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Modeling the Transport of Contaminants Originating from the Dissolution of DNAPL Pools in Aquifers in the Presence of Dissolved Humic Substances

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Abstract. A two-dimensional finite difference numerical model was developed to describe the transport of dissolved organics originating from nonaqueous phase liquid (NAPL) pool dissolution in saturated porous media in the presence of dissolved humic substances. A rectangular NAPL pool was considered in a homogeneous porous medium with unidirectional interstitial groundwater velocity. It was assumed that dissolved humic substances and aqueous phase contaminants may sorb onto the solid matrix under local equilibrium conditions. The contaminant in the aqueous phase may undergo first-order decay. Also, the dissolved contaminant may sorb onto humic substances. The transport properties of dissolved humic substances are assumed to be unaffected by sorbing contaminants, because dissolved humic macromolecules are much larger than dissolved contaminants and sorption of nonpolar contaminants onto humic substances do not affect the overall surface charge of humic substances. The sorption characteristics of dissolved humic substances onto clean sand were determined from column experiments. An effective local mass transfer rate coefficient accounting for the presence of dissolved humic substances was developed. Model simulations indicate that dissolved humic substances substantially increase NAPL pool dissolution, and consequently reduce the required pump-and-treat aquifer remediation time.

Key words: contaminant transport, transport of humic substances, NAPL pool dissolution, dissolved organic carbon, aquifer remediation, numerical modeling.

Abbreviations: DNAPL – dense nonaqueous phase liquid, DDT – dichlorodiphenyltrichloroethane, DOC – dissolved organic carbon, HCBD – hexachlorobutadiene, NAPL – nonaqueous phase liquid, PCE – perchloroethylene, TCE – trichloroethylene.

Nomenclature

c	advection number, defined in (31a) [–].
C	aqueous phase solute concentration (solute mass/liquid volume) [M/L^3].
C_a	apparent aqueous phase solute concentration in the presence of DOC [M/L^3].

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C_s	aqueous solubility [M/L^3].
C^*	sorbed solute concentration onto the solid matrix (solute mass/solids mass) [–].
C^*_doc	solute concentration sorbed onto DOC (solute mass/liquid volume) [M/L^3].
C^{**}_doc	solute–humic concentration sorbed onto the solid matrix (solute mass/solids mass) [–].
d	diffusion number, defined in (31b) [–].
$\mathcal{D}$	molecular diffusion coefficient [L^2/t].
$\mathcal{D}_\mathrm{e}$	effective molecular diffusion coefficient [L^2/t].
D_x	longitudinal hydrodynamic dispersion coefficient [L^2/t].
D_z	vertical hydrodynamic dispersion coefficient [L^2/t].
f_oc	insoluble organic carbon fraction in the solid matrix (mass of organic carbon per mass of sorbent) [–].
H	concentration of humic substances in the aqueous phase expressed as DOC [M/L^3].
H_0	source concentration of humic substances expressed as DOC [M/L^3].
I( )	integer mode arithmetic operator [–].
k	local mass transfer coefficient [L/t].
k_e	effective local mass transfer coefficient [L/t].
$\overline{k}_\mathrm{e}$	average (or overall) effective mass transfer coefficient [L/t].
K_d	solute partition coefficient between the solid matrix and the aqueous phase [L^3/M].
K_doc	solute partition coefficient between the DOC and aqueous phase [L^3/M].
K_h	humic substance partition coefficient between the solid matrix and the aqueous phase [L^3/M].
K_oc	organic carbon partition coefficient [L^3/M].
K_ow	octanol–water partition coefficient (concentration of octanol per unit aqueous concentration) [–].
ℓ_x	pool dimension in the longitudinal direction [L].
ℓ_{x_0}	x Cartesian coordinate of pool origin [L].
ℓ_y	pool width in the transverse direction [L].
L_h	humic substance source height [L].
m	summation index [–].
m_f	total number of time steps [–].
$\mathcal{M}$	total contaminant mass dissolved in the aqueous phase [M].
Pe	cell Peclet number [–].
Q	flowrate [L^3/t].
R_s	retardation factor of the solute [–].
R_h	retardation factor of the humic substances [–].
t	time [t].
U	average interstitial velocity [L/t].
x, y, z	spatial Cartesian coordinates [L].

Greek Symbols

α_L	longitudinal dispersivity [L].
Δt	time interval [t].
ζ	conductivity [S/L].
θ	porosity (liquid volume/porous medium volume) [–].
λ	first-order decay coefficient [t^{-1}].

ρ_b	dry bulk density of the solid matrix (dry solids mass/aquifer volume) [M/L^3].
τ	tortuosity ($\geqslant 1$) [–].

Subscripts

h	indicates a dissolved humic substance.
s	indicates a solute.
sh	indicates solute-humic substance.

Superscript

n	finite-difference scheme time step.

1. Introduction

Leaking underground gasoline tanks, hazardous waste dump sites, industrial waste outlets, and accidental land spills are just a few possible sources of man-made groundwater contamination. As the number of contaminated sites around the world increases, the public becomes more aware of the environmental impact that groundwater contamination has on present and future generations. In particular, nonaqueous phase liquids (NAPLs) are the focus of many studies (e.g., Miller *et al.*, 1990; Geller and Hunt, 1993; Mayer and Miller, 1993; Chrysikopoulos *et al.*, 1994; Powers *et al.*, 1994; Imhoff *et al.*, 1994; Chrysikopoulos, 1995; Illangasekare *et al.*, 1995; Lee and Chrysikopoulos, 1995, 1998; Holman and Javandel, 1996; Chrysikopoulos and Lee, 1998; Kim and Chrysikopoulos, 1999).

Once NAPLs are released into the environment, they migrate through the unsaturated zone until they reach the groundwater table. If large quantities of NAPLs are released, contaminant pools can form. Light nonaqueous phase liquids (LNAPLs, specific gravity <1) form pools on top of the water table, whereas dense nonaqueous phase liquids (DNAPLs, specific gravity >1) may form pools on top of semi-impermeable subsurface formations, often at the bottom of aquifers. Dissolution from these NAPL pools occurs slowly, creating plumes of contamination in the direction of the groundwater movement.

Due to the slow dissolution rate of DNAPL pools and the difficulty in locating these pools, environmental engineers are especially concerned with the quality of groundwater once these NAPLs penetrate into subsurface formations. As a result, a substantial amount of effort has been expended to develop treatment technologies to increase NAPL dissolution rates, thereby improving aquifer remediation efficiencies.

Humic substances are natural polydisperse organic materials exhibiting solubility enhancement behavior for oils and other relatively water insoluble compounds. The ability of humic substances to interact with hydrophobic organic compounds is widely accepted, and they enhance hydrophobic organic solubility by a partitioning process (Chiou *et al.*, 1986). Numerous experimental studies suggest that a linear relationship exists between NAPL solubility and dissolved humic substance concentration (e.g., Wershaw *et al.*, 1969; Carter and Suffet, 1982; Chiou *et al.*, 1986, 1987; Chin and Weber, 1989; Abdul *et al.*, 1990; Tell and Uchrin, 1991; Kopinke *et al.*, 1995; Chin *et al.*, 1997; Tanaka *et al.*, 1997). Several authors have modeled hydrophobic contaminant transport in the presence of humic substances (Lafrance *et al.*, 1989; Rav-Acha and Rebhun, 1992; Johnson *et al.*, 1995; Sojitra *et al.*, 1995, 1996; Rebhun *et al.*, 1996). However, all of the experimental and modeling efforts have been one-dimensional. Furthermore, the case of NAPL pool dissolution in the presence of dissolved humic substances has not been explored yet. This work explores the capability of dissolved humic substances to increase DNAPL pool dissolution rates, and enhance contaminant transport in a two-dimensional, homogeneous porous formation.

