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Modeling of Co-Existing Anaerobic-Aerobic Biotransformation of Chlorinated Ethenes in the Subsurface

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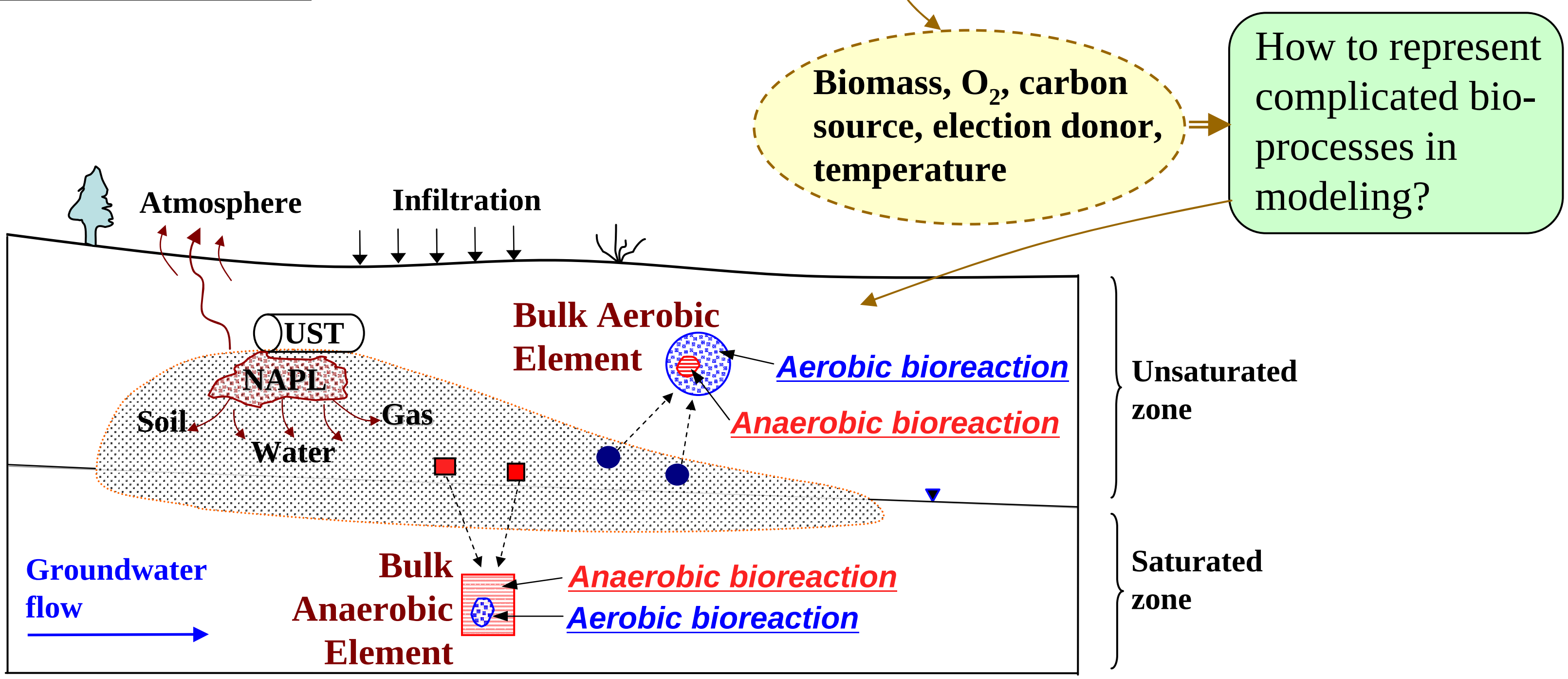
Introduction

- Soil and groundwater contamination is often initiated by accidental spills or leakage of volatile organic compounds, including chlorinated ethenes (CEs: e.g., tetrachloroethylene, PCE, and trichloroethylene, TCE), from underground storage tanks (USTs) and hazardous landfills.
- CEs can be biologically transformed by <u>indigenous microorganisms under anaerobic and/or aerobic environments</u>.



