Effect of spreading coefficient on three-phase relative permeability of nonaqueous phase liquids

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[1] Three-phase flow conditions are encountered regularly, for example, during migration of released NAPL through the vadose zone, certain stages of soil vapor extraction, bioslurping, or generation of gases by microbes. To model three-phase flow, a common approach is to construct three-phase relative permeabilities based on a combination of two-phase relative permeabilities. Although this circumvents a lack of experimental data, it can lead to serious underprediction or overprediction of residual NAPL saturation. This can mislead decision makers that need to predict whether a particular spill will reach the water table or predict the speed of a NAPL front or conduct an assessment of the performance of remediation actions. Experimental data to estimate three-phase relative permeabilities is sparse. A study by DiCarlo et al. [2000a] generated significant experimental information. Their analysis focused on the high NAPL saturation region, given their emphasis on oil reservoir engineering. For environmental applications the low saturation region is of more interest. Using this data set, we derived a set of empirical relations that relate NAPL three-phase relative permeability \( k_{rn} \) to NAPL saturation \( S_r \) and spreading coefficient \( C_s \) for \( S_r \) less than about 0.1, such that:

\[
A_{k_r} = \frac{A_1 S_r^{A_{25}}}{A_1 S_r^{A_{25}}} \exp \left(-1.3 C_s\right) + A_2 (2.1 - 0.60 C_s + 0.036 C_s^2).
\]

At higher \( S_r \), \( k_{rn} \approx S_r^4 \), independent of \( C_s \). We present a pore-scale conceptual model that provides a phenomenological basis for the use of \( C_s \) as a predictor of \( k_{rn} \) at low \( S_r \). We then present a number of simulated case studies that highlight the effect of these three-phase relative permeabilities on risk assessment or remediation design. INDEX TERMS: 1831 Hydrology: Groundwater quality; 1832 Hydrology: Groundwater transport; 1829 Hydrology: Groundwater hydrology; 1803 Hydrology: Anthropogenic effects; KEYWORDS: residual saturation, multiphase flow, numerical simulation, risk assessment, remediation


1. Introduction

[2] Three-phase flow conditions occur in a number of environmental situations that are relevant for risk assessment, conceptual model definition, active remediation design, as well as monitored natural attenuation. These conditions are encountered, for example, as light or dense nonaqueous phase liquids (LNAPL or DNAPL) migrate through the unsaturated zone, displacing air and water from the pore space, or when LNAPL pools are subjected to a rising and falling water table and capillary fringe, thus smearing the organic contaminants and allowing for further NAPL displacement under three-phase flow conditions. In some cases, three-phase flow conditions are generated during dewatering operations, in an attempt to reduce the water saturation in preparation for NAPL vapor extraction. Bioslurping, where a lance is inserted into the soil formation at the NAPL pool-capillary fringe interface to remove the NAPL and provide for additional air movement for biodegradation, generates three-phase flow conditions. In addition, the generation of gases from biogeochemical processes (e.g., \( \text{H}_2\text{S}, \text{CO}_2, \text{CH}_4, \text{H}_2 \)) as the organic pollutants degrade or as a result of inorganic transformations, can also lead to three-phase flow conditions, which result in additional NAPL migration.

[3] Why is it important to consider three-phase flow conditions? There is a need to make accurate prediction of the time needed for a NAPL spill to reach groundwater, so that appropriate risk management actions can be undertaken. It is also important to determine whether a NAPL spill will reach residual saturation before it reaches the capillary fringe or the water table, since in many instances regulations are written such that action is taken only if there is a concern that groundwater resources are vulnerable. Lack of adequate methods for estimating the three-phase relative permeabilities or the residual saturation under these conditions often leads to the simplifying assumption that two-phase information is adequate. Assuming that NAPL flows under two-phase (NAPL/air) conditions in the vadose zone will result in inaccurate estimates, and may thus lead to an incorrect assessment. If the residual saturation under three-phase flow conditions is significantly lower than under two-phase conditions, the NAPL will travel much further than anticipated and at a significantly different rate.

