The impact of local diffusion upon mass arrival of a passive solute in transport through three-dimensional highly heterogeneous aquifers

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ABSTRACT

Fluid flow and solute transport take place in a porous formation. The spatial variability of the hydraulic conductivity \( K \) has a large impact on the velocity field and advective spreading of solute. The logconductivity \( Y = \ln K \) is modeled as a stationary random space function, of normal distribution of mean \( \mu \) and variance \( \sigma^2 \), and of isotropic autocorrelation of finite integral scale \( L \). The stationary velocity field is of uniform mean \( U \). Transport of an ergodic plume is quantified by the mass arrival (breakthrough curve) at control planes normal to \( U \). First-order solutions in \( \sigma^2 \), applicable to weak heterogeneity \( (\sigma^2 < 1) \), have been investigated extensively in the past. However, many natural formations are highly heterogeneous \( (\sigma^2 > 1) \) and the more complex flow and transport problems have been attacked only recently. The present study investigates the impact of local diffusion, quantified by the Peclet number \( Pe = U(l) \), upon the breakthrough curve (BTC), both by numerical simulations and an analytical approach based on the self consistent approximation. The latter is an extension to finite Peclet of a method that we have developed in the past, in which we solved the 3D problem of flow and advective transport by modeling the structure as an ensemble of densely packed spherical inclusions of uniform radius \( R \) and independent random \( \alpha \).

Unlike the first-order solution, diffusion has a large impact on the BTC, even for the common values \( Pe \gg 1 \). Two mechanisms associated with finite \( Pe \) are identified and quantified: removal of the solute captured by low \( K \) blocks (characterized by “slow” flow) and exchange between the fluid flowing past inclusions (i.e. “fast” flow) and their interior. The first mechanism affects primarily the tail of the BTC, while the second one impacts both the peak and the tail. All the parameters of the model \( (U, \sigma^2, Pe, l) \) are physically based and depend on the structural and flow characteristics solely.

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1. Introduction and background

Transport of solutes by fluid flow in natural porous formations (aquifers, petroleum reservoirs) is a subject of intensive research of the last three decades. The focus was on investigating the impact of the spatial variability of the hydraulic conductivity \( K \) upon the fluid velocity field and the spreading of solute plumes in a stochastic framework. Various quantitative models of flow and transport have been advanced in the past (see, e.g., the monographs [5,15, 24]). The traditional approach to solving transport problems, which is adopted here as well, follows a few steps: a model of the aquifer hydraulic conductivity structure, based on field data, is selected; the stochastic equations of water flow are solved with appropriate boundary and initial conditions, rendering the random velocity field; the transport equations comprising advection by the velocity field and other physical processes, e.g., local diffusion or reaction, are solved in order to derive the random concentration field \( C(x,t) \). As a starting point, the logconductivity \( Y = \ln K \) is commonly modeled as a random space function, characterized by the univariate pdf \( f(Y) \) and the associated mean \( \mu \) and variance \( \sigma^2 \), the two point autocorrelation \( \rho(x_i,x_j) \) and higher order and multipoint covariances. This structure-based approach, which starts from the definition of the spatially variable \( K \) and solves the flow equation is the only one considered here.

The simplest and basic configuration which was investigated extensively in the past and here as well is: stationary and statistically isotropic \( Y \) of a finite integral scale \( l \), flow driven by a mean uniform head gradient and of mean constant velocity \( U \), an inert solute (tracer) undergoing both large-scale advection and local diffusion and a domain and plume that are large at the \( l \) scale. This may apply to natural gradient flow and constitutes the starting point for solving more complex problems. The concentration field of a solute plume injected in the aquifer is quantified here by the breakthrough curve (BTC) at a given control surface and the associated temporal moments. Generally speaking these entities are...
random, but under the assumed ergodic hypothesis these measures in any given realization can be exchanged with their ensemble mean, i.e. they can be determined with the aid of \( C(x,t) \) field. Such global characterizations of spreading shall be distinguished from the statistical moments of \( C \), which reflect mixing, and are not considered here.

Even under these idealized conditions the problem is difficult and various approximation were adopted in the past in order to solve it. The most common is a first-order approximation in \( \sigma_i^2 \) (for brevity FOA, see the above monographs), which may apply to weakly heterogeneous aquifers. For the commonly assumed log-normal conductivity distribution, it was found that \( C \) is Gaussian and entirely characterized by the centroid velocity \( U \) and by the macrodispersion coefficients related to the second spatial moments of the plume or equivalently to the temporal moments of the BTC. In particular, the longitudinal macrodispersivity \( \lambda_i \) was found to be a function of travel time [5], tending to a constant value after a travel distance of a few integral scales. The latter regime was coined as Fickian and then \( C(x,t) \) satisfies an advection–dispersion equation with constant coefficients. A few important properties of the FOA based solution are: \( \lambda_i/L \) depends linearly on \( \sigma_i^2 \) and consequently \( C \) depends in a simple manner on the parameters \( \sigma_i^2, L \), which can be identified in the field; for the common values of \( Pe = UI/D \gg 1 \) (where \( D \) is the local diffusion coefficient) it was found that it has a small effect on \( \lambda_i \) (but it is impacting mixing) [3].

