

# **An Integrated Groundwater Model using Multicomponent Multiphase Theory (III) - Parameter Studies in Multiphase Flow and Transport of Organic Contaminants -**

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## **ABSTRACT**

This work demonstrates a comprehensive model of organic contaminant flow and transport in porous media. The model allows for the simulation of multicomponent and multiphase processes as governed by the following phenomena: 1) capillary pressure and relative permeability; 2) hydrodynamic dispersion; 3) dissolution; 4) volatilization; and 5) sorption. The multiphase flow component of the model uses established permeability-saturation-pressure relationships. The contaminant transport component of the model enables simulation of hydrodynamic dispersion as well as both equilibrium and nonequilibrium interfacial mass transfer processes (dissolution, volatilization and sorption). Model capabilities will be demonstrated in a series of simulations employing an increasingly complex view of a hypothetical flow and transport scenario. The sensitivity of simulations to variations of key parameters will be tested at each step of the modeling sequence.

## **INTRODUCTION**

Groundwater models and computational capabilities have evolved rapidly over the last decade, and now allow for simulations ranging from simple groundwater flow to complex multiphase, multicomponent flow and transport. The complexity of a model is usually dictated by the level of resolution required in a particular modeling effort, and by the desired level of computational efficiency. For example, in a contamination scenario involving the release of mixture of solvents into the subsurface, a multiphase flow model would account for the vast majority of the contaminant mass. Solute transport contributions, such as dispersion, dissolution and sorption, could be assumed to be related to a minimal amount of contaminant mass, and neglected in the governing equations. Later, when the driving force behind the intruding solvent phase diminished, the need for a more detailed description of the solute transport processes would gain prominence at the expense of multiphase flow descriptions. A model incorporating both multiphase flow and contaminant transport aspects would be most applicable to the scenario.

It has become accepted that soil and groundwater remediation is, in most cases, a long-term endeavor [Mackay and Cherry, 1989]. Extraction of the contaminated groundwater (pump-and-treat) is the most commonly implemented remediation strategy. Several researchers have demonstrated theoretically that remediation via pump-and-treat, if successful, can require several decades to complete [e.g., Haley et al., 1991; Kong et al., 1993; Rabideau and Miller, 1994]. In the face of shrinking economic resources, researchers have begun to examine other remediation strategies.

This work employs the recently formulated multicomponent, multiphase model of Kim and Stenstrom [1994a] in a study of the interrelation of contaminant flow and transport behavior. The numerical model [Kim and Stenstrom, 1994b] is capable of simulating the following phenomena: 1) multiphase flow; 2) hydrodynamic dispersion; 3) nonaqueous phase dissolution; 4) organic species volatilization; and 5) organic species sorption. With parameter estimates gleaned from the literature, this model was used to generate a sequence of increasingly detailed model realizations for the same contamination scenario. The objectives of the study were: 1) to present a comprehensive expression of the system parameters required for the integrated model; and 2) to gain insight into the relationship between flow and transport parameters through a parameter sensitivity analysis. The following section reviews the constitutive equations and submodels that have used to describe the pertinent flow and transport phenomena. In each case, the discussion includes a brief review of the underlying theory, and of experimental and theoretical research aimed at parameter estimation.

In this paper, previous research related to parameter studies of multicomponent multiphase theory are reviewed, and in the companion papers [Kim and Stenstrom, 1994a,b], theoretical and numerical studies are surveyed. Previous developments of parameter studies can be classified as follows: 1) relation between capillary pressure-saturation, and fluid conductivity, 2) hydrodynamic dispersion coefficients, 3) sorption equilibrium and rate coefficient, 4) mass dissolution, 5) volatilization, 6) chemical reactions, 7) biological reactions, and 8) heterogeneity of porous media.

