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# Modeling kinetic non-equilibrium using the first two moments of the residence time distribution

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Abstract: A method for simulating field scale transport of kinetically adsorbing solutes is described. The non-equilibrium adsorption is modeled as a birth and death process and is coupled with the particle tracking approach using the first two moments of the distribution of the particle residence time, i.e., the time that a solute particle stays in the liquid phase. A single residence time distribution, regardless of the initial and final phase, is demonstrated to yield an accurate description of chemical kinetics in the vast majority of field scale problems. The first two moments of the residence time distribution are derived as a function of chemical reaction rates and the transport time interval $\Delta t$. It is shown that the first moment of the residence time represents a measure of the speed of the chemical reaction relative to the transport time scale $\Delta t$ which is chosen depending on the velocity field. The second moment of the residence time reflects the relative importance of the chemical kinetics versus local equilibrium conditions for the given transport time step $\Delta t$. The simulated spatial moments of the contaminant plume are compared in the one-dimensional case with available analytical solutions to demonstrate the accuracy of the proposed technique. A two-dimensional case for stratified formations is presented to study the transport behavior for heterogeneous velocity fields and variable distribution coefficient, hypothesized as being negatively correlated with hydraulic conductivity. The results show that the enhanced plume spreading and the statistics of the arrival time distribution appear to be more sensitive to the spatially variable distribution coefficient than to the kinetics alone. In fact, the second spatial moment was almost doubled in the case of spatially variable distribution coefficient.

Key words: Kinetic non-equilibrium, residence time, spatially variable chemical reactions.

## 1 Introduction

Pollutant fate and transport in natural aquifers is highly dependent on the physical, chemical, and biological processes governing solute transport. A solute partitioning between solid and liquid phase, such as a surface-chemical reaction, is one of the most important processes influencing the fate of many organic pollutants whose transport is generally retarded by the presence of such a sorption mechanism. The local equilibrium assumption (LEA) has been widely used to date to describe chemical reactions between moving fluid and active sorption sites when these reactions are much faster than the fluid flow rate. Several recent investigations (e.g. Jennings and Kirkner, 1984; Valocchi, 1985; Bahr and Rubin, 1987) reported the conditions for which LEA is applicable. Other studies (e.g. Miller and Weber, 1986; Hutzler et al., 1986; Bouchard et al., 1988; Roberts, et al., 1986) have observed the deviations from local equilibrium in the spreading and tailing of breakthrough curves in laboratory experiments. Non-equilibrium phenomena or rate limited sorption models have been examined extensively in laboratory experiments for homogeneous soil columns focusing on the kinetic non-equilibrium (e.g., the chemical will be adsorbed slowly) and/or physical non-equilibrium (van Genuchten and Wierenga, 1976; Nkedi-Kizza et al., 1984) which describes the physical resistances encountered by a chemical trying to reach the sorption sites of the porous medium during its movement through the soil.

We adopt in this paper the scale description of porous media as laboratory or pore scale, local or formation scale, and regional scale (Dagan, 1986). The local scale refers to the scale of the aquifer (depositional unit). The regional scale usually refers to cases where the areal dimension is much larger then the aquifer thickness. Most of the local and regional scale problems can be described as field scale problems and this term will be used throughout this paper. The degree of spatial variability of the hydraulic conductivity is measured by the heterogeneity scale defined as the distance over which e.g., the core plug values of hydraulic conductivity are still correlated (order of several meters). The heterogeneity of hydrogeological parameters (hydraulic conductivity, porosity) in field scale problems causes the spatial variability in the flow field. The dispersion which results from the spatial variation of the velocity field has been named macrodispersion (Gelhar and Axness, 1983; Dagan, 1986) to distinguish it from the pore-scale dispersion. Therefore the overall plume spreading of reactive solutes in the field scale comes from a combination of spreading due to heterogeneity in the velocity field and to the possible non-equilibrium processes which may also exhibit spatial heterogeneity. As a consequence of the heterogeneity in the hydrogeology and possible heterogeneity in the chemical reactions the modeled concentration point value is highly erratic and for practical purposes sometimes meaningless. For that reason the spatial characteristics of the moving plume i.e., the spatial and/or temporal moments are more informative tools for analyzing the reactive transport and will be employed in this study.

In order to study coupled phenomena of non-equilibrium chemistry and transport at the field scale the employed numerical technique needs to posses negligible numerical dispersion and be computationally efficient for three dimensional applications. The particle tracking approach meets these requirements (Kinzelbach, 1988) and is especially attractive for problems involving chemical reactions. Apart from being free from numerical dispersion ( in the classical sense), the treatment of chemical reactions at the particle level provides more flexibility for spatial and temporal moment analysis and allows better insight from the chemical modeling standpoint. This technique typically represents the solute mass as a large collection of particles; each particle is moved with deterministic and random displacements over discrete increments of time. The magnitude of each displacement depends upon the velocity and dispersion field.

Coupling the chemical reaction process with the transport model usually involves integrating the chemical reaction rate over the transport time scale represented by the time step $\Delta t$ whose choice depends on the velocity field. The smaller the time scale of the reaction process relative to $\Delta t$, the more sophisticated an integration scheme is needed (Tompson and Dougherty, 1990). Integrating the chemical reaction rate over $\Delta t$ is equivalent to solving the chemical reaction process in a stochastic framework by estimating the particle residence time in the liquid phase. The importance of accurately estimating the residence time in the liquid phase stems from the fact that only dissolved solutes participate in the transport. Several recent investigations (Kinzelbach, 1988; Valocchi and Quinodoz, 1989) have employed a stochastic description of the chemical reaction process. Their approaches differ in the way the transition probabilities and waiting times in the liquid phase are estimated.

This paper follows the line of coupling the particle tracking technique with a stochastic description of a chemical reaction. A field scale transport model of kinetically adsorbing solutes is presented where the kinetic non-equilibrium is generally described as a birth and death process which in the case of one solute and two states reduces to a two-state continuous time Markov process. The main focus of this paper is to examine the possibility of modeling kinetic non-equilibrium using the first two moments of the distribution of the solute residence time in the liquid phase. The particle residence time per time step $\Delta t$ is defined as the random sum of random variables and its first two moments are analytically approximated. We demonstrate that the use of the first two moments of the residence time distribution per $\Delta t$ provides an accurate description of the first two spatial moments of the contaminant plume for most field scale transport problems. The use of the first two moments of the residence time distribution is computationally efficient and particularly attractive if spatially variable chemical reactions are employed. The first moment of the residence time distribution represents a measure of the chemical reaction speed relative to the transport time step $\Delta t$ and the second moment indicates the relative importance of kinetic non-equilibrium with respect to $\Delta t$, where $\Delta t$ depends on the velocity field. One-and two-dimensional examples are presented to illustrate the accuracy and limitations of the proposed technique when modeling reactive field scale transport in heterogeneous media.

