Pore Scale Determination of the Rate of NAPL Dissolution or Volatilization

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1. Introduction

Non-Aqueous Phase Liquids (NAPLs), such as chlorinated solvents and hydrocarbon fuels, have been used extensively in private industry, military installations and DOE facilities. NAPL spills during transport and leaks from underground storage tanks have inevitably occurred and represent a major risk to water supply, since even a small amount of NAPLs can contaminate large volumes of groundwater. NAPL ganglia (blobs) trapped in the porous soil or rock matrix at “residual” saturation (Dawson, 1992; Kueper et al., 1993) are a continuous source of contamination to the aquifer or the soil vapor, through dissolution or vaporization (Garg and Rixey, 1999; Rixey, 1996; Smith et al., 1996). NAPL may also be present in large pools either above the water table (in the case of lighter-than-water NAPLs, LNAPLs) or resting at the bottom of the aquifer on the confining bedrock (in the case of denser-than-water NAPLs, DNAPLs), slowly transferring to the surrounding water or vapor phase (Chrysikopoulos and Lee, 1998; Seagren et al., 1999).

To design a remediation scheme, it is important to understand at a basic level the physicochemical processes that govern inter-phase mass transfer of NAPLs in the subsurface, both in the unsaturated and the water-saturated regions. The rate at which NAPLs dissolve or volatilize in large part determines the time required to clean up a contaminated site, whether via Soil Vapor Extraction (SVE) (Falta et al., 1993; Gomez-Lahoz et al., 1994b; Lingineni and Dhir, 1997; Rathfelder et al., 1996; Wilson et al., 1994), bioremediation and its many variants (bioventing, bioslurping, etc.) (Ghoshal and Luthy, 1998; Ghoshal et al., 1996; Mukherji and Weber, 1998; Seagren et al., 1993; Sekelsky and Shreve, 1999; Yang et al., 1995) and pump-and-treat (Gomez-Lahoz et al., 1994a). Non-equilibrium conditions are most important during active remediation, when the rate of inter-phase mass transfer can significantly limit the effectiveness of any treatment scheme, but may also play a role during natural attenuation (Grathwohl, 1998; Libelo et al., 1998; Reichert et al., 1998; Stauffer et al., 1998).

Modeling and experimental work (Armstrong et al., 1994; Geller, 1990; Geller and Hunt, 1993; Grathwohl et al., 1990; Hunt et al., 1990; Imhoff et al., 1990; Imhoff et al., 1993; Imhoff and Miller, 1996; Imhoff et al., 1996; Mayer and Miller, 1992; McKay and Gillham, 1993; Wilkins et al., 1995) indicates that inter-phase mass transfer may be a limiting factor when the NAPL saturations are low, the aqueous or vapor phase velocities are large or the NAPL is only slightly soluble, conditions which are typical during soil remediation of many common organic pollutants. Many remediation proposals consider that mass-transfer is not rate limiting; up to
recently, few numerical models have included this important consideration in their simulations, with the corresponding potential error in determining the required clean-up time and/or risk to drinking water supplies or human/ecological exposure. There are a number of recent models that do consider the rate of mass transfer in their formulation (Abriola et al., 1993; Abriola and Pinder, 1985; Forsyth and Sudicky, 1998; Forsyth et al., 1998; Rathfelder et al., 1996; Rubin et al., 1997; Wilkins et al., 1995).

1.1 Conceptual Model

The conceptual model of a typical contaminant spill into porous and fractured media has been put forward by several researchers (Abriola, 1989; Kueper and McWhorter, 1991; Mercer and Cohen, 1990; Parker and Cherry, 1994). In some cases, the contaminant is dissolved in water and thus travels through the aquifer as a solute. More typically a contaminant enters the subsurface as a liquid phase separate from the gaseous or aqueous phases present (Figure 1.1). NAPLs may be leaking from a damaged or decaying storage vessel (e.g. in a gasoline station, refinery, dry-cleaning operation), improperly constructed storage and distribution systems, a waste disposal lagoon, or may be spilt during transport and use in a manufacturing process (e.g. during degreasing of metal parts, in the electronics industry to clean semiconductors, or in an airfield for cleaning jet engines).

The NAPL travels first through the unsaturated zone, under three-phase flow conditions, displacing air and water. The variations in matrix permeability, due to the heterogeneity of the porous medium, result in additional deviations from vertical flow. If the NAPL encounters layers of slightly less permeable materials (e.g. silt or clay lenses, or even tightly packed sand), or materials with smaller pores and thus a higher capillary entry pressure (e.g. NAPL entering a tight, water-filled porous medium), it will tend to flow mostly in the horizontal direction until it encounters a path of less resistance, either more permeable or with larger pores. Microfractures in the soil matrix are also important in allowing the NAPL to flow through low-permeability lenses. In the either the unsaturated or saturated zones, NAPLs traveling downward may reach a low enough saturation to become disconnected and immobile (forming drops or “ganglia”), as shown in Figure 1.2. NAPLs are trapped within the porous medium when the capillary forces are sufficiently strong to overcome the viscous and gravitational forces acting on the NAPLs.

Denser than water NAPLs (e.g. chlorinated organic solvents, polychlorinated biphenyls, tars and creosotes), which are denominated DNAPLs, forms a mound once they reach the water table, and spread horizontally until either there is enough mass to overcome the capillary entry pressure or the DNAPL finds a path of less resistance into the water-saturated matrix, either a fracture or a more porous/permeable region. Once in the saturated zone, DNAPLs travel downward until either they reach a low enough saturation to form immobile ganglia, or they find a low-permeability layer. If the layer does not extend very far, the DNAPL will flow horizontally around it. In many cases, the DNAPL reaches bedrock or a tight clay layer. These layers usually contain fractures into which the DNAPL flows readily, displacing water. The capillary entry pressure into most fractures is quite low, on the order of a few centimeters of DNAPL head (Kueper and Frind, 1991). Flow into the fractures continues until either the fracture becomes highly DNAPL saturated, or the fracture is filled or closed below, or the DNAPL spreads thin.
enough to become disconnected. The DNAPL may flow into horizontal fractures within the fracture network.

In terms of remediation strategies, DNAPLs in fractured bedrock are probably one of the most intractable problems (NRC, 1996). They are a continuous source of dissolved contaminants for years or decades, making any pumping or active bioremediation alternative a very long term and costly proposition. Excavation down to the fractured bedrock is very expensive in most cases, and removal of the contaminated bedrock even more so. Potential remediation alternatives include dewatering the contaminated zone via high-rate pumping and then applying Soil Vapor Extraction to remove volatile DNAPLs, applying steam to mobilize and volatilize the DNAPL towards a collection well, or using surfactants to mobilize the NAPLs to a collection well or trench. Other alternatives include isolating the NAPL source zone using impermeable barriers, with mixed success (Jefferis, 1991).

1.2 Mass Balance Considerations

This macroscopic model of NAPL movement and mass transfer to the surrounding gaseous or aqueous phases can be described mathematically using mass conservation considerations. First, a general mass balance equation for in phase p, which may be composed of one or more components, c, can be expressed as (Abriola, 1989):

\[ \frac{\partial}{\partial t} (\varphi \rho_p s_p) + \nabla \cdot (\varphi \rho_p s_p v_p) = \varphi \sum_c \sum_{p1} j_{pp1c} + \rho_p \sum_c r_{pc} \]

(1)

where:

- \( \varphi \) is the matrix porosity [-];
- \( \rho_p \) is the mass density of phase p [M L\(^{-3}\)];
- \( s_p \) is the saturation of phase p in the void space of the porous medium [-];
- \( t \) is the time [T];
- \( v_p \) is the pore velocity of phase p [L T\(^{-1}\)];
- \( j_{pp1c} \) is the rate of mass transfer of component c from phase p to phase p1, per unit pore volume [M L\(^{-3}\) T\(^{-1}\)];
- \( r_{pc} \) is the sum of rates of reaction of component c in phase p, for various transformation processes (biotic or abiotic) per unit aquifer volume per unit time [T\(^{-1}\)]; and
- \( p \) is the subscript that denotes the various phases in the porous medium (g = gas, w = aqueous, n = NAPL, s = solid, b = biophase).

The saturations are subject to the constraint:

\[ s_w + s_n + s_g + s_b = 1 \]  

(2)
The solid phase has no saturation since it is not part of the void space. The phase velocity is formulated using a modified Darcy’s Law, considering the simultaneous flow of various phases through the porous media, thus interfering with each other and reducing the absolute permeability:

\[ V_p = \frac{q_p}{\phi S_p} = -\frac{k k_{rp}}{\mu_p} \left( \nabla P_p - \rho_p g \nabla z \right) \]  \hspace{1cm} (3)

where:
- \( q_p \) is the specific discharge of phase \( p \) \([L \, T^{-1}]\);
- \( k \) is the intrinsic permeability tensor of the porous medium \([L^2]\);
- \( k_{rp} \) is the relative permeability of phase \( p \) \([-]\);
- \( \mu_p \) is the dynamic viscosity of phase \( p \) \([M \, L^{-1} \, T^{-1}]\);
- \( P_p \) is the pressure of phase \( p \) \([M \, L^{-1} \, T^{-2}]\); and
- \( g \) is the gravitational acceleration vector \([L \, T^{-2}]\).

For the purposes of our study, we do not consider biotic or abiotic transformations, and focus specifically on the interphase mass transfer rates under various conditions. In most of the work we will present, the NAPL phase has reached a “residual” saturation and is immobile, such that \( V_n = 0 \) (since \( k_n = 0 \)). However, as Keller et al., (1997) have pointed out using highly detailed observations of NAPL flow under two- and three-phase flow conditions, even “residual” NAPL may mobilize within the pore space if the conditions are modified. This will be discussed in the results section in more detail. We will also not consider a biophase, assuming that in our studies \( S_b = 0 \). Equation 1 is presented in this more general form to indicate the possibility that these other phases and processes may occur, and that they need to be considered when we transfer the results of our studies to larger scales.

A mass balance for component \( c \) in phase \( p \) can thus be expressed as:

\[ \frac{d}{dt} \left( \phi S_p C_p^c \right) + \nabla \cdot \phi S_p \left( V_p C_p^c - D_{pc}^h \nabla C_{pc} \right) = \phi \sum_{c} \sum_{p1} J_{pp1c} \]  \hspace{1cm} (4)

where:
- \( C_p^c \) is the mass concentration of \( c \) in phase \( p \) \([M \, L^{-3}]\);
- \( D_{pc}^h \) is the hydrodynamic dispersion tensor of component \( c \) in phase \( p \) \([L^2 \, T^{-1}]\), which includes molecular diffusion and kinematic dispersion.

