The Semi-Analytical Solution for Non-Equilibrium Solute Transport in Dual-Permeability Porous Media

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Abstract This study presents a conceptual Dual-Permeability Non-Equilibrium (DPNE) model that accounts for both physical and chemical nonequilibria to describe the reactive solute transport through a porous medium. A semi-analytical solution of the DPNE model is derived in the Laplace domain, which is then numerically inverted to obtain concentrations in different domains at different times and depths. The derived semi-analytical solution is validated using experimental data and existing analytical (for simple problems) and numerical solutions. The Global Sensitivity Analysis (GSA) is performed to identify model parameters with an impact on nonreactive tracer breakthrough curves (BTC) for a selected data set. A sensitivity-based calibration of the DPNE model's parameters is carried out to simulate a BTC with multiple inflection points. The DPNE model can better describe the experimental datasets than the model based on the dual-porosity (MIM) concept with first-order mass transfer. Since the DPNE model considers detailed sorption and mass transfer dynamics, it is suitable for process-based investigations.

1. Introduction

Transport of contaminants through porous media often experiences non-equilibrium conditions and remains a challenging problem for groundwater hydrologists. The porous media heterogeneity is associated with irregular stratification, dead-end pores, fractures, and lenses with different hydraulic conductivities (Bai & Roegiers, 1994, 1997; Bai et al., 1993; Kartha & Srivastava, 2008). It has been widely recognized that heterogeneities in porous media's physical and chemical properties significantly influence transport processes and result in an anomalous transport behavior (Brusseau et al., 1989; Brusseau & Rao, 1989; Coats & Smith, 1964). The solute transport through such porous media is distinguished by asymmetry, early breakthrough, and extensive tailing in breakthrough curves (BTC) (Brusseau, 1992; Brusseau et al., 1989). Classical advection-dispersion equation-based models fail to capture the solute plume behavior under the non-Fickian and nonequilibrium conditions. Brusseau and Srivastava (1997) reported several factors affecting the transport of organic solutes, including physical and chemical heterogeneity and nonlinear and rate-limited sorption. Several conceptual models have been developed to analyze the fate of solutes in heterogeneous porous media by considering nonequilibrium, multi-rate mass transfer, and/or non-Fickian transport behavior (Brusseau et al., 1989; Haggerty & Gorelick, 1995; Pot et al., 2003; Selim et al., 1999; Sharma et al., 2015, 2016; Srivastava & Brusseau, 1996; van Genuchten & Wierenga, 1976). The nonequilibrium transport can be categorized as physical nonequilibrium (PNE) or chemical nonequilibrium (CNE). PNE is associated with transport-related non-equilibrium and affects both sorbing and non-sorbing solutes (Brusseau et al., 1989; van Genuchten et al., 1977; van Genuchten & Wierenga, 1976). PNE is often modeled using dual- (multi-) porosity and/or dual- (multi-) permeability approaches (Šimůnek et al., 2003; Šimůnek & van Genuchten, 2008).

The dual-porosity models divide the porous medium into two interacting continua (Coats & Smith, 1964; Gaudet et al., 1977; Gerke & van Genuchten, 1993, 1996; Goltz & Roberts, 1986; Gwo et al., 1995; Selim et al., 1999; Selim & Ma, 1998). While the first region is associated with macropores or fractures, the second region is associated with micropores or rock matrix. The dual-porosity models assume that advective flow is limited to the fracture domain and that dissolved solutes can move in and out of micropores or rock matrix due to molecular diffusion or first-order mass transfer (van Genuchten & Wierenga, 1976; Swami et al., 2014, 2016, 2018). The most popular model based on the dual-porosity approach is the

The dual-permeability models consider flow and transport in both macropore and micropore regions (Gerke & van Genuchten, 1993). These models assume that water flows relatively faster in the macropore region and slower in the micropore region. The dual-permeability models can be further extended to account for the immobile region in the matrix domain (e.g., Šimůnek & van Genuchten, 2008). The solute exchange between the fracture and matrix regions and between the matrix and its immobile region occurs due to molecular diffusion. Most studies considering the dual-permeability concept solve the governing equations using numerical techniques (Gerke & van Genuchten, 1996; Zimmerman et al., 1993).

A few conceptual models incorporate CNE into a dual-permeability model (Kartha & Srivastava, 2008; Šimůnek & van Genuchten, 2008). CNE is often incorporated using two-site sorption conceptualization, which divides the sorption sites into two fractions with equilibrium and kinetic sorption (van Genuchten & Wagenet, 1989). Kartha and Srivastava (2008) developed a dual-permeability model that considers porous domains with slow and fast-moving liquid and an immobile zone. Their model's conceptualization was analogous to the multi-process non-equilibrium (MPNE) model of Brusseau et al. (1989). The two-site conceptualization represented the sorption process. They assumed that both equilibrium and kinetic sites exist in the immobile and slow regions and that no sorption occurs in the fast region. A dual-permeability model with an immobile zone inside of the matrix domain and two-site sorption in both domains was also incorporated into the HYDRUS-1D software (Gerke & van Genuchten, 1993; Šimůnek et al., 2003, 2008) and successfully applied to multiple experimental datasets (e.g., Dousset et al., 2007; Köhne et al., 2006; Pot et al., 2005). Equilibrium and kinetic sorption can take place in both macropore and micropore regions in HYDRUS-1D.

Several studies developed analytical or semi-analytical solutions for the dual-porosity model incorporating PNE and CNE (Carnahan & Remer, 1984; Gao et al., 2009, 2010; Goltz & Roberts, 1986; Joshi et al., 2012; Leij et al., 1993; Neville et al., 2000; Toride et al., 1993; van Genuchten & Wagenet, 1976, 1989). However, only a few studies developed analytical/semi-analytical solutions for the dual-permeability model (Leij & Bradford, 2013; Leij et al., 2012; Liang et al., 2019; Skopp et al., 1981). To the best of our knowledge, an analytical model considering a dual-permeability system with an immobile region and chemical non-equilibrium (referred to here as the DPNE model) has not yet been reported. The present study aims to fill this research gap and develop a semi-analytical solution for the DPNE model. The developed semi-analytical solution is verified against the semi-analytical solution for the MIM and MPNE models (i.e., simpler problems) and the numerical solution in HYDRUS-1D (i.e., a more complex problem). To identify the most sensitive DPNE model parameters, the global sensitivity analysis was performed, and its results were then applied to analyze the existing experimental data set from the literature.

### 2. Conceptualization of the DPNE Model and Its Semi-Analytical Solution

The concept of the DPNE model with an immobile liquid zone in porous media and its implications for the solute transport is mathematically described in this section. The water movement in the porous media is categorized into fast, slow, and immobile liquid fractions. The fast and slow-moving liquids exist in separate hydraulically connected pore regions having $v_f$ and $v_s$ velocities.

The conceptual approach of the DPNE model is similar to that of the multi-process non-equilibrium model developed by Brusseau et al. (1989). The conceptual model considers advection, dispersion, first-order mass transfer, and sorption processes. The schematic of the conceptual model is presented in Figure 1. The solute is assumed to coexist in the liquid and sorbed phases in the fast, slow, and immobile pore regions (zones). The existence of three liquid domains results in three different liquid phase solute concentrations: Immobile ($c_{im}$), slow ($c_s$), and fast ($c_f$) domain concentrations (Figure 1).

