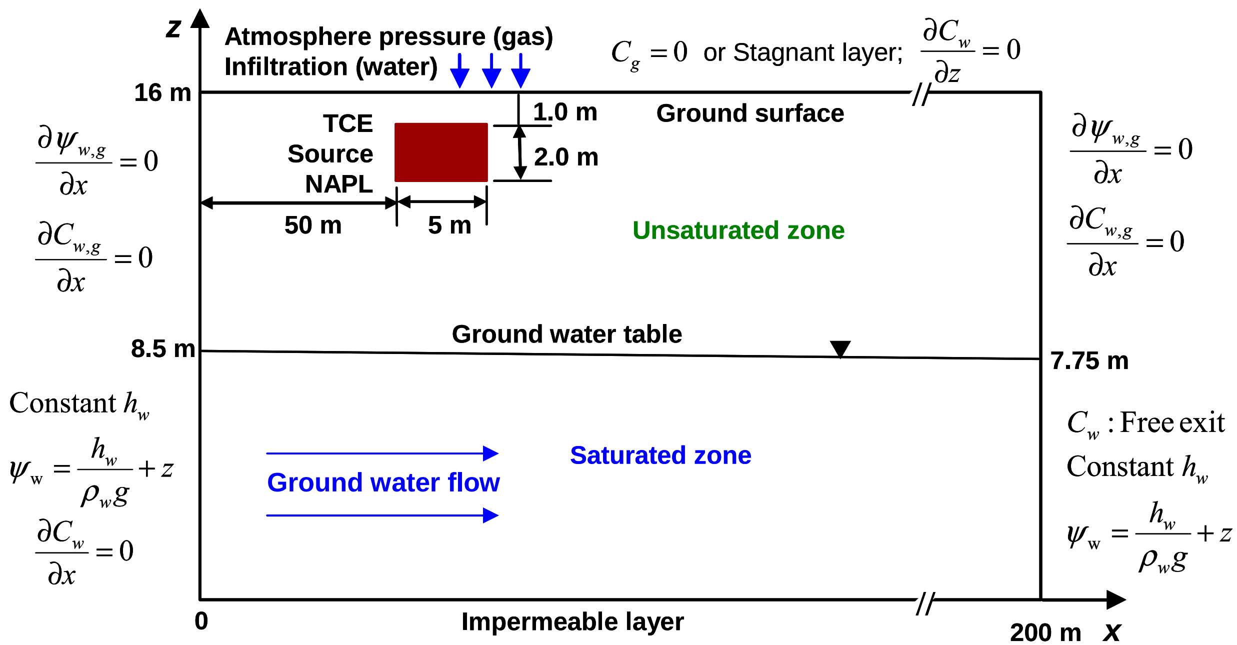


Density-driven transport with Biotransformation

- **The simulation of this study considered:**
  - Both unsaturated and saturated zones in the domain
  - Biotransformation for long-term simulation
  - Quantitative analysis
    - The contributions of important factors to ground water pollution

Modeling domain

- **Simulation of TCE transport in the variably saturated zone**
  - Model domain (unsaturated + saturated zone)



TCE source
Initial NAPL saturation = 5%
Initial TCE mass as NAPL = 64.9 kg

Parameters and properties

Parameters	TCE (C_2HCl_3)	cDCE ($C_2H_2Cl_2$)	VC (C_2H_3Cl)
Molecular weight	131.39	96.94	62.50
Vapor density, kg/m^3	5.56	4.10	2.64
Vapor dynamic viscosity, Pa s $\times 10^6$	9.38	9.29	9.27
Henry constant, dimensionless	0.227	0.097	0.756
Molecular diffusion in air, m^2/s $\times 10^6$	7.87	8.84	10.42
Molecular diffusion in water, m^2/s $\times 10^{10}$	8.206	8.711	10.65
Sorption coefficient, K_{oc}, L/g	0.1	0.049	0.003
Vapor pressure, mmHg	41.27	129.2	2136.30
max. C_g, kg/m^3	0.302	0.697	7.434
max. C_w, kg/m^3	1.33	7.19	9.83

TCE: Trichloroethylene
cDCE: cis-Dichloroethylene
VC: Vinyl chloride

Porous medium	
Permeability, k	1.0×10^{-10} m^2
Porosity, ϕ	0.35
Residual water saturation, s_m	0.
Bulk density, ρ_b	1.6 g/cm^3
Temperature, T	15 °C
Longitudinal dispersivity, α_L	1.0 m
Transverse dispersivity, α_T	0.01 m
Soil organic content, f_{oc}	0.0025
Parameters for the unsaturated zone	
n	2.0
α_{gw}	5.0 m^{-1}