At the length scale of the current studies, molecular diffusion becomes very important, as will be discussed in more detail later.

The rate of mass transfer between phases is generally modeled using a linear driving force (Schwarzenbach et al., 1993):
\[ J_{pp1c} = T_{pp1c} \left( C_{c}^{e,pp1} - C_{c}^{p} \right) \]  

(5)

where:
- \( T_{pp1c} \) is the overall (or lumped) mass transfer coefficient for component \( c \), from phase \( p \) to phase \( p_1 \) \([T^{-1}]\); and
- \( C_{c}^{e,pp1} \) is the mass concentration of \( c \) in phase \( p \), in equilibrium with phase \( p_1 \) \([M L^{-3}]\).

It is possible to interchange between mass concentrations and mole fractions by using the relation:

\[ C_{c}^{p} = \frac{M_{c}x_{c}^{p}}{M_{p}} \]  

(6)

where:
- \( M_{c} \) is the molecular weight of \( c \) \([M \text{ mole}^{-1}]\); 
- \( M_{p} \) is the molecular weight of phase \( p \) \([M \text{ mole}^{-1}]\); and
- \( x_{c}^{p} \) is the mole fraction of component \( c \) in phase \( p \) \([\text{mole mole}^{-1}]\).

This provides an additional constraint, since the sum of the component mole fractions must add up to one:

\[ \sum_{c} x_{c}^{p} = 1 \]  

(7)

### 1.3 Equilibrium Partitioning

If the phases are allowed to come in contact for sufficiently long time, the partitioning of the NAPL components between the various phases will be constant, achieving thermodynamic equilibrium. The equilibrium or partitioning coefficients between the various phases are derived in (Schwarzenbach et al., 1993). The partitioning between NAPL and gas is based on Raoult’s Law:

\[ P_{c}^{g} = \gamma_{c}^{n} x_{c}^{n} P_{c}^{vap} \]  

(8)

where:
- \( P_{c}^{g} \) is the partial pressure of component \( c \), \([M L^{-1} T^{-2}]\); 
- \( \gamma_{c}^{n} \) is the activity coefficient of component \( c \) in NAPL, [-]; 
- \( x_{c}^{n} \) is the mole fraction of \( c \) in NAPL, \([\text{mole mole}^{-1}]\); and
- \( P_{c}^{vap} \) is the vapor pressure of component \( c \), \([M L^{-1} T^{-2}]\).
The activity coefficient is used to capture nonideal behavior of some components within the NAPL mixture. For most NAPL mixtures, ideal behavior is assumed, such that \( \gamma_c^n \approx 1 \) (Schwarzenbach et al., 1993). \( p_c^g \) can be related to the mole fraction in the gas phase, \( x_c^g \), using the ideal gas law:

\[
p_c^g = \frac{\rho_g x_c^g RT}{M_p}
\]

where:

- \( R \) is the ideal gas law coefficient, \([L^2 M T^{-2} K^{-1} \text{ mole}^{-1}]\); and
- \( T \) is the temperature \([K]\).

Combining Equations 8 and 9 and rearranging, one obtains the NAPL/gas partitioning coefficient for component \( c \), \( K_{gn,c}^e \), which is a function of temperature:

\[
K_{gn,c}^e = \frac{x_c^g}{x_c^n} = \frac{M_p P_{c,vap}}{\rho_g RT}
\]

The dissolution of NAPL constituents from a mixture of organic liquids can be expressed by:

\[
x_c^w = \frac{1}{\gamma_c} \frac{n_c x_c^w}{x_c^n}
\]

where:

- \( \gamma_c^w \) is the activity coefficient of component \( c \) in water, [-].

In most cases (Schwarzenbach et al., 1993),

\[
\frac{1}{\gamma_c^w} \approx x_c^{w,sat}
\]

where:

- \( x_c^{w,sat} \) is the saturation mole fraction of component \( c \) in water, [-], also denominated the molar solubility of \( c \) in water.

These assumptions are valid for most organic compounds with low solubilities \((< 1 \text{ kg m}^{-3})\) and similar NAPL components (e.g. petroleum hydrocarbons, mixture of chlorinated alkyls). Thus, the NAPL/water partitioning coefficient for component \( c \), \( K_{wn,c}^e \), is:

\[
K_{wn,c}^e = \frac{x_c^w}{x_c^n} = x_c^{w,sat}
\]
Partitioning between the aqueous and gas phase can be estimated by combining Equations 10 and 13 to obtain the gas/water partitioning coefficient for component c, $K_{wg,c}^e$:

$$K_{wg,c}^e = \frac{x_c^w}{x_c^g} = \frac{K_{wn,c}^e}{K_{gn,c}^e} = \frac{x_c^{w,sat}}{K_p^RT} = \frac{M_p^vap}{x_c^w}$$ (14)

$K_{wg,c}^e$ is equivalent to the dimensionless Henry’s Law coefficient (Schwarzenbach et al., 1993).

Although the present studies do not consider sorption, the water/solid partitioning coefficient for component c, $K_{sw,c}^e$, would be:

$$K_{sw,c}^e = \frac{x_c^s}{x_c^w} = \frac{C_c^sM_w}{C_c^wM_s} = \frac{K_{oc}^{oc}f_{oc}M_w}{\rho_wM_s}$$ (15)

where:

- $K_{oc}^{oc}$ is the partitioning coefficient between component c and organic carbon, [-]; and
- $f_{oc}$ is the fraction of organic carbon in the soil, [-].

Other relationships have been used to describe the sorption behavior of organic solutes, including the Freundlich and Langmuir isotherms (Schwarzenbach et al., 1993).

### 1.4 Rate of Mass Transfer

The linear relationship presented in Equation 5 can be explicitly expressed for the various exchanges of mass. For example, for rate limited mass transfer between NAPL and gas (volatilization rate), the linear driving force is:

$$J_{gn,c} = M_c\rho_gT_{gn,c}\left(K_{gn,c}^e x_c^n - x_c^g\right)$$ (16)

An implicit assumption in Equation 16 is that the rate of volatilization is controlled by resistance in the gas phase, since it is assumed that there is no boundary film within the NAPL phase (Weber and DiGiano, 1996). This is generally true for a well-mixed NAPL, or where the volume of the NAPL phase is relatively small, as may be the case for residual NAPL blobs trapped in the porous medium.

Similarly, the rate of dissolution is:

$$J_{wn,c} = M_c\rho_wT_{wn,c}\left(K_{wn,c}^e x_c^n - x_c^w\right)$$ (17)

In this case, the rate of dissolution is assumed to be controlled by the aqueous phase, based on similar considerations (Weber and DiGiano, 1996).
The overall mass transfer coefficient, $T_{pp1,c}$, can be separated into a mass transfer coefficient $\tau_{pp1,c}$ [L T$^{-1}$], that depends on physicochemical properties of the mixed phase, properties of the porous media and fluid phase velocity, and a specific interfacial contact area, $a_{pp1}$, [L$^{-1}$], as follows:

$$T_{pp1,c} = \tau_{pp1,c} a_{pp1}$$  \hspace{1cm} (18)

The specific interfacial contact area refers to the actual interfacial area [L$^2$] divided by the volume of the porous media [L$^3$].

There has been significant work in the last few years to obtain precise expressions for $\tau_{pp1,c}$ (Brusseau, 1992; Geller and Hunt, 1993; Miller and Mayer, 1990; Pfannkuch, 1984; Powers et al., 1991). However, it has proven impossible up to now to measure the interfacial contact area experimentally. The empirical correlations available for calculating the inter-phase mass transfer coefficient, $\tau_{pp1,c}$, have used “surrogates” for the interfacial contact area, such as grain size (Pfannkuch, 1984), drainage and imbibition soil parameters (Miller et al., 1998) and more recently NAPL saturation (Miller and Mayer, 1990; Powers et al., 1992), with varying degrees of success. Although it appears that NAPL saturation is an acceptable surrogate for $a_{pp1}$, in reality as the dissolution or volatilization process advances, $S_n$ (which depends on the volume of NAPL present in the blob or NAPL pool) decreases at a different rate than $a_{pp1}$. In addition, even for two equivalent NAPL saturations, not all the interfacial area is in contact with flowing fluid (water or vapor) in the same proportions, since each pore space is likely to be different and some pores provide more contact area than others.

The mass transfer coefficient is a function of many parameters (Miller and Mayer, 1990):

$$T_{pp1,c} = f(\mu_p, \rho_{p1}, \rho_p, \rho_{p1}, d_s, V_p, D_{mol}^{p,c}, \sigma_{wn}, g, S_p, S_{p1})$$ \hspace{1cm} (19)

where:

- $D_{mol}^{p,c}$ is the molecular diffusion coefficient of component c in phase p, [L$^2$ T$^{-1}$]; and
- $d_s$ is the diameter of particles in the porous medium, [L], typically the median grain size, $d_{50}$.

and since there is no fundamental theoretical model to describe the mass transfer phenomenon, empirical correlations have been developed for the mass transfer coefficient as a function of physicochemical properties of c, fluid flow velocity and the properties of the medium, which are typically captured in dimensionless parameters such as the Schmidt number, $Sc$:

$$Sc = \frac{\mu_p}{\rho_p D_{mol}^{p,c}}$$ \hspace{1cm} (20)

and the Reynolds number, $Re$:

$$Re = \frac{V_p \rho_p d_s}{\mu_p}$$ \hspace{1cm} (21)
The mass transfer coefficient is embedded in the Sherwood number, $Sh$:

$$Sh = \frac{T_{pp,c} d_s^2}{D_{P,c}^{mol}}$$  \hspace{1cm} (22)

Table 1.1 presents a number of mass transfer correlations formulated using this approach. As can be seen, the progression over the years has been to include more parameters that influence the rate of mass transfer, since the available empirical correlations do not accurately predict mass transfer rates. Starting with the work by (Miller and Mayer, 1990), the correlations begin to consider the effect of $S_n$, by including a term for the NAPL volume fraction, [-]:

$$\theta_n = \phi S_n$$  \hspace{1cm} (23)

