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Mass Transfer From Nonaqueous Phase Organic Liquids in Water-Saturated Porous Media

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Abstract

Results of dissolution experiments with trapped nonaqueous phase liquids (NAPLs) are modeled by a mass transfer analysis. The model represents the NAPL as isolated spheres that shrink with dissolution and uses a mass transfer coefficient correlation reported in the literature for dissolving spherical solids. The model accounts for the reduced permeability of a region of residual NAPL relative to the permeability of the surrounding clean media that causes the flowing water to partially bypass the residual NAPL. The dissolution experiments with toluene alone and a benzene-toluene mixture were conducted in a water-saturated column of homogeneous glass beads over a range of Darcy velocities from 0.5 to 10 m d⁻¹. The model could represent the observed effluent concentrations as the NAPL underwent complete dissolution. The changing pressure drop across the column was predicted following an initial period of NAPL reconfiguration. The fitted NAPL sphere diameters of 0.15 to 0.40 cm are consistent with the size of NAPL ganglia observed by others and are the smallest at the largest flow velocity.

Introduction

The widespread production and use of industrial solvents and liquid petroleum products have provided ample opportunity for subsurface contamination from leaking underground storage tanks and pipelines, hazardous waste sites, and surface spills. The aqueous solubility of these organic liquid contaminants is low enough for them to exist in the subsurface as nonaqueous phase liquids (NAPLs) but large enough to seriously degrade water quality. NAPL contaminants include a wide range of industrial compounds such as gasoline, fuel oils, chlorinated and fluorinated hydrocarbons, creosote, and transformer oils [Mercer and Cohen, 1990]. Many NAPLs, such as gasoline, creosote, and waste liquids, are multicomponent, with the constituents having a broad distribution of chemical properties.

The chemical and physical properties of the organic liquids and the physical characteristics of the subsurface govern their transport and fate [e.g., Schwillie, 1967; Hunt *et al.*, 1988; Mercer and Cohen, 1990]. As the contaminant migrates through the subsurface, residual segments of organic liquid, or ganglia, break off from the main flow of the liquid and are held in the pore spaces of the aquifer by capillary forces. Upon encountering the groundwater table, liquids denser than water may migrate through the water-saturated zone leaving residual ganglia or blobs behind their flow path [Schwillie, 1981]. Liquid contaminants that are less dense than water form a lens along the capillary fringe and water table fluctuations vertically distribute residual NAPL [e.g., McKee *et al.*, 1972; Schwillie, 1967, 1984]. An analysis of the capillary and viscous forces acting on ganglia in aquifers by Hunt *et al.* [1988] shows that the trapped residual is immobile under typical hydraulic gradients. The NAPL is therefore a long-term source of contamination as it dissolves into the surrounding groundwater.

Modeling groundwater contamination by NAPLs has evolved considerably over the last few years. Many multiphase transport models assume equilibrium partitioning among all fluid and solid phases [e.g., *Pinder and Abriola*, 1986; *Corapcioglu and Baehr*, 1987; *Kaluarachchi and Parker*, 1990]. The justification for assuming equilibrium has come from the column studies of the dissolution of homogeneously distributed organic liquid residuals [*van der Waarden et al.*, 1971; *Fried et al.*, 1979]. Observations at NAPL-contaminated sites of aqueous phase concentrations less than solubility have been attributed to the irregular distribution of the NAPL in the aquifer [*Mackay et al.*, 1985; *Wilson et al.*, 1990, *Anderson et al.*, 1992a, b]. The flowing water partially bypasses regions of residual NAPL such that concentrations downgradient represent a mixture of contaminated and uncontaminated water, a feature not represented in the aforementioned column studies. In an experiment that allowed the flow of water through, as well as around a zone of residual NAPL embedded in a sand box, the portion of water flowing through the NAPL zone reached near solubility for seepage velocities less than 0.1 m d^{-1} [*Anderson et al.*, 1992a]. Models that account for diffusional limitations to mass transfer in the aqueous phase predict that aqueous concentrations can be orders of magnitude lower than equilibrium for certain residual NAPL blob sizes and flow velocities [*Hunt et al.*, 1988; *Powers et al.*, 1991]. For multicomponent NAPLs, reported simulations assume a uniform NAPL composition [e.g., *Mackay et al.*, 1991]. The possibility that internal gradients in composition may limit dissolution has been recognized [*Mackay et al.*, 1991; *Conrad et al.*, 1992] but has not been investigated analytically or experimentally.

This paper investigates the dissolution of residual organic liquids in water-saturated, homogeneous porous media under conditions where chemical equilibrium between the organic liquid and aqueous phases is not achieved. The combination of mechanistic analysis and experimental investigation arrives at a model for mass transfer limited dissolution of organic liquids entrapped in porous media.

Background

NAPL Distribution

When an invading NAPL contaminant displaces water, regions of water-saturated media are bypassed by the flowing NAPL and part of the NAPL may become separated from the bulk flow as a result of interfacial instabilities and media heterogeneities [*Kueper and Frind*, 1988]. When the capillary forces acting on a NAPL segment are greater than the gravity forces that drive its movement, the NAPL is immobile. The subsequent flow of water through a NAPL-contaminated region may cause the trapped NAPL segments to be displaced or broken up into smaller blobs. When viscous forces induced by the flowing water overcome interfacial forces, the fraction of pore space occupied by the NAPL, or residual saturation, is a function of the capillary number $Ca[U\mu_w/(\sigma n)]$, where U is the Darcy velocity, μ_w is the viscosity of water, σ is the interfacial tension between the NAPL and water, and n is the porosity of the porous media. When Ca is less than 10^{-6} , the upper limit in most aquifers, experiments have shown that residual saturation is independent of Ca [*Morrow and Chatzis*, 1982]. However, models have indicated that viscous forces may affect blob configuration at capillary numbers as low as 10^{-7} [*Dias and Payatakes*, 1986]. This suggests that the residual saturation and ganglia configuration may change in response to a change in flow velocity that may occur during aquifer remediation.