Nonaqueous phase liquid (NAPL)

Biological Processes of PCE

- **Bio-processes**
  - Anaerobic condition
  - Aerobic condition

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

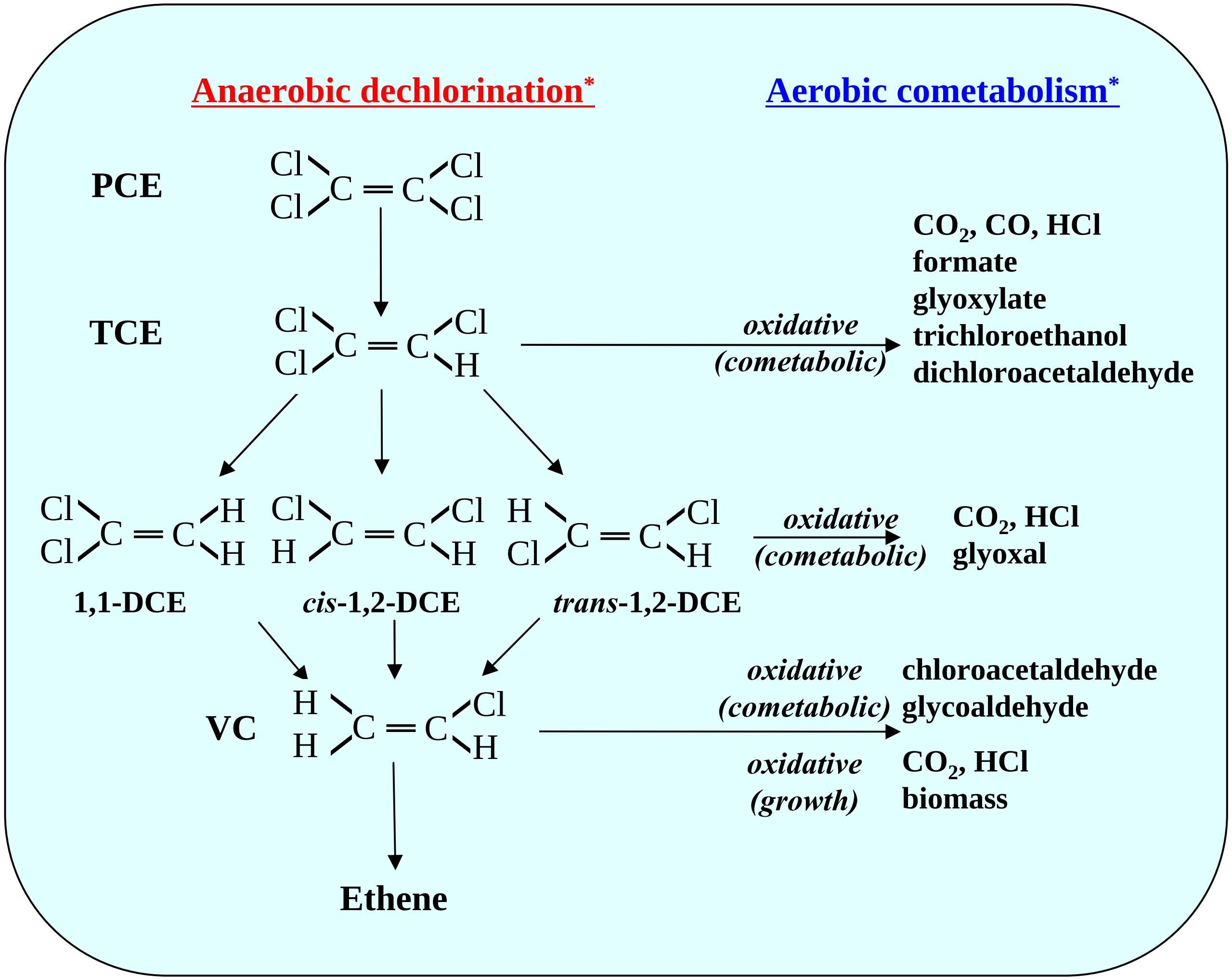


*Diagram from van Htlckama Vlieg and Janssen, 2001.

Study objectives

- To develop a method to represent co-existing aerobic and anaerobic biological transformations of CEs in the subsurface.

- To investigate the effect of the co-existing biological processes on the fate and transport of CEs.

Subsurface System

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

Multiphase flow

- Multiple contaminants
  - Advection
  - Dispersion/diffusion
  - Biological processes
  - Physical/chemical reactions

Multi-species transport in multiphase flow

Numerical Approach on Multiphase Flow

- **From mass conservation and continuity equations**

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

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**

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

Contaminant concentration in gas phase (C_g^i)

- Dense contaminant concentration increases in gas phase near NAPL-contaminant sources.
  ⇒ Density-driven flow is generated.*

*Jang and Aral, 2006.

Contaminant Transport Equation

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

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

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

Monod kinetics for dechlorination

$$I_w^i = \phi s_w \varepsilon_X \left(-\frac{k_B^i C_w^i}{K_S^i + C_w^i} + \frac{y_{i/i-1} k_B^{i-1} C_w^{i-1}}{K_S^{i-1} + C_w^{i-1}} \right); \quad \varepsilon_X = \left(\frac{K_I^{O_2}}{K_I^{O_2} + C_w^{O_2}} \right)$$

Coefficient for anaerobic bio-reaction.

