

## **Stochastic transport of reactive pollutants in groundwater: effective parameters approach**

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**Abstract** The impact of small scale heterogeneity or spatial variability upon field-scale transport is widely recognized as a key problem in groundwater research and practice. Although initial research in this topic focused upon non-reactive solutes and variability of physical properties of the aquifer (namely, hydraulic conductivity and porosity), recent work has emphasized reactive solutes and variability of chemical properties (namely, adsorption parameters). Uncertainty about the precise values of the chemical properties of the soil will lead to uncertainties in transport calculations. These uncertainties will play a key role in the analysis of the environmental impact of reactive contaminants moving through a real porous formation. Temporal moments analysis, in addition to an effective parameters approach, is used in this paper to explain the effect of chemical heterogeneity upon the transport of reactive pollutants.

### **INTRODUCTION**

It is now widely recognized that groundwater aquifers exhibit significant small-scale variability in their hydraulic and chemical properties. Some well-known field-scale experiments (Borden and Cape Cod) have shown that this spatial variability or heterogeneity of the porous formation plays a very important role in the spreading and dispersion of contaminants at the field scale. Analytical and numerical techniques can be used to characterize the overall effect of chemical heterogeneity upon the transport of reactive pollutants. In both cases, a stochastic description is used to characterize the spatial distribution of adsorption parameters (adsorption and desorption rates for linear kinetic adsorption) in a one dimensional system. In this particular approach the aquifer is assumed to be comprised of two distinct zones: reactive and non reactive; a Bernoulli random process is used to describe the distribution of reactive zones along the aquifer. Adsorption is allowed only along the reactive zones. Physical properties of the porous medium are assumed to be constant in space and time (flow velocity and dispersion coefficient).

Analytical solutions based on a small-perturbations approach are developed to study the distribution of the ensemble mean of the dissolved concentration after an instantaneous injection of contaminant (a Dirac pulse). These solutions are very useful to study the temporal evolution of the pollutant concentration at different positions inside the aquifer, but they do not provide a complete insight as to the global effect of the different mechanisms taking place in the transport process (advection, dispersion, adsorption and chemical heterogeneity). Analytical techniques, such as temporal and spatial moments analyses, have been used in the past to study the combined effect of

advection, dispersion and adsorption in homogeneous aquifers (Valocchi, 1985; Goltz, 1986). In this paper an application of the temporal moments analysis of the specific impact of chemical heterogeneity in the transport process is presented.

## GOVERNING EQUATIONS

The starting point for this derivation is the well known Advection-Dispersion equation (ADE) written in a one dimensional formulation as:

$$\frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} - u \cdot \frac{\partial C}{\partial x} \quad (1)$$

where  $C(x,t)$  is the dissolved or aqueous concentration,  $S(x,t)$  is the adsorbed concentration,  $D$  is the mechanical dispersion coefficient,  $u$  is the flow velocity,  $x$  is the spatial coordinate and  $t$  is time. The adsorption is a kinetic process which can be represented by the following expression:

$$\frac{\partial S}{\partial t} = k_F \cdot C - k_R \cdot S = k_R (K_d \cdot C - S) \quad (2)$$

where  $k_F$  and  $k_R$  are the forward and reverse adsorption rates, respectively, and  $K_d$  is the distribution coefficient. In this derivation we assume a physically homogeneous (i.e. flow velocity and mechanical dispersion are constant through the aquifer), but chemically heterogeneous, porous medium (i.e. adsorption takes place on a limited portion of the aquifer). Following this assumption equation (2) must be modified:

$$\frac{\partial S}{\partial t} = k_F \cdot \phi \cdot C - k_R \cdot S = k_R (\phi \cdot K_d \cdot C - S) \quad (3)$$

where  $\phi(w;x)$  is a random process which describes the distribution of adsorption zones along the aquifer. The statistical characteristics of this stochastic process are known *a priori* (mean =  $\bar{\phi}$ , variance =  $\sigma_{\phi\phi}^2$ ). The argument  $w$  in the distribution of adsorption sites,  $\phi(w;x)$ , shows the random nature of the stochastic process. Boundary conditions for this problem are specified as null concentration on the extremes of the domain, i.e.:

$$C(\pm\infty, t) = 0, \quad S(\pm\infty, t) = 0 \quad (4)$$

and, for the initial condition we assume the contaminant is incorporated into the aquifer instantaneously. Hence, the dissolved and adsorbed concentrations can be described by:

$$C(x,0) = C_0 \cdot \delta(x), \quad S(x,0) = 0 \quad (5)$$

where  $\delta(x)$  is the Dirac function. Due to the random nature of  $\phi(x;w)$  the original system of partial differential equations described by (1) and (2) is transformed into a stochastic partial differential equation given by (1) and (3). The solution to this problem is no longer deterministic and therefore classical techniques to solve differential equations must be modified to account for the random component.