2. Background

Humic substances are probably the most abundant polymers in nature. They are brown, acidic materials formed by oxidation and condensation reactions between polyphenols, polysaccharides, and polyamino acids of plant and microbial origin (Larson and Weber, 1994). Humic substances found in groundwater originate from infiltrating surface water and from paleo-soils that were buried during geological sedimentation.

The important characteristics of humic substances are their ability to partition with high molecular weight hydrophobic organics and to form complexes with heavy metals. Organic matter in soil and natural water consists of humic substances with molecular weights ranging from several hundreds to tens of thousands. By weight, humic substances may also be considered colloids, exhibiting similar behavior. Humic substances are divided into three diverse groups of compounds on the basis of their solubility in dilute acid and dilute base: fulvic acids are soluble in both dilute acids and dilute bases, humic acids are soluble in dilute bases but are precipitated by dilute acids, and humin, which is insoluble (Krishnamurthy, 1992).

Humic substances were considered for solubility enhancement of contaminants when pesticide pollution was a major concern in the 1960s. The use of humic substances was first implemented in solubilization studies of dichlorodiphenyltrichloroethane (DDT). Wershaw *et al.* (1969) have shown that with the addition of 0.5% sodium humate, the solubility of DDT in water was increased by at least 20 times. Chiou *et al.* (1987) used humic substances to increase the solubility of various extremely insoluble organic solutes including p, p'-DDT, 2,4,5,2′,5′-PCB, 2,4,4′-PCB, 1,2,3-trichlorobenzene, and lindane.

In view of the fact that humic substances are relatively high molecular weight species containing nonpolar organic moieties, a partition-like interaction of a solute with the ‘microscopic organic environment’ of dissolved humic molecules is a reasonable explanation for the observed solubility enhancement of solutes. However, the exact solubility enhancement mechanism is not well understood. The apparent aqueous solubility enhancement of a solute, at the NAPL–water interface, in the presence of dissolved humic substances for a two-dimensional system can be expressed as (Chiou *et al.*, 1986)

$$C_{\mathrm{a}}(t, x, z)|_{z\to 0} = C_{\mathrm{s}}[1 + K_{\mathrm{doc}} H(t, x, z)]|_{z\to 0}, \tag{1}$$

where $C_{\mathrm{a}}(t, x, z)$ is the apparent aqueous phase solute concentration in the presence of dissolved organic carbon (DOC); C_{s} is the aqueous solubility of the solute; $H(t, x, z)$ is the DOC concentration attributable to humic substances; K_{doc} is the solute partition coefficient between humic substances and the aqueous phase (based on the DOC concentration); x and z are the spatial coordinates in the longitudinal and vertical directions, respectively; and t is time.

Sorption of dissolved humic substances onto solids is often described mathematically as a linear equilibrium, Langmuir, or Freundlich process (Murphy *et al.*, 1990, 1992; Liljestrand *et al.*, 1992; Jardine *et al.*, 1992; McCarthy *et al.*, 1993). The major factors affecting the sorption behavior of humic substances are soil type (i.e., clay or clean sand), ionic strength, pH, average effective diameter of the humic macromolecules, and the source of humic substances (i.e., rivers, natural soils, or chemical company).

One detrimental effect of humic acids is that chloroform and other trihalomethanes may form when water containing humic substances is treated by chlorination (Coleman *et al.*, 1992). However, this is not a major concern in pump-and-treat systems because chlorination is rarely used in this process (Kerr, 1990). To remove humic substances from drinking water where chlorination treatment is necessary, activated carbon can be used effectively (Qiu, 1989).

3. Model Development

The physical system considered in this study is a two-dimensional, homogenous, saturated aquifer with a DNAPL pool located onto a bedrock as shown in Figure 1. The dissolved solute is assumed to sorb onto the solid matrix as well as onto particles suspended in the aqueous phase (e.g., humic substances). Contaminant–humic particles and humic substances may sorb onto the solid matrix. The dissolved solute is assumed to undergo first-order decay. Furthermore, the humic substances are introduced into the aquifer from a line source.

The appropriate mathematical model for the physical system considered here consists of three coupled transport equations. One equation describes the transport of the contaminant originating from the dissolving NAPL pool in the presence of dissolved humic substances, another equation describes the transport of dissolved humic substances, and the third equation describes the cotransport of contaminant–humic particles.

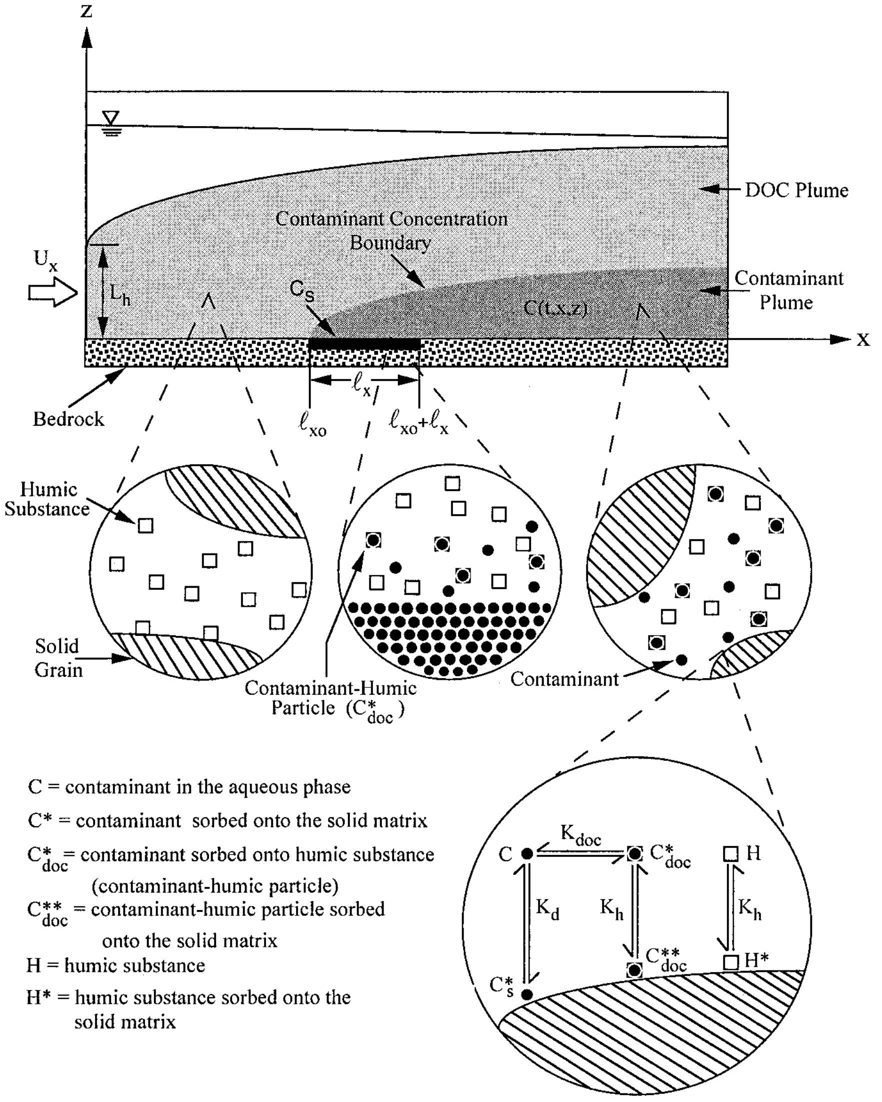

Figure 1. Schematic diagram of the conceptual model showing the unidirectional velocity U_x, the DNAPL pool with aqueous saturation concentration C_s, the humic substance line source of height L_h, and the modes of interaction between dissolved contaminant, dissolved humic substances, and the solid matrix.

