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The Effect of Oxygen Transport on Biotransformation of Trichloroethylene in the Subsurface

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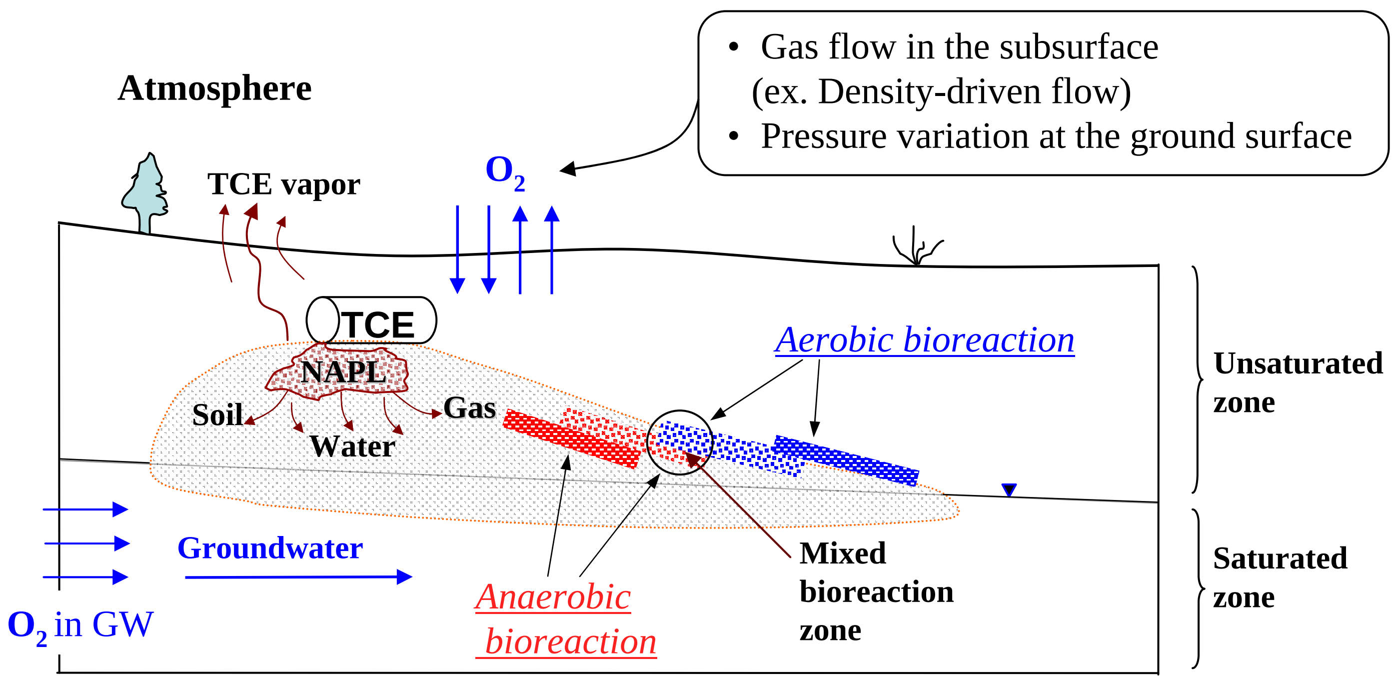
Oxygen and Groundwater Contamination

- Trichloroethylene (TCE) at contaminated sites can be biologically transformed by indigenous microorganisms under **aerobic** and **anaerobic** environments.
- **Oxygen** transport (influx and outflux) from the atmosphere to the subsurface can play an important role in determining oxygen levels in the contaminated zone.

