Transport in Heterogeneous Media: Tracer Dynamics in Complex Flow Networks

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Large-scale inhomogeneities in natural porous media profoundly affect the dynamic response of conveyed tracers. It is proposed that tracer dynamics in heterogeneous porous media can be represented by temporal moments based on parallel and series unit models of homogeneous columns, stirred volumes, or mass-transfer-connected closed compartments. The rules of combining the moments for elementary volumes are based on units (1) in series, where output from the preceding units is the input to the succeeding unit, and (2) in parallel, where the splitting or joining flow paths control the response. For a network of elementary volumes in series or parallel, fate and transport of contaminants in heterogeneous media can be analyzed simply in a deterministic framework. Results for several simple series and parallel models show the wealth of responses that can be quantitatively described by this procedure.

Introduction

Effects of heterogeneity on transport processes are commonly observed in nature and in the laboratory. Transport processes in physically and chemically heterogeneous media are characterized by interactions on multiple length scales. Mass transport in subsurface porous media, for example, may involve diffusion through silty soil, permeation through gravel beds, and flow around impermeable units. Adsorption and chemical reaction may occur simultaneously with diffusion and permeation. In the laboratory, chromatographic separations and measurements are based on flows through columns or porous media that retard chemical species differently because of differences in adsorption, permeation, diffusion, and flow. In column chromatography, nonuniformities in packing lead to deterioration in the separation resolution. An approach to describing porous-media transport in homogeneous or slightly nonhomogeneous media is by averaged, or upscaled, transport equations and coefficients. When the system becomes heterogeneous on several length scales, however, such effective medium approaches are less accurate and less useful. The development of quantitative representations of transport in heterogeneous media is an important challenge that has attracted considerable attention recently, particularly from water resources and environmental engineers.

Subsurface physical heterogeneity manifests as spatial variations in hydraulic conductivities associated with spatial variations in size and type of aquifer materials. Often, such heterogeneity occurs on large (such as, meter) scales at high amplitudes (many orders of magnitude range in hydraulic conductivities), giving rise to complicated aquitard (semipervious) aquifer systems that act as multiply connected flow networks. When such a heterogeneous flow system is divided into a series of coupled homogeneous subsystems with relatively uniform hydrogeological properties, the general characteristics of breakthrough curves (response parameters) in each homogeneous subsystem can be estimated directly through temporal moment analysis (Valocchi, 1985). Four response

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parameters, related to temporal moments, that are commonly used for risk analysis are: (1) the total mass; (2) the mean residence time; (3) the variance (spread) of the breakthrough curve; and (4) a potential delay associated with the sorption properties of contaminants and porous media along the heterogeneous flow paths, also known as tailing effects. Low mean residence time and low tailing effect, for example, indicate an immediate risk for areas downstream of the contaminant-source area (Delay et al., 1998). Hence, the main goal of this research is to couple the moment equations, written for each homogeneous subsystem, to estimate the aforementioned response parameters for the entire heterogeneous system without computing actual breakthrough curves.

A considerable amount of work has been reported in the literature on the problem of strong heterogeneities in subsurface flow systems. Variations in hydraulic conductivities in heterogeneous aquifer systems may lead to channeling (branching) and bifurcation along the subsurface flow paths, rather than unidirectional straight and smooth flow paths (Scheibe and Freyberg, 1995). Federspiel (1992) considered diffusional transport in a network of branching conduits. A perturbation analysis yielded an effective transport equation for species concentration. Although the study was initially directed toward describing gas diffusion in the lung, the result is analogous to later techniques in water-resources fields, which use network representations of flow systems when dealing with contaminant transport in porous media.

Simmons et al. (1995) employed a streamtube approach to solve a one-dimensional stochastic reactive convective-transport model for physically heterogeneous media. In their model, they represented the entire heterogeneous system as a parallel ensemble of independent stream tubes, each characterized by a travel time and associated constant effective pore water velocity with no inter- or intratube dispersion. The relative fraction of solute flux in each streamtube was computed from an advective-travel-time distribution function, obtained by breakthrough analysis of an inert tracer in the effluent from the heterogeneous medium. After calculating the concentration in each streamtube by solving the transport equation without the dispersive term, they weighted them by the advective-travel-time distribution function and then added them together. To overcome shortcomings associated with negligence of the dispersive term, Cirpka and Kitanidis (2000) proposed an advective-dispersive streamtube approach. In their approach, they assumed a constant apparent Peclet number of mixing for all streamtubes at the outlet. They also computed the distribution function of arrival times using information from both local and integrated breakthrough curves. Subsequently, they solved the transport equation for each streamtube, including the dispersive term. In the end, they weighted the results by the arrival-time distribution and then summed them up.

Ginn (2001) directly incorporated dispersion within (but not between) streamtubes by assuming Fickian-type kinematic dispersion with the dispersion coefficient proportional to the constant effective velocity in a streamtube. The inert tracer breakthrough is expressed as a serial Voltera–Fredholm integral that generalizes the summing up per relative flux to include effects of intrastream dispersion. Ginn (1999) also generalized the streamtube method to accommodate multicomponent reaction networks. The method is applied to biodegradation [in Ginn et al. (2001)] for experiments in porous media exhibiting bimodal hydraulic conductivity distribution (Murphy et al., 1997).

The main advantage of the streamtube approach is it reduces a 3-D transport problem to an ensemble of 1-D transport problems with constant coefficients that reflect global transport properties. Thus, earlier streamtube models can be viewed as nonparametric in the sense that a detailed representation of heterogeneities of flow and transport parameters (such as hydraulic conductivities) across a flow domain is not used. In this article, however, the system's heterogeneities will be represented with a network of streamtubes (conduits) connected to each other in series or parallel, different from previously developed streamtube models. Furthermore, the earlier streamtube models ignored the mass transfer between the streamtubes in a bundle. This work can potentially address this issue using various network layouts generated by changing the number, size, and configuration of elementary volumes, and can potentially be used to mimic effects of mass transfer among the compartments on the overall contaminant transport process.