## 2 Particle tracking model of reactive solutes

Consider the transport model given by the advection-dispersion equation which describes the large scale movement of pollutants in groundwater. The transport equation of the conservative solute in two horizontal dimensions (Bear, 1979) is given by:

$$\frac{\partial c}{\partial t}+u_x\frac{\partial c}{\partial x}+u_y\frac{\partial c}{\partial y}=\frac{\partial}{\partial x}(D_{xx}\frac{\partial c}{\partial x}+D_{xy}\frac{\partial c}{\partial x})+\frac{\partial}{\partial y}(D_{yy}\frac{\partial c}{\partial x}+D_{yx}\frac{\partial c}{\partial x}) \tag{1}$$

where $c$ is the concentration ($M/L^3$), $u_x$ is the velocity ($L/T$) in $x$ direction, and $D$ is the dispersion tensor with $D_{xx}$, for example, being the dispersion coefficient ($L^2/T$) in the $x$ direction.

The random walk method, as a special case of the particle tracking approach, has a full analogy with the Fokker-Plank equation (Tompson et al., 1989). In particular, the two-dimensional particle distribution can be obtained from a random walk model with step equations of the form (Kinzelbach, 1988)

$$x(t+\Delta t)=x(t)+u_x^*\Delta t+z_1\sqrt{2\alpha_1 u\Delta t}\frac{u_x}{u}-z_2\sqrt{2\alpha_t u\Delta t}\frac{u_y}{u} \tag{2a}$$

$$y(t+\Delta t)=y(t)+u_y^*\Delta t+z_1\sqrt{2\alpha_1 u\Delta t}\frac{u_y}{u}-z_2\sqrt{2\alpha_t u\Delta t}\frac{u_x}{u} \tag{2b}$$

where

$$u_x^*=u_x+\partial D_{xx}/\partial x+\partial D_{xy}/\partial y$$

$$u_y^*=u_y+\partial D_{yy}/\partial x+\partial D_{yx}/\partial y$$

$$u=\sqrt{u_x^2+u_y^2}$$

and $z_1$ and $z_2$ are random deviates from a standard Normal distribution $N(0,1)$, and $\alpha_1$ ($L$) and $\alpha_t$ ($L$) are the longitudinal and transversal local dispersivities, respectively. The second term in (2) represents the convective displacement while the third and fourth terms denote the dispersive displacement. The velocity term in the step equation has been augmented with the dispersion gradient in order to account for stagnation zones in the case of variable velocity field. Around a stagnation point the convective and dispersive displacements vanish and the dispersion gradient generates the additional velocity components to move particles out of stagnation zones. However, in a slow varying velocity field the dispersion gradient can be neglected.

In order to describe the kinetic non-equilibrium the transport equation (1) needs to be modified. For illustration purposes, we will present the case of one-dimensional steady flow in a homogeneous porous medium

$$\frac{\partial c}{\partial t}+\frac{\rho}{\theta}\frac{\partial s}{\partial t}=D_x\frac{\partial^2 c}{\partial x^2}-u_x\frac{\partial c}{\partial x} \tag{3}$$

where $c$ is the fluid concentration (species mass/fluid volume), $s$ is the solid concentration (species mass/solid mass), $\rho$ is the bulk density (solid mass/aquifer volume), and $\theta$ is the porosity (fluid volume/aquifer volume). In the process of coupling a chemical reaction with the transport model there is a need to describe the chemical reaction rate which is now a part of the transport equation (3). In this study the first order reversible linear reaction rate is used as described by

$$\frac{\partial S}{\partial t}=k_2(K_d c-S) \tag{4}$$

where $S=\rho s/\theta$ is the concentration of the solid matrix represented in the same units as $c$, $K_d$ is a dimensionless equilibrium distribution coefficient, and $k_2$ is the kinetic rate coefficient ($T^{-1}$). Equation (4) can also be written as

$$\frac{\partial S}{\partial t}=k_1 c-k_2 S \tag{5}$$

where $k_1$ ($T^{-1}$) and $k_2$ ($T^{-1}$) are the forward and reverse rate coefficients, respectively, related to the distribution coefficient with $K_d=k_1/k_2$. The rate law (4) approaches the local equilibrium condition with the linear adsorption isotherm $S=K_d c$ and retardation factor $R=1+K_d=1+k_1/k_2$ when the reaction rates $k_1$ and $k_2$ approach infinity at constant $K_d$ (Jennings and Kirkner, 1984).

The boundary conditions for (3) are:

$$c=0,\ s=0,\ \frac{\partial c}{\partial x}=0,\text{ and }\frac{\partial s}{\partial x}=0\ at\ x\to\pm\infty$$

We assume that at $t=0$ there is no solute in the aquifer and that the pollutant is injected as an instantaneous, fully penetrating source implying the initial condition

$$c=C_0\delta(x)\text{ and }s=0\ at\ t=0$$

where $\delta(\cdot)$ is the Dirac delta function and $C_0$ represents a normalizing constant proportional to the total input mass.

Ahlstrom et al. (1977) applied the discretized form of (5) in space to determine the adsorbed concentration and then solved the transport problem using the random walk method. This approach evidently requires very small time step to justify the decoupling of the two processes. Valocchi and Quinodoz (1989) used a continuous time two-state Markov chain to describe (5) and compared three different methods of generating the waiting times in the liquid phase. The most efficient method of acceptable accuracy was that of sampling the waiting times from the four conditional probability distribution functions of the fraction of time that a particle spends in the liquid phase during a time interval $\Delta t$ (Keller and Giddings, 1960). Each distribution was conditioned on the initial and final phase, and a value of the fraction (between 0 and 1) was obtained going through a three-step procedure applied for each particle. This approach particularly emphasizes the situation where particles undergo very few (or even none) transitions from solid to liquid phase.

