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# Reactive Transport with Wellbore Storages in a Single-Well Push-Pull Test

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**Abstract.** Using the single-well push-pull (SWPP) test to determine the in situ biogeochemical reaction kinetics, a chase phase and a rest phase were recommended to increase the duration of reaction, besides the injection and extraction phases. In this study, we presented multi-species reactive models of the four-phase SWPP test considering the wellbore storages for both groundwater flow and solute transport and a finite aquifer hydraulic diffusivity, including three isotherm-based models (Freundlich, Langmuir and linear sorption models), one-site kinetic sorption model, two-site sorption model, which were also capable of describing the biogeochemical reactive transport processes, e.g. Monod or Michaelis-Menten kinetics. The models of the wellbore storage for solute transport were derived based on the mass balance, and the results showed that ignoring it might produce great errors in the SWPP test. In the injection and chase phases, the influence of the wellbore storage increased with the decreasing aquifer hydraulic diffusivity. The peak values of the breakthrough curves (BTCs) increased with the increasing aquifer hydraulic diffusivity in the extraction phase, and the arrival time of the peak value became shorter with a greater aquifer hydraulic diffusivity. Meanwhile, the Robin condition performed well at the rest phase only when the chase concentration was zero and the solute in the injection phase was completely flushed out of the borehole into the aquifer. The Danckwerts condition was better than the Robin condition even when the chase concentration was not zero. The reaction parameters could be determined by directly best fitting the observed data when the non-linear reactions were described by piece-wise linear functions, while such an approach might not work if one attempted to use non-linear functions to describe such non-linear reactions. The field application demonstrated that the new model of this study performed well in interpreting BTCs of a SWPP test.

## 1 Introduction

Single-well push-pull (SWPP) test is a popular technique to characterize the in situ geological formations and the biogeochemical reaction kinetics of the aquifer (Istok, 2012;Phanikumar and McGuire, 2010;Schroth and Istok, 2006), through which the parameters of concern could be estimated by best fitting the observed breakthrough curves (BTCs) with analytical/numerical models in the well (Snodgrass and Kitanidis, 1998;Haggerty et al., 1998). As a result, the accuracy of the parameter estimation is not only dependent on the experimental operation, but also on the conceptual model which is expected to represent the proper physical and biogeochemical processes. Unfortunately, most previous studies of the multi-species reactive transport were based on some assumptions which may not be satisfied in actual applications, although those assumptions usually simplified the mathematical treatment of the problem (Istok, 2012;Wang et al., 2017).

As for the analytical solutions of the SWPP test, they have been widely used for applications, due to the high efficiency and great accuracy of the solutions, e.g. the model of Gelhar and Collins (1971) for a fully penetrating well, the model of Schroth and Istok (2005) for a point source/sink well, the model of Huang et al. (2010) for a partially penetrating well, assuming that advection, dispersion and the first-order reaction were involved in the transport processes. Haggerty et al. (1998) and Snodgrass and Kitanidis (1998) presented a simplified method based on a well-mixed reactor to estimate the first-order and zero-order reaction rate coefficients, without involving complex numerical modeling. Schroth and Istok (2006) provided two alternative models, one of them was a plug-flow model and the other was a variably mixed reactor model. Schroth et al. (2000) presented a simplified method for estimating retardation factors, based on the model of Gelhar and Collins (1971). Istok et al. (2001) extended the models of Haggerty et al. (1998) and Snodgrass and Kitanidis (1998) to estimate the Michaelis-Menten kinetic parameters which were used to describe the microbial respiration in the aquifer. Recently, Jung and Pruess (2012) presented a closed-form analytical solution for heat transport in a fracture aquifer involving a push-and-pull procedure. However, the mentioned-above analytical or semi-analytical solutions of the SWPP test were based on some over-simplified assumptions. For instance, the hydraulic diffusivity of the aquifer was assumed to be infinite, resulting in a time-independent flow velocity. The wellbore storage effect on the flow field was assumed to be negligible as well. Recently, Wang et al. (2017) found that the influences of a finite hydraulic diffusivity on the results might be significant, since both advective and dispersive transport were related to the flow velocity, which was closely related to it, in addition to the boundary and initial conditions of the flow. However, such model only considered the wellbore storage for groundwater, not for solute transport.

The wellbore storage for solute transport refers to the variation of the solute injected in the wellbore during the processes of the test. A complete SWPP test contains four principle phases: injection of a prepared solution (tracer) into a targeted aquifer; injection of a chaser; rest period; extraction of the mixture solution. The second and third phases are optional but are recommended to extend the reaction time of the tracer in the aquifer. In the injection phase, the concentration of the solute in the wellbore is smaller than the original concentration of the solute at the early stage, since the original solute could be diluted by the original water in the wellbore, due to the mixing effect. In the chaser phase, the concentration of the solute in the wellbore may be greater than the concentration of the chaser, due to the mixing effect. Similarly, in the rest phase, the concentration is also not 0. All these effects occurring in the wellbore is named wellbore storage for the solute transport, which was ignored by the analytical solutions and numerical solutions by Wang et al. (2017).

Actually, the above-mentioned assumptions used in the analytical and semi-analytical solutions can be relaxed in the numerical models, such as MODFLOW/MT3DMS (Zheng and Wang, 1999;Harbaugh et al., 2000), FEFLOW (Diersch, 2014), SUTRA (Voss, 1984), STOMP (Nichols et al., 1997), and so on. Huang et al. (2010), Sun (2016), Haggerty et al. (1998), and Schroth and Istok (2006) respectively employed such four software packages to carry out numerical simulations of SWPP tests, mainly involving advection, dispersion and first-order reaction. Unfortunately, the commercial numerical packages may create some errors in describe the solute transport in the region around the well, for instance, the volume of the water in the wellbore calculated by MODFLOW/MT3DMS may be not accurate. Meanwhile, none of these four software packages could deal with multi-species reactive transport problems with non-linear reactions. Therefore, Phanikumar and McGuire (2010) presented several multi-species reactive models of the SWPP test, which had the capability to describe user-defined reaction rates, including the Monod/Michaelis-Menten kinetics which was used to simulate the microbial processes. However, such model assumed that the hydraulic diffusivity was infinite and the wellbore storage was negligible for both groundwater and solute transport. For instance, Phanikumar and McGuire (2010) employed a Robin condition (or a third-type condition) with a constant concentration in the wellbore to describe the boundary condition of transport at wellbore during first three phases of the test, so did Wang et al. (2017). Specifically, the concentration of the solute in the wellbore was the same with the concentration of the original solute in the injection phase, and was 0 in the chaser and rest phases.

Obviously, the assumption of ignoring the wellbore storage is not reasonable for the solute transport. For instance, excluding the wellbore storage may overestimate the concentration in the wellbore in the injection phase, since the finite volume of water in the wellbore could dilute the solute concentration in the early stage before the pre-test water inside the wellbore was completely flushed out of the borehole into the aquifer. Similarly, one may conclude that such a treatment could underestimate the concentration in the wellbore in the early stage of the chase phase, due to the high concentration of solute in the wellbore at the end of the injection phase. Such an effect is called storage effect of solute transport in this study. As for the boundary condition of the wellbore in the rest phase, the concentration at the well screen may not be zero in the early stage of the rest phase, especially when the chase concentration was not zero.

This study addresses multi-species reactive transport associated with SWPP tests with a better conceptual model that acknowledges the realistic circumstances that have been either overlooked or overly simplified in previous investigations. Firstly, we will employ a more realistic finite hydraulic diffusivity instead of an infinite hydraulic diffusivity to describe the flow field. Secondly, we will propose a better way to handle the boundary condition of transport at the wellbore by consider the wellbore storage effect for both groundwater and solute transport during the SWPP tests. Thirdly, the new model is tested using the a field test dataset reported in McGuire et al. (2002).

## 2 Problem statement of the SWPP test

A cylindrical coordinate system is adopted with the *r*-axis horizontal and the *z*-axis vertically upward, as shown in Figure 1. The origin is at the center of the well and located in the plane of symmetry of the aquifer. The well fully penetrates a confined aquifer with a constant thickness. The aquifer is homogeneous, and the influence of the regional flow could be ignored.

### 2.1 Revisit of the previous model

Phanikumar and McGuire (2010) established a multi-species reactive transport model of the SWPP test, including three isotherm-based models (Freundlich, Langmuir and linear sorption models), one-site kinetic sorption and two-site sorption models. Meanwhile, the model could be used to describe biogeochemical reactive transport of an arbitrary number of species including Monod/Michaelis-Menten kinetics, and the model is

$$\frac{\partial C_i}{\partial t}+\frac{\rho_b}{\theta}\frac{\partial S_i}{\partial t}=-\sum_{j=1}^{N-1}\left[\mathcal{H}\left(t-t_j^*\right)-\mathcal{H}\left(t-t_{j+1}^*\right)\right]\lambda_j\,C_i^{n_j}\pm F_j, \tag{1}$$

where $C_i$ is the aqueous phase concentration of the $i^{\text{th}}$ reactive solute [ML$^{-3}$], $S_i$ is the solid phase concentration of the $i^{\text{th}}$ reactive solute [ML$^{-3}$], $t$ is the time in the SWPP test [T], $\rho_b$ is the bulk density, $\theta$ is the porosity, $\mathcal{H}$ is the Heaviside step function, $\lambda_j$ and $n_j$ are the constant and orders, $N$ is the number of the segment, $t_j^*$ and $t_{j+1}^*$ are the times at two ends of segment $j$, and $F_j$ Monod/Michaelis-Menten kinetics. For the purpose of the simplicity, we only present the reactive processes of the chemicals as described by Eq. (1), while the expressions of the transport (e.g. dispersion, diffusion, and advection) could be seen in Phanikumar and McGuire (2010).

However, the model of Phanikumar and McGuire (2010) contained several assumptions which may be debatable in actual applications and could be the source of errors. Firstly, the transport model is composed of a set of advection-dispersion equations (ADEs) built on the basis of flow velocity which is assumed to be time-independent:

$$v_r=\frac{Q}{2\pi rB\theta},\ r\geq r_w, \tag{2}$$

where $r_w$ is the well radius [L]; $r$ is the radius distance from the center of the well [L]; $\theta$ represents the porosity [dimensionless]; $B$ is the aquifer thickness [L]; $Q$ is the flow rate of the well [L$^3$T$^{-1}$]; $v_r=u_r/\theta$ is the average radial pore velocity [LT$^{-1}$] and $u_r$ is the radial Darcian velocities [LT$^{-1}$]. Eq. (2) implies that the hydraulic diffusivity of the aquifer is infinite, thus the flow velocity is independent of time. Meanwhile, the wellbore storage is negligible or the well radius $r_w$ is assumed to be infinitesimal in formulating Eq. (2).