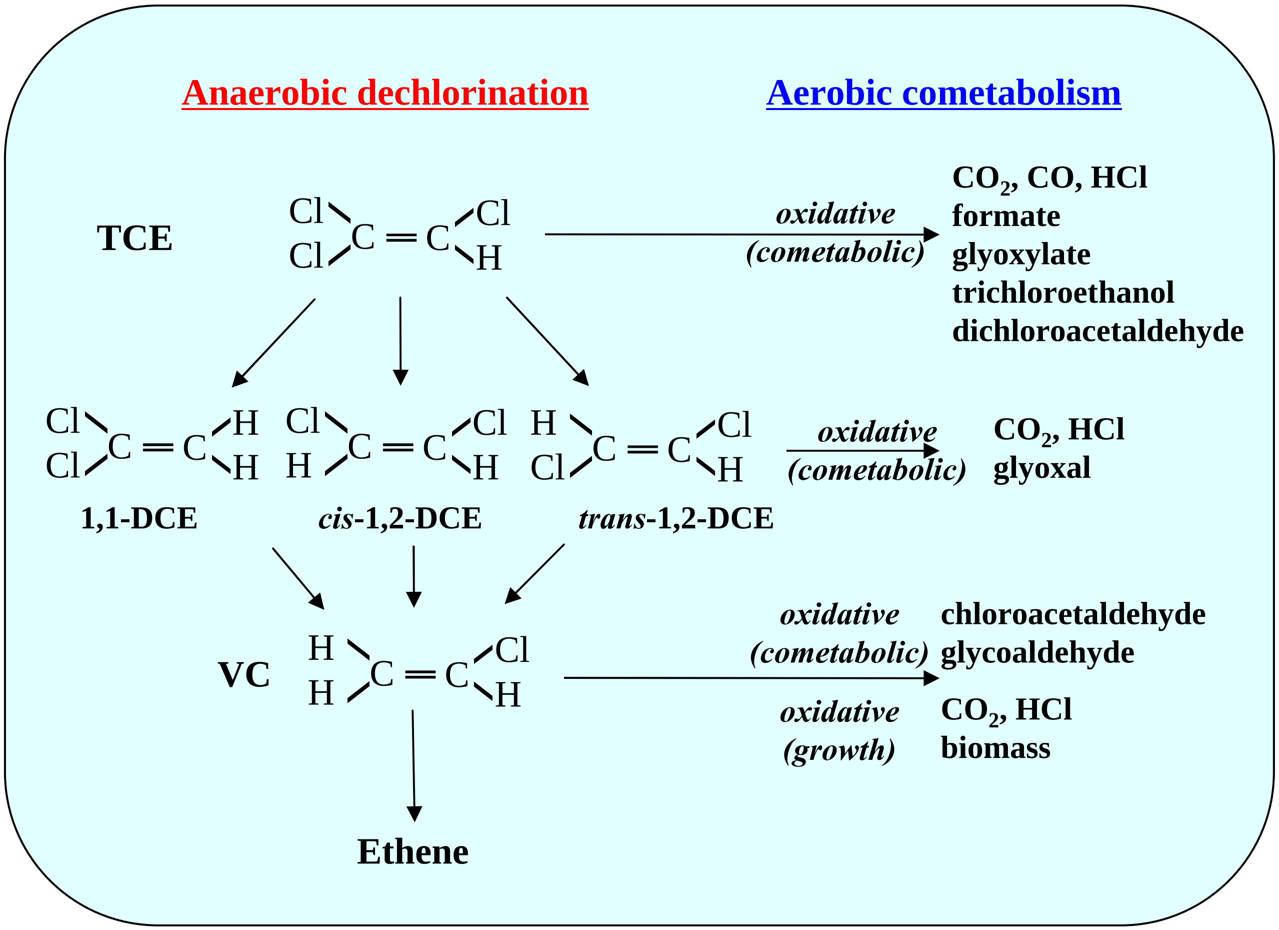


NAPL = Nonaqueous phase liquid

Biological Processes of TCE

- **Bioreactions**
  - Anaerobic dechlorination
  - Aerobic cometabolism

- **Target contaminants**
  - Trichloroethylene (TCE)
  - cis-1,2-Dichloroethylene (cDCE)
  - Vinyl chloride (VC)



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Study objectives

- This study investigates:
  - The effect of oxygen transport on the aerobic and anaerobic biological transformations of TCE and associated byproducts
    - O_2 transport in the unsaturated zone by gas flow with air influx from the atmosphere into the subsurface.
    - O_2 transport in the saturated zone by the groundwater flow.
  - The fate of TCE, cDCE, and VC in the subsurface.

Subsurface System

- Multiple phases
  - Groundwater
  - Soil
  - Gas/vapor in the unsaturated zone
  - NAPL

Multiphase flow

- Multiple contaminant transport
  - Advection
  - Dispersion/diffusion
  - Biological processes
  - Physical/chemical reactions

Multi-species transport in multiphase flow

Multiphase Flow

- **From mass conservation and continuity equations**

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

Subscript *f* = fluid phases (water, gas)
ψ_f = Pressure head of fluid
s_f = Saturation
k_{rf} = Relative permeability
ρ_f = Density

i = contaminants
N= total number of contaminants

- **Gas density**

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

- The density of soil vapor near NAPL TCE sources can increase due to its evaporation.
 $\Rightarrow$ Density-driven gas flow will be generated.*

Jang and Aral, 2007.

Multispecies Transport

- **Multi-species in water and gas phases**

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

- **Biological processes: 1st order kinetics**

1st order kinetics for dechlorination

$$I_w^i = \phi s_w \varepsilon_X \left(\lambda_B^{i-1} C_w^{i-1} - \phi s_w \lambda_B^i C_w^i\right) \qquad \varepsilon_X = \left(\frac{K_I^{O_2}}{K_I^{O_2} + C_w^{O_2}}\right)$$

Coefficient for anaerobic bioreaction.

1st order kinetics for cometabolism

$$I_w^i = -\phi s_w \varepsilon_O \lambda_w C_w^i \qquad \varepsilon_O = \left(\frac{C_w^{O_2}}{K_S^{O_2} + C_w^{O_2}}\right)$$

Coefficient for aerobic bio-reaction.

Oxygen utilization by cometabolism

$$I_w^{O_2} = \phi s_w \sum_{TCE,cDCE,VC}^{i} y_{O_2/i}\, \varepsilon_O \frac{k_B^i C_w^i}{K_S^i + C_w^i}$$

subscript i = by-product contaminant;
i-1 = parent contaminant.

Numerical Method & Codes

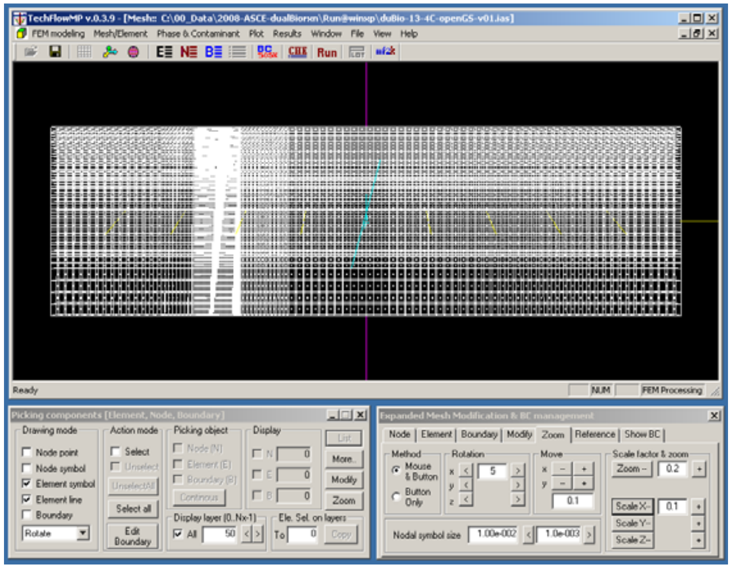
- **Galerkin Finite Element Method**
  - Modified Picard method
  - Element of domain
  - Rectangular prism (8 nodes each element)