(Miller and Mayer, 1990) identify the difficulty in measuring $a_{pp1}$, or even define it mathematically. They correctly point out that the interfacial area will change with time as the NAPL dissolves or volatilizes. In addition, it is difficult to determine an average $a_{pp1}$, since NAPL blobs have very complex shapes. Finally, they address the issue of the effective interfacial contact area, since it is clear that in many cases most of the NAPL surface area is not in contact with a significant amount of air or water, which reduces the rate of mass transfer. By including $S_n$ within their empirical correlation, they attempt to capture the role of NAPL saturation in determining the characteristic length found in $Re$ and $Sh$, since as they point out, it is the NAPL that is providing the transferred mass, not the solid phase of the porous medium. Their power law relationship,

$$Sh = \beta_0 R_e^{\beta_1} \theta_n^{\beta_2} Sc^{1/2}$$  \hspace{1cm} (24)

where:

$$\beta_0 = 12 \pm 2;$$

$$\beta_1 = 0.75 \pm 0.08;$$

$$\beta_2 = 0.60 \pm 0.21;$$

$\beta_0$, $\beta_1$, and $\beta_2$ are fitting parameters from over 70 column experiments. Note that this model predicts that $Sh \rightarrow 0$ as $Re \rightarrow 0$, which is not quite correct, since there is dissolution even for the case where there is no advective flow. The value of $\beta_2$ indicates that as NAPL saturation increases, the mass transfer coefficient increases but not in the same proportion. This is intuitively correct, since one would expect that as $S_n$ approaches unity, the rate of mass transfer would reach an asymptotic value, given that the aqueous phase cannot come into contact with much of the available NAPL. There is however a large variance in $\beta_2$, suggesting that this might not be a completely correct approach for accounting for the interfacial area.
### Table 1.1 Mass Transfer Correlations, from Jia et al., (1999)

<table>
<thead>
<tr>
<th>References</th>
<th>Equation</th>
<th>Valid conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friedlander, 1957</td>
<td>$Sh = 0.89 Re^{0.33} Sc^{0.33}$</td>
<td>$Pe &gt; 1000$</td>
</tr>
<tr>
<td>Levich, 1962</td>
<td>$Sh = \frac{1}{\sqrt{6\pi}} Re^{0.5} Sc^{0.5}$</td>
<td>$Re &lt; 1$</td>
</tr>
<tr>
<td>Pfeffer and Happel, 1964</td>
<td>$Sh = b Re^{0.33} Sc^{0.33}$</td>
<td>all $Pe$</td>
</tr>
<tr>
<td>Wako and Kaguse, 1982</td>
<td>$Sh = \frac{2 + 1.1 Re^{0.5} Sc^{0.33}}{b}$</td>
<td>$2 &lt; Re &lt; 3000$</td>
</tr>
<tr>
<td>Miller et al., 1990</td>
<td>$Sh = 425 Re^{0.7} Sc^{0.66}$</td>
<td>$0.015 &lt; \theta_e &lt; 0.07$</td>
</tr>
<tr>
<td>Parker et al., 1991</td>
<td>$Sh = 1240 Re^{0.79} Sc^{0.90}$</td>
<td>$0.02 &lt; \theta_e &lt; 0.03$</td>
</tr>
<tr>
<td>Powers et al., 1992</td>
<td>$Sh = 57.7 [(\phi - \theta_e) Re^{0.61} J_{20}^{0.34} J_{41}^{0.41}]$</td>
<td>$0.1 &lt; Re &lt; 0.2$</td>
</tr>
<tr>
<td>Gumana et al., 1992</td>
<td>$Sh' = 107 [(Re)/(\phi - \theta_e)]^{0.96} a^{2.54}$</td>
<td>$0.002 &lt; Re (\phi - \theta_e) &lt; 0.017$</td>
</tr>
<tr>
<td>Imhoff et al., 1993</td>
<td>$Sh' = 340 a^{0.87} Re^{0.71} [(\phi - \theta_e)]^{-0.31}$</td>
<td>$0.1 &lt; \theta_e &lt; 0.056$</td>
</tr>
<tr>
<td>Geller and Hunt, 1995</td>
<td>$Sh' = 70.5 Re^{0.82} Sc^{0.69} [(\phi - \theta_e)]^{-0.27} [(\frac{d}{d_p})]^{0.53}$</td>
<td>$0 &lt; \theta_e &lt; 0.056$</td>
</tr>
<tr>
<td>Powers et al., 1994</td>
<td>$Sh' = a Re^{0.87} Sc^{0.21} \frac{\theta_e}{\theta_{ao}}$</td>
<td>$0.039 &lt; \theta_e &lt; 0.060$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 4.13 \pm 0.01$, $\beta_1 = 0.598 \pm 0.073$, $\beta_2 = 0.673 \pm 0.156$, $\beta_3 = 0.369 \pm 0.119$</td>
<td>$0.013 &lt; Re &lt; 0.058$</td>
</tr>
</tbody>
</table>

- $\beta_n = 0.667$ sphere
- $\beta_n = 0.50$ long cylinder with changing dimension of diameter
- $\beta_n = 0.8 - 1.0$ long cylinder with changing dimension of length
- $\beta_n = 0.87$ Disk shaped cylinder with changing dimension of diameter

*a* Boundary layer flow around single spheres.
*b* Boundary layer flow in packed beds.
*c* Combination of experimental data.
*d* Oil dissolution in porous media.
Powers et al., (1994) address the transient nature of the dissolution process, considering that the effective interfacial area of the NAPL blobs is not directly related to saturation, but rather changes with time. Previous models had been developed mostly using data from the initial dissolution period, and only a few consider the changes that occur towards the end of the dissolution process. Their empirical model developed by the authors considers $Re$, $\theta_n$, and other porous medium characteristics:

$$Sh = \frac{T_{wn,c} d_{S0}^2}{D_{w,c}^{mol}} = \beta_0 R e^{\beta_1 \delta} \beta_2 U_i^{\beta_3} \left( \frac{\theta_n}{\theta_{n,0}} \right)^{\beta_4} \quad (25)$$

where:

$\delta$ is a normalized grain size, $\delta = d_{S0}/d_M$, where $d_M$ is the diameter of a "medium" sand grain (0.5 mm) as defined by the US Department of Agriculture (Driscoll, 1986);

$U_i$ is the particle size uniformity index, $U_i = d_{60}/d_{10}$, [-];

and

$\beta_0 = 4.13 \pm 1.01$;

$\beta_1 = 0.598 \pm 0.073$;

$\beta_2 = 0.673 \pm 0.156$;

$\beta_3 = 0.369 \pm 0.119$;

For $\beta_4$, Powers et al., (1994) use geometric considerations. If the NAPL blob is a sphere, then $\beta_4 = 0.667$. This can be derived from the well-known fact that the surface area of a sphere is proportional to volume to the two-thirds power. For cylindrical NAPL blobs where the diameter is decreasing, $\beta_4 = 0.5$. If the length is decreasing, then $\beta_4 = 0.8-1.0$. Experimentally, Powers et al., (1994) obtained a value of $\beta_4 = 0.750 - 0.960$, depending on the porous medium. These experimental values would indicate that NAPL blobs would be closer to a cylindrical shape, with their length decreasing. Based on four different soil types, they obtained the following correlation:

$$\beta_4 = 0.518 + 0.114\delta + 0.10U_i \quad (26)$$

which indicates the $\beta_4$ increases with particle size and particle size distribution. Coarser soils with a mixture of coarse and fine particles would result in a larger dependence of $Sh$ on $\theta_n$.

These studies highlight the need to understand how the effective interfacial contact area changes during the mass transfer process. Since it is not practical to measure or estimate the effective interfacial contact area in the field, it has to be related to measurable parameters. $S_h$ is a logical choice, but it is still important to understand how the NAPL blobs evolve during the mass transfer process, and how the changing shape affects saturation and effective interfacial area. Along these lines, interfacial partitioning tracers are being used in the field to estimate the effective interfacial area (Saripalli et al., 1997; Saripalli et al., 1998). Although the objective of
these studies is to mobilize residual NAPL using surfactants, the interfacial partitioning tracers (IPT) can also be used to estimate the effective interfacial area and thus make a better estimate of the rate of mass transfer. To measure the effective interfacial area using IPT, the retardation of the tracer relative to non-partitioning tracers is used:

$$R_{\text{ift}} = 1 + \frac{a_{nw} K_o}{\theta_w}$$

(27)

where:

- \( R_{\text{ift}} \) is the retardation factor of the interfacial tracer, [-]; and
- \( K_o \) is the interfacial adsorption coefficient, calculated as the ratio of interfacial tracer concentration in the sorbed phase at the NAPL-water interface to that in the aqueous phase, at equilibrium, [L].

It should be noted that there are still some practical issues to be resolved with IPT, since the tracers will also partition to organic carbon present in the soil, not only to NAPL. In this case, Equation 27 must be adjusted to consider the additional retardation, but in addition to this modification, on a practical basis it implies that the tracer signal might be too weak, or large amounts of tracer are needed in this case. However, if successful, these tracers can be combined with partitioning tracers to determine \( S_n \) and \( a_{nw} \) in the field, extending the present studies.

The following sections present a theoretical derivation of the rate of mass transfer at the pore scale, as well as experimental evidence to support our model.

### 2. Objective

Our objective in this study was to theoretically predict and experimentally observe the dissolution and volatilization processes at the pore scale as a function of saturation and pore space geometry for various Non-Aqueous Phase Liquids (NAPLs), and then to determine how the mass transfer coefficient can be derived from pore scale processes, which can then be scaled to field dimensions, and to understand the functional relationship between mass transfer and hydrologic and physicochemical properties and processes. We also sought to determine the relationship between NAPL saturation, \( S_n \), and the effective interfacial contact area between, \( a_{pp1} \), and how well this correlates with. Our hypothesis was that the relationship between \( a_{pp1} \) and \( S_n \) varies with time, is non-linear, but can be expressed as a power function. Our specific objectives are to:

- Develop a conceptual and mathematical model of mass transfer based on pore scale processes;
- Provide a methodology for scaling up our pore scale model to the field scale;
- Confirm our model using pore scale observations of the mass transfer process
3. Building a Conceptual Model of Mass Transfer from the Pore Scale

The discussion presented in the introduction began with the classical conceptual model, starting from a large-scale view of the processes, and focusing on the mathematical description of the details using empirical observations. Here, our intent is to build the conceptual model of mass transfer (volatilization or dissolution) starting from the pore scale and then comparing our resulting model against the empirical observations, from this study as well as from previous work.

Consider the pore space depicted in Figure 3.1, where capillary forces trap a blob of NAPL, water is flowing in the surrounding media (from left to right), and NAPL is dissolving into the aqueous phase. The same processes can be considered for volatilization, but for the moment we consider NAPL to water mass transfer. For simplicity, we have depicted a very homogeneous porous media that consists of solid grains that when packed produces pore bodies (large cavities) and pore throats that connect the pore bodies. In a three-dimensional representation, each pore body would be connected to six other pore bodies through six pore throats. We will later explore the implications of the pore space geometry. As shown in Figure 3.2, water flows mostly around the pore body that contains NAPL, since those pathways represent a lower resistance to flow. Nevertheless, it is important to consider the possibility that a certain fraction of the water flows in the crevices surrounding the NAPL blob, at least until we have proven that this process is insignificant under certain circumstances.

