A Review of Multidimensional, Multifluid Intermediate-Scale Experiments: Nonaqueous Phase Liquid Dissolution and Enhanced Remediation

M. Oostrom,* J. H. Dane, and T. W. Wietsma

ABSTRACT

A review is presented of original multidimensional, intermediate-scale experiments involving NAPLs (nonaqueous phase liquids). The experimental approach at this scale can be viewed as an important intermediary between column studies and field trials. The primary advantage of intermediate-scale flow cell experiments is that field-scale processes can be simulated under controlled conditions. The experiments are conducted to provide data sets to test and verify numerical and analytical flow and transport models. The controlled setting and laboratory instrumentation reduces the uncertainty in parameter estimation, allowing comparisons between simulation and experimental results to focus on flow and transport processes. A total of about 125 original contributions were identified and reviewed. Depending on the main topic of NAPL experimental research, the papers were divided into the following sections: (i) aqueous dissolution, (ii) enhanced remediation, (iii) flow behavior, (iv) quantification, and (v) imaging. In this review, the first two categories are discussed and suggestions for future research are provided. In a companion review, experimental work related to the other three categories is investigated. The aqueous dissolution category includes experiments in which pooled and entrapped NAPL removal occurs due to water flushing. The enhanced remediation section contains experimental contributions investigating surfactant flushing, alcohol flushing, surfactant and alcohol flushing combinations, dense brine strategies, hydraulic NAPL recovery, soil vapor extraction, air sparging, heat-based remediation, bioremediation, and other techniques.

SOIL AND GROUNDWATER POLLUTION by NAPLs (nonaqueous phase liquids) pose a persistent environmental problem as it affects our use of groundwater as a source of drinking or irrigation water. Nonaqueous phase liquids exist either as LNAPLs (light NAPLs) or DNAPLs (dense NAPLs) and enter the subsurface through spills and leaking storage facilities. Remediation efforts are often hampered by our inability to define contaminated subsurface regions, a prerequisite for any remediation attempt. Johnson et al. (2004) stated that DNAPL remediation has not been resolved for the good reason that it is still the most challenging class of problems facing the environmental sciences community.

Bench-scale laboratory research on NAPL flow and remediation occurs at the pore scale in micromodels, the one-dimensional column scale, and the multidimensional intermediate aquifer model scale. Column studies are important because they provide an important initial understanding of a multifluid problem; however, column studies lack representiveness to field situations (Conrad et al., 2002). For instance, dissolution of entrapped NAPL in a column does not represent field conditions, because the flushing solutions are forced through the contaminated zone. Another example is the unfavorable mobilization of DNAPL following surfactant or alcohol flushing, often an apparent phenomenon in multidimensions, but masked in column studies. Two- and three-dimensional aquifer model experiments are an important intermediary between column studies and field trials.

The focus of this review is multifluid intermediate-scale flow cell experimentation. Lenhard et al. (1995) defined the conditions needed before an experiment can be classified as “intermediate-scale”: (i) the experimental configuration has to allow small-scale processes to manifest themselves at a larger scale so that their relative contributions to flow and transport phenomena can be studied and quantified; (ii) the size of the experiment has to be small enough for the environment to be controlled; and (iii) the experimental-cell dimensions have to be compatible with measurement and sampling techniques.

The primary advantage of intermediate-scale experiments is that field-scale processes can be mimicked under controlled conditions (Lenhard et al., 1995). Chevalier and Petersen (1999) noted that laboratory investigations of NAPL flow in porous media are studied under the same capillary, viscous, and buoyancy forces as full-scale systems. Flow cell experiments are also conducted to provide data sets to test and verify numerical (e.g., Waddill and Parker, 1997) and analytical (Chrysikopoulos et al., 2000) multifluid flow and transport models. Waddill and Parker (1997) argued that the controlled setting and laboratory instrumentation would reduce the uncertainty in parameter estimation, thus allowing the comparisons between model simulations and experiments to focus on flow processes. Another purpose of intermediate-scale experiments is to provide the necessary data to compute parameters associated with theoretical models. For instance, parameter values for Gilland–Sherwood kinetic mass transfer models of entrapped NAPL were computed by Saba and...
Illangasekare (2000), and Brusseau et al. (2002) using data from flow cell experiments. Conrad et al. (2002) stressed the importance of performing flow cell visualization experiments to evaluate the performance of proposed techniques for DNAPL remediation.

