Three-Dimensional Flow and Transport Modeling of an Aquifer Contaminated by Perchloroethylene Subject to Multi-PRB Remediation

Zengguang Xu, YanqingWu, Fei Yu, 2012.

Transp Porous Med (2012) 91:319–337 DOI 10.1007/s11242-011-9847-1.

Student: Yu-Chieh Ho

Advisor: Jui-Sheng Chen

Date: 112/05/05

Outline

PART 01.

Introduction

PART 02.

Mathematical Model

PART 03.

Parameter Estimation for PRB's Reactive Media

PART 04.

Model Verification

PART 05.

Three-Dimensional Modeling of PCE in Groundwater Subject to Multi-PRB

1. Introduction

Issue of chlorinated solvents

- With the development of chemical industries and chemical products, many synthetic organic compounds have polluted groundwater.
  - Japan: 30% wells contaminated by PCE and TCE, 3% wells exceed drinking water standard
  - US: chlorinated solvents are detected at 80% of Superfund sites
- PCE and TCE, like other VOCs, frequently exceeded drinking-water standards, and were the 2nd and 4th most frequently detected VOCs in samples(Partick et al. 1987; USGS 2006).

How? Biochemical degradation can effectively remove organic matter from groundwater, and natural attenuation often degrades organic contaminants to innocuous compounds.

1. Introduction

Enhanced natural attenuation

- Bio-augmentation technology has become popular for speeding the rate and broadening the extent of microbial degradation.
  - Cultures proven by bio-augmentation technology grow efficiently and can dechlorinate efficiently chlorinated solvents(ESTCP 2005).
  - Injection of emulsified soybean oil was effective in enhancing reductive dechlorination in columns study(Borden, 2006).
- The research group carried PCE's screening tests using 5 reactive materials in batch reactors:
  - ✓ Zn : zero-valent zinc
  - ✓ Fe : zero-valent iron
  - ✓ MB : a microbial community
  - ✓ ZnMB : zinc and a microbial community
  - ✓ **FeMB** : iron and a microbial community

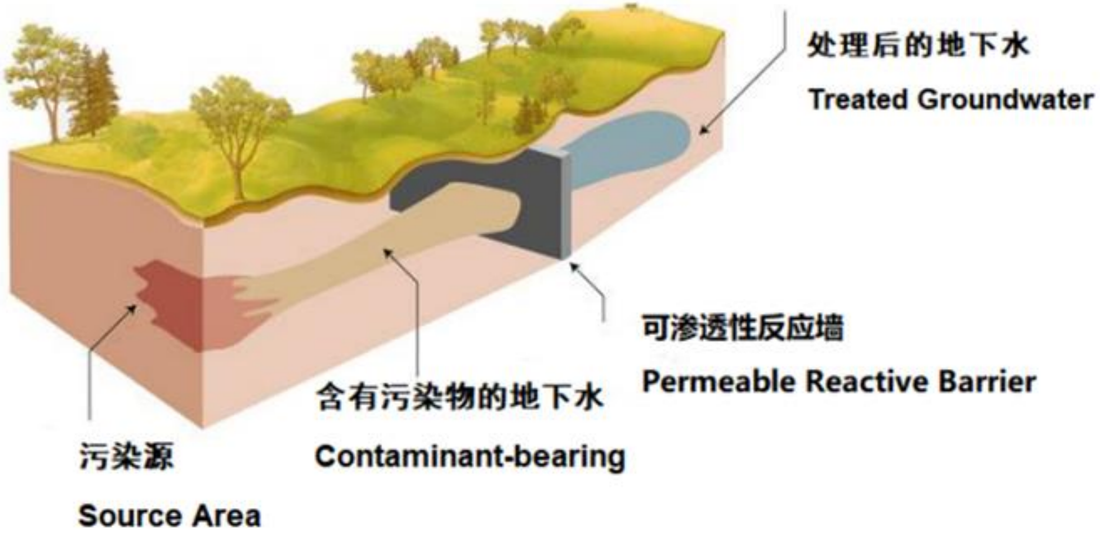
Pathway for PCE degradation :

PCE → TCE → 1,1DCE → ethylene → ethane

1. Introduction

PRB Technology

- Groundwater remediation is being augmented at many sites by innovative techniques including permeable reactive barriers (PRBs)
- PRBs are in-situ treatments with reactive materials that can degrade or immobilize contaminant plumes.
  - mixing iron and bentonite Wadley et al. (2005)
  - zero-valent iron Lai et al. (2006)
  - emulsified oil substrate Borden (2007)



Limitation: Losses of reactivity and permeability are common causes of PRB failure(Henderson and Demond, 2007).

1. Introduction

Groundwater and transport modeling

- Sun et al. (1999;2004) suggest use of simulation as a tool to avoid potential design flaws.
  - Lu et al. (2003): 1-D analytic solution for dechlorination reaction network including PCE and its degradation products
  - Lai et al. (2006): model of transport and transformation of PCE and TCE using the GMS on the basis of a column test
  - MODFLOW has also been widely used for groundwater flow. RT3D and MT3D99 can simulate chain kinetic reactions for contaminant transport.
- Developing a model without limits on number of species based on MODFLOW/MT3DMS is very helpful for transport simulation.

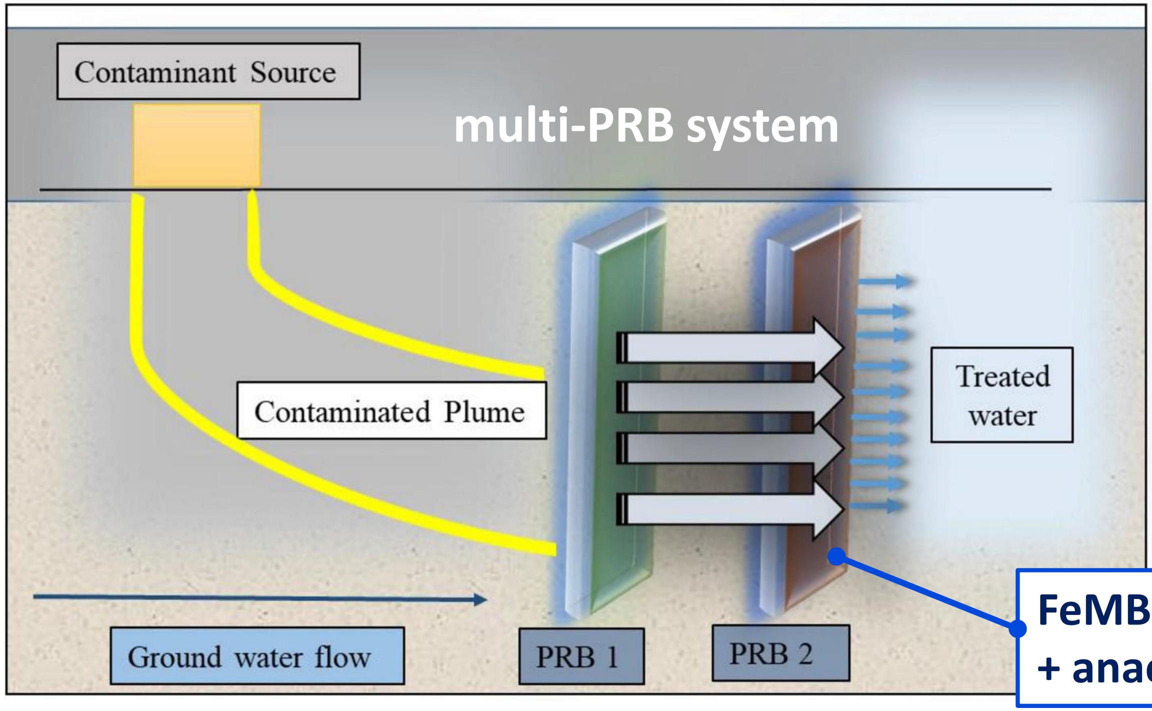
Pathway for PCE degradation :

