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Characterization of residual NAPL using partitioning tracers: temporal moment analysis

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Abstract A stochastic Lagrangian methodology is used to derive expressions for the temporal moments associated with transport of partitioning tracers through an aquifer of spatially variable hydraulic conductivity that contains a heterogeneously distributed residual nonaqueous phase liquid (NAPL) phase. The resulting statistical moments of the Lagrangian variables are expressed in terms of the statistics of the hydraulic conductivity and the NAPL content for the special case of a perfectly stratified aquifer.

INTRODUCTION

In recent years, several new techniques that use various reactive tracers to characterize subsurface contamination and the associated transport processes have been developed (Rao *et al.*, 1998). Partitioning tracer tests for characterization of residual nonaqueous phase liquid (NAPL) contamination is one of these innovative tracer techniques (Jin *et al.*, 1995); it has recently been applied under field conditions (Annable *et al.*, 1998). This technique uses tracers that partition into the NAPL, whereby the retardation of a partitioning tracer relative to a nonreactive one is used to quantify the amount of residual NAPL present within the aquifer volume swept by the tracers.

In this paper, we consider an aquifer of spatially variable hydraulic conductivity that contains a heterogeneously distributed residual NAPL phase. A stochastic Lagrangian methodology is used to derive expressions for the first and second temporal moments associated with the breakthrough curves of nonreactive and partitioning tracers in the extraction wells in a hypothetical tracer test configuration. The moment equations are expressed in terms of the statistical moments of two integrated Lagrangian variables: the advective travel time and the integral of the volumetric NAPL content along the stream-tube. The sensitivity of the temporal moments to the statistics of the hydraulic conductivity and the NAPL content is illustrated for the special case of a perfectly stratified formation.

THEORY

Basic configuration and assumptions

The transport domain considered extends between two planes perpendicular to the mean flow direction, the x direction: the plane $x = 0$, which is referred to as the injection plane

(IP), and the plane $x = x_{cp}$, referred to as the control plane (CP). The IP and the CP are taken to represent lines of injection and extraction wells, respectively, in a hypothetical tracer test configuration. The area within which the tracer plumes cross the CP is denoted as Ω and has the size A. This configuration is a somewhat idealized form of that used in some previous field experiments with partitioning tracers (Annable *et al.*, 1998).

The aquifer volume between the IP and the CP is characterized using the breakthrough curves (BTC) of nonreactive and partitioning tracers. Thus, we assume that a number of different tracers are injected at the IP at time $t = 0$, and that the flux-averaged concentrations of these tracers are measured at the CP. The groundwater velocity field, $\mathbf{v}(v_x,v_y,v_z)$, is assumed steady and the volumetric water content, θ_w, is approximated as a constant. Furthermore, the flow is assumed to be driven by a uniform mean gradient in the x direction, implying that the mean velocity is $\langle \mathbf{v} \rangle = (u,0,0)$ where $\langle v_x \rangle \equiv u$ is constant ($\langle\ \rangle$ denotes ensemble average).

The heterogeneous hydraulic properties of the aquifer are described as a spatially variable hydraulic conductivity field, $K(\mathbf{x})$, where $\mathbf{x}(x,y,z)$. In addition, the aquifer contains a residual NAPL with a heterogeneous spatial distribution, which is expressed in terms of a spatially variable NAPL content, $\theta_n(\mathbf{x})$ (volume NAPL per unit total volume of the medium). Spatial variability is here described statistically, such that $K(\mathbf{x})$ and $\theta_n(\mathbf{x})$ are statistically stationary random space functions, characterized by their point statistics and spatial auto- and cross-correlation structures.

The use of partitioning tracer BTCs for quantification of the NAPL content requires that the partitioning process is known, such that relevant transport equations can be formulated. Similar to other researchers (Jin *et al.*, 1995; Annable *et al.*, 1998), we consider linear equilibrium partitioning, and define the dimensionless distribution coefficient for tracer i as:

$$K_{di}(\mathbf{x}) = \frac{K_{ni}\theta_n(\mathbf{x})}{\theta_w} = \lambda_i \theta_n(\mathbf{x}) \tag{1}$$

where K_{ni} is the NAPL–water partitioning coefficient and λ_i is a tracer-specific constant. By regarding θ_w as constant and θ_n as spatially variable, we neglect the effects of the variability in NAPL content on flow, whereas the effect of this variability on tracer retardation is accounted for (James *et al.*, 1997).

Flux-averaged concentrations

The conceptual model of groundwater flow that underlies the stochastic Lagrangian models of solute transport is a flow field resolved into a collection of flow paths or streamtubes. Solute transport is modelled by following "solute parcels" as they move by advection and undergo mass transfer and transformation processes along the streamtubes (Cvetkovic & Dagan, 1994). The transport equations are formulated in Lagrangian coordinates, which can be expressed by a temporal parameterization in terms of trajectories, $\mathbf{X}(t)$, or a spatial one in terms of travel time, $\tau(x)$, and transverse coordinates, $\eta(x)$ and $\varsigma(x)$, at a given longitudinal position.

