Effects of source zone heterogeneity on surfactant-enhanced NAPL dissolution and resulting remediation end-points

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Abstract

The effectiveness of removal of nonaqueous phase liquids (NAPLs) from the entrapment source zone of the subsurface has been limited by soil heterogeneity and the inability to locate all entrapped sources. The goal of this study was to demonstrate the uncertainty of degree of source removal associated with aquifer heterogeneity. In this demonstration, source zone NAPL removal using surfactant-enhanced dissolution was considered. Model components that simulate the processes of natural dissolution in aqueous phase and surfactant-enhanced dissolution were incorporated into an existing code of contaminant transport. The dissolution modules of the simulator used previously developed Gilland–Sherwood type phenomenological models of NAPL dissolution to estimate mass transfer coefficients that are upscaleable to multidimensional flow conditions found at field sites. The model was used to simulate the mass removal from 10 NAPL entrapment zone configurations based on previously conducted two-dimensional tank experiments. These entrapment zones represent the NAPL distribution in spatially correlated random fields of aquifer hydraulic conductivity. The numerical simulations representing two-dimensional conditions show that effectiveness of mass removal depends on the aquifer heterogeneity that controls the NAPL entrapment and delivery of the surfactant to the locations of entrapped NAPLs. Flow bypassing resulting from heterogeneity and the reduction of relative permeability due to NAPL entrapment reduces the delivery efficiency of the surfactant, thus prolonging the remediation time to achieve desired end-point NAPL saturations and downstream dissolved concentrations. In some extreme cases, the injected surfactant completely bypassed the NAPL source zones. It was also found that mass depletion rates for different NAPL source...
configurations vary significantly. The study shows that heterogeneity result in uncertainties in the mass removal and achievable end-points that are directly related to dissolved contaminant plume development downstream of the NAPL entrapment zone.

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Keywords: NAPL dissolution; Heterogeneity; Numerical simulation; Upscaling

1. Introduction

The focus of this paper is on problems dealing with potential contamination of groundwater by organic waste chemicals that are in the form of nonaqueous phase liquids (NAPLs). Many investigators have demonstrated the complex flow, entrapment, and transport behavior of these chemicals in heterogeneous subsurface systems (e.g., Kueper and Gerhard, 1995; Illangasekare et al.1995a,b; Held and Illangasekare, 1995; Illangasekare, 1998). Important to the site assessment and risk analysis investigations involving NAPLs is the realization that the contamination will be distributed between free-phase NAPL (pools, residual, and potentially in fractures); sorbed onto the soil matrix; and dissolved in the aqueous phase. Unless removed, the mass present as free phase and sorbed onto the media will provide ongoing sources of dissolved contamination in the aqueous phase. Depending on the physical and chemical characteristics of the contaminant, these sources can be expected to “deliver” mass to the aquifer for extended periods of time. Because of the enormous concerns for long-term groundwater contamination from NAPL sources and the long-term costs associated with pump-and-treat schemes, interest has increased in the application of aggressive free-phase removal technologies such as surfactant-enhanced dissolution and mobilization, chemical oxidation, and steam injection. However, these technologies cannot completely remove NAPLs, especially in complex, heterogeneous aquifers (USEPA, 1992; Grubb and Sitar, 1994). Several factors contribute to incomplete NAPL removal including viscous and capillary resistance of entrapped NAPL, incomplete contact of reactive agents (e.g., surfactant, microorganisms, chemical oxidants) with NAPL at all locations, complexity of NAPL morphology (pools or residual fingers and blobs), and changes in NAPL morphology (e.g., remobilization) and chemical composition during application of remediation technologies. Additionally, in the case of DNAPLs, the complex distribution controlled by unstable fingering makes it difficult to locate all entrapped sources. It is likely that a fraction of the NAPL will remain after source remediation, thus prolonging the potential risks from contamination and subsequent long-term human exposure. The goal of this study was to demonstrate the uncertainty in the degree of source removal associated with aquifer heterogeneity. In this demonstration, source zone NAPL removal using surfactant-enhanced dissolution was considered. The impact of aquifer heterogeneity on the effectiveness of surfactant-enhanced aquifer remediation (SEAR) is evaluated. A numerical model of aqueous and surfactant-enhanced dissolution, in combination with experimental data generated in intermediate-scale laboratory test tanks, is used in this
evaluation. The numerical model predicts the achievable end-point NAPL saturations in the entrapment zone and the downstream dissolved concentrations in the solute plume.