3.1. CONTAMINANT TRANSPORT

The two-dimensional transient transport of contaminants resulting from the dissolution of a DNAPL pool in saturated, homogeneous, porous media under uniform interstitial groundwater flow and in the presence of dissolved humic substances is governed by

$$\begin{aligned}\frac{\partial}{\partial t}[R_{\mathrm{s}}(t,x,z)C(t,x,z)] \;=\;& D_{x_{\mathrm{s}}}\frac{\partial^2 C(t,x,z)}{\partial x^2}+D_{z_{\mathrm{s}}}\frac{\partial^2 C(t,x,z)}{\partial z^2}-\\ &-U_x\frac{\partial C(t,x,z)}{\partial x}-\lambda_{\mathrm{s}}R_{\mathrm{s}}(t,x,z)C(t,x,z),\end{aligned}\tag{2}$$

where $C(t,x,z)$ is the aqueous phase solute concentration; $D_{x_{\mathrm{s}}}$ and $D_{z_{\mathrm{s}}}$ are the longitudinal and vertical hydrodynamic dispersion coefficients of the solute, respectively; U_x is the average interstitial pore water velocity in the longitudinal direction; λ_{s} is the first-order decay coefficient of the solute; $R_{\mathrm{s}}(t,x,z)$ is the time and space dependent dimensionless retardation factor of the solute given by

$$R_{\mathrm{s}}(t,x,z)=1+\frac{\rho_b K_d}{\theta}+K_{\mathrm{doc}}H(t,x,z),\tag{3}$$

where K_d is the solute partition coefficient between the solid matrix and the aqueous phase; ρ_b is the dry bulk density of the porous medium; θ is the porosity; and subscript s indicates the solute. It should be noted that the dispersion coefficients for the dissolved contaminant are differentiated from the dispersion coefficients for the solute–humic substances because of their differences in molecular size and structure.

The governing contaminant transport equation (Equation (2)) assumes that solute can sorb onto the solid matrix under linear equilibrium conditions described by

$$C^*(t,x,z)=K_dC(t,x,z),\tag{4}$$

and that solute sorption onto dissolved humic substances, in view of (1), is described by the following relationship:

$$C^*_{\mathrm{doc}}(t,x,z)=K_{\mathrm{doc}}C(t,x,z)H(t,x,z),\tag{5}$$

where $C^*(t,x,z)$ is the solute concentration sorbed onto the solid matrix, and $C^*_{\mathrm{doc}}(t,x,z)$ is the solute concentration sorbed onto DOC. It should be noted that for $z\neq 0$ the aqueous solubility, C_{s}, present in (1) should be replaced by the aqueous phase solute concentration, $C(t,x,z)$.

Assuming that the thickness of the NAPL pool is insignificant relative to the thickness of the aquifer, the appropriate initial and boundary conditions for contaminant transport originating from a dissolving DNAPL pool in a two-dimensional porous medium in the absence of initial dissolved solute concentration are

$$C(0,x,z)=0,\tag{6}$$

$$\frac{\partial C(t,\pm\infty,z)}{\partial x}=0,\tag{7}$$

$$-\mathcal{D}_{\mathrm{e_s}}\frac{\partial C(t,x,0)}{\partial z}=\begin{cases}k_{\mathrm{e}}(t,x)[C_{\mathrm{s}}-C(t,x,\infty)], & \ell_{x_0}\leqslant x\leqslant \ell_{x_0}+\ell_x,\\ 0, \text{ otherwise},\end{cases} \tag{8}$$

$$\frac{\partial C(t,x,\infty)}{\partial z}=0, \tag{9}$$

where $\mathcal{D}_{\mathrm{e_s}} = \mathcal{D}_{\mathrm{s}}/\tau$ is the effective molecular diffusion coefficient ($\mathcal{D}_{\mathrm{s}}$ is the molecular diffusion coefficient, $\tau \geqslant 1$ is the tortuosity); ℓ_x is the pool length; ℓ_{x_0} indicates the x coordinate of the pool origin; and $k_{\mathrm{e}}(t,x)$ is the effective local mass transfer coefficient dependent on time and distance along the NAPL–water interface. Note that the surface of the NAPL–water interface is at $z = 0$, and $z \to \infty$ corresponds to any location above the contaminant concentration boundary layer.

3.2. MASS FLUX AT THE NAPL–WATER INTERFACE

Assuming that the bulk contaminant concentration outside the boundary layer is zero, $C(t,x,\infty) = 0$, the appropriate expression for the effective local mass transfer coefficient is given by

$$\begin{aligned} k_{\mathrm{e}}(t,x) &= -\frac{\mathcal{D}_{\mathrm{e_s}}}{C_{\mathrm{s}}}\frac{\partial}{\partial z}[C(t,x,0)+C^{*}_{\mathrm{doc}}(t,x,0)]\\ &= -\frac{\mathcal{D}_{\mathrm{e_s}}}{C_{\mathrm{s}}}\frac{\partial C_{\mathrm{a}}(t,x,0)}{\partial z}. \end{aligned} \tag{10}$$

If there is no dissolved humic acid present, then in view of (1) and (5) the preceding equation reduces to the local mass transfer coefficient derived by Chrysikopoulos *et al.* (1994):

$$k(t,x)=-\frac{\mathcal{D}_{\mathrm{e_s}}}{C_{\mathrm{s}}}\frac{\partial C(t,x,0)}{\partial z}. \tag{11}$$

Furthermore, the average (overall) effective mass transfer coefficient $\overline{k}_{\mathrm{e}}(t)$, applicable to the entire pool, can be expressed as (Incropera and DeWitt, 1996, p. 286; Chrysikopoulos and Lee, 1998)

$$\overline{k}_{\mathrm{e}}(t)=\frac{1}{\ell_x}\int_0^{\ell_x}k_{\mathrm{e}}(t,x)\,\mathrm{d}x. \tag{12}$$

The amount of contaminant mass, $\mathcal{M}^{\circ}(t)$, that has partitioned across the NAPL–water interface can be calculated by the following expression (Chrysikopoulos and Lee, 1998):

$$\mathcal{M}^{\circ}(t)=\sum_{m=1}^{m_f}\overline{k}_{\mathrm{e}}(m\Delta t)C_{\mathrm{s}}\ell_x\ell_y\theta\Delta t, \tag{13}$$

where ℓ_y is the width of the NAPL pool, which is equal to unity for the case considered in this study; Δt is a time interval; m is a summation index; and $m_f = \mathrm{I}(t/\Delta t)$ is an integer indicating the total number of time steps (where I( ) is an integer mode arithmetic operator truncating off any fractional part of the numeric argument).