PCE → TCE → 1,1DCE → ethylene → ethane

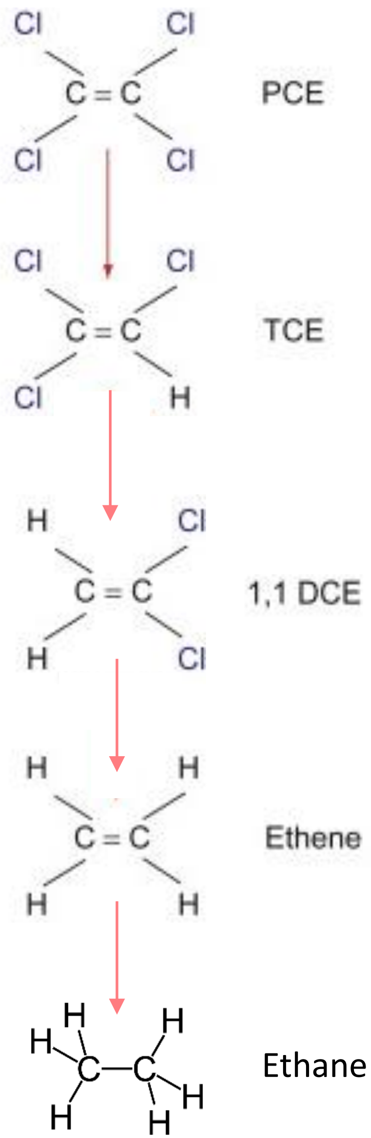
1. Introduction

Purpose of the work

❖ To use FeMB as multi-PRB's reactive media, develop a modified MODFLOW/MT3DMS that can simulate a 3-D aquifer contaminated by PCE and its daughters.



FeMB = zero-valent iron
+ anaerobic microbial communities



2. Mathematical Model

Assumptions
(a) effective porosity keeps constant
(b) the adsorption follows Langmuir isotherm
(c) the biological/chemical reaction follows first-order kinetics model

- Contaminant fate and transport in groundwater is written as:

$$R\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\theta\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i\theta C) - \lambda\theta C$$

where ADS DSP ADV BCR

C : dissolved contaminant concentration (ML^{-3})
θ : effective porosity (-)
D_{ij}: hydrodynamic dispersion tensor (L2T−1) ($L^2 T^{-1}$)
v_i : average pore velocity (LT^{-1})
λ : first-order reaction rate (T^{-1})
R : retardation factor (-)

(Zheng, 2006)

- Using FeMB as PRB's reactive media, a contaminated aquifer is composed of PRB zones and non-PRB zones:

$$\begin{cases}
\text{Non-PRB}: R_m\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_m}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C_m) \quad m = \text{PCE,TCE}, \ldots, \text{ethane} \\
\text{PRB} \begin{cases}
\text{PCE}: R_{\text{PCE}}\frac{\partial C_{\text{PCE}}}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_{\text{PCE}}}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C_{\text{PCE}}) - \lambda_{\text{PCE}}C_{\text{PCE}} \\
\text{TCE}: R_{\text{TCE}}\frac{\partial C_{\text{TCE}}}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_{\text{TCE}}}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C_{\text{TCE}}) + Y_{\text{PCE/TCE}}\lambda_{\text{PCE}}C_{\text{PCE}} \\
\qquad - \lambda_{\text{TCE}}C_{\text{TCE}} \\
1,1\text{−DCE}: R_{1,1\text{−DCE}}\frac{\partial C_{1,1\text{−DCE}}}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_{1,1\text{−DCE}}}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C_{1,1\text{−DCE}}) \\
\qquad + Y_{\text{TCE/1,1−DCE}}\lambda_{\text{TCE}}C_{\text{TCE}} - \lambda_{1,1\text{−DCE}}C_{1,1\text{−DCE}} \\
\text{Ethylene}: R_{\text{ethylene}}\frac{\partial C_{\text{ethylene}}}{\partial t} \\
\quad = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_{\text{ethylene}}}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C_{\text{ethylene}}) \\
\qquad + Y_{1,1\text{−DCE/ethylene}}\lambda_{1,1\text{−DCE}}C_{1,1\text{−DCE}} - \lambda_{\text{ethylene}}C_{\text{ethylene}} \\
\text{Ethane}: R_{\text{ethane}}\frac{\partial C_{\text{ethane}}}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_{\text{ethanee}}}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C_{\text{ethane}}) \\
\qquad + Y_{\text{ethylene/ethane}}\lambda_{\text{ethylene}}C_{\text{ethylene}}
\end{cases}
\end{cases}$$

where R_m is a dimensionless factor defined as: $R_m = 1 + \frac{\rho}{\theta}\frac{\partial \overline{C}_m}{\partial C_m} = 1 + \frac{\rho}{\theta}\left[\frac{K_l^m S_0^m}{(1+K_l^m C_m)^2}\right]$

ρ : bulk density (ML^{-3})
C_m : adsorbed contaminant concentration (ML^{-3})
K_m^l: Langmuir constant (L^3M^{-1})
S_m^0: total concentration of sorption sites (MM^{-1})
$Y_{m-1/m}$: stoichiometric yield factor that describes the fraction of parent species m transformed into daughter species $m-1$

3. Parameter Estimation for PRB's Reactive Media

Experimental Description

❖ To obtain adsorption and degradation characteristics of FeMB as PRB's reactive media, the degradation test of PCE in a sand column with FeMB was executed.

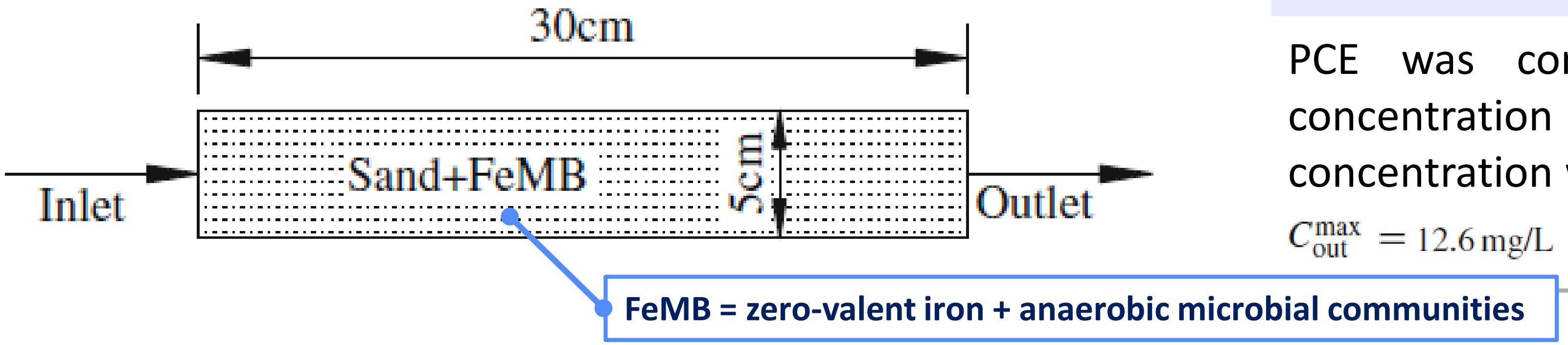


Table 1 Parameters in the sand column (Ma 2007)

Parameters	Values	Parameters	Values
Bulk density (g/cm^3)	1.45	Column length (cm)	30
Effective porosity	0.41	Inlet concentration (mg/L)	65.2
Average pore velocity (cm/day)	16.75	Hydrodynamic dispersion coefficient (cm^2/day)	2.034×10^2

Step1.

