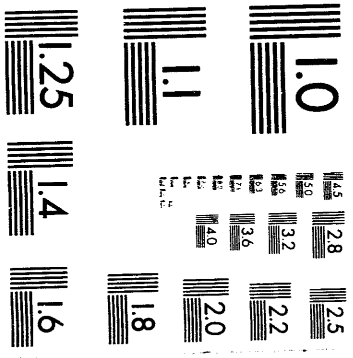
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TRANSPORT OF SORBING SOLUTES IN RANDOMLY HETEROGENEOUS FORMATIONS: SPATIAL MOMENTS, MACRODISPERSION, AND PARAMETER UNCERTAINTY

by

Roko Andricevic

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ABSTRACT

Expressions for the spatial moments and macrodispersion tensor for sorbing solutes in heterogeneous formations were presented using a probabilistic model of a fluid residence time coupled with the particle position analysis. The fluid residence time was defined as a fraction of the actual time during which the particle stayed in the mobile fluid phase of the aquifer. The fluid residence time is a random variable whose variability comes as a result of the non–equilibrium sorption properties. The sorbing solute was assumed to be governed with first–order linear kinetics. The closed–form expressions were based on the stationarity in the kinetic process and on the first–order approximation in the hydraulic conductivity field and in the fluid residence time. The non–equilibrium effects were presented as a function of the spatial variability in hydraulic conductivity and temporal variability in the fluid residence time. The importance of the non–equilibrium processes in the field scale was found to be dependent on reaction rates, retardation factor, mean velocity, and on variance and correlation scale of the hydraulic conductivity. The time needed to reach the asymptotic macrodispersivity is dependent on the degree of non–equilibrium processes and distribution coefficient. The impact from the uncertainty in parameters upon the spatial moments was examined and compared with the organic tracer used in the Borden field experiment.

INTRODUCTION

To accurately predict the movement of pollutants in natural formations is necessary to develop effective strategies for groundwater quality management and restoration programs. Solute transport by groundwater results from complex interactions between physical, chemical, and biological processes occurring in natural aquifers. A solute partitioning between solid and fluid phase, such as surface chemical reaction, is one of the most important processes influencing the fate of many pollutants. On a microscopic scale and in laboratory experiments, this sorption mechanism has been extensively studied and, although complex in nature, has been reasonably well understood for predictive purposes. The common approach in simulating the transport of reactive solutes is to consider either local equilibrium assumption (LEA) when reaction rates are much faster than the fluid flow rate, or first–order non–equilibrium models. The wide use of LEA models was prompted mainly because of significant mathematical simplifications, however, many researchers pointed out obvious limitations and studied important deviations of such an assumption (Valocchi, 1985, 1988; Bahr and Rubin, 1987; Bouchard et al., 1988; Roberts et al., 1986; Jennings and Kirkner, 1984; Brusseau et al., 1989). Non–equilibrium processes or rate–limited mechanisms have also been examined at the laboratory scale, focusing either on the chemical non–equilibrium (chemical kinetics) and/or physical or transport related non–equilibrium (van Genuchten and Wierenga, 1976; Nkedi–Kizza et al., 1984; Goltz and Roberts, 1986; Brusseau and Rao, 1989), which describes the physical resistance encountered by solute trying to reach the sorption sites of the porous medium as transported by groundwater. The occurrence of non–equilibrium processes of any origin may have significant impact on groundwater remediation efforts and on the risk assessment of radionuclide migration. The non–equilibrium process results in much longer time for aquifer restoration because of increased "tailing" (slow desorption) of the solute plume and the larger horizontal spreading may impact the prediction for the water supply protective area.

Studying reactive transport at the laboratory scale is usually restricted with the homogeneous soil and governing equations applicable for such porous media (e.g., the advection–dispersion equation with constant dispersivity). However, the major difficulty occurs when trying to extrapolate the findings from the laboratory scale to a field–scale problem. The field data analysis from the Borden aquifer revealed the difficulties in interpreting the reactive solute transport (Roberts et al., 1986; Curtis et al., 1986) which was attributed to the spatial variability of the porous media and non–equilibrium behavior. Valocchi (1989) applied the Aris method of spatial moment analysis (Aris, 1958) to the perfectly stratified aquifer and observed that LEA validity depends on the spatial variability of pore–water velocity, as well as the reaction rates.

It is now generally accepted that spatial variability in hydraulic properties of natural aquifers has a strong impact on the solute plume movement (e.g., Dagan, 1982, 1984; Gelhar and Axness, 1983). In addition, the sorption mechanism, regardless of its origin (chemical or physical), also affects the solute movement and may significantly alter the transport characteristics. It is, therefore, of great practical interest to understand the field–scale transport properties of the solute undergoing sorption in conjunction with the spatial variability of aquifer properties. Several numerical simulation experiments recently examined some impacts of the kinetically sorbing solutes on transport characteristics at large scale (Valocchi and Quinodoz, 1989, in a one–dimensional case; Andricevic and Foufoula–Georgiou, 1991, for stratified formations; and Selroos and Cvetkovic, 1992, for two–dimensional heterogeneous formations). The solute flux approach (which provides one–dimensional mass breakthrough curves by integrating over the plane perpendicular to the mean flow direction) coupled with kinetically sorbing solutes was employed by Cvetkovic and Shapiro (1990) for a saturated medium and by Destouni and Cvetkovic (1991) in an unsaturated medium. Sposito and Jury (1988) studied a movement of sorptive solutes using the concept of the lifetime probability density function in heterogeneous porous media and Chrysikopoulos et al. (1992) employed Taylor–Aris–Brenner moment analysis to derive the macrodispersion tensor for solute transport with spatially periodic retardation factor and velocity field.

The main focus of this paper is on the solute particle displacement moments and macrodispersive characteristics for kinetically sorbing solutes in a heterogeneous porous formation and large–scale problems. The probabilistic model is presented and coupled with the Lagrangian description of the particle displacement to obtain closed–form expressions of the first two spatial moments. The uncertainty in the reaction parameter estimates is considered and its impact on the spatial moments is investigated. The presented results assume (but are not limited to) the uniform mean flow, isotropic heterogeneity of the aquifer, and first–order approximation in hydraulic conductivity variance. The non–equilibrium effects are presented as a function of the spatial variability in hydraulic conductivity and temporal variability in the fluid residence time. The LEA validity for the field–scale problems is analyzed and a non–equilibrium index is introduced which can be seen as a field–scale version of the Damkohler number. The importance of the non–equilibrium processes in the field scale is found to be dependent on reaction rates, retardation factor, mean velocity, and on variance and correlation scale of the hydraulic conductivity. The presented approach is also applicable in the case of transport related nonequilibrium processes if they can be approximated by first–order kinetics.

BASIC TRANSPORT FORMULATION

We assume that the solute undergoes transport by convection by steady groundwater velocity, by dispersion, and by non–equilibrium sorption described with the first–order reversible linear kinetics, i.e., $c(\mathbf{x},t)$; the volumetric concentration (species mass/fluid volume) satisfies the macroscopic mass balance equation

$$\frac{\partial(\theta c)}{\partial t} + \mathbf{V} \cdot \nabla(\theta c) = \nabla \cdot \left[\mathbf{D}_d \nabla(\theta c)\right] - \frac{\partial(\varrho s)}{\partial t} \tag{1}$$

$$\frac{\partial(\varrho s)}{\partial t} = k_1(\theta c) - k_2(\varrho s) = k_2\left[k_d(\varrho c) - (\varrho s)\right] \tag{2}$$

where s is the adsorbed species concentration (species mass/solid mass); ϱ is the bulk density (solid mass/aquifer volume); θ is the porosity (fluid volume/aquifer volume); $\mathbf{D}_d$ is a hydrodynamic dispersion tensor (each entry has units L^2/T); k_1 is the forward rate coefficient (T^{-1}); k_2 is the reverse rate coefficient (T^{-1}); k_d is the equilibrium distribution coefficient (fluid volume/solid mass); $\mathbf{V}(\mathbf{x}) = (K/\theta)\nabla h$ is Eulerian seepage velocity (L/T) in space coordinate $\mathbf{x}$; K is the hydraulic conductivity; and h is the hydraulic head. Note that parameters ϱ and θ are introduced in (1) by passing from the mass balance equation at the microscopic scale to the one at the macroscopic scale by performing either spatial averaging (e.g., over the representative elementary volume (rev) (Bear, 1979)) or ensemble averaging over the number of realizations of the porous media. A common approach is to consider the spatial variability in the hydraulic conductivity as a dominant aquifer spatial variability, and to assume ϱ and θ to be constant in (1). Dividing, then, (2) with θ and assigning $S = \varrho s/\theta$ as a transformed adsorbed phase concentration with same units as c, the first–order linear rate reduces to (Valocchi, 1989)

$$\frac{\partial S}{\partial t} = k_1 c - k_2 S = k_2(K_d c - S) \tag{3}$$

where $K_d = (\varrho k_d/\theta) = k_1/k_2$ is the dimensionless equilibrium distribution coefficient. Although simple, with respect to the complex chemical and physical reactions occurring at the solid–fluid interface, the first–order linear rate expression in (2) and (3) is a reasonably accurate approximation of the more complex non–equilibrium models based on diffusive transport between mobile and stagnant fluid zones (Nkedi–Kizza et al., 1984; van Genuchten, 1985; Parker and Valocchi, 1986). The rate law (3) approaches the local equilibrium condition with the linear adsorption isotherm, $S = K_d c$, when the reaction rates, k_1 and k_2, approach infinity at constant K_d (Jennings and Kirkner, 1984). In this case, the reaction rates are fast relative to the rate of concentration changes resulting from the transport mechanism (convection and dispersion). Then, the LEA can be used to solve (1), yielding essentially the same formulation as in the non–reactive case with velocity (or time) scaled by retardation coefficient $R = 1 + K_d$. The simplicity of this formulation attracted many researchers to widely use the LEA for modeling sorptive solute. Since the LEA is an approximation, its use may easily result in erroneous prediction of the plume movement having serious consequences, particularly in the aquifer remediation programs. The usual concern about validity of the local equilibrium comes from the fact that under conditions of steady or transient groundwater flow and estimated actual speed of chemical reactions for given solute, the contact time available to achieve sorption equilibrium may be insufficient. The other reason to cast doubt on the validity of the LEA, particularly in the field–scale problems, is a fact that after averaging over space or over an ensemble of realizations, the macroscopic mass balance equations (1) under LEA assume that the rate of concentration changes due to reactions is fast (instantaneous) over the entire averaging volume, i.e., the LEA implies its validity over the entire size of REV. Although frequently overlooked, this condition is seldom satisfied in modeling field–scale transport problems.

The occurrence of non–equilibrium processes may have significant impact on delineating groundwater contamination and aquifer remediation efforts. For example, during the pump–and–treat activity, the induced flow field may easily cause nonequilibrium processes to become significant, resulting in much longer time for aquifer restoration due to the increased "tailing" (slow desorption) of the solute plume. Determining the impact of non–equilibrium sorption on the solute transport in two– and three–dimensional heterogeneous aquifers is the main goal of the present study.