[4] There is a considerable body of literature on two-phase relative permeabilities, using theoretical and empiri-
cular approaches, for example, work by Burdine [1953], Wyllie, [1962], and Mualem [1976]. The U.S. Department of Agriculture Salinity Laboratory has compiled data from numerous experiments with many different soils, to develop an extremely useful data set for predicting two-phase relative permeabilities using the van Genuchten-Mualem model [van Genuchten, 1980]; this data can be accessed through the Rosetta model (http://www.usdl.ars.usda.gov/ MODELS/rosetta/rosetta.htm) to estimate the relation between two-phase relative permeability (air-water) and saturation of either phase. These air-water relative permeabilities can be scaled using the Leverett J-function approach [Leverett, 1941] in conjunction with Mualem’s method, to estimate the corresponding NAPL-water relative permeabilities. The work by Demond and Roberts [1987, 1993] underscored the need to normalize the effective permeabilities by the NAPL permeability, \( k_m \), at residual water saturation, \( S_{wr} \), to obtain a better fit. 

Only a few experimental investigations of three-phase relative permeability relations have been conducted [e.g., DiCarlo et al., 2000b]. Given the lack of experimental data on three-phase relative permeabilities, a number of investigators have developed models to generate them from available or calculated two-phase relative permeabilities, for example the work by Stone [1973], Faust [1985], or Parker and Lenhard [1990a]. Other researchers have attempted to generate the three-phase relative permeabilities using network or percolation models, such as the work by Fenwick and Blunt [1998], Blunt et al. [1995], Celia and Ferrand [1989], Soll and Celia [1989], Held and Celia [2001]. While these approaches are useful to conceptualize the processes involved during multiphase flow, it is important to incorporate experimental findings into any generalized relation between relative permeability and phase saturation.

In this study, we review the existing literature on three-phase flow relations and reevaluate the experimental results of Sahni et al. [1999] and DiCarlo et al. [2000a, 2000b]. We then develop a relation between NAPL relative permeability, NAPL saturation and spreading coefficient under three-phase flow conditions, with particular emphasis on the behavior at low NAPL saturations, which tend to determine the long-term behavior of a NAPL spill. To illustrate the behavior of different NAPLs with rather different three phase relative permeabilities, we conducted numerical simulations using a modified version of UTCChem version 6.0 [De Blanc et al., 1996].

2. Conceptual and Mathematical Model

The conceptual model of a typical contaminant spill into porous and fractured media has been put forward by several researchers, including Abriola [1989], Mercer and Cohen [1990], Parker et al. [1994]. In either the unsaturated or saturated zones, NAPL traveling downstream may reach a low enough saturation to become disconnected and immobile, forming ganglia. 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. From a mass balance of each phase and the application of Darcy’s Law, we obtain the following governing equations for a three-phase system in porous media [Abriola and Pinder, 1985; Van Geel and Sykes, 1997], neglecting interphase mass transfer, reactions or sorption at this stage of the spill, since we are mostly interested in multiphase flow processes:

\[
\frac{\partial}{\partial t} (\phi S_p) + \nabla \cdot \left( \frac{k_{pp}}{\mu_p} (\nabla P_p + \rho_g g \nabla z) \right) + q_p = 0 \tag{1}
\]

where

- \( \phi \) the matrix porosity (dimensionless);
- \( S_p \) the saturation of phase \( p \) in the void space of the porous medium (dimensionless);
- \( t \) the time [T];
- \( k \) the intrinsic permeability tensor of the porous medium [L\(^2\)];
- \( k_{pp} \) the relative permeability of phase \( p \) (dimensionless);
- \( \mu_p \) the dynamic viscosity of phase \( p \) [M L\(^{-1}\) T\(^{-1}\)];
- \( P_p \) the pressure of phase \( p \) [M L\(^{-1}\) T\(^{-2}\)];
- \( \rho_p \) the mass density of phase \( p \) [M L\(^{-3}\)];
- \( g \) the gravitational acceleration vector [L T\(^{-2}\)];
- \( z \) the vertical dimension [L];
- \( q_p \) any source or sink term for phase \( p \) [L T\(^{-1}\)];
- \( p \) the subscript that denotes the various phases in the porous medium (\( g \) = gas, \( w \) = aqueous, \( n \) = NAPL).