The approach applied in this paper is similar to the method employed by Valocchi and Quinodoz (1989) in that the concentration plume spatial moments are computed by the particle tracking technique and the chemical reaction is modeled in a stochastic framework. The main difference is that in our study the residence time distribution is approximated by its first two moments which are derived as functions of the transport time step $\Delta t$ and the chemical reaction parameters $k_1$ and $k_2$. The accuracy of this approximation is demonstrated and discussed by comparing the marginal probability density function obtained by properly weighing the above mentioned four conditional distributions (Keller and Giddings, 1960) to a normal distribution with mean and variance equal to the derived moments. The applicability and accuracy of using the first two moments of the residence time distribution for field scale transport problems is evaluated by comparing the simulated first two spatial moments of the concentration plume with the available closed form analytical solution (Valocchi, 1988).

### 2.1 *Stochastic description of kinetic non-equilibrium*

The chemical reaction in (5) represents a simplified version of a non-equilibrium model based on diffusive solute transport between mobile and stagnant fluid zones (van Genuchten and Wierenga, 1976). In general, kinetic non-equilibrium represents the chemical process of several interacting species in the mobile and immobile phase. Some possible examples are cation exchange systems between several chemical components or the biodegradation processes where, for example, the heterotrophic denitrification is carried out by bacteria microorganisms. Most of these processes represent chemical kinetics which can be described as a birth and death process with corresponding forward and reversible rates (Erdi and Toth, 1989; Goel and Rihter-Dyn, 1974)

$$A_0 \underset{\mu_1}{\overset{\lambda_0}{\rightleftharpoons}} A_1 \underset{\mu_2}{\overset{\lambda_1}{\rightleftharpoons}} A_2 \cdots \underset{\mu_n}{\overset{\lambda_{n-1}}{\rightleftharpoons}} A_n \tag{6}$$

where $A_i, i = 0,1,\ldots,n$, stands for different chemical species in the mobile and immobile phases and various $\lambda$'s and $\mu$'s are the reaction rate constants. Let $P_{i,j}(t)$ be the transition probability that process is at state $i$ at time $t$, given that it was at state $j$ at $t = 0$. The probabilistic description of the reaction above is given by

$$dP_{i,j}(t)/dt = \lambda_{j-1}P_{i,j-1}(t)+\mu_{j+1}P_{i,j+1}(t)-(\lambda_j+\mu_j)P_{i,j}(t) \tag{7}$$

where $i = 0,1,\ldots,n$ and $j = 0,1,\ldots,n$ are the states of the process. Equations (7) are known as the Kolmogorov differential equations or master equations whose solution may be obtained subject to an initial condition, e.g., $P_{i,j}(0) = \beta_{i,j}$. If $\beta_j$ denotes the probability of the process initially being in state $j$ (with $\sum_j \beta_j = 1$, then $P_i(t)$ (the probability that the solute is in state $i$ at time $t$) is given by

$$P_i(t) = \sum_j P_{i,j}(t)\beta_j \tag{8}$$

For the simple case of one component and two states (solid and liquid) the general birth and death process reduces to a two-state continuous time Markov chain as also employed by Valocchi and Quinodoz (1989). Although in this paper only a two-state example is presented, in which case the birth and death process reduces to a Markov chain, we retain the generality of the birth and death type process which can deal with more complex cases, as for example with the case of modeling bacteria population growth and decay when a biodegradation process is considered. In that case the bacteria population is represented with a finite number of particles and the birth and death reaction rates are used to model the population growth or decay marching through the transport time scale.

The two-state chemical process as described in (5) (with state 2 meaning that solute is in the solid phase and state 1 that it is in the liquid phase) has the following parameters.

Birth or arrival rate $\lambda = k_1$ and $\lambda_2 = 0$

Death or departure rate $\mu_1 = 0$ and $\mu_2 = k_2$

The Kolmogorov equations in this case can be written as

$$dP_{1,1}(t)/dt = k_2P_{1,2}(t) - k_1P_{1,1}(t) \tag{9a}$$

$$dP_{1,2}(t)/dt = k_1P_{1,1}(t) - k_2P_{1,2}(t) \tag{9b}$$

$$dP_{2,1}(t)/dt = k_2P_{2,2}(t) - k_1P_{2,1}(t) \tag{9c}$$

$$dP_{2,2}(t)/dt = k_1P_{2,1}(t) - k_2P_{2,2}(t) \tag{9d}$$

With a given initial condition $P_{1,1}(0) = 1$ (all particles in the liquid phase – instantaneous injection) the above set of equation can be solved (Ross, 1985) yielding four transition probabilities

$$P_{1,1}(\Delta t) = \frac{k_2}{k_1+k_2} + \frac{k_1}{k_1+k_2} exp[-(k_1+k_2)\Delta t] \tag{10a}$$

$$P_{2,2}(\Delta t) = \frac{k_1}{k_1+k_2} + \frac{k_2}{k_1+k_2} exp[-(k_1+k_2)\Delta t] \tag{10b}$$

$$P_{2,1}(\Delta t) = 1 - P_{2,2}(\Delta t) = \frac{k_2}{k_1+k_2}[1 - exp[-(k_1+k_2)\Delta t]] \tag{10c}$$

$$P_{1,2}(\Delta t) = 1 - P_{1,1}(\Delta t) = \frac{k_1}{k_1+k_2}[1 - exp[-(k_1+k_2)\Delta t]] \tag{10d}$$

where instead of $t$ we have used $\Delta t$ which is the time step of the particle tracking step equation (2). To obtain the total probability that a particle is in the liquid phase at $t+\Delta t$, equation (8) yields

$$P_1(t+\Delta t) = P_{1,1}(\Delta t)P_1(t) + P_{1,2}(\Delta t)P_2(t); \quad P_1(0) = 1, \ P_2(0) = 0 \tag{11}$$

where $P_1(t)$ and $P_2(t)$ are the probabilities that a particle is in the liquid and solid phase at time $t$, respectively, and $P_1(t+\Delta t)$ is the probability that a particle will be in the liquid phase at time $t+\Delta t$. Equations (10a-d) and (11) must be coupled with the transport model to provide at each time step the fraction of the particles adsorbed on the solid phase.