- **Material balance calculation**
  - Accuracy and error checking

- **Numerical codes**
  - TechFlowMP: 3D multiphase flow and multispecies transport codes.
  - Program language: C/C++ and Microsoft Visual C++
  - Supporting platform: Linux/Unix with OpenMP, and Microsoft Windows

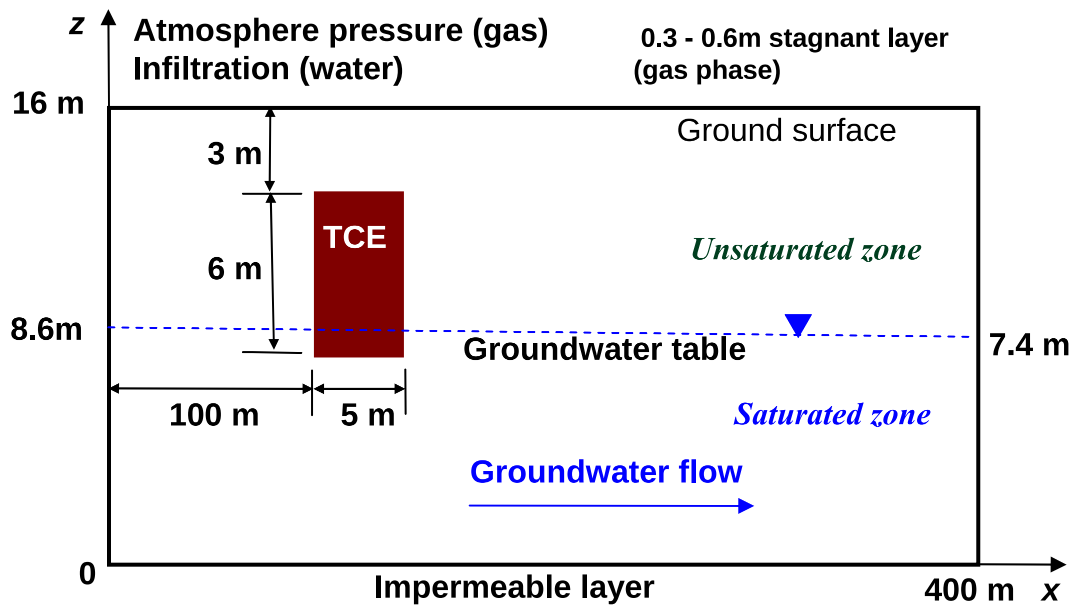
TechFlowMP

(Graphical user interface and 3D mesh)



Simulation for TCE and its Byproducts

- Source contaminant: nonaqueous-phase-liquid TCE
- Model domain: the unsaturated and saturated zones



TCE source: Initial NAPL saturation = 5 %

Modeling Scenarios and Parameters

Simulation scenarios

- Case 1 : No free-flux at the ground surface and no density-driven advection of gas phase.
- Case 2 : Limited flux at the ground surface with the density-driven advection of gas phase.
- Case 3 : Free-flux at the ground surface with the density-driven advection of gas phase.

Bioreaction coefficients* and oxygen consumption

	TCE	DCE	VC
Anaerobic bioreaction (d^{-1})	3.0×10^{-3}	2.5×10^{-3}	3.8×10^{-3}
Aerobic biodegrdation (Cometabolism) (d^{-1})	7.4×10^{-4}	4.5×10^{-3}	7.9×10^{-3}
Oxygen consumption†	0.55	0.83	1.41

†stoichiometric coefficient.

$$\text{TCE}:\ 2C_2H_3Cl+\frac{11}{2}O_2\rightarrow 4CO_2+3H_2O+Cl^-$$

Parameters of Soil and Chemicals

Porous soil medium	
Permeability	5.3×10^{-11} m^2
Porosity, ϕ	0.35
Longitudinal dispersivity, α_L	1.0 m
Transverse dispersivity, α_T	0.01 m

Parameters	TCE	cDCE	VC
Molecular weight	131.4	96.9	62.5
Vapor density, kg/m^3	5.56	4.10	2.64
Henry constant, dimensionless	0.227	0.097	0.756
Sorption coefficient, K_{oc}, L/g	0.1	0.049	0.003
Vapor pressure, mmHg	45.1	129.3	2178.6

