



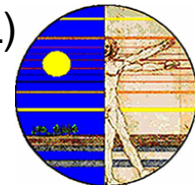
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# **Modeling of Co-Existing Anaerobic- Aerobic Biotransformation of Chlorinated Ethenes in the Subsurface**

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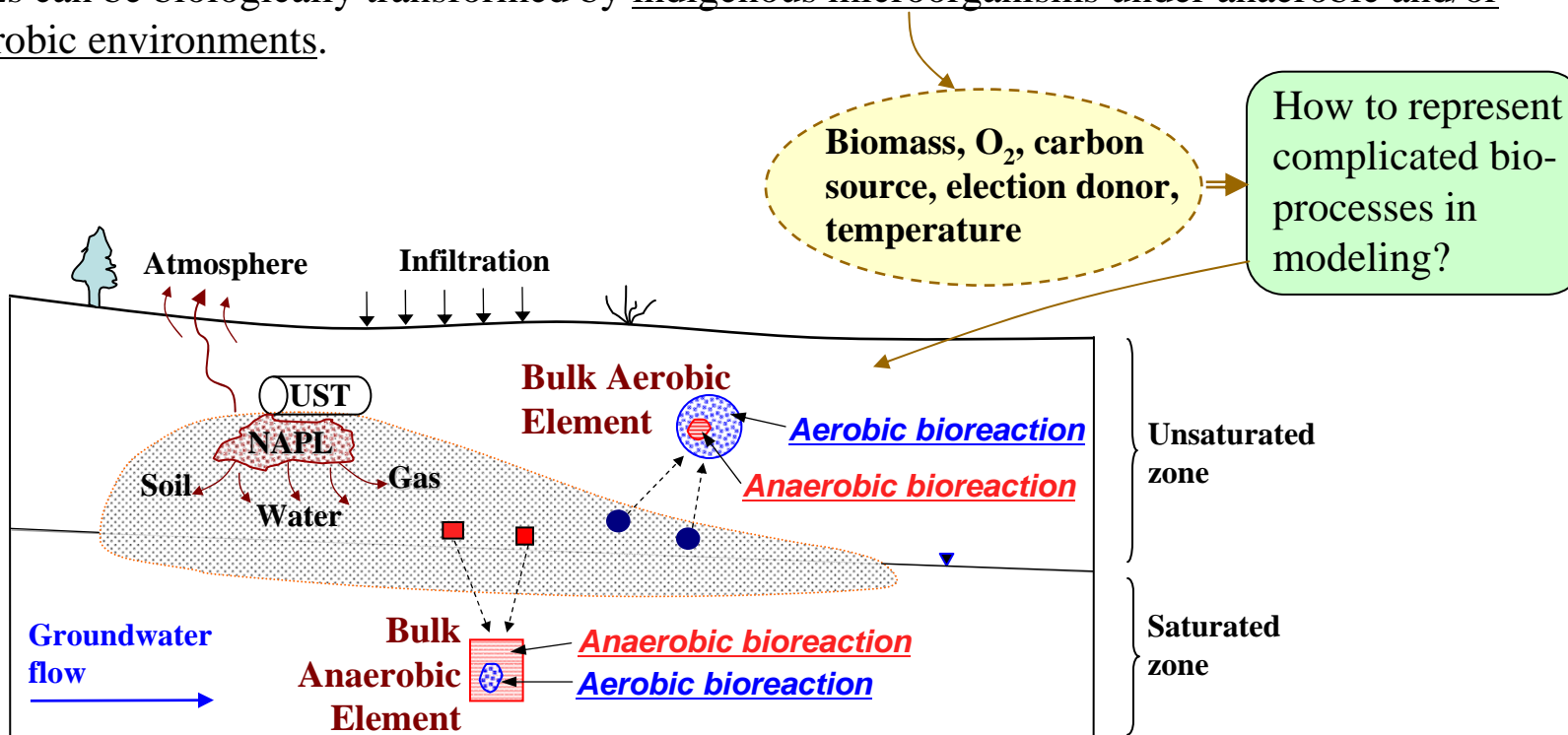
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# Table of Contents

- Introduction
  - Study objectives
  - Governing equations
    - Multiphase flow through porous media
    - Contaminant transport
  - Numerical method
  - Simulation scenarios and results
    - Anaerobic-only biotransformation
    - Coexisting anaerobic-aerobic biological processes
  - Summary
-

# 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 indigenous microorganisms under anaerobic and/or aerobic environments.



