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Nonaqueous Phase Liquid Dissolution in Porous Media: Current State of Knowledge and Research Needs

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Abstract. Our understanding of nonaqueous phase liquid (NAPL) dissolution in the subsurface environment has been increasing rapidly over the past decade. This knowledge has provided the basis for recent developments in the area of NAPL recovery, including cosolvent and surfactant flushing. Despite these advances toward feasible remediation technologies, there remain a number of unresolved issues to motivate environmental researchers in this area. For example, the lack of an effective NAPL-location methodology precludes effective deployment of NAPL recovery technologies. The objectives of this paper are to critically review the state of knowledge in the area of stationary NAPL dissolution in porous media and to identify specific research needs. The review first compares NAPL dissolution-based mass transfer correlations reported for environmental systems with more fundamental results from the literature involving model systems. This comparison suggests that our current understanding of NAPL dissolution in small-scale (on the order of cm) systems is reasonably consistent with fundamental mass transfer theory. The discussion then expands to encompass several issues currently under investigation in NAPL dissolution research, including: characterizing NAPL morphology (i.e. effective size and surface area); multicomponent mixtures; scale-related issues (dispersion, flow by-passing); locating NAPL in the subsurface and enhanced NAPL recovery. Research needs and potential approaches are discussed throughout the paper. This review supports the following conclusions: (1) Our knowledge related to local dissolution and remediation issues is maturing, but should be brought to closure with respect to the link between NAPL emplacement theory (as it impacts NAPL morphology) and NAPL dissolution; (2) The role of nonideal NAPL mixtures, and intra-NAPL mass transfer processes must be clarified; (3) Valid models for quantifying and designing NAPL recovery schemes with chemical additives need to be refined with respect to chemical equilibria, mass transfer and chemical delivery issues; (4) Computational and large-scale experimental studies should begin to address parameter up-scaling issues in support of model application at the field scale; and (5) Inverse modeling efforts aimed at exploiting the previous developments should be expanded to support field-scale characterization of NAPL location and strength as a dissolving source.

Key words: NAPL, dissolution, mass transfer, morphology, multicomponent, up-scaling, inverse modeling.

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Nomenclature

d_{50}	median particle diameter [L].
D	solute diffusivity [L^2/T].
k_f	mass transfer coefficient [L/T].
K	mass transfer rate constant [1/T].
l_c	length scale [L].
n	porosity [-].
u	superficial velocity [L/T].
U_i	uniformity index [-].
x	distance into column [L].
Pe	Peclet number, ReSc [-].
Re	Reynolds number, ul_c/ν [-].
Re*	modified Reynolds number, ul_c/ν $(\theta_n(1-n))$.
Sc	Schmidt number ν/D [-].
Sh	Sherwood number, $(k_f)(l_c)/D$ [-].
Sh*	modified Sherwood number $(K)(l_c^2)/D$ [-].

Greek Letters

β_4	fitting parameter [-].
δ	normalized grain size [-].
λ	dimensionless length of active zone [-].
ν	kinematic viscosity [L^2/T].
θ_n	NAPL saturation, volume NAPL/volume pore space [-].
θ_{n_0}	initial NAPL saturation, initial NAPL volume/volume pore space [-].

1. Introduction

Environmental research over the past decade has succeeded in elucidating many issues regarding the problem of nonaqueous phase liquids (NAPL) in the subsurface environment. In many cases, field observations depict dilute contaminant plumes, while spillage estimates and failed pump-and-treat operations attest to the persistence of dissolving NAPL sources (Mackay *et al.*, 1985; Keely, 1989). Different phenomena contribute to the dilute nature of these plumes, including: (1) Mass transfer-limited dissolution at various observational scales; (2) Multicomponent NAPL, for which there is an apparent solubility reduction; (3) Solute dilution caused by advection and dispersion in heterogeneous media; and (4) Natural attenuation caused by solute transformation. These processes have been examined to varying extents, and have yielded useful information regarding NAPL dissolution. More importantly to practicing engineers, promising methods for remediating NAPL contaminated sites through injection of heat or chemical additives are at various stages of research and development.

Despite the recent research advances, a key practical observation is that NAPL in the subsurface environment cannot be effectively located using observed aqueous concentrations. In cases where the NAPL location is known, the problem of adequately modeling engineered NAPL recovery process in the presence of chemical additives is not yet fully developed. These observations underscore the need for

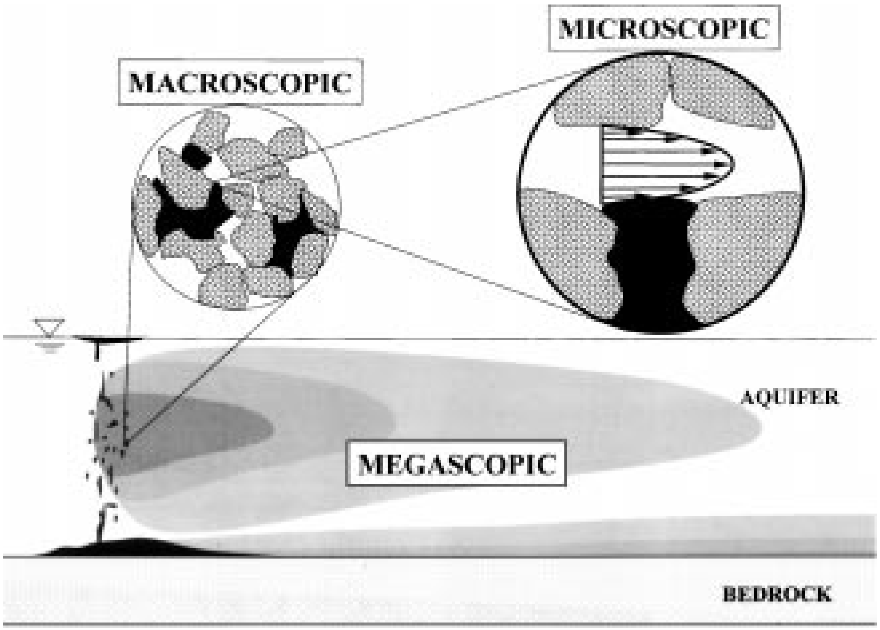

Figure 1. Schematic diagram of NAPL dissolution at several different observational scales in porous media. At the microscopic scale, the pore-scale hydrodynamics and mass transfer can be evaluated. However, detailed information regarding geometry and size is required. Most laboratory experiments mimic the macroscopic scale. Unfortunately, extrapolation from this to the megascopic scale may be problematic due to large-scale issues in contaminant transport.

continued research aimed at honing our understanding of NAPL dissolution processes. The objectives of this paper are to critically review the state of knowledge in the area of NAPL dissolution in porous media, and to identify specific research areas in support of this topic.

The problem of NAPL dissolution in natural porous media may be examined at several scales (Figure 1). To understand the underlying processes, one must study them microscopically, that is, at the scale of the pore-NAPL interface. We can resolve local mass transfer behavior at this scale, but only if the NAPL and pore geometry are known. Because this geometry is difficult to know, engineers have mainly pursued NAPL dissolution modeling using traditional soil column (or macroscopic scale) studies. The majority of the literature reviewed here is pertinent to this scale. NAPL dissolution rate behavior at the field or megascopic scale has yet to be explored in detail. Description of this larger-scale behavior will be central to the prospect of locating NAPL sources using observed aqueous concentrations.