A tracer test with KCl was performed to obtain hydrodynamic dispersion coefficient and average pore velocity estimated by CXTFIT2.1.

Step2.

PCE was continuously injected at a constant concentration of C_0 = 65.2mg/L, and degraded concentration was measured at the outlet with

$C_{out}^{max} = 12.6$ mg/L

3. Parameter Estimation for PRB's Reactive Media

Parameters' Estimation by Means of a Genetic Algorithm

Genetic Algorithms (GAs)

- Adaptive search algorithm premised on evolutionary ideas of natural selection and genetics.
- The basic idea is to mimic natural selection to optimize model fitting to data.

Langmuir constant K_l^{PCE}

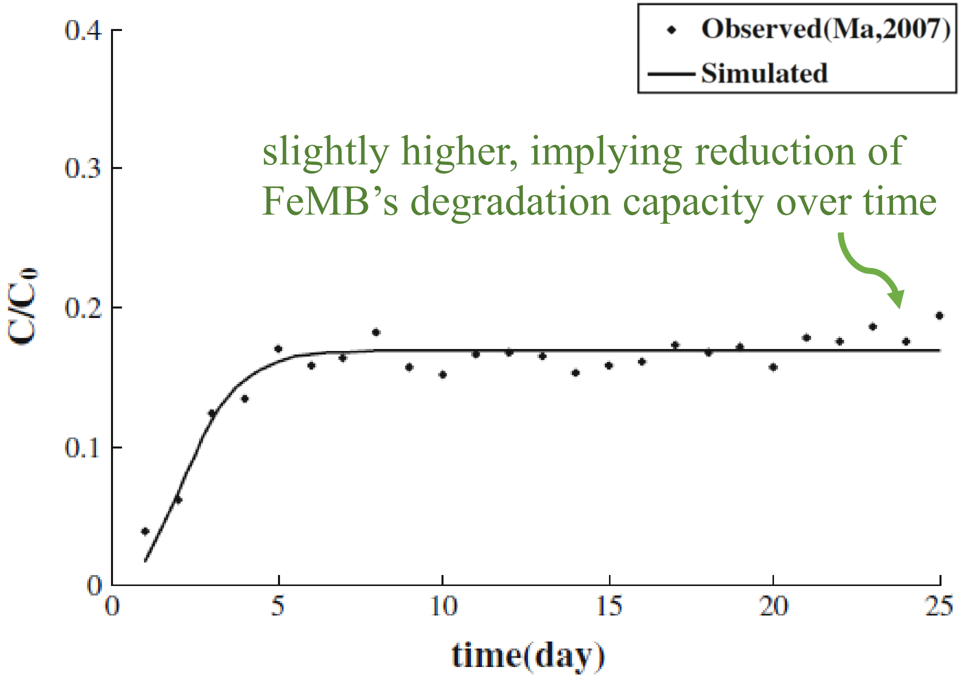
total concentration of sorption sites S_0^{PCE}

first-order reaction rate λ_{PCE}

❖ The goal of the procedure was to find the values of K_l^{PCE}, S_0^{PCE}, and λ_{PCE} , which could minimize the objective function, the sum of squared residuals between simulated and observed values.

Table 2 Estimated parameters in the sand column

Parameters	K_l^{PCE} (L/mg)	S_0^{PCE} (mg/g)	λ_{PCE} (day^{-1})	Linear correlation coefficient	Coefficient of efficiency
Values	3.5×10^{-3}	7.24×10^{-2}	1.365	0.95	0.90



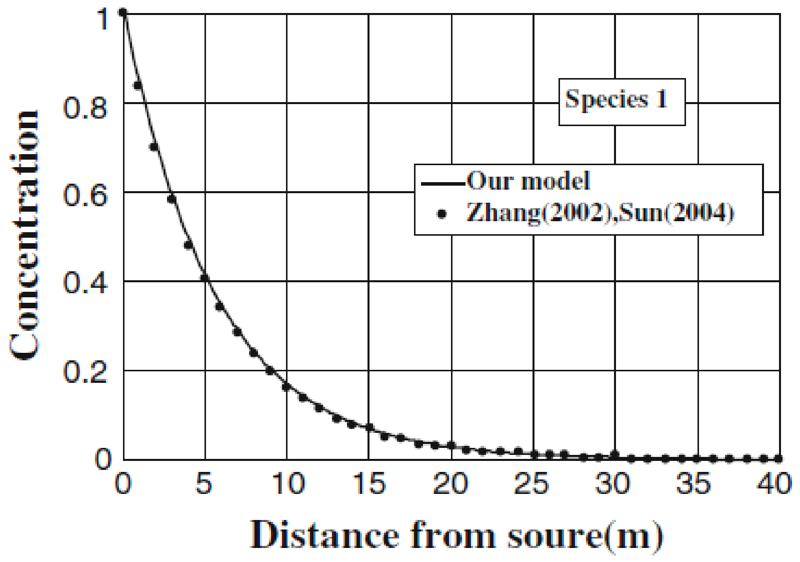
4. Model verification

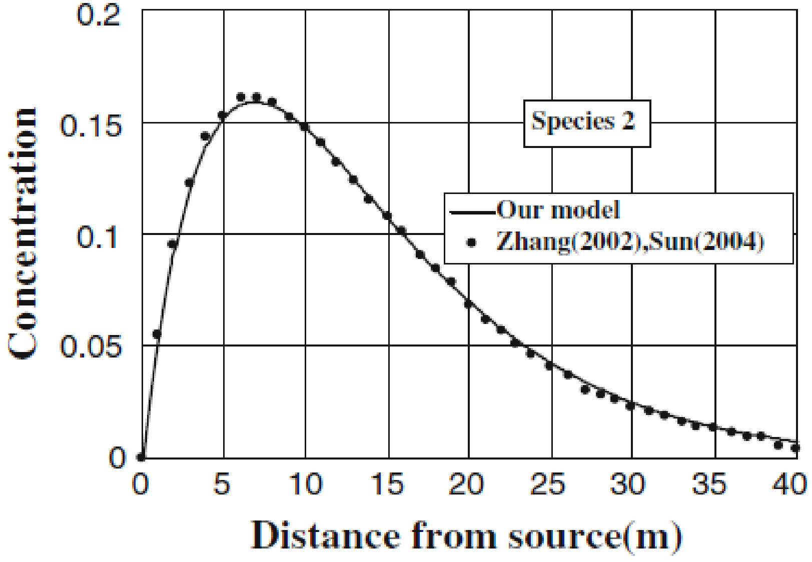
Two species

- Verification of computer codes focuses on transformation from mother to daughter products.
- A problem of 1-D transport from Zhang and Woodbury(2002) and Sun et al. (2004) is selected.
- The model domain is a rectangular column ($0.4 \times 0.4 \times 50 m^3$), discretized into 100 hexahedral elements of $0.4 \times 0.4 \times 0.5 m^3$.