Nonaqueous phase liquid (NAPL)

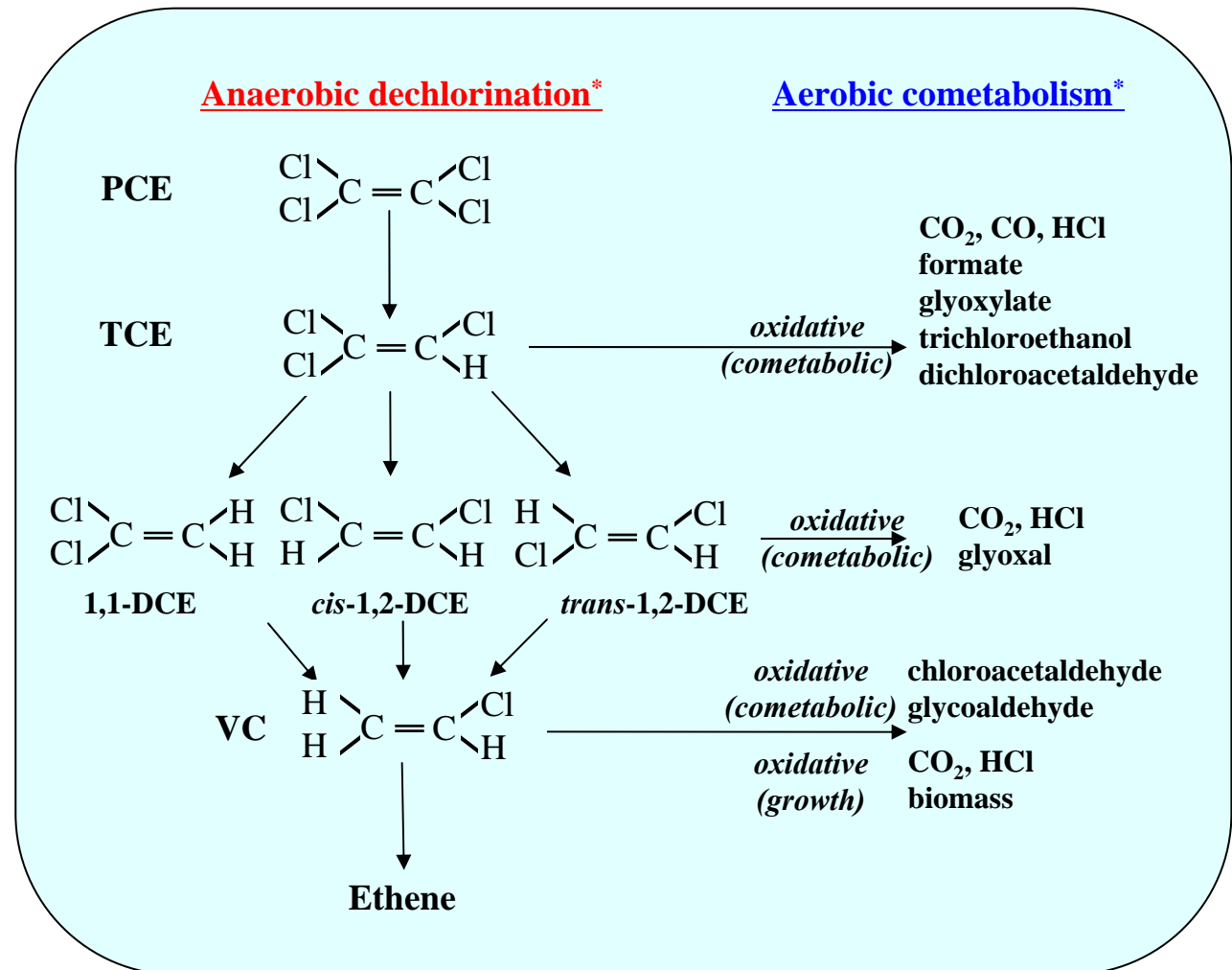
# Biological Processes of PCE

## ■ Bio-processes

- Anaerobic condition
- Aerobic condition

## ■ Target contaminants

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



\*Diagram from van Hiltkama Vlieg and Janssen, 2001.

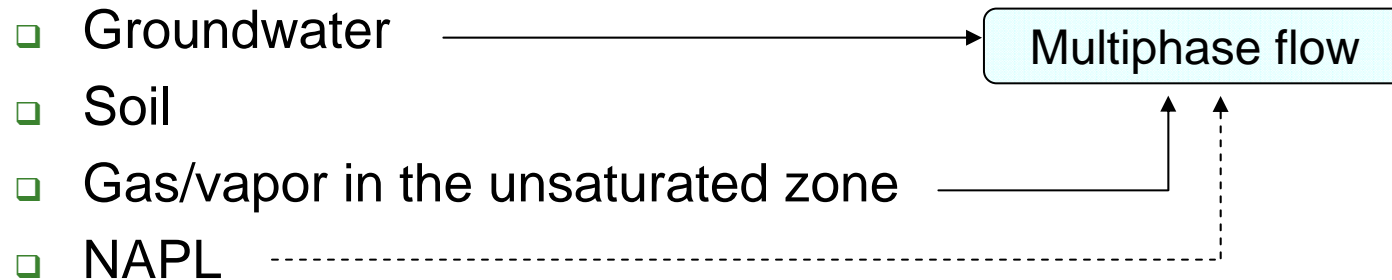
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## Study objectives

