

# An analytical model for carrier-facilitated solute transport in weakly heterogeneous porous media



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## ABSTRACT

Carrier-facilitated solute transport in heterogeneous aquifers is studied within a Lagrangian framework. Dissolved solutes and carriers are advected by steady random groundwater flow, which is modeled by Darcy's law with uncertain hydraulic conductivity that is treated as a stationary random space function. We derive general expressions for the spatial moments of the dissolved concentration and the concentration associated with the carrier phase. In order to reduce the computational effort, we use previously derived solutions for the flow field. This enables us to obtain closed-form solutions for the spatial moments of the two concentration fields. The mass and center of gravity of the two propagating plumes depend only on the mean velocity field and chemical/degradation processes. The higher (second and third) moments are affected by the coupling between reactions (sorption/desorption and degradation) among the three phases (i.e., dissolved, carrier and sorbed concentrations) and the aquifer's heterogeneity. We investigate the potentially enhancing effect of carriers by comparing spatial moments of the two propagating plumes. The forward/backward mass transfer rates between the liquid and carrier phases, and the degradation coefficients are identified as critical parameters. The carrier's role is most prominent when detachment from carrier sites is slow, provided that degradation on the carriers is smaller than that in the liquid phase.

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## 1. Introduction

Numerous particles freely moving in aquifers may act as carriers for many solutes. Groundwater contamination as a result of the widespread use of industrial chemicals as well as of the geological media for final disposal of spent nuclear materials has attracted the attention of hydrologists (a recent overview on the topic can be found in [2]). Their interest is particularly motivated by the fact that carriers can facilitate transport of strongly sorbing contaminants (e.g., [3,4]). Dissolved pollutants may “sorb” on the carriers, whose advection can significantly enhance pollutant transport in the subsurface [5]. Transport of pesticides and hydrophobic chemicals mediated by the presence of carriers has been documented in [6]. In other cases carriers (such as pathogenic bacteria and viruses) are contaminants themselves (e.g., [7,8]). Thus, simulation

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models accounting for mobility enhancement of dissolved solutes have been extensively studied in the past (a review can be found in [9] and references therein).

Generally, contaminant concentration(s) are predicted by accounting simultaneously for the relevant physico-chemical processes. As a consequence, carrier-facilitated transport involves a large number of equations and parameters. After their release, solutes may undergo a number of physical/chemical transformations (e.g., sorption, desorption, degradation, filtration, removal, etc.). The governing equations for mass transfer between phases are generally very difficult to parametrize because of the data scarcity and difficulty of carrying out batch experiments [10]. Several mathematical models have been developed to describe mass exchanges between the species, and the majority of them assume equilibrium conditions between the carrier and liquid phase (e.g., [5] and references therein). Such models predict a reduction of the retardation depending on both the carrier concentration and the partition coefficient on the carrier sites. If equilibrium is applicable, as carriers bearing solutes move into a solute-free porous medium, they are rapidly stripped of solutes due to the high sorption capacity of the matrix. In contrast, if desorption kinetics from carriers is slow, the assumption of equilibrium would underestimate the impact of carriers on enhancing transport [4].

In addition to the above mentioned complexity, one has to account for spatial heterogeneity of the transport parameters. This observed heterogeneity is mainly reflected in the erratic spatial variations of the hydraulic conductivity (a wide exposition can be found in [11]). In principle, one could adopt a “detailed” description of the observed variations, but in practice the cost and time of obtaining the necessary field data would be unrealistic. Furthermore, such an approach is excessive if one is interested in global quantities (like the plume moments or mean contaminant fluxes) instead of local concentration values. Hence, carrier-facilitated solute transport in natural porous media can be realistically modeled by means of a stochastic approach. In absence of carriers a considerable work has been done (e.g., [12,13] and references therein) by applying the Lagrangian approach [14]. Despite the enormous achievements obtained in this case, very little has been done when dealing with three (or more) moving phases under the same field uncertainties. A mathematical formulation of colloid-facilitated solute transport in heterogeneous porous formations (which represents an important case of carriers facilitated solute transport) has been presented in [5].

The present paper aims at investigating carrier-enhanced solute transport in heterogenous porous formations. Unlike [5], we study carrier-facilitated solute transport by means of spatial moments similarly to Severino et al. [4]. We generalize their analysis in several respects: i) we incorporate the impact of solute degradation (within both the liquid and carrier phase) and illustrate how this mechanism combines with chemical reactions and heterogeneity; ii) we analytically compute transverse moments (lateral dispersion), iii) we provide a closed-form expression for the longitudinal third moment (to quantify the departure from Gaussianity), and iv) we derive asymptotic results which are of utility in the practical applications.

## 2. Phenomenological assumptions and mathematical statement

In heterogeneous porous media, both the conductivity  $K(\mathbf{x})$  and porosity  $\vartheta(\mathbf{x})$  vary in space  $\mathbf{x} \in \mathbb{R}^3$ . However, our analysis focuses on transport in aquifers where  $K(\mathbf{x})$  often varies by orders of magnitude, and is heavily under-sampled (e.g., [15,16]). It is common (see [11,14] and references therein) to characterize this uncertainty by treating  $K(\mathbf{x})$  as a random space function (RSF). In particular, the log-conductivity  $Y = \ln K$  is modeled as a second-order stationary (statistically homogeneous), multi-variate Gaussian field with given mean  $\langle Y \rangle$  (hereafter  $\langle \cdot \rangle$  represents the ensemble average operator), variance  $\sigma_Y^2$  and autocorrelation function  $\rho_Y \equiv \rho_Y(\mathbf{r})$ . We choose

$$\rho_Y(\mathbf{r}) = \exp\left(-\sqrt{\frac{r_1^2 + r_2^2}{I^2} + \frac{r_3^2}{I_v^2}}\right) \quad \mathbf{r} \equiv (r_1, r_2, r_3), \quad (1)$$

where  $I$  and  $I_v$  are the horizontal and vertical integral scales, respectively. The statistical anisotropy arising from the fact that  $I \neq I_v$  is a salient feature of many aquifers (reflecting the formation processes), and it influences to a great extent the flow field (e.g., [17–20]). The spatial variability of porosity  $\vartheta$  is often much smaller than that of  $Y$  (e.g., [15]), and therefore can be neglected. In the present study, we follow this trend as well, and regard  $\vartheta$  as a deterministic constant.

We consider steady groundwater flow driven by a constant gradient  $\nabla\Phi$  of the hydraulic head  $\Phi$  into an unbounded aquifer (such that one may neglect the impact of the boundary conditions). The velocity  $\mathbf{V} \equiv (V_1, V_2, V_3)^T$  is related to the hydraulic conductivity, the porosity and the head via Darcy's law  $\mathbf{V} = -\frac{K}{\vartheta} \nabla\Phi$ . Since  $Y$  is regarded as a RSF, the velocity will also be a RSF, and we shall assume that its mean value  $\langle \mathbf{V} \rangle$  is uniform and aligned to the  $x_1$ -axis, i.e.  $\langle \mathbf{V} \rangle = (U, 0, 0)^T$ . A dissolvable solute injected into an aquifer through an “injection plane” (Fig. 1). We assume that carriers are advected by groundwater, and may bind part of the dissolved solute as a result of complex chemical processes, such as sorption/desorption. Thus, the retention due to possible sorption on the soil matrix is reduced (as compared with the case where carriers are supposed not to exist), or equivalently *the solute mobility is enhanced*. Our aim here is to provide a model for carrier facilitated solute transport accounting for the aquifer heterogeneity on one hand, and physico-chemical involved processes on the other in order to build up a simple as well as reliable tool for quick assessment of the potential impact of carriers on the migration of solute(s) in the subsurface.

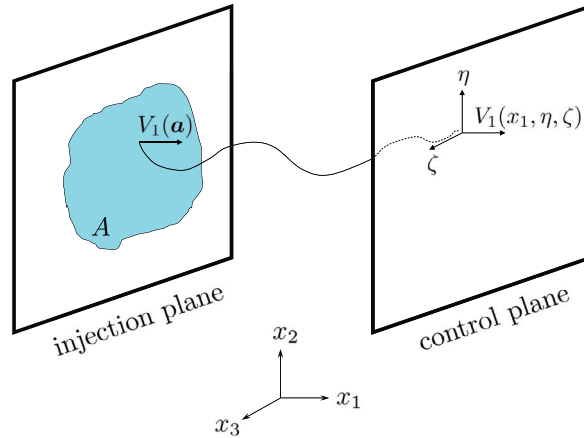


Fig. 1. Definition sketch of a particle path starting at the injection area  $A$  with velocity  $V_1(\mathbf{a})$ , and arriving to the control plane with velocity  $V_1(x_1, \eta, \zeta)$ .