## 1. Permeability-Saturation-Pressure Relations

A relatively insoluble, nonaqueous phase liquid (NAPL) infiltrates the subsurface under the influence of three forces: 1) gravity, or buoyant force; 2) frictional forces, or viscous forces; and 3) capillary forces. The latter of these three forces is related to the interfacial tension between the wetting and nonwetting fluids in the pore spaces. In general, the difference between the buoyant and viscous forces will govern the flow of the NAPL, while capillary forces will serve to immobilize, or entrap, NAPL in the form of residual saturation. Microscopic models underlying the flow and entrapment of the NAPL phase have been summarized elsewhere [e.g., Demond and Roberts, 1991; Dawson, 1992]. These models are constructed by balancing the aforementioned forces expressed in terms of interfacial tension, contact angle, characteristic length scales, liquid density difference, hydraulic gradient, and capillary pressure [Dawson, 1992]. Macroscopic flow and entrapment models are formed by expressing the hydraulic gradient in terms of Darcy's Law (introducing the relative permeability parameter), and substituting an equilibrium capillary pressure-saturation function for the pore scale capillary pressure term. Relative permeability, like capillary pressure, is a function of the NAPL saturation in the porous medium. Thus, constitutive equations for permeability-saturation-pressure relations are required for the solution of the multiphase flow equations, and numerical solutions have been demonstrated [e.g., Abriola and Pinder, 1985; Faust, 1985]. Because it is fairly difficult to measure, numerous attempts have been made to correlate relative permeability with more readily observed parameters, such as saturation and capillary pressure. In many methods, a closed-form expression [e.g., van Genuchten, 1980], involving one or more fitting parameters, is required in describing the saturation-capillary pressure function. Recently, Demond and Roberts [1993] compared relative permeabilities predicted by five such correlations to measured relative permeability-saturation data [Demond and Roberts, 1991]. They concluded that while the correlations provided reasonable estimates of the wetting-phase relative permeability (water), they overestimated that for the nonwetting phase (n-dodecane, o-xylene, and n-butyl acetate in separate experiments). The measurements clearly indicated that the maximum value of relative permeability for the nonwetting phase was on the order of 0.4, as opposed to a value of unity predicted by all of the correlations tested. Demond and Roberts noted that another shortcoming of the correlations was their inability to describe the hysteretic behavior that was observed for the nonwetting phase.

Models for predicting relative permeability-saturation-pressure functions for three-phase systems (i.e., water, air, and organic liquid) from parametric capillary pressure-saturation functions, calibrated with two-phase observations, have been developed predictive models requiring two-phase system measurements for calibration [e.g., Leverett and Lewis, 1941; Stone, 1973]. Others have developed an approach which requires only the measured pressure-saturation relations to calibrate relative permeability-saturation-pressure relationships for three-phases [Corey et al., 1956; Parker et al., 1987a]. Calibration in the latter method requires considerably less experimental work than in the former method. Parker and coworkers [Parker et al., 1987a] applied the parametric pressure-saturation model of van Genuchten [1980] in their approach. They also extended the approach to capture the effects of hysteresis and nonwetting phase entrapment [Parker and Lenhard, 1987a; 1987b]. Their constitutive equations were adopted for use in the present model, and are shown in more detail in the following two sections.

The constitutive equations for the permeability-saturation-pressure relation of the three phases have been derived by the extension of the experimental results of the two phases [Leverett and Lewis, 1941; Brooks and Cory, 1964; Stone et al., 1970; Aziz and Settari, 1979; van Genuchten, 1980; Parker et al., 1987a,b; Aleman and Slattery, 1988]. Parker et al. [1987a] developed the closed form of capillary pressure-saturation relations in two and three phase system using effective saturation concept, and derived the expression of relative permeability extending the method of van Genuchten [1981]. Parker and Lenhard [1987b] derived a general expression for fluid saturation, relative permeability, and pressure including residual saturation. Lenhard and Parker [1988a,b] experimentally validated the extension theory of two phase to three phase for capillary pressure-saturation relationships. Lenhard et al. [1988c] performed an experiment in sand using Soltrol 170 and compared it to one-dimensional finite element code. Saturation derivative was evaluated analytically from capillary head-saturation relationship. Lenhard et al. [1991] analyzed simulated and experimental hysteretic two-phase flow, including hysteresis in saturation-pressure relations caused by contact angle, irregular pore geometry, and nonwetting fluid entrapment effects. The water table in a 72 cm vertical soil column was fluctuated to scan S-P paths. Water contents were measured via a gamma radiation system, and water pressure were measured via a tensiometers inserted in the soil column. One more parameter was improvised to model hysteretic fluid behavior than nonhysteretic case. Pruess and Tsang [1990] obtained capillary pressure from lognormal aperture distributions of two-phase system, and calculated relative permeability numerically. Nimmo and Mello [1991] applied centrifugal techniques to measure saturated hydraulic conductivity less than 10<sup>-9</sup> m/s for constant- and falling-head cases. Baehr and Hult [1991] showed that the air flow in the unsaturated zone is complicated because of air compressibility, Klinkerberg effect, variation in air density and viscosity that results from temperature fluctuations. They

