Analytical model of three-dimensional multiple contaminant transport with complex reaction pathways subject to time-dependent source boundary conditions

Zhong-Yi Liao[1], Jui-Sheng Chen[1,2]

[1]Graduate Institute of Applied Geology, National Central University

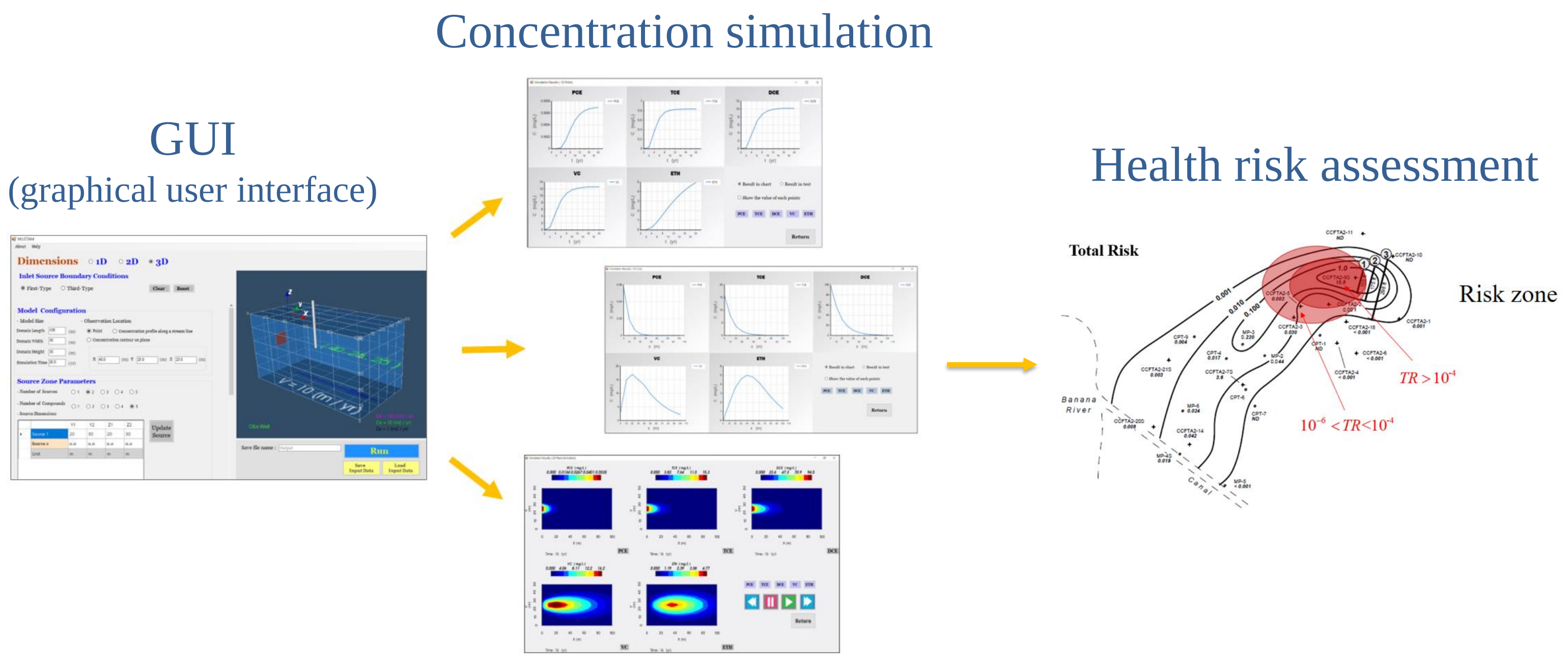
[2]Center for Advanced Model Research Development and Applications, National Central University

Introduction

Groundwater contamination is an important issue of global concern. Chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE) have been frequently found as contaminants in groundwater and can produce stepwise degradation compounds, which can be more toxic and mobile. Thus, it is essential to understand the transport processes that affect the contaminant migration in subsurface.