The scope of this paper is limited to the dissolution behavior of stationary or entrapped NAPL in residual or pooled configurations. The entrapment process is governed by multiphase flow phenomena (for review, see Mercer and Cohen, 1990; Mayer and Miller, 1992, 1993; Miller *et al.*, 1998; Fenwick and Blunt, 1998), and clearly dictates the initial geometry of the dissolving NAPL. A recent review

(Miller *et al.*, 1998) provides a particularly strong discussion of NAPL dissolution from the perspective of multiphase flow concepts. The tone of the discussion here will favor research progress and directives related to the dissolution process of an existing NAPL distribution from the perspective of the contaminant plume that it has generated. We begin with a discussion of some of the fundamental mass transfer research that serves as background to recent efforts attempting to correlate NAPL dissolution rates with groundwater flow conditions. This background review serves as a point of departure for the following issues: characterizing NAPL morphology; multicomponent mixtures; scale-related issues; locating NAPL in the subsurface and enhanced NAPL recovery.

2. Correlating Dissolution Mass Transfer with Hydrodynamics

Much of the early work of relevance to NAPL dissolution can be found in studies pertaining to mass transfer in engineered packed bed systems. The earliest studies concentrated on ideal systems, that is, either perfect spheres packed in columns or theoretical investigations assuming ideal geometry. The following two sections present a brief chronology of early theoretical and experimental studies, respectively, and the insight they provide for the NAPL dissolution problem. A subsequent section discusses the analogous body of literature pertaining directly to NAPL dissolution. The reader is referred to chemical engineering texts for more thorough review of the fundamentals of mass transfer (Bird *et al.*, 1960; Geankoplis, 1972; Sherwood *et al*., 1975; Clift *et al*., 1978), and to Dwivedi and Upadhyay (1977) for a summary of early experiments associated with this topic.

2.1. MODEL SYSTEMS (THEORETICAL WORK)

Classical studies dealt with mass transfer into fluids flowing around single cylinders (Dobry and Finn, 1956) or spheres (Ranz and Marshall, 1952) at low Reynolds numbers. Expressions correlating mass transfer behavior, as summarized by the dimensionless group Sh (Sherwood number), with flow and solute diffusion behavior, as summarized by the dimensionless groups Re (Reynolds number) and Sc (Schmidt number), respectively, are listed in Table I. Friedlander (1957) examined these ideal systems theoretically by using boundary layer theory and assuming a hyperbolic concentration profile to derive an expression relating Sh to the Peclet number ($\mathrm{Pe} = \mathrm{ReSc}$). He assumed advection-dominated conditions (high Pe values), avoiding potential natural convection effects. His correlation for high Pe values underestimated experimental results by 10–40%. Levich (1962) analyzed the same problem for similarly high Pe values, making no assumptions as to the shape of the concentration profile. Levich’s Pe-based correlation is sometimes mistakenly applied at low Pe flow conditions. At low Pe values, the Sh value asymptotically approaches a value of 2 for a sphere (Clift *et al*., 1978) (more specifically, Levich discusses the asymptotic approach of the mass flux, which

Table I. Correlations obtained from the chemical engineering literature.

System	Correlation		Ref.
Theoretical work			
Single sphere	$\mathrm{Sh} = 0.89\,\mathrm{Pe}^{1/3}$	$\mathrm{Pe} \gg 1$	1
	$\mathrm{Sh} = \dfrac{4}{\mathrm{Pe}} \ln\left(\dfrac{1}{1-\frac{\mathrm{Pe}}{2}}\right)$	$\mathrm{Pe} \ll 1$	
Single sphere*	$\mathrm{Sh} = 2 + 1.24\,\mathrm{Pe}^{1/3}$	$0 < \mathrm{Pe} \ll 1000$	2
Single sphere	$\mathrm{Sh} = (4 + 1.21\,\mathrm{Pe}^{2/3})^{1/2}$	$0 < \mathrm{Pe} \ll 10000$	3
Multiparticle †	$\mathrm{Sh} \to 2.0(2\,\mathrm{Pe}/\lambda)^{1/3}$	$\mathrm{Pe} \to \infty$, creeping flow	4
Multiparticle ‡	$\mathrm{Sh} = 1.26\left[\dfrac{1-(1-n)^{5/3}}{W}\right]^{1/3} \mathrm{Pe}^{1/3}$	$1 \ll \mathrm{Pe} < 1000$	5
Experimental work			
Benzoic acid-water	$\mathrm{Sh} = \dfrac{1.09}{n}\,\mathrm{Pe}^{1/3}$	$0.0016 < \mathrm{Re} < 55$ $0.35 < n < 0.75$	6
Correlation of 11 experiments	$\mathrm{Sh} = 2 + 1.1\,\mathrm{Sc}^{1/3}\mathrm{Re}^{0.6}$	$3 < \mathrm{Re} < 2000$	7
Correlation of 16 experiments	$\mathrm{Sh} = \left[\dfrac{0.765}{\mathrm{Re}^{0.82}} + \dfrac{0.365}{\mathrm{Re}^{0.386}}\right] \dfrac{u}{n\,\mathrm{Sc}^{0.58}}$	$0.01 < \mathrm{Re} < 15000$	8
Correlation of 15 experiments	$\mathrm{Sh} = \dfrac{1.17u}{\mathrm{Re}^{0.415}\mathrm{Sc}^{2/3}}$	$10 < \mathrm{Re} < 2500$	3

[*] The original text reported a coefficient of 1.28 for the Pe term because of an incorrect evaluation of a Γ function.

[†] λ is the dimensionless length of active region.

[‡] $W = 2 - 3(1-n)^{1/3} + 3(1-n)^{5/3} - 2(1-n)^2$.

References: 1. Friedlander, 1957; 2. Levich, 1962; 3. Sherwood *et al.*, 1975; 4. Sorensen and Stewart, 1974; 5. Pfeffer, 1964; 6. Wilson and Geankoplis, 1966; 7. Wakao and Funazkri 1978; 8. Dwivedi and Updhyay 1977.

converts to $\mathrm{Sh} \to 2$). As suggested by Levich, a linear combination of this limiting value and the Pe-based correlation could represent the dissolution process over the entire range of Pe.

Mass transfer behavior in a packed bed is significantly different from the ideal systems discussed above. The inclusion of a solid matrix provides an external control on boundary layer formation, that is phenomena such as flow separation are less pronounced in multi-particle systems (Pfeffer, 1964). For example, the theoretically calculated limiting Sh value as $\mathrm{Pe} \to 0$ in a regularly packed bed of spheres is 3.89 (Sorensen and Stewart, 1974a). However, this is only the case for a packed bed of completely active spheres. For a diluted bed (in which not all particles are dissolving), the limiting Sh number can be quite different. For example, Rexwinkel *et al.* (1997) calculated a limiting value of 0.5 for a packed bed of diluted spheres. Many other investigators have studied this problem from a theoretical standpoint, including Griffith (experimental as well) (1960), Bowman *et al.* (1961), Kusik and Happel (1962), Pfeffer and Happel (1964), Pfeffer (1964), Sorensen and Stewart (1974a, b), Batchelor (1979) and Csanady (1986).