A common approach for solving (1) and (2) is to follow the Eulerian framework, which considers c as a dependent variable in a mass balance equation. Along these lines, several techniques have been applied: analytical solutions for homogeneous aquifers using suitable transformations (van Genutchen and Wierrenga, 1976; Cameron and Klute, 1977; van Genutchen, 1981; Rao and Jessup, 1983; Valocchi, 1985; Goltz and Roberts, 1986; among others); Taylor–Aris method of moments for evaluating temporal and spatial moments of the fluid–phase concentration (Sudicky, 1983 and Guven et al., 1984, for non–reactive solute; Goltz and Roberts, 1987, for homogeneous aquifer and non–equilibrium models; Valocchi, 1988, 1989, for kinetically sorbing solutes in idealized stratified systems; and Chrysikopoulos et al., 1992, for spatially periodic retardation factor and velocity field, solute flux approach (Cvetkovic and Shapiro, 1990, for saturated porous media; and Destouni and Cvetkovic, 1991, for unsaturated porous media); and numerical solutions, which usually involve integrating the chemical reaction rate over the transport time scale (Ahlstrom et al., 1977; Jennings and Kirkner, 1984; Bahr and Rubin, 1987; Brusseau et al., 1989; Valocchi and Quinodoz, 1989; Andricevic and Foufoula–Georgiou, 1991; Selroos and Cvetkovic, 1992).

In the Lagrangian framework, the equivalent of integration over time for solving (2) is the estimation of the particle residence time, t_*, in the fluid phase. A solute particle is transported by groundwater only while residing in the mobile fluid phase of the porous media. Thus, the determination of the particle fluid residence time as a fraction of the actual time is crucial to accurately predicting the solute movement. Both physical and chemical non–equilibrium processes occurring in the porous medium will directly affect the particle fluid residence time and therefore will make direct impact on the spreading of the solute plume. In this paper, the fluid residence time of the solute particle will be described with a probabilistic model and defined as a random variable which depends on reactive parameters.

In heterogeneous aquifers, the velocity field is uncertain and spatially variable resulting from the uncertainty in the transport mechanism (estimation of parameters characterizing flow and location of boundaries) and spatial variability of the aquifer properties (permeability, porosity). Therefore, the Lagrangian approach for transport of sorbing solutes in heterogeneous aquifers can be described with the motion of the indivisible solute particle in the velocity field during the random fluid residence time, t_*, that a particle stays in the velocity field. In other words, the transport of kinetically sorbing solutes is affected by spatial variability of the velocity field and temporal variability of the fluid residence time. Spatial variability comes as a result of tortuous pathways in heterogeneous formations, while temporal variability results from non–equilibrium processes. We focus on the steady state velocity field $\mathbf{V(x)}$, in the space coordinate $\mathbf{x}$, which satisfies Darcy's law, together with continuity equation $\nabla \cdot \mathbf{V} = 0$, and possess a statistical homogeneity which results in decomposing $\mathbf{V(x)} = \langle \mathbf{V(x)} \rangle + \mathrm{v}(\mathbf{x})$, where $\langle \mathbf{V(x)} \rangle = \mathbf{U}$ denotes the ensemble average vector of the velocity field and $\mathrm{v}(\mathbf{x})$ is a random fluctuation with zero mean and covariance matrix $R_v(x_i - x_j)$, depending only on the separation between two points. Following the Lagrangian formulation for the non–reactive solute (Dagan, 1982, 1984, 1987), the random displacement vector $X(t)$ of the kinetically sorbing solutes can be expressed with a modified kinematic relation

$$X(t) \;=\; \int_0^{t_*} V[X(\tau_*)]d\tau_* + X_d \;=\; \mathbf{U}t_* + \int_0^{t_*} v[X(\tau_*)]d\tau_* + X_d \qquad t_* \le t \tag{4}$$

where $X(t)$ is a three–dimensional displacement vector, X_d is the pore–scale dispersion (molecular diffusion is neglected), and τ_* is the integration variable going from 0 to t_* where $t_* \le t$. Thus, the right–hand side of (4) is expressed in the new time variable t_* which is a fraction of the actual time t. Since the particle is sorbing with the soil, the random fluid residence time appears as an upper limit in the integration of the velocity field. In (4), the particle random displacement is initially for $t = 0$ at $X(0) = 0$ and it is permanently transported by the random velocity field. The difficulties and possible approximative solution of the kinematic relation for the non–reactive case (4) replacing t_* with t) was extensively discussed by Dagan (1989). In the case of kinetically sorbing solute, the additional random variable t_* appears in the kinematic relation.

We start our solution process with formal first–order approximation of the Lagrangian displacement by expanding the right–hand side of (4) in the Taylor series up to the first order around the ensemble mean fluid residence time, $\langle t_*(t)\rangle$, and the ensemble mean displacement, $\langle X(t)\rangle$, and by neglecting the pore scale dispersion; this yields

$$\begin{aligned} X(t) &= \mathrm{U}t_* + \int_0^{t_*} v[X(\tau_*)]d\tau_* \cong \mathrm{U}\langle t_*\rangle + \int_0^{\langle t_*\rangle} v\left[\langle X(\tau_*)\rangle\right]d\tau_* + \\ &+ t_*'\nabla_{\tau_*}\cdot\left.\left\{\mathrm{U}t_* + \int_0^{t_*} v[X(\tau_*)]d\tau_*\right\}\right|_{\substack{t_*=\langle t_*\rangle \\ X(t)=\langle X(t)\rangle}} + \\ &+ X'(t)\nabla_X\cdot\left.\left\{\mathrm{U}t_* + \int_0^{t_*} v[X(\tau_*)]d\tau_*\right\}\right|_{\substack{t_*=\langle t_*\rangle \\ X(t)=\langle X(t)\rangle}} + \ldots \end{aligned} \qquad (5)$$

where $t_*' = t_* - \langle t_*\rangle$ denotes the fluctuations around the mean residence time, $X'(t)$ is the residual displacement, and ∇_{τ_*} and ∇_X denote the gradient of (4) with respect to the fluid residence time and particle displacement, respectively. The neglect of the pore–scale dispersion coefficient compared to other terms in (4) implies that the case with large Peclet numbers is considered. Neuman et al. (1987) have considered other cases with small Peclet numbers, but these special cases are not considered here.

After taking differentiation, t_* and X(t) are replaced with corresponding mean values such that the first displacement moment, $\langle X(t)\rangle = \mathrm{U}\langle t_*\rangle$, is obtained by taking the ensemble average of (5) and assuming the independence between the random velocity field and fluid residence time. Keeping only first–order terms, the displacement residual is, then, given with

$$X'(t) \simeq X(t) - \langle X(t) \rangle \simeq \int_{0}^{\langle t_* \rangle} v[U\tau_*] d\tau_* + Ut'_* \tag{6}$$

The second moment of the particle displacement follows by taking the ensemble average of $X'(X')^T$

$$\begin{aligned} X_{ij}(t) &= \langle X'(X')^T \rangle = \langle (X(t) - \langle X(t) \rangle)(X(t) - \langle X(t) \rangle)^T \rangle \\ &= 2 \int_{0}^{\langle t_* \rangle} \left[\langle t_* \rangle - \tau_* \right] R_v[\mathrm{U}\tau_*] d\tau_* + \mathrm{U}\sigma^2_{t_*}(t)\mathrm{U}^T \end{aligned} \tag{7}$$

where $R_v[\mathrm{U}\tau_*]$ is the covariance matrix of the velocity field for two points separated by the displacement $\mathrm{U}\tau_*$, where τ_* is the integration variable going from 0 to $\langle t_* \rangle$. The first term in (7) is the first–order estimate of the displacement covariance evaluated at the first moment of the fluid residence time. The second term represents the contribution coming from the kinetically sorbing activity of the particle which follows the first–order reaction rate given in (2). These two terms combined are the main reason for the additional spreading which occurs in the case of the kinetically sorbing solutes. The magnitude of the variance $\sigma^2_{t_*}$, relative to the first term in (7), will determine the importance of the kinetics process over the local equilibrium condition.

To evaluate (7), the first two moments of the fluid residence time have to be derived. In the next section, we present a probabilistic model used to evaluate the first two moments of the fluid residence time.

PROBABILISTIC MODEL FOR KINETICALLY SORBING SOLUTES

In this section, the probabilistic model for kinetically sorbing solutes applicable for two– or three–dimensional flow in heterogeneous formations is presented. Coupled with Lagrangian formulation of the transport, this approach provides a way to evaluate the particle displacement moments for kinetically sorbing solutes.

Let Z_t denote the binary (indicator) process defined as follows:

$$Z_t = \begin{cases} 0 & \text{particle attached to the solid matrix} \\ 1 & \text{particle travels with the fluid} \end{cases} \tag{8}$$

where $t > 0$ and Z_t will be modeled as a time–homogeneous stochastic process. Specifically, Z_t is a two–state Markov process with state 1 indicating the particle is in the fluid phase and state

0 that it is in the solid phase. Vallochi and Quinodoz (1989) in their numerical simulation study employed the two–state continuous Markov chain to generate the fraction of time step Δt from the four conditional probability distributions (see also Keller and Giddings, 1960). The extension of their work is reported by Andricevic and Foufoula–Georgiou (1991), who employed the two–state Markov chain as a subclass of a more general birth and death process which may be used for multi–component solute transport and modeling bioremediation activity. Recently, Selroos and Cvetkovic (1992) employed the solute flux approach with particle tracking technique to simulate breakthrough curves for kinetically sorbing solutes. In contrast to above numerical studies, we present a closed–form derivation of the first two moments of the fluid residence time distribution for any time instant t, $t > 0$ as a direct function of reaction rates. This will allow the derivation of the first two moments of the particle displacement undergoing the non–equilibrium sorption described with linear kinetics.