Motivation

- Mathematical models based on advection-dispersion equations (ADEs) are widely used for understanding plume migration in the subsurface.
- A study of 45 chlorinated solvent sites found that mathematical models were used at 60% of these sites (McGuire et al., 2004) .
- The most popular models for coupled multispecies transport is BIOCHLOR (Aziz et al., 2000), however, it only valid for that each contaminant must have the same retardation factor value.
- Recently, Liao et al. (2021) developed exact three dimensional analytical solutions to multi-species transport involving distinct retardation factors.



Concentration simulation

GUI
(graphical user interface)

Health risk assessment

Fig. 1. Development of graphical user interface for three dimensional analytical model.

- Most of multispecies transport analytical models are limited to considering a straight reaction network and a constant source concentration.
- However, the realistic transport behavior of contaminants may involve both divergent and convergent reactions.

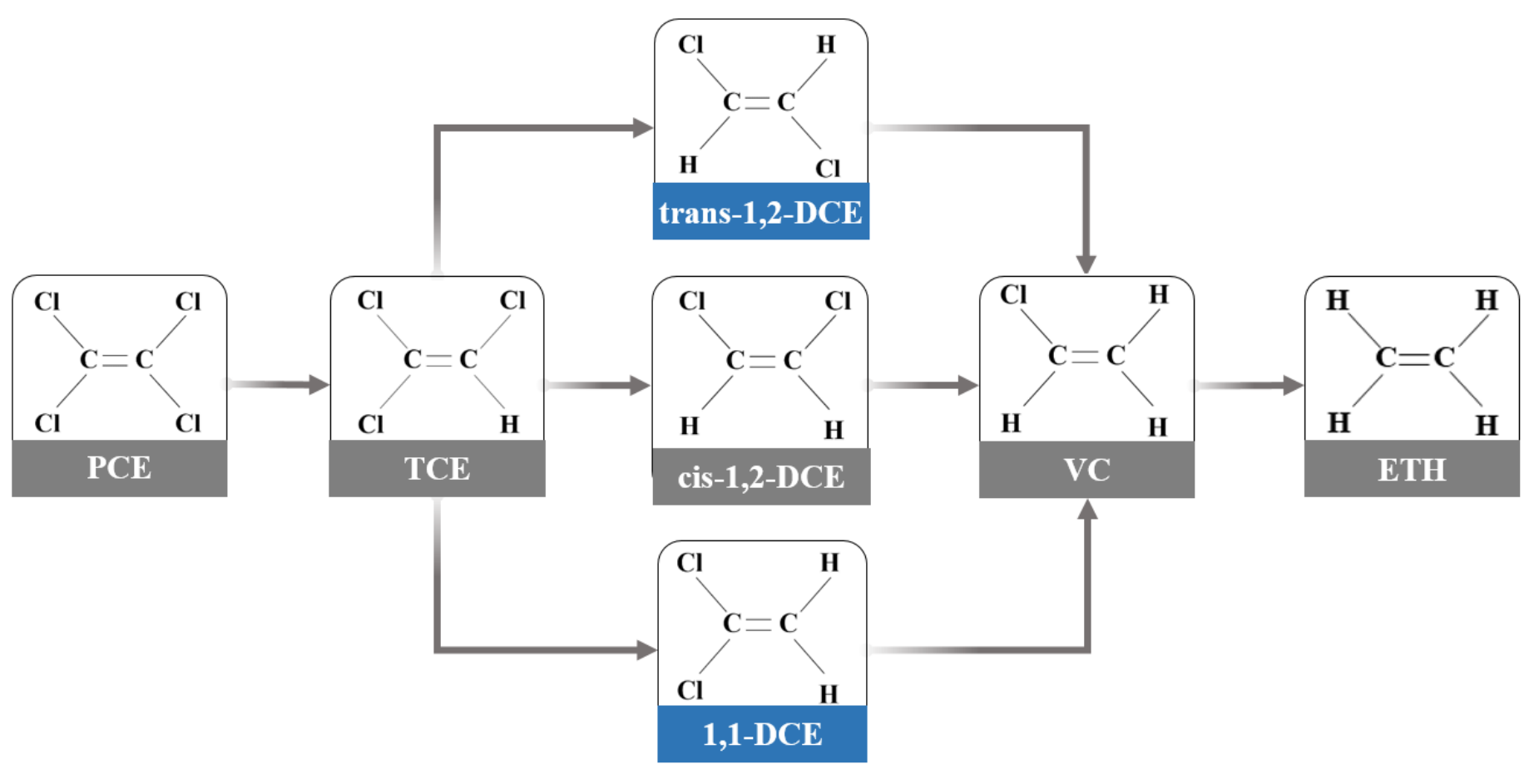


Fig. 2. Complex degradation pathway of PCE.