Table 3 System parameters (Zhang and Woodbury 2002; Sun et al. 2004)

Parameters	Values	Parameters	Values
Average pore velocity (m/day)	0.4	First-order reaction rate λ_2 (day^{-1})	0.1
Longitudinal dispersivity (m)	10	Stoichiometric yield factor $Y_{1/2}$	0.5
First-order reaction rate λ_1 (day^{-1})	0.2		





good agreements between models

5. Modeling of PCE in Groundwater Subject to Multi-PRB

Calculation Conditions

- Constant head at left and right boundaries
- A point source of PCE (65.2mg/L) at left boundary (for 20 days)
- 3-stage PRB with reactive FeMB and thicknesses of 10 cm
- 2 horizontal sections (1-1 and 2-2)
- 1 observation point

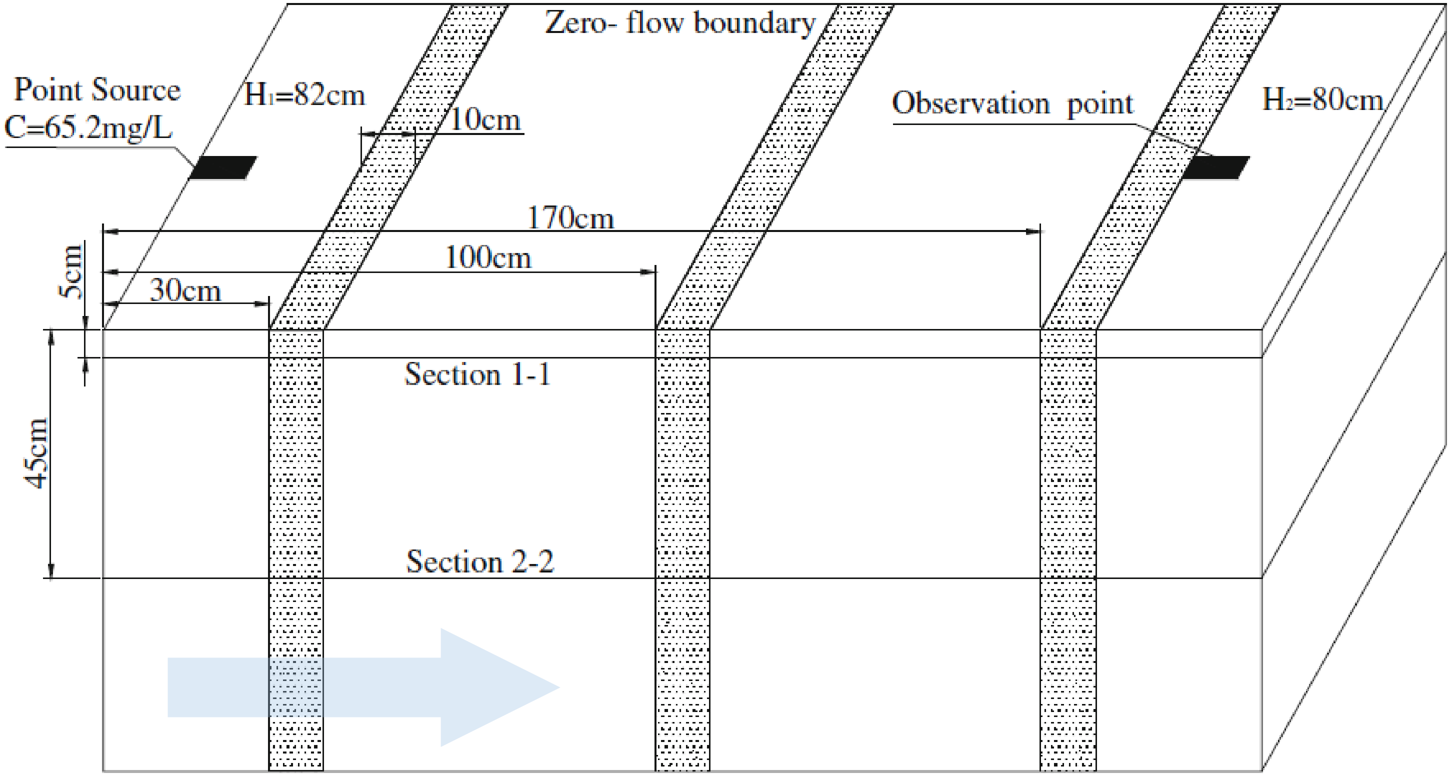


Fig. 6 Model schematic

- rectangular parallelepiped: $80 \times 150 \times 210$ cm^3
- 2,520 elements with dimensions $10 \times 10 \times 10$ cm^3
- simulation time: 50 days

Calculation Results and Analysis

Comparative Analysis of Various Factors in Contaminant Transport

❖ To analyze the contribution of each factor

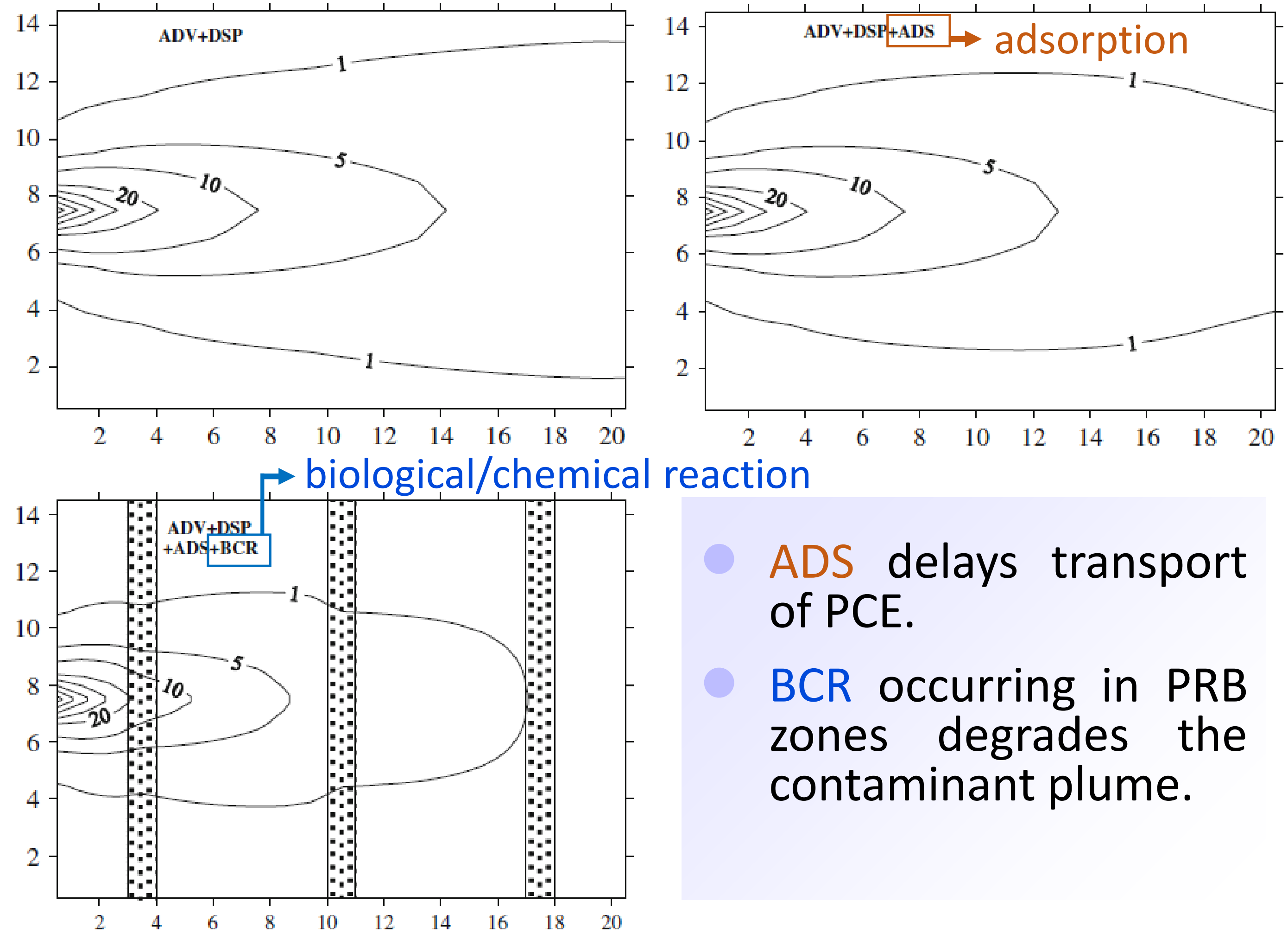


Fig. 7 Concentration profiles of PCE after 20 days at section 1-1 (mg/L)

- ADS delays transport of PCE.
- BCR occurring in PRB zones degrades the contaminant plume.