3.3. TRANSPORT OF DISSOLVED HUMIC SUBSTANCES

The two-dimensional transient transport of dissolved humic substances in saturated, homogeneous porous media under uniform interstitial groundwater flow is governed by the following partial differential equation:

$$R_{\mathrm{h}} \frac{\partial H(t,x,z)}{\partial t} = D_{x_{\mathrm{h}}} \frac{\partial^2 H(t,x,z)}{\partial x^2} + D_{z_h} \frac{\partial^2 H(t,x,z)}{\partial z^2} - U_x \frac{\partial H(t,x,z)}{\partial x}, \tag{14}$$

where $D_{x_{\mathrm{s}}}$ and $D_{z_{\mathrm{s}}}$ are the longitudinal and vertical hydrodynamic dispersion coefficients of the dissolved humic substances, respectively; R_{h} is the retardation factor for humic substances defined as follows:

$$R_{\mathrm{h}} = 1 + \frac{\rho_b K_{\mathrm{h}}}{\theta} \tag{15}$$

(K_{h} is the humic substance linear equilibrium partition coefficient between the solid matrix and the aqueous phase); and subscript h indicates the dissolved humic substance. It should be noted that K_{h} is based on the assumption that the sorption of dissolved humic substances onto the solid matrix is described by the following linear relationship:

$$H^*(t,x,z) = K_{\mathrm{h}} H(t,x,z), \tag{16}$$

where $H^*(t,x,z)$ is the DOC concentration sorbed onto the solid matrix. Decay of humic substances are not considered because they are usually stable and persistent in the environment.

The appropriate initial and boundary conditions for transport of dissolved humic substances in a homogenous, saturated formation with a continuous line source of height L_{h}, located at $x = 0$, $y = 0$ (see Figure 1) are

$$H(0,x,z) = 0, \tag{17}$$

$$H(t,0,z \leqslant L_h) = H_0, \tag{18}$$

$$\frac{\partial H(t,\pm\infty,z)}{\partial x} = 0, \tag{19}$$

$$\frac{\partial H(t,x,\infty)}{\partial z} = 0, \tag{20}$$

$$\frac{\partial H(t,x,0)}{\partial z} = 0, \tag{21}$$

where H_0 is the source concentration of dissolved humic substances expressed as DOC. The initial condition (17) establishes that there is no initial dissolved humic substances within the two-dimensional porous formation. The boundary condition (18) implies a constant humic substance concentration throughout the line source. Conditions (19) and (20) preserve concentration continuity for an infinite system along the x direction, and a semi-infinite system along the z direction, respectively. Finally, condition (21) represents an impervious boundary at $z = 0$.

3.4. COTRANSPORT OF SOLUTE–HUMIC SUBSTANCES

The two-dimensional transient cotransport of solute–humic substances in saturated, homogeneous porous media under uniform interstitial groundwater is governed by the following partial differential equation:

$$\begin{aligned} R_{\mathrm{sh}} \frac{\partial C^*_{\mathrm{doc}}(t,x,z)}{\partial t} &= D_{x_{\mathrm{sh}}} \frac{\partial^2 C^*_{\mathrm{doc}}(t,x,z)}{\partial x^2} + D_{z_{\mathrm{sh}}} \frac{\partial^2 C^*_{\mathrm{doc}}(t,x,z)}{\partial z^2} - \\ &\quad - U_x \frac{\partial C^*_{\mathrm{doc}}(t,x,z)}{\partial x} - \lambda_{\mathrm{sh}} R_{\mathrm{sh}} C^*_{\mathrm{doc}}(t,x,z), \end{aligned} \tag{22}$$

where R_{sh} is the retardation factor for the dissolved solute–humic substances; $D_{x_{\mathrm{sh}}}$ and $D_{z_{\mathrm{sh}}}$ are the longitudinal and vertical dispersion coefficients of the dissolved solute–humic substances; λ_{sh} is the first-order decay coefficient of the solute-humic; and subscript sh indicates the solute–humic substance. Solute–humic substances are assumed to share the same transport properties as humic substances because humic substances are much larger than the contaminants considered in this study and that sorption of nonpolar compounds onto humic substances most likely will not significantly affect the overall surface charge or sorption characteristics of humic macromolecules. Therefore, $D_{x_{\mathrm{h}}}=D_{x_{\mathrm{sh}}}$, $D_{z_{\mathrm{h}}}=D_{z_{\mathrm{sh}}}$, and the solute–humic substances retardation factor, R_{sh}, is defined as

$$R_{\mathrm{sh}} = 1 + \frac{\rho_b K_{\mathrm{h}}}{\theta}, \tag{23}$$

which is based on the assumption that the sorption of solute–humic substances onto the solid matrix is described by the following linear equilibrium relationship:

$$C^{**}_{\mathrm{doc}}(t,x,z) = K_{\mathrm{h}} C^*_{\mathrm{doc}}(t,x,z), \tag{24}$$

where $C^{**}_{\mathrm{doc}}(t,x,z)$ is the solute–humic concentration sorbed onto the solid matrix. Here it is assumed that the partition coefficient for solute–humic substances between the solid matrix and the aqueous phase, K_{h}, is identical to the partition coefficient for humic substances between the solid matrix and the aqueous phase. Furthermore, it is assumed that the decay of solute–humic substances is dictated by the decay of the solute. Therefore, the decay of solute–humic substances is described by the following expression:

$$\frac{\partial C^*_{\mathrm{doc}}}{\partial t} = -\lambda_{\mathrm{sh}} C^*_{\mathrm{doc}}, \tag{25}$$

where $\lambda_{\mathrm{sh}} = \lambda_{\mathrm{s}}$.

The appropriate initial and boundary conditions for the cotransport of solute–humic substances in a homogenous, saturated, two-dimensional formation are

$$C^*_{\mathrm{doc}}(0, x, z) = 0, \tag{26}$$

$$\frac{\partial C^*_{\mathrm{doc}}(t, \pm\infty, z)}{\partial x} = 0, \tag{27}$$

$$\frac{\partial C^*_{\mathrm{doc}}(t, x, \infty)}{\partial z} = 0, \tag{28}$$

$$\frac{\partial C^*_{\mathrm{doc}}(t, x, 0)}{\partial z} = 0, \tag{29}$$

where the boundary conditions (27)–(29) are analogous to the conditions (19)–(21).

3.5. NUMERICAL SOLUTION

The partial differential equations describing the transport of the dissolved solute and humic substances are solved numerically by an unconditionally stable, fully implicit finite difference discretization method. All flux boundary conditions were estimated using a second-order accurate one-sided approximation (Strikwerda, 1989). The fully implicit algorithm leads to a set of algebraic equations that form a banded square matrix, which is solved by subroutines *bandec* and *banbks* provided by Press *et al.* (1992). In order to avoid numerical dispersion, nodal separation distances and numerical time steps are selected so that the following criteria are satisfied (Hoffman, 1992):

$$\mathrm{Pe}_x = \frac{U_x \Delta x}{D_x} \leqslant 2, \qquad \mathrm{Pe}_z = \frac{U_x \Delta z}{D_z} \leqslant 2, \tag{30a, b}$$

$$c = \frac{U_x \Delta t}{\Delta x} \leqslant 1, \qquad d = \frac{D_x \Delta t}{\Delta x^2} \leqslant 1, \tag{31a, b}$$

where Pe is the cell Peclet number; c is the advection number; and d is the diffusion number.

