New Model of Reactive Transport in Single-well Push-Pull Test with Aquitard Effect

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Supplementary Materials

S1. Derivation of analytical solutions for the SWPP test

To reduce the complexity in analyzing the influence of input parameters on the output, the dimensionless parameters are introduced as follows: $C_{mD} = \frac{c_m}{c_0}$, $C_{imD} = \frac{c_{im}}{c_0}$, $C_{inj,mD} = \frac{c_{inj,m}}{c_0}$, $C_{inj,imD} = \frac{c_{inj,im}}{c_0}$, $C_{cha,mD} = \frac{c_{cha,m}}{c_0}$, $C_{cha,imD} = \frac{c_{cha,im}}{c_0}$, $C_{res,mD} = \frac{c_{res,m}}{c_0}$, $C_{res,imD} = \frac{c_{res,im}}{c_0}$, $C_{ex,mD} = \frac{c_{ex,m}}{c_0}$, $C_{ext,imD} = \frac{c_{ext,im}}{c_0}$, $C_{umD} = \frac{c_{um}}{c_0}$, $C_{uimD} = \frac{c_{uim}}{c_0}$, $C_{limD} = \frac{c_{lim}}{c_0}$, $C_{limD} = \frac{c_{lim}}{c_0}$, $t_D = \frac{|A|}{\alpha_r^2 R_m} t$, $r_D = \frac{r}{\alpha_r}$, $r_{WD} = \frac{r_w}{\alpha_r}$, $z_D = \frac{z}{B}$, $\mu_{md} = \frac{\alpha_r^2 \mu_m}{A}$, $\mu_{imD} = \frac{\alpha_r^2 \mu_{im}}{R_{im} A}$, $\mu_{umD} = \frac{\alpha_r^2 \mu_{um}}{A}$, $\mu_{limD} = \frac{\alpha_r^2 \mu_{lim}}{R_{im} A}$, where the subscript “D” represents the dimensionless parameter hereinafter, $A = \frac{Q}{4\pi B \theta_m}$. By substituting these dimensionless parameters into the governing equations, one could obtain the dimensionless model of the SWPP test:

$$\frac{\partial C_{mD}}{\partial t_D} = \frac{1}{r_D} \frac{\partial^2 C_{mD}}{\partial r_D^2} - \frac{1}{r_D} \frac{\partial C_{mD}}{\partial r_D} - \epsilon_m (C_{mD} - C_{imD}) - \mu_{mD} C_{mD} - \left(\frac{\theta_{um} \alpha_r^2 \nu_{um}}{2A\theta_m B} C_{umD} - \frac{\partial u m_{D} \partial C_{umD}}{2A\theta_m B^2} \right) \bigg|_{z_D=1}, r_D \geq r_{WD}, \quad (S1a)$$

$$\frac{\partial C_{imD}}{\partial t_D} = \frac{\partial C_{imD}}{\partial t_D} = \epsilon_{im} (C_{mD} - C_{imD}) - \mu_{imD} C_{imD}, r_D \geq r_{WD}, \quad (S1b)$$

$$\frac{\partial C_{umD}}{\partial t_D} = R_m \alpha_r^2 D_u \frac{\partial^2 C_{umD}}{\partial z_D^2} - R_m \nu_{um} \alpha_r^2 \frac{\partial C_{umD}}{\partial z_D} - \epsilon_{um} (C_{umD} - C_{uimD}) - \mu_{umD} C_{umD}, \quad (S2a)$$

$$\frac{\partial C_{uimD}}{\partial t_D} = \epsilon_{uim} (C_{umD} - C_{uimD}) - \mu_{uimD} C_{uimD}, z_D \geq 1, \quad (S2b)$$

$$\frac{\partial C_{limD}}{\partial t_D} = \frac{R_m \alpha_r^2 D_l}{AB^2 R_{im}} \frac{\partial^2 C_{limD}}{\partial z_D^2} + \frac{R_m \nu_{lim} \alpha_r^2}{AB R_{im}} \frac{\partial C_{limD}}{\partial z_D} - \epsilon_{im} (C_{limD} - C_{limD}) - \mu_{limD} C_{limD}, \quad (S3a)$$

$$z_D \leq -1,$$
The analytical solution will be derived using the Laplace transform method and the Green’s functions method, and the detailed information could be seen in the following sections.

S1.1 Solutions in the injection phase: Eqs. (25a) and (25f)

Substituting the dimensionless parameters into Eqs. (5) - (6), one could obtain the dimensionless boundary conditions and dimensionless initial conditions for the injection phase:

\[ C_{mD}(r_D, t_D)|_{t_D=0} = C_{imD}(r_D, t_D)|_{t_D=0} = C_{umD}(r_D, z_D, t_D)|_{t_D=0} = C_{лимD}(r_D, z_D, t_D)|_{t_D=0} = 0, \]  

\[ C_{mD}(r_D, z_D, t_D)|_{r_D \to \infty} = C_{имD}(r_D, z_D, t_D)|_{r_D \to \infty} = C_{umD}(r_D, z_D, t_D)|_{z_D \to \infty} = 0, \]  

\[ C_{uимD}(r_D, z_D, t_D)|_{z_D \to \infty} = C_{лимD}(r_D, z_D, t_D)|_{z_D \to \infty} = 0, \]  

\[ C_{mD}(r_D, t_D) = C_{umD}(r_D, z_D = 1, t_D), \]  

\[ C_{mD}(r_D, t_D) = C_{имD}(r_D, z_D = -1, t_D). \]

Conducting Laplace transform to Eqs. (S2a) - (S2b), one has:

\[ s\tilde{C}_{имD} = \frac{R_m\alpha^2 u_D}{AB^2 R_{um}} \frac{\partial^2 \tilde{C}_{имD}}{\partial z_D^2} - \frac{R_m\nu_{um}\alpha^2 D}{ABR_{um}} \frac{\partial \tilde{C}_{имD}}{\partial z_D} - (\varepsilon_{um} + \mu_{umD}) \tilde{C}_{имD} + \varepsilon_{um} \tilde{C}_{uимD}, \]

\[ z_D \geq 1, \]  

\[ s\tilde{C}_{uимD} = \varepsilon_{uимD}(\tilde{C}_{имD} - \tilde{C}_{uимD}) - \mu_{uимD} \tilde{C}_{имD}, z_D \geq 1, \]  

Substituting Eq. (S7b) into Eq. (S7a) will lead to:

\[ s\tilde{C}_{имD} = \frac{R_m\alpha^2 u_D}{AB^2 R_{um}} \frac{\partial^2 \tilde{C}_{имD}}{\partial z_D^2} - \frac{R_m\nu_{um}\alpha^2 D}{ABR_{um}} \frac{\partial \tilde{C}_{имD}}{\partial z_D} - (\varepsilon_{um} + \mu_{umD}) - \frac{\varepsilon_{um}\varepsilon_{uимD}}{s + \mu_{uимD} + \varepsilon_{uимD}} \tilde{C}_{имD}, \]
\[ z_D \geq 1, \quad \text{(S8)} \]

Similarly, Eqs. (S3a) - (S3b) become:

\[ s\tilde{C}_{lmD} = \frac{R_m \alpha_r^2 D_l}{A B^2 R_{lm}} \frac{\partial^2 \tilde{C}_{lmD}}{\partial z_D^2} + \frac{R_m v_m \alpha_f^2}{A B R_{lm}} \frac{\partial \tilde{C}_{lmD}}{\partial z_D} - \left( \varepsilon_{lm} + \mu_{lmD} \right) \tilde{C}_{lmD} + \varepsilon_{lm} \tilde{C}_{lmD}, \]

\[ z_D \leq -1, \quad \text{(S9a)} \]

\[ s\tilde{C}_{lmD} = \varepsilon_{lm} \left( \tilde{C}_{lmD} - \overline{\tilde{C}}_{lmD} \right) - \mu_{lmD} \overline{\tilde{C}}_{lmD}, \quad z_D \leq -1, \quad \text{(S9b)} \]

Substituting Eq. (S9b) into Eq.(S9a) results in:

\[ s\tilde{C}_{lmD} = \frac{R_m \alpha_r^2 D_l}{A B^2 R_{lm}} \frac{\partial^2 C_{lmD}}{\partial z_D^2} + \frac{R_m v_m \alpha_f^2}{A B R_{lm}} \frac{\partial C_{lmD}}{\partial z_D} - \left( \varepsilon_{lm} + \mu_{lmD} - \frac{\varepsilon_{lm} \varepsilon_{lm}}{s + \mu_{lmD} + \varepsilon_{lm}} \right) \overline{C}_{lmD}, \]

\[ z_D \leq -1, \quad \text{(S10)} \]

where overbar represents the variables in Laplace domain hereinafter; \( s \) is the Laplace transform parameter in respect to dimensionless time.