Objectives and Methods

The present objective is to develop a mathematical procedure to characterize complex tracer responses in heterogeneous media by proper superposition of temporal moments of those tracer responses from elementary units represented in the heterogeneous media. A temporal moment approach for the superposed elementary units—columns, stirred vessels, and connected compartments—provides expressions for building the model to simulate the transport in a heterogeneous medium. The method of combining column and stirred-vessel modules to represent complex and nonideal flow behavior has a precedent in chemical engineering analysis (Fogler, 1999). Transport in strongly heterogeneous systems, in general, displays a non-Fickian behavior, which usually involves spatial nonlocality (dependence of flux at a given position x on not just the local values of controlling properties such as velocity and gradient of concentration at that position, but on the values of these properties in a wider neighborhood around x) in the constitutive theory describing the dispersive flux (Cushman and Ginn, 1993; Irwin et al., 2000). In this study, to overcome the potential difficulties due to the non-Fickian dispersion, the entire heterogeneous system is represented as a network of homogeneous units where the Fickian transport is valid in each unit. Certain characteristics of breakthrough curves for the entire system can then be obtained by coupling the temporal moments of elementary volumes through transfer functions. The use of conventional transport theory in network components (at the small scale) does not imply conventional transport in the network as a whole (large scale).

Temporal moments are useful in exploring the mean retention time, spreading, and tailing of contaminant distributions in homogeneous (Valocchi, 1985) and heterogeneous (Naff, 1992) systems. These moments are critical measures in environmental risk analysis. The use of temporal moments in finding general trends of solute breakthrough curves and the actual concentration distribution in non-Fickian heterogeneous systems was addressed in Naff (1992). Berglund and

Fiori (1997) applied temporal moments to a convective–dispersive equation with first-order sorption kinetics for heterogeneous systems with non-Fickian behavior based on the premise that particle movement at large travel distances is uncorrelated.

In this article, we focus on linear mathematics for dilute tracers with the assumption that reaction and adsorption processes are first order, and system properties are constant in each elementary unit. The idealized flow network can be constructed using streamtube-mixing plug-flow and continuous-flow stirred-tank reactor elementary components. The rationale for this approach lies in its construction as a compromise between the fully Eulerian approach requiring complete characterization of hydraulic conductivity and the fully Lagrangian streamtube approach (Ginn, 2001), given that full characterization of a realistic hydraulic conductivity field is almost never feasible. The fully Lagrangian approach restricts the modeling question to provide only a simulated breakthrough at one observation location, for which the distribution of flux over travel time is required. The determination of the distribution flux over travel time requires either field-scale experimentation (tracer test), or estimation via deterministic or stochastic approaches (Dagan, 1989). The present approach requires only partial characterization of the large-scale, dominant heterogeneity to restrict the number of networks possibly representing transport at multiple observation locations. Furthermore, this approach may provide a valuable alternative to either stochastic Eulerian or streamtube Lagrangian approaches, because of the different characterization needs and reduced computational requirements in the former case and because it intrinsically incorporates streamtube interaction (splitting and rejoining) within the network.

Theory

The fundamental concept of this work is that a heterogeneous porous medium can be represented by linked homogeneous units whose temporal moments can be readily calculated. The solute transport in an individual homogeneous unit can be simulated using a well-known one-dimensional advection–dispersion equation (ADE) accompanied with a first-order reaction and a linear equilibrium sorption isotherm

$$R\frac{\partial C}{\partial t} = F(C) = D_e\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - kC \qquad (1)$$

$$R = 1 + \frac{\rho_b K_d}{\theta} \qquad (2)$$

where $C(x,t)$ is the aqueous phase concentration $[M/L^3]$; R is the dimensionless retardation coefficient; F represents various transport operators as a function of fluid velocity and system geometry, where D_e is the dispersion coefficient $[M/L^2]$; v is the linear average velocity $[L/T]$; k is the first-order reaction coefficient $[1/T]$; ρ_b is the ratio of the mass of sorbent to the bulk volume $[M/L^3]$; K_d is the distribution coefficient defined as the ratio of the aqueous volume to the mass of sorbent $[L^3/M]$; θ is the porosity (volume of aqueous phase per bulk volume); x is the spatial position index $[L]$; and t is the time index $[T]$. It should be noted that Eq. 1 is not applicable to the entire heterogeneous system due to spatial nonlocality in the constitutive theory describing the diffusive flux. Equation 1 is, however, applicable to individual homogeneous volumes in the network, because they satisfy the Fickian constitutive theory built on the local dispersive flux.

The Laplace transform for linear F gives $R[s\tilde{C} - C(t=0)] = \tilde{F}$, in terms of the initial condition, which we take to be zero for a system initially clear of tracer. The Laplace transform serves as a temporal moment generator (Aris, 1958; Simmons, 1982; Valocchi, 1985; McCoy and Rolston, 1991; Harvey and Gorelick, 1995; Dogu et al., 1996; Espinoza and Valocchi, 1997) for both resident and flux-averaged concentration

$$\lim\nolimits_{s\to 0}(-1)^n\frac{d^n\tilde{C}(x,s)}{ds^n} = \int_0^\infty C(x,t)t^n\,dt = C^{(n)}(x) \qquad (3)$$

where s is the Laplace parameter and the tilde represents the Laplace transform of variables with respect to time. The nth normalized moment, $\hat{C}^{(n)}(x)$, can then be calculated as $\hat{C}^{(n)}(x) = C^{(n)}(x)/C^{(0)}(x)$, in which the zeroth moment, $C^{(0)}(x)$, represents the total concentration of tracer. Hence, $M = QC^{(0)}(x)$ represents the total mass flux of tracer at x, where Q is the steady volumetric flux rate. The nth normalized central temporal moment is

$$\bar{C}^{(n)}(x) = \frac{1}{C^{(0)}}\int_0^\infty \left[t - \hat{C}^{(1)}(x)\right]^n C(x,t)\,dt \qquad n \geq 2 \qquad (4)$$

where the temporal mean, $\hat{C}^{(1)}(x)$, presents the average time of response (average retention time). The second normalized central moment (variance), $\bar{C}^{(2)}(x)$, is a measure of the temporal width of the response. The third normalized central moment of the breakthrough curve, $\bar{C}^{(3)}(x)$, identifies the extended tailing. In this study, we will focus only on the first four moments, that is, $n \leq 3$.

