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CONTAMINANT TRANSPORT IN THE SUBSURFACE AT THE PORE-MICROPORE INTERFACE

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ABSTRACT

The field of contaminant transport and remediation has achieved a great deal of advancements in recent years. However, practice has shown that remediation efforts are often plagued by extremely long breakthrough curve tails, an indication of almost infinite time requirements for the remediation efforts to bring the level of contaminants below the regulatory standards. It has been postulated that this is due to the effect of micropores. This paper proposes a method to forecast effects of micropores on contaminant transport at both macroscopic and microscopic levels and to establish a link between the two different approaches.

INTRODUCTION

In the field of subsurface contaminant remediation, techniques applicable to mobile and, to a lesser extent, immobile zones are readily available and proven economically feasible. However, practice has shown that remediation efforts are usually plagued by extremely long breakthrough curve tails, an indication of almost infinite time requirements for the remediation efforts to bring the level of contaminants below the regulatory standards. One hypothesis is that these long tails are the manifestation of very slow diffusive processes in soil micropore zones (Wood, 1996). Micropores are small voids within the solid matrix of individual soil grains and are essentially small stagnation zones. Transport in micropore zones experiences negligible advection and, therefore, is predominantly diffusive. This is a big problem in the remediation process because removing contaminants from micropores is an extremely difficult and costly process due to the fact that micropores have a capacity to store contaminants against a moving flow. The inability to correctly identify and account for effects of diffusion in micropores is one of the main causes of failure in achieving desired levels of remediation.

Understanding and ultimately simulating the contaminant transport phenomenon in micropore zones will help further the advancement of the subject as well as facilitate the efficient design and implementation of future remediation techniques. Although some innovative flushing and extraction techniques that remove contaminants mainly from mobile and immobile zones have been developed, sophisticated and cost-effective techniques to address the removal of the contaminants in micropores ought to be a topic of future research.

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MACROSCOPIC VIEW OF CONTAMINANT TRANSPORT IN MULTIPLE-POROSITY MEDIA

1. Conceptual Model

Although a model is hardly a true representation of nature, it describes an approximate state of reality. Likewise, the conceptual model involved in a macroscopic study of contaminant transport attempts to capture the reality and complex structure of porous media. Using pore size difference as the discriminant factor, a domain of interest, such as sand and clay, is divided into mobile, immobile, and micropore zones. De Smedt and Wierenga (1979) qualitatively described that mobile zone is the primary zone of water and solute transfer, and immobile zone is the zone where the movement of water and solute is stagnant. In addition, the mobile zone is described as a zone where advective and dispersive transport takes place whereas the immobile zone is where primarily diffusive transport takes place and serves as sink/source for sorption/desorption process of solutes (van Genuchten and Wierenga, 1976).

Although many attempts have been made to quantitatively categorize the zones, a qualitative description is more important in this study because the quantitative pore size of each zone may differ for different porous media and also from one point in space to another. In order to construct a mathematical model from the conceptual model, it is essential to identify the dominant processes in each zone. The dominant transport processes in each zone are as follows:

- Mobile zone – advection, mechanical dispersion, diffusion, degradation, and exchange with immobile zone
- Immobile zone – adsorption, degradation, and exchanges with mobile zone and micropores
- Micropores – adsorption, degradation, and exchange with immobile zone.

2. Mathematical Model

The mathematical formulation of contaminant transport in the mobile, immobile, and micropore zones of a domain starts with the Advection Dispersion Reaction Equation (ADRE). In addition, using the dominant processes mentioned in the previous section for each zone, a mathematical model is formulated. Since it is very difficult, and often impossible, to mathematically describe true heterogeneous transport phenomena, the mathematical model is based on the following assumptions and simplifications: 1. One-dimensional (1D) transport is analyzed; 2. Diffusion-based transport between zones is proportional to concentration differences between zones; 3. The solute exchange between the three domains is described using first-order kinetics where the rate of mass transfer depends on the concentration gradient; 4. The direct solute exchange between mobile zones and micropores is insignificant; 5. The adsorption is assumed to be instantaneous and to follow a linear isotherm model; 6. Degradation is represented as a first order decay term in each of the domains. A more detailed analysis on the validity of the first order decay term as an approximation for biodegradation can be found in Bouwer and McCarty (1985); 7. The initial concentration in the aqueous and sorbed phases is in equilibrium; and 8. Dead-end micropores are not accounted for in this study. Dead-end micropores refer to those that are not in contact with the surface of the immobile zone.

