



TCE and PCE plume persistence based on different clay types

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STUDY RATIONALE

Diffusion of dense non-aqueous phase liquid (DNAPL) has been recognized as an important process of contaminant transport in a single aquifer-aquitard system. Forward diffusion is a mass storage process from the aquifer to the aquitard (Fig. 1a). While, back diffusion indicates a mass release process from the aquitard to the aquifer due to the reversal of the concentration gradient between the aquifer and aquitard (Fig. 1b). Back diffusion from the aquitard can cause long-term plume persistence with a long remediate period, likely many decades. Thus, aquitards contaminated with DNAPL paly a significant role in groundwater quality due to DNAPL release from aquitards. This study was performed to understand DNAPL persistence by the back diffusion from the three types of clay using one-dimensional analytical solutions.

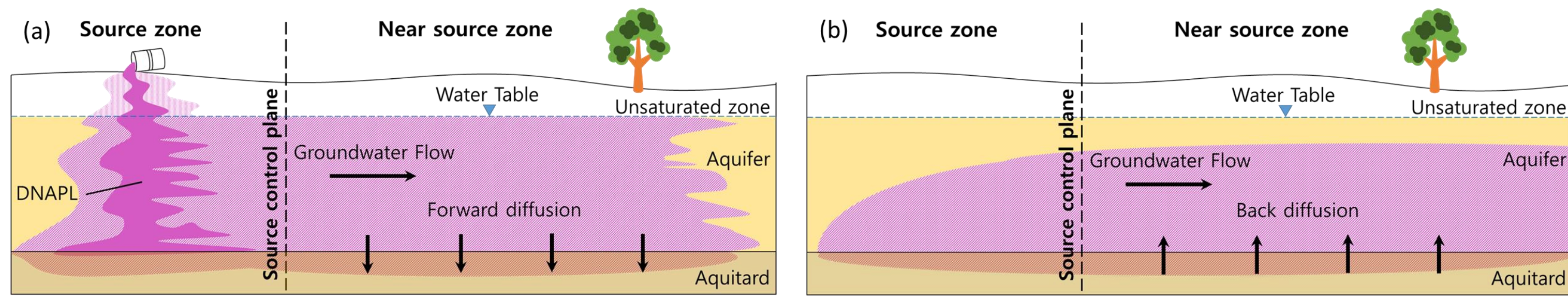


Fig. 1. Conceptual illustration of DNAPL source and near-source zones. (a) Forward and (b) back diffusion occurs for negative and positive concentration gradients between the aquifer and aquitard.

OBJECTIVE

The aims of this study are to...

1. Provide 1D analytical solutions for aquitard concentration profiles and BTC
2. Estimate the total accumulated mass on the clay types
3. Predict DNAPL tailings due to the back diffusion based on different clay types of the aquitard

SCENARIO

A conceptual model was designed with 5 m thickness of an aquifer underlain by 0.7 m thickness of an aquitard (Fig. 2). The aquitard was considered to be a finite domain boundary at the bottom of bentonite (B), kaolinite (K), and montmorillonite (M) layers. The tortuosity of each clay was assumed to be 0.95 (B), 0.55 (K), and 0.05 (M). A diffusion model scenario assumed a step change in concentration boundary condition representing complete removal of trichloroethylene (TCE) and tetrachloroethylene (PCE), after 10 years of source loading (Fig. 3).