The second assumption of the model is the boundary condition of the well screen in the rest phase of the SWPP test, in which a Robin condition (or a third-type condition) is employed to describe the aqueous solute transport (Phanikumar and McGuire, 2010;Wang et al., 2017):

$$\left(v_rC-D_r\frac{\partial C}{\partial r}\right)\Big|_{r\to r_w}=0,\ t_{inj}+t_{cha}<t\leq t_{inj}+t_{cha}+t_{res}, \tag{3}$$

where $t_{inj}$, $t_{cha}$, $t_{res}$, and $t_{ext}$, represent the durations [T] of the injection, chase, rest, and extraction phases, respectively; $C$ is resident concentration of the aqueous phase [ML$^{-3}$] to represent $C_i$ in Eq. (1); $D_r$ is the dispersion coefficient [L$^2$T$^{-1}$], which is

$$D_r = \alpha_r v_r + D_0, \quad (4)$$

in which $\alpha_r$ is the radial dispersivity [L]; $D_0$ is the effective diffusion coefficient in the aquifer [L$^2$T$^{-1}$].

Thirdly, a constant solute concentration in the wellbore is applied in the injection and chase phases without considering the solute diluted effect in the wellbore (Gelhar and Collins, 1971;Istok, 2012;Phanikumar and McGuire, 2010;Wang et al., 2017)

$$\left.\left(v_r C - D_r \frac{\partial C}{\partial r}\right)\right|_{r \to r_w} = v_r C_0^{inj}, \ 0 < t \le t_{inj}, \quad (5a)$$

$$\text{or } C|_{r \to r_w} = C_0^{inj}, \ 0 < t \le t_{inj}, \quad (5b)$$

$$\left.\left(v_r C - D_r \frac{\partial C}{\partial r}\right)\right|_{r \to r_w} = v_r C_0^{cha}, \ t_{inj} < t \le t_{inj} + t_{cha}, \quad (6a)$$

$$\text{or } C|_{r \to r_w} = C_0^{cha}, \ t_{inj} < t \le t_{inj} + t_{cha}, \quad (6b)$$

where $C_0^{inj}$ and $C_0^{cha}$ represent the solute concentrations injected into the wellbore during the injection and chase phases, respectively. A detailed discussion about mentioned-above assumptions can be seen in Phanikumar and McGuire (2010).

### 2.2 A revised model with a finite hydraulic diffusivity

As for the first assumption of Phanikumar and McGuire (2010), Wang et al. (2017) demonstrated that it might result in non-negligible errors in parameter estimation, particularly for the estimation of dispersivity. A minor point to note is that the model of Wang et al. (2017) mainly focused on conservative solute transport, rather than reactive transport. Nevertheless, the Darcian velocity is calculated by Darcy's law

$$u_r = K_r \frac{\partial s}{\partial r}, \quad (7)$$

where $K_r$ is the radial hydraulic conductivity [LT$^{-1}$]; $s$ is drawdown [L], which could be obtained by solving the following mass balance equation with the proper initial and boundary conditions

$$\frac{\partial u_r}{\partial r} + \frac{u_r}{r} = S_s \frac{\partial s(r,t)}{\partial r}, \ r \ge r_w, \quad (8)$$

$$s(r, t = 0) = 0, \quad (9)$$

$$u_r|_{r \to \infty} = 0, \quad (10)$$

$$2\pi B u_r|_{r \to \infty} - \pi r_w^2 \frac{ds_w(t)}{dt} = Q, \quad (11)$$

where $S_s$ is the specific storage of aquifer [L$^{-1}$]; $s_w$ is the drawdown inside the wellbore [L].

As for the second assumption in the rest phase, as shown Eq. (3), it implies that the concentration of solute is zero in the wellbore. This assumption works when the chase concentration is zero and the prepared solution is completely pushed out of the borehole into the aquifer at the end of the chase phase. Otherwise, the concentration in the early stage of the rest phase, which is close to the concentration at the end of the chase phase, is not zero. This is because the water level in the wellbore is greater than the hydraulic head in the surrounding aquifer due to the wellbore storage, resulting in a positive flux from the wellbore into the aquifer. Correspondingly, when the chase concentration is not zero or the prepared solution in the injection phase is not completely pushed out of the wellbore, the concentration in the wellbore may not be zero in the early stage of the rest phase.

In this study, we employed the Danckwerts condition for transport at the well screen in the rest period (Danckwerts, 1953)

$$\left.\frac{\partial C}{\partial r}\right|_{r\to r_w} = 0,\ t_{inj} + t_{cha} < t \le t_{inj} + t_{cha} + t_{res}. \tag{12}$$

Actually, Eq. (12) acknowledges the continuity of concentration and continuity of mass flux simultaneously across the well screen, namely, $C|_{r\to r_w^-} = C|_{r\to r_w^+}$ and $(v_r C)|_{r\to r_w^-} = \left.\left(v_r C - D_r \frac{\partial C}{\partial r}\right)\right|_{r\to r_w^+}$, where – and + signs in the subscript of $r_w$ represent approaching the well screen from inside the well and outside the well, respectively.

The third assumption mentioned in Section 2.1 seems not reasonable at the early stage of the injection and chase phases, because the concentration of the injected solute will be affected by the finite volume of water in the wellbore. Take the chase phase as an example: it is impossible to immediately reduce the solute concentration inside the wellbore from a certain level during the tracer injection phase to zero when switching to the chase phase, even when the solute concentration in the chase phase is zero. This is because the wellbore with a finite radius contains a certain finite mass of solute at the moment of switching from injection of a tracer to injection of a chaser. Therefore, it will take some time to completely flush out the residual tracer inside the wellbore after the start of the chase phase, and a larger wellbore will take a longer time to flush out the residual tracer inside the wellbore. This means that the concentration at the wellbore/aquifer interface will not drop to zero immediately after the start of the chase phase. Instead, it will take a finite period of time to gradually approach zero during the chase phase. Similarly, the boundary condition of the well screen in the injection phase might not be appropriate in previous studies if the wellbore storage effect is of a concern. Therefore, the value of solute concentration inside the wellbore should be smaller or equal to $C_0^{inj}$ in the injection phase and greater or equal to $C_0^{cha}$ in the chase phase.

Here, we will develop a new approach to take care of the concentration in the wellbore in the injection and chase phases based on the mass balance principle, i.e.,

$$\Delta m = C_0^{inj} Q \Delta t = C_w^{t+\Delta t}(V^t + Q\Delta t) - C_w^t V^t,\ 0 < t \le t_{inj}, \tag{13}$$

$$\Delta m = C_0^{cha} Q \Delta t = C_w^{t+\Delta t}(V^t + Q\Delta t) - C_w^t V^t,\ t_{inj} < t \le t_{inj} + t_{cha}, \tag{14}$$

where $\Delta m$ represents the mass entering into the well during time interval$\Delta t$; $C_w^t$ and $C_w^{t+\Delta t}$ represent the solute concentrations in the wellbore at the time $t$ and $t + \Delta t$, respectively; $V^t$ represents the volume of water in the wellbore at the time $t$. The initial values of $C_w^t$ and $V^t$ at the injection phase are

$$C_w^t|_{t=0} = 0, \tag{15}$$

$$V^t|_{t=0} = \pi r_w^2 (H_w|_{t=0}), \tag{16}$$

where $H_w$ represents the water depth of the wellbore.

In the chase phase, one has

$$C_w^t|_{t=t_{inj}^-} = C_w^t|_{t=t_{inj}^+}, \tag{17}$$

$$V^t|_{t=t_{inj}^+} = \pi r_w^2 \left(H_w|_{t=t_{inj}^+}\right), \tag{18}$$

where the - and + signs in the subscripts of Eqs. (17) - (18) hereinafter represent approaching the limit from left and right sides of $t_{inj}$, respectively.

## 2.3 Capability of the new SWPP model of this study

Different from the model of Wang et al. (2017), the multi-species reactive transport models are used to describe the non-linear biogeochemical reactive processes with considering the wellbore storage not only for the groundwater flow but also for the solute transport. The new model of this study is an extension of Phanikumar and McGuire (2010) that ignored the wellbore storage for both groundwater flow and solute transport, and considered an infinite aquifer hydraulic diffusivity. The Danckwerts condition rather than the Robin condition is applied at the well screen in the rest phase of this study. Therefore, the new model is more powerful in describing an arbitrary number of species and user-defined reaction rate expressions, including Monod/Michaelis-Menten kinetics.

## 3 Numerical solution of the SWPP test

In this study, we will use a finite-difference method to solve the model of the SWPP test, where the finite-difference scheme of the groundwater flow is the same with Wang et al. (2017), and the scheme of the transport governing equation (ADE) is similar to the model of Phanikumar and McGuire (2010). However, the flow velocity used in the advective term of ADE is computed by solving the model of groundwater flow rather than directly using Eq. (2), which was employed by Phanikumar and McGuire (2010).

To minimize numerical errors and to increase computational efficiency, we employ a non-uniform grid system for simulations (Wang et al., 2014), which is:

$$r_i = \frac{r_{i-1/2}+r_{i+1/2}}{2}, i = 1, 2, 3, \cdots, N, \tag{19}$$

where $N$ represents the number of nodes in discretization of the spatial domain [$r_w$, $r_e$], $r_w$ and $r_e$ respectively represent the distances of inner and outer boundary nodes; $r_i$ is the radial distance of node; $r_{i+1/2}$ is calculated as follows

$$log_{10}(r_{i+1/2}) = log_{10}(r_w) + i\left[\frac{log_{10}(r_e)-log_{10}(r_w)}{N}\right], i = 0, 1, 2, \cdots, N. \tag{20}$$

The value of $r_{i-1/2}$ can be calculated using the similar way. Eqs. (19) - (20) represent a space domain discretized logarithmically, and the spatial steps are smaller near the wellbore and become progressively greater away from the wellbore.

Similarly, we logarithmically discretize the temporal domain:

$$t_i = \frac{t_{i-1/2}+t_{i+1/2}}{2}, i = 1, 2, 3, \cdots, M, \quad (21)$$

where $M$ represents the number of nodes in discretization of the temporal domain; $t_i$ is the time of node $i$; $t_0$ is a very small positive value representing the first time step, such as $1.0\times10^{-7}$ days, $t_{i+1/2}$is calculated as follows in the injection phase

$$log_{10}(t_{i+1/2}) = log_{10}(t_0) + i\left[\frac{log_{10}(t_{inj})-log_{10}(t_0)}{M}\right], i = 1, 2, 3, \cdots, M. \quad (22)$$

As for the chase, one has

$$t_{i+1/2} = 10^{log_{10}(t_0)+i\left[\frac{log_{10}(t_{cha})-log_{10}(t_0)}{M}\right]} + t_{inj}, i = 1, 2, 3, \cdots, M. \quad (23)$$

Similarly, in the rest phase, one has

$$t_{i+1/2} = 10^{log_{10}(t_0)+i\left[\frac{log_{10}(t_{res})-log_{10}(t_0)}{M}\right]} + t_{inj} + t_{cha}, i = 1, 2, 3, \cdots, M. \quad (24)$$

In the extraction phase, one has

$$t_{i+1/2} = 10^{log_{10}(t_0)+i\left[\frac{log_{10}(t_{ext})-log_{10}(t_0)}{M}\right]} + t_{inj} + t_{cha} + t_{res}, i = 1, 2, 3, \cdots, M. \quad (25)$$

Before the use of the new model of this study, it is necessary to evaluate the numerical errors (like artificial oscillation and numerical dispersion) of the solution. Unfortunately, the benchmark analytical solutions of the SWPP test with a finite hydraulic diffusivity are not available up to date. Alternatively, the accuracy of the finite-difference solution could be tested by comparing with the numerical solution of Wang et al. (2017) which was proven to be accurate and robust. Figure 2 shows the comparison of BTCs between the solution of Wang et al. (2017) and of this study, where the parameters used are similar to Figure 3 of Phanikumar and McGuire (2010): $B$=8 m, $r_w$=0.052 m, $\alpha_r$=1 m, $\theta$=0.38 m, $D_0$=0 m$^2$/day, $t_{inj}$=94.32 day, $t_{cha}$=0 day, $t_{res}$=0 day, $t_{ext}$=405.6 day, injection flow rate $Q_{inj}$=2.587 m$^3$/day, and extraction flow rate $Q_{ext}$=-2.282 m$^3$/day.