An earlier literature review of 2-D (two-dimensional) laboratory experiments in NAPL flow, transport, and remediation was presented by Chevalier and Petersen (1999). They reviewed about 20 papers with the most recent contribution from 1997. Besides the fact that numerous papers have appeared in the literature after 1997, the review by Chevalier and Petersen (1999) did not provide a comprehensive review of intermediate-scale flow cell experiments before 1997.

We have reviewed about 125 original contributions. Depending on the main topic of research, the papers were divided into the following categories: (i) aqueous dissolution, (ii) enhanced remediation, (iii) flow behavior, (iv) quantification, and (v) imaging. The dissolution category includes experiments where NAPL removal occurs due to water flushing. The enhanced remediation section contains experimental contributions investigating surfactant flushing, alcohol flushing, surfactant and alcohol flushing combinations, dense brine strategies, hydraulic NAPL removal, soil vapor extraction, air sparging, heat-based remediation, bioremediation, and other techniques. The flow behavior papers involve investigations of NAPL flow and transport phenomena. The smaller quantification and imaging categories discuss experiments conducted to detect and quantify NAPL using tracers and experiments performed to provide images of fluid saturations in flow cells, respectively.

Table 1. Overview of NAPL (nonaqueous phase liquid) aqueous dissolution experiments.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Dimensions (L × H × W), cm</th>
<th>Wall material (F = front; B = back)</th>
<th>NAPL</th>
<th>NAPL configuration</th>
<th>Saturation</th>
<th>Homogeneous or heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anderson et al., 1992</td>
<td>100 × 100 × 75</td>
<td>glass or lucite</td>
<td>tetrachloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Brusseau et al., 2002</td>
<td>220 × 110 × 5.3</td>
<td>F: glass B: Kynar</td>
<td>trichloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>heterogeneous</td>
</tr>
<tr>
<td>Oostrom et al., 1999a</td>
<td>100 × 100 × 10</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>heterogeneous</td>
</tr>
<tr>
<td>Oostrom et al., 2005b</td>
<td>17.8 × 12 × 2.9</td>
<td>F: glass B: stainless steel</td>
<td>trichloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Pearson et al., 1994</td>
<td>65 × 34 × 21</td>
<td>F: glass B: stainless glass</td>
<td>trichloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>heterogeneous</td>
</tr>
<tr>
<td>Powers et al., 1998</td>
<td>17.8 × 10 × 2.9</td>
<td>F: stainless steel</td>
<td>trichloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Reynolds et al., 1996</td>
<td>100 × 50 × 10</td>
<td>stainless steel</td>
<td>toluene, trichloroethylene, o-toluidine</td>
<td>entrapped</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Saba and Illangasekare, 2000</td>
<td>220 × 110 × 5.08</td>
<td>F: Plexiglas B: stainless steel</td>
<td>para-xylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Schvill, 1988</td>
<td>150 × 30 × 50</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Vondrias and Yeh, 1994</td>
<td>85 × 30 × 20</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Whelan et al., 1994</td>
<td>75 × 36.8 × 21.1</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>entrapped</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
</tbody>
</table>
Table 2. Overview of NAPL (nonaqueous phase liquid) enhanced remediation experiments.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Remediation technique</th>
<th>Dimensions (L × H × W), cm</th>
<th>Wall material</th>
<th>NAPL</th>
<th>Saturation</th>
<th>Homogeneous or heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adamson et al., 2003</td>
<td>reductive dechlorination</td>
<td>540 × 183 × 213</td>
<td>Stainless steel</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Boyd et al., 2006</td>
<td>alcohol flushing</td>
<td>110 × 405 × 2.85</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Catalan and Dullien, 1995</td>
<td>gravity drainage, oil pumping</td>
<td>69 × 120 × 1.27</td>
<td>glass</td>
<td>Solvco 110</td>
<td>unsaturated</td>
<td>both</td>
</tr>
<tr>
<td>Chevalier et al., 1998</td>
<td>surfactant flushing</td>
<td>100 × 100 × 5</td>
<td>glass</td>
<td>toluene; xylene</td>
<td>unsaturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Chu et al., 1999</td>
<td>surfactant flushing</td>
<td>14 × 10.5 × 0.25</td>
<td>Plexiglas</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Conrad et al., 2002</td>
<td>surfactant flushing, in situ chemical oxidation</td>
<td>60.5 × 30 × 10</td>
<td>glass</td>
<td>trichloroethylene; tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Dai and Reifsnena, 2002</td>
<td>in situ chemical oxidation</td>
<td>38 × 80 × 2.5</td>
<td>F: glass; B: aluminum</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Dong et al., 2004</td>
<td>surfactant flushing</td>
<td>30 × 5 × 1</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Field et al., 1999</td>
<td>surfactant flushing</td>
<td>183 × 50 × 2.85</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Field et al., 2000</td>
<td>alcohol flushing</td>
<td>76 × 76 × 2</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Gnbob et al., 1997</td>
<td>alcohol flushing</td>
<td>76 × 76 × 2</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Gnbob et al., 1999a</td>
<td>alcohol flushing</td>
<td>51.5 × 10 × 2</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Gnbob and Sitar, 1999</td>
<td>surfactant flushing</td>
<td>122 × 58 × 5.8</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Heron et al., 2002</td>
<td>air sparging</td>
<td>116 × 56 × 4</td>
<td>F: glass; B: aluminum</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Hill et al., 2001</td>