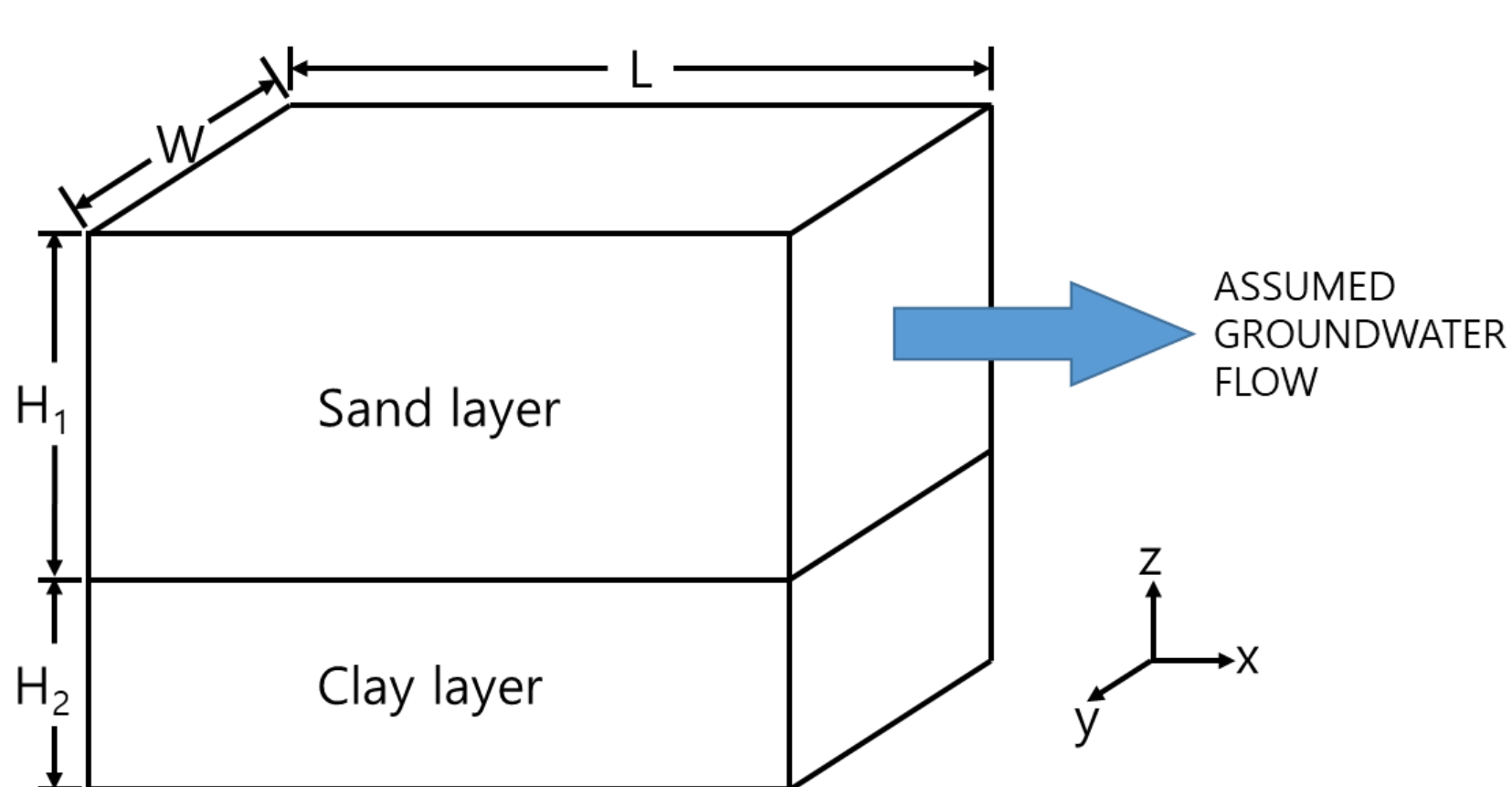


Fig. 2. Schematic configuration of the single aquifer-aquitard system; $L = 15$ m, $W = 10$ m, $H_1 = 5$ m, and $H_2 = 0.7$ m.