The presence of the NAPL blob reduces the available cross-sectional area for water flow, reducing $k_{rw}$. For this discussion, the NAPL blob is assumed to be held in place by capillary forces, and thus has zero relative permeability. If a larger fraction of the pore space was occupied by NAPL blobs (Figure 3.3), $k_{rw}$ would sharply decrease, until most of the water flow in this region of the pore space would essentially be through thin films around the crevices of the pore space (Keller et al., 1997). Note that even under these circumstances, $k_{rn}$ would still be zero, despite the significant change in $S_n$. Our underlying assumption is that the porous media is water wetting, such that water preferentially covers the grains. Although this assumption is not always valid, in particular for soil grains with significant organic content, it is applicable to most soils and permeable consolidated media, unless they have been in contact with oily layers for a considerable time. Seen from a larger scale, Figure 3.3 is very similar to Figure 3.2, with water flowing through the outside of a larger NAPL source zone. Since water will preferentially fill the small pore bodies and throats (displacing any NAPL that might be momentarily trapped in the throats), the NAPL blobs rapidly become disconnected and are thus trapped. A significant change in conditions is needed to remobilize the NAPL blobs (e.g. very high hydraulic gradient, increase in NAPL hydraulic head from a new spill, change in interfacial tension due to the introduction of surfactants via the aqueous phase, decreased viscosity due to the introduction of heat via steam injection).

In Figure 3.4, we present a cross-section of the pore body that contains NAPL. For simplicity, we begin with a discussion of the phase distribution using a rectangular pore cross-section, although we later relax this assumption and consider other pore geometries. A rectangular cross-section captures some of the important features of natural pore cross-sections, where small crevices allow for flow of the most wetting fluid phase past the non-wetting phase(s).
distribution of the two fluid phases is such that the wetting fluid is near the solid surface and the non-wetting phase is in the middle of the pore space. Experimental evidence of this arrangement can be seen in Figure 3.5 for a NAPL blob surrounded by water in a realistic physical model of porous media. Note that although the assumption that the pore body is rectangular is not correct, it is closer to reality than the assumption that the pore body has a circular cross-section, which would reduce flow through water films to practically zero. The radius of curvature of the NAPL/water interface, $r_{n/w}$, is dictated by the interfacial tension and the contact angle, as described in the Young-Laplace’s equation (Adamson, 1982):

$$P_{cap} = \frac{2\gamma_{nw} \cos \phi_{nw}}{r_{cap}} = \frac{2\gamma_{nw}}{r_{n/w}}$$

(28)

where

- $P_{cap}$ is the capillary pressure difference between NAPL and water, [$M L^{-1} T^{-2}$];
- $r_{cap}$ is the capillary radius, [L];
- $\gamma_{nw}$ is the interfacial tension between NAPL and water, [$M T^{-2}$];
- $\phi_{nw}$ is the contact angle between NAPL and water, [$^\circ$].

A similar formulation can be derived for the NAPL-air interface.

To determine the resistance for water to flow in the corners of the porous media, we consider the areas occupied by each phase. The total pore body cross-section is

$$A_t = L_{p1}L_{p2} = abr_{n/w}^2$$

(29)

where

- $L_{p1}$, $L_{p2}$ are the dimensions of the rectangular cross-section, [L]; and
- $a$, $b$ are the number of interfacial radii across each direction of the pore space, [-].

The cross-sectional area of NAPL in the pore body can be shown to equal:

$$A_n = \left[a(b-2) + 2(a-2) + \pi\right] r_{n/w}^2$$

(30)

so that the cross-sectional area for water flow is simply:

$$A_w = A_t - A_n = \left\{ab - \left[a(b-2) + 2(a-2) + \pi\right]\right\} r_{n/w}^2$$

(31)

For example, for a square cross-section where the NAPL blob happens to form a perfectly circular blob, this reduces to the expected $A_w = (4 - \pi)r_{n/w}^2$, with $a = b = 2$. The circular cross-section is the lower limit of a NAPL blob cross-section. The radius of curvature of the interface thus plays an important role in limiting the flow of water past the NAPL blob. Combining Equations 28 and 31, it can be shown that $A_w$ depends on $\gamma_{nw}$ and $P_{cap}$. 
\[ A_w = A_t - A_n = \left\{ ab - \left[ a(b - 2) + 2(a - 2) + \pi \right] \right\} \left( \frac{2\gamma_{nw}}{P_{cap}} \right)^2 \]  

(32)

To put into perspective the area occupied by water in a typical corner, consider the interfacial tensions and contact angles presented in Table 3.1. Figure 3.6 presents the decrease in \( A_w \) as \( P_{cap} \) increases for a number of common organic liquids in water-wetting media. Chemicals with a large interfacial tension will result in larger areas for water flow. Using Equations 29 and 32, one can determine that in a square pore body \( 30 \times 30 \mu m^2 \), \( r_{nw} = 15 \mu m \) and \( P_{cap} \) for n-Dodecane would be 7 kPa, indicating a relatively small \( A_w = 193 \mu m^2 \), approximately 21% of the original pore body cross-section. However, it should be noted that the values presented in Table 3.1 are for pure compounds, and as the dissolution process proceeds, the interfacial tension drops, since there are now more organic molecules in the aqueous phase. This would decrease the cross-sectional area for water flowing past the NAPL blob. In addition, natural surfactants in porous media, for example those produced by endogenous bacteria, may result in a significant decrease in \( \gamma_{nw} \) and thus \( A_w \).

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Surface tension ( \gamma_{na} ) (mN m(^{-1}))</th>
<th>Interfacial tension ( \gamma_{nw} ) (mN m(^{-1}))</th>
<th>Contact Angle ( \phi_{nw} ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-chlorobutane</td>
<td>24.40</td>
<td>36.1</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>40.04</td>
<td>15.5</td>
<td>69 ± 2</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>35.8</td>
<td>39.8</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>26.92</td>
<td>43.3</td>
<td>30 ± 4</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>32.96</td>
<td>37.4</td>
<td>38 ± 3</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>29.05</td>
<td>37.6</td>
<td>11 ± 3</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>25.58</td>
<td>52.8</td>
<td>17 ± 0</td>
</tr>
<tr>
<td>n-Octane</td>
<td>21.68</td>
<td>51.5</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>30.04</td>
<td>36.1</td>
<td>25 ± 6</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>31.74</td>
<td>47.5</td>
<td>66 ± 2</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>29.5</td>
<td>34.5</td>
<td>38 ± 3</td>
</tr>
<tr>
<td>Water</td>
<td>72.75</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

adapted from Demond (1988)

Poiseuille’s Law for single-phase flow in a pipe is given by (Bird and Stewart, 1960):

\[ Q_p = g_p \Delta P \]  

(33)

where

- \( Q_p \) is the flow of fluid phase \( p \), \([L^3 T^{-1}]\);  
- \( g_p \) is the conductance of the pipe \([L^4 T M^{-1}]\); and
\( \Delta P \) is the pressure gradient across the pipe segment, \([ML^{-1}T^{-2}]\).

The conductance can be expressed as:

\[
g_p = \frac{\pi r_{eq}^4}{8 \mu_p L_t}
\]

(34)

where

- \( L_t \) is the length of the tube or pipe through which fluid flows, \([L]\);
- \( r_{eq} \) is the equivalent radius for cross-sections that are not circular, \([L]\), which can be defined such that the volume of water in the tube is equal to \( \pi r_{eq}^2 L_t \).

The conductance between two pore bodies (e.g., \( i \) and \( j \)), \( g_{ij}^{ij} \), is calculated by summing the series of resistances to flow, considering the conductance of the pore throat connecting the two pore bodies, \( g_p^t \) and the conductivity of the two pore bodies, \( g_p^i \) and \( g_p^j \):

\[
\frac{1}{g_{ij}^{ij}} = \frac{1}{g_p^t} + \frac{1}{g_p^i} + \frac{1}{g_p^j}
\]

(35)

Under most conditions, \( g_p^t \) is smaller and thus dominates the overall conductance, although for small pore bodies, their contribution to \( g_{ij}^{ij} \) is significant. For flow from one pore body to the next, Equation 33 can be rewritten as:

\[
Q_p^y = g_p^y (P_i - P_j)
\]

(36)

and subject to the constraint that mass (and volume) are conserved in each pore space:

\[
\sum_{j=1}^{N} Q_p^{ij} = 0
\]

(37)

Fenwick and Blunt, (1998) have shown that this approach can be used to obtain a very good approximation of the absolute permeability of a porous medium knowing the grain size distribution and using a network model that captures the heterogeneity of the pore body and pore throat dimensions.

In the two-phase system described earlier, the conductance of water, \( g_{ij}^{ij} \), through the corners of the rectangular cross-section is (Ransohoff and Radke, 1988):

\[
g_{w}^{ij} = \frac{A_w r_n^{w}}{\mu_w \chi L_t}
\]

(38)

where
χ is a resistance factor, approximately 250 for a no-slip boundary, [Ransohoff and Radke, 1988].

χ accounts for additional resistance to flow due to the small size of the “tube”, which makes viscous forces much more important. For NAPL, the conductance, \( g_{ij}^n \), is given by:

\[
g_{ij}^n = \frac{\pi r_{eq}^4}{8 \mu_n L_t}
\]

Returning to our example with a pore body of 30 x 30 µm², and \( L_t = 100 \) µm, then \( g_{ij}^w = 1.7 \times 10^{-15} \) m⁴ s kg⁻¹, and \( g_{ij}^n = 1.3 \times 10^{-13} \) m⁴ s kg⁻¹ for n-dodecane if it could be mobilized (i.e. if it was not trapped by capillary forces). For these calculations, \( \mu_w = 1.01 \) g m⁻¹ s⁻¹ and \( \mu_n = 1.58 \) g m⁻¹ s⁻¹. For reference, the conductivity for water in this pore body, if NAPL were not present, would be \( 3.2 \times 10^{-11} \) m⁴ s kg⁻¹. Thus, the reduction in conductivity for the NAPL is roughly two orders of magnitude since water occupies the crevices, and for water the conductivity is reduced by more than four orders of magnitude as it is forced to flow through a much smaller cross-section.