Surfactant-enhanced source removal technologies are based on the ability of surfactant molecules to create low water/oil interfacial tension to reduce capillary forces and thus mobilize entrapped NAPLs. The mobilized NAPLs are surrounded by surfactant molecules forming stable micelles when surfactant concentration is above the critical micelle concentration (CMC). As a result, the apparent aqueous solubility of an NAPL can significantly increase in the presence of surfactants allowing a more rapid cleanup than is typically observed in conventional pump-and-treat techniques. SEAR processes have been tested in a small scale (usually 1-D column experiments), and have been proven to be successful in cleaning up contaminated soils (Pennell et al., 1993, 1994). Taylor et al. (2001) report that although considerable effort has been devoted to surfactant selection and design, field testing at DNAPL sites have achieved mixed results. The effectiveness of SEAR in field applications is usually hindered by the inability of the surfactant to access all the entrapped free-phase NAPL in the source zone.

The developed numerical model is based on an existing three-dimensional finite difference groundwater flow and contaminant transport codes: MODFLOW (McDonald and Harbaugh, 1988; Harbaugh et al., 2000) and MT3D (Zheng, 1990; Zheng and Wang, 1999). The model has the capability to simulate nonequilibrium mass transfer from entrapped NAPL in heterogeneous aquifers taking into consideration the fact that the mass transfer coefficients have to be upscaled to a larger simulation scale. The mass transfer coefficients for natural and enhanced dissolution used for the simulations are based on Gilland–Sherwood type models that were previously developed (Saba and Illangasekare, 2000; Saba et al., 2001).

2. Background

Mass transfer phenomena have been the focus of considerable attention in the literature, but there are still many unresolved issues. While dimensional analysis has shown the mass transfer rate to be a function of several nondimensional groups (Bird et al., 1960), most laboratory work to date have only investigated a few of these. A majority of the laboratory studies have used a first-order rate model to simulate mass transfer in homogeneous porous media with length scales on the order of centimeters (e.g., Miller et al., 1990; Powers et al., 1992, 1994; Imhoff et al., 1994; Imhoff and Miller, 1996). Results from these studies support the establishment of near-equilibrium conditions over relatively short length and time scales. However, field-scale observations do not typically show groundwater plumes to be near equilibrium conditions. Observed concentrations that are much smaller than the equilibrium solubility limit is attributed to dilution by the water coming from the cleaner zones of the aquifer (Sorens et al., 1998). Recent research has focused on investigating mass transfer phenomena in two dimensions (Saba and Illangasekare, 2000; Nambi and Powers, 2000) that allow for more realistic representation of nonuniform flow field in the NAPL entrapment zone.
Miller et al. (1990), based on single-film dissolution models, proposed an expression for mass transfer between the aqueous and organic phases as:

\[ J = \hat{k}(C_s - C) \]  

where \( J \) \([\text{ML}^{-3} \text{ T}^{-1}]\) is the solute mass flux from the immiscible liquid phase to an aqueous phase, \( \hat{k} \) \([\text{T}^{-1}]\) is a lumped mass transfer coefficient, \( C_s \) \([\text{ML}^{-3}]\) is the aqueous solubility of the organic phase, and \( C \) \([\text{ML}^{-3}]\) is the solute concentration in the bulk aqueous phase. As the lumped mass transfer coefficient contains terms that cannot be easily measured at the pore-scale, methods to determine values of \( \hat{k} \) at the macroscopic scale are usually based on empirical correlations containing a modified form of Sherwood number \((Sh)\). The modified Sherwood number that is used in porous media applications is defined as (Bird et al., 1960):