The saturations are subject to the constraint that \( S_w + S_g + S_n = 1 \). In addition, capillary pressure relations can relate the various pressures, \( P_{ij} = P_i - P_j \), where \( i \) and \( j \) are any two of the three phases and \( P_{ij} \) is the capillary pressure between the two phases. There are two key relations (constitutive equations) imbedded in equation (1), namely the capillary pressure-saturation \((P_c-S)\) and relative permeability-saturation relations \((k_r-S)\). A significant amount of work has already been done on three-phase \( P_c-S \) relations, including theoretical and experimental studies [e.g., Lenhard and Parker, 1987; Celia and Ferrand, 1989; Parker and Lenhard, 1990b; Kalaydjian, 1992; Soll et al., 1993; Busby et al., 1995; Hofstee et al., 1997; Fenwick and Blunt, 1998]. As mentioned earlier, much less is known or understood about the three-phase \( k_r-S \) relationship.

The \( P_c-S \) functions are based on a scaled variant of the van Genuchten [1980] function:

\[
S_i = \left[ 1 + \frac{(\alpha h_{ij}^n)\beta_j}{S_{ij}} \right]^{-m} \tag{2}
\]

where \( S_i \) is a scaled saturation, \( S_i = (S_i - S_{iw})/(1 - S_{iw}) \) for phase \( i \) (dimensionless); \( S_{iw} \) is a residual or minimum phase saturation for phase \( I \) (dimensionless); \( h_{ij} = \beta_j h_{ij} = \beta_j (P_i - P_j)\) is a scaled capillary head between phases \( i \) and \( j \) [L]; \( \beta_j \) is a scaling factor specific for each fluid pair, (dimensionless); \( h_{ij} \) is the capillary head between phases \( i \) and \( j \) [L]; \( \rho^p \) is a reference density, usually the wetting fluid [M L\(^{-3}\)]; \( \alpha \) and \( n \) is parameters that capture hydraulic properties of the porous media (see Rosetta model information for more details), (dimensionless); \( m = 1 - 1/n \), (dimensionless).

The scaling coefficients are derived from Lenhard and Parker [1987], namely,

\[
\beta_{gw} = \alpha_{gw}/\sigma_{gw} \tag{3}
\]
\[
\beta_{sw} = \alpha_{gw}/\sigma_{sw} \tag{4}
\]
where $\sigma_{gw}$ is the uncontaminated air-water interfacial tension (i.e., surface tension of the pure phases), $\sigma_{gw}$ is the interfacial tension between gas and NAPL and $\sigma_{nw}$ is the interfacial tension between NAPL and water. To account for the effect of organic components in the gas and water phases, the scaling factor is adjusted as follows:

$$\beta_{gw} = \frac{\beta_{gw}^\prime}{(\sigma_{gw} + \sigma_{nw})}$$

As a reference, the scaling factor for the air-water system $\beta_{gw} \equiv 1$, considering pure air as the gas phase.

[13] Implicit in the approach by Parker and Lenhard [1990a] is the need to have well-established residual saturations for all three phases, under three-phase flow conditions. The gas or water phases essentially reach the same residual saturation under two-or three-phase flow conditions. Since the gas phase is the least wetting phase in all cases, it is mostly constrained by the total liquid saturation that fills up the smaller pore bodies and pore throats, such that $k_{rg}$ is only a function of $S_g (= 1 - S_L)$. When water is the wetting phase, it can flow (slowly) even through thin water layers coating the porous media, but strong capillary forces in small crevices hold residual water in place. Thus water flow depends more on pore size distribution and media wetting properties, such that the two-phase relation between $k_{rw}$ and $S_w$ can be used to predict $k_{rw}$ for three-phase flow conditions with reasonable accuracy.

[14] However, the NAPL residual saturation under three-phase flow conditions is very difficult to determine a priori, which limits the usefulness of Parker and Lenhard’s approach, particularly at low $S_n$, Work by Blunt et al. [1994], Blunt et al. [1995], Keller et al. [1997], and Fenwick and Blunt [1998] on the role of thin NAPL layers between gas and water indicates that NAPL can reach very low “residual” saturations under three-phase flow conditions, for spreading and even for many nonspreading organic liquids.