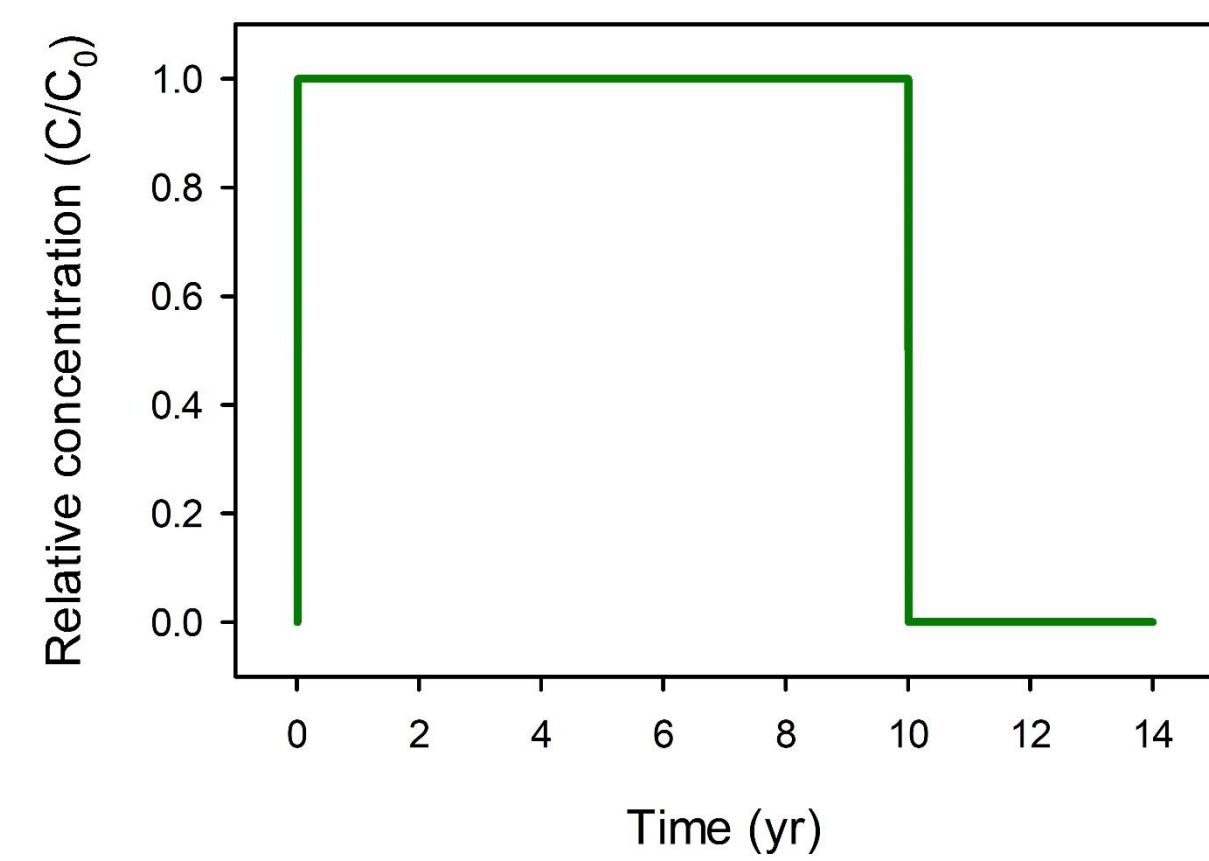


Fig. 3. Aquifer concentrations at the source control plane. The scenario is assumed to be the clean aquifer due to complete remediation process after DNAPL loading in the aquifer for 10 years.

MODELING APPROACH

Concentration profiles (C/C_0)

In order to simulate the concentration profiles in the aquitard, a analytical solution can be expressed by Fick's second law of diffusion:

$$\frac{\partial \eta C}{\partial t} = \eta D^* \frac{\partial^2 C}{\partial z^2} \quad (1)$$

where η [dimensionless] is the porosity of the aquitard, C [M/L³] is the concentration in the aquitard, t [T] is the period during the DNAPL diffusion, z [L] is the vertical distance into the aquitard, and D^* [L²/T] is the effective diffusion coefficient, defined in this study as

$$D^* = \frac{D\tau}{R} = \frac{D\tau}{1 + \frac{\rho_b K_d}{\eta}} \quad (2)$$

where D [L²/T] is the molecular diffusion coefficient, τ [dimensionless] is the matrix tortuosity, R [dimensionless] is the retardation factor, ρ_b [M/L³] is bulk density, and K_d [L³/M] is distribution coefficient.

