

COMPARATIVE EVALUATION OF MODELS FOR NON-FICKIAN TRANSPORT IN UNSATURATED POROUS MEDIA

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ABSTRACT

Understanding solute transport in unsaturated porous media is essential for a wide range of scientific and engineering applications. This study investigates non-Fickian transport in unsaturated porous media using pore-network modelling to simulate quasi-static two-phase flow and tracer transport. The pore-network model was first validated against experiments in glass bead packing. Then the validated model was used to simulate transport in three different hypothetical network structures with three different correlated pore-size distributions (characterized by correlation lengths), different Péclet (Pe) numbers, and saturation values. Breakthrough curve (BTC) analysis reveals an expected shift from anomalous long-tailed behavior at low saturation to Fickian transport as saturation approaches unity. The simulation results were interpreted using three continuum-scale approaches: Mobile-Immobile (MIM), Multirate Mass Transfer (MRMT), Continuous-Time Random Walk (CTRW), and their predictions were compared against each other and to direct estimations (DE) obtained from the pore-network simulations. Estimates of stagnant zone saturation from the MIM and MRMT models show strong sensitivity to saturation and flow conditions, at times yielding unrealistic values. Dispersion coefficients derived from the MIM and DE exhibit non-monotonic variation with saturation, consistent with both simulation trends and previously reported experimental observations, while the MRMT and CTRW models fail to capture this behavior. The DE analysis demonstrates that mass transfer coefficients vary with time, challenging the assumption of constant rates in the MIM and MRMT formulations. The findings underscore limitations of continuum-scale models and emphasise the role of two-phase flow distributions, time-dependent mass transfer, and saturation-dependent dispersion in accurately predicting transport in unsaturated media.

KEYWORDS

Non-Fickian transport, Pore-network modelling, Direct estimation, Mobile-immobile model, MIM, Multirate mass transfer, MRMT, Continuous-time random walk, CTRW

WHY THIS PAPER MATTERS

Predicting how dissolved substances move through partially saturated porous media is challenging because uneven flow can cause some material to move rapidly while some is retained for much longer. We use detailed pore-scale simulations to test whether commonly used larger-scale models can reliably represent these underlying transport processes. Our results show that models can reproduce observed breakthrough behaviour while still producing parameters that do not accurately reflect the physical processes occurring within the pore space. This matters for improving predictions of solute and contaminant transport in environmental and engineering applications, including groundwater and subsurface systems.



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1. INTRODUCTION

Fluid flow and mass transfer in porous media are ubiquitous phenomena in a wide range of natural and engineered systems, including hydrology, agriculture, chemical engineering, biology, and the energy sector (6, 46, 60). Accurate quantification and prediction of the performance of such processes require a profound understanding of how a tortuous assembly of interconnected pores would affect the transport of a solute by a carrying fluid through them (63, 75). Solute transport by a carrying fluid occurs through advection, governed by fluid velocity, and diffusion, driven by concentration gradients and Brownian motion of solute molecules. Each mechanism has its own characteristic timescale, and their relative importance is characterized by the Péclet number (Pe), which is the ratio of advective to diffusive transport.

Solute transport in saturated (single phase) porous media is complex, primarily due to the interaction of the carrying fluid with the spatially variable pore size and hydraulic conductivity, resulting in a non-uniform velocity field and solute dispersion, a behavior typically described by a single advection-dispersion equation (2, 18, 28, 29, 76). Further complexities arise in unsaturated (multiphase) and/or heterogeneous porous media, in which, depending on the flow conditions, the connectivity of the pore space, and the distribution of the carrying phase, preferential flow pathways (mobile zones) provide a substantial contribution to the fluid flow and transport through the advection mechanism, whereas stagnant regions (immobile zones) may poorly contribute through the diffusion mechanism. These complexities lead to multiple characteristic transport timescales, hence anomalous or non-Fickian behaviors, such as long tails in the solute breakthrough curve (BTC), nonlinear evolution of dispersion and its dependence on the phase saturation topology (5, 10, 15, 16).

The advection-dispersion equation (ADE) is unable to describe non-Fickian transport in unsaturated porous media at the continuum scale because it does not incorporate two-phase flow properties, which significantly impact transport characteristics (42). Thus, alternative approaches, such as the mobile-immobile model (MIM), the multirate mass transfer model (MRMT), and the continuous-time random walk model (CTRW), have been adapted as inverse modelling tools to characterize non-Fickian dispersive transport in porous media under two-phase conditions (25, 31). In the MIM and MRMT models, considering non-equilibrium mass transfer between mobile and immobile

zones enables capturing early solute breakthrough through mobile zones and long tails in solute BTCs caused by diffusive mass transfer from immobile zones to mobile regions (8, 20, 34, 70). The average pore velocity, longitudinal dispersion coefficient, stagnant saturation, and mass transfer rate(s) are determined by fitting the BTC to the transport models (19, 53, 57, 74, 77). The MRMT model can be viewed as a generalized form of the MIM approach, introducing multiple immobile zones, each characterized by different mass transfer rates. This allows MRMT to account for different rate coefficients rather than a single value, making it particularly suitable for highly heterogeneous systems, such as fractured porous structures, where solutes experience a wide range of residence behaviors (65). The CTRW model has been developed based on the fact that the residence time of a solute particle in low-velocity regions is longer than in high-velocity zones and that the velocity changes in space only (not in time) on a characteristic length scale (13, 59, 61). In this model, the solute transport is described through spatiotemporal particle transitions, steps where a particle moves a certain distance and pauses for a random residence time, whose time distribution reflects mass transfer behavior (10). The CTRW model does not relate solute transport in diffusive-dominated zones to stagnant saturation and mass transfer rate(s); instead, it uses a power-law equation to capture the behavior over time. This is why stagnant saturation and mass transfer rates estimated from the CTRW model cannot be directly compared against those estimated by the MIM and MRMT models (17, 31). The CTRW model has been successfully used as an inverse model to characterize non-Fickian transport due to heterogeneity (12, 14, 23, 31) and solute transport under unsaturated conditions (10, 17, 78). While the above models have been extensively used to describe non-Fickian transport, their physical consistency still needs to be comprehensively evaluated (38).

Recent experimental and numerical studies have demonstrated that stagnant zone saturation and mass transfer between mobile and immobile zones can be directly estimated by characterizing solute transport in low- and high-velocity regions within unsaturated porous media (5, 37, 42, 43, 72). This approach, referred to as Direct Estimation (DE), uses a passive tracer as the solute, and its transport is characterized under steady-state saturation conditions, meaning that phase saturation values remain constant. Comparisons between DE-derived transport parameters and those obtained from the MIM model revealed that the stagnant saturation estimated by the MIM model varies with changes in the hydrodynamic conditions (characterized by Pe), even when the saturation topology remains unchanged (37). Furthermore, it was shown that the MIM model cannot explicitly incorporate two-phase flow properties in describing solute transport, as it is a phenomenological model that infers stagnant saturation solely from the BTC shape. In this work, we extend the above findings by systematically comparing the performance of the MIM, MRMT, and CTRW in predicting solute transport properties under two-phase flow conditions, and by evaluating their predictions against those obtained from the DE. We use pore-network modelling (PNM), owing to its ability to simulate transport in large domains with manageable computational cost, as an upscaling tool to simulate solute transport in three-dimensional (3D) unsaturated porous media, thereby obtaining BTCs and directly determining stagnant saturation, mass transfer rates, and solute concentrations in flowing and stagnant regions under different hydrodynamic conditions. This work provides new insight into the accuracy, validity, and applicability of the above commonly used non-Fickian models for describing solute transport in unsaturated porous media.

2. THE PHYSICAL FRAMEWORK OF CONTINUUM-SCALE TWO-PHASE TRANSPORT MODELS

In this section, we provide a brief review of the physical framework of the MIM, MRMT, and CTRW models, which are extensively used to characterize solute transport in unsaturated porous media. Additionally, we review the physical framework of the DE approach, focusing on the procedures for obtaining stagnant saturation and mass transfer rates.

2.1. Mobile-immobile model (MIM)

The MIM model was first developed by van Genuchten et al. (70) to characterize chemical transport through an unsaturated porous medium. In this model, the pore space is divided into two distinct regions based on pore velocity: (i) flowing (mobile) zones and (ii) stagnant (immobile) zones (3, 58). The full set of equations for non-reactive solute transport in the MIM model can be written as:

$$\frac{\partial C_f}{\partial t} + \left(\frac{S_s}{S - S_s} \right) \frac{\partial C_s}{\partial t} = D \frac{\partial^2 C_f}{\partial x^2} - v \frac{\partial C_f}{\partial x} \quad (1)$$

$$S_s \phi \frac{\partial C_s}{\partial t} = \gamma (C_f - C_s) \quad (2)$$

where C is concentration, S is saturation of the solute-carrying fluid phase, and the subscripts f and s denote its flowing and stagnant portions, respectively ($S = S_f + S_s$). D is the longitudinal dispersion coefficient, v is the average mobile pore velocity, γ is the first-order mass transfer coefficient, and ϕ is porosity. It can be seen that **Equation 1** extends the classical ADE by incorporating the non-equilibrium mass transfer between the flowing and stagnant zones, herein referred to as the source-sink term, and **Equation 2** accounts for this new term. Several experimental and modelling studies have employed the MIM model to describe non-Fickian transport in unsaturated porous media (7, 27, 30, 50, 55, 64, 66). In this work, transport parameters (S_s , D , v , and γ) were estimated by inverse modelling using a modified version of the CXTFIT code implemented in the STANMOD package (67, 69). In this framework, **Equations 1** and **2** are reduced to analytical solutions under the prescribed initial and boundary conditions by reformulating the governing equations in dimensionless form, following the approach of Toride et al. (67). These analytical solutions serve as the forward model in the inverse problem. Parameter estimation is then carried out by minimizing the squared difference between the simulated BTCs and the model predictions using a non-linear least-squares optimization algorithm.

2.2. Multirate mass transfer model (MRMT)

The long tailing of BTC in non-Fickian transport through a non-adsorbing porous system can result from the presence of several stagnant zones, each with unique characteristics and mass transfer rate (34, 35). To account for this, **Equations 1** and **2** can be extended to include N stagnant zones, each characterized by a unique mass transfer coefficient γ_j :

$$\frac{\partial C_f}{\partial t} + \sum_{j=1}^N \sigma_j \frac{\partial (C_s)_j}{\partial t} = D \frac{\partial^2 C_f}{\partial x^2} - v \frac{\partial C_f}{\partial x} \quad (3)$$

$$(S_s)_j \phi \frac{\partial (C_s)_j}{\partial t} = \gamma_j (C_f - (C_s)_j) \quad (4)$$

in which σ_j is the capacity coefficient of the stagnant zone j , defined as the ratio of its saturation to the flowing saturation (34):

$$\sigma_j = \frac{(S_s)_j}{S - (S_s)_j}. \quad (5)$$

While the source-sink term is typically expressed as the derivative of stagnant concentration with respect to time, as shown in **Equations 3** and **4**, an alternative formulation proposed by Haggerty et al. (36) uses a convolution integral to express the source-sink in terms of a memory function, $g(t)$:

$$g(t) = \int_0^\infty \gamma b(\gamma) e^{-\gamma t} d\gamma \quad (6)$$

and the derivative of flowing concentration with respect to time. In **Equation 6**, $b(\gamma)$ is a density function of the mass transfer coefficient γ , which can be described by a power-law equation:

$$b(\gamma) = \frac{\sum_{j=1}^N \sigma_j (k-2)}{\gamma_{max}^{k-2} - \gamma_{min}^{k-2}} \gamma^{k-3} \quad k > 0, k \neq 2, \gamma_{min} \leq \gamma \leq \gamma_{max} \quad (7)$$

where k is an exponent, and γ_{min} and γ_{max} are the minimum and maximum mass transfer coefficients, respectively (36). In the MRMT framework, the governing transport equations are reformulated using a memory function that represents the superposition of mass transfer processes associated with a continuous distribution of stagnant regions. Under the prescribed initial and boundary conditions, this formulation yields a semi-analytical solution in which the source-sink term is expressed through a convolution integral involving the memory function (**Eq. 6**). These semi-analytical expressions serve as the forward model for inverse analysis. Transport parameters, including the dispersion coefficient D and the parameters defining the mass transfer rate distribution (e.g. γ_{min} , γ_{max} , and k), are estimated by fitting the model predictions to the breakthrough curves using a non-linear least-squares optimization algorithm. In this study, the inverse modelling was performed using the STAMMT-L code (33), which efficiently evaluates the semi-analytical MRMT solution without requiring explicit numerical discretization of the governing equations.