The residual saturation does not describe the shape and size distribution of NAPL blobs, which is important in mass transfer. The description of NAPL displacement mechanisms at the pore level provides more insight into NAPL distribution. Snap-off produces organic liquid blobs that occupy one- or two-pore bodies, called singlets and doublets, respectively [*Chatzis et al.*, 1983], and occurs when the ratio of the pore body to pore throat diameter of the media, or aspect ratio, is above a critical value [*Li and Wardlaw*, 1986]. More complex, branched ganglia

result when the wetting phase bypasses the nonwetting phase [Chatzis *et al.*, 1983]. The shape of residual NAPL ganglia following displacement by water has been observed by polymerizing residual styrene blobs [Morrow and Chatzis, 1982; Chatzis *et al.*, 1983; Conrad *et al.*, 1992]. In a glass bead pack following a water flood at a capillary number of 10^{-6} , Morrow and Chatzis [1982] reported that approximately 60% of the residual NAPL blobs occupied single-pore bodies, but most of the residual NAPL volume was contained in blobs that extended over more than nine pore bodies. Conrad *et al.* [1992] found a qualitatively similar size distribution for residual NAPL in sand columns.

Mass Transfer Coefficient

The aqueous phase concentration for the one-dimensional flow of water through a region of residual NAPL can be described by the following equation:

$$n \frac{\partial (S_w C)}{\partial t} = -U \frac{\partial C}{\partial x} + k_l a (C^* - C) + D_x \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where C is the aqueous phase concentration of organic and S_w is the residual saturation of water. The term $k_l a (C^* - C)$ represents the rate of mass transfer of organic from the NAPL to the aqueous phase, where k_l is the mass transfer coefficient and a is the specific interfacial area, which is the NAPL-water interfacial area per unit volume. The aqueous phase concentration at the NAPL-water interface, C^* , is assumed to be in equilibrium with the nonaqueous phase [Levich, 1962; Turitto, 1963]. For a pure organic liquid, the aqueous concentration at the NAPL-water interface equals the liquid's aqueous solubility, C^s . The longitudinal dispersion coefficient D_x appears in the last term on the right-hand side of (1). If an experimentally measured mass transfer coefficient is used, this term may not be necessary as discussed later.

The evaluation of the mass transfer coefficient and the interfacial area is problematic because of the complex interfacial geometry. Mass transfer coefficients are frequently described by nondimensional expressions derived from experimental data. The nondimensional form of the mass transfer coefficient is the Sherwood number ($k_l L/D$), where D is the molecular diffusivity of the contaminant in water and L is a length scale of the system. The Sherwood number is expressed as a function of the Reynolds number [$UL\rho_w/\mu_w$] or the quotient of the Peclet number [UL/D] and the Schmidt number $E\mu_w/(\rho_w D)$. In porous media the length scale is equal to the media grain diameter d_g .

Miller *et al.* [1990] and Powers *et al.* [1991] reviewed theoretical and experimentally derived expressions for mass transfer coefficients, mostly from the chemical engineering literature for dissolving spheres and cylinders either in packed beds or suspended in fluids. One correlation, by Wilson and Geankoplis [1966], was derived from the dissolution of solid benzoic acid spheres:

$$Sh = 1.09 n^{-1} Pe^{1/3} \quad (2)$$

This correlation was measured using the steady state, one-dimensional plug flow equation, which is equivalent to (1) without the dispersion term. The effect of local dispersion is embedded within the mass transfer coefficient. Other mass transfer correlations for dissolving spheres indicate a similar dependence of the Sherwood number on the Peclet number [Friedlander, 1957; Bowman *et al.*, 1961]. In a summary of 17 correlations for particle-liquid mass transfer in packed columns and fluidized beds [Dwivedi and Upadhyay, 1977], (2) was the only correlation derived from data measured at Reynolds numbers over the range of 0.002–0.1 for spherical particles. The application of these relationships to mass transfer from

nonspherical residual NAPL blobs has not been verified experimentally. In addition, the experiments by *Wilson and Geankoplis* [1966] were not conducted over a long enough time to observe the effect of shrinking spheres on mass transfer.

Hunt et al. [1988] applied the mass transfer coefficient from (2) to predict the dissolution of residual NAPLs. The results illustrated the sensitivity of aqueous concentrations to Darcy velocity and the NAPL spheroid diameter. *Powers et al.* [1991] conducted an extensive sensitivity analysis regarding the influence of NAPL blob shape on dissolution. Spherical and cylindrical shapes resulted in different values for the specific interfacial area and consequently affected the rate of dissolution in the same manner as the predictions by *Hunt et al.* [1988]. The results provided no justification for assuming more complex blob shapes in models. The analysis by Powers et al. also showed that dissolution is sensitive to the mass transfer coefficient correlation. Simulations using (2) and an earlier measurement by *Williamson et al.* [1963] were compared; however, they are the same correlation, with the only difference being that *Williamson et al.* [1963] used a constant porosity.

The mass transfer coefficient cannot be measured directly from the dissolution of NAPL residuals because the interfacial area is unknown. An approach taken by *Miller et al.* [1990] was to measure a mass transfer rate coefficient, which is the product of the mass transfer coefficient and the interfacial area. The use of the mass transfer rate coefficient eliminates the need for evaluating the interfacial area; however, the rate coefficient is dependent upon the interfacial area itself which was controlled by physically stirring the organic liquid into a water-saturated glass bead pack. Their approach did not represent the complete history of NAPL dissolution, but only examined effluent concentrations at various, fixed NAPL saturations. They measured mass transfer rate coefficients and correlated them with residual saturation and Reynolds number. Their emplacement mechanism did not represent subsurface processes, and their correlation cannot be used to simulate mass transfer as the trapped residual NAPL dissolves and shrinks because of the short duration of their experiments.

In light of the uncertainties of the pore scale NAPL geometry and the dearth of measurements made for systems that represent residual NAPLs at the low Reynolds numbers encountered in groundwater flow, the Wilson and Geankoplis correlation best describes the conditions of interest in this investigation.