## SMALL RANDOM PERTURBATIONS

One of the simplest approaches to deal with a stochastic differential equation is to use a small random perturbation approach. In this analysis the dependent variables and random parameters are expanded in terms of their mean and a small random perturbation (Gelhar, 1994), such as:

$$C(w; x, t) = \bar{C}(x, t) + C'(w; x, t) \quad (6)$$

$$S(w; x, t) = \bar{S}(x, t) + S'(w; x, t) \quad (7)$$

$$\phi(w; x) = \bar{\phi}(x) + \phi'(w; x) \quad (8)$$

After substitution of these approximations into the ADE equation we can use algebra to obtain the following equation in terms of the mean value of  $C(x, t)$  and  $S(x, t)$ :

$$\frac{\partial \bar{C}}{\partial t} + \frac{\partial \bar{S}}{\partial t} = D \cdot \frac{\partial^2 \bar{C}}{\partial x^2} - u \cdot \frac{\partial \bar{C}}{\partial x} \quad (9)$$

Subtracting equations (1) and (9) we find the following equation in terms of the random perturbations of  $C$  and  $S$ :

$$\frac{\partial C'}{\partial t} + \frac{\partial S'}{\partial t} = D \cdot \frac{\partial^2 C'}{\partial x^2} - u \cdot \frac{\partial C'}{\partial x} \quad (10)$$

Now we can substitute approximations (6) to (8), into the governing equation (3) to obtain the following equation to represent the kinetic adsorption in terms of the mean of  $C$ ,  $S$ , and  $\phi$ :

$$\frac{\partial \bar{S}}{\partial t} = k_F \cdot \bar{\phi} \cdot \bar{C} - k_R \cdot \bar{S} + k_F \cdot \overline{C' \phi'} \quad (11)$$

The first and second terms on the right hand side of equation (11) are the same as for the original ADE, but in terms of the mean value of the random variables. The additional term, covariance  $\overline{C' \phi'}$ , represents the contribution of the chemical heterogeneity into the adsorption reaction. An approximation for the actual ensemble mean dissolved concentration can be found by neglecting the covariance term in equation (11). Such an approximation is usually called a *first-order* solution, and represents the solution of a homogeneous equivalent problem.

After some algebra it is possible to obtain the following differential equation to describe the kinetic adsorption process in terms of the perturbation of the dependent variables and parameters:

$$\frac{\partial S'}{\partial t} = k_F \cdot \bar{\phi} \cdot \bar{C} - k_R \cdot S' + k_F \cdot \bar{C} \cdot \phi' \quad (12)$$

Using the same procedure it is possible to obtain expressions for the boundary and initial conditions for both the mean and perturbation equations.

By using appropriate assumptions the system of partial differential equations described by (10) and (12) can be solved to compute the additional term  $\overline{C' \phi'}$ , needed

to determine the actual solution of  $C(x,t)$  and  $S(x,t)$  in equations (9) and (11). To completely describe  $\overline{C'\phi'}$  the spatial dependence among the adsorption zones,  $\phi(w;x)$ , must be described by means of a correlation function. As presented in the introduction, a Bernoulli random process with the following correlation function is used to compute the analytical solution:

$$E[\phi'(x) \cdot \phi'(x')] = \begin{cases} \sigma_{\phi\phi}^2 & \text{if } |x - x'| < \frac{\lambda}{2} \\ 0 & \text{otherwise} \end{cases} \quad (13)$$

where  $\sigma_{\phi\phi}^2$  and  $\lambda$  are the variance and correlation length of  $\phi(w;x)$ , respectively. The solution to this problem will be called the *complete* analytical solution.