In line with the existing literature on the topic (e.g., [21]), we assume that the concentration  $C_c$  (mass of carrier per volume of liquid) of the advected carriers does not drastically change with the time  $t$  (quasi steady state regime), and consequently the mass balance equation for the carrier phase can be written as

$$V_i \frac{\partial C_c}{\partial x_i} = -\varepsilon C_c + \mu, \tag{2}$$

(hereafter Einstein’s summation convention is adopted), where  $\varepsilon$  and  $\mu$  quantify the irreversible removal and generation of carriers, respectively. Estimating the pair  $(\varepsilon, \mu)$  is difficult since field scale data are limited. In the case of colloidal particles, it is customary (e.g., [1,5,10,22]) to assume that removal is compensated by generation, i.e.,  $\varepsilon C_c \approx \mu$ . Based on this, we shall regard the carrier concentration as uniform. Generally, it is more likely to be that  $\varepsilon C_c > \mu$ , i.e., carrier removal dominates generation, and therefore the enhancing impact of carriers upon solute transport might be reduced. Nevertheless, even when this is the real case, our assumptions would lead to an upper bound for carrier facilitated transport, thus leading to a conservative prediction. This aspect is quite important when the solute is a contaminant.

We define the fluid concentration, hereafter denoted by  $C^{(X)}$ , as mass of dissolved solute per volume of liquid, and the carrier concentration, hereafter denoted by  $C^{(Y)}$ , as mass (per volume of liquid) of solute bound to the carrier. Generally, the change in time and space of  $C^{(m)}$  (in what follows  $m \equiv X, Y$ ) is assumed to be controlled by: i) groundwater advection, ii) chemical processes, and iii) pore scale dispersion (PSD). This latter in general impacts both moments [23] and concentration(s) [24–26]. However, moments are significantly influenced by the PSD when the plume is originated by a point-like source [27], a typical configuration of flows from/toward wells (for details, see [28,29]). Instead, in the case of a mean uniform flow (typical of groundwater flows) the plume is generated by a relatively (as compared to the heterogeneity scale of  $Y$ ) large source for which PSD has a very minor effect. Since this is the case in the problem at stake, hereafter we neglect the PSD.

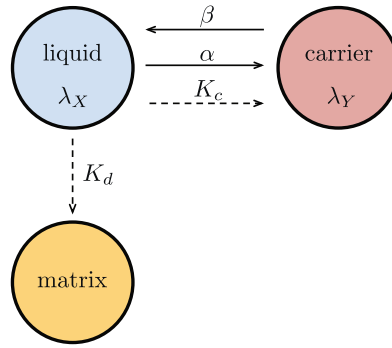
Characterization of any mass transfer process requires specification of the thermodynamic kinetics, and a relation to represent the dynamics of approaching the equilibrium. Sorption/desorption reactions have received a significant attention [30,31]. These reactions are associated with parameters that are very difficult to measure [10,32]. Hence, it is common to treat them according to simplified models. In particular, we shall assume that solutes are in equilibrium with the porous matrix. Such an assumption seems reasonable as many solutes (such as Neptunium and Plutonium as well as some agro-chemicals) obey the linear equilibrium model [10,22,33], and nevertheless even more complex reactions (like sorption/desorption) may tend to the equilibrium on relatively short times (see [34,35]).

Let us denote by  $N^{(X)} \equiv K_d C^{(X)}$  the solute concentration sorbed onto the matrix defined per unit of bulk volume. The mass balance equations then can be written as [4]

$$\frac{\partial}{\partial t} \left[ C^{(X)} + \frac{N^{(X)}}{R_c} \right] + V_i \frac{\partial C^{(X)}}{\partial x_i} = R_c^{-1} \psi(C^{(X)}, C^{(Y)}) - \left[ C^{(X)} + \frac{N^{(X)}}{R_c} \right] \lambda_X \tag{3a}$$

$$\frac{\partial C^{(Y)}}{\partial t} + V_i \frac{\partial C^{(Y)}}{\partial x_i} = -R_c^{-1} \psi(C^{(X)}, C^{(Y)}) - \lambda_Y C^{(Y)}, \quad N^{(X)} = K_d C^{(X)}, \tag{3b}$$

where  $R_c = 1 + K_c$  is referred to as (carrier) retardation factor. The dimensionless parameters  $K_c$  and  $K_d$  are the linear partitioning coefficients on the porous matrix and carrier sites, respectively. In addition, solutes may undergo reactions like precipitation (especially for organic compounds) or radioactive decay (typically of radionuclides). Modeling such type of reactions is quite complex. Thus, we assume that the loss of mass in the liquid and carrier phase is regulated by a first-order decay law with degradation rates equal to  $\lambda_X$  and  $\lambda_Y$ , respectively.



**Fig. 2.** Sketch of the liquid-carrier-porous matrix with indication of: i) forward,  $\alpha$ , ii) backward,  $\beta$ , rates pertaining to the sorption/desorption (continuous), and iii) coefficients,  $K_c - K_d$ , showing the linear partitioning between each phase (dashed). In addition,  $\lambda_X$  and  $\lambda_Y$  refer to the degradation in the liquid and carrier phase, respectively.

Mass transfer (generically represented by the function  $\psi$ ) from/toward the carrier and liquid phase is a mechanism of central importance. While the equilibrium assumption has been a common assumption at laboratory scale, at field scale the experimental observations do not usually support its validity [22], and therefore kinetic effects have to be considered. A fairly general kinematical model is that of Langmuir which accounts for the fact that the number of binding sites upon the carrier surface is limited. However, the concentrations  $C^{(m)}$  relevant in the applications are often relatively low, and therefore the Langmuir model can be linearized, i.e.,

$$\psi(C^{(X)}, C^{(Y)}) \approx -\alpha C^{(X)} + \beta C^{(Y)}, \tag{4}$$

$\alpha$  and  $\beta$  being the forward and backward rate, respectively (Fig. 2). In the discussion below, we shall refer to (4) as sorption/desorption between  $C^{(X)}$  and  $C^{(Y)}$ . When there is no kinetically controlled mechanism between the two phases, one has  $\psi = 0$ , and consequently the concentrations  $C^{(m)}$  change due to advection combined with pure equilibrium, solely.

We rewrite (3) a Lagrangian framework. Following [36], we replace the independent variables  $x_i$  with variables  $\xi_i$ , which are defined as

$$\xi_1 = \tau(x_1; \mathbf{a}), \quad \xi_2 = x_2 - \eta(x_1; \mathbf{a}), \quad \xi_3 = x_3 - \zeta(x_1; \mathbf{a}), \quad \mathbf{a} \in A, \tag{5}$$

where  $\tau$  represents the “travel time” of a fluid particle starting at a given position on the injection area  $A$  and reaching a given accessible environment (termed as *control plane*) located at  $x_1$  (Fig. 1). The Lagrangian coordinates  $\eta$  and  $\zeta$  fix the position of the fluid particle at the control plane, i.e.,  $x_2 = \eta(x_1; \mathbf{a})$  and  $x_3 = \zeta(x_1; \mathbf{a})$ . The functions  $\tau$ ,  $\eta$ , and  $\zeta$  depend upon the velocity field  $\mathbf{V}$  through the system of equations [36]

$$\frac{d\tau}{dx_1} = \frac{1}{V_1(\xi)}, \quad \frac{d\eta}{dx_1} = \frac{V_2(\xi)}{V_1(\xi)}, \quad \frac{d\zeta}{dx_1} = \frac{V_3(\xi)}{V_1(\xi)}. \tag{6}$$

Application of the chain rule of derivation and accounting for (6) yields:

$$\frac{\partial}{\partial x_1} = \frac{1}{V_1(\xi)} \frac{\partial}{\partial \xi_1}, \quad \frac{\partial}{\partial x_i} = \frac{1}{V_i(\mathbf{x})} \left[ V_i(\mathbf{x}) - V_i(\xi) \frac{V_1(\mathbf{x})}{V_1(\xi)} \right] \frac{\partial}{\partial \xi_i} \quad (i = 2, 3), \tag{7}$$

so that (3) can be written as

$$R \frac{\partial C^{(X)}}{\partial t} + \frac{V_1(\mathbf{x})}{V_1(\xi)} \frac{\partial C^{(X)}}{\partial \xi_1} + \left[ V_i(\mathbf{x}) - V_i(\xi) \frac{V_1(\mathbf{x})}{V_1(\xi)} \right] \frac{\partial C^{(X)}}{\partial \xi_i} = \frac{\psi}{R_c} - R \lambda_X C^{(X)} \tag{8a}$$

$$\frac{\partial C^{(Y)}}{\partial t} + \frac{V_1(\mathbf{x})}{V_1(\xi)} \frac{\partial C^{(Y)}}{\partial \xi_1} + \left[ V_i(\mathbf{x}) - V_i(\xi) \frac{V_1(\mathbf{x})}{V_1(\xi)} \right] \frac{\partial C^{(Y)}}{\partial \xi_i} = -\frac{\psi}{R_c} - \lambda_Y C^{(Y)}, \tag{8b}$$

where  $R = 1 + K_d/R_c$ . By setting  $\xi_2 = \xi_3 = 0$ , i.e., for  $x_2 = \eta$  and  $x_3 = \zeta$  (see Eq. (5)), one has  $\mathbf{V}(\mathbf{x}) \equiv \mathbf{V}(\xi)$  and (8a) and (8b) become (see (4))

$$R \frac{\partial C^{(X)}}{\partial t} + \frac{\partial C^{(X)}}{\partial \tau} = -\left( R \lambda_X + \frac{\alpha}{R_c} \right) C^{(X)} + \frac{\beta}{R_c} C^{(Y)} \tag{9a}$$

$$\frac{\partial C^{(Y)}}{\partial t} + \frac{\partial C^{(Y)}}{\partial \tau} = \frac{\alpha}{R_c} C^{(X)} - \left( \lambda_Y + \frac{\beta}{R_c} \right) C^{(Y)}. \tag{9b}$$

Summarizing, adoption of the Lagrangian parametrization (5) enables us to convert system (3a) and (3b) (with a three dimensional nature) into one-dimensional system (9a) and (9b). The advantage of such a methodology (for details, see [36]) is that one can significantly reduce the computational burden. In particular, one may use just one (i.e., Laplace) integral transform to fully solve the transport problem.

