WATER RESOURCES RESEARCH, VOL. 39, NO. 4, 1086, doi:10.1029/2002WR001399, 2003

Travel time moments for sorbing solutes in heterogeneous domains under nonuniform flow conditions

Xavier Sanchez-Vila
Department of Geotechnical Engineering and Geosciences, Technical University of Catalonia, Barcelona, Spain

Yoram Rubin
Department of Civil and Environmental Engineering, University of California, Berkeley, California, USA

Received 24 April 2002; revised 17 October 2002; accepted 30 January 2003; published 4 April 2003.

[1] A methodology for evaluating the unconditional and conditional moments of travel time for a sorbing solute is presented. The approach is applicable for any flow configuration and for a wide range of mass transfer rate-limited linear processes. The methodology is applicable to the general case of spatially variable hydrological and chemical parameters. The sorption model used to derive the temporal moments is that of a continuous distribution of mass rate coefficients [*Haggerty and Gorelick*, 1998]. Models such as instantaneous equilibrium, first-order and two-site sorption kinetics, among others, can be considered as particular cases of this general model. Using a deterministic approach, the low-order moments of the breakthrough curves for reactive solutes can be obtained as a function of those for conservative tracers. Using a stochastic approach, the unconditional low-order statistics of the travel time moments can be obtained. These moments depend on the statistics of two Lagrangian functions, the travel time for a conservative solute, and an integral of the variations of the chemical parameters weighted by the inverse local velocity along the trajectory. Finally, conditional temporal moments are derived. Moments can be conditioned to any type of information, hard or soft, hydraulic or geochemical. Conditioning is found to reduce uncertainty, characterized by a reduction in the variance of the travel time. The general results are particularized for both uniform in the mean and convergent flow conditions and for simple sorption models such as linear instantaneous equilibrium and first-order kinetics. In all such cases, close-form results, based on small perturbations expansions, are presented for the travel time moments. *INDEX TERMS:* 1829 Hydrology: Groundwater hydrology; 1832 Hydrology: Groundwater transport; 1869 Hydrology: Stochastic processes; 5114 Physical Properties of Rocks: Permeability and porosity; *KEYWORDS:* groundwater, heterogeneity, reactive transport, conditional temporal moments, multirate sorption

Citation: Sanchez-Vila, X., and Y. Rubin, Travel time moments for sorbing solutes in heterogeneous domains under nonuniform flow conditions, *Water Resour. Res.*, *39*(4), 1086, doi:10.1029/2002WR001399, 2003.

1. Introduction

[2] Traditional sorption models used in the hydrogeological literature consider that mass transfer between the solute in the mobile and the immobile zones is either in instantaneous equilibrium, or characterized by a single mass transfer rate (first-order kinetics). In the last few years new models have arisen. These models incorporate the possibility that sorption can be characterized by multiple rates at any single location, related to the presence of a nonuniform distribution of grain sizes [*Connaughton et al.*, 1993; *Pedit and Miller*, 1994; *Culver et al.*, 1997; *Cunningham and Roberts*, 1998; *Haggerty and Gorelick*, 1998; *Deitsch et al.*, 2000]. The most general model assumes a continuous distribution of mass transfer rates [*Haggerty and Gorelick*, 1998] and was developed as an extension of various particular continuous and discrete models. A particular case of the continuous model has recently been applied to the interpretation of single-well and convergent flow tracer tests [*Haggerty et al.*, 2001; *McKenna et al.*, 2001].

[3] The study of travel time moments for solutes undergoing sorption processes has been the subject of attention in the literature in the past few years. The first studies considered either instantaneous equilibrium or first-order kinetics [*Cvetkovic and Shapiro*, 1990; *Selroos and Cvetkovic*, 1992; *Cvetkovic et al.*, 1992]. *Rubin et al.* [1997] [see also *Rubin*, 2003] develop a general methodology that could be extended to a large variety of mass transfer models, considering spatially uniform reactive parameters. Their work was extended by *Lawrence et al.* [2002] to incorporate the continuous distribution of mass transfer rates and to evaluate the effect of conditioning the moments of travel time on hydraulic conductivity measurements. *Cvetkovic et al.* [1998] provide a framework to incorporate spatial variability in the sorption parameters to obtain the unconditional moments of travel time under mean uniform flow conditions, including nonlinear equilibrium processes. *Cvetkovic and Haggerty* [2003] analyze transport with multiple-rate exchange in terms of the crossing-time density function to an exit surface.

0043-1397/03/2002WR001399

[4] In this paper we develop a methodology to obtain the moments of travel time for a sorbing solute. The methodology is an extension of the formulation of *Rubin et al.* [1997] to incorporate, first, the general continuous model of *Haggerty and Gorelick* [1998], and second, spatial variability in the sorption parameters. The approach allows obtaining moments conditioned on measurements. The methodology is not restricted to any particular flow configuration.

[5] The outline of the paper is as follows. First, we aim at finding a general expression for the moments of a breakthrough curve for a solute undergoing heterogeneous sorption kinetics in a given realization (deterministic approach) of a hydraulically heterogeneous medium. Second, this development is then used to find the statistics of travel time in a stochastic framework by ensemble averaging. The general expressions found are particularized for two sorption models, those of linear instantaneous equilibrium and first-order kinetics, and for different examples, covering convergent and uniform in the mean flow conditions. Some ideas about other sorption models are also presented. In all the examples close-form solutions for the mean and variance of travel time, based on small perturbations expansions, are obtained. In the last section we extend the general methodology to find expressions for the conditional temporal moments.

2. General Solution

2.1. Problem Statement

[6] The initial mathematical problem is obtaining the moments of the breakthrough curve (BTC) of a reactive tracer advected along a streamline, from an injection point to a discharge point (e.g. convergent flow), a plane (e.g. uniform on the mean flow), or a surface. Discharges to a point or a plane are the typical situations in forced-flow and natural-flow tracer tests, respectively. Even in the absence of local dispersion, the path followed by any solute particle will not be a straight line due to spatial heterogeneity of the hydraulic parameters, such as hydraulic conductivity.

[7] The transport equation along a streamline for a sorbing solute under steady flow conditions and in dimensionless form is given by the following set of coupled equations [*Haggerty and Gorelick*, 1998]:

$$\frac{\partial C_1}{\partial T} + \beta_{tot} \int_0^\infty p \frac{\partial C_2}{\partial T} d\alpha + V \frac{\partial C_1}{\partial \eta} = 0, \tag{1a}$$

$$\frac{\partial C_2}{\partial T} = \alpha (C_1 - C_2). \tag{1b}$$

where $C_1(\eta, t)$ is the dimensionless aqueous concentration (actual concentration -mass per unit volume of fluid- divided by a reference value); α is a (dimensionless) normalized mass rate coefficient, given as, $\alpha = \alpha_a I/U$, α_a being the actual mass rate coefficient $[T^{-1}]$, U some reference velocity $[L\,T^{-1}]$, and I some normalizing distance [L] (e.g. some integral distance); $C_2(\eta, t, \alpha)$ is the dimensionless immobile concentration corresponding to the part of the solid that reacts at rate α (in this sense C_2 is also defined per unit volume of fluid and then normalized by the concentration reference value); $V(\eta)$ (dimensionless) is normalized velocity ($V = v/U$, $v(\eta)$ $[L\,T^{-1}]$ being the actual velocity); T (dimensionless) is normalized time ($T = U\,t/I$, t being real time [T]); and η (dimensionless) is the normalized (again by I) coordinate along the streamline; $\beta_{tot}(\eta)$ (dimensionless) is the total capacity coefficient, that is the ratio of the total mass in the immobile zone to the total mass in the mobile zone at equilibrium [*Haggerty and Gorelick*, 1998]. As an example, when porosity in the immobile zone is neglected, $\beta_{tot} = \rho_b K_d/\phi$, where ϕ is the porosity of the mobile zone, ρ_b $[M\,L^{-3}]$ is the bulk density, and K_d $[L^3\,M^{-1}]$ is the distribution coefficient. Finally, $p(\alpha, \eta)$ corresponds to the volumetric fraction of the sorbing part of the solid that reacts at a particular rate, so that $\int_0^\infty p(\alpha, \eta) d\alpha = 1$ and $\int_0^\infty p(\alpha, \eta) C_2(\eta, t, \alpha) d\alpha = C_{2tot}(\eta, t)$. With this last definition, $C_{2tot}(\eta, t)$ (dimensionless) is recognized to be the total immobile concentration at a given location and time. In our notation it has been made explicit that both β_{tot} and p can be heterogeneous, and therefore depend on η. In equation (1) the effects of local dispersion have been neglected, which would be a valid approximation for large Peclet numbers.

[8] In this paper we concentrate on the problem of a solute that is injected in an initially clean aquifer (the initial concentrations, $C_1(\eta, t = 0)$ and $C_2(\eta, t = 0, \alpha)$, are zero). Applying Laplace transform to equations (1a) and (1b) under these initial conditions and combining them, the resulting equation for the concentration in the mobile phase is:

$$s(1 + h(\eta, s))\overline{C}_1 = -V \frac{\partial \overline{C}_1}{\partial \eta}, \tag{2}$$

where s is the Laplace variable, $\overline{C}_1(\eta, s)$ the Laplace transform of $C_1(\eta, t)$, and $h(\eta, s)$ is a dimensionless auxiliary function given by

$$h(\eta, s) = \beta_{tot}(\eta) \int_0^\infty \frac{\alpha p(\alpha, \eta)}{s + \alpha} d\alpha. \tag{3}$$

[9] Defining $\overline{C}_{2tot}(\eta, s)$ as the Laplace transform of $C_{2tot}(\eta, t)$, and using the Laplace transformed version of equation (1b), we get:

$$\begin{aligned} \frac{\beta_{tot}(\eta)\overline{C}_{2tot}}{\overline{C}_1} &= \beta_{tot}(\eta) \int_0^\infty p(\alpha, \eta) \frac{\overline{C}_2(\alpha, \eta, s)}{\overline{C}_1(\eta, s)} d\alpha \\ &= \beta_{tot}(\eta) \int_0^\infty \frac{\alpha p(\alpha, \eta)}{s + \alpha} d\alpha = h(\eta, s), \end{aligned} \tag{4}$$

so that $h(\eta, s)$ depends on the ratio between the Laplace transforms of the total immobile and mobile concentrations, similar to the auxiliary functions defined by *Rubin et al.* [1997] and *Cunningham* [1999]. An equation similar to (3) appears in the work of *Sardin et al.* [1991], but in their case the p() function accounts for mass transfer times instead of reaction rates.

2.2. Deterministic Approach

[10] The next step is to solve (2) for a given set of boundary conditions. The problem we consider is that of solute injected at point $\eta = 0$. We denote with F(t) the injection function, that is, the time series of the concentration at the source. This is common in tracer tests, where

the solute is injected in a very small portion of the aquifer (e.g. a well or a portion of it), while the tracer injection takes from a few minutes to hours. In these tests the input function is usually recorded.