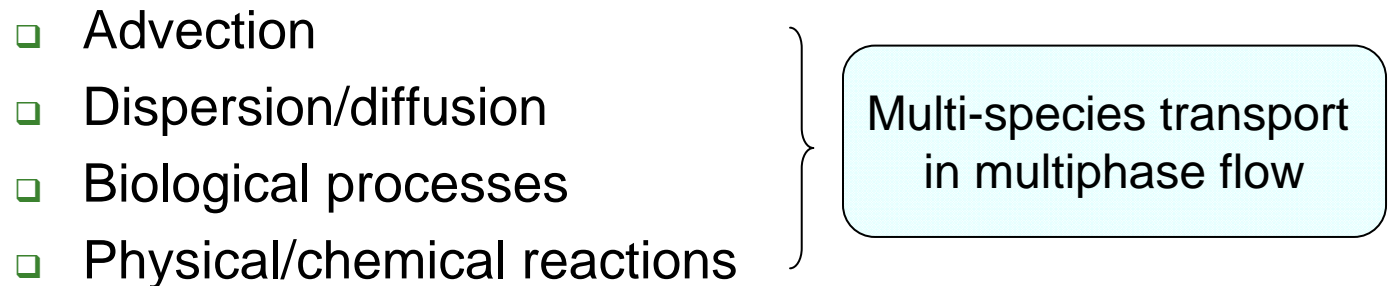
- To develop a method to represent co-existing aerobic and anaerobic biological transformations of CEs in the subsurface.
  - To investigate the effect of the co-existing biological processes on the fate and transport of CEs.
-

# Subsurface System

## ■ Multiple phases



## ■ Multiple contaminants



# Numerical Approach on Multiphase Flow

- From mass conservation and continuity equations

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

Subscript  $f$  = fluid phases (water, gas)

$\psi_f$  = Pressure head of fluid

$s_f$  = Saturation

$k_{rf}$  = Relative permeability

$\rho_f$  = 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

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

# Contaminant Transport Equation

- Multi-species in water and gas phases

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

- Biological processes: 1<sup>st</sup> order & Monod kinetics

Monod kinetics  
for dechlorination

$$I_w^i = \phi_s \varepsilon_X \left( -\frac{k_B^i C_w^i}{K_S^i + C_w^i} + \frac{y_{i/i-1} k_B^{i-1} C_w^{i-1}}{K_S^{i-1} + C_w^{i-1}} \right); \quad \varepsilon_X = \left( \frac{K_I^{O_2}}{K_I^{O_2} + C_w^{O_2}} \right) \text{ Coefficient for anaerobic bio-reaction.}$$

Monode kinetics  
for cometabolism

$$I_w^i = \phi_s \varepsilon_O \left( -\frac{k_B^i C_w^i}{K_S^i + C_w^i} \right); \quad \varepsilon_O = \left( \frac{C_w^{O_2}}{K_S^{O_2} + C_w^{O_2}} \right) \text{ Coefficient for aerobic bio-reaction.}$$

1<sup>st</sup> order kinetics  
for dechlorination

$$I_w^i = \phi_s \varepsilon_X (\lambda_B^{i-1} C_w^{i-1} - \phi_s \lambda_B^i C_w^i)$$

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

Oxygen utilization  
by cometabolism

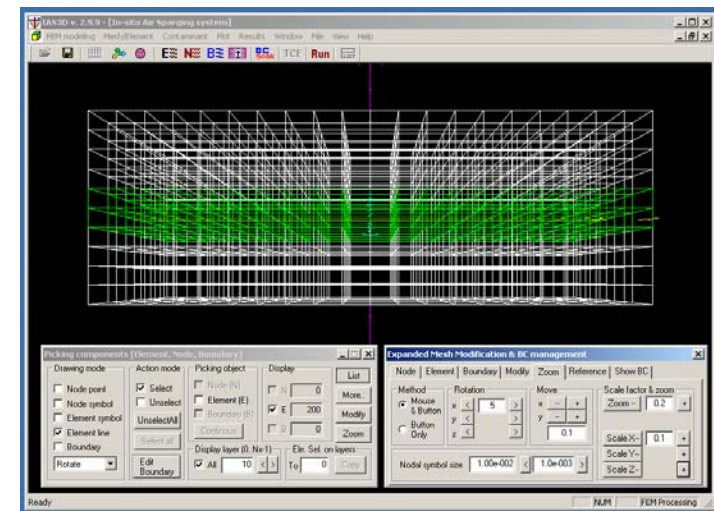
$$I_w^{O_2} = \phi_s \sum_{TCE, cDCE, VC}^i y_{O_2/i} \varepsilon_O \frac{k_B^i C_w^i}{K_S^i + C_w^i}$$