2.3. Continuous-time random walk model (CTRW)

In the CTRW model, the ADE for solute transport is represented by a Generalized Master Equation in the Laplace transformed space of the time variable t , with the Laplace variable denoted by u and Laplace transformed quantities by $\sim$ (22, 24):

$$u\tilde{c}(x, u) - c_0(x) = -\tilde{M}(u) \left[v_\psi \frac{\partial \tilde{c}(x, u)}{\partial x} - D_\psi \frac{\partial^2 \tilde{c}(x, u)}{\partial x^2} \right] \quad (8)$$

In the above equation, D_ψ and v_ψ are the Laplace transformed dispersion coefficient and the pore velocity, respectively, $c_0(x)$ is the initial concentration and $\tilde{c}$ is the Laplace transformed concentration. $\tilde{M}(u)$ is a memory function accounting for the unknown heterogeneities at the pore scale, defined as:

$$\tilde{M}(u) = \bar{t} u \frac{\tilde{\psi}(u)}{1 - \tilde{\psi}(u)} \quad (9)$$

where $\bar{t}$ is the characteristic time. $\tilde{\psi}(u)$ in **Equation 9** is the Laplace transform of a truncated power-law (TPL) probability distribution function $\psi(t)$, describing each solute particle transition with time:

$$\tilde{\psi}(u) = (1 + \tau_2 u t_1)^\beta \exp(t_1 u) \Gamma(-\beta, \tau_2^{-1} + t_1 u) / \Gamma(-\beta, \tau_2^{-1}) \quad (10)$$

In the above equation, $\tau_2 \equiv t_2/t_1$, β is the exponent determining the nature of the dispersion (Fickian at $\beta > 2$ and non-Fickian at $0 < \beta < 2$) (22, 25), and Γ is the incomplete Gamma function (22). The parameter t_1 is the average time for a solute particle to move from one pore to another (25), and t_2 is the cut-off time, separating transport in advective-dominated (flowing) zone from that in diffusive-dominated (stagnant) zone (25).

The CTRW governing equation is formulated in the Laplace domain and is transformed numerically into the time domain under the prescribed initial and boundary conditions. In this study, the time-domain solution was evaluated using the CTRW MATLAB Toolbox v4.0 (21), which employs numerical Laplace inversion techniques to compute breakthrough curves. Model parameters β , t_1 , t_2 , v_ψ , and D_ψ were estimated via inverse modelling by fitting the simulated breakthrough curves to the numerical CTRW solution. Parameter optimization was performed using the toolbox's built-in error minimization algorithm, which iteratively adjusts the CTRW parameters to minimize the misfit between the predicted and observed BTCs.

2.4. Direct estimation (DE)

The direct estimation (DE) approach was first introduced by Karadimitriou et al. (42) and used to characterize non-Fickian solute transport in two-dimensional (2D) unsaturated porous media, and expanded to 3D porous media by Hasan et al. (37) and An et al. (3). To directly estimate the stagnant saturation in the DE, steady-state two-phase saturation conditions must first be established, ensuring that the saturation values of the phases remain constant over time. Under these conditions, a tracer is injected into one of the fluid phases, typically the aqueous/non-wetting phase. As the tracer moves through the porous medium, two distinct zones appear: the flowing zone, dominated by advective transport, and the stagnant zone, where transport is predominantly diffusion-controlled. This means that, unlike the above models that rely solely on breakthrough curve (BTC) fitting, DE requires detailed spatial information about flow and/or transport within the domain. Although this makes the approach more data intensive, it also allows the underlying pore-scale physics to be explicitly incorporated, leading to more physically consistent and reliable estimates of transport parameters (4, 42).

To evaluate transport characteristics, local pore velocities obtained from PNM are extracted, and their histogram is plotted at different S values, which typically shows a bimodal distribution at intermediate saturations ($0 \ll S \ll 1$) with the first peak representing the stagnant zone and the second peak representing the flowing zone, and a unimodal distribution when $S \rightarrow 0$ or 1 (3, 5, 37, 73). The grouped plot of the local pore velocity histograms is then analyzed to find a threshold velocity that separates the first and second peaks. Using this threshold as a guide, a search algorithm is applied to obtain the stagnant saturation, which is defined as:

$$S_s = \frac{\sum_{u < \bar{v}} r_{ij}^2 l_{ij}}{\sum r_{ij}^2 l_{ij}} + \frac{\sum_{u < \bar{v}} R_i^3}{\sum R_i^3} \quad (11)$$

In this equation, $\bar{v}$ is the threshold velocity, l_{ij} is the length of the pore throat connecting pore bodies i and j , r_{ij} and R_i are the radii of pore throats ij and pore bodies i , respectively, and u represents the local pore velocity. Hasan et al. (37) proposed that relative permeability-saturation curves bear important information about the stagnant saturation and established a scaling between their stagnant saturation and total relative permeability. The stagnant saturation can be also directly estimated by using real-time visualization of solute transport, through identifying zones delayed in mixing (stagnant zones) and those that have reached the injection solute concentration (flowing zones) (41, 42, 72).

In this work, we utilized the first approach, in which the histogram of local pore velocities is obtained at different saturations to find $\bar{v}$, followed by using **Equation 11** to calculate S_s , and **Equation 12**:

$$C_f = \frac{\sum_{u \geq \bar{v}} C_i V_i}{\sum V_i} \quad (12)$$

and **Equation 13**:

$$C_s = \frac{\sum_{u < \bar{v}} C_i V_i}{\sum V_i} \quad (13)$$

to obtain C_f and C_s , respectively. In **Equations 12** and **13**, C_i and V_i denote the solute concentration and volume, respectively, of the control volume comprising pore body i and one-half of each neighboring pore throat. Eventually, **Equation 2** is rearranged to determine γ :

$$\gamma(t) = \frac{S_s \phi}{C_f - C_s} \frac{\partial C_s}{\partial t}. \quad (14)$$

When using DE, we first characterize the stagnant and flowing zones for a given saturation. A threshold time, defined as the time when the solute in the flowing zone reaches 0.99, is then identified to separate the solute transport in these two zones. Using this time, the portion of the effluent flux-averaged BTCs affected by solute transport in the flowing zone, attributed to the Fickian transport (4), is fitted to the analytical solution of the advection-dispersion equation (54):

$$\langle C_{OB}^f(x, t) \rangle = \frac{1}{2} C_{\max} \left[\operatorname{erfc} \left(\frac{x - vt}{2\sqrt{Dt}} \right) + \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left(\frac{x + vt}{2\sqrt{Dt}} \right) \right] \quad (15)$$

to obtain D and v .

At a given saturation S , the presence of stagnant zones can cause breakthrough curves to exhibit strong skewness at early and/or late times, which may adversely affect the inverse optimization used to fit the transport models. The quantity $\langle C^f(t) \rangle$ is normalized by the inlet concentration and therefore varies between 0 and 1. Values of $\langle C^f(t) \rangle$ smaller than 10^{-5} and larger than 0.99 were excluded from the fitting procedure solely to improve numerical robustness and parameter identifiability, as these extreme early- and late-time data points are particularly sensitive to tailing effects and numerical noise.

The DE is inherently more computationally demanding than continuum-scale inverse models, as it requires detailed pore-scale information on velocity fields, saturation distributions, and/or transient solute concentrations. In this work, these quantities are obtained from pore-network simulations, although equivalent information may also be acquired experimentally using high-resolution imaging and tracer visualization techniques (41, 42, 72). From a computational perspective, the dominant cost arises from resolving steady-state two-phase flow and transient solute transport at the pore scale, followed by post-processing steps such as velocity histogram analysis, phase partitioning, and time-dependent mass transfer estimation. These requirements currently limit the direct application of DE to small domains, typically at the millimeter scale, where pore-scale resolution is feasible. Nevertheless, DE is not intended as a replacement for continuum-scale transport models in field applications. Rather, it provides a physically grounded benchmark that enables direct quantification of stagnant saturation, dispersion, and mass transfer dynamics based on pore-scale transport mechanisms. Recent advances in pore-scale modelling and high-performance computing have demonstrated that pore-resolved simulations can be extended to centimeter-scale domains, such as core-scale systems, thereby expanding the range of conditions under which DE-derived insights can be obtained (49).