Nevertheless, many formations are highly heterogeneous (\( \sigma_i^2 > 1 \); see, e.g., [14]) and the FOA is not applicable; the solution of the much more difficult nonlinear transport problem has been addressed only recently. Most structure based systematic studies were of a numerical nature, assumed multi-Gaussian \( Y \) fields and addressed 2D flows [2,25,7,1]. In the recent years we have pursued solutions of 3D flow and transport by a model coined as multi-indicator: the formation is modeled as an ensemble of blocks of independent, random, conductivities [6]. Our previous works mainly dealt with advective transport [3,10], with neglect of local diffusion.

Most existing works on transport in highly heterogeneous media led to the conclusion that the BTC become highly skewed when \( \sigma^2 \) is large, displaying considerable tailing and anomalous-like features. These features cannot be captured by FOA. Contrary to the prediction of FOA, local dispersion or diffusion may impact the BTC and macrodispersivity when \( \sigma_i^2 \gg 1 \) (see, e.g., the 2D macrodispersivity analysis of Salandin and Fiorotto [26], and Beaudoin et al. [1], and the 3D numerical simulations of LaBolle and Fogg [20]), as local processes may cause solute to explore zones of the aquifer characterized by significantly different velocities.

The scope of the present work is to analyze the impact of local diffusion (i.e. finite \( Pe = UI/D \)) on the BTC for transport in strongly heterogeneous (i.e. \( \sigma_i^2 \gg 1 \)) 3D formations. This will be done through accurate numerical simulations and approximate analytical solutions. In both cases we shall make use of our multi-indicator model. While multi-indicator model can represent any structure of given \( f(Y) \) and integral scale \( L \), it differs from the multi-Gaussian one for higher-order moments. The great advantages of the model is the ability to achieve accurate numerical solutions of flow and advective transport for large values of \( \sigma^2 \), allowing for a systematic analysis of its impact. Furthermore, the method leads to a useful semi-analytical approximation (coined as the self-consistent, SCA for brevity). In the SCA solution we shall make use of the results of Jankovic et al. [18] for macrodispersivity associated with an isolated inclusion. While the multi-indicator structure model is an idealized one, it is as valid as the commonly adopted multi-Gaussian one, as long as field data are not detailed enough to allow for identification of moments higher than the second ones; we point out however that solutions of flow and transport may be different in media with same second-order statistics but different higher-order statistical moments. Furthermore, representation of the formation by an ensemble of blocks may be quite realistic in some cases, e.g., when detailed lithologic maps are available. In any case, at present we regard the multi indicator structural model primarily as a systematic tool for gaining understanding of the complex transport processes occurring in highly heterogeneous formations rather than a realistic representation of given particular aquifers.

Our multi-indicator structure assumes that all classes of conductivity have the same degree of correlation (or connectivity), expressed by the integral scale \( L \). This is different from the multivariate normal model or other approaches in which certain classes of \( K \) are more correlated than others (see, e.g., [27]). Nevertheless, as shown recently by Fiori and Jankovic [12], the multi-indicator model adopted here leads to strongly connected flow fields when heterogeneity is high. This is related to connectivity being often a flow-related feature, which manifests also in presence of poorly connected \( K \) fields. At any rate, the emergence of flow related connected paths affects the early arrival of the BTC, which is captured in the present work. The issue is further discussed in Fiori and Jankovic [12].

The plan of the paper is as follows: the new accurate numerical simulations for a dense ensemble of spherical inclusions are presented in Section 2; Section 3.1 recalls the semi-analytical self-consistent approximation as applied to advective transport, while Section 3.2 quantifies the effect of diffusion on removal of slow particles from low conductivity inclusions. The mechanism of diffusion between the fast flow and low conductivity inclusions is quantified in Section 3.3; the main new results concerning advective–diffusive transport through the heterogeneous medium are illustrated in Section 4, while Section 5 concludes the study.

2. Numerical simulations of advective–diffusive transport in isotropic formations

2.1. The numerical setup

Numerical simulations serve as a laboratory for solving test cases toward identification of mechanisms and for deriving approximate simplified solutions. The steps are parallel to those mentioned before: (i) a model of the random hydraulic conductivity of the medium is adopted; (ii) the equations of flow (mass conservation and Darcy’s Law) are solved under conditions of mean uniform flow, rendering the Eulerian velocity field; (iii) a thin tracer plume of large transverse dimension, made from discrete particles, is inserted in the injection plane; (iv) transport is solved by tracking a large number of particles which move by advection and local diffusion; they make up the plume which is quantified by the mass arrival, i.e. breakthrough curve (travel time distribution), at various control planes normal to the mean flow. These steps were carried out in our previous works for the case of advection and results were reported in a few papers [17,11]. We include here local diffusion, and we outline in the following the main features of the numerical procedure and results. The procedure is developed for the case of isotropic formations, for which existing flow solutions are available. The anisotropic case, which is perhaps more relevant for applications, is definitely more complex and requires a new formulation of the procedure to solve the flow problem, and is deferred to future studies.