During each "visit," a particle stays in the fluid or solid phase an amount of time, ω, which is exponentially distributed as

$$f_i(\omega_i) = k_i \exp(-k_i \omega_i), \omega_i > 0; i = 0,1 \tag{9}$$

where k_i denotes the reaction parameters as given in (2). The probabilistic description of this two–state process is given by the following Kolmogorov differential equation

$$dP_{i,j}/dt = \lambda_{j-1} P_{i,j-1}(t) + \mu_{j+1} P_{i,j+1}(t) - (\lambda_j + \mu_j) P_{i,j}(t) \tag{10}$$

where $i = 0,1$ and $j = 0,1$ are the states of the process and $P_{i,j}(t)$ denotes the transition probability that process is at state i at time t, given that it was at state j at $t = 0$. For the two–state chemical process as described in (2), the parameters are $\lambda_1 = k_1$, $\lambda_o = 0$, $\mu_1 = 0$, and $\mu_o = k_2$. With this parameter description, the above Kolmogorov equations can be easily solved (see Ross, 1985) yielding the transition probability matrix **P** whose elements are:

$$P_{00}(t) = \frac{k_1}{k_1 + k_2} + \frac{k_2}{k_1 + k_2} \exp[-(k_1 + k_2)t] = \frac{1}{R}[K_d + \exp(-Rk_2 t)] \tag{11}$$

$$P_{11}(t) = \frac{k_2}{k_1 + k_2} + \frac{k_1}{k_1 + k_2} \exp[-(k_1 + k_2)t] = \frac{1}{R}[1 + K_d \exp(-Rk_2 t)] \tag{12}$$

$$P_{01}(t) = \frac{k_2}{k_1 + k_2}\left[1 - \exp[(k_1 + k_2)t]\right] = \frac{1}{R}[1 - \exp(-Rk_2 t)] \tag{13}$$

$$P_{10}(t) = \frac{k_1}{k_1 + k_2}\left[1 - \exp[-(k_1 + k_2)t]\right] = \frac{K_d}{R}[1 - \exp(-Rk_2 t)] \tag{14}$$

The above transition probabilities represent the probability of transitions across the solid–surface interface and it is of interest to analyze their temporal behavior. It has been shown that after the solute particle has been introduced in the porous formation with availability of exchange sites, the relaxation time for the first attachment of the adsorbate molecules on the solid interface is of the order between 10 and 100μsec (e.g., Ruzic, 1987). This results in reaching the stationary transition probabilities quickly, particularly in the field–scale transport problems. Mathematically, this can be written that after enough transitions across the solid–fluid interface, the following limiting probabilities are reached

$$P_{00}(t) \rightarrow P_{10}(t) \rightarrow p_0 \rightarrow \frac{k_1}{k_1 + k_2} = \frac{K_d}{R} \quad k_2 t > 2 \tag{15}$$

$$P_{11}(t) \rightarrow P_{01}(t) \rightarrow p_1 \rightarrow \frac{k_2}{k_1 + k_2} = \frac{1}{R} \quad k_2 t > 2 \tag{16}$$

where p_0 and p_1 are the elements of the stationary probability row vector $\tilde{\mathbf{p}}$ of unconditional probabilities of the particle being in fluid and solid phase, respectively. It can be easily shown using (11)–(14), (15), and (16) that the stationary vector $\tilde{\mathbf{p}}$ has the unique and non–negative solution of the form:

$$\tilde{\mathbf{p}}\mathbf{P} = \tilde{\mathbf{p}}\left[p_0 P_{00} + p_1 P_{10} \quad ; \quad p_0 P_{01} + p_1 P_{11}\right] \tag{17}$$

Differentiating the first element of the row vector $\tilde{\mathbf{p}}$ from the above and using (10) yields

$$\frac{\partial p_0}{\partial t} = k_1 p_1 - k_2 p_0 \tag{18}$$

which demonstrates the full analogy (3) if unconditional probabilities p_0 and p_1 are substituted for the S and c, respectively. Note that the above stationary probabilities, in the field–scale transport problems of the kinetically sorbing solutes, are reached rather quickly. In the probabilistic terminology it means that the process is of very short memory and the initial state (e.g., when and how is the solute introduced in the aquifer) of the sorbing particle quickly becomes irrelevant. Figure 1 shows the necessary time for attaining the limiting probability for three different K_d values as a function of the wide range of the dimensionless time $k_2 t$. It is clear from Figure 1 that for all practical purposes the dimensionless time $k_2 t > 2$ will guarantee near limiting probabilities. The stationarity of transition probabilities is reached even sooner for $K_d > 2$. Furthermore, since the focus of this study is on the large–scale transport in the natural formation, the limiting probability and stationarity condition for the kinetic process almost always prevails. This results from the fact that the time scale of the kinetic process is several orders of magnitude smaller than the time scale of the regional transport problems. Andricevic

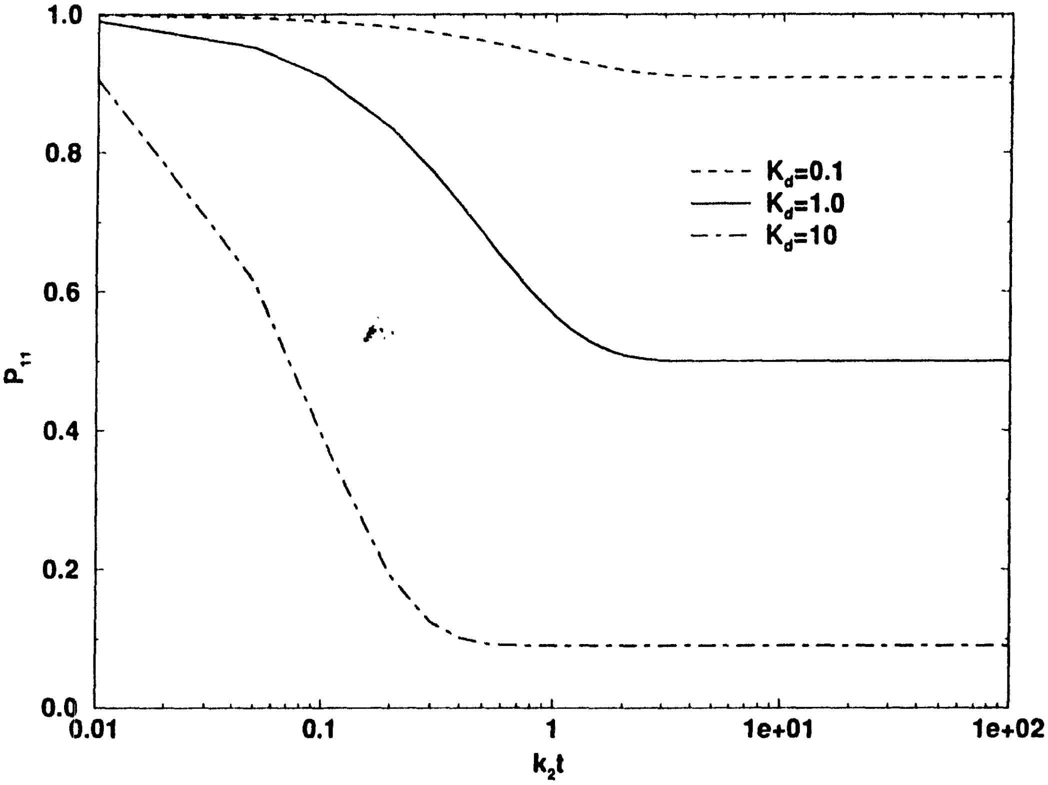


Figure 1. Temporal behavior of the transition probability P_{11}.

and Foufoula–Georgiou (1991) defined the counting process $N(t)$ of transitions across the solid–fluid interface, as an indicator of the speed of the kinetic process with the expected value $\langle N(t) \rangle$ equal to $k_2 K_d t/R$. They demonstrated through numerical experiments that the limiting probability of the kinetic process is reached after only several transitions (e.g., 3–4), and in the natural aquifers this happens on the time scale much smaller than the transport time scale of interest (e.g., for relatively slow rate $k_2 = 0.01(hr^{-1})$, it is easy to demonstrate that a single sorbing particle introduced into the groundwater at time $t = 0$ will reach $k_2 t > 2$ in 9 days, which in terms of the field–scale transport may still be considered as a short transport travel time; in practice, the plume often has not yet been discovered).

Besides its direct applicability in the field–scale transport problems in the stationary form, (18) can be also used for studying the small–scale or laboratory experiments. However, in that case, the unconditional probabilities p_0 and p_1 are time dependent and should be evaluated through propagation in time by knowing initial conditions, i.e., when and how the sorbing solute was introduced into the porous medium. These type of problems (e.g., laboratory column experiments and small-scale field tracer tests) are not considered in this study.

If the interesting increment of time extends from 0 to t, we define the fluid residence time (traveling with the fluid) $t_*(t)$ as

$$t_*(t) = \int_{t=0}^{t} Z_\tau d\tau \tag{19}$$

where the Z_t is a binary process as defined in (8). The expected value, $\langle t_*(t) \rangle$ can be obtained by taking the expected value of (19)

$$\langle t_*(t) \rangle = \int_{t=0}^{t} \langle Z_\tau \rangle d\tau \tag{20}$$

Since Z_t is a binary process

$$\langle t_*(t) \rangle = \int_{t=0}^{t} Prob[Z_\tau = 1] d\tau = \int_{t=0}^{t} p_1 d\tau = \frac{k_2}{k_1 + k_2} t = \frac{1}{R} t \tag{21}$$

where $R = 1 + K_d$ is the retardation factor. Therefore, after the stationarity is reached, the mean displacement is linearly related to the time with slope of R^{-1}. However, before the stationarity is reached, the mean displacement is nonlinearly related to time and reaction parameters (Quinodoz and Valocchi, manuscript submitted 1992), since the evaluation of $Prob[Z_t = 1]$ involves the transition probabilities. This early time-scale characteristic of the kinetic process may be important in the laboratory column experiments and in some small-scale field tests, but its impact on the regional transport characteristics and macrodispersion is becoming negligible when the stationarity prevails. Thus, using (21), the first term in (7) represents the displacement second moment of the sorbing solute particle satisfying the local equilibrium condition.

The second moment of the fluid residence time is of particular interest to this study because it is precisely this variability that causes the increased spreading and tailing of the contaminant plume. Applying the variance operator to both sides of (19) yields

$$Var[t_*(t)] = \sigma^2_{t_*}(t) = \int_{\tau=0}^{t} \int_{\tau'=0}^{t} Cov[Z_\tau, Z_{\tau'}]d\tau d\tau' \tag{22}$$

where *Cov* denotes the auto–covariance of the binary process Z_t. The above expression is evaluated in the Appendix and takes the final form

$$\begin{aligned} \sigma^2_{t_*}(t) &= \frac{2k_2k_1}{(k_1+k_2)^4}\left[(k_1+k_2)t - 1 + \exp[-(k_1+k_2)t]\right] \\ &= \frac{2K_d}{R^3k_2}\left[t - \frac{1}{Rk_2}[1 - \exp(-Rk_2t)]\right] \end{aligned} \tag{23}$$

The variance of t_* shows the symmetry of k_1 and k_2. This implies that the $Var[t_*(t)]$ is equal to $Var[t - t_*(t)]$. In other words, we can state that regardless of the magnitude of reaction rates, the variability about the mean time spent in the fluid or solid phase is the same.

It is always of interest to examine the $Var[t_*(t)]$ for small– and long–time limit. Consider first the behavior for the small–time limit. Expanding the exponential in (23) about $t = 0$ up to the second order yields

$$\begin{aligned} Var[t_*(t)] &\rightarrow \frac{2k_1k_2}{(k_1+k_2)^4}\left[(k_1+k_2)t - 1 + 1 - (k_1+k_2)t + \frac{1}{2}(k_1+k_2)^2t^2\right] \\ &= \frac{k_1k_2}{(k_1+k_2)^2}t^2 = \frac{K_d}{R^2}t^2 \end{aligned} \tag{24}$$

indicating that the standard deviation of the small–time limits of the residence time is proportional to the time.