Multicomponent NAPLs

When an organic liquid contains more than one chemical, the aqueous phase concentration of compound j in equilibrium with the organic liquid mixture C_j^e is

$$C_j^e = \gamma_{N,j} X_{N,j} C_j^s \quad (3)$$

where $\gamma_{N,j}$ is the activity coefficient of j in the NAPL, $X_{N,j}$ is the mole fraction of j in the NAPL, and C_j^s is the aqueous solubility of pure liquid j [e.g., *Prausnitz et al.*, 1986]. For an ideal organic liquid mixture comprised of structurally related hydrophobic liquids, the activity coefficient for each component equals unity [*Banerjee*, 1984]. Equation (3) indicates that when an organic liquid mixture contains components with different aqueous solubilities, C_j^e changes as the NAPL dissolves. As the more soluble components dissolve, the mole fraction of the less soluble components, and consequently their aqueous solubility, increases. The aqueous solubility of one hydrophobic organic chemical is not enhanced by the presence of another chemical as long as they have aqueous solubilities less than 0.001 mole fraction [*Banerjee*, 1984; *Burris and MacIntyre*, 1986a, b; *Munz and Roberts*, 1986].

Most predictions of multicomponent dissolution have assumed that there is equilibrium between the liquid phases and that the organic liquid composition is homogeneous over the length of the organic liquid region [van der Waarden *et al.*, 1971; Shiu *et al.*, 1988; Sitar *et al.*, 1990; Feenstra *et al.*, 1991; Mackay *et al.*, 1991; Zalidis *et al.*, 1991]. Cases where changes in NAPL volume are significant and nonequilibrium conditions arise have not been reported in the literature. Nonequilibrium conditions may arise because of diffusion within the aqueous phase as discussed above, or due to diffusional limitations within the NAPL itself. A mathematical analysis by deZabala and Radke [1986] indicated that diffusional mass transfer limitations within 10- μm -diameter oil globules had no significant effect on the effectiveness of alkaline surfactant flooding. This represents the pore body size of consolidated sandstones typical of petroleum reservoirs but is 1 to 3 orders of magnitude smaller than the size of trapped NAPL blobs that would be expected in medium grain-sized unconsolidated media, typical of fluvial aquifers.

Analytical Description of NAPL Dissolution

Mass Transfer Zone

Instead of empirically correlating experimental results with characteristic dimensionless numbers of the system, NAPL dissolution is modeled by representing the organic liquid as initially equal-sized spheres that shrink with time. If the NAPL-contaminated region is sufficiently long in the direction of water flow, aqueous concentrations will be in equilibrium with the NAPL. Figure 1 illustrates the spatial distribution of ganglia spheres undergoing dissolution at time t_1 and at a later time t_2 . At time t_1 there has been sufficient flow so that ganglion diameters at the upstream end approach zero and ganglia are at their initial size at some downstream distance where the aqueous concentration has reached solubility. The flow distance necessary to reach near equilibrium in the aqueous phase for a single-component NAPL is the length of the mass transfer zone, L_{mtz} . For a fully developed mass transfer zone and a constant water velocity, the mass transfer zone propagates at a velocity v_{mtz} given by

$$v_{mtz} = \frac{UC^s}{\rho_N n S_{N,0}} \quad (4)$$

which is the ratio of the dissolved flux leaving the mass transfer zone to the initial mass concentration of NAPL, where ρ_N is the NAPL density and $S_{N,0}$ is the initial NAPL saturation of the pore space.

In a coordinate system moving at the velocity of the mass transfer zone, $\xi = x - v_{mtz}t$, steady state profiles of sphere diameter and aqueous concentrations are expected. A differential equation for the NAPL sphere diameter d_N within the mass transfer zone is derived from a mass balance on the spheres over a differential volume for the moving coordinate system. Equating the advection of spherical NAPL drops into the control volume with the rate of dissolution gives

$$v_{mtz} \frac{d}{d\xi} \left(\rho_N N \frac{\pi}{6} d_N^3 n \right) = k_l N \pi d_N^2 (C^s - C) \quad (5)$$

where N is the number of NAPL spheres per volume of porous media. For a NAPL sphere that is larger than the media grain, the volume of NAPL contained within a sphere of diameter d_N is equal to the pore space within the NAPL sphere. Given the initial diameter of the NAPL sphere is $d_{N,0}$, N is expressed as follows:

$$N = \frac{6S_{N,0}}{\pi d_{N,0}^3} \quad (6)$$

Since the spheres do not break up as they dissolve, N is not a function of ξ .

Assuming that the aqueous organic concentration is much less than its aqueous solubility and simplifying, (5) reduces to

$$\frac{d(d_N)}{d\xi} \approx \frac{2k_l C^s}{\rho_N v_{mtz} n} \quad (7)$$

Following on the work of *Hunt et al.* [1988], the Wilson and Geankoplis mass transfer correlation in (2) in dimensional form becomes

$$k_l = \frac{1.09}{n} U^{1/3} \left(\frac{D}{d_N} \right)^{2/3} \quad (8)$$

Substituting (4) for the mass transfer zone velocity and integrating (7) with the boundary condition

$$d_N(\xi=0) = 0 \quad (9)$$

gives

$$d_N^{5/3}(\xi) \approx \frac{3.63}{n S_{N,0}} \left(\frac{D}{U} \right)^{2/3} \xi \quad (10)$$

Equation (10) provides an estimate for the length of the mass transfer zone, L_{mtz} , because at $\xi = L_{mtz}$, the sphere diameter is $d_{N,0}$, or

$$L_{mtz} \approx \frac{0.275n}{S_{N,0}} \left(\frac{U}{D} \right)^{2/3} d_{N,0}^{5/3} \quad (11)$$

Equation (11) underestimates the length of the mass transfer zone because the analysis assumes that the aqueous concentration is much less than solubility. In addition, the porosity in (8) is not corrected for the presence of the immobile NAPL. Because reported values of residual saturation are less than 0.3 [*Chatzis et al.*, 1983; *Wilson et al.*, 1990], the effect of the reduced porosity on the mass transfer coefficient is neglected. The length of the mass transfer zone indicates when the equilibrium partitioning assumption is valid within the NAPL region and illustrates how a change in flow velocity may render that assumption invalid. L_{mtz} is inversely proportional to $S_{N,0}$ and increases with $d_{N,0}$ as a result of their effect on the specific interfacial area. Evaluating (11) for a Darcy velocity of 1 m d⁻¹, a molecular diffusivity of 10⁻⁹ m² s⁻¹ and an initial residual saturation of 0.2 and substituting values for initial drop diameters of 0.1, 1, and 10 cm, the length of the mass transfer zone is approximately 0.003, 0.1, and 6 m, respectively. At a Darcy velocity of 10 m d⁻¹ these values increase by a factor of 4.6.