Eqs. (S5), (S6a)-(S6b) and (S8) compose a model of the second-order ordinary differential equation (ODE) with boundary conditions, the general solution of Eq. (S8) is:

\[ \bar{C}_{lmD} = A_1 e^{a_1 z_D} + B_1 e^{a_2 z_D}. \quad \text{(S11a)} \]

Similarly, the general solution of Eq. (S10) is:

\[ \bar{C}_{lmD} = A_2 e^{b_1 z_D} + B_2 e^{b_2 z_D}. \quad \text{(S11b)} \]

where

\[ a_1 = \frac{\sqrt{\left( \frac{R_m v_m \alpha_f^2}{A B R_{lm}} \right)^2 + 4 \left( \frac{R_m \alpha_r^2 D_l}{A B^2 R_{lm}} \right)^2 \left( s + \varepsilon_{lm} + \mu_{lmD} \right) - \frac{\varepsilon_{lm} \varepsilon_{lm}}{s + \mu_{lmD} + \varepsilon_{lm}}}}{2 \frac{R_m \alpha_r^2 D_l}{A B^2 R_{lm}}}, \]

\[ a_2 = \frac{\sqrt{\left( \frac{R_m v_m \alpha_f^2}{A B R_{lm}} \right)^2 + 4 \left( \frac{R_m \alpha_r^2 D_l}{A B^2 R_{lm}} \right)^2 \left( s + \varepsilon_{lm} + \mu_{lmD} \right) - \frac{\varepsilon_{lm} \varepsilon_{lm}}{s + \mu_{lmD} + \varepsilon_{lm}}}}{2 \frac{R_m \alpha_r^2 D_l}{A B^2 R_{lm}}}, \]

\[ b_1 = \frac{\sqrt{\left( \frac{R_m v_m \alpha_f^2}{A B R_{lm}} \right)^2 + 4 \left( \frac{R_m \alpha_r^2 D_l}{A B^2 R_{lm}} \right)^2 \left( s + \varepsilon_{lm} + \mu_{lmD} \right) - \frac{\varepsilon_{lm} \varepsilon_{lm}}{s + \mu_{lmD} + \varepsilon_{lm}}}}{2 \frac{R_m \alpha_r^2 D_l}{A B^2 R_{lm}}}, \]

and
\[ b_2 = \frac{R_m v_{im}\alpha_T^2}{AB\mathcal{R}_m} \sqrt{\frac{R_m v_{im}\alpha_T^2}{AB\mathcal{R}_m} + \frac{4R_m\alpha_T^2D_l}{AB^2\mathcal{R}_m}\left(s + \epsilon_{lim} + \mu_{limD} - \frac{\epsilon_{lim} - \epsilon_{lim}}{s + \mu_{limD} + \epsilon_{lim}}\right)} \]  

Substituting Eqs. (S11a) - (S11b) into Eqs. (S5)-(S6) leads to:

\[ \tilde{c}_{umD} = B_1 e^{a_2 z_D}. \quad (S12a) \]

\[ \tilde{c}_{lmD} = A_2 e^{b_1 z_D}. \quad (S12b) \]

where \( B_1 = \tilde{c}_{mD} \exp(-a_2), B_2 = 0, A_1 = 0 \) and \( A_2 = \tilde{c}_{mD} \exp(b_1) \).

Thus, we could obtain the solutions for the aquitards as:

\[ \tilde{c}_{umD} = \tilde{c}_{mD} \exp(a_2 z_D - a_2). \quad (S13a) \]

\[ \tilde{c}_{uimD} = \frac{e_{um}}{s + \epsilon_{um} + \mu_{umD}} \tilde{c}_{umD}. \quad (S13b) \]

\[ \tilde{c}_{lmD} = \tilde{c}_{mD} \exp(b_1 z_D + b_1). \quad (S14a) \]

\[ \tilde{c}_{limD} = \frac{\epsilon_{lim}}{s + \epsilon_{lim} + \mu_{limD}} \tilde{c}_{lmD}. \quad (S14b) \]

In the injection phase, the dimensional boundary conditions Eq. (8) and Eqs. (12a)-(12b) are transformed into their dimensionless forms:

\[ \left[ C_{mD} \left( \frac{\partial C_{mD}(r_D,t)}{\partial r_D} \right) \right]_{r=r_{wd}} = C_{inj,mD}(t_D), 0 < t_D \leq t_{inj,D} \quad (S15) \]

\[ \beta_{inj} \frac{dC_{inj,mD}(t_D)}{dt_D} = 1 - C_{inj,mD}(t_D), 0 < t_D \leq t_{inj,D} \quad (S16a) \]

\[ C_{inj,mD}(t_D = 0) = 0. \quad (S16b) \]

where \( \beta_{inj} = \frac{v_{inj}r_{wd}}{\xi R_m \alpha_r}. \)

Conducting Laplace transform to Eqs. (S1a) - (S1b), one has:

\[ s \tilde{C}_{mD} = \frac{1}{r_D} \frac{\partial^2 \tilde{C}_{mD}}{\partial r_D^2} - \frac{1}{r_D} \frac{\partial \tilde{C}_{mD}}{\partial r_D} - (\epsilon_m + \mu_{mD}) \tilde{c}_{mD} + \epsilon_m \tilde{c}_{lmD} - \]

\[ \left( \frac{\theta_{um} \alpha_T^2 v_{um}}{2A\theta_m B} \tilde{C}_{umD} - \frac{\theta_{um} \alpha_T^2 D_u \partial \tilde{C}_{umD}}{2A\theta_m B^2 \partial z_D} \right) \bigg|_{z_D = 1} + \left( \frac{\theta_{lm} \alpha_T^2 v_{lm}}{2A\theta_m B} \tilde{C}_{lmD} - \frac{\theta_{lm} \alpha_T^2 D_l \partial \tilde{C}_{lmD}}{2A\theta_m B^2 \partial z_D} \right) \bigg|_{z_D = -1}, \]
\[ r_D \geq r_{WD}. \quad (S17a) \]

\[ \tilde{c}_{imD} = \frac{\varepsilon_{im}}{(s+\mu_{imD}+\mu_{im})} \tilde{c}_{mD}, \quad r_D \geq r_{WD}. \quad (S17b) \]

Substituting Eqs. (S13a), (S14a) and (S17b) into Eq. (S17a), one has:

\[ \frac{1}{r_D} \frac{\partial^2 \tilde{c}_{mD}}{\partial r_D^2} - \frac{1}{r_D} \frac{\partial \tilde{c}_{mD}}{\partial r_D} - E \tilde{c}_{mD} = 0. \quad (S18) \]

where

\[ E = s + \varepsilon_m + \mu_{mD} - \frac{s \varepsilon_{im}}{s+\mu_{imD}+\mu_{im}} + \frac{\theta_{um} a^2 u_m}{2A \theta_m B} - \frac{\theta_{im} a^2 i_m}{2A B \theta_m} - \frac{a_2 \theta_{um} a^2 u_l}{2A B \theta_m} + \frac{b_2 \theta_{im} a^2 i_l}{2A B^2 \theta_m}. \]

The boundary conditions of the wellbore and infinity in the Laplace domain are:

\[ \left[ \tilde{c}_{mD} - \frac{\partial \tilde{c}_{mD}(r_D, s)}{\partial r_D} \right]_{r = r_{WD}} = \tilde{c}_{inj, mD}(s), \quad (S19a) \]

\[ \tilde{c}_{mD}(r_D, s) \bigg|_{r_D \to \infty} = 0. \quad (S19b) \]

Conducting Laplace transform on Eqs. (S16a)- (S16b), one has:

\[ \tilde{c}_{inj, mD}(r_w, s) = \frac{1}{s(s \beta_{inj} + 1)}. \quad (S20) \]

Eqs. (S18), (S19a)-(S19b), and (S20) compose a model of the second-order ordinary differential equation (ODE) with boundary conditions. The general solution of Eq. (S18) is:

\[ \tilde{c}_{mD}(r_D, s) = \phi_1 \exp \left( \frac{\varepsilon_{inj}}{2} \right) A_1 \left( E^{1/3} y_{inj} \right) + \phi_2 \exp \left( \frac{\varepsilon_{inj}}{2} \right) B_1 \left( E^{1/3} y_{inj} \right). \quad (S21) \]

where \( y_{inj} = r_D + \frac{1}{4E}, \) \( y_{inj, w} = r_{WD} + \frac{1}{4E}, \) \( \phi_1 \) and \( \phi_2 \) are constants which could be determined by the boundary conditions; \( A_1(\cdot) \) and \( B_1(\cdot) \) are the Airy functions of the first kind and second kind, respectively. As \( B_1(r_D) \) diverges when \( r_D \to \infty, \phi_2 \) has to be zero.

Substituting Eqs. (S21), (S20) and \( \phi_2 = 0 \) into Eq. (S19a), the value of \( \phi_1 \) is:

\[ \phi_1 = \frac{1}{s(s \beta_{inj} + 1)} \exp \left( \frac{\varepsilon_{inj}}{2} \right) \left[ A_1 \left( E^{1/3} y_{inj, w} \right) \right] \left[ B_1 \left( E^{1/3} y_{inj} \right) \right] \quad (S22) \]

where \( A_1'(\cdot) \) is the derivative of the Airy function.
Substituting Eq. (S22) and $\phi_2 = 0$ into Eqs. (S21) and (S17b), one could obtain the Laplace-domain analytical solution of solute transport in the injection phase of the SWPP test.