The long–time behavior is more interesting, particularly when travel time distribution analysis is needed for the environmental regulatory standards. Taking the limit in (23), the exponential term and singleton 1 are rendered insignificant, yielding

$$Var[t_*(t)] \rightarrow \frac{2k_1k_2}{(k_1+k_2)^3}t = \frac{2K_d}{R^3k_2}t \tag{25}$$

The standard diviation of the residence time for the long–time limit seems to obey a $t^{1/2}$ law, similar to that of the Brownian motion. In Figure 2, the first two moments of the residence time distribution and the coefficient of variation (CV) are plotted in the dimensionless form for $K_d = 0.1$ (Figure 2a), $K_d = 1.0$ (Figure 2b), and $K_d = 10$ (Figure 2c). The mean residence time

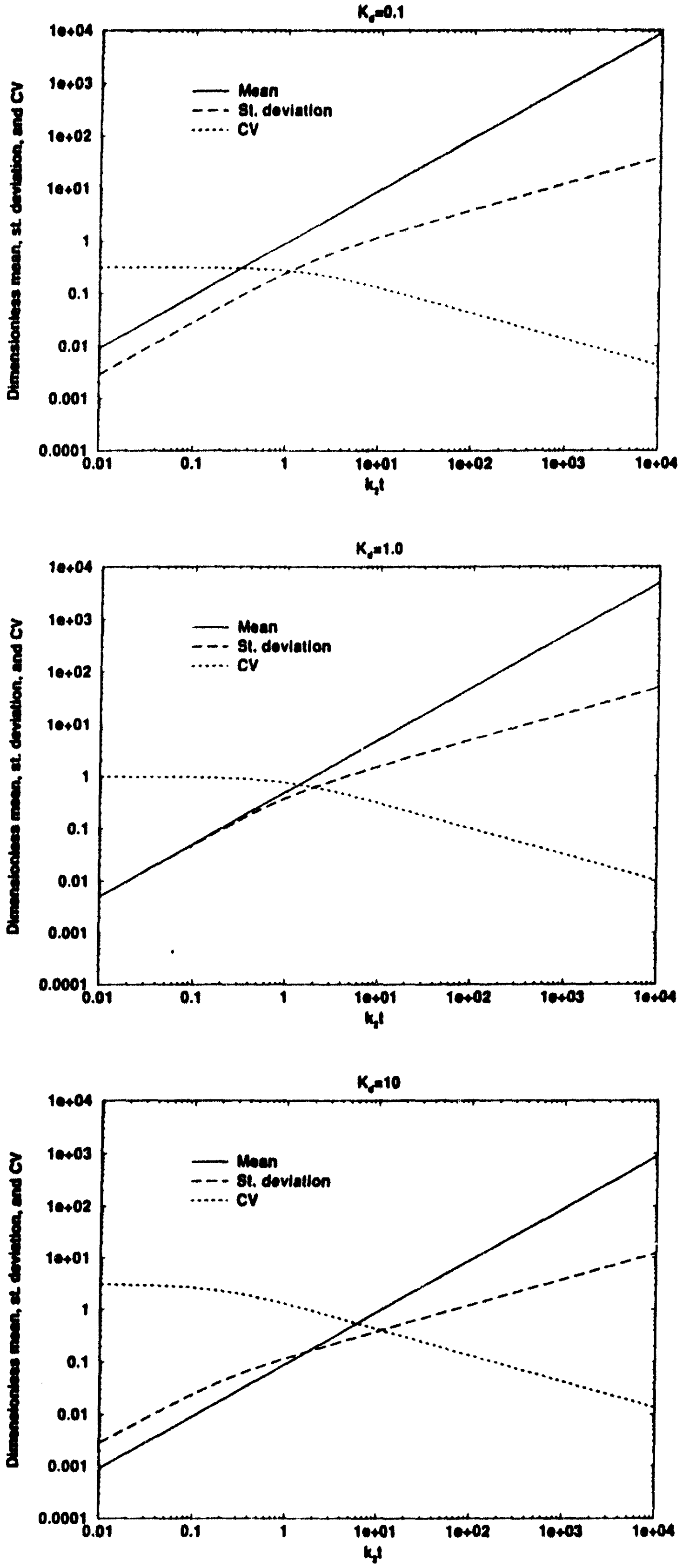


Figure 2. Dimensionless mean ($\langle t_* \rangle k_2$), standard deviation ($\sigma_{t_*} k_2$) and coefficient of variation (CV=($\langle t_* \rangle k_2/\sigma_{t_*} k_2$) of the fluid residence time distribution; (a) K_d=0.1; (b) K_d=1.0; (c) K_d=10.

is normalized with $\langle t_*\rangle k_2$ such that it is represented with a straight line of the slope equal to $1/R$. The standard deviation of the fluid residence time is normalized with $\sigma_{t_*} k_2$, and for large values of the argument $k_2 t$ shows a growth proportional to $\sqrt{t}$, while close to zero it behaves proportional to t. It is interesting to note that a point when σ_{t_*} begins to grow proportional to $\sqrt{t}$ (like Brownian process) is around $k_2 t > 2$, which corresponds, as we have seen from Figure 1, to a point when limiting probabilities are reached. The CV of the random process $t_*(t)$ maintains approximately a constant value of $\lim_{t\to\infty} CV = \sqrt{K_d}$ for $k_2 t > 2$, and decays proportional to $\sqrt{t^{-1}}\left(\lim_{t\to\infty} CV = \sqrt{2K_d/Rk_2}\sqrt{t^{-1}}\right)$ for $k_2 t > 2$. Figure 2 also indicates that the random process $t_*(t)$ is underdispersed (e.g., more regular process) after limiting probabilities are reached.

LONGITUDINAL PLUME SPREADING

The expression for the second moment of the particle displacement (7) shows that the variance of the fluid residence time $\sigma_{t_*}^2$ is a driving force for the plume increased spreading resulting from non–equilibrium processes. In fact, by allowing $\sigma_{t_*}^2$ to approach zero, (7) approaches the solution for the second moment of the particle displacement satisfying LEA. Analyzing the long–time limits of the fluid residence time variance, it can be shown that the $\sigma_{t_*}^2$ will go to zero only when k_2 becomes very large (keeping K_d constant)

$$\lim_{k_2\to\infty}\left[\lim_{t\to\infty}\sigma_{t_*}^2\right] = \lim_{k_2\to\infty}\left[\frac{2K_d}{R^3 k_2}t\right] = 0 \tag{26}$$

In the case for $k_2 < \infty$ with large travel time, the residence time variance approaches (25), which exhibits the linear growth of the residence time second moment.

Therefore, the spatial distribution of the kinetically sorbing particle at the field scale is affected by two major mechanisms. One is the non–equilibrium sorption process which results from the variability in fluid residence time and the other is the spreading caused mainly by the spatial variability of the velocity field, which in turn is caused by the spatial variability of the hydraulic conductivity in the three–dimensional space. If the formation hydraulic conductivity can be characterized following a log–normal distribution, $Y = \ln K$, with constant mean and its stationary isotropic covariance function of the exponential form.

$$C_Y(i,j) = \sigma_n^2[1 - H(r)] + \sigma_Y^2\exp\left(-r^2/\lambda^2\right) \tag{27}$$

where σ_n^2 represents the small–scale variability (the nugget effect), H is the Heaviside step function, σ_Y^2 is the variance attributable to the spatial separation, λ is the integral scale of the hydraulic conductivity. Although this representation neglects the aquifer anisotropy, for the sake of simplicity and illustration purposes, we shall adopt in this study the isotropic type of the exponential correlation in (27).

After mean displacement, $\langle \mathbf{X}(t) \rangle = \mathbf{U}\langle t_* \rangle$, the other most informative characteristic of the transport of the kinetically sorbing particle is the second moment given in (7). Using the fluid residence time variance (23), horizontal flow $\mathbf{U}(U,0,0)$, and derivation for the first term in (7) obtained by Dagan (1989, p. 315) modified by considering (21), we obtain the closed–form solution of the dimensionless displacement second moment for kinetically sorbing solutes in a three–dimensional heterogeneous aquifer:

$$X_{11}^*(t') = \frac{X_{11}(t)}{\lambda^2} = \frac{2K_d}{R^3}\left[\frac{t'}{\omega} - \frac{1}{R(\omega)^2}[1 - \exp(-Rt'\omega)]\right] \\ + \sigma_Y^2\left[2\frac{t'}{R} - 2\left[\frac{8}{3} - \frac{4R}{t'} + \frac{8R^3}{t'^3} - \frac{8R^2}{t'^2}\left(1 + \frac{R}{t'}\right)\exp(-t'/R)\right]\right] \tag{28}$$

and for the two–dimensional isotropic transport in the horizontal plane

$$X_{11}^*(t') = \frac{X_{11}(t)}{\lambda^2} = \frac{2K_d}{R^3}\left[\frac{t'}{\omega} - \frac{1}{R(\omega)^2}[1 - \exp(-Rt'\omega)]\right] \\ + \sigma_Y^2\left[2\frac{t'}{R} + \frac{3}{2} - 3\left[Ei\left(-\frac{t'}{R}\right) - \ln\left(\frac{t'}{R}\right) - E\right] + 3\frac{\exp\left(\frac{t'}{R}\right)\left(1 + \frac{t'}{R}\right) - 1}{\left(\frac{t'}{R}\right)^2}\right] \tag{29}$$

where Ei denotes the exponential integral, $E = 0.577..$ is the Euler number, and dimensionless variables t' and ω are

$$t' = \frac{tU}{\lambda} \; ; \qquad \omega = k_2\frac{\lambda}{U} \tag{30}$$

where ω is an index for the non–equilibrium sorption. The magnitude of this index determines the importance of non–equilibrium over the LEA solution. Note that ω depends not only on the desorption rate coefficient k_2 but also on the mean heterogeneity scale residence time ($t_\lambda = \lambda/U$), such that it can be seen as a field–scale version of a Damkohler number, which is here determined by the ratio of the heterogeneity scale residence time to the reaction time and, as such, characterizes the degree of non–equilibrium in heterogeneous formations. The mean residence time of the heterogeneity scale can be explained as a time the solute particle needs for traveling one aquifer heterogeneity correlation scale (correlation scale of the *lnK* field). Damkohler numbers have been used in the past extensively to evaluate LEA validity criteria (Rao and Jessup, 1983; Jennings and Kirkner, 1984; Valocchi, 1985; Bahr and Rubin, 1987; Brusseau et al., 1989). All of these studies were concentrated on one–dimensional homogeneous systems and/or laboratory column experiments which can be described by the advection–dispersion equation (ADE) with constant dispersivity. As a direct consequence, in those studies, the Damkohler number indicated that far from the source the non–equilibrium effects are lost and transport approaches LEA solution. For field–scale applications, the ADE with constant dispersivity is not an appropriate model unless the domain size is not sufficiently large compared to the heterogeneity integral scale. In the present study, the development leading to ω in (30) captures the three–dimensional field–scale behavior of sorbing solutes in a spatially variable flow field.