The isotropic hydraulic conductivity structure for numerical simulations was created by replacing heterogeneous cubes of equal dimensions that tessellate the entire volume by densely packed spherical inclusions of high volume fraction, set to \( n = 0.7 \), of independent conductivities generated at random from the univariate
lognormal distribution \((K_c, \sigma^2_c)\). The inclusions of uniform radii \(R\) were placed on a cubic face centered periodic lattice into a homogeneous background of \(K_{de}\) where the effective conductivity \(K_d/K_c = \text{func}(\sigma^2_c)\). The matrix may be viewed as representative of a medium of conductivity variations of same univariate distribution but of much smaller integral scales, manifesting in a finite value at the origin (“nugget”) of the conductivity variogram or a spike of \(\rho(r)\) at \(r = 0\). Further details on the adopted medium structure and relation with other approaches are given in Dagan et al. [6]. For the selected values of \(\sigma^2_c = 2\), \(\sigma^2_c = 4\) and \(\sigma^2_c = 8\), the values of \(K_{de}/K_c\) were determined as 1.291, 1.558 and 2.095, respectively. The 2-point autocorrelation function of blocks conductivity has the exact analytical expression [16]

\[
\rho(r) = \begin{cases} 
1 - \frac{3r^2}{4R^2} + \frac{r^4}{16R^4} & (r < 2R) \\
0 & (r \geq 2R)
\end{cases} \quad r = |x_i - x_j|
\]

with integral scale \(I = 3/4R\). A large number of 100,000 spherical inclusions were placed in a flow domain \(\Omega\) (a large spheroid), subject to uniform flow from infinity. Interactions between inclusions were accounted for by using a highly precise numerical method that satisfied mass balance exactly at each point in the domain. The mean velocity \(U\) inside this heterogeneous body was found to be equal to uniform velocity at infinity, while streamlines are not perturbed outside \(\Omega\), except a boundary layer \(O(R)\) near \(\partial \Omega\) (this is illustrated in Figs. 1 and 2 of Jankovic et al. [16]). This serves as a check of model consistency prior to running transport simulations.

The transport simulations were carried in a transport domain of large size, 1211 long and 441 wide in both transverse directions, within the core of stationarity of \(V\) in \(\Omega\). We checked in previous work that the domain size is large enough to ensure ergodicity of the random velocity field. We used 62,500 particles placed at \(x = 0\) with spacing of 0.18I. For the selected flux proportional injection mode, each particle mass was set proportional to the local velocity \(V_s\). The variable time steps of 4th order Runge–Kutta method were selected to yield constant space steps of \(R/100\). Few simulations were carried with smaller space steps to investigate sensitivity of results to selected steps, and none was found. Ergodicity was also checked by simulations of equally likely \(K\) fields, obtaining identical results. The diffusive displacements, modeled by a random walk algorithm, were added to advective ones each time a particle is moved. As expected, in absence of inclusions the algorithm reproduced accurately the inverse-Gaussian travel time distribution.

It is worthwhile to mention here that these numerical simulations have a few distinctive properties: the 3D domains are of sufficiently large size to eliminate the effect of boundaries and permit exchange of one realization and ensemble statistics in the core of stationarity; high accuracy of the flow solution with exact fulfillment of mass conservation; modeling of large ergodic plumes; large number of particles to ensure accurate representation of the entire BTC; large distance to the control planes relative to the integral scale such as to eliminate the near injection zone local effects; solving for highly heterogeneous formations of large \(\sigma^2_c\).

The various results and subsequent analysis of advective transport (i.e. without local diffusion) are given in our aforementioned works. The main results are encapsulated by the BTC (travel time distribution) \(\mu(t,x; \sigma^2_c) = \partial \mu(1 - M/M_0)\) where \(M_0\) is the total mass of particles injected in the plane \(x = 0\) at \(t = 0\) and \(M_0 - M(t,x)\) is the mass of solute particles which have crossed the control plane (CP) at \(x\) until time \(t\). Similar results for different other values of these parameters can be found elsewhere [10]. As found in our previous works, the agreement with the semi-analytical approximation (see next section) is indeed good.

Local diffusion is modeled as an isotropic Brownian motion type of constant diffusion coefficient \(D\). As we shall show later, one of the major effects of diffusion is the removal of particles immobilized in blocks of low conductivity in which the velocity is very small and molecular diffusion becomes the dominant mechanism. Hence, \(D\) shall be regarded as the average effective molecular diffusion coefficient in the porous medium. Furthermore, the main effect of local diffusion manifests through the transverse component, and its modeling as isotropic is not influential. Hence, \(\mu/lU\) depends on the additional parameter \(Pe = UI/D\) which is finite, but usually very large, typically \(O(10^5)\) or larger.

### 2.2. Illustration of the numerical results

The results of the numerical simulations are encapsulated in (Figs. 1–3, dots; the solid and dot-dashed lines pertain to the SCA model and will be discussed later.) representing the BTC \(\mu_lU\) as a function of \(tU/l\) at a fixed control plane at \(x/l = 116\). The nine graphs illustrates different combinations of parameters values \(\sigma^2_c = 2, 4, 8\) and \(Pe = UI/D = 750, 375, 75\). The advective results for \(Pe = \infty\), based on the SCA are represented as well (dashed lines).

Starting with the bulk of \(\mu\), for say \(tU/l < 250\), it is seen that the main effect of local diffusion is a diminishing of the peak of the infinite \(Pe\) distribution and its retardation. This effect is maximal for the largest \(\sigma^2_c = 8\) and the lowest \(Pe = 75\) (Fig. 3c) for which the attenuation is by a factor of 0.65 and the retardation by 1.2, while it becomes weaker for the larger \(Pe\) values (Fig. 3b and 3c). These effects are diminished with decreasing degree of heterogeneity: for \(\sigma^2_c = 2\) the \(\mu\) is very close to the one pertinent to \(Pe = \infty\), justifying in retrospective the neglect of local diffusion on longitudinal spread in the FOA. The physical mechanism underlying these effects are discussed in the next section.