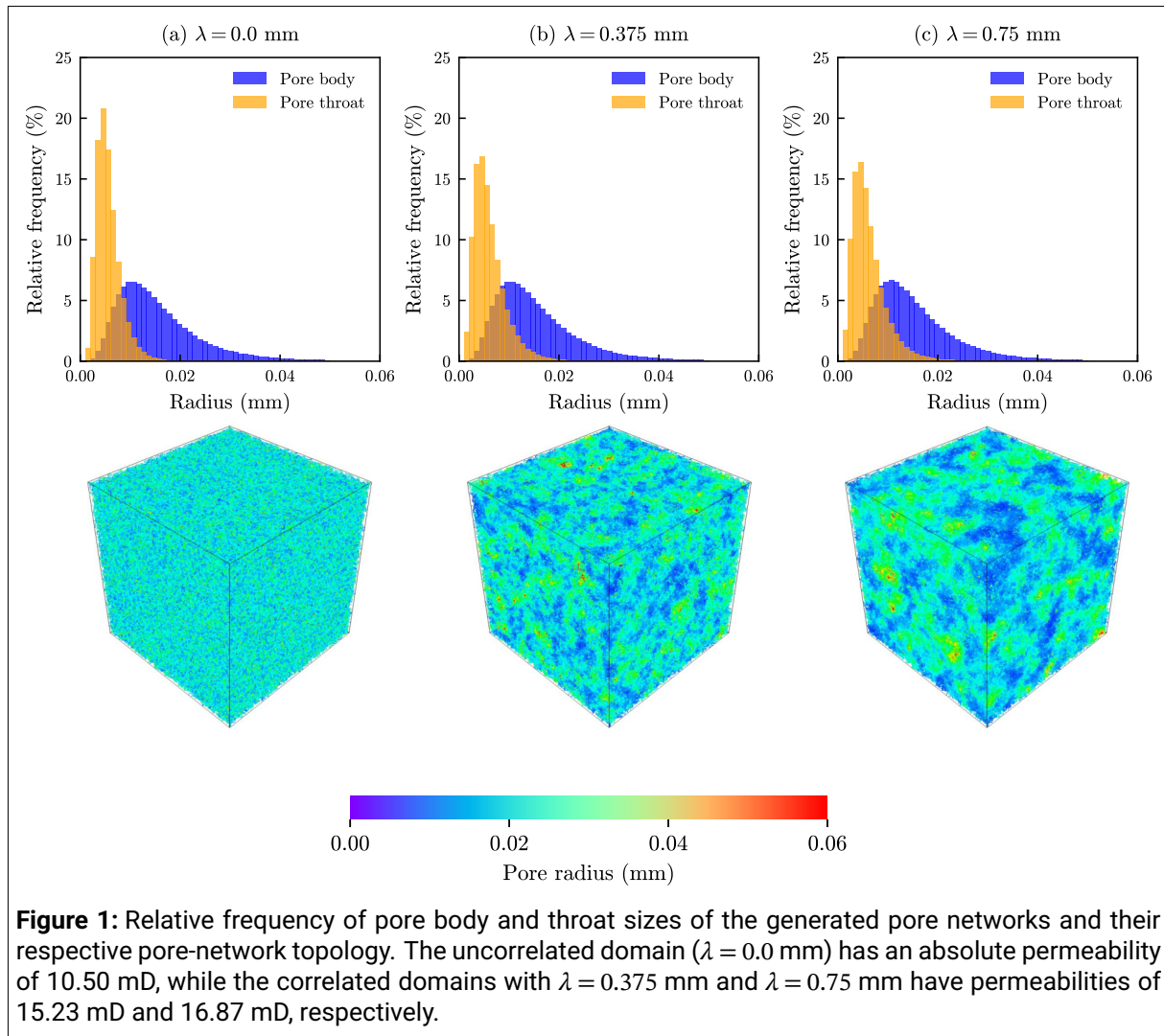
3. METHODOLOGY

3.1. Pore-network models

In this study, we adopted the procedure detailed by Babaei and Niasar (6) to generate pore networks. Briefly, the topology of the networks was first created using 3D Delaunay triangulation, where the vertices represent the positions of pore bodies and the edges represent the pore throats. Next, excessively long pore throats were identified and removed such that a realistic mean coordination number is generated. Finally, a correlation length (λ) field generator was used to specify the sizes of the pore bodies and throats. Following the above procedure, three pore networks with dimensions of $15 \times 15 \times 15 \text{ mm}^3$ and over a million pore bodies were generated: a homogeneous uncorrelated network ($\lambda = 0.0 \text{ mm}$) and two heterogeneous correlated ($\lambda = 0.375 \text{ mm}$ and 0.75 mm) networks. The corresponding absolute permeabilities were 10.50 mD, 15.23 mD, and 16.87 mD, respectively (4). The generated networks and their relative frequency of the pore body and throat sizes are shown in **Figure 1** and their statistical details are tabulated in **Table 1**. It is emphasized that the pore networks have the same topology but different spatial distribution of pore bodies and throats.

Table 1: Statistical details of the pore body and throat sizes of the generated pore networks; λ denotes the spatial correlation length of the pore sizes.

λ (mm)	Pore body statistics		Pore throat statistics	
	Mean (mm)	Standard deviation (mm)	Mean (mm)	Standard deviation (mm)
0	0.0156	8.61×10^{-3}	0.0056	2.45×10^{-3}
0.375	0.0156	8.58×10^{-3}	0.0061	3.24×10^{-3}
0.75	0.0156	8.53×10^{-3}	0.0063	3.45×10^{-3}

**Figure 1:** Relative frequency of pore body and throat sizes of the generated pore networks and their respective pore-network topology. The uncorrelated domain ($\lambda = 0.0$ mm) has an absolute permeability of 10.50 mD, while the correlated domains with $\lambda = 0.375$ mm and $\lambda = 0.75$ mm have permeabilities of 15.23 mD and 16.87 mD, respectively.

3.2. Steady state two-phase flow and solute transport simulation

We followed the methodology detailed by An et al. (3) to simulate solute transport in a pore network under two-phase flow conditions. The process starts by establishing steady-state saturation conditions, achieved by displacing the receding fluid (wetting phase) with the invading fluid (non-wetting phase). The displacement is governed by the entry capillary pressure, calculated for pore throats using the Young-Laplace equation. Different saturation states are obtained by progressively invading the pore network according to the entry capillary pressure criterion until a target steady-state saturation is reached. Upon establishing the steady-state saturation field throughout the domain, solute, dissolved in the invading fluid, is injected from the inlet. We highlight that the solute is assumed to be soluble only in the invading fluid; therefore, no inter-phase mass transfer is considered during solute transport. Such a configuration is representative of situations in which solutes are transported within non-wetting carrier fluids, including surfactant or tracer transport

in aqueous phases during enhanced oil recovery in oil-wet reservoirs (1), and organic contaminant transport within non-aqueous phase liquids (NAPLs) in subsurface remediation (44, 51).

To simulate solute transport, the classical ADE with the Taylor-Aris dispersion correction factor (9, 37, 39) is solved only for pores occupied by the invading fluid, with Dirichlet boundary conditions being applied at the inlet ($C|_{\text{in}} = 1.0$) and zero-gradient boundary conditions imposed at the outlet ($C_i - C|_{\text{out}} = 0.0$), to compute temporally evolving local pore concentrations. For pore body i , the conservation equation for the concentration can be expressed as follows:

$$V_i \frac{\partial C_i}{\partial t} = \sum_{q_{ij} < 0} q_{ij} C_i + \sum_{q_{ij} > 0} q_{ij} C_j + \sum_{j \in N_i} \pi r_{ij}^2 D_{ij} \left(\frac{C_j - C_i}{l_{ij}} \right), \quad \{i, j\} \in \Omega_{\text{invading fluid}} \quad (16a)$$

$$D_{ij} = D_m (1 + \kappa Pe_{ij}^2), \quad \kappa = 1/192 \quad (16b)$$

where C_i is the solute concentration in pore body i , D_{ij} is the Taylor-Aris dispersion coefficient, D_m represents molecular diffusion, and N_i denotes the coordination number of pore body i (the number of pore throats connected to pore body i). The summation over $j \in N_i$ therefore accounts for diffusive mass exchange between pore body i and all its directly connected neighbouring pore bodies through the associated pore throats. The local Pe number is defined as $Pe_{ij} = v_{ij} r_{ij} / D_m$ with v_{ij} being the average pore velocity in the pore throat ij . The volumetric flow rate q_{ij} between pore bodies i and j is obtained by solving the steady-state flow problem on the pore network, restricted to regions occupied by the invading phase, prior to the transport simulation. Flow through each pore throat is assumed to be laminar, and q_{ij} is calculated using a Hagen-Poiseuille-based conductance formulation as a function of the pressure difference between connected pore bodies (68):

$$q_{ij} = \frac{A_{ij}^2 G_{ij}}{2\mu l_{ij}} (P_i - P_j) \quad (17)$$

where A_{ij} is the cross-sectional area of the pore throat, μ is the viscosity of the carrying fluid, and P_i and P_j are the pressures in pore bodies i and j , respectively. The shape factor G_{ij} accounts for the throat geometry and is determined directly from the extracted pore-network geometry as $G_{ij} = V_{ij} l_{ij} / A_s^2$, where V_{ij} is the pore throat volume and A_s is its surface area. These geometric quantities are obtained from image-processing-based pore-network extraction methods following the procedure described by Dong and Blunt (26).

The ADE is solved under the following simplifying assumptions: (i) the flow through pore throats is considered laminar, hence the Hagen-Poiseuille equation can be used to compute the pore velocities, (ii) pore bodies are spherical and pore throats are cylindrical, (iii) pore bodies have no resistance against the flow compared to the pore throats, and (iv) complete mixing occurs in pore bodies. Under these assumptions, **Equation 16b** follows from the classical Taylor-Aris dispersion theory, which predicts that dispersion in a cylindrical tube scales with the square of the mean fluid velocity, and hence with Pe^2 . A further requirement of the Taylor-Aris formulation is that transverse diffusive mixing across the pore throat cross-section occurs sufficiently rapidly compared to axial advection. For the pore throat sizes and molecular diffusion coefficient considered here, the characteristic transverse diffusion timescale, $t_d \sim r_{ij}^2 / D_m$, is much smaller than the advective residence time within individual pore throats. The use of the Taylor-Aris dispersion correction is therefore appropriate over the temporal and spatial scales investigated in this study. We note that in real porous media, dispersion commonly exhibits a weaker, sub-quadratic dependence on Pe due to pore-scale heterogeneity, tortuous flow paths, and enhanced mixing in complex geometries. Such effects are not explicitly represented in idealized Poiseuille tube models and may lead to deviations from the Pe^2 scaling observed in experimental systems (45, 47, 62).

Table 2: Péclet (Pe) numbers for the three pore networks at different saturation (S) and differential pressure (ΔP) conditions.

<i>Pe</i> values for uncorrelated network ($\lambda = 0.0$ mm)					
ΔP (kPa)	$S = 0.41$	$S = 0.49$	$S = 0.62$	$S = 0.75$	$S = 0.94$
10	1.95	4.20	14.25	37.65	92.40
50	9.75	21.45	71.85	187.80	461.85
100	19.50	42.75	143.70	375.60	923.70

<i>Pe</i> values for correlated network ($\lambda = 0.375$ mm)					
ΔP (kPa)	$S = 0.35$	$S = 0.48$	$S = 0.61$	$S = 0.80$	$S = 0.95$
10	2.10	7.35	20.55	71.85	136.80
50	10.95	36.75	102.75	359.70	684.15
100	21.90	73.65	205.50	719.40	1368.45

<i>Pe</i> values for correlated network ($\lambda = 0.75$ mm)				
ΔP (kPa)	$S = 0.31$	$S = 0.59$	$S = 0.80$	$S = 0.96$
10	4.20	27.60	83.10	147.30
50	21.30	138.45	415.35	736.95
100	42.75	276.90	830.85	1474.35

The average resident concentration $\langle C^r(t) \rangle$ at time t is then calculated by averaging the pore concentrations, weighted by the pore volume V_i :

$$\langle C^r(t) \rangle = \frac{\sum C_i(t)V_i}{\sum V_i}, i \in \Omega_{\text{invading fluid}}. \quad (18)$$

The effluent flux-averaged concentration $\langle C^f(t) \rangle$ is also calculated by averaging the concentrations at outlet pores C_{ij} , weighted by q_{ij} :

$$\langle C^f(t) \rangle = \frac{\sum C_{ij}(t)q_{ij}}{\sum q_{ij}}, ij \in \Omega_{\text{outflow boundary}} \quad (19)$$

The parameters $\langle C^r(t) \rangle$ and $\langle C^f(t) \rangle$ can then be plotted against time to obtain the resident and flux-averaged BTCs. Finally, the effluent flux-averaged concentration BTC is fitted to the solute transport models (see Section 2) to obtain the fitting parameters and characterize the nature of the transport. A criterion of $R^2 > 0.98$ was applied in this work for BTC fitting and inverse modelling to ensure the reliability of the fitted parameters (R^2 values available in the **Supplementary Material, available online**).