Figure 3 represents the dependence of the three–dimensional X^*_{11} and t' for a range of values of the non–equilibrium index ($\omega = 0.1 - 10$), with the LEA solution and the non–reactive case also presented for a comparison. Notice that the non–reactive case is reached when k_2 and K_d go to zero in (28) and (29). Figure 3a displays the case for $K_d = 0.1$, Figure 3b the case for $K_d = 1$, and Figure 3c the case for $K_d = 4$. In all three cases there is clear additional spreading as a result of non–equilibrium sorption. As expected, by increasing ω, the longitudinal spreading approaches the LEA solution and asymptotically (28) and (29) equals the LEA when $\omega \rightarrow \infty$. However, for all practical purposes, the longitudinal spreading for $\omega > 10$ closely follows the LEA solution, and may be considered as a point when non–equilibrium effects are unimportant in the direction of the mean flow. This criterion is in general agreement with the previous studies of one–dimensional homogeneous systems reported by Rao and Jessup (1983), Jennings and Kirkner (1984), Valocchi (1985), Bahr and Rubin (1987) and Brusseau et al. (1989). The important difference is, however, that the field–scale Damkohler number ω is now obtained as a function of the correlation scale of the *lnK* field. The consequence of this formulation is that the increased spreading of the kinetically sorbing solutes is continuously present for large travel times. Thus, the non–equilibrium sorption in longitudinal direction depends on the heterogeneity scale of the natural aquifer formation such that the larger the *lnK* correlation scale, the smaller the influence from the kinetically sorbing solutes. The accurate estimation of the *lnK* correlation scale in the field–scale transport studies is of major importance not only from the point of modeling convection and dispersion, but also from the point of assessing the importance of non–equilibrium processes. The choice of problem dimensionality may have strong

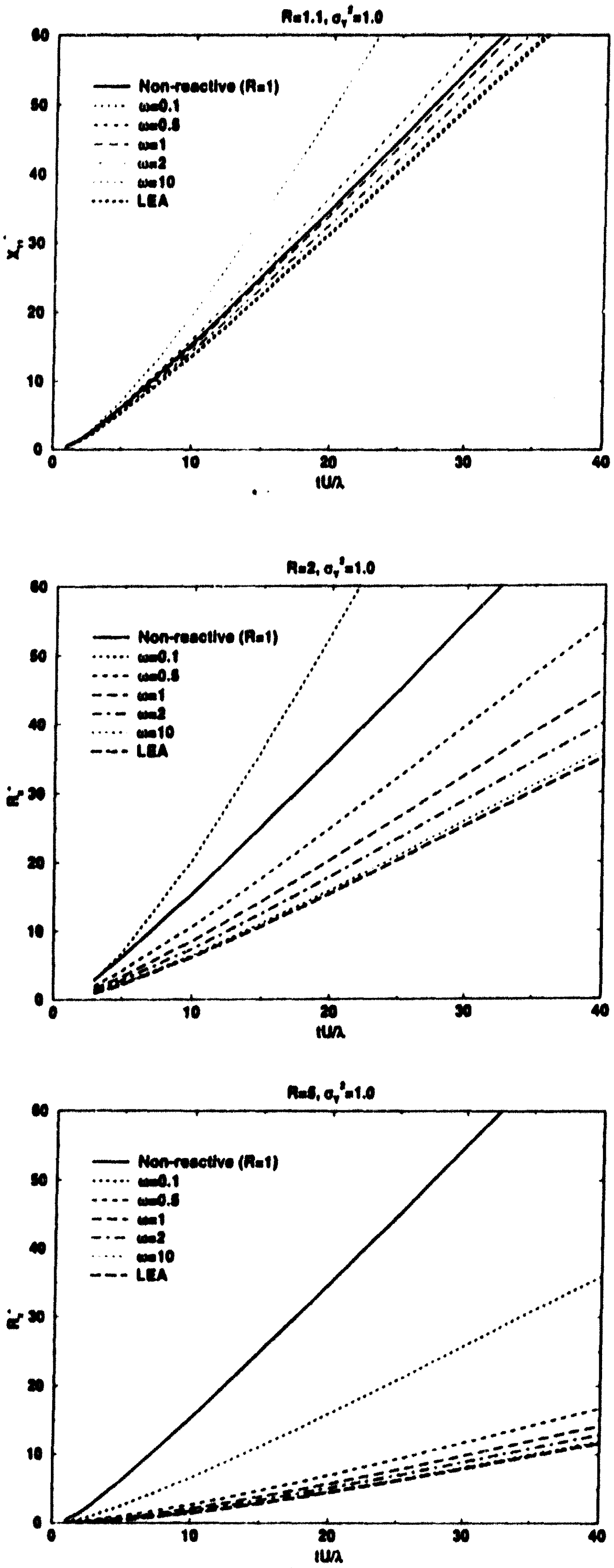


Figure 3. Longitudinal displacement variance X^*_{11}; (a) K_d=0.1; (b) K_d=1.0; (c) K_d=4.

implications on the importance of non–equilibrium effects. If the field–scale problem has domain size of the order of the aquifer depth in the vertical direction and of the similar size in the horizontal plane, the correlation scale of *lnK* is found to be in few available field studies of the order of meters. In such cases, the non–equilibrium index ω may easily take values below 1, resulting in the strongly increased plume spreading. In contrast, the regional–scale efforts where the *lnK* is averaged vertically yielding the transmissivity as a point variable, the correlation scale has been found (Hoeksema and Kitanidis, 1985) to be of the order of kilometers. At this scale, the importance of non–equilibrium effects, in the longitudinal direction, may sooner diminish to the point that the LEA solution is an acceptable one. Note that the above discussion is not limited only to the chemical non–equilibrium, but also applies in the case of physical non–equilibrium processes, when mass transfer resistance can be approximated by the first–order kinetics.

Figures 3a, 3b, and 3c also indicate the influence from the retardation factor upon the longitudinal spreading. For strongly sorbing solutes, the non–equlibrium effects are less pronounced compared to the case of $K_d = 1$. The similar conclusion can be made for the case of the weak retardation ($K_d = 0.1$ – Figure 3a). This indicates that the LEA model is more likely to be violated for the transport of solutes whose distribution coefficient is around one.

Since the focus of this study is at the transport on the large scale, the long–time limits are of particular interest to analyze. For $t' \rightarrow \infty$ we obtain

$$X^{*}_{11} \rightarrow \frac{2K_d t'}{R^3 \omega} + 2\sigma^2_Y \frac{t'}{R} \tag{31}$$

The long–time limits show the influence resulting from the non–equilibrium sorption as a result of the magnitude of the first term in (31), which is a function of the non–equilibrium index ω. It is clear that when $\omega \rightarrow \infty$, the LEA solution is obtained and for practical purposes the accurate assessment of ω is needed before any statement about the importance of non–equilibrium processes is made. Note also that the additional spreading coming from the non–equilibrium sorption is additive to the LEA spreading, but only as X^{*}_{11} approaches its asymptotic limit.

Thus, the impact of non–equilibrium processes in the natural formations depends not only upon the reaction rate parameter and mean velocity, but also on the retardation factor, correlation scale of aquifer heterogeneity, and the degree of aquifer heterogeneity. These results support observations by Valocchi (1989) who observed that the deviation from the LEA solution depends on the vertical spatial variability of the pore–water velocity. This study provides a way to quantify the non–equilibrium effects resulting from the spatial variability in hydraulic conductivity and temporal variability in the fluid residence time in terms of the Lagrangian description of particle displacement moments. With this approach, the importance of non–equilibrium sorption is presented as a function of the correlation scale of the *lnK* field, introducing the index, ω, as a measure of LEA applicability in heterogeneous aquifer systems. However, although ω appears to be a simple criterion for LEA validity, its determination in the field settings is far from an easy task. Being dependent on λ and mean velocity U, its determination is subject to error due to the erroneous estimation process for the correlation scale of the hydraulic conductivity in field settings. In fact, one can argue that ω is by no means a constant variable for the field–scale transport (due to ever changing data availability for estimating λ and choice for the scale of a domain size) resulting in potential problems in defining whether the non–equilibrium is important in natural formations.

Transport described using the LEA can be adequate for fast adsorption and desorption rates relative to the rates of concentration changes. For slow desorption processes (e.g., in case of organic chemicals), the mean velocity has to be decreased or correlation scale increased (in other words the residence time within one heterogeneity scale increased) to achieve sorption equilibrium. Furthermore, the sorption equilibrium will be sooner attained if the solute is strongly sorbing and has a higher degree of heterogeneity. These conditions are very often violated in the field–scale problems, particularly during the pump–and–treat designs for aquifer remediation, where induced flow field of the extraction wells can increase significantly the velocity. This increase in the velocity may easily be sufficient to cause departures from the equilibrium transport model commonly used for the pump–and–treat feasibility study (see Bahr, 1989).

EFFECTIVE DISPERSION COEFFICIENT

The effective dispersion coefficient or macrodispersion, D_{ij}, for the non–reactive solute is known to depend on the travel time from the source and is expected to reach the constant value after experiencing all variations in the random velocity field. For the kinetically sorbing solutes, besides the random velocity field, the macrodispersion should have an additional dependence on the non–equilibrium index ω and distribution coefficient K_d. This is the case, since from the first–order approximation of the displacement second moment (7) and (23) the dispersion tensor is given by

$$D_{ij}(t) = \frac{1}{2}\frac{dX_{ij}(t)}{dt} = \int_{0}^{t/R} R_v\left[U(t/R - \tau)\right]d\tau + \frac{K_d U^2}{R^3 k_2}\left[1 - \exp(-Rk_2 t)\right] \tag{32}$$

The first term on the right–hand side represents the dispersion resulting from the spatially variable velocity field combined with the first moment of the fluid residence time, while the second term is a pure increase in the dispersion resulting from the kinetics process described with the first–order reversible reaction. Note that only under the assumption of the horizontal flow aligned in x–direction, the transversal dispersion has only the first term from (32) and is affected through the first moment of the fluid residence time. Instead of dealing with the dispersion coefficient directly, it is common practice to introduce the dispersivity, which is equal to the dispersion coefficient normalized relative to the mean velocity. Furthermore, we introduce the dimensionless macrodispersivity, $A_{ij}(t)$, by normalizing it relative to the logconductivity correlation scale λ as follows

$$A_{ij}(t) = \frac{D_{ij}(t)}{U\lambda} \tag{33}$$

Figures 4a and 4b show the evolution of the dimensionless longitudinal macrodispersivity, $A_{11}(t')$ as a function of t' for $K_d = 1$ (Figure 4a) and $K_d = 4$ (Figure 4b). To present dimensionless macrodispersivity as a function of the dimensionless time t', we simply divide the second moment of the particle displacement, X^*_{11}, by $2t'$ and obtain the macrodispersivity with $X_{11}/2Ut\lambda$. Figure 4 shows that the apparent macrodispersivity grows with the travel time and its rate of growth is a function of the non–equilibrium index ω and distribution coefficient K_d. The macrodispersivity of the kinetically sorbing solute is tending toward the constant limit considerably slower than the LEA solution and particularly slower than the non–reactive plume which attains its constant value in the shortest time. This slow transition towards the asymptotic macrodispersion for the non–equilibrium transport is more pronounced for smaller ω. For the case of $Kd = 1$ (Figure 4a), the overall growth of macrodispersivity is larger in magnitude and slower than in the case of $K_d = 4$ (Figure 4b), which, again, indicates that for the distribution coefficient around 1, the transport mechanism may have the strong impact from the non–equilibrium processes.