# Numerical Method

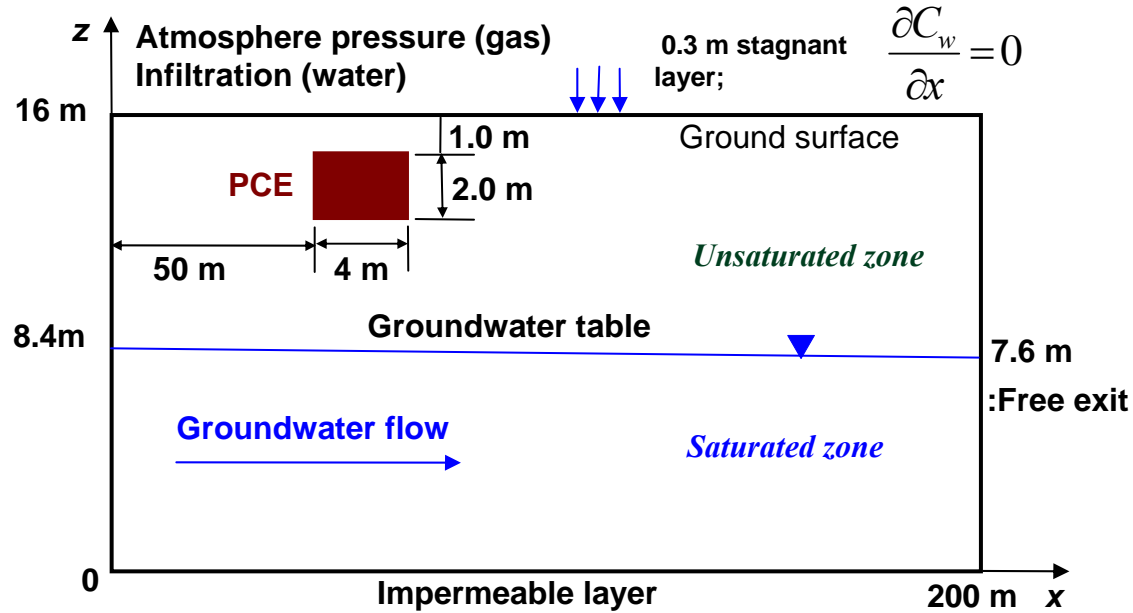
- **Galerkin Finite Element Method**
  - Modified Picard method
  - Element of domain
  - Rectangular prism (8 nodes each element)
- **Material balance calculation**
  - Accuracy and error checking
- **Numerical codes**
  - TechFlowMP: 3D multiphase flow and multispecies transport codes.
  - Program 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

## 1<sup>st</sup> order bioreaction coefficients\*

Rate(day <sup>-1</sup> )	PCE	TCE	DCE	VC
	$2.9 \times 10^{-3}$	$3.0 \times 10^{-3}$	$2.5 \times 10^{-3}$	$3.8 \times 10^{-3}$

## 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

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

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

# Parameters of Soil and Chemicals

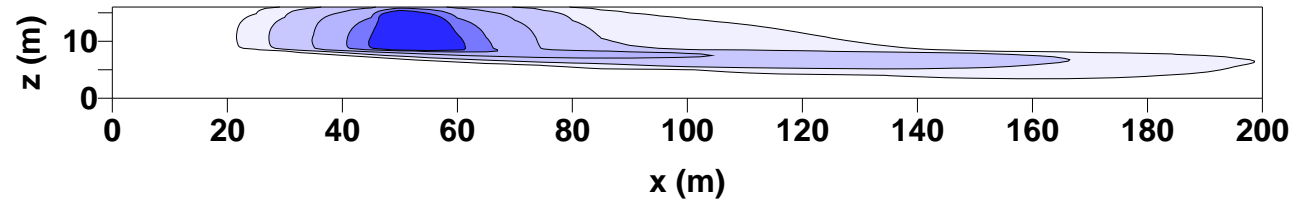
Porous soil medium	
Permeability	$5.0 \times 10^{-11} \text{ m}^2$
Porosity, $\phi$	0.35
Longitudinal dispersivity, $\alpha_L$	1.0 m
Transverse dispersivity, $\alpha_T$	0.01 m

Parameters	PCE	TCE	cDCE	VC
Molecular weight	465.8	131.4	96.9	62.5
Vapor density, $\text{kg/m}^3$	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

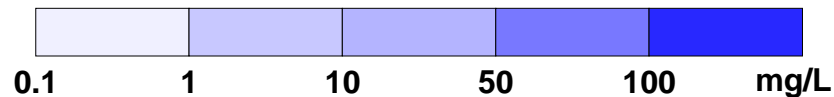
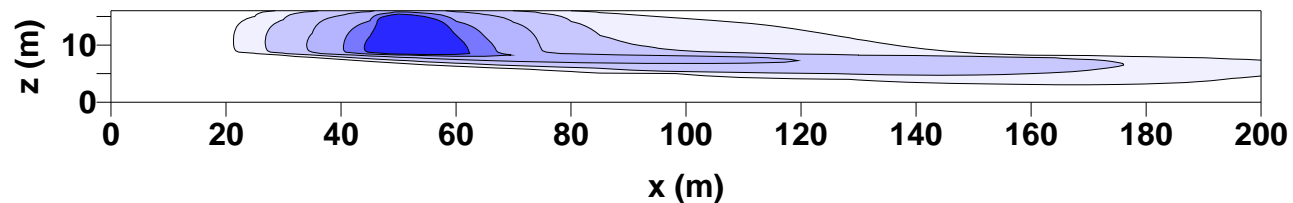
## Case F-1:

Anaerobic-only  
bioreaction with 1<sup>st</sup>  
order kinetics



## Case F-2:

Coexisting  
anaerobic/aerobic  
bioreaction with  
1<sup>st</sup> order kinetics



In Case F-2, the anaerobic biotransformation of PCE decreased due to  $\varepsilon_x$ .