Monode kinetics for cometabolism

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

$$\varepsilon_O = \left(\frac{C_w^{O_2}}{K_S^{O_2} + C_w^{O_2}} \right)$$

Coefficient for aerobic bio-reaction.

1st order kinetics for dechlorination

$$I_w^i = \phi s_w \varepsilon_X \left(\lambda_B^{i-1} C_w^{i-1} - \phi s_w \lambda_B^i C_w^i \right)$$

Oxygen utilization by cometabolism

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

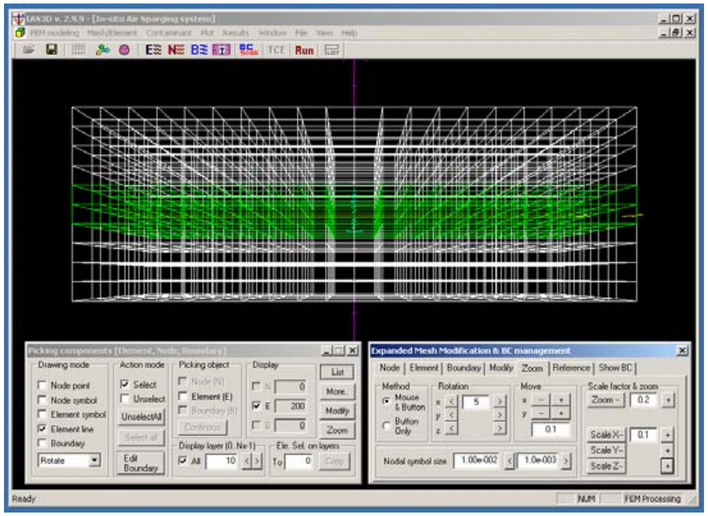
subscript i = by-product contaminant; i-1 = parent contaminant.

Numerical Method

- **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++/Microsoft Visual C++
  - Supporting platform: Linux, Unix with OpenMP, and Microsoft Windows

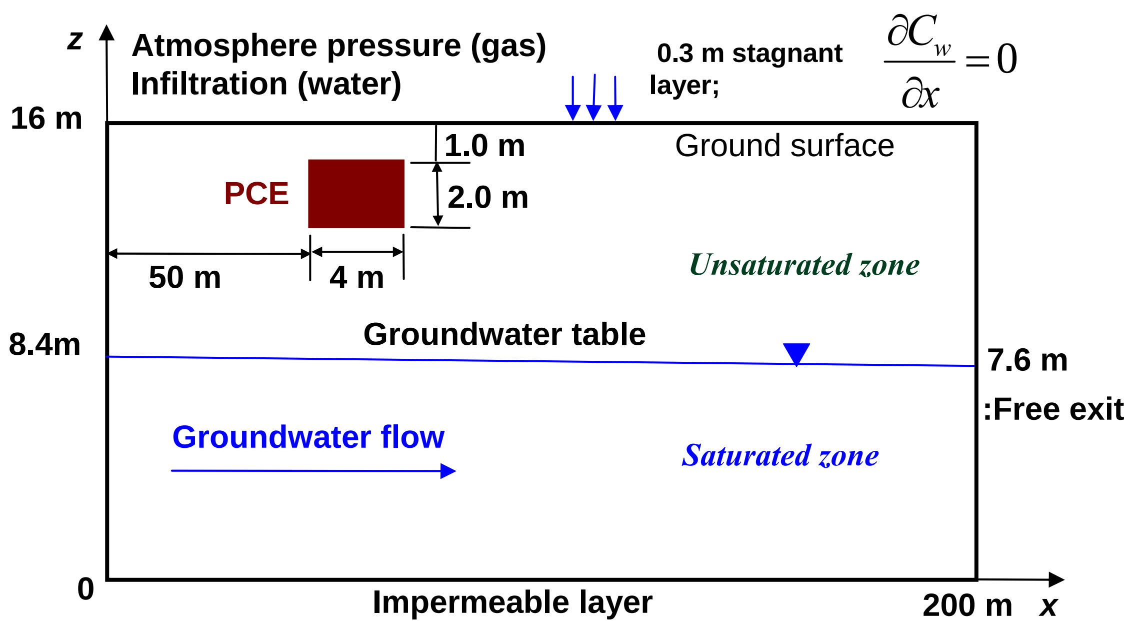
TechFlowMP

(Graphical user interface and 3D mesh)



Simulation for PCE and its Byproducts

- Source contaminant: NAPL PCE
- Model domain: Unsaturated + Saturated zones



PCE source: Initial NAPL saturation = 10%

Modeling Scenarios and CeParameters

Simulation scenarios

- Case F-1 : Anaerobic-only bioreaction with 1st order kinetics
- Case F-2 : Coexisting anaerobic/aerobic bioreaction with 1st order kinetics
- Case M-1 : Anaerobic-only bioreaction with Monod kinetics
- Case M-2 : Coexisting anaerobic/aerobic bioreaction with Monod kinetics