Forward diffusion - C/C_0 of aquitard

Eq. (1) with a boundary conditions of $C(z = l, t > 0) = C_0$ and an initial conditions of $C(0 < z < l, t = 0) = 0$ is obtained from Carslaw and Jaeger (1959) and modified to simulate aquitard concentration profiles during forward diffusion:

$$\frac{C(z, t)}{C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{\zeta t} \cos \theta \quad (3)$$

where $\zeta = -D^*(2n+1)^2\pi^2/4l^2$, $\theta = (2n+1)\pi z/2l$, C_0 [M/L³] is the constant concentration, and l [L] is the aquitard thickness.

Back diffusion - C/C_0 of aquitard

In case of the complete removal of DNAPL from the source zone, DNAPL transfers from the aquitard to aquifer, and the analytical solution is expressed as:

$$\frac{C(z, t)}{C_0} = \frac{-4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \theta \left(e^{\zeta t} - e^{\zeta(t-T)} \right) \text{ for } t > T \quad (4)$$

where T [T] is the loading period during the forward diffusion.

Diffusive flux

The diffusive flux that moves the aquitard inside can be expressed by Fick's first low:

$$j = -\eta D^* \frac{\partial C}{\partial z} \quad (5)$$

where j [M/L²/T] is the solute diffusive flux between the aquifer and aquitard.

Forward and back diffusion - flux

In order to simulate the diffusive flux in the aquitard, a analytical solutions can be expressed by substituting Eq. (3) and Eq. (4) into Eq. (5).

$$j_F(z, t) = \frac{-2C_0\eta D^*}{l} \sum_{n=0}^{\infty} -(-1)^n e^{\zeta t} \sin \theta \quad (6)$$

$$j_B(z, t) = \frac{2C_0\eta D^*}{l} \sum_{n=0}^{\infty} [(-1)^n \sin \theta (e^{\zeta t} - e^{\zeta(t-T)})] \text{ for } t > T \quad (7)$$

where j_F [M/L²/T] is the forward diffusion flux, and j_B [M/L²/T] is the back diffusion flux. When $z = l$, the diffusive flux at the interface between the aquifer and aquitard can be calculated.

Total accumulated mass - forward

The total accumulated mass of DNAPL into the aquitard during the forward diffusion is defined by integrating Eq. (6) over t .

$$m_F(z, t) = \varepsilon - \frac{2C_0\eta D^*}{l} \sum_{n=0}^{\infty} \frac{(-1)^n e^{\zeta t} \sin \theta}{\zeta} \quad (8)$$

where m_F [M/L²] is the total accumulated mass and ε is the integral constant. Similar to flux, when $m_F(z = l, t = 0) = 0$, ε and m_F at the interface between the aquifer and aquitard can be calculated.

Breakthrough curve (BTC)

The analytical solution for estimating the DNAPL persistence of aquifer due to back diffusion is expressed as

$$C_e = \frac{j_B A_i}{q A_c} \quad (9)$$

where C_e [M/L³] is the effluent concentration, A_i [L²] is the interfacial area between the aquifer and aquitard, A_c [L²] is the cross-sectional area of the aquifer, and q [L/T] is the Darcy flux of the aquifer.

MODELING APPLICATION TO FIELD STUDIES

The input parameters for DNAPL diffusion in the aquitard are summarized in Table 1. The molecular diffusion coefficients, porosity, and retardation factor were acquired from previous studies (Chapman and Parker, 2005; Fetter et al., 2018).