⇒ Greater PCE plume in the domain.

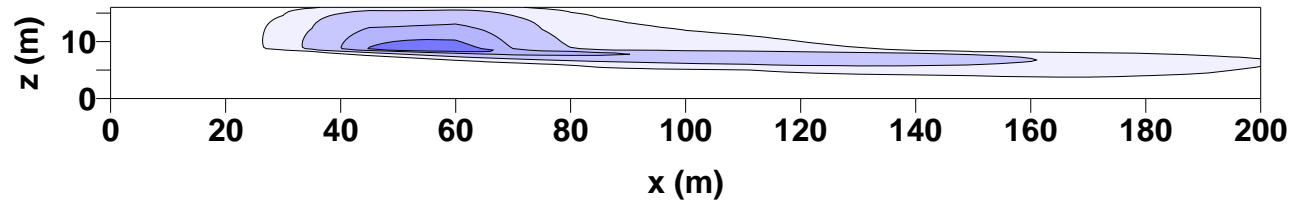
(PCE is not biodegradable under aerobic conditions.)

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

# Concentration of TCE in Water Phase

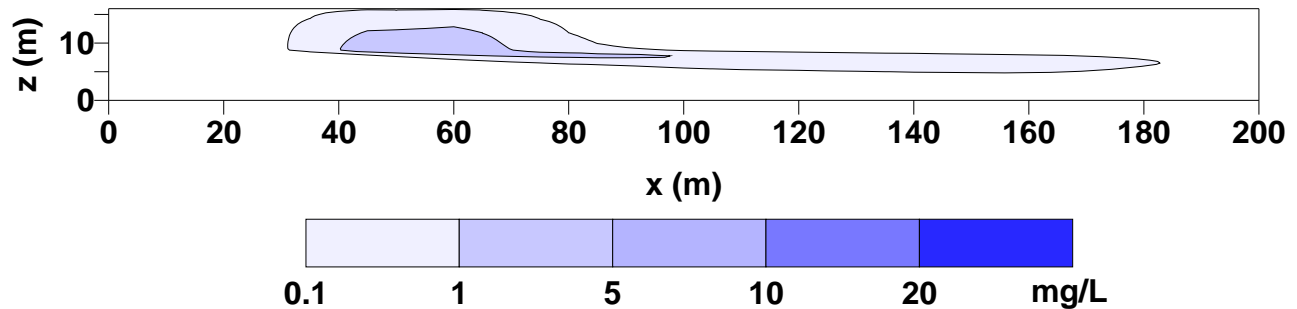
## Case F-1:

Anaerobic-only  
bioreaction with 1<sup>st</sup>  
order kinetics



## Case F-2:

Coexisting  
anaerobic/aerobic  
bioreaction with  
1<sup>st</sup> order kinetics

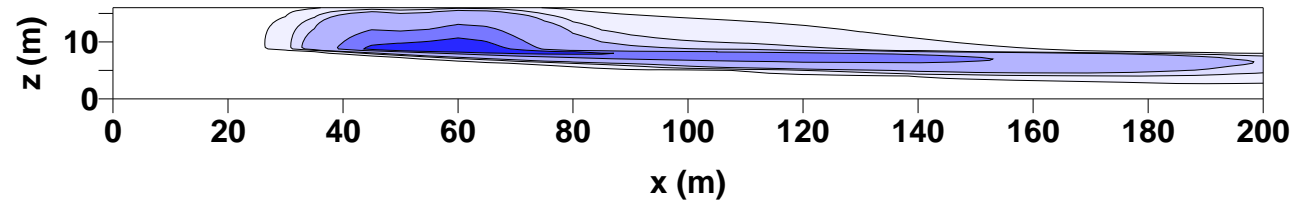


In Case F-2, the anaerobic biotransformation of PCE decreased due to  $\varepsilon_x$ .  
⇒ **Low TCE generation.**