By comparing the solution of this study with Wang et al. (2017), one may conclude that the solution of this study appears to be accurate and reliable. In the wellbore ($r = r_w$), the concertation is equal to $C_0^{inj}$, as shown in Figure 2. This is due to the boundary condition of the wellbore, e.g.,

$$C|_{r\to r_w} = C_0^{inj}, 0 < t \leq t_{inj}. \quad (26)$$

In the aquifer, the values of BTCs increase with the decreasing distance from the wellbore.

## 4 Discussions

Revisiting the assumptions used in previous studies as mentioned in Sections 2.1 and 2.2, one may find that the flow field is a key factor for the SWPP test. This is not surprising, since the flow velocity is not only included in the advective term, but also in the dispersive term. Meanwhile, the volume of pre-test water in the wellbore (i.e., the wellbore storage) may influence the concentration of the solute injected into the wellbore. In this section, we mainly investigate the influence of the flow field and the boundary conditions on the multi-species reactive transport in the SWPP test.

Subject to the discharge or recharge of the well, the flow field is mainly controlled by the hydraulic diffusivity of the aquifer and the wellbore storage. In the following discussion, we choose three representative types of porous media to test the influence of the hydraulic diffusivity on the results of the SWPP test, including fine sand, medium sand, and coarse sand. According to Domenico and Schwartz (1990) and Batu (1998), one could obtain the values of the hydraulic diffusivity for above mentioned three types of media: $1.0\times10^3$ $m^2$/day (with $K_r$ = $1.0\times10^{-1}$ m/day and $S_s$ = $1.0\times10^{-4}$ $m^{-1}$) for the fine sand, $1.0\times10^4$ $m^2$/day (with $K_r$= 1.0 m/day and $S_s$ = $1.0\times10^{-4}$ $m^{-1}$) for the medium sand, and $1.0\times10^6$ $m^2$/day (with $K_r$= 10.0 m/day and $S_s$ = $1.0\times10^{-5}$ $m^{-1}$) for the coarse sand. Generally, the hydraulic diffusivity of the aquifer correlates to the grain size of the media, and the value is smaller for the smaller grain size, e.g., fine sand.

The parameters related to the solute transport mainly come from the studies of Phanikumar and McGuire (2010), who interpreted the field experimental data of the SWPP test conducted by McGuire et al. (2002). Except for parameters specifically mentioned otherwise, the default values used in the following section are $C_0^{inj}$=100.0 mg/L, $C_0^{cha}$=10.0 mg/L, $B$=0.1 m, $r_w$=0.0125 m, $\alpha_r$=0.01 m, $\theta$ =0.33 m, $D_0$=0 $m^2$/day, $t_{inj}$=0.6 hour, $t_{cha}$=0.067 hour, $t_{res}$=0.0333 hour, $t_{ext}$=3.6 hour, $Q_{inj}$=0.0333 $m^3$/hour, $Q_{cha}$=0.0255 $m^3$/hour, and $Q_{ext}$=-0.011 $m^3$/hour, which can be found in Figure 5 of Phanikumar and McGuire (2010).

## 4.1 Effect of boundary condition in the rest phase

Figures 3A and 3B show the comparison of BTCs between the Robin and Danckwerts conditions at the wellbore for different porous media, where $C_0^{cha}$=10.0 mg/L in Figure 3A and $C_0^{cha}$=0.0 mg/L in Figure 3B. For the purpose of comparison, the boundary conditions at the wellbore in the injection and chase phases are still described by Eqs. (5) - (6). The chemical reaction is not included in the comparison study of this section.

Figure 3A shows that the difference of BTCs between two boundary conditions is significant at the early stage of the extraction phase when $C_0^{cha}$=10.0 mg/L, and BTCs of the Danckwerts condition are above BTCs of the Robin condition. With time going, such a difference becomes negligible. As for the curves of the Robin condition, the solute concentration in the wellbore is 0 in the chase phase, correspondingly, the concentration starts from 0 at the early stage of the extraction phase. Actually, the solute concentration in the wellbore may be not 0 in the rest phase due to the wellbore storage and finite hydraulic diffusivity when $C_0^{cha}$=10.0 mg/L. Another interesting observation is that the properties of the porous media could also influence the difference of BTCs between two boundary conditions. Obviously, a smaller hydraulic diffusivity would result in a larger difference between them, e.g., such a difference is greater for the fine sand aquifer.

Figure 3B shows the comparison of BTCs for different boundary conditions in the wellbore when $C_0^{cha}$=0.0, and one could find that the difference of BTCs between the Robin and Danckwerts conditions is negligible, which implies that the Robin condition performs well when $C_0^{cha}$=0.0, while not for the case $C_0^{cha}$ $\neq$0.0.

### 4.2 Effect of boundary condition in the injection and chase phases

Figure 4 shows the comparison of BTCs in the wellbore for different boundary conditions and different porous media. The parameters used in this case are the same as ones in Section 4.1. The initial head is 1 m. The boundary condition of the wellbore in the rest phase is described by the Danckwerts condition. The chemical reaction is not included in this comparison study.

Two interesting observations can be seen. Firstly, the difference of BTCs between the two boundary conditions at the wellbore is obvious, and such a difference is larger for the medium sand than for the coarse sand, implying that it increases with the decreasing hydraulic diffusivity. Secondly, the values of BTCs obtained from Eqs. (13) - (14) are greater at the early stage of the extraction phase, while the peak values of BTC are smaller. In another word, the model of Eqs. (13) - (14) may underestimate the concentration in the early stage of the extraction phase, while overestimate the peak values of BTCs.

These observations can be explained as follows. The model of Eqs. (5) - (6) assumes that the volume of water in the wellbore is negligible, and the concentration in the wellbore is close to10.0 mg/L in the rest phase, due to $C_0^{cha}$=10.0 mg/L. As for the model of Eqs. (13) - (14), the volume of water in the wellbore is non-negligible and could dilute the concentration in the injection phase; namely, the solute concentration in the wellbore could not immediately rises to $C_0^{inj}$ at the early stage of the injection phase, thus resulting in smaller peak values of BTCs. Similarly, the concentration in the wellbore could not immediately reduce to $C_0^{cha}$ at the early stage of the chase phase, which makes the concentration larger at the early stage of the extraction phase based on the model of Eqs. (13) - (14).

### 4.3 Effect of the flow field on the chemical reactions

The complex biogeochemical reactions are still active research subjects in subsurface hydrology, and one of the simplest models of such reactions may be the first-order reaction

$$\frac{\partial C}{\partial t} = -\lambda C, \tag{27}$$

where $\lambda$ is the first-order reaction rate constant. Beside the first-order reaction, Eq. (27) could be used to describe the first-order biodegradation and radioactive decay. Haggerty et al. (1998) presented a simplified method to estimate $\lambda$ for the SWPP test:

$$\ln\left(\frac{C_{rec}(t^*)}{C_{tra}(t^*)}\right) = \ln\left(\frac{1-exp(-\lambda t_{inj})}{\lambda t_{inj}}\right), \tag{28}$$

where $t^*$ is time since the end of injection; $C_{rec}(t^*)$ is the reactant concentration; $C_{tra}(t^*)$ is the concentration of a conservative tracer. To obtain the value of $\lambda$, the reactant and the conservative tracer should be fully mixed and injected into the aquifer simultaneously to conduct the SWPP test. After measuring the data of $C_{rec}(t^*)$ and $C_{tra}(t^*)$ in the extraction phase, one could fit the data of $\ln\left(\frac{C_{rec}(t^*)}{C_{tra}(t^*)}\right) \sim t^*$ using a linear function and the slope of $t^*$is the estimation of $\lambda$. Snodgrass and Kitanidis (1998) derived a similar model for estimating $\lambda$:

$$\ln\left(\frac{C_{rea}(t^*)}{C_{tra}(t^*)}\right) = \ln\left(\frac{C_{rec}^0}{C_{tra}^0}\right) - \lambda t^*. \tag{29}$$

Comparing Eq. (28) with Eq. (29), one could find that the difference is the first terms on the right sides of equations, while $\lambda$ is the slope for both Eqs. (28) and (29). Although the accuracy of both models has been tested by a number of investigators, previous studies on reactive transport were based on an assumption that the aquifer hydraulic diffusivity was infinite (e.g. Eq. (1) of Reinhard et al. (1997) , and Eq. (2) of Haggerty et al. (1998)).

To test the validation of Eqs. (28) - (29) with a finite aquifer hydraulic diffusivity, we will use the model of this study to reproduce the data of $\ln(C_{rec}/C_{tra})\sim t^*$ based on a set of given parameters, and then using Eqs. (28) - (29) (which is based on an infinite hydraulic diffusivity presumption) to estimate $\lambda$ (denoted as $\tilde{\lambda}$) by best fitting $\ln(C_{rec}/C_{tra})\sim t^*$. Two species involved in this case are $Cl^{-1}$ and $SO_4^{-2}$, in which $C_{tra}$ and $C_{rec}$ represent the concentrations of $Cl^{-1}$ and $SO_4^{-2}$, respectively. Figure 5 shows the fitness of the simulated $\ln(C_{rec}/C_{tra})\sim t^*$ in the wellbore using a linear function, with the detailed information shown in Table 1. Two sets of $\lambda$ are employed in the discussions for the reactant, e.g. $\lambda$ =0.1 hour$^{-1}$ and 0.2 hour$^{-1}$. One may conclude that the simplified models of Eqs. (28) - (29) with an infinite hydraulic diffusivity perform well in the estimation of $\lambda$ for reactive transport under the finite hydraulic diffusivity condition.

This simplified model of Eq. (29) has been widely used to estimate $\lambda$, due to the advantages that $\lambda$ could be determined directly by best fitting observed $\ln(C_{rec}/C_{tra})\sim t^*$, without the knowledge of the aquifer properties, such as porosity, dispersivity, hydraulic diffusivity. However, this model is proposed based on the first-order reaction, which is a linear reaction, as shown in Eq. (27). Whether this approach still work for non-linear reactions is still questionable, and will be investigated in the following section.

Assuming that the extraction time since the rest phase ended could be divided into $N$-1 segments, Phanikumar and McGuire (2010) employed the Heaviside unit step function to describe a type of non-linear biogeochemical reaction:

$$\frac{\partial C}{\partial t} = -\sum_{j=1}^{N-1}\left[\mathcal{H}\left(t-t_j^*\right) - \mathcal{H}\left(t-t_{j+1}^*\right)\right]\lambda_j C_i^{n_j}, \tag{30}$$

where $\lambda_j$ is the reaction constant in the temporal segment $j$, and the Heaviside step function $\mathcal{H}(\cdot)$ is:

$$\mathcal{H}\left(t-t_j^*\right) - \mathcal{H}\left(t-t_{j+1}^*\right) = \begin{cases} 0 & if\ t < t_j^* \\ 1 & if\ t_j^* < t < t_{j+1}^* \\ 0 & if\ t_{j+1}^* < t \end{cases}. \tag{31}$$

Eq. (30) is a series of piece-wise linear ($n_j$ =1) or non-linear ($n_j \neq$ 1) functions, which are an extension of Eq. (27).