\[ Sh = \frac{\hat{k}d_{50}^2}{D_m} \]  

where \( D_m \) \([\text{L}^2 \text{ T}^{-1}]\) is the molecular diffusion coefficient for the soluble constituent, and \( d_{50} \) \([\text{L}]\) is the mean particle diameter. Several researchers have proposed dimensionless correlations of interphase mass transfer \((Sh)\) to be a function of various dimensionless groups such as Reynolds \((Re)\), Schmidt \((Sc)\), and Peclet \((Pe)\) numbers, etc. (Miller et al., 1990; Powers et al., 1992, 1994; Imhoff et al., 1994). It should be noted that the lumped mass transfer coefficients that are estimated using the modified Sherwood number quantifies the mass transfer that occurs at observation scales larger than the pore-scale when water passes through NAPL entrapment zone (the net rate of mass transfer per unit mass of water flowing). These empirical correlations used in chemical engineering applications are referred to as Gilland–Sherwood models. Although these models developed from data generated in 1-D columns allow for the estimation of mass transfer coefficients to predict NAPL dissolution, they may not provide accurate mass transfer predictions in larger field scales where the groundwater flow is three-dimensional. Saba (1999), Saba and Illangasekare (2000), and Saba et al. (2001) developed upscaleable mass transfer coefficients for both natural and surfactant-enhanced dissolution. A series of experiments were conducted in which externally prepared NAPL \((p\text{-xylene})\) samples with known saturations were placed in a test tank. Several NAPL-source samples with different lengths were used to investigate the scale dependency on mass transfer rate. Aqueous phase \(p\text{-xylene}\) concentrations were measured downstream of the NAPL source and breakthrough curves were analyzed to estimate the rate of mass depletion. Following a tracer test to determine media dispersivity, dissolution behavior under different groundwater velocities was investigated for each of three entrapped source lengths. Through inverse modeling using UCODE (Poeter and Hill, 1998), the transient mass transfer rate coefficients were determined based on the transient values of Reynolds number \((Re)\), Schmidt number \((Sc)\), and volumetric NAPL content during the simulation of the dissolution process. The resulting equation was of the form:

\[ Sh_{\text{nat}} = \alpha (Re)^\beta (Sc)^\gamma \left( \frac{\theta n d_{50}}{\tau L^*} \right)^\eta \]
The parameter $\tau$ is the tortuosity factor of the porous medium, and $L^* [L]$ is the dissolution length. $L^*$ accounts for the path length of the contaminated numerical soil block in the flow direction. This characteristic length parameter allows for the correction of the scale-dependent mass transfer coefficient. The Schmidt ($Sc$) and Reynolds ($Re$) numbers are the properties of flowing fluids where $Sc = \nu D_m^{-1}$ and $Re = d_{50} U^n v^{-1}$. $U^n [L T^{-1}]$ and $v [L^2 T^{-1}]$ are the average linear pore velocity and the kinematic viscosity of the flowing fluid, respectively. $\theta_n$ is the volumetric NAPL content. The constants $\alpha$, $\beta$, $\gamma$, $\eta$, and $\xi$ are empirical fitting parameters that are determined from a multiple, nonlinear regression analysis of the experimental data. Table 1 shows the empirical fitting parameters used for the numerical simulations; these values were determined from the two-dimensional tank experiments reported in Saba et al. (2001).