### 3. Spatial moments

We wish to characterize the evolution of the propagating plumes originated at the injection plane by means of spatial moments. In order to compute spatial moments we consider a pulse-injection of solute,

$$C^{(X)}(\mathbf{a}, t) = \frac{\rho_0(\mathbf{a})}{V_1(\mathbf{a})} \delta(t), \quad C^{(Y)}(\mathbf{a}, t) = 0 \quad (\mathbf{a} \in A), \tag{10}$$

(where  $\rho_0$  is the injected solute mass per unit area  $A$ ) into an aquifer which is initially solute free,  $C^{(m)}(\mathbf{x}, 0) = 0$ . Starting from the reaction functions  $\gamma_m$ , the Lagrangian concentration associated with a solute particle started at a given position  $\mathbf{a}$  over the injecting plane can be written as

$$\Delta C^{(m)} = \frac{\vartheta \rho_0(\mathbf{a})}{V_1(x_1, \eta, \zeta)} \gamma_m(\tau, t) \delta(x_2 - \eta) \delta(x_3 - \zeta). \tag{11}$$

Therefore the entire field  $C^{(m)}$  is obtained by integrating over  $A$ , i.e.,

$$C^{(m)}(\mathbf{x}, t) = \vartheta \int_A d\mathbf{a} \frac{\rho_0(\mathbf{a}) \gamma_m(\tau, t)}{V_1(x_1, \eta, \zeta)} \delta(x_2 - \eta) \delta(x_3 - \zeta). \tag{12}$$

For the Lagrangian concentration (12) spatial moments are defined as

$$\mathcal{M}_{pqr}^{(m)}(t) = \int d\mathbf{x} x_1^p x_2^q x_3^r C^{(m)}(\mathbf{x}, t) = \vartheta \int_A d\mathbf{a} \rho_0(\mathbf{a}) \int_0^\infty dx_1 \frac{x_1^p \eta^q \zeta^r}{V_1(x_1, \eta, \zeta)} \gamma_m(\tau, t). \tag{13}$$

The key to computing  $\mathcal{M}_{pqr}^{(m)}$  is to exchange the variable  $x_1$  with  $\tau$  with the aid of  $V_1 = dx_1/d\tau$ , i.e.,

$$\mathcal{M}_{pqr}^{(m)}(t) = \vartheta \int_A d\mathbf{a} \rho_0(\mathbf{a}) \int_0^\infty d\tau X_1^p(\tau; \mathbf{a}) X_2^q(\tau; \mathbf{a}) X_3^r(\tau; \mathbf{a}) \gamma_m(\tau, t), \tag{14}$$

where  $\mathbf{X}(\tau; \mathbf{a}) \equiv (x_1(\tau; \mathbf{a}), \eta(\tau; \mathbf{a}), \zeta(\tau; \mathbf{a}))$  is the Lagrangian trajectory of a fluid particle starting at the injection plane at  $t = 0$ , and crossing the control plane at  $x_1$  in the point  $(\eta, \zeta)$  at  $t \equiv \tau$  (Fig. 1). Since the fluid velocity  $\mathbf{V}$  is assumed to be a RSF,  $(\tau, \eta, \zeta)$  are also RSFs, as are the spatial moments  $\mathcal{M}_{pqr}^{(m)}$ . Assuming that both the liquid and the carrier plumes are “ergodic”, we restrict our analysis to the ensemble average of (14). Before going further, it is worth recalling that Fiori and Bellin [37] have shown that the attainment of ergodic conditions is favored by the presence of the sorption/desorption reaction. Moreover, the validity of the ergodic argument is further corroborated by the fact that the characteristic length of the source is significantly larger than the horizontal heterogeneity scale of  $Y$  (i.e.  $A \gg l^2$ ), which corresponds to the requirement suggested by Dagan [38] to regard transport of a passive scalar (i.e., inert) as ergodic. As a consequence, either when transport is dominated by the ongoing chemical/physical reactions or when reactions are rapidly exhausted (and therefore solutes behave like inert), in the present study transport can be considered as ergodic.

Let us define auxiliary functions

$$\Gamma_n^{(m)}(t) = \int_0^\infty d\tau \tau^n \gamma_m(\tau, t) \quad (n = 0, 1, 2, \dots), \tag{15}$$

that are computed as

$$\Gamma_n^{(m)}(b, t) = (-1)^n \frac{d^n}{ds^n} \widehat{\gamma}_m(s, t) \Big|_{s=b}, \tag{16}$$

where  $\widehat{\gamma}_m(s, t)$  is the Laplace transform of  $\gamma_m$  (over the travel time  $\tau$ ).

The zero-order moment (mass) of the liquid and carrier phase is computed by setting  $p = q = r = 0$  in (14) and taking the ensemble average,

$$M^{(m)}(t) = M_0 \Gamma_0^{(m)}(0, t), \quad M_0 = \vartheta \int_A d\mathbf{a} \rho_0(\mathbf{a}). \tag{17}$$

The center of gravity  $\mathbf{R}^{(m)}$  is computed by setting  $p = q = r = 1$  in (14) and normalizing by (17) to account for the effective mass confined into the  $m$ -phase (recall that, due to the ongoing physical/chemical reactions, the mass in each phase is changing at any  $t$ ):

$$\mathbf{R}^{(m)}(t) = \frac{\vartheta}{M^{(m)}(t)} \int_A d\mathbf{a} \rho_0(\mathbf{a}) \int_0^\infty d\tau \mathbf{X}(\tau; \mathbf{a}) \gamma_m(\tau, t). \tag{18}$$

The ensemble average of (18) is

$$\langle \mathbf{R}_i^{(m)}(t) \rangle = R_i^{(m)}(0) + U \frac{\Gamma_1^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} \delta_{1i} \quad (i = 1, 2, 3), \tag{19}$$

where we have used the fact that for the considered problem one has:  $\mathbf{X}(t) = \mathbf{X}(0) + \langle \mathbf{V} \rangle t + \mathbf{X}'(t)$  [14], with  $\mathbf{X}'$  the fluctuation of the trajectory  $\mathbf{X}$ . It is seen that the zero, (17), and first, (19), moments do not depend upon the heterogeneity. Instead,

they are influenced only by the chemical/physical reactions (through the presence of the  $\Gamma$ -functions), and by the mean flow (via the velocity  $U$ ). The second and third moments are computed in a similar fashion. Thus, the second longitudinal central moment reads as

$$\langle S_{11}^{(m)}(t) \rangle = \Psi_{11}^{(m)}(t) + \frac{1}{\Gamma_0^{(m)}(0, t)} \int_0^\infty d\tau X_{11}(\tau) \gamma_m(\tau, t), \tag{20a}$$

$$\Psi_{11}^{(m)}(t) = S_{11}^{(m)}(0) + U^2 \left\{ \frac{\Gamma_2^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} - \left[ \frac{\Gamma_1^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} \right]^2 \right\}, \tag{20b}$$

whereas the transverse ones are

$$\langle S_{ii}^{(m)}(t) \rangle = S_{ii}^{(m)}(0) + \frac{1}{\Gamma_0^{(m)}(0, t)} \int_0^\infty d\tau X_{ii}(\tau) \gamma_m(\tau, t) \quad (i = 2, 3). \tag{21}$$