To test the influence of the hydraulic diffusivity on the accuracy of this approach in estimating $\lambda_j$ for the non-linear reactions, the model of this study is used to reproduce the data of $\ln(C_{rec}/C_{tra})\sim t^*$ with a set of specific $\lambda_j$, $n_j$ and $t_j^*$ for three types of porous media. Figures 6 and 7 represent the computed $\ln(C_{rec}/C_{tra})\sim t^*$ based on the model of the chemical reactions described by the piece-wise linear and the non-linear functions, respectively. The values of $\lambda_j$ and $t_j^*$ of Figure 6 are obtained by fitting the observation data using a piecewise linear function (e.g., $n_j$ =1) proposed by Phanikumar and McGuire (2010). The circle represents the experiments data observed by McGuire et al. (2002). The parameters related to the chemical reactions in Figure 7 are from Phanikumar and McGuire (2010) by fitting the observation data using a nonlinear function: $\lambda_j$ =0.25, $n_j$ =0.25, $N$=$j$=1. Comparing Figures 6 and 7, one may find that the influence of the hydraulic diffusivity on the computed $\ln(C_{rec}/C_{tra}){\sim}t^*$ is negligible for the chemical reaction described by the piecewise linear function, which is similar to the first-order reaction as shown in Figure 5. However, the influence of the hydraulic diffusivity on the relationship of $\ln(C_{rec}/C_{tra}){\sim}t^*$ cannot be ignored if one attempts to use nonlinear functions to describe such a chemical reaction. The difference between the curves of different porous media is obvious in Figure 7. The agreement between the observed and computed data is well for the medium and coarse sands, but not for the fine sand in Figure 7. This is because the hydraulic diffusivity values of the medium and coarse sands are larger than that of the fine sand, thus are close to the assumption of an infinite hydraulic diffusivity used in Phanikumar and McGuire (2010).

Therefore, one may conclude that $\lambda_j$, $n_j$ and $t_j^*$ could be determined by directly best fitting the observed $\ln(C_{rec}/C_{tra}){\sim}t^*$ when the non-linear reactions are described by the piece-wise linear functions, in a similar way to estimate the linear reaction rate by Eq. (29). However, such an approach may not work if one attempts to use non-linear functions to describe such non-linear reactions.

## 5 Field applications

To test the model of this study, the field data of a SWPP test conducted in a single well by McGuire et al. (2002) will be employed. In this test, the prepared solution contains $Na_2SO_4$ (as a reactant) and NaCl (as a conservative tracer). The reactant and the tracer were well mixed and then injected into a targeted aquifer.

### 5.1 Revisit of previous model

Phanikumar and McGuire (2010) interpreted such data using a model containing several assumptions mentioned in Section 2.1. The parameters used in their model were $B$=0.1 m, $r_w$=0.0125 m, $\alpha_r$=0.001 m, $\theta$ =0.33 m, $D_0$=0 m$^2$/day, $t_{inj}$=0.6 hour, $t_{cha}$=0.067 hour, $t_{res}$=0.0333 hour, $t_{ext}$=3.6 hour, $Q_{inj}$=0.0333 m$^3$/hour, $Q_{cha}$=0.0255 m$^3$/hour, and $Q_{ext}$=-0.011 m$^3$/hour. The concentrations of NaCl were $C_0^{inj}$=100.0 mg/L in the injection phase and $C_0^{cha}$=10.0 mg/L in the chase phase. As for the reactant of $Na_2SO_4$, the concentrations were $C_0^{inj}$=20.0 mg/L and $C_0^{cha}$=2.0 mg/L. The results showed that the fitness between the computed and observed BTCs was very well, as shown in Figure 8A of this study, or Figure 5 of Phanikumar and McGuire (2010). Figure 8A of this study shows the comparison of the observed BTCs, the computed BTCs by PPTESE in the aquifer at $r$= $r_w$+0.15 m, and the computed BTCs of this study in the aquifer at $r$= $r_w$+0.15 m. The legend of “PPTEST” represents the solution of Phanikumar and McGuire (2010), and the others are produced by the solution of this study. Figure 8B shows the computed BTCs of this study in the well for different hydraulic diffusivities. The parameters of these two figures related to the solute transport are the same with the model of Phanikumar and McGuire (2010). For the purpose of comparison, Eqs. (5) - (6) are used as the boundary conditions at the well screen.

Interestingly, we have observed an unusual feature that the initial concentrations of $Na_2SO_4$ and NaCl are not zero in Figure 8A of this study or Figure 5 of Phanikumar and McGuire (2010), while they are far greater than the chase concentration. It seems difficult to interpret such an observation in the wellbore using previous models, as shown in Figure 8B. By carefully checking the report of Phanikumar (2010), we found that the computed BTCs were at a radial distance of 0.15 m from the wellbore, rather than at the wellbore itself in Phanikumar (2010).

From Figures 8A and 8B, several interesting observations could be made. Firstly, the difference of BTCs among different porous media is obvious. BTCs of the coarse sand aquifer are close to the solution of PPTEST, as shown in Figure 8A. This is because the hydraulic diffusivity of the coarse sand aquifer is the largest, which is close to the assumption used in the PPTEST that hydraulic diffusivity is infinity. Secondly, the wellbore concentration is 10 mg/L at the early stage of the extraction phase for $Cl^-$. This is mainly due to the chosen boundary condition at the well screen, which has been discussed in details in Section 4.1. Thirdly, the peak values of BTCs increase with the decreasing hydraulic diffusivity, and the arrival times of peak values increase with the decreasing hydraulic diffusivity. Such an observation is also found in Figures 3A and 3B. Fourthly, the configuration of BTCs in the aquifer (at $r= r_w$+0.15 m) computed by the model of this study shows that the concentration firstly decreases with time, then increases with time, as shown in Figure 8A. This observation could be explained by the corresponding flow field, as shown in Figure 9. Looking at the flow velocity in the aquifer at $r= r_w$+0.15 m, one may find that the flow direction is still outward from the wellbore in the early stage of the extraction phase, due to the finite hydraulic diffusivity. The outward flow will persist for a finite period of time, depending on the value of the hydraulic diffusivity, and then reverse its direction to flow towards the wellbore for the rest of the extraction phase. This feature is very different from the results with an infinite hydraulic diffusivity assumption, in which the flow direction is always towards the wellbore for the entire extraction phase.

### 5.2 Fitness of this study

In this study, we try to use the new model of this study to interpret BTCs of the SWPP test, considering a finite hydraulic diffusivity, a finite wellbore storage, and new boundary conditions of the wellbore at the injection, chase and rest phases. Assuming the initial head of the flow field is 1 m. In a trial and error process of best fitting the observed BTC data, we only estimate parameters of $K_r$, $S_s$ and $\alpha_r$, while the other parameters are the same with those used for producing Figure 5 of Phanikumar and McGuire (2010). Figure 10 demonstrates the fitness of the observed BTC data in the wellbore when $K_r$ = 1.0 m/hour, $S_s$ = $1.0\times10^{-5}$ $m^{-1}$ and $\alpha_r$=0.015 m. Comparing with $\alpha_r$=0.001 m estimated by Phanikumar and McGuire (2010), the dispersivity estimated in this study is 15 times greater. The significant difference of dispersivity estimated in this study ($\alpha_r$=0.015 m) and that of Phanikumar and McGuire (2010) ($\alpha_r$=0.001 m) is probably because of the fundamental difference in the mathematical model of flow and transport, as this study acknowledges the influences of finite aquifer hydraulic diffusivity and wellbore storage not only on flow, but also on transport process, while such influences were ignored in previous study of Phanikumar and McGuire (2010).

## 6 Summary and conclusions

A complete SWPP test includes injection, chase, rest and extraction phases, where the second and third phases are not necessary but are recommended to increase the duration of reaction. Due to the complex mechanics of biogeochemical reactions, aquifer properties, and so on, previous mathematic or numerical models contain some assumptions which may over simplify the actual physics, for instance, the hydraulic diffusivity of the aquifer is infinite. The Robin or the third-type boundary condition was often used in previous studies at the well screen in the injection, chase and rest phases by ignoring the mixing effect of the volume of water in the wellbore (namely, wellbore storage). In this study, we presented a multi-species reactive SWPP model considering the wellbore storage for both groundwater flow and solute transport, and a finite aquifer hydraulic diffusivity. The models of wellbore storage for both solute transports are derived based on the mass balance. The Danckwerts boundary condition instead of the Robin condition is employed for solute transport across the well screen in the rest phase. The robustness of the new model is tested by the field data. The following conclusion can be made from this study:

(1) The influence of wellbore storage for the solute transport increases with the decreasing hydraulic diffusivity in the injection and chase phases, and the model of Eqs. (13) - (14) underestimates the concentration in the early stage of the injection phase, while overestimates the peak values of BTCs.

(2) The values of $\lambda_j$, $n_j$ and $t_j^*$ could be determined by directly best fitting the observed $\ln(C_{rec}/C_{tra}) \sim t^*$ when the non-linear reactions are described by the piece-wise linear functions, while such an approach may not work if one attempts to use non-linear functions to describe such non-linear reactions.

(3) The Robin condition used to describe the wellbore flux in the rest phase works well only when the chase concentration is zero and the prepared solution in the injection phase is completely pushed out of the borehole into the aquifer, while the Danckwerts boundary condition performs betters even when the chase concentration is not zero.

(4) In the extraction phase, the peak values of BTCs increase with the decreasing hydraulic diffusivity, and the arrival time of the peak value becomes shorter when the hydraulic diffusivity is smaller.