<td>dense brine strategies</td>
<td>22.5 × 24 × 16.5</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Ho and Udell, 1992</td>
<td>soil vapor extraction</td>
<td>25 × 20 × 2.54</td>
<td>glass</td>
<td>toluene; o-xylene</td>
<td>unsaturated</td>
<td>both</td>
</tr>
<tr>
<td>Hunter, 2001</td>
<td>deinduration</td>
<td>210 × 100 × 8.5</td>
<td>glass</td>
<td>vegetable oil</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Kashusky and Udell, 2005</td>
<td>surfactant flushing</td>
<td>98 × 92 × 5</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Kostarelos et al., 1998</td>
<td>surfactant–alcohol flushing combination</td>
<td>103 × 40 × 5.1</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Lee et al., 2003</td>
<td>in situ chemical oxidation</td>
<td>160 × 90 × 60</td>
<td>&quot;plastic&quot;</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Li and Schwartz, 2004a</td>
<td>in situ chemical oxidation</td>
<td>30.5 × 5 × 0.3</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Li and Schwartz, 2004b</td>
<td>in situ chemical oxidation</td>
<td>30.5 × 5 × 0.3</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Lunn and Kueper, 1997</td>
<td>alcohol flushing</td>
<td>20 × 125 × 3</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Lunn and Kueper, 1999a</td>
<td>alcohol flushing</td>
<td>20 × 125 × 3</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Lunn and Kueper, 1999b</td>
<td>alcohol flushing</td>
<td>20 × 125 × 3</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>MacKinnon and Thompson, 2002</td>
<td>in situ chemical oxidation</td>
<td>250 × 45 × 15</td>
<td>stainless steel</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Miller et al., 2000</td>
<td>dense brine strategies</td>
<td>15 × 20 × 2</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Ostrom et al., 1999b</td>
<td>surfactant flushing</td>
<td>167 × 100 × 5</td>
<td>F: glass; B: Kynar</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Ostrom et al., 2005a</td>
<td>soil vapor extraction</td>
<td>100 × 75 × 5</td>
<td>glass</td>
<td>carbon tetrachloride–lact oil di-buty</td>
<td>saturated</td>
<td>heterogeneous butyl-phosphate–tributyl phosphate mixture</td>
</tr>
<tr>
<td>Palomino and Grubb, 2004</td>
<td>alcohol flushing</td>
<td>76 × 76 × 2</td>
<td>F: glass</td>
<td>dodecane, octane, toluene</td>
<td>unsaturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Ramsburg and Pemnell, 2001</td>
<td>surfactant–alcohol flushing combination</td>
<td>61 × 40 × 1.4</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Ramsburg and Pemnell, 2002</td>
<td>surfactant–alcohol flushing combination</td>
<td>63.5 × 38 × 1.4</td>
<td>glass</td>
<td>trichloroethylene, chlorobenzene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Ramsburg et al., 2004</td>
<td>surfactant–alcohol flushing combination</td>
<td>63.5 × 38 × 1.4</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Reitma and Marshall, 2000</td>
<td>in situ chemical oxidation</td>
<td>76.8 × 30.6 × 2.8</td>
<td>glass</td>
<td>trichloroethylene; tetrachloroethene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Rodder et al., 2001</td>
<td>alcohol flushing</td>
<td>100 × 70 × 6</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Rogers and Oet, 2000</td>
<td>air sparging</td>
<td>38 × 57 × 5.05</td>
<td>F: Plexiglas; B: aluminum</td>
<td>p-xylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Saha et al., 2001</td>
<td>surfactant flushing</td>
<td>38 × 57 × 5.05</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Sanchez and Ely, 1998</td>
<td>dense brine barrier strategies</td>
<td>15 × 125 × 4</td>
<td>not reported</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Schaerackens and Feyen, 2004</td>
<td>surfactant flushing</td>
<td>80 × 60 × 4</td>
<td>not reported</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Schmidt et al., 2002</td>
<td>steam injection</td>
<td>110 × 74 × 8.5</td>
<td>F: glass; B: stainless steel</td>
<td>1,3,5-trimethylbenzene, 1,2-dichlorobenzene</td>
<td>unsaturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Schwille, 1967</td>
<td>hydraulic recovery, surfactant flushing</td>
<td>260 × 80 × 20, 105 × 105 × 15</td>
<td>glass</td>
<td>heating oil, kerosene</td>
<td>unsaturated</td>
<td>both</td>
</tr>
<tr>
<td>She and Skeep, 1999</td>
<td>steam injection</td>
<td>1105 × 575 × 30</td>
<td>F: glass; B: stainless steel</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Sleep et al., 2000</td>
<td>hydraulic recovery</td>
<td>300 × 350 × 1.70</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Taylor et al., 2001</td>
<td>surfactant flushing</td>
<td>61.7 × 32 × 1.5</td>
<td>Glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Taylor et al., 2004</td>
<td>surfactant–alcohol flushing combination</td>
<td>60.7 × 36 × 1.4</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Van Stempess et al., 2002</td>
<td>humic acid enhanced dissolution</td>
<td>650.7 × 130 × 180</td>
<td>glass</td>
<td>trichloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Van Valkenburg and Annable, 2002</td>
<td>alcohol flushing</td>
<td>61 × 39.4 × 1.4</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Wadid and Parker, 1997</td>
<td>hydraulic recovery</td>
<td>152 × 108 × 8.2</td>
<td>stainless steel</td>
<td>Solvco 110</td>
<td>unsaturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Wadige et al., 2004</td>
<td>air sparging</td>
<td>120 × 80 × 15</td>
<td>F: glass; B: stainless steel</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Walker et al., 1998a</td>
<td>surfactant–alcohol flushing combination</td>
<td>170 × 100 × 15</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Walker et al., 1998b</td>
<td>surfactant flushing</td>
<td>170 × 100 × 15</td>
<td>glass</td>
<td>tetrachloroethylene</td>
<td>saturated</td>
<td>homogeneous</td>
</tr>
</tbody>
</table>