The large time tail of the BTC, for \(tU/l\) as large as 1000, is represented on a logarithmic scale in the inserts of the different figures. The affected mass is very low and as a result the numerical points start to oscillate around the mean due to limited number of solute particles contributing to each class, for say \(tU/l > 500\) (a non-ergodic effect, despite the large dimension of the injected plume; the issue is thoroughly discussed in Jankovic et al. [17]). It is seen that the finiteness of \(Pe\) manifests in diminishing of \(\mu/lU\) at the tail, as compared to the advective case, clearly illustrating the impact of diffusion on the tail, depending on the degree of heterogeneity.

Although the simulations serve as an invaluable experimental basis of a numerical nature, the heavy numerical burden limits use of simulations as a routine tool. An approximate method which simplifies the procedure on one hand and allows for insight in the physical mechanism is described next.

### 3. The self-consistent semi-analytical approximation (SCA)

#### 3.1. Brief recapitulation of previous results for advective transport \((Pe = \infty)\)

We have used this approach extensively in our previous works for \(Pe = \infty\). It can be traced back to the classical method to derive \(K_d\) by the self-consistent or effective medium approach: flow is solved first separately for each block of conductivity \(K\) by replacing the surrounding medium by a homogeneous one of \(K = K_d\). Besides the self consistent argument, the method displays similarities with the dilute medium approach forwarded by Koch and Brady [19] and Eames and Bush [8]. The velocity field for an isolated sphere of radius \(R\) is given exactly by

\[
\begin{align*}
\mathbf{u}^\alpha &= \nabla \phi^\alpha; & \phi^\alpha &= \frac{\rho^n}{2} \mathbf{U} \cdot \mathbf{V} |\mathbf{x} - \mathbf{x}_j|^2 & (|\mathbf{x} - \mathbf{x}_j| > R) \\
\mathbf{u}^m &= \nabla \phi^m = 2/lU & (|\mathbf{x} - \mathbf{x}_j| < R)
\end{align*}
\]
where \( \mathbf{V} = \mathbf{U} + \mathbf{u} \), \( \mathbf{U}(0,0) \) is the mean velocity, \( \mathbf{u} \) is the perturbation, \( \mathbf{x}_c(x_c, y_c, z_c) \) is the coordinate vector of the inclusion center, \( f = (\kappa - 1)/(2 + \kappa) \), \( \kappa = K/K_{ef} \) and \( K = \exp(Y) \). The velocity field for the ensemble of inclusions is the superposition of (2) for spheres of different \( Y \) and centroid location \( \mathbf{x}_c \), and this analytical solution constitutes a tremendous simplification of the general one, which can be derived only numerically for large \( \sigma_T^2 \) and dense settings.

Starting with the effective conductivity, it was obtained from the self-consistent argument \( \int u^2 f(Y) dY = 0 \) leading for a normal \( Y = Y - \langle Y \rangle \) to the well known relationship (e.g., [5])

\[
\sigma_X^2 = \frac{\mu}{U}
\]

\[
\sigma_Y^2 = \frac{2}{1 + \frac{20}{2 + 1/2}}
\]

\[
\sigma_Z^2 = \frac{1}{2}
\]

\[
\sigma_T^2 = \frac{\mu}{U}
\]

\[
\sigma_Y^2 = \frac{2}{1 + \frac{20}{2 + 1/2}}
\]

\[
\sigma_Z^2 = \frac{1}{2}
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\[
\sigma_Y^2 = \frac{2}{1 + \frac{20}{2 + 1/2}}
\]

\[
\sigma_Z^2 = \frac{1}{2}
\]
The integral equation (3) can be easily solved iteratively and the solution was found to be very accurate in comparison with the complete numerical solution [16]. In particular, at first order, (3) recovers the well known result $K_{ef}/K_G = 1 + \sigma_f^2/6$. 

\[
\int_{-\infty}^{\infty} \frac{K - K_{ef}}{K + 2K_{ef}} f(Y') dY' = 0; \quad K = K_G \exp(Y'); \\
\langle Y' \rangle = \frac{\exp\left[-Y'^2/(2\sigma_Y^2)\right]}{(2\pi)^{1/2}\sigma_Y}.
\]
It is worthwhile to recall a few properties of the velocity field (2) for an inclusion of low conductivity, which is of particular interest. The constant interior velocity $V_{in}/U = 3\kappa/(2 + \kappa) \approx 3\kappa/2 = 0.015$ for $\kappa = 0.01$ is very small, while $|V_{in}|/U = 0(1)$ along the streamlines circumventing the inclusion, with a sharp discontinuity on the envelope. The fluid entering the sphere originates from and is discharged through a thin wake, of radius $R_{w}/R = (V_{in}/U)^{1/2} = 0.12$ sufficiently far from the sphere (Fig. 4a). A similar figure is
displayed for a high conductivity inclusion in [6], for which, however, the interior velocity is bounded by $V^0/U = 3$ for $k \to \infty$ and the maximal wake radius becomes $R_{\text{w}}/R = 1.73$.