Simulation scenarios

- **Scenario 1. Diffusion vs. Density-driven transport**

- **Scenario 2. Sequential biological transformations**

  : TCE → cDCE → VC

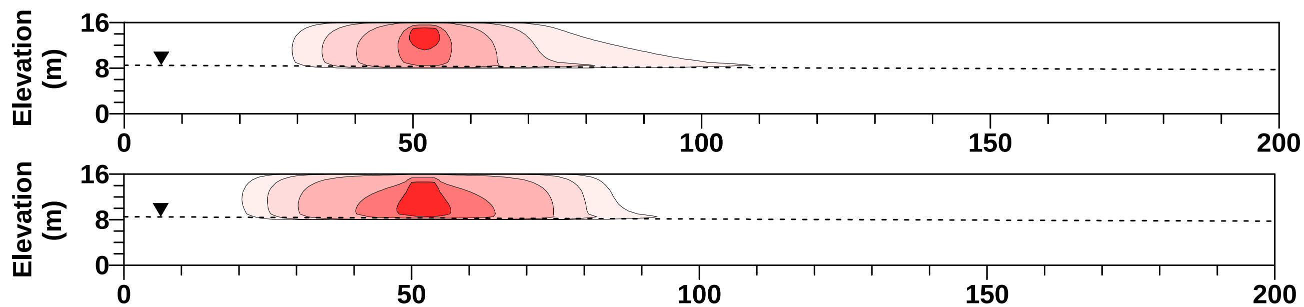
Scenario 1. Diffusion vs. Density-driven transport

Red = Contaminant in gas phase

- **Concentration of TCE in gas phase**
  - t=100 days

Diffusion (no advection)

Density-driven Transport (Adv.+Disp.)

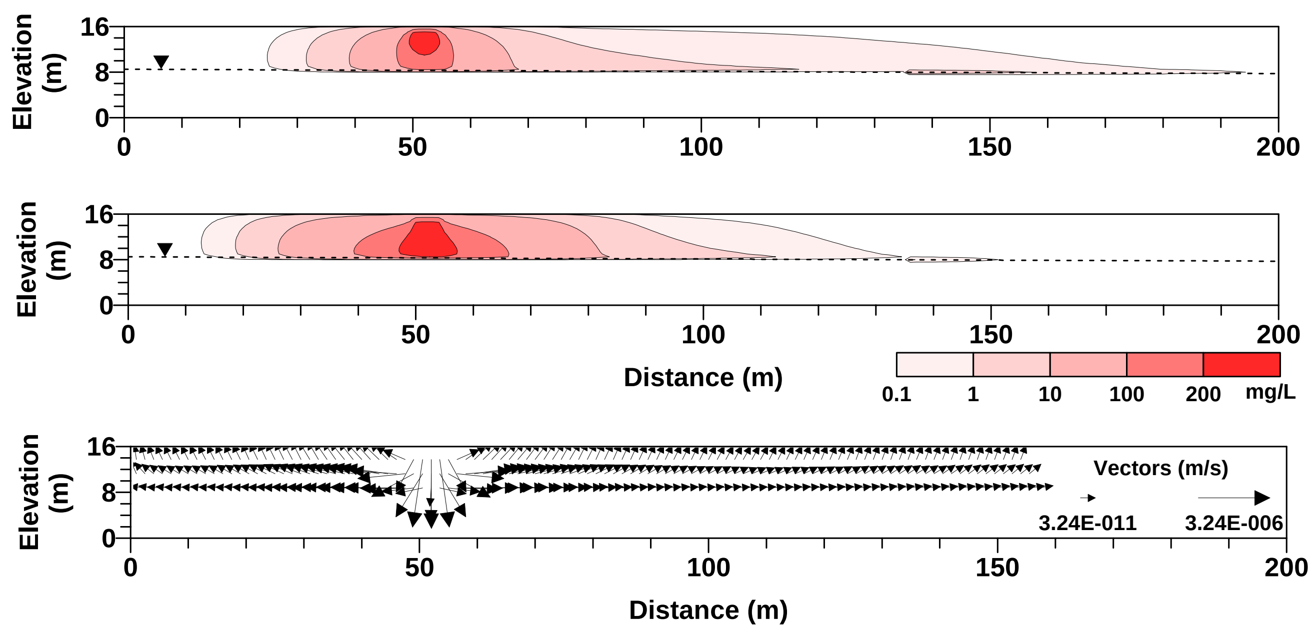


  - t=200 days

Diffusion

Density-driven transport

Gas phase Density-driven flow



Scenario 1. Diffusion vs. Density-driven transport (continued)