2.2. MODEL SYSTEMS (EXPERIMENTAL WORK)

Williamson *et al.* (1963) were among the first to systematically study mass transfer coefficients in a well-characterized packed bed reactor. They constructed benzoic acid spheres of constant radii enabling them to use exact areas to obtain mass transfer coefficients. A correlation was presented to describe their data. Wilson and Geankoplis (1966) also studied this system and presented another correlation that superceded that of Williamson *et al.* The effects of natural convection were not considered in either of these studies and may have influenced the data at lower Re values. Dwivedi and Upadhyay (1977) analyzed a series of mass transfer experiments and were able to use a single correlation to describe the entire data set. Their correlation demonstrates a transition zone at Re $\sim$10, indicating fundamentally different mass transfer properties (or differing hydrodynamics). Earlier in the development of such correlations, it became evident that mass transfer from a single sphere can be used as a surrogate for mass transfer in multi-sphere systems (Griffith, 1960, and references therein). However, experiments in packed beds typically yield mass transfer coefficients lower than those predicted from the extrapolation of correlations developed from single sphere systems. These discrepancies can be accounted for by assuming a nonuniform distribution of the void fraction (Martin, 1978) (i.e. the void fraction increases closer to the column walls) or by modifying the boundary conditions used (Nelson and Galloway, 1975). Such corrections are not routinely applied, and potential users should exercise caution in applying single sphere correlations to multi-particle systems.

2.3. ENVIRONMENTAL SYSTEMS

A key early issue in the study of NAPL dissolution by environmental scientists relates to the validity of the equilibrium assumption in model formulations. At the microscopic scale, the equilibrium assumption supports the presence of saturated aqueous concentrations at the NAPL–water interface. This assumption has been shown to be valid experimentally (Levich, 1962). Moving up in scale, the question then becomes whether or not dissolution driven by this process is sufficiently fast, relative to groundwater flow rates, to achieve equilibrium with that flow. In an early study, van der Waarden *et al.* (1971) reported equilibrium concentrations emanating from a NAPL mixture for Re $\sim$ 0.01. Fried *et al.* (1979) and Imhoff *et al.*

(1993) reported that relatively small spatial scales (on the order of a few cm) were required to achieve equilibrium conditions. Pfannkuch (1984), in his analysis of others' data, found that approximately 15 min were necessary to attain equilibrium concentrations for $\mathrm{Re} < 0.2$ (estimated). Miller *et al.* (1990) found concentrations very close to equilibrium in homogeneously packed columns of glass beads and toluene. The homogeneity was achieved by mechanically mixing the toluene *in situ*. Also, Schwille (1988) found that for blobs at residual saturation, equilibrium concentrations could be achieved quickly. In contrast to this, Hunt *et al.* (1988a) determined through order-of-magnitude analysis that nonequilibrium dissolution may be a factor when dealing with large ganglia (on the order of 5 cm) at relatively high velocities ($\mathrm{Re} \sim 0.05$). The theoretical work by Powers *et al.* (1991) suggested that nonequilibrium mass transfer is expected for small contact times, large NAPL blobs, and small NAPL saturations. Later, Powers *et al.* (1992) were able to produce experimental nonequilibrium conditions in short columns at high velocities ($\mathrm{Re} > 0.01$). As these results suggest, the question of achieving equilibrium is highly system specific. This conclusion has led many researchers to endeavor to develop generalized NAPL-based mass transfer expressions.

Mass transfer correlations developed in the environmental engineering literature (Table II) were patterned after those for more ideal systems (Table I). Some environmental researchers have enjoyed success explaining their data using chemical engineering-based correlations (Geller and Hunt, 1993; Baldwin and Gladden, 1996). Others have developed new correlations based on steady state effluent concentration data from soil column experiments (Miller *et al.*, 1990; Powers *et al.*, 1992; Imhoff *et al.*, 1993; Powers *et al.*, 1994a). In one case, the correlation developed using steady state data is applied to transient dissolution data with the inclusion of a time-dependent NAPL saturation term (Powers *et al.*, 1994a). Most of the newly developed correlations are strongly dependent on the experimental conditions employed and a universally applicable theory for NAPL dissolution in natural systems does not exist.

A complicating factor in comparing the environmental engineering correlations to the classical versions was introduced by environmental investigators who chose to summarize results in terms of a modified Sherwood number (Sh^*). This version of the dimensionless mass transfer group is based on the mass transfer rate constant, the product of the mass transfer rate coefficient and the interfacial surface area. The reason for lumping these two parameters is that the interfacial surface area is difficult to estimate with much accuracy. Casual (and incorrect) comparison of the recently derived Sh^*-based correlations (Table II) with the Sh-based expressions (Table I) would seem to suggest substantial discrepancies in the mass transfer behavior of the environmental and more ideal systems, as depicted in Figure 2. However, by making a few assumptions regarding the geometry of the NAPL in the systems for which Sh^* is employed, we can roughly estimate the corresponding Sh values for the correlations based on steady concentration observations. First, we assumed that large ganglia, of the type frequently observed in experimental

Table II. Correlations obtained from experimental work in the environmental engineering literature[†].

System	Correlation		Ref.
Blobs/Ganglia			
TCE-water Styrene-water	$\mathrm{Sh}^* = 57.7\mathrm{Re}^{0.61} d_{50}^{0.64} U_{\mathrm{i}}^{0.41}$	$10 < \mathrm{Pe} < 250$	1
TCE-water Styrene-water	$\mathrm{Sh}^* 4.13\,\mathrm{Re}^{0.598} \delta^{0.673} U_{\mathrm{i}}^{0.369} \left(\frac{\theta_{\mathrm{n}}}{\theta_{\mathrm{n}_0}}\right)^{\beta_4}$ and $\beta_4 = 0.518 + 0.114\delta + 0.10U_{\mathrm{i}}$	$10 < \mathrm{Pe} < 170$	2
Naphthalene-water	$\mathrm{Sh} = 77.6\,\mathrm{Re}^{0.658}$	$1 < \mathrm{Pe} < 200$	3
TCE-water	$\mathrm{Sh}^* = 340\theta_{\mathrm{n}}^{0.87} (\mathrm{Re}^*)^{0.71} (d_{50}/x)^{0.31}$	$1 < \mathrm{Pe} < 25$, $0 < \theta_n < 0.04$, $1.4 \leqslant x/d_{50} \leqslant 180$	4
Pools			
Oils in water	$\mathrm{Sh} = 0.55 + 0.025\,\mathrm{Pe}^{3/2}$	$0.5 < \mathrm{Pe} < 50$	5
Theoretical rectangular pools	$\mathrm{Sh} = 1.58(\mathrm{Pe}_x)^{0.34}(\mathrm{Pe}_y)^{0.43}$	$1.25^* < \mathrm{Pe} < 50^*$	6
Theoretical circular/elliptical pools	$\mathrm{Sh} = 1.74(\mathrm{Pe}_x)^{0.33}(\mathrm{Pe}_y)^{0.40}$	$1.25^* < \mathrm{Pe} < 50^*$	6

[†] The valid ranges for the correlations are usually presented in graphical form and with Re. These numbers are changed to Pe by multiplying by Sc as calculated from given data. Large Pe values are rounded to the nearest 10 whereas, small Pe values are rounded to the nearest digit. For correlations developed using more than one compound, the largest span of Pe is presented.