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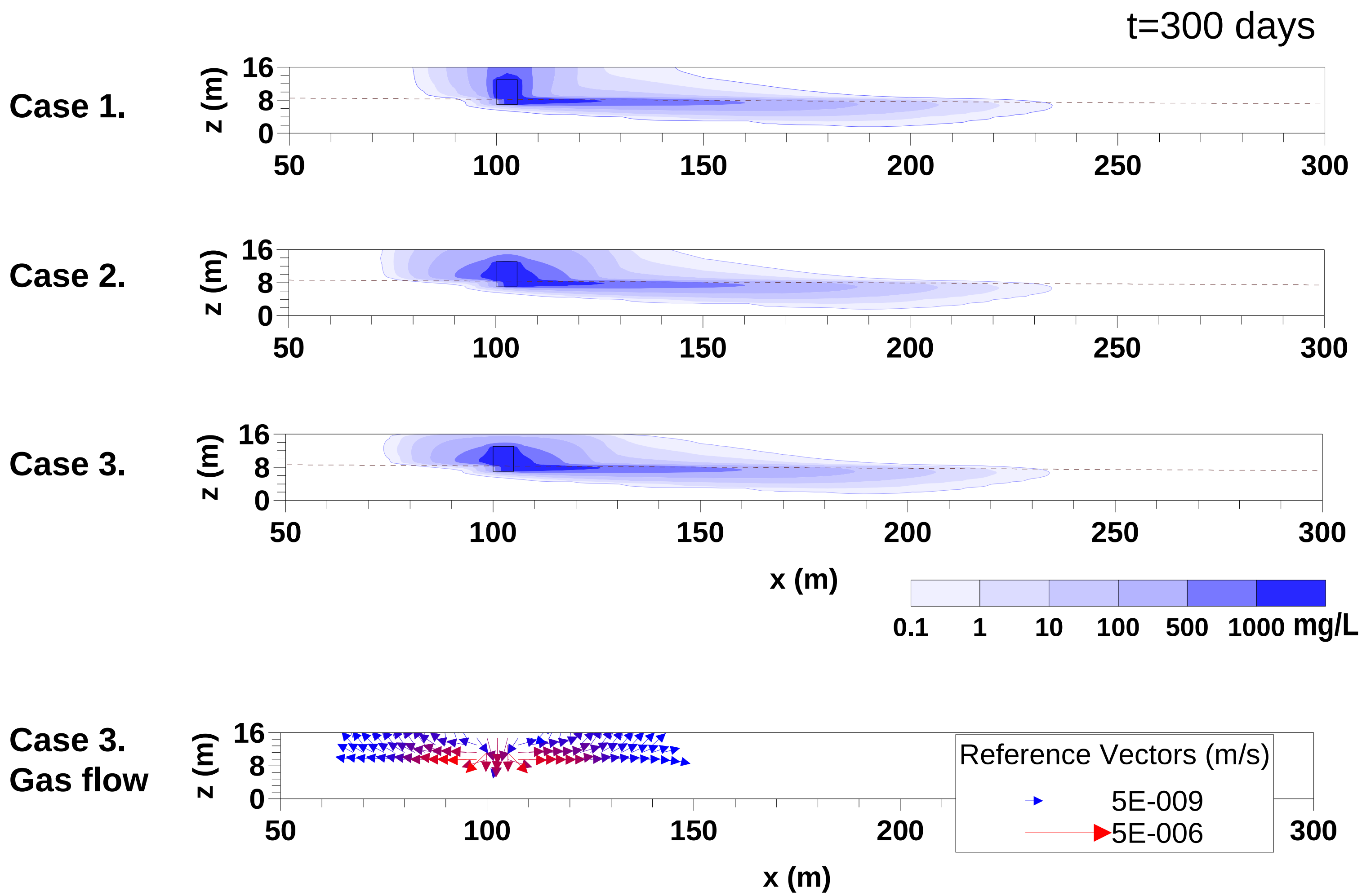
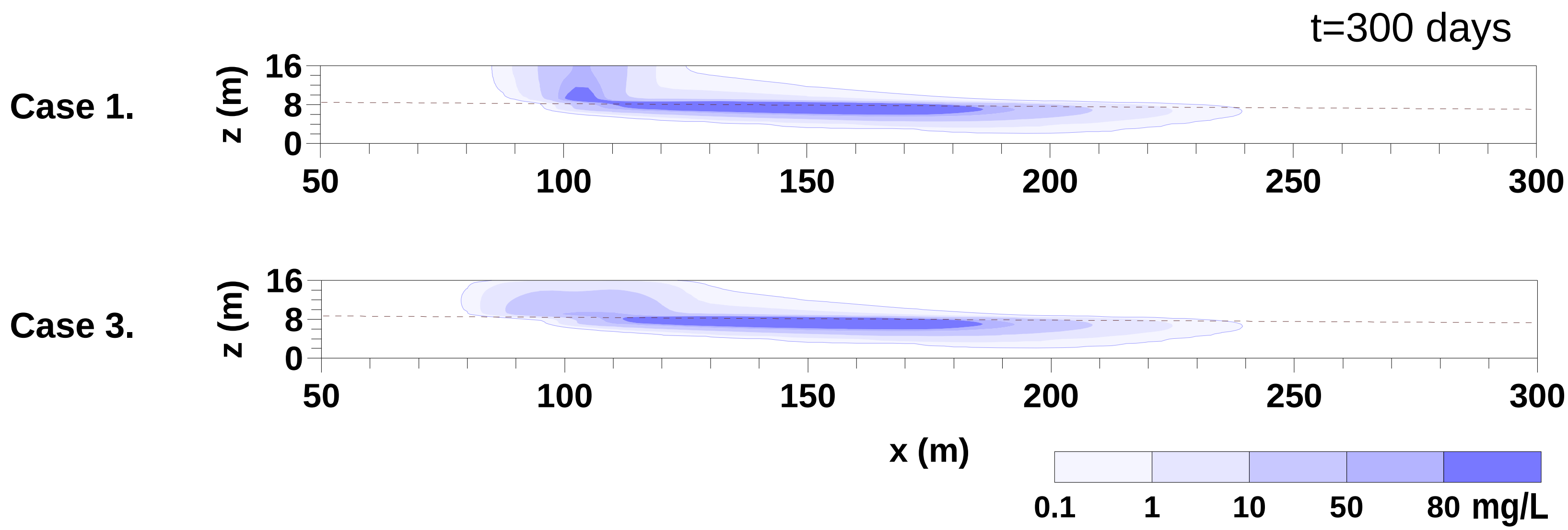
TCE Transport in Water Phase