1st order bioreaction coefficients*

Rate(day^{-1})	PCE	TCE	DCE	VC
	2.9×10^{-3}	3.0×10^{-3}	2.5×10^{-3}	3.8×10^{-3}

Monod kinetic coefficients**

	PCE	TCE	DCE	VC
k_B (μM/d)	0.01	0.008	0.0019	0.0017
K_s (μM)	0.11	1.4	3.3	2.6

$$K_S^{O_2} = 2mg/L$$

**Suna et al, 2001; **Haston and McCarty, 1999.*

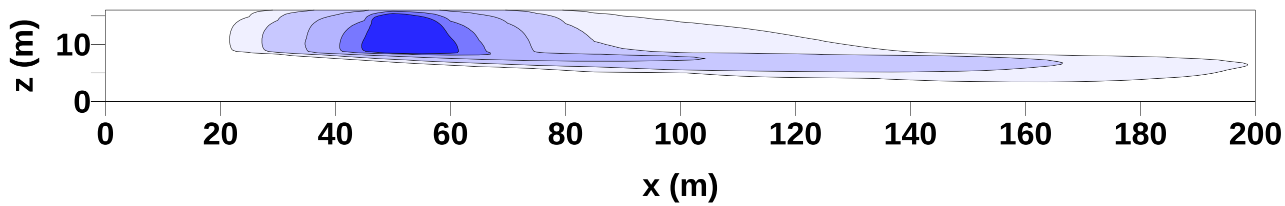
Parameters of Soil and Chemicals

Porous soil medium	
Permeability	5.0×10^{-11} m^2
Porosity, ϕ	0.35
Longitudinal dispersivity, α_L	1.0 m
Transverse dispersivity, α_T	0.01 m

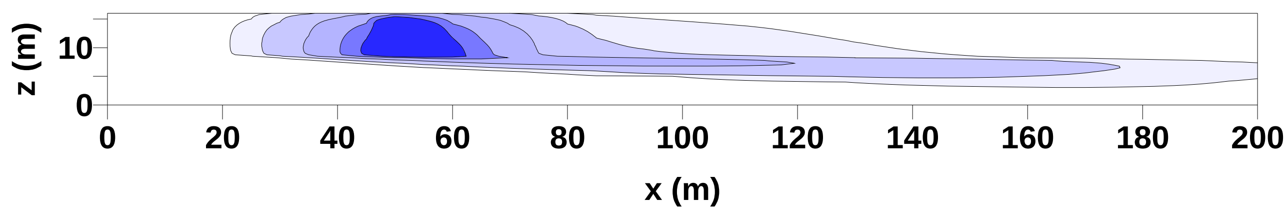
Parameters	PCE	TCE	cDCE	VC
Molecular weight	465.8	131.4	96.9	62.5
Vapor density, kg/m^3	7.02	5.56	4.10	2.64
Henry constant, dimensionless	0.35	0.227	0.097	0.756
Sorption coefficient, K_{oc}, L/g	0.14	0.1	0.049	0.003
Vapor pressure, mmHg	10.6	45.1	129.3	2178.6