[15] The balance of forces at the interface determines the spreading behavior of an organic liquid placed on a water film in the presence of air. The spreading coefficient, $C_s$, is defined as [Adamson, 1990]:

$$C_s = \sigma_{gw} - \sigma_{nw} - \sigma_{nn}$$

[16] Typically, $\sigma_{gw} > \sigma_{nn} > \sigma_{nw}$, but the magnitude of the sum of interfacial tensions $\sigma_{nn} + \sigma_{nw}$ can be larger than $\sigma_{gw}$, resulting in a negative spreading coefficient, as is the case for many hydrocarbons (e.g., decane and higher hydrocarbons) and some chlorinated solvents (e.g., tetrachloro-

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**Table 1.** Parameters $\sigma_{nw}$, $\sigma_{gw}$, $\sigma_{nw}$ and $C_s$ for Selected NAPLS, Based on the Compilation by Dendrom and Linther [1993]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma_{nw}$ mN m</th>
<th>$\sigma_{gw}$ mN m</th>
<th>$\sigma_{nw}$ mN m</th>
<th>$C_s$ mN m</th>
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<tr>
<td>Alkanes</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>n-pentane</td>
<td>49.0</td>
<td>15.5</td>
<td>72.2</td>
<td>7.7</td>
</tr>
<tr>
<td>Cyclohexane</td>
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<td>24.7</td>
<td>72.0</td>
<td>-2.6</td>
</tr>
<tr>
<td>n-hexane</td>
<td>51.1</td>
<td>18.4</td>
<td>72.4</td>
<td>2.9</td>
</tr>
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<td>n-heptane</td>
<td>50.2</td>
<td>19.7</td>
<td>72.6</td>
<td>2.7</td>
</tr>
<tr>
<td>n-octane</td>
<td>50.8</td>
<td>21.6</td>
<td>72.7</td>
<td>0.2</td>
</tr>
<tr>
<td>n-decane</td>
<td>52.0</td>
<td>23.8</td>
<td>72.7</td>
<td>-3.1</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>52.8</td>
<td>24.9</td>
<td>72.7</td>
<td>-5.0</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>52.2</td>
<td>26.6</td>
<td>72.7</td>
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</tr>
<tr>
<td>n-hexadecane</td>
<td>53.3</td>
<td>27.0</td>
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<td>Isopentane</td>
<td>49.6</td>
<td>15.0</td>
<td>72.0</td>
<td>7.4</td>
</tr>
<tr>
<td>Isooctane</td>
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<td>18.3</td>
<td>72.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Diisooaryl</td>
<td>46.8</td>
<td>22.5</td>
<td>71.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Aromatics</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>35.0</td>
<td>28.9</td>
<td>60.6</td>
<td>-3.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>36.1</td>
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<td>61.7</td>
<td>-2.3</td>
</tr>
<tr>
<td>Styrene</td>
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<td>32.0</td>
<td>62.5</td>
<td>-5.0</td>
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<tr>
<td>o-xylene</td>
<td>37.2</td>
<td>29.8</td>
<td>64.2</td>
<td>-2.8</td>
</tr>
<tr>
<td>m-xylene</td>
<td>37.9</td>
<td>29.0</td>
<td>64.6</td>
<td>-2.4</td>
</tr>
<tr>
<td>p-xylene</td>
<td>37.8</td>
<td>28.6</td>
<td>62.8</td>
<td>-3.5</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>38.4</td>
<td>28.8</td>
<td>64.4</td>
<td>-2.7</td>
</tr>
<tr>
<td>Halogenated Aliphatics</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>45.0</td>
<td>27.0</td>
<td>72.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>32.8</td>
<td>27.3</td>
<td>72.6</td>
<td>12.4</td>
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<tr>
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<td>27.8</td>
<td>72.1</td>
<td>16.0</td>
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<tr>
<td>Tetrachloroethylene</td>
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<td>31.7</td>
<td>72.8</td>
<td>-6.5</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>34.5</td>
<td>28.8</td>
<td>72.7</td>
<td>9.4</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>29.6</td>
<td>34.0</td>
<td>72.6</td>
<td>9.0</td>
</tr>
<tr>
<td>Halogenated Aromatics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>37.4</td>
<td>33.6</td>
<td>71.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>
ethylene) 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 (e.g., fresh gasoline spill). Table 1 presents typical values of $s_{nw}$, $s_{gn}$ and $s_{gw}$ for hydrocarbons and chlorinated hydrocarbons, as well as spreading coefficients for these compounds, considering contact with an aqueous solution already at equilibrium with the organic phase, based on data collected by Demond and Lindner [1993].