Toward solving transport, the travel time residual $S_M(k) = \int_{-\infty}^{\infty} [1/V_x(x,0,0) - 1/U] \, dx$ of a fluid particle moving along the center line $y = z = 0$ (with $x_c = 0$) was determined analytically from (2) the result being [9]

$$\frac{\tau_M U}{K} = \frac{2}{3} (1 - k) \left[ \frac{2}{k} + \frac{3}{2} + \frac{5}{3} Z \right] F_1 \left( \frac{2}{3}, 1, \frac{5}{3}, Z \right); \quad Z = 2 \beta = \frac{2(1 - k)}{(2 + k)} \quad (4)$$

Fig. 4. Streamlines ensuing from the wake of a low conductivity spherical inclusion ($k = 0.01$) and snapshots of an advected thin plume: (a) general view and velocity distribution and (b) snapshots of plume and outline of the two diffusion mechanisms.
where \( F_1(z) \) is the hypergeometric function, given by

\[
F_1(\frac{2}{3}, \frac{1}{3}, Z) = \begin{cases} 
\frac{1}{3} & \text{if } Z \leq 1 \\
\frac{\ln \left( \frac{1 + \sqrt{1 + 4Z}}{2} \right)}{2\sqrt{Z}} - 2\sqrt{3} \arctan \left( \frac{1}{\sqrt{3}} \right) & (1 \leq Z \leq 3) \\
\frac{\ln \left( \frac{1 + \sqrt{1 + 4Z}}{2} \right)}{2\sqrt{Z}} - 2\sqrt{3} \arctan \left( \frac{1}{\sqrt{3}} \right) & (Z \geq 3)
\end{cases}
\]

with \( z = |Z|^{1/2} \). For a sufficiently large distance between the injection and control plane \(|x| > 1\), (4) represents the travel time residual of a particle crossing the inclusion and reaching the control plane, provided that the sphere is not close to it. Next, the distribution of travel time residuals \( \tau_k = t - \langle t \rangle \) of particles moving on other streamlines (Fig. 4a) was replaced by a simple expression within the wake, \( \tau_k/L \) being assumed to be proportional to the segment intercepted in the sphere, while \( \tau_k = 0 \) outside the wake [9]. The pdf of \( \tau_k \) was obtained subsequently by summation of contributions from spheres of different random \( \kappa \), their volume fraction being proportional to the pdf \( f(\kappa) \). The final result for flux weighted injection is given by [10], Eq. (11) as follows

\[
f'(\tau_k) = 6\tau_k \int_0^{\infty} \frac{1}{2 + \kappa - \frac{1}{\kappa}} \frac{\kappa}{2} f(\kappa) d\kappa \quad \text{for } \tau_k > 0
\]

\[
f(\tau_k) = -6\tau_k \int_0^{\infty} \frac{1}{2 + \kappa - \frac{1}{\kappa}} \frac{\kappa}{2} f(\kappa) d\kappa \quad \text{for } \tau_k < 0
\]

where \( \kappa = \eta(\tau_k) \) is obtained by inverting the relationship \( \tau_0(\kappa) \) (4) with \( 0 < \kappa < \infty \). The pdf can be obtained by a numerical quadrature for a given \( f(\kappa) \) which is taken here as lognormal, i.e. \( \kappa = \text{Kc}_\text{log} / \text{Kc}_\text{exp}(\text{Y}) \) (3). It is worthwhile to recall here that \( f(\tau_k) \) is highly skewed; the transition of \( f(\tau_k) \) from a distribution close to an inverse Gaussian one (for small or moderate \( \sigma^2 \)) to a highly skewed one (for increasing \( \sigma^2 \)) is illustrated in Fig. 2 of [10].

Finally, according to the model, the travel time residual of a particle moving through the ensemble of spheres between \( x=0 \) and \( x \) is the sum of residuals \( \tau_k \) pertaining to the \( N \) different inclusions encountered on the trajectory. Approximating the plume for the ensemble by the sum of those resulting from different inclusions was forwarded in the pioneering work of Eames and Bush [8], who assumed a dilute medium \((n \ll 1)\) and analyzed numerically the spatial trajectories distribution. Since \( \tau_k \) are independent random variables in our model, the Fourier Transform (FT) of the pdf \( \mu(t; x) \) was determined as a number of \( N \) convolutions of that of \( f(\tau_k) \) [6], i.e.

\[
\mu(t - T; x; \text{Pe} = \infty) = FT^{-1}[\tilde{f}(\tau_k)]
\]

where \( T = x/U \) is the mean arrival time, \( \tilde{f}(\tau_k) \) is the FT of \( f(\tau_k) \). For sufficiently large \( x/kR > 1 \) this number stabilizes at the value \( N = \text{N}(3x/4kR) \approx 0.4kR \) where \( n = 0.7 \) is the volume density achieved at the dense packing of the numerical simulations. Correspondingly, the value \( N = x/(2kR) \approx x/kR \) pertains to cubes of side \( 2kR \) packed at the maximum density \( n = 1 \) [11]. The ensuing semi-analytical procedure renders the pdf of \( \mu(t; x) \) (which is identical to that of \( U(t)/l \)) depending on \( x/kR \) and \( \sigma^2 \), for the given lognormal distribution. It was explored in our previous works [10] displaying a good agreement with the numerical simulations.