Objective

To develop analytical model for three-dimensional reactive transport incorporating the process of complex reaction pathways and time-varying source functions.

Mathematical model

- Governing equations and boundary conditions :

$$D_x \frac{\partial^2 C_{ij}\left(x,y,z,t\right)}{\partial x^2}+D_y \frac{\partial^2 C_{ij}\left(x,y,z,t\right)}{\partial y^2}+D_z \frac{\partial^2 C_{ij}\left(x,y,z,t\right)}{\partial z^2}-v\frac{\partial C_{ij}\left(x,y,z,t\right)}{\partial x}$$

$$-\mu_{ij}R_{ij}C_{ij}\left(x,y,z,t\right)+\sum_{k_{i-1}=1}^{n_{i-1}} f_{(i-1)k_{i-1}\to ij}\, g_{i-1\to i}\,\mu_{(i-1)k_{i-1}}R_{(i-1)k_{i-1}}C_{(i-1)k_{i-1}}\left(x,y,z,t\right)=R_{ij}\frac{\partial C_{ij}\left(x,y,z,t\right)}{\partial t},$$

$$g_{0\to 1}=0 \qquad i=1,2,\ldots,5 \quad j=1,2,\ldots,N$$

$$C_{ij}\left(x,y,z,t=0\right)=0$$

$$C_{ij}\left(x=0,y,z,t\right)= f_{ij,0}\left(t\right)$$

$$-D_x\frac{\partial C_{ij}\left(x=0,y,z,t\right)}{\partial x}+vC_{ij}\left(x=0,y,z,t\right)=vf_{ij,0}\left(t\right)$$

$$C_{ij}\left(x\to\infty,y,z,t\right)=0$$

$$\frac{\partial C_{ij}\left(x,y=0,z,t\right)}{\partial y}=0,\quad \frac{\partial C_{ij}\left(x,y=W,z,t\right)}{\partial y}=0$$

$$\frac{\partial C_{ij}\left(x,y,z=0,t\right)}{\partial z}=0,\quad \frac{\partial C_{ij}\left(x,y,z=H,t\right)}{\partial z}=0$$