[17] 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 thin organic layers over the gas/water interface (if $C_s > 0$), result in a decrease in $s_{gw}$ that is usually larger than the changes in $s_{gn}$ and $s_{nw}$, 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, $C_s^e ≤ 0$ [Adamson, 1990], since $s_{gw} ≥ s_{nw} + s_{gn}$.

[18] Free-energy calculations and experimental work by Dong and Chatzis [1995] have shown that NAPL layers may exist in a porous matrix for $C_s^e ≤ 0$, and that NAPL will imbibe into crevices of the porous medium, between the air and water phases. The constraint of the narrow distance between pore walls in the porous medium crevices will force the NAPL to form a layer when air is also present in the pore space, rather than to form a droplet. Fenwick and

Figure 2. Power law fit of relative permeabilities based on experimental observations. Hexane (circles), octane (diamonds), and decane (squares) are presented separately.

Figure 3. Relationship between power law exponent and spreading coefficient.

Figure 4. Relationship between power law coefficient and spreading coefficient.

Figure 5. Comparison between experimental data and predicted three-phase relative permeabilities for hexane, octane, and decane using equations (11)–(13).
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. These conditions have been observed experimentally in micro-models [Dong and Chatzis, 1995; Keller et al., 1997]. The observation of NAPL layers in crevices has led to the prediction that $k_{rn}$ decreases continuously as $S_n$ decreases to very low values for many NAPL-water-gas systems [Blunt et al., 1994; Fenwick and Blunt, 1998].

3. Experimental Evidence

[19] DiCarlo et al. [2000a] and Sahni et al. [1999] presented measurements of three phase relative permeabilities using X-ray CT scanning. Details of the experimental work are discussed in the respective papers. In summary, water-wet sand (sieved to size 120) was packed into a rubber sleeve 7.6 cm in diameter and 87 cm long. The CT measurements were calibrated by scanning the sand dry, saturated with water or saturated with the NAPL of interest. CT scans every 2 cm along the length of the core were analyzed, and using a linear interpolation of the X-ray attenuations at two energy levels (80 and 140 kV), the water, gas and NAPL saturations were obtained. For a set of experiments, sand was saturated with water and then 5 pore volumes of NAPL were passed through to reach $S_{wr}$. Then air which had been saturated with NAPL vapors and water (by bubbling it through two reservoirs) was slowly injected through the top of the system, while water and oil drained out the bottom under gravity. Similar experiments were conducted starting from an $S_{nr}$ initial condition, achieved by first saturating the media with water, then injecting 5 pore volumes of NAPL, then water flooding for 5 pore volumes to reach $S_{nr}$. The data was interpreted using [Sahni et al., 1999]:

$$k_{rn} = -\frac{\mu_n \phi}{k} \int_0^Z \alpha \frac{\partial S_n}{\partial \tau} dz \left( \frac{\partial P_{cm}}{\partial Z} + \Delta P_{gwg} \right)$$

which required the measurement of the NAPL saturations over an extended period of time, on the order of weeks.

Table 2. Sessile Drop Contact Angle on Various Mineral Surfaces From USGS-OFR-90-409a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quartz</th>
<th>Calcite</th>
<th>Biotite</th>
<th>Clay</th>
</tr>
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<td>Cyclohexane</td>
<td>8.5</td>
<td>8.5</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Benzene</td>
<td>11.5</td>
<td>21.5</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>10.5</td>
<td>14</td>
<td>10.5</td>
<td>6</td>
</tr>
<tr>
<td>Toluene</td>
<td>9</td>
<td>14</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>m-xylene</td>
<td>5</td>
<td>6</td>
<td>10.5</td>
<td>N.A.</td>
</tr>
<tr>
<td>o-xylene</td>
<td>8</td>
<td>10.5</td>
<td>12</td>
<td>N.A.</td>
</tr>
<tr>
<td>p-xylene</td>
<td>5</td>
<td>6.5</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>8.5</td>
<td>13.5</td>
<td>10.5</td>
<td>6</td>
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<td>Chloroform</td>
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<td>8</td>
<td>7</td>
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<td>Chlorobenzene</td>
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<td>5</td>
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<td>o-dichlorobenzene</td>
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<td>p-dichlorobenzene</td>
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<td>1, 2, 4-trichlorobenzene</td>
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<td>29.5</td>
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<tr>
<td>Average CHC</td>
<td>18</td>
<td>21</td>
<td>18</td>
<td>6</td>
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aSee Ethington [1990].