These three solute concentrations (in different pore regions) have corresponding instantaneous and rate-limited sorbed concentrations since sorption is assumed to occur in all three zones. Additionally, the solute mass transfer between the liquid and sorbed phases in the same porous region and between liquid phases in different pore regions is considered. The mass transfer between sorbed phases in two different
pore regions is not considered. The mass transfer between fast and slow-moving liquids is governed by the first-order rate process, $\omega_{sf} (t^{-1})$. Similarly, as shown in Figure 1, the mass transfer between slow and immobile liquids is governed by the first-order rate process, $\omega_{im} (t^{-1})$. Instantaneous sorption in the three pore regions is defined by the three distribution coefficients $K_{im}$, $K_{sl}$, and $K_{fs}$. The mass transfer for rate-limited sorption in the three pore regions is defined by $k_{im}$, $k_{sl}$, and $k_{fs}$. The model assumes that the mass transfer rates $\omega_{sf}$ and $\omega_{im}$ are constant and independent of time and space. The upper-case $K$ represents distribution coefficients for linear sorption, the lower case $k$ represents rate-limited sorption, the symbol $\omega$ represents mass transfer coefficients, and subscripts $fs$, $sl$, and $im$ represent fast, slow, and immobile zones.

### 2.1. Governing Equation of DPNE

Three coupled one-dimensional equations represent the transport processes in porous media with different flow rates in the fast, slow, and immobile regions. The processes of advection and dispersion in the longitudinal direction in both slow and fast regions and mass transfer are considered. The first-order mass transfer is the coupling process between two different pore regions. Also, both instantaneous equilibrium sorption and first-order rate-limited sorption occur in all pore regions, corresponding to the classical two-site sorption model of van Genuchten and Wierenga (1976).

The governing solute transport equation for the fast region can be given as:

$$
\left(\theta_{fl} + f_{fl}F_{fl}\rho_{fl}K_{fl}\right)\frac{\partial C_{fl}}{\partial t} + q_{fl}\frac{\partial C_{fl}}{\partial x} = \theta_{fl}D_{fl}\frac{\partial^2 C_{fl}}{\partial x^2} - \omega_{sf}\left(C_{fl} - C_{sl}\right) - f_{fl}\rho_{fl}\frac{\partial S_{sf2}}{\partial t}
$$

(1)

The solute transport equation for the slow region can be given as:

$$
\left(\theta_{sl} + f_{sl}F_{sl}\rho_{sl}K_{sl}\right)\frac{\partial C_{sl}}{\partial t} + q_{sl}\frac{\partial C_{sl}}{\partial x} = \theta_{sl}D_{sl}\frac{\partial^2 C_{sl}}{\partial x^2} - \omega_{sl}\left(C_{sl} - C_{fs}\right) - f_{sl}\rho_{sl}\frac{\partial S_{sl2}}{\partial t}
$$

(2)

The mass balance equation for the immobile zone in the slow region can be given as:

$$
\left(\theta_{im} + f_{im}F_{im}\rho_{im}K_{im}\right)\frac{\partial C_{im}}{\partial t} + f_{im}\rho_{im}\frac{\partial S_{im2}}{\partial t} = \omega_{im}\left(C_{sl} - C_{im}\right)
$$

(3)

The rate-limited sorption kinetics in fast, slow, and immobile regions can be represented as:

$$
\frac{\partial S_{fs2}}{\partial t} = k_{fs}\left[1 - F_{fs}\right]K_{fs}C_{fs} - S_{fs2}
$$

(4)
respectively. The kinetic sorption model described by Equations 4–6 allows for different sorption and desorption rates.

2.2. Initial and Boundary Conditions

A semi-infinite domain is considered for obtaining the analytical solution. Initially, it is assumed that the media is free of contamination in all regions and phases.

\[ C_{fs}(x,0) = C_{sl}(x,0) = C_{im}(x,0) = S_{fs}(x,0) = S_{sl}(x,0) = S_{im}(x,0) = 0 \]  

(7)

The inflow boundary condition for the fast and slow regions are:

\[ v_f C_{fs}(0,t) - \delta D_f \frac{\partial C_{fs}(0,t)}{\partial x} = v_f C_0 \left(1 - \left(t - t_0\right)\right) \]  

(8)

\[ v_s C_{sl}(0,t) - \delta D_s \frac{\partial C_{sl}(0,t)}{\partial x} = v_s C_0 \left(1 - \left(t - t_0\right)\right) \]  

(9)

where \( C_0 \) is the source concentration, \( \delta = 0 \) represents a constant concentration (Dirichlet) boundary condition, and \( \delta = 1 \) represents a constant flux (Cauchy) boundary condition.

For the outflow boundary, a semi-infinite domain is considered. The outflow boundary condition for the fast region is:

\[ C_{fs}(\infty,t) = 0 \]  

(10)

and for the slow region is:

\[ C_{sl}(\infty,t) = 0 \]  

(11)

2.3. Solution in the Laplace Domain

The analytical solution is derived in the Laplace domain. A detailed derivation is given in Appendix A. The numerical inversion of the Laplace domain solution is done using de Hoog’s algorithm (de Hoog et al., 1982). de Hoog’s algorithm is used extensively for numerous solute transport problems (Joshi et al., 2012; Neville et al., 2000; Sudicky & Frind, 1982; Tang et al., 1981). This algorithm uses Fourier series approximation based on the quotient difference algorithm for the approximation of the inverse Laplace transform and is given as:

\[ C_{fs}(x,t) = \frac{1}{T} \exp(\rho t) \operatorname{Re} \left( \frac{\tilde{C}_{fs}(x, \rho)}{2} + \sum_{k=1}^{2M} \frac{\tilde{C}_{fs}(x, p_k + i\pi/2)}{p_k + i\pi/2} \right) \]  

(12)

where \( T \) defines the period of approximating Fourier series and \( T = 0.80t \) (Neville et al., 2000), \( \tilde{C}_{fs} \) represents the fast region concentration in the Laplace domain.

\[ s = -\ln\left(\frac{E_s}{2T}\right) \]  

(13)
Table 1
Values of Different DPNE Model Parameters Used to Compare the Proposed Model With Other (MIM, MPNE, and HYDRUS-1d) Models

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameter</th>
<th>Units</th>
<th>MIM</th>
<th>MPNE</th>
<th>HYDRUS (without immobile water)</th>
<th>HYDRUS (with immobile water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$L$</td>
<td>cm</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>$\rho$</td>
<td>g/cm$^3$</td>
<td>1.30</td>
<td>1.36</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>3</td>
<td>$D$</td>
<td>cm$^2$/day</td>
<td>30</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>$\alpha$</td>
<td>cm</td>
<td>–</td>
<td>0.34</td>
<td>5.74</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>$\theta_0$</td>
<td>–</td>
<td>0.26</td>
<td>0.439</td>
<td>0.082</td>
<td>0.002</td>
</tr>
<tr>
<td>6</td>
<td>$\theta_d$</td>
<td>–</td>
<td>0.14</td>
<td>0.034</td>
<td>0.316</td>
<td>0.063</td>
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<tr>
<td>7</td>
<td>$\theta_{im}$</td>
<td>–</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.333</td>
</tr>
<tr>
<td>8</td>
<td>$q_f$</td>
<td>cm/day</td>
<td>10</td>
<td>5.11</td>
<td>6.19</td>
<td>0.771</td>
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<tr>
<td>9</td>
<td>$q_d$</td>
<td>cm/day</td>
<td>0</td>
<td>0</td>
<td>1.20</td>
<td>6.62</td>
</tr>
<tr>
<td>10</td>
<td>$\omega_f$</td>
<td>day$^{-1}$</td>
<td>0.15</td>
<td>0.075</td>
<td>1.063</td>
<td>0.072</td>
</tr>
<tr>
<td>11</td>
<td>$\omega_{im}$</td>
<td>day$^{-1}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.470</td>
</tr>
<tr>
<td>12</td>
<td>$f_f$</td>
<td>–</td>
<td>0.4</td>
<td>0.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>$f_d$</td>
<td>–</td>
<td>0.6</td>
<td>0.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>$f_{im}$</td>
<td>–</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>$F_f$</td>
<td>–</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>$F_d$</td>
<td>–</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>$F_{im}$</td>
<td>–</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>$k_f$</td>
<td>day$^{-1}$</td>
<td>0</td>
<td>0.663</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>$k_d$</td>
<td>day$^{-1}$</td>
<td>0</td>
<td>0.663</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>$k_{im}$</td>
<td>day$^{-1}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td>$K_f$</td>
<td>cm$^3$/g</td>
<td>0.5</td>
<td>0.429</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>$K_d$</td>
<td>cm$^3$/g</td>
<td>0.5</td>
<td>0.416</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>$K_{im}$</td>
<td>cm$^3$/g</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

de Hoog et al. (1982) suggested the following values of constants for accelerating the convergence of the Fourier series: $\epsilon = 0$, $Er = 0.001$, and $M = 7$.