[11] From (2), the concentration at the discharge point or plane located at a normalized Euclidean distance L along the mean flow direction is given by:

$$\overline{C}_1(L,s)=f(s)\exp\left(-s\left(\tau(L)+\int_0^{\eta(L)}\frac{h(\eta',s)}{V(\eta')}d\eta'\right)\right), \qquad (5)$$

where τ, given by $\tau(L)=\int_0^{\eta(L)}\frac{d\eta'}{V(\eta')}$, is the travel time from the injection point ($\eta = 0$) to the discharge point, located at distance $\eta = \eta(L)$. η is the distance along the trajectory, which is unknown, while L is the Euclidean distance measured along the mean trajectory, which is known; these two distances would be equal in a perfectly homogeneous medium. The function f(s) is the Laplace transform of the injection function, F(t). If in (5) we consider homogeneous h, and we further consider an injection of a concentration pulse area of one (selecting appropriately the normalizing concentration) in an infinitely short time (so that f(s) = 1), we recover exactly the expression by *Rubin et al.* [1997]. Equation (5) is a generalization to nonuniform flow of equation (5.12) of *Cvetkovic et al.* [1998]. As $\eta(L)$ is uncertain, so is τ. Also the values of h and V at any particular location are not known unless measured.

[12] $C_1(L, t)$ is the breakthrough curve (BTC) at the discharge location in actual space, and could be obtained by back transforming (5). But in order to obtain the temporal moments of BTC ($t_i(L)=\int_0^\infty t^iC_1(L,t)dt/\int_0^\infty C_1(L,t)dt$), it is more convenient to work in Laplace space. From the work by *Aris* [1958], the noncentral temporal moments can be obtained by taking the s → 0 limits of successive derivatives of (5) with respect to s:

$$t_i(L)=(-1)^i d^i\overline{C_1}(L,s)/ds^i\big|_{s=0}/\overline{C_1}(L,0). \qquad (6)$$

[13] The central moments, $T_i(L)$, can be obtained from the noncentral ones by algebraic expressions. From (6), assuming that f(s) is twice differentiable and $h(\eta, s)$ is at least once differentiable, the first two central and noncentral dimensionless temporal moments of the BTC are obtained as follows:

$$t_1(L)=\overline{t_{inj}}+\tau(L)+\int_0^{\eta(L)}\frac{h(\eta',0)}{V(\eta')}d\eta', \qquad (7a)$$

$$t_2(L)=\frac{f''(0)}{f(0)}+2\overline{t_{inj}}\left(\tau(L)+\int_0^{\eta(L)}\frac{h(\eta',0)}{V(\eta')}d\eta'\right) + \left(\tau(L)+\int_0^{\eta(L)}\frac{h(\eta',0)}{V(\eta')}d\eta'\right)^2 -2\frac{d}{ds}\int_0^{\eta(L)}\frac{h(\eta',s)}{V(\eta')}d\eta'\Bigg|_{s=0}, \qquad (7b)$$

$$T_2(L)=t_2(L)-(t_1(L))^2=s_{inj}^2-2\frac{d}{ds}\int_0^{\eta(L)}\frac{h(\eta',s)}{V(\eta')}d\eta'\Bigg|_{s=0}, \qquad (7c)$$

where, $f'(0)=\frac{df}{ds}\big|_{s=0}$, $f''(0)=\frac{d^2f}{ds^2}\big|_{s=0}$, $\overline{t_{inj}}=-f'(0)/f(0)$ corresponds to the (dimensionless) time where 50% of the total mass has been injected, and $s_{inj}^2 = f''(0)/f(0) - (f'(0)/f(0))^2$ is a measure of the spread in the injection function. As an example, for constant injection between $t = a_1$ and $t = a_2$, $\overline{t_{inj}} = (a_1 + a_2)/2$ and $s_{inj}^2 = (a_2 - a_1)^2/12$.

[14] The first moment of the BTC (equation 7a) is the sum of three terms, corresponding respectively to the injection history, the advective travel time for a conservative solute (τ), and an additional Lagrangian function that accounts for the variation of the sorption parameters along the trajectory weighted by the inverse local velocity. The central second moment (equation 7c) is the sum of two terms: one corresponding to the injection history, and the other incorporating both the flow configuration and the sorption model. All the expressions in (7) depend on h and its derivatives (provided they exist) evaluated at s = 0, which is mathematically analogous to $t \to \infty$. The important implications of this will be explored later. The expressions given in (7) are valid regardless of flow configuration or dimensionality of the problem.

[15] A particular case of (7) corresponds to h being independent of s (e.g. assuming linear instantaneous equilibrium between the mobile and the immobile phases); in this case:

$$t_1(L)=\overline{t_{inj}}+\tau(L)\left(1+\int_0^{\eta(L)}\frac{h(\eta',0)}{V(\eta')}d\eta'\Big/\tau(L)\right), \qquad (8a)$$

$$T_2(L)=\sigma_{inj}^2. \qquad (8b)$$

[16] Equations (8a) and (8b) indicate that the BTC is retarded with respect to that for a conservative solute, but with no additional dispersion. Defining the retardation factor, R, as the average time taken by a retarded solute particle to travel some distance divided by the one for a conservative solute [*Rajaram*, 1997], we have $R(L)=1+\tau(L)^{-1}\int_0^{\eta(L)}h(\eta',0)V(\eta')^{-1}d\eta'$. Furthermore, from (4) we have $h(\eta', 0) = \beta_{tot}(\eta')$. As β_{tot} and V are always positive, it follows that $R(L) > 1$ (except for the trivial case $\beta_{tot} = 0$, where $R(L) = 1$). Notice that from this definition the retardation factor is a heterogeneous, nonlocal parameter, as it incorporates information along the trajectory. Only in the particular case where β_{tot} = constant, the retardation factor becomes homogeneous, $R(L) \equiv R = 1 + \beta_{tot}$. Note that for $\beta_{tot}=\frac{\rho_b}{\phi}K_d$, we get $R=1+\frac{\rho_b}{\phi}K_d$, which is the classical expression for retardation factor under linear instantaneous equilibrium conditions [e.g., *Domenico and Schwartz*, 1990].

2.3. Stochastic Approach

[17] Up to this point the approach taken has been deterministic. Due to the inherent heterogeneity of nature, it is not possible to obtain the exact values for the BTC moments unless a full knowledge of the heterogeneous hydrological and geochemical parameters is invoked. To account for our improper knowledge of the subsurface we adopt a stochastic approach. Therefore the hydraulic conductivity (or transmissivity depending on the dimensionality of the problem) as well as the sorption parameters are considered Space Random Functions (SRF). Consequently, the dependent

variables V, η, τ, h and C_1 become random variables as well.

[18] Let us express now the mass transfer function (η, s) as the sum of an expected value and a zero mean perturbation, $h(\eta, s) = H(s) + h'(\eta, s)$, with $H(s) = \langle h(\eta, s)\rangle$. In this expansion h is assumed to be a second-order stationary random process, resulting in spatially uniform H. A sufficient condition for that is that all the sorption parameters involved in the definition of $h(\eta, s)$ are also second-order stationary. Now, taking the expected values of (5), and assuming a deterministic f(s), we can write the expression for the expected breakthrough curve:

$$\langle \overline{C_1}(L, s)\rangle = f(s)\langle \exp(-s(\tau(L)(1 + H(s)) + \psi(L, s)))\rangle. \tag{9}$$

[19] In (9) we have included a new SRF, $\psi(L, s) = \int_0^{\eta(L)} \frac{h'(\eta', s)}{V(\eta')} d\eta'$. This Lagrangian function involves velocity, which may or may not be stationary (e.g. convergent flow), and therefore its expected value, $\Psi(L, s) = \langle \psi(L, s)\rangle$, may depend on location.

[20] Under ergodic conditions, the BTC is equivalent to the pdf (probability density function) of the travel time from a point source injected instantaneously at time zero ($f(s) = 1$, $\overline{t_{inj}} = \sigma^2_{inj} = 0$). From (9), using again the methodology by *Aris* [1958], and after some algebraic manipulation, the mean and variance of the dimensionless travel time for sorbing solutes become:

$$\langle \tau^R(L)\rangle = (1 + H(0))\langle \tau^{NR}(L)\rangle + \Psi(L, 0), \tag{10a}$$

$$\sigma^{2,R}_\tau(L) = (1 + H(0))^2\sigma^{2,NR}_\tau(L) + 2(1 + H(0))\sigma_{\tau\psi}(L, 0) + \sigma^2_\psi(L, 0) - 2\langle \tau^{NR}(L)\rangle \left.\frac{dH(s)}{ds}\right|_{s=0} - 2\left.\frac{d\Psi(L, s)}{ds}\right|_{s=0}, \tag{10b}$$

where R and NR stand for reactive and nonreactive (conservative) tracers, respectively. In (10b) $\sigma^2_\tau(L) = \langle \tau^2(L)\rangle - \langle \tau(L)\rangle^2$, $\sigma_{\tau\psi}(L, 0) = \langle \tau(L)\psi(L, 0)\rangle - \langle \tau(L)\rangle\, \langle \psi(L, 0)\rangle$, and $\sigma^2_\psi(L, 0) = \langle \psi^2(L, 0)\rangle - \langle \psi(L, 0)\rangle^2$.

[21] From (10a), the expected value of the travel time for a reactive solute is the sum of two terms. The first one corresponds to the expected value of the travel time for a conservative solute times a mean retardation factor (1 + H(0)) (= 1 + $\langle \beta_{tot}\rangle$). The second term ($\Psi(L, 0)$) represents the contribution of the correlation between the sorption parameters and groundwater velocity. When $h'(\eta', s)$ and $V(\eta')$ are positively correlated (higher local retardation values correspond on average to high velocities), $\Psi(L, 0)$ becomes negative, and contrariwise. Another important property from the mean travel time can be related to the inequality: $H(s) + h'(\eta, s) \geq 0$, as it can be proven that for all linear sorption models $\langle \tau^R(L)\rangle \geq \langle \tau^{NR}(L)\rangle$. A similar type of enhanced retardation such as the one given by (10a) is reported by *Bellin et al.* [1993] and *Bellin and Rinaldo* [1995] in their analysis of plume location of linearly adsorbing solutes in heterogeneous formations.