The solution for solute transport is obtained by approximating the three transport equations (2), (14), (22) and corresponding initial and boundary conditions (6)–(9), (17)–(21), and (26)–(29) simultaneously. For the case where dissolved humic substances are not present, the L_h term is set equal to zero. For this special case ($L_h = 0$), numerical model simulations of solute transport originating from DNAPL pool dissolution in homogeneous, saturated porous media have been compared to the analytical solution presented by Chrysikopoulos *et al.* (1994). An excellent agreement between the numerical and analytical solution is observed.

4. Evaluation of Model Parameters

The majority of the parameters used for model simulations presented here are taken directly from the literature or determined using existing empirical relationships. The humic substance partition coefficient between a clean solid matrix and the aqueous phase was determined experimentally, because there were no empirical relationships available for K_h.

In order to characterize the sorption behavior of the humic substances, flow-through experiments were conducted with columns packed with kiln dried Monterey sand (RMC Lonestar, Monterey, California). The columns were packed with 20–40 size sand, the sand fraction that passed through the #20 sieve (0.850 mm) but was retained on the #40 sieve (0.425 mm). The dry bulk density of the sand was determined gravimetrically to be 1.47 g/cm^3, with a porosity of 0.40. The humic substance used was a humic acid sodium salt obtained from Aldrich Chemical Company, with an average organic carbon content of 50.2% (Chin and Weber, 1989). The effective molecular diffusion coefficient used in this study, $\mathscr{D}_{e_h} = 0.009$ cm^2/h, was estimated by Dycus *et al.* (1995) for similar experimental conditions (pH, filter size, and humic substance source). It should be noted, however, that for the advection dominated numerical simulations conducted here, the $\mathscr{D}_{e_h}$ value will not significantly affect the main conclusions of this research.

The sorption experiments were conducted under constant ionic strength and pH. The pH of the humic acid solution was adjusted to 6.0 using hydrochloric acid (HCl). Sodium chloride (NaCl) was used to raise the conductivity, ζ, of the humic acid solution more than twenty times. Consequently, the resulting ionic strength is attributed primarily to NaCl, and the humic acid contribution is negligible. Subsequently, the humic acid solution was filtered to remove any precipitate that may have formed. The column experiments were conducted in a constant temperature chamber (Forma Scientific, Murietta, Ohio) at 20°C.

4.1. SORPTION EXPERIMENTS

A borosilicate glass column (Omnifit, Cambridge, England) with an inner diameter of 25 mm and 250 mm in length was packed with sand under a constant upflow of deionized water. The dispersivity of the column was determined by tracer experiments with potassium bromide salt (KBr).

Two syringe infusion pumps (model KDS200) were used, one for delivering deionized water to the column and the other for delivering the tracer or humic acid solution. A switching valve (Upchurch Scientific, Oak Harbour, Washington) was used to alter the flow between the two pumps. Liquid samples (approximately 1/2 ml) were collected periodically from the column effluent.

The bromide concentrations in the column effluent were detected using a Dionex ion chromatograph. The longitudinal hydrodynamic dispersion coefficient,

$$D_{\mathrm{L}} = \alpha_{\mathrm{L}} U + \mathcal{D}_{\mathrm{e}} \tag{32}$$

(where α_{L} is the longitudinal dispersivity), was determined by fitting an available one-dimensional analytical solute transport model (US Geological Survey, 1992) to the tracer breakthrough data. Assuming that $\tau = 1.43$, which is appropriate for fine to medium grained sand (de Marsily, 1986), and the molecular diffusion coefficient for bromide is $\mathcal{D} = 7.24 \times 10^{-2}$ cm^2/h (Domenico and Schwartz, 1990), then the effective molecular diffusion coefficient of bromide is estimated to be $\mathcal{D}_{\mathrm{e}} = 5.06 \times 10^{-2}$ cm^2/h. In view of the fitted D_{L} and the estimated $\mathcal{D}_{\mathrm{e}}$, the corresponding value of α_{L} is determined from (32).

Two humic acid flowthrough experiments were performed under the laboratory conditions listed in Table I. Assuming that the sorption of humic substances onto sand is described by a linear equilibrium isotherm, the humic substance retardation factor was estimated by fitting the analytical solution of the standard one-dimensional advection dispersion equation to the humic acid breakthrough experimental data. The best estimate of R_{h} for the column experiments 1 and 2 is 1.40 and 1.46, respectively. The average R_{h} value of 1.43 was used for the numerical simulations presented in this study. The experimental data as well as the simulated concentration breakthrough curves are shown in Figure 2.

4.2. CONTAMINANT PROPERTIES

The three DNAPLs employed in this work are trichloroethylene (TCE), perchloroethylene (PCE), and hexachlorobutadiene (HCBD). The effective molecular dif-

Table I. Parameter values for the humic acid column experiments

Parameter	Experiment 1	Experiment 2
Filter size (μm)	0.40	11.0
Humic acid (mg DOC/l)	245	245
pH	6.0	6.0
Q (cm^3/min)	0.65	0.65
U (cm/min)	0.3457	0.3457
α_{L} (cm)	0.069	0.073
ζ (mS/cm)	16.0	16.0
θ	0.40	0.40

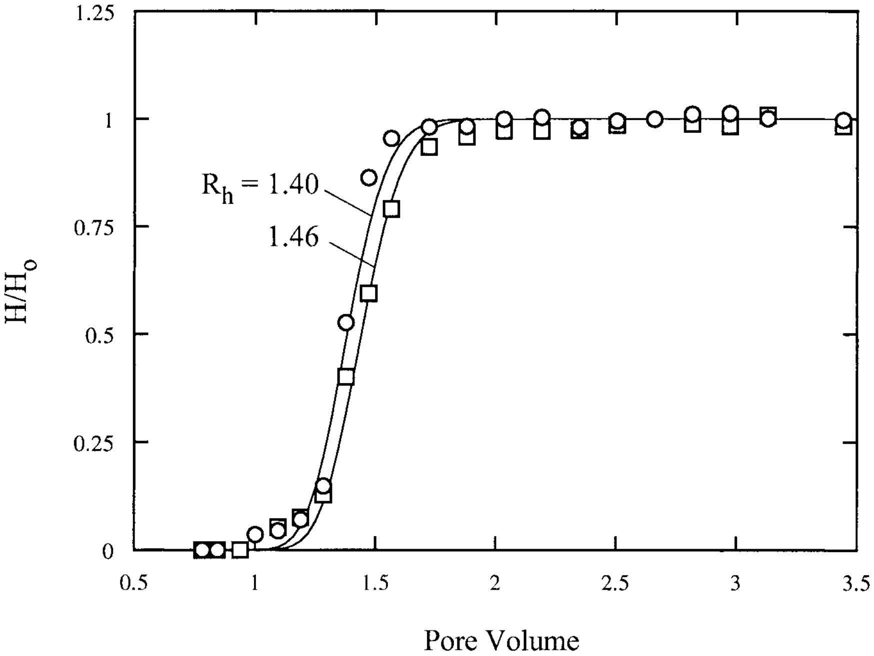

Figure 2. Humic acid breakthrough data from column experiment 1 (circles), experiment 2 (squares), and the simulated concentration histories (solid lines).

fusion coefficients of these organics listed in Table II were calculated using the Hayduk and Laudie (1974) relationship, and the required molar volumes were estimated using the LeBas method (Lyman *et al.*, 1982). For additional details refer to Lee and Chrysikopoulos (1995).