3. Verification of the Developed Solution
This section demonstrates the DPNE model's capabilities in reproducing BTCs obtained by a range of models based on the dual-porosity and dual-permeability concepts. Two analytical solutions from the literature (Neville et al., 2000; van Genuchten & Wierenga, 1976) are used to verify the DPNE model for the dual-porosity system. For this verification, the DPNE model is converted/simplified into the MIM and MPNE models by selecting specific values of various coefficients. The numerical HYDRUS-1D model is used to fully verify the DPNE model for the dual-permeability system with or without an additional immobile region.

The analytical solution for the MIM model considered here is limited to instantaneous equilibrium sorption. Therefore, the governing equations of the DPNE model are simplified by taking $F_f = F_d = F_{im} = 1$. When $F_f = F_d = F_{im} = 0$, sorption in the fast, slow, and immobile porous regions is reduced to first-order kinetics. Only physical non-equilibrium without sorption is considered for the dual-permeability system and the comparison with HYDRUS-1D. Therefore, the governing equations of the DPNE model are simplified by taking $K_f = K_d = K_{im} = k_f = k_d = k_{im} = 0$. Table 1 shows a list of input parameters for all three modeling setups.

3.1. Comparison With the MIM Solution Developed by van Genuchten and Wierenga (1976)
van Genuchten and Wierenga (1976) developed an analytical solution for a physical non-equilibrium model considering a bi-continuum liquid phase concentration, that is, a dual-porosity model. The concentration difference between two hydraulically connected regions governs the first-order mass transfer between them. The DPNE model is converted to the MIM model by considering $\omega_{im} = 0$ in the governing equations of the DPNE model (shown in Appendix C). In the dual-porosity approach, the mobile and immobile pore regions are hydraulically connected. The fast region processes (in the DPNE model) are analogous to the mobile region processes (in the MIM model), while the slow region processes are analogous to the immobile region processes. This is achieved by considering $q_d = 0$ and the reaction parameters $F_f = F_d = F_{im} = 1$ and $k_f = k_d = k_{im} = 0$ as the rate-limited sorption is not considered. The list of additional parameters is listed in the MIM column of Table 1. Figure 2 shows that the results of the downscaled DPNE model and the MIM model are identical.

3.2. Comparison With the Semi-Analytical Solution for the Multi-Process Non-Equilibrium Model (MPNE)
The MPNE model is an extension of the bi-continuum model by including site-specific sorption. The MPNE model thus considers both physical and chemical non-equilibria. A semi-analytical solution for the MPNE model incorporating instantaneous and rate-limited sorption was presented by Neville et al. (2000). The semi-analytical solution of the DPNE model can be reduced to the MPNE model by switching off the immobile...
region by substituting \( \omega_{im} = 0 \) and \( q_d = 0 \), similarly as in the previous section. To convert the DPNE model to the MPNE model, additional instantaneous and rate-limited sorption parameters were considered in both mobile and immobile domains. A list of input parameters is shown in Table 1. Figure 3 shows an excellent agreement between the DPNE and MPNE models.

### 3.3. Comparison With the Numerical Solution for the Dual-Permeability System With Immobile Water in the Matrix

The DPNE model is further validated in this section using the numerical solution for solute transport in a dual-permeability porous medium incorporated in the HYDRUS-1D model (Šimůnek et al., 2003, 2008). A soil column experiment involving the transport of the CaCl\(_2\) solution containing Br (Pot et al., 2005) is used for the validation. The undisturbed soil column 30 cm long was collected from a soil layer with hydromorphic silt loam (with 24% clay, 40% silt, and 36% sand). The experiment was conducted under unsaturated, steady-state flow conditions. The effluent was collected at 0.5 h intervals. More details can be found in Pot et al. (2005), who analyzed the collected BTC using the dual-permeability model with or without an immobile region in the soil matrix implemented in HYDRUS-1D. The list of parameters used to validate the DPNE model that considers the dual-permeability system with and without an immobile region in the soil matrix is shown in Table 1 (the last column). Figure 4 shows an excellent agreement between the results of the DPNE model and those simulated by the HYDRUS-1D model.

### 4. Global Sensitivity Analysis

Being a complex, process-based model, the DPNE model requires a large number of input parameters. In its full complexity (i.e., multiple porosities, multiple processes), many of these model parameters may not be identifiable using typically collected information (i.e., outflow breakthrough curves). Under such conditions, various assumptions about different parameters need to be considered. For example, some parameters can be eliminated to simplify the model by neglecting one or two pore domains or considering only instantaneous or kinetic sorption (as shown in the examples above). For less sensitive parameters, typical values may be obtained from the literature. Similar parameters can be linked, such as assuming the same sorption and/or degradation parameters in different phases or regions. Multiple parameter optimization steps can be used to estimate various parameters. For example, Pot et al. (2005) first used the non-reactive tracer BTCs to estimate flow parameters (fluxes and mass transfer between different regions). The reactive tracer BTCs were then used to estimate reaction parameters (for equilibrium and kinetic sorption). Such strategies and assumptions will depend on the system’s complexity and the information content of collected data.

In the case of a process-based model, the simulated output may not be similarly sensitive to all input parameters simultaneously. Before estimating or calibrating the model for a particular system (e.g., MIM, MPNE, DPNE) against the field/laboratory data, it is important to identify the most sensitive parameters, that is, those that have the largest impact on the results and are thus pivotal for the model deployment, especially in case of a complex modeling approach (Ceriotti et al., 2019). This can be accomplished by performing the Global Sensitivity Analysis (GSA). Such practice outlines a basic framework for the model-based interpretation to design the experimental work (Fajraoui et al., 2011).

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**Figure 3.** Verification of the downscaled DPNE model with the MPNE model. Experimental data are from Neville et al. (2000). DPNE, dual-permeability non-equilibrium; MPNE, multi-process non-equilibrium.

**Figure 4.** Verification of the DPNE model with the Hydrus-1D model (the dual-permeability model with (DP_IM) and without (DP) immobile water in the matrix). Experimental data are from Pot et al. (2005). DPNE, dual-permeability non-equilibrium.
Different sensitivity analysis (SA) approaches have been proposed for various research areas related to groundwater and environmental sciences (e.g., Cukier et al., 1973; Dell’Oca et al., 2020; Hamby, 1994; Norton, 2008; Pianosi et al., 2016), hydrogeological models (Wainwright et al., 2014), complex kinetic systems (Turanji, 1990), building energy analysis (Tian, 2013), and radioactive waste disposal models (Helton, 1993). For a complex model, an increase in the number of input parameters is imperative. It is important to opt for an appropriate sensitivity analysis (SA) approach, specific to the type of the model input-output configuration (Nguyen & Reiter, 2015).