[22] The variance of travel time for a reactive solute is given by (10b). The first term in (10b) corresponds to the variance of travel time for a conservative solute times the mean retardation factor squared. This term would be the only contribution to (10b) if the sorption parameters were homogeneous and $h(\eta, s)$ were not a function of s. The next two terms in (10b) are the contributions of the spatial variability in the sorption parameters and their cross correlation with the hydraulic conductivity. The last two terms in (10b) correspond to the effects of kinetics ($h(\eta, s)$ being time dependent). The mean and variance of travel time for a conservative solute, which appear in (10), can be obtained from the cdf (cumulative distribution function) of τ, $G(\tau(L))$ [see *Rubin et al.*, 1997], as follows:

$$\langle \tau^{i,NR}(L)\rangle = \int_0^\infty i\tau^{i-1}(1 - G(\tau(L)))d\tau. \tag{11}$$

[23] The other terms in (10) include $\langle \psi\rangle$, and the auto and cross-correlation functions for τ and ψ. All (cross-)moments involving ψ depend on s (and therefore on time), but from (10) only the behavior for $s \to 0$ (equivalent to $t \to \infty$) is important. One approach to obtaining these moments is through Monte Carlo simulations [e.g., *Burr et al.*, 1994]. For this purpose, autocorrelation and cross-correlation models for hydraulic conductivity and the sorption parameters need to be established. Then a number of realizations of the two correlated heterogeneous fields can be obtained, and transport simulated. From the ensemble of numerical simulations the statistics of τ and ψ can be computed. The advantage of this method is that it can be applied to different flow configurations, with no restriction on the degree of heterogeneity. A second approach is to compute the moments analytically. In the following sections this point is further addressed.

3. Application of the General Method to Common Sorption Models

3.1. Linear Instantaneous Equilibrium Model (LIE)

3.1.1. General Solution

[24] The linear instantaneous equilibrium model assumes that the local relation between the mobile and sorbed concentrations is linear [e.g., *Domenico and Schwartz*, 1990]. The LIE model is equivalent to considering in the general formulation (in section 2) that $\beta_{tot}(\eta) = \frac{\rho_b}{\phi}K_d(\eta)$, $p(\alpha, \eta) = \delta(\alpha - \alpha_1)$, with $\delta(\bullet)$ being Dirac's delta function, and setting $\alpha_1 \to \infty$. This model corresponds to a single reversible sorption rate which is fast relative to a solute advection time, so that mass transfer can be considered instantaneous. From (4), $h(\eta, s) = \frac{\rho_b}{\phi}K_d(\eta)$, and therefore: $H(s) = \frac{\rho_b}{\phi}\langle K_d\rangle, h'(\eta, s) = \frac{\rho_b}{\phi}K'_d(\eta), \psi(L, s) = \frac{\rho_b}{\phi} \int_0^{\eta(L)} K'_d(\eta')V(\eta')^{-1}d\eta'$ and $\Psi(L, s) = \frac{\rho_b}{\phi}\langle \int_0^{\eta(L)} K'_d(\eta')V(\eta')^{-1}\, d\eta'\rangle$ with $K'_d(\eta) = K_d(\eta) - \langle K_d\rangle$. Defining a mean retardation factor, $\langle R\rangle = 1 + \frac{\rho_b}{\phi}\langle K_d\rangle$, the dimensionless travel time moments for the LIE model become:

$$\langle \tau^{LIE}(L)\rangle = \langle R\rangle\langle \tau^{NR}(L)\rangle + \Psi(L, 0), \tag{12a}$$

$$\sigma^{2,LIE}_\tau(L) = \langle R\rangle^2\sigma^{2,NR}_\tau(L) + 2\langle R\rangle\sigma^{LIE}_{\tau\psi}(L, 0) + \sigma^{2,LIE}_\psi(L, 0), \tag{12b}$$

[25] The expression for the mean travel time (12a) is identical to (10a). The variance, given in (12b), is a combination of the variances of the two Lagrangian quantities, $\langle R\rangle\tau$ (mean retardation times conservative travel time)

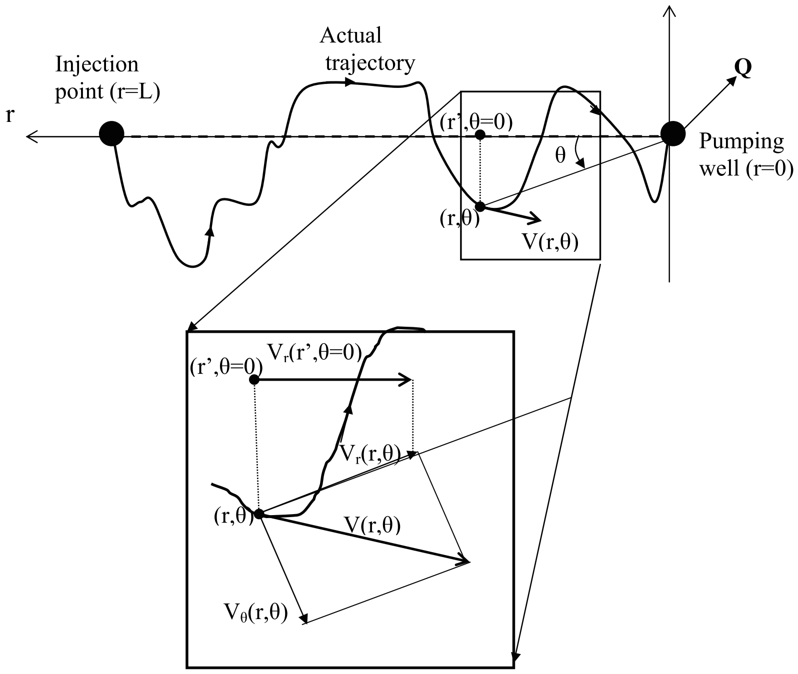

Figure 1. Conceptual sketch for solute transport along a streamline under convergent flow conditions. Water is pumped at a rate Q at r = 0, and the solute is injected at r = L. The mean trajectory is the one corresponding to the straight line (dashed line), but the actual trajectory is tortuous (solid line). The main approximation used to develop the results from example 1 is to consider that $V_r(\eta') \equiv V_r(r, \theta)$ is equivalent to $V_r(r', \theta = 0)$.

and ψ, and their cross-variance. τ and ψ must be evaluated numerically in most cases, but in some cases we may obtain analytical approximations using low-order expansions of the Lagrangian quantities, as shown in the next example.

3.1.2. Radial Flow Example

[26] This example is an extension of the study of transport of a conservative solute under radial flow conditions from *Riva et al.* [1999]. In that paper the authors performed several sets of Monte Carlo simulations for convergent flow in heterogeneous media with no background flow. Travel time statistics for a conservative solute were computed for different values of aquifer porosity ϕ, pumping rate (Q [$L^3 T^{-1}$]), and log-hydraulic conductivity variance σ_Y^2, with Y = log-K.

[27] To compute low-order approximations of the integrals that appear in (12) it is convenient to project all quantities (velocity and distribution coefficient) along the mean trajectory. This is sketched in Figure 1 for convergent flow conditions. This type of projection is equivalent to neglecting the tangential component of the local velocity. The normalized radial velocity is expressed as the sum of its mean value $\overline{V}(r)$ (radial), plus the residual, $V'(r)$. An expression for $\overline{V}(r)$, under the assumption that the aquifer saturated thickness (b) is much larger than the vertical integral scale for Y, is provided by *Indelman and Dagan* [1999]:

$$V(r) = -\frac{\overline{Q}}{2\pi\phi}\frac{1}{r} + V'(r), \qquad (13)$$

where we use the normalized variables from *Riva et al.* [1999], that is velocities are normalized by K_G [LT^{-1}], which is the geometric mean of the hydraulic conductivity values. All distances are normalized by I, and the (dimensionless) pump rate, $\overline{Q}$, is given as $\bar{Q} = \frac{Q}{bIK_G}$. Substituting (13) into (12), expanding the different terms and retaining only the terms up to second order, the final equations for the travel time moments for a reactive solute under convergent flow conditions are obtained. The final expressions as well as the main steps of the derivation are outlined in Appendix A. The resulting expressions are written in terms of the travel time moments for a conservative solute, with a few additional terms. These terms include integrals of the covariances and cross-covariances of the velocity and the distribution coefficient. Expressions for the covariance of velocity for radial flow conditions are available in the literature [*Fiori et al.*, 1998] but not in a close form.

[28] Let us particularize the general expressions given in (12) to the case where fluid velocity and the distribution coefficient are statistically independent. Then the travel time moments for a particle to travel from a point located initially at distance L and traveling toward the well are (see Appendix A):

$$\left\langle \tau^{LIE}(L) \right\rangle = \langle R \rangle \left\langle \tau^{NR}(L) \right\rangle, \qquad (14a)$$

$$\sigma_\tau^{2,LIE}(L) = \langle R \rangle^2 \sigma_\tau^{2,NR}(L) + \left(\frac{2\pi\rho_b}{\overline{Q}}\right)^2 \int_0^L \int_0^L r'r''\langle K_d'(r')K_d'(r'')\rangle dr'dr''. \qquad (14b)$$

[29] In the expression for the mean travel time now $\Psi = 0$ due to the independence between K and K_d. For the dimensionless variance we get a first term that accounts for the variance for the conservative solute times the mean

retardation factor squared plus an additional term due to the heterogeneity in K_d. This second term in (14b) can be shown to be positive for any given covariance model. Therefore the heterogeneity in K_d increases the variance of travel time, indicating the increase in uncertainty in the actual travel time for a single solute particle.

[30] Equation (14b) can be evaluated analytically for a given autocorrelation function for K_d. Based on the work by *Allen-King et al.* [1998], we assume K_d is lognormal and select an exponential isotropic model for the autocovariance. Denoting $K_{d,G}$ as the geometric mean of the K_d values, we can write $\langle K'_d(r')K'_d(r'')\rangle = K^2_{d,G}\,\sigma^2_{\ln\ kd}\exp(-|r' - r''|/I_k)$, with $\sigma^2_{\ln\ kd}$ the variance of log-K_d, and I_k its integral scale. Finally, the double integral in (14b) becomes:

$$\int_0^L\int_0^L r'r''\langle K'_d(r')K'_d(r'')\rangle dr'dr'' = 2K^2_{d,G}\,\sigma^2_{\ln kd}\left(\frac{L^3I_k}{3} + I_k^4 - \frac{L^2I_k^2}{2} - I_k^4\exp(-L/I_k) - LI_k^3\exp(-L/I_k)\right), \tag{15}$$

where again all distances are normalized by some characteristic distance I. We evaluate now the relative impact of the term given in (15) on the travel time variance. We select one of the set of simulations from *Riva et al.* [1999], with $\overline{Q} = 14.4$ and $\phi = 0.3$. Travel times for this simulation are given in Figure 8 from *Riva et al.* [1999] as travel time probabilities and as a function of distance, from where it is possible to approximate the travel time cdf for a conservative solute. Therefore the data allows getting an estimation of the travel time moments for different travel distances and σ^2_Y values. We consider some additional parameters to characterize the properties of the sorbing solute: $\rho_b = 1.8$ T/m^3; $\langle K_d\rangle = 0.20$ m^3/T; $\sigma^2_{\ln\ kd} = 1$; $I_k = I$, and assume statistical independence between hydraulic conductivity and distribution coefficient. With these values $\langle R\rangle = 2.2$ and $K_{d,G} = \exp(\ln\langle K_d\rangle - \frac{\sigma^2_{\ln kd}}{2}) = 0.121$.