* These ranges are dependent on the directional Pe used. For more information see Kim and Chrysikopoulos, 1999.

References: 1. Powers *et al*., 1992; 2. Powers *et al*., 1994a; 3. Powers *et al*., 1994b; 4. Imhoff *et al*., 1993; 5. Pfannkuch 1984, reevaluating others' data; 6. Kim and Chrysikopoulos, 1999.

systems (Conrad *et al.*, 1992; Powers *et al.*, 1992), controlled the observed steady state dissolution data (Mayer and Miller, 1996). More specifically, we assumed the ganglia length scale to be 20 times greater than the reported average grain diameter. For simplicity, we assumed that the largest ganglia are spherical in shape. This is clearly unrealistic given photographic evidence of the shapes of the large ganglia (Ng *et al.*, 1978; Chatzis *et al.*, 1983; Conrad *et al.*, 1992; Powers *et al.*, 1992). However, the idea behind the scaling procedure remains the same regardless of the assumed shape. Finally, we adjusted the Re value in the Sh*-based correlations to include porosity and NAPL saturation in order to reduce system effects. The transformed correlations are plotted in Figure 3 to demonstrate that the discrepancy between the general mass transfer behavior in environmental systems and that in the classical systems may be less than one might expect. Furthermore, the discrepancy may not be as important in the overall context of transport modeling. A recent numerical study (Mayer and Miller, 1996) demonstrated that mass removal

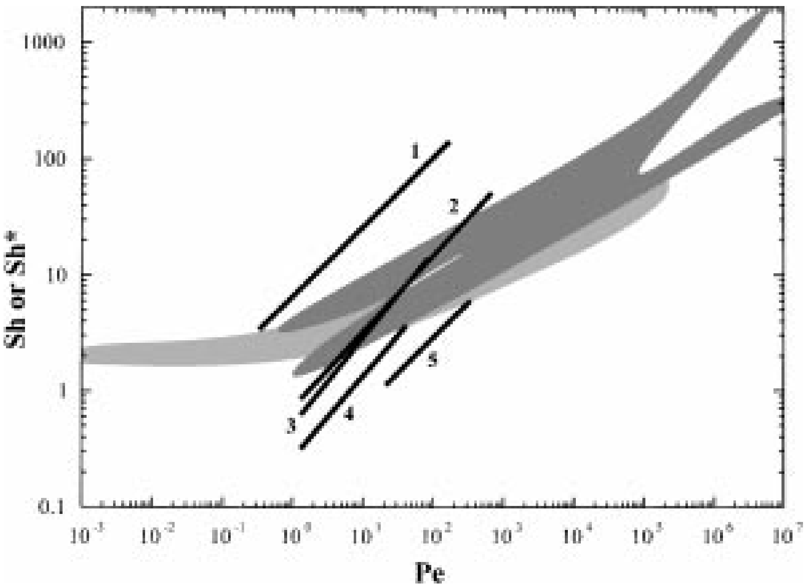

Figure 2. A plot of existing correlations relating Sh and Sh* to Pe for mass transfer from spherical and residual NAPL geometry. The light gray area represents theoretical work from the chemical engineering literature (Friedlander, 1957; Levich, 1962; Pfeffer, 1964; Sorensen and Stewart, 1974; Sherwood *et al.*, 1974; Clift *et al.*, 1978) and the dark gray area represents experimental work (Wilson and Geankoplis, 1966; Wakao and Funazkri, 1974). The lines represent experimental work of 1. Powers *et al.*, 1994a; 2. Powers *et al.*, 1994b; 3. Miller *et al.*, 1990; 4. Imhoff *et al.* ($x/d_{50} = 1.4$); and 5. Powers *et al.*, 1992.

rates in a homogeneous porous medium were fairly insensitive to the correlation used.

Developing mass transfer correlations for describing the dissolution of NAPL in pooled geometry is even more difficult because it is a three-dimensional problem. For this reason, contributions regarding pooled NAPL have not kept pace with those for residual NAPL. Nonetheless, there is a growing body of literature on the dissolution of NAPL pools (Pfannkuch, 1984 (see Table II); Anderson *et al.*, 1992b; Johnson and Pankow, 1992, Voudrias and Yeh, 1994; Chrysikopoulos *et al.*, 1994; Chrysikopoulos, 1995; Longino and Kueper, 1995; Holman and Javandel, 1996; Mason and Kueper, 1996; Chrysikopoulos and Lee, 1998; Kim and Chrysikopoulos, 1999). In contrast to residual NAPL dissolution modeling efforts, those for pooled NAPL have undertaken a more rigorous account of the increasing boundary layer thickness from the upstream to downstream positions along the pool (Chrysikopoulos, 1995). Based on a theoretical study of pool dissolution from square and circular/elliptical pool geometries, Kim and Chrysikopoulos (1999) derived two correlations for mass transfer from these pools (Table II). The correlations were written in terms of two Pe; one for the x-direction (direction of flow) and one for the y-direction. The plot in Figure 4 allows for comparison of Sh–Pe type correlations developed from pooled NAPL systems with those developed from

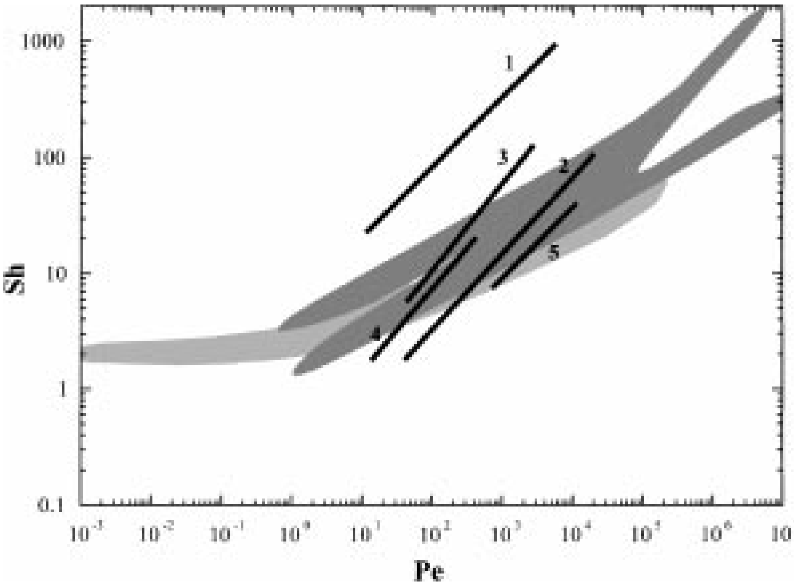

Figure 3. A plot of existing correlations relating Sh only to Pe for mass transfer from spheres and residual NAPL. The light and dark gray areas are the same as for Figure 2. The lines are estimates based on the experimental work of 1. Powers *et al.*, 1994a; 2. Powers *et al.*, 1994b; 3. Miller *et al.*, 1990; 4. Imhoff *et al.* ($x/d_{50} = 1.4$); and 5. Powers *et al.*, 1992; where Sh* values have been transformed to approximate Sh values as described in the text.