The governing equation for an elementary homogeneous unit thus yields a moment expression that can be combined (superposed) with those of adjoining units. Consider units in series so that the exit flow from one unit is the inlet flow to the next unit. The total mass is conserved between the units, whether they are columns, stirred vessels, or connected compartments

$$C_{j+1}^{(0)} = C_j^{(0)} \qquad (5)$$

where the downstream moment from position j is denoted $j+1$ (Figure 1).

Elementary Units

Well-mixed vessels in a series

A mass-balance equation for well-mixed vessels can be written by modifying Eq. 1 (such as Sardin et al., 1991) for a spatially integrated reactor

$$Q(C_{j-1} - C_j) = V\theta R\frac{\partial C_j}{\partial t} + V\theta kC_j \qquad (6)$$

where Q is the volumetric flux rate at the entrance and exit end of the vessel $[L^3/T]$; $(Q = A\theta v)$, A is the average cross-sectional area normal to the flow direction $[L^2]$; and V is the volume of the vessel [L^3]. Equation 6 is based on the premise that effluent concentrations at the exit end of the well-mixed vessel are equal to resident concentration within the vessel. In real systems, well-mixed vessels (Figure 1a) can be used to represent the contaminant transport that takes place in non-Darcy (such as turbulent) flow zones or any network components that have no well-specified advection. Fissures, large openings, or joints in sedimentary or volcanic units along the main flow paths across the flow domain may lead to well-mixed turbulent flows in certain parts of the subsurface flow domain.

Streamtubes (columns) in a series

A one-dimensional advective–dispersive transport equation with an equilibrium reaction for an initially uncontaminated streamtube can be written as

$$R\frac{\partial C}{\partial t}+v\frac{\partial C}{\partial x}=D_e\frac{\partial^2 C}{\partial x^2}-kC \tag{7}$$

with the following auxiliary conditions

$$C(0,t)=C_{\text{in}} \tag{8}$$

$$C(x\rightarrow\infty,t)=0 \tag{9}$$

$$C(x,0)=0 \tag{10}$$

where C_{in} is the influx concentration into the compartment. The boundary condition given in Eq. 9 is usually valid for high Peclet systems. Streamtubes (Figure 1b) can be used to simulate contaminant transport characterized predominantly by advection and dispersion across the coarse-grained (sand and gravel) aquifer layers. As opposed to well-mixed vessels, streamtubes allow the consideration of spatial variations in concentrations along the homogeneous porous subsystems via conventional transport operations.

Well-mixed compartment attached to a streamtube

Some isolated "dead-end zones," located off the main advective transport pathways, may entrap solutes in uniformly mixed compartments that also may sequester solutes via reversible sorption. Such a configuration appears in layered sand-shale sequences in the presence of silt and/or clay units, and other geological structures. In such cases, a potential mass-interaction between the compartments and nearby streamtubes (Figure 1c) can be described as

$$R\frac{\partial C}{\partial t}+v\frac{\partial C}{\partial x}=-k_p(C-C_p)-k_1C \tag{11}$$

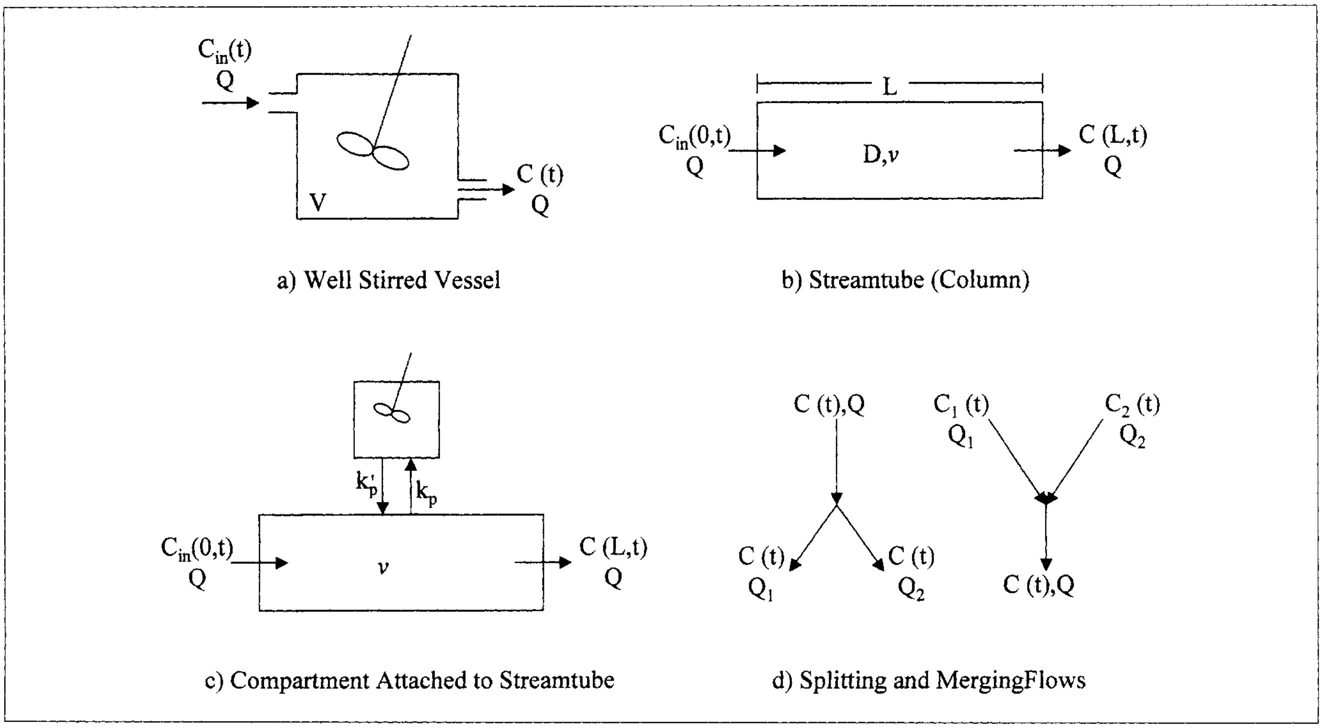
$$\frac{\partial C_p}{\partial t}=k'_p(C-C_p)-k_2C_p \tag{12}$$

with the following auxiliary conditions

$$C(0,t)=C_{\text{in}}(t) \tag{13}$$

$$C(x,0)=0 \quad C_p(t=0)=0 \tag{14}$$

where k'_p and k_p are the mass-transfer rates between the streamtube and the well-mixed vessel [T^{-1}] (Figure 1c); k_1



a) Well Stirred Vessel

b) Streamtube (Column)

c) Compartment Attached to Streamtube

d) Splitting and MergingFlows

Figure 1. Elementary units for modeling tracer transport in heterogeneous media.