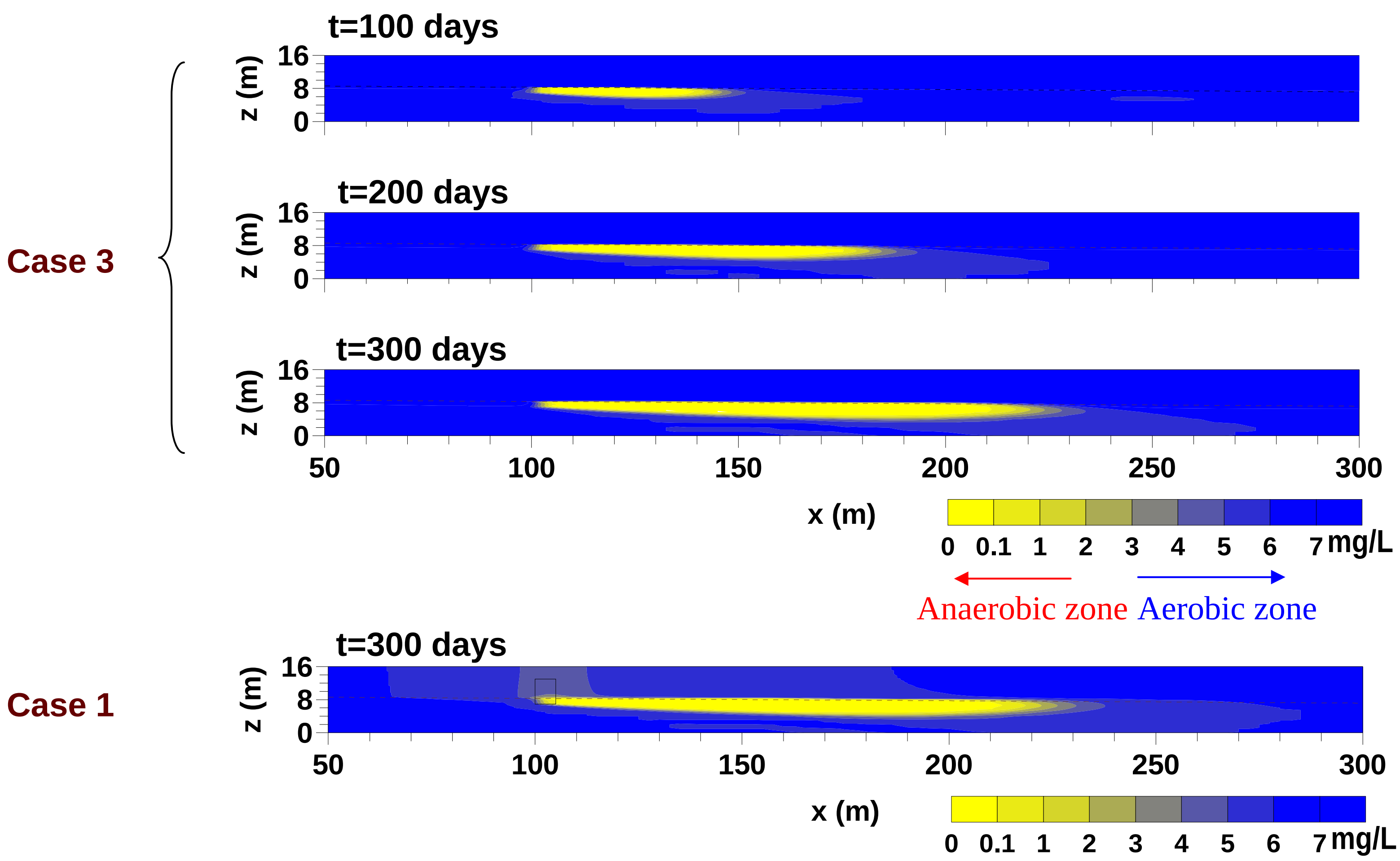
□ : NAPL TCE source

DCE Transport in Water Phase

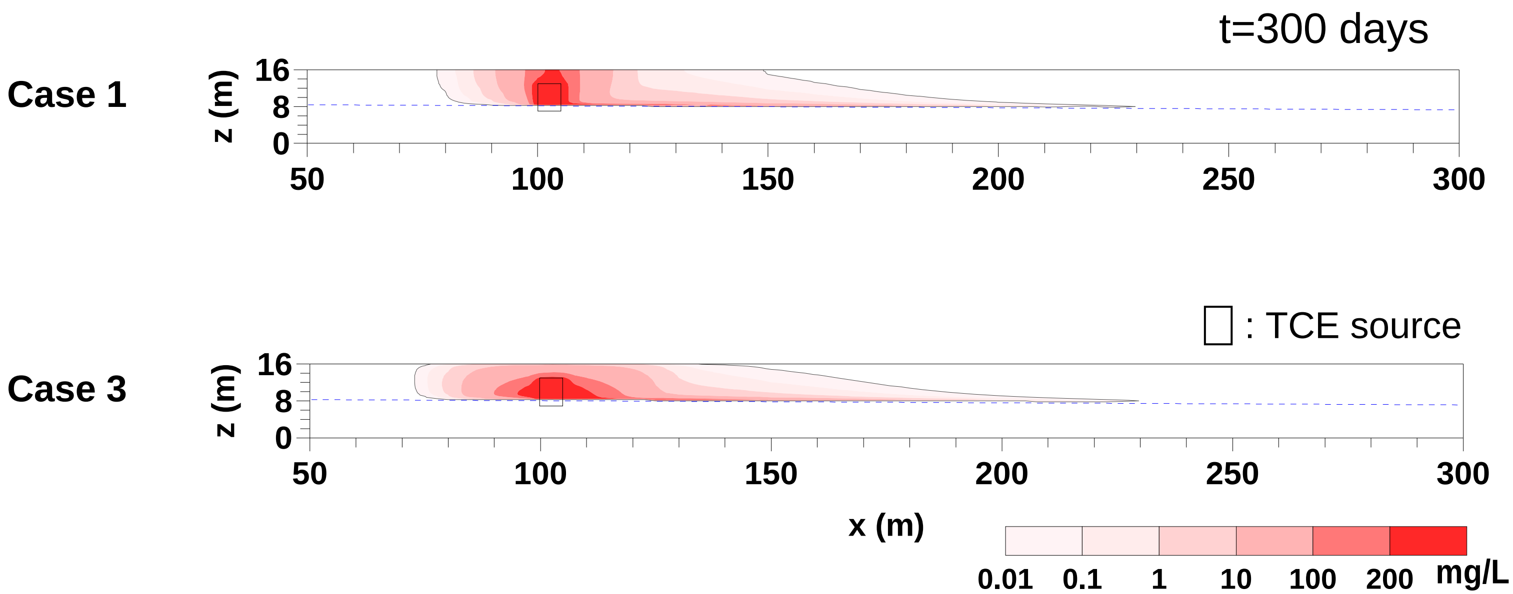


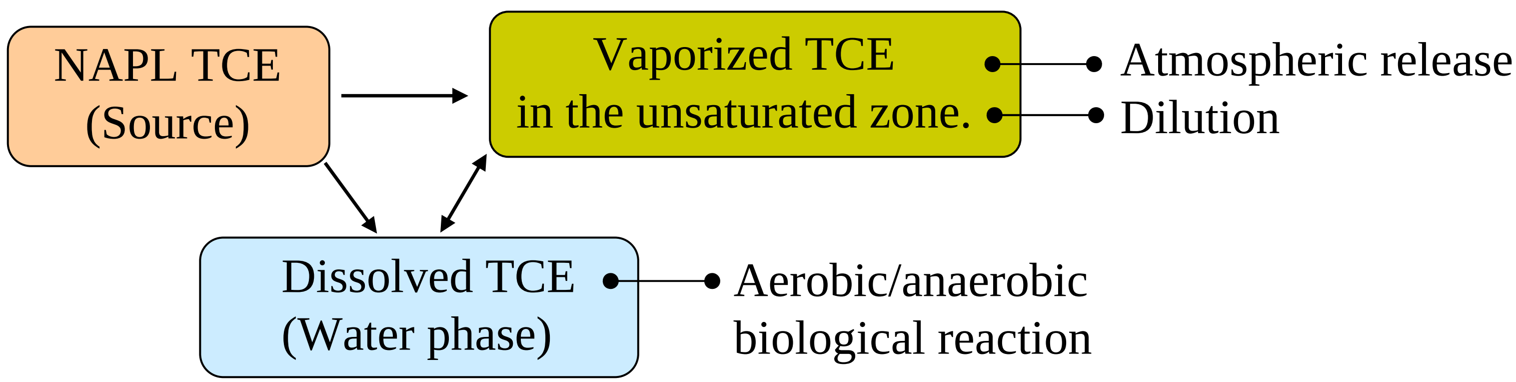
- The cDCE concentrations at the source area are lower in Case 3 than in Case 1.
- The dilution and the atmospheric release of cDCE contribute to decreasing its concentration at and near the source area.