The Fourier Amplitude Sensitivity Test (FAST) is a variance-based method to quantify the effect of different parameters on the output of the non-linear models (Cukier et al., 1973, 1975). The FAST model decomposes the model output variance into fractions within a Fourier amplitude integration framework and attributes the model output variance to particular parameters (assumed to be uncorrelated) or their subsets. The details of the FAST formulation and calculation details are given in Appendix B.

In this section, the global sensitivity analysis for the DPNE model is carried out to determine the most sensitive model parameters for a particular selected data set so that these parameters can be estimated effectively. The sensitivity analysis is based on Miyamoto et al.’s (2003) data set involving conservative solute transport experiments on the Andisol soil column. Andisols, developed from volcanic ash, constitute 17% of Japan’s land and are commonly used for agriculture. Due to unique physical and chemical properties, Andisol’s flow and transport properties are of prime interest. Andisol has a distinct interaggregate and intra-aggregate pore space arrangement due to its composition of non-crystalline minerals. The Andisol experiment was conducted on a 26 cm long soil column with an internal diameter of 4.4 cm. An aqueous solution of CaCl₂ of 0.06M (considered to be a non-reactive solute) was eluted at a steady-state saturated flow rate of 0.56 cm/min. Four electrical conductivity probe sensors were inserted horizontally at 7.72 cm, 9.96 cm, 14.05 cm, and 16.87 cm along the column to monitor the electrical conductivity (Toride et al., 2003) and experimental breakthrough curves. All depths were considered for investigating the sensitivity of parameters. Please refer to Section 4 of Leij et al. (2012) for further details about the experiment.

Table 2 lists the DPNE model parameters, their means, and lower and upper limits considered in the global sensitivity analysis. The mean values of these parameters were obtained by preliminary fitting of BTCs at all four depths simultaneously. The lower and upper limits of these parameters were selected to ensure that wide intervals in the parameter space were explored and to minimize the chance of sampling negative values.

The quantitative results illustrated in this section show the general relative importance of the input parameters and that model output sensitivity varies spatially and temporally for different input transport parameters. The results may vary based on the flow characteristics and transport properties.

Figure 5 compares the breakthrough curve profiles reported by Miyamoto et al. (2003) and related total sensitivity indices of the DPNE model parameters. Figures 5 A-D show relative sensitivities for five unknown parameters q₀, qᵢ, ωᵣᵢ, ωᵢₘᵢ, and α. Figures 5 E-H then show relative sensitivities of three parameters ωᵣᵢ, ωᵢₘᵢ, and α, when the seepage velocities in the slow and fast flow regions are assumed to be known.

Figures 5A–5D show the FAST sensitivity indices for five DPNE parameters (q₀, qᵢ, ωᵣᵢ, ωᵢₘᵢ, and α) at distances of 7.72, 9.96, 14.05, and 16.87 cm. In all cases, the sensitivity indices for qᵢ and q₀ are significantly larger than those for the other three parameters. It is also interesting to point out that the sensitivity indices for qᵢ and q₀ show an inverse correlation, identifiable by local peaks. Figure 5 also indicates that the dispersivity α has negligible sensitivity during the initial and late stages of the BTC.

Figures 5E–5H show the FAST sensitivity indices for three less sensitive parameters (ωᵣᵢ, ωᵢₘᵢ, and α), assuming that water fluxes are known. In Figures 5E and 5F, the sensitivity is governed by α, revealing the importance of dispersivity at earlier times. At farther distances (Figures 5G and 5H), ωᵣᵢ dominates the sensitivity index. The sensitivity index for ωᵣᵢ attains sharp peaks at the BTC’s inflection points due to the impact of...
diffusive processes between primary and secondary porosities. Figures 5E–5H also illustrate that the model output is sensitive to the parameter $\omega_{im}$ during later stages of the BTC.

Figures 5E–5H reveal important information about $\omega_{sf}$, $\omega_{im}$, and $\alpha$. Figures 5E–5H clearly show that at all distances, overall sensitivity is mainly affected by $\alpha$. Both parameters $\omega_{sf}$ and $\alpha$ show independent behavior, and the sensitivity of BTC at later stages is governed by both $\omega_{im}$ and $\alpha$. A careful observation of Figures 5E–5H reveals temporal locations of inflection points and sharp peaks and drops in the FAST index of $\omega_{sf}$ and $\alpha$. At a short distance (7.72 cm), the sensitivity index of $\omega_{sf}$ has a single point of inflection. It has two at middle distances (9.96 and 14.05 cm) and three at a large distance (16.9 cm). The sensitivity associated with $\omega_{im}$ is reduced at larger distances. The findings of Figure 5 imply that all five parameters, that is, $q_s$, $q_f$, $\omega_{sf}$, $\omega_{im}$, and $\alpha$ are relevant. When the BTC has multiple peaks/inflections, these parameters contain essential information about the model response variance for model calibration.

5. Simulation of Experimental Data

The experimental data set for Andisol (Miyamoto et al., 2003), considered above in the global sensitivity analysis, is analyzed in this section to evaluate the applicability of the developed model. The calibration of the DPNE model parameters for BTCs collected at four observed locations is carried out based on GSA’s results discussed above. A set of sensitive parameters for a nonreactive tracer was identified in the previous section using the sensitivity analysis. Breakthrough curves at all observation points were assigned equal weights.
The observed data were analyzed using the DPNE model, and its results were compared with those of the dual-porosity (MIM) model. The MIM and DPNE transport parameters were estimated using PEST (Doherty & Christensen, 2011) and are shown in Table 3. Since Darcy’s discharge \( q \) and total porosity were experimentally measured (Leij et al., 2012), they were fixed at 0.56 cm/min and 0.57, respectively. The dispersivity \( \alpha \), mass transfer coefficient \( \omega \), mobile \( \theta_m \) and immobile \( \theta_{im} \) water contents were optimized for the MIM model. For the DPNE model, six parameters were optimized \( \theta_{sl}, \theta_{fs}, \theta_{im}, \omega_{sf}, \omega_{im}, \) and \( \alpha \). The estimation was carried out with two constraints, that is, the total flux \( q = q_{sl} + q_{fs} \) and the total porosity \( \theta = \theta_{sl} + \theta_{fs} + \theta_{im} \), which were defined in the objective function in PEST. The estimated parameters are shown in Table 3.

The DPNE model parameters acquired by simultaneously optimizing BTCs at four depths are shown in Table 3. Figure 6 demonstrates that the DPNE model performs better than the MIM model, specifically for BTCs with multiple inflections at greater depths. It appears that the contaminant moves through three hydraulically connected domains more or less independently, which is evident from small values of mass transfer coefficients. It can also be observed that the volume fractions of the fast and slow regions are equal. Most of the solute transport is governed by the slow region, which is apparent from the estimated \( \theta_{sl} \). Mass transfer between the fast and slow regions is faster than between the slow and immobile regions, as shown by the corresponding mass transfer coefficients’ values. It is important to highlight the MIM model’s limitations to capture the complex behavior of BTCs affected by multiregional transport phenomena. The optimized values of dispersivity and mass transfers coefficient are higher for MIM compared to DPNE.