We will now focus on estimating the mass transfer from the NAPL blob in Figure 3.1 to the surrounding aqueous phase. Three important processes need to be considered: (1) molecular diffusion from the blob to upstream and downstream water; (2) dissolution into pore water trapped in the crevices which is then transported advectively downgradient; and (3) mixing of waters with different concentrations of dissolved NAPL constituents. We will address each one of them separately and then combine the solution to understand the relative importance of each process.

**Molecular Diffusion**

Consider the pore space presented in Figure 3.7, which is a close-up of Figure 3.1. As soon as organic molecules transfer from the NAPL blob to the surrounding water phase, they begin to diffuse by Brownian motion towards upstream and downstream regions, which we will indicate with subscripts \( u \) (upstream) and \( d \) (downstream). Consider an “inlet” location far enough upgradient that upstream diffusion is insignificant. The concentration of organic at that point is \( C_{c,u}^w \). The concentration at a point just upstream of the NAPL blob (point U in Figure 3.6, which is at a junction between pore bodies), \( C_{c,u}^w \), may be different from \( C_{c,u}^w \) due to molecular diffusion. The concentration next to the NAPL blob is at the solubility limit (i.e. in equilibrium, as described in Equations 5 and 12), \( C_{c,u}^{sw} \). If we assume that the distance between NAPL and point U is \( L_u \), then the concentration gradient is:

\[
\frac{(C_{c,u}^{sw} - C_{c,u}^w)}{L_u}
\]
Applying a mass balance around this point, we can see that the mass of solute c transported by water flowing past point U is:

\[
Q_w (C_{c,u}^w - C_{c,j}^w) = -D_{w,c}^{mol} A_p^u \left( \frac{C_c^{e,w} - C_{c,a}^w}{L_u} \right)
\]  

(41)

where

- \( D_{w,c}^{mol} \) is the molecular diffusion of c in water, \([L^2 T^{-1}]\);
- \( A_p^u \) is the cross-sectional area for water flowing past point U, \([L^2]\).

Equation 41 indicates that the mass of solute transported by molecular diffusion (due to the concentration gradient) is swept away by the water flowing past point U, once we account for the mass of c that was already in the water at the inlet. At this point, we neglect the small flow of water through the crevices, which we address later on.

By definition,

\[
\frac{Q_w}{A_p^u} = \frac{q_w}{\phi S_w}
\]  

(42)

and using the definition of the Peclet number, \( Pe \):

\[
Pe = \frac{q_w L_u}{D_{w,c}^{mol}}
\]  

(43)

which is the dimensionless ratio of the advective to diffusive transport, we can rearrange Equation 41 to express the difference in concentrations as a function of \( Pe \):

\[
C_{c,u}^w - C_{c,j}^w = \frac{C_{c,u}^{e,w} - C_c^{e,w}}{1 + \frac{Pe}{\phi S_w}}
\]  

(44)

From Equation 44, we can see that for very low flowrates (\( Pe \ll 1 \)), the concentration around the pore blob approaches the equilibrium concentration, \( C_{c,e}^{e,w} \). For very large flowrates (\( Pe \gg 1 \)), the right hand side becomes very small, which indicates that \( C_{c,u}^w \rightarrow C_{c,j}^w \), i.e. the concentration at the upstream point is very close to the inlet concentration, since solute c is being swept away much faster than it can diffuse from the NAPL blob.

The exact same derivation can be used to derive the formulation for the downstream point D, assuming a symmetrical geometry in our idealized porous medium:

\[
C_{c,d}^w - C_{c,j}^w = \frac{C_{c,d}^{e,w} - C_c^{e,w}}{1 + \frac{Pe}{\phi S_w}}
\]  

(45)
Again, for very low flowrates \((Pe \ll 1)\), the concentration around the pore blob approaches the equilibrium concentration, \(C_{c}^{e,w}\). For very large flowrates \((Pe \gg 1)\), \(C_{c,d}^{w} = C_{c,j}^{w}\), since solute \(c\) is again being swept away much faster than it can diffuse from the NAPL blob.

**Transport from Crevice**

Transport of solute \(c\) out of the crevice by water creeping past the NAPL blob is governed by the advective flow of water past the NAPL. We can assume that the water is flowing slowly enough for complete mixing of the water in the crevice such that the concentration everywhere within this region is \(C_{c}^{e,w}\). The mass transported out of the crevice is then:

\[
Q_{w}^{ud}C_{c}^{e,w} = g_{w}^{ud}(P_{u} - P_{d})C_{c}^{e,w}
\]  

(46)

The change in concentration from Point U to Point D due to this mass flux is then:

\[
\frac{\partial C_{c}^{w}}{\partial x} = \frac{C_{c,u}^{w} - C_{c,d}^{w}}{L_{ud}} = \frac{g_{w}^{ud}(P_{u} - P_{d})C_{c}^{e,w}}{A_{p}}
\]  

(47)

where

- \(L_{ud}\) is the length between Point U and Point D, \([L]\); and,
- \(A_{p}\) is the cross-section of the pore body, \([L^2]\).

At very low flowrates \((Pe \ll 1)\), the pressure differential between Point U and Point D is quite small, and given that the conductance through this path is much lower than through “NAPL-free” pore bodies, the change in mass from Point U to Point D due to transport through the crevice is quite small. In the limit, as \(Pe \to 0\), \(C_{c,u}^{w} = C_{c,d}^{w} = C_{c}^{e,w}\).

**Mixing of Pore Water**

Water from different pathways mixes again after the NAPL blob, as shown in Figures 3.6 and 3.2. Water at \(C_{c,u}^{w}\) mixes with water at \(C_{c,i}^{w}\) to form water at the next point below Point \(i\), to produce water at a concentration \(C_{c,i+1}^{w}\). The change in concentration from \(i\) to \(i+1\) is then:

\[
C_{c,i+1}^{w} - C_{c,i}^{w} = M(C_{c}^{e,w} - C_{c,i}^{w})
\]  

(48)

where

\[
M = \hat{\vartheta} \left[ \frac{g_{w}^{ud}L_{p}(P_{u} - P_{d})C_{c}^{e,w}}{A_{p}} \right] + (1 - \hat{\vartheta}) \left[ \frac{1}{1 + \frac{Pe}{\phi S_{w}}} \right];
\]

\(\hat{\vartheta}\) is the fraction of water flow through the crevice, \([-\]]; and
$L_p$ is the distance between Point $i$ and Point $i + 1$, [L], approximately the length of a pore body.

In the limit, for a small distance,

$$\frac{C_{c,i+1}^w - C_{c,i}^w}{L_p} \approx \frac{\partial C_c^w}{\partial x}$$

From Equations 4 and 5, the rate of mass transfer is approximately equal to the advective flux, neglecting dispersion at the pore scale. Then,

$$q_w \frac{\partial C_c^w}{\partial x} \approx \tau_{mv,c} a_{nw} (C_c^{e,w} - C_c^w)$$

(50)

Comparing Equations 48 and 50, the mass transfer coefficient, $\tau_{mv,c}$, can be related to $M$ using:

$$\tau_{mv,c} a_{nw} = \frac{Mq_w}{L_p}$$

(51)

Finally, using the definition of $Sh$ (Equation 22) and $Pe$ (Equation 43),

$$Sh = \frac{\tau_{mv,c} a_{nw} d_{50}^2}{D_{mol}^{nw,c}} \approx \frac{Mq_w L_p^2}{D_{mol}^{nw,c} L_p} = \frac{Mq_w L_p}{D_{mol}^{nw,c}} = MPe$$

(52)

where we make the assumption that $d_{50} \sim L_p$, since these two dimensions are of the same order of magnitude. We have thus derived an expression for $Sh$ (and thus the mass transfer coefficient) that depends on $Pe$ and the parameters included $M$, which combine molecular diffusion, transport of solute out of the crevices and mixing of pore waters after passing the NAPL blob. Through $M$, we have also captured a dependence of $Sh$ on $S_n (= 1 - S_w)$, thus accounting for the change in the rate of mass transfer with decreasing $S_n$.

By looking at the two extreme conditions, we can see how the model behaves. When $Pe \ll 1$, $M$ is nearly 1, since the most important process is molecular diffusion and the concentration around the NAPL blob is essentially the same, nearly $C_c^{e,w}$. In this case, $Sh$ is directly proportional to $Pe$. When $Pe \gg 1$, $M$ can be shown to be proportional to $Pe^{-1/2}$, and thus $Sh$ is proportional to $Pe^{1/2}$.

It should be noted that the model is valid for either dissolution or volatilization. However, in the case of volatilization, air transport through the crevices is no longer a valid process, since the crevices are likely filled with a thin water film that is strongly bound by capillary forces. For extremely dry soils, NAPL will be the most wetting phase, so there will still be no air flow in the crevices until the mass of the NAPL blob is small enough to allow air to pass through.

How does this model compare with the empirical observations? First, a comparison of $Re$, $Sc$ and $Pe$, using Equations 20, 21 and 43, indicates that:
\[ Pe = \frac{q_p d_{50}}{D_{p,c}^{mol}} = \frac{\mu_p}{\rho_p D_{p,c}^{mol}} \frac{q_p \rho_p d_{50}}{\phi S_p \mu_p} \]  

(53)

Since the empirical studies of mass transfer referenced above have been conducted using the same fluid and at constant pressure and small differences in temperature, \( \mu_p \) and \( \rho_p \) have not varied significantly, and thus it is logical that \( Sh \) appears to be insensitive to \( Sc \). For the (Miller and Mayer, 1990) and (Powers et al., 1994) empirical correlations presented above in Equations 24 and 25 respectively, \( Sh \) appears to depend on \( Pe \) to a power of from 0.6 to 0.75. The model derived from a consideration of pore scale processes varies from 0.5 to 1 as \( Pe \) decreases, which is consistent with the empirical observations, which have typically been performed at \( Pe \) ranging from 10 to 1000. The observed variability in the exponent of the empirical correlations may be explained by the fact that the underlying processes for mass transfer are changing as \( Pe \) varies.

If we relax the assumption that the pore body is rectangular, and consider a more complex pore geometry with nooks and crevices, we will see that there will be regions of the crevice where the NAPL practically “squeezes” out the water film, since the crevice is round and approximately equal in radius to \( r_{n/w} \). In other areas of the pore space, the crevice will actually allow a significantly larger cross-sectional area for water flow, in particular for crevices with angles less than 90°, where NAPL cannot penetrate as far. However, it is clear from our analysis that water flow through the crevices is very slow and thus mass transport here is not very significant.