Blue = Contaminant in water phase

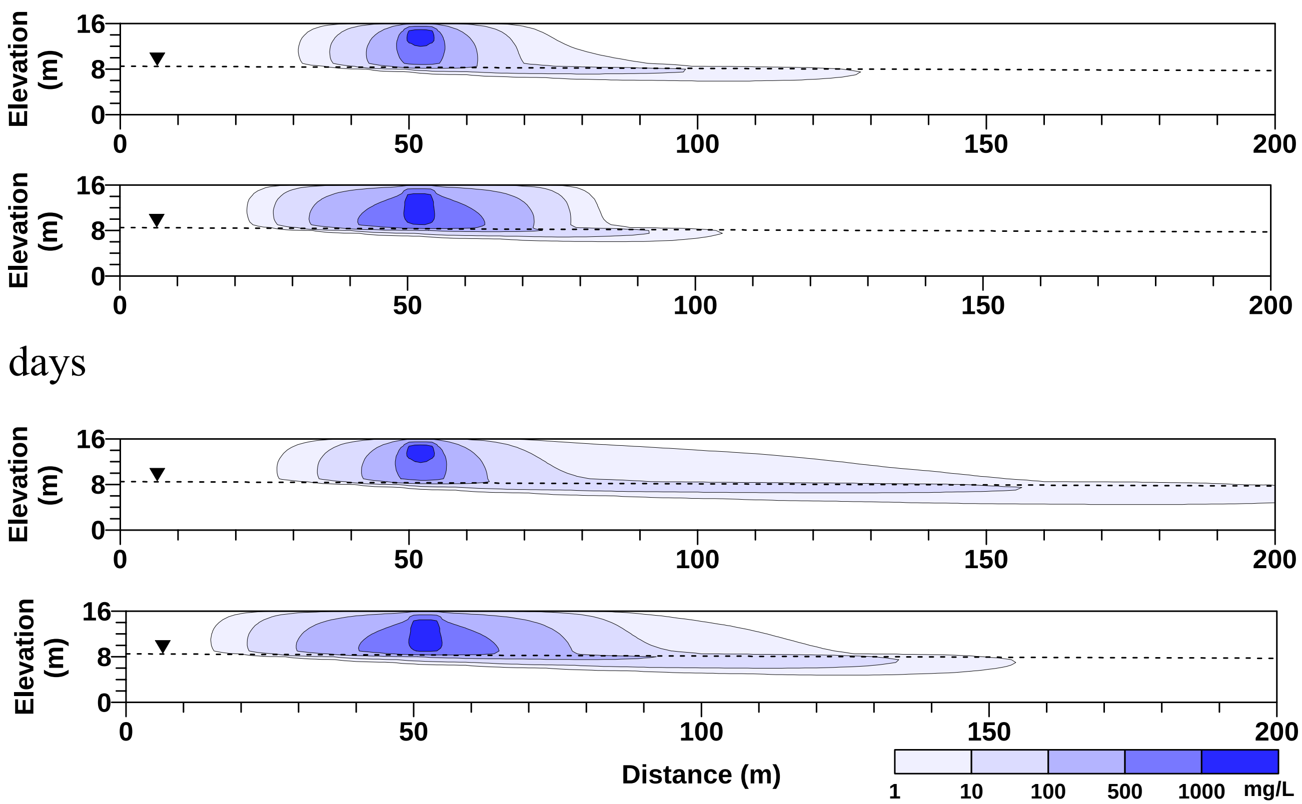
- **Concentration of TCE in water phase**
  - t=100 days
  - t=200 days

Diffusion

Density-driven transport

Diffusion

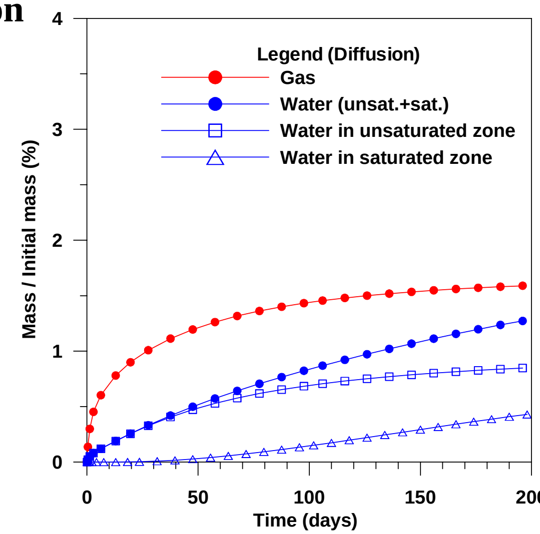
Density-driven transport



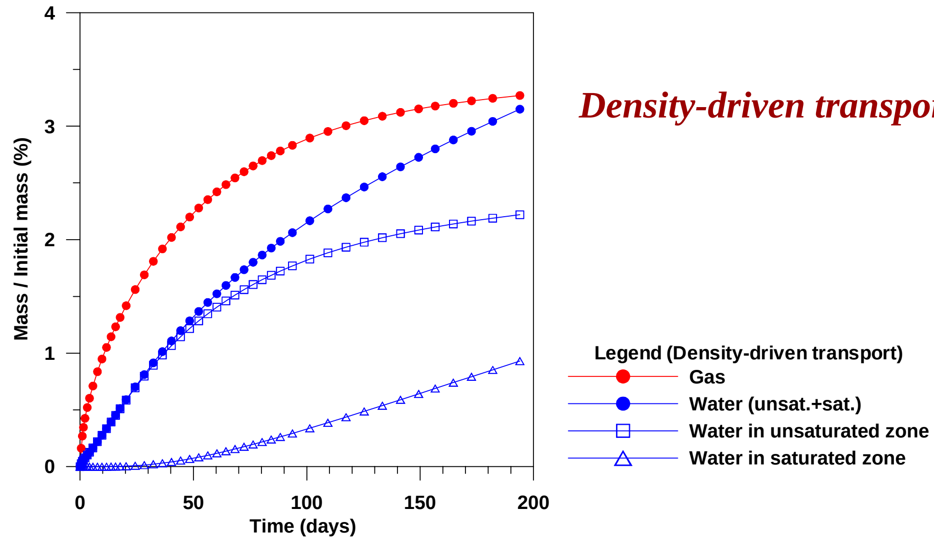
Scenario 1. Diffusion vs. Density-driven transport (continued)