The two models’ performance and suitability are compared in Table 4 to identify whether a simpler MIM model can better describe the experimental data than a more complex DPNE model while using fewer computational resources and fewer parameters. This is assessed by calculating the root mean square error (RMSE), determination coefficient \( R^2 \), Nash-Sutcliffe efficiency (NSE), Akaike information criterion (AIC), and Modified Akaike information criterion (AICc) using the following set of equations:

\[
RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (C_{obs} - C_{sim})^2}
\]  

\( C_{obs} \) is the observed concentration, \( C_{sim} \) is the simulated concentration, and \( n \) is the number of observations.
Figure 6. Experimental data (Miyamoto et al., 2003) and their fits at distances of 7.72, 9.96, 14.05, and 16.87 cm using the DPNE and MIM models with parameters optimized using data from all depths. DPNE, dual-permeability non-equilibrium; MIM, mobile-immobile model.

Table 4
The Goodness of Fit for Different (MIM and DPNE) Models to Simulate Experimental Data

<table>
<thead>
<tr>
<th>Distance (cm)</th>
<th>$R^2$</th>
<th>RMSE</th>
<th>NSE</th>
<th>AIC</th>
<th>AICc</th>
<th>Pearson coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.72</td>
<td>0.993</td>
<td>0.998</td>
<td>0.026</td>
<td>0.016</td>
<td>0.993</td>
<td>0.997</td>
</tr>
<tr>
<td>9.96</td>
<td>0.997</td>
<td>0.995</td>
<td>0.02</td>
<td>0.03</td>
<td>0.996</td>
<td>0.992</td>
</tr>
<tr>
<td>14.05</td>
<td>0.994</td>
<td>0.96</td>
<td>0.038</td>
<td>0.051</td>
<td>0.988</td>
<td>0.969</td>
</tr>
<tr>
<td>16.87</td>
<td>0.996</td>
<td>0.94</td>
<td>0.023</td>
<td>0.091</td>
<td>0.996</td>
<td>0.94</td>
</tr>
</tbody>
</table>

$$R^2 = \left[ \frac{\sum_{i=1}^{n} (C_{obs} - \bar{C}_{obs}) \sum_{i=1}^{n} (C_{sim} - \bar{C}_{sim})}{\sqrt{\sum_{i=1}^{n} (C_{obs} - \bar{C}_{obs})^2 \sum_{i=1}^{n} (C_{sim} - \bar{C}_{sim})^2}} \right]^2$$

$$NSE = 1 - \frac{\sum_{i=1}^{n} (C_{obs} - C_{sim})^2}{\sum_{i=1}^{n} (C_{obs} - \bar{C}_{obs})^2}$$

$$AIC = N \cdot \ln(\sigma^2) + 2\varphi$$

$$AICc = N \cdot \ln(\sigma^2) + 2\varphi + \frac{2\varphi(\varphi + 1)}{n - \varphi - 1}$$
where \( C_{\text{obs}} \) and \( C_{\text{sim}} \) are \( i \)th observed and simulated concentrations, respectively; \( \bar{C}_{\text{obs}} \) and \( \bar{C}_{\text{sim}} \) are the means of observed and simulated concentrations, respectively, \( n \) is the number of observations taken at any particular observation point, \( N \) is the sample size, \( \varphi \) is the number of parameters in the model plus 1, and \( \sigma^2 \) is the residual sum of squares/\( N \).

The DPNE model, which also considers transfer processes in the immobile zone, can better describe observed BTCs than the MIM model when the dual-porosity concept is used. To evaluate whether it is beneficial to use a more complex model, statistical measures such as \( \text{AIC} \) and \( \text{AIC}_c \) are shown in Table 4. It is concluded that the DPNE model outperforms the MIM model at all distances in simulating BTCs with multiple inflection points. \( \text{AIC} \) and \( \text{AIC}_c \) also show the maximum likelihood criteria are in favor of DPNE.

6. Temporal Moments

This section compares temporal moments for the MIM and DPNE models derived from observed BTCs. Temporal moments can describe the distribution of solute mass within a porous medium and have proven useful in analyzing the solute mass response to various transport processes. The zeroth temporal moment gives the mass of solute recovered at the sampling location. The first \( (T_1) \) and second \( (T_{11}) \) temporal moments normalized by a zeroth temporal moment give the mean arrival time and variance of BTCs, respectively. The numerical expressions for temporal moments are as follows (Kendall & Stuart, 1977):

\[
M_n(x) = \int_0^x \tau^{n-1} C(x, \tau) d\tau
\]

\[
T_1(x) = \frac{M_1}{M_0}
\]

\[
T_{11}(x) = \frac{M_2}{M_0} - \left( \frac{M_1}{M_0} \right)^2
\]

where \( M_n(x) \) represents the \( n \)th absolute temporal moment, \( T_1(x) \) is the normalized first temporal moment (by zeroth temporal moment), and \( T_{11}(x) \) is the normalized second temporal moment or variance of the BTC.

Figures 7–9 show the moment analysis for the models compared. The solute mass in the advective domain at various distances is shown using the zeroth temporal moment in Figure 7. Note that the solute mass decreases with distance as some solute is transferred from the advective domain to the immobile domain. The mass accumulated at all distances is predicted precisely by the DPNE model. The estimation of mass at 14.05 and 9.96 cm is more precise by MIM compared to DPNE. At other distances, MIM overestimated the mass. The zeroth temporal moments show that the DPNE model, due to its consideration of detailed transport processes, performs best for the BTC with complex behavior, which is observed at 16.87 cm. At other distances, the estimation of mass by the MIM and DPNE models is comparable.

The residence time of the solute mass within the system and its mean arrival time at different depths capture various transport processes occurring in the porous medium. The mean arrival time of reactive solutes at any given observation location will be higher than for tracers. For
nonreactive solutes, such as the one considered here, the mass transfer processes between different pore regions will determine the mean arrival time. Shorter mean arrival times are expected for soils with multiple porosities and limited mass exchange. Such a phenomenon can be observed using the first temporal moment. The MIM model slightly overestimates mean arrival time at longer distances, whereas the DPNE model estimates the exact mean arrival time. This is due to the inclusion of physical transport processes and secondary and immobile pore regions. Hydraulically connected fast-slow and slow-immobile regions actively participate in the mass transfer processes, which causes a delayed mean arrival time.

Preferential flow through a complex porous medium causes larger spatial spreading of the solute plume. This spreading will be higher if PNE processes such as solute mass transfer between domains are involved. For nonreactive solutes, these processes are mostly diffusion-based and include intra- and inter-domain mass transfers and intra-particle diffusion. For reactive solutes, in addition to diffusion-based processes, there are chemical transformation reactions that will also cause larger spatial spreading.

Better estimation of variance is done using DPNE compared to MIM, as shown in Figure 9. Both DPNE and MIM models estimate higher variances at shorter distances and lower variances at larger distances. A comparison of the MIM and DPNE parameters in Table 3 shows the overestimation of the MIM parameters, which resulted in higher variance estimation. The lower variance estimated by the DPNE model at 16.87 cm is due to the higher liquid fraction of the slow region than the fast region (Figure 6).

From the analysis of temporal moments, it is evident that the DPNE model outperforms the MIM model. The inclusion of additional physically based parameters is required to fully describe experimental BTCs, which cannot be accomplished by the MIM model, which neglects relevant transport processes.

7. Conclusions

A semi-analytical solution for solute transport with non-equilibrium physical and chemical processes under steady-state water flow conditions in a dual-permeability porous medium is presented in this manuscript. The semi-analytical solution was derived in the Laplace domain and numerically inverted in the time domain. The semi-analytical solution was validated using existing analytical (MIM and MPNE) solutions for simpler conditions and numerical solutions (HYDRUS-1D) for more complex conditions. Excellent agreements between the new semi-analytical solution and existing analytical and numerical solutions were obtained in all evaluated cases.