$C(t)$ is the time-dependent tracer concentration and Q is the volumetric flow rate for steady flows.

and k_2 are the first-order decay rates along the streamtube and the attached compartment; and C_p is the concentration in the attached well-mixed vessel $[M/L^3]$. For this particular application, the dispersive transport in Eq. 11 was ignored to simplify computations. It should be noted that, in reality, the aging effect might be a critical factor in determining the contribution of sorbed (Ginn, 1999) or sequestered (Alexander, 2000) contaminants to the overall contaminant transport process across the porous media. However, the aging effect is beyond the scope of this article.

Transfer Functions and Temporal Moments

The concept of transfer functions (known also as Green's functions, kernel functions, or response functions) has been commonly used in linear solute-transport problems to relate injected concentrations (input) to output concentrations (response), when linearity holds for the flow domain under consideration (Jury, 1982; Valocchi, 1985)

$$\tilde{C}_k(s) = \tilde{C}_{k-1}(s)T_k(s) \tag{15}$$

where $T(s)$ is the transfer function, which depends only on the governing transport equation, and k is the order of the elementary volume in the network. Because transfer functions are independent of the loading (input) function, they are customarily computed by assuming a Dirac-loading type of boundary condition. The transfer functions and the corresponding temporal moments for the aforementioned elementary volumes are given in the subsequent sections.

First, the transfer function for the *well-mixed vessel*, $T_{wv}(s)$, is

$$T_{wv}(s) = \frac{1}{1+\tau(Rs+k)} \tag{16}$$

where τ is the holding time $(V\theta/Q)$. Here, it is assumed that the flux-averaged concentration at the outlet of the perfectly mixed zone is equal to its volume-averaged resident concentration. Then, the corresponding response parameters are

$$M = QC^{(0)} = \frac{QC_{\text{in}}}{1+\tau k} \tag{17}$$

$$\hat{C}^{(1)} = \hat{C}_{\text{in}} + \frac{\tau R}{1+\tau k} \tag{18}$$

$$\bar{C}^{(n)} = \bar{C}_{\text{in}}^{(n)} + (n-1)\left(\frac{\tau R}{1+\tau k}\right)^n \quad \text{for} \quad n = 2,3 \tag{19}$$

The transfer function for the flux-averaged concentration at the outlet of a *streamtube* $T_{st}(x,s)$, is

$$T_{st}(x,s) = \exp\left(\frac{\left(v - \sqrt{v^2 + 4D(Rs+k)}\right)x}{2D}\right) \tag{20}$$

The corresponding response parameters are

$$M = QC^{(0)} = QC_{\text{in}}^{(0)} \exp\left(0.5xD^{-1}\left[v - \xi^{1/2}\right]\right) \tag{21}$$

$$\hat{C}^{(1)} = \hat{C}_{\text{in}} + xR\xi^{-1/2} \tag{22}$$

$$\bar{C}^{(2)} = \bar{C}_{\text{in}}^{(2)} + 2DxR^2\xi^{-3/2} \tag{23}$$

$$\bar{C}^{(3)} = \bar{C}_{\text{in}}^{(3)} + 12D^2xR^3\xi^{-5/2} \tag{24}$$

where $\xi = v^2 + 4Dk$. It should be noted that both the variance and skew are functions of the dispersion coefficient in the preceding equations. The response parameters at the outlet of each streamtube can be found simply by substituting the length of the streamtube L for x in Eqs. 21 through 24.

Finally, the transfer function for the flux-averaged concentration at the outlet of a purely advective streamtube hydraulically connected to a immobile dead-end zone $T_{cst}(x,s)$, is

$$T_{cst}(x,s) = \exp\left(\left(-Rs - (k_p + k_1) + \frac{k_p k_p'}{s + k_p' + k_2}\right)\frac{x}{v}\right) \tag{25}$$

and the corresponding response parameters are

$$M = QC^{(0)} = QC_{\text{in}}^{(0)} \exp\left(\left(k_1 + \frac{k_p k_2}{k_p' + k_2}\right)\frac{x}{v}\right) \tag{26}$$

$$\hat{C}^{(1)} = \hat{C}_{\text{in}} + \frac{x}{v}\left(R + \frac{k_p k_p'}{\left(k_p' + k_2\right)^2}\right) \tag{27}$$

$$\bar{C}^{(n)} = \bar{C}_{\text{in}}^{(n)} + \frac{xn!}{v}\frac{k_p k_p'}{\left(k_p' + k_2\right)^{n+1}} \quad \text{for} \quad n = 2,3 \tag{28}$$

It should be noted that, unlike the first- and second-type elementary units, the spread and skew of breakthrough curves across the third-type elementary unit are not influenced by the sorption-induced retardation factor, but are affected by the relative magnitude of forward and reverse mass-transfer rates. However, storage of the contaminant within the attached compartments can cause effects similar to the sorption process, leading to a delay in breakthrough curves. Equation 28 indicates that high-order response parameters increase proportionally with a decrease in k_p', which highlights the effects of slow releases from an attached compartment on the variance and skew of breakthrough curves in the streamtube nearby.

Once the transfer functions for a Dirac-delta input are derived, an elemental response to any arbitrary input can be computed using the convolution theorem, and the temporal moments corresponding to any arbitrary loading can be computed following the procedure described in Valocchi (1985).