Table 1 Model input parameters

Parameters	TCE	PCE	Units
Molecular diffusion coefficient, D	7.17×10^{-5}	6.48×10^{-5}	m ² /d
Retardation factor, R	1.2	1.7	-
Solubility, C_0	1100	200	mg/L
Aquitard porosity, η	0.6	0.6	-
Source duration, T	10	10	years
Darcy flux of aquifer, q	2.07	2.07	m/d
Tortuosity of bentonite, τ_B	0.95	0.95	-
Tortuosity of kaolinite, τ_K	0.55	0.55	-
Tortuosity of montmorillonite, τ_M	0.05	0.05	-

RESULTS AND DISCUSSION

Concentration profiles

The relative concentration of TCE and PCE in aquitard is shown in Fig. 4 at two steps (10 and 11 years). The TCE and PCE during forward diffusion (10 years) moved into the aquitard. After the complete removal of TCE and PCE, the instantaneous concentration change in the aquifer at 10 years reversed the concentration gradient, which triggered TCE and PCE back diffusion from the aquitard to the aquifer. The back diffusion in TCE and PCE profiles showed characteristic shapes of zero concentration at the aquifer-aquitard interface, increasing with depth in the aquitard to a peak and then decreasing again with depth. Also, the discrepancy of concentration profiles on the clay types is due to different tortuosity, which contributed to behavior passing the aquitard.