determined air-phase permeability from an inverse solution of the air flow equation using pneumatic test data. Ferrand and Celia [1992] presented a network percolation model to overcome the problems related to the extension of laboratory experiments of capillary pressure-saturation relations to larger scales in heterogeneous media. Pore scale physics were directly incorporated into the model. Kuepper and McWhorter [1992] investigated the application of macroscopic percolation theory to large-scale capillary pressure curves, and concluded that an arithmetic average is only valid through the range of fluid saturation where no trapping occurs, based on the comparison of percolation-derived capillary pressure curves to those based on a direct arithmetic average. Demond and Roberts [1993] measured drainage and imbibition relative permeabilities of several organic-water systems to assess the accuracy of two-phase relative permeabilities in five common methods. The organic liquid phase showed hysteresis. Shan and Stephens [1993] developed an analytical solution to use either the observed steady state pressure heads at several points due to a single injection, or steady pressure heads at a single point to multiple injections to determine the unsaturated hydraulic conductivity. Soll et al. [1993] developed a two-dimensional grid channeled glass box with three fluid reservoir, and measured saturation changes between pressure steps and movement of isolated fluids to investigate percolation theory. The data was acquired using digital image analysis. Soll and Celia [1993] used percolation and network theories to determine the movement of the fluids under capillary driven transport for two- and three-fluid systems. The model utilized the displacement rules, and could account for the effect of a wetting films, hysteresis, trapping of fluids, and gravity. The model was verified against two- and three-fluid experimental data. Essaid et al. [1993] showed that the discrepancy between the observed and simulated oil distributions was due to the uncertainty in model parameters and boundary conditions based on 146 samples collected from 7 boreholes along a 120-m at a crude oil spill for 10 years. Demond et al. [1994] measured the change of sorption and zeta potential of o-xylene-water-quartz systems containing a cationic surfactant entyltrimethyl ammonium bromide with respect to interfacial tension and contact angle. The modified Leverett's function was verified against experimental results, and roughness and curvature corrections were incorporated into the intrinsic contact angle.

### 1.1 Capillary Pressure-Saturation Functions

In this study, the saturation and relative permeability are computed from the effective saturation of each phase. The effective saturation is calculated from the constitutive relation between the saturation and capillary pressure [ Brooks and Corey, 1964; Parker et al., 1987]. The relative permeability is defined from the effective saturation for each phase. The constitutive equations for the relation of the capillary pressure and the saturation are as follows :

- Brooks and Corey [1964]

$$S_w^e = (P_{dow} / P_{cow})^\lambda \quad \text{for } P_{cow} - P_{dow} > 0, \quad = 1 \quad \text{for } P_{cow} - P_{dow} \leq 0 \quad (1.1.1)$$

$$S_l^e = (P_{dgo} / P_{cgo})^\lambda \quad \text{for } P_{cgo} - P_{dgo} > 0, \quad = 1 \quad \text{for } P_{cgo} - P_{dgo} \leq 0 \quad (1.1.2)$$

$$S_g^e = 1 - S_l^e \quad (1.1.3)$$

- Parker et al. [1987]

$$S_w^e = \left(1 + (\alpha_{ow} h_{ow})^n\right)^{-m} \quad \text{for } h_{ow} > 0, \quad = 1 \quad \text{for } h_{ow} \leq 0 \quad (1.1.4)$$

$$S_l^e = \left(1 + (\alpha_{lo} h_{lo})^n\right)^{-m} \quad \text{for } h_{lo} > 0, \quad = 1 \quad \text{for } h_{lo} \leq 0 \quad (1.1.5)$$

$$S_a^e = \left(1 + (\alpha_{aw} h_{aw})^n\right)^{-m} \quad \text{for } h_{aw} > 0, \quad = 1 \quad \text{for } h_{aw} \leq 0 \quad (1.1.6)$$

### 1.2 Relative Permeability-Saturation Functions

- Brooks and Corey [1964]

$$K_{rw} = (S_w^e)^{(2+3\lambda)/\lambda} \quad (1.2.1)$$

$$K_{ro} = (S_l^e - S_w^e)^2 \left( S_w^e - (S_w^e)^{(2+\lambda)/\lambda} \right) \quad (1.2.2)$$

$$K_{ra} = (1 - S_w^e)^2 \left( 1 - (S_w^e)^{(2+\lambda)/\lambda} \right) \quad (1.2.3)$$