[31] In Figure 2 we present the variance of normalized travel time for a sorbing solute versus normalized distance in this example. *Riva et al.* [1999] show that the first term in (14b) is proportional to σ^2_Y, while from (15) we see that the second term in (14b) is proportional to $\sigma^2_{\ln\ kd}$ (and independent of σ^2_Y). From the plot, the total variance increases with distance as $L^{3.5}$, which is also true for the conservative case.

3.2. Application to First-Order Kinetics (KIN)

3.2.1. General Solution

[32] In the general formulation (section 2), the first-order kinetics model is equivalent to considering again $\beta_{tot}(\eta) = \frac{\rho_b}{\phi}K_d(\eta)$, and $p(\alpha, \eta) = \delta(\alpha - k_2)$ (similar to the LIE model), but now assuming k_2 is a finite value. Thus from (4), $h(\eta, s) = \frac{\rho_b}{\phi}\frac{K_d(\eta)k_2(\eta)}{s+k_2(\eta)}$, and therefore contrary to the LIE model, h is a function of s. After some manipulation the travel time moments become:

$$\left\langle\tau^{KIN}(L)\right\rangle = \langle R\rangle\left\langle\tau^{NR}(L)\right\rangle + \frac{\rho_b}{\phi}\left\langle\int_0^{\eta(L)}\frac{K'_d(\eta')}{V(\eta')}d\eta'\right\rangle, \tag{16a}$$

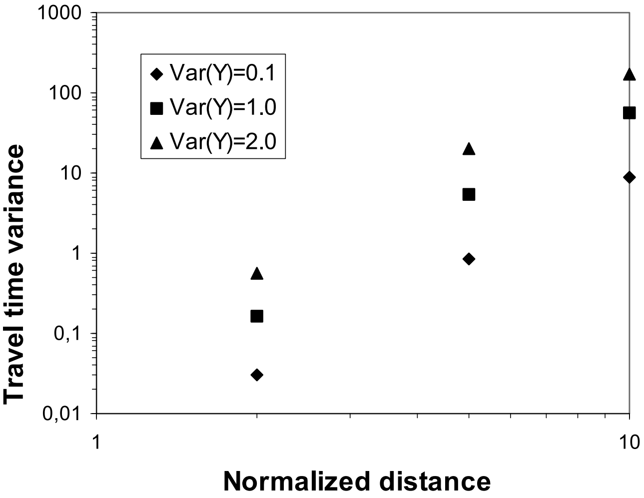

Figure 2. Variance of travel time as a function of normalized distance for a sorbing solute under convergent flow conditions (equation 14b) for different values of the variance of Y (σ^2_Y). The sorption model is that of linear instantaneous equilibrium. Data for the conservative solute was extracted from *Riva et al.* [1999]. Values for the different parameters can be found in the text.

$$\sigma^{2,KIN}_\tau(L) = \langle R\rangle^2\sigma^{2,NR}_\tau(L) + 2\langle R\rangle\sigma^{KIN}_{\tau\psi}(L,0) + \sigma^{2,KIN}_\psi(L,0) + 2\frac{\rho_b}{\phi}\left\langle\int_0^{\eta(L)}\frac{K_d(\eta')}{k_2(\eta')}\frac{d\eta'}{V(\eta')}\right\rangle. \tag{16b}$$

[33] The mean travel time (equation 16a) corresponds exactly to that of the LIE case. The consequence is that even though sorption is not instantaneous, on average the solute spends the same amount of time sorbed as in the LIE case. In the expression for the dimensionless travel time variance (16b), there is an additional term compared to (12b). This term, which incorporates the effect of k_2, is always positive. Due to the normalization process (see section 2.1), k_2 (dimensionless) corresponds to Damköhler number I (D_I), that is the ratio between the scale of the reaction process and the advective velocity [e.g., *Domenico and Schwartz*, 1990]. When $D_I = k_2 \to \infty$, mass transfer is instantaneous, the last term in (16b) becomes zero, and we recover the LIE case. At the other limit, $D_I \to 0$, advection is dominant and thus any particle that is adsorbed stays sorbed a relatively very large time, enhancing tailing. *Cunningham* [1999] compared terms similar to those in (16b) to define a criterion for the relative importance of sorption kinetics in plume spread.

[34] The last term in (16b) involves three parameters: the two corresponding to the sorption model plus the velocity. Thus an additional hypothesis should be made regarding the three parameters cross correlations in order to get analytical or numerical results for $\sigma^{2,KIN}_\tau(L)$.

[35] Both $\sigma^{KIN}_{\tau\psi}(L, s)$ and $\sigma^{2,KIN}_\psi(L, s)$ are functions of s, but in (16b) both terms are evaluated at s = 0, leading to the same expressions as for the LIE model; that is $\sigma^{KIN}_{\tau\psi}(L, 0) = \sigma^{LIE}_{\tau\psi}(L, 0)$ and $\sigma^{2,KIN}_\psi(L, 0) = \sigma^{2,LIE}_\psi(L, 0)$. This can be useful in some situations. If these terms have been evaluated (analytical or numerically) for a certain flow configuration

assuming LIE, the values obtained can be transferred directly to a similar problem with the same flow configuration but using the KIN model.

3.2.2. Uniform in the Average Flow Example

[36] This second example corresponds to reactive transport in a uniform in the average flow field. The goal is to get analytical expressions for the mean and variance of travel time (equations 16a and 16b) for two- and three-dimensional heterogeneous domains and to compare the results with those in the literature. The initial step is to write the velocity as the sum of the expected value (constant, as opposed to the radial flow case) plus a perturbation ($V_1(x', y', z') = U_1 + V_1'(x', y', z')$). The mean travel time for a conservative solute is given by *Rajaram* [1997] (his equation 31):

$$\langle \tau^{NR}(L)\rangle = \frac{1}{U_1}\int_0^L \left(1+\frac{C_{V_1V_1}(x',0,0)}{U_1^2}\right)dx', \qquad (17)$$

with $C_{V_1}V_1(x', 0, 0)$ the covariance of velocities at a lag distance x' along the mean trajectory (x being the mean flow direction). Rajaram's formulation accounts for a non linear relation between mean travel time and travel distance, found in the numerical works of *Selroos and Cvetkovic* [1992] and *Cvetkovic et al.* [1996]. This nonlinearity is found whenever uniform resident injection conditions are considered [*Demmy et al.*, 1999].

[37] To obtain approximations of the remaining terms in (16) we need expanding $\tau^{NR}(L)$ and $\psi(L, s)$ up to second order in perturbations. Following *Cvetkovic et al.* [1998], we substitute the velocity perturbation at the actual location by the one at the projection point $V_1'(x', y', z') \approx V_1'(x', 0, 0)$. Similarly, we consider $K_d(x', y', z') \approx Kd(x', 0, 0)$, so that:

$$\begin{aligned}\tau^{NR}(L) &\approx \int_0^L \frac{dx'}{U_1+V_1'(x',0,0)}\\ &= \frac{1}{U_1}\int_0^L\left(1-\frac{V_1'(x',0,0)}{U_1}+\frac{V_1'^2(x',0,0)}{U_1^2}-\ldots\right)dx', \qquad (18a)\end{aligned}$$

$$\begin{aligned}\psi(L,s) &\approx \frac{\rho_b}{\phi}\int_0^L \frac{K_d'(x',0,0)}{V_1(x',0,0)}dx'\\ &\approx \frac{\rho_b}{\phi}\frac{1}{U_1}\int_0^L K_d'(x',0,0)\left(1-\frac{V_1'(x',0,0)}{U_1}+\ldots\right)dx'. \qquad (18b)\end{aligned}$$

[38] From here the resulting expressions for the various terms that appear in (16) become:

$$\sigma_\tau^{2,NR}(L) = \frac{1}{U_1^2}\int_0^L\int_0^L C_{V_1V_1}(x',x'')dx'dx'', \qquad (19a)$$

$$\Psi(L,0) = -\frac{\rho_b}{\phi}\frac{1}{U_1^2}\int_0^L C_{K_dV_1}(x',x')dx', \qquad (19b)$$

$$\sigma_{\tau\psi}^{LIE}(L,0) = -\frac{\rho_b}{\phi}\frac{1}{U_1^3}\int_0^L\int_0^L C_{K_dV_1}(x',x'')dx'dx'', \qquad (19c)$$

$$\sigma_\psi^{2,LIE}(L,0) = \left(\frac{\rho_b}{\phi}\right)^2\frac{1}{U_1^2}\int_0^L\int_0^L C_{K_dK_d}(x',x'')dx'dx'', \qquad (19d)$$

with $C_{V_1V_1}(x', x'') = \langle V_1'(x', 0, 0)V_1'(x'', 0, 0)\rangle$, $C_{K_dV_1}(x', x'') = \langle K_d'(x', 0, 0)V_1'(x'', 0, 0)\rangle$and $C_{K_dK_d}(x', x'') = \langle K_d'(x', 0, 0)K_d'(x'', 0, 0)\rangle$. To get close-form expressions for the different terms in (19) plus some additional terms in (16b) we need to specify a correlation model for K_d, and the cross-correlation models for K_d, k_2, and Y.

[39] *Robin et al.* [1991] proposed a lognormal distribution for K_d of the type:

$$K_d = K_{d,G}\exp(\beta Y' + W), \qquad (20)$$

with $Y' = Y - \langle Y\rangle$, and $\beta \in [-1, 1]$ is a measure of the degree of correlation between K_d and Y. Negative β implies negative correlation; that is, the solute is less retarded in high conductive zones, and more retarded in low conductive areas. The opposite holds for positive β. In this expression W is a zero-mean Gaussian random process $W = N(0, \sigma_W^2)$ independent of Y, intended to introduce imperfect correlation between K_d and Y. Finally, k_2 is considered uncorrelated to either Y or W (as suggested by *Hu et al.* [1995]). From these correlation models, the different terms in (16) can be computed, provided the correlation structure of Y is defined. The computations are carried out in Appendix B for an isotropic exponential correlation structure in a three-dimensional domain, and in Appendix C for the two-dimensional case. The resulting expressions are similar to those obtained by *Cvetkovic et al.* [1998], except for three things: (1) we consider $I_W \neq I_Y$; (2) these authors use an expression for $\langle\tau^{NR}(L)\rangle$ which is different from (17); and (3) they set the simplification $\Psi = 0$, while we evaluate this term for both the isotropic 3-D model (equation B6) and the isotropic 2-D model (equation C3). Actually Ψ provides a contribution which is $O(\sigma_Y^2)$, and therefore should not be discarded in a consistent second-order perturbation expansion.