The global sensitivity analysis was used to identify model parameters, which the model output is the most sensitive to, using an experimental data set of Miyamoto et al. (2003). The results of the sensitivity analysis were then used in model calibration. The fluxes in slow and fast regions, that is, $q_s$ and $q_f$, were identified as the most important parameters during the entire experiment. On the other hand, the $\omega_f$ and $\alpha$ parameters were found to affect the BTC mainly during the initial breakthrough and at inflection points, respectively. It was concluded that all five DPNE parameters played an important role when analyzing BTCs with multiple inflection points.

The DPNE and MIM model parameters were estimated for an experimental data set of Miyamoto et al. (2003) involving BTCs with multiple inflection points. The DPNE model outperformed the MIM model. The temporal moment analysis illustrated that the DPNE model could better capture the mass, mean arrival time, and spreading of the BTC than the DPM model.

Since the DPNE model incorporates two distinct flow regions and considers both physical and chemical nonequilibria, it can be readily applied to analyze experimental data collected at the field scale. Additionally, the semi-analytical solution presented here can be used to verify complex numerical models considering

![Figure 9. Comparison of the second temporal moments for experimental data (Miyamoto et al., 2003) (Exp) and the DPNE and MIM model fits. DPNE, dual-permeability non-equilibrium; MIM, mobile-immobile model.](image-url)
multiple overlapping porous flow regions with simultaneous physical and chemical nonequilibrium processes.

**Appendix A: Analytical Solution of the DPNE Model in the Laplace Domain**

Taking the Laplace transform of Equation 6 and solving it leads to:

\[
pS_{im2} = k_{im} \left[ (1 - F_{im})K_{im}C_{im} - \bar{S}_{im2} \right]
\]

where \( p \) is the Laplace operator.

Further solving Equation A1 we get:

\[
\bar{S}_{im2} = \frac{k_{im} (1 - F_{im})K_{im}C_{im}}{p + k_{im}}
\]

Taking the Laplace transform of Equation 3 and solving it results in:

\[
R_{im}p\bar{C}_{im} + f_{im}\rho_{b}p\bar{S}_{im2} = \omega_{im} \left( \bar{C}_{sl} - \bar{C}_{im} \right)
\]

\[
R_{im} = \theta_{im} + F_{im}f_{im}\rho_{b}K_{im}
\]

\[
\bar{C}_{im} = A_0\bar{C}_{sl}
\]

where

\[
A_0 = \frac{\omega_{im}}{pR_{im} + J_1 + \omega_{im}}
\]

\[
J_1 = f_{im}\rho_{b}pK_{im} \frac{(1 - F_{im})K_{im}}{p + k_{im}}
\]

Taking the Laplace transform of Equation 5 and solving it leads to:

\[
\bar{S}_{sl2} = \left( \frac{k_{sl} (1 - F_{sl})K_{sl}}{p + k_{sl}} \right)\bar{C}_{sl}
\]

Taking the Laplace transform of Equation 2 and solving it:

\[
-q_{sl} \frac{d^2\bar{C}_{sl}}{dx^2} + q_{sl} \frac{d\bar{C}_{sl}}{dx} + A_0\bar{C}_{sl} - \omega_{sf}\bar{C}_{fs} = 0
\]

where:

\[
A_2 = R_{sl}p + \alpha_{sl} + \omega_{im} - \omega_{im}A_1 + J_2
\]

\[
R_{sl} = \theta_{sl} + f_{sl}\rho_{b}F_{sl}K_{sl}
\]

\[
J_2 = f_{sl}\rho_{b}pk_{sl} \frac{(1 - F_{sl})K_{sl}}{p}
\]

Solving Equation A9, we get:

\[
\alpha \frac{d^2\bar{C}_{sl}}{dx^2} - \frac{d\bar{C}_{sl}}{dx} = \frac{A_2}{q_{sl}}\bar{C}_{sl} - \frac{\omega_{sf}}{q_{sl}}\bar{C}_{fs}
\]
Similarly, the solution for the fast region can be obtained as:

\[
\frac{d^2 \bar{C}_{fs}}{dx^2} - \frac{d \bar{C}_{fs}}{dx} = \frac{A_3}{q_{fs}} \bar{C}_{fs} - \frac{\omega_{sf}}{q_{sl}} \bar{C}_{sl}
\]  

(A14)

where

\[
A_3 = R_{fs} p + \omega_{sf} + J_3
\]  

(A15)

\[
R_{fs} = \theta_{fs} + f_{fs} \rho_s F_{fs} K_{fs}
\]  

(A16)

\[
J_3 = f_{fs} \rho_s p k_{fs} \left(1 - F_{fs}\right) K_{fs} \left(p + k_{fs}\right)
\]  

(A17)

Now, Equations A13 and A14 are solved simultaneously using Eigenvalue and Eigenvector as shown:

\[
L \{C\} = AC
\]  

(A18)

where operator \(L\) is:

\[
L = \alpha \frac{d^2}{dx^2} - \frac{d}{dx}
\]  

(A19)

\[
A = \begin{bmatrix}
    \frac{A_3}{q_{fs}} & -\frac{\omega_{sf}}{q_{sl}} \\
    \frac{\omega_{sf}}{q_{sl}} & \frac{A_3}{q_{fs}} \\
    \frac{\omega_{sf}}{q_{fs}} & \frac{A_3}{q_{fs}} \\
\end{bmatrix}
\]  

(A20)

As the transformed concentration vector \(C\) is \(\bar{C}_{sl} \bar{C}_{fs}\), Eigenvalues (\(\lambda_1\) and \(\lambda_2\)) and Eigenvectors (\(\xi_1\) and \(\xi_2\)) corresponding to matrix \(A\) are obtained using the Mathematica software. They are given as:

\[
\lambda_1 = \frac{A_4 - \sqrt{A_3 + A_5}}{2q_{fs} q_{sl}}
\]  

(A21)

\[
\lambda_2 = \frac{A_4 + \sqrt{A_3 + A_5}}{2q_{fs} q_{sl}}
\]  

(A22)

\[
v_1 = \begin{bmatrix} \xi_{11} \\ \xi_{21} \end{bmatrix} = \begin{bmatrix} -\frac{A_4 - \sqrt{A_3 + A_5}}{2\omega_{sf} q_{sl}} \\ 1 \end{bmatrix}
\]  

(A23)

\[
v_2 = \begin{bmatrix} \xi_{12} \\ \xi_{22} \end{bmatrix} = \begin{bmatrix} -\frac{A_4 + \sqrt{A_3 + A_5}}{2\omega_{sf} q_{sl}} \\ 1 \end{bmatrix}
\]  

(A24)

where
\[ A_4 = A_2 q_{f,1} + A_3 q_{d} \]  
(A25)

\[ A_5 = A_2^2 q_{f,1}^2 - 2A_2 A_3 q_{f,1} q_{d} \]  
(A26)

\[ A_6 = 4A_2^2 q_{f,1} q_{d} + A_3^2 q_{d}^2 \]  
(A27)

\[ A_7 = A_2 q_{f,1} - A_3 q_{d} \]  
(A28)

There exists a modal matrix \( P \), using which matrix \( A \) is diagonalizable because matrix \( A \) will have distinct roots. These roots can be calculated as:

\[ A - \lambda I = 0 \]  
(A29)

Modal matrix \( P \) is defined from the Eigen vectors as:

\[ P = \begin{bmatrix} \zeta_{11} & \zeta_{12} \\ \zeta_{21} & \zeta_{22} \end{bmatrix} \]  
(A30)

Also, the modal matrix \( P \) has a property that allows the diagonalization of matrix \( A \):

\[ P^{-1}AP = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} \]  
(A31)