- Parker et al. [1987]

$$K_{rw} = (S_w^e)^{1/2} \left\{ 1 - \left( 1 - (S_w^e)^{1/m} \right)^m \right\}^2 \quad (1.2.4)$$

$$K_{ro} = (S_i^e - S_w^e)^{1/2} \left\{ 1 - \left( 1 - (S_w^e)^{1/m} \right)^m \right\}^2 \left( S_w^e - (S_w^e)^{(2+\lambda)/\lambda} \right) \quad (1.2.5)$$

$$K_{ro} = (1 - S_w^e)^2 \left( 1 - (S_w^e)^{(2+\lambda)/\lambda} \right) \quad (1.2.6)$$

### 1.3 Related Modeling Efforts

Several researchers developed early models based on Darcy's Law for multiphase flow and the constitutive equations discussed in the previous sections [Abriola and Pinder, 1985a; 1985b; Faust, 1985; Corapcioglu and Baehr, 1987]. The models emphasize multiphase flow phenomena over NAPL dissolution (see section 3) volatilization (see section 4) and sorption of the dissolved species (see section 5). For example, Abriola and Pinder [1985a] included only equilibrium partitioning expressions in modeling transfer of a NAPL species to the aqueous phase and vapor phases, and chose to ignore sorption phenomena altogether. Faust [1985] ignored all interfacial transfer of NAPL components. These early efforts have contributed greatly to the development of numerical techniques for solving the highly nonlinear partial differential equations. More recent models are formulated in the same manner as the earlier versions, but have been extended to encompass the more recently developed theory regarding the constitutive relations. Parker and coworkers [Parker and Lenhard, 1989; Kaluarachchi et al., 1990] developed a model for the areal migration of NAPL that is less dense than water (LNAPL). However, these models are concerned with the extent of spreading of LNAPL on the water table, and, thus, also neglect interphase mass transfer.

## 2. Hydrodynamic Dispersive Coefficient Tensor

Corapcioglu and Baehr [1987] proposed a formulation of the hydrodynamic coefficient tensor based on the void fraction, the soil type, and phase velocity. Plumb and Whitaker [1988] acquired the large scale dispersive coefficient using volume averaging, including local heterogeneity of the domain. Baehr and Bruell [1990] showed that a Fickian-based transport model can significantly overestimate soil tortuosity because of the organic vapor phase based upon sand column experiments. Newman [1990] presented a universal scaling rule using a hierarchy based on a semivariogram and a fractal dimension. Gelhar et al. [1992] reviewed 59 sites and concluded that longitudinal dispersivity increased with 10-2 m for site 10-1 m to 104 m for site 105 m. Hess et al. [1992] measured hydraulic conductivity to estimate macrodispersivities (longitudinal dispersivity : 0.35-0.78 m). Rehefeldt and Gelhar [1992] used stochastic continuum theory to predict longitudinal and transverse macrodispersivities of a three-dimensional plume, whose magnitude similar to Borden, Cape Cod, and Columbus tracer test. Strack [1992] presented non-Fickian constitutive equation for macroscopic dispersion, containing diffusive and inertia terms. Grandrod and Impey [1993] used three models to assess the relative contributions of Fickian dispersal processes and channeling in fractal medium. They found fast-channel dominated at early stage, later Fickian dominated. Grattoni et al. [1993] determined dispersion and adsorption parameters by matching numerical solution to experimental effluent curves.

The result of the dispersion is similar to the diffusion of chemical species and traditional Fickian-type flux is used for the evaluation of the diffusion. The diffusive flux is caused by the difference of solute concentration. The dispersive flux is caused by the microscopic velocity fluctuation, as well as the difference in chemical concentration. In the derivation of macroscopic averaged transport equation [Kim and Stenstrom, 1994], the character of dispersive flux appears as the difference between the microscopic species phase velocity. The dispersion coefficient has the directional property of velocity of each phase and can be different for each component species. The traditional formulation of dispersion coefficient tensor [Bear, 1979; Voss, 1984] can be expanded for this species dependency as follows [Kim, 1989; Abriola et al., 1993]:

$$D_{ij,\alpha}^d = a_{T,\alpha}^i |v_\alpha| \delta_{ij} + (a_{L,\alpha}^i + a_{\alpha,T}^i) \frac{v_{i,\alpha}^j v_{j,\alpha}^i}{|v_\alpha|} + D_{m,\alpha}^i \quad (2.1)$$