Incorporating all assumptions and simplifications, the governing equations take the form:

Mobile water zone:

$$\theta_m \frac{\partial C_m}{\partial t} = \theta_m D_0 \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} - \alpha_m (C_m - C_{im}) - \theta_m \mu_m C_m \quad (1)$$

Immobile water zone:

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + f\rho_b \frac{\partial S_{im}}{\partial t} = \alpha_m (C_m - C_{im}) - \alpha_{im} (C_{im} - C_{ip}) - \theta_{im} \mu_{im} C_{im} \quad (2)$$

Micropore zone:

$$\theta_{ip} \frac{\partial C_{ip}}{\partial t} + (1-f)\rho_b \frac{\partial S_{ip}}{\partial t} = \alpha_{im} (C_{im} - C_{ip}) - \theta_{ip} \mu_{ip} C_{ip} \quad (3)$$

C is solute concentration; v_m is transport velocity; θ is water content; D_0 is dispersion coefficient; f is fraction of adsorption associated with the immobile zone; α is exchange rate coefficient between two neighboring zones; μ is degradation rate coefficient; S is sorbed concentration; ρ_b is bulk density of porous medium; t is time; and x is spatial coordinate. The subscripts, *m*, *im*, and *ip*, represent the mobile, immobile, and micropore zone, respectively. Based on our conceptual model, the adsorption of contaminants into the solid matrix would occur from the immobile and micropore zones. Since the layers of immobile water and micropores are typically of small volumes, the adsorption is assumed to be instantaneous and to follow a linear isotherm model. Initially, the contaminant concentrations in all three different zones are assumed either uniform throughout the control volume or zeros depending on whether contamination or remediation is simulated.

The following initial and boundary conditions, expressed in dimensionless space coordinate X, are used:

$$C_m(X,0) = C_{im}(X,0) = C_{ip}(X,0) = \phi \quad (4)$$

$$\left.\frac{\partial C_m}{\partial X}\right|_{X=1} = 0, \quad \left. C_m - D\frac{\partial C_m}{\partial X}\right|_{X=0} = 1 - \phi \quad (5)$$

where ϕ is either 0 or 1, depending on where the soil is assumed to be initially clean or contaminated.

3. Analytical Solution

Solving a set of complicated partial differential equations is challenging. Fortunately, mathematical tools such as the eigenfunction integral equations method and Laplace transforms are available to help solve such a task. Applying the Laplace transform allows one to change a set of partial differential equations to a set of algebraic equations. Applying the Laplace transform to equations (1) – (3), we obtain the Laplace-transformed concentration in all the zones as follows.

Micropore Zone:

$$\overline{C}_{ip} = \frac{\omega_{im}\overline{C}_{im} + \beta_{ip} R_{ip} \phi}{\beta_{ip} R_{ip} s + \omega_{im} + \frac{\Gamma_{ip}}{\Gamma_m}\mu_{ip}} \quad (6)$$

Immobile Water Zone:

$$\overline{C}_{im} = A + B\overline{C}_m \quad (7)$$

where A and B are given by

$$A = \frac{\beta_{im} R_{im} \phi + \dfrac{\omega_{im}\beta_{ip} R_{ip} \phi}{\beta_{ip} R_{ip} s + \omega_{im} + \frac{\Gamma_{ip}}{\Gamma_m}\mu_{ip}}}{\beta_{im} R_{im} s + \omega_m + \omega_{im} + \frac{\Gamma_{im}}{\Gamma_m}\mu_{im} - \dfrac{\omega^2{}_{im}}{\beta_{ip} R_{ip} s + \omega_{im} + \frac{\Gamma_{ip}}{\Gamma_m}\mu_{ip}}} \quad (8)$$

$$B = \frac{\omega_m}{\beta_{im} R_{im} s + \omega_m + \omega_{im} + \frac{\Gamma_{im}}{\Gamma_m}\mu_{im} - \dfrac{\omega^2{}_{im}}{\beta_{ip} R_{ip} s + \omega_{im} + \frac{\Gamma_{ip}}{\Gamma_m}\mu_{ip}}} \quad (9)$$