### S1.2 Solutions in the chaser phase: Eqs. (26a) - (26g)

For the chaser phase, conducting Laplace transform on Eqs. (S2a)-(S2b), one has:

$$C_{umD}(r, z, t_{in,j, D}) = 0, \quad z_D \geq 1,$$

(S23a)

$$s\tilde{C}_{umD} - C_{umD}(r, z, t_{in,j, D}) = \epsilon_{um}(\tilde{C}_{umD} - \tilde{C}_{imD}) - \mu_{umD}\tilde{C}_{umD},$$

(S23b)

Eq. (S23b) could be rewritten as:

$$\tilde{C}_{umD} = \frac{\epsilon_{um}}{s + \epsilon_{um} + \mu_{umD}}\tilde{C}_{umD} + \frac{\epsilon_{um}(r, z, t_{in,j, D})}{s + \epsilon_{um} + \mu_{umD}},$$

(S23c)

Substituting Eq. (S23c) into Eq. (S23a), one has:

$$C_{umD}(r, z, t_{in,j, D}) + \frac{\epsilon_{um}(r, z, t_{in,j, D})}{s + \epsilon_{um} + \mu_{umD}} = 0, \quad z_D \geq 1,$$

(S24)

Similarly, Eqs. (S3a) - (S3b) become:

$$C_{lmD}(r, z, t_{in,j, D}) = 0, \quad z_D \leq -1,$$

(S25a)

$$s\tilde{C}_{lmD} - C_{lmD}(r, z, t_{in,j, D}) = \epsilon_{lm}(\tilde{C}_{lmD} - \tilde{C}_{imD}) - \mu_{lmD}\tilde{C}_{lmD},$$

(S25b)

Eq. (S23b) could be rewritten as:

$$\tilde{C}_{lmD} = \frac{\epsilon_{lm}}{s + \epsilon_{lm} + \mu_{lmD}}\tilde{C}_{lmD} + \frac{C_{lmD}(r, z, t_{in,j, D})}{s + \epsilon_{lm} + \mu_{lmD}},$$

(S25c)

Substituting Eq. (S25c) into Eq. (S25a), one has:
\[
\frac{R_m\alpha_D^2}{AB^2R_{lim}} \frac{d^2\tilde{c}_{limD}}{dz_D^2} + \frac{R_m\nu_{lim}\alpha_D^2}{ABR_{lim}} \frac{d\tilde{c}_{limD}}{dz_D} - \left(S + \epsilon_{lim} + \mu_{limD} - \frac{\epsilon_{lim}e_{im}}{s + \epsilon_{lim} + \mu_{limD}}\right)\tilde{c}_{limD} +
\]

where \( C_{umD}(r_D, z_D, t_{inj,D}) \) and \( C_{uimD}(r_D, z_D, t_{inj,D}) \) are respectively the mobile and immobile concentrations [ML\(^{-3}\)] of the upper aquitard at the end of the injection phase, \( C_{limD}(r_D, z_D, t_{inj,D}) \) and \( C_{limD}(r_D, z_D, t_{inj,D}) \) are respectively the mobile and immobile concentrations [ML\(^{-3}\)] of the lower aquitard at the end of the injection phase. In this study, we use the Green’s function method to derive the analytical solution of Eqs. (S24) and (S26).

Notice that the boundary condition of Eq. (S6a) is inhomogeneous, thus we need to homogenize it first. Letting \( \tilde{c}_{umD} = \kappa(z_D) + \varsigma_1 + \varsigma_2 z_D \), and substituting them into Eqs. (S5) and (S6a) yields:

\[
[k(\kappa(z_D))]_{z_D=\infty} = 0, \quad (S27a)
\]

\[
[k(\kappa(z_D))]_{z_D=1} = 0, \quad (S27b)
\]

where \( \varsigma_1 = -\varsigma_2 z_{eD} \) and \( \varsigma_2 = \frac{C_{umD}(r_D,s)}{1-z_{eD}} \).

Defining the spatial operator: \( L_u = -\left[\frac{R_m\alpha_D^2}{AB^2R_{um}} \frac{d^2}{dz_D^2} - \frac{R_m\nu_{um}\alpha_D^2}{ABR_{um}} \frac{d}{dz_D} - E_u\right] \), one has:

\[
L_u \tilde{c}_{umD} = L_u [\kappa(z_D) + \varsigma_1] = F_u(z_D), \quad (S28)
\]

Let \( f_u(z_D) = F_u(z_D) - L_u [\varsigma_1 + \varsigma_2 z_D] \), one has:

\[
\frac{R_m\alpha_D^2}{AB^2R_{um}} \frac{d^2f_u}{dz_D^2} - \frac{R_m\nu_{um}\alpha_D^2}{ABR_{um}} \frac{df_u}{dz_D} - E_u f_u = -f_u(z_D), \quad (S29)
\]

where \( E_u = S + \epsilon_{um} + \mu_{umD} - \frac{\epsilon_{um}e_{um}}{s + \epsilon_{um} + \mu_{umD}} \),

\[
F_u(z_D) = C_{umD}(r_D, z_D, t_{inj,D}) + \frac{\epsilon_{um}C_{uimD}(r_D,z_D,t_{inj,D})}{s + \epsilon_{um} + \mu_{umD}} \quad \text{and} \quad f_u(z_D) = C_{umD}(r_D, z_D, t_{inj,D}) +
\]

\[
\frac{\epsilon_{um}C_{uimD}(r_D,z_D,t_{inj,D})}{s + \epsilon_{um} + \mu_{umD}} - \frac{R_m\nu_{um}\alpha_D^2}{ABR_{um}} \varsigma_2 - E_u (\varsigma_1 + \varsigma_2 z_D).
\]
The general solution of Eq. (S24) is:

\[
\tilde{c}_{umD} = \int_1^\infty g_u(z_D, E_u; \eta_u) f_u(\eta_u) d\eta_u + \frac{z_D - z_{ed}}{1 - z_{ed}} \tilde{c}_{mD}(r_D, s), \quad z_D \geq 1. \tag{S30}
\]

where \( f_u(\eta_u) = C_{umb}(r_D, \eta_u, t_{in,j,D}) + \frac{\varepsilon_{um} e_{umD}(r_D, \eta_u, t_{in,j,D})}{s + \varepsilon_{uml} + \mu_{umlD}} - \frac{R_{m_{um}} e_{um}^2}{A R_{um}} s_2 - E_u(s_1 + s_2 \eta_u), \eta_u \)

is a positive value varying between 1 and \( \infty \) (e.g. \( 1 \leq \eta_u \leq \infty \)); \( g_u(z_D, E_u; \eta_u) \) is the Green's function, and could be expressed as:

\[
g_u(z_D, E_u; \eta_u) = \begin{cases} 
  g_{u1}(z_D, E_u; \eta_u) = N_1 \exp(a_1 z_D) + N_2 \exp(a_2 z_D) & 1 \leq z_D < \eta_u \\
  g_{u2}(z_D, E_u; \eta_u) = N_3 \exp(a_1 z_D) + N_4 \exp(a_2 z_D) & \eta_u \leq z_D < \infty 
\end{cases} \tag{S31}
\]

where \( N_1, N_2, N_3 \) and \( N_4 \) are coefficients to be determined using the following conditions:

\[ (Chen \text{ and Woodside}, 1988): \]

a) \( g_{u}(z_D, E_u; \eta_u) \) satisfying the model of Eqs. (S29) and (S27a)-(S27b);

b) \( g_{u1}(z_D, E_u; \eta_u) = g_{u2}(z_D, E_u; \eta_u); \)

c) \[ \frac{dg_{u2}}{dz_D} \bigg|_{z_D=\eta_u} + \frac{dg_{u1}}{dz_D} \bigg|_{z_D=\eta_u} = -\frac{AB^2 R_{um}}{R_m a_{\infty}^2 D_u}. \] (S32)

Substituting Eq. (S31) into Eq. (S27a), one has:

\[ N_3 = 0, \tag{S32} \]

Substituting Eq. (S31) into Eq. (S27b), one has:

\[ N_1 \exp(a_1) + N_2 \exp(a_2) = 0, \tag{S33a} \]

According to Eq. (S33a), one has:

\[ N_1 = -N_2 \exp(a_2 - a_1), \tag{S33b} \]

According to above condition of b), one has:

\[ N_1 \exp(a_1 \eta_u) + N_2 \exp(a_2 \eta_u) = N_4 \exp(a_2 \eta_u), \tag{S34} \]