TCE distribution

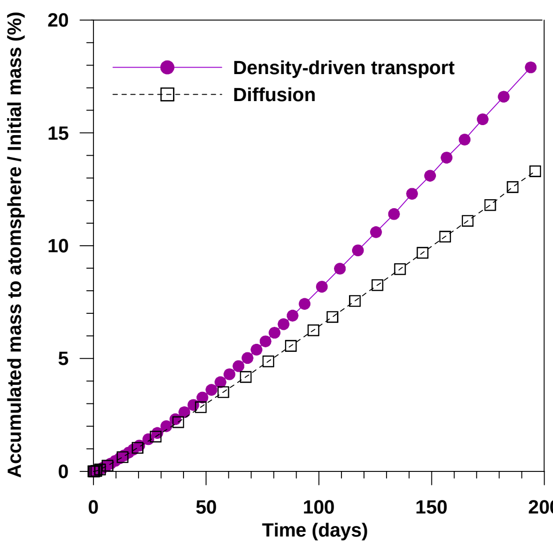
Diffusion



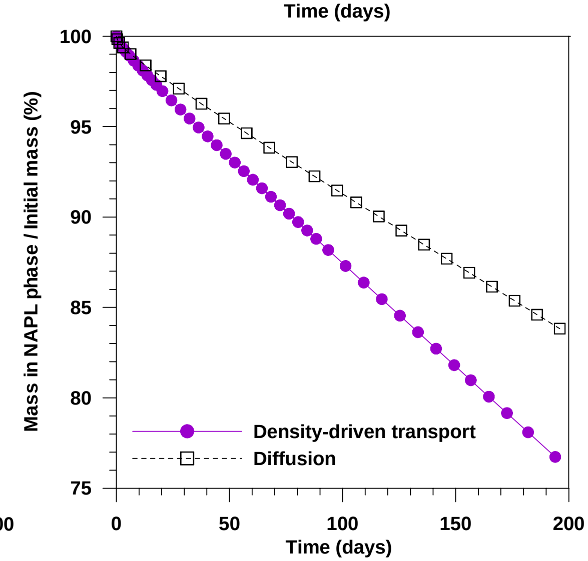
Density-driven transport



Release of TCE to the atmosphere



Mass reduction in NAPL source



Mass balance:
$$\sum^{Source} TCE_{NAPL}^{Initial\ mass(t=0)} - \sum_{t=0}^{t} TCE_{Atmosphere} - \sum^{Element} TCE_{Water}^{(t)} - \sum^{Element} TCE_{Gas}^{(t)} - \sum^{Element} TCE_{Soil}^{(t)} - \sum^{Source} TCE_{residual\ NAPL}^{(t)} \approx 0$$

Scenario 2. Biotransformation

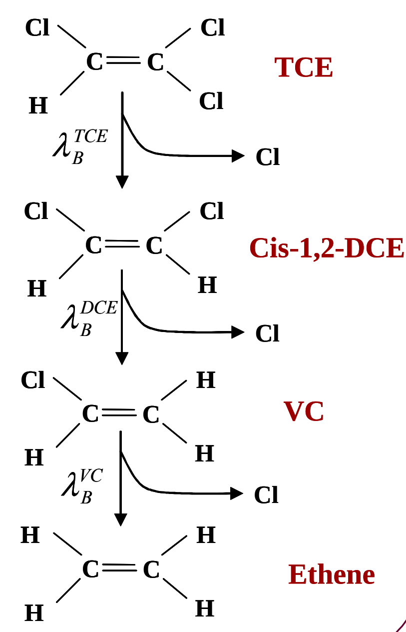
- **Assumed TCE is dehalogenated via sequential reactions**
  - It occurred under the anaerobic condition
  - First-order reactions

- **Effect of biological transformation of TCE**
  - To investigate byproducts
    - DCE and VC
  - First-order bioreaction coefficients (Three cases)

Rate(day^{-1})	TCE	DCE	VC
Case I*	3.0×10^{-3}	2.5×10^{-3}	3.8×10^{-3}
Case II	1.5×10^{-3}	1.3×10^{-3}	1.9×10^{-3}
Case III**	1.1×10^{-4}	1.6×10^{-3}	1.0×10^{-3}

*Suna et al. [2001]
**Clement et al. [2000]