[40] In both cases the resulting expressions for $\langle\tau^{LIE}(L)\rangle$ depend on four parameters ($K_{d,G}$, β, σ_Y^2, σ_W^2), while $\sigma_\tau^{2,LIE}(L)$ depends also on $\langle k_2^{-1}\rangle$ and the ratio I_W/I_Y. The dependence of $\langle\tau^{LIE}(L)\rangle$ on β can be seen in Figure 3 (Figures 3 to 7 correspond to the isotropic three-dimensional case, but a 2-D study would lead to similar plots). From Figure 3, negative correlation between K_d and Y ($\beta < 0$) results in larger travel time for a reactive solute compared to the noncorrelated case ($\beta = 0$). On the contrary, positive correlation ($\beta > 0$) has a smaller influence and the results are closer to the uncorrelated ($\beta = 0$) case. The reason is that on one hand positive correlation tends to retard the mean movement, while on the other hand a larger β value results in a larger $\langle K_d\rangle$ value (with remaining parameters constant). Therefore the minimum is not attained at $\beta = 1$, but at some different value which actually depends on σ_W^2.

[41] Both σ_Y^2 and σ_W^2 have strong effects on the mean travel time. In Figure 4 we plot mean travel time versus distance for different values of the two variances, with constant $\beta = -0.5$. From Figure 4, the mean travel time increases with either σ_Y^2 or σ_W^2. The last parameter to consider is $K_{d,G}$; the larger it is, the more significant the retardation.

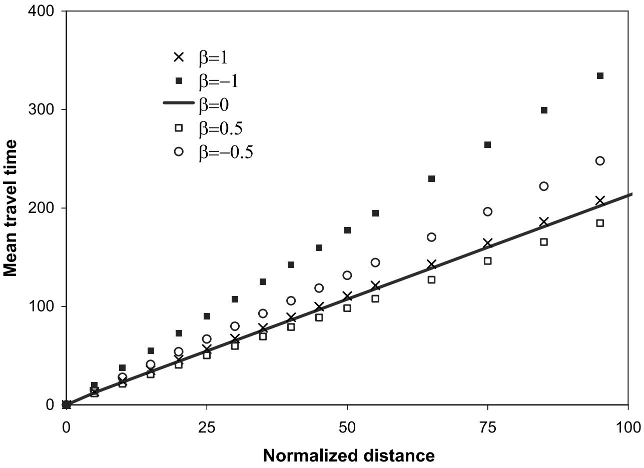

Figure 3. Influence of the degree of correlation between hydrogeological and chemical parameters (β) on mean travel time. The remaining parameters are held constant ($\rho_b K_{d,G}/\phi = 1$; $\sigma_Y^2 = 1$; $\sigma_W^2 = 0.2$; $I_W/I_Y = 1$).

[42] Similar analysis can be done with respect to the travel time variance. Regarding the dependence of $\sigma_\tau^{2,\mathrm{LIE}}(L)$ with β (see Figure 5), negative correlation between K_d and Y results in larger variance (as compared to the uncorrelated case), and contrariwise (this result was already found by *Bellin and Rinaldo* [1995]). The largest variance is obtained for $\beta = -1$ (maximum negative correlation), but the minimum is not obtained for $\beta = +1$ (maximum positive correlation). This result is independent on the choice of additional sorption parameters.

[43] The full expression for the variance of travel time obtained from (16) is given as a sum of terms that are linear in σ_Y^2, plus some additional terms linear in σ_W^2. As a consequence the variance of travel time increases when either of the variances of Y and W do so (Figure 6). On the contrary, the influence of the ratio between I_W/I_Y is not significant, as shown in Figure 7.

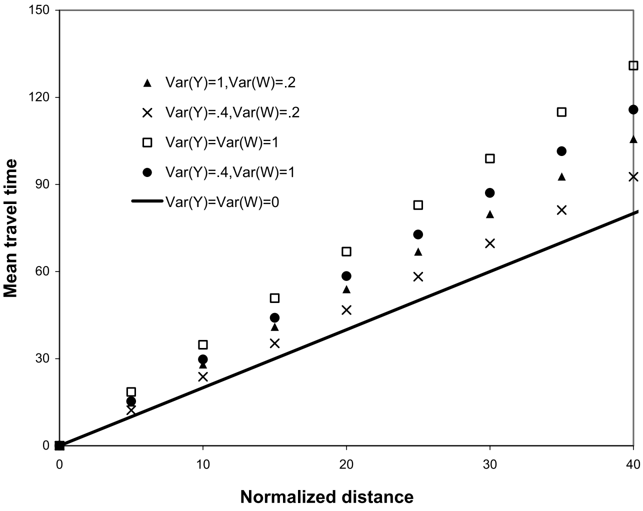

Figure 4. Mean travel time versus distance for different values of the variances of Y and W. Additional parameters are $\rho_b K_{d,G}/\phi = 1$; $I_W/I_Y = 1$; $\beta = 0.5$. The case $\sigma_Y^2 = \sigma_W^2 = 0$ corresponds to a homogeneous aquifer with homogeneous distribution parameter K_d and $\rho_b K_d/\phi = 1$; therefore $\langle \tau^{\mathrm{LIE}}(L)\rangle = 2\,\langle \tau^{\mathrm{NR}}(L)\rangle$.

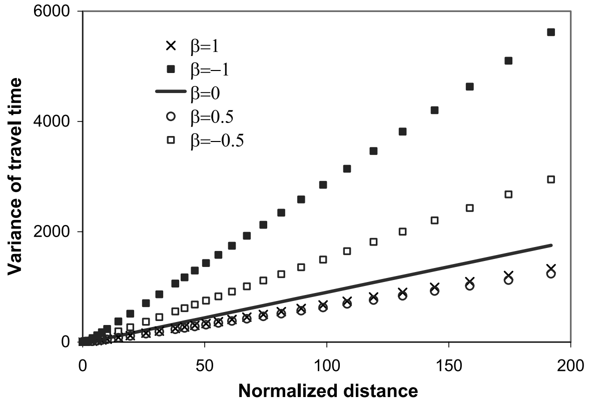

Figure 5. Influence of the degree of correlation between the hydrogeological and the chemical parameters β on the variance of travel time. Additional parameters are $\rho_b K_{d,G}/\phi = 1$; $\sigma_Y^2 = 1$; $\sigma_W^2 = 0.2$; $I_W/I_Y = 1$; $\langle k_2^{-1}\rangle = 0$.

3.3. Application to Other Continuous and Noncontinuous Sorption Models

[44] For other sorption models it would be enough to define the $p(\alpha)$ function, use equation (3) to derive the $h(\eta, s)$ function and find the moments of travel time from (10). *Lawrence et al.* [2002] provide the $h(\eta, s)$ function for two additional continuous sorption models such as the lognormal or the gamma models. In some sorption models $p(\alpha)$ is not a continuous function but an infinite summation of weighted Dirac functions.

[45] An alternative to this approach is to define directly the $h(\eta, s)$ function based on its physical meaning (the ratio between the Laplace transforms of the immobile and mobile concentrations). This approach has been taken, for example, by *Sardin et al.* [1991] or *Harvey and Gorelick* [1995] to account for diffusion into grains, aggregates, and immobile

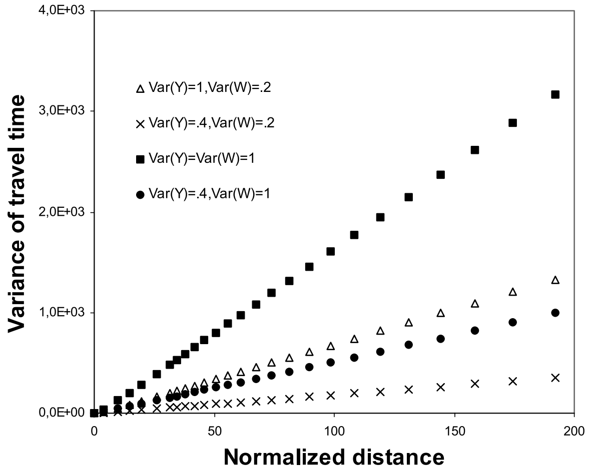

Figure 6. Variance of travel time for different values of the variances of Y and W. Additional parameters are $\rho_b K_{d,G}/\phi = 1$; $I_W/I_Y = 1$; $\beta = 1$; $\langle k_2^{-1}\rangle = 0$.

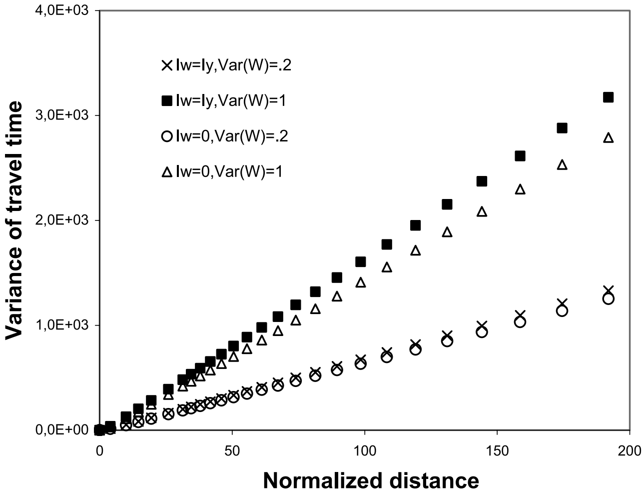

Figure 7. Influence of the integral distance ratio I_W/I_Y on the travel time variance for two different values of σ_W^2. Additional parameters are $\rho_b K_{d,G}/\phi = 1$; $\sigma_Y^2 = 1$; $\beta = 1$; $\langle k_2^{-1}\rangle = 0$.

regions and by *Rubin et al.* [1997] for the two-site kinetic model.

4. Conditional Temporal Moments

4.1. General Equations

[46] One of the important characteristics of the methodology presented in this paper is that the travel time moments for sorbing solutes can be directly conditioned to all available hard measurements, such as hydraulic conductivity values, heads, velocities or mass transfer parameters, or on soft information, such as geophysical data. One advantage of conditioning is the reduction in uncertainty, which has been demonstrated in several examples [e.g., *Rubin*, 1991; *Harvey and Gorelick*, 1995].

[47] Let us consider first a conservative solute. The conditional temporal moments for this case can be derived from the conditional cdf of τ, $G^C(L, \tau)$, which in itself can be obtained from the unconditional one ($G(L, \tau)$) using Bayesian principles [*Rubin and Dagan*, 1992]. Then, the ith-order conditional temporal moments is given by (similarly to 11):

$$\left\langle \tau^i(L)\right\rangle^C = \int_0^\infty i\tau^{i-1}\left(1 - G^C(L,\tau)\right)d\tau. \tag{21}$$

[48] From the approach presented in this paper it is possible to write an immediate extension of (9) for the conditional moments of travel time for a sorbing solute, which will be given as:

$$\left\langle \tau^R(L)\right\rangle^C = \left\langle \tau^{NR}(L)\right\rangle^C(1 + H(0)) + \Psi^C(L,0), \tag{22a}$$

$$\begin{aligned}\sigma_\tau^{2,R,C}(L) &= (1 + H(0))^2\sigma_\tau^{2,NR,C}(L) + 2(1 + H(0))\sigma_{\tau\psi}^C(L,0)\\ &\quad + \sigma_\psi^{2,C}(L,0) - 2\left\langle \tau^{NR}(L)\right\rangle^C \frac{dH(s)}{ds}\bigg|_{s=0}\\ &\quad - 2\frac{d\Psi^C(L,s)}{ds}\bigg|_{s=0}.\end{aligned} \tag{22b}$$

where the superscript C stands for conditional values. Therefore the conditional temporal moments for a sorbing solute are given in terms of those for a conservative solute (given by 21), the unconditional mean retardation coefficient ($1 + H(0)$), the conditional mean and variance of Ψ, and the conditional cross-variance of τ and ψ. All these terms could be evaluated numerically in any given case.