3.2. The impact of finite Pe: removal of advected particles from low-conductive blocks (first mechanism)

It is clear that the extension of the SCA approximation to transport of finite Pe has to address first of all the impact of diffusion on the removal of solute particles which enter the low conductivity blocks by advection through the wake and are practically immobilized inside them. To illustrate the large difference between the distance travelled by fluid particles captured by the wake and those moving outside, we have represented in Fig. 4b the streamlines associated with \( V(2) \) as well snapshots of a thin plume at different times, for \( \kappa = 0.01 \).

It is important to emphasize that while in applications \( Pe \gg 1 \), what counts for this mechanism is the interior \( Pe^\text{in} = U(\text{V})/D \), based in the velocity inside the sphere \( V = U + u_0 = 3Uk/(2 + \kappa) \), leading to \( Pe^\text{in} = [3k/(2 + \kappa)]Pe \). Thus, \( Pe^\text{in} \) can be quite small for the low \( \kappa \) inclusions, justifying the reference to the effective molecular diffusion coefficient as representing the dominant mechanism. In order to quantify this effect, we have to solve the problem of advective–diffusive transport for an isolated sphere surrounded by a homogeneous matrix for conductivity ratio \( \kappa \ll 1 \) and for \( Pe \gg 1 \). This problem, though considerably simpler than the one pertinent to the dense ensemble of spheres, is still complex and was not solved before. We have undertaken this task by the same numerical tools and presented the results in [18]. Thus, we have considered a thin plume injected upstream of a spherical inclusion, advected by the velocity field (2) and diffusing (Fig. 4b). The global impact of diffusion was assessed with the aid of the travel time dimensionless variance \( \sigma^2 = \sigma^2 U^2 / R^2 \), after subtracting the small diffusive component which prevails in the matrix for uniform flow. It was found that a diffusion–dominated regime emerges for \( \kappa < \kappa_c \) with \( \kappa_c(\text{Pe}) \) a cutoff threshold: in this regime removal of solute which enters the inclusion takes place by diffusion, advection inside the sphere by \( V \) playing a negligible role. The cutoff \( \kappa_c \) was identified from the numerical simulations in [18], leading to the expression \( \kappa_c \approx 3.6/\text{Pe} \). This value can be translated to the one of \( \text{Pe}^\text{in} \), the interior Pe number at the transition, by using the relationships \( V^\text{in} / U \approx 3k/(2 + \kappa) \), to yield

\[
\kappa_c \approx 3.6/\text{Pe} \Rightarrow \text{Pe}^\text{in} = 5.4
\]

In words (8) states that for \( \text{Pe}^\text{in} < 5.4 \) removal of solute is diffusion dominated whereas for \( \text{Pe}^\text{in} > 5.4 \) advection prevails.

This result was applied to the derivation of the travel time pdf with a cutoff adjustment of (6) to account for diffusion impact upon the tail at high Pe: the residual \( \tau_0(\kappa) \) (4) is maintained for \( \kappa > \kappa_c \) and it is replaced by the constant \( \tau_0(\kappa_c) \) for \( \kappa < \kappa_c \). In turn this modified \( \tilde{f}(\tau_k) \) was used in the Fourier Transform convolutions (7) leading to the travel time distributions depicted in Figs. 1–3 (dot-dashed lines).

3.3. The impact of finite Pe: diffusion into low-conductive blocks from outer flow (second mechanism)

There is an additional mechanism, related to the rapid flow outside the same inclusions, as illustrated in Fig. 4b by the snapshots of the plume portion advected outside and in the neighborhood of the inclusion. Thus, solute particles swept along the streamlines neighboring the sphere diffuse inside and subsequently back. This mechanism leads to a macroscopic “retardation”, which is sometimes modeled through suitable “memory functions” in the literature. Modeling this complex process can be simplified by observing that a similar one was considered in the past in the frame of models of exchange between mobile and immobile zones in soil, or matrix sorption in aquifers or fractured rocks (see discussion in [4]), as a kinetic process described macroscopically by linear mass transfer. This effect was modeled in terms of solute travel time by Cvetkovic and Dagan [4] with the aid of the function \( \gamma(t; \kappa) \) which can be defined as the concentration along a streamline at time \( t \) for a pulse of solute of unit concentration injected at \( t = 0 \) and reaching the control plane by advection at time \( \tau \), with \( \tau \gg \tau \). The function \( \gamma \) adopted by Cvetkovic and Dagan [4] is based on the approximate solution of Rosen [23] for diffusion into spherical immobile zones, the result being (4); Eq. 5.8)
\[
\gamma(\tau, t; K_d, \xi) = \frac{4\xi}{\pi} \int_0^\infty \exp[-3K_d\xi\tau I_1(\lambda)]\cos[2\xi(t-\tau)]^2 \\
- 3K_d\xi\tau H_2(\lambda) j d\lambda
\]

with

\[
H_1(\lambda) = \frac{j(\sinh 2\lambda + \sin 2\lambda)}{(\cosh 2\lambda - \cos 2\lambda)}; \quad H_2(\lambda) = \frac{j(\sinh 2\lambda - \sin 2\lambda)}{(\cosh 2\lambda - \cos 2\lambda)}
\]

