Application of the random walk method to simulate the transport of kinetically adsorbing solutes

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ABSTRACT A new random walk method is presented for simulating the transport of kinetically adsorbing solutes. The method incorporates adsorption directly into the particle tracking algorithm by utilizing an analytical formula for the probability density function of the fraction of time a particle spends in the aqueous phase. The new method is compared to two other techniques for one-dimensional, nondispersive test cases. The new method is shown to be more accurate and computationally efficient for moderate to fast reaction rates. Future extension to two-dimensional, randomly heterogeneous media is discussed.

INTRODUCTION

Adsorption reactions in porous media transport can be described using either an equilibrium or kinetic approach; however, the former has been most widely utilized to date due to its conceptual and mathematical simplicity. Nonequilibrium adsorption phenomena have been examined extensively on the laboratory scale for homogeneous soil columns; the important kinetic limitation at this scale involves microscopic transport from the flowing pore fluid to the soil-solution interface where the reaction occurs. Such kinetic effects cause increased spreading and tailing of contaminant plumes and breakthrough curves (Valocchi, 1985). However, the spatial variability of real field aquifers causes additional kinetic limitations involving macro-scale mixing among zones of differing permeability. Data from a recent field study show deviations from equilibrium sorption behavior even for low velocity, natural gradient conditions (Roberts et al., 1986). Therefore, at present, field-scale behavior of reactive contaminants is not well-understood.

Most theoretical studies of nonequilibrium transport are limited to homogeneous media. However, preliminary analyses of perfectly stratified aquifers show that there are strong interactions between adsorption kinetics and hydrogeological variability; for example, Valocchi (1988) has shown that deviations from local equilibrium behavior diminish as the hydraulic conductivity heterogeneity increases. We are currently extending these studies to two- and three-dimensional, randomly heterogeneous aquifers. Our initial goal is to develop a numerical transport model which will be used to examine the relative contribution of kinetics and spatial variability to the overall spreading of a solute plume. It is crucial for the numerical technique to possess negligible numerical dispersion and to be computationally efficient for three-dimensional applications. With these two criteria in mind, we have selected the random walk method. Also, Tompson et al. (1987) have recently reported successful implementation of the random walk method for
investigating macrodispersive phenomena for nonreactive transport in three-dimensional, randomly heterogeneous aquifers.

Ahlstrom et al. (1977) and Kinzelbach (1988) have discussed extension of random walk methods to handle chemically reactive transport problems. However, for the simple first-order kinetic adsorption reaction considered in our work, those techniques are not always computationally efficient. The purpose of this paper is to present a new random walk method for kinetically adsorbing solute transport. The accuracy and efficiency of the new method is demonstrated through several example simulations.

RANDOM WALK METHOD - THEORY

For simplicity, we will initially review the case of one-dimensional, steady flow in a homogeneous porous medium. In this case, the governing advection-dispersion equation (ADE) for a nonreactive solute is

\[
\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x}
\]  

(1)

where \( c \) is the aqueous concentration (aqueous species mass/fluid volume), \( D_x \) is the hydrodynamic dispersion coefficient (L\(^2\)/T), and \( v_x \) is the pore water velocity (L/T).

Next, consider a random walk where at each step the position of an individual particle is adjusted according to

\[
x_p(t + \Delta t) = x_p(t) + v_x \Delta t + Z \sqrt{2D_x \Delta t}
\]

(2)

where \( x_p(t) \) is the position of particle "p" at time \( t \), \( \Delta t \) is the time step, and \( Z \) is a random draw from a normally distributed random variable having mean zero and standard deviation one. In the limit of a large number of particles, the frequency distribution of the number of particles per unit length satisfies the transport equation (1). In practice, a finite number of particles are moved according to the deterministic advective and stochastic dispersive steps embodied in Eqn. (2). Then the concentration distribution is estimated as

\[
c(x,t) = M' \cdot \frac{n(x,t)}{N(t) \Delta x}
\]

(3)

where \( M' \) is a normalizing constant, \( n(x,t) \) is the number of particles at time \( t \) within a line segment \( \Delta x \) centered at \( x \), and \( N(t) \) is the total number of particles at time \( t \). Tompson et al. (1987) and Kinzelbach (1988) provide discussion of the formal equivalence between Eqns. (1) and (2), as well as important generalizations to three-dimensional heterogeneous media.