The model presented here should be valid for high \( S_n \), since the assumptions are essentially the same, although in those cases at the local scale water flow through the crevices would be more important (and thus the rationale for considering it in the model). At a larger scale, the larger NAPL zone looks just like a big blob which most of the water will flow around, very similar to what is presented in Figure 3.7. In those cases, mass transfer occurs mostly at the periphery of the NAPL zone.

In the case that three fluid phases are present (NAPL, water and air), which is common in the vadose zone since there is generally some water content, one has to consider the spreading coefficient, \( C_{se} \), of the three-phase system. Although it was initially considered that only spreading NAPLs could form films in a porous medium, (Dong and Chatzis, 1995b) have theoretically predicted and experimentally verified that non-spreading NAPLs can form thick films in the crevices of the pore space, depending not only on the spreading coefficient and capillary pressures but also on the geometry of the crevice. Thick NAPL films may provide additional channels for NAPL flow at low NAPL saturations, resulting in very low residual NAPL saturations. Because many NAPLs of environmental significance are non-spreading, the role of NAPL films is important in modeling the flow of three phases in the subsurface. Blunt et al., (1995) observed rapid NAPL (iso-octane) film flow in the corners using capillary tubes with square cross-section, in a time-frame that is environmentally significant. In micromodel studies, NAPL films have been observed for Soltrol, which is spreading (Oren and Pinczewski, 1995). For non-spreading NAPLs, Oren and Pinczewski (1995) and Oren and Pinczewski (1992) did not observe NAPL films.

The spreading coefficient, \( C_S \) is defined as:
\[ C_s = \gamma_{gw} - (\gamma_{nw} + \gamma_{gn}) \]  

Typically, \( \gamma_{gw} > \gamma_{nw} > \gamma_{gn} \), but the magnitude of the sum of interfacial tensions \( \gamma_{gn} + \gamma_{ow} \) can be larger than \( \gamma_{gw} \), resulting in a negative spreading coefficient, as is the case for many hydrocarbons (e.g. decane and higher hydrocarbons) and chlorinated solvents (e.g. carbon tetrachloride, trichloroethylene, tetrachloroethylene) as well as for some NAPL mixtures. This means that on a flat surface, NAPL will form droplets and will not spread. If \( C_s > 0 \), the NAPL will spread between water and gas, as occurs for the lighter hydrocarbons.

The interfacial tensions can change as the interfaces age, i.e. they become contaminated with molecules from the other fluids. Even for fairly immiscible fluids, the dissolution of NAPL in water, the volatilization of NAPL and water to the gas phase, and the formation of molecular NAPL films over the gas/water interface (if \( C_s > 0 \)), result in a decrease in \( \gamma_{gw} \) that is usually larger than the changes in \( \gamma_{gn} \) and \( \gamma_{nw} \), resulting in a change in the spreading coefficient. The aged spreading coefficient is considered here as the equilibrium spreading coefficient, \( C_s^e \). When thermodynamic equilibrium is reached, \( C_s^e \leq 0 \) (Adamson, 1990).

Free-energy calculations and experimental work by Dong and Chatzis (1995b) have shown that NAPL layers may exist in a porous matrix for \( C_s^e \leq 0 \), and that the NAPL phase will imbibe into crevices in the porous medium. Fenwick and Blunt (1998) have shown theoretically that layers of NAPL may be present in a crevice, provided that the geometry and ratio of capillary pressures are within certain ranges. Figure 3.8 presents the situation for (a) a circular cross-section, (b) a square cross-section and (c) a more realistic pore space configuration. In the case of the circular cross-section, only a film will exist if \( C_s > 0 \), and will be very thin, of molecular thickness. Flow through these thin films is very slow, and may result in drainage of NAPL phase from the porous media only over very long time frames. On the other hand, these very thin films present a large surface area for volatilization of the NAPL to the gas phase. For the configurations in Figures 3.8b and 3.8c, thick NAPL layers may be present.

For the geometry of a crevice shown in Figure 3.9, an NAPL layer will be present as long as the ratio of the NAPL-water interfacial radius, \( r_{nw} \), to the gas-NAPL radius, \( r_{gn} \), is below a critical ratio, \( R_c \). Fenwick and Blunt (1996) assumed that the NAPL layer would disappear when the NAPL/water and gas/NAPL contacts with the solid surface coincided, i.e. when points A and B in Figure 3.9 meet. Thus:

\[ R_c = \left( \frac{r_{nw}}{r_{gn}} \right)_c = \left( \frac{\gamma_{nw}P_{gn}}{\gamma_{gn}P_{c\text{w}c}} \right)_c = \cos(\theta_{gn} + \beta) / \cos(\theta_{nw} + \beta) \]  

where

- \( \beta \) is the half-angle of the crevice, [°]
- \( \theta_{gn} \) is the gas/NAPL contact angle, [°]; and
- \( \theta_{nw} \) is the NAPL/water contact angle, [°];
and assuming that $\theta_{gn} \geq \theta_{nw}$. Having three phases in equilibrium imposes a constraint on the contact angles and interfacial tensions (Zhou and Blunt, 1997):

$$\gamma_{gw} \cos \theta_{gw} = \gamma_{gn} \cos \theta_{gn} + \gamma_{nw} \cos \theta_{nw}$$  \hspace{1cm} (56)

where $\theta_{gw}$ is the gas/water contact angle measured at thermodynamic equilibrium.

For a completely water-wet surface, $\theta_{gw} = \theta_{nw} = 0$, and from Equations 54 and 55 we find (Kalaydjian, 1992):

$$\cos \theta_{gn} = 1 + C^{e} \mathcal{M}_{gn}$$  \hspace{1cm} (57)

Keller et al., (1997) have shown experimentally that these NAPL and water films are present and that they do in fact play a role in the movement of these fluid phases through the porous media under three-phase flow conditions. With respect to the mass transfer processes, in the case of non-spreading NAPLs the situation is very similar for the two-phase (NAPL-water) case presented above, except that air is now the fluid phase which carries most of the component c in the gas phase, and that the flow of air through the crevices is practically zero for most cases.

For the case of a spreading NAPL, the situation is quite different. As shown in Keller et al., (1997), NAPL will spread around the gas phase, forming a very thin layer between the water film on the porous media surface and the gas phase. Thus, under these conditions mass transfer is expected to be extremely rapid, since the interfacial contact area between NAPL and air is very large. The rate of mass transfer is then limited by the rate at which the gas flow removes the volatilized NAPL components, which is a function of the relative permeability of the gas phase, and thus of $S_{n}$, $S_{w}$ and $S_{g}$.
4. Experimental Approach

To study in detail the dynamic dissolution and volatilization processes at the pore scale and to be able to quantitatively measure NAPL saturation and interfacial area requires a setup that non-intrusively permits the observation and recording of pore scale processes. In this project, we developed a micromodel setup, which we had previously successfully applied to observe pore scale displacement of NAPL during two- and three-phase flow conditions (Keller et al., 1997). Micromodels have up to now been used mostly for studying two- and three-phase flow behavior, with petroleum engineering and environmental applications (Chatzis et al., 1988; Dong and Chatzis, 1995a; Oren and Pinczewski, 1992; Oren and Pinczewski, 1995; Wan and Wilson, 1994; Wilson, 1994). Micromodels are well suited for studying mass transfer processes at the pore scale. A recent paper by Jia et al., (1999) uses glass micromodels to study NAPL solubilization in pore networks. Previous work (Mayer et al., 1999; Miller and Mayer, 1990; Pfannkuch, 1984; Powers et al., 1992; Powers et al., 1994; Wilkins et al., 1995) was performed at larger scales (sand packs and cores), such that $S_n$ is measured macroscopically and there is practically no possibility of determining the actual $a_{pp1}$. Work by Powers et al., (1992) was the closest to determining actual saturation, using a castable NAPL to obtain solidified polystyrene blobs, but the method used to generate the solid blobs results in a modification of the actual NAPL saturation (due to shrinkage and change of interfacial tensions) and the correlation between $S_n$ and $a_{pp1}$ is inferred rather than observed.

The micromodel setup (Figure 4.1) allows us to observe the mass transfer processes within a controlled pore scale geometry, with a known fluid (water or vapor) flow rate. We capture the images dynamically through a video camera for either immediate numerical processing or storage for future numerical processing of the digitized images. From the micromodel images we can directly and simultaneously determine both $S_n$ and $a_{pp1}$ as a function of time. We measure the outlet concentration of dissolved or volatilized NAPL in the flowing phase using Gas Chromatography. Given the small pore volume in the micromodel, we make the assumption that the outlet concentration is the same as the bulk concentration in the flowing fluid within the micromodel.

**Micromodel construction**

The micromodels planned for this work were designed with the following objectives in mind:

- produce a realistic representation of actual pore geometry
- generate a model with the correct dimensions for pore scale processes
- use a media which simulates typical wetting properties of natural media
- allow easy reproduction of the micromodels, for comparison studies

To achieve these objectives, a thin slice of Berea sandstone was imaged through an optical microscope and then digitized, by Hornbrook et al. (1991). To improve the connectivity in the micromodel, the digitized image was modified slightly. The pattern was then repeated 100 x 100 times. The digital image of the pore space was then transferred to a chrome plated glass mask, at no magnification from the original sandstone thin slice. Using technology similar to the
manufacture of microchips, the image was photochemically etched on a silicon wafer, at a constant etching thickness (micromodels have been constructed with etching depths ranging from 15 to 60 µm, for different studies). The final etched repeat pattern is shown on Figure 4.2. Pore diameters range from 3 to 30 µm. Figure 4.3 is a scanning electron micrograph of a section of the repeat pattern, which shows the shape of the grain walls and the regularity of the etching depth. The porosity of the micromodel has been experimentally determined to be 42%. We are able to make identical micromodel reproductions.

The etched silicon wafer is then placed between two glass plates. The top glass plate is attached to the silicon wafer using anodic bonding, to avoid contamination from organic adhesives. Four ports are constructed on the top plate to allow independent injection of three phases and an outlet port. The bottom plate is attached with epoxy to the silicon wafer, and is mainly to provide support for the micromodel.

The silicon surface is oxidized by oxygen after etching, leaving a water-wetting silica surface, approximately 10 nm deep. To ensure that the model remains water-wet, carbon dioxide is introduced to displace the air, and then water is injected, which eventually dissolves the carbon dioxide, allowing the wetting fluid to saturate the model completely. This is typically followed by injection of a 10% acetic acid solution into the micromodel for at least 50 pore volumes. The acetic acid is flushed out with distilled water for at least 100 pore volumes. In all cases the model is strongly water-wet in the presence of air.