# Concentration of DCE in Water Phase

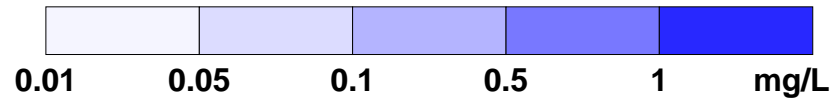
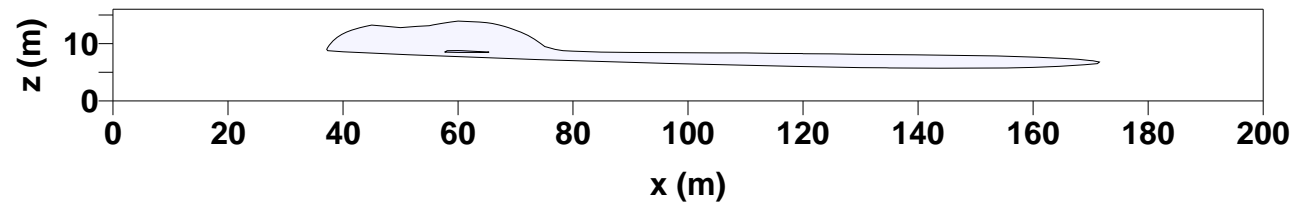
## Case F-1:

Anaerobic-only  
bioreaction with 1<sup>st</sup>  
order kinetics



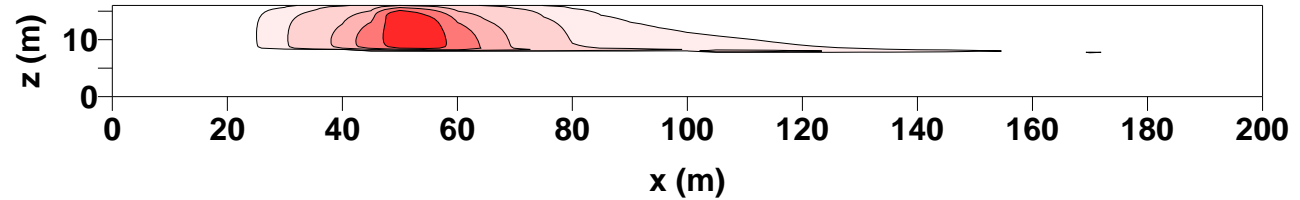
## Case F-2:

Coexisting  
anaerobic/aerobic  
bioreaction with  
1<sup>st</sup> order kinetics

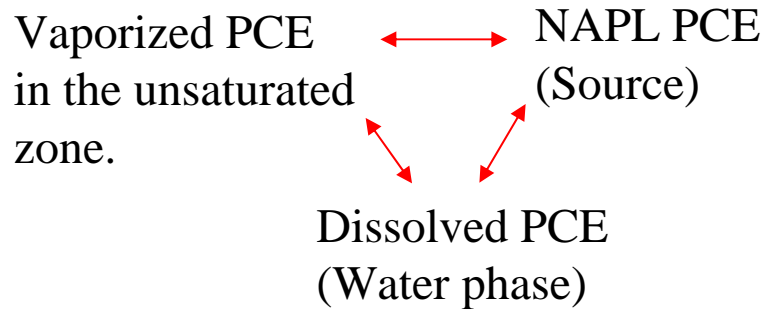
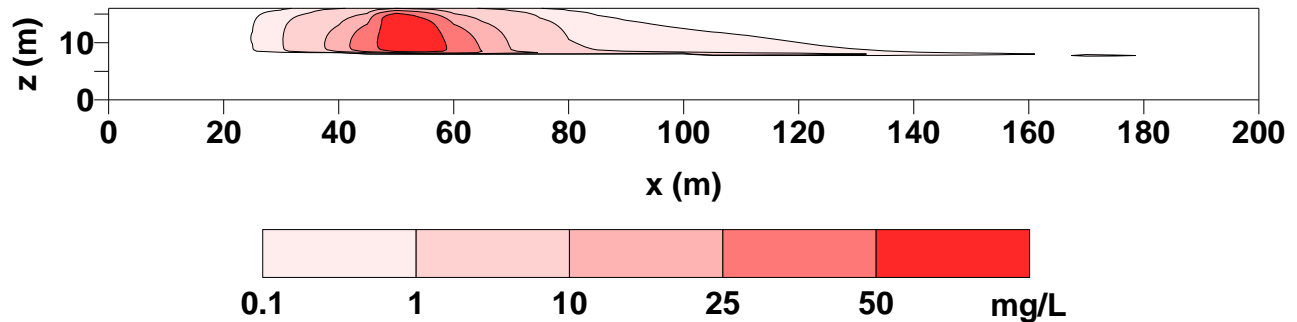