## 3 Residence time distribution in the liquid phase

The crucial step in applying the random model of chemical kinetics in transport of reactive solutes is the accurate estimation of the residence time of each particle in the liquid phase. During a time step $\Delta t$ (determined as a function of the velocity field) each particle will make transitions (phase changes) between solid and liquid phase depending on the considered reaction rates for the partitioning process. Between transitions each particle stays in the liquid or solid phase an amount of time (in the liquid phase $w_1$ and in the solid phase $w_2$) which is exponentially distributed as

$$f_1(w_1) = k_1 exp(-k_1w_1), \quad w_1 \geq 0 \tag{12}$$

$$f_2(w_2) = k_2 exp(-k_2 w_2)\,, \quad w_2 \geq 0 \tag{13}$$

The times $w_1$ and $w_2$ are independent random variables. This directly implies that the counting process $N(t)$ of transitions from liquid to solid or solid to liquid phase is a renewal process with interarrival times $w = w_1 + w_2$. The renewal process $N(t)$ represents the number of phase changes in a time interval $(0,t)$ and can be viewed as an indicator of the speed of the underlying chemical process relative to the time $t$. The first two moments of the interarrival time $w$ are easily obtained as

$$E(w) = \frac{k_1+k_2}{k_1 k_2} \tag{14}$$

$$Var(w) = \frac{1}{k_1^2} + \frac{1}{k_2^2} \tag{15}$$

The key problem is to determine the total time each particle stays in the liquid phase (residence time) during a time step $\Delta t$.

We difine $\Delta t^*$ as the residence time of each particle in the liquid phase during a given actual transport time step $\Delta t$. $\Delta t^*$ is a random variable which by definition can be expressed as

$$\Delta t^* = \sum_{i=1}^{N(\Delta t)} w_{1,i} \tag{16}$$

where $N(\Delta t)$ is the random number of transitions from solid to liquid phase during the actual time interval $\Delta t$ and $w_{1,i}$ is the time spent in the liquid phase during the transition $i$. Figure 1 depicts a schematic diagram of the liquid to solid transitions and the residence time representation.

The random number of transitions from solid to liquid phase, $N(\Delta t)$, represents the counting renewal process evaluated at time interval $\Delta t$. The first two moments of $N(\Delta t)$ can be obtained from the mean and variance of the interarrival times $w$ making use of some asymptotic results (e.g., see Taylor and Karlin, 1975 p. 289 for an interpretation of the asymptotics of the renewal theorem)

$$\lim_{t\to\infty} E[N(t+\Delta t)-N(t)] = \lim_{t\to\infty} E[N(\Delta t)] \approx \frac{\Delta t}{E(W)} = \frac{k_1 k_2}{k_1+k_2}\Delta t = \frac{k_1}{1+Kd}\Delta t = \frac{k_1}{R}\Delta t \tag{17}$$

$$\begin{aligned}\lim_{t\to\infty} Var[N(t+\Delta t)-N(t)] &= \lim_{t\to\infty} Var[N(\Delta t)] \approx \frac{Var(W)}{(E(W))^3}\Delta t \\ &= \frac{k_1 k_2 (k_1^2+k_2^2)}{(k_1+k_2)^3}\Delta t = \frac{k_1(1+Kd^2)}{R^3}\Delta t\end{aligned} \tag{18}$$

Notice that the large time requirement for the validity of the above approximations is not a limiting factor particularly in field scale transport problems, since the "large time" for chemical reactions (large number of transitions) is usually achieved after only a few transport time steps $\Delta t$. It is also worth noting that by analyzing the above first two moments it appears that the index of dispersion of $N(\Delta t)$,

$$I(\Delta t) = Var[N(\Delta t)]/E[N(\Delta t)] = \frac{1+Kd^2}{R^2} = \frac{1+Kd^2}{1+2Kd+Kd^2} \tag{19}$$

is (as was expected) always less than one suggesting that $N(\Delta t)$ is an under-dispersed process (more regular process) relatively to the Poisson process with the same rate of

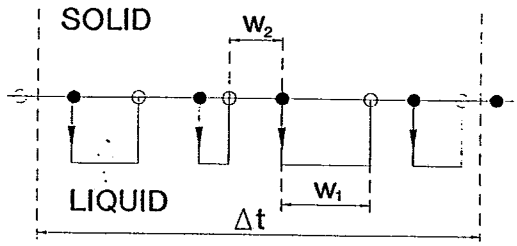

**Figure 1.** Schematic of the phase transitions during the transport time interval $\Delta t$

occurrence. The average number of transitions, $E[N(\Delta t)]$, can be seen as an indication of *the speed of the chemical reaction process relative to the transport time scale.* In other words the term $R/k_1$ in (17) represents the fraction of the transport time step $\Delta t$ needed for one chemical reaction (on the average) which in this case refers to one transition from solid to liquid phase. Also, note that the waiting times $w_1$, in liquid phase between transitions, are independent and identically distributed random variables and that the counting process $N(\Delta t)$ of transitions from solid to liquid phase depends on the magnitude of the waiting times $w_1$. The first moment of the residence time in the liquid phase per time step $\Delta t$ can be derived as (Benjamin and Cornell, 1970)

$$E[\Delta t^*] = E[N(\Delta t)]E[w_1] = \frac{k_2}{k_1+k_2}\Delta t = \frac{1}{R}\Delta t \tag{20}$$

and the second moment can be approximated by

$$Var[\Delta t^*] \approx (E[w_1])^2 Var[N(\Delta t)] = \frac{k_2(k_1^2+k_2^2)}{k_1(k_1+k_2)^3}\Delta t = \frac{1+Kd^2}{k_1 R^3}\Delta t \tag{21}$$

The accuracy of the above approximation was found very satisfactory as will be discussed in detail in the numerical example.

It is important to notice that by considering the residence time in the liquid phase only through its first moment, the chemical kinetic are reduced to local equilibrium conditions, where the entire solute transport is just retarded by the factor $R$ (same as scaling the time of nonreactive transport by the factor $R$). The second moment (variance of $\Delta t^*$) represents the variability in the liquid residence time. It is precisely this variability that results in the increased spreading and tailing of contaminant plumes and breakthrough curves as is shown and quantitatively examined in the numerical examples.