Serially Connected Elements

With the transfer functions thus established for each elementary homogeneous unit, the units are connected to form the network. The outlet of a preceding unit is considered inlet to the subsequent unit, and the outflux concentration can be related to the inlet concentration through transfer functions using Eq. 15 with the assumption of linearity. The mass-balance equation for each serial compartment (such as a contiguous group of elements) can then be written sequentially as

$$
\begin{aligned}
&\tilde{C}_1(s) = \tilde{C}_{\text{in}}(s)T_1(s)\\
&\tilde{C}_2(s) = \tilde{C}_1(s)T_2(s) = \tilde{C}_{\text{in}}(s)T_1(s)T_2(s)\\
&\tilde{C}_3(s) = \tilde{C}_2(s)T_3(s) = \tilde{C}_{\text{in}}(s)T_1(s)T_2(s)T_3(s)\\
&\vdots\\
&\tilde{C}_k(s) = \tilde{C}_{k-1}(s)T_3(s) = \tilde{C}_{\text{in}}(s)\prod_{i=1}^{k} T_i(s)
\end{aligned}
\tag{29}
$$

For a group of elements in serial connection, the total mass, normalized first, and central second and third moments of the breakthrough curve that characterize the mass transport across the entire heterogeneous media, become

$$M = QC_k^{(0)} = QC_{\text{in}}^{(0)}\prod_{i=1}^{k} T_i(s=0) \tag{30}$$

$$\hat{C}_k^{(1)} = \hat{C}_{\text{in}}^{(1)} - \left(\sum_{i=1}^{k} \frac{d^n \ln T_i(s)}{ds}\right)_{s\to 0} \tag{31}$$

$$\overline{C}_k^{(1)} = \overline{C}_{\text{in}}^{(n)} + (-1)^n\left(\sum_{i=1}^{k} \frac{d^n \ln T_i(s)}{ds^n}\right)_{s\to 0} \quad \text{for} \quad n = 2,3 \tag{32}$$

In Eqs. 30–32, the product of the zeroth moment and flow rate represents the total tracer mass within the entire heterogeneous system. The normalized first and central second moments (mean and variance, respectively) are the mean residence time and the tracer spread. The central third moment (skew) identifies potential delay risk (that is, extended tailing effect) associated with the sorption properties of contaminants and porous medium along the heterogeneous flow paths.

Splitting and Merging Streamtubes

The procedure described in the previous section can be used to simulate contaminant transport along a *single* flow path that consists of a number of stirred vessels and streamtubes to mimic the system's heterogeneities. In reality, however, there exist many hydrogeological systems, such as large alluvial deposits with complicated sedimentary architecture, in which a number of flow conduits merge at certain points and form a single flow conduit after that point. Similarly, a flow conduit also may split into a number of flow conduits in such systems, for example, when the flow path embodies large lenses of low permeability zones along the flow direction (Figure 1d). Thus, in order to simulate the contaminant transport in heterogeneous media, the temporal moment equations for splitting and merging streamtubes need to be derived and used in conjunction with Eqs. 30–32.

Splitting streamtubes

It is assumed that concentrations are not changed by a split, but volumetric flow rates will be different, so that the mass at the multifurcation point will be apportioned in accordance with the flow rates. The mass-balance equation at a splitting point is simply

$$Q_{k-1} = \sum_{m=1}^{N_s} Q_{\text{in},m} \tag{33}$$

where Q_{k-1} is the volumetric flow rate available to the multifurcation point $[L^3/T]$, N_s is the number of streamtubes leaving the multifurcation point, and $Q_{\text{in},m}$ is the fractional volumetric flow rate entering the *m*th elementary unit downstream of the splitting point. Here *m* serves as a local index of elementary units. When a steady flow regime (time-invariant velocity field) is assumed, we obtain from Eq. 33

$$C_{k-1}^{(n)} = \sum_{m=1}^{NS} C_{\text{in},m}^{(n)}\cdot(Q_{\text{in},m}/Q_{k-1}) = C_{k-1}^{(n)} \sum_{m=1}^{NS} (Q_{\text{in},m}/Q_{k-1}) \tag{34}$$

where $C_{k-1}(t)$ is the total concentration available to the multifurcation point $[M/L^3]$, assumed to be equal to concentrations entering the streamtube diverging at the multifurcation point, and $C_{\text{in},m}$ is the concentration leaving the multifurcation point into the *m*th elementary unit.

The total mass and response parameters can be obtained directly from Eqs. 3, 4, and 34. As can be observed from these equations, the mean residence, variance, and skew of the breakthrough curve in the streamtube approaching the multifurcation point are equal to that of the breakthrough curves in all streamtubes leaving the multifurcation point.

Merging streamtubes

It is assumed that the total flow rate at the merging point is equal to the sum of volumetric flow rates in the merging streamtubes. The mass-balance equation at the merging point is

$$\sum_{m=1}^{N_m} C_m(t)Q_m = C_{\text{in},k}(t)Q_{\text{in},k} \tag{35}$$

where N_m is the number of merging streamtubes, C_m is the concentration $[M/L^3]$, Q_m is the volumetric flow rate leaving the streamtube $[L^3/T]$, $C_{\text{in},k}$ is the concentration entering the elementary unit downstream of the merging point $[M/L^3]$, and $Q_{\text{in},k}$ is the fractional volumetric flow rate entering the elementary unit downstream of the merging point $[L^3/T]$. Similar to splitting streamtubes, when flow is assumed to be steady state, the temporal moment equation can be obtained from Eq. 35

$$\sum_{m=1}^{N_m} \overline{C}_m^{(n)}\cdot(Q_m/Q_{\text{in},k}) = \overline{C}_{\text{in},k}^{(n)} \tag{36}$$

The total mass, residence time, variance, and skew of the breakthrough curve representing the solute transport process in the streamtube at the merging point are

$$M = QC^{(0)}_{\text{in},k} = Q \sum_{m=1}^{NM} C^{(0)}_m \cdot (Q_m/Q_{\text{in},k}) \tag{37}$$

$$\hat{C}^{(1)}_{\text{in},k} = \sum_{m=1}^{NM} C^{(1)}_m \cdot Q_m \bigg/ \sum_{m=1}^{NM} C^{(0)}_m \cdot Q_m \tag{38}$$

$$\overline{C}^{(2)}_{\text{in},k} = \frac{\sum_{m=1}^{NM} C^{(2)}_m \cdot Q_m}{\sum_{m=1}^{NM} C^{(0)}_m \cdot Q_m} - \left(\hat{C}^{(1)}_{\text{in},k}\right)^2 \tag{39}$$

$$\overline{C}^{(3)}_{\text{in},k} = \frac{\sum_{m=1}^{NM} C^{(3)}_m \cdot Q_m}{\sum_{m=1}^{NM} C^{(0)}_m \cdot Q_m} - 3\frac{\left(\sum_{m=1}^{NM} C^{(2)}_m \cdot Q_m\right)\left(\sum_{m=1}^{NM} C^{(1)}_m \cdot Q_m\right)}{\left(\sum_{m=1}^{NM} C^{(0)}_m \cdot Q_m\right)^2} + 2\left(\hat{C}^{(1)}_{\text{in},k}\right)^3 \tag{40}$$

When the distribution of the velocity field is known for a steady-state flow regime across the heterogeneous medium, the average residence time, spread, and the skew of the breakthrough curve at the merging and splitting streamtubes can be computed using Eqs. 35–40.