Oxygen Concentration Profiles

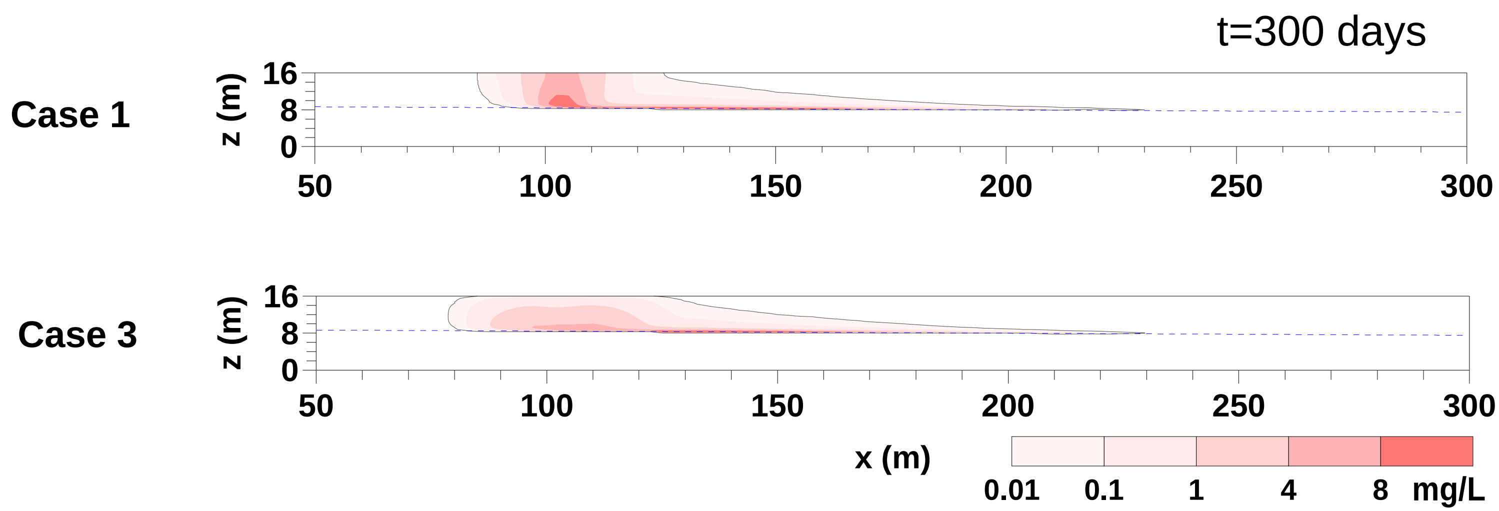


Concentration of TCE in Gas Phase





Concentration of DCE in Gas Phase



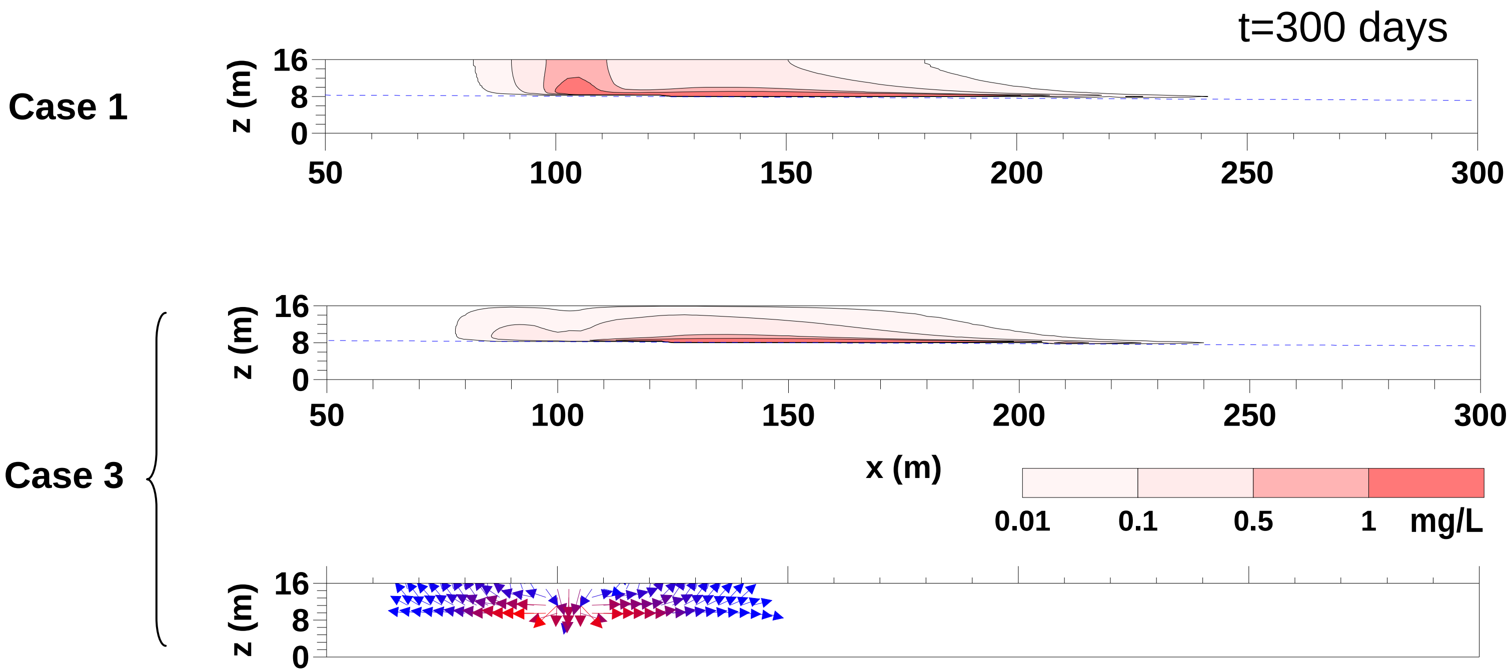
Vaporized cDCE in the unsaturated zone.

- Atmospheric release
- Dilution

Dissolved cDCE (Water phase) generated by TCE dechlorination

- Aerobic/anaerobic biological reaction

Concentration of VC in Gas Phase

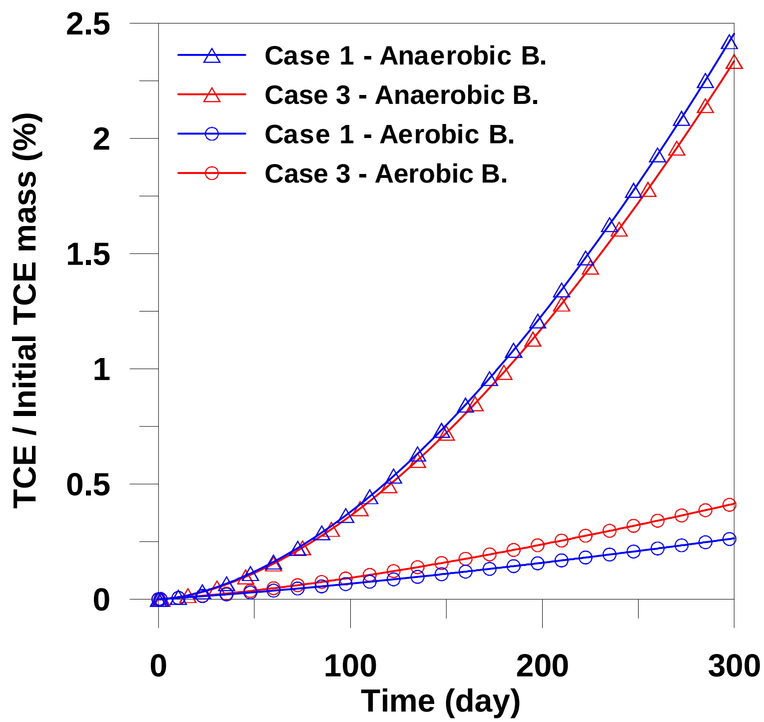


Vaporized VC
in the unsaturated zone.