The simulations were conducted at a wide range of the invading (solute-carrying) non-wetting phase saturation values and differential pressures of 10, 50, and 100 kPa for all three pore networks, corresponding to the pressure gradients of 0.667, 3.333, and 6.667 MPa/m, respectively. Only saturation values $S > 0.3$ were considered, which were chosen to be well above the percolation threshold of the invading phase, thereby ensuring the presence of a continuous spanning cluster that enables solute transport across the domain. It should be noted that varying saturation through the immiscible displacement process modifies pore-scale connectivity and flow pathways, leading to systematic variations in characteristic velocities and transport regimes under a given differential pressure. Under pressure-driven conditions, this behavior is consistent with Darcy's law for multiphase flow, $\mathbf{v}^\alpha = -(k k_r^\alpha / \mu^\alpha) \nabla P$, where k is the absolute permeability, k_r^α is the relative permeability of phase α , and μ^α is its viscosity (3). For a fixed imposed pressure gradient, the characteristic velocity of the solute-carrying phase therefore scales with its relative permeability, i.e. $\mathbf{v}^\alpha \propto k_r^\alpha$. Such conditions are representative of subsurface transport problems in partially saturated porous media, where a prescribed pressure gradient is applied, and solute migration occurs within the connected phase while saturation-dependent pore connectivity evolves.

For each imposed ΔP , the corresponding Pe numbers were calculated at different S values using the **Equation (20)**:

$$Pe = \frac{v_{in} l_c}{D}, \quad (20)$$

where v_{in} is the average inlet velocity, $l_c = 15$ mm is the characteristic length, and $D = 10^{-9}$ m²s⁻¹ is the diffusion coefficient. The characteristic length l_c corresponds to the length of the pore network and is used here to define a macroscopic (continuum-scale) Pe number based on the advective residence time across the domain. This definition is consistent with the MIM, MRMT, and CTRW models discussed in Section 2, which work at the continuum scale and do not explicitly resolve pore-scale length scales. While saturation alters pore-scale connectivity and local transport pathways, its effect on the macroscopic Pe number is captured through the saturation-dependent inlet velocity v_{in} rather than through a variable characteristic length. A similar definition of l_c was adopted by Huysmans and Dassargues (40). **Table 2** summarizes the calculated Pe numbers for each pore network under varying saturation and differential pressure conditions.

3.3. Validation of the pore-network model

We validated the above methodology by comparing its performance in predicting solute transport behavior in a porous medium against the experimental results reported by Van Offenwert et al. (71). The experimental study used fast X-ray micro-CT imaging to quantify transient solute concentration fields in a saturated porous medium (sintered glass with pore sizes of 150 - 250 μm ^a). An X-ray micro-CT image of the dry sample, with dimensions of 6.0 mm in diameter and 5.0 mm in length and a porosity of 0.23, was used to extract a pore-network model using the distance map, maximal ball, and watershed algorithms (56). The extracted network had cylindrical pore throats and spherical pore bodies, with a porosity of 0.22, similar to that of the real porous medium.

Solute transport was simulated in the pore network at two injection rates of 0.25 and 0.50 $\mu\text{l s}^{-1}$, identical to the experimental conditions (71). To account for the delay in solute concentration reaching unity at the inlet, which was observed experimentally (possibly due to the solute dispersion within the injection line), **Equation 21** was used to specify the concentration values at the inlet pores:

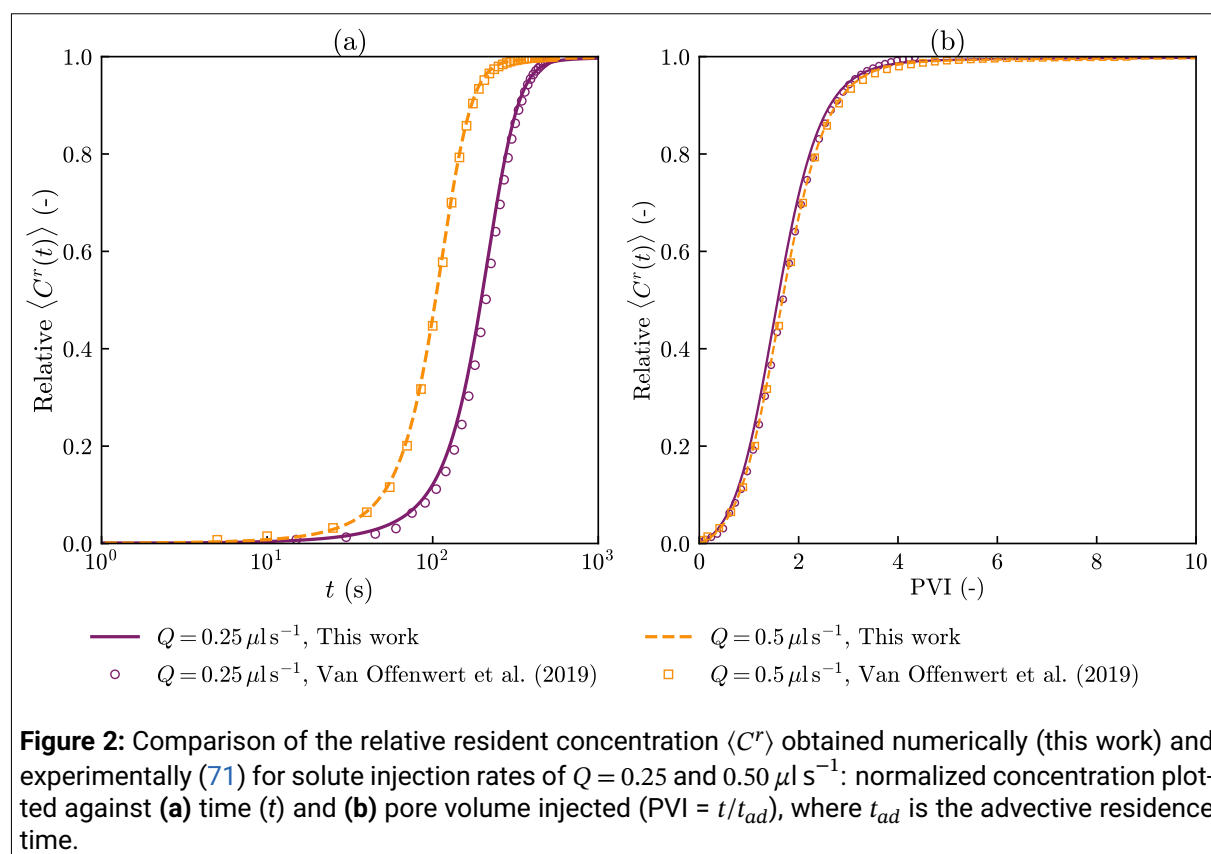
$$C(t)|_{in} = \frac{\exp(a(t - b))}{\exp(a(t - b)) + 1} \quad (21)$$

in which a and b are the fitting coefficients, determined by fitting the equation to the experimental data (see **Supplementary Material** for more details, [available online](#)). The steady-state volumetric flow rates q_{ij} , computed using **Eq. 17**, were then used to formulate the mass balance for each pore body and to resolve advective solute transport and the temporal evolution of C_i . Eventually, the relative $\langle C^r(t) \rangle$ (**Eq. 18**) was obtained and plotted against time and the injected pore volume of the invading fluid, PVI, obtained by scaling t by the advective characteristic time:

$$t_{ad} = \frac{V_p S}{Q} \quad (22)$$

The resulting BTCs are compared with the experimentally determined results in **Figure 2**. As can be seen, the simulation results are in excellent agreement with the experimental data at both solute injection rates, confirming the accuracy of the approach. We highlight that although the validation is performed under fully saturated conditions, it remains relevant because the solute transport simulations in the unsaturated cases are conducted only after the immiscible displacement process has reached steady state (see Section 3.2), with the solute assumed to be soluble exclusively in the invading phase.

^aROBU P0, Germany; <https://www.robuglas.com/>



4. RESULTS AND DISCUSSION

4.1. Breakthrough curves

Figure 3 illustrates $\langle C^f(t) \rangle$ against PVI at different ΔP and S values for the three pore networks. It is evident that the breakthrough curves transition from non-Fickian behavior, characterized by pronounced tailing, to more Fickian behavior as S increases towards unity, irrespective of λ and ΔP . This trend is expected because, at different S values, imposing a constant ΔP results in different flow rates and characteristic velocities, and hence different Pe numbers (**Table 2**). Similar behavior has been observed experimentally by Padilla et al. (55) and numerically by Hasan et al. (37) and An et al. (3), highlighting the critical role of saturation in shaping the magnitude and distribution of the pore-scale velocity field under a given hydrodynamic forcing, thereby governing solute transport dynamics in partially saturated porous media. **Figures 4** and **5** show the evolution of the average concentrations in the flowing and stagnant regions, C_f and C_s , as a function of PVI for the same ΔP and S conditions. As expected, concentrations in both regions evolve over time; however, their rates of change differ due to contrasting transport mechanisms. In the flowing region, concentration evolution is primarily controlled by advection, leading to a rapid increase towards the unity at small PVI. In contrast, transport in the stagnant region is diffusion dominated, resulting in a slower approach. Moreover, the evolution of C_s is non-linear in time, which is consistent with a temporally varying mass transfer rate between the flowing and stagnant regions.

To quantify the role of S in controlling non-Fickian transport, we define τ as the PVI required for $\langle C^f(t) \rangle$ to increase from 0.0 to 0.99 and plot it against S for different values of λ and ΔP in **Figure 6**. As observed, τ decreases with increasing S for all λ and ΔP values, consistent with the BTC trends in **Figure 3**. This declining behavior is because higher S values provide greater interconnected pore space for the invading fluid flow, and accordingly, solute transport. At lower S , more pores act as dead-ends, reducing hydraulic conductivity, increasing tortuosity, and thereby limiting effective solute transport and promoting non-Fickian behavior. Furthermore, for a given λ and S , τ generally

decreases with increasing ΔP , as higher pressure gradients increase mean and local pore velocities (and thus Pe), accelerating advective transport and reducing the PVI required to reach $\langle C^f(t) \rangle = 0.99$. In addition, for a given ΔP , higher τ values are observed at larger λ . This behavior reflects the fact that increasing spatial correlation in pore sizes promotes the formation of extended preferential flow pathways coexisting with larger and more persistent low-velocity or stagnant regions. Given these stagnant regions are less efficiently accessed by advective transport and rely predominantly on diffusive mass exchange with the flowing zones, which slows solute equilibration and prolongs late-time tailing in the BTCs. As a result, a larger injected pore volume is required for $\langle C^f(t) \rangle$ to approach unity, leading to increased τ values and more pronounced non-Fickian behavior (4). As S approaches unity, the τ values converge across all λ and ΔP cases, indicating that most of the pore space becomes accessible to the solute, thereby reducing non-Fickian transport characteristics. We emphasize that the above comparative discussion reflects transport behavior under two-phase flow conditions, in which saturation, pore connectivity, velocity distributions, and Pe are intrinsically coupled.