The parameters \(\xi, K_d\) are defined in the original derivation as follows

\[
\xi = \frac{R}{D}; \quad K_d = \frac{\theta_m}{1 - \theta_m}
\]

with \(\theta_m\) the relative volume fraction of the immobile zones. These parameters can be related in a straightforward manner with the ones characterizing the ensemble of spherical inclusions in the present model. Indeed, by its definition (11) \(\zeta/R = (3/4)\rho^{-1}\). As for \(\theta_m\), it can be related in a simple manner to the volume fraction of inclusions characterized by \(k \leq k_c\), for which \(V_m\) is so small, that the fluid is practically immobilized inside the spheres. Since the pdf \(f(k)\) is precisely the lognormal distribution of relative volumes of inclusions of different \(k\), we get \(\theta_m = P_x(k_c)\) with \(P_x = \int_0^1 f(k) k\) the CDF of \(k\). Hence, the two parameters in (9) are given by

\[
\zeta/R = (3/4)\rho^{-1} \quad \text{and} \quad K_d = \frac{P_x(k_c)}{1 - P_x(k_c)}
\]

The function \(\gamma(9)\) is often denoted as “reaction function” and it is represented in Cvetkovic and Dagan [4] (Fig. 2a) as function of \(\tau/t < 1\) for a few values of \(\zeta\). At the extreme \(\rho \rightarrow \infty\) (\(\zeta \rightarrow 0\)), of advection solely, \(\gamma \rightarrow \delta(t - \tau)\), whereas for finite \(\rho\) and sufficiently large \(t (\zeta \gg 1)\), \(\gamma \rightarrow \delta(t - t/R)\) and the retardation coefficient is given by \(R = 1 + K_d\). With these preparatory steps, the second mechanism is incorporated into the distribution \(\mu\) determined previously by applying the following integral

\[
\mu(t; x; Pe) = \int_0^T f(\tau; x; Pe) \gamma(\tau; t) d\tau
\]

where \(f(\tau; x; Pe)\) is the travel time pdf affected by the tail cutoff discussed above (first mechanism).

4. Implementation, comparison with numerical simulations and discussion

For easiness of the discussion, we recapitulate briefly the steps followed in order to implement the SCA semi-analytical model: (i) for a normal distribution \(f(Y)\) characterized by \(K_c\) and \(\sigma_y^2\), the lognormal \(f(k)\) is determined by deriving first \(K_{ef}\) (3) and plugging \(k = K\) \(K_{ef}\) into \(f(k)\) (6); (ii) for a given value of the \(Pe = UI/D\) the cutoff value \(k_c\) is determined from \(k_c = 3.6\rho^{-1}\) (8); (iii) the Fourier Transform is applied numerically to \(f(t_k)\) (6), with \(t_k = \epsilon(k)/(4)\) replaced by the constant \(t_{m(k)}(k)\) for \(k < k_c\); (iv) for a given distance to the control plane \(x/l\) a number of convolutions \(N = 0.4x/l\) is applied numerically to the previous FT in order to obtain the FT of \(f(t; x; Pe)\), the latter being obtained subsequently by the inversion of the FT; (v) the function \(\gamma(9)\) is determined for the selected value of \(Pe\) by (12) and \(f(t; x; Pe)\) is numerically integrated (13) in order to arrive at the final expression of \(\mu(t; x; Pe)\). Although this process involves a few numerical quadratures and Fourier Transforms, it is considerably simpler than the full numerical solution described in Section 2. We emphasize again that the method is formally valid for any \(\sigma_y^2\).

In order to validate the SCA, the procedure was applied to the control plane at \(x/l = 116\) (which is far enough from the injection plane to warrant neglect of boundary effects) and to same governing parameters \(\sigma_y^2 = 2, 4, 8\) and \(Pe = 75, 375, 750\) as in the numerical simulations (Section 2). The distribution \(\mu(t; x; Pe)\) is represented as function of \(t/l\) in the nine graphs (Figs. 1–3) pertaining to the different combinations of parameters values. In each case we have depicted three graphs, besides the dots representing the numerical simulations: the one pertaining to advection only (\(Pe = \infty\)) as described in Section 3.1, a second one for \(f(t; x; Pe)\) for which the impact of finite Pe is due only to the first mechanism through the cutoff \(k_c\) and finally the complete \(\mu(t; x; Pe)\) for which Pe impacts also via the second mechanism.

Starting with the lowest \(\sigma_y^2 = 2\) it is seen that for the highest \(Pe = 750\) and \(Pe = 375\) (Fig. 1a and b), diffusion has little impact and the BTC based on the SCA is practically identical to the one pertinent to \(Pe = \infty\). Only at the lowest \(Pe = 75\) (Fig. 1c) diffusion has a small influence and the two SCA based BTC, \(f\) and \(\mu\), differ somewhat, both in the bulk and the tail. However, the complete SCA \(\mu(t; x)\) (13) is very close to the numerical simulation. The negligible impact of diffusion is easily understood from the SCA developments: the rapid decay of the lognormal distribution (3) wipes out the fraction of low \(k < k_c\) which are affected by both mechanisms of diffusion. Indeed, the volume fractions are \(P_x(k_c) = 0.052, 0.083, 0.208\) for \(Pe = 750, 375, 75\), respectively. Once again, this finding justifies the neglect of diffusion in the FOA as assumed in the past for weakly heterogeneous formations of lognormal conductivity.