The modeling approach adopted here is sufficiently different from that of Powers *et al.* [1991] and Miller *et al.* [1990] to preclude quantitative comparison. In both works the NAPL saturation is constant in the direction of flow. This results in a higher specific interfacial area than for the fully developed mass transfer zone shown in Figure 1. Two additional differences in the simulation of Powers *et al.* [1991] would produce a longer mass transfer zone than predicted by (11). First, the interfacial area was multiplied by a factor to estimate the surface area actually available for mass transfer. Second, a dispersion term was incorporated in the simulation despite the fact that Wilson and Geankoplis mass transfer correlation used was for the one-dimensional plug-flow equation.

Dissolution of a NAPL-Contaminated Region Embedded in Clean Media

The geometry of the experimental system, described in detail later, can be idealized as a cylindrical residual NAPL region embedded coaxially within a cylinder of clean media as illustrated in Figure 2. Initially, before any NAPL dissolution, the water flow is distributed with some water passing through the NAPL region at a reduced flow velocity and the remainder flowing through the annular region. As flow in the NAPL region continues, some NAPL dissolves at the upstream region and local NAPL saturation decreases. The decrease in the local NAPL saturation causes more water to flow through that region, but since little NAPL has dissolved downstream, the water flow is partially redistributed into the annular region, carrying dissolved organic with it. An increasing amount of flow enters the NAPL region until a quasi-steady mass transfer zone develops and propagates downstream at the velocity given in (4). Effluent concentrations decline when the length of residual NAPL is less than the length of the mass transfer zone.

The flow velocity through the NAPL region, U_N and the flow velocity through the annular region surrounding the NAPL cylinder, U_a are described by Darcy's law:

$$U_N = \frac{k k_{rw} \rho_w g}{\mu_w} i \quad (12)$$

$$U_a = \frac{k \rho_w g}{\mu_w} i \quad (13)$$

where k is the media permeability, k_{rw} is the relative permeability of water through the NAPL region, and i is the negative hydraulic gradient. The relative permeability to water is estimated from a correlation by Wyllie [1962]:

$$k_{rw} = \left(\frac{S_w - S_{w,irr}}{1 - S_{w,irr}} \right)^3 \quad (14)$$

where $S_{w,irr}$ is the irreducible water saturation. This correlation has been shown to describe measured relative permeabilities in several similar systems. Measurements by Morrow and Songkran [1981] and Morrow *et al.* [1985] of the relative permeability of water in glass bead packs having discontinuous, nonwetting phase residual saturations equal to and less than 0.15 fit the Wyllie correlation [Geller, 1990]. Demond [1988] measured the relative permeability of water in a sand pack as a function of xylene saturation, compared the data to three different correlations and found that (14) best described the data. The relative permeability is assumed to be independent of flow velocity based on experimental results by Larson *et al.* [1981] for

capillary numbers less than 10^{-6} . The water saturation is a function of the NAPL sphere diameter and the number concentration of NAPL drops as follows:

$$S_w = 1 - S_N = 1 - \frac{N\pi}{6} d_N^3 \quad (15)$$

For the simplification of one-dimensional flow the hydraulic gradient across the NAPL region is approximately equal to the hydraulic gradient across the annular region and can be derived from a flow balance as follows:

$$UA = \frac{k\rho_w g i}{\mu_w} (A_a + k_{rw} A_N) \quad (16)$$

where U is the Darcy velocity upstream of the NAPL region and A , A_N , and A_a are the total cross-sectional areas of the column, the NAPL-contaminated region, and annular region, respectively. During dissolution, the shrinkage of A_N is neglected because dissolution from the NAPL region's outer surface is much less than the amount dissolved by flow through the NAPL region. Solving for i gives

$$i = \frac{UA\mu_w}{k\rho_w g (A_a + A_N k_{rw})} \quad (17)$$

Substituting (17) into (12) gives

$$U_N = \frac{k_{rw} UA}{A_a + A_N k_{rw}} \quad (18)$$

The aqueous organic concentration within the NAPL region, C_N , is described by the following equation:

$$n \frac{\partial (S_w C_N)}{\partial t} = \frac{\partial (C_N U_N)}{\partial x} + C_N \frac{\partial U_N}{\partial x} + k_l a (C^s - C_N) \quad (19)$$

where k_l is described by (8). The term $C_N \partial U_N / \partial x$ represents the advection of dissolved organic out of the NAPL region and into the annular region. Further simplification results in

$$n \frac{\partial (S_w C_N)}{\partial t} = -U_N \frac{\partial C_N}{\partial x} + k_l a (C^s - C_N) \quad (20)$$

The aqueous organic concentration within the annular region, C_a is described as follows:

$$n \frac{\partial C_a}{\partial t} = -\frac{\partial (C_a U_a)}{\partial x} - \frac{A_N}{A_a} C_N \frac{\partial U_N}{\partial x} \quad (21)$$

where the second term on the right-hand side represents the advection of dissolved organic into the annular region from the NAPL region. The change in each NAPL sphere mass is equal to

the flux at the NAPL-water interface, multiplied by the interfacial area, which becomes upon simplification

$$\frac{\partial d_N}{\partial t} = -2 \frac{k_l}{n\rho_N} (C^s - C_N) \quad (22)$$

For a fixed fluid flow rate, (18) and (20) through (22) couple flow redistribution with NAPL dissolution from a cylindrical region surrounded by a clean annular region and will be applied to the simulation of the experimental results. The equations are solved numerically by forward difference using an element length equal to $d_{N,0}$. The initial conditions are

$$d_N(x, t=0) = d_{N,0} \quad (23)$$

$$C_N(x, t=0) = C_a(x, t=0) = 0 \quad (24)$$

with the following boundary conditions

$$C_N(x=0, t) = C_a(x=0, t) = 0 \quad (25)$$

Assuming steady state dissolution during each time step, the equations are solved explicitly for concentration. At the end of the time step, the change in NAPL sphere diameter in each element is computed from (22) and the resulting values are used to compute aqueous concentrations in the next time step.