Now, a setting is done:

\[ C = PY \]  
(A32)

Substituting \( C \) in Equation A18:

\[ L(PY) = A(PY) \]  
(A33)

As \( P \) is linear:

\[ PL(Y) = APY \]  
(A34)

Pre-multiplying Equation A34 with \( P^{-1} \) leads to:

\[ L(Y) = P^{-1}APY \]  
(A35)

Using Equation A19 and A31, Equation A35 becomes:

\[
\begin{bmatrix}
\frac{d^2 Y_1}{dx^2} - \frac{dY_1}{dx} \\
\frac{d^2 Y_2}{dx^2} - \frac{dY_2}{dx}
\end{bmatrix} =
\begin{bmatrix}
\lambda_1 & 0 \\
0 & \lambda_2
\end{bmatrix}
\begin{bmatrix}
Y_1 \\
Y_2
\end{bmatrix}
\]  
(A36)

Solving the above equation for \( Y_1 \), we get:

\[ \frac{d^2 Y_1}{dx^2} - \frac{dY_1}{dx} = \lambda_1 Y_1 \]  
(A37)

\[ \left( \alpha D^2 - D - \lambda_1 \right) Y_1 = 0 \]  
(A38)

So,
\[ D_{1,2} = \frac{1 + \sqrt{1 + 4\alpha \lambda_1}}{2\alpha} \]  
(A39)

\[ D_{3,4} = \frac{1 + \sqrt{1 + 4\alpha \lambda_2}}{2\alpha} \]  
(A40)

\[ \therefore Y_1 = m_1 e^{\delta_1} + m_2 e^{\delta_2} \]  
(A41)

and

\[ Y_2 = m_3 e^{\delta_3} + m_4 e^{\delta_4} \]  
(A42)

For solving Equation A41, we need the boundary condition in terms of \( Y \). Since \( C = PY \):

\[ C = \begin{bmatrix} \zeta_{11} & \zeta_{12} \\ \zeta_{21} & \zeta_{22} \end{bmatrix} \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix} \]  
(A43)

At the boundary condition corresponding to \( C \), from Equations 7–11, it follows:

\[ C_{(0,i)} = C_0 \]  
(A44)

\[ \frac{\partial C}{\partial x}(x,t) = 0 \]  
(A45)

Therefore, at the boundary condition corresponding to \( \bar{C} \):

\[ \bar{C}_{(0,p)} = \frac{C_0}{p} \]  
(A46)

\[ \frac{\partial \bar{C}}{\partial x}(x,p) = 0 \]  
(A47)

When the boundary conditions are transformed corresponding to \( Y \), since \( C = PY \), we get:

\[ Y = P^{-1} C \]  
(A48)

Now

\[ P^{-1} = \frac{\text{adj} \{P\}}{|P|} \]  
(A49)

Using the values of \( P \) from Equation A30, we get:

\[ P^{-1} = \begin{bmatrix} \zeta_{22} & -\zeta_{12} \\ -\zeta_{21} & \zeta_{11} \end{bmatrix} \left( \zeta_{11} \zeta_{22} - \zeta_{12} \zeta_{21} \right) \]  
(A50)

Substituting \( P^{-1} \) in Equation A48:

\[ \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix} = \frac{1}{\left( \zeta_{11} \zeta_{22} - \zeta_{12} \zeta_{21} \right)} \begin{bmatrix} \zeta_{22} & -\zeta_{12} \\ -\zeta_{21} & \zeta_{11} \end{bmatrix} \begin{bmatrix} \bar{C}_{sl} \\ \bar{C}_{fs} \end{bmatrix} \]  
(A51)

which gives a value of:
\( Y_1 = \frac{\zeta_{12}C_{sl} - \zeta_{12}C_{fs}}{\zeta_{11}S_{22} - \zeta_{12}S_{21}} \) \hspace{1cm} (A52)

and

\( Y_2 = \frac{\zeta_{11}C_{fs} - \zeta_{21}C_{sl}}{\zeta_{11}S_{22} - \zeta_{12}S_{21}} \) \hspace{1cm} (A53)

The outlet conditions suggest that \( m_1 = m_3 = 0 \) and thus \( Y_1 = m_2 e^{\frac{d \xi}{2}} \).

At \( x = 0 \):

\[ m_2 = Y_1 = \left( \frac{\zeta_{22} - \zeta_{12}}{\zeta_{11}S_{22} - \zeta_{12}S_{21}} \right) \frac{C_0}{p} \] \hspace{1cm} (A54)

Therefore:

\[ Y_1 = \frac{C_0}{p} \left( \frac{\zeta_{22} - \zeta_{12}}{\zeta_{11}S_{22} - \zeta_{12}S_{21}} \right) e^{\frac{d \xi}{2}} \] \hspace{1cm} (A55)

and

\[ Y_2 = \frac{C_0}{p} \left( \frac{\zeta_{11} - \zeta_{21}}{\zeta_{11}S_{22} - \zeta_{12}S_{21}} \right) e^{\frac{d \xi}{4}} \] \hspace{1cm} (A56)

Using \( C = PY \):

\[
\begin{bmatrix}
C_{sl} \\
C_{fs}
\end{bmatrix} = \begin{bmatrix}
\zeta_{11} & \zeta_{12} \\
\zeta_{21} & \zeta_{22}
\end{bmatrix} \begin{bmatrix} Y_1 \\ Y_2 \end{bmatrix} \] \hspace{1cm} (A57)

\[ C_{sl} = \zeta_{11}Y_1 + \zeta_{12}Y_2 \] \hspace{1cm} (A58)

\[ C_{fs} = \zeta_{22}Y_2 + \zeta_{21}Y_1 \] \hspace{1cm} (A59)

**Appendix B: Details About the FAST Sensitivity Index**

The expected value of the output \( E[y] \) for a function \( f(x_1, x_2, \ldots, x_m) \) containing \( x_1, x_2, \ldots, x_m \) parameters can be evaluated by:

\[ E\{y\} = \int \cdots \int f(x_1, x_2, \ldots, x_m) P(x_1, x_2, \ldots, x_m) dx_1 \cdots dx_m \] \hspace{1cm} (B1)

where \( P \) is the \( m \)-dimensional probability density for \( x \). The FAST method expands the model into a Fourier series where Fourier coefficients are used to calculate the mean and the variance of the model.

\[ f(X) = \sum_{k_1=-\infty}^{\infty} \sum_{k_2=-\infty}^{\infty} \cdots \sum_{k_m=-\infty}^{\infty} C_{k_1 k_2 \cdots k_m} e^{\frac{j2\pi(k_1 x_1 + k_2 x_2 + \ldots + k_m x_m)}{\sigma^2}} \] \hspace{1cm} (B2)

with

\[ C_{k_1 k_2 \cdots k_m} = \int f(X) e^{-\frac{j2\pi(k_1 x_1 + k_2 x_2 + \ldots + k_m x_m)}{\sigma^2}} dX \] \hspace{1cm} (B3)
Using Equation 74, component \( f_{i1} \ldots f_{in} (x_{1i} \ldots x_{il}) \) of the analysis of variance (ANOVA), decomposition can be presented as Fourier series having \( k_{i1} \ldots k_{in} \) as the only non-null indices (Sobol’, 1990, 1993). Applying this method, the variance can be expressed as the sum of modulus of the Fourier coefficients.

\[
\text{var}\{f_{i1} \ldots f_{in}\} = \sum_{k_{i1} = -\infty}^{\infty} \ldots \sum_{k_{in} = -\infty}^{\infty} \left| C_{k_{i1} \ldots k_{in}} \right|
\]  