Sequential bioreaction of TCE

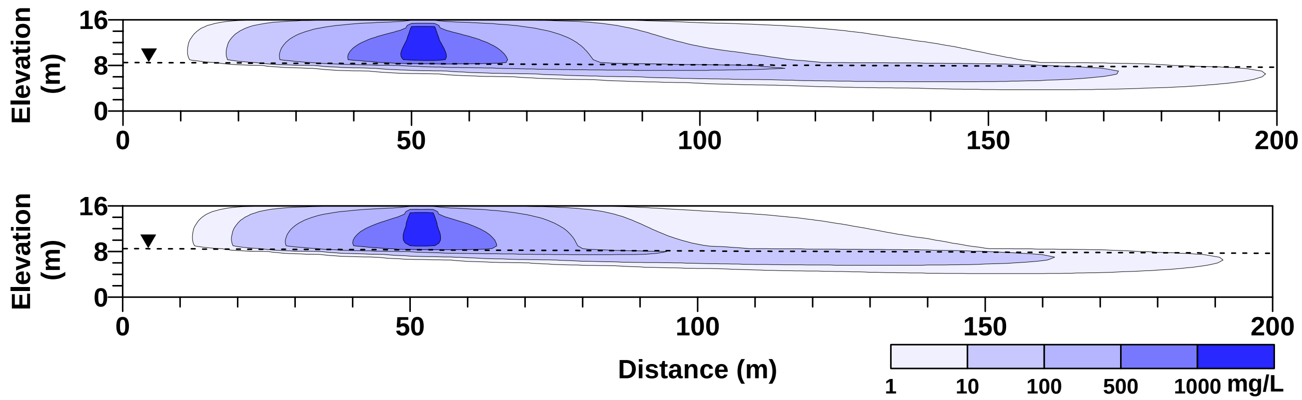


Scenario 2. Biotransformation (continued)

- **TCE concentration in water phase at 280 days**

No biorxn

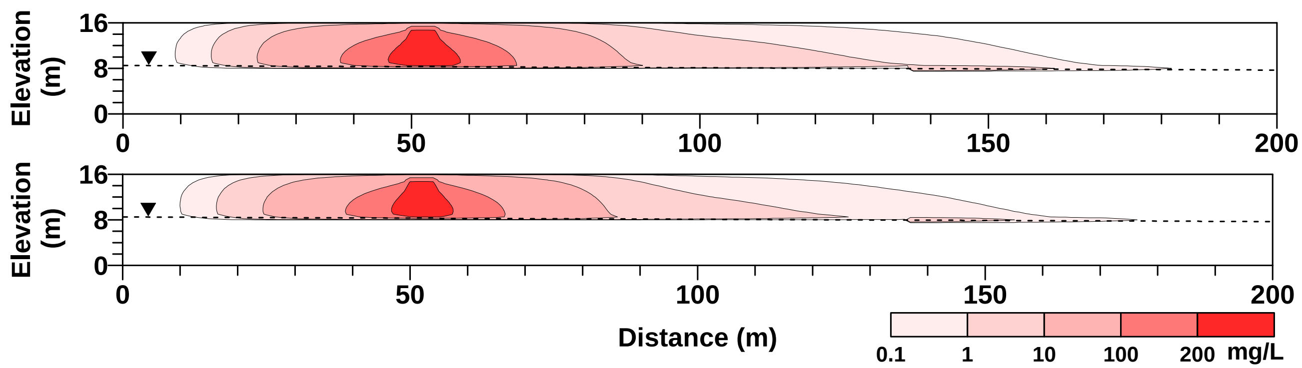
Case I.



- **TCE in gas phase at 280 days**

No biorxn

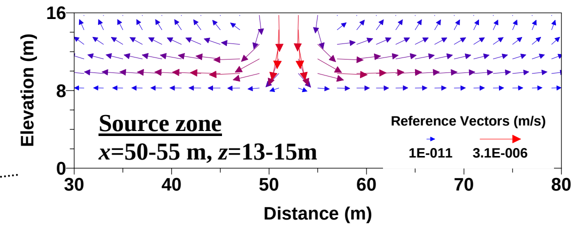
Case I.



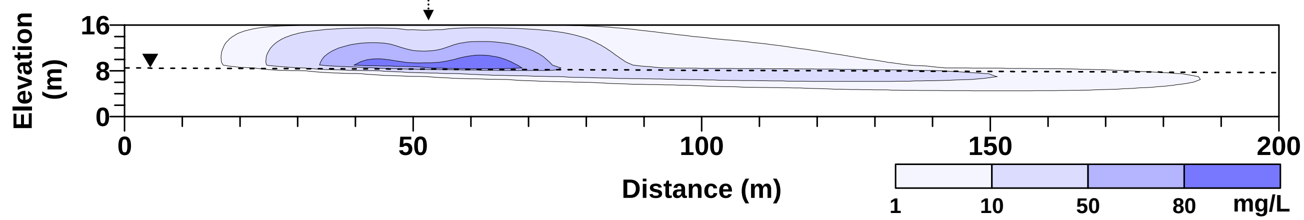
Scenario 2. Biotransformation (continued)