In (20a) and (21)  $X_{ii}(t) \equiv \langle X_i'^2(t) \rangle$  represents the variance of the trajectory  $\mathbf{X} \equiv (X_1, X_2, X_3)$  whose expression has been derived at the first-order of approximation in the variance  $\sigma_V^2$ , i.e.,

$$X_{ii}(t) = 2 \int_0^t d\tau (t - \tau) u_{ii}(\tau) \quad (i = 1, 2, 3), \tag{22}$$

where  $u_{ii}$  is the velocity covariance (for details, see [14]). Finally, the longitudinal third central moments are given by

$$\langle S_{111}^{(m)}(t) \rangle = \Psi_{111}^{(m)}(t) + \frac{3U}{\Gamma_0^{(m)}(0, t)} \int_0^\infty d\tau X_{11}(\tau) \gamma_m(\tau, t) \left[ \tau - \frac{\Gamma_1^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} \right], \tag{23a}$$

$$\Psi_{111}^{(m)}(t) = S_{111}^{(m)}(0) + U^3 \left\{ \frac{\Gamma_3^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} - 3 \frac{\Gamma_2^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} \frac{\Gamma_1^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} + 2 \left[ \frac{\Gamma_1^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} \right]^3 \right\}. \tag{23b}$$

It is seen from (20a), (21) and (23a) that to evaluate the second and third longitudinal moments the  $\gamma_m$ -functions are also needed. Generally, system (3a) and (3b) can be solved only numerically. Alternatively, one can analytically solve such a system in the Laplace domain, and subsequently, by a numerical inversion of Laplace transform, compute  $\gamma_m$ . Even if such a numerical inversion can be in principle carried out, it does not represent an easy task, and it poses many problems in terms of stability as well as convergence [39]. In order to avoid any numerical steps, we propose a different approach which leads to very simple (closed form) solutions. More precisely, we take advantage approximate expressions for  $X_{ii}$ ,

$$X_{ii}(t') = 2 (\sigma_V I)^2 u_{ii}(0) \begin{cases} \frac{1}{u_{11}(0)} \left\{ t' + \frac{\exp[-u_{11}(0)t'] - 1}{u_{11}(0)} \right\} & i = 1 \\ b_{ii}^2 \left[ 1 - \left( 1 + \frac{t'}{b_{ii}} \right) \exp\left(-\frac{t'}{b_{ii}}\right) \right] & i = 2, 3 \end{cases} \quad (t' = t/t_h), \tag{24}$$

obtained by [1] by replacing in (22) the velocity covariance with

$$u_{ii}(r) = (\sigma_V U)^2 u_{ii}(0) \begin{cases} \exp[-u_{11}(0)r/I] & i = 1 \\ [1 - r/(b_{ii}I)] \exp[-r/(b_{ii}I)] & i = 2, 3, \end{cases} \tag{25}$$

where  $t_h = I/U$  is the characteristic heterogeneity time scale,  $u_{ii}(0)$  are the scaled exact  $\sigma_V^2$ -order velocity variances [40]:

$$u_{11}(0) = 1 + \frac{e}{16(1 - e^2)^2} [(19 - 10e^2)e - (13 - 4e^2)\chi], \tag{26a}$$

$$u_{22}(0) = \frac{e^2}{16(1 - e^2)^2} \left[ (1 - 4e^2) \frac{\chi}{e} + 1 + 2e^2 \right], \tag{26b}$$

$$u_{33}(0) = \frac{e}{4(1 - e^2)^2} [(1 + 2e^2)\chi - 3e], \tag{26c}$$

and

$$\chi = \frac{\arcsin \sqrt{1 - e^2}}{\sqrt{1 - e^2}}, \quad b_{ii} = \begin{cases} 2 \sqrt{\frac{(1 - e^2)[1 + (1 - 2e^2)\chi/e]}{(1 - 4e^2)\chi/e + 1 + 2e^2}} & i = 2 \\ \sqrt{\frac{2(1 - e^2)(\chi - e)}{(1 + 2e^2)\chi - 3e}} & i = 3. \end{cases} \quad (27)$$

In (26a)–(26c)  $e = l_v/l \leq 1$  is the anisotropy ratio. The accuracy related to the adoption of the approximate expressions (24) has been assessed by Severino et al. [1] who quantified the relative error between the exact (first order) moments with the analytical expressions obtained by adopting (24). In particular, these latter compare very well (with a relative error less than 0.1%) for  $t' \leq 1$  and  $t' \geq 100$ . Instead, in the intermediate regime  $1 < t' < 100$ , it is shown that the maximum relative error does not exceed 20%. Since in the present paper one is mainly interested into predictions over large times, the proposed approximate expressions lead to very robust results.

We are now in position to demonstrate how Eq. (24), combined with the Laplace transform of the reaction functions, enable us to evaluate the second and third spatial moments. More specifically, insertion of (24) into (20a), (21), and (23a) implies the evaluation of the following integrals:

$$\int_0^\infty d\tau X_{11}(\tau) \tau^n \gamma_m(\tau, t) = \frac{U}{I} \lambda_{11} \left\{ \Gamma_{n+1}^{(m)}(0, t) + c_1^{-1} \left[ \int_0^\infty d\tau \beta_i(\tau) \tau^n \gamma_m(\tau, t) - \Gamma_n^{(m)}(t) \right] \right\}, \quad (28a)$$

$$\int_0^\infty d\tau X_{ii}(\tau) \gamma_m(\tau, t) = \lambda_{ii} \left[ \Gamma_0^{(m)}(0, t) - \int_0^\infty d\tau \beta_i(\tau) (1 + c_i \tau) \gamma_m(\tau, t) \right], \quad (28b)$$

with  $n = 0, 1$ , and,

$$\lambda_{11} = 2(\sigma_Y I)^2, \quad \lambda_{ii} = 2u_{ii}(0)(\sigma_Y I b_{ii})^2, \quad \beta_i(\tau) = \exp(-c_i \tau), \quad c_1 = \frac{U}{I} u_{11}(0), \quad c_i = \frac{U}{I b_{ii}}, \quad (29)$$

( $i = 2, 3$ ). The integrals on the right hand side of (28a)–(28b) are now calculated by observing that

$$\int_0^\infty d\tau \exp[-(b + s)\tau] \tau^n \gamma_m(\tau, t) = (-1)^n \frac{\partial^{(n)}}{\partial s} \hat{\gamma}_m(s + b, t), \quad (30)$$

which, after taking the limit  $s \rightarrow 0$  on both sides, leads to

$$\int_0^\infty d\tau \exp(-b\tau) \tau^n \gamma_m(\tau, t) = (-1)^n \frac{\partial^{(n)}}{\partial s} \hat{\gamma}_m(s + b, t) \Big|_{s=0} = \Gamma_n^{(m)}(b, t). \quad (31)$$

Summarizing, the second and third moments become

$$\langle S_{11}^{(m)}(t) \rangle = \Psi_{11}^{(m)}(t) + (I\sigma_Y)^2 \left\{ \frac{R_1^{(m)}(t)}{I} - \frac{1}{u_{11}(0)} \left[ 1 - \frac{\Gamma_0^{(m)}(c_1, t)}{\Gamma_0^{(m)}(0, t)} \right] \right\}, \quad (32a)$$

$$\langle S_{ii}^{(m)}(t) \rangle = S_{ii}^{(m)}(0) + 2u_{ii}(0) (I\sigma_Y b_{ii})^2 \left[ c_i \frac{\Gamma_1^{(m)}(c_i, t)}{\Gamma_0^{(m)}(0, t)} + 1 - \frac{\Gamma_0^{(m)}(c_i, t)}{\Gamma_0^{(m)}(0, t)} \right] \quad (i = 2, 3), \quad (32b)$$

$$\langle S_{111}^{(m)}(t) \rangle = \Psi_{111}^{(m)}(t) + 6I(U\sigma_Y)^2 \Lambda_{111}^{(m)}(t), \quad (32c)$$

where

$$\Lambda_{111}^{(m)}(t) = \frac{\Gamma_2^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} - \left[ \frac{\Gamma_1^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} \right]^2 - c_1^{-1} \frac{\Gamma_0^{(m)}(c_1, t)}{\Gamma_0^{(m)}(0, t)} \left[ \frac{\Gamma_1^{(m)}(0, t)}{\Gamma_0^{(m)}(0, t)} + \frac{\Gamma_1^{(m)}(c_1, t)}{\Gamma_0^{(m)}(c_1, t)} \right]. \quad (33)$$

It follows from (32) that to evaluate spatial moments it is sufficient to find the Laplace transform  $\hat{\gamma}_m(s, t)$  of the Lagrangian reaction functions  $\gamma_m(\tau, t)$ . In particular, the longitudinal second and third moments are represented as the sum of two terms: i) one (of deterministic nature) depending only upon the chemical reactions, and ii) another that accounts for the coupling between the reactions and the heterogeneity of the porous formation.