It is also of interest to derive the closed–form expression for the asymptotic macrodispersion coefficients, which in the case of the longitudinal direction follows from (32)

$$A^* = A_{11}(\infty) = \frac{1}{2U\lambda}\lim_{t\to\infty}\frac{d}{dt}X_{11} = \frac{K_d}{R^3\omega} + \frac{\sigma_Y^2}{R} \tag{34}$$

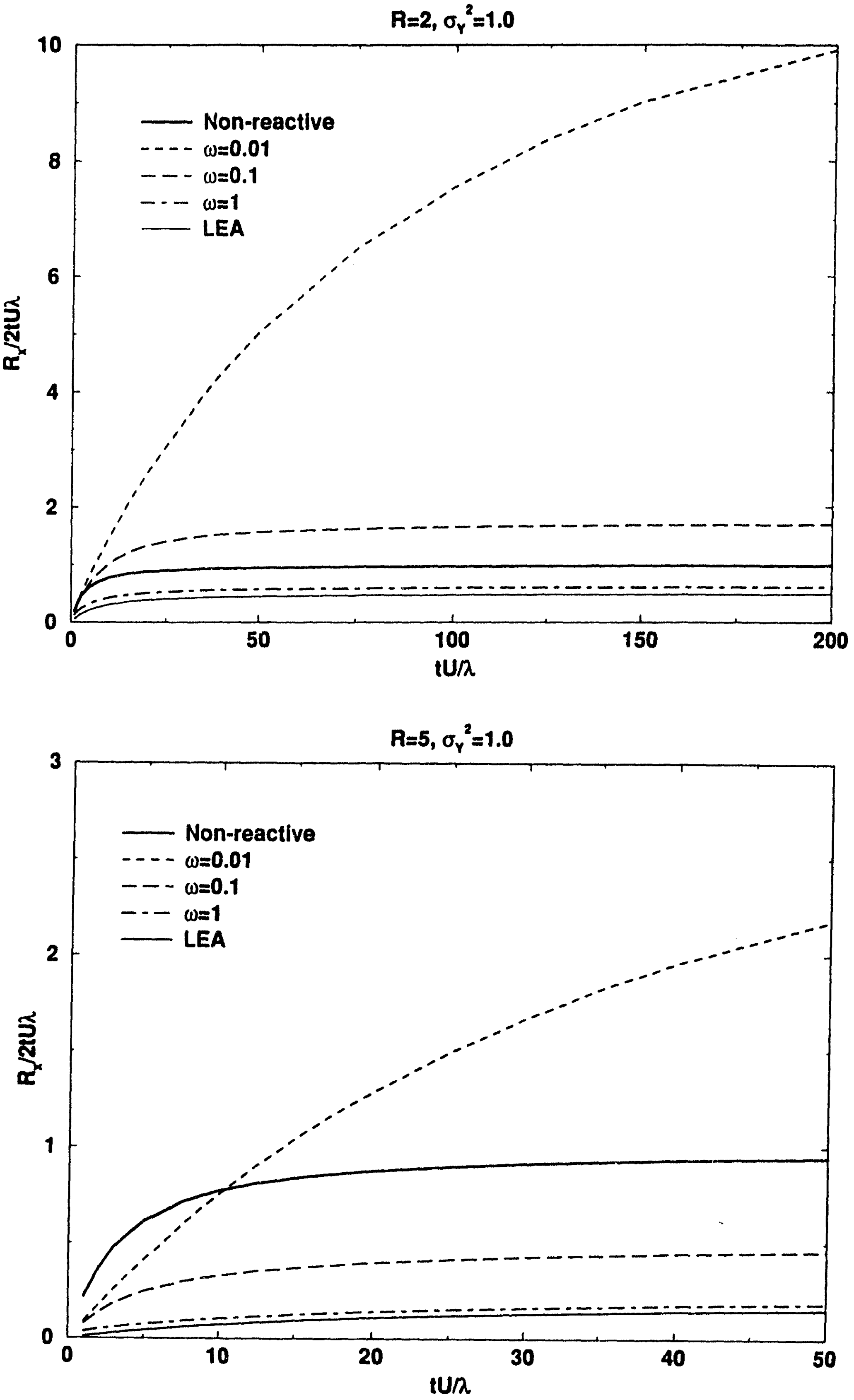


Figure 4. Longitudinal macrodispersivity $A_{11}(t')$; (a) K_d=1; (b) K_d=4.

This expression for the constant macrodispersion can be employed in the advection–dispersion equation

$$\frac{\partial\langle c\rangle}{\partial t} = -\frac{\mathbf{U}}{R}\cdot\nabla\langle c\rangle + \nabla\cdot\left[A^{*}\cdot\nabla\langle c\rangle\right] \qquad (35)$$

to model the transport of $\langle c\rangle$ (ensemble averaged volumetric concentration) for kinetically sorbing solute after the plume has experienced all variations in the flow field and fluid residence time. The elapsed time for the above ADE to become valid (and basically replace (1) and (2) with one Fickian ADE) is usually called the relaxation time (Chrysikopoulos et al., 1992). It can be seen from Figure 4 that this relaxation time in the case of kinetically sorbing solutes depends strongly on the non–equilibrium index ω and on the distribution coefficient K_d. The direct practical importance of the constant macrodispersion coefficient and the Fickian ADE is, for example, in problems studying the migration of radionuclides from the nuclear waste disposal sites where the transport scale of interest is at a very large time scale and first–order kinetics might be used to describe a mass transfer resistance between the fracture plane and porous solid matrix. In such cases, it is unreasonable to assume that the relaxation time is reached. The travel time aspect of such a transport problem combined with the risk assessment analysis for radionuclides (Andricevic et al., 1992) reveals the important impact coming from the non–equilibrium processes as well as from the parameter uncertainty. In other cases of the local scale and significant non–equilibrium effects, the relaxation time necessary for (35) to become valid may be large, such that it is unlikely that within the one geologic unit (for which the flow field variability is defined) the solute plume will ever behave according to the above ADE. However, even if the asymptotic conditions are not reached, it is useful to know the converging limits of the transport parameters.

The asymptotic macrodispersivity, A^{*}, as a function of the non–equilibrium index ω is presented in Figure 5 for three values of K_d. This plot clearly shows the increased macrodispersivity (e.g., order of magnitude) for low values of ω. Note that low values of ω result either from low k_2 or small heterogeneity scale residence time λ/U. By increasing ω, the effective macrodispersivity does not change with non–equilibrium index, and Figure 5 indicates again, that for $\omega > 10$, the asymptotic macrodispersivity becomes totally insensitive to ω. This limit is equal to the macrodispersivity of the LEA solution which from (34) is equal to σ_Y^2/R.

THE EFFECT OF PARAMETER UNCERTAINTY

The preceding section presented the development of the spatial moments and macrodispersion of the kinetically sorbing solutes in the randomly heterogeneos formation. The

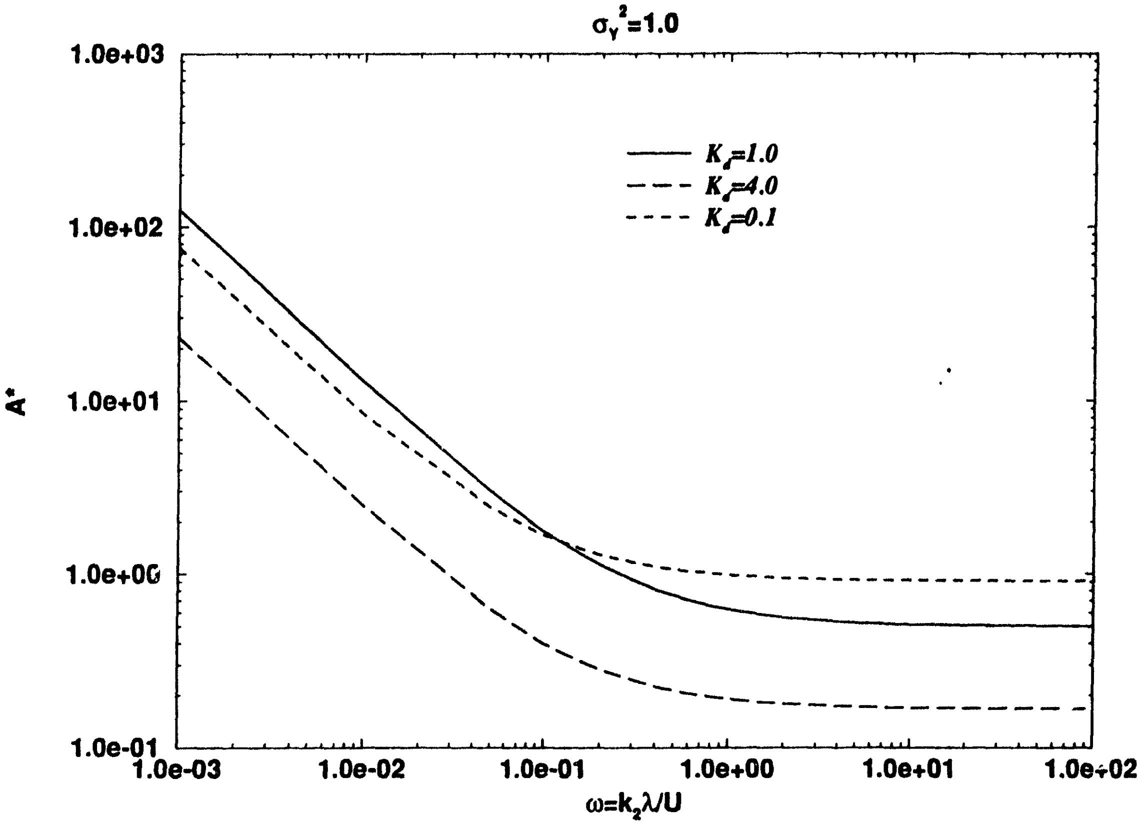


Figure 5. Constant longitudinal macrodispersive cofficient A_{11}^* as a function of the non–equilibrium index ω.

impact coming from the non–equilibrium processes is quantified using the closed–form expression of the first two moments of the fluid residence time. These expressions together with spatial moments depend, however, on a few parameters which are commonly estimated from the field data or laboratory experiments. The estimates are subject to the uncertainty, which directly affects the accuracy of provided tools in predicting the concentration plume in a given natural formation. Dagan (1988) suggested an approach for studying the impact of parameter uncertainty and Woodbury and Sudicky (1991) applied it to the second displacement moment of the non–reactive plume at the Borden field experiment, by considering the uncertainty in the estimates of the geostatistical parameters, namely σ_Y^2 and λ. This study is focused on the kinetically sorbing solutes and the impact from the uncertainty of the reactive parameters will be examined.

Recently, investigators studied the spatial variability in the distribution coefficient K_d (Garabedian et al., 1988; Valocchi, 1989; Robin et al., 1991; Chrysikopoulos et al., 1992) analyzing the effect such variability may have on the transport characteristics. In the particular case of radionuclides, the work of Sheppard and Thibault (1990) reported a detailed description of the variability in the distribution coefficient (found in the laboratory and field experiments), its distributional characteristics, and correlation with several soil characteristics like clay content, soil–to–plant concentration ratio, and pH factor. Consequently, the transport of sorbing solutes is clearly affected by the estimated mean distribution coefficient, $\langle K_d \rangle$, and with the uncertainty of such estimate, $\sigma^2_{\langle K_d \rangle}$. In what follows, the effect of uncertainty in K_d on the second spatial moment will be analyzed. The role of the non–equilibrium process in this case can be seen also as a result of the mass transfer resistance between the mobile fractured void space and the immobile porous solid matrix.