## 4 Assessment of the accuracy of the proposed approximation

Our approach has introduced an approximation resulting from the use of a single residence time distribution (instead of four conditional distributions) with the first two moments obtained from (20) and (21). Assessment of the accuracy of this approximation is done in two steps. First, in this section we directly compare the residence time distribution described with the first two moments computed from (20) and (21) and the marginal residence time distribution obtained by properly weighing the four conditional distributions of Keller and Giddings (1960) also employed by Valocchi and Quinodoz (1989). In the next section we assess the accuracy of this approximation by examining the conditions under which the use of only the first two moments of the residence time distribution provides an accurate description of field scale transport problems in terms of accurately approximating the spatial moments of the contaminant plume.

(a)

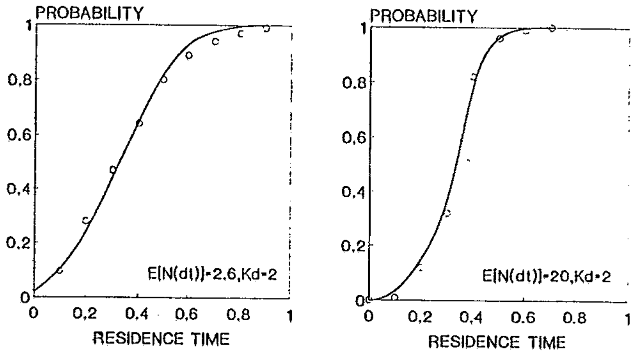

Figure 2a

(b)

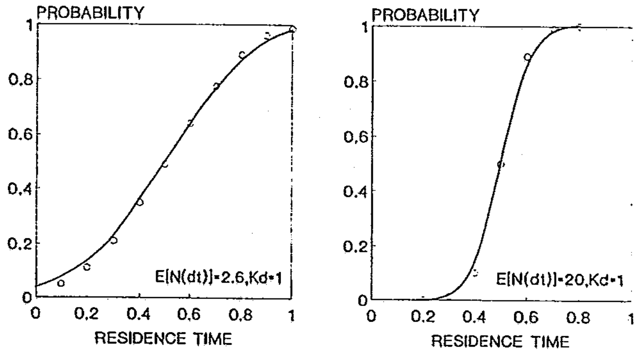

Figure 2b

(c)

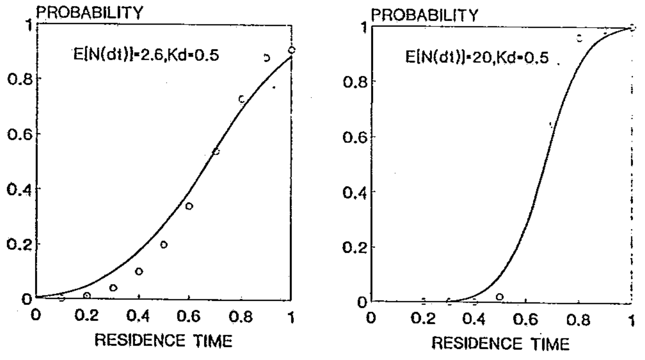

Figure 2c

**Figure 2.** Comparison between the proposed residence time distribution (solid line) and marginal distribution obtained by weighing the four conditional distributions depending on final and initial phase (circles). (a) $K_d = 2$; (b) $K_d = 1$; (c) $K_d = 0.5$

In our approach the residence time $\Delta t^*$ is described in (19) as the sum of a random number ($N(\Delta t)$) of exponentially distributed random variables $w_1$ (Figure 1), where $N(\Delta t)$ is a counting process evaluated at the transport time scale $\Delta t$ i.e., it counts the number of state transitions from solid to liquid within an interval $\Delta t$. Keller and Giddings (1960) studied chemical reactions that do not undergo a transport mechanism and observed that after only "several transitions" solid $\rightleftharpoons$ liquid the residence time distribution approaches a Gaussian distribution. We argue that by including the field scale transport mechanism on top of the kinetics, the requirement for several transitions is easily satisfied as can be seen form (17) where the transport time step $\Delta t$ is in days and $k_1$ in inverse hours. In other words, even for a relatively slow intrinsic chemical reaction, e.g., $k_1 = 0.1\ hr^{-1}$, which undergoes transport described by a time step $\Delta t = 5$ days, several transitions between solid and liquid phase are obtained (e.g., 6 transitions from solid to liquid on the average for R=2). This is the reason for introducing $E[N(\Delta t)]$ as a measure of the speed of the chemical reaction relative to the transport time scale $\Delta t$. At the resolution of $\Delta t$ the speed of chemical reactions will determine the influence of kinetics upon the transport and this is captured by the first moment of the counting process $N(\Delta t)$. With several transitions taking place the starting and ending phase of a particle become insignificant and a marginal distribution approximation is appropriate. The marginal distribution of the residence time in the liquid phase can be obtained as

$$f(\xi) = p_1[f_{11}(\xi)+f_{12}(\xi)]+p_2[f_{21}(\xi)+f_{22}(\xi)], \quad 0<\xi<1 \tag{22a}$$

$$f(\xi=1) = p_1 exp(-k_1\Delta t) \tag{22b}$$

$$f(\xi=0) = p_2 exp(-k_2\Delta t) \tag{22c}$$

where $\xi$ denotes the fraction (between 0 and 1) of the residence time $\Delta t^*$ to the transport time step $\Delta t$; $f_{ij}(\xi), i,j=1,2$ are the four conditional pdfs of the residence time with $f_{12}(\xi)$, for example, being the conditional pdf of the particle starting in liquid phase and ending in solid phase after at least one transition; and $p_1$ and $p_2$ denote the probability of the particle being in the liquid and solid phase, respectively.

Figure 2a shows the comparison between the marginal residence time cumulative distribution calculated from (22) (circles) and approximated as a normal distribution with the first two moments evaluated from (20) and (21) (solid line) for the case of $K_d$ equal 2. Two different average number of transitions per $\Delta t$ are considered (i) $E[N(\Delta t)] = 2.6$ which may represent a slow reaction relative to the transport time step $\Delta t$ (e.g., $E[N(\Delta t)] = 2.6$ following (17) may describe a transport problem with intrinsic speed of chemical reaction equal to $k_1 = 0.065\ h^{-1}$, retardation factor $R = 1+K_d = 3$, and transport time step $\Delta t = 5$ days), (ii) $E[N(\Delta t)] = 20$ representing fast reactions relative to the time step $\Delta t$. In both cases the cumulative distribution obtained using the derived first two moments exhibits an acceptable accuracy and good agreement with the marginal residence time distribution. By increasing the average number of transitions per $\Delta t$ this agreement is more pronounced.