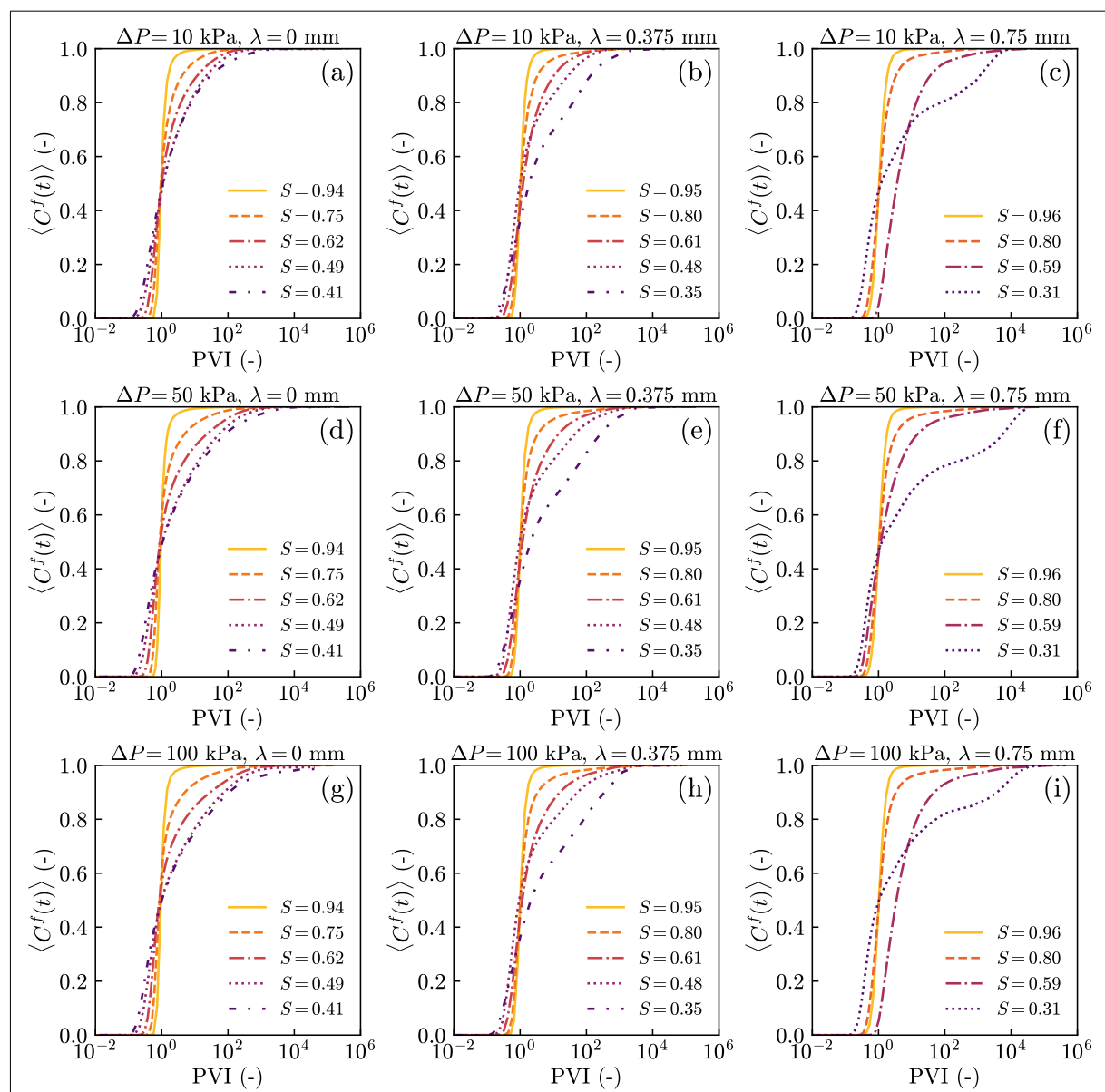
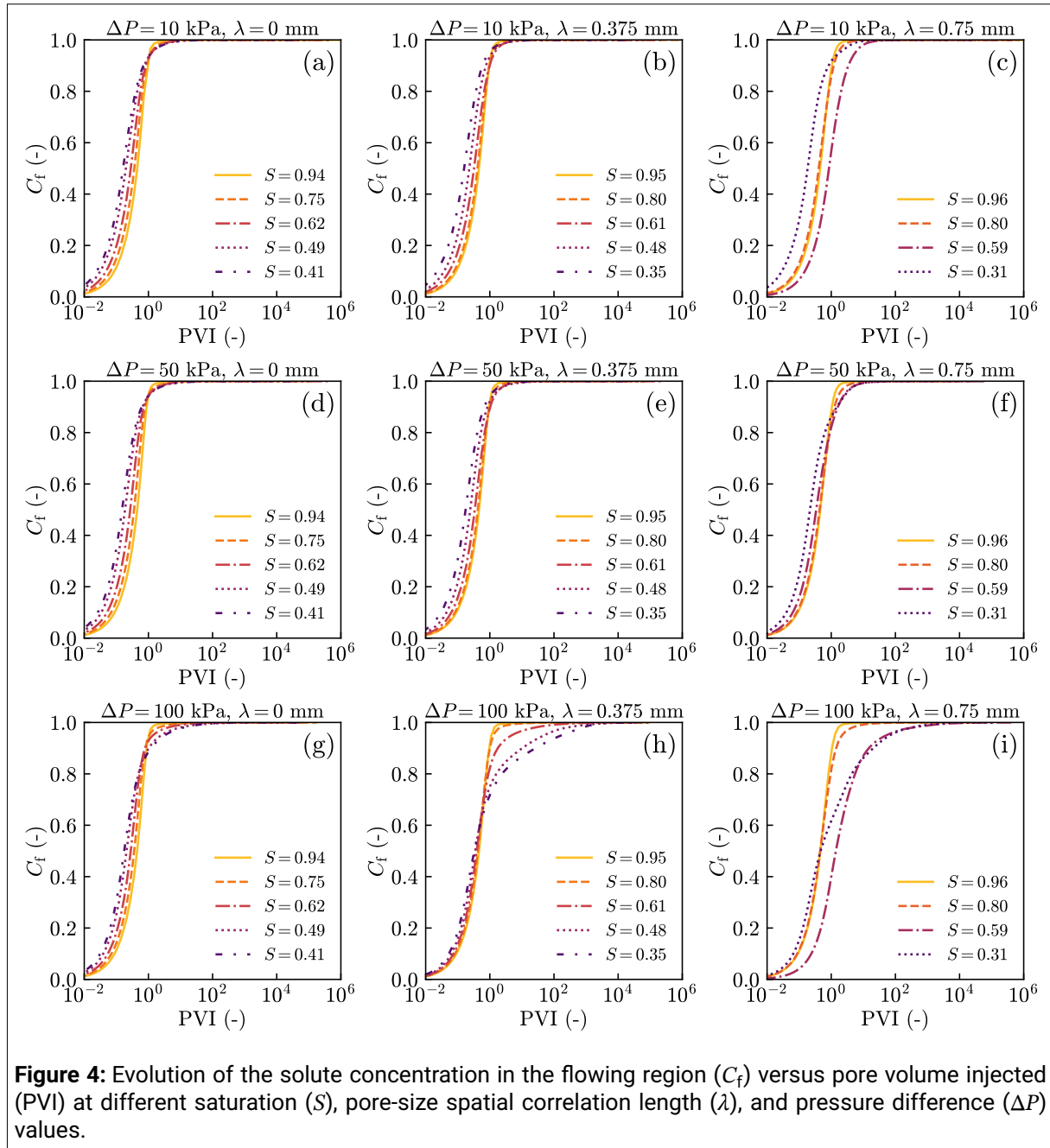
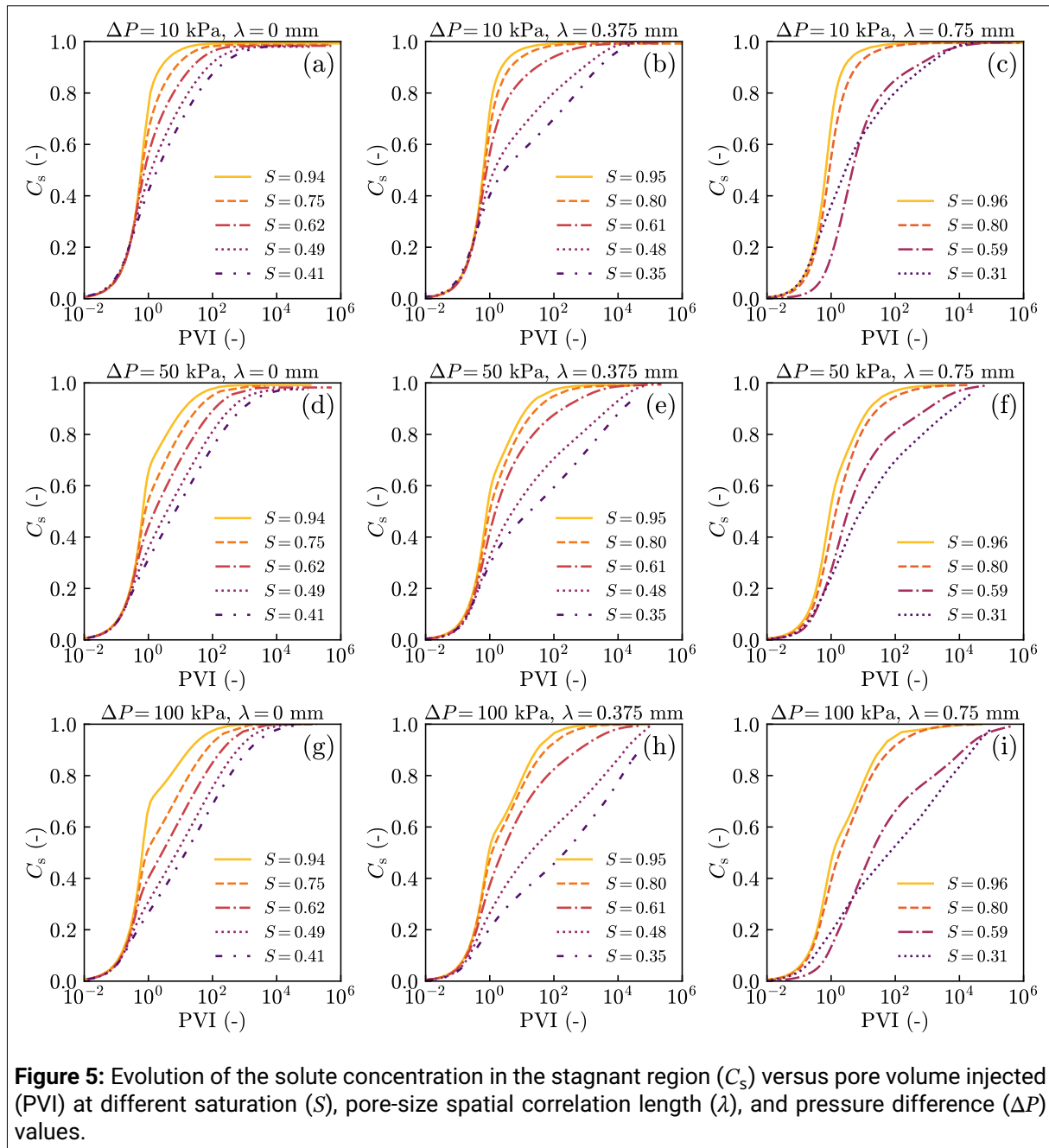


Figure 3: Evolution of effluent flux-averaged concentration ($\langle C^f(t) \rangle$) versus pore volume injected (PVI) at different saturation (S), pore-size spatial correlation length (λ), and pressure difference (ΔP) values. The corresponding Péclet (Pe) numbers for each case are provided in Table 2.