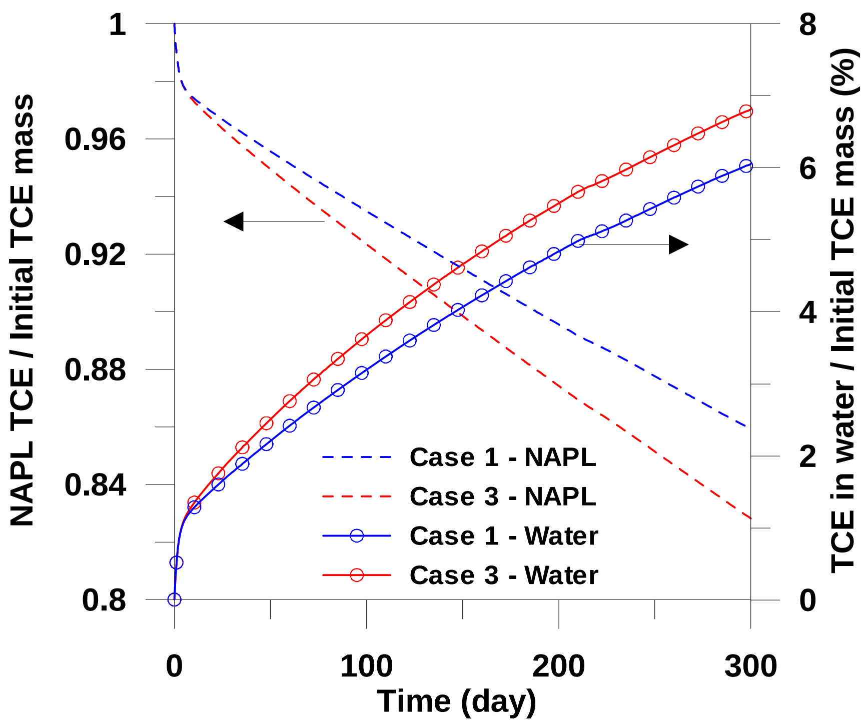
Dissolved VC (Water phase)
generated by cDCE
dechlorination

Fate of TCE

Biotransforamtion

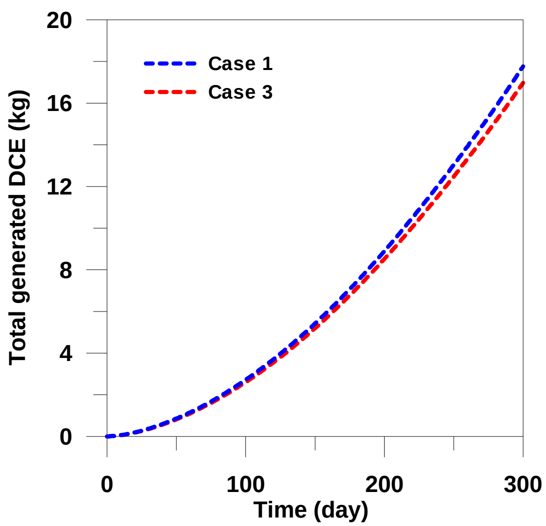


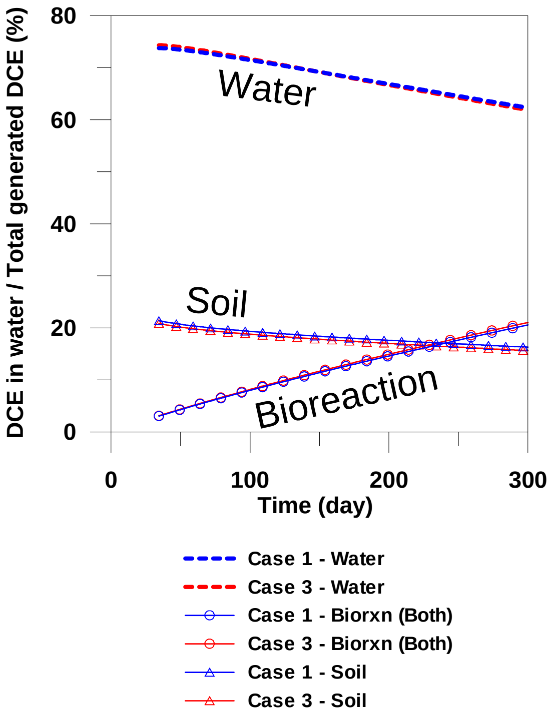
TCE in NAPL and Water

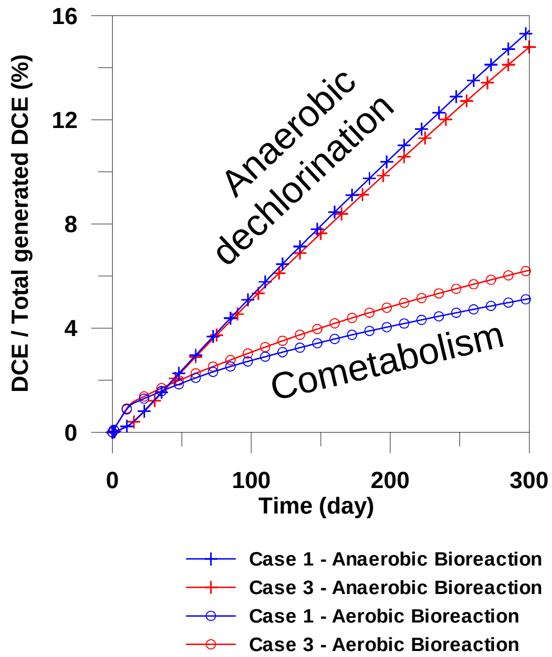


Fate of cDCE

cDCE Generation







Summary

- Air flux into the ground, initiated by the density-driven advection of gas phase, increased oxygen levels in the unsaturated zone and accelerated aerobic biodegradation of TCE and its byproducts.

- The size of the anaerobic zone increased as contaminated groundwater plume spread out. The bioreaction processes became more important with time. The anaerobically-dechlorinated contaminants were much greater than the aerobically-cometabolized contaminants.

- Oxygen levels could be an important factor to determine the concentrations of TCE and its byproducts. The coexisting anaerobic-aerobic-bioreaction approach can be used to model heterogeneous biological processes of organic compounds in the subsurface.

- The density-driven advection decreased contaminant concentrations near the ground surface around the source area. This is mostly due to advective contaminant-transport, dilution, atmospheric release, and biological processes.

Thank you