[49] It is important to note that the travel time variance represents both the variability between realizations due to uncertainty in the hydraulic conductivity and/or the sorption parameters, and the actual spread due to kinetic sorption, which is present in every single realization. Therefore even in the case of perfect knowledge of the heterogeneous fields (total conditioning) the variance of travel time would not be zero.

4.2. A Simplified Example on the Importance of Conditioning

[50] For illustrative purposes let us consider a simple example of radial flow in a homogeneous conductivity field. The sorption model selected is first-order kinetics (KIN), with heterogeneous distribution coefficient and reaction rate. An immediate consequence of the homogeneity in K is the independence between velocities and the sorption parameters. The solute is injected at a certain normalized distance from the well, L, the well is of negligible radius and pumps at a constant rate $\overline{Q}$ (defined as in section 3.1).

[51] Due to the homogeneity of the K field, the unconditional and conditional expectations of the travel time for a nonreactive solute are identical, and are given by: $\langle\tau^{NR}(L)\rangle^C = \pi\phi L^2/\overline{Q}$, with no uncertainty ($\sigma_\tau^{2,NR,C}(L) = 0$). From (22a), the expression for the mean travel time is:

$$\left\langle \tau^{KIN}(L)\right\rangle^C = \left(1 + \frac{\rho_b}{\phi}\langle K_d\rangle\right)\frac{\pi\phi L^2}{\overline{Q}} + \frac{2\pi\rho_b}{\overline{Q}}\int_0^L r\left\langle K_d'(r)\right\rangle^C dr. \tag{23}$$

[52] The first term corresponds to the travel time for a conservative solute times the mean retardation factor. The second term is the correction due to the variations in the conditional mean along the trajectory. As the unconditional expectation $\langle K_d'(r)\rangle$ is equal to zero, the contribution of the integral in (23) extends only to the places where conditional expectations differ from the unconditional ones (that would be a function of the integral distances of the conditioning parameters). If the K_d' values measured along the trajectory are mostly positive this last term will also be positive and an additional retardation in $\langle\tau^{KIN}(L)\rangle^C$ is expected.

[53] A point should be made whether the location of the measurement points with respect to the well location has any influence upon the mean travel time. To illustrate this point, let us consider a single measurement of K_d for conditioning. We select the variogram for K_d to be isotropic exponential, with unit integral distance (as we use the integral distance for K_d as the normalizing distance) and we assume $L > 1$. We consider two cases: conditioning at the well, and conditioning upon a measurement taken at the injection point. For the first case and after performing

kriging we get $\langle K'_d(r)\rangle^C = \exp(-r)K'_d(0)$. Introducing this expression in (23) we finally get:

$$\left\langle \tau^{KIN}(L)\right\rangle^C = \langle R\rangle\tau(L) + \frac{2\pi\rho_b}{\overline{Q}}\left(1-(1+L)e^{-L}\right)K'_d(0). \qquad (24a)$$

[54] If the injection point value is used for conditioning $\langle K'_d(r)\rangle^C = \exp(-(L-r))K'_d(L)$, and:

$$\left\langle \tau^{KIN}(L)\right\rangle^C = \langle R\rangle\tau(L) + \frac{2\pi\rho_b}{\overline{Q}}\left(L-1+e^{-L}\right)K'_d(L). \qquad (24b)$$

[55] From (24a) and (24b) the effect of the measurement on the conditional mean travel time is quite different depending on the measurement point location. In fact, for any given value of L (with $L > 1$), the term in brackets in (24b) is always larger than that in (24a). Therefore it follows that the effect of conditioning is stronger when data are taken far from the well. The reason is that as flow is convergent, velocities are higher close to the well. On the other hand, travel time is an integration of the inverse of velocities along the trajectory, and therefore lower velocities have a larger impact on travel time. If retardation were enhanced at the low velocity points a very significant retarding effect would arise, which would be larger than an enhanced value of retardation near the well. This effect could be of importance when selecting or designing a monitoring network.

[56] Finally, as $\langle K'_d(r)\rangle^C \geq -\langle K_d\rangle$ due to physical considerations ($K_d \geq 0$ at every point), it can be shown from (23) that $\langle\tau^{KIN}(L)\rangle^C \geq \langle\tau^{NR}(L)\rangle^C$.

[57] Next, we analyze the travel time variance. In the example presented here $\sigma_{\tau\psi}^{KIN} \equiv 0$ and therefore from (22b) (and after some manipulation), the variance of travel time at the well is:

$$\sigma_\tau^{2,KIN,C}(L) = \left(\frac{\rho_b}{\phi}\right)^2 \int_0^L\int_0^L \frac{1}{V(r')V(r'')}\left\langle K'_d(r')K'_d(r'')\right\rangle^C dr'dr''$$
$$+\frac{2\rho_b}{\phi}\int_0^L \frac{1}{V(r)}\left\langle\frac{K_d}{k_2}(r)\right\rangle^C dr \qquad (25)$$

where the conditional terms would normally be evaluated numerically.

5. Additional Discussion

[58] From (10a) and (4) the mean travel time can be written as:

$$\left\langle\tau^R(L)\right\rangle = \langle R\rangle\left\langle\tau^{NR}(L)\right\rangle + \left\langle\int_0^{\eta(L)}\frac{\beta'_{tot}(\eta')}{V(\eta')}d\eta'\right\rangle. \qquad (26)$$

[59] In summary, the normalized mean travel time for the reactive solute depends on the mean travel time for a conservative solute, the mean retardation, and the expected value of a Lagrangian variable that incorporates the residuals of the total capacity factor, weighted by the inverse local velocity and integrated along the trajectory. This result does not depend on the sorption model, but only on the spatial distribution of the surface available for sorption. The last term in (26) will generally be evaluated numerically, but in the paper we present the analytical expressions for purely convergent and uniform in the mean flow conditions (common flow configurations in tracer tests).

[60] Defining two auxiliary functions: $\xi(\eta, s) = (1 + H(s))\tau(\eta) + \psi(\eta, s)$ and $\zeta(\eta) = \xi(\eta, 0)$, the variance of travel time (10b) can be written in a very concise form:

$$\sigma_\tau^{2,R}(L) = \sigma_\zeta^2(L) - 2\left.\frac{d\langle\xi\rangle}{ds}\right|_{s=0}. \qquad (27)$$

[61] The first term in (27) is the variance of the Lagrangian quantity ζ. This quantity incorporates the conservative travel time retarded by a mean time-independent retardation value, plus the integral along the trajectory of the residuals of the total capacity factor, weighted by the inverse local velocity. The second term in (27) can be written as

$$-2\left.\frac{d\langle\xi\rangle}{ds}\right|_{s=0} = 2\left\langle\int_0^{\eta(L)}\frac{\beta_{tot}(\eta')}{V(\eta')}\cdot\left[\int_0^\infty\frac{p(\alpha,\eta')}{\alpha}d\alpha\right]d\eta'\right\rangle, \qquad (28)$$

and therefore depends on the sorption model selected. In the LIE model this term becomes identically zero, but in other models it may be significant. Actually, there is a common model in the desorption literature where (28) becomes infinity. This corresponds to the so-called gamma model [*Connaughton et al.*, 1993; *Pedit and Miller*, 1994; *Chen and Wagenet*, 1995; *Culver et al.*, 1997; *Deitsch et al.*, 2000], where $p(\alpha) = \frac{\alpha^{a-1}}{b^a\Gamma(a)}\exp\left(-\frac{\alpha}{b}\right)$ (a, b are model parameters and Γ corresponds to the gamma function). As a consequence in this model the variance travel time for a reactive solute is unbounded. This result has also been found by *Cvetkovic and Haggerty* [2003] using an alternative way which does not need the definition of $h(\eta, s)$.

6. Conclusions

[62] We present a concise and integrated methodology for evaluating the moments of travel time for a solute that undergoes mass transfer rate-limited linear sorption processes. The methodology accounts for heterogeneous media in the sense that hydraulic conductivity is a spatially randomly variable. It also accounts for heterogeneity in the parameters characterizing the sorbing behavior. The methodology has been developed for a general sorption model that accounts for a continuous of mass transfer rates at any given point [*Haggerty and Gorelick*, 1998]. A wide range of mass transfer rate-limited linear processes, such as instantaneous equilibrium, first-order sorption kinetics, or diffusion into different element shapes can be considered particular cases of the general model.

[63] One of the novel contributions of the methodology presented in this paper is that it can be applied for any flow configuration. While the general expressions are written in integral form, close-form results can be derived for different flow configurations, such as convergent flow and parallel mean flow using a perturbations approach. In the former type of flow, and under some simplifications, the travel time

moments computed using perturbations agree with those from *Cvetkovic et al.* [1998].

[64] Another advantage of the method is the possibility of considering unconditional and conditional statistical moments in a unified framework. The influence of conditioning has been addressed in an example, which consists of convergent flow in a hydraulically homogeneous 2-D aquifer. In this case we have found that the conditional expected travel time is mostly influenced by measurements taken far from the well. In the parallel flow case all independent measurements would have the same effect on travel time, as the unconditional mean velocity is uniform throughout the domain.