Using similar laboratory and modeling procedures that were used in the development of correlations for natural dissolution, a relationship was developed by Saba et al. (2001) for surfactant-enhanced dissolution. This relationship is given as:

$$Sh_{surf} = \alpha (Re)^\beta (Sc)^\gamma \left( \frac{\theta_n}{1 - \theta_n} \right)^\eta \left( \frac{d_{50}}{\tau L^*} \right)^\xi \quad (4)$$

The parameters used for the simulations were determined from the tank experiments reported in Saba (1999). As the rate-limited mass transfer depends on the NAPL during mass removal, a dual-gamma system was used in the experiments to monitor the changes in NAPL saturation in the source zone during surfactant-enhanced dissolution. The $\theta_n/(1 - \theta_n)$ term in Eq. (4) effectively takes this NAPL depletion into consideration. The determination of fluid saturations in multiphase systems using the dual-gamma system is described in Illangasekare et al. (1994). The parameters of the model in Eq. (4) are given in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Natural</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>11.34</td>
<td>0.4727</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.2767</td>
<td>0.2793</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.3333</td>
<td>0.5</td>
</tr>
<tr>
<td>$\eta$</td>
<td>1.037</td>
<td>1.642</td>
</tr>
<tr>
<td>$\xi$</td>
<td>–</td>
<td>0.1457</td>
</tr>
</tbody>
</table>

#### 3. Numerical model

Complex models exist for the simulation of surfactant-enhanced dissolution, e.g., UTCHEM by Delshad et al. (1996). A simplified model that has the capability of upscaling the mass transfer processes in heterogeneous systems was developed in this study to demonstrate the effect of heterogeneity on surfactant delivery and hence, the efficiency of source zone treatment.

The mixing of the dissolved NAPL in the source zone and the subsequent downstream migration of the dissolved NAPL are controlled by the local groundwater flow field within
the entrapment zone, regional groundwater flow field, advection, dispersion, and reactive processes. In this study, three-dimensional finite difference groundwater flow model, MODFLOW was used to model the local and regional groundwater flow fields. The solute transport is simulated using MT3D.

A dissolution modeling package developed by Okeson (1995) and Saba (1999) was modified and coupled to MT3D to simulate dissolution of NAPL under conditions of natural groundwater flow and surfactant-enhanced remediation. This modified package allows MT3D to solve for NAPL dissolution based on Eqs. (1) and (2) and the phenomenological models given in Eqs. (3) and (4). The schematic coupling of the major model components is shown in Fig. 1. Given an initial NAPL saturation in each grid block, MODFLOW solves the groundwater flow equation based on modified hydraulic conductivity field resulting from NAPL entrapment. The partially water-saturated or modified hydraulic conductivity ($K_{rw}$), and saturated hydraulic conductivity ($K_{sat}$) can be expressed in terms of the relative permeability ($k_{rw}$) as:

$$K = k_{rw}K_{sat}$$  \hspace{1cm} (5)

Wyllie (1962) proposed the relationship between the relative permeability of the wetting phase and NAPL saturation using Eq. (6) as:

$$k_{rw} = \left( \frac{1 - S_n - S_r}{1 - S_r} \right)^3$$  \hspace{1cm} (6)

where $S_n$ is the NAPL saturation, and $S_r$ is the residual saturation of the aqueous phase. The NAPL saturation $S_n$ as appearing in Eq. (6) and the volumetric NAPL content $\theta_n$ in Eqs. (3) and (4) are related by $S_n = n\theta_n$, where $n$ is the soil porosity. Wyllie’s equation was chosen in the model because it was found to best describe the relative permeability measurement data for the test sands used in our past laboratory investigations (Saba, 1999; Saba and Illangasekare, 2000).

The value of hydraulic conductivity is time-dependent since NAPL content decreases during surfactant-enhanced dissolution. Consequently, during the simulation, the flow field within the NAPL entrapment zone will change accordingly with the updated hydraulic conductivity.