In the present work, we employ a stochastic Lagrangian methodology which essentially comprises the following three steps: (a) solution of the transport equation for a single streamtube, (b) spatial averaging to obtain the flux-averaged concentration, and (c) derivation of the temporal moment equations. We assume ergodic conditions, which implies that the spatial averaging in step (b) is replaced by ensemble averaging over the relevant random space functions (cf. below). Furthermore, local dispersion, and hence mass transport between streamtubes, is neglected.

Using the spatially variable distribution coefficient, equation (1), the transport equation for tracer i along a single streamtube that crosses the CP at $\mathbf{a}(a_y, a_z)$ within Ω can be written as (cf. Cvetkovic *et al.*, 1998):

$$\{1+\lambda_i \theta_n [\mathbf{X}(\tau)]\}\frac{\partial C}{\partial t}+\frac{\partial C}{\partial \tau}=0 \tag{2}$$

where C is the aqueous concentration, and the argument of θ_n is the position along the streamtube that corresponds to τ. The transport equation for a nonreactive tracer is obtained for $\lambda_i = 0$. The advective travel time between the IP and the plane at x can be expressed as an integration along the streamtube:

$$\tau(x;\mathbf{a})=\int_0^x \frac{\mathrm{d}x'}{v_x[x',\eta(x';\mathbf{a}),\varsigma(x';\mathbf{a})]} \tag{3}$$

We consider tracer injection at a constant concentration during a finite time interval into an initially tracer-free domain; the initial condition is $C(0,\tau)=0$, whereas the boundary condition is $C(t,0)=C_0$ for $0<t<\Delta t_0$ and $C(t,0)=0$ otherwise. The solution of equation (2) for these initial and boundary conditions is:

$$C(t,\tau;\mu)=\begin{cases} C_0 & \text{for } \tau+\lambda_i\mu<t<\tau+\lambda_i\mu+\Delta t_0 \\ 0 & \text{otherwise} \end{cases} \tag{4}$$

where μ is the integrated NAPL content along the streamtube. In the t,τ space, μ is a function of τ. However, in analogy with equation (3), it can also be represented as a function of x (Cvetkovic *et al.*, 1998):

$$\mu(x;\mathbf{a})=\int_0^x \frac{\theta_n[x',\eta(x';\mathbf{a}),\varsigma(x';\mathbf{a})]}{v_x[x',\eta(x';\mathbf{a}),\varsigma(x';\mathbf{a})]}\mathrm{d}x' \tag{5}$$

The field-scale, flux-averaged concentration, C_f, is defined as the total solute discharge through Ω, i.e. the integral of the local tracer discharge $\theta_w v_x C \mathrm{d}\mathbf{a}$ over all area elements $\mathrm{d}\mathbf{a}$ within Ω, divided by the corresponding water discharge; C_f is the concentration in the effluent through Ω after complete mixing. Since $\mathbf{v}$ and θ_n are random, the integrated Lagrangian variables τ and μ are also random. Under the assumed conditions of statistical stationarity and ergodicity, the expression for the flux-averaged concentration at the CP can be written as:

$$C_f(t,x_{cp})=\frac{1}{u}\left\langle v_{cp} C[t,\tau(x_{cp});\mu(x_{cp})]\right\rangle \tag{6}$$

where v_{cp} is the velocity in the x direction at the CP ($u=\langle v_{cp}\rangle$), and the random v_{cp},τ,μ are for the same streamtube.

Temporal moments

The absolute temporal moment of order p of the BTC for C_f is defined as:

$$m_p(x_{cp}) = \int_0^{\infty} t^p C_f(t, x_{cp}) \mathrm{d}t \tag{7}$$

In the present work, we focus on the normalized first moment, $T_{BTC} = m_1 / m_0$, and the second, centred moment, $S^2_{BTC} = m_2 / m_0 - (T_{BTC})^2$; T_{BTC} and S^2_{BTC} quantify the mean residence time and the spreading around the mean residence time, respectively.

Using equations (4) and (6), the temporal moment equations are readily derived from equation (7); the resulting expressions can be written as:

$$T_{BTC}(x_{cp}) = T_\tau(x_{cp}) + \lambda_i T_\mu(x_{cp}) + \frac{\Delta t_0}{2} \tag{8}$$

$$S^2_{BTC}(x_{cp}) = S^2_\tau(x_{cp}) + 2\lambda_i S_{\tau\mu}(x_{cp}) + \lambda_i^2 S^2_\mu(x_{cp}) + \frac{\Delta t_0^2}{12} \tag{9}$$

where, again, the equations for a nonreactive tracer are obtained by setting $\lambda_i = 0$. The temporal moments in equations (8) and (9) depend on a set of velocity-weighted statistical moments of τ and μ, defined as:

$$T_\tau = \frac{1}{u}\langle v_{cp}\tau\rangle; \quad T_\mu = \frac{1}{u}\langle v_{cp}\mu\rangle \tag{10}$$

$$\begin{aligned} S^2_\tau &= \frac{1}{u}\langle v_{cp}(\tau - T_\tau)^2\rangle = \frac{1}{u}\langle v_{cp}\tau^2\rangle - (T_\tau)^2 \\ S_{\tau\mu} &= \frac{1}{u}\langle v_{cp}(\tau - T_\tau)(\mu - T_\mu)\rangle = \frac{1}{u}\langle v_{cp}\tau\mu\rangle - T_\tau T_\mu \\ S^2_\mu &= \frac{1}{u}\langle v_{cp}(\mu - T_\mu)^2\rangle = \frac{1}{u}\langle v_{cp}\mu^2\rangle - (T_\mu)^2 \end{aligned} \tag{11}$$