According to above condition of c), one has:

\[ N_4 a_2 \exp(a_2 \eta_u) - [N_1 a_1 \exp(a_1 \eta_u) + N_2 a_2 \exp(a_2 \eta_u)] = -\frac{AB^2 R_{um}}{R_m a_{\infty}^2 D_u}. \tag{S35} \]
In the chaser phase, the values of $N_1$, $N_2$, $N_3$ and $N_4$ could be determined by Eqs. (S33a) - (S35), namely:

$$N_1 = -N_2 \exp(a_2 - a_1), \quad N_2 = \frac{-AB^2 R_{um}}{R_m \alpha_r^2 D_0 (a_1 - a_2) \exp(a_2 - a_1) \exp(a_1 \eta_u)}$$

$$N_3 = 0$$

$$N_4 = N_2 - N_2 \exp(a_2 - a_1) \exp(a_1 \eta_u - a_2 \eta_u).$$

As for the analytical solution of the lower aquitard, one could use a similar approach as that used for deriving the analytical solution of the upper aquitard to obtain, and the general solution of Eq. (S26) could be described as:

$$\bar{C}_{lmD} = \int_{-1}^{\infty} g_1(z_D, E_i; \eta_i) f_i(\eta_i) d\eta_i + \frac{\varepsilon_{D0} + \varepsilon_D}{\varepsilon_{D0} - 1} \bar{C}_{mD}(r_D, z_D, s), z_D \leq -1.$$  \hspace{1cm} (S36a)

$$g_i(z_D, E_i; \eta_i) = \begin{cases} g_{i1}(z_D, E_i; \eta_i) = M_1 \exp(b_1 z_D) + M_2 \exp(b_2 z_D) - 1 \leq z_D < \eta_i \vspace{1mm} \\ g_{i2}(z_D, E_i; \eta_i) = M_3 \exp(b_1 z_D) + M_4 \exp(b_2 z_D) \eta_i \leq z_D < -\infty \end{cases}$$  \hspace{1cm} (S36b)

$$f_i(\eta_i) = C_{lmD}(r_D, \eta_i, t_{inj,D}) \frac{\varepsilon_{lm} C_{lim}(r_D, \eta_i, t_{inj,D}) + \varepsilon_{lm} \bar{C}_{mD} - \varepsilon_{D0} \varepsilon_{D0} \bar{C}_{mD}}{\varepsilon_{D0} - 1},$$  \hspace{1cm} (S36c)

where $\eta_i$ is a negative value varying between $-1$ and $-\infty$ (e.g. $-1 \leq \eta_i \leq -\infty$); $g_i(z_D, E_i; \eta_i)$ is the Green’s function, $E_i = s + \varepsilon_{lm} + \mu_{limD} - \frac{\varepsilon_{lm} \varepsilon_{lim}}{s + \varepsilon_{lim} + \mu_{limD}}$, and the values of $M_1$, $M_2$, $M_3$ and $M_4$ could be described as:

$$M_1 = -M_2 \exp(b_1 - b_2), \quad M_2 = \frac{-AB^2 R_{lm}}{R_m \alpha_r^2 D_0 [\exp(b_2 \eta_i - b_1 \eta_i) - b_2 \exp(b_2 \eta_i)]},$$

$$M_3 = M_2 \exp(b_2 \eta_i - b_1 \eta_i) - M_2 \exp(b_1 - b_2), \quad M_4 = 0,$$

the values of $a_1, a_2, b_1$ and $b_2$ are the same as used in the injection phase.

In the chaser phase, the dimensional boundary conditions Eqs. (15a)-(15b) are transformed into dimensionless forms as:

$$\beta_{cha,D} \frac{\partial C_{mD}(r_D, t_D)}{\partial t_D} \bigg|_{r_D = r_{wd}} = C_{mD}(r_D, t_D), t_{inj,D} < t_D \leq t_{cha,D},$$  \hspace{1cm} (S37a)

$$C_{cha,mD}(r_D, t_D) \bigg|_{t_D = t_{inj,D}} = C_{inj,mD}(r_D, t_D) \bigg|_{t_D = t_{inj,D}}, t_{inj,D} < t_D \leq t_{cha,D}.$$  \hspace{1cm} (S37b)

where $\beta_{cha,D} = \frac{v_{w,cha} / w_{WD}}{\xi R_m \alpha_r}$.
Conducting Laplace transform on Eqs. (S1a)-(S1b) in the chaser phase, one has:

\[
s\tilde{C}_{mD} - C_{mD}(r_D, t_{inj,D}) = \frac{1}{\tau_D} \frac{\partial^2 \tilde{C}_{mD}}{\partial \tau_D^2} - \frac{1}{\tau_D} \frac{\partial \tilde{C}_{mD}}{\partial \tau_D} - (\epsilon_m + \mu_{mD}) \tilde{C}_{mD} + \epsilon_m \tilde{C}_{imD} - \\
\left( \frac{\theta_{um} \alpha^2 v_{um}}{2\theta_m B} \tilde{C}_{umD} - \frac{\theta_{um} \alpha^2 v_{um}}{2\theta_m B^2} \frac{\partial \tilde{C}_{umD}}{\partial \tau_D} \right) \bigg|_{z_D=1} + \left( \frac{\theta_{im} \alpha^2 v_{im}}{2\theta_m B} \tilde{C}_{imD} - \frac{\theta_{im} \alpha^2 D_l}{2\theta_m B^2} \frac{\partial \tilde{C}_{imD}}{\partial \tau_D} \right) \bigg|_{z_D=1},
\]

\[
r_D \geq r_{WD}.
\]

\[
\tilde{C}_{imD} = \frac{\epsilon_{im}}{(s + \mu_{imD} + \epsilon_{im})} \tilde{C}_{mD} + \frac{c_{imD}(r_D, t_{inj,D})}{(s + \mu_{imD} + \epsilon_{im})} r_D \geq r_{WD},
\]

where \( C_{mb}(r_D, t_{inj,D}) \) and \( C_{imD}(r_D, t_{inj,D}) \) are respectively the mobile and immobile concentrations [ML\(^{-3}\)] of the aquifer at the end of the injection phase, which could be calculated by Eqs. (S21) and (S17b).

After substituting Eqs. (S30), (S36a)-(S36c) and (S38b) into Eq. (S38a), one has:

\[
\frac{1}{\tau_D} \frac{\partial^2 \tilde{C}_{mD}}{\partial \tau_D^2} - \frac{1}{\tau_D} \frac{\partial \tilde{C}_{mD}}{\partial \tau_D} - E_a \tilde{C}_{mD} + F = 0, r_D \geq r_{WD},
\]

where \( E_a = s + \epsilon_m + \mu_{mD} - \frac{\epsilon_m \epsilon_{im}}{s + \mu_{imD} + \epsilon_{im}} + \frac{\theta_{um} \alpha^2 v_{um}}{2\theta_m B} - \frac{\theta_{im} \alpha^2 v_{im}}{2\theta_m B^2} - \frac{1}{1 - \epsilon_D} \frac{\theta_{um} \alpha^2 D_u}{2\theta_m B^2} + \frac{1}{1 - \epsilon_D^{-1}} \frac{\theta_{im} \alpha^2 D_l}{2\theta_m B^2} \)

and \( F = C_{mD}(r_D, t_{inj,D}) + \frac{\epsilon_m c_{imD}(r_D, t_{inj})}{s + \mu_{imD} + \epsilon_{im}} \).

The boundary conditions of Eqs. (S37a)-(S37b) in Laplace domain becomes:

\[
\tilde{C}_{\text{cha},mD}(r_{WD}, s) = \frac{\beta_{\text{cha},D}}{s \beta_{\text{cha},D} + 1} C_{inj,mD}(r_D, t_D) \bigg|_{t_D=t_{inj,D}}.
\]

The boundary conditions of the wellbore and infinity in Laplace domain are:

\[
\left[ \frac{\partial \tilde{C}_{mD}}{\partial \tau_D} \right]_{r=r_{WD}} = \frac{\beta_{\text{cha},D}}{s \beta_{\text{cha},D} + 1} C_{inj,mD}(r_D, t_D) \bigg|_{t_D=t_{inj,D}}.
\]

\[
\tilde{C}_{\text{cha},mD}(r_{WD}, s) \bigg|_{r_D \to \infty} = 0,
\]

Similar to the model of the SWPP test in the injection phase, Eqs. (S39) and (S40)-(S41b) compose a model of the second-order ordinary differential equation (ODE) with boundary
conditions, however, the governing equation is an inhomogeneous differential equation. In this
study, we use the Green’s function method to derive the analytical solution of Eq. (S39).