Application

The moment equations derived in the previous sections were applied to an aquifer profile shown in Figure 2 to determine a set of response variables that involves the total mass, the average travel time, and the spreading and tailing of contaminant distribution at different locations across the profile. The profile shown in Figure 2 involves (1) well-connected main flow paths (displayed in white with no pattern), which might be characterized by coarse-grained sediments such as sand and gravel; (2) non-Darcy flow zones (represented by dashed lines) that may characterize fractured sedimentary or volcanic units; and (3) impervious or semi-impervious zones (shaded in gray) that might characterize silt or clay layers. It should be stressed that the network representation of the synthetic heterogeneous medium in Figure 2 is not unique. The number, scale, and configuration of the elementary volumes can possibly be modified in accordance with the objective of the study, desired accuracy, and quantity and quality of the measured data available for calibration. A likely useful approach to restricting the number of feasible networks is the incorporation of large-scale geophysical characterization data.

In the absence of injection to/or withdrawal from an aquifer, the spatial variations in the velocity field are mainly caused by spatial variations in lithologies and the boundary conditions. The velocity field can be calculated independently of contaminant transport, when the system does not involve complex chemical reactions (such as precipitation, biomass accumulation) that alter the flow field. In such systems, well-documented and widely used groundwater flow simulation models, such as MODFLOW (McDonald and Harbough, 1988), can be used to compute the velocity field in the modeled heterogeneous medium. Thus, the moment analysis method presented herein can potentially be applied

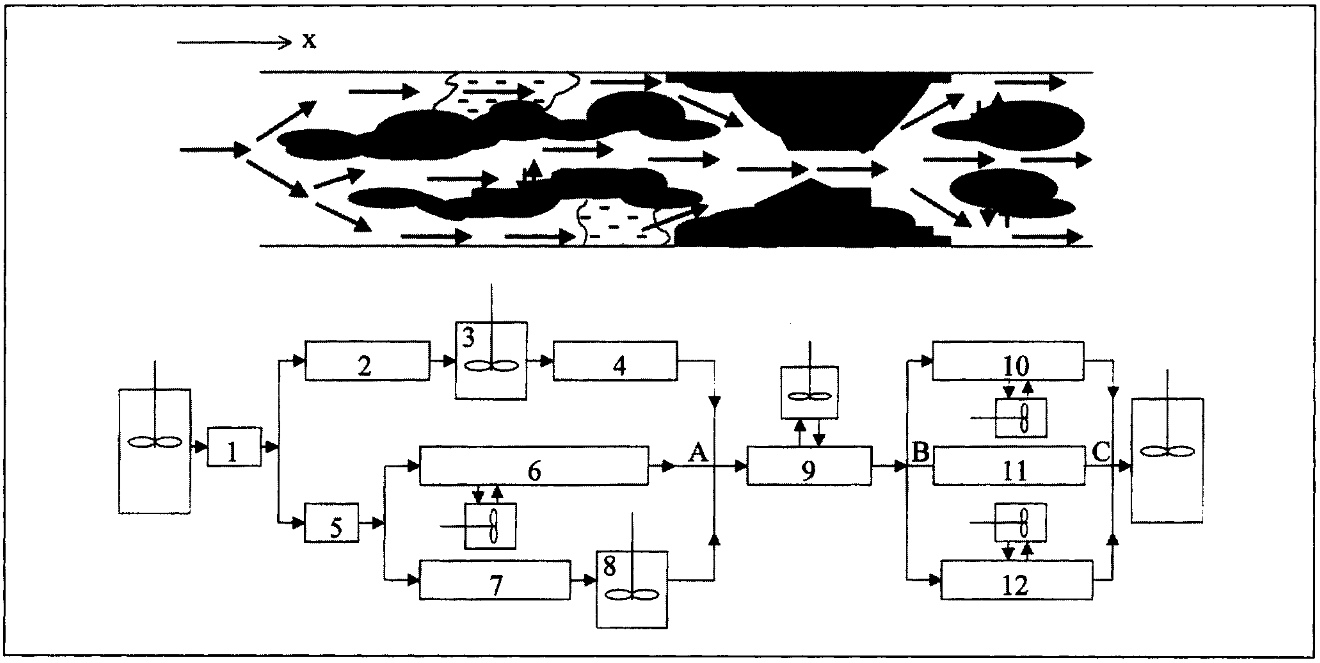


Figure 2. Network of elementary units for a synthetic aquifer profile.

to any subsurface velocity field. For this particular application, we assume time-invariant prespecified velocities across the hypothetical system for simplicity.

In Figure 2, the physical heterogeneity is represented by a total of twelve elementary units. Unlabeled first and last well-stirred vessels represent the input and exit ends of the system (these two compartments are shown as zeroth and thirteenth compartments in the figures). In this particular application, the aforementioned response parameters will be computed at the exit end of elementary units using Eqs. 30–32, 34, and 37–40. Equations 21–24 and 26–28 can be used to compute the response parameters at arbitrary points along the streamtubes.