Injection of water or surfactant solution is simulated using the well package of MODFLOW. The delivery of surfactant to the NAPL entrapment zone is simulated by solving the advection–dispersion equation using MT3D for surfactant concentrations. For simplicity, the aqueous phase and the micro-emulsion phase were combined, treating them as a single aqueous phase. In addition, the viscosity and density of the surfactant solution were assumed to be the same as that of water. At the end of each surfactant transport simulation step, finite difference blocks having surfactant concentration greater than the critical micelle concentration are flagged and identified as zones of enhanced dissolution. Within these flagged computational blocks, the mass transfer coefficients are calculated using Eq. (4). In the unflagged blocks where the surfactant concentrations have not reached the CMC, the mass transfer is modeled using Eq. (3) that estimates the mass transfer coefficient for natural dissolution.
When the modified MT3D solves for the mass transfer of NAPL to aqueous phase, it keeps track of the rate of dissolution of the NAPL into the flowing aqueous phase and hence, the rate of depletion of the NAPL mass. Temporal variation of NAPL saturation, effective porosity for the aqueous phase, and relative permeability are updated at the end.
of each simulation time step. With an updated hydraulic conductivity field, MODFLOW simulates the new groundwater flow field within the NAPL source zone.

In order to take the surfactant–NAPL interaction into consideration, the surfactant concentrations within the blocks where the surfactant is used to enhance dissolution were updated at the end of each time step for the subsequent surfactant transport calculation. In a previous research, Ewing (1996) found the solubility of \( p \)-xylene (the NAPL that is used in this study) is proportional to the amount of surfactant (Tween-80) in groundwater. Based on laboratory batch studies, Ewing (1996) proposed the following relationship:

\[
\frac{C}{C_s} = 1 + 2637.3C_{\text{surf}}
\]

where \( C \) is the \( p \)-xylene concentration, \( C_s \) is the solubility of \( p \)-xylene in pure water, and \( C_{\text{surf}} \) is the surfactant concentration (g cm\(^{-3}\)). The surfactant concentrations were updated using Eq. (7).

4. Numerical model simulations

The effect of the local groundwater flow field within a heterogeneous NAPL entrapment zone was investigated using the developed numerical model. A set of numerical simulations was conducted in a two-dimensional system. A test setup was selected to represent a proposed experimental simulation that will be conducted in a two-dimensional intermediate-scale tank (Fig. 2). The selection of this test problem is more appropriate for this demonstration as the soils that will be used in the planned laboratory simulations have been well characterized (Illangasekare et al., 1995b; Barth et al., 2001).

The intermediate-scale test tanks with dimensions 9.75-m long and 1.22-m high is filled homogeneously with a test sand except in the source zone where a heterogeneous NAPL entrapment configuration will be created through an NAPL spill onto a heterogeneous packing. Two constant-head supply tanks are used to maintain a steady hydraulic gradient along the length of the tank. An injection well is placed upstream of the NAPL source that

Fig. 2. Schematic of the proposed intermediate-scale two-dimensional test tank.
will be used for surfactant delivery. Three monitoring wells are located downstream as shown in Fig. 2 to act as the points of compliance.

4.1. Definition of source zones

The present simulation utilizes data generated in a set of spill experiments conducted in one of our earlier investigations (Compos, 1998). The spill experiments were conducted in a 91 × 61-cm test tank packed with five well-characterized sands to represent a spatially correlated random field (sand properties are listed in Table 2). NAPL spills were conducted in five packing configurations to represent five realizations of the same random field stochastic parameters. The parameters are: (1) mean of the logarithm of hydraulic conductivity, \( \ln K_{\text{avg}} = 3.46 \) (m day \(^{-1}\)), (2) variance of logarithm of hydraulic conductivity, \( \sigma_{ln K}^2 = 1.10 \) (m\(^2\) day \(^{-2}\)), (3) vertical correlation length, \( \lambda_v = 0.0254 \) m, and (4) horizontal correlation length, \( \lambda_h = 0.0508 \) m. Fig. 3 shows the packing configuration based on one of the realizations.