The effluent concentration C is computed from a mass balance at the end of the NAPL region:

$$C = \frac{C_a U_a A_a + C_N U_N A_N}{U A} \quad (26)$$

Two-component dissolution—To model the dissolution of a multicomponent NAPL, (19) through (22) are written for each component j :

$$n \frac{\partial (S_w C_{N,j})}{\partial t} = -U_N \frac{\partial C_{N,j}}{\partial x} + k_{l,j} a (X_{N,j} C_j^s - C_{N,j}) \quad (27)$$

$$n \frac{\partial C_{a,j}}{\partial t} = -\frac{\partial (C_{a,j} U_a)}{\partial x} - \frac{A_N}{A_a} C_{N,j} \frac{\partial U_N}{\partial x} \quad (28)$$

$$\frac{\partial (d_N)}{\partial t} = -2 \frac{k_l}{n} \sum_j \frac{(X_{N,j} C_j^s - C_{N,j})}{\rho_{N,j}} \quad (29)$$

The mole fraction of each component in the NAPL is updated by mass balance at the end of each time step. The effluent concentration is

$$C_j = \frac{C_{a,j}U_aA_a + C_{N,j}U_NA_N}{UA} \quad (30)$$

Experimental Procedures

Methods

The dissolution of an immobile NAPL in water-saturated porous media was measured for a pure contaminant, toluene, and an initially equal-mole mixture of toluene and benzene. The aqueous solubilities of toluene and benzene at 25°C are 515 and 1780 mg L⁻¹, respectively [McAuliffe, 1966]. These chemicals were selected because they represent the most soluble components of gasoline, their chemical structure is similar so that their mixture is ideal, and their solubilities differ enough so that the effect of changing NAPL composition with dissolution of the mixture would be observed. Because of the low aqueous solubilities of benzene and toluene, their dissolution does not alter the viscosity or density of water. Homogeneous glass beads were chosen for the porous media in order to achieve the simplest, most replicable distribution of the organic liquid. At the beginning of each experiment the NAPL was slowly injected into the center of the water-saturated column, and then water was pumped through at a constant velocity. The intent of this emplacement method was to represent two important features of subsurface contamination: the slow flow velocity of a subsurface leak, and a NAPL-contaminated region surrounded by uncontaminated material.

The experimental apparatus was constructed of materials inert to ultrapure water and the organic liquids used: 316 stainless steel, Teflon, glass, and viton. The Pyrex column was 5 cm ID × 15 cm long. A stainless steel screen supported the porous media. The Teflon endplates had a shallow cone to ensure even distribution of flow over the column cross section. The column was packed with 40–45 mesh soda-lime silica glass beads (0.35–0.42 mm diameter). The beads were specified to be 90% true spheres and to contain no more than 2% irregularly shaped particles. The beads were acid-washed according to a method described by Tobiasson [1987]. The column was packed with the NAPL injection needle in place which extended to the center of the column. The needle remained in the column throughout the experiment. The porosity was calculated knowing the mass of beads added to the column, the specific density of the beads and the internal volume of the column. In order to eliminate air, the packed column was initially flooded with CO₂ before pumping water upward through the column. All process water was deionized, filtered and deaerated before use. Further details regarding the experimental apparatus are given by Geller [1990].

A syringe pump injected the desired volume of organic liquid into the center of the column at a constant rate of 0.1 mL min⁻¹ while no water flowed. The toluene was spectographic grade (Aldrich Chemical Co., Milwaukee, Wis.) and the benzene was analytical reagent grade (Malinkrodt Inc., Paris, Ky.); the chemicals were used as purchased. To verify that the NAPL did not reach the column wall or endplates, its emplacement was observed by injecting dyed toluene into a 2.54 cm ID column made of two sections that opened at the injection point. The column was prepared according to the procedures described above. After injection the column was opened into the two sections and excavated. The NAPL was found to occupy a continuous region around the injection point that was approximately cylindrical and surrounded by uncontaminated media [Geller, 1990].

Following the NAPL injection, water was pumped through the column at a constant rate. The water flow probably caused a redistribution of the NAPL to a lower residual saturation, but the

length of continuous NAPL was insufficient to actually induce the flow of the NAPL given the capillary numbers of the experiments. Column effluent was sampled in 1 or 5 mL glass luer-lok syringes attached to a syringe valve at the sample port and filled by the force of the flow. The sample was transferred to an autosampler vial and sealed with a crimper. To minimize volatilization of sample into the headspace of the autosampler vial, samples were stored at 4°C and analyzed within several hours of collection by direct aqueous injection into a gas chromatograph (model 5880A, Hewlett Packard Co., Avondale, Pa.).

Continuous measurements were made of flow rate, temperature and pressure drop. The pressure drop across the apparatus was corrected to 20°C and for headloss due to the endplates. Experiments were run until the NAPL was completely dissolved in order to observe the effect of the decrease in volume of the trapped phase on effluent concentrations. Flow velocity and the amount of NAPL emplaced into the column were varied.

Mass Recoveries

The mass recoveries for the toluene dissolution experiments are listed in Table 1. These recoveries were calculated by integrating the effluent concentration over the course of the experiments. Several factors may have contributed to the low mass recovery. In runs 1 through 6, the precise amount of organic liquid injected was uncertain due to the large 100-mL syringe pump used. In runs 7 through 9 the use of the 5-mL syringe pump enabled a more accurate determination of the injected volume by weighing the syringe before and after injection.

The low mass recovery may have resulted from the displacement of organic liquid droplets from the column during the initial reconfiguration of the NAPL with the onset of flowing water. This reconfiguration is indicated by the relatively high pressure gradients measured over the first several pore volumes that subsequently declined. The pressure data are shown in Figure 6 and discussed in more detail in the following section. If the organic liquid droplets appeared intermittently in the effluent, the measured sample concentrations would not recover all of the organic liquid. In runs 7 and 8, 2–5 mL samples were divided into 1-mL fractions and analyzed. In run 7 the variability in aqueous concentration among the fractions of a given sample was of the order of 20% of the mean compared to better than the 5% precision of the analytical methods [Geller, 1990]. Fractions with higher concentrations presumably contained organic liquid droplets that dissolved by the time of analysis. In subsequent runs the flow was directed downward in order to keep droplets from escaping. In addition, a 0.01 M CaCl₂ solution was used for the process water to compress the electric double layer on the glass beads in hopes that this would promote sticking of the mobilized drops to the beads. This concentration of electrolyte does not alter significantly the aqueous solubility of toluene and benzene and these measures did produce a decrease in sample variability in run 8.