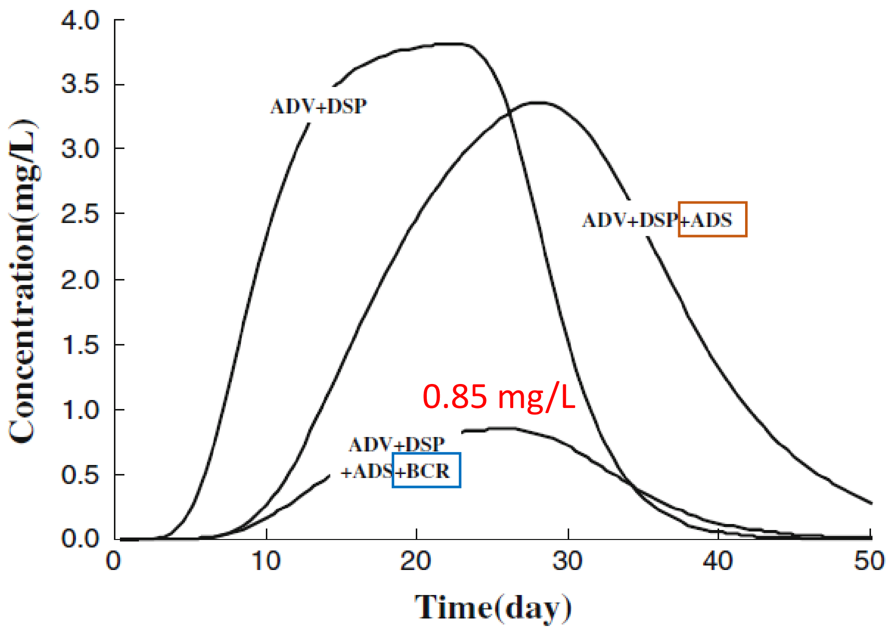


Fig. 8 Breakthrough curves of PCE at observation point

- ADS slows the plume spreading rate.
- peak value of ADV+DSP+ADS+BCR: 65.2 → 0.85 mg/L (98.7%↓)

Calculation Results and Analysis

Comparative Analysis of Various Factors in Contaminant Transport

❖ To analyze the contribution of each factor

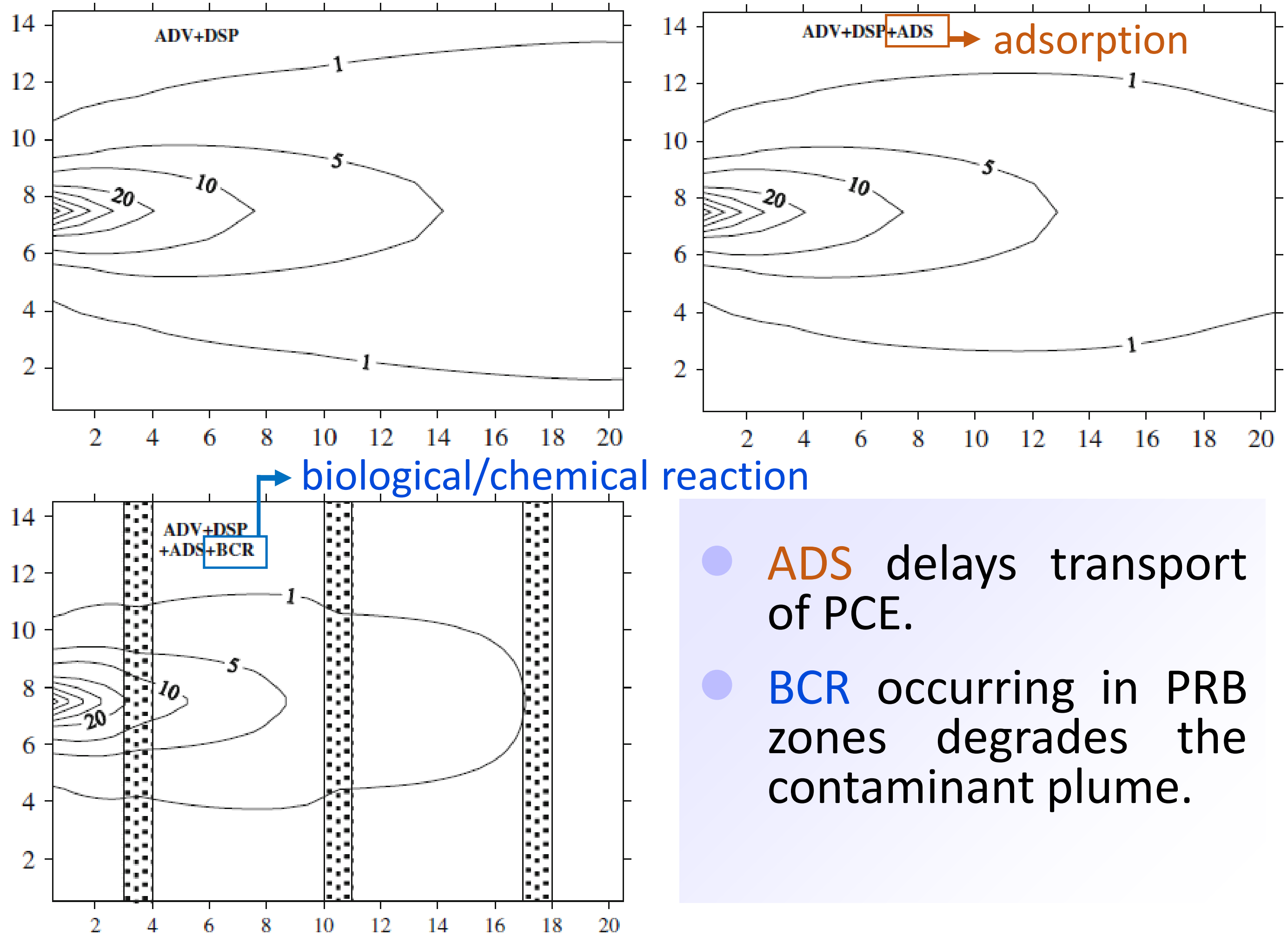


Fig. 7 Concentration profiles of PCE after 20 days at section 1-1 (mg/L)

- ADS delays transport of PCE.
- BCR occurring in PRB zones degrades the contaminant plume.