The expected value of the second displacement moment of kinetically sorbing solutes, as a result of uncertainty in the distribution coefficient estimate, is given with

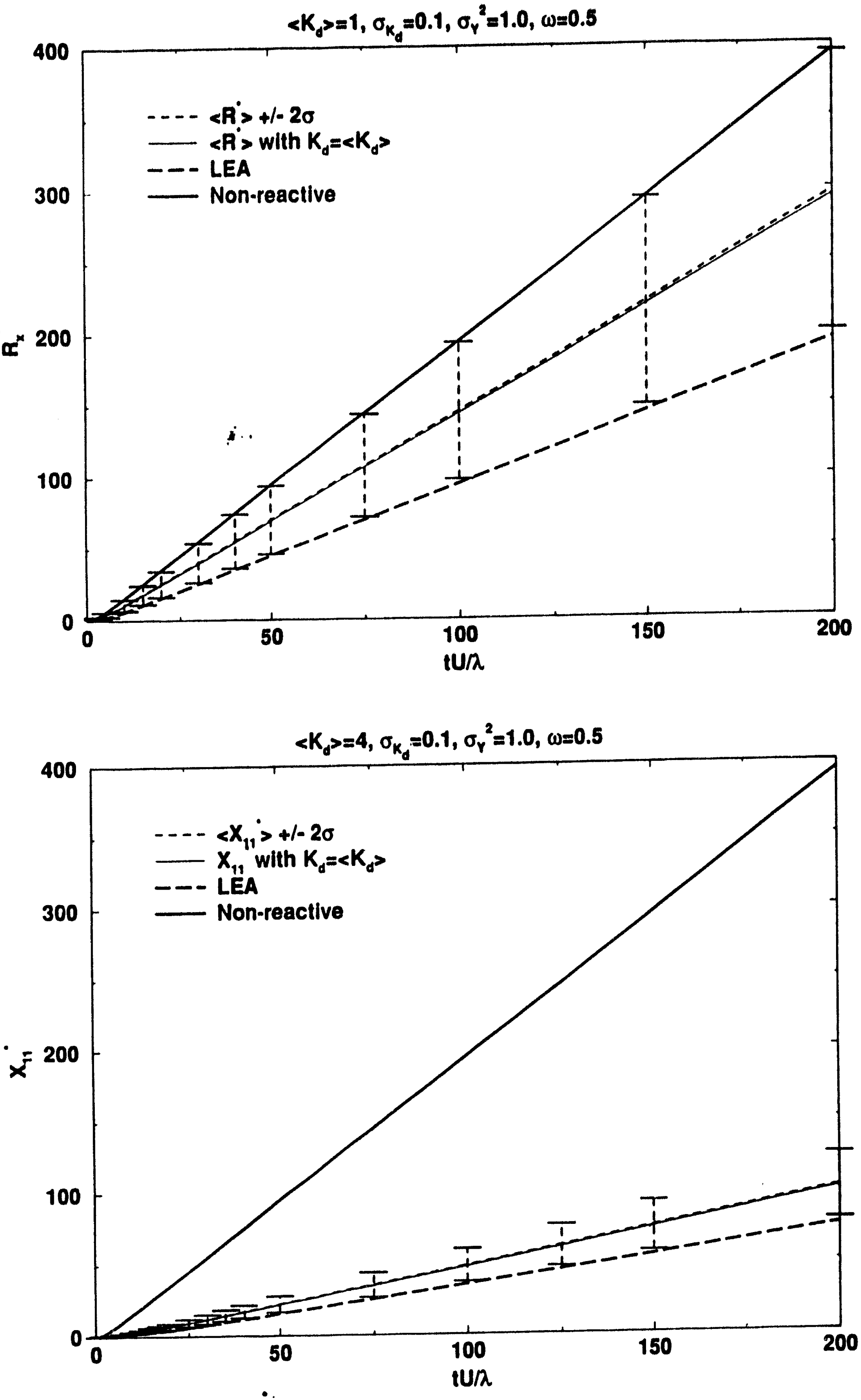
$$\langle X^*_{ij}(t') \rangle = \int X^*_{ij}(t' \mid K_d) f(K_d) dK_d \tag{36}$$

where $f(K_d)$ is the pdf of the distribution coefficient estimate. With this, the variance of X^*_{ij} is obtained as

$$\sigma^2_{X^*_{ij}}(t') = \int \left[X^*_{ij}(t' \mid K_D) \right]^2 f(K_d) dK_d - \left[\langle X^*_{ij}(t') \rangle \right]^2 \tag{37}$$

Although other parameters (e.g., U, σ^2_Y, and λ) are also subject to uncertainty (see Woodbury and Sudicky, 1991; Dagan and Nguyen, 1989; Andricevic et al., 1992), in this study, we limit the analysis on examining the impact coming from the uncertainty in the mean distribution coefficient estimate. Since this work was partially motivated by studying the migration of radionuclides for which the strong spatial variability was documented (see Sheppard and Thibault, 1990), the impact on the solute spreading was expected to be important, particularly due to the strong nonlinear interactions.

Figure 6 shows the expected rate of plume spreading in the longitudinal direction, $\langle X^*_{11} \rangle$, with $\pm\, 2\sigma_{X^*_{11}}$ error bars which form approximately the 95 percent confidence limit. The non–reactive and LEA spreading is also plotted for the reference. The confidence limit interpretation assumes that *a posteriori* distribution for K_d is Gaussian, which is warranted in

$<K_d>=1$, $\sigma_{K_d}=0.1$, $\sigma_Y^2=1.0$, $\omega=0.5$

$<K_d>=4$, $\sigma_{K_d}=0.1$, $\sigma_Y^2=1.0$, $\omega=0.5$

Figure 6. The expected value of the second displacement moment in the direction of the mean flow with error bars equal to 2σ; (a) $\langle K_d \rangle=1$; (b) $\langle K_d \rangle=4$.

the case of a large number of data. The pdf $f(K_d)$ is assumed, thus, normal with mean $\langle K_d = 1\rangle$ (Figure 6a) and $\langle K_d = 4\rangle$ (Figure 6b). The estimation standard deviation, $\sigma_{\langle K_d\rangle}$, is assumed 10 percent of the mean value, which represents the very low bound estimated from the reported variability in K_d for radionuclides for the sand soil (Sheppard and Thibault, 1990). For the mean distribution coefficient $K_d = 1$ and non–equilibrium index $\omega = 0.5$, the 95 percent confidence limit of the longitudinal spreading almost captures the entire range between the LEA and non–reactive case (Figure 6a). This reveals how sensitive the second displacement moment in the longitudinal direction is on the uncertainty in the estimated mean distribution coefficient, even for relatively small variability in the mean K_d estimate. However, for $K_d = 4$ (higher retardation), the longitudinal spreading envelopes are reduced and positioned just above the LEA solution, indicating that strongly sorbing solute besides reducing the non–equilibrium effect also reduces the effect from the uncertainty in the parameter estimate. Although this analysis assumes other parameters, like mean velocity, U, σ_Y^2, and λ known with certainty, it is easy to see what effect those parameters would have on the confidence limit. For example, by considering error in the mean velocity estimate together with K_d (Andricevic et al., 1992), the difference between $\langle X_{11}^*\rangle$ and X_{11}^* using $\langle K_d\rangle$ as deterministic value would be more apparent, particularly if K_d is assumed to be negatively correlated with the velocity field.

The three–dimensional transversal second moment is affected by the uncertainty in the K_d estimate (Figure 7). Figure 7a and 7b depict cases for $\langle K_d\rangle = 1$ and $\langle K_d\rangle = 4$, respectively. In the case of $\langle K_d\rangle = 1$, the second transversal moment, with its error bars, shows the strong impact coming from the relatively small error in the K_d estimate ($\sigma_{K_d}^2$). Also, the plot of X_{11}^* for the non–reactive solute indicates that in the case of sorbing solutes, the constant macrodispersion is approached slower in the transverse direction and the 95 percent confidence limit may easily extend over the non–reactive spreading. In the case of $\langle K_d\rangle = 4$, the error bars are reduced and they seem to approach the constant limit even slower. The fact that the large t' error bars are becoming smaller is due to the independence of $X_{22}(\infty) = 2\sigma_Y^2\lambda^2/3$ on the mean velocity and distribution coefficient. However, the error in the estimate σ_Y^2 and λ will make a significant effect on the transversal spreading (see Woodbury and Sudicky, 1991).

In the recent field experiment at the Borden site several reactive compounds were used and their behavior in time and space was extensively analyzed (Roberts et al., 1986; Curtis et al., 1986). One of their observations was related to the variability in the retardation factor found in the field experiment, which may be attributed to several reasons, among which is the spatial variability in the distribution coefficient and some non–equilibrium effects. Ball (1989), in his

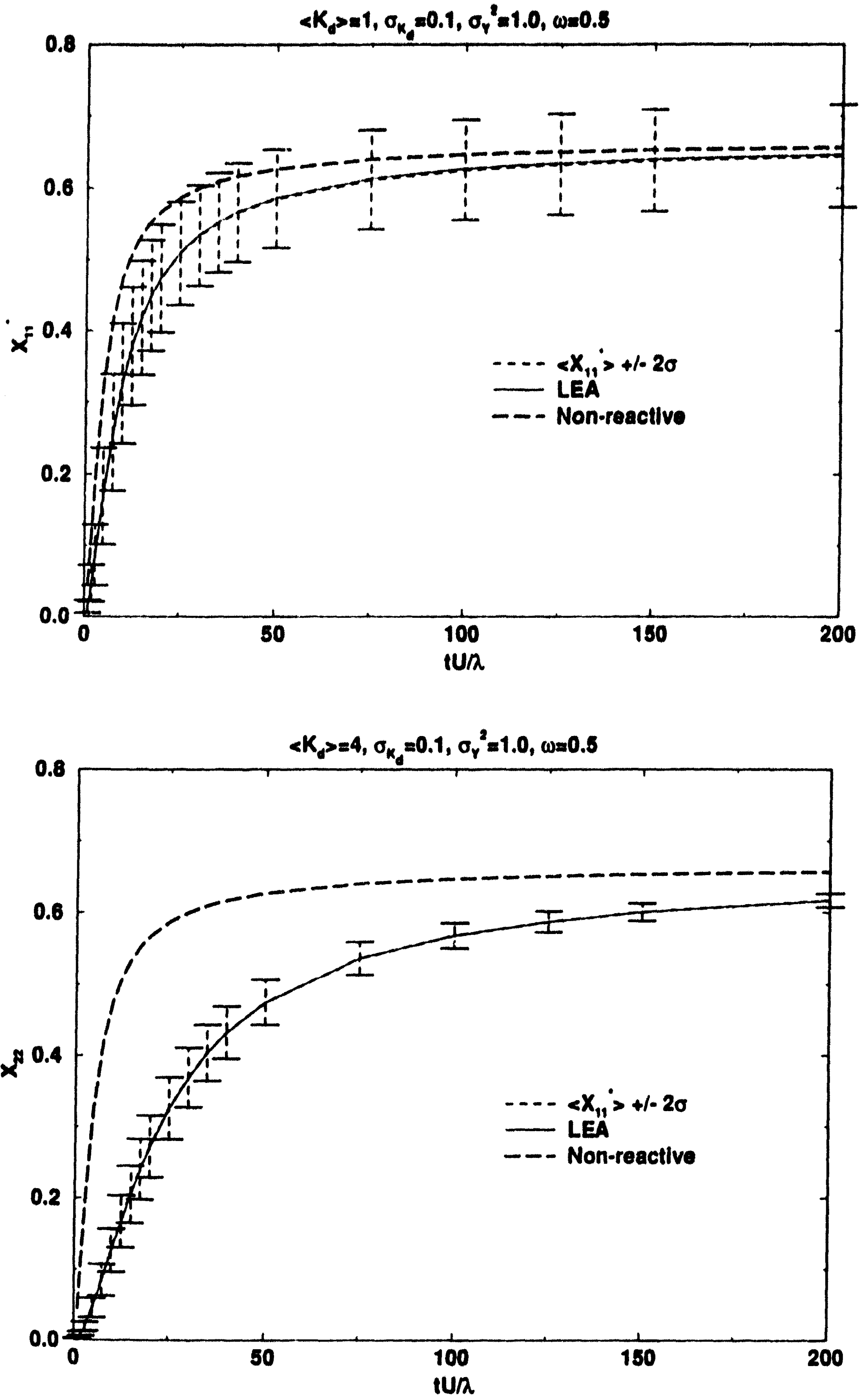


Figure 7. The expected value of the tranverse second displacement moment with error bars equal to 2σ; (a) $\langle K_d \rangle = 1$; (b) $\langle K_d \rangle = 4$.