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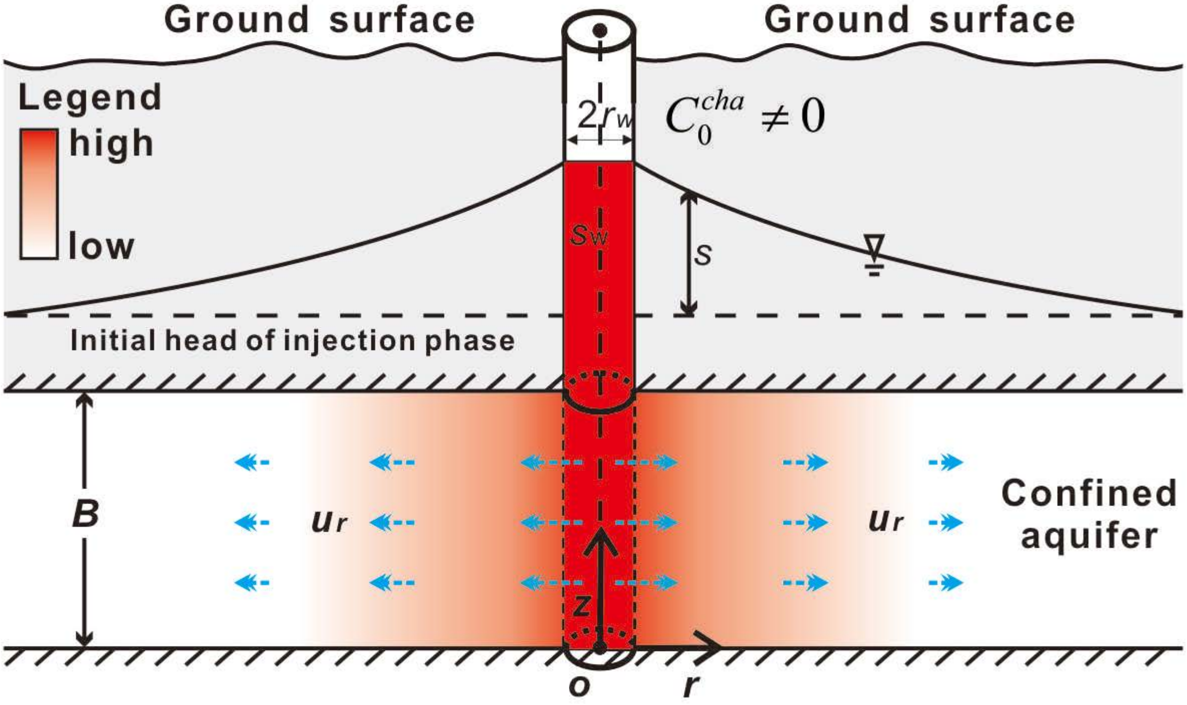


**Figure 1. The schematic diagram of the SWPP test at the beginning of the rest phase when the chase concentration is not 0.**

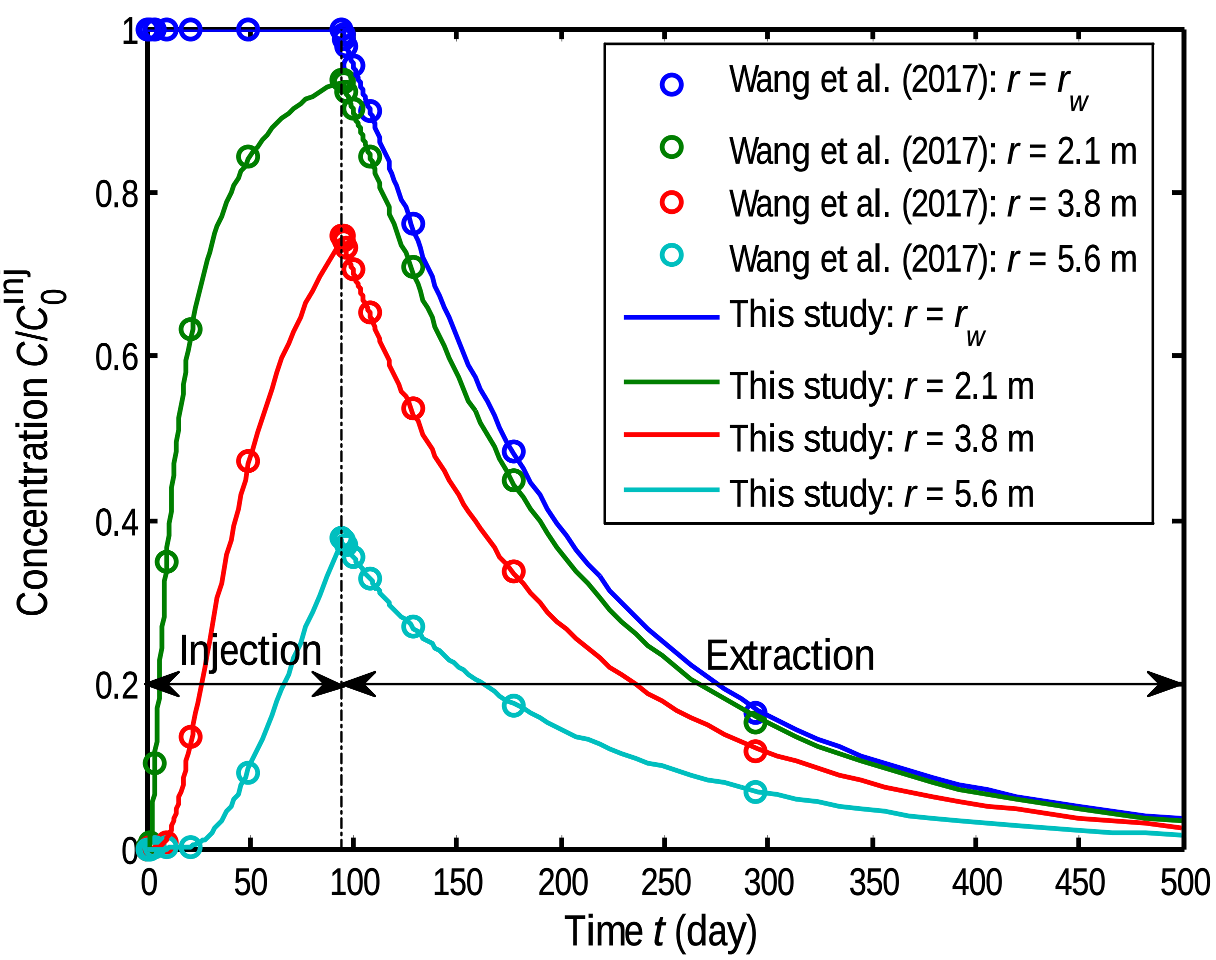
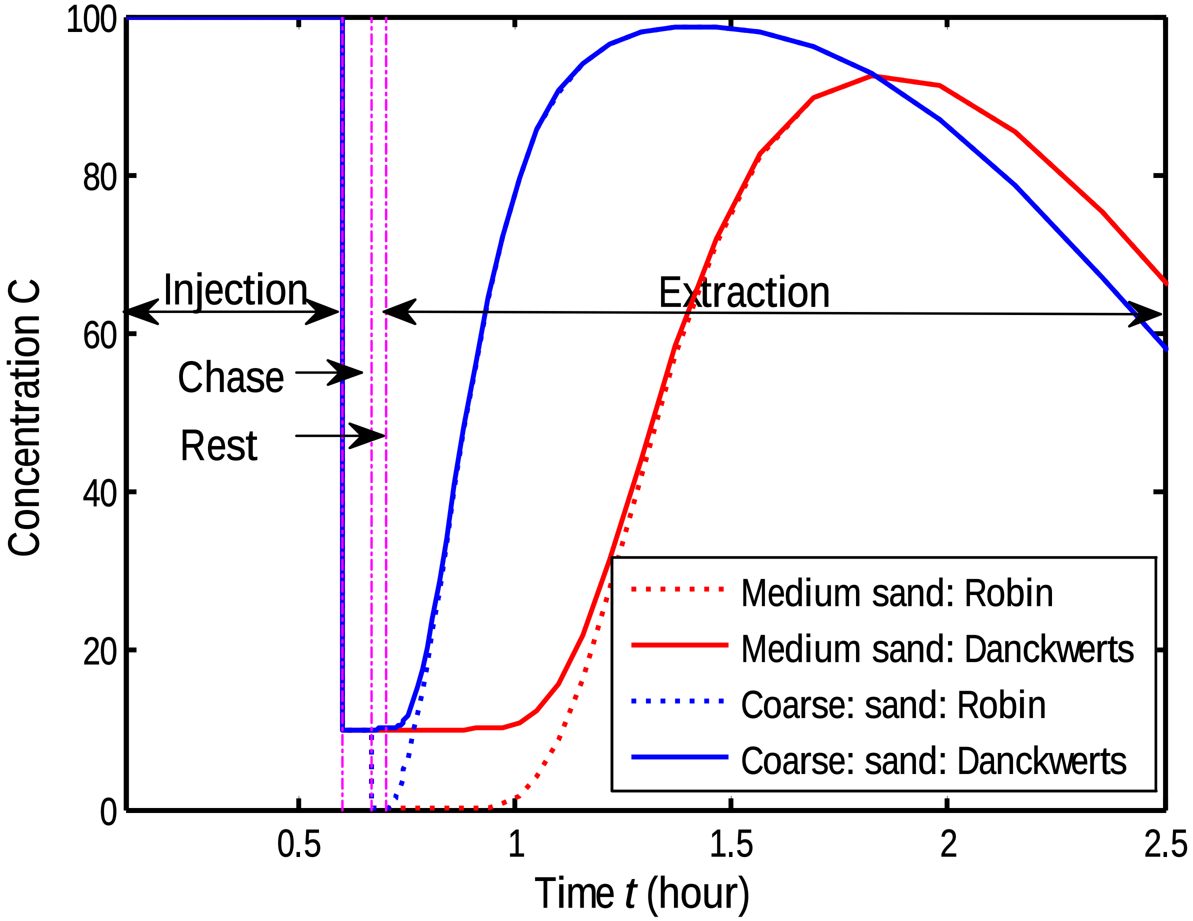
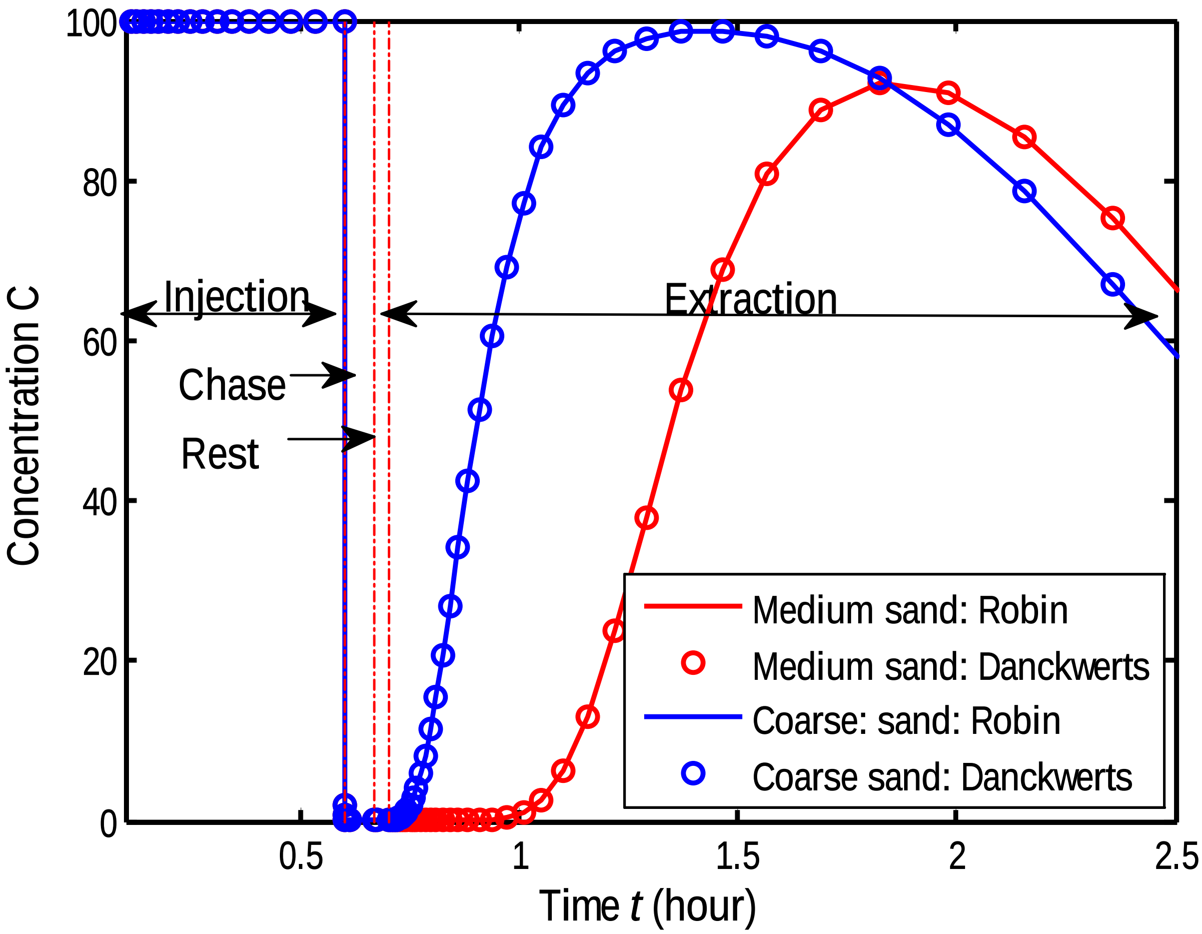