4.2. Transport parameters

In this section, the transport parameters estimated via inverse modelling by fitting the BTCs to each transport model are compared with one another and with those obtained using the DE. The transport parameters in the MIM and MRMT models, and DE, include S_s , D , and γ , whereas those in the CTRW model include β , D , and t_2 .

4.2.1. Stagnant saturation and transport behavior

As S_s quantifies stagnant zones (dead-ends, narrow throats, cul-de-sacs) which contribute poorly to flow and transport, its variation is expected to reflect the trends observed in the BTCs (section 4.1). **Figure 7** presents the values of S_s estimated by the DE as well as MIM and MRMT models as a function of S for the three pore networks at different ΔP values. As observed, the DE estimates a negligible increase in S_s at low S values, followed by a steeper decline as S approaches unity

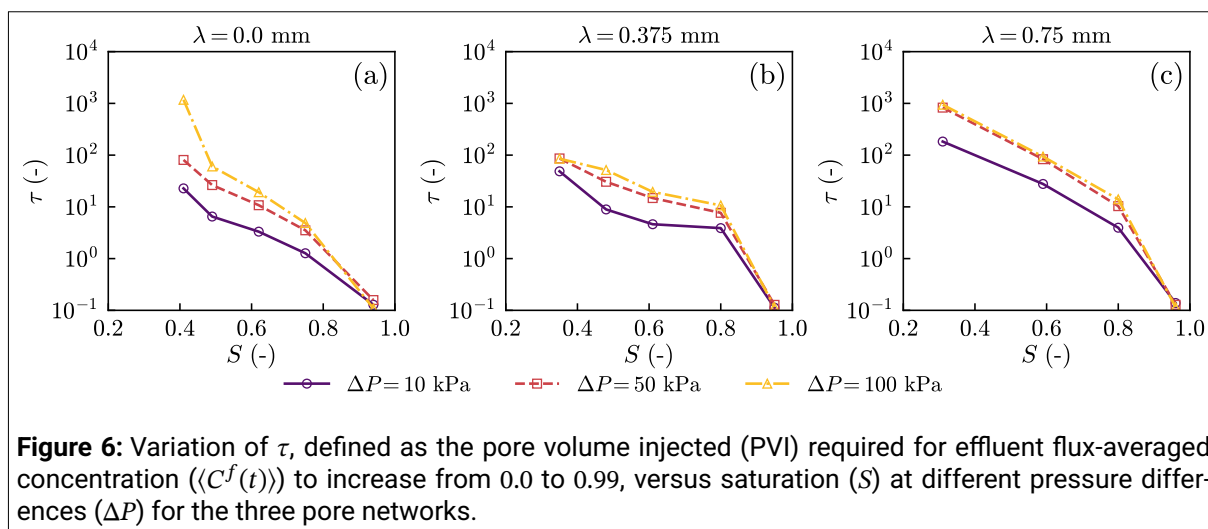


Figure 6: Variation of τ , defined as the pore volume injected (PVI) required for effluent flux-averaged concentration ($\langle C^f(t) \rangle$) to increase from 0.0 to 0.99, versus saturation (S) at different pressure differences (ΔP) for the three pore networks.

(Fig. 7a-c), whereas regardless of ΔP and λ , S_s follows a concave trend in the MIM and MRMT models (Fig. 7d-f and g-i, respectively). The initial slight increase in S_s estimated by the DE aligns with percolation theory, which suggests that the fraction of dead-end pores reaches its maximum between the percolation threshold and a fully connected network (37). The subsequent decrease at higher S values can be attributed to the increasing presence of interconnected pores. However, the pronounced increase in S_s predicted by the MIM and MRMT models at low to intermediate saturations contradicts the trends observed in Figure 3 and Figure 6. In some cases, this trend may not even be physically meaningful - for example, at $\lambda = 0.0$ mm, $\Delta P = 100$ kPa, and $S = 0.62$, the predicted $S_s = 0.56$ implies $S_f = 0.06$, which is unrealistic. This discrepancy shows that the MIM and MRMT frameworks may not adequately distinguish the contributions of flowing and stagnant zones to fluid flow and solute transport at low and intermediate saturations when fitting the BTC data.

The predicted S_s values in the MIM and MRMT models also show sensitivity to ΔP in all pore networks, whereas the DE estimates values that remain unaffected by hydrodynamic conditions. Sensitivity of S_s to ΔP , i.e. Pe (see Table 2), is unexpected here because solute injection occurs after the steady-state saturation field has been established. This again highlights a key limitation of the MIM and MRMT models - since S_s is determined exclusively through fitting the solute BTC to the transport models, its prediction is strongly influenced by BTC evolution. As a result, variations in S_s at different ΔP values are observed, even though steady-state saturation conditions require S_s to remain constant. In contrast, the DE distinguishes stagnant regions from flowing zones based on local residence times rather than BTC fitting. This further supports the argument that estimating S_s purely through inverse modelling and BTC fitting to continuum-scale transport models may be insufficient, as noted by Griffioen et al. (32) and Hasan et al. (37).

Since the steady-state saturation field and the distribution of dead-end zones are governed by entry capillary pressure, which in turn, depends on pore size distribution and heterogeneity, S_s is expected to vary with λ at fixed ΔP and S (3, 58). Figure 7a-c confirms that the DE captures this dependence, estimating lower S_s at higher λ . In contrast, while the MIM and MRMT models also yield different S_s values for varying λ , no consistent trend emerges.

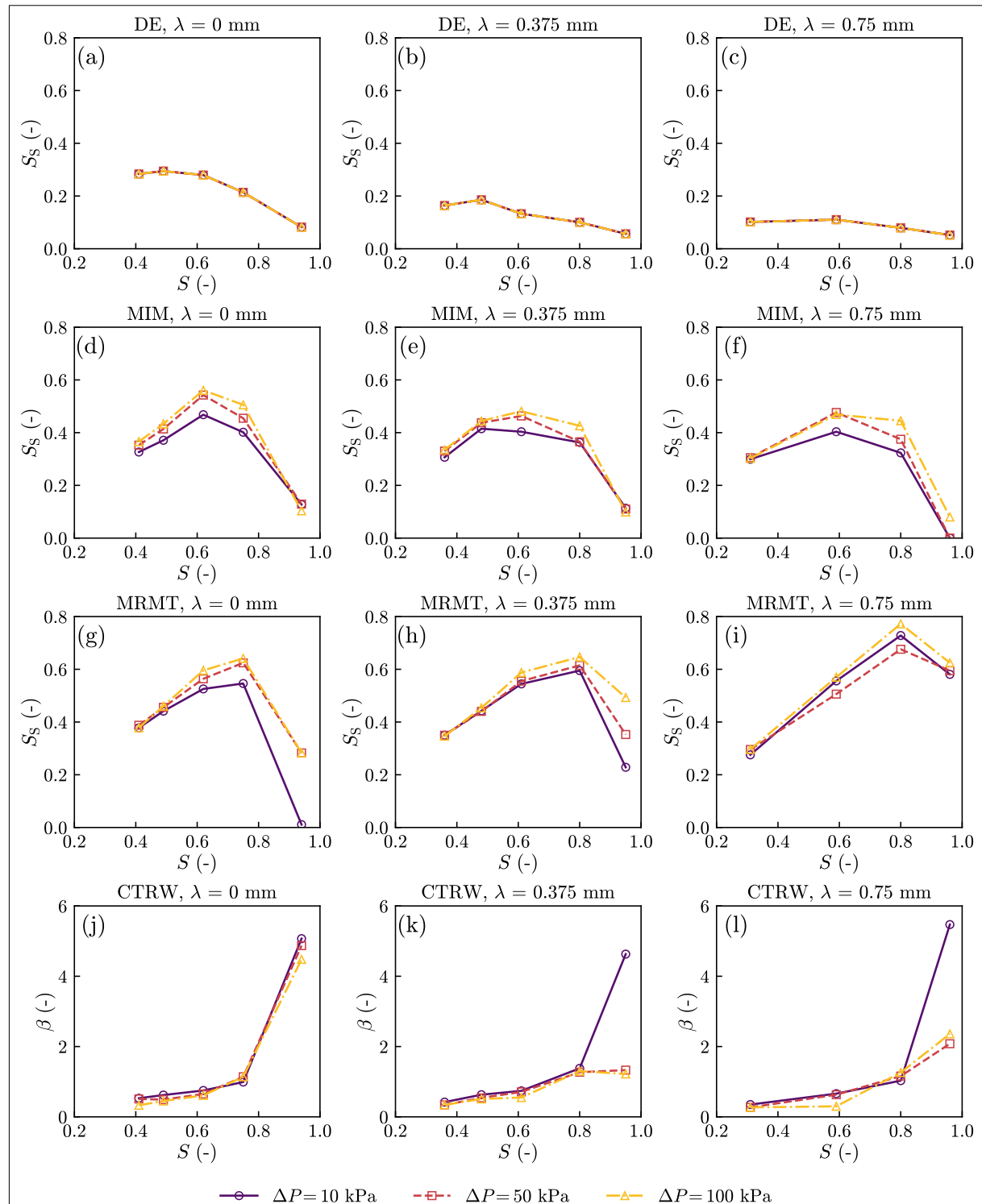


Figure 7: Stagnant saturation (S_s) estimated from the direct estimation (DE) and predicted by the mobile-immobile (MIM) and multirate mass transfer (MRMT) models, together with the CTRW anomalous dispersion exponent (β) predicted by the continuous-time random walk (CTRW) model, plotted against total saturation (S) for various pressure differences (ΔP) and pore-size spatial correlation lengths (λ); the DE results overlap for different ΔP at a given λ value.

Unlike the other models, the CTRW model does not estimate S_s but instead employs a TPL probability distribution function (Eq. 10) to determine β and characterize solute transport. Figure 7j-l presents β as a function of S for the three pore networks at different ΔP values. As observed, β

generally increases with S , indicating a transition toward Fickian transport. This trend is consistent with previous studies (22, 23) and aligns with trends in the BTCs (Fig. 3) and τ values (Fig. 6). At low to intermediate S values, $\beta < 2$ suggests non-Fickian transport with minimal sensitivity to hydrodynamic conditions. However, as S approaches unity, β becomes hydrodynamically dependent. Specifically, for $S > 0.9$, β sharply reaches ~ 5 at all ΔP values in the uncorrelated pore network (Fig. 7j), signifying strong Fickian transport. In the correlated pore networks, transport remains strongly Fickian at $\Delta P = 10$ kPa, as reflected by $\beta \gg 2$. At higher ΔP values, although the BTCs at high saturation appear increasingly Fickian (Fig. 3), the corresponding CTRW fits yield β values that approach, but do not significantly exceed, $\beta = 2$. This indicates that while the macroscopic BTCs exhibit near-Fickian behavior, the CTRW framework becomes less sensitive in distinguishing fully Fickian transport once advective transport dominates and residence-time distributions narrow.