Ten entrapment configurations based on five spills were used in the numerical simulations. The entrapment configuration was recorded continuously using an automated scanning dual-gamma system (Illangasekare et al., 1994). Two observed configurations (one at an intermediate time period and the second at the end of the spill propagation) for each spill were used to come out with the 10 test configurations. The same volume of NAPL was used in all of the spill experiments. To avoid the generation of waste, and for safety reasons, an LNAPL (Soltrol) was injected at the bottom of the tank instead of a DNAPL (e.g., TCE or PCE). The LNAPL migrated vertically upwards due to buoyancy forces, creating entrapment configurations controlled by fingering and preferential channeling. At different time periods during the

<table>
<thead>
<tr>
<th>Sand type</th>
<th>#16</th>
<th>#30</th>
<th>#50</th>
<th>#70</th>
<th>#110</th>
</tr>
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<tbody>
<tr>
<td>( K_{\text{sat}} ) (m day (^{-1}))</td>
<td>694.1</td>
<td>171.4</td>
<td>35.1</td>
<td>21.0</td>
<td>4.56</td>
</tr>
<tr>
<td>( d_{50} ) (mm)</td>
<td>1.08</td>
<td>0.5</td>
<td>0.32</td>
<td>0.2</td>
<td>0.12</td>
</tr>
<tr>
<td>( S_r )</td>
<td>0.07</td>
<td>0.26</td>
<td>0.29</td>
<td>0.3</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Fig. 3. Sand configuration of realization #2.
migration of the NAPL, the saturation distribution was recorded using the automated scanning dual-gamma system. Table 3 lists the packing realizations and the time after the spill when the saturation measurements were recorded for the 10 entrapment configurations. Fig. 4 shows the measured saturation distribution for two of the data sets (Sets 3 and 5). Although the exact NAPL entrapment configurations may be different between Soltrol and \( p \)-xylene due to the differences in their physical properties, the NAPL entrapment configurations from real spills were used for the simulations.

<table>
<thead>
<tr>
<th>Data set</th>
<th>Realization</th>
<th>Day</th>
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<tr>
<td>1</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>26</td>
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</tr>
<tr>
<td>10</td>
<td>5</td>
<td>45</td>
</tr>
</tbody>
</table>

Fig. 4. NAPL distribution of data sets #3 and #5.
4.2. Dissolution modeling

The model parameters for the numerical simulations are based on the proposed intermediate-scale experiments schematically shown in Fig. 2. The physicochemical properties of the NAPL and the surfactant will be the same as those that will be used in the spill experiments and enhanced dissolution experiments. Table 4 summarizes model parameters and physicochemical properties of the test NAPL (\(p\)-xylene) and surfactant (Tween-80). For the dissolution length \(L^*\) in Eqs. (3) and (4), the horizontal correlation length \(\lambda_h = 0.0508\) m was used.

Three simulations for each of the 10 data sets (Table 3) were conducted. First, the natural dissolution of the NAPL under a natural gradient of 0.0154 was simulated using Eq. (3). In the second simulation, it was assumed that the surfactant is delivered to all of the entrapped NAPL; all the numerical blocks used Eq. (4) to calculate the mass transfer rate. This scenario of complete delivery will not occur under realistic conditions, but it provides a basis of comparison to demonstrate the uncertainty of NAPL cleanup under heterogeneous conditions. The last simulation represents the more realistic condition of surfactant delivery constrained by heterogeneity of the medium and changes in the relative permeability due to NAPL entrapment, as described in Section 3. A surfactant solution (Tween-80) at a concentration of 8000 mg l\(^{-1}\) (greater than CMC of 16 mg l\(^{-1}\)) was injected continuously through a well placed upstream of the NAPL entrapment zone. An injection rate of \(2.16 \times 10^{-3}\) m\(^3\) day\(^{-1}\) was used in order not to disturb the natural flow field giving the average groundwater flow velocity of 2.53 m day\(^{-1}\). A high surfactant concentration was used in the simulations to allow the NAPL sources to deplete within a reasonable time during the proposed tank experiments. The simulations were conducted over a 30-day period. The initial \(p\)-xylene dissolved concentrations in the tank were assumed to be zero.