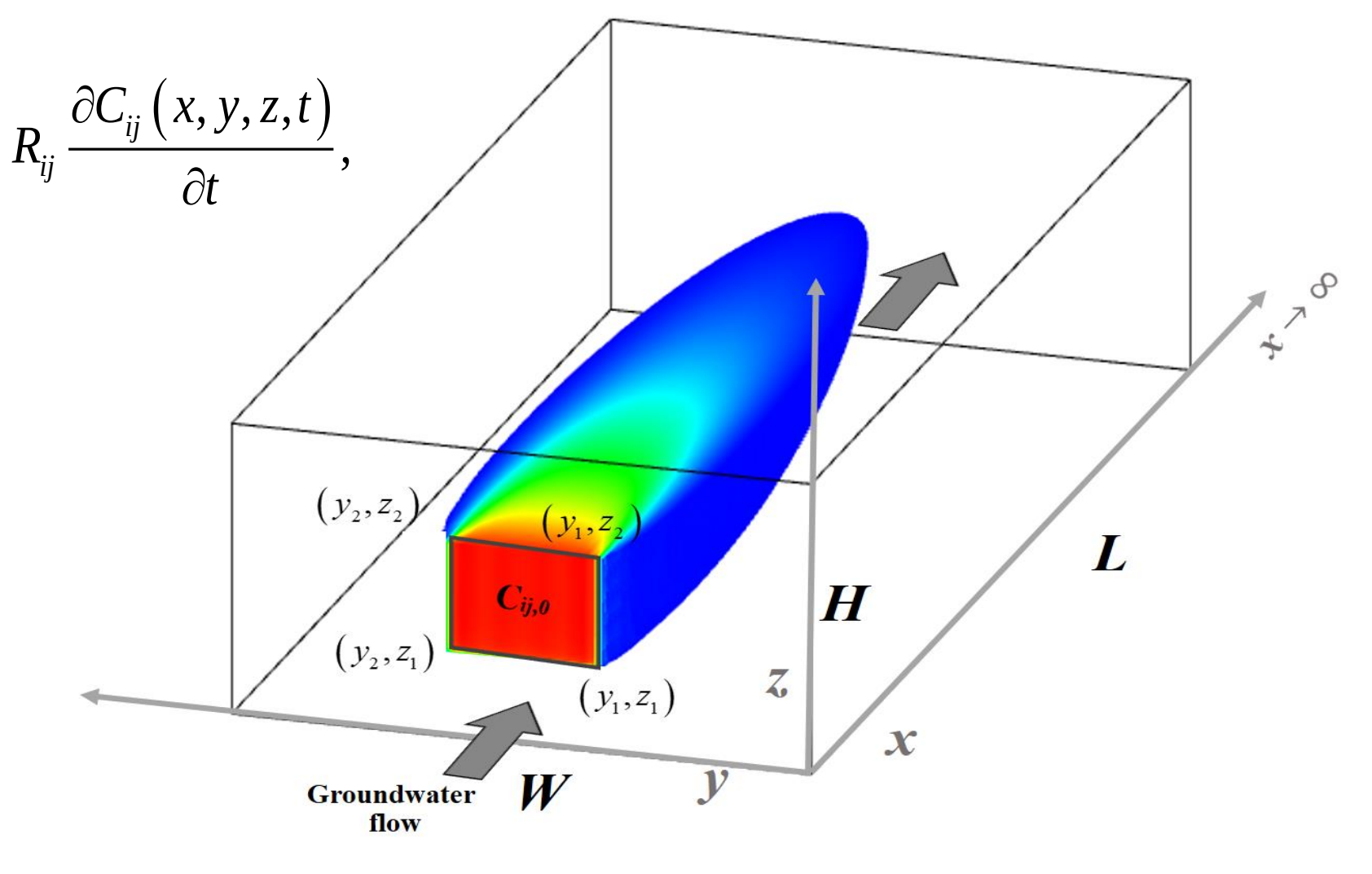


Fig. 3. Schematic view of the three-dimensional multispecies plume migration in a groundwater system.