Mobile Water Zone:

$$\overline{C}_m = K_1 \exp(\lambda_1 X) + K_2 \exp(\lambda_2 X) - \frac{F}{E} \quad (10)$$

$$E(s) = \Gamma_m s + \omega_m + \mu_m - \omega_m B \quad (11)$$

$$F(s) = -\Gamma_m \phi - \omega_m A \quad (12)$$

$$\lambda_1 = \frac{1 + \sqrt{1 + 4ED}}{2D}, \ \lambda_2 = \frac{1 - \sqrt{1 + 4ED}}{2D} \quad (13\text{ a, b})$$

$$K_1 = \frac{-\lambda_2 K_2 \exp(\lambda_2)}{\lambda_1 \exp(\lambda_1)}, \quad K_2 = \frac{\dfrac{F}{E} + \dfrac{(1-\phi)}{s}}{1 - D\lambda_2 - \dfrac{\lambda_2}{\lambda_1}\dfrac{\exp(\lambda_2)}{\exp(\lambda_1)}(1 - D\lambda_1)} \qquad (14\text{ a, b})$$

where

$$X = \frac{x}{L}; \quad D = \frac{1}{Pe} = \frac{D_0}{v_m L} \qquad (15\text{ a, b})$$

$$\mu_m = \frac{\mu_m L}{v_m}; \quad \mu_{im} = \frac{\mu_{im} L}{v_m}; \quad \mu_{ip} = \frac{\mu_{ip} L}{v_m} \qquad (16\text{ a, b, c})$$

$$\Gamma_m = \frac{\theta_m}{\theta}; \quad \Gamma_{im} = \frac{\theta_{im}}{\theta}; \quad \Gamma_{ip} = \frac{\theta_{ip}}{\theta} \qquad (17\text{ a, b, c})$$

$$\omega_m = \frac{\alpha_m L}{\theta_m v_m}; \quad \omega_{im} = \frac{\alpha_{im} L}{\theta_m v_m} \qquad (18\text{ a, b})$$

$$R_{im} = 1 + \frac{\rho_b K_{im}}{\theta}; \quad \beta_{im} = \frac{\theta_{im} + f\rho_b K_{im}}{\theta + \rho_b K_{im}} \qquad (19\text{ a, b})$$

$$R_{ip} = 1 + \frac{\rho_b K_{ip}}{\theta}; \quad \beta_{ip} = \frac{\theta_{ip} + (1-f)\rho_b K_{ip}}{\theta + \rho_b K_{ip}} \qquad (20\text{ a, b})$$

where L is the domain length.

4. Laplace Inversion

The Laplace transform helps transform the original set of partial differential equations to the manageable set of solutions given by ordinary differential equations. Now the transformed solutions must be inverted back to the original domain. Of the many Laplace inversion methods, we experimented with the Stehfest inversion method (Stehfest, 1970), a numerical inversion technique that is popular in groundwater engineering and is based on a delta convergent series (Cheng *et al.*, 1994).

MICROSCOPIC FLOW SIMULATION USING A NAVIER-STOKES EQUATION SOLVER

Flow is simulated with a numerical code that is a 2D finite volume Navier-Stokes solver using a structured colocated grid on a Cartesian system. The structured grid is used because it is the simplest one to program and can handle discretization schemes of the type that we intend to run. The time discretization is performed using a one-step explicit Euler method and has been made more efficient using the Adams-Bashforth predictor-corrector scheme. A Quadratic Upwind Interpolation scheme with a second-order spatial derivative is used for the spatial discretization of the advective terms, while a central derivative scheme is used for the convective terms. The Poisson equation for the pressure is solved by the Gauss-Seidel or Successive-Over-Relaxation (SOR) iterative methods. SOR accelerates the iterative procedures but is usually a refinement to the Gauss-Seidel method. The pressure coupling is obtained following the Kim and Moin (1985) fractional step procedure. In the numerical code described above, the rate of convergence is heavily dependent on several parameters, such as the Reynolds number (R_e), viscosity, the mesh size and shape, and the number of computational points.

CONTAMINANT TRANSPORT WITH THE RANDOM WALK PARTICLE TRACKING METHOD

Once flow information is obtained from the Navier-Stokes solver, the transport process is simulated, and predictions as to the rate with which contaminants get adsorbed or desorbed by the soil grains can be made. Macroscopically, this is accomplished semi-analytically following the method, presented in the previous section. In order to simulate contaminant transport at the microscopic level, we employ the flow patterns and boundary conditions provided by the Navier-Stokes simulation results together with the Random Walk Particle Tracking (RWPT) method. This will allow us to relax the dependence of the contaminant source and sink terms on semi-analytical techniques and simulate the diffusive process and the exchange at the pore-micropore interface explicitly. The RWPT method is composed of two parts, namely particle tracking and the random walk method. Two methods are integrated to simulate contaminant (solute) transport using the random movement of particles. In other words, contaminants are represented by particles moving under the influence of flow, and the transport mechanism is based on the random movement of the particles.