**Figure 2. Comparison of BTCs between the solutions of Wang et al. (2017) and of this study, where $C_0^{inj}$ represents the concentration of the prepared solute in the injection phase.**

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-181
Manuscript under review for journal Hydrol. Earth Syst. Sci.
Discussion started: 22 June 2018



**A**



**B**

**Figure 3. Comparison of BTCs in the wellbore between the Robin and Danckwerts conditions: A.** $C_0^{cha}$ **=10.0 mg/L, B.** $C_0^{cha}=0$.

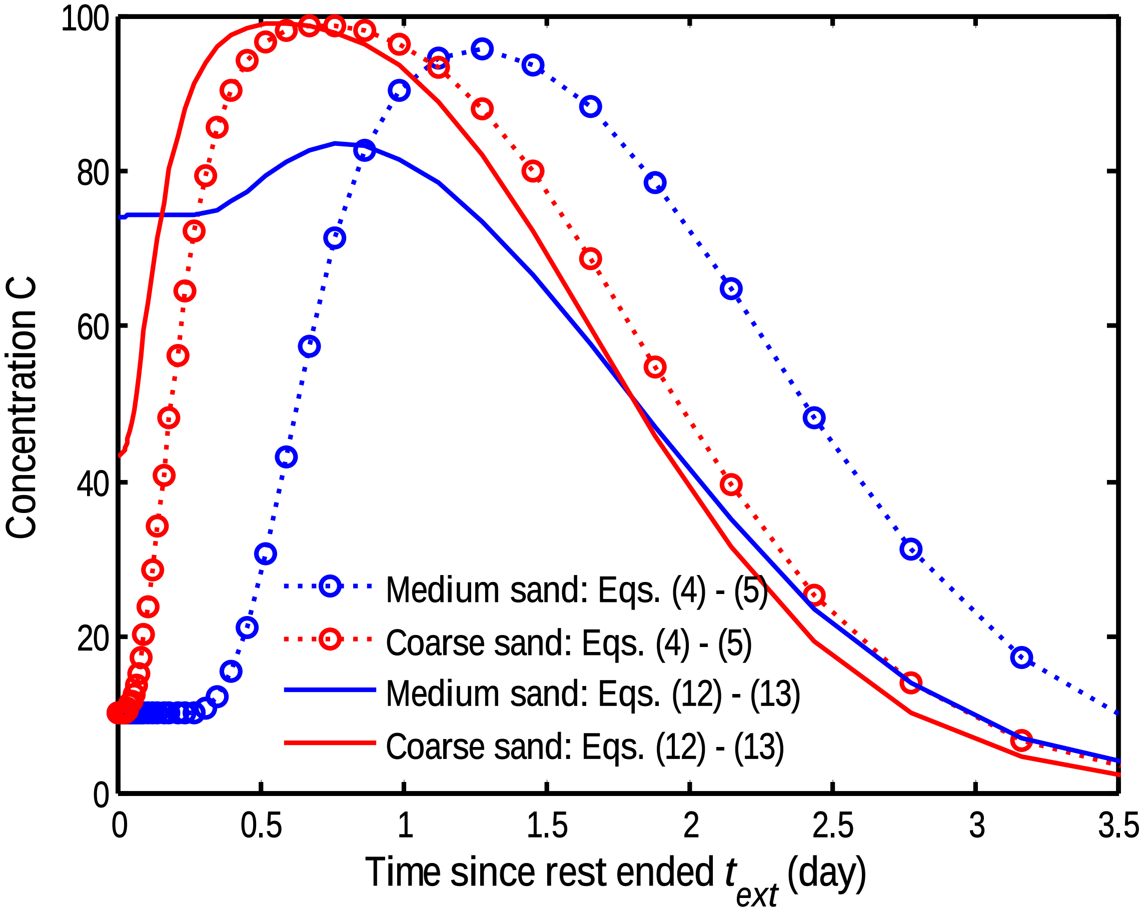


**Figure 4. The BTCs in the wellbore for the different boundary conditions at the wellbore in the injection and chase phases.**

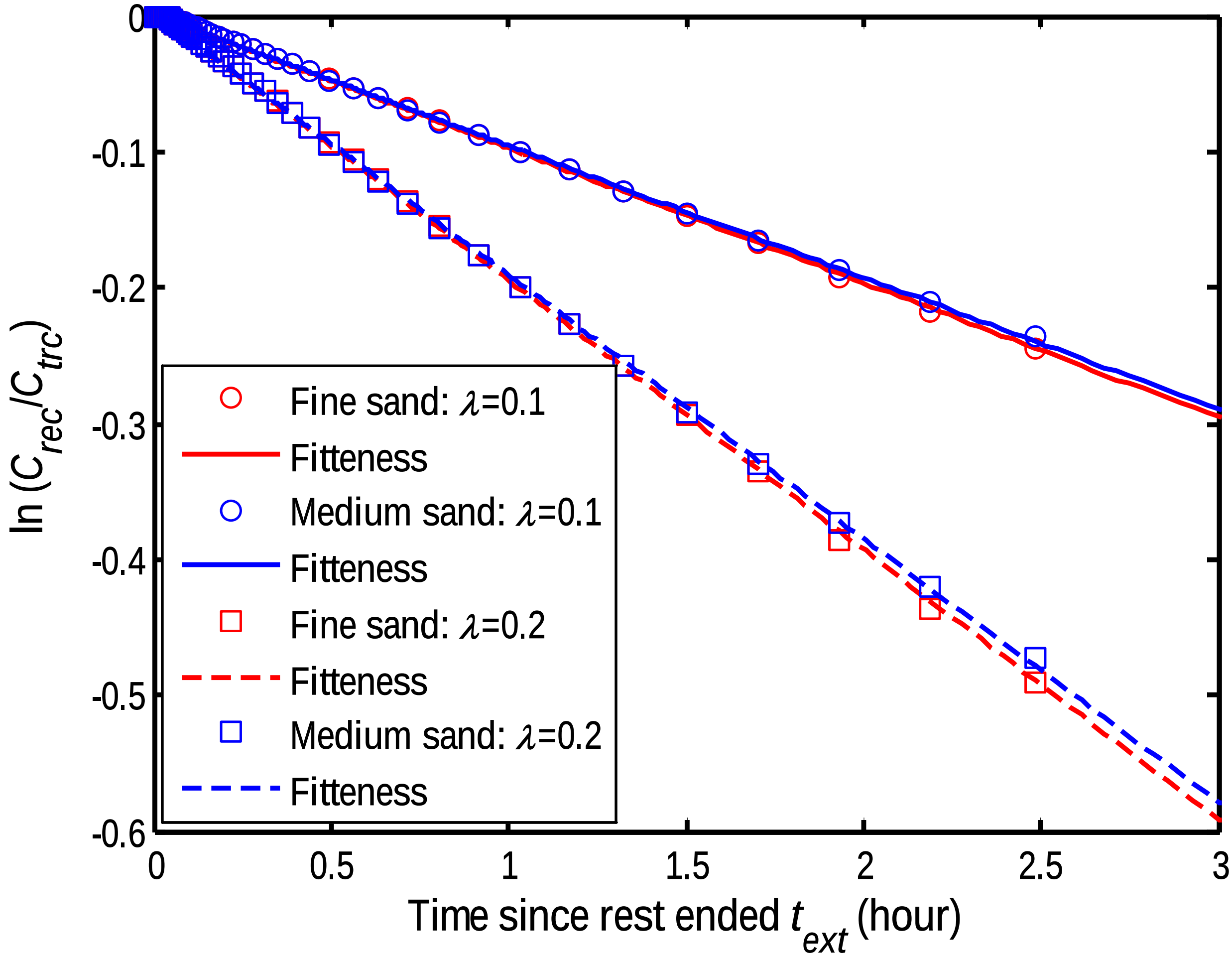


**Figure 5. Fitness of $\ln\left[C_{rec}/C_{tra}\right] \sim t^{*}$ produced by the numerical solution of this study with the first order reaction in the different porous media.**