Notice that the boundary condition of Eq. (S41a) is inhomogeneous, and we need to
homogenize it first. Assigning \( \tilde{C}_{mD} = \Psi(r_D) + \delta_1 + \delta_2 r_D \), and substituting it into Eqs. (S41a)
and (S41b) yields:

\[
\left. \left[ \Psi(r_D, s) - \frac{\partial \Psi(r_D, s)}{\partial r_D} \right] \right|_{r=r_{WD}} = 0, \quad (S42a)
\]

\[
\left. \Psi(r_D, s) \right|_{r_D \to \infty} = 0, \quad (S42b)
\]

where \( \delta_1 = - \frac{\beta_{cha,D}}{s \beta_{cha,D+1}} \frac{r_D}{r_{WD} - r_D} C_{inj,mD}(r_D, t_D) \big|_{t_D = t_{inj,D}} \) and

\[
\delta_2 = \frac{\beta_{cha,D}}{s \beta_{cha,D+1}} \frac{1}{r_{WD} - r_D} C_{inj,mD}(r_D, t_D) \big|_{t_D = t_{inj,D}}.
\]

Defining a spatial operator: \( L = - \left[ \frac{d^2}{dr_D^2} - \frac{d}{dr_D} - r_D E_a \right] \), one has:

\[
L \tilde{C}_{mD} = L[\Psi(r_D) + \delta_1 + \delta_2 r_D] = Fr_D, \quad (S43)
\]

Let \( \varphi(r_D) = Fr_D - L(\delta_1 + \delta_2 r_D) \), one has:

\[
\frac{\partial^2 \Psi}{\partial r_D^2} - \frac{\partial \Psi}{\partial r_D} - r_D E_a \varphi = -\varphi(r_D). \quad (S44)
\]

where \( \varphi(r_D) = Fr_D - [\delta_2 + r_D E_a (\delta_1 + \delta_2 r_D)] \).

The general solution of Eqs. (S42a) - (S44) is:

\[
\Psi(r_D, E_a; \eta) = \int_{r_{WD}}^{\infty} g(r_D, E_a; \eta) \varphi(\eta) d\eta. \quad (S45)
\]

where \( \eta \) is a positive value varying between \( r_{WD} \) and \( \infty \) (e.g. \( r_{WD} \leq \eta \leq \infty \)); \( g(r_D, E_a; \eta) \) is the
Green's function, and could be expressed as:

\[
g(r_D, E_a; \eta) = \begin{cases} 
  g_1(r_D, E_a; \eta) = T_1 \exp\left( \frac{\chi_{cha}}{2} \right) A_1 \left( E_a \gamma_{cha} \right) + T_2 \exp\left( \frac{\chi_{cha}}{2} \right) B_1 \left( E_a \gamma_{cha} \right) r_{wb} \leq \gamma_{cha} \leq \eta \\
  g_2(r_D, E_a; \eta) = T_3 \exp\left( \frac{\chi_{cha}}{2} \right) A_1 \left( E_a \gamma_{cha} \right) + T_4 \exp\left( \frac{\chi_{cha}}{2} \right) B_1 \left( E_a \gamma_{cha} \right) \eta \leq \gamma_{cha} \leq \infty
\end{cases} \quad (S46)
\]
where \( \varphi(\eta) = F\eta - [\delta_2 + \eta E_a(\delta_1 + \delta_2\eta)] \), \( y_{cha} = r_D + \frac{1}{4E_a} \). As \( B_i(r_D) \) diverges when \( r_D \to \infty \), \( T_2 \) has to be zero. Substituting Eq. (S45) into Eq. (S42a), one has:

\[
\left[ g_1 - \frac{\partial g_1}{\partial r_D} \right]_{r_D=r_{wD}} = 0, \quad (S47)
\]

According to Eq. (S47), one has:

\[
T_1 = -T_2 X. \quad (S48)
\]

where \( X = \frac{1}{2}B_i(E_a^{1/3}y_{cha,w}) - E_a^{1/3}B_i'(E_a^{1/3}y_{cha,w}) \) and \( y_{cha,w} = r_{wD} + \frac{1}{4E_a} \).

According to above condition of \( b) \), one has:

\[
T_i A_i \left( E_a^{\frac{1}{3}}y_{cha\mid r_D=\eta^+} \right) + T_2 B_i \left( E_a^{\frac{1}{3}}y_{cha\mid r_D=\eta^+} \right) = T_3 A_i \left( E_a^{\frac{1}{3}}y_{cha\mid r_D=\eta^-} \right). \quad (S49)
\]

According to above condition of \( c) \), one has:

\[
\left[ \frac{1}{2} T_3 \exp \left( \frac{y_{cha}}{2} \right) A_i \left( E_a^{\frac{1}{3}}y_{cha} \right) + E_a^{\frac{1}{3}} T_3 \exp \left( \frac{y_{cha}}{2} \right) A_i' \left( E_a^{\frac{1}{3}}y_{cha} \right) \right]_{r_D=\eta^-} - \]

\[
\left[ 0.5 T_1 \exp \left( \frac{y_{cha}}{2} \right) A_i \left( E_a^{\frac{1}{3}}y_{cha} \right) + E_a^{\frac{1}{3}} T_1 \exp \left( \frac{y_{cha}}{2} \right) A_i' \left( E_a^{\frac{1}{3}}y_{cha} \right) \right]_{r_D=\eta^+} - \]

\[
\left[ \frac{1}{2} T_2 \exp \left( \frac{y_{cha}}{2} \right) B_i \left( E_a^{\frac{1}{3}}y_{cha} \right) + E_a^{\frac{1}{3}} T_2 \exp \left( \frac{y_{cha}}{2} \right) B_i' \left( E_a^{\frac{1}{3}}y_{cha} \right) \right]_{r_D=\eta^+} = -1. \quad (S50)
\]

For solution in the chaser phase, the values of \( T_1, T_2, T_3 \) and \( T_4 \) could be determined by Eqs. (S48) - (S50), namely:

\[
T_3 = \frac{\pi A_i(y_{ext\mid r_D=\eta^+})}{E_a^{1/3}} X, \quad T_2 = \frac{\pi A_i(y_{ext\mid r_D=\eta^+})}{E_a^{1/3}}, \quad T_3 = \frac{\pi A_i(y_{ext\mid r_D=\eta^+})}{E_a^{1/3}} \left[ B_i(y_{ext\mid r_D=\eta^+}) - X \right] \quad \text{and}
\]

\[
T_4 = 0. \quad (S50)
\]

\[ S1.3 \text{ Solutions in the rest phase: Eqs. (27a) - (27f)} \]
In the rest phase, the flow velocity become zero, and the advection and dispersion terms drop out of the governing equations. After conducting Laplace transform on Eqs. (S2a)-(S2b), the following equations would be obtained:

\[
(s + \varepsilon_{um} + \mu_{umD})c_{umD} - \varepsilon_{um}\tilde{c}_{umD} - C_{umD}(r_D, z_D, t_{cha,D}) = 0, \quad z_D \geq 1. \quad (S51a)
\]

\[
\tilde{c}_{umD} = \frac{\varepsilon_{um}}{s + \varepsilon_{um} + \mu_{umD}}c_{umD} + \frac{C_{umD}(r_D, z_D, t_{cha,D})}{s + \varepsilon_{um} + \mu_{umD}}, \quad z_D \geq 1, \quad (S51b)
\]

Substituting Eq. (S51b) into Eq. (S51a), one has:

\[
(s + \varepsilon_{um} + \mu_{umD})c_{umD} - \varepsilon_{um}\tilde{c}_{umD} - C_{umD}(r_D, z_D, t_{cha,D}) - \frac{\varepsilon_{um}C_{umD}(r_D, z_D, t_{cha,D})}{s + \varepsilon_{um} + \mu_{umD}} = 0, \quad z_D \geq 1. \quad (S52)
\]

Similarly, Eqs. (S3a) - (S3b) become:

\[
(s + \varepsilon_{lm} + \mu_{lmD})\tilde{c}_{lmD} - \varepsilon_{lm}\tilde{c}_{lmD} - C_{lmD}(r_D, z_D, t_{cha,D}) = 0, \quad z_D \leq -1. \quad (S53a)
\]

\[
\tilde{c}_{lmD} = \frac{\varepsilon_{lm}}{s + \varepsilon_{lm} + \mu_{lmD}}c_{lmD} + \frac{C_{lmD}(r_D, z_D, t_{cha,D})}{s + \varepsilon_{lm} + \mu_{lmD}}, \quad z_D \leq -1, \quad (S53b)
\]

Substituting Eq. (S45b) into Eq. (S45a), one has:

\[
(s + \varepsilon_{lm} + \mu_{lmD})c_{lmD} - \varepsilon_{lm}\tilde{c}_{lmD} - C_{lmD}(r_D, z_D, t_{cha,D}) - \frac{\varepsilon_{lm}C_{lmD}(r_D, z_D, t_{cha,D})}{s + \varepsilon_{lm} + \mu_{lmD}} = 0, \quad z_D \leq -1. \quad (S54)
\]

According to Eqs. (S52) and (S54), one has:

\[
c_{umD} = \frac{C_{umD}(r_D, z_D, t_{cha,D}) + \varepsilon_{um}C_{umD}(r_D, z_D, t_{cha,D})}{s + \varepsilon_{um} + \mu_{umD}} \quad (S55a)
\]

\[
c_{lmD} = \frac{C_{lmD}(r_D, z_D, t_{cha,D}) + \varepsilon_{lm}C_{lmD}(r_D, z_D, t_{cha,D})}{s + \varepsilon_{lm} + \mu_{lmD}} \quad (S55b)
\]

where \(C_{umD}(r_D, z_D, t_{cha,D})\) and \(C_{lmD}(r_D, z_D, t_{cha,D})\) are respectively the mobile and immobile concentrations \([\text{ML}^{-3}]\) of the upper aquitard at the end of the chaser phase. \(C_{lmD}(r_D, z_D, t_{cha,D})\)
and \( C_{imD}(r_D, z_D, t_{cha,D}) \) are respectively the mobile and immobile concentrations [ML\(^{-3}\)] of the lower aquitard at the end of the chaser phase.