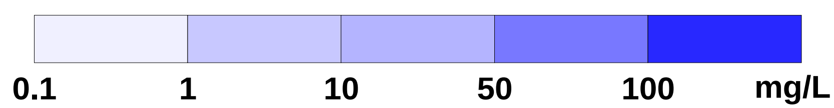
Concentration of PCE in Water Phase

Case F-1:
Anaerobic-only bioreaction with 1st order kinetics



Case F-2:
Coexisting anaerobic/aerobic bioreaction with 1st order kinetics





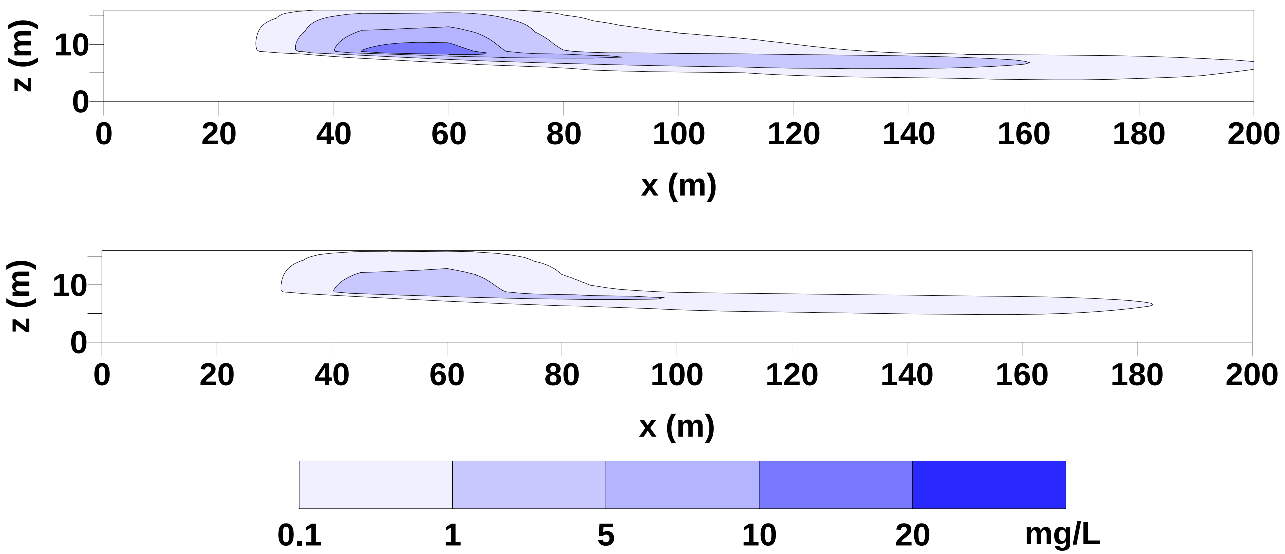
In Case F-2, the anaerobic biotransformation of PCE decreased due to ε_x.
⇒ Greater PCE plume in the domain.
(PCE is not biodegradable under aerobic conditions.)

$$\varepsilon_X = \left(\frac{K_I^{O_2}}{K_I^{O_2} + C_w^{O_2}} \right)$$

Concentration of TCE in Water Phase

Case F-1:
Anaerobic-only bioreaction with 1st order kinetics

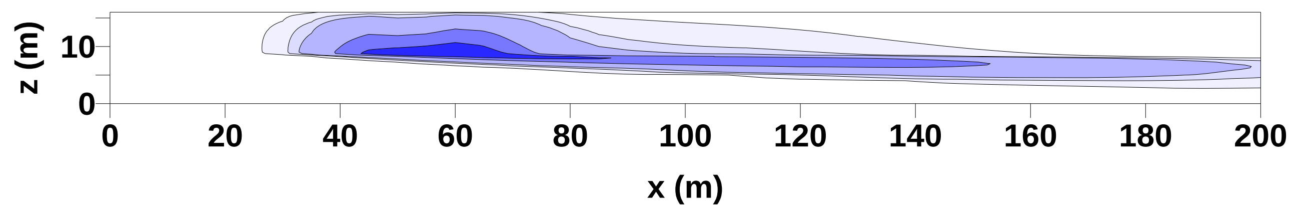
Case F-2:
Coexisting anaerobic/aerobic bioreaction with 1st order kinetics



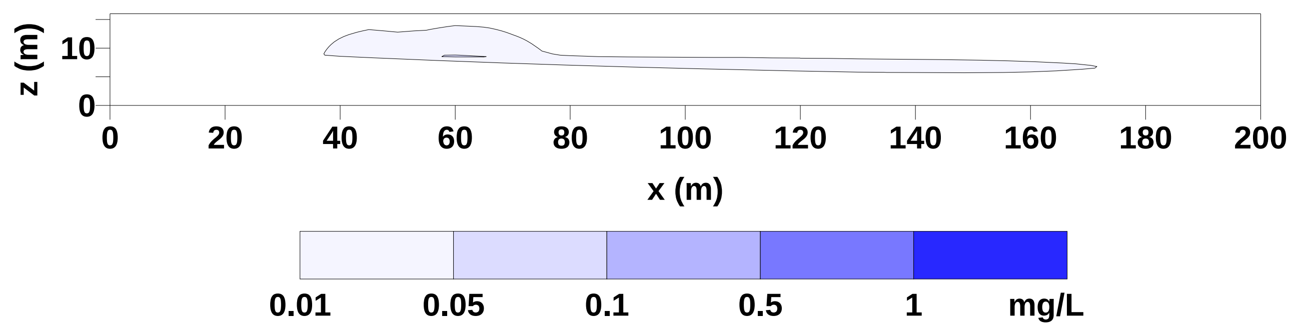
In Case F-2, the anaerobic biotransformation of PCE decreased due to ε_x.
⇒ Low TCE generation.