where,  $D_{ij,\alpha}^d$  is the dispersion coefficient tensor of species  $i$  in  $\alpha$  phase (m/day<sup>2</sup>),  $a_{T,\alpha}^i$  and  $a_{L,\alpha}^i$  are the transverse and longitudinal dispersivities of species  $i$  in  $\alpha$  phase (m),  $|v_\alpha|$  is the absolute velocity of  $\alpha$  phase ( $= \sqrt{v_{i,\alpha}^2 + v_{j,\alpha}^2}$ ),  $ij$  is the index for direction,  $\delta_{ij}$  is the Kronecker delta ( $\delta_{ij} = 1$  when  $i = j$ ,  $\delta_{ij} = 0$  when  $i \neq j$ ), and  $D_{m,\alpha}^i$  is the molecular diffusivity of species  $i$  in  $\alpha$  phase.

Corapcioglu and Baehr [1987] proposed an alternative formulation for the mechanical dispersion and the molecular diffusivity as follows :

$$D_{\alpha}^j = d_{\alpha} \lambda_{\alpha} + D_{m\alpha}^j \theta_{\alpha} \xi_{\alpha} \quad (2.2)$$

where,  $d_{\alpha}$  is the matrix of factors depending upon the fluid velocity,  $\lambda_{\alpha}$  is the product of  $\theta_{\alpha}$  and the dispersivity, and  $\xi_{\alpha}$  is the complexity tensor of  $\alpha$  phase.

Although many forms of equations have been developed for the dispersion coefficient, no generally accepted evaluation procedure exists. The tortuosity of the geometry makes the analysis very difficult to perform and the microscopic phase velocity is almost impossible to postulate. The only method used heretofore relies on soil sample tests and the tracer tests. These results can be combined with parameter estimation techniques. Often only approximate results can be obtained, and additional research is required to better estimate this parameter.

### 3. Mass Dissolution

Mass dissolution in the subsurface environment usually refers to the transfer of species from organic liquids (NAPL) to the aqueous phase. The process can also refer to the dissolution of solid organic phases, or precipitated inorganic solids. In this section, discussion is limited to NAPL dissolution, which occurs when entrapped NAPL blobs are contacted by soil or ground water, and when NAPL pools spread over the water table (LNAPL) or penetrate the aquifer itself (DNAPL). One approach to incorporating NAPL dissolution in a transport model is to assume that local equilibrium exists between the organic liquid and aqueous phases. However, results from recent studies indicate that a nonequilibrium approach may, in most cases, be more appropriate.

#### 3.1 NAPL-Water Equilibrium Partitioning

The majority of organic contaminants of environmental interest are often categorized as sparingly soluble. Solubility values range from about  $10^{-3}$  to 0.7 mol/L, for one- and two-carbon halogenated compounds, from about  $10^{-8}$  to  $10^{-3}$  mol/L, for aliphatic hydrocarbons, and can be as low as  $10^{-10}$  and  $10^{-11}$  mol/L, for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), respectively [Schwarzenbach et al., 1993]. Exceptionally soluble organics include ionic and polar species. For example, methanol is infinitely soluble in water, and can act as a cosolvent, increasing the apparent solubility of a sparingly soluble organic species [Yalkowsky et al., 1976]. The NAPL phase often consists of a mixture of several organic species. In such cases, the aqueous solubility of each component of the NAPL phase is proportional to its mass fraction in the multicomponent mixture.

$$x_w^i = \frac{\gamma_o^i x_o^i}{\gamma_w^i} \quad (3.1.1)$$

where  $x_w^i$  is the mole fraction of organic species  $i$  in the water [-],  $x_o^i$  is the mole fraction of organic species  $i$  in the NAPL phase [-],  $\gamma_o^i$  is the activity coefficient of organic species  $i$  in the NAPL phase,  $\gamma_w^i$  is the activity coefficient of organic species  $i$  in the water.

The activity coefficients account for the nonideality associated with a species in the respective solution. The organic species is expected to exhibit fairly ideal behavior in the NAPL phase, and the activity coefficient in the numerator (equation 3.1.1) is often assumed to be equal to 1. However, the greater the dissimilarity between the molecules in the mixture, the greater the deviation from 1 will be. The activity coefficient for the organic species in water is a function of the aqueous concentration, and can be difficult to estimate. It is generally the same order of magnitude as the inverse of the aqueous solubility for the pure species [see Schwarzenbach et al., 1993], and, thus, can span a wide range of values for the various organics of interest. If  $\gamma_w^i$  is approximated by the inverse of solubility, and  $\gamma_o^i$  by 1, then equation 3.1.1 simplifies to

$$x_w^i = x_w^i s_o^i \quad (3.1.2)$$

where  $x_w^i$  is the mole fraction of species  $i$  in water at the solubility.