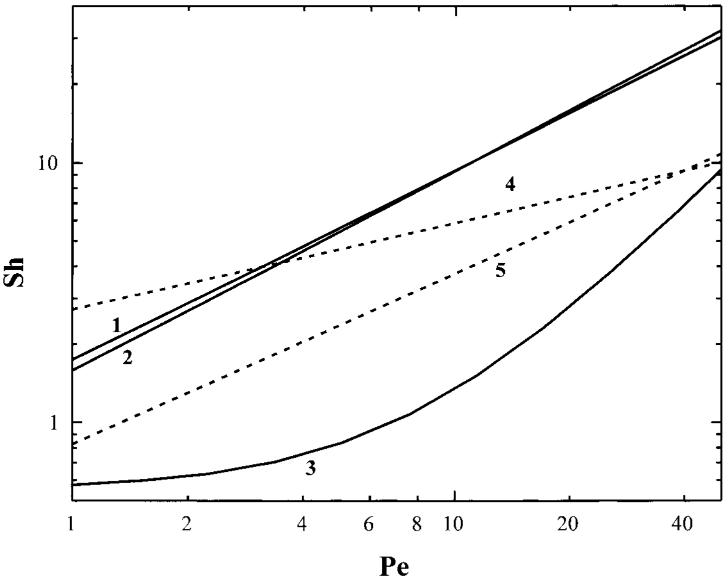

Figure 4. A plot of correlations relating Sh to Pe for NAPL pools of assumed flat-plate geometry for 1. Kim and Chrysikopoulos, 1999; 2. Kim and Chrysikopoulos, 1999; and 3. Pfannkuch, 1984. Correlations for spheres 4. Wilson and Geankoplis, 1966; and residual NAPL 5. Powers *et al.*, 1994b; are provided for comparison.

residual NAPL systems. Relative to the plots in Figures 2 and 3, there is clearly a dearth of information regarding dissolution behavior for NAPL in pooled geometry. This point notwithstanding, estimates for mass transfer from pools suggest Sh values similar to those for residual NAPL. If this is true, then the lower specific interfacial areas associated with pools will produce slower overall dissolution rates, as suggested by others (Anderson *et al.*; 1992, Johnson and Pankow, 1992; Mayer and Miller, 1996).

The abundance of NAPL dissolution correlations in the literature, and their general agreement with more fundamentally based correlations, suggests that our knowledge at the soil column scale has matured, but has yet to yield a universal theory. Improved techniques for defining the NAPL–water interface in natural porous media will aid in this respect, and this topic is the subject of discussion in the following section.

3. NAPL Morphology

This section focuses on research aimed at describing the length scale and interfacial geometry of entrapped NAPL. A detailed discussion on NAPL infiltration theory, which clearly affects NAPL morphology, has been provided in several other papers (Mayer and Miller, 1996; Fenwick and Blunt, 1998; Miller *et al*. 1998). In general, the size, shape and surface area of the NAPL blobs greatly influence the mass transfer characteristics (Clift *et al.*, 1978; Conrad *et al.*, 1992). Many investigators have tried to infer mass transfer behavior from direct or indirect observations of the NAPL ganglia geometry. Methods used include: NMR imaging (Baldwin and Gladden, 1996), gamma radiation (Imhoff *et al.*, 1993), photography (Griffith, 1960; Kennedy and Lennox, 1997; Jia *et al.*, 1998), styrene polymerization (Chatzis *et al.*, 1983; Mayer and Miller, 1992; Powers *et al.*, 1992), and freezing of bromoform (Kennedy and Lennox, 1997). Noninvasive techniques are useful because they enable one to look at the kinetics of the dissolution process at the pore scale. Photography is also useful since actual pictures of the processes are taken, and excellent photographs of NAPL shapes and sizes are available in the literature (Ng *et al*., 1978; Chatzis *et al*., 1983; Conrad *et al*., 1992; Powers *et al*., 1992; Jia *et al*., 1998). However, photography is limited to use in two-dimensional visualization systems, or in invasive techniques for retrieving frozen or polymerized ganglia. The polymerization of styrene and freezing of bromoform gives insight into NAPL size distribution and location within a column. However, the viscosity, density, and interfacial tensions of the styrene or bromoform need to be similar to the NAPL of interest because these parameters can significantly influence NAPL size, geometry, and location. In the other two noninvasive methods (NMR and gamma radiation), measurements lead to inferred NAPL properties. The shortcoming of these methods is that only NAPL quantity and not shape or size can be measured.

Methods for accurately estimating the interfacial areas available to dissolution, as mentioned previously, have yet to be defined. This is true for both residual and pooled NAPL. As evidence of this point, the fraction of the NAPL available to dissolution cannot be independently estimated, and is frequently used as a fitting parameter for experimental results. In the subsurface environment, there is a greater tendency for the NAPL ganglia to attain irregular, elongated, and branched shapes. This is because the percolation of NAPLs in the ground is a stochastic process and the particles are often reasonably well graded in the unconsolidated deposits subject to NAPL infiltration. This combination results in heterogeneous NAPL size and shape distributions. Chatzis *et al.* (1983) found that 30% of the blobs were larger than the pore sizes of the packing material with only 5% occupying over three times the pore size. They also found that the branched blobs occupied three to eight pore bodies. Powers *et al.* (1992) found that a significant fraction of the NAPL blobs were multi-pore ganglia. In their micromodel experiments, Kennedy and Lennox (1997) froze bromoform ganglia and found three distinct types of ganglia: blobs of one pore space, complex ganglia of several pore spaces, and a body of larger ganglia. Powers *et al.* (1992) found that the absolute size of NAPL blobs is strongly dependent on grain size, while Chatzis *et al.* (1983) found that the NAPL saturation is independent of absolute pore size. NAPL ganglia up to 10 pore bodies in size have also been observed (Conrad *et al.*, 1992).

Several investigators have used NAPL saturation as a surrogate for size and, more specifically, the interfacial area available to dissolution (Miller *et al.*, 1990; Powers *et al.*, 1992; Imhoff *et al.*, 1993; Powers *et al.*, 1994a). While this approach is pragmatic, the complex geometry of the NAPL ganglia is not captured by the saturation, and will affect its mass transfer and mobilization properties. Other surrogate measures for the residual NAPL geometry have been studied. For example, Powers *et al.* (1992, 1994a) noted that inclusion of the uniformity index (see Table II) improved dissolution model fits to data based on observations that this parameter is correlated to the NAPL size distribution found in their columns. However, this improvement might be inherent in their methodology as they also used the mean grain diameter as the defining length scale for their modified Sherwood number.