In general, the number of parameters in the model depends on the heterogeneous system. If the geologic structure and hydrologic properties are known, one can estimate volumes, porosities, and permeabilities. Any realistic model for a complex heterogeneous medium requires detailed information about the constituency. Our model may actually minimize the number of parameters needed for a quantitative description. For this particular application, the hydrogeological parameters for all homogeneous elementary volumes, shown in Figure 2, are listed in Table 1. Dispersivity coefficients and velocities were chosen close to the values reported in Mulla et al. (1996) for sandy loam. In practice, the effective hydraulic conductivities, and thus velocities, can be assigned to Darcy-flow zones, based on the correlation lengths of the hydraulic conductivity field (Mukhopadhyay and Sahimi, 2000). The steady flow rate across the subsurface system was set to 1,500 cm^3/d. A percent contribution of steady flows from elementary units 4, 6, and 8 to the flow from the merging point *A* to the elementary unit 9 were set to 0.35, 0.35, and 0.3. Similarly, the ratios of steady flows leaving the elementary units 10, 11, and 12 to the flow downgradient of the merging point *C* were set to 0.35, 0.3, and 0.35, respectively. The other parameters listed in Table 1 were chosen arbitrarily.

Four scenarios were considered for this particular application with or without chemical decay and retardation processes (Table 2). In the first and fourth scenarios, the contaminant with a presumed half-life of 600 days is assumed to undergo a decay process with a uniform decay rate throughout the system (($k = \ln 2/\varphi$), where φ is the half-life of the contaminant $[T]$). In the first and second scenarios, a relatively smaller retardation coefficient was assumed in well-stirred cells than in the other homogeneous units based on the premise that well-mixed compartments may be associated with slower sorption processes. In the second and third scenarios, the chemical decay process was turned off to ensure that the total mass across the entire system is conserved. In all scenarios, 0.1 ppb/d (1 ppb = 1 mg/m^3) contaminant was assumed to be released continuously from the left most CSTR in Figure 2 during a year (365 days). Thus, the zeroth, and the associated central moments of the loading, are $C^{(0)} = 36.5$ ppb, $\hat{C}^{(1)} = 182.5$ day, $\overline{C}^{(2)} = 11{,}100$ day^2; and $\overline{C}^{(3)} = 0$ day^3, relatively. For the aforementioned scenarios, variations in four response parameters across the flow domain are shown in Figure 3.

When the chemical decay process was not considered, Figure 3a shows that the total mass across the heterogeneous system was conserved. In this figure, the total mass leaving compartments 4, 6, and 8 (as well as 10, 11, and 12) added up to 0.055 mg in the second and third scenarios, which was equal to the total mass entering the system. Figure 3b compares the mean retention times (MRT) of the contaminant at certain points in the aquifer, obtained from four scenarios. Low MRT, suggesting the rapid excursion of contaminant to downgradient sites, was observed in the third scenario where the retardation process was turned off. The second scenario yielded higher MRT than the first scenario, because some portion of the mass was removed from the system due to the decay process in the first scenario, which lessened the residence time of the contaminant in the system. Moreover, the lowest MRTs observed in the fourth scenario resulted from the loss of contaminant due to the decay process, in addition to a lack of retardation.

Figure 3c compares the variances, a measure of spread of breakthrough curves, at the prespecified points across the aquifer. Figure 3 suggests that prior to the confluence at the upstream side of the homogeneous unit 9 (denoted by *A* in Figure 2), both the chemical decay and retardation contributed to the variance. A discontinuity in the variance at *A* resulted from large variations in the second central moments (such as up to 29% in the second scenario) as well as mean retention times (Figure 3b) of the effluents leaving homogeneous units 4, 6 and 8. At and after *B* (Figure 2), the variance reduced by the chemical decay in the attached compart-

Table 1. Hydrogeological and Transport Parameters for Homogeneous Volumes

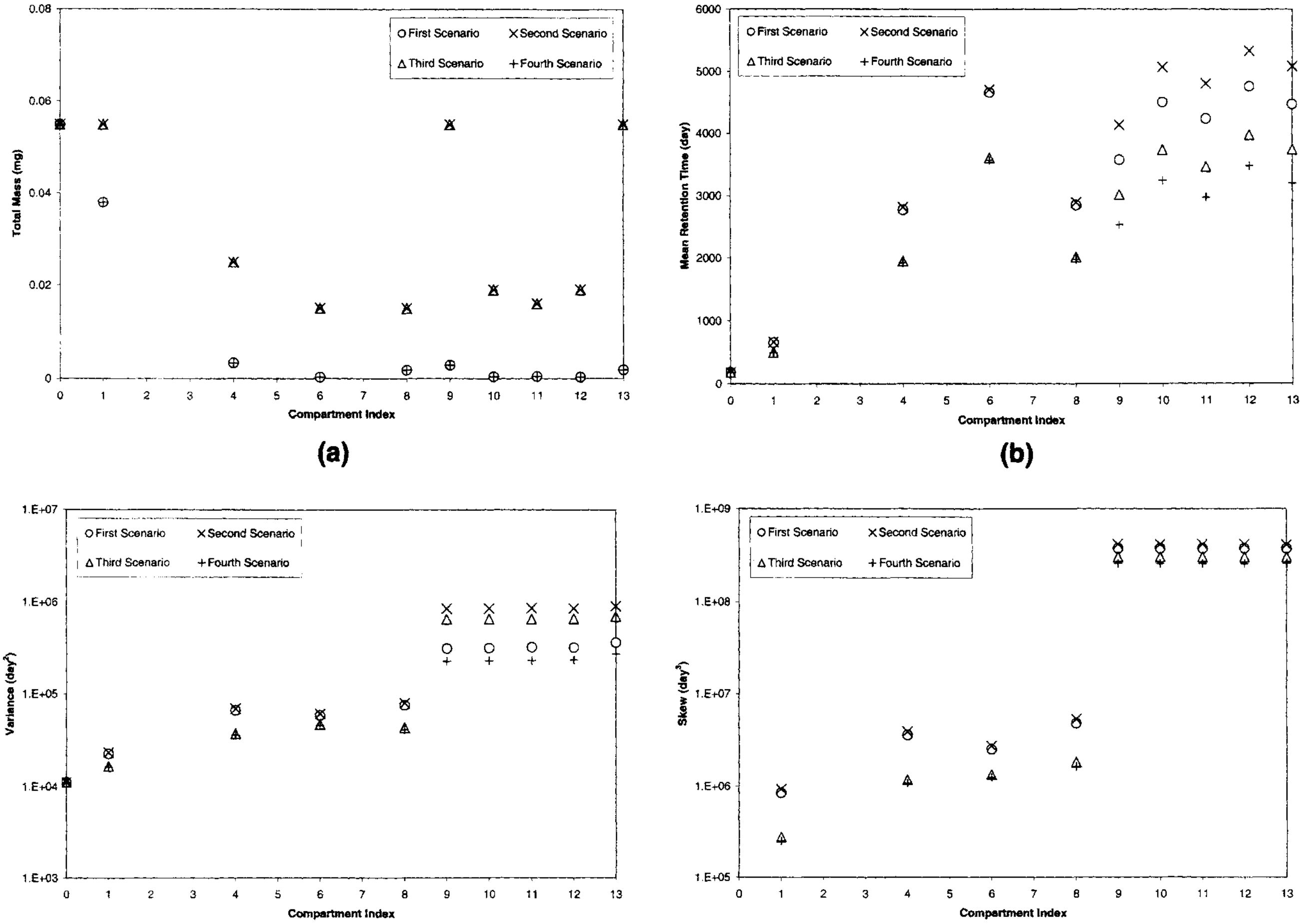
	Hydrogeological and Transport Parameters						
Compartment No.	L (cm)	v (cm/d)	D (cm^2/d)	R	k_p (1/d)	k'_p (1/d)	τ (d)
1	200	0.62	3.24	1.5	—	—	—
2	600	0.68	3.49	1.5	—	—	—
3	—	—	—	1.1	—	—	25
4	400	0.75	3.60	1.5	—	—	—
5	200	0.60	3.20	1.5	—	—	—
6	1,000	0.56	—	1.5	0.08	0.1	—
7	700	0.63	3.10	1.5	—	—	—
8	—	—	—	1.1	—	—	80
9	250	0.78	—	1.5	0.06	0.13	—
10	350	0.81	—	1.5	0.1	0.15	—
11	350	0.78	3.7	1.5	—	—	—
12	350	0.73	—	1.5	0.1	0.1	—