Assuming that solute sorption onto the solid matrix can be modeled as a linear equilibrium process, the solute partition coefficient, K_d, can be estimated as (Karickhoff, 1979)

$$K_d = f_{\mathrm{oc}} K_{\mathrm{oc}}, \tag{33}$$

where f_{oc} is the organic carbon fraction of the solid matrix and K_{oc} is the organic carbon partition coefficient, which can be estimated by the following expression (Karickhoff *et al.*, 1979):

$$\log K_{\mathrm{oc}} = 1.00 \log K_{\mathrm{ow}} - 0.21, \tag{34}$$

where K_{ow} is the octanol–water partition coefficient. In this work, it is assumed that $f_{\mathrm{oc}} = 0.02\%$, $\theta = 0.40$, and $\rho_b = 1.47$ g/cm^3.

The equilibrium partition coefficient for hydrophobic compounds onto dissolved humic acid is determined by the following empirical relationship (Chin and Weber, 1989):

$$K_{\mathrm{doc}} = [\log^{-1}(0.82 \log K_{\mathrm{ow}} + 0.1923)] \times 10^{-6}, \tag{35}$$

Table II. Parameter Values for Model Simulations

Parameter	Value	Units
$C_s^{\dagger}$	1100[a], 150[b], 2[c]	mg/l
$\mathcal{D}_{e_s}$	0.0243[a], 0.0219[b], 0.0236[c]	cm^2/h
$\mathcal{D}_{e_h}$	0.009	cm^2/h
D_{x_s}	1.224[a], 1.222[b], 1.224[c]	cm^2/h
D_{x_h}	1.209	cm^2/h
D_{z_s}	0.624[a], 0.622[b], 0.624[c]	cm^2/h
D_{z_h}	0.609	cm^2/h
H_0	250	mg DOC/l
K_d	0.0324[a], 0.310[b], 7.43[c]	l/kg dry solids
K_{doc}	1.50 E^{-4} [a], 9.56 E^{-4} [b], 1.29 E^{-2} [c]	l/mg DOC
K_h	0.117	l/kg dry solids
$\log K_{ow}^{\dagger}$	2.42[a], 3.40[b], 4.78[c]	–
ℓ_x	8.0	cm
ℓ_{x_0}	7.2	cm
L_h	10	cm
U_x	2.0	cm/h
α_x	0.6	cm
α_z	0.3	cm
Δt	0.5	h
Δx	0.8	cm
Δz	0.5	cm
ρ_b	1.47	g/cm^3
τ	1.43	–
θ	0.40	–

[a] Data for TCE. [b] Data for PCE. [c] Data for HCBD.
† Mackay *et al.*, 1993.

where the value 1×10^{-6} is just a unit conversion factor. The preceding empirical relationship is valid for $\log K_{ow}$ values ranging from approximately 2.4 to 6.0.

5. Simulations and Discussion

Consider a PCE pool located at the bottom of a two-dimensional sandy aquifer on top of an impermeable aquitard. The origin of the pool is at $\ell_{x_0} = 7.2$ cm, and its length is $\ell_x = 8.0$ cm. It is assumed that the NAPL does not diffuse into the aquitard. Initially there is neither dissolved PCE nor dissolved humic substances present in the aquifer. At $t = 0$, a 250-mg DOC/l humic acid solution is injected into the aquifer from a line source ($L_h = 10$ cm). At this instant, the effective mass transfer rate coefficient is at its peak value because the concentration gradient

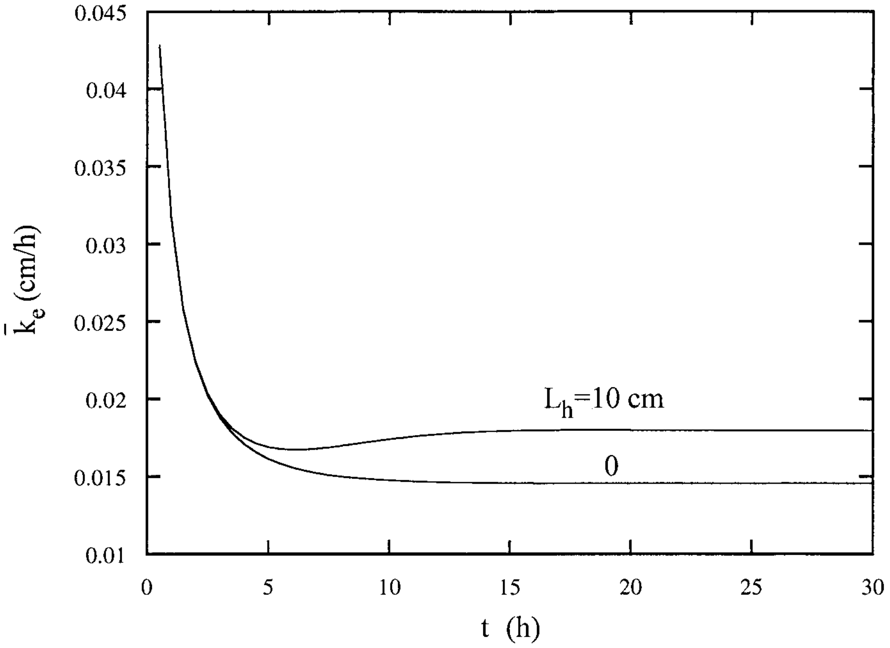

Figure 3. Variation of the effective average mass transfer coefficient with increasing time evaluated for a PCE pool in the presence ($L_h = 10$ cm) and absence ($L_h = 0$) of humic substances.

at the NAPL–water interface is maximum. As the concentration boundary layer is established, the concentration gradient decreases until steady state conditions are reached. The thickness of the boundary layer depends on the hydrodynamic conditions and physical properties of the porous formation. The greater the concentration gradient at the NAPL–water interface the greater the mass transfer of the dissolving contaminant. Therefore, the mass transfer coefficient decreases with increasing distance away from the front edge of the NAPL pool, and its peak value is at the front, or upstream edge of the pool (Chrysikopoulos and Lee, 1998). Consequently, the leading edge of a NAPL pool dissolves faster than the downstream edge. Figure 3 illustrates the behavior of $\bar{k}_e$, defined in (12), as a function of time in the presence and absence of humic substances. Clearly, the presence of humic substances increases the mass transfer from the NAPL pool into the aqueous phase. Similarly, Figure 4 presents the distribution of k_e along the NAPL–water interface in the presence and absence of humic substances. For the conditions considered here, $\bar{k}_e$ is greater than $\bar{k}$ ($\bar{k}$ corresponds to the case where $L_h = 0$).