The governing ADE (1) must be modified for the case where the solute undergoes adsorption reactions. The modified ADE is

\[
\frac{\partial c}{\partial t} + \frac{\partial s}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x}
\]

(4)

where \( s \) is the adsorbed species concentration (adsorbed species
mass/fluid volume). Following Valocchi (1988), we assume that the adsorption rate \( \frac{\partial s}{\partial t} \) can be described by a first-order, reversible, linear rate expression

\[
\frac{\partial s}{\partial t} = k_f c - k_r s
\]

(5)

where \( k_f (T^{-1}) \) and \( k_r (T^{-1}) \) are the forward and reverse rate coefficients, respectively.

Ahlstrom et al. (1977) presented a decoupled approach for handling a broad class of chemical reactions in the random walk method. Their decoupled approach is a continuum based one. In the context of the single species adsorption problem here, particles representing aqueous phase mass would advect and disperse according to the nonreactive random walk [Eqn. (2)], then a smooth aqueous phase concentration field would be calculated, and finally a discretized form of Eqn. (5) would be solved locally in space for the adsorbed phase concentration. The aqueous phase mass would then need to be adjusted for any net adsorption or desorption before proceeding to the next time step. Although the decoupled approach is versatile, it is prone to numerical errors unless the time step size is small. However, we now show how the linear rate expression given by Eqn. (5) can be handled in a direct, particle-based fashion by the random walk method.

Two-State Markov Chain

Using results presented by Parzen (1962), we can show that the stochastic analogue of Eqn. (5) is a homogeneous, continuous-time, two-state Markov chain. Consider a sequence of phase changes experienced by a single particle. At any single instant, the particle can exist in either of two states or phases: state 1 (aqueous phase) or state 2 (adsorbed phase). We denote this Markov chain as \( (Y(t), t > 0) \) with state space \( \{1, 2\} \). The rates at which the particle leaves states 1 and 2 (so-called intensities of passage) are \( k_f \) and \( k_r \), respectively; the time the particle spends in either state prior to making a transition is an exponentially distributed random variable with a parameter equal to the appropriate rate of change (\( k_f \) or \( k_r \)).

A continuous-time Markov chain is completely specified if we know both the intensities of passage and the transition probability functions. These functions measure the probability of transition between any combination of the two states, given the initial and final times. There are four such combinations, namely 1-1, 1-2, 2-1, 2-2. When the Markov chain is homogeneous, it is only the difference \( t \) between the initial and final times that is important. The transition probability functions are usually found by solving a system of differential equations, called the Kolmogorov differential equations, which for our problem read:

\[
\begin{align*}
\frac{dp_{1,1}(t)}{dt} &= -k_f p_{1,1}(t) + k_r p_{1,2}(t) \\
\frac{dp_{1,2}(t)}{dt} &= -k_r p_{1,2}(t) + k_f p_{1,1}(t) \\
\frac{dp_{2,2}(t)}{dt} &= -k_r p_{2,2}(t) + k_f p_{2,1}(t) \\
\frac{dp_{2,1}(t)}{dt} &= -k_f p_{2,1}(t) + k_r p_{2,2}(t)
\end{align*}
\]

(6)
The notation used for the above probabilities uses as sub-indices the two phases associated with the transition: the first index is for the initial phase and the second index for the final phase. Note that each of the above equations can be interpreted as a stochastic gain-loss equation for the transition probabilities between two states. Parzen (1962) solved the above system of equations and obtained the four transition probabilities; his results are as follows:

\[ p_{2,1}(t) = P[Y(t+s) = 1 \mid Y(s) = 2] = \frac{k_r}{k_f + k_r} \left[ 1 - e^{-(k_f+k_r)t} \right] \quad (7) \]

\[ p_{1,2}(t) = P[Y(t+s) = 2 \mid Y(s) = 1] = \frac{k_f}{k_f + k_r} \left[ 1 - e^{-(k_f+k_r)t} \right] \quad (8) \]

\[ P_{1,1} = 1 - p_{1,2} \quad (9) \]

\[ P_{2,2} = 1 - p_{2,1} \quad (10) \]

The above four transition probabilities do not depend upon the number of phase changes during time \( t \); that number can take on any value compatible with the initial and final state. However, because the waiting time in each state is exponentially distributed, we can easily compute the probability of zero phase changes within time \( t \). Denoting this by a superscript \( z \), we have

\[ p_{1,1}^z = e^{-k_f t}, \quad p_{2,2}^z = e^{-k_r t} \quad (11) \]