Results and discussion

- A chlorinated solvent example

$v=0.4m/\text{day}$

$D_x=0.4m^2/day$

$D_y=0.04m^2/\text{day}$

$D_z=0.04m^2/day$

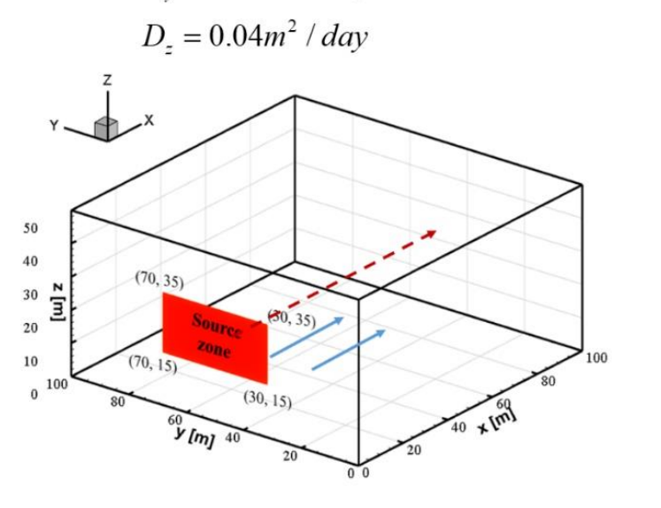
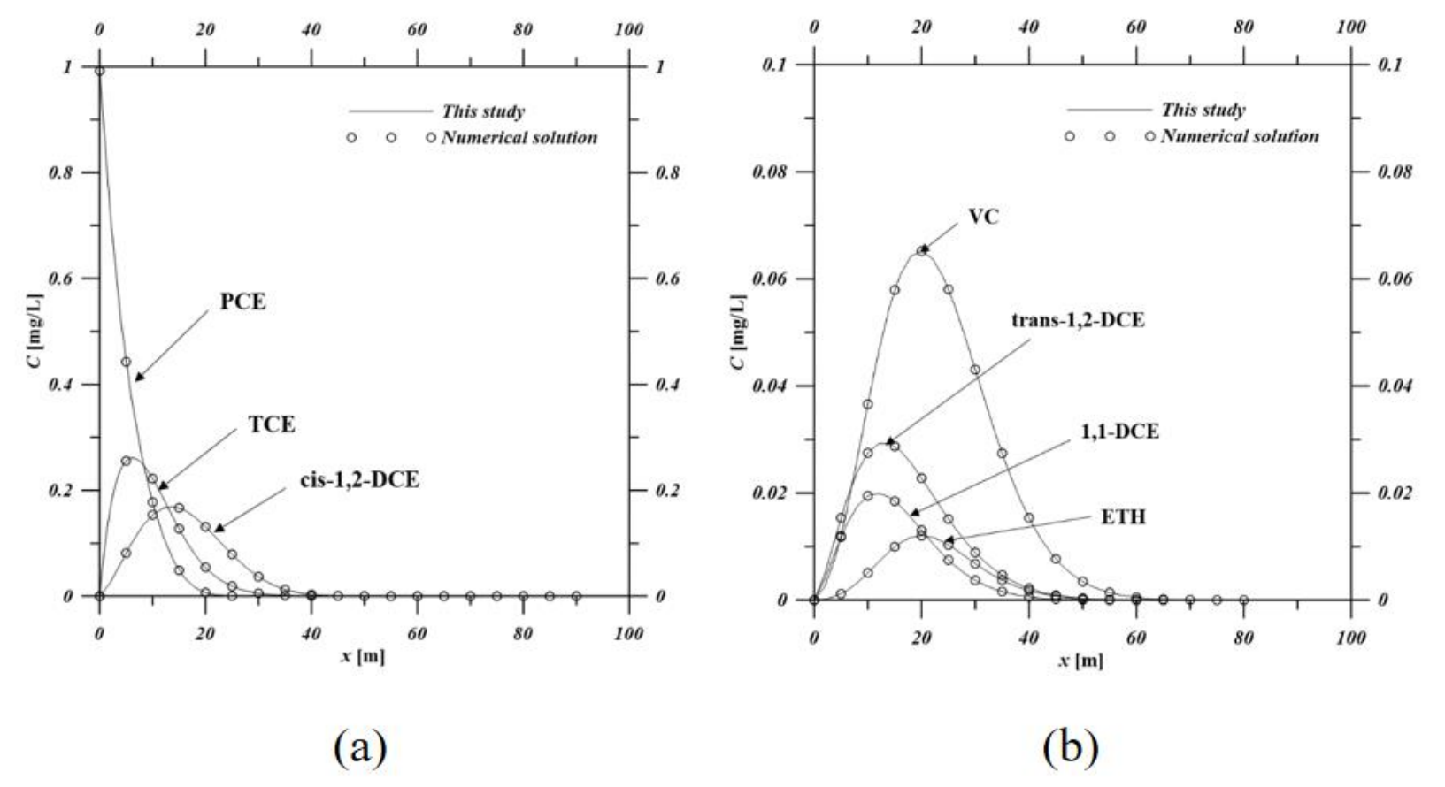


Fig. 4. Schematic diagram of the scenario.

Table 1. Reaction parameters.