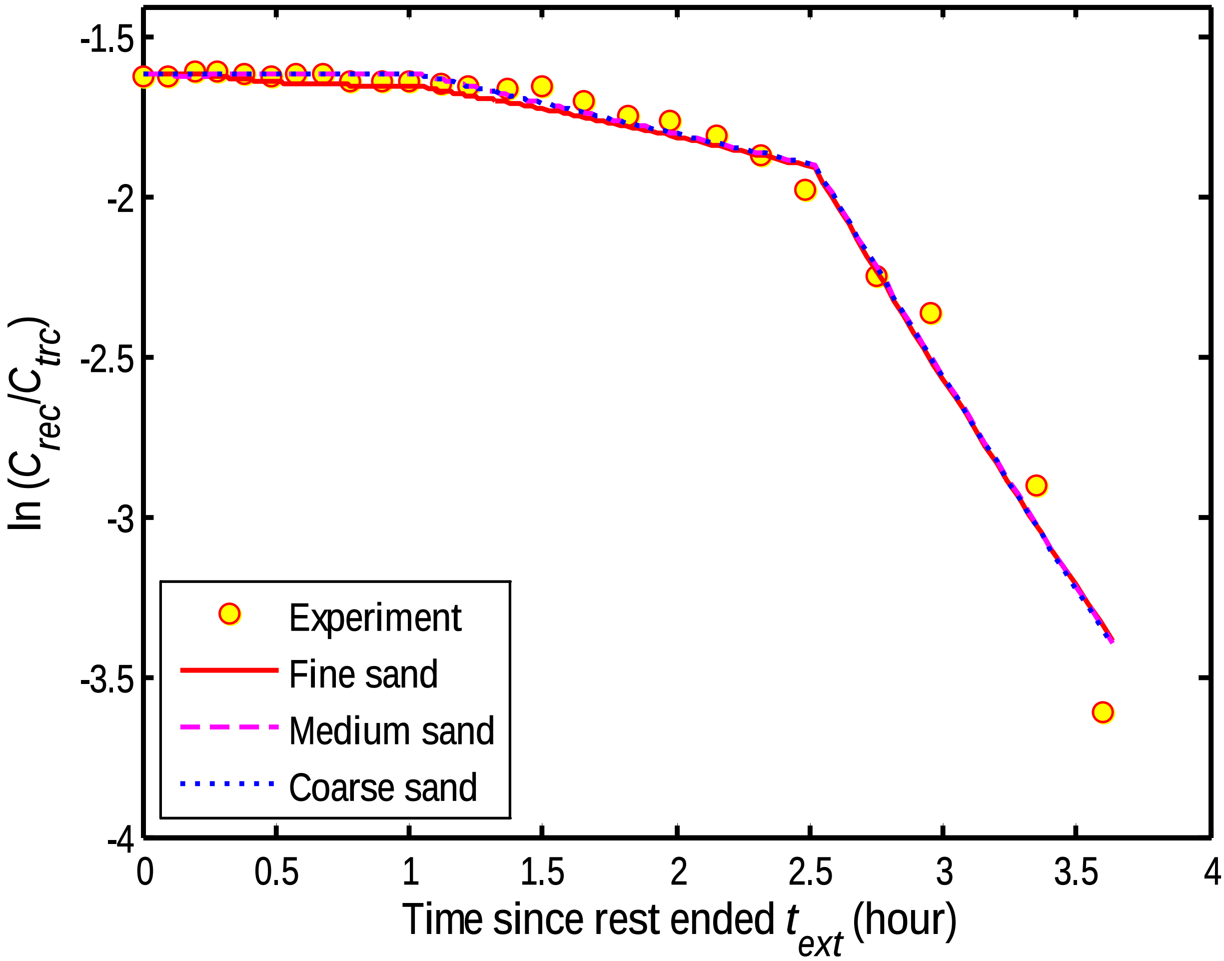


**Figure 6. Computed $\ln\left[C_{rec}/C_{tra}\right] \sim t^{*}$ by the model of this study using a piecewise linear function to describe the nonlinear chemical reactions.**

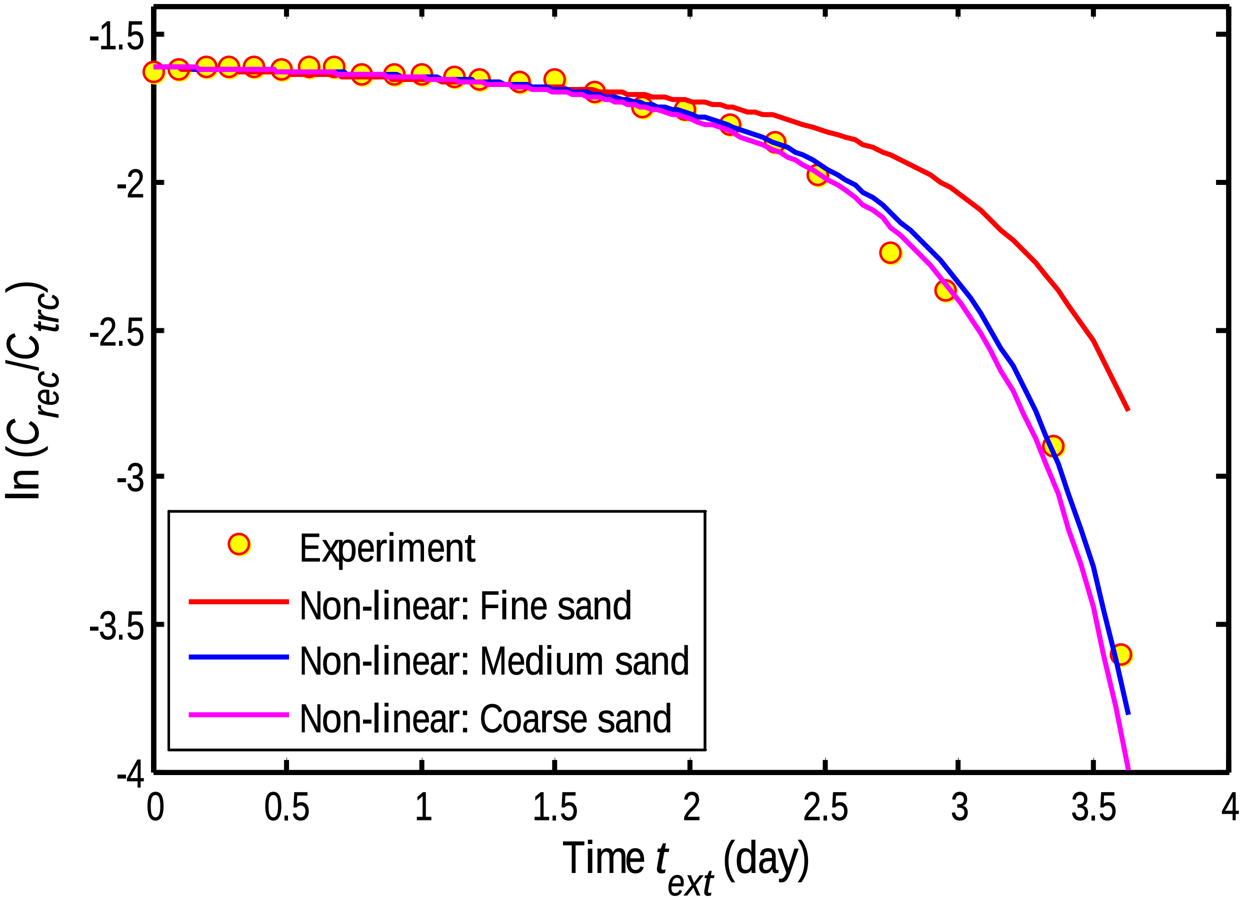
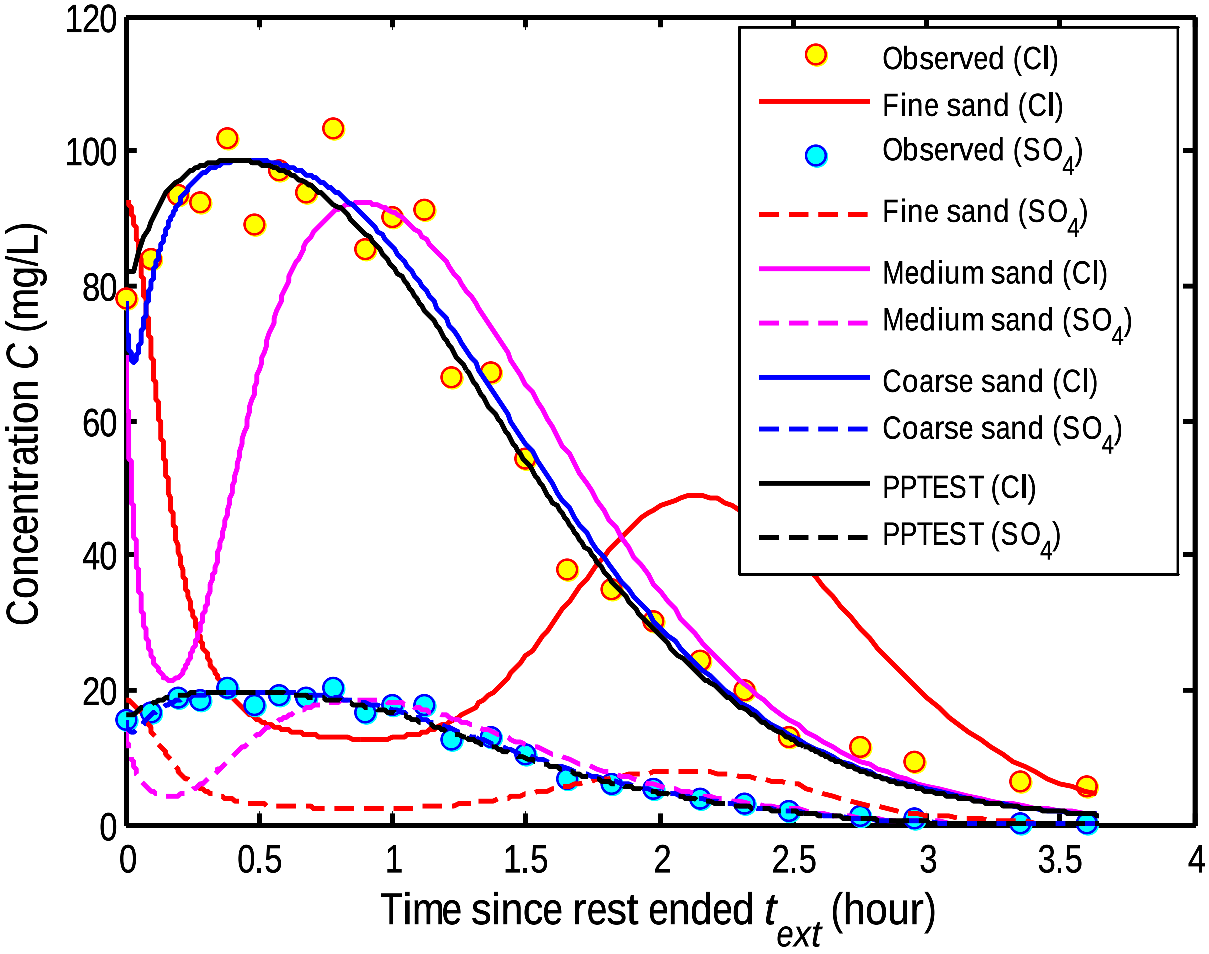
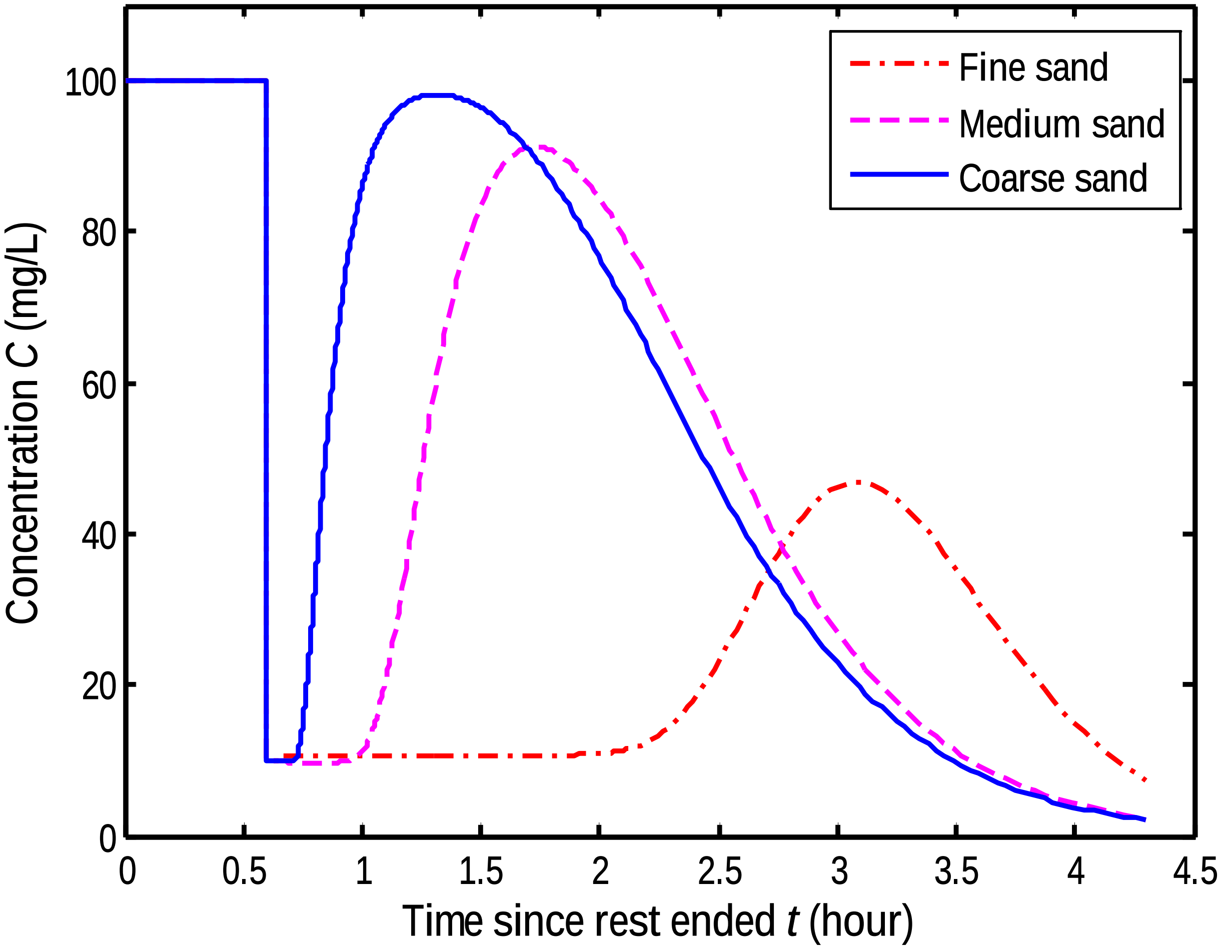