### Table 4
Model parameters used in natural and surfactant-enhanced dissolution simulations

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Natural</th>
<th>Surfactant</th>
<th>Units</th>
</tr>
</thead>
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<tr>
<td>Cell width along row ((\Delta x))</td>
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<td>5.08</td>
<td>cm</td>
</tr>
<tr>
<td>Cell width along column ((\Delta y))</td>
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<td>5.08</td>
<td>cm</td>
</tr>
<tr>
<td>Layer thickness ((\Delta z))</td>
<td>2.54</td>
<td>2.54</td>
<td>cm</td>
</tr>
<tr>
<td>Longitudinal dispersivity ((a_L))</td>
<td>0.1</td>
<td>0.1</td>
<td>cm</td>
</tr>
<tr>
<td>Transverse dispersivity ((a_T))</td>
<td>0.01</td>
<td>0.01</td>
<td>cm</td>
</tr>
<tr>
<td>Average groundwater velocity ((v))</td>
<td>2.53</td>
<td>2.53</td>
<td>m day(^{-1})</td>
</tr>
<tr>
<td>NAPL density ((\rho_{nw}))</td>
<td>0.8611</td>
<td>0.8611</td>
<td>g cm(^{-3})</td>
</tr>
<tr>
<td>NAPL diffusion coefficient ((D_m))</td>
<td>(7.2 \times 10^{-6})</td>
<td>(7.2 \times 10^{-6})</td>
<td>cm(^2) s(^{-1})</td>
</tr>
<tr>
<td>Critical micelle concentration</td>
<td>–</td>
<td>16.0</td>
<td>mg l(^{-1})</td>
</tr>
<tr>
<td>NAPL partition coefficient in water or in surfactant solution ((K_p))</td>
<td>6410.0</td>
<td>60.2</td>
<td>cm(^3) g(^{-1})</td>
</tr>
<tr>
<td>Aqueous solubility ((C_s))</td>
<td>156.0</td>
<td>(^{\text{a}})</td>
<td>mg l(^{-1})</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\) To be determined by Eq. (4) in the simulation.
5. Results and discussion

The expected concentration of dissolved NAPL in the observation wells (see Fig. 2 for the locations) was calculated using the discharge-weighted average of the concentration in all computational cells that are intercepted by the well screen. The time-varying NAPL mass of the source zone was also calculated during each simulation time step.

Fig. 5 shows the simulated downstream concentration breakthrough curves at the three monitoring wells for data set 2 (observed NAPL distribution 26 days after spill in realization #2; see Table 3). These results show that, under natural dissolution, the downstream concentration reaches a steady-state value of 10.7 mg l\(^{-1}\). The steady-state values obtained from the other data sets ranged between 9.2 and 17.3 mg l\(^{-1}\). However, these steady-state concentrations are still much lower than the aqueous (equilibrium) solubility of \(p\)-xylene (156 mg l\(^{-1}\)) indicating rate-limited mass transfer.

Fig. 6 shows surfactant-enhanced dissolution breakthrough curves at monitoring well #2 (MW2) assuming both complete and incomplete delivery of surfactant for the same data set (data set #2). In the case of complete delivery, the observed \(p\)-xylene concentration remains initially high but dramatically decreases as NAPL mass is depleted. Even though the breakthrough curve is smooth, it shows different zones of transitions reflecting the model’s ability to simulate dissolution in zones of varying entrapment saturations. That is, surfactant will first remediate zones where NAPL saturations are low (high relative permeability, \(k_{rw}\)) and then deplete mass in high saturation zones. In this case, dissolved

![Fig. 5. Concentration breakthrough at monitoring wells due to natural dissolution (data set #2).](image-url)
Fig. 6. Concentration breakthrough at monitoring well #2 due to enhanced dissolution: complete vs. incomplete delivery (data set #2).