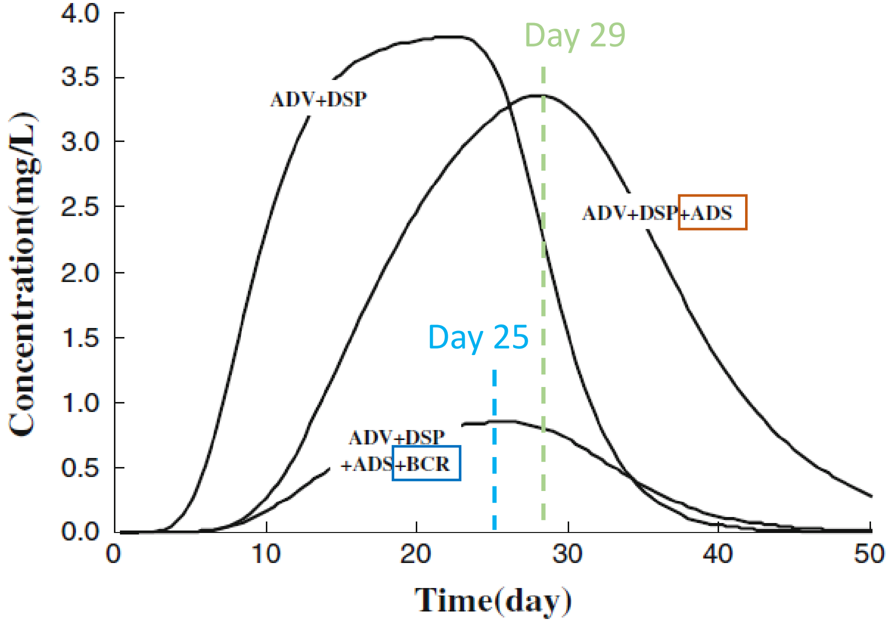


Fig. 8 Breakthrough curves of PCE at observation point

- ADS slows the plume spreading rate.
- peak value of ADV+DSP+ADS+BCR:
  65.2 → 0.85 mg/L (98.7%↓)
- The peak arrives faster, which is led by higher permeability in BCR zone.

Calculation Results and Analysis

Comparing Multi-PRBs

- Compare model results for single-, two-, and three-stage PRBs to remove PCE and its daughters

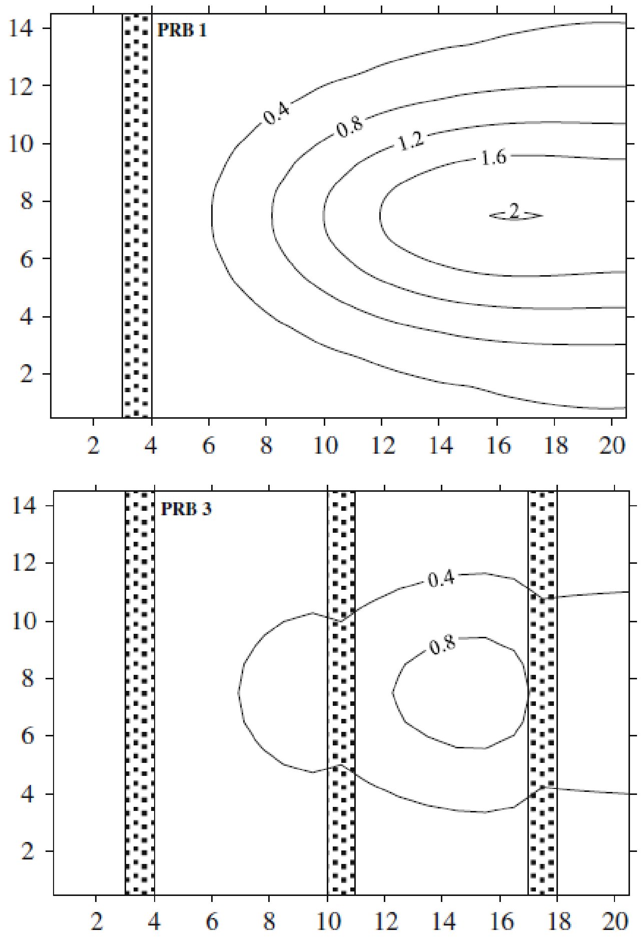


Fig. 9 Concentration profiles of PCE after 30 days at section 1-1 (mg/L)

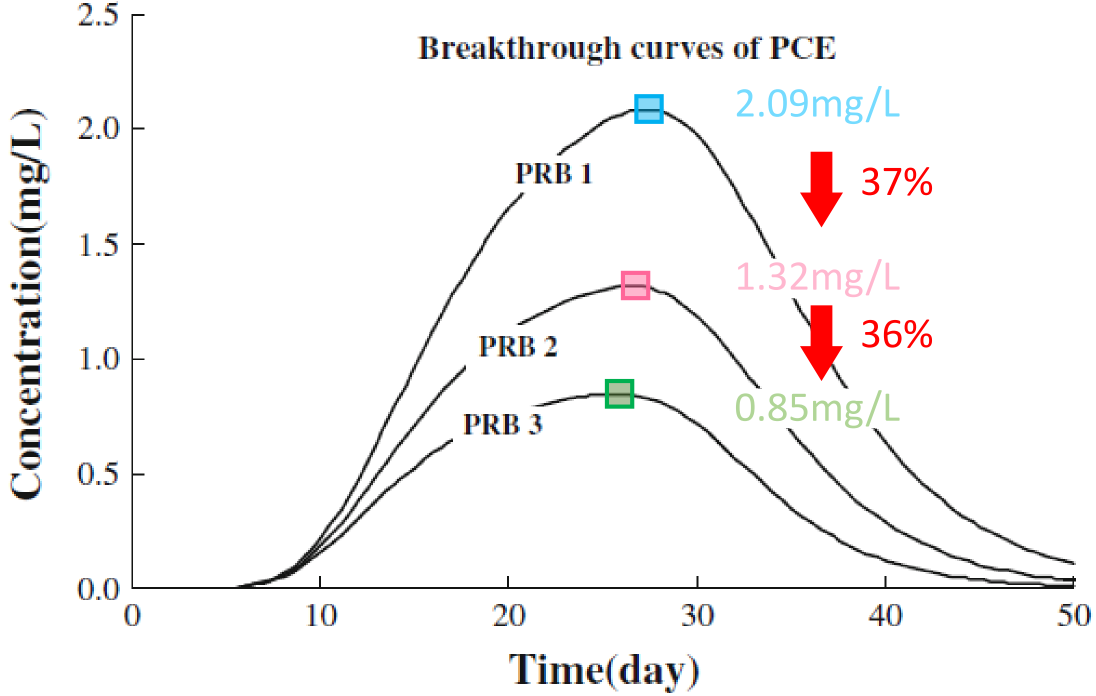


Fig. 10 Breakthrough curves of PCE at observation point

- The concentrations of PCE in treated water are: three-stage<two-stage<single-stage.
- Multi-PRB can degrade more noxious species to innocuous species.
- The issue of optimal cost and effectiveness should be taken into account during designing PRBs.

Calculation Results and Analysis

Sensitivity Analysis for the Losses of Reactivity and Permeability

- During restoring a contaminated aquifer using biochemical degradation, clogging due to and precipitation may cause a loss of hydraulic conductivity (Long and Borden, 2006).
- The reactivity of material could have a decline over time.