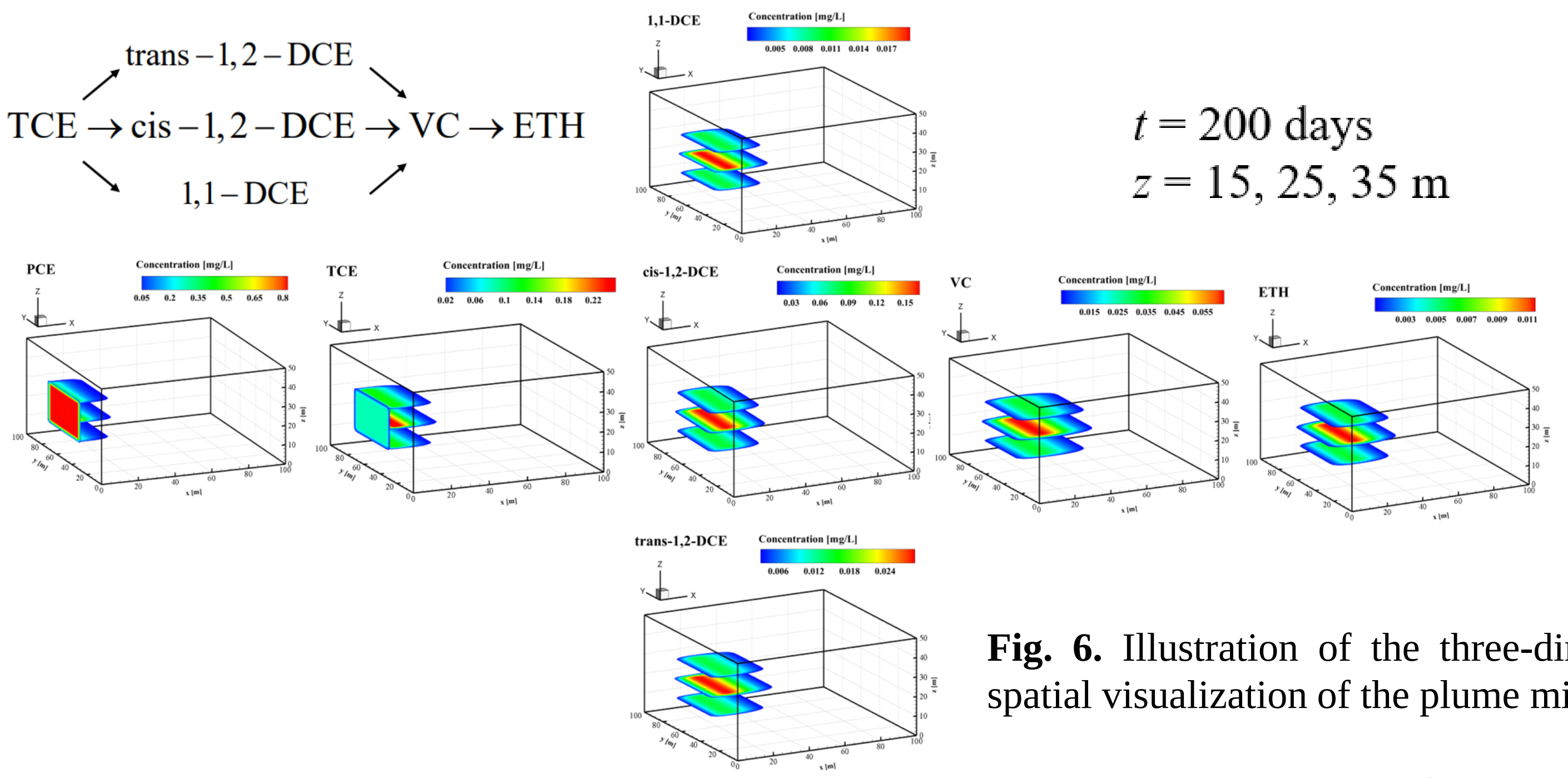
Parameter	Value
Degradation reaction rate constant [day^{-1}]	
PCE	0.075
TCE	0.070
cis-1,2-DCE	0.020
trans-1,2-DCE	0.035
1,1-DCE	0.055
VC	0.030
ETH	0.000001
Retardation factor [-]	
PCE	7.13
TCE	2.87
cis-1,2-DCE	2.80
trans-1,2-DCE	1.76
1,1-DCE	1.85
VC	1.43
ETH	5.35
Yield coefficient PCE→TCE	0.79
Yield coefficient TCE→DCE	0.74
Yield coefficient DCE→VC	0.64
Yield coefficient VC→ETH	0.45



(a) (b)

Fig. 5. Comparisons of the spatial concentration profiles of seven species at t = 200 days obtained from the derived analytical solutions and numerical solution.

$$\begin{tikzcd}[column sep=small] & & \text{trans}-1,2-\text{DCE} \arrow[dr] & & \\ \text{PCE} \arrow[r] & \text{TCE} \arrow[ur] \arrow[r] \arrow[dr] & \text{cis}-1,2-\text{DCE} \arrow[r] & \text{VC} \arrow[r] & \text{ETH} \\ & & 1,1-\text{DCE} \arrow[ur] & & \end{tikzcd}$$



t = 200 days

z = 15, 25, 35 m

Fig. 6. Illustration of the three-dimensional spatial visualization of the plume migration.