Concentration of DCE in Water Phase

Case F-1:
Anaerobic-only bioreaction with 1st order kinetics



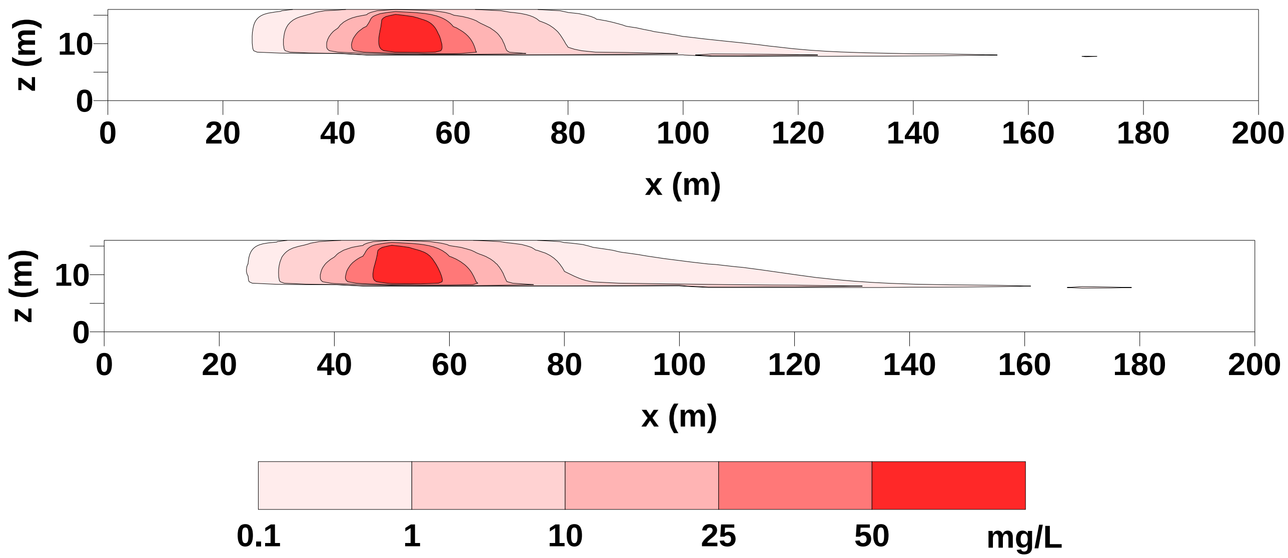
Case F-2:
Coexisting anaerobic/aerobic bioreaction with 1st order kinetics