**Figure 7. Computed $\ln\left[C_{rec}/C_{tra}\right] \sim t^{*}$ by the model of this study using a nonlinear function to describe the nonlinear chemical reactions.**


Concentration C (mg/L)
0
20
40
60
80
100
120
Time since rest ended $t_{ext}$ (hour)
0
0.5
1
1.5
2
2.5
3
3.5
4
Observed (Cl)
Fine sand (Cl)
Observed ($SO_4$)
Fine sand ($SO_4$)
Medium sand (Cl)
Medium sand ($SO_4$)
Coarse sand (Cl)
Coarse sand ($SO_4$)
PPTEST (Cl)
PPTEST ($SO_4$)

**A**



**B**

**Figure 8. BTCs for the different porous media with a piecewise linear function to describe chemical reactions: A. $Cl^{1-}$ and $SO_4^{2-}$ in the aquifer at $r = r_w$ +0.15 m, B. $Cl^{1-}$ in the wellbore.**

Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-181
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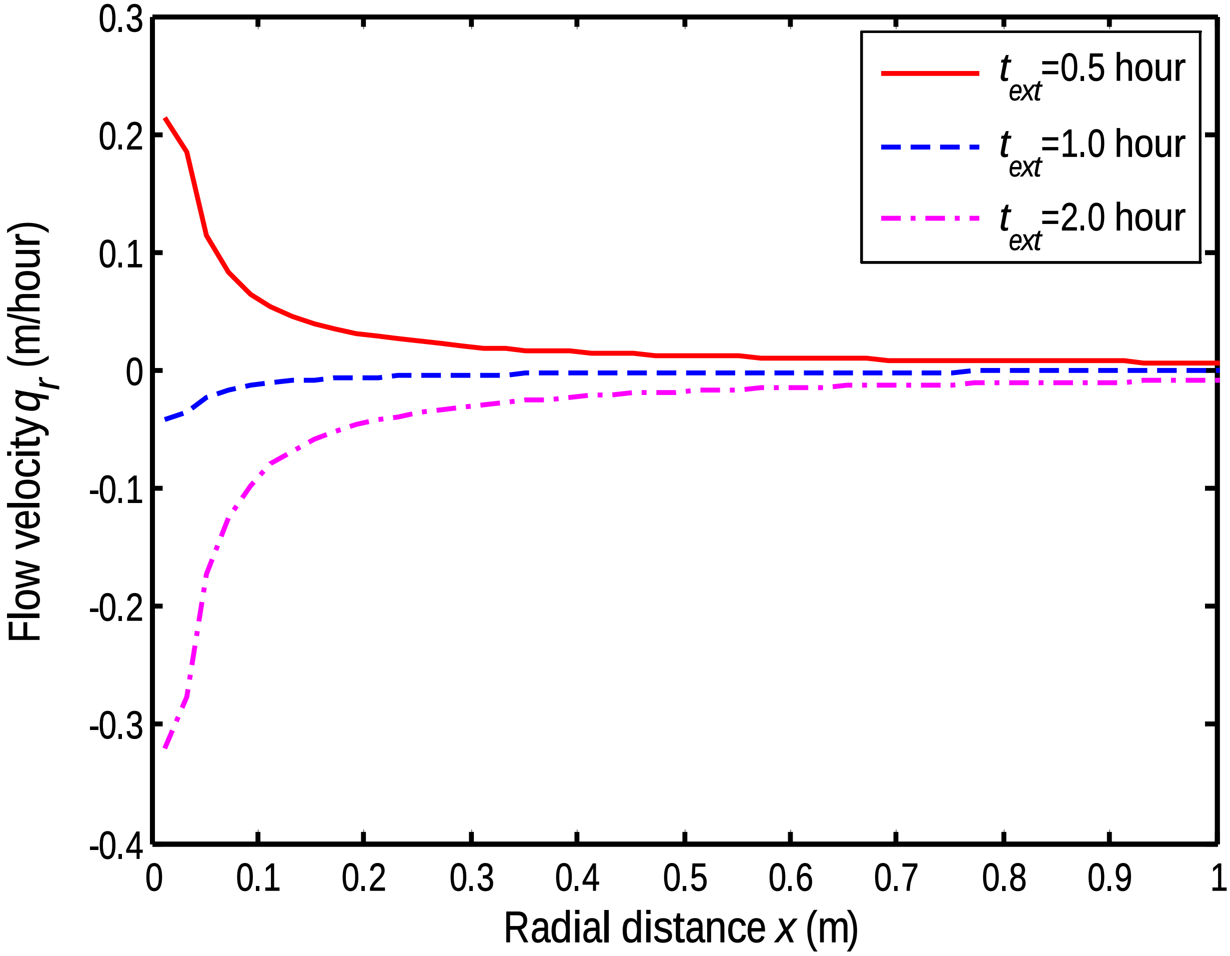

**Figure 9. Spatial distribution of the flow velocity in the extraction phase.**

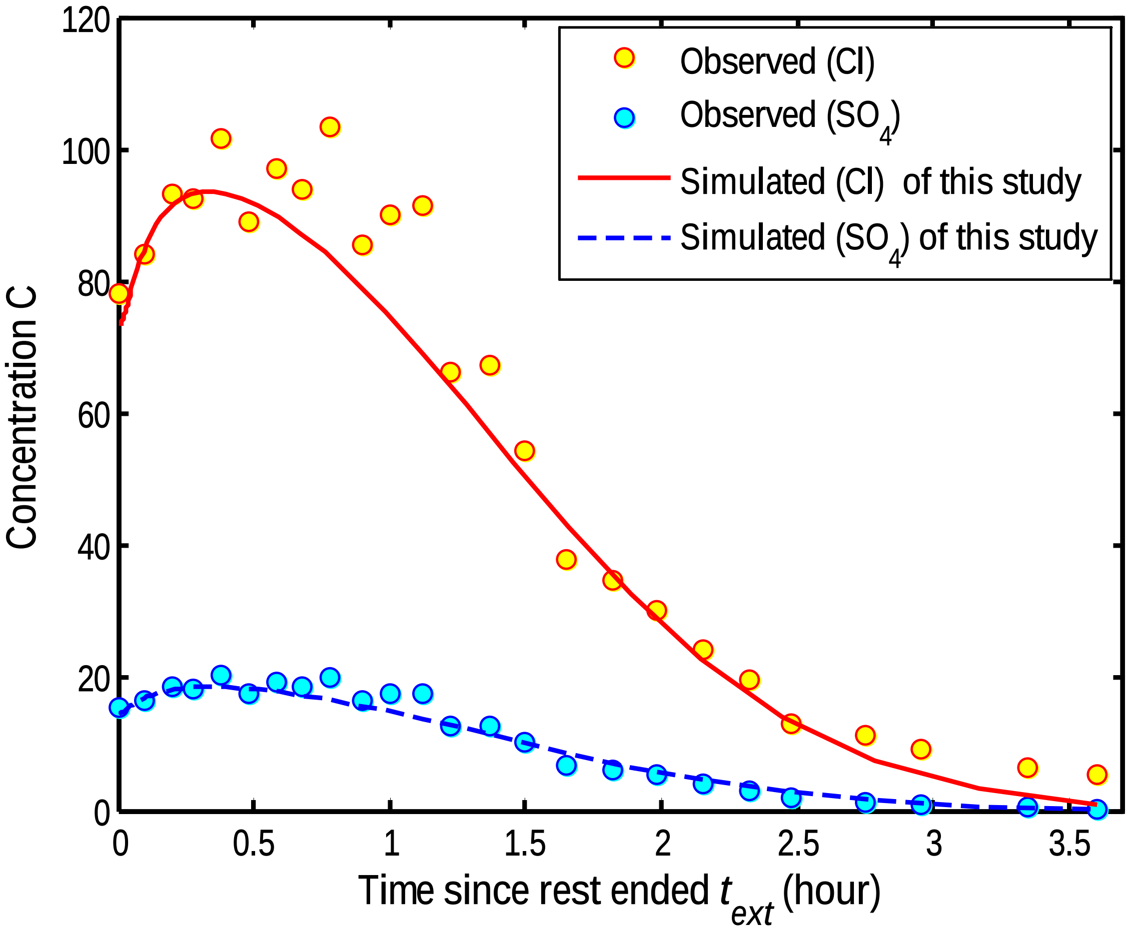

**Figure 10. Fitness of the field SWPP test data by the new model of this study.**

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Discussion started: 22 June 2018

**Table 1. Reaction parameters estimated by linear functions.**

| $K$ (m/day) | $S_s$ (m$^{-1}$) | $\lambda$ (hour) | $\tilde{\lambda}$ (hour) | Intercept of linear function | $\ln\left(\frac{1-\exp(-\lambda t_{inj})}{\lambda t_{inj}}\right)$ | $\ln\left[\frac{C_{rec}^{0}}{C_{trc}^{0}}\right]$ |
|---|---|---|---|---|---|---|
| 0.1 | 0.0001 | 0.1 | 0.0991 | 0.0017 | -0.0299 | 0 |
| 1 | 0.0001 | 0.1 | 0.0970 | 0.0016 | -0.0299 | 0 |
| 0.1 | 0.0001 | 0.2 | 0.1981 | 0.0034 | -0.0594 | 0 |
| 1 | 0.0001 | 0.2 | 0.1939 | 0.0031 | -0.0594 | 0 |