Figure 2b depicts the same type of comparison for the case of $K_d = 1$ ($R = 2$) and Figure 2c for $K_d = 0.5$ ($R = 1.5$). It is observed that in the case of $K_d = 0.5$, which corresponds to weakly retarded transport, a statistically significant difference between the two distributions is found which is due to the approximation introduced in evaluating the second moment of the residence time. Nevertheless, even in this case the spatial moments of the resulting concentration plume are in acceptable agreement with the closed-form analytical solution as evidenced by the numerical examples presented in the next section.

The above discussion and comparisons clearly demonstrate that the proposed technique is applicable to field scale transport problems when the velocity field allows the time step $\Delta t$ in transport simulations to be large enough to guarantee, on the average, several transitions between solid and liquid phase. Notice that this is the case for most field scale transport problems and thus for these problems the advantage of using a residence time distribution given by its first two moments is threefold:

a) Computational effort is significantly reduced since the residence time for each particle is generated directly from a normal distribution with known first two moments explicitly expressed as functions of the chemical reaction rates and transport time step $\Delta t$.

b) For multi-component cases or cases involving biodegradation the choice of a single distribution for the residence time and the use of a birth and death formulation provide a computationally attractive way of coupling stochastic models for chemical reactions and the particle tracking approach even for three dimensional applications when the four conditional distribution approach would be computationally prohibitive.

c) In the case of heterogeneous chemical reaction rates the single residence time distribution formulation is completely independent of the reaction rates and the computational implementation is straightforward. The computational effort is not increased compared to the homogeneous case.

## 5 Numerical examples

### *5.1 One-dimensional case*

The first numerical example considers a one-dimensional case and is presented to illustrate that the introduced approximation of the residence time distribution results in accurate description of the solute movement in terms of the spatial moments of the solute plume. This case was chosen based on the availability of a closed-form analytical solution of spatial moments (Valocchi, 1988; Goltz and Roberts, 1987). The computational flow domain is depicted on Figure 3 and consists of 100 cells of length $\Delta x = 1(L)$. A constant uniform velocity $v = 0.67$ $(L/T)$ was used in the one-dimensional form of (2), to move 5000 particles initially distributed uniformly in the fifth cell. A constant dispersivity $\alpha_1 = 0.2(L)$ and an actual time step $\Delta t = 1(T)$ were chosen to complete an input set of necessary variables for the transport problem. The proposed coupled model tested different kinetic reaction rates $k_1$ and $k_2$ while keeping the ratio $K_d = k_1/k_2$ equal to 0.5, 1.0, and 2.0. Following the proposed approach of the single residence time distribution each particle will be advected and dispersed in the transport model with the time step

$$\Delta t^* = E(\Delta t^*) + z\sqrt{Var(\Delta t^*)} \tag{23}$$

where $z$ is a standard normal random deviate and the mean and variance of $\Delta t^*$ are estimated by (20) and (21), respectively.

The simulation results of the numerical example are analyzed and compared with the analytically derived spatial moments of the contaminant plume. The first spatial moment provides information about the mean location of the plume and the second moment (displacement variance) provides information of the spreading of the contaminant plume about its mean displacement. Figure 4 represents the mean displacement of the solute plume for different $K_d$ values and for different speeds of chemical reactions expressed in terms of the expected number of transitions from solid to liquid phase during the transport time step $\Delta t$. As expected the mean location of the concentration plume using the first two moments of $\Delta t^*$ shows almost perfect match with the analytical solution regardless of the chemical reaction speed. The same result is also true for different values of the distribution coefficient $K_d$.

In Figure 5 the displacement variance is depicted for different expected number of transitions $E[N(\Delta t)]$, and different values of $K_d$. Figure 5a depicts the displacement variance for the case of $E[N(\Delta t)] = 2.6$ which represents slow kinetics relative to the transport time scale. In fact by considering $\Delta x = 1$ *m*, $\Delta t = 1$ *day*, and distribution coefficient

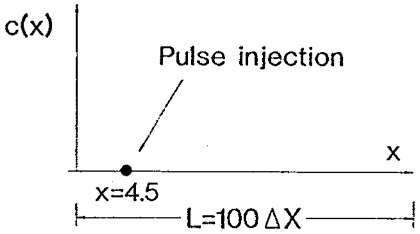

**Figure 3.** Numerical example layout for the one-dimensional case

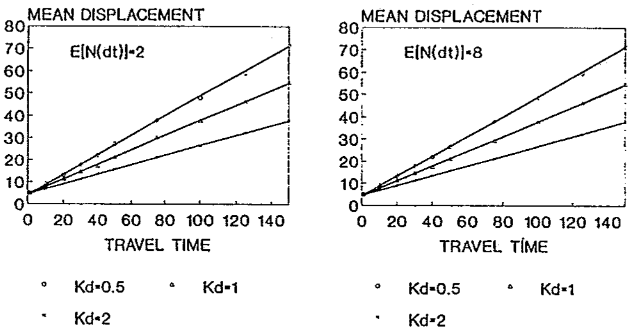

**Figure 4.** Mean plume displacement obtained by simulation using the first two moments of the residence time $\Delta t^*$ (points) compared with the analytical solution (solid line) for three different values of $E[N(\Delta t)]$

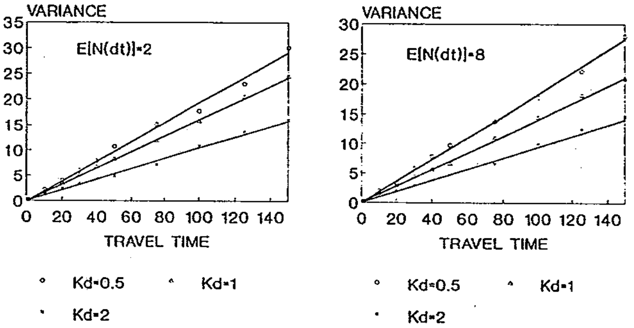

**Figure 5.** Displacement variance obtained by simulation (points) compared to the analytical solution (solid line)

$K_d = 1$, from (17) the reaction rate $k_1$ equals $0.2\,h^{-1}$ which may be considered as corresponding to a slow intrinsic adsorption process. Even for this slow kinetics the displacement variance shows an acceptable small deviation from the analytical solution justifying the use of the introduced single distribution approximation of the residence time. Notice that in Figure 5a the second moment of the particle cloud is also depicted for the case of slow reaction ($E[(N(\Delta t)] = 2.6$) and $K_d = 0.5$ for which we found (see previous section) the highest differences between the residence time distribution approximated with its first two moments and the marginal distribution obtained by weighing the four conditional distributions. It is observed that even in this case the simulated spatial moments still provide an acceptable accuracy compared to the analytical solution.