#### 3.2 NAPL-Water Mass Transfer

Aqueous concentrations approaching the solubility of organic contaminants are seldom observed at contaminated sites [Schwille, 1975; Mackay et al., 1985; Feenstra and Coburn, 1986]. Research that examined water moving through a stationary NAPL phase [Miller et al., 1990; Powers et al., 1991; 1992; Mayer et al., 1991; Imhoff et al., 1993] has shown that the local equilibrium approach is typically not valid for NAPL dissolution. Most of these re-

searchers interpreted their results by using a film transfer mechanism to model the rate of mass transfer from the NAPL phase to the aqueous phase. This approach was adopted for implementation into the present model.

The film transfer model describes the diffusion of an organic species away from the interface of the organic phase and the bulk aqueous phase. The equation for mass flux depicts film diffusion using a linear driving force approximation:

$$J = k_f(C_w^o - C_{ow}^o) \quad (3.2.1)$$

where  $J$  is the mass flux of the organic species in the direction normal to the interface ( $M \cdot L^{-2} \cdot T^{-1}$ ),  $k_f$  is the external, or film, mass transfer coefficient [ $L/T$ ],  $C_{ow}^o$  is the organic species concentration at the interface.

The interfacial concentration can be approximated by aqueous solubility ( $C_s$ ). Equation (3.2.1) can be rewritten as

$$J = \frac{1}{A_o} \frac{\partial m}{\partial t} = \frac{U_w}{A_o} \frac{\partial C_w^o}{\partial t} = k_f(C_s - C_w^o) \quad (3.2.2)$$

where  $\frac{\partial m}{\partial t}$  is the mass rate of change for the aqueous phase [ $M/T$ ],  $A_o$  is the interfacial surface area between the NAPL and the aqueous phase [ $L^2$ ],  $U_w$  is the volume of the aqueous phase,  $\frac{U_w}{A_o} = a_o$  is the specific interfacial surface area [ $L$ ]. For the dissolution of NAPL blobs in a porous medium, the specific interfacial surface area is defined as (deZabala and Radke, 1986):

$$a_o = \phi S_o \left( \frac{A}{V} \right)_{blob} f \quad (3.2.3)$$

where  $\left( \frac{A}{V} \right)_{blob}$  is the ratio of the surface area to volume of NAPL blob [ $L^{-1}$ ],  $f$  is the fraction of blob surface area exposed to mobile water [-].

Use of equation (3.2.3) requires an assumption of blob geometry, and an estimate of the exposed blob surface area. A simple geometry (e.g., spheres) is usually assumed, and the entire surface area is usually assumed to be exposed to flow ( $f=1$ ). The assumption regarding exposed surface area is probably not a bad one. However, Powers et al. (1992) examined residual NAPL ganglia, and found a complex geometry, strongly dependent on pore structure and aqueous phase velocity. The mass transfer coefficient in equation (3.2.2) is correlated to the diffusivity and velocity of the aqueous phase using the dimensionless Sherwood number (Welty, 1969):

$$Sh = \frac{k_f l_c}{D_l} = a Re^m Sc^n \quad (3.2.4)$$

where  $Sh$  is the Sherwood number [-],  $D_l$  is the free aqueous diffusivity of the organic species [ $L^2/T^2$ ],  $l_c$  is the characteristic length scale [ $L$ ],  $Re$  is the Reynolds number [-],  $v_w$  is the Darcy velocity of the aqueous phase [ $L/T$ ],  $Sc = \left( \frac{\mu_w}{D_l \rho_w} \right)$

is the Schmidt number [-], and  $a$ ,  $m$  and  $n$  are empirical constants.

The characteristic length scale is most frequently chosen as the representative grain diameter for the porous medium. It is worthwhile to note that equation (3.2.4) indicates a nonzero value of the mass transfer coefficient under no-flow conditions. Several of the recent soil column studies regarding NAPL dissolution (Miller et al., 1990; Powers et al., 1992; 1994; Imhoff et al., 1994) have provided regressions, similar in form to equation (3.2.4), for estimating the mass transfer coefficient. More specifically, most approaches provide a means of estimating a mass transfer rate constant ( $k_{ow}^o = k_f a_o$ ).