Fig. 7. Normalized mass depletion as a function of time for natural and surfactant-enhanced dissolution (complete delivery).
NAPL concentration eventually reaches zero, indicating that the source zone is fully remediated.

In practical situations, it is not possible for surfactant to reach all of the entrapment zones, and some locations of NAPL entrapment may not undergo remediation within a reasonable length of time. This is shown by the incomplete surfactant delivery cases. As surfactant delivery is controlled by the heterogeneity of the entrapment zone, the breakthrough curve is not smooth (see Fig. 6). This is due to the fact that the surfactant concentration will not reach CMC in all of the computational blocks containing free-phase NAPLs and that the flow field is continuously changing with the NAPL depletion.

The NAPL mass depletion in the source zone as a function of time for the 10 simulations are plotted in Figs. 7 and 8 for complete and incomplete surfactant delivery, respectively. Mass depletion in the case of natural dissolution is also included in Fig. 7. As expected, natural dissolution results in negligible depletion of NAPL mass and the concentrations downstream will remain at a steady value for a long period of time. Mass depletion during surfactant-enhanced dissolution for the 10 cases shows a range of variability due to the uncertainty of NAPL distribution and soil heterogeneity. For complete surfactant delivery, although the variability of mass depletion is evident, the total mass of NAPL will eventually decrease to zero for all cases. In reality, however, soil heterogeneity as well as high NAPL saturation can create flow bypassing of the injected surfactant solution. As a result, the cleanup takes place slowly in the NAPL entrapment zones where bypassing occurs. This is shown in Fig. 8 for the incomplete delivery cases.

Fig. 8. Normalized mass depletion as a function of time for surfactant-enhanced dissolution (incomplete delivery). The gray lines represent complete delivery cases.
In some extreme cases, the surfactant will not access the entrapment zones and the NAPL will never be remediated (e.g. data set #3 in Fig. 8 shows mass of NAPL in the source zone remains constant after ~13 days of surfactant injection). A much greater mass depletion variability is observed for incomplete surfactant delivery compared with the case where complete delivery is assumed.

Numerical simulations can also be used to visualize flow bypassing of the delivered surfactant solution around the source zone. Fig. 9 illustrates the 3-D contour mesh of the hydraulic head near the source zone, and contours of surfactant concentration for data set #1. Thus, the effect of flow bypassing is evident.

6. Conclusions

The issue of the benefits of partial source zone treatment with respect to reduction of risk has received considerable attention recently. Sale and McWhorter (2000) suggested the limited near-term benefits of partial source zone treatment with respect to achieving
cleanup goals with expected reduction of dissolved contaminants downstream of source zone. They supported the conclusion that mass removal from source zone is ineffective unless a large mass of the free phase is removed. As the Sale and McWhorter (2000) study was conducted under very simplistic conditions, it is premature to generalize the applicability their findings to field sites with much more complex geohydrologic conditions and NAPL entrapment configurations. Rao et al. (2001) pointed out that different conclusions would be reached for heterogeneous flow fields. The findings of the study presented in this paper further illustrate the uncertainty of source zone mass removal associated with the aquifer heterogeneity and the resulting nonuniform flow field.

This study specifically illustrates the effect of heterogeneity on the effectiveness of surfactant delivery to the source zone of NAPL undergoing remediation. A comparison of complete and incomplete surfactant delivery as controlled by heterogeneity and relative permeability effects shows a much greater variability in the mass depletion when incomplete surfactant delivery is accomplished. The primary hypothesis that the heterogeneity controls the delivery of the surfactant was tested. The results establish that when the heterogeneity cannot be fully characterized, there exists significant uncertainty regarding the achievement of cleanup goals and the reduction of risk.

Even though a simplified model was used in the analysis, the model captures the basic processes adequately to arrive at these conclusions. An experimental study in an intermediate-scale test tank is planned to generate an accurate data set to validate the model in the laboratory before applying it to field situations for further validation of the findings of this paper.

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