The addition of a biocide in run 4 did not improve the mass recovery, therefore it is unlikely that part of the toluene was degraded biologically. The extraction of the media into pentane at the end of runs 6 through 9 indicated that less than 1% of the initially injected mass of toluene was left in the column once effluent concentrations reached the limits of the analytical methods (details of the extraction procedure are given by Geller [1990]).

Results and Model Predictions

Single Component

This section presents the results and analysis of the toluene dissolution experiments. Two-component dissolution is discussed in the following section.

Effluent concentrations—In Figures 3 through 6, the experimentally measured effluent concentrations are compared with predictions according to (20) through (26). The initial drop diameter $d_{N,0}$ and the cross-sectional area of the NAPL region, A_N , were determined from the best fit with the experimental data. The volume of NAPL recovered, listed in Table 1, was used for the initial volume of NAPL in the column $V_{N,0}$. The input value for the initial organic liquid saturation $S_{N,0}$ was set near 0.15 to represent residual NAPL saturations achieved in glass bead columns at similar capillary numbers [Morrow and Chatzis, 1982]. Measurements by Morrow and Chatzis [1982] showed that there was less than a 10% variability in $S_{N,0}$ over the range of capillary numbers of 10^{-6} to 10^{-5} . Table 1 indicates slight variations in $S_{N,0}$ because the initial volume of NAPL was distributed into discrete element lengths. A value of 0.1 for the irreducible wetting saturation was selected based upon experimental measurements in glass bead packs by Morrow [1970]. A value of $1.02 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was used for the molecular diffusion coefficient based on a reported value for benzene in water [Thibodeaux, 1979].

Figure 3 shows the data and prediction for the dissolution of 1.5-mL toluene with a Darcy velocity of 0.5 m d^{-1} . During the first 10 pore volumes, measured effluent concentrations were noisy as a result of the reconfiguration of the organic liquid with the onset of the water flow and possibly the production of NAPL droplets in the effluent. The effluent concentration then slowly increased up to about 50 pore volumes where nearly steady, but variable concentrations were measured out to 70 pore volumes. After that, effluent concentrations declined. The simulation depicts these three regions of (1) increasing effluent concentration as the mass transfer zone develops, (2) a steady region as the mass transfer zone propagates through the NAPL region, and (3) a declining concentration caused by the length of the NAPL region being less than the length of the mass transfer zone.

Figure 4 illustrates the sensitivity of predicted effluent concentrations to the input parameters $d_{N,0}$, A_N , and $S_{N,0}$. These simulations used the input values for run 2 listed in Table 1 except for the noted variation of the designated parameter. In Figure 4a, increasing the initial NAPL sphere diameter from 0.4 to 0.5 cm results in a smaller specific NAPL surface area. The initial effluent concentrations are lower and complete recovery requires a greater volume of water. An increase in the NAPL cross-sectional area, as shown in Figure 4b, uniformly accelerates dissolution because more flow is forced through the NAPL contaminated region. The major effect of a change in $S_{N,0}$ is on the relative permeability of the NAPL region, shown in Figure 4c. A smaller value of $S_{N,0}$ produces a more permeable NAPL region which allows a greater portion of the water to flow through it, higher effluent concentrations and consequently a shorter NAPL lifetime. The data could be described by different combinations of values for $S_{N,0}$ and A_N ; however, the fit of $d_{N,0}$ is unique.

In Figures 5 and 6 the experimental measurements and predictions for Darcy velocities of 5 and 10 m d^{-1} are shown for different injected NAPL volumes. Runs 7 and 8 were conducted for the same injected NAPL volumes and the plotted data points are the average of two to five fractions analyzed for a given sample. The similarity of the data for runs 7 and 8 indicates that the NAPL emplacement procedure was reproducible and that the change in flow direction and water composition described in the methods section did not affect mass transfer. The concentrations over the first 50 to 70 pore volumes are greater for the larger volumes of injected toluene, due to the greater cross-sectional area occupied by the organic liquid which allowed a greater portion of the total flow through the column to contact the NAPL. A steady concentration region was not established as in the 0.5 m d^{-1} run due to the longer mass transfer zone at the higher flow velocities. The model does not exactly reproduce the tailing of the data. This may be a result of the equal initial diameter assumed for all drops; larger drops will persist for longer times. The results for the 10 m d^{-1} velocities in Figure 6 show similar trends of an initial increase in effluent concentrations followed by declines.

Table 1 also summarizes the parameters used in the simulations. All experiments at a given velocity used the same initial drop diameter and only the cross sectional area was varied to account for variations in injected volume. The size of the initial NAPL drop diameter is largest at the 0.5 m d^{-1} Darcy velocity and decreases at the higher velocities. The inverse correlation between the drop diameter and flow velocity may be an indication that smaller sized blobs are formed at increased capillary numbers. The initial drop diameter size ranges from 3.5 to 10 times the grain diameter of the media and this is consistent with experimental observations [Morrow and Chatzis, 1982; Conrad *et al.*, 1992]. Conrad *et al.* [1992] hypothesized that only a fraction of the surface area of a branched blob may be exposed to flowing groundwater. The success of the simulation suggests that the spherical blob shape adequately represents the interfacial area that is available for mass transfer. In addition, the larger blobs which contain most of the NAPL volume control dissolution while the single-pore body-sized blobs dissolve quickly because of their high specific interfacial area.

Differential pressure—The differential pressure measurements and predictions from the integration of (17) are plotted in Figure 7 for experiments conducted at 10 m d^{-1} . The pressure data are consistent with the trends observed in the concentration data. The higher differential pressures measured over the first ten to twenty pore volumes were not predicted because the model did not account for ganglia reconfiguration. Subsequent to that period, the decrease in differential pressure as the NAPL dissolves is predicted by Wyllie's [1962] correlation. When no NAPL remains, differential pressures equal a constant baseline value for the clean column. The baseline values differ for each run due to the imprecision of the transducer calibration and do not reflect a significant difference in media permeability. Pressure data for the 5 and 0.5 m d^{-1} flow rates were not meaningful due to the greater relative fluctuation in measurements as pressures approached the sensitivity limits of the transducer diaphragm.