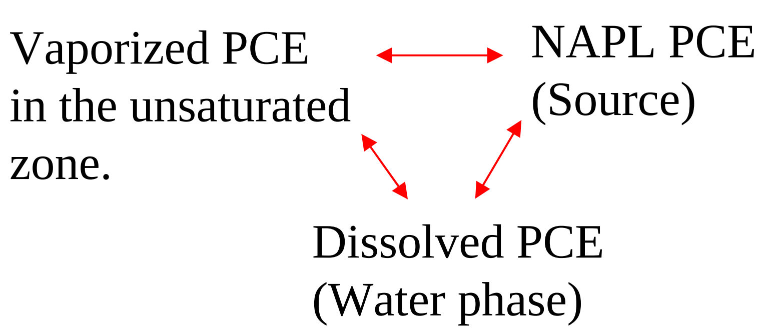


Concentration of PCE in Gas Phase

Case F-1:
Anaerobic-only bioreaction with 1st order kinetics

Case F-2:
Coexisting anaerobic/aerobic bioreaction with 1st order kinetics

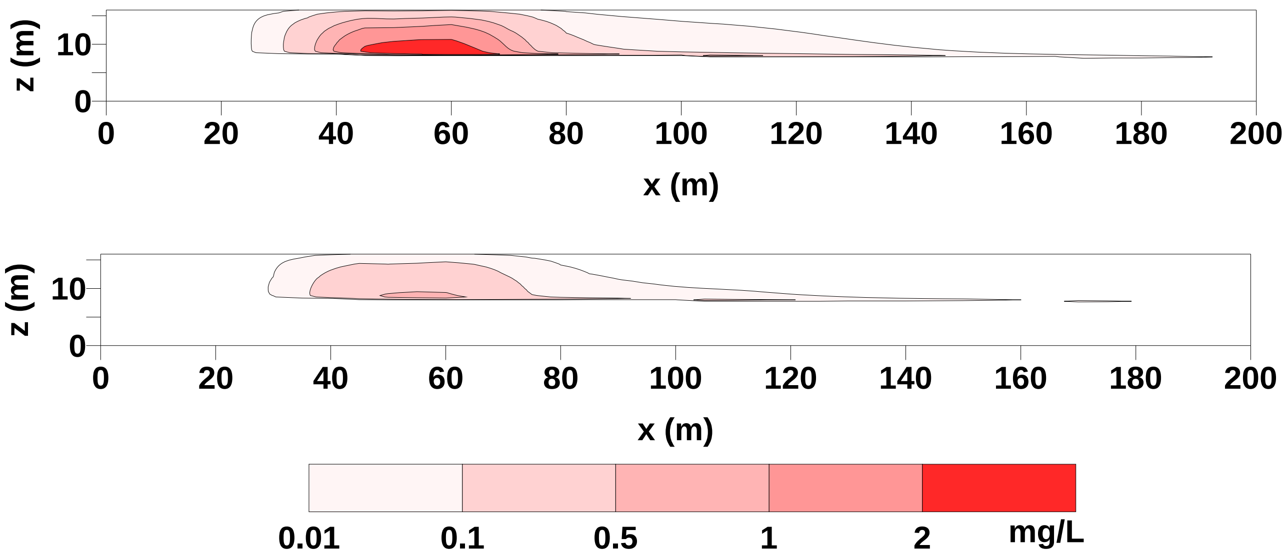




Concentration of TCE in Gas Phase

Case F-1:
Anaerobic-only bioreaction with 1st order kinetics

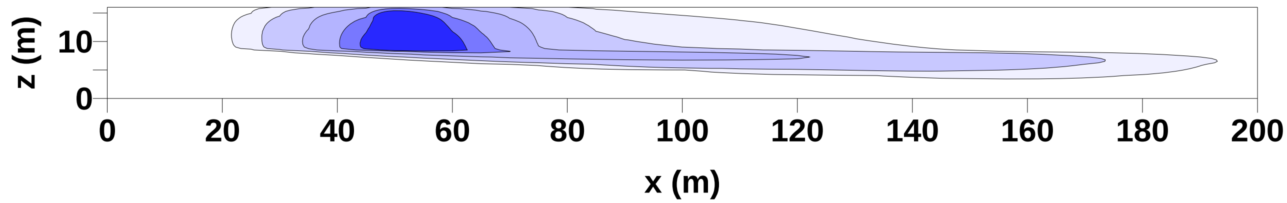
Case F-2:
Coexisting anaerobic/ aerobic bioreaction with 1st order kinetics



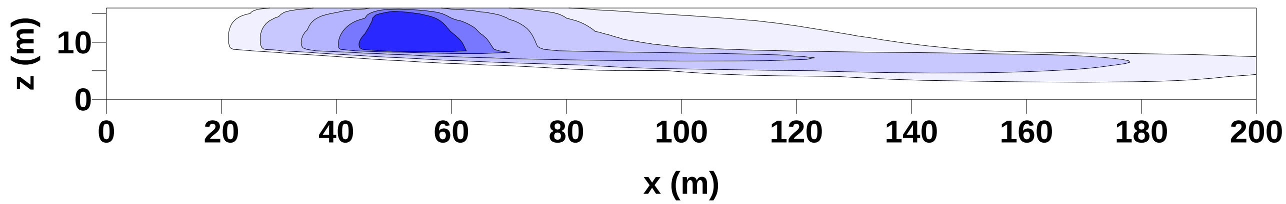
Vaporized TCE in the unsaturated zone. ↔ Dissolved TCE (Water phase), generated from the dechlorination of PCE