Finally, we develop the correspondence between Eqn. (5) and the two-state, continuous-time Markov chain described above. Let \( \alpha_1(0) \) and \( \alpha_2(0) \) denote the probability that a particle is in state 1 and 2, respectively, at time equal to zero. Then the probability that a particle is in the adsorbed phase (state 2) at time \( t \), \( P_2(t) \), is

\[ P_2(t) = p_{1,2}(t) \cdot \alpha_1(0) + p_{2,2}(t) \cdot \alpha_2(0) \]

A similar expression can be derived for \( P_1(t) \). Differentiating the above equation with respect to time, and substituting (6) for \( dp_{1,2}/dt \) and \( dp_{2,2}/dt \) yields

\[ \frac{d}{dt} P_2(t) = k_f P_1(t) - k_r P_2(t) \quad (12) \]

Equation (12) is identical to Eqn. (5) if the probability that a particle is in a particular phase is interpreted as the phase concentration. In practice, the time history of phase changes of a large number of independent particles can be simulated; \( P_1(t) \) is then estimated as the fraction of particles in phase 1 at time \( t \).
RANDOM WALK METHOD-IMPLEMENTATION

In this section, we present three alternative approaches to implementing the two-state, continuous-time, Markov chain representation of the adsorption-desorption reaction. Depending upon the nonuniformity of the velocity field, a certain maximum timestep ($\Delta t$) will be dictated for the advection and dispersive steps in Eqn. (2) (Tompson et al., 1987). Since only aqueous-phase particles are mobile, the key problem is to determine the fraction of the timestep that each particle remains in the aqueous phase.

Method 1: Continuous Time History Method

This method takes the natural approach of simulating the history of phase changes for each particle during $\Delta t$. This can be accomplished in a straightforward manner by generating a sequence of exponential waiting times with parameters alternating between $k_f$ and $k_r$ (or vice versa if the initial state of the particle is adsorbed). The process stops when the total time elapsed is larger than $\Delta t$; at that point the waiting times for each state are summed and the particle is advected/dispersed using a time step equal to the time spent in the aqueous phase.

The method is computationally simple since the exponential distribution has a closed form inverse which allows efficient generation of random variables by the inverse transform method (Rubinstein, 1981). The main difficulty occurs for fast reaction rates, which requires generation of an unacceptably large number of waiting times.

Method 2: Small Time Step Method

In the limit of small $(k_f\Delta t + k_r\Delta t)$, the transition probabilities, Eqns. (7) and (8), become

$$P_{21} = k_r \Delta t$$

For a given $k_f$ and $k_r$, Eqn. (13) holds for "small enough" $\Delta t$. Since the number of phase transitions can be considered a Poisson process, the probability of having more than one phase change in a small $\Delta t$ is negligible (Parzen, 1962). Therefore, a particle is assumed to remain in its initial state for the entire $\Delta t$, and its final state is adjusted by a Bernoulli trial where a uniform (0,1) random variate is compared to the appropriate transition probability in Eqn. (13). This method has been previously presented by Kinzelbach (1988). The main drawback of this approach is that $\Delta t$ must be chosen to guarantee that $p_{1,2}$ and $p_{2,1}$ above are much smaller than one; for fast reactions, this may require an excessively small $\Delta t$.

Method 3: Arbitrary Time Step Method

For an arbitrary $\Delta t$, Keller and Giddings (1960) have determined probability distributions for $\beta(\Delta t)$, the fraction of time that a particle spends in the aqueous phase. Their results for the probability density functions depend upon the initial and final phases and are as follows:
where $a = k_f \Delta t$ and $b = k_r \Delta t$, and $I_0$ and $I_1$ are modified Bessel functions of order 0 and 1, respectively.

The algorithm involves three different steps. First, we determine if there is a phase change by performing a Bernoulli trial using the appropriate zero-transition probabilities in Eqn. (11). Second, if there is a phase change, we determine the final phase by performing a Bernoulli trial using the transition probabilities in Eqns. (7)-(10), which are first adjusted to exclude the probability of zero-transition used in the first step. Finally, we determine the time spent in the aqueous phase by applying the inverse transform method to the cumulative distribution functions derived from the density functions in Eqns. (14)-(17). These three steps will result in a value of $\beta$ between zero and one for each particle. The advective and dispersive steps can then be performed for each particle with $\beta \Delta t$ instead of $\Delta t$ in Eqn. (2). A distinct advantage of this method over the previous two techniques is that the overall computational effort is more or less independent of the reaction rate.