Table 3. Contact Angle Through Aqueous Phase on Various Surfaces From Demond [1988]

<table>
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<th>Calcite</th>
<th>Albite</th>
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<td>N.A.</td>
<td>N.A.</td>
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<tr>
<td>n-dodecane</td>
<td>17</td>
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<td>21</td>
</tr>
<tr>
<td>o-xylene</td>
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<td>28</td>
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<tr>
<td>Ethylbenzene</td>
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<td>N.A.</td>
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<tr>
<td>Carbon tetrachloride</td>
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<td>N.A.</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>38</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>1-chlorobutane</td>
<td>10</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>66</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>1, 1, 2-trichloroethane</td>
<td>36</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>38</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>22</td>
<td>31</td>
<td>29</td>
</tr>
<tr>
<td>Average HC</td>
<td>17</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Average CHC</td>
<td>34</td>
<td>31</td>
<td>29</td>
</tr>
</tbody>
</table>

Figure 6. Predicted three-phase relative permeabilities for a number of compounds using equations (11)–(13).

Figure 7. Relative position of NAPL, air and water in a pore.
The initial $C_s$ is used for the correlation, first because it is easier to determine from published interfacial tension data, and second because in many cases the equilibrium (aged) spreading coefficient is close to zero, which would not provide a useful correlation with basic physicochemical properties. The equilibrium $C_s$ is also likely to be influenced by the properties of the medium, such as wettability and organic content; it would be difficult to generalize equations (11)–(13) to all these conditions. Although there is considerable scatter in the experimental data at low $S_n$, it can be seen in Figure 5 that this simple model can be used to more accurately predict $k_{rn}$ in particular at low $S_n$. Figure 5 presents a piecewise fit of the high and low $S_n$ regions to the experimental data, piecing together the high $S_n$ power law behavior ($k_{rn} = S_n^{4}$) with equations (11)–(13). The three-phase relative permeability model predicts that $k_{rn}$ decreases to lower $S_n$ decreases, but is always positive.

In Figure 6 we present the expected behavior of five common organic compounds. This set of equations can be used to determine the "residual saturation" of a given NAPL under three phase flow conditions. Note that this approach can also be used to estimate $k_{rn}$ for organic mixtures, as long as their initial $C_s$ is known, can be measured or estimated. Although additional experimental validation is warranted, this approach is more consistent with the experimental data than three-phase relative permeabilities constructed from two-phase information.

Hui and Blunt [2000] have shown that for a stable NAPL layer to exist, the ratio must meet the following condition

$$\left(\frac{r_{nw}/r_{jn}}{r_{jn}}\right)_{crit} = \cos(\theta_{jn} + \varphi)/\cos(\theta_{jn} + \varphi)$$

where $\varphi$ is the half-angle of the crevice, and $\theta_{jn}$ is the contact angle between phases $i$ and $j$. Tables 2 and 3 present some

### Table 4. Simulated Cases

<table>
<thead>
<tr>
<th>Simulated NAPLs</th>
<th>Hexane</th>
<th>Hexadecane</th>
<th>TCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual saturation</td>
<td>0.001</td>
<td>0.001</td>
<td>0.2</td>
</tr>
<tr>
<td>Injection rate (m³/d)</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

### Table 5. Physicochemical Properties at 20°C

<table>
<thead>
<tr>
<th></th>
<th>Hexane</th>
<th>Hexadecane</th>
<th>TCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>639.7</td>
<td>770</td>
<td>1462</td>
</tr>
<tr>
<td>Viscosity (mN·s/m²)</td>
<td>0.3189</td>
<td>3.24</td>
<td>0.63</td>
</tr>
<tr>
<td>Solubility (mg/L)</td>
<td>9.523</td>
<td>0.0031</td>
<td>1138</td>
</tr>
<tr>
<td>Vapor pressure (kN/m²)</td>
<td>16.02</td>
<td>0.00062</td>
<td>7.30</td>
</tr>
<tr>
<td>Henry’s constant (atm m³/mol)</td>
<td>0.6463</td>
<td>0.074</td>
<td>0.007</td>
</tr>
</tbody>
</table>
Figure 9. Hexane spill in vadose zone with a release rate of 0.1 m$^3$/d. On the right we present the NAPL saturation profile and on the left the corresponding aqueous concentration of the organic compound, for water in the vadozone and in the saturated zone. See color version of this figure at back of this issue.