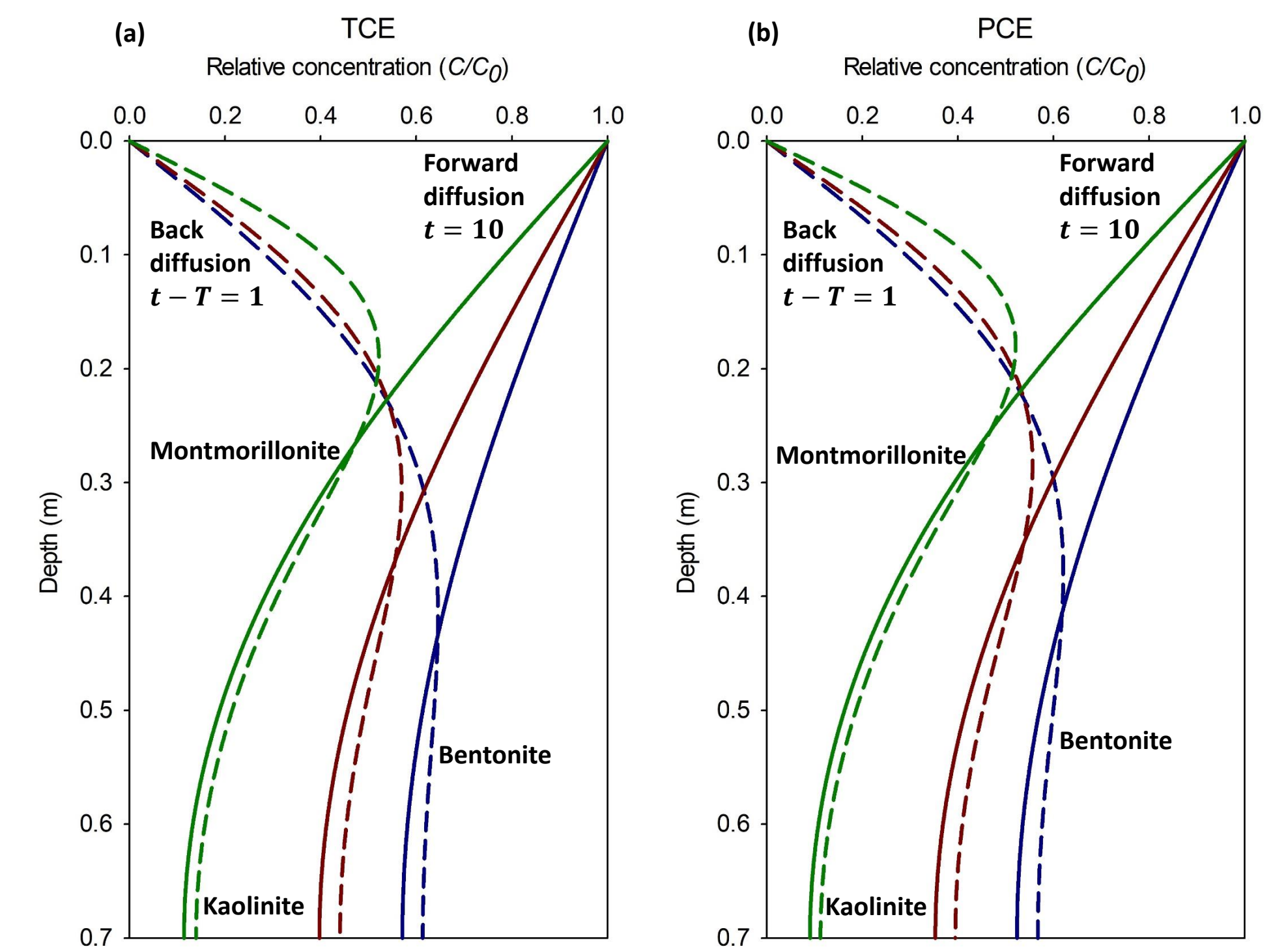


Fig. 4. Simulations with forward (solid line) and back (dashed line) diffusion of TCE (a) and PCE (b). Aquitard concentration profiles at bentonite (blue), kaolinite (red), and montmorillonite (green) using Eq. (3) and (4).

Total accumulated mass

The total accumulated mass in the aquitard during the forward diffusion showed that PCE was 57.3 (B), 44.3 (K), 13.3 (M) g/m², and TCE was 329.2 (B), 256.2 (K), 76.8 (m) g/m². The order of total accumulated mass coincides with the order of tortuosity on the clay, both TCE and PCE ($\tau_B > \tau_K > \tau_M$).