Table 2. Scenarios With/Without Retardation and Decay Processes

Scenario	Retardation	Decay
1	On	On
2	On	Off
3	Off	Off
4	Off	On

ments (Eq. 25), given that homogenous units 9, 10 and 12 allow temporary storage in their attached compartments. Although not shown in Figure 3c, a 10% increase in the chemical decay rate in the attached compartments along units 9, 10, and 12 in the second scenario, for example, the variance at the exit end of these units decreased by 0.5–2.2%. A reduction in the variance due to chemical decay is more obvious in the last scenario when retardation was neglected. The chemical decay in the attached compartment reduces the mass to be released slowly back into the nearby streamtube. Thus, when the third-type elementary unit with and without chemical decay receives the same amount of input, a higher portion of the mass is expected to release back to the nearby streamtube in the latter case over a relatively longer time, which yields higher temporal variance and skew measures. It should also be noted that because a high variance has already been achieved at *B* (Figure 2), the streamtubes at the confluence *C* makes a relatively slight contribution to the overall variance.

The third central moment given in Figure 3d is a measure of delay risk caused by the tailing effects of the breakthrough curves. The third central moment is a critical measure for predicting success of the pump and treatment remediation techniques in real systems (Cunningham and Roberts, 1998). As should be expected, the minimum skew was found for the third and fourth scenarios where the retardation process was not considered. As in the variance, a discontinuity was observed in the third central moments after the first merging point near homogeneous unit 9. This can be attributed to the large variations in the third (such as, up to 91% in the second scenario) and second central moments, as well as large variations in the mean retention times of the effluents entering the merging point at the homogeneous unit 9. Although a linear sorption isotherm was assumed in all streamtubes and well-mixed compartments, the profound tailing was also greatly affected by the mass transfer between attached well-mixed compartments and nearby stream tubes, which is analogous to the concept of matrix diffusion. Carrera et al. (1998) noted that a reversible first-order kinetic sorption process is indistinguishable from the first-order matrix diffusion. Thus,



(a)

(b)

(c)

(d)

Figure 3. Four response parameters from four scenarios: (a) first; (b) second; (c) third; and (d) fourth.

the overall tailing across the entire heterogeneous system can be viewed as the combined effect of a linear sorption kinetics along the first two elementary units and pseudokinetic reversible sorption kinetics across the third elementary units.

Conclusions

Tracer dynamics in a heterogeneous porous system were analyzed using a temporal moment analysis. The hypothetical porous medium was represented as a network of homogenous units with varying characteristics. Contaminant transport in each homogeneous element was then coupled through transfer functions to identify the basic characteristics of the breakthrough curves for the entire system, which can potentially be used in subsequent risk analysis. The traditional ADE is valid in each component but not across the heterogeneous medium. The potential use of merging and splitting streamtubes and flexibility in choosing the size, number, and configuration of compartments allows consideration of various mass-transfer processes among the various layers in real systems, as opposed to the traditional streamtube models that usually neglect the mass transfer between the streamtubes. This approach is expected to be particularly useful in the presence of large-scale, large-amplitude structural heterogeneities, such as arise in alluvial deposits. Even though only certain characteristics of the breakthrough curve representing the entire heterogeneous system were analyzed in this article, the actual breakthrough curves can be obtained by numerical inverse Laplace transform algorithms, once the temporal moments are computed.

In this article, the impacts of the retardation coefficient, chemical decay rate, and the mass transfer into the dead-end zones on the general characteristics of the breakthrough curves were analyzed. For this particular application, the variations in the total mass across the heterogeneous media were found to be controlled by the chemical decay rate. The mean retention time (MRT) of the contaminant in certain portions of the aquifer was found to be shortened by low retardation and/or high chemical decay. Although low MRT triggered by low retardation may impose a high risk to downstream sites due to extended tailing effects, it imposes less risk when it is triggered by high chemical decay. A mass transport into the dead-end pores was also found to increase MRT. A low decay rate in the attached vessels and a low reverse mass-transfer rate between the attached vessels and the nearby streamtubes were found to increase the higher-order central moments. Retardation was found to be a critical process in predicting the skew of the breakthrough curves. As opposed to MRT, a sharp increase (discontinuity) was observed in higher central moments, especially at the first confluence. A dramatic increase in the variance and the skew of the breakthrough curves at the first confluence was mainly due to significant deviations in the lower-order moments of the effluents carried in the merging streamtubes.

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