Similarly, the dimensionless governing equation of the mobile zone during the rest phase is:

\[
\frac{\partial C_{md}}{\partial t_D} = -\varepsilon_m(C_{mD} - C_{imD}) - \mu_{mD} C_{mD}, \quad r_D \geq r_{WD}. \tag{S56a}
\]

\[
\frac{\partial C_{imD}}{\partial t_D} = \varepsilon_{im}(C_{mD} - C_{imD}) - \mu_{imD} C_{imD}, \quad r_D \geq r_{WD}, \tag{S56b}
\]

Conducting Laplace transform to Eqs. (S56a) and (S56b) for the rest phase, one has:

\[
s\tilde{C}_{mD} - C_{mD}(r_D, t_{cha,D}) = -\varepsilon_m(\tilde{C}_{mD} - \tilde{C}_{imD}) - \mu_{mD}\tilde{C}_{mD}, \quad r_D \geq r_{WD}. \tag{S57a}
\]

\[
s\tilde{C}_{imD} - C_{imD}(r_D, t_{cha,D}) = \varepsilon_{im}(\tilde{C}_{mD} - \tilde{C}_{imD}) - \mu_{imD}\tilde{C}_{imD}, \quad r_D \geq r_{WD}. \tag{S57b}
\]

According to Eqs. (S57a)-(S57b), one has:

\[
\tilde{C}_{mD} = \frac{C_{mD}(r_D, t_{cha,D}) + \varepsilon_{im}C_{imD}(r_D, t_{cha,D})}{s + \varepsilon_{im} + \mu_{mD} s^{\varepsilon_{im}} + \mu_{mD} s^{\varepsilon_{im}}}, \tag{S58a}
\]

\[
\tilde{C}_{imD} = \frac{C_{imD}(r_D, t_{cha,D})}{s + \mu_{imD} + \varepsilon_{im}} + \frac{\varepsilon_{im}\tilde{C}_{mD}}{s + \mu_{imD} + \varepsilon_{im}}. \tag{S58b}
\]

\[\text{S1.4 Solutions in the extraction phase: Eqs. (28a) - (28g)}\]

Contrary to the injection and chaser phases, the direction of advective flux is reversed in the extraction stage, Eqs. (S2a) and (S3a) are modified as:

\[
\frac{\partial C_{umD}}{\partial t_D} = \frac{R_m\alpha^2 u_D}{AB^2 R_{um}} \frac{\partial^2 C_{umD}}{\partial z_D^2} + \frac{R_m\psi_{um}\alpha^2}{ABR_{um}} \frac{\partial C_{umD}}{\partial z_D} - \varepsilon_{um}(C_{umD} - C_{uimD}) - \mu_{umD} C_{umD}, \quad z_D \geq 1, \tag{S59a}
\]

\[
\frac{\partial C_{imD}}{\partial t_D} = \frac{R_m\alpha^2 u_D}{AB^2 R_{im}} \frac{\partial^2 C_{imD}}{\partial z_D^2} - \frac{R_m\psi_{im}\alpha^2}{ABR_{im}} \frac{\partial C_{imD}}{\partial z_D} - \varepsilon_{im}(C_{imD} - C_{limD}) - \mu_{imD} C_{imD}, \quad z_D \leq -1, \tag{S59b}
\]

Conducting Laplace transform on Eqs. (S2b) and (S59a), one has:
\[ s\tilde{C}_{umD} - C_{umD}(r_D, z_D, t_{res,D}) = \frac{R_m \alpha_T^2 D_u}{AB^2 R_{um}} \frac{\partial^2 C_{umD}}{\partial z_D^2} + \frac{R_m \nu_{um} \alpha_T^2}{ABR_{um}} \frac{\partial C_{umD}}{\partial z_D} - \varepsilon_{um}(\tilde{C}_{umD} - \bar{C}_{umD}) - \varepsilon_{um} \]

\[ \mu_{umD}\tilde{C}_{umD}, z_D \geq 1, \quad (S60a) \]

\[ \tilde{C}_{umD} = \frac{\varepsilon_{uin} \hat{C}_{umD}}{s + \varepsilon_{uin} + \mu_{uinD}} - \frac{C_{uinD}(r_D, z_D, t_{res,D})}{s + \varepsilon_{uin} + \mu_{uinD}}, z_D \geq 1, \quad (S60b) \]

Substituting Eqs. (S60b) into Eq. (S60a), one can has:

\[ \frac{R_m \alpha_T^2 D_u}{AB^2 R_{um}} \frac{\partial^2 C_{umD}}{\partial z_D^2} + \frac{R_m \nu_{um} \alpha_T^2}{ABR_{um}} \frac{\partial C_{umD}}{\partial z_D} - \left( s + \varepsilon_{um} + \mu_{umD} - \frac{\varepsilon_{um} \varepsilon_{uin}}{s + \varepsilon_{uin} + \mu_{uinD}} \right) \tilde{C}_{umD} + \]

\[ C_{umD}(r_D, z_D, t_{res,D}) = \frac{\varepsilon_{uin} \hat{C}_{uinD}}{s + \varepsilon_{uin} + \mu_{uinD}} + \frac{C_{uinD}(r_D, z_D, t_{res,D})}{s + \varepsilon_{uin} + \mu_{uinD}} = 0. z_D \geq 1, \quad (S61) \]

Similarly, conducting Laplace transform on Eqs. (S3b) and (S59b), one has:

\[ s\tilde{C}_{lmD} - C_{lmD}(r_D, z_D, t_{res,D}) = \frac{R_m \alpha_T^2 D_l}{AB^2 R_{lm}} \frac{\partial^2 C_{lmD}}{\partial z_D^2} - \frac{R_m \nu_{lm} \alpha_T^2}{ABR_{lm}} \frac{\partial C_{lmD}}{\partial z_D} - \varepsilon_{lm}(\tilde{C}_{lmD} - \bar{C}_{lmD}) - \]

\[ \mu_{lmD}\tilde{C}_{lmD}, z_D \leq -1, \quad (S62a) \]

\[ \tilde{C}_{lmD} = \frac{\varepsilon_{lim} \hat{C}_{lmD}}{s + \varepsilon_{lim} + \mu_{limD}} + \frac{C_{limD}(r_D, z_D, t_{res,D})}{s + \varepsilon_{lim} + \mu_{limD}}, z_D \leq -1, \quad (S62b) \]

Substituting Eqs. (S62b) into Eq.(S62a), one has:

\[ \frac{R_m \alpha_T^2 D_l}{AB^2 R_{lm}} \frac{\partial^2 C_{lmD}}{\partial z_D^2} - \frac{R_m \nu_{lm} \alpha_T^2}{ABR_{lm}} \frac{\partial C_{lmD}}{\partial z_D} - \left( s + \varepsilon_{lm} + \mu_{lmD} - \frac{\varepsilon_{lm} \varepsilon_{lim}}{s + \varepsilon_{lim} + \mu_{limD}} \right) \tilde{C}_{lmD} + \]

\[ C_{lmD}(r_D, z_D, t_{res,D}) = \frac{\varepsilon_{lim} \hat{C}_{limD}}{s + \varepsilon_{lim} + \mu_{limD}} + \frac{C_{limD}(r_D, z_D, t_{res,D})}{s + \varepsilon_{lim} + \mu_{limD}} = 0. z_D \leq -1, \quad (S63) \]

where \( C_{umD}(r_D, z_D, t_{res,D}) \) and \( C_{uinD}(r_D, z_D, t_{res,D}) \) are respectively the mobile and immobile concentrations [ML\(^{-3}\)] of the upper aquitard at the end of the rest phase, \( C_{lmD}(r_D, z_D, t_{res,D}) \) and \( C_{limD}(r_D, z_D, t_{res,D}) \) are respectively the mobile and immobile concentrations [ML\(^{-3}\)] of the lower aquitard at the end of the rest phase.