Neither direct nor surrogate measurements for characterizing pooled NAPL surface areas have been studied. Instead, models describing pool dissolution have generally assumed the presence of a sharp, flat NAPL–water interface (e.g. Chrysikopoulos *et al.*, 1994; Kim and Chrysikopoulos, 1998). The dissolution process in such models is considered in terms of boundary layer theory, where the mass transfer coefficient varies locally along the pool with the varying boundary layer thickness. Three-dimensional experimental data to test this assumption are only now emerging in the literature (Lee *et al.*, 1998; Dela Barre *et al.*, 1998).

The importance of NAPL surface area available to the dissolution process points to the need for continued effort in this area. Furthermore, the manner in which residual NAPL affects flow patterns in various pore networks links this problem to the issue of flow bypassing and its role in the dissolution process. Given the complexity of the geometry in a natural porous media, it may be most fruitful to continue to explore the use of more measurable surrogates, such as saturation, for the interfacial area available to dissolution (Miller *et al.*, 1990; Powers *et al.*, 1992, 1994a; Imhoff *et al.*, 1993). However, current results in this area are far from generalized, and may hinge on the development of new noninvasive techniques for accurately describing NAPL geometry at the laboratory scale.

4. Multicomponent NAPL

There is a growing body of literature on the dissolution equilibrium and kinetics of NAPL mixtures (Mackay *et al.*, 1991; Borden and Kao, 1992; Borden and Piwoni, 1992; Geller and Hunt, 1993; Lesage and Brown, 1994; Mukherji *et al.*, 1997). In some cases, the apparent solubility reduction of an organic chemical in an ideal mixture is readily estimated using Raoult's law. Mackay *et al.* (1991) and Borden and Piwoni (1992) have studied real systems (crude oil, and an aviation fuel contaminated site, respectively) and reported that the dissolution of the NAPL mixtures supports the ideal mixture assumption qualitatively. Results from several experimental studies demonstrate that nonidealities exist in some contaminant mixtures (e.g. Lesage and Brown, 1994; Mukherji *et al.*, 1997). These nonidealities are a function of the chemical characteristics of the compounds in the mixture (i.e. shape, size, polarity, etc.). The value of incorporating NAPL components' activity coefficients into transport models has not been fully investigated for nonideal NAPL systems. Relevant examples may be additives such as methyl tert-butyl ether (MTBE) in fuel mixtures, and alcohol-solvent mixtures that form during cosolvent flushing operations. Such nonideal behavior must be addressed if researchers are to link aqueous concentrations to their NAPL source.

Mass transfer resistance within a multicomponent NAPL may further complicate interpretation of thermodynamic issues associated with such mixtures. For a well-mixed NAPL, incorporating accurate activity coefficient estimates into expressions for the apparent solubility of a component would presumably enable estimation of that component's mass transfer coefficient, independent of the mixture composition (Mukherji *et al.*, 1997). However, the assumption of a well-mixed NAPL may also be suspect for real systems, where internal NAPL circulation may be limited by low momentum transfer from creeping groundwater flow (Clift *et al.*, 1978). Intra-NAPL diffusion (i.e. diffusion of the components from within the NAPL to the NAPL–water interface) may then limit the interfacial concentration value (deZabala and Radke, 1986; Conrad *et al.*, 1992; Geller and Hunt, 1993). Clearly, rigorous modeling of multicomponent diffusive interactions is implausible for all but the simplest binary and ternary NAPL mixtures, and probably unwarranted (Cussler, 1997). A few researchers have begun to examine intra-NAPL diffusion for independently diffusing components during NAPL vaporization (Lingineni and Dhir, 1997) and dissolution (Holman and Javandel, 1996). Their results suggest that intra-NAPL diffusion can significantly impact mass transfer. Obviously, incorporation of an intra-NAPL diffusion mechanism into a transport model for NAPL dissolution would underscore the importance of adequately characterizing NAPL size and shape, as this would determine the appropriate diffusion length scale.

5. Scale-Related Issues: Dispersion and Flow Bypassing

The discussion here is in the context of modeling NAPL dissolution in porous media at increasingly realistic scales. There is a relatively small body of work that is beginning to address larger scale issues associated with residual (Anderson *et al.*, 1992a; Illangasekare, 1998) and pooled NAPL (Kim and Chrysikopoulos, 1999; Dela Barre *et al.*, 1998; Lee *et al.*, 1998). As Miller *et al.* (1998) noted, there has been very little work on the problem of up-scaling the NAPL dissolution rates to better equip contaminant transport models at the field scale. Reliable up-scaling procedures will be needed if the NAPL location problem discussed below is to be solved at a large scale. Clearly, development of dissolution rate up-scaling procedures will involve quantifying the effects of other scale-dependent modeling parameters, such as dispersivity.

Many investigators have reported that dispersion in the column does not significantly affect the dissolution process (Wakao and Funazkri, 1978; Miller *et al.*, 1990; Powers *et al.*, 1991; Imhoff *et al.*, 1993; Pennell *et al.*, 1993; Powers *et al.*, 1994). Order of magnitude analysis by Lin *et al.* (1974) (as used in Imhoff *et al.*, 1993), corroborates these results. More specifically, Powers *et al.* (1991) and Pennel *et al.* (1993) conducted sensitivity analyses and found that the effluent concentrations are insensitive to dispersivities in the range of 0.01 and 1 cm. There are conditions under which dispersion contributions are important to consider. For example, Wakao and Funazkri (1978) postulated that, for $\mathrm{Re} < 3$ in liquid systems, dispersion begins to effect mass transfer-related interpretations. Also, Rexwinkel *et al.* (1997) recently demonstrated that the exclusion of axial dispersion for Pe values less than about 200 (about $\mathrm{Re} = 0.2$) can result in erroneous interpretation of data. Overall, the literature suggests that at relatively large Re values (roughly, $\mathrm{Re} > 3$), dispersion can be neglected. However, Re values characteristic of groundwater flow can be much smaller than unity (Pfannkuch, 1984; Domenico and Schwartz, 1990) and, thus, dispersion may become significant. The contribution may be more substantial for larger scale dispersive processes, as has clearly been the case for other subsurface fate and transport phenomena (e.g. sorption and biodegradation).

A related up-scaling issue is flow bypassing of a NAPL-impacted zone. Flow bypassing refers to the preferential flow of water around contaminated zones because of the reduced permeabilities in these zones (Kueper and Frind, 1991; Anderson *et al.*, 1992a; Geller and Hunt, 1993; Soerens *et al.*, 1998). Kueper and Frind (1991) estimated relative permeabilities for the PCE water system after the onset of fingering to be between 0.3 and 0.8. Wheatcraft and Winterberg (1985) give an expression for the fraction of flow through a cylinder as a function of the relative permeability. Using this expression in calculations for their own experiments (in which the water was free to flow around the contaminated zone), Anderson *et al.*

(1992a) estimated the relative permeability of the NAPL-impacted zone to be about 0.82. Soerens *et al*. (1998) treated the problem mathematically in a similar way; they divided the theoretical column into two zones, one with NAPL, and one with clean water. They were able to capture experimentally observed tailing behavior by including different exchange coefficients between these columns and by changing the fraction of flow in each column.