### 3.1. Analytical expression for the $\hat{\gamma}_m$ -functions

In absence of carriers, solutions in the Laplace domain of transport equations are available [34,35]. Furthermore, in the case of colloid facilitated radionuclide transport [5] has derived analytical solutions for  $\hat{\gamma}_m$ . In the following, we analytically calculate  $\hat{\gamma}_m$  assuming linear non-equilibrium sorption (see (4)) combined with degradation. Although the main steps of



such a procedure can be found in [4], the latter is limited to the derivation of  $\gamma_Y$ . Instead, we provide the full derivation leading to  $\hat{\gamma}_m$ . Thus, the governing system of equations is derived from (9a) and (9b) as

$$\begin{cases} R \frac{\partial \gamma_X}{\partial t} + \frac{\partial \gamma_X}{\partial \tau} = -\left(R\lambda_X + \frac{\alpha}{R_c}\right)\gamma_X + \frac{\beta}{R_c}\gamma_Y \\ \frac{\partial \gamma_Y}{\partial t} + \frac{\partial \gamma_Y}{\partial \tau} = \frac{\alpha}{R_c}\gamma_X - \left(\lambda_Y + \frac{\beta}{R_c}\right)\gamma_Y, \end{cases} \tag{34}$$

which is solved subject to the homogeneous initial condition,  $\gamma_m(\tau, 0) = 0$ , and solute pulse injection in the liquid phase,  $\gamma_X(0, t) = \delta(t)$ . The Laplace transforms  $\hat{\gamma}_m$  (see the Appendix for detailed derivations) are  $\hat{\gamma}_m(s, t'') = \hat{F}(s, t'') \hat{F}^{(m)}(s, t'')$ , where

$$\hat{F}(s, t'') = \frac{\exp\left\{-\left[\omega(s) + \sqrt{1 + \chi^2(s)}\right]t''\right\}}{2R\sqrt{1 + \chi^2(s)}}, \quad \hat{F}^{(Y)}(s, t'') = \sqrt{R\alpha/\beta}[1 - \theta(s, t'')], \tag{35}$$

$$\hat{F}^{(X)}(s, t'') = \sqrt{1 + \chi^2(s)} + \chi(s) + \left[\sqrt{1 + \chi^2(s)} - \chi(s)\right]\theta(s, t''), \tag{36}$$

where  $t'' = \frac{t}{t_r}$  (the characteristic reaction timescale  $t_r$  is defined in the Appendix) and

$$\chi(s) = \chi + s t_r \left(\frac{R-1}{2R}\right), \quad \omega(s) = \omega + s t_r \left(\frac{R+1}{2R}\right), \tag{37}$$

$$\chi, \omega = \frac{1}{2}\sqrt{\frac{R}{\alpha\beta}}\left(\beta + R_c\lambda_Y \mp \frac{\alpha + R_c\lambda_X}{R}\right), \quad \theta(s, t'') = \exp\left[-2\sqrt{1 + \chi^2(s)}t''\right]. \tag{38}$$

With  $\hat{\gamma}_m(s, t)$  calculated in closed forms, we compute the spatial moments via (17), (19), and (32).

**4. Discussion**

We consider carrier-facilitated solute transport in a 3-D statistically anisotropic heterogeneous aquifer under the flow field conditions discussed above. We wish to assess the interplay between heterogeneity and chemical/physical processes and its effect on possible enhancement of solute transport. This will be accomplished with the aid of the spatial moments previously derived. The zeroth-moments  $M^{(m)}(t'')$  represent the most important quantities since they represent the solute mass associated with each phase. In order to assess the effect of sorption/desorption and degradation on solute partition between the two phases, we have calculated the ratio  $\mu$  between  $M^{(Y)}$  and  $M^{(X)}$ ,

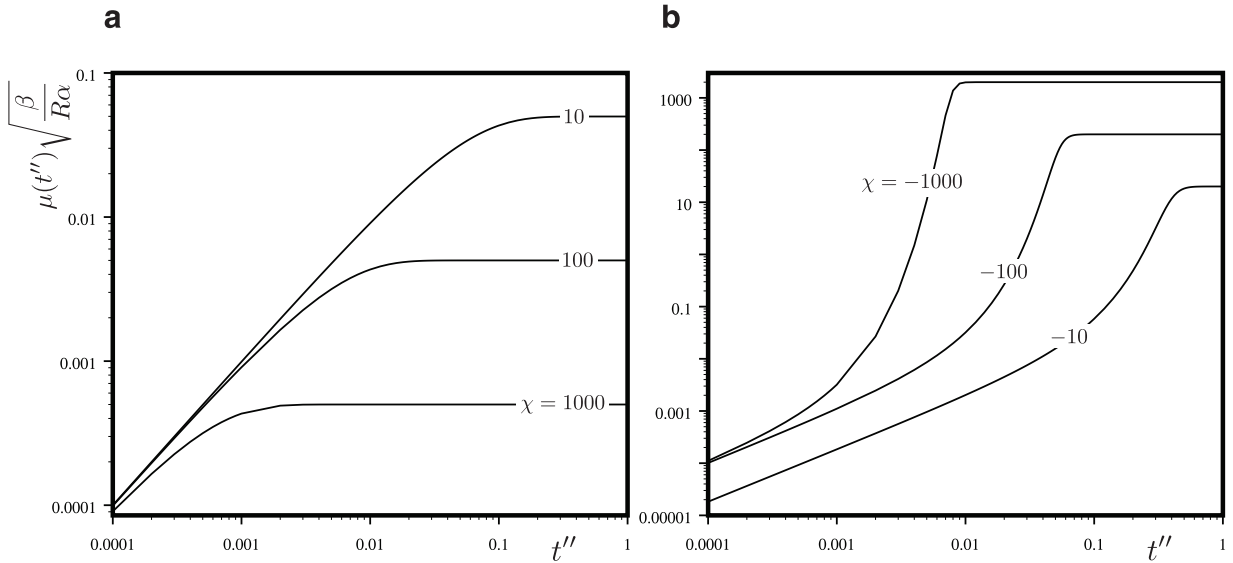
$$\mu(t'') = \frac{M^{(Y)}(t'')}{M^{(X)}(t'')} = \frac{\sqrt{R\alpha/\beta}[1 - \theta(0, t'')]}{\sqrt{1 + \chi^2} + \chi + (\sqrt{1 + \chi^2} - \chi)\theta(0, t'')}. \tag{39}$$

The parameter

$$\chi = \frac{1}{2}\sqrt{\frac{R}{\alpha\beta}}\left(\beta + R_c\lambda_Y - \frac{\alpha + R_c\lambda_X}{R}\right), \tag{40}$$

is referred to as a *modified Damköhler number* (MDN); it combines the effects of degradation and sorption/desorption in the  $m$ -phases. More precisely,  $\chi > 0$  indicates that the solute release/degradation mechanisms acting in the carrier phase are quicker than the ones in the liquid phase, and *viceversa* ( $\chi < 0$ ). The role of chemical processes and degradation is shown in Fig. 3a where for positive values of MDN the corresponding part of the initial injected mass  $M_0$  is fluid-advected for almost all the time. On the other hand, for negative MDN (Fig. 3b) the solute mass in the carrier concentration is at least 10 times (provided that  $t > t_r$ ) the solute mass present in the liquid phase. The lower is  $\chi$ , the higher is the quantity of solute mass which is in the carrier phase. Thus, very slow desorption from the carrier concentration coupled with a very low degradation as compared with the same mechanisms acting in the fluid one (Fig. 2), i.e.,  $\beta + R_c\lambda_Y \ll (\alpha + R_c\lambda_X)/R$ , would result in “inert” transport. This feature has a profound impact on contaminant transport since it implies that even very strongly sorbing pollutants (like some radionuclides), which are expected to be very immobile in the groundwater, may behave like tracers. This would explain for instance why Noell et al. [41] recovered unretarded breakthrough curves of cesium in the presence of silica (acting as carriers). Similar results were observed by Saiers and Hornberger [42] who recovered early breakthrough curves of cesium in the presence of kaolinite particles. Even if the mass partition depends on both the MDN and time  $t$ , Figs. 3a and b show that for  $t'' > 1$  the quantity  $\mu$  becomes practically constant implying that the mass partition between the two phases is at equilibrium. Thus, the value  $\mu_\infty \equiv \lim_{t \rightarrow \infty} \mu(t)$  represents an important parameter





**Fig. 3.** Scaled relative zeroth-order moment  $\mu(t'')\sqrt{\beta/(R\alpha)}$  versus dimensionless time  $t'' \equiv t/t_r = t\sqrt{\alpha\beta}/(R_c\sqrt{R})$ , for positive (a) and negative (b) values of the MDN  $\chi$ .

for applications (especially when estimating the long term fate of carrier-facilitated contaminant transport). It is calculated from (39) as

$$\mu_\infty = \lim_{t \rightarrow \infty} \mu(t) = \frac{\sqrt{R\alpha/\beta}}{\sqrt{1 + \chi^2 + \chi}}. \tag{41}$$

For very large MDN all the mass is confined in the liquid phase, and therefore we recover  $\mu_\infty \simeq 0$ . At the other extreme of very negative  $\chi$  (41) yields  $\mu_\infty \gg 1$ . Such behavior is due to the fact that the linear kinetic model (4), as stated before, does not account for the fact that the number of binding carrier sites is limited.