- Branching vs. straight chain reaction

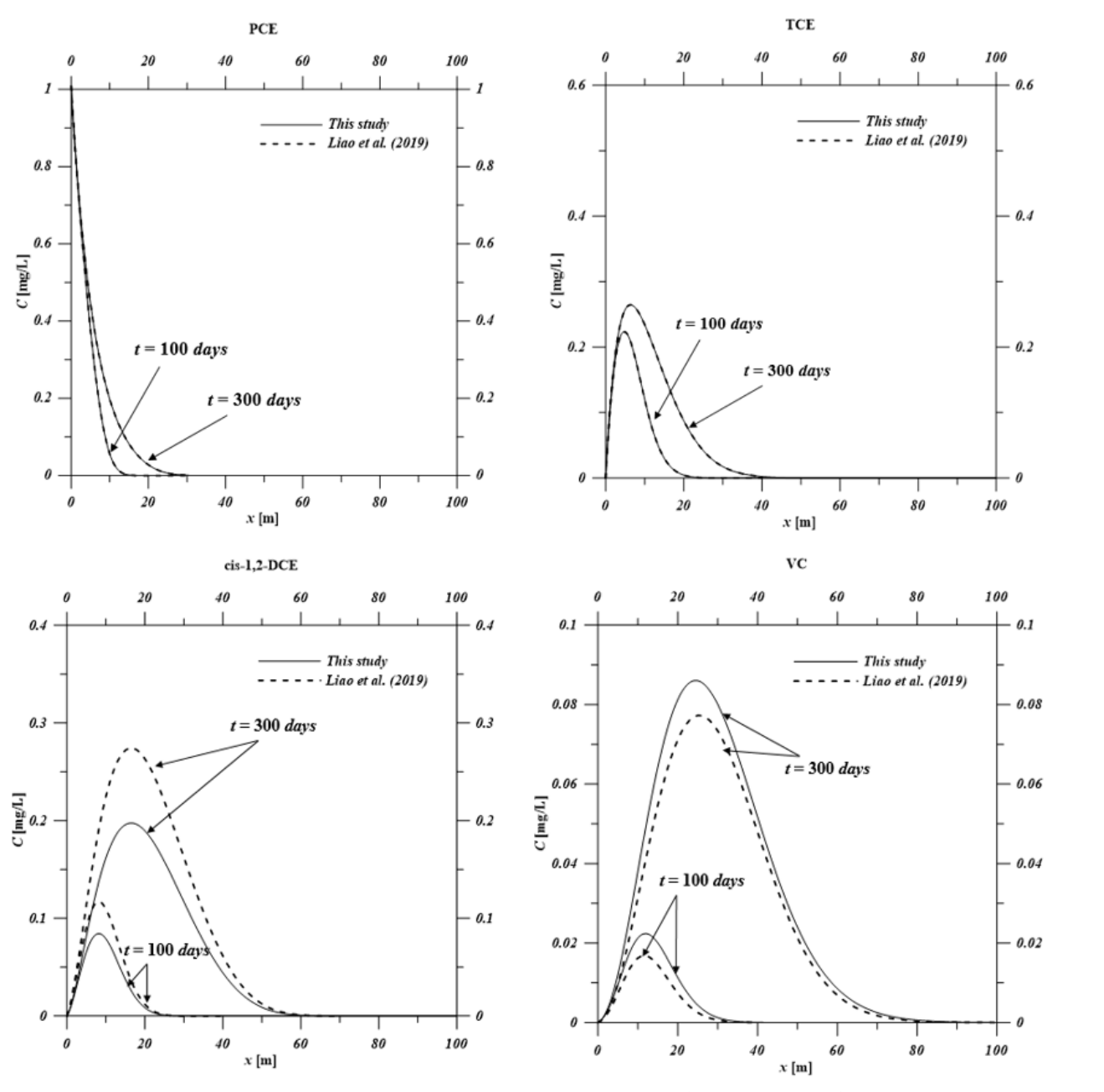
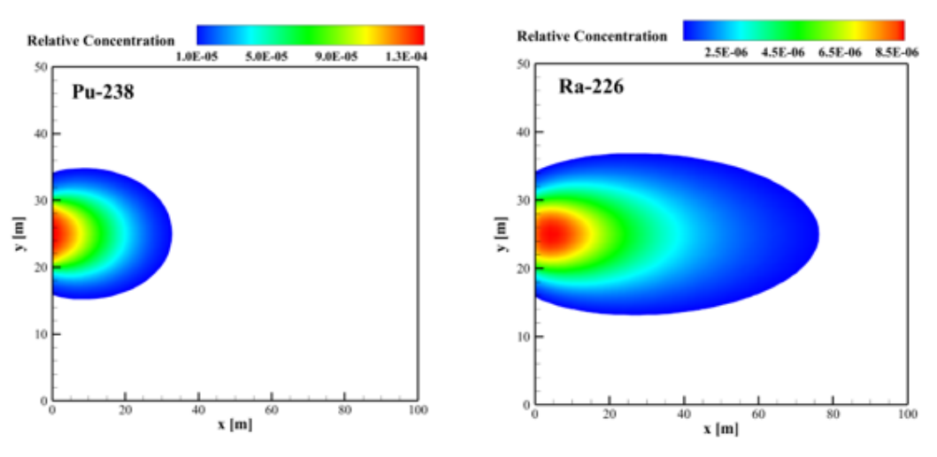