Dissolution within mass transfer zone—The parameters that provide the best fit to the data can now be used to estimate the length of the mass transfer zone using (11). The Darcy velocity used in this equation is the velocity leaving the NAPL region, or $U_{N,0}$. Table 1 shows that for run 2 the length of the mass transfer zone is less than the initial length of the NAPL region, $L_{N,0}$, which was calculated by

$$L_{N,0} = \frac{V_{N,0}}{nA_N S_{N,0}} \quad (31)$$

At higher flow velocities the mass transfer zone is longer than $L_{N,0}$. Qualitatively, the experiments by Miller *et al.* [1990] found mass transfer zones of the order of a centimeter, their column length. This is shorter than found in this work, which is reasonable given their more energetic emplacement mechanism.

The predictions of the aqueous toluene concentrations and NAPL sphere diameter along the length of the NAPL region for the 0.5 m d^{-1} run are shown in Figures 8a and 8b after different pore volumes of water have passed through the column. In the numerical simulation, computed concentrations and sphere diameters are constant over each element of length $d_{N,0}$, and these values are plotted at the end of a given element. Aqueous concentrations in the first element are set equal to zero. The same shape and equal distance between the simulated profiles at 40, 60, and 80 pore volumes indicate the development of a steady mass transfer zone. The front velocity as estimated from the distance between these profiles is equal to $4.6 \times 10^{-3} \text{ m d}^{-1}$. This is slightly larger than the value of $3.6 \times 10^{-3} \text{ m d}^{-1}$ calculated from (4), using the Darcy velocity, $U_{N,0}$, listed in Table 1, because (4) does not account for the flux of dissolved organic from the mass transfer zone into the annular region. Aqueous concentrations at the downstream end of the NAPL region are nearly equal to the aqueous solubility up to approximately 60 pore

volumes of flow, at which time the mass transfer zone breaks through the end of the NAPL region and concentrations decrease.

Once the mass transfer zone is developed, its length can be estimated from the distance over which the NAPL drop diameter increases from zero to its initial value. The NAPL drop diameter profiles at different pore volumes are shown in Figure 8b. The profile at 40 pore volumes indicates a mass transfer zone length of approximately 3 cm, which is close to the value predicted by (11).

Two-Component NAPL

The mass transfer model is applied to the dissolution of the two-component NAPL. The model prediction is first compared with the experimental data and then is used to describe dissolution within the mass transfer zone.

Effluent concentrations—The effluent concentrations from the dissolution of a benzene and toluene mixture at a Darcy velocity of 5 m d^{-1} are plotted in Figure 9. The data points represent the average of five fractions for a given sample. The mass concentration of benzene shown in Figure 9 was initially higher than toluene's because of its higher aqueous solubility. Consequently, the mole fraction of benzene in the organic liquid phase decreased relative to the mole fraction of toluene. The effluent concentration of toluene increased as the concentration of benzene decreased; once all the benzene dissolved, toluene concentrations decreased due to the reduction in interfacial area.

The dissolution of the benzene-toluene mixture is modeled by assuming that the NAPL is homogeneous within each element. The values of 0.20 cm and 3.5 cm^2 for $d_{N,0}$ and A_N , respectively, best reproduced the data. The initial NAPL sphere diameter has the same value used in the single component 5 m d^{-1} runs. The predicted benzene concentrations are initially slightly higher than the measured data, which may be an indication that diffusion within the NAPL sphere limited the mass transfer of benzene to a small degree. However, the general agreement between the prediction and data indicates that concentration gradients within the NAPL sphere may be neglected in this application.

Dissolution within mass transfer zone—Predictions for the NAPL composition and the NAPL sphere diameter along the NAPL region are shown in Figures 10a and 10b. The mole fractions of benzene and toluene at various pore volumes illustrate the selective depletion of the more water soluble benzene from the upstream end and the corresponding increase in the mole fraction of toluene. The changing NAPL composition with distance shows that the estimation of NAPL composition from aqueous phase concentrations is not straightforward, particularly if the NAPL region is sufficiently long. The length of the NAPL region in this experiment is not long enough to achieve chemical equilibrium between the liquid phases. By the time the upstream drop diameter is almost zero at 40 pore volumes, the downstream drop diameter is less than the initial value of 0.20 cm .

For a two-component NAPL of sufficient length, two mass transfer zones would develop. At the upstream end the NAPL is depleted of benzene, there is a large driving force for toluene dissolution, but the NAPL drops are small. Further downstream, the NAPL drops are larger and the benzene mole fraction is greater, causing more rapid benzene dissolution into the water and toluene partitioning back into the NAPL. The evolution of benzene and toluene concentrations within the mass transfer zones can be viewed as a chromatographic process, where the mass transfer zone velocity of each component through the region is a function of its local solubility.

Summary and Conclusions

Laboratory experiments have measured the complete dissolution of trapped NAPLs, and the data are successfully fit to a quantitative model. The NAPL saturation is modeled as discrete spheres that are initially uniform in size. From the experimental data, ganglia size and the cross-sectional area of the NAPL region are obtained by fitting the model to the data and assuming a fixed initial NAPL saturation. This two-parameter model, when combined with known magnitudes of residual saturation and relative permeability functions represented experimental observations of (1) increasing aqueous concentration during initial water flooding as the mass transfer zone is established, (2) a quasi-steady effluent concentration as the mass transfer zone propagates downstream, and (3) the decline in effluent concentration as the NAPL-containing region shrinks to less than the length of the mass transfer zone. The model was applied to a two-component NAPL without changing the initial NAPL sphere diameter determined from single component dissolution experiments. Further advances in NAPL dissolution kinetics will require improved theories supported by experimental data for NAPL ganglia size distributions, ganglia reconfiguration by flow, ganglia mobilization as droplets, and three-dimensional imaging of ganglia during dissolution.

The experimental data and modeling effort illustrate mechanisms that limit the remediation of NAPL-contaminated aquifers. There is a complex dependency of groundwater contaminant concentration on flow velocity. High flow rates will likely reconfigure ganglia into smaller sizes with higher interfacial areas, but the length of the mass transfer zone increases at higher velocities. Furthermore, multicomponent NAPLs undergo chromatographic separation with multiple mass transfer zones that will complicate the estimation of NAPL composition from the analysis of pumped groundwater.