As expected for faster reactions ($E[N(\Delta t)] = 8$) the observed deviation from the analytical solution in Figure 5b is further reduced. By further increasing $E[N(\Delta t)]$ the numerical simulation results would give perfect match with the analytical solution due to the decreased variance of $\Delta t^*$ indicating also that the underlying process approaches the local equilibrium condition.

### *5.2 Stratified aquifer*

The second numerical example examines the case of a two-dimensional transport problem in a perfectly stratified formation composed of distinct layers. Since the continuity of such layers over large distances in field problems is not warranted the theoretical results may be unrealistic. Nevertheless, the study of stratified formations is a usual starting point for grasping more complex cases, and it can serve as a benchmark for numerical simulations (Dagan 1989).

The coordinate system used is given in Figure 6, namely $z$ is a vertical coordinate normal to the bedding, $x$ is a horizontal coordinate, $B$ is the formation thickness, and $\partial h/\partial x = -J$ is a constant head gradient parallel to the bedding. The flow is horizontal and the velocity vector $u = U+u'(z)$ (mean plus perturbation) can be easily obtained from

$$U = \frac{JK_a}{n}; \quad u'(z) = U\frac{K'(z)}{K_a} \tag{24}$$

where $K_a = E[K(z)]$ is the hydraulic conductivity arithmetic mean, $K'(z)$ is the conductivity perturbations, and $n$ is the porosity. A total of 10000 particles were injected at the source (Figure 6) and moved with the heterogeneous velocity field using a constant local longitudinal dispersivity $\alpha_l = 0.2$ $(L)$ and constant transversal dispersivity $\alpha_t = 0.02$ $(L)$. Thus, vertical transport is allowed only due to the local transversal dispersion.

Besides studying the reactive transport behavior under the heterogeneous velocity field, in this example we also examined the case of spatially variable distribution coefficient $K_d$. We assumed that $K_d$ is stationary with constant mean $\overline{K}_d$, and perturbations $K'_d(z)$. Following some of the recent studies (Garabedian, 1987) we assumed that $K_d$ is negatively correlated to the hydraulic conductivity field. The correlation between $K'_d$ and $K'$ is assumed to be a linear one $K'_d(z) = \alpha K'(z)$.

To illustrate the impact of chemical kinetics upon the transport in heterogeneous formations we evaluated the second spatial moment (displacement variance) of the solute plume. The simulation was performed by generating fifty realizations of the log-hydraulic conductivity fields with variance level $\sigma_y^2 = 0.8$. The porosity, constant hydraulic gradient, and mean hydraulic conductivity are chosen to give a mean horizontal velocity $U = 0.67$ $(L/T)$. The formation thickness is $B = 35\lambda_y$ ($\lambda_y$ represents the vertical correlation scale of the log-hydraulic conductivity), the mean value of the distribution coefficient $\overline{K}_d = 1$, and the average number of transitions is $E[N(\Delta t)] = 5$. The degree of correlation, $\alpha$, ($K'_d(z) = \alpha K'(z)$) is chosen to produce a coefficient of variation of 0.2 in the distribution coefficient $K_d$.

In Figure 7 the horizontal displacement ensemble variance is depicted for three case. We compare the solute plume spreading due to local equilibrium assumption (constant $K_d$, linear isotherm), kinetic nonequilibrium (constant $K_d$), and kinetic non-equilibrium

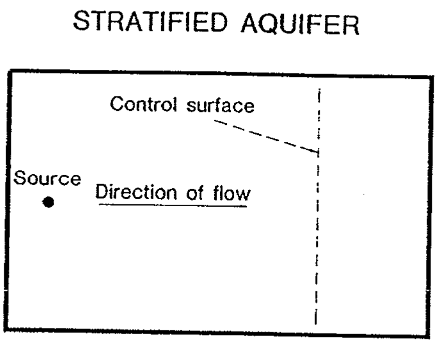

Figure 6

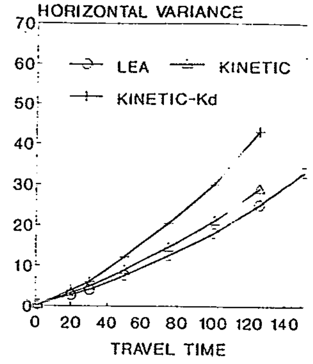

Figure 7

**Figure 6.** Numerical example layout for the two-dimensional case of stratified formation

**Figure 7.** Longitudinal displacement variance for local equilibrium assumption (LEA) (circles), kinetic non-equilibrium with constant $K_d$ (triangles), and kinetic non-equilibrium with variable $K_d$ (crosses)