The issue of groundwater flow circumventing NAPL-impacted zones or promoting dissolution fingers as it accesses more permeable portions of those zones has received a good deal of attention at the laboratory scale. As the observational scale of interest extends outside of soil columns to the real subsurface, the likelihood of flow bypassing and dissolution fingering the NAPL impacted zone increases. Anderson *et al*. (1992a) found concentrations close to solubility in a system where a cylindrical NAPL source was placed in a larger square column. This result suggests that either flow bypassing does not occur or that the mass transfer kinetics are fast enough so that flow bypassing does not effect the effluent concentrations. In contrast, Geller and Hunt (1993) specifically accounted for flow bypassing in their soil column study, and found significantly lower concentrations ($\sim$20% of solubility in all runs). In addition to direct effects on the dissolution problem, the effects of flow bypassing may become more pronounced when remediation technologies such as cosolvent or surfactant injection are implemented.

An issue intertwined with flow bypassing and dissolution fingering phenomena is the effect of heterogeneity on NAPL geometry and dissolution. Recently, a numerical study by Mayer and Miller (1996) showed that heterogeneity in the porous medium leads to the formation of NAPL pools that were implicated in slow dissolution rates. These authors also compared mass removal rates using different published correlations. They found that in the homogeneous medium, all but one of the published correlations gave similar removal rates. However, in the heterogeneous medium, the differences between the correlations were more pronounced. Heterogeneity also causes scale-dependence in dispersive behavior, which will also affect the mass transfer rates from NAPL sources. Such factors will also undoubtedly hinder the effective delivery of chemical additives to the NAPL locations. Thus, while homogeneous column experiments on NAPL dissolution yield insightful information on the mass transfer properties, heterogeneity (from the pore scale to field scale) remains a crucial issue in determining the shape, size, and dissolution properties of NAPL sources as well as the flow characteristics around NAPL contaminated regions. Both experimental and theoretical investigations are needed to find the best methods for describing NAPL dissolution behavior in the field.

6. Locating NAPL in the Subsurface

Directly related to the scale issues is the problem associated with locating NAPL-impacted zones in the setting of large, dilute plumes. In contrast with the literature regarding the physical modeling efforts, that related to the identification of NAPL location is sparse. One promising geophysical technique is to probe for relatively low radon levels in pore water, as this radioactive species is naturally present and tends to partition into NAPL (Semprini *et al.*, 2000, this issue). One drawback to employing this approach on a large scale is potential heterogeneity in the background radon signal. Another promising approach for locating NAPL in the subsurface is the partitioning interwell tracer tests (Jin *et al*., 1995; James *et al*., 1997; Dwarakanath and Pope, 1998). Tracers of different affinities for the NAPL (or different partition coefficients) are introduced to the NAPL contaminated zone and the breakthrough of these tracers is analyzed to infer the NAPL saturation. These tracer techniques are currently limited to applications where the NAPL location is reasonably well known. More work is needed to extend their application to the problems where the NAPL location is highly uncertain. These problems await the formulation and solution of inverse models emphasizing NAPL dissolution dynamics.

Classical inverse modeling techniques (Yeh, 1986) have not yet been applied to NAPL dissolution scenarios to identify parameters such as location and strength of NAPL sources. Two related papers (Butcher and Gauthier, 1994; Jin *et al*., 1995) determine NAPL mass based on aqueous plume observations. There has been some movement toward the problem of identifying parameters associated with contaminant sources. Most of the work has involved geostatistical and optimization approaches for determining the location, magnitude and disposal period of point releases (Gorelick, 1982; Gorelick and Remson, 1982; Wagner, 1992; Snodgrass and Kitanidis, 1997). Skaggs and Kabala (1994, 1995) have investigated the problem of recovering the contaminant release history for a one-dimensional domain. Sidauruk *et al*. (1998) employed the inverse method for estimating pollutant mass, initial location and time of injection in a two-dimensional, homogeneous porous medium. They employed instantaneous and continuous source terms, avoiding explicit descriptions for NAPL dissolution. The solution of the inverse problem for identifying NAPL location will involve estimating dissolution parameters in addition to conventional flow and transport modeling parameters. Thus, we can expect the inverse problem to be much more difficult to solve in real cases. Nonetheless, successful deployment of the remediation technologies discussed throughout this paper would benefit immensely from the development of effective NAPL-locating algorithms. These algorithms should optimize the use of available field data, or identify data needs for identifying NAPL location within an acceptable range of uncertainty. Successful development of these types of algorithms will depend greatly on the development of up-scaled dissolution rate models.

7. Enhanced NAPL Recovery

NAPL persistence due to relatively low aqueous solubility has motivated the feasibility assessment of various remedial technologies aimed at more efficient NAPL removal. Hot water flushing has received some attention. However, the most actively investigated technologies involve flushing the NAPL-impacted zone with cosolvents or surfactants.

In a study involving a modest water temperature increase to 40°C, Imhoff *et al.* (1997) reported a dissolution enhancement that was accounted for by increase in NAPL solubility (i.e., dissolution driving force). The influence of temperature on mass transfer coefficients in such systems would be limited for this range of temperatures, and can be estimated by calculating the temperature dependence of the relevant Schmidt number (Sc). The relatively low potential increase in the driving force for dissolution over modest temperature ranges may render this a noncompetitive approach. Higher temperature NAPL recovery approaches, such as steam injection (Hunt *et al.*, 1988a, 1988b), might be more attractive if the NAPL location is well-characterized and accessible.

There is a significant body of literature dealing with the effects of cosolvents in NAPL–water systems (Yalkowsky *et al.*, 1976; Yalkowsky and Valvani, 1979; Nkedi-Kizza *et al.*, 1985; Mackay *et al.*, 1991; Augustijn *et al.*, 1994; Imhoff *et al.*, 1995; Hayden and van der Hoven, 1996). Cosolvents are organic solutes that are present in sufficient quantities in the water ($>$ approximately 10% by volume) to render the aqueous phase more hydrophobic in nature. At these levels cosolvents can increase the apparent aqueous solubility of each NAPL component. For example, Imhoff *et al.* (1995) studied the dissolution of PCE in the presence of a 60% methanol/water mixture. They found mass transfer correlations developed in pure water were able to predict (to within 30%) mass transfer coefficients in the presence of this mixture. This result is surprising given that they report a decrease in interfacial tension between the NAPL and water from 43 dyne/cm to approximately 10 dyne/cm. Also, the solubility of PCE (and thus, the driving force for dissolution) was reportedly increased from 225 mg/l to $\sim$9000 mg/l. Moreover, the molecular diffusivity of PCE changed in the presence of methanol. It seems fortuitous that aqueous-based models were able to predict cosolvent enhanced dissolution data.