It can be seen in equations (8) through (11) that the first and second temporal moments can be obtained from the statistical moments of the Lagrangian variables, provided these variables are weighted by the corresponding local velocities in the CP. If the correlation lengths of the random space functions are finite, the effect of this weighting decreases with increasing distance to vanish in the limit $x \to \infty$.

APPLICATION OF THE MOMENT EQUATIONS

In order for the moment equations to be useful in a parameter estimation scheme, the various joint moments in equations (10) and (11) must be related to the (Eulerian) statistical moments of K (or v) and θ_n. Using equations (3) and (5), and by application of flow continuity along a single streamtube and for the whole plume, the following simple expressions for the moments in equation (10) are obtained:

$$T_\tau = \frac{x_{cp}}{u}; \quad T_\mu = \frac{x_{cp}}{u}\langle\theta_n\rangle \tag{12}$$

which are exact results, and not derived on the basis of first-order approximations.

General, closed-form expressions for the terms in equation (9) for the second moment are not available. In principle, a parameter estimation procedure based on numerical simulations of nonreactive transport (cf. Cvetkovic *et al.*, 1998) could be developed. However, a particular complication is that the correlation lengths associated with K and θ_n cannot be inferred from observations in a single control plane; hence, independent information on the correlation structures would be required. An alternative, which may be useful for preliminary studies, is to assume some simple heterogeneity structure, such as that of a stratified formation.

For illustrative purposes, we consider a perfectly stratified aquifer, i.e. K and θ_n are spatially variable in the vertical direction (z) only, with flow and transport in the x direction. The correlated K and θ_n fields are described as:

$$K(z) = K^G \exp[Y(z)]; \ \theta_n(z) = \theta_n^G \exp[\beta Y(z) + W(z)] \tag{13}$$

where Y and W are two normally distributed, uncorrelated random fields, β determines the strength of correlation, and superscript "G" denotes geometric mean. The first moment of a partitioning tracer is given by equations (8) and (12), whereas the various terms in equation (11), required for the second moment (equation (9)), are:

$$\begin{aligned} S_\tau^2 &= (T_\tau)^2\left[\exp(\sigma_Y^2) - 1\right] \\ S_{\tau\mu} &= T_\tau T_\mu \left\{\exp\left[\sigma_Y^2(1-\beta)\right] - 1\right\} \\ S_\mu^2 &= (T_\mu)^2\left\{\exp\left[\sigma_Y^2(1-\beta)^2 + \sigma_W^2\right] - 1\right\} \end{aligned} \tag{14}$$

where σ_Y^2 and σ_W^2 are the variances of Y and W, respectively.

It can be observed that in order to infer the three variability parameters in equation (14) from a tracer experiment, we must have data on the second moments of one nonreactive and two partitioning tracers. The sensitivity of the second temporal moment to β and σ_W^2 is illustrated in Fig. 1, where we consider an instantaneous injection ($\Delta t_0 \to 0$) with all other parameters set to unity. It is seen that the second moment increases with decreasing β and with increasing σ_W^2. The results in Fig. 1 indicate a relatively high sensitivity to β, implying that the strength of the $K-\theta_n$ correlation has a significant effect on the second moment.

CONCLUSIONS

For the injection and detection conditions considered in the present study, the temporal moments of a partitioning tracer can be expressed as velocity-weighted ("flux-averaged") statistical moments of the integrated Lagrangian variables τ and μ. The relation between the moments of the Lagrangian variables and those associated with

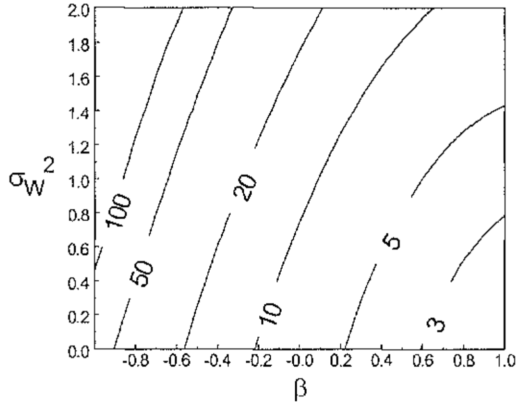

Fig. 1 Sensitivity of the second moment (equation (9)) to β and the variance of W.

the hydraulic conductivity and the NAPL content is illustrated here for the special case of a stratified aquifer. Our work in progress focuses on the development of estimators that are applicable to more general heterogeneity structures.

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