Figure 10. Hexane spill in vadose zone with a release rate of 0.3 m$^3$/d. See color version of this figure at back of this issue.
measured values of $\theta_{nw}$, $\theta_{gn}$ for hydrocarbons and chlorinated hydrocarbons, based on work by Ethington [1990] and Demond [1988]. For a flat surface, $\varphi = 90^\circ$, and spreading as defined by equation (9) will occur as long as the balance of forces is positive. For a square crevice (a useful conceptual model although not common place in porous media), $\varphi = 45^\circ$. As the crevice becomes narrower, a wider range of NAPLs can form a layer between air and water.

A NAPL with a positive spreading coefficient (e.g., hexane) will form a layer between air and water, continuing to flow through the porous medium, albeit at a slower rate since the resistance to flow increases significantly as the thickness of the layer decreases to only a few molecules thick. Flow is also possible for NAPLs with a small negative spreading coefficient due to the crevice configuration. However, for NAPLs with a more negative spreading coefficient (e.g., decane or hexadecane), there is a point where $S_n$ is low enough to allow the NAPL blob to reconfigure within the pore space to a less energetic configuration. The surface energy of the NAPL layer between air and water becomes greater than the surface energy of the NAPL in a blob (quasi-spherical), resulting in snap-off of the blob from the rest of the organic phase, forming a residual [Keller et al. 1997]. From Figure 2 this appears to occur at $S_{\text{decane}}$ slightly below 10% in this sand. We expect this to occur at $S_{\text{hexadecane}} \approx 0.2$ (Figure 6).

Equations (11)–(13) can be used to generate three-phase relative permeabilities for numerical simulation. Operationally, we found it easiest to create a look up table for each NAPL or NAPL mixture based on their initial $C_s$. Since most multiphase flow simulators require a “residual” saturation, $k_{rn}^{\text{res}}$, even under spreading conditions, one can use Figure 6 to estimate the lowest practical NAPL saturation. For example, $k_{rn}^{\text{res}} = 10^{-5}$ is a practical lower value, but note that the “residual” saturation varies significantly for each NAPL type, ranging from around 0.001 for hexane to 0.20 for hexadecane.

4. Numerical Modeling

We selected UTCHEM version 6.0 for our simulations since it is a multiphase, multicomponent, three-dimensional numerical flow model. The full development of the
UTCHEM model is described in detail by Delshad et al. [1996]. We added default boundary configurations suitable for studies of fluid flow and transport in the vadose zone. An analytic method for calculating the soil thermal profile was also added, and then incorporated temperature-dependent physicochemical properties as well as the three-phase relative permeabilities derived above.

The boundary conditions were designed to allow the movement of gaseous and aqueous phases across the top boundary. Pressure is specified for the lower portion of the right-hand boundary to fix the water table level and allow discharge. All other boundaries are impermeable to fluid flow. A constant head is maintained on the left-hand side of the saturated zone. The modeled area is shown in Figure 8. The 38 m x 12 m domain is discretized with 38 grid blocks in the horizontal direction (x) and 37 grid blocks in the vertical direction (z). The ground surface is at z = 0 m. The initial water table is set at −10 m (red line in Figure 8), with $S_w = 1.0$ at $z = -10.0$. The water saturation above the water table is initially at capillary equilibrium, with $S_w = 0.34$ at $z = 0$. Groundwater flows from left to right. The assumed leaking underground storage tank (UST) is located 19 m away from the left boundary (black polygon in Figure 8). The tank is a cylinder with diameter $D = 0.3$ m.

Figure 12. Hexadecane spill with a release rate of 0.3 m$^3$/d. See color version of this figure at back of this issue.
height $H = 2.8$ m and the top surface is $1$ m below the ground surface. Although a heterogeneous soil could be modeled, for simplicity of the analysis a homogeneous soil with an absolute permeability of $3 \times 10^{-9}$ m$^2$ (silty to clean sand) was considered.