One could use a similar approach of obtaining the analytical solution of aquitards in the chaser phase to derive the solution of aquitards in the extraction phase. The general solution of (S61) is:
\[ \tilde{C}_{umD} = \int_{1}^{\infty} g_u(z_D, E_u; \beta_u) f_u(\beta_u)d\beta_u + \frac{z_D - z_{eD}}{1 - z_{eD}} \tilde{c}_{mD}(r_D, s), z_D \geq 1, \]  
\[ g_u(z_D, E_u; \beta_u) = \begin{cases} 
    g_{u1}(z_D, E_u; \beta_u) = H_1 \exp(m_1 z_D) + H_2 \exp(m_2 z_D), & 1 \leq z_D < \beta_u, \\
    g_{u2}(z_D, E_u; \beta_u) = H_3 \exp(m_1 z_D) + H_4 \exp(m_2 z_D), & \beta_u \leq z_D < \infty. 
\end{cases} 
\]  
\[ f_u(\beta_u) = \]  
\[ C_{umD}(r_D, \beta_u, t_{res,D}) + \frac{\epsilon_{um}c_{mum}(r_D, \beta_u, t_{res,D})}{s + \epsilon_{um} + \mu_{umD}} + \frac{R_m v_{um} \alpha_f^2}{ABR_{um}} \frac{\tilde{c}_{mD}(r_D, s)}{1 - z_{eD}} - \frac{\beta_u - z_{eD}}{1 - z_{eD}} E_u \tilde{C}_{mD}(r_D, s), \]  
\[ \tilde{C}_{ImD} = \int_{-1}^{\infty} g_i(z_D, E_i; \beta_i) f_i(\beta_i)d\beta_i + \frac{z_{D} + z_{eD}}{z_{eD} - 1} \tilde{c}_{mD}(r_D, s), z_D \leq -1, \]  
\[ g_i(z_D, E_i; \beta_i) = \begin{cases} 
    g_{i1}(z_D, E_i; \beta_i) = l_1 \exp(n_1 z_D) + l_2 \exp(n_2 z_D), & 1 \leq z_D < \beta_i, \\
    g_{i2}(z_D, E_i; \beta_i) = l_3 \exp(n_1 z_D) + l_4 \exp(n_2 z_D), & \beta_i \leq z_D < -\infty. 
\end{cases} 
\]  
\[ f_i(\beta_i) = \]  
\[ C_{mD}(r_D, \beta_i, t_{res,D}) + \frac{\epsilon_{im}c_{mim}(r_D, \beta_i, t_{res,D})}{s + \epsilon_{im} + \mu_{imD}} - \frac{R_m v_{im} \alpha_f^2}{ABR_{im}} \frac{\tilde{c}_{mD}(r_D, s)}{1 - z_{eD}} - \frac{\beta_i + z_{eD}}{z_{eD} - 1} E_i \tilde{C}_{mD}(r_D, s), \]  
where \( \beta_u \) is a positive value varying between 1 and \( \infty \); \( \beta_i \) is a negative value varying between \(-1 \) and \(-\infty \); \( g_u(z_D, E_u; \beta_u) \) and \( g_i(z_D, E_i; \beta_i) \) are the Green's functions, \( H_1 \sim H_4 \) and \( I_1 \sim I_4 \) are constants which could be determined by the boundary conditions and conditions of a)-c), the values of \( H_1 \sim H_4 \) and \( I_1 \sim I_4 \) are as follows: 
\[ H_2 = \frac{-AB_{um} R^2}{R_m \alpha_f^2 D_u (m_1 - m_2) \exp(m_2 - m_1) \exp(m_1 \beta_u)} , H_3 = 0, H_4 = H_2 - H_2 \exp(m_2 - m_1) \exp(m_1 \beta_u - m_2 \beta_u), \]  
\[ l_1 = -l_2 \exp(n_1 - n_2), l_2 = \frac{-AB^2 R_{im}}{R_m \alpha_f^2 D_i [\exp(n_2 \beta_i - n_1 \beta_i) - n_2 \exp(n_2 \beta_i)]}, \]  
\[ l_3 = l_2 \exp(n_2 \beta_i - n_1 \beta_i) - l_2 \exp(n_1 - n_2), l_4 = 0, \]  
\[ m_1 = \frac{R_m v_{um} \alpha_f^2}{ABR_{um} (s + \epsilon_{um} + \mu_{umD}) \frac{z_{um} c_{umD}}{z + \epsilon_{umD} + \mu_{umD}}}, \]
\[ m_2 = \frac{-R_m \nu u m^2}{AB^2 R_{um}} \left( \frac{R_m \nu u m^2}{AB^2 R_{um}} \right)^2 + \frac{4R_m \nu u m^2 D_u}{AB^2 R_{um}} \left( s + \frac{\epsilon u m + \mu u m D}{s + \mu u m D + \epsilon u m} \right) \]

\[ n_1 = \frac{-R_m \nu u m^2}{AB^2 R_{um}} \left( \frac{R_m \nu u m^2}{AB^2 R_{um}} \right)^2 + \frac{4R_m \nu u m^2 D_l}{AB^2 R_{um}} \left( s + \frac{\epsilon l m + \mu l m D}{s + \mu l m D + \epsilon l m} \right) \]

\[ n_2 = \frac{-R_m \nu u m^2}{AB^2 R_{um}} \left( \frac{R_m \nu u m^2}{AB^2 R_{um}} \right)^2 + \frac{4R_m \nu u m^2 D_l}{AB^2 R_{um}} \left( s + \frac{\epsilon l m + \mu l m D}{s + \mu l m D + \epsilon l m} \right) \]

Similarly, contrary to the injection and chaser phases, the direction of advective flux is reversed in the extraction stage, and Eq. (S1a) is modified as:

\[ \frac{\partial c_{mD}}{\partial t_D} = \frac{1}{r_D} \frac{\partial^2 c_{mD}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial c_{mD}}{\partial r_D} - \epsilon_m (c_{mD} - c_{l mD}) - \mu_{mD} c_{mD} - \left( -\frac{\theta_u m \alpha^2 v u m}{2A \theta_m b} c_{u m D} - \right) \]

\[ \frac{\theta_u m \alpha^2 v u m}{2A \theta_m b} \frac{\partial c_{mD}}{\partial z_D} \right|_{z=1} + \left( -\frac{\theta_l m \alpha^2 v l m}{2A \theta_m b} c_{l mD} - \frac{\theta_l m \alpha^2 D_l}{2A \theta_m b} \frac{\partial c_{l mD}}{\partial z_D} \right) \right|_{z=-1}, \quad r_D \geq r_{WD}. \quad (S66) \]

In the extraction phase, the dimensional boundary conditions Eqs. (14a)-(14b) are transformed to the dimensionless format:

\[ \beta_{ext,D} \frac{\partial c_{mD}(r_D,t_D)}{\partial t_D} \bigg|_{r_D=r_{WD}} = \frac{\partial c_{mD}(r_D,t_D)}{\partial r_D} \bigg|_{r_D=r_{WD}}, \quad t_{res,D} < t_D \leq t_{ext,D} \quad (S67a) \]

\[ c_{mD}(r_D, t_D) \big|_{t_D=t_{res,D}} = c_{res,mD}(r_D, t_D) \big|_{t_D=t_{res,D}}. \quad (S67b) \]

where \( \beta_{ext,D} = - \frac{V_{w,ext} r_{WD}}{\xi R_m \alpha_r} \).

Conducting Laplace transform on Eqs. (S58) and (S1b) in the extraction phase, one has:

\[ s \tilde{c}_{mD} - c_{mD}(r_D, t_{res}) = \frac{1}{r_D} \frac{\partial^2 \tilde{c}_{mD}}{\partial r_D^2} + \frac{1}{r_D} \frac{\partial \tilde{c}_{mD}}{\partial r_D} - (\epsilon_m + \mu_{mD}) \tilde{c}_{mD} + \epsilon_m \tilde{c}_{l mD} - \]

\[ \left( -\frac{\theta_u m \alpha^2 v u m \tilde{c}_{u m D}}{2A \theta_m b} - \frac{\theta_l m \alpha^2 D_l \tilde{c}_{l m D}}{2A \theta_m b} \right) \bigg|_{z_D=1} - \left( \frac{\theta_l m \alpha^2 v l m \tilde{c}_{l m D}}{2A \theta_m b} + \frac{\theta_l m \alpha^2 D_l \tilde{c}_{l m D}}{2A \theta_m b} \right) \bigg|_{z_D=-1}, \]

\[ r_D \geq r_{WD}. \quad (S68a) \]
\[ \tilde{C}_{imD} = \frac{\epsilon_{im}}{(s+\mu_{imD}+\epsilon_{im})}\tilde{C}_{mD} + \frac{c_{imD} (r_{D,t_{res}})}{s+\mu_{imD}+\epsilon_{im}}, r_{D} \geq r_{WD}, \quad (S68b) \]