- **DCE concentration in water**

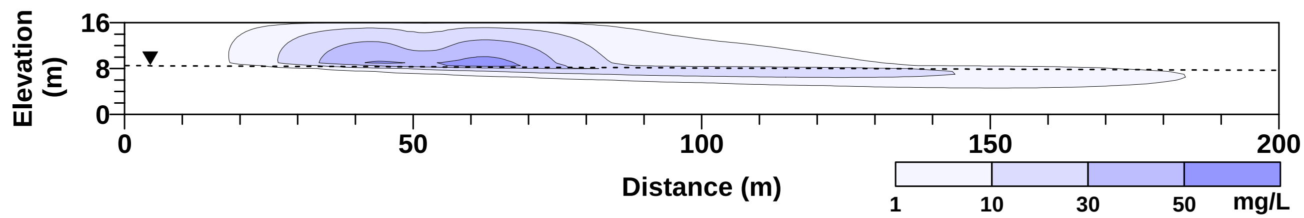
Gas flow



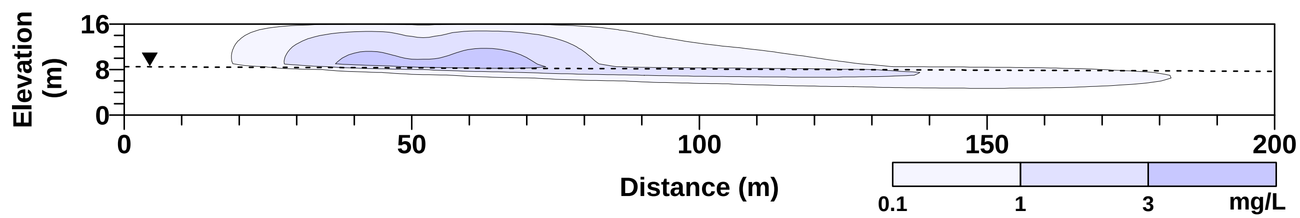
Case I.



Case II.



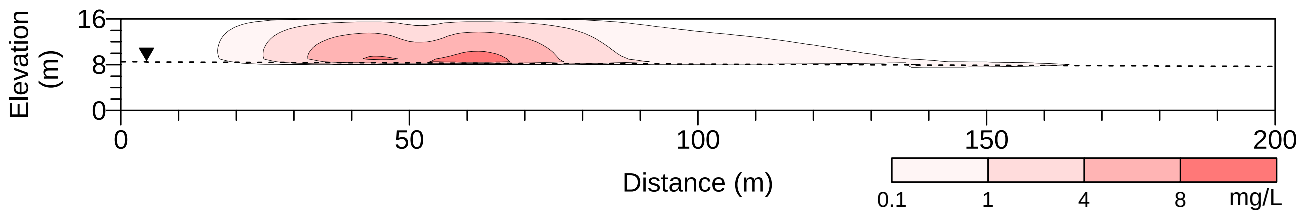
Case III.



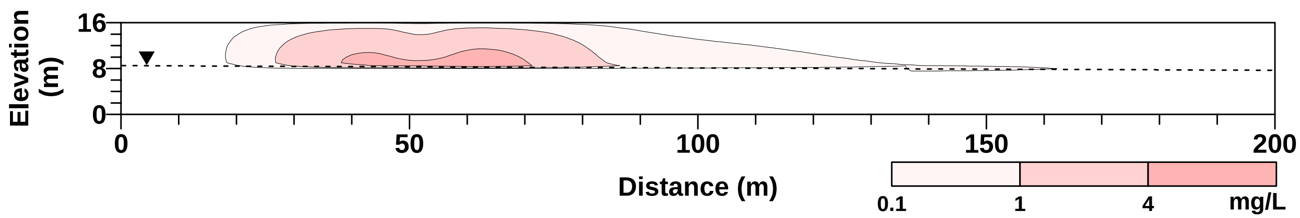
Scenario 2. Biotransformation (continued)

- **DCE concentration in gas phase**

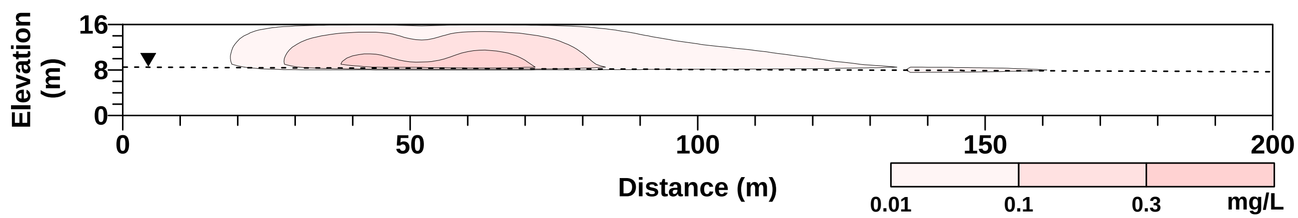
Case I.



Case II.