In one variation (Powers et al., 1994), researchers included soil particle size distribution data explicitly in the correlation. Most of the experiments in these studies were conducted using relatively high flow velocities (e.g.,  $v_w > 3.5m/d$ , Powers et al., 1994). These velocities are more closely associated with forced gradient flow, such as that occurring during a pump and treat remediation effort. Under such conditions, the results clearly demonstrate in invalidity of the local equilibrium assumption for NAPL dissolution in porous media. Observed values of the dissolution rate constant ranged from about  $0.1 d^{-1}$  to several hundred  $d^{-1}$  in the most recent studies (Powers et al., 1994; Imhoff et al., 1994). The specific value depends on strongly on the flow rate and NAPL-pore geometry. In the framework of the present model, the single-component NAPL dissolution rate expression from equation (3.2.2) takes the following form:

$$\frac{\partial w_w^o}{\partial t} = k_{ow}^o (w_w^o - w_w^o) \quad (3.2.5)$$

where  $k_{ow}^o$  is the NAPL dissolution rate constant [ $T^{-1}$ ],  $w_w^o$  is the mass fraction of the organic species at the aqueous solubility limit [-].

Equation (3.2.5) is incorporated into the overall transport model as an interfacial mass transfer term. Within the overall model, the dissolution rate constant will be retarded by a factor related to equilibrium partitioning of the dissolved organic species between the aqueous and the soil phases (see section 5.1).

### 3.3 Related Modeling Efforts

On the other hand, there are many evidences which suggest that local equilibrium assumption is not valid. Many researchers realized that the concentrations of organic solutes in groundwater containing NAPL residual were lower than their equilibrium concentrations [ Mackay et al., 1985; Feenstra and Coburn, 1986; Schwillie, 1975 ]. Fields and laboratory studies also showed that local equilibrium conditions were not consistent to the results of the column and field tests [ Miller and Weber, 1986; Roberts et al., 1986; Valocchi, 1988]. Miller et al. [1990] performed an experiment to isolate and measure mass transfer between toluene and water in glass bead media systems. The interfacial mass transfer rate was represented as a function of aqueous phase velocity, and nonaqueous-phase fluid saturation level. No significant relation to mean particle size was found. Equilibrium was achieved rapidly over a wide range of nonaqueous phase fluid saturation and aqueous phase velocities. Conrad et al. [1992] used etched glass micromodels to visually observe dynamic multiphase displacement of residual organic liquid trapped in aquifers. Experimental results revealed that the size shape, and spatial distribution of isolated blobs affected the dissolution of organic liquid into water phase and the biotransformation of organic components. Powers et al. [1991] showed that nonequilibrium dissolution of nonaqueous phase liquids could play a significant role in some contamination scenarios, primarily for large blob sizes and relatively high velocities. The steady and transient behavior and the sensitivity of the system were investigated for various parameters including mass transfer coefficient, blob size and shape, and Darcy velocity using one-dimensional analytical and numerical models. Powers et al. [1992] studied steady column dissolutions by the examination of polymerized blobs, and found that NAPL dissolutions rates are highly dependent upon pore structure characteristics and aqueous phase velocity. Powers et al. [1994] proposed a general correlation for transient dissolutions rates, incorporating porous medium properties, Reynolds number, and volumetric fraction of NAPL. Imhoff et al. [1993] used gamma attenuation technique to determine mass transfer rate of TCE ganglia trapped within a porous medium, and found the coefficients to be a function of Darcy flux, TCE volumetric fraction, and distance into the region of residual TCE. Geller and Hunt [1993] obtained ganglia size and cross-sectional area of trapped NAPL by fitting two-parameter models to the experimental data.

## CONCLUSIONS

The parameters, constitutive equations and partition concepts of previous research have been addressed as broadly as possible, and some of the evaluation techniques have been improved for the parameters such as the fluid conductivity tensor, storage coefficient about compressibility of soil matrix and fluid, dispersion and partition coefficients.

The governing equations have been developed from averaged parameters, and the groundwater system is very dependent upon these averaging parameters. Therefore, sensitivity analysis, simplification and estimation of these parameters are exceedingly important.

Accompanying paper of this issue shows how the numerical implementation of the governing equation is matched to experimental results.

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