Similarly to the previous case, we study the relative distance between the centers of gravity of the two moving plumes by computing the quantity  $\varrho = R_1^{(Y)} - R_1^{(X)}$ ,

$$\varrho(t'') = \frac{I_r(R-1)}{2R\sqrt{1+\chi^2}} \left[ \frac{\sqrt{1+\chi^2} + \chi - (\sqrt{1+\chi^2} - \chi)(1 + 2\chi t'')\theta(0, t'')}{\sqrt{1+\chi^2} + \chi + (\sqrt{1+\chi^2} - \chi)\theta(0, t'')} - \frac{2\chi t''\theta(0, t'')}{1 - \theta(0, t'')} \right], \tag{42}$$

where  $I_r = Ut_r = UR_c\sqrt{R/(\alpha\beta)}$  is the reaction characteristic length. When there is no sorption on the matrix ( $R = 1$ ), we recover  $\varrho \equiv 0$ , i.e., the two centroids occupy the same position at each time (irrespective of the chemical/degradation processes). When  $R > 1$  the center of gravity of the liquid phase always trails that of the carrier phase ( $\varrho > 0$  at any  $t$ ). This is to be expected since linear partitioning on the matrix implies a retardation in the dissolved solute migration but not on the carriers (and hence on the solute bound to them). The dimensionless relative distance  $\frac{R\varrho(t'')}{I_r(R-1)}$  is depicted in Figs. 4a and b versus  $t''$ , for several values of  $\chi$ . At  $t'' \ll 1$  the behavior of  $\varrho$  is assessed by expanding (42) in a power series:

$$\varrho(t'') = \frac{I_r(R-1)}{2R}t'' + \mathcal{O}(t''^2). \tag{43}$$

Since both the kinematic and degradation effects are “time-dependent”, it follows from (43) that at the very early times the relative distance  $\varrho$  does not depend upon  $\chi$ . For larger times (and provided that  $t'' < 0.01$ ),  $R_1^{(Y)}$  moves at a velocity higher than that of  $R_1^{(X)}$  (i.e.,  $\dot{\varrho} > 0$ ). For  $t'' \geq 0.01$  the behavior of  $\varrho$  at positive values of the MDN is significantly different from that at negative values. More precisely, for  $\chi > 0$  (Fig. 4a) retardation due to the linear partitioning is dominant (since positive  $\chi$ -values imply that most of the solute mass is confined in the liquid phase), and therefore the distance between  $R_1^{(Y)}$  and  $R_1^{(X)}$  increases until equilibrium conditions (both in the liquid and carrier phase) are reached. From here on the relative distance stabilizes, and consequently  $\varrho$  does not change with time. In particular, the faster the sorption/desorption (large  $\chi$ -values), the sooner the attainment of such stable conditions.

For  $\chi < 0$  (Fig. 4b) a reduction in the velocity is observed at certain time (depending on  $\chi$ ). This is attributed to the fact that the very strong sorption on carrier sites causes a very high retardation, and thus after an initial period in which  $\varrho$

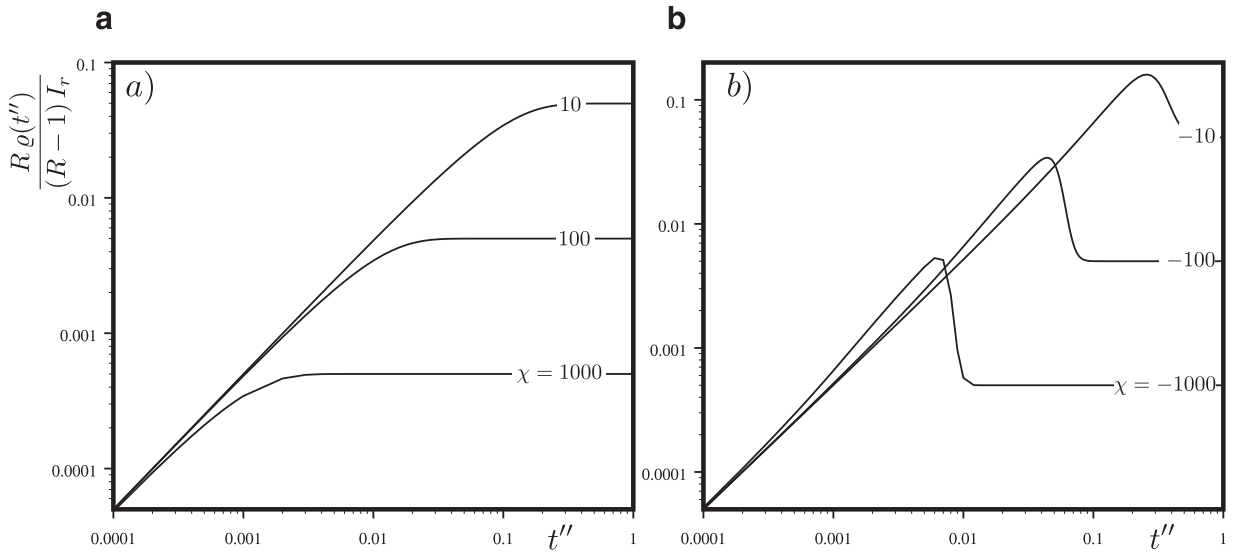


Fig. 4. Scaled first-order moment  $\frac{R \varrho(t'')}{(R-1)I_r}$  versus the dimensionless time,  $t'' \equiv t/t_r = t\sqrt{\alpha\beta}/(R_c\sqrt{R})$ , for positive (a) and negative (b) values of the MDN  $\chi$ .

increases (since most of the solute mass is being transferred to the carrier phase), the center of gravity  $R_1^{(Y)}$  advances with a velocity less than that of  $R_1^{(X)}$ .

In order to analyze the asymptotic behavior of  $\varrho(t'')$ , we neglect  $\mathcal{O}(\exp(-t''))$ -terms in (42), to obtain

$$\varrho_\infty = \lim_{t \rightarrow \infty} \varrho(t) = \frac{I_r(R-1)}{2R\sqrt{1+\chi^2}}. \tag{44}$$

The first important feature of the asymptotic relative distance is that it is “finite”. Furthermore,  $\varrho_\infty$  is maximum at  $\chi = 1$ , and it does not depend upon the the sign of  $\chi$ , i.e., upon the dominant direction of the reaction/degradation processes. Even if  $\varrho_\infty$  may be relatively high, we have to account for the solute mass which is going to be really carried. Thus, it is clear that the case  $\chi < 0$  is the most critical one especially when the solute is a contaminant.

The second-order spatial moments (32a) and (32b) depend on two different timescales:  $t_h$  and  $t_r$ . Various particular cases may be considered depending on the ratio  $t_r/t_h$ . In particular, if  $t$  is much larger than the rescaled characteristic heterogeneity time  $t_h$  and simultaneously  $t = \mathcal{O}(t_r)$ , then  $t_h \ll t_r$ . Such a condition is known as the *Fickian regime* (e.g., [36]) for which the trajectory variances (24) can be approximated by

$$X_{ii}(t) \approx 2(I\sigma_Y)^2 \begin{cases} t & i = 1 \\ u_{ii}(0) b_{ii}^2 & i = 2, 3. \end{cases} \tag{45}$$

It is worth noting that (45) accounts also for the asymptotic behavior of the second-order moments of a passive (i.e., inert) solute. However, in the case of reactive transport this is not anymore the case (although  $X_{ii}$  are involved in the computation of moments, as shown below).

Inspection of the first expansion in (45) shows that in the Fickian regime the anisotropy does not impact the longitudinal dispersion  $\langle S_{11}^{(m)} \rangle$ . Substituting (45) into (20) and (21) yields

$$\langle S_{11}^{(m)}(t) \rangle \approx \Psi_{11}^{(m)}(t) + 2I\sigma_Y^2 \langle R_1^{(m)}(t) \rangle, \tag{46a}$$

$$\langle S_{ii}^{(m)}(t) \rangle \approx (I\sigma_Y)^2 \begin{cases} \frac{e[e + (1 - 2e^2)\chi]}{2(1 - e^2)} & i = 2 \\ \frac{e(\chi - e)}{1 - e^2} & i = 3. \end{cases} \tag{46b}$$

where for simplicity we set  $R_i^{(m)}(0) = S_{ii}^{(m)}(0) \equiv 0$ . The first term on the right hand side of (46a) is deterministic (see (20b)), and depends upon reactions and the mean velocity. Instead, the second term is related to the heterogeneity, and is identical to the one obtained when carriers are not accounted for, provided that  $Ut$  is replaced with  $\langle R_1^{(m)} \rangle$ . The transverse