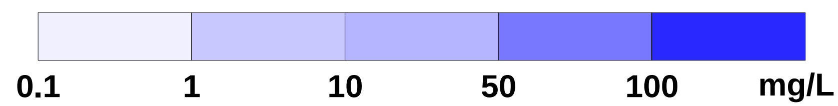
Concentration of PCE in Water Phase

Case M-1:
Anaerobic-only bioreaction with Monod kinetics

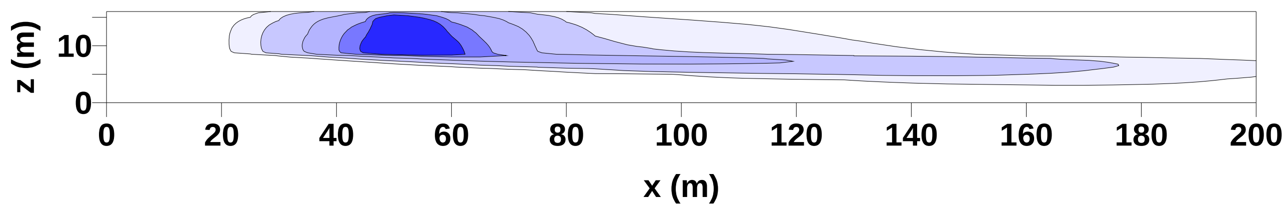


Case M-2:
Coexisting anaerobic/aerobic bioreaction with Monod kinetics

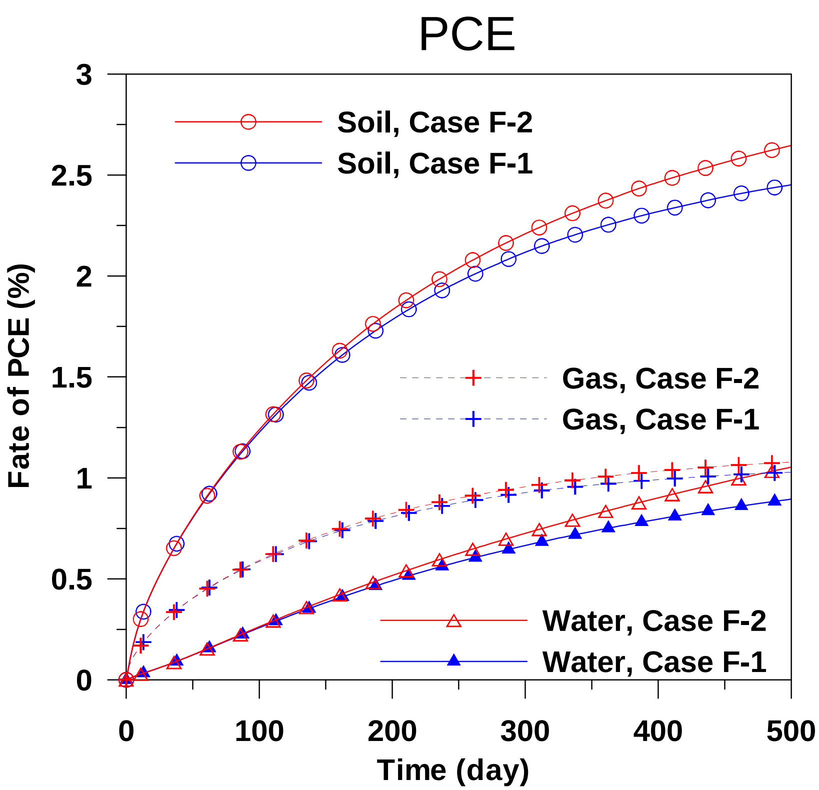


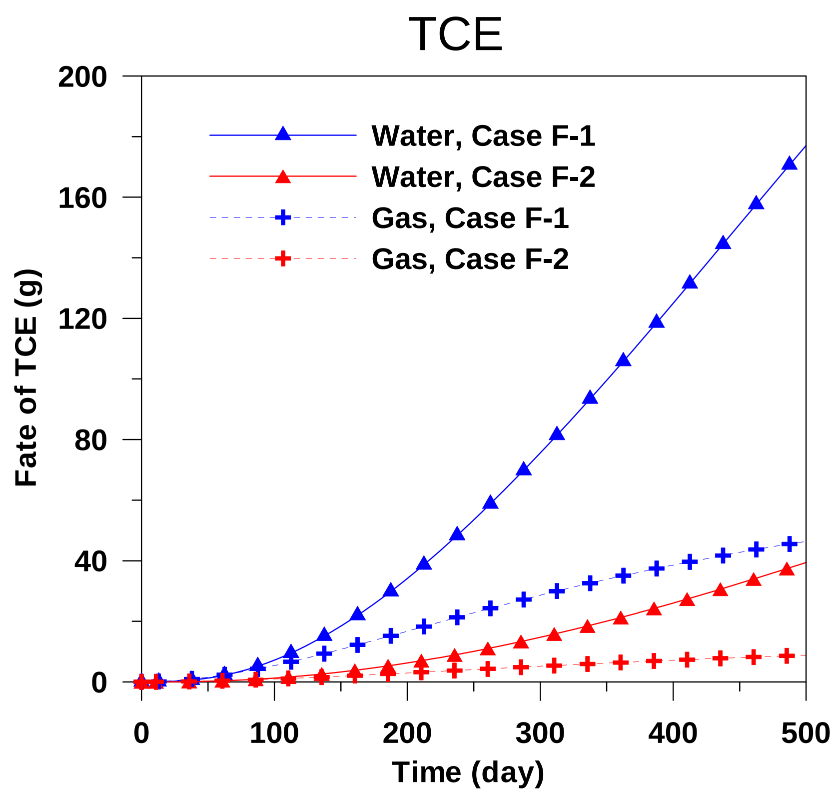


Case F-2



Fate of PCE and TCE





Summary

- The coefficient ε was implemented to define the ratio between aerobic and anaerobic biological processes of organic contaminants.

- Compared to the anaerobic-only bioreaction case, the case of coexisting anaerobic-aerobic bioreaction of CEs showed the higher PCE concentration in the subsurface due to reduced PCE biotransformation rates under the presence of oxygen.

- The availability of oxygen is an important factor to determine the concentrations of PCE and its byproducts. The concept of coexisting anaerobic-aerobic bioreaction could be used to effectively delineate complex biological processes in the transport modeling of organic compounds in the subsurface.

Thank you

Reference

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