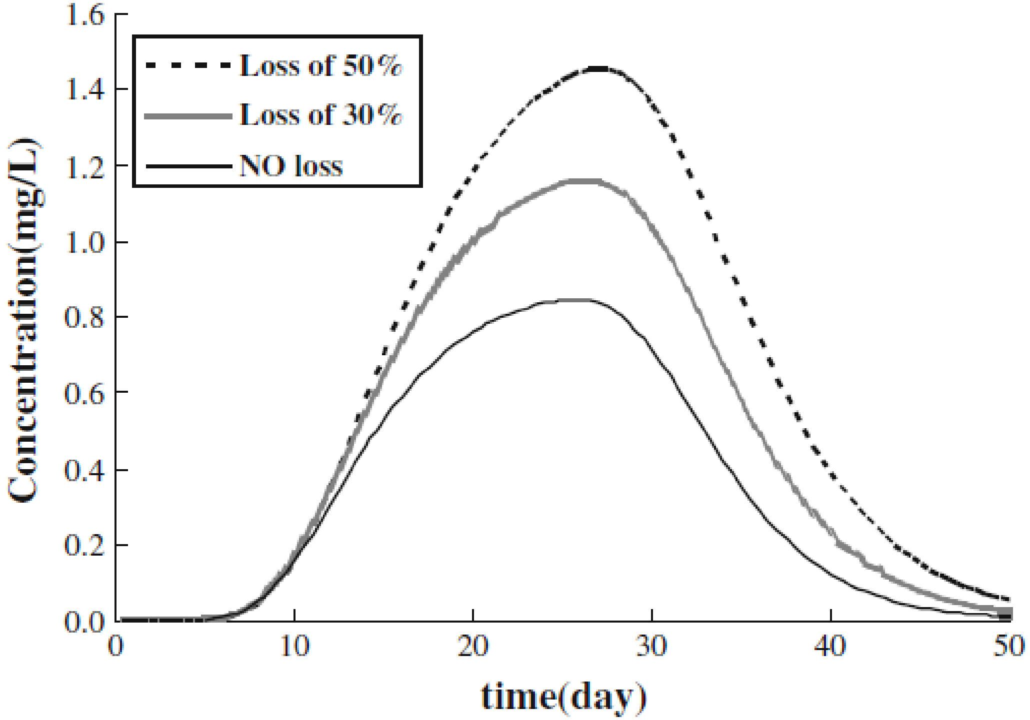


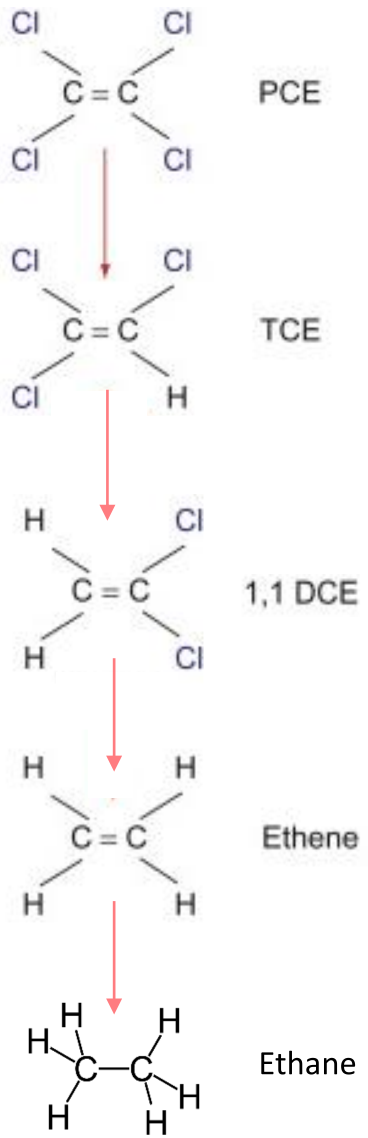
Fig. 18 Breakthrough curves of PCE for sensitivity analyses at observation point

- First-order reaction rate and hydraulic conductivity in PRB zones are assumed to decrease by 30 or 50%.
- The losses could cause a decline of remediation effect.

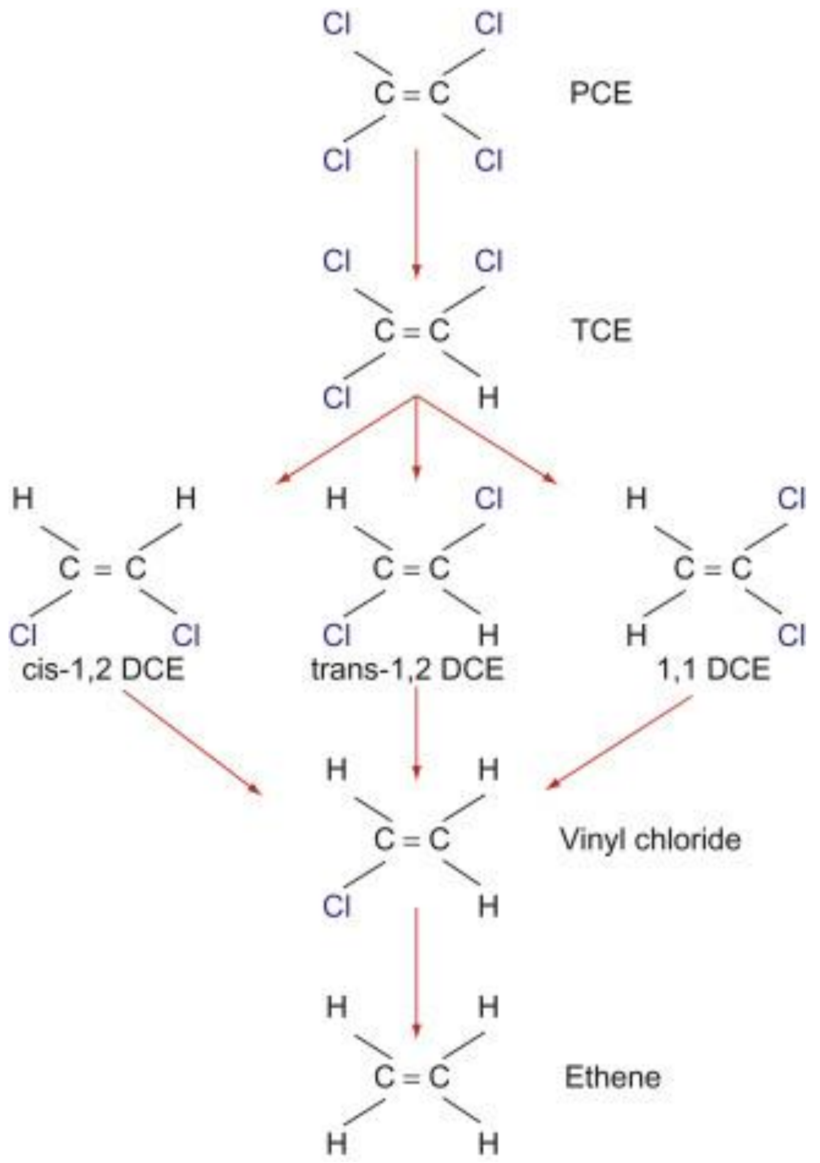
6. Conclusions

- The multi-species transport model of a multi-PRB has been built and applied to a 3-D model to analyze the treatment efficiency of multi-PRBs.
  - FeMB is a potential reactive media for PCE-contaminated groundwater.
  - When contamination causes secondary pollution during remediation process, multi-PRB could be a technology of preferred option.
  - The modified MODFLOW/MT3DMS can effectively simulate multispecies chain kinetic reactions with arbitrary number of species.
  - Losses of reactivity and permeability have a significant effect on remediation's success.