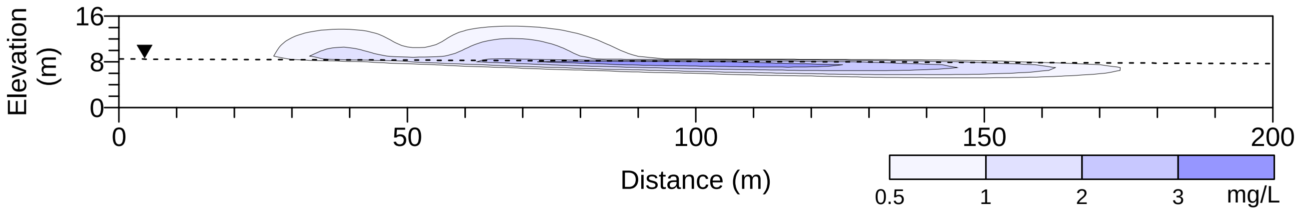
Case III.



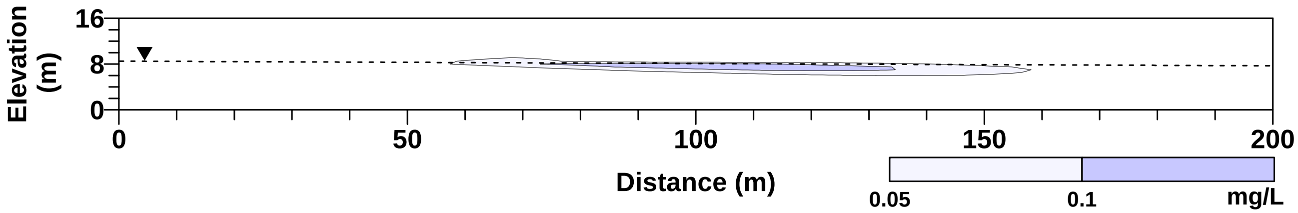
Scenario 2. Biotransformation (continued)

- **VC concentration in water phase at t=280 days**

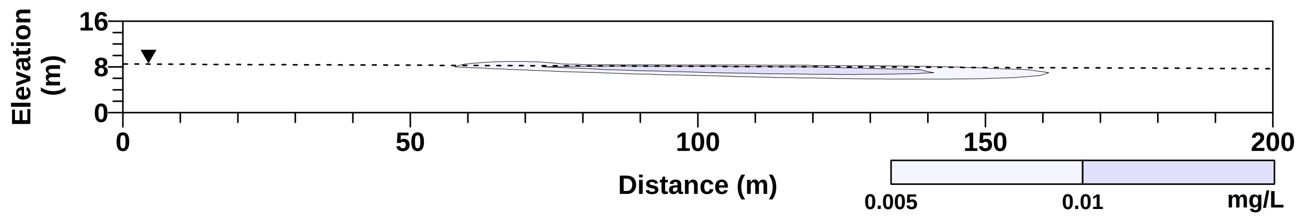
Case I.



Case II.

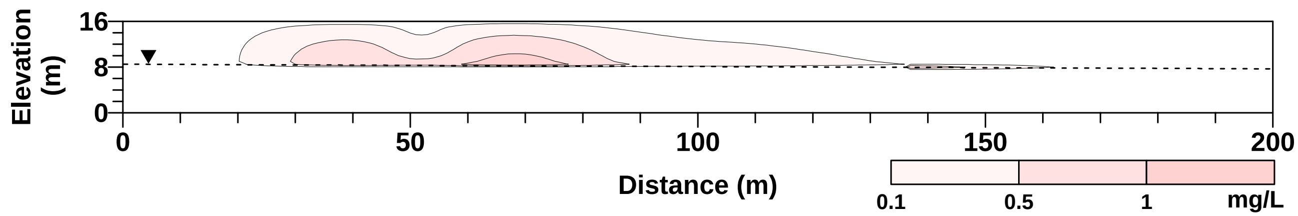


Case III.



- **VC in gas phase**

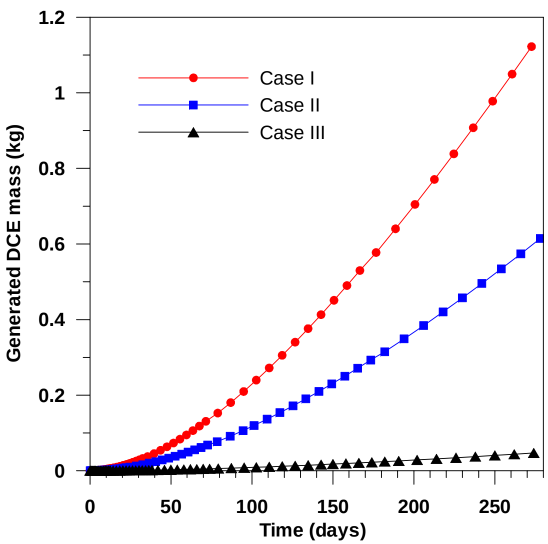
Case I.