# Concentration of PCE in Gas Phase

**Case F-1:**  
Anaerobic-only  
bioreaction with 1<sup>st</sup>  
order kinetics



**Case F-2:**  
Coexisting  
anaerobic/aerobic  
bioreaction with  
1<sup>st</sup> order kinetics

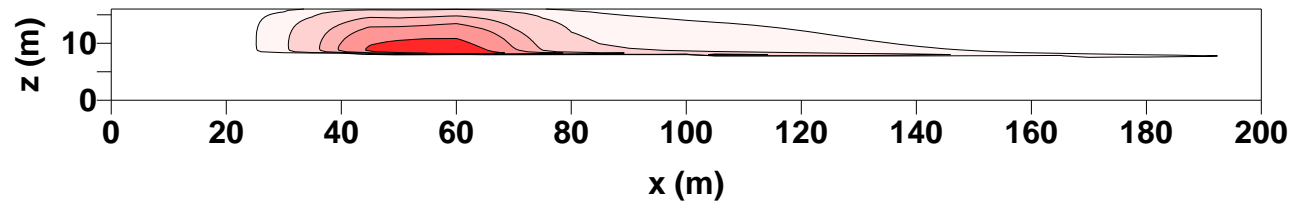




# Concentration of TCE in Gas Phase

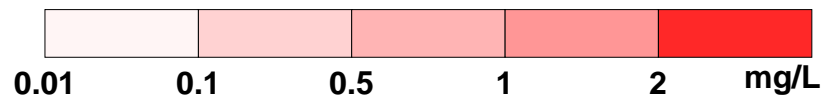
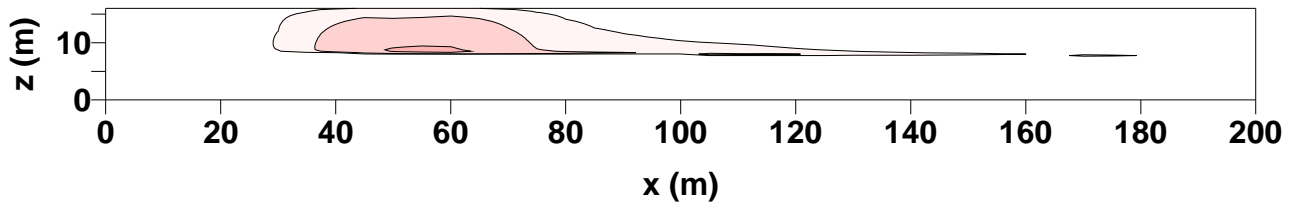
## Case F-1:

Anaerobic-only  
bioreaction with 1<sup>st</sup>  
order kinetics



## Case F-2:

Coexisting  
anaerobic/ aerobic  
bioreaction with  
1<sup>st</sup> order kinetics



Vaporized TCE  
in the unsaturated  
zone.

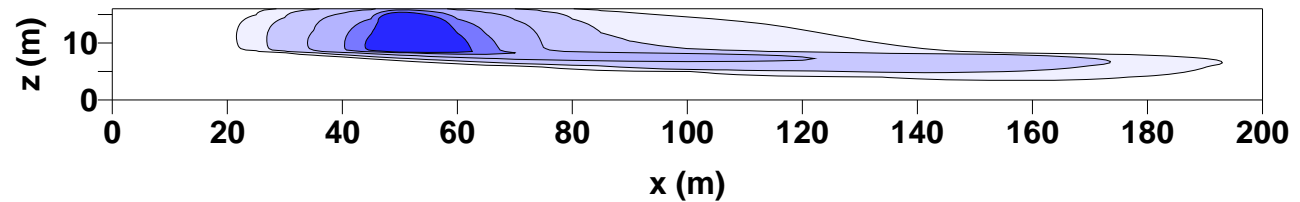


Dissolved TCE (Water phase),  
generated from the  
dechlorination of PCE

# Concentration of PCE in Water Phase

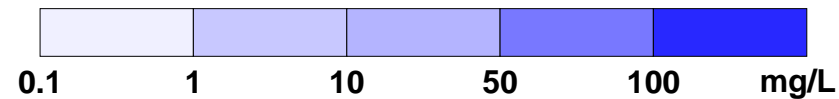
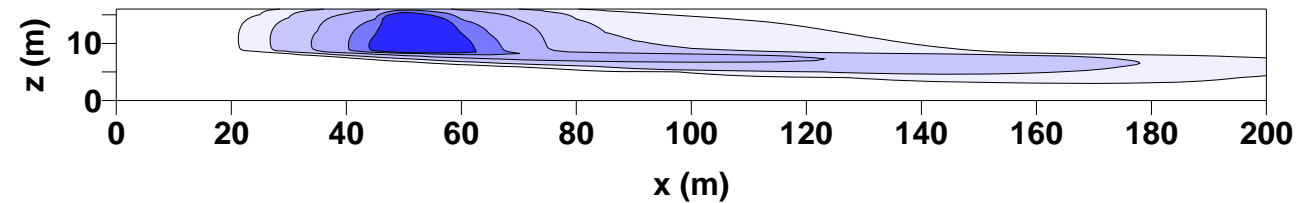
## Case M-1:

Anaerobic-only  
bioreaction with  
Monod kinetics

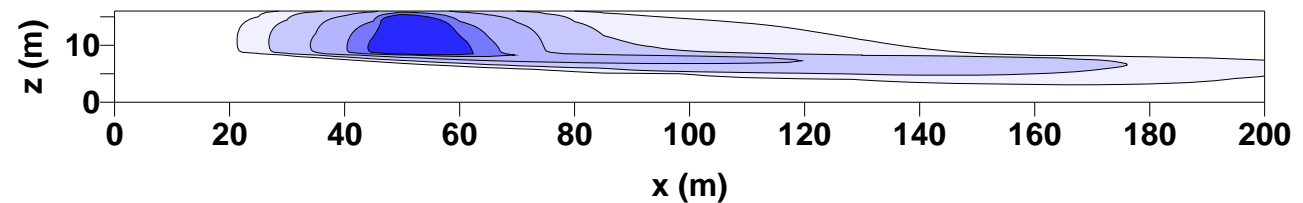


## Case M-2:

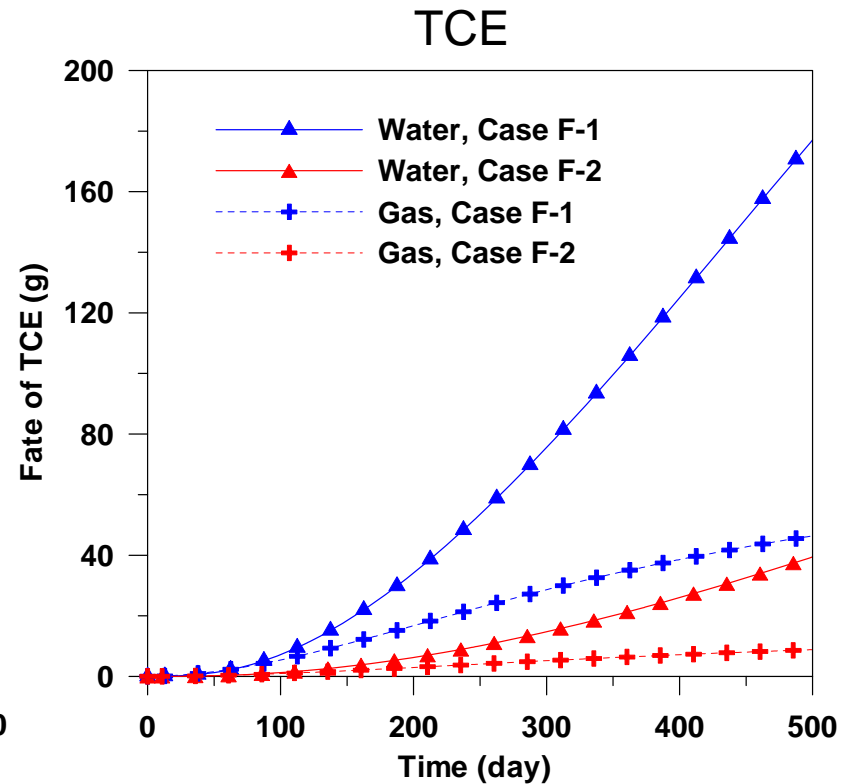
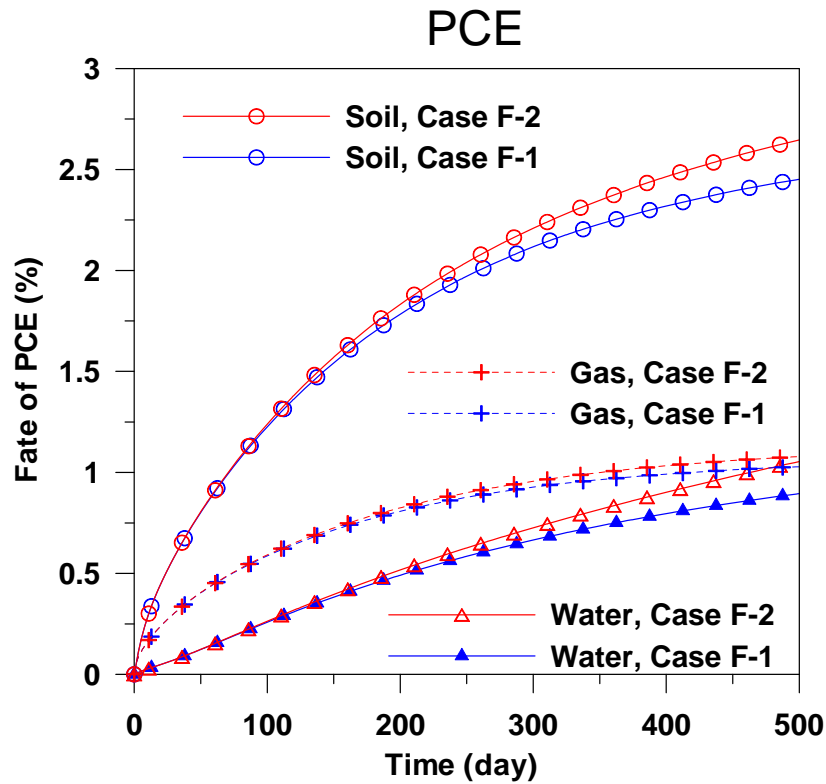
Coexisting  
anaerobic/aerobic  
bioreaction with  
Monod kinetics



## Case F-2



# Fate of PCE and TCE



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# Summary

- The coefficient  $\varepsilon$  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.
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# *Thank you*

## **Reference**

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