Surfactants are also receiving a great deal of attention in the NAPL recovery literature (Edwards *et al.*, 1991; Holsen *et al.*, 1991; Liu *et al.*, 1991; Abriola *et al.*, 1993; Pennell *et al.*, 1993, 1994; Edwards *et al.*, 1994; Grimberg *et al.*, 1994, 1995, 1996; Martel and Gelinas, 1996; Mason and Kueper, 1996; Yeom *et al.*, 1996; Anonymous, 1997; Kanga *et al.*, 1997). A suitable surfactant will markedly affect NAPL–water partitioning when present at levels above its critical micelle concentrations (CMC). Above the CMC, surfactants form micelles that are also very suitable environments for the organic NAPL. The NAPL will partition into the micelle core, causing an apparent increase in aqueous solubility. Through proper selection of surfactant, this apparent solubility increase can be substantial. Even greater NAPL removal efficiency may be brought about by surfactant-induced mobilization of NAPL-surfactant macroemulsions (Okuda *et al.*, 1996; Fortin *et al.*, 1997), or through mobilization of larger NAPL bodies after a sufficient reduction of interfacial tension (Fortin *et al.*, 1997; Rothmel *et al.*, 1998). Mass transfer in the presence of surfactants displays some interesting characteristics. For example, Pennell *et al*. (1993) observed that mass transfer coefficients in the presence of surfactants are significantly less than those observed in corresponding surfactant-free systems. Experiments by Yeom *et al*. (1995) required longer equilibration times between coal tar and the surfactant solution at higher surfactant concentrations, suggesting a mass transfer rate reduction by the surfactant. In accord with this finding, Grimberg *et al*. (1995) reported that the mass transfer coefficient characterizing the solid organic phase dissolution asymptotically decreased as a function of surfactant concentration. Grimberg *et al*., (1996) reported steady-state effluent phenanthrene concentrations which decreased more with increasing flow rate in the presence of surfactants than with water alone, suggesting a greater mass transfer rate-limitation in the presence of surfactants. An additional complicating factor is that a kinetic control on the mass transfer mechanism can also be present. For example, Mason and Kueper (1996) found that approximately seven days were required to reach a steady interfacial tension between a NAPL and surfactant/water solution. This was observed in a controlled experiment in the laboratory.

In terms of research needs, mass transfer aspects of cosolvent and surfactant additives have not been thoroughly investigated. Several proposed cosolvents tend to partition strongly into the NAPL phase (Brandes and Farley, 1993; Imhoff *et al*., 1995), reducing the NAPL–water interfacial tension. However, while reduced surface tension may play a role in altering NAPL dissolution rate, it is probably less significant in the face of the potential for NAPL mobilization (Imhoff *et al*., 1995). Another research need which may supercede cosolvent-related NAPL dissolution issues is that associated with efficient delivery of these inhomogeneous but water-miscible fluids to the desired subsurface location (Rao *et al*., 1997; Harmon *et al*., 1998). Similarly for surfactants, the causes and effects of macroemulsions and NAPL mobilization may supercede the need for a better understanding of solubilization rates. Nonetheless, several interesting and potentially important surfactant-related effects on NAPL dissolution are not fully understood. First, surfactant accumulation at the NAPL–water interface can reduce the internal circulation of the NAPL ganglia (Griffith, 1960; Levich, 1962; Clift *et al*., 1978; Pfannkuch, 1984; Quintana, 1990; Kennedy and Lennox, 1997). With a reduced internal circulation, the mass transfer properties of the NAPL blob will more closely resemble that of a solid (Clift *et al*., 1978; Pfannkuch, 1984). All of the referenced studies suggest that the mass transfer coefficient is reduced in the presence of surfactants. Clift *et al*. (1978) show that a solid sphere of a given size can have a five-fold reduced mass transfer coefficient when compared to a similar liquid droplet (dependent on viscosity). However, Grimberg *et al*. (1996) observed that the maximum dissolution rate (product of mass transfer coefficient and the aqueous solubility) increased linearly with the surfactant concentration, suggesting that the solubility enhancement by the surfactant overshadows the mass transfer reduction. Investigators have generally ignored the effects of accumulation of the surfactants at the NAPL–water interface. Thus, the correlations developed under surfactant flushing conditions may not be universally applicable. The fundamental changes in mass transfer due to surfactants needs more attention. Once this aspect of the problem is fully understood, generalizing correlations should be quite straightforward.

It is worthwhile to note that surfactant-induced mass transfer reduction can be a source of experimental artifacts. For example, many investigators use colored dye in the organic phase to enhance visualization in their system (Schwille, 1988; Anderson *et al.*, 1992a; Powers *et al.*, 1992; Imhoff *et al.* 1995; Mason and Kueper, 1996; Fortin *et al.*, 1997; Kennedy and Lennox, 1997). Such a dye can change interfacial tension significantly (by 10 to 30%) (Powers *et al.*, 1992) and may affect mass transfer rates as well. It is apparent that impurities in the water can effect the interfacial tension in the NAPL–water system. In turn, the momentum transport through the water–NAPL interface is altered, changing the mass transfer characteristics. Caution must be exercised in applying dyes for visual experiments as they may have surface-active properties. In a related problem, Pfannkuch (1984) states that a differential solubilization of compounds (more soluble ones leaving the NAPL phase first) can result in the formation of a 'skin' around the NAPL, changing its mass transfer properties. Luthy and others have also found reduced mass transfer of naphthalene from 'aged' coal tar experiments (Luthy *et al.*, 1993; Ramaswami *et al.*, 1994). Nelson *et al.* (1996) found that aging coal tar for three days results in the formation of a semi-gelatinous film around the tar globule. They attribute this to the accumulation of water at the surfaces which is a fundamentally different mechanism than that presumed by Pfannkuch (1984). In comparing column data to field data, the aging of field NAPL sources cannot be neglected.

8. Summary and Conclusions

There now exists an extensive body of literature summarizing the results of environmentally based research on the problem of NAPL dissolution in the subsurface environment. Pertinent issues recounted here include: residual and pooled NAPL dissolution rates and correlations; quantifying residual NAPL geometry; the effect of dispersion and flow bypassing phenomena on the dissolution process; multicomponent mixtures; and enhanced NAPL extraction technologies. Research and development is relatively advanced on this array of issues, and results are in reasonable accord with those from similar but more mature fields. Despite this significant amount progress, there remains extensive potential for refinement in many areas. Specifically, we propose the following research directives:

1. There is work to be done in establishing the link between NAPL geometry (length scale and interfacial area) and NAPL infiltration and entrapment processes. The latter were not addressed in detail in this paper, but clearly will play a key role in establishing interfacial surface area and in NAPL-induced flow bypassing.

2. As our understanding of the issues in (1) reaches completion, investigations into multicomponent equilibrium and mass transfer (e.g. intra-NAPL diffusion) issues, and their impact on the overall transport scenario, will be necessary.
3. Continued research into the fundamental interactions between NAPL recovery enhancing additives and dissolution equilibrium and mass transfer processes is needed to support the development of additive delivery and NAPL recovery design models.
4. There is a need for a large amount of computational modeling and model validation to be done in the area of up-scaling NAPL dissolution rate behavior to accomodate field-scale simulations.
5. Finally, as we gain confidence in field-scale forward modeling approaches, inverse modeling techniques can then be meaningfully investigated to help identify NAPL residual and pool locations at large sites.

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