Moving to highly heterogeneous formations of \(\sigma_y^2 = 4\), at the highest \(Pe = 750\) (Fig. 2a), the influence of diffusion is negligible and the travel time distribution is close to the advective one. There is some impact on the tail for \(Pe = 375\) (Fig. 2b) and again the complete SCA (13) is a good approximation of the numerical simulations. At the lowest \(Pe = 75\) (Fig. 2c) diffusion becomes quite influential and the BTC differs from the \(Pe = \infty\) result both in the bulk and the tail. In this case incorporation of the second mechanism (13) leads to a marked improvement of the comparison between the SCA and the numerical simulations.

Lastly, for the very high \(\sigma_y^2 = 8\), the effect of diffusion is still weak for \(Pe = 750\) (Fig. 3a), but it becomes significant both in the bulk and tail of the BTC for the lower Pe values (Fig. 3b and c). The largest impact for the entire set is observed at the lowest \(Pe = 75\) (Fig. 4c), as discussed in Section 2. Here again the SCA result (13) is in excellent agreement with the numerical simulations and accounting for the second mechanism via the \(\gamma(9)\) function is needed. The relative impact of the first and second mechanisms on transport is similar to the one observed in the previous cases.

To further assess the impact of the finite Pe upon transport we have represented the retardation coefficient \(R = 1 + K_d\) as function of \(\sigma_y^2\) for the considered values of \(Pe\) in Fig. 5. It reflects the impact of the second mechanism (Section 3.3) for \(x/l > 1\). It is seen that this effect is significant only for highly heterogeneous formations (say \(\sigma_y^2 > 2\)), and it is not a property of the medium as it strongly depends on Pe. The retardation of the mean time manifests in that of the peaks of \(\mu\) displayed in Figs. 1–3, as the early times behavior is influenced primarily by the second mechanism.

In our previous work [18] we have determined the asymptotic equivalent longitudinal macrodispersivity

\[
\chi_{eq}(x) = U^2 \sigma_y^2 \frac{2x}{\sigma_x^2}
\]

as function of \(\sigma_y^2\) and Pe, where \(\sigma_y^2\) is the variance of the travel determined from the pdf \(f\) (6) accounting for the first mechanism only. Since this is the main process affecting the reduction of \(\chi_{eq}\) as compared to advection only, the reader is referred to [18, Fig. 6] for results. In any case, the results led to the conclusion that the macrodispersivity (14) is not an adequate measure of solute
spread in highly heterogeneous formations as it depends strongly on the tail of the BTC (whose prediction is imprecise) and on \( Pe \).

5. Summary and conclusions

The present study addresses the effect of local diffusion on the breakthrough curve (BTC) of passive solutes. The analysis is performed by accurate numerical simulations, which serve as numerical laboratory, and by developing a simplified analytical solution. Diffusion is quantified by \( Pe = UI/D \), and the analysis is focused on strongly heterogeneous media. The structure model is of a dense ensemble of inclusions with random hydraulic conductivity, of log-normal distribution.

Accurate numerical simulations (Figs. 1–3) revealed two major effects when comparing the BTC with the one ensuing from advective transport: a considerable reduction of the BTC tail on one hand, and an apparent diminishing and retardation of the peak, on the other. These effects are determined by the interplay between large scale macro-advection and transfer of mass between “fast” and “slow” flows by local diffusion. They were captured on the other. These effects are determined by the interplay between large scale macro-advection and transfer of mass between “fast” and “slow” flows by local diffusion. They were captured accurately by a semi-analytical model based on the self consistent approximation (SCA) by incorporating (i) a physically based cutoff \( \kappa_c \) in the low \( \kappa \) tail of the conductivity distribution, which separates regions of diffusion- and advection-dominated transport, and (ii) a macroscopic model of exchange between mobile-immobile zones available in the literature (similar to a memory function).

All parameters of the model are physically based and depend only on the structural and flow characteristics, quantified by \( U, \sigma_y^2, Pe = UI/D, I \) for the adopted model. While estimates of the mean velocity \( U \) and \( D \) are generally feasible, the inference of the logconductivity variance \( \sigma_y^2 \) and its integral scale \( I \) from field data is usually more problematic since they require more detailed information. In the field experiments carried out in the past this was achieved by laboratory measurement of a large number of samples extracted from batteries of observation wells. More efficient methods have been advanced recently, e.g., direct push (e.g., [22,21]) or interpretation of pumping test in the context of heterogeneous media (e.g., [13]). Hence, the main conclusion of the present study is that the main features of transport in highly heterogeneous formations can be explained by physical mechanisms which are directly related to the medium structure and local diffusion solely. Furthermore, the BTC can be quantified in terms of two measurable parameters: the logconductivity variance \( \sigma_y^2 \) and the \( Pe \) number, representing the degree of the medium heterogeneity and effect of molecular diffusion, respectively. The next step of the present research in making the model comparable with field experiments, in which we are engaged, is its extension to statistically anisotropic heterogeneous media, as encountered in most natural formations. Examples of additional topics to be explored in the future are: non-ergodic behavior related to plume size, impact of the choice of the model structure (e.g., present one versus continuous multi-Gaussian), extension to reactive transport and nonstationary velocity field.

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