**Image Capture and Processing**

An industrial microscope (Nikon Optiphot-M) is used to image the micromodel pore space. Since the silicon wafer is too thick to transmit light; we use reflected light to view the fluids in the pore space. The setup also allows capture of fluorescence from fluids or tagged colloids in the pore space. The images are captured using a CCD TV-camera (Optronics DEI-470) at a high resolution (1/2" CCD Color Image Sensor, 470 Line Horizontal Resolution). The video image is acquired by a computer using a video frame grabber (Flashpoint by Integral Technologies).

The images are processed using MATLAB (The Math Works, Inc.) or NIH Image, to determine saturation and interfacial area. To calculate saturation and interfacial area, we subtract the image of the micromodel with only one phase (typically the air phase) from the image with two or more saturations, to isolate the fluid phases from the pore grains in the image. We then distinguish from the fluid phases (air, water or NAPL) based on the small but measurable differences in color and opacity. We calibrate this information from observations of each phase directly through the microscope. We can then use numerical integration to determine the volume associated with each phase in a particular pore space (and thus obtain the saturation), as well as the interfacial area. We use again the image of the micromodel grains to subtract the area that is not in contact with flowing fluid. Once the procedure is coded, we efficiently process many images to generate a map of saturation and interfacial contact area for the entire micromodel, as a function of time (i.e. as the mass transfer process advances).
Concentration in Aqueous or Gaseous Phase

The concentration in the aqueous or gaseous phase, depending on the particular experiment, is sampled at the micromodel outlet port. The samples are collected using a gas-tight 1 µL syringe, and the concentrations are measured using a GC/MS (HP5890/5970B).

Flow Rate and Pressure Drop

Flow rate is measured at the outlet, using digital flowmeters (ADM2000, J&W Scientific for the gas phase and Fischer Scientific Model 1000 for the aqueous phase). Pressure is measured for the inlet and outlet lines using calibrated pressure transducers (Celesco DP-25). Given knowledge of the flow rate and pressure drop from single phase flow (water or gas), we can determine the relative permeability-saturation relationship when the NAPL phase is present, which is dynamic given the change in NAPL saturation as the dissolution or volatilization process advances. Our experience with micromodels indicates that the best mode of operation is to have a constant pressure drop across the micromodel, supplying the flowing fluid (air or water) from a constant pressure reservoir. Typically the outlet is at atmospheric pressure. This avoids sudden surges in pressure that are caused with a constant flow rate using a pumping arrangement; the surges are due to rapid changes in local relative permeability based on local changes in phase saturation, either during the movement of NAPLs or during their dissolution or volatilization.
5. Experimental Results

The experimental studies were divided into two sections: (1) volatilization experiments; and (2) dissolution experiments.

5.1 Experimental Observation of Volatilization at the Pore Scale

A number of experiments were conducted using hexane, acetone and hexadecane volatilizing to air. In general, the volatilization process is fast at this scale, since these organic compounds are all relatively volatile.

The first set of sequences presents the volatilization of acetone to air (Figures 5.1 to 5.3) in various regions of the pore space presented in Figure 4.2. As can be seen in Figure 5.1a,b, we obtain a relatively large visual contrast between the acetone blob (light color) and the pore grains and air (darker color). With a little training, one can easily recognize the pore grains since they are typically closed figures, while the flowing fluid (air in this case) appears to have no boundaries. In addition, the flowing fluid is slightly lighter than the pore grains. The conditions for this set of experiments were a pressure drop across the micromodel of 8.3 kPa (12 psi) and a temperature of 23 °C. Since the micromodels have previously been wetted with water, we assume that a thin film of water covers the surface, and thus NAPL is not in direct contact with the grain surface. Since the water film is only a few tens of nanometers thick, it is not visible under the present conditions.

At the beginning of the sequence in Figure 5.1a, we observe several NAPL blobs, including one which spans over two pore bodies, since the connecting pore throat has dimensions which are of similar size as one of the pore bodies, and the snap-off effect observed by Keller et al., 1997) and Lenormand and Zarcone (1988) has not yet occurred. As can be seen in this sequence, the effective interfacial contact area is mostly at the pore throats, which represents a much smaller area than the total surface area of the NAPL blobs. After 99 seconds, the NAPL blobs have shrunk in size and the large blob on the left has reconfigured, withdrawing to a single pore body, which is logically the larger of the two. Further rearrangements occur throughout the volatilization process as the NAPL blob finds positions of lower energy. Note for example how the NAPL blob adopts a spherical shape (circular in this quasi-two-dimensional porous media) once it does not have enough volume to occupy the entire pore body (e.g. 204, 379, 390, and 401 s).

The rate of mass transfer at the pore scale is strongly dependent on the diffusion of mass in the upstream and downstream directions. For example, molecules leaving the NAPL blob highlighted with a circle in Figure 5.1a must diffuse out through some rather small pore throats (on the order of 3 to 5 µm). Once past the pore throats, these molecules are swept away by the flowing gas phase, so the rate-controlling step is molecular diffusion through these thin throats. Note however the longer time required to volatilize this particular NAPL blob with respect to the surrounding blobs, where diffusion is not so constrained. It is possible to appreciate within this relatively rectangular pore body with some narrow crevices how there is the possibility for the flowing fluid to move into these regions. In a three-dimensional porous medium, these
crevices might be sufficiently large to allow continuous airflow, sweeping away molecules that have transferred to the gas phase.

The general pattern observed in Figures 5.1 to 5.3 is a gradual rearrangement of the NAPL blob to a lower surface energy configuration. The NAPL blob eventually becomes spherical and might move to a corner within the pore body if the surrounding fluid flow is sufficiently rapid to displace it. We have even observed the movement of the very small spherical NAPL blobs out through some of the larger pore throats at the end of the mass transfer process. Figures 5.1 to 5.3 represent three sets of series collected at separate locations of the micromodel, as the mass transfer zone swept through the micromodel. However, one can compare Figures 5.2a,b,c,d and 5.3a,b, and see that these rearrangements are fairly consistent for equivalent regions of the porous medium (remembering that in the micromodel we have 100 x 100 equal representative pore volumes (REV)). The main difference is the concentration of the gas phase sweeping through the particular region. Since Series 2 (Figure 5.2) was captured near the inlet of the micromodel, the gas phase contains little acetone, and the volatilization process occurs readily. Further downgradient, (Figure 5.3, Series 3), the concentration of acetone in the gas phase is higher, and the volatilization process does not proceed significantly until fresh air sweeps this region.

We have captured these observations in a schematic description of the sequence of rearrangements in our simplified quasi-rectangular pore body, connected to other pores through the corners, as shown in Figures 5.4 and 5.5. The generalized behavior of the NAPL/air (or in the case of dissolution NAPL/water) effective interfacial contact area, \( a_{pp1} \), as a function of \( S_n \) is shown in Figure 5.6. The units for \( a_{pp1} \) in Figure 5.6 are not relevant, although they are in \( \mu m^2 \). Initially the pore is highly saturated with NAPL and the only contact with the flowing fluid is through the exposed interface in the pore throats. Once mass begins to transfer to the flowing fluid (via molecular diffusion through the pore throats), \( a_{pp1} \) increases, since the flowing fluid is now exposed to more of the NAPL surface area. Active flushing of the free pore space may occur, although in general fluid flow through this region is expected to be slow, given that there is not a significant pressure gradient across the pore body. As the mass transfer process proceeds and the NAPL blob slowly recedes, \( a_{pp1} \) remains generally constant, until the point where the NAPL blob reconfigures to a spherical shape. At that point, there is a sudden increase in the effective interfacial contact area, as more of the flowing fluid can contact the NAPL blob. However, this increase is short-lived, since \( a_{pp1} \) begins to sharply decrease as the NAPL sphere becomes smaller and smaller. Thus, although the behavior of \( a_{pp1} \) with respect to \( S_n \) is highly non-linear, it can be understood and generalized.

Series 1 depicts a number of NAPL blobs that resided in the upper left-hand corner of the REV presented in Figure 4.2. The image analysis indicates that the total area of the image is 307,200 pixels, of which 133,909 pixels are filled by pore space, resulting in a porosity of 0.44 for this region. The area of the pore space initially filled with acetone in Series 1 is 49.3% (i.e. \( S_t = 0.493 \)). As shown in Figure 5.7, \( S_t \) decreases for this set from 0.493 to 0.135 in 423 s. Figure 5.8 presents the non-linear behavior of The effective interfacial contact area as a function of time. The effective interfacial contact area as a function of NAPL saturation (Figure 5.9) shows the expected behavior predicted by our conceptual mass transfer model (Figures 5.4 to 5.6), decreasing gradually at first, then rising sharply when the NAPL blobs in general are
spherical, and then decreasing rapidly since at this point the exposed surface is much larger, relative to the volume of the NAPL blobs.

Series 2 comprises several NAPL blobs, which were located in the lower right-hand corner of the REV presented in Figure 4.2. Presented is the almost complete disappearance of NAPL during the volatilization process, controlled mostly by three large NAPL blobs trapped in this region. Note how the accessibility of the pore bodies (i.e. the relative widths of the pore throats leading to the pore bodies) determines to a large extent which NAPL blob disappears first. Eventually all the blobs follow the same predictable transition from a somewhat rectangular shape that fills the entire pore body and even a fraction of the pore throat, to a spherical shape which then disappears relatively fast. The same general behavior is observed for Series 3.

Figure 5.10 presents the rate at which NAPL saturation decreases for these two series. Series 2 disappears faster than Series 3 given its proximity to the inlet port of the micromodel. The initial decrease in saturation with time (i.e. the rate of mass transfer) is essentially linear in both cases, since the flowrate of the sweeping gas phase is constant; the pressure drop across the micromodel is constant at 8.3 kPa. The difference in the initial slope between Series 2 and 3 is due to the smaller concentration gradient experienced by the NAPL blobs in Series 3. While $S_n$ is initially decreasing at a rate of $1.73 \times 10^{-2}$ $\%$ s$^{-1}$ for Series 2, $S_n$ is decreasing at a rate of $1.01 \times 10^{-2}$ $\%$ s$^{-1}$ for Series 2. Thus the concentration gradient is 59 $\%$ smaller for the blobs in Series 3. The effective interfacial contact area exhibits the behavior described earlier, rising slowly (or almost constant) during the initial phase of the volatilization, then changing rather abruptly as the NAPL blobs become spherical, and then dropping rapidly as mass is lost at the end (Figure 5.11). The general relationship between $S_n$ and $a_{ng}$ (Figures 5.12 and 5.13) follows our expectations, but is highly non-linear and cannot be captured by a power law relationship. A phenomenological explanation is required, such as the sequence presented in Figure 5.4.