In describing the Particle Tracking Method, PTM hereinafter, it is imperative to clarify the definition of particles in solute transport phenomena. The term, *particle models*, is used for the simulation models whose interacting particles are the discrete representation of physical phenomena (Hockney and Eastwood, 1988). The PTM uses a number of particles to represent the distribution or movement of physical properties with respect to time.

The random walk method is one of few purely stochastic processes that describe the diffusive-dispersive part of the particle transfer. It does not directly solve partial differential equations that describe solute transport, but is based on the concept that random processes play a fundamental role in dispersion in porous media. The theoretical foundation of the random walk model derives from Einstein's explanation of Brownian motion, which describes the motion of suspended particles under the influence of a fluctuating force (Einstein, 1926).

If velocity (*v)* and dispersion (*D*) are constant, the RWPT equation is given as:

$$X^{n+1} = X^{n} + v\Delta t + \sqrt{24 D\Delta t}\,(0.5 - R^{n}) \tag{21}$$

where R^n is a random number uniformly distributed between 0 and 1; the index n indicates time t_n; X is the particle position vector.

RESULTS AND DISCUSSION

With the macroscopic and microscopic approaches established, 2D modeling around a spherical soil grain is simulated using both methods. After a careful parametric study allowed making the two methods compatible, simulations are performed to compare the macroscopic approach with the microscopic approach. Although the micropore zone concentration is omitted from the comparison, the mobile and immobile zone concentration is plotted in the following figures.

Figure 1 is the average concentration breakthrough profile using the microscopic approach, and figure 2 is the macroscopic result obtained with parameters equivalent to those being used in the NS-RWPT approach. Although only mobile and immobile concentrations are compared, they are in a good agreement considering that only four slices are used to represent a sphere in the NS-RWPT method. Jagged curves in figure 1 suggest that using more slices can improve the smoothness of the curves, such as shown in figure 2. In addition, using a higher resolution in the simulations will certainly improve the accuracy of results. Furthermore, inclusion of micropore concentration will make the comparison more complete.

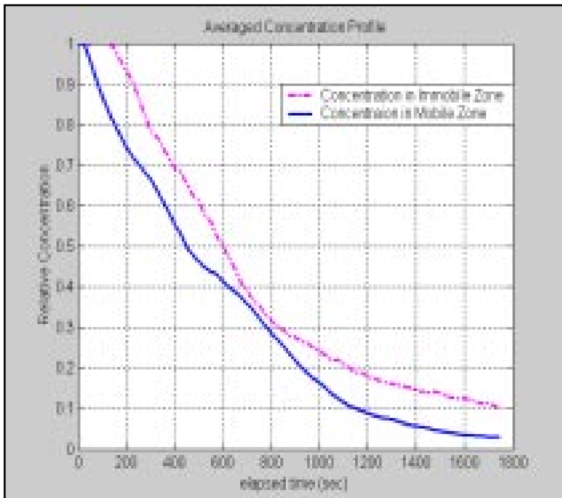

Figure 1: Averaged concentration profile from the microscopic approach

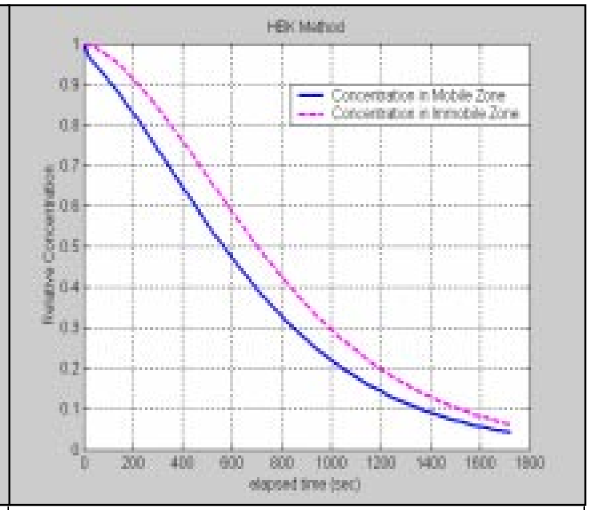

Figure 2: Concentration profile from the macroscopic approach

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