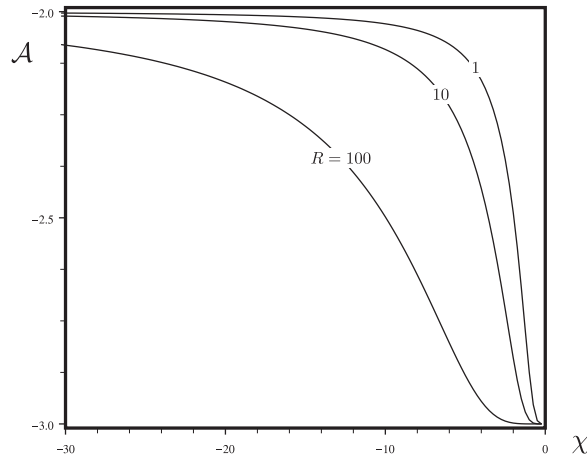


Fig. 5. Nondimensional parameter  $\mathcal{A}$  versus the MDN  $\chi$ , for three values of the retardation factor  $R$ .

moments (46b) do not depend on reactions, and are identical for both phases. Thus, as far as the transverse dispersion is accounted for in the Fickian regime, the two plumes behave like “noninteracting” solute bodies [43]. To complete the large-time analysis, we computed the nondimensional quantity  $\mathcal{A} \equiv \lim_{t \rightarrow \infty} (S_{111}^{(X)}(t)) / (R_1^{(X)}(t))^3$  in order to assess the deviation from the Gaussianity in the Fickian regime. By omitting the very lengthy algebraic derivations, the final result reads as

$$\mathcal{A} = -\left(2 + \frac{\beta_3}{\beta_1^3}\right), \tag{47}$$

where

$$\beta_1 = (1 + \chi^2) \left[ R + 1 + \frac{(R - 1)\chi}{\sqrt{1 + \chi^2}} \right], \tag{48}$$

$$\beta_3 = (R + 1)^3 + 4(R^3 - 1)\chi^6 + 3(R + 1)\chi^2[2(R^2 + 1)(1 + \chi^2) + (R - 1)^2\chi^2] + (R - 1)\chi(1 + \chi^2)^{3/2}[3(R + 1)^2 + 4(R^2 + R + 1)\chi^2]. \tag{49}$$

The striking result is that in the Fickian regime the chemical/physical processes completely overtake the heterogeneity. Such behavior was already observed in transport of both linearly [36] and nonlinearly [44] reacting solutes. Fig. 5 depicts the dependence of  $\mathcal{A}$  on the MDN, and a few values of the retardation factor  $R$ . Asymptotically the solute plume always displays a negative asymmetry, since the following bounds hold:

$$-3 \equiv \mathcal{A}(0) \leq \mathcal{A}(\chi) \leq \mathcal{A}(-\infty) \equiv -2. \tag{50}$$

In particular, the higher value of  $\mathcal{A}$  is attained for very negative MDN, since most of the solute is in the liquid phase as consequence of the strong retention on the carrier sites. On the other hand, for  $\chi \rightarrow 0$  the solute mostly sorbs on the matrix due to the linear partitioning, and this produces a longer tail as manifested in the more negative asymmetry. The transition between these two limiting cases is regulated by the retardation coefficient  $R$ . Finally, we investigate the slight dependence of  $\mathcal{A}$  on the retardation coefficient in the range  $\chi \in [0, +\infty)$ . Within this interval  $\mathcal{A}$  is a monotonically increasing function of  $\chi$  and satisfies the following bounds:

$$-3 \equiv \mathcal{A}(0) \leq \mathcal{A}(\chi) \leq \mathcal{A}(+\infty) \equiv -3(1 - R^{-3}). \tag{51}$$

Since usually  $R \gg 1$ ,  $\mathcal{A} \simeq -3$  at any  $\chi \geq 0$ .

### 5. Concluding remarks

The main objective of the present study was to investigate transport of reactive solute by steady random groundwater flow when potential carriers are accounted for. By adopting the Lagrangian procedure employed in the past for similar problems, we derive general expressions for spatial moments of the solute concentration dissolved in the liquid phase and the solute concentration attached to the moving carriers. In order to reduce the computational effort, we use approximate expressions for the fluid particles variances  $X_{ij}$  obtained in [1]. Such approximate expressions for  $X_{ij}$  enable one to obtain closed-form analytical solutions for the spatial moments of the moving plumes for a wide class of chemical/physical processes occurring between carriers and dissolved solutes.

The structure of spatial moments, and the mutual effect of chemical/degradation processes combined with heterogeneity is analyzed. In order to emphasize when the presence of carriers may drastically enhance solute transport, we focused mainly on the first two moments. The modified Damköhler number  $\chi$  is shown to be the critical parameter. Positive values of  $\chi$  imply that solute transport is taking place mostly in the liquid phase, and therefore the impact of carriers is modest. On the contrary, negative values of  $\chi$  mean that the solute is mainly “located” on the moving carriers, and thus the most significant effect of carriers on transport is expected when sorption on carrier sites is irreversible, provided that degradation there is slower than in the other phase(s). Simple asymptotic results enabling one to assess the evolution of the propagating plumes in the Fickian (large time) regime are also analyzed. Useful bounds for the asymmetry of the solute plume are obtained, and its dependence upon the MDN is discussed.

Finally we remark (in view of the practical applications) a few specific features of the present study:  $\diamond$  the proposed methodology provides a relatively simple and robust tool for carrying out a contaminant risk assessment;  $\diamond$  a comparison between the linear and nonlinear sorption/desorption models for carrier-facilitated transport (e.g., [22]) indicates that the linear model provides a reasonable (upper bound) approximation even in cases where nonlinear effects are relevant.

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**Appendix. Analytical derivation of the  $\hat{\gamma}_m$  functions**

Application of the Laplace transform (denoted with “hat” symbol) over  $\tau$  (the corresponding complex variable is  $s$ ) to (34) yields

$$\begin{cases} \frac{d}{dt} \hat{\gamma}_X + \left(s + \frac{\alpha}{R_c} + R\lambda_X\right) \hat{\gamma}_X = \frac{\beta}{R_c} \hat{\gamma}_Y + \frac{\delta(\bar{t})}{R} \\ \frac{1}{R} \frac{d}{dt} \hat{\gamma}_Y + \left(s + \frac{\beta}{R_c} + \lambda_Y\right) \hat{\gamma}_Y = \frac{\alpha}{R_c} \hat{\gamma}_X \end{cases} \quad \hat{\gamma}_m(s, 0) = 0, \tag{A1}$$

where retardation due to  $R$  is encapsulated in the scaledtime  $\bar{t} = t/R$ . We apply again the Laplace transform (denoted with “tilde” symbol) over  $\bar{t}$  (the corresponding complex variable is  $q$ ) to (A1) to obtain

$$\tilde{\gamma}_X(s, q) = \frac{q + \xi_Y}{R P_2(q)}, \quad \tilde{\gamma}_Y(s, q) = \frac{\alpha}{R_c P_2(q)}, \tag{A2}$$

in which  $P_2(q) = (q + \xi_X)(q + \xi_Y) - \frac{\alpha \beta R}{R_c^2}$ , and

$$\xi_X = s + \frac{\alpha}{R_c} + R\lambda_X, \quad \xi_Y = R \left( s + \frac{\beta}{R_c} + \lambda_Y \right). \tag{A3}$$

By observing that

$$\tilde{\gamma}_X(s, q) = \frac{R^{-1}}{q_1 - q_2} \left( \frac{q_1 + \xi_Y}{q - q_1} - \frac{q_2 + \xi_Y}{q - q_2} \right), \quad \tilde{\gamma}_Y(s, q) = \frac{\alpha R_c^{-1}}{q_1 - q_2} \left( \frac{1}{q - q_1} - \frac{1}{q - q_2} \right), \tag{A4}$$

where  $q_{1,2}$ ,

$$q_{1,2} = \frac{1}{2} \left[ -(\xi_Y + \xi_X) \pm \sqrt{(\xi_Y - \xi_X)^2 + 4 \frac{\alpha \beta R}{R_c^2}} \right], \tag{A5}$$

are the roots of  $P_2(q)$ , we calculate the inverse of tilde Laplace transform of (A4),

$$\hat{\gamma}_m(s, t) = \hat{F}(s, t) \hat{F}^{(m)}(s, t), \quad \hat{F}(s, t) = \frac{1}{q_1 - q_2} \exp\left(\frac{q_1}{R} t\right) \tag{A6}$$

$$\hat{F}^{(X)}(s, t) = \frac{1}{R} \left[ q_1 + \xi_Y - (q_2 + \xi_Y) \exp\left(-\frac{q_1 - q_2}{R} t\right) \right] \tag{A7}$$

$$\hat{F}^{(Y)}(s, t) = \frac{\alpha}{R_c} \left[ 1 - \exp\left(-\frac{q_1 - q_2}{R} t\right) \right]. \tag{A8}$$

Normalizing the current time  $t$  by the characteristic timescale  $t_r = R_c \sqrt{R/(\alpha\beta)}$ , and accounting for (A5), enables us to rewrite (A6)–(A8) as (35)–(36).