Appendix A: Close-Form Expressions for the Temporal Moments in the Radial Flow Example

[65] This Appendix is devoted to develop some of the analytical expressions that lead to equations (14a) and (14b). From (13), the inverse of velocity will be given approximately by:

$$\frac{1}{V(r)} = \frac{1}{\overline{V}(r)} \frac{1}{\left(1+V'(r)/\overline{V}(r)\right)} \approx \frac{1}{\overline{V}(r)}\left(1-\frac{V'(r)}{\overline{V}(r)}+\frac{V'^2(r)}{\overline{V}^2(r)}\right). \tag{A1}$$

[66] In the expression for the mean travel time (12a) it is necessary to evaluate the term $\Psi(L, 0)$. Using (A1), and keeping only the terms up to second order:

$$\begin{aligned}\Psi(L,0) &= \frac{\rho_b}{\phi}\left\langle \int_0^{\eta(L)} \frac{K_d'(\eta')}{V(\eta')}d\eta' \right\rangle \\ &\approx \frac{2\pi\rho_b}{\overline{Q}} \int_L^0 r'\left\langle K_d'(r')\left(1-\frac{V'(r')}{\overline{V}(r')}+\ldots\right)\right\rangle dr' \\ &= \frac{2\pi\rho_b}{\overline{Q}} \int_0^L r'\left\langle K_d'(r')\frac{V'(r')}{\overline{V}(r')}\right\rangle dr' \\ &= -\frac{4\pi^2\phi\rho_b}{\overline{Q}^2}\int_0^L r'^2\langle K_d'(r')V'(r')\rangle dr' \end{aligned} \tag{A2}$$

[67] For the travel time variance (12b) we need to develop the expressions for $\sigma_{\tau\psi}^{LIE}(L, 0)$ and $\sigma_{\psi}^{2,LIE}(L, 0)$:

$$\begin{aligned}\sigma_{\tau\psi}^{LIE}(L,0) &= \frac{-\rho_b}{\phi}\left\langle \int_0^{\eta(L)} \frac{V'(\eta')}{\overline{V}^2(\eta')}d\eta' \int_0^{\eta(L)} \frac{K_d'(\eta')}{V(\eta')}d\eta' \right\rangle \\ &\approx -\frac{\rho_b}{\phi}\int_0^L\int_0^L \left\langle \frac{K_d'(r')}{\overline{V}(r')}\frac{V'(r'')}{\overline{V}^2(r'')}\right\rangle dr'dr'' \\ &= -\frac{\rho_b}{\phi}\left(\frac{2\pi\phi}{\overline{Q}}\right)^3 \int_0^L\int_0^L r'r''^2\langle K_d'(r')V'(r'')\rangle dr'dr'' \end{aligned} \tag{A3}$$

$$\begin{aligned}\sigma_{\psi}^{2,LIE}(L,0) &= \frac{\rho_b^2}{\phi^2}\left\langle \int_0^{\eta(L)} \frac{K_d'(\eta')}{V(\eta')}d\eta' \int_0^{\eta(L)} \frac{K_d'(\eta')}{V(\eta')}d\eta' \right\rangle \\ &= \left(\frac{2\pi\rho_b}{\overline{Q}}\right)^2 \int_0^L\int_0^L r'r''\langle K_d'(r')K_d'(r'')\rangle dr'dr'' \end{aligned} \tag{A4}$$

[68] In the particular case used in the body of the text, K_d and V are uncorrelated. Then both the expressions in (A2) and (A3) are equal to zero, and we get the final expressions in (14).

Appendix B: Close-Form Expressions for the Temporal Moments in 3-D Domains

[69] The first step in the derivation is writing the covariance functions involving K_d in terms of covariances involving Y and W. Expanding the exponential in (20) and subtracting the expected values we get to first-order $K_d' = K_{d,G}(\beta Y' + W')$ and therefore

$$\langle K_d\rangle = K_{d,G}\exp\left(\frac{\beta^2\sigma_Y^2}{2}\right)\exp\left(\frac{\sigma_W^2}{2}\right). \tag{B1}$$

[70] Furthermore, as $\langle V_1'W'\rangle = \langle Y'W'\rangle = 0$, we have $\langle V_1'K_d'\rangle = K_{d,G}(\beta\langle Y'V_1'\rangle)$ and $\langle K_d'K_d'\rangle = K_{d,G}^2(\beta^2\langle Y'Y'\rangle + \langle W'W'\rangle)$. The next step is to select a covariance model for Y and W. A most common model for Y is the exponential model, where the covariance of Y is given by $\langle Y'(\mathbf{x}')\,Y'(\mathbf{x}'')\rangle = \sigma_Y^2\exp(-|\mathbf{x}' - \mathbf{x}''|)$ with $\mathbf{x}$, $\mathbf{x}'$ already normalized by the integral distance I_Y which would be the normalizing distance in this example. The normalizing velocity will be $\langle V\rangle$, which in this example is a constant value. Similarly, an exponential covariance model for W could also be considered, $C_W(\mathbf{x}'-\mathbf{x}'') = \sigma_W^2\exp\left(-|\mathbf{x}'-\mathbf{x}''|\frac{I_Y}{I_W}\right)$, where the integral distance for W (I_W) needs not necessarily be equal to I_Y.

[71] The only additional expression needed to evaluate the integrals in (19) is the cross correlation between V_1 and Y. For this particular configuration, in a three-dimensional isotropic domain, and up to first order in σ_Y^2 the solution is [*Zhang and Neuman*, 1992]

$$C_{YV_1}(\mathbf{x}',\mathbf{x}'') = \sigma_Y^2U_1\left(\frac{4}{r^3}+\exp(-r)\left(-\frac{2}{r}-\frac{4}{r^2}-\frac{4}{r^3}\right)\right), \quad \text{with } r = |\mathbf{x}'-\mathbf{x}''|. \tag{B2}$$

[72] By double integration and after some manipulation we get the expressions up to first order in σ_Y^2 and σ_W^2 for $\sigma_{\tau\psi}^{LIE}$ (equation 19c) and $\sigma_{\psi}^{2,LIE}$(19d):

$$\sigma_{\tau\psi}^{LIE}(L,0) = \frac{-1}{U_1^2}\frac{\rho_b}{\phi}K_{d,G}\sigma_Y^2\left[\frac{4}{L}(1-\exp(-L))+2L-4\right], \tag{B3}$$

$$\sigma_{\psi}^{2,LIE}(L,0) = 2\left(\frac{\rho_bK_{d,G}}{\phi U_1}\right)^2\left[\beta^2\sigma_Y^2(L-1+\exp(-L)) + \sigma_W^2\frac{I_w}{I_Y}\left(L+\frac{I_w}{I_Y}\left(\exp\left(-\frac{I_Y}{I_W}L\right)-1\right)\right)\right]. \tag{B4}$$

[73] The variance of the travel time for a conservative solute in a 3D isotropic domain can be obtained from (19a). *Cvetkovic et al.* [1996] provide the solution:

$$\sigma_{\tau}^{2,NR}(L) = \frac{1}{U_1^2}\sigma_Y^2\left[2L-\frac{16}{3}+\frac{8}{L}-\frac{16}{L^3}+16\left(\frac{1}{L^3}+\frac{1}{L^2}\right)\exp(-L)\right]. \tag{B5}$$

[74] Finally, the resulting expression for $\Psi(L, 0)$ and $\left\langle \int_0^{\eta(L)} \frac{K_d(\eta')}{k_2(\eta')} \frac{d\eta'}{V(\eta')} \right\rangle$, to second order in σ_Y, are:

$$\Psi(L, 0) = -\frac{\rho_b}{\phi} \frac{1}{U_1^2} \int_0^L C_{K_d V_1}(x', x') dx' = -\frac{2}{3} \frac{\rho_b K_{d,G} \beta L \sigma_Y^2}{\phi U_1}. \tag{B6}$$

$$\begin{aligned} \left\langle \int_0^{\eta(L)} \frac{K_d(\eta')}{k_2(\eta')} \frac{d\eta'}{V(\eta')} \right\rangle &= \langle k_2^{-1} \rangle \Bigg(\langle K_d \rangle \langle \tau^{NR}(L) \rangle \\ &\quad + \left\langle \int_0^{\eta(L)} \frac{K'_d(\eta')}{V(\eta')} d\eta' \right\rangle \Bigg) \\ &= \langle k_2^{-1} \rangle \left(\langle K_d \rangle \langle \tau^{NR}(L) \rangle - \frac{2 K_{d,G} \beta L \sigma_Y^2}{3 U_1} \right), \end{aligned} \tag{B7}$$

[75] The substitution of (B3) to (B7) into (16) provides close-form solutions for the first and second temporal moments of a reactive solute undergoing heterogeneous first-order sorption kinetics in a three dimensional statistically isotropic domain.

Appendix C: Close-Form Expressions for the Temporal Moments in 2-D Domains

[76] Some of the 3-D results are also valid for the 2-D case. In particular, $\sigma_\Psi^{2,LIE}$ (L, 0)and $\langle K_d \rangle$ remain the same. The expression for $\sigma_\tau^{2,NR}$ in an isotropic 2-D domain can be found in the work by *Sanchez-Vila* [1995] or *Cvetkovic et al.* [1996] and is given by

$$\begin{aligned} \sigma_\tau^{2,NR}(L) = \frac{3}{U_1^2} \sigma_Y^2 \bigg[&\frac{2}{3} L - \ln L + \frac{1}{2} - \gamma + Ei(-L) \\ &- \frac{1}{L^2} + \frac{(1+L)}{L^2} \exp(-L) \bigg], \end{aligned} \tag{C1}$$

γ being Euler's constant, and Ei(x) the exponential integral function. To get the additional terms in (12) we need the cross correlation between V_1 and Y. For uniform mean flow, in a two-dimensional isotropic domain, and up to second order in σ_Y, the solution is [*Rubin*, 1991]:

$$C_{YV_1}(\mathbf{x}', \mathbf{x}'') = \sigma_Y^2 U_1 \left(\frac{1}{r^2} - \exp(-r) \left(\frac{1}{r} + \frac{1}{r^2} \right) \right), \quad \text{with } r = |\mathbf{x}' - \mathbf{x}''|. \tag{C2}$$

[77] By integration and after some manipulation the different expressions in (16a) become, up to second order in σ_Y:

$$\Psi(L, 0) = -\frac{1}{2} \frac{\rho_b K_{d,G} \beta L \sigma_Y^2}{\phi U_1}, \tag{C3}$$

$$\sigma_{\tau\Psi}^{LIE}(L, 0) = \frac{-2\rho_b}{\phi U_1^2} K_{d,G} \sigma_Y^2 [L - E_1(L) - \ln L - \gamma], \tag{C4}$$

$$\left\langle \int_0^{\eta(L)} \frac{K_d(\eta')}{k_2(\eta')} \frac{d\eta'}{V(\eta')} \right\rangle = \langle k_2^{-1} \rangle \left(\langle K_d \rangle \langle \tau^{NR}(L) \rangle - \frac{K_{d,G} \beta L \sigma_Y^2}{2 U_1} \right), \tag{C5}$$

with $E_1(L) = \int_L^\infty \frac{e^{-t}}{t} dt.$ The substitution of (B4), (C1), (C3), (C4), and (C5) into (16a) provides close-form solutions for the first and second moments of travel time for a reactive solute undergoing first-order sorption kinetics in a two-dimensional statistically isotropic domain.