4.2.2. Dispersion Coefficient

Figure 8 shows the dispersion coefficient (D) estimates from the DE as well as predictions from the MIM, MRMT, and CTRW models as a function of S for the three pore networks at different ΔP values. Consistent with previous experimental findings (52, 55) and in agreement with DE estimates (Fig. 8a-c), the MIM model predicts a non-monotonic relationship between D and S in all cases, with higher D values at intermediate saturations (Fig. 8d-f). This behavior arises from the competing influences of increasing advective transport strength and the evolution of stagnant regions with saturation. At very low S , dispersion remains small because, regardless of S_s , advective transport is highly restricted by low effective permeability and poor phase connectivity, resulting in small Pe (Table 2). As S increases toward intermediate values, additional pores become accessible to the invading phase; consequently, effective permeability and average pore velocity increase, strengthening advective transport (and hence Pe , see Table 2), while preferential flow pathways coexist with stagnant or poorly connected regions. The interaction between fast-moving and slow-moving zones enhances solute spreading, leading to a peak in dispersion. As $S \rightarrow 1$, the fraction and influence of stagnant regions decrease substantially (see Fig. 7). This reduction in mass-exchange contrast between flowing and stagnant zones outweighs the comparatively modest increase in advective strength, resulting in a decrease in dispersion. This behavior has also been observed experimentally by Karadimitriou et al. (43). It can be seen that the MRMT and CTRW models fail to accurately capture this behavior in most cases, despite successfully predicting the overall range of D variations (Fig. 8g-i and j-l, respectively). In the MRMT model, the predicted dispersion reflects the superposition of multiple mass transfer rates associated with a prescribed distribution of immobile regions, which can lead to deviations from the physically expected saturation dependence. The inability of the CTRW model to reproduce the non-monotonic dependence of D on saturation stems from its formulation (2.3). The CTRW model does not reproduce the non-monotonic dependence of D on saturation because dispersion in CTRW is controlled by the statistics of particle transition times through the memory function $\tilde{M}(u)$ and TPL probability distribution function $\psi(t)$, rather than by explicit saturation-dependent reorganization of pore-scale velocity fields. As a result, changes in saturation primarily affect the fitted parameters β and t_2 , while the dispersion coefficient D_ψ remains insensitive to the competition between preferential flow pathways and stagnant regions that gives rise to peak dispersion at intermediate saturations.

For low to intermediate S and a given ΔP , the MRMT model estimates higher D values than the DE, MIM, and CTRW models, with the CTRW model predicting the lowest D values, even as $S \rightarrow 1$. The high dispersion coefficient predicted by the MRMT model in this saturation range is due to its consideration of multiple mass transfer rates from stagnant regions (Eq. 4), leading to an overestimation of dispersion, as noted in previous studies (48, 53). The low dispersion coefficients predicted by the CTRW model is due to its definition, which is based on the timescale of transport (see Eq. 8), offering a distinct physical interpretation compared to the other models (11, 14).

Although previous studies have not fully explained the physical meaning of the CTRW dispersion coefficient, one study classified the average pore velocity in CTRW as the average particle velocity of a solute particle moving between two pores (22). Assuming that D is defined as dispersivity (α) multiplied by pore velocity (v), D in the CTRW model can be interpreted as a particle dispersion coefficient.

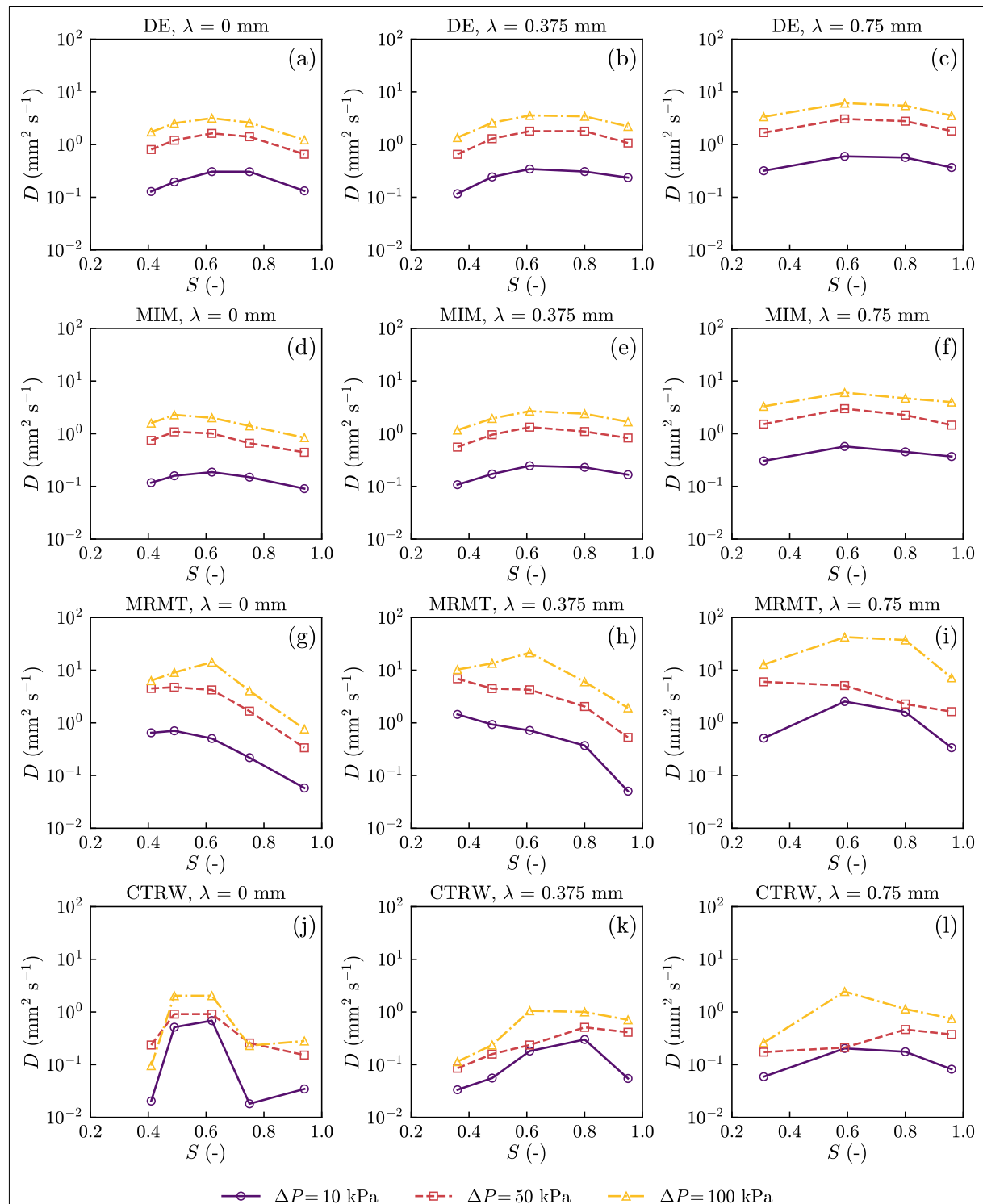
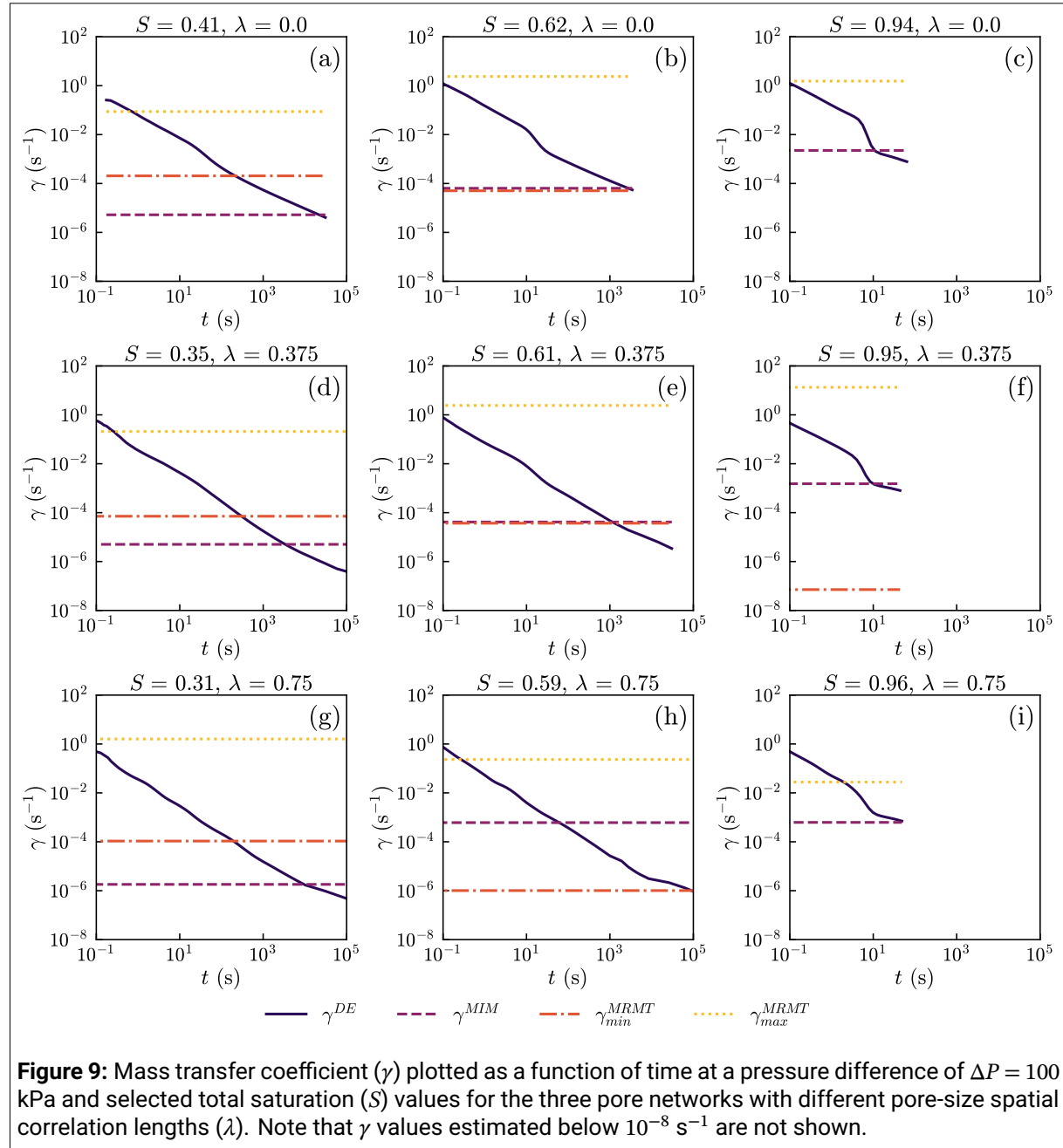


Figure 8: Dispersion coefficient (D) estimated from the direct estimation (DE) and predicted by the mobile-immobile (MIM), multirate mass transfer (MRMT), and continuous-time random walk (CTRW) models, plotted against total saturation (S) for various pressure differences (ΔP) and pore-size spatial correlation lengths (λ).

4.2.3. Mass transfer rate

In this section, we first compare the mass transfer coefficients (γ) estimated by the DE with those predicted by the MIM and MRMT models. The γ values, presented in **Figure 9**, are plotted as a function of time at $\Delta P = 100$ kPa and selected S values for the three pore networks. The selected S values are the lowest, intermediate, and highest S values for each pore network in **Table 2**. Since the trends observed at $\Delta P = 10$ kPa and $\Delta P = 50$ kPa are similar, these results are included in the **Supplementary Material** (available online) for brevity.