Now consider that the NAPL pool is of unit width, $\ell_y = 1$ cm. The mass of contaminant dissolving into the aqueous phase across the NAPL–water interface is calculated for several humic acid line source lengths ($L_h = 0, 1, 5$, and 10 cm) and the results are presented in Figure 5. The case where humic substances are not present in the aquifer is represented by $L_h = 0$. The total contaminant mass

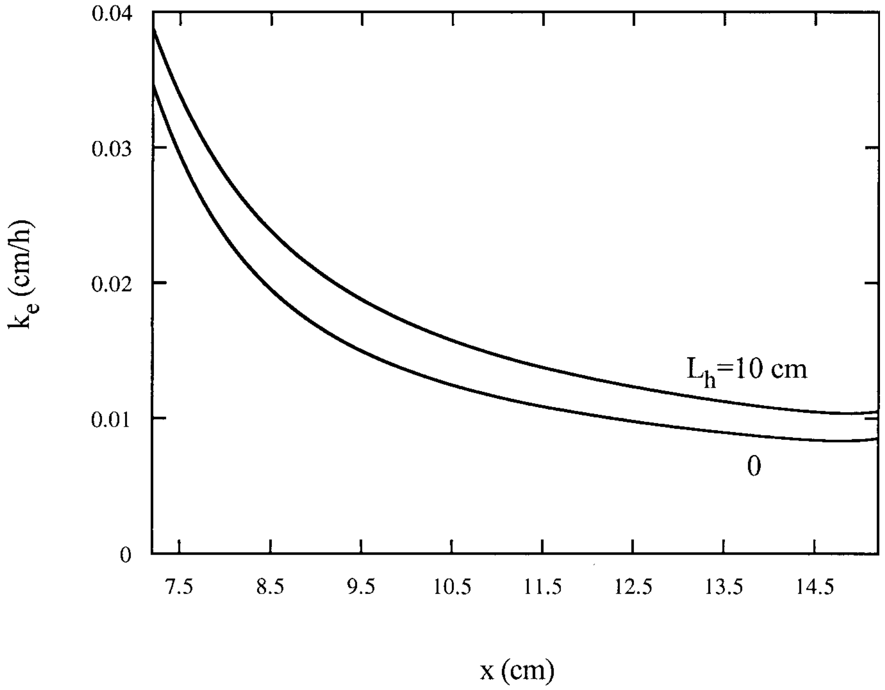

Figure 4. Variation of the local mass transfer coefficient with distance along the PCE pool surface at steady state conditions in the presence ($L_h = 10$ cm) and absence ($L_h = 0$) of humic substances.

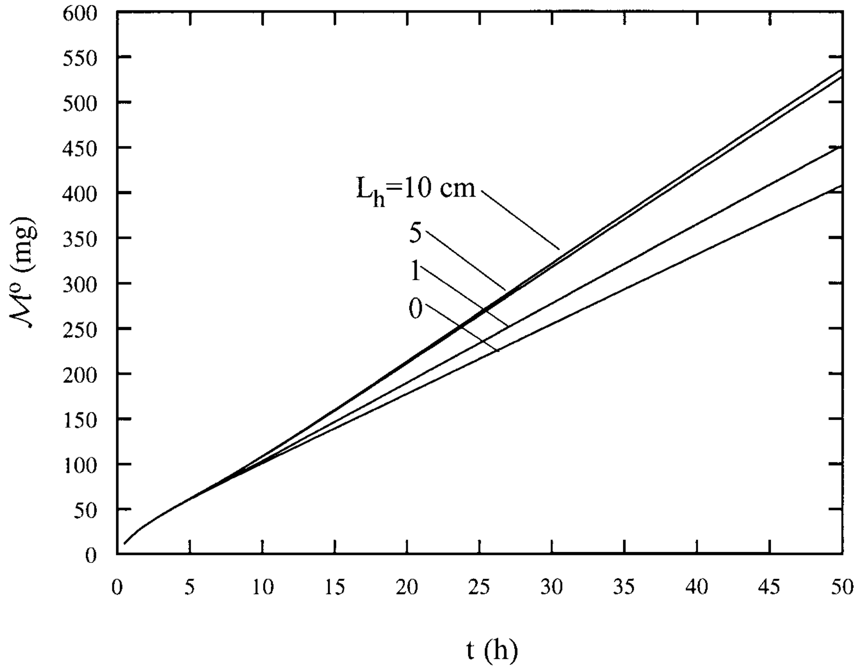

Figure 5. Total contaminant mass dissolved from the PCE pool as a function of time for different humic substance source heights.

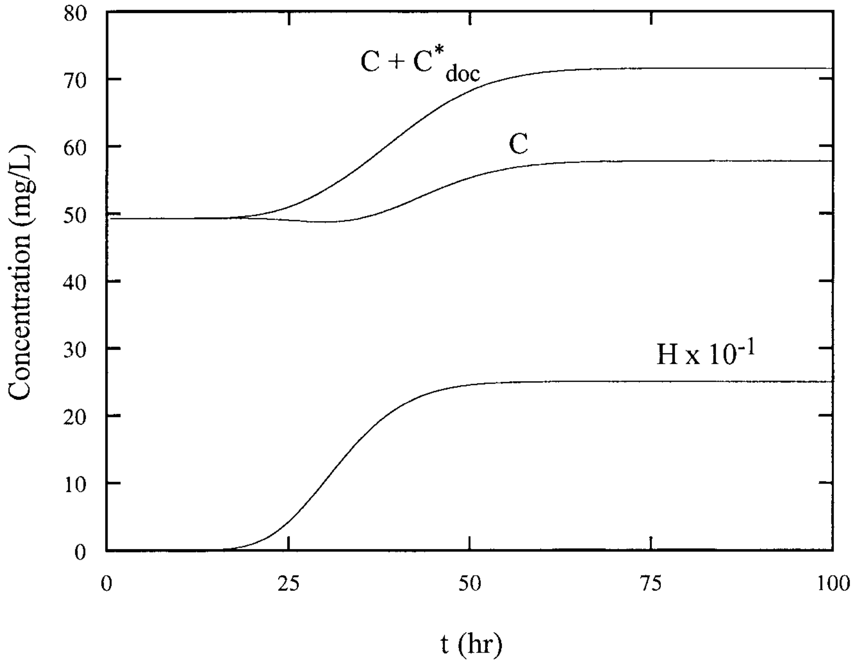

Figure 6. Breakthrough curves of the aqueous PCE concentration, C, total PCE concentration, $C + C^*_{\text{doc}}$, and DOC concentration, H, at a point within the aquifer with coordinates $x = 39.2$ cm, $z = 1$ cm (here $L_{\text{h}} = 10$ cm).

that partitions across the NAPL–water interface as a function of time for the four different cases considered here is evaluated by (13). It is evident from Figure 5 that the presence of humic substances increases the dissolved mass of the contaminant in the aqueous phase. Furthermore, the contaminant mass in the aqueous phase increases with increasing L_{h}. However, it is important to note that increasing L_{h} beyond a certain length does not contribute significantly to the total mass dissolved. Actually, the optimum injection geometry for humic substances is case specific.

To further illustrate the effects of humic substances on NAPL pool solubility enhancement, dissolved PCE concentrations as a function of time were determined for an arbitrary point within the aquifer with coordinates $x = 39.2$ cm and $z = 1.0$ cm. The results are presented in Figure 6, where the total PCE concentration represents the sum of the PCE sorbed onto DOC, C^*_{doc}, and the aqueous PCE concentration, C. The DOC $(\times 10^{-1})$ concentration is also presented in Figure 6. As the dissolved humic substances pass over the NAPL–water interface, NAPL dissolution is enhanced due to sorption of the dissolved contaminant onto suspended humic substances. However, the aqueous phase contaminant concentration at the pool–water interface is assumed to remain equal to C_{s}. When contaminant–humic substances travel through sections of the aquifer with low aqueous phase contaminant concentrations, the contaminant desorbs from suspended humic substances into the aqueous phase, thus increasing the aqueous phase contaminant concentration.