Notation

a, b	parameters of the sorption gamma model.
$C_1(\eta, t)$	mobile concentration in the physical space [M L^{-3}].
$C_2(\eta, t, \alpha)$	immobile concentration in noninstantaneous equilibrium with the mobile concentration and reacting at a certain mass transfer rate α[M L^{-3}].
$C_{2tot}(\eta, t)$	total immobile concentration [M L^{-3}].
C_{AB}	covariance between spatial random functions A and B.
D_I	Damköhler number (dimensionless).
$E_1(L)$	exponential integral function.
$g(L, \tau)$	probability density function (pdf) of travel time.
$G(L, \tau)$	cumulative distribution function (cdf) of travel time.
h	auxiliary function in Laplace space defined by (3).
H	expected value of h.
h'	perturbation of h.
I_i	integral scale of some hydraulic or sorption parameter [L].
K_d	distribution coefficient [L^3 M^{-1}].
K_G	geometric mean of the hydraulic conductivity values [L T^{-1}].
$K_{d,G}$	geometric mean of the distribution coefficient values [L^3 M^{-1}].
L	distance from injection to control plane (dimensionless).
$p(\alpha)$	volumetric fraction of the solid that reacts at a particular rate α.
Q	pumping rate [L^3 T^{-1}].
s	Laplace's variable.
T	dimensionless time.
$T_i^R(L)$	ith noncentral moment of the deterministic breakthrough curve.
t	real time [T].
t_i	temporal moment i of the deterministic breakthrough curve [T].
u	velocity fluctuation around the mean (dimensionless).
U	mean velocity (dimensionless).
v	actual velocity along the trajectory [L T^{-1}].
V	dimensionless velocity along the trajectory.
x	coordinate along mean flow direction (dimensionless).
W	random component of K_d.
Y	natural log of hydraulic conductivity.
α or α_i	mass transfer rate coefficients (dimensionless).
β	factor controlling the degree of correlation between K_d and Y.
β_{tot}	total capacity factor (dimensionless).
γ	Euler's constant.
$\Gamma(\bullet)$	gamma function.
$\delta(\bullet)$	Dirac's delta function.

ζ	auxiliary function.
η	dimensionless coordinate along the streamline.
ξ	auxiliary function.
ρ_b	bulk density [M L^{-3}].
$\sigma_\bullet^2$	variance.
τ	travel time (dimensionless).
ϕ	porosity in the mobile zone.
ψ	Lagrangian quantity.
Ψ	expected value of ψ.
ψ'	perturbation of ψ.
$\langle\bullet\rangle$	expected value.
Superscripts	
C	conditional.
KIN, LIE, NR	the sorption model, respectively, first-order kinetics, linear instantaneous equilibrium, and nonreactive (conservative) solute.
–	variable in Laplace space.

[78] **Acknowledgments.** This work was partially supported by ENRESA and the Spanish Ministry of Education. The authors thank Monica Riva and Alberto Guadagnini for providing the data used in the radial flow example in section 3.

References

Allen-King, R. M., R. M. Halket, D. R. Gaylord, and M. L. Robin, Characterizing the heterogeneity and correlation of perchloroethene and hydraulic conductivity using a facies-based approach, *Water Resour. Res.*, *34*(3), 385–396, 1998.

Aris, R., On the dispersion of linear kinematic waves, *Proc. R. Soc. London, Ser. A*, *245*, 268–277, 1958.

Bellin, A., and A. Rinaldo, Analytical solutions for transport of linearly adsorbing solutes in heterogeneous formations, *Water Resour. Res.*, *31*(6), 1505–1511, 1995.

Bellin, A., A. Rinaldo, W. J. P. Bosma, S. E. A. T. M. van der Zee, and Y. Rubin, Linear equilibrium adsorbing solute transport in physically and chemically heterogeneous porous formations, 1, Analytical solution, *Water Resour. Res.*, *29*(12), 4019–4030, 1993.

Burr, D. T., E. A. Sudicky, and R. L. Naff, Nonreactive and reactive solute transport in three-dimensional heterogeneous porous media: Mean displacement, plume spreading, and uncertainty, *Water Resour. Res.*, *30*(3), 791–815, 1994.

Chen, W., and R. J. Wagenet, Solute transport in porous media with sorption-site heterogeneity, *Environ. Sci. Technol.*, *29*(11), 2725–2734, 1995.

Connaughton, D. F., J. R. Stedinger, L. W. Lion, and M. L. Shuler, Description of time-varying desorption kinetics: Release of naphthalene from contaminated soils, *Environ. Sci. Technol.*, *27*(12), 2397–2403, 1993.

Culver, T. B., S. P. Hallisey, D. Sahoo, J. J. Deitsh, and J. A. Smith, Modeling the desorption of organic contaminants from long-term contaminated soil using distributed mass transfer rates, *Environ. Sci. Technol.*, *31*(6), 1581–1588, 1997.

Cunningham, J. A., Sorption and desorption of organic contaminants by aquifer solids: Mechanisms, rates, and implications for transport in groundwater, Ph.D. dissertation, Stanford Univ., Stanford, Calif., 1999.

Cunningham, J. A., and P. V. Roberts, Use of temporal moments to investigate the effects of nonuniform grain-size distribution on the transport of sorbing solutes, *Water Resour. Res.*, *34*(6), 1415–1425, 1998.

Cvetkovic, V., and R. Haggerty, Transport with multiple-rate exchange in disordered media, *Phys. Rev. E*, in press, 2003.

Cvetkovic, V. D., and A. M. Shapiro, Mass arrival of sorptive solute in heterogeneous porous media, *Water Resour. Res.*, *26*(9), 2057–2067, 1990.

Cvetkovic, V., A. M. Shapiro, and G. Dagan, A solute flux approach to transport in heterogeneous formations, 2, Uncertainty analysis, *Water Resour. Res.*, *28*(5), 1377–1388, 1992.

Cvetkovic, V., H. Cheng, and X.-H. Wen, Analysis of nonlinear effects on tracer migration in heterogeneous aquifers using Lagrangian travel time statistics, *Water Resour. Res.*, *32*(6), 1671–1680, 1996.

Cvetkovic, V., G. Dagan, and H. Cheng, Contaminant transport in aquifers with spatially variable hydraulic and sorption properties, *Proc. R. Soc. London, Ser. A*, *454*, 2173–2207, 1998.

Deitsch, J. J., J. A. Smith, T. B. Culver, R. A. Brown, and S. A. Riddle, Distributed-rate model analysis of 1,2-dichlorobenzene batch sorption and desorption rates for five natural sorbents, *Environ. Sci. Technol.*, *34*(8), 1467–1469, 2000.

Demmy, G., S. Berglund, and W. Graham, Injection mode implications for solute transport in porous media: Analysis in a stochastic Lagrangian framework, *Water Resour. Res.*, *35*(7), 1965–1973, 1999.

Domenico, P. A., and F. W. Schwartz, *Physical and Chemical Hydrogeology*, 824 pp., John Wiley, New York, 1990.

Fiori, A., P. Indelman, and G. Dagan, Correlation structure of flow variables for steady flow toward a well with application to highly anisotropic heterogeneous formations, *Water Resour. Res.*, *34*(4), 699–708, 1998.

Haggerty, R., and S. M. Gorelick, Modeling mass transfer processes in soil columns with pore-scale heterogeneity, *Soil Sci. Soc. Am. J.*, *62*(1), 62–74, 1998.

Haggerty, R., S. W. Fleming, L. C. Meigs, and S. A. McKenna, Tracer tests in a fractured dolomite, 2, Analysis of mass transfer in single-well injection-withdrawal tests, *Water Resour. Res.*, *37*(5), 1129–1142, 2001.

Harvey, C. F., and S. M. Gorelick, Temporal moment-generating equations: Modeling transport and mass transfer in heterogeneous aquifers, *Water Resour. Res.*, *31*(8), 1895–1911, 1995.

Hu, B. X., F.-W. Deng, and J. H. Cushman, Nonlocal reactive transport with physical and chemical heterogeneity: Linear nonequilibrium sorption with random Kd, *Water Resour. Res.*, *31*(9), 2239–2252, 1995.

Indelman, P., and G. Dagan, Solute transport in divergent radial flow through heterogeneous media, *J. Fluid Mech.*, *384*, 159–182, 1999.

Lawrence, A. E., X. Sanchez-Vila, and Y. Rubin, Conditional moments of the breakthrough curves of kinetically sorbing solute in heterogeneous porous media using multirate mass transfer models for sorption and desorption, *Water Resour. Res.*, *38*(11), 1248, doi:10.1029/2001WR001006, 2002.

McKenna, S. A., L. C. Meigs, and R. Haggerty, Tracer tests in a fractured dolomite, 3, Double-porosity, multiple-rate mass transfer processes in convergent flow tracer tests, *Water Resour. Res.*, *37*(5), 1143–1154, 2001.

Pedit, J. A., and C. T. Miller, Heterogeneous sorption processes in subsurface systems, 1, Model formulations and applications, *Environ. Sci. Technol.*, *28*(12), 2094–2104, 1994.

Rajaram, H., Time and scale dependent effective retardation factors in heterogeneous aquifers, *Adv. Water Res.*, *20*(4), 217–230, 1997.

Riva, M., A. Guadagnini, and F. Ballio, Time-related capture zones for radial flow in two dimensional randomly heterogeneous media, *Stochastic Environ. Res. and Risk Assess.*, *13*(3), 217–230, 1999.

Robin, M. J. L., E. A. Sudicky, R. W. Gillham, and R. W. Kachanoski, Spatial variability of strontium distribution coefficients and their correlation with hydraulic conductivity in the Canadian Forces Base Borden aquifer, *Water Resour. Res.*, *27*(10), 2619–2632, 1991.

Rubin, Y., Prediction of tracer plume migration in disordered porous media by the method of conditional probabilities, *Water Resour. Res.*, *27*(6), 1291–1308, 1991.

Rubin, Y., *Applied Stochastic Hydrogeology*, Oxford Univ. Press, New York, 2003.

Rubin, Y., and G. Dagan, Conditional estimation of solute travel time in heterogeneous formations: Impact of transmissivity measurements, *Water Resour. Res.*, *28*(4), 1033–1040, 1992.

Rubin, Y., M. A. Cushey, and A. Wilson, The moments of the breakthrough curves of instantaneously and kinetically sorbing solutes in heterogeneous geologic media: Prediction and parameter inference, *Water Resour. Res.*, *33*(11), 2465–2481, 1997.

Sanchez-Vila, X., On the geostatistical formulation of the groundwater flow and the solute transport equations, Ph.D. dissertation, Univ. Politèc. de Catalunya, Barcelona, Spain, 1995.

Sardin, M., D. Schweich, F. J. Leij, and M. T. Van Genuchten, Modeling the nonequilibrium transport of linearly interacting solutes in porous media: A review, *Water Resour. Res.*, *27*(9), 2287–2307, 1991.

Selroos, J.-O., and V. Cvetkovic, Modeling solute advection coupled with sorption kinetics in heterogeneous formations, *Water Resour. Res.*, *28*(5), 1271–1278, 1992.

Zhang, D., and S. P. Neuman, Comment on "A note on head and velocity covariances in three-dimensional flow through heterogeneous anisotropic porous media" by Y. Rubin and G. Dagan, *Water Resour. Res.*, *28*(12), 3343–3344, 1992.

Y. Rubin, Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720, USA.

X. Sanchez-Vila, Department of Geotechnical Engineering and Geosciences, Technical University of Catalonia, 08034 Barcelona, Spain. (xavier.sanchez-vila@upc.es)