After substituting Eqs. (S64a)-(S65c) and Eq. (S68b) into Eq. (S68a), one has

\[ \frac{\partial^2 \tilde{c}_{mD}}{\partial r_{D}^2} + \frac{\partial \tilde{c}_{mD}}{\partial r_{D}} - r_{D}\tilde{\zeta} \tilde{c}_{mD} + r_{D}\Lambda = 0. \quad (S69) \]

where \( \tilde{\zeta} = s + \epsilon_{m} + \mu_{mD} - \frac{\epsilon_{im} \epsilon_{m}}{s+\mu_{imD}+\epsilon_{im}} - \frac{\theta_{um}\alpha_{2}^{2} v_{um}}{2A\theta_{m}B} + \frac{\theta_{lm}\alpha_{2}^{2} v_{lm}}{2AB^{2}\theta_{m}} - \frac{1}{1-2e_{D}} \frac{\theta_{um}\alpha_{2}^{2} D_{u}}{2A\theta_{m}b} + \frac{1}{2}\frac{\theta_{lm}\alpha_{2}^{2} D_{l}}{2AB^{2}\theta_{m}} \)

\[ \Lambda = \frac{c_{mD}(r_{D}, t_{res})}{s+\mu_{imD}+\epsilon_{im}}; c_{imD}(r_{D}, t_{res}) \text{ and } c_{mD}(r_{D}, t_{res}) \text{ represent the initial concentrations in the immobile and mobile domains of the SWPP test in the rest phase.} \]

The boundary condition of Eqs. (S67a)-(S67b) in Laplace domain becomes:

\[ s\beta_{ext,D} \tilde{c}_{mD}(r_{D}, s)|_{r_{D}=r_{WD}} - \beta_{ext,D} \tilde{C}_{res,m}(r_{D}, t_{D})|_{t_{D}=t_{res,D}} = \frac{\partial \tilde{c}_{mD}(r_{D}, s)}{\partial r_{D}}|_{r_{D}=r_{WD}}. \quad (S70) \]

Similar to the model of the SWPP test in the injection phase, Eqs. (S5), (S61) and (S70) compose a model of the second-order ordinary differential equation (ODE) with boundary conditions. However, the governing equation is an inhomogeneous differential equation. In this study, we use the Green’s function method to derive the analytical solution of Eq. (S69).

Similar to Chen and Woodside [1988], Eq. (S69) could be transferred into a self-adjoint form:

\[ \frac{\partial^2 g}{\partial r_{D}^2} - \frac{1}{4} G = -\ell(r_{D}). \quad (S71) \]

where \( G = \exp(r_{D}/2)\tilde{c}_{mD} \) and \( \ell(r_{D}) = \exp(r_{D}/2)r_{D}\Lambda. \)

The boundary conditions of Eqs. (S5) and (S70) could be rewritten as:

\[ G(r_{D}, s)|_{r_{D}=\infty} = 0, \quad (S72a) \]

\[ \left[s\beta_{ext,D} + \frac{1}{2} G - \frac{\partial g}{\partial r_{D}}\right]|_{r_{D}=r_{WD}} = \beta_{ext,D}\exp(r_{WD}/2)C_{mD}(r_{WD}, t_{res,D}). \quad (S72b) \]
One could find that the boundary condition of Eq. (S72b) is inhomogeneous, and we need to homogenize it first. Assigning $G = U(r_D) + V(r_D)$ and $V(r_D) = \sigma_1 + \sigma_2 r_D$, and substituting them into Eqs. (S72a) and (S72b) yields:

$$U(r_D, s)|_{r_D=\infty} = 0,$$  \hfill (S73a)

$$\left[ (s\beta_{ext,D} + \frac{1}{2}) U - \frac{\partial U}{\partial r_D} \right]_{r_D=r_{WD}} = 0,$$  \hfill (S73b)

where $\sigma_1 = -\frac{\beta_{ext,D} \exp(r_{WD}/2)c_{MD}(r_{WD}, \lambda_{res,D})}{(s\beta_{ext,D} + \frac{1}{2})r_{WD} - 1 - (s\beta_{ext,D} + \frac{1}{2})}r_D|_{r_D=\infty}$,

$$\sigma_2 = \frac{\beta_{ext,D} \exp(r_{WD}/2)c_{MD}(r_{WD}, \lambda_{res,D})}{(s\beta_{ext,D} + \frac{1}{2})r_{WD} - 1 - (s\beta_{ext,D} + \frac{1}{2})}r_D|_{r_D=\infty}.$$

After defining a spatial operator $L = -\frac{d^2}{dr_D^2} + (r_D \zeta + \frac{1}{4})$, one has:

$$LG = LU(r_D) + LV(r_D) = \ell(r_D).$$  \hfill (S74)

and

$$LU(r_D) = \ell(r_D) - LV(r_D).$$  \hfill (S75)

Let $f(r_D) = \ell(r_D) - LV(r_D)$, one has:

$$\frac{\partial^2 U}{\partial r_D^2} - \left( r_D \zeta + \frac{1}{4} \right) U = -f(r_D).$$  \hfill (S76)

where $f(r_D) = \exp(r_D/2)r_D \Lambda - \left( r_D \zeta + \frac{1}{4} \right) (\sigma_1 + \sigma_2 r_D)$.

Right now, the model with an inhomogeneous boundary condition becomes a regular Sturm-Louisville problem. The general solution of Eqs. (S73a) - (S73b) and (S76) is:

$$U(r_D, \zeta; \varepsilon) = \int_{r_{WD}}^{\infty} g(r_D, \zeta; \varepsilon) f(\varepsilon) d\varepsilon.$$  \hfill (S77)

where $\varepsilon$ is a positive value varying between $r_{WD}$ and $\infty$ (e.g. $r_{WD} \leq \varepsilon \leq \infty$); $g(r_D, \zeta; \varepsilon)$ is the Green's function, and could be expressed as:

$$g(r_D, \zeta; \varepsilon) = \begin{cases} g_1(r_D, \zeta; \varepsilon) = P_1 A_1(y_{ext}) + P_2 B_1(y_{ext}) & r_{WD} \leq y_{ext} \leq \varepsilon \\ g_2(r_D, \zeta; \varepsilon) = P_3 A_1(y_{ext}) + P_4 B_1(y_{ext}) & \varepsilon \leq y_{ext} \leq \infty \end{cases}.$$  \hfill (S78)
388 where \( f(\varepsilon) = \exp(\varepsilon/2)\varepsilon \Lambda - \left( \varepsilon \zeta + \frac{1}{4} \right)(\sigma_1 + \sigma_2 \varepsilon), \ y_{\text{ext}} = \zeta^{1/3}(r_D + \frac{1}{4\zeta}), \ P_1, P_2, P_3 \) and \( P_4 \) are coefficients to be determined. As \( B_i(r_D) \) diverges when \( r_D \to \infty \), \( P_4 \) has to be zero.

Substituting Eq. (S78) into Eq. (S73b), one has:

\[
\left[ (s\beta_{\text{ext}D} + \frac{1}{2}) g_1 - \frac{\partial g_1}{\partial r_D} \right]_{r_D = r_{wD}} = 0. \tag{S79}
\]

which leads to

\[ P_1 = -P_2 W. \tag{S80} \]

where \( W = \frac{(s\beta_{\text{ext}D} + \frac{1}{2})B_i(y_{\text{ext}w}) - \zeta^{1/3}B'_i(y_{\text{ext}w})}{(s\beta_{\text{ext}D} + \frac{1}{2})A_i(y_{\text{ext}w}) - \zeta^{1/3}A'_i(y_{\text{ext}w})}, \ y_{\text{ext}w} = \zeta^{1/3}(r_{wD} + \frac{1}{4\zeta}). \]

According to the properties of Green’s function, one has:

\[ P_1A_i(y_{\text{ext}}|_{r_D = \varepsilon^+}) + P_2B_i(y_{\text{ext}}|_{r_D = \varepsilon^+}) = P_3A_i(y_{\text{ext}}|_{r_D = \varepsilon^-}). \tag{S81} \]

\[ [P_3\zeta^{1/3}A'_i(y_{\text{ext}})]_{r_D = \varepsilon^-} = \left[ P_1\zeta^{1/3}B'_i(y_{\text{ext}}) + P_2\zeta^{1/3}B'_i(y_{\text{ext}}) \right]_{r_D = \varepsilon^+} = -1. \tag{S82} \]

The values of \( P_1, P_2 \) and \( P_3 \) could be determined by Eqs. (S69) - (S71), namely:

\[ P_1 = -\frac{\pi A_i(y_{\text{ext}}|_{r_D = \varepsilon^+})}{\zeta^{1/3}} W, \ P_2 = \frac{\pi A_i(y_{\text{ext}}|_{r_D = \varepsilon^+})}{\zeta^{1/3}}, \]

\[ P_3 = \frac{\pi A_i(y_{\text{ext}}|_{r_D = \varepsilon^+})}{\zeta^{1/3}} \left[ \frac{B_i(y_{\text{ext}}|_{r_D = \varepsilon^+})}{A_i(y_{\text{ext}}|_{r_D = \varepsilon^+})} - W \right]. \]

**References**


**S2. Numerical simulations**
Figure S1. The grid mesh of the aquifer-aquitard system used in the Galerkin finite element program using COMSOL Multiphysics.

S3. References for Table 4


[g]. Javadi, S., Ghavami, M., Zhao, Q., and Bate, B.: Advection and retardation of non-polar contaminants in compacted clay barrier material with organoclay amendment, Applied Clay Science, S0169131716304628, 2017.