RESULTS

The three methods described in the previous section were tested for two different cases of one-dimensional, steady, uniform flow without dispersion. The first case considered a constant input of solute at the upstream boundary. This case was chosen because of its simplicity and because of the availability of an analytical solution (Bolt, 1982). Simulations with all three methods used 10,000 particles, a pore water velocity $v=1$, and $k_f = k_r = 1.0$. Concentration profiles were obtained for selected times and compared to the analytical solution. A graphical comparison of the profiles at $T = 100$ is shown in Fig. 1 for Method 3. The fluctuating nature of the numerical solution represents statistical noise associated with the finite number of particles used (Kinzelbach, 1988). The other two methods produced results of nearly identical quality, although the required CPU time was about 5 times larger for Method 2, for which it was necessary to reduce the time step by a factor of 10 relative to the other two methods.

The second case consists of an instantaneous point discharge of aqueous-phase solute as the initial condition. This case was selected because there is an analytical solution available for the evolution in time of the first two spatial moments of the cloud of particles in the mobile phase (Valocchi, 1988). The test used different rates for each phase, while keeping the ratio $k_f/k_r$ equal to 0.5. The individual rates were varied to cover the range of slow to fast reaction rates. The flow velocity was $v=1$, and the number
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of particles was varied in the different experiments.

All three methods are compared using the first two moments of the position of the particle cloud: mean and variance, as well as the total CPU time on a DEC-Vaxstation II. The error in the values of the mean position were very small in general, and only results for the variance are discussed here. Table 1 summarizes the results for a time $T=100$. Results of comparable quality were obtained with both the continuous time history (Method 1) and arbitrary time step (Method 3) methods, while the small time step method (Method 2) produced larger errors. Computing times are comparable only for slow reaction rates; for moderate and fast rates Method 2 is the most time consuming, followed by Method 1. The accuracy of Method 2 is improved when $\Delta t$ is reduced, but this results in an increased CPU time. Overall, the most efficient and accurate method for all reaction rates is Method 3.

<table>
<thead>
<tr>
<th>$k_r$</th>
<th>$N$</th>
<th>Time step</th>
<th>Relative error (%)</th>
<th>CPU time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow reaction rate</td>
<td>$k_r = 0.1$</td>
<td>1</td>
<td>1.0</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>$N = 100,000$</td>
<td>2</td>
<td>1.0</td>
<td>5.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>1.0</td>
<td>0.79</td>
</tr>
<tr>
<td>Moderate reaction rate</td>
<td>$k_r = 1.0$</td>
<td>1</td>
<td>1.0</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>$N = 100,000$</td>
<td>2</td>
<td>0.1</td>
<td>7.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>1.0</td>
<td>0.55</td>
</tr>
<tr>
<td>Fast reaction rate</td>
<td>$k_r = 10.0$</td>
<td>1</td>
<td>1.0</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>$N = 10,000$</td>
<td>2</td>
<td>0.01</td>
<td>8.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>1.0</td>
<td>1.49</td>
</tr>
</tbody>
</table>

The agreement between numerical and analytical solutions is very good; however, the relative error in the variance estimation is sensitive to the number of particles ($N$) and to the reaction rates.
Table 1 shows the relative error is larger than 1% for all methods when using 10,000 particles. A single run with fast rates was repeated with 100,000 particles using Method 3 which effectively lowered the error to 0.37%.

FUTURE DIRECTIONS

Because of its accuracy, robustness, and efficiency, Method 3 has been used in the development of a two-dimensional transport code. The code has been modified and optimized to run on an Alliant FX-8 computer which is a shared-memory, parallel (8 processors) machine. About 95% of the code is multi-taskable and sample test problems run approximately forty times faster on the Alliant than on the Vaxstation. We next plan to use the code to examine the impact of various rate coefficients upon the particle cloud variance for fixed patterns of heterogeneity. We will initially use spatially uniform rate parameters. Although the methods described above are valid for spatially variable reaction rates, computational implementation would be considerably more difficult.

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REFERENCES