kinetic adsorption study with aquifer solids from the Borden site, reported a K_d value for tetrachloroethylene (PCE) of 3.1 and desorption rate $k_2 = 0.3\ d^{-1}$. Here we attempt to model the data for the PCE plume by considering the uncertainty in the laboratory estimate of K_d and k_2, as well as their negative correlation as suggested by Brusseau et al. (1989). The uncertainty in the K_d and k_2 estimate is assumed 20 and 25 percent of the corresponding mean values, respectively. The three-dimensional anisotropic structure of the Borden aquifer is adjusted to the horizontal isotropy by considering factor 0.74 as a result of vertical averaging (Woodbury and Sudicky, 1991). The mean velocity $U = 0.091 m/d$, $\sigma_Y^2 = 0.244$, and $\lambda = 5.14m$ are the flow parameters assumed perfectly known. The field data are also adjusted for the displacement variance at $t = 0$ (experiment had a finite injection zone), which for the bromide tracer was estimated by Freyberg (1986) as $1.8m^2$.

Therefore, the function $f(K_d, k_2)$ of the parameter estimates now is the two–dimensional joint pdf between K_d and k_2. The expected value and the variance of the second moment of the particle displacement are obtained using (36) and (37), with the pdf $f(K_d, k_2)$ assumed jointly normal. The integration over the two–dimensional parameter space is performed numerically using the Gaussian quadrature. The final result is presented in Figure 8 and compared with field data points for the PCE plume. The longitudinal spreading and field data points are presented in the dimensionless form to be consistent with the previous presentations. Figure 8 shows how strong an impact the uncertainty in the K_d and k_2 estimates can have on the second spatial moment. The reason for this can be seen from the highly nonlinear interactions K_d and k_2 have in (28). The error bounds are again equal to $\pm 2\sigma$ and may be seen (under the assumption of the Gaussian *aposteriori* process) as confidence limits. Almost all data points are within those limits except one outlier at the early time of $t = 85 days$.

CONCLUDING REMARKS

In this work, the macrodispersion characteristics for kinetically sorbing solutes are analyzed. The probabilistic model is developed and coupled with advective transport to obtain closed–form expressions for the first two moments of the particle displacement. The effect from the uncertainty in estimating the mean distribution coefficient K_d upon the second displacement moment is examined. The theoretical developments and presented results reveal the following characteristics of transport of kinetically sorbing solutes in the field scale:

1. Coupling advective transport with the first two moments of the fluid residence time provides a way to obtain the closed–form expression for displacement moments and asymptotic macrodispersion tensor. The solute plume spreading results from the spatial variability in the velocity field and the temporal variability in the actual time

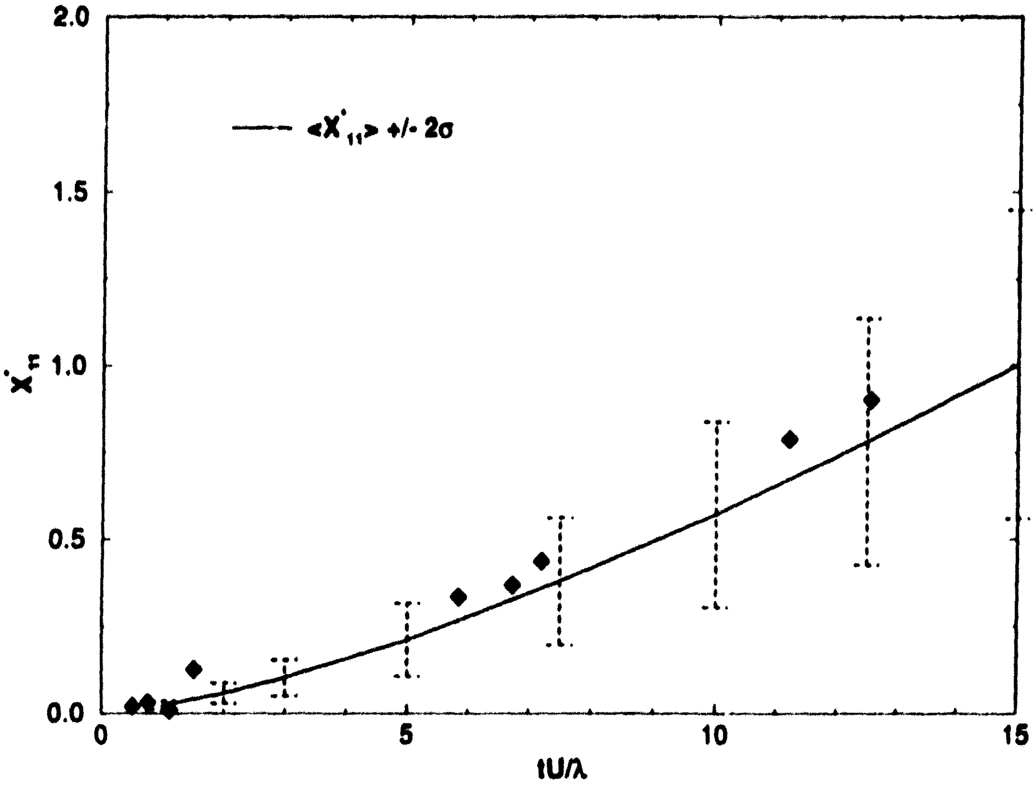


Figure 8. The expected longitudinal displacement variance with error bars (2σ) resulting from the variability in K_d and k_2 for the PCE plume in the Borden field experiment. Solid line represents the model with parameter uncertainty and diamonds field data.

the particle stays in the mobile fluid phase while being transported by groundwater. The non-equilibrium index $\omega = k_2\lambda/U$ is introduced, which can be considered as field-scale Damkohler number, since it relates the reaction time k_2 to the residence time of the aquifer heterogeneity scale λ/U.

2. The importance of the non-equilibrium sorption at field scale depends not only upon the magnitude of the reaction rate parameter, but also upon the correlation scale of the *lnK* field λ, the retardation factor, and variance of the *lnK* field.

3. The longitudinal spreading of the kinetically sorbing plume shows an increase compared to the LEA model, however, for $\omega > 10$, for all practical purposes, the LEA model can be used for spreading estimates in the direction of the mean flow.

4. The magnitude of the asymptotic macrodispersion is a function of the non–equilibrium index ω and may increase significantly by decreasing ω. The relaxation time needed for macrodispersion to reach its asymptotic limit is highly sensitive on the ω and K_d, and may be very large for the smaller ω. This is particularly evident for the cases of the distribution coefficient K_d around 1.

5. Due to the non–linear interactions, the uncertainty in estimating reaction parameters (K_d and k_2) has a strong impact on the expected value of the spatial moments, particularly on the moment of inertia. For the smaller ω, the effect of the parameter uncertainty on the second displacement moment may be very significant. When comparing with the field data, the parameter uncertainty may play a dominant role.

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APPENDIX

DERIVATION OF THE SECOND MOMENT OF THE FLUID RESIDENCE TIME

The variance of the fluid residence time is formulated in (22) and the evaluation of the auto-covariance $Cov[Z_\tau, Z_{\tau'}]$ is the first step. Since Z_τ is a stationary, binary process, we have $\langle Z_\tau \rangle = p_1$, such that

$$\langle Z_\tau Z_{\tau'} \rangle = Prob\left[Z_\tau = 1 \cap Z_{\tau'} = 1\right] \tag{38}$$

If $\tau \leq \tau'$, the above becomes

$$\langle Z_\tau Z_{\tau'} \rangle = Prob\left[Z_\tau = 1\right] Prob\left[Z_{\tau'} = 1 \mid Z_\tau = 1\right] = p_1 P_{11}(\tau' - \tau) \tag{39}$$

and by setting $\tau \leq \tau'$, the above solution is reversed to yield $p_1 P_{11}(\tau - \tau')$. Therefore, the general auto-covariance of the binary process can be evaluated with the following expression

$$Cov\left[Z_\tau, Z_{\tau'}\right] = \langle Z_\tau Z_{\tau'} \rangle - \langle Z_\tau \rangle \langle Z_{\tau'} \rangle = p_1 P_{11}(|\tau - \tau'|) - p_1 p_1 \tag{40}$$

Combining (12) and (40), we obtain

$$Cov\left[Z_\tau, Z_{\tau'}\right] = p_1\left[p_1 + p_0 \exp(-Rk_2 |\tau - \tau'|)\right] - p_1 p_1 = p_0 p_1 \exp(-Rk_2 |\tau - \tau'|) \tag{41}$$

Then, substituting the above in (22) yields

$$\sigma_{t_*}^2(t) = p_0 p_1 \int_{\tau=0}^{t} \int_{\tau'=0}^{t} \exp(-Rk_2 |\tau - \tau'|) d\tau d\tau' = 2 \int_{\tau=0}^{t} (t - \tau) \exp(-Rk_2 \tau) d\tau \tag{42}$$

Using the substitution $x = t - \tau$, the above can be rewritten as

$$\sigma_{t_*}^2(t) = \frac{2K_d}{R^2} \int_0^t x \exp(-Rk_2(t - x)) dx = \frac{2K_d}{R^2} \exp(-Rk_2 t) \int_0^t x \exp(Rk_2 x) dx \tag{43}$$

Integrating by parts, the last integral from above can be analytically solved yielding

$$\sigma_{t_*}^2(t) = \frac{2K_d}{R^2} \exp(-Rk_2 t) \left\{ \frac{t}{Rk_2} \exp(Rk_2 t) - \frac{1}{R^2 k_2^2}\left[\exp(Rk_2 t) - 1\right] \right\} \tag{44}$$

which can be further rearranged to yield

$$\sigma_{t_*}^2(t) = \frac{2K_d}{R^3 k_2}\left[t - \frac{1}{Rk_2}\left[1 - \exp(-Rk_2 t)\right] \right] \tag{45}$$

which completes the derivation of the variance of the fluid residence time as given in (23).

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