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NOTATION

A	column cross-sectional area, L^2
A_a	cross-sectional area of annular region, L^2
A_N	cross-sectional area of NAPL region, L^2
a	specific interfacial area, $L^2 L^{-3}$
C	aqueous concentration, $M L^{-3}$
C_j	aqueous concentration of j , $M L^{-3}$
$C_{a,j}$	aqueous concentration of j within annular region, $M L^{-3}$
$C_{N,j}$	aqueous concentration of j within NAPL region, $M L^{-3}$
C^*	aqueous concentration at NAPL-water interface, $M L^{-3}$
C^s	aqueous solubility of single-component organic liquid, $M L^{-3}$
Ca	capillary number [$U\mu_w/(\sigma n)$]
D	molecular diffusion coefficient, $L^2 t^{-1}$
D_x	longitudinal dispersion coefficient, $L^2 t^{-1}$
d_g	grain diameter, L

d_N	NAPL drop diameter, L
g	acceleration of gravity, $L t^{-2}$
i	negative hydraulic gradient
k	permeability, L^2
k_l	mass transfer coefficient, $L t^{-1}$
L	length scale, L
L_N	length of NAPL region, L
L_{mtz}	length of mass transfer zone, L
M	mass, M
n	porosity
N	number of organic liquid drops per unit volume of porous media, L^{-3}
Pe	Peclet number $[UL/D]$
Re	Reynolds number $[UL\rho_w/\mu_w]$
S	saturation as fraction of pore space
Sc	Schmidt number $[\mu_w/(\rho_w D)]$
Sh	Sherwood number $[k_l L/D]$
t	time, t
U	Darcy velocity, $L t^{-1}$
U_a	Darcy velocity through annular region, $L t^{-1}$
U_N	Darcy velocity through NAPL region, $L t^{-1}$
V	volume, L^3
V_{mtz}	velocity of mass transfer zone, $L t^{-1}$
X	mole fraction
x	direction of flow, L
γ	activity coefficient
μ	dynamic viscosity, $M^{-1} t^{-1}$
ρ	density, $M L^{-3}$
σ	interfacial tension, $M L^{-1} t^{-2}$
ξ	moving coordinate system variable, L

Subscripts

g	grain
j	solute
a,j	solute j in aqueous phase
N,j	solute j in NAPL
mtz	mass transfer zone
N	NAPL or within NAPL region

N_0	NAPL, initial value
N_{inj}	NAPL, injected
r_w	relative, wetting phase (water)
w	wetting phase (water)
w_{irr}	wetting phase, irreducible

Superscripts

e	equilibrium
s	solubility of single component
*	interface

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Fig. 1. The propagation of the mass transfer zone (L_{mtz}) through residual NAPL at time t_1 and at a later time t_2 . The circles represent the residual NAPL, the arrows indicate the flow of water.

Fig. 2.

Axial cross section of NAPL-contaminated region embedded in clean media. The length of the arrow qualitatively indicates the relative magnitude of the flow velocity.

Fig. 3.
Measured (circles) and predicted (line) toluene effluent concentrations at $U = 0.5 \text{ m d}^{-1}$ (run 2).

Fig. 4.

(Opposite) Sensitivity of predicted effluent concentrations to input parameters (run 2). Symbols are measured data, lines are predictions. All parameters are as in Figure 3 except as noted in legend. (a) Initial NAPL sphere diameter. (b) Cross-sectional area of NAPL region. (c) Initial residual saturation.

Fig. 5.
Measured (symbols) and predicted (lines) toluene effluent concentration at $U = 5 \text{ m d}^{-1}$ runs 3, 7, and 8).

Fig. 6.
Measured (symbols) and predicted (lines) toluene effluent concentration at $U = 10 \text{ m d}^{-1}$ (runs 1, 4, and 6).

Fig. 7.
Measured (symbols) and predicted (lines) differential pressure across column (20°C) at $U = 10 \text{ m d}^{-1}$ (runs 1, 4, and 6).

Fig. 8. Simulation of toluene dissolution within the NAPL region at $U = 0.5 \text{ m d}^{-1}$, (a) Dissolved toluene concentration. (b) NAPL drop diameter.

Fig. 9. Measured (symbols) and predicted (line) column effluent concentrations for the dissolution of the benzene/toluene mixture at $U = 5 \text{ m d}^{-1}$.

Fig. 10. Simulation of initially equimolar benzene/toluene mixture dissolution within the NAPL region, $U = 5 \text{ m d}^{-1}$. PV: pore volumes. (a) NAPL mole fraction. (b) NAPL drop diameter.

TABLE 1

Experimental Summary, Mass Recovery, and Model Parameters

U , md^{-1}	Ca , $\times 10^6$	Run ^b	n	$V_{N,\text{inj}}^c$, mL	NAPL Recovered			Model Parameters			Calculated Quantities ^d			
					mL	$\%$	d	$d_{N,0}$, cm	A_N , cm^2	$S_{N,0}$, md^{-1}	$U_{N,0}$ (12), md^{-1}	$L_{N,0}$ (31), cm	L_{mz} (11), cm	
0.5	0.16	2	0.374	1.5	1.30	87	0.40	5.0	0.145	0.33	4.80	3.2		
5	1.6	3	0.374	1.5	1.44	96	0.20	4.5	0.148	3.22	5.80	7.2		
5	1.6	7	0.367	3.06	2.32	76	0.20	10.0	0.148	3.67	4.20	7.8		
5	1.6	8	0.371	3.18	2.27	71	0.20	10.0	0.148	3.67	4.20	7.8		
5	1.6	9	0.378	0.76(T)	0.83	109	0.20	3.5	0.149	3.13	7.81	<i>na</i> ^e		
				0.63(B)	0.71	113								
10	3.2	1	0.377	1.5	1.17	78	0.15	5.0	0.148	6.5	4.20	8.7		
10	3.2	4	0.378	3.0	2.08	69	0.15	7.0	0.150	6.78	5.25	8.8		
10	3.2	6	0.375	6.0	2.61	44	0.15	11.0	0.151	7.48	4.20	9.3		

^aParentheses indicate equation numbers in text.^bThere is no run 5.^cNAPL in runs 1 through 8 was toluene. NAPL in run 9: (T) is toluene and (B) is benzene^dPercent of NAPL injected, $V_{N,\text{inj}}$.^eNot applicable.