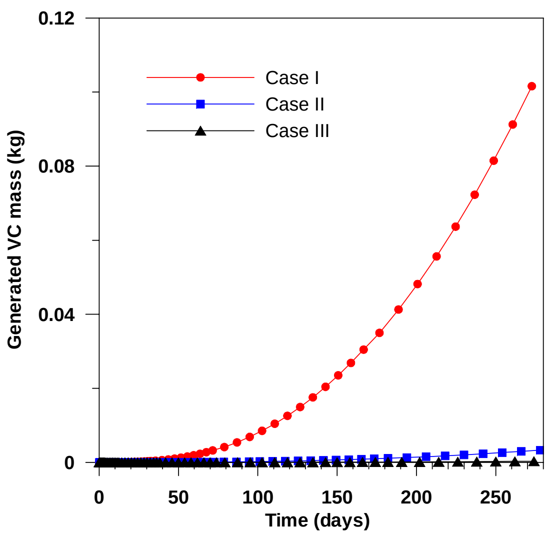
MESL@GT

Scenario 2. Biotransformation (continued)

DCE production



VC production



Mobilized TCE at 300 days

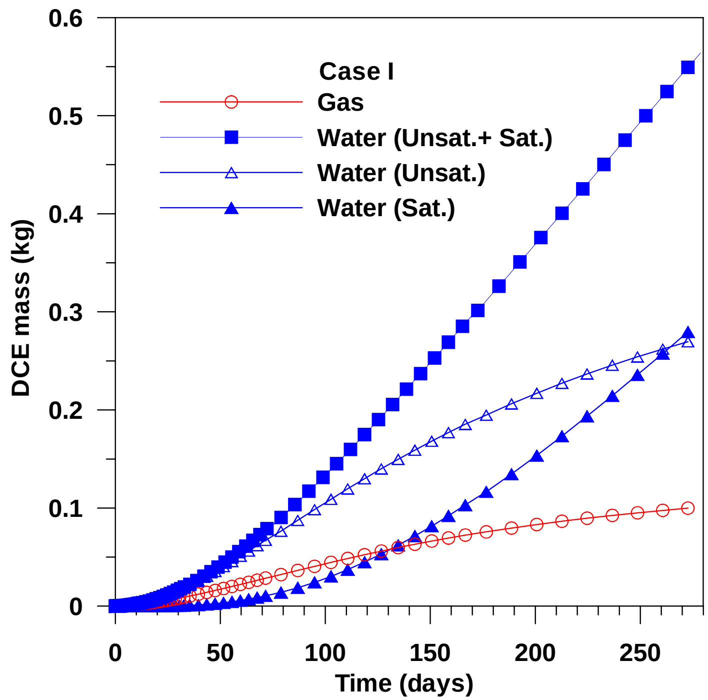
Bioreaction	Mobilized TCE (Dissolved + Vaporized TCE)	
	Mass[1], Kg	Ratio, %[2]
Case I	**21.43**	**33.55**
Case II	**21.30**	**33.35**
Case III	**21.18**	**33.16**

1) Mobilized TCE (kg) =Dissolved + Vaporized TCE from NAPL source

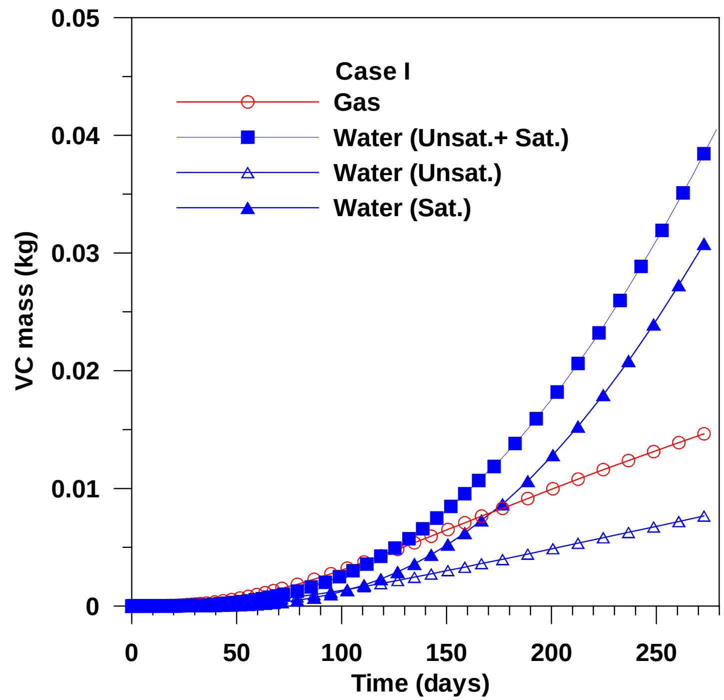
2) %=Mass of mobilized TCE (kg) / Inital TCE mass (kg)

Scenario 4. Biotransformation (continued)

- **Distribution of DCE and VC**



Dichloroethylene



Vinyl chloride

Summary

- **Density-driven transport in the unsaturated zone increases**
  - The spreading of contaminants
  - Contaminant transport to groundwater
  - Contaminant removal to atmosphere

- **Biotransformation**
  - Can generates new toxic contaminants
  - Is important near/in the saturated zone
  - Have an important influence on the distribution of new contaminants
  - Should be considered for long-period simulations.

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