Figures 5.14 and 5.15 present two series for the volatilization of hexadecane to air. The general volatilization process is similar to that observed for acetone, although the rearrangement of the NAPL blob and the location of the spherical residual varies somewhat. We don’t consider this to be a significant factor in the overall rate of mass transfer. Note the significantly greater time needed to volatilize essentially the same mass, due to the lower $P_{sat}$ for hexadecane, which sharply reduces the concentration gradient.

In Figures 5.16 to 5.20, five different hexane blobs are volatilized to air in different regions of the micromodel. The corresponding relationship between NAPL saturation, $S_n$, and effective interfacial contact area, $a_{ng}$, is presented in Figures 5.21 to 5.25. As can be seen, the individual NAPL blobs follow the generalization made in Figures 5.4 to 5.6. In particular the sequence captured in Figure 5.18 (and its corresponding relationship in Figure 5.23) follows quite closely our conceptual model.

We feel quite confident that these images present a generalizable behavior of NAPL volatilization, which we have captured in Figures 5.4 to 5.6 under “ideal” conditions, which serve to synthesize our observations.
5.2 Experimental Observation of Dissolution at the Pore Scale

To study the dissolution process, we used the toluene/water and hexadecane/acetone pairs. The rationale was that toluene dissolves relatively fast in water, but hexadecane dissolves much more slowly. Thus, we choose a solvent which was closer to hexadecane, to increase the rate of dissolution, but which was still polar enough to result in the right configuration in the porous medium.

First we present two series that capture the dissolution process for toluene into water. Figure 5.26 presents a NAPL blob near the lower right-hand corner of the REV (Figure 4.2). As can be seen, in general there is not a significant difference in NAPL blob morphology between NAPL blobs in water and those in contact with air. The most important difference is the slightly greater cross-sectional area available for water flow around the NAPL blob, since water strongly wets the surface. Similar to the volatilization process, $S_n$ follows a relatively predictable decrease with time, accelerating in the last steps of the dissolution process (Figure 5.27), whereas $a_{nw}$ increases at the beginning of the dissolution process, then remains relatively constant for some time, rises sharply once the blob becomes spherical and then declines rapidly as the spherical blob quickly loses mass to the surrounding flowing fluid (Figure 5.28). This results in an overall relationship between $S_n$ and $a_{nw}$ (Figure 5.29) that follows closely the generalized model presented in Figures 5.4 to 5.6. The dissolution process follows the same general pattern observed earlier for the volatilization process.

Figures 5.30 (a-y) present an important variant on the normal sequence presented so far. In this case, the initial NAPL blob clearly spans over two pore spaces, connected through a rather stretched section spanning the connecting pore throat, which is approximately 12 µm in width. As the dissolution process advances, the bridge of NAPL across the pore throat stretches until after about 200 s it snaps-off, as expected (Figure 5.30c). The NAPL blob on the right-hand side of the image disappears sooner (Figure 5.30d), since it is closer to the inlet port (i.e. the mass transfer zone reaches it sooner). The sequence continues until the blob on the right-hand side becomes spherical and eventually disappears, while the one on the left-hand side only slowly begins to decrease in size (Figure 5.30n). Note how the NAPL blob on the right-hand side begins to travel towards the left, presumably due to the small but non-negligible flow of water towards the left-hand side of the image (Figure 5.30q). Finally after 1267 s, the left-hand side NAPL blob is completely gone (Figure 5.30y). When the aggregate behavior is observed (Figure 5.31), $S_n$ appears to be atypical to the previous observations, since it first follows the typical decline but then stabilizes for a while at a particular $S_n$ ( ~ 0.18). However, the analysis of the $S_n$ for each NAPL blob is more aligned with our previous observations (Figure 5.32). This sequence serves to illustrate how $S_n$ decreases only slightly while the NAPL blob is in contact with water close to the solubility limit, and only begins to decrease significantly in size (i.e. mass transfer becomes very important) when the NAPL blob is exposed to mostly fresh water (i.e. $C_{w,d}^w \approx 0$). The behavior of $a_{nw}$ relative to $S_n$ also appears somewhat atypical for the complete blob, but follows closely our previous experience for the individual blobs (Figure 5.33). This is a reminder that the aggregate (macroscopic) behavior may be more difficult to explain, since it is a combination of many simple events which on aggregate don’t seem to follow a simple pattern.
The last set we present is the dissolution of hexadecane in acetone (Figure 5.34). The dissolution process proceeds in the expected manner, albeit much slower. Four hexadecane blobs can be appreciated, which are highlighted with red circles in the first image of this sequence. The dissolution of the large NAPL blob in the center of the pore space follows the predictable pattern from our conceptual model. Note the movement of the NAPL blobs once they become spherical, as they respond to the pressure gradient in the flowing fluid (acetone in this case). The rate of mass transfer can be appreciated in Figure 5.35. The rate of mass transfer is fairly constant until about 1800 s, and then once the NAPL blobs become spherical the rate accelerates since $a_{nv}$ increases substantially. As we have seen before, the conceptual model for mass transfer from a NAPL blob to the surrounding flowing fluid follows the same general pattern regardless of the NAPL/fluid pair.
6. Conclusions and Discussion

In Section 3 we present a mathematical model that phenomenologically describes mass transfer (whether volatilization or dissolution) at the pore scale. The model can be scaled up to the dimensions of a laboratory core or a field site. The model predicts that $Sh$ depends on $Pe$ to a power of one-half when the flowrate of the flowing fluid (air or water) is very slow ($Pe << 1$). As $Pe$ increases, the model predicts that the dependence of $Sh$ on $Pe$ increases, until at very large flowrates ($Pe >> 1$), $Sh$ is directly proportional to $Pe$. Since $Pe$ is the ratio between advective and diffusive processes, this indicates that at the higher flowrates typical of laboratory core experiments it would be likely to observe a dependence greater than 0.5. In fact, most recent experiments (Miller and Mayer, 1990; Powers et al., 1994) indicate that the dependence of $Sh$ on $Pe$ in laboratory experiments ranges from 0.6 to 0.75, well in line with the prediction of the phenomenological model. One would expect that for field studies of the rate of mass transfer, the correct exponent would be closer to 0.5, since most field sites operate at low $Pe$ values. Under these conditions, the assumption that local equilibrium (LEA) exists seems to be justified. However, for active remediation (e.g. Soil Vapor Extraction, vigorous pump and treat, or soil flushing with surfactants which raise the solubility limit), LEA may not be valid, and $Sh$ is likely to depend more on $Pe$ (i.e. a higher exponent would be warranted, closer to the laboratory experiments).

The model includes considerations for advective transport around the NAPL blob (both within the pore body where the NAPL blob resides and outside that pore body), as well as diffusive transport from the NAPL blob to the region where fresh water flows, removing the dissolved organic molecules. It also considers mixing of different pore water downgradient from the NAPL blob. The combination of these processes is sufficient to explain most of the mass-transfer behavior at the pore scale. From calculations of the conductance of water through the thin cross-sectional area within the pore body crevices surrounding the NAPL blob, we conclude that advective transport through these crevices is not a very significant contributor to the overall mass transfer process, and that most of the mass transfer is done through molecular diffusion from the NAPL blob to the external flowing fluid through the narrow pore throats.

In addition to the dependence of $Sh$ on $Pe$, it also depends on $S_n$, via the molecular diffusion process. The dependence of $Sh$ on $S_n$ is not as easily explained, given that the underlying relationship is between $Sh$ and $a_{nv}$, which up to now had been difficult to characterize. However, an evaluation of the functional relationship indicates that as $S_n$ becomes smaller, the rate of mass transfer (and thus $Sh$) increases, so there is an inverse relationship between $Sh$ and $S_n$. It is also readily seen that as $S_n$ becomes very small, the flowing fluid can more easily flow past the NAPL blob, and a larger interfacial area is contacted, also increasing the rate of mass transfer.

In Section 5 we present evidence that the phenomenological model described in Section 3 is correct. Even at the low $Pe$ of these micromodel experiments, advective transport through the crevices is small relative to the diffusive transport, since the cross-sectional area for the flowing fluid is very small, in particular when the cross-section is a complex mixture of geometries. We observe how the mass transfer process follows essentially a power law behavior, with an increasing exponent as the end of the mass transfer occurs. This acceleration in mass transfer can be explained by the fact that once the NAPL blob begins to shrink, it allows more crevice
transport, the surface area contacted by the flowing fluid increases, and overall mass transfer grows.

We present a model for the dependence of $a_{nw}$ on $S_n$, which is based on our observations and generalization of the mass transfer process. This model predicts that, at the pore scale, initially as $S_n$ decreases, $a_{nw}$ begins to increase, since the NAPL blob shrinks slightly and exposes more interfacial contact area. Once the NAPL blob has shrunk enough to become spherical (thereby reducing its surface energy), $a_{nw}$ sharply increases, only to decrease as the spherical blob rapidly loses size. Thus in large part explains the observed acceleration of mass transfer at the end of the mass transfer process for an individual NAPL blob. This behavior appears to be generalizable to any fluid/fluid pair (NAPL/gas, NAPL/water, and probably air/water), and can be easily codified for further analysis in a network model.

One important consideration is that the aggregate behavior of a combination of NAPL blobs is more complex, even though it is only the sum of simple processes. This macroscopic complexity is responsible for the empirical approach undertaken to date to explain mass transfer, and also the variance between different experimentalists. The use of numerical modeling tools (e.g. network models) based on these observations at the pore scale can serve to explain the macroscopic behavior, and elucidate the relative importance of the various processes and the degree of NAPL saturation.

This project has served to establish a fundamental understanding of mass transfer, which is of relevance under many natural and engineered systems, including site remediation through a variety of methods. The phenomenological model serves to underpin the empirical models, and explain their variance. The experimental observations from this project will serve to develop more complete numerical models that can be used for prediction of the rate of mass transfer under a variety of conditions, including different soils, fluid pairs, saturation and factors that affect the physicochemical properties of the compounds of interest.

The results of this project suggest several exciting new research directions. Future research will be directed at:

- Codifying the mathematical model derived in this study into a network model, to study the interactions between different pore bodies, and predict the aggregate behavior of NAPL blobs;
- Incorporating our mathematical model into a macroscopic numerical model that simulates multiphase flow and mass transfer, such as UTCHEM, to study field sites where mass transfer limitations are important and evaluate the accuracy of our model in predicting the rate of mass transfer;
- Developing further the limitations that moisture content would pose on the rate of volatilization of NAPL, as the water fills some of the pore throats and constrains the rate at which the flowing gas phase can remove the diffusing organic molecules.
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