Fig. 7. Spatial concentration profiles of contaminants along x direction obtained from the derived analytical solutions and the analytical solutions with a straight chain reaction network.

- Time-dependent source functions

Exponentially decaying function $f_{ij}\left(t\right)=C_{ij}e^{-\lambda_{ij}t}$ t = 1000 years



Variable concentration $f_{ij}\left(t_k\right)=C_{ij,t1},C_{ij,t2}\cdots$

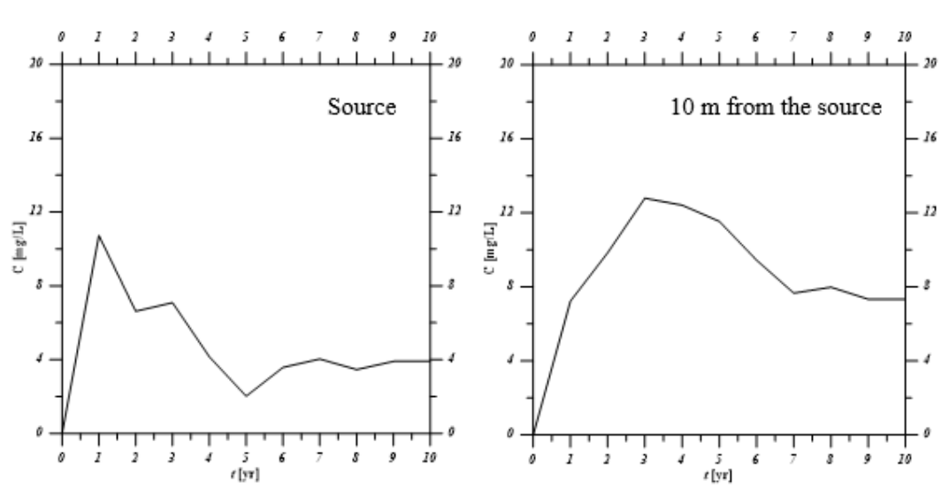


Fig. 8. The plume migration and breakthrough curve of contaminants obtained from the derived analytical solutions subject to time-dependent source concentration.

Conclusions

This study presents exact analytical solutions to three-dimensional contaminants transport with complex reaction pathway which can provide more realistic for simulating the transport of the contaminants and its degradation-related byproducts. The time-dependent source functions have more practical applicability for matching historical concentration at contaminated sites remediation work. In the future, we will design a friendly graphical user interface (GUI) coupled with the transport and risk assessment models which can greatly enhance the added value of the model and become a popular modeling software.