We simulated three NAPLs with significantly different $C_s$: hexane, hexadecane and trichloroethylene (TCE). The NAPL residual saturation was estimated from Figure 6 and was considered constant throughout the model simulation (Table 4). Other input parameters and initial conditions were the same in all cases. For simplicity, the surface soil temperature remained at $20^\circ$C throughout the simulation and rainfall infiltration rate was assumed to be zero at all times (e.g., a paved surface). We simulated a NAPL release lasting 10 days beginning at $t = 0$. Biodegradation of dissolved NAPL constituents was considered negligible in this timeframe, to strictly compare only the physicochemical processes, although the model is capable of simulating biodegradation. Of interest to us was whether the NAPL spill would reach the groundwater table and, if so, in what timeframe, to determine the amount of time available to respond.

We present these simulations based on the three different NAPLs and two injection rates to illustrate: (1) contrasts between transport behavior in the vadose zone for different amount of spills and for different NAPLs, hence different physicochemical properties (Table 5); (2) the effect of the release rate on the arrival time of each NAPL at the groundwater level. For these simulations, we created lookup tables for the relative permeabilities based on our empirical model (equations (11)–(13)) for the low $S_n$ range using the corresponding initial $C_s$, and $k_{rn} = S_n^4$ for high $S_n$.

5. Simulation Results

Figures 9 and 10 present snapshots of the travel of a hexane spill through the vadose zone to the water table at two different release rates. Since the simulated residual hexane saturation is 0.001, only a small amount of hexane is retained in the pores of the vadose zone as the hexane
passes downward. It takes about 220 days for the hexane spill to reach the capillary fringe and spread at the lower release rate (Figure 9) but only 30 days at the higher spill rate, given that the overall travel velocity is much higher as the NAPL front moves at higher relative saturation (Figure 10).

A comparable hexadecane spill would take between 2,400 and 15,000 days to reach the water table (assuming no biodegradation, which of course would have to be considered for this case). Hexadecane would reach the water table much sooner dissolved in pore water and via gas-phase transport (Figures 11 and 12). The TCE spill (Figures 13 and 14) would produce a rather different “footprint”, given the higher dissolution rate of TCE. For the smaller spill (Figure 13) the NAPL pool would be much smaller at all times and, although it is a DNAPL, does not necessarily pass through the capillary fringe since the mass of DNAPL pool is small. The larger TCE spill reaches the water table in about 90 days, or three times longer than hexane, based on the differences in relative permeability (Figure 14). This larger TCE spill would continue to move through the water table and down to a lower permeability lens.

6. Conclusions

We presented empirical correlations for three-phase relative permeability of NAPLs, which can be used to model the behavior of a release in the vadose zone. Although these empirical correlations are based on a relative small number of organic compounds, the conceptual model of the location of NAPL, aqueous and gas phases in the pore spaces and the corresponding surface areas provide a basis for correlating the three-phase relative permeabilities with initial spreading coefficient. To assume that a relative permeability can be constructed from the two-phase relative permeabilities and without considering the differences in properties of the compounds of interest can lead to significant errors in simulation.

The simulations conducted using UTChem and our empirical three-phase relative permeability correlations provide a better understanding of the importance of the differences in three-phase relative permeability for managing an accidental release of NAPL. Spreading NAPLs will migrate very fast, with a high likelihood of impacting groundwater. As the spreading coefficient becomes more and more negative, the likelihood of directly impacting the water table decreases, and other processes such as volatilization and air-water equilibrium become the dominant transport process for these NAPL constituents. Biodegradation would naturally be of importance in the vadose zone.

These results need to be corroborated with controlled laboratory and field experiments, but they highlight the need for understanding in more detail the behavior of NAPLs in the vadose zone.

Acknowledgments. The authors also wish to acknowledge funding by U.S. EPA Exploratory Research grant R826268 and U.S. EPA grant...
References


Figure 8. Finite difference space grid of modeled area (X: 38 m, 38 grids; Z: 12 m, 37 grids; variable grid size).
Figure 9. Hexane spill in vadose zone with a release rate of 0.1 m³/d. On the right we present the NAPL saturation profile and on the left the corresponding aqueous concentration of the organic compound, for water in the vadozone and in the saturated zone.

Figure 10. Hexane spill in vadose zone with a release rate of 0.3 m³/d.
Figure 11. Hexadecane spill with a release rate of 0.1 m$^3$/d.
Figure 12. Hexadecane spill with a release rate of 0.3 m$^3$/d.
Figure 13. TCE spill with a release rate of 0.1 m³/d.
Figure 14. TCE spill with a release rate of 0.3 m$^3$/d.