The formulations of γ in different models (see Section 2) inherently require its variability over time, as both the solute concentrations in flowing and stagnant zones and the time derivative of the stagnant concentration evolve due to solute transport and mixing within the pore space (see **Fig. 4** and **5**).

This behavior is effectively captured by the DE at different cases, as shown in **Figure 9**, in agreement with recent modelling and experimental studies (3, 37, 42). In contrast, the MIM model predicts a

single constant value for γ over time, and the MRMT model estimates a range of constant γ values, with the minimum and maximum values indicated in **Figure 9**. Although these constant values do not reflect the inherently time-dependent nature of mass transfer between flowing and stagnant zones, they generally fall within the range of time-dependent γ values estimated by DE, thus can be considered as time-averaged approximations and exhibit interesting trends. For instance, at a given λ , the constant γ^{MIM} values generally increase with increasing S . This trend can be attributed to the fact that at higher S , the reduction of S_s enhances mass transfer between stagnant and flowing zones. A similar trend is observed for $\gamma_{\max}^{MRMT}$, except at $\lambda = 0.75$, where a decreasing trend is noted. Meanwhile, $\gamma_{\min}^{MRMT}$ decreases with increasing S , indicating a broader range of γ^{MRMT} values as S increases.

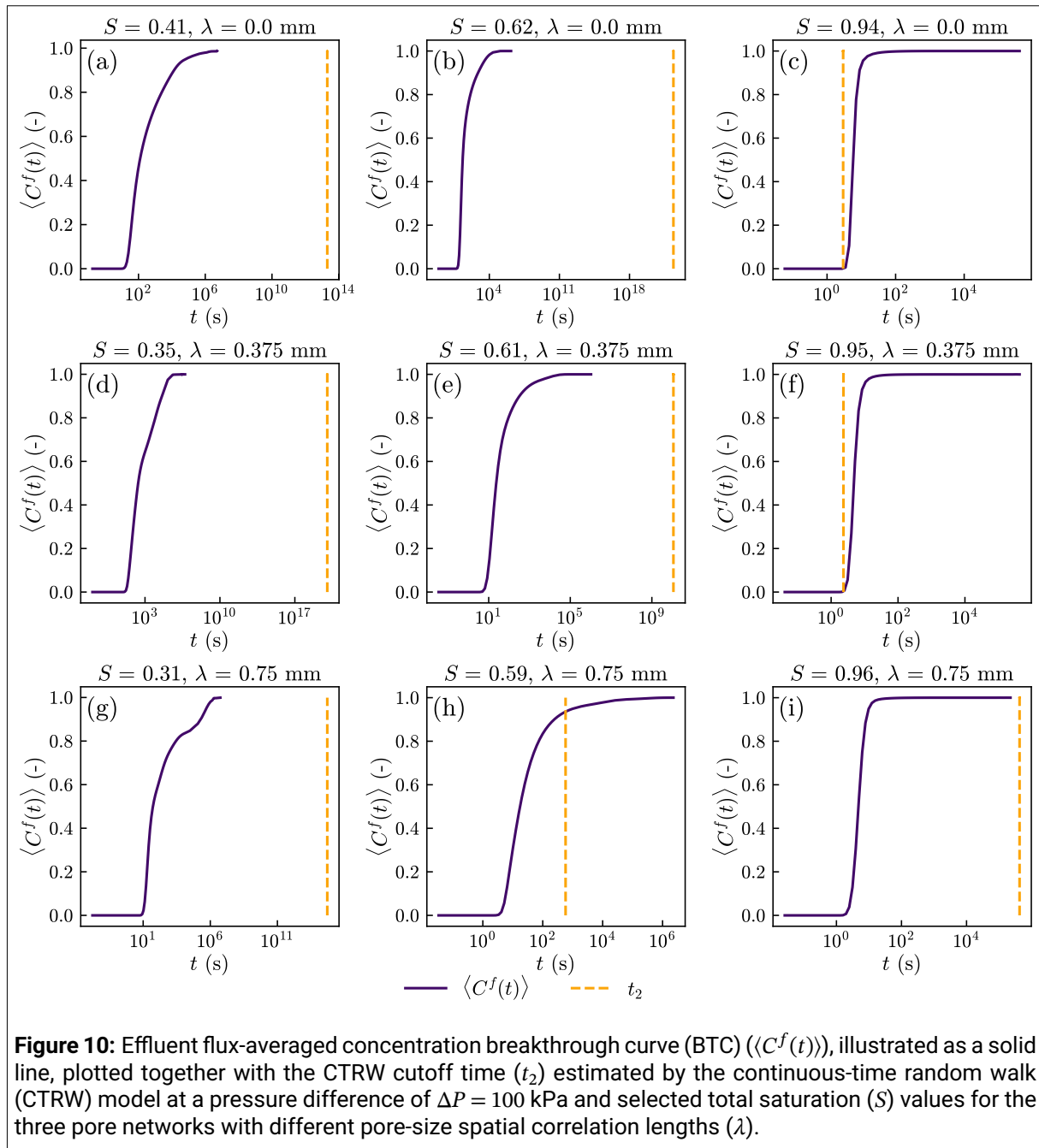
In **Figure 9**, the time-dependent γ values predicted by the DE follow a power-law decay, $\gamma \propto t^{-\vartheta}$, where ϑ is the correlation exponent. The exponent ϑ was found to range from 0.972 to 1.228 for $\lambda = 0.0$, 1.046 to 1.109 for $\lambda = 0.375$, and 1.052 to 1.119 for $\lambda = 0.75$, indicating a slightly faster decline of γ at higher saturations. However, no clear correlation between ϑ and λ was observed at a given saturation, suggesting that further studies at larger correlation lengths are needed to better understand the impact of heterogeneity on the temporal evolution of γ . The observed power-law behavior highlights the need to revisit continuum-scale models and to incorporate a time-dependent mass transfer coefficient to more accurately represent solute exchange between flowing and stagnant regions.

As mentioned, the CTRW model does not explicitly estimate the mass transfer rate but instead employs a TPL probability distribution function (**Eq. 10**) to characterize solute transport by fitting the solute BTC to the CTRW model and obtaining β , t_1 , and t_2 . **Figure 10** presents the temporal evolution of $\langle C^f(t) \rangle$ versus time, along with t_2 , at $\Delta P = 100$ kPa and selected S values for the three pore networks. The selected S values correspond to the lowest, intermediate, and highest S values for each pore network in **Table 2**. Since the trends observed at $\Delta P = 10$ kPa and $\Delta P = 50$ kPa are similar, these results are included in the **Supplementary Material** ([available online](#)) for brevity. In **Figure 10**, it can be seen that t_2 consistently exceeds the final time of the BTC at $\lambda = 0.0$ and 0.375, in agreement with previous conceptual studies (22, 24), which suggest that t_2 acts as a cutoff time distinguishing transport in the advective-dominated (flowing) zone from that in the diffusion-dominated (stagnant) zone. This is true for low and intermediate saturation cases; however, at high saturation, t_2 is underestimated, indicating that its definition does depend on saturation of the carrying phase. This dependence of t_2 on saturation has been noted by Dentz et al. (25) and Berkowitz et al. (11), who reported that when the transport time is much greater than t_2 , transport behavior becomes Fickian, whereas when the transport time is much smaller than t_2 , transport remains anomalous (non-Fickian).

5. CONCLUSION

In this work, we investigated non-Fickian solute transport in unsaturated porous media using pore-network modelling under steady-state two-phase flow conditions. Simulations were conducted in three pore networks with different heterogeneity, characterized by correlation lengths (λ), and differential pressures (ΔP), demonstrating a clear transition from anomalous, long-tailed breakthrough behavior at low to intermediate saturations to Fickian transport as saturation approaches unity.

A comparative analysis of commonly used continuum-scale models, Mobile-Immobile (MIM), Multirate Mass Transfer (MRMT), and Continuous-Time Random Walk (CTRW) was carried out to characterize solute transport properties, and their predictions were compared with each other and against those obtained with the direct estimations (DE). The results showed that the MIM and MRMT, as two traditional inverse modelling approaches, are highly sensitive to the hydrodynamic



conditions and, in some cases, yielded physically unrealistic estimates for stagnant saturation (S_s) and mass transfer parameters. The DE, however, consistently captured the expected dependencies on saturation and heterogeneity owing to its use of detailed pore-scale flow and transport information. Moreover, the DE showed a time-dependent mass transfer coefficient (γ), in line with theoretical expectations, whereas the MIM and MRMT models produced constant values that failed to represent the transient dynamics of solute transport.

The CTRW model, as an alternative to traditional approaches, successfully characterized the transition from non-Fickian to Fickian transport with increasing saturation. However, it did not adequately reproduce the non-monotonic variations in dispersion with respect to saturation, a behavior observed both in our simulations and in available experimental data. While showing some similarities to the MIM and MRMT frameworks, the CTRW model did not fully capture the complex, time-dependent, and heterogeneous features of mass transfer in porous media.

This study demonstrates that commonly used continuum-scale inverse models are fundamentally limited in their ability to infer physically meaningful transport parameters under unsaturated two-phase flow conditions. While such models can reproduce certain macroscopic features of BTCs, their fitted parameters are often sensitive to hydrodynamic conditions, lack physical uniqueness, and do not reliably represent the underlying pore-scale transport mechanisms. As a result, interpreting inverse-model parameters as physically representative quantities can be misleading, particularly in heterogeneous and partially saturated systems. When only breakthrough curve data are available, as is typically the case in field-scale applications, inverse modelling remains a pragmatic but inherently indirect approach. In this context, the present results provide clear guidance on the regimes in which these models are most likely to fail and highlight the risks associated with over-interpreting fitted parameters. The DE, which explicitly incorporates pore-scale velocity fields and residence-time distributions, provides a physically robust basis for quantifying mass transfer, dispersion, and stagnant-zone dynamics. Although its application is currently restricted to systems where detailed pore-scale data are accessible, the insights obtained from DE establish a clear pathway for improving continuum-scale transport models by embedding pore-scale physics rather than relying solely on phenomenological fitting to BTCs.

Taken together, these findings argue for a shift away from purely phenomenological inverse modelling toward hybrid and multiscale approaches that explicitly account for pore-scale heterogeneity and two-phase flow effects. Such a shift is essential for improving predictive reliability in subsurface transport problems, including groundwater contamination, soil remediation, and enhanced oil recovery, where accurate representation of transport processes under partial saturation is critical.

STATEMENTS AND DECLARATIONS

Supplementary Material

The following information is provided in the Supplementary Material, which is [available online](#): (i) the averaged resident concentration at the inlet, (ii) the breakthrough curves plotted versus time, (iii) the coefficient of determination (R^2) values obtained from fitting the DE and MIM, MRMT, and CTRW models, (iv) mass transfer coefficients at $\Delta P = 10$ kPa and $\Delta P = 50$ kPa, and (v) the temporal evolution of breakthrough curves with t_2 .

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Author Contributions

SH: Part-conceptualisation, Investigation, Methodology, Software, Validation, Formal analysis, Writing - original draft. **MVF:** Investigation, Methodology, Formal analysis, Visualisation, Writing - Review & Editing. **SVO:** Validation, Writing - Review & Editing. **TB:** Validation, Writing - Review & Editing. **VN:** Conceptualisation, Methodology, Formal analysis, Supervision, Funding acquisition, Writing - review and editing.

Conflicts of Interest

The authors report no conflict of interest.

Data, Code & Protocol Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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