(B4)

To find the Fourier coefficients, the multi-dimensional integral in Equation B3 needs to be solved. Ergodic theorem is used to convert this equation into a one-dimensional integral by expressing every parameter as a function of a new independent variable ‘\( s \)’ (Saltelli et al., 1999).

\[
x_i(s) = \frac{1}{2} + \arcsin(\sin(\omega_i s))
\]  

(B5)

Here, \( \omega_i \) is the frequency assigned to \( x_i \), and \( s \) is the search variable. As Equation B5 is periodic in nature, \( s \) varying between \(-\infty\) and \( \infty \) traverses the entire curve (McRae et al., 1982). Hence, the expected output value is calculated as

\[
E\{y\} = \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x) \cdot ds
\]  

(B6)

Similarly, the variance of the first-order function, which only depends on the input parameter, can be represented by Fourier coefficients.

\[
E\{ y \mid x_i \} = \sum_i C_{ki}
\]  

(B7)

where coefficients can be calculated as:

\[
C_{ki} = \frac{1}{2\pi} \int_{-\pi}^{\pi} f(x) e^{-j2\pi k_i s} \cdot ds
\]  

(B8)

Results from Equations B6 and B7 are used to calculate the first-order sensitivity index, denoted as \( S_i \), which measures the effect of input parameter \( x_i \) on the output variance, ignoring the interaction with other parameters (Sobol’, 1993). It is estimated to be:

\[
S_i = \frac{\text{var}\{E\{ y \mid x_i \}\}}{\text{var}\{y\}}
\]  

(B9)

The value of \( S_i \) varies from 0 to 1. An increase in this value represents an increase in the corresponding parameter’s importance in the model outcome.

Appendix C: Comparison of the DPNE Model With Simpler Models

Comparison with the multi-process non-equilibrium model (MPNE) presented by Neville et al. (2000)

We start with the governing equations in the DPNE model. The governing solute transport equations for the fast, slow, and immobile regions are given as follows, respectively:

\[
\left( \theta_f + f_{pf} \rho_r K_f \right) \frac{\partial C_{fi}}{\partial t} + q_f \frac{\partial C_{fi}}{\partial x} = \theta_f D_f \frac{\partial^2 C_{fi}}{\partial x^2} - \omega_f \left( C_{fi} - C_{fi} \right) - f_{pf} \rho_r \frac{\partial S_{fi} \omega_f}{\partial t}
\]  

(C1)
The rate-limited sorption kinetics in the fast, slow, and immobile regions is represented as follows, respectively:

\[
\frac{\partial S_{f2}}{\partial t} = k_{f2} \left[ (1 - F_{f2}) K_{f2} C_{f2} - S_{f2} \right] \tag{C4}
\]

\[
\frac{\partial S_{s2}}{\partial t} = k_{s2} \left[ (1 - F_{s2}) K_{s2} C_{s2} - S_{s2} \right] \tag{C5}
\]

\[
\frac{\partial S_{im2}}{\partial t} = k_{im2} \left[ (1 - F_{im2}) K_{im2} C_{im2} - S_{im2} \right] \tag{C6}
\]

Now, we convert the DPNE model into the MPNE model. First, the immobile region in the slow domain is turned off by substituting \(\omega_{im} = 0\). As a result, Equation (C3) is eliminated, and Equation (C2) is modified as follows:

\[
\left( \theta_d + f_d F_d \rho_b K_d \right) \frac{\partial C_d}{\partial t} + q_d \frac{\partial C_d}{\partial x} = \theta_d D_d \frac{\partial^2 C_d}{\partial x^2} - \omega_d \left( C_d - C_{f2} \right) - \omega_{im} \left( C_d - C_{im} \right) - f_d \rho_b \frac{\partial S_{f2}}{\partial t} \tag{C7}
\]

Second, the slow region Equation (C7) is converted into an equation describing the immobile region by substituting \(q_d = 0\) (which also leads to \(D_d = 0\)):

\[
\left( \theta_d + f_d F_d \rho_b K_d \right) \frac{\partial C_d}{\partial t} + \frac{\partial C_d}{\partial x} = \theta_d D_d \frac{\partial^2 C_d}{\partial x^2} - \omega_d \left( C_d - C_{f2} \right) - f_d \rho_b \frac{\partial S_{f2}}{\partial t} \tag{C8}
\]

Equations (C1) and (C8) represent the MPNE model, in which \(\frac{\partial S_{f2}}{\partial t}\) and \(\frac{\partial S_{s2}}{\partial t}\) are calculated from Equations (C4) and (C5), respectively. The conceptual model of the MPNE model is shown in Figure C1.
Comparison With the MIM Model Developed by van Genuchten and Wierenga (1976)

The DPNE model can be further simplified into the MIM model. The MIM model developed by van Genuchten and Wierenga (1976) considers only instantaneous equilibrium sorption, that is, \( k_{fs} = k_{sl} = 0 \) in Equations C4 and C5 and \( F_{fs} = F_{sl} = 1 \) in Equations C1 and C8, resulting in:

\[
\left( \theta_{fs} + f_{fs} \rho_b K_d \right) \frac{\partial C_{fs}}{\partial t} + q_{fs} \frac{\partial C_{fs}}{\partial x} = \theta_{fs} D_{fs} \frac{\partial^2 C_{fs}}{\partial x^2} - \omega_{sf} \left( C_{fs} - C_d \right) \tag{C9}
\]

\[
\left( \theta_{sl} + f_{sl} \rho_b K_d \right) \frac{\partial C_{sl}}{\partial t} = \omega_{sf} \left( C_{fs} - C_d \right) \tag{C10}
\]

Additionally, \( f_{fs} = (1 - f_{fs}) \). Equations C9 and C10 represent the MIM model with instantaneous sorption. The simplified conceptual model is shown in Figure C2.

![Conceptualization of the MIM model.](image)

**Figure C2.** Conceptualization of the MIM model.

**List of Symbols**

- **Subscript “fs”** Parameters of the fast region
- **Subscript “sl”** Parameters of the slow region
- **Subscript “im”** Parameters of the immobile region
- **\( D \)** Dispersion coefficient \( (L^2 T^{-1}) \)
- **\( \omega_{sf} \)** Mass transfer coefficient between slow and fast regions \( (T^{-1}) \)
- **\( \omega_{im} \)** Mass transfer coefficient between slow and immobile regions \( (T^{-1}) \)
- **\( \theta \)** Porosity
- **\( Q \)** Darcy’s velocity \( (LT^{-1}) \)
- **\( V \)** Seepage velocity \( (LT^{-1}) \)
- **\( F \)** Fraction of sorption sites available
- **\( F \)** Fraction of sites for which sorption is instantaneous
- **\( C \)** Volume-averaged dissolved concentration in the liquid phase \( (ML^{-3}) \)
- **\( \bar{C} \)** Concentration in the Laplace domain
- **\( \rho_b \)** Bulk density of the porous medium \( (ML^{-3}) \)
- **\( \alpha \)** Dispersivity \( (L) \)
- **\( K_d \)** Sorption coefficient \( (L^3 M^{-1}) \)
- **\( K \)** First-order rate-limited sorption coefficient \( (T^{-1}) \)
- **\( S \)** Sorbed phase concentration \( (ML^{-3}) \)
- **\( P_e \)** Peclet number
- **\( D_m \)** Damkohler’s number
- **\( t_0 \)** Duration of the pulse-type input \( (T) \)
- **\( t_{max} \)** Maximum experimental duration \( (T) \)
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References


Datasets for this research are included in this paper (and its supplementary information files): Miyamoto et al. (2003) and referred at s. no. 39.