## References

- [1] G. Severino, V. Cvetkovic, A. Coppola, On the velocity covariance for steady flows in heterogeneous porous formations and its application to contaminants transport, *Comput. Geosci.* 9 (4) (2005) 155–177.
- [2] R. Murali, Colloid Mediated Contamination of Ground Water and its Remediation, The M. S. University of Baroda, Vadodara, India, 2011 Ph.D. thesis.
- [3] H. Van de Weerd, A. Leijnse, W. Van Riemsdijk, Transport of reactive colloids and contaminants in groundwater: effect of nonlinear kinetic interactions, *J. Contam. Hydrol.* 32 (3) (1998) 313–331.
- [4] G. Severino, V. Cvetkovic, A. Coppola, Spatial moments for colloid-enhanced radionuclide transport in heterogeneous aquifers, *Adv. Water Resour.* 30 (1) (2007) 101–112.
- [5] V. Cvetkovic, Colloid-facilitated tracer transport by steady random ground-water flow, *Phys. Fluids* 12 (9) (2000) 2279–2294.
- [6] B. Gjettermann, C. Petersen, C.B. Koch, N.H. Spliid, C. Grøn, D. Baun, M. Styczen, Particle-facilitated pesticide leaching from differently structured soil monoliths, *J. Environ. Qual.* 38 (6) (2009) 2382–2393.
- [7] L.L.C. Rehmann, C. Welty, R.W. Harvey, Stochastic analysis of virus transport in aquifers, *Water Resour. Res.* 35 (7) (1999) 1987–2006, doi:10.1029/1999WR900059.
- [8] S. Bhattacharjee, J.N. Ryan, M. Elimelech, Virus transport in physically and geochemically heterogeneous subsurface porous media, *J. Contam. Hydrol.* 57 (3) (2002) 161–187.
- [9] P. Knabner, I. Kögel-Knabner, K. Totsche, *The Modeling of Reactive Solute Transport with Sorption to Mobile and Immobile Sorbents*, Citeseer, Berlin, 1992.
- [10] S. Painter, V. Cvetkovic, D. Pickett, D. Turner, Significance of kinetics for sorption on inorganic colloids: modeling and experiment interpretation issues, *Environ. Sci. Technol.* 36 (24) (2002) 5369–5375.
- [11] Y. Rubin, *Applied Stochastic Hydrogeology*, Oxford University Press, Oxford, 2003.
- [12] A. Fiori, F. Boso, F.P. de Barros, S. De Bartolo, A. Frampton, G. Severino, S. Suweis, G. Dagan, An indirect assessment on the impact of connectivity of conductivity classes upon longitudinal asymptotic macrodispersivity, *Water Resour. Res.* 46 (8) (2010).
- [13] G. Severino, D.M. Tartakovsky, G. Srinivasan, H. Viswanathan, Lagrangian models of reactive transport in heterogeneous porous media with uncertain properties, *Proc. Roy. Soc. A* 468 (2140) (2012) 1154–1174.
- [14] G. Dagan, *Flow and Transport in Porous Formation*, Springer-Verlag, New York, 1989.
- [15] G. Severino, A. Comegna, A. Coppola, A. Sommella, A. Santini, Stochastic analysis of a field-scale unsaturated transport experiment, *Adv. Water Resour.* 33 (10) (2010) 1188–1198.
- [16] C. Fallico, S. De Bartolo, M. Veltri, G. Severino, On the dependence of the saturated hydraulic conductivity upon the effective porosity through a power law model at different scales, *Hydrol. Process.* 30 (13) (2016) 2366–2372.
- [17] G. Severino, A. Santini, A. Sommella, Steady flows driven by sources of random strength in heterogeneous aquifers with application to partially penetrating wells, *Stoch. Environ. Res. Risk Assess.* 22 (4) (2008) 567–582.
- [18] G. Severino, Stochastic analysis of well-type flows in randomly heterogeneous porous formations, *Water Resour. Res.* 47 (3) (2011).
- [19] G. Severino, S. De Bartolo, G. Toraldo, G. Srinivasan, H. Viswanathan, Travel time approach to kinetically sorbing solute by diverging radial flows through heterogeneous porous formations, *Water Resour. Res.* 48 (12) (2012).
- [20] G. Severino, S. De Bartolo, Stochastic analysis of steady seepage underneath a water-retaining wall through highly anisotropic porous media, *J. Fluid Mech.* 778 (2015) 253–272.
- [21] L. Lührmann, U. Noseck, C. Tix, Model of contaminant transport in porous media in the presence of colloids applied to actinide migration in column experiments, *Water Resour. Res.* 34 (3) (1998) 421–426.
- [22] V. Cvetkovic, S. Painter, D. Turner, D. Pickett, P. Bertetti, Parameter and model sensitivities for colloid-facilitated radionuclide transport on the field scale, *Water Resour. Res.* 40 (6) (2004) W06504.
- [23] A. Fiori, Finite pecllet extensions of dagan's solutions to transport in anisotropic heterogeneous formations, *Water Resour. Res.* 32 (1) (1996) 193–198.
- [24] V. Kapoor, P.K. Kitaniadis, Concentration fluctuations and dilution in aquifers, *Water Resour. Res.* 34 (5) (1998) 1181–1193.
- [25] A. Fiori, G. Dagan, Concentration fluctuations in aquifer transport: a rigorous first-order solution and applications, *J. Contam. Hydrol.* 45 (1) (2000) 139–163.
- [26] A. Bellin, G. Severino, A. Fiori, On the local concentration probability density function of solutes reacting upon mixing, *Water Resour. Res.* 47 (1) (2011).
- [27] G. Severino, Macrodispersion by point-like source flows in randomly heterogeneous porous media, *Transp. Porous Media* 89 (1) (2011) 121–134.
- [28] M. Dentz, H. Kinzelbach, S. Attinger, W. Kinzelbach, Temporal behavior of a solute cloud in a heterogeneous porous medium: 1. Point-like injection, *Water Resour. Res.* 36 (12) (2000) 3591–3604.
- [29] G. Severino, A. Santini, A. Sommella, Macrodispersion by diverging radial flows in randomly heterogeneous porous media, *J. Contam. Hydrol.* 123 (1) (2011) 40–49.
- [30] M.L. Brusseau, P. Rao, R.W. Gillham, Sorption nonideality during organic contaminant transport in porous media, *Crit. Rev. Environ. Sci. Technol.* 19 (1) (1989) 33–99.
- [31] W.J. Weber, P.M. McGinley, L.E. Katz, Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport, *Water Res.* 25 (5) (1991) 499–528.
- [32] S. Gómez, G. Severino, L. Randazzo, G. Toraldo, J. Otero, Identification of the hydraulic conductivity using a global optimization method, *Agric. Water Manag.* 96 (3) (2009) 504–510.
- [33] P. Indelman, I. Touber-Yasur, B. Yaron, G. Dagan, Stochastic analysis of water flow and pesticides transport in a field experiment, *J. Contam. Hydrol.* 32 (1) (1998) 77–97.
- [34] G. Severino, P. Indelman, Analytical solutions for reactive transport under an infiltration–redistribution cycle, *J. Contam. Hydrol.* 70 (1) (2004) 89–115.
- [35] G. Severino, V. Monetti, A. Santini, G. Toraldo, Unsaturated transport with linear kinetic sorption under unsteady vertical flow, *Transp. Porous Media* 63 (1) (2006) 147–174.
- [36] V. Cvetkovic, G. Dagan, Transport of kinetically sorbing solute by steady random velocity in heterogeneous porous formations, *J. Fluid Mech.* 265 (1994) 189–215.
- [37] A. Fiori, A. Bellin, Non-ergodic transport of kinetically sorbing solutes, *J. Contam. Hydrol.* 40 (3) (1999) 201–219.
- [38] G. Dagan, Dispersion of a passive solute in non-ergodic transport by steady velocity fields in heterogeneous formations, *J. Fluid Mech.* 233 (1991) 197–210.
- [39] D. Ang, J. Lund, F. Stenger, Complex variable and regularization methods of inversion of the Laplace transform, *Math. Comput.* 53 (188) (1989) 589–608.
- [40] D. Russo, On the velocity covariance and transport modeling in heterogeneous anisotropic porous formations: 1. Saturated flow, *Water Resour. Res.* 31 (1) (1995) 129–137.
- [41] A.L. Noell, J.L. Thompson, M.Y. Corapcioglu, I.R. Triay, The role of silica colloids on facilitated cesium transport through glass bead columns and modeling, *J. Contam. Hydrol.* 31 (1) (1998) 23–56.
- [42] J.E. Saiers, G.M. Hornberger, The role of colloidal kaolinite in the transport of cesium through laboratory sand columns, *Water Resour. Res.* 32 (1) (1996) 33–41.
- [43] G. Severino, A. Santini, V.M. Monetti, Modelling water flow water flow and solute transport in heterogeneous unsaturated porous media, in: *Advances in Modeling Agricultural Systems*, Springer, 2009, pp. 361–383.
- [44] G. Severino, G. Dagan, C. van Duijn, A note on transport of a pulse of nonlinearly reactive solute in a heterogeneous formation, *Comput. Geosci.* 4 (3) (2000) 275–286.