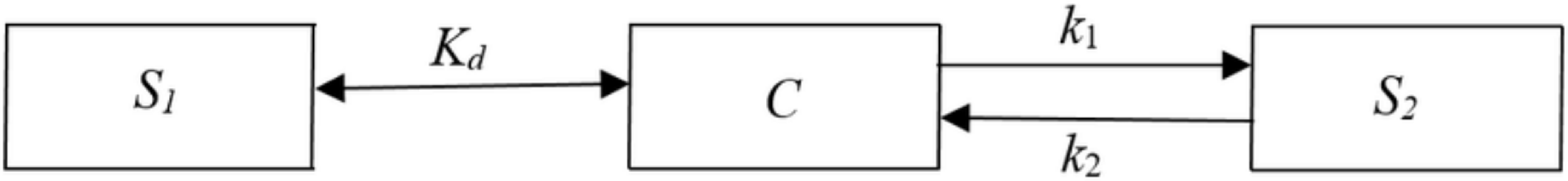
Thanks for your attention!



PCE
TCE
1,1 DCE
Ethene
Ethane



PCE
TCE
cis-1,2 DCE
trans-1,2 DCE
1,1 DCE
Vinyl chloride
Ethene



Schematic diagram of the two-site sorption model. C is the concentration in the solution, S1 is the amount of solute sorbed on equilibrium sites, S2 is the amount of solute sorbed on kinetic sites, k1 and k2 are the rates of reactions (Zhang and Selim 2005)

吸附模式 (Batch Method)

- 等溫吸附模式
  - Langmuir isotherm（Q_m, ΔG, ΔH, ΔS）
  - Freundlich isotherm
  - BET isotherm（多層吸附）
  - Tekim isotherm (不勻質表面之吸附)
  - Dubinin-Radushkevich isotherm (不勻質表面之吸附)
- 動力吸附模式
  - Pseudo-first-order equation（k_1, E_a）
  - Pseudo-second-order equation（k_2, E_a）
  - Elovich equation

Langmuir isotherm

1. 吸附位址均勻分佈於吸附劑固體表面，每一個吸附位址只能吸附一個分子。
2. 各吸附位址對吸附質之親和力相同。
3. 一個位置上吸附分子後，並不會影響其餘分子之吸附效應。
4. 固體表面單一分子層最大吸附容量為單層之飽和吸附效應。
5. 被吸附之分子不會脫附。
6. 每個吸附位址之吸附能均相同。
7. 吸附能是定值。

Langmuir isotherm

$$q=Q_mK_LC_e/(1+K_LC_e)$$

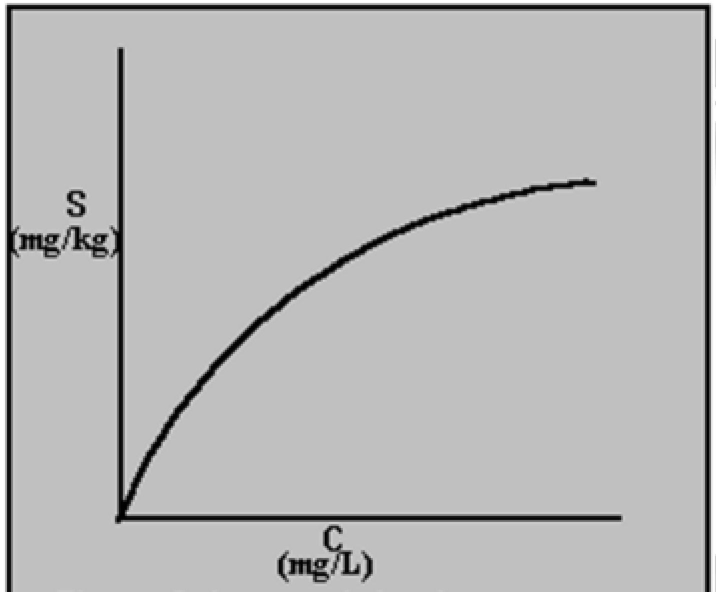


Figure 3: Langmuir Isotherm

2.2. Coefficient of Efficiency E

The coefficient of efficiency E has been widely used to evaluate the performance of hydrologic models [e.g., *Leavesley et al.*, 1983; *Wilcox et al.*, 1990]. *Nash and Sutcliffe* [1970] defined the coefficient of efficiency which ranges from minus infinity to 1.0, with higher values indicating better agreement, as

$$E = 1.0 - \frac{\sum_{i=1}^{N} (O_i - P_i)^2}{\sum_{i=1}^{N} (O_i - \bar{O})^2}. \tag{2}$$

Physically, E is the ratio of the mean square error,

$$\mathrm{MSE} = N^{-1} \sum_{i=1}^{N} (O_i - P_i)^2,$$

to the variance in the observed data, subtracted from unity. For example, if the square of the differences between the model simulations and the observations is as large as the variability in the observed data, then $E = 0.0$, and if it exceeds it, then $E < 0.0$ (i.e., the observed mean is a better predictor than P_i). Thus a value of zero for the coefficient of efficiency indicates that the observed mean $\bar{O}$ is as good a predictor as the model, while negative values indicate that the observed mean is a better predictor than the model [*Wilcox et al.*, 1990].

The coefficient of efficiency represents an improvement over the coefficient of determination for model evaluation purposes in that it is sensitive to differences in the observed and model-simulated means and variances; that is, if $P_i = (AO_i + B)$, then E decreases as A and B vary from 1.0 and 0.0, respectively. Because of the squared differences, however, E is overly sensitive to extreme values, as is R^2.

Abstract

Background

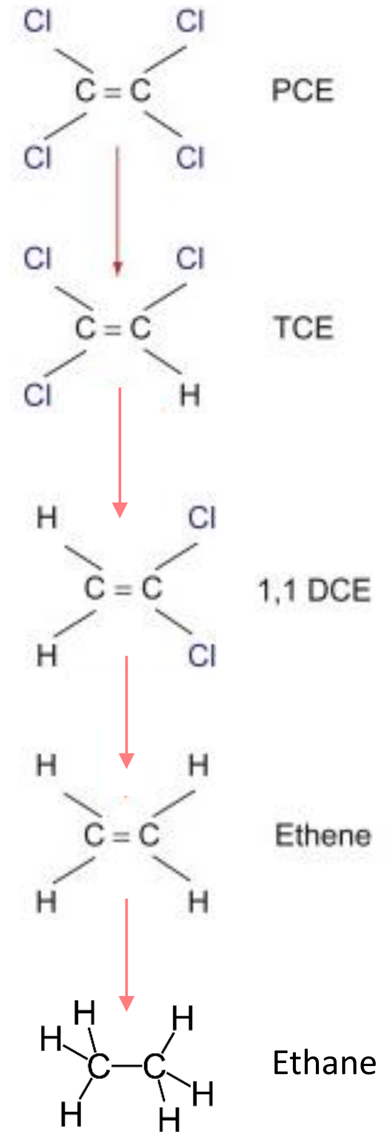
- Permeable reactive barrier (PRB) as a typical in-situ remediation technology is successful at many sites, which are contaminated by organic chemicals .
- PCE can be dechlorinated by FeMB, and the degradation pathway is: PCE → TCE → 1, 1-DCE →ethylene → ethane

Purpose

- Use FeMB as multi-PRB's reactive media, and develop a modified MODFLOW/MT3DMS that can simulate a 3-dimensional aquifer contaminated by PCE and its daughters.
  - Adsorption and degradation parameters were estimated by means of genetic algorithm.

Results

- FeMB is potential for PCE-contaminated groundwater. Multi-PRB is a preferred option for secondly pollution caused by application of one-stage PRB.
- Losses of reactivity and permeability have a significant effect on remediation's success.



FeMB =
zero-valent iron
+ anaerobic microbial communities