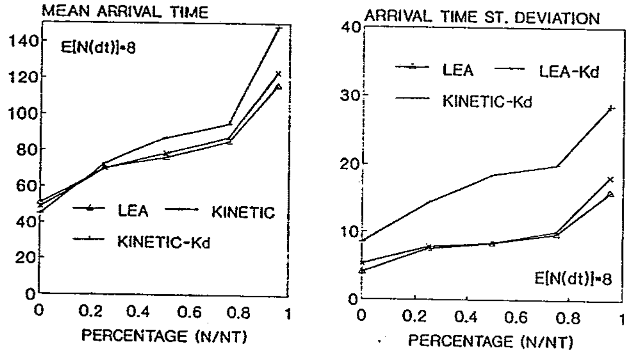

**Figure 8.** First two moments of the arrival time distribution of the particle cloud at the control surface

with spatially variable distribution coefficient $K_d$. Chemical kinetics are modeled with the first two moments of the residence time distribution as discussed previously. As expected in all three cases the displacement variance grows non-linearly with time and therefore the transport exhibits non-Fickian behavior in this range of travel time simulations. The kinetic non-equilibrium did show some increase in spreading over the LEA. However, on the average, that additional spreading does not seem to have significant impact on the solute plume second moment. On the contrary, the third case with spatially variable distribution coefficient $K_d$, shows a significant additional spreading of the solute plume. In fact, in this relatively small travel time (120 $\Delta t$'s) the spreading of the solute plume due to the negatively correlated distribution coefficient was almost doubled. It is important to note that this simulation example illustrates that an additional spreading over LEA can arise from chemical kinetics and negative correlation between the distribution coefficient $K_d$ and the hydraulic conductivity. This appears to be in agreement with similar findings reported by Valocchi (1989) who analytically derived the spatial moments for a stratified formation. The results reveal furthermore that the importance of chemical kinetics in field scale transport problems depends on the speed of adsorption kinetics relative to the transport time scale $\Delta t$. The enhanced plume spreading due to the negative correlation between $K_d$ and $K$ also appears to be a major reason for the increased second moment of the contamination plume over the LEA case.

To better grasp the solute plume behavior under variable $K_d$, we next analyze the arrival time for the particle cloud i.e., the time required for the arrival of the first particle and of 25, 50, 75, and 95% (the percentages are computed as the number of particles $N$ crossing the control surface over the total number of particles $NT$) of the particles at the control surface (see Figure 6). Smith and Schwartz (1980) used a similar analysis for a non-reactive transport problem. Fifty solutions of the transport problem were obtained and the mean and standard deviation were calculated for the above five arrival times. In Figure 8 the same three cases are examined. In the case of negatively correlated $K_d$ and $K$ the particles are first crossing and last exiting the control surface, which supports the previously observed increased spreading in Figure 7. Notice, however, that the late exiting (higher mean arrival time for higher $N/NT$) is more pronounced than the early arrival which indicates stronger tailing. The same conclusion is also supported by observing higher variance of the arrival time for higher values of $N/NT$. The second moment of the arrival time increases with increasing total mass passing through the control surface. In the case of spatially variable $K_d$ the arrival time standard deviation is almost twice as high compared to the case of LEA and adsorption kinetics with constant $K_d$.

## 6 Conclusions

In this paper we have used the first two moments of the distribution of the particle residence time in the liquid phase, $\Delta t^*$, to study the field scale transport of kinetically adsorbing solutes. The first two moments of $\Delta t^*$ are expressed as functions of the kinetic reaction rates and the actual transport time step $\Delta t$. The comparison between the residence time distribution approximated by the first two moments and the distribution obtained by appropriately weighing the four conditional distributions (conditioned on the initial and final phase (Valocchi and Quinodoz, 1989) shows an acceptable agreement in most cases. Numerical simulations were performed in one- and two-dimensional cases to examine the accuracy of the proposed approximation in terms of providing an accurate description of the spatial moments of the contaminant plume. The results in the one-dimensional case showed close agreement with the analytical solutions of Valocchi (1988).

The use of a single residence time distribution has a clear computational advantage. We found (using an Apollo DN 10000 workstation) that the increase in CPU time from solving non-reactive transport to solving transport of kinetically adsorbing solutes is less than 7%. Furthermore the presented birth and death process framework for modeling chemical kinetics can be easily extended to non-trivial chemical processes (multicomponent and bioremediation) and three dimensional applications. In that case the additional computational requirements are proportional to the computational requirements of the particle tracking technique. The increase in computation, by considering the birth and death process with the first two moments of the residence time distribution, is moderate even for spatially variable chemical reactions. More precisely, the example with stratified formations was run on the Cray-2 Supercomputer and required in CPU times 47 sec for the LEA case, 53 sec for the chemical kinetics - constant $K_d$, and 67 sec for the case with variable $K_d$.

It has been shown that the spreading (dispersion) of a contaminant plume is due to three components: one which depends on the mean value of $\Delta t^*$, a second one which is related to the variability in the residence time distribution relative to the transport time scale $\Delta t$, and a third one which results from the possible negative correlation between $K_d$ and $K$. The first component is due to the retardation factor given by the first moment of

$\Delta t^*$. The second component represents the additional dispersion caused by the slow kinetic reaction rates relative to $\Delta t$ and is expressed in terms of the second moment of $\Delta t^*$. The third component may arise in cases of negative correlation between the distribution coefficient $K_d$ and the hydraulic conductivity $K$. The results from the numerical simulations furthermore revealed that the possible negative correlation between $K_d$ and $K$ may be a major factor which enhances the plume spreading in addition to the kinetics alone, particularly in field scale problems where the transport time scale $\Delta t$ is large (i.e., $E[N(\Delta t)] \geq 10$) compared to the intrinsic chemical reaction time.

The arrival time statistics also showed the effects from the three different spreading components. The effects from the variable $K_d$ were more pronounced than the effects of kinetics themselves and in particular the second moment of the arrival time exhibited higher values for higher percentages of total mass that exited a cross-section, indicating the high degree of uncertainty in estimating the travel time for kinetically adsorbing solutes in heterogeneous media.

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**Table of contents**

| | |
|---|---|
| Chapter I: | Probability and stochastic processes |
| Chapter II: | More on probability and stochastic processes |
| Chapter III: | Ito stochastic calculus |
| Chapter IV: | Ito stochastic differential equations |
| Chapter V: | The stochastic Taylor formula |
| Chapter VI: | Modelling with stochastic differential equations |
| Chapter VII: | Applications of stochastic differential equations |
| Chapter VIII: | Time discrete approximations of deterministic equations |
| Chapter IX: | Introduction to stochastic time discrete approximations |
| Chapter X: | Time discrete strong Taylor approximations |
| Chapter XI: | General time discrete strong approximations |
| Chapter XII: | Further results on strong approximations (eg Newton, Talay) |
| Chapter XIII: | Strong approximation of first exit times |
| Chapter XIV: | Time discrete Taylor approximations |
| Chapter XV: | General time discrete weak approximations |
| Chapter XVI: | Unbiased weak approximations (Wagner) |
| Chapter XVII: | Variance reduced weak approximations (Wagner) |
| Chapter XVIII: | Evaluation of Wiener integrals |
| Chapter XIX: | Evaluation of invariant measures |
| Chapter XX: | Ito processes with jump components |
| Chapter XXI: | Jump adapted time discrete approximations |
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