## TEMPORAL MOMENTS

In order to analyse the specific impact of the chemical heterogeneity on the transport of a reactive pollutant we use temporal moments. We can define the  $i$ th temporal order moment of the ensemble mean dissolved concentration,  $C(x,t)$ , as:

$$M_i(x) = \int_0^{\infty} t^i \cdot C(x,t) dt \quad (14)$$

We can use the zero-th, first, and second temporal moments to compute the asymptotic effective velocity and dispersion ( $V_{eff}$  and  $D_{eff}$  respectively) using the following definitions:

$$V_{eff} = \lim_{x \rightarrow \infty} \frac{x}{M_1(x) / M_0(x)} \quad (15)$$

$$D_{eff} = \frac{1}{2} \lim_{x \rightarrow \infty} \frac{M_2(x) / M_0(x) - (M_1(x) / M_0(x))^2}{M_1(x) / M_0(x)} V_{eff}^2 \quad (16)$$

Instead of using the definition of the temporal moment presented in equation (14) we can use a relationship between the temporal moments and the Laplace domain solution for  $C(x,t)$ . Following Valocchi (1985) we can write:

$$M_i(x) = (-1)^i \lim_{p \rightarrow 0} \frac{d^i C(x,p)}{dp^i} \quad (17)$$

in which  $M_i(x)$  is  $i$ th temporal moment of the mean dissolved concentration,  $C(x,t)$ , and,  $p$  is the Laplace transform parameter.

In order to get analytical expressions for  $V_{eff}$  and  $D_{eff}$  we solve the system of differential equations described by (9) and (11) using a Fourier transform for the coordinate  $x$ , and a Laplace transform for time. After some algebra we obtain an analytical expression for  $C(x,t)$ , in the Laplace space. This solution can be used to evaluate the temporal moments of  $C(x,t)$  by means of equation (16). Finally, the effective velocity and dispersion can be computed using equations (15) and (16).

Using the expressions presented above we can evaluate the effective parameters for the *first-order* and *complete* analytical solutions. For the effective velocity we found the same expression for both solutions:

$$V_{eff} = \frac{u}{\bar{R}} \tag{18}$$

where  $\bar{R}$  is the mean retardation factor ( $=1 + \bar{\phi} \cdot K_d$ ). The effective dispersion for the *first-order* problem is:

$$D_{eff} = \frac{D}{R} + \frac{\bar{\phi} \cdot K_d \cdot u^2}{\bar{R} \cdot k_R} \tag{19}$$

and for the *complete* analytical solution:

$$D_{eff} = \frac{D}{R} + \frac{\bar{\phi} \cdot K_d \cdot u^2}{\bar{R} \cdot k_R} + \frac{D \cdot \sigma_{\phi\phi}^2 \cdot K_d^2}{R^3} \cdot \left( 1 - e^{-\frac{u \cdot \lambda}{2 \cdot D}} + \frac{u \cdot \lambda}{2 \cdot D} \right) \tag{20}$$

We observe in the case of the effective velocity that chemical heterogeneity does not introduce any new information about the global properties of the pollutant plume. In this case the solution shows that, far from the initial injection, the plume will move at a velocity which is much smaller than the velocity of the groundwater flow,  $u$ . This retardation is a consequence of the adsorption process taking place along the aquifer. In the case of the *first-order* solution the effective dispersion is comprised of two terms. The first shows that the local dispersion is decreased due to the adsorption process, while the second shows the effect of kinetic adsorption into the system. In effect, as the pollutant migrates through the aquifer the plume becomes longer as some material which was initially adsorbed by the soil matrix is being released into the groundwater. This result shows that if the adsorption process is very slow the plume becomes very elongated as the contaminant moves through the aquifer. On the other hand, if the kinetic adsorption is very fast ( $k_R$  very large, keeping  $K_d$  constant) the second term eventually disappears. The effect of the chemical heterogeneity is clearly observed in the effective dispersion computed for the *complete* solution. If we compare equations (19) and (20) we observe that the two expressions are the same except for the additional term in equation (20). This new term shows that chemical heterogeneity produces an increase in the apparent dispersion of the pollutant. In this case we observe that this additional dispersion is a combination of local dispersion, correlation length, flow velocity, and the spatial variability of the adsorption sites. A second important observation is that this new term is not affected by the kinetics of the adsorption process. In effect, we observe that this term is not a function of either the adsorption or desorption rates ( $k_F$  or  $k_R$ ), but it is a function of the distribution coefficient  $K_d$  which measures the relative amount of contaminant in the dissolved and adsorbed phases, at equilibrium.

## SUMMARY AND CONCLUSIONS

The effect of chemical heterogeneity in the transport of a reactive pollutant in groundwater is explained by means of effective parameters, which are computed using

a temporal moments technique. The main effect of chemical heterogeneity is to increase the rate of dispersion experienced by an adsorbing pollutant as it moves through the aquifer. The asymptotic effective velocity does not seem to be affected by the heterogeneity.

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