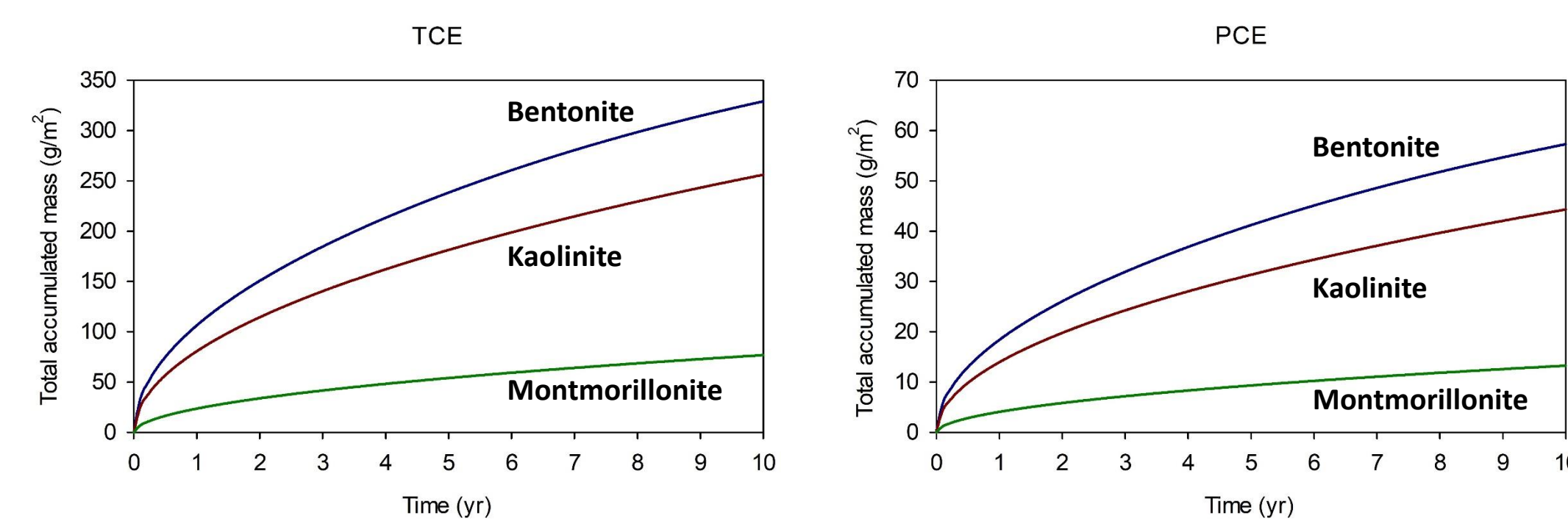


Fig. 5. Total accumulated mass at the interface ($z = l$ m) for TCE (left) and PCE (right) during forward diffusion.

Breakthrough curve (BTC)

The calculated tailing concentration of TCE and PCE at the aquifer during the back diffusion maintained higher concentrations than the maximum contaminant level (MCL, TCE and PCE = 5 µg/L for 38 (B), 43 (K), 19 (M) and 22 (B), 16 (K), 11 (M) years, respectively. When compared to BTC and tortuosity, the order of TCE differed only.

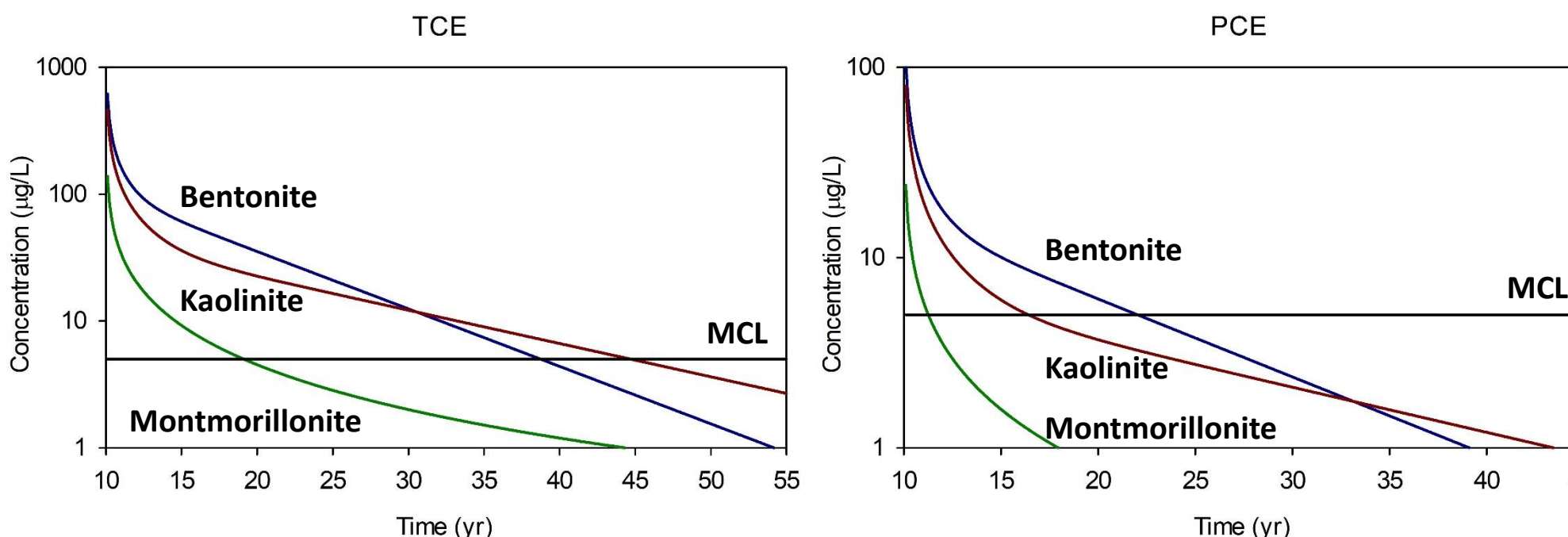


Fig. 6. Breakthrough curve for TCE (left) and PCE (right) during the back diffusion from the aquitard.