† Wedge: 125 cm long by 20 cm high, 5 cm at narrow end, 50 cm at wide end.
flow cell experiments, recognizing that they have been called several names, including physical aquifer model (Field et al., 1999), lab-scale reactor (Rogers and Ong, 2000), soil tank (Waduge et al., 2004), model sand aquifer (Van Stemponckt et al., 2002), sand pack (Ho and Udell, 1992), 2-D box (Taylor et al., 2004), trough (Schwille, 1967), sand box (Dai and Reitsma, 2002), soil flume (Saba and Illangasekare, 2000), and flow tank (Li and Schwartz, 2004). In addition, following the terminology proposed by Lenhard et al. (2004), we will refer to pore-scale NAPL that is occluded by water as entrapped NAPL, and pore-scale NAPL that is not entrapped by water, but does not drain from the pore spaces, as residual NAPL. Both forms of NAPL are assumed to be immobile. Residual NAPL can be continuous or discontinuous throughout the pore spaces, but entrapped NAPL is always discontinuous (Lenhard et al., 2004). The term macroentrapped NAPL is used to describe NAPL in systems where free NAPL is located in a relatively coarse porous medium surrounded by finer grained materials. Examples of such configurations were discussed by Manivannan et al. (1996), Powers et al. (1998), and Nambi and Powers (2000).

AQUEOUS DISSOLUTION
Dissolution of Pooled Nonaqueous Phase Liquids

The first intermediate-scale dissolution experiments of DNAPL pools were reported by Schwille (1988). Other DNAPL pool dissolution experiments were conducted by Chrysikopoulos et al. (2000), Dela Barre et al. (2002), Pearce et al. (1994), and Whelan et al. (1994). Voudrias and Yeh (1994) discussed a LNAPL pool dissolution experiment. Eberhardt and Grathwohl (2002) studied both pooled and entrapped coal tar dissolution. Oostrom et al. (1999a) discussed an experiment including the dissolution of a pool developed after a spill.

The main goal of the experiments by Schwille (1