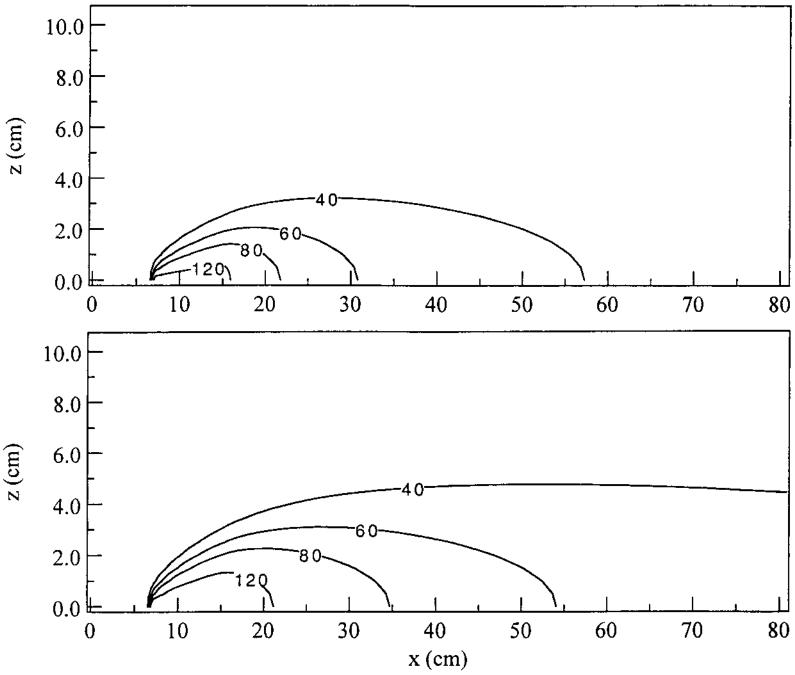

Figure 7. Steady state aqueous phase PCE concentration contours in the aquifer (a) before and (b) after the injection of humic substances (here $L_h = 10$ cm, $\ell_{x_0} = 7.2$ cm, and $\ell_x = 8$ cm).

The concentration of PCE sorbed onto dissolved humic substances is the difference between the total PCE concentration and the aqueous phase PCE concentration.

Figure 7 presents steady state total PCE concentration contours throughout the aquifer in the xz plane for two different cases. The first case represents an aquifer clean of humic substances (Figure 7(a)), whereas for the second case the transport of humic substances is also accounted for (Figure 7(b)). Comparison of the results suggests that vertical and longitudinal spreading of PCE throughout the aquifer is greatly increased in the presence of the dissolved humic substances. Note that contours are closer together at the leading edge of the pool where concentration gradients are larger than the tailing edge of the pool.

In addition to the PCE pool, TCE and HCBD pools are considered in this study. With the exception of C_s, $\mathcal{D}_{e_s}$, D_{x_s}, D_{z_s}, K_d, K_{doc}, K_{ow} which depend on the specific NAPL (see Table II) all other parameter values used for the model simulations are identical. The normalized aqueous phase concentration for each NAPL in the presence of humic substances, as a function of distance downstream from the NAPL pool, at a vertical height of $z = 1$ cm, is illustrated in Figure 8. Note that concentrations are normalized by the corresponding aqueous solubility, $(C + C^*_{doc})/C_s$. The dissolved concentrations are evaluated at steady state conditions ($t = 150$ h). It is evident from Figure 8 that peak normalized concentrations occur at the downstream end of the pool, whereas further away from the pool, lon-

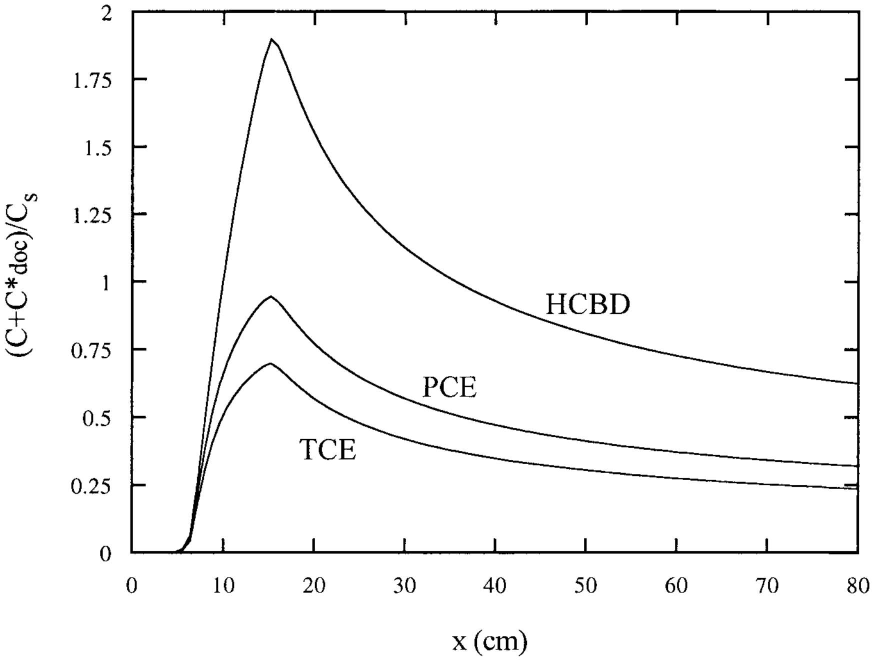

Figure 8. Normalized PCE, TCE, and HCBD aqueous phase concentrations as a function of distance from the pool 150 h since the injection of humic substances into the aquifer (here $z = 1$ cm, $\ell_{x_0} = 7.2$ cm, $\ell_x = 8$ cm, $L_h = 10$ cm).

Table III. PCE pool removal time

L_h (cm)	Time to remove 250 g of PCE (days)
0	169.6
1	149.2
5	123.2
10	120.8

gitudinal and vertical dispersion cause the concentrations to decline with distance. Furthermore, among the NAPLs considered, the normalized dissolved concentration is greatest for HCBD followed by PCE and TCE. This is attributed to the level of hydrophobicity of these organics. The partition coefficient for a dissolved contaminant between DOC and water is strongly related to the contaminant's hydrophobicity. In view of (35), it is evident that, for the transport model developed here, K_{ow} is the only parameter that affects the ability of a solute to sorb onto DOC. The K_{ow} values presented in Table II indicate that HCBD is the most hydrophobic and TCE is the least hydrophobic.

In order to evaluate the ability of humic substances to reduce aquifer pump-and-treat times, a 8 × 8 cm NAPL pool, containing 500 g of PCE is considered.

The NAPL pool surface area is assumed to remain constant throughout the model simulation period. The time required to remove 50% of the PCE pool was evaluated for several different L_h values and the results are listed in Table III. For $L_\mathrm{h} = 10$ cm the time required to remove 250 g of PCE is approximately 30% faster than the case where humics are not present in the aquifer ($L_\mathrm{h} = 0$ cm).

6. Summary

A two-dimensional finite difference numerical model was developed to simulate the dissolution of a single component NAPL pool in a homogeneous, saturated aquifer in the presence of dissolved humic substances. It was assumed that the NAPL pool is located at the bottom of the aquifer on top of an impermeable aquitard. Furthermore, it was assumed that the dissolved contaminant and humic substances may sorb onto the solid matrix under local equilibrium conditions following a linear sorption process. The dissolved contaminant may sorb onto humic substances. Furthermore, contaminant sorption onto dissolved humic substances is assumed to be a function of both contaminant and dissolved humic substance concentration. Model simulations indicate that dissolved humic substances may increase considerably NAPL pool dissolution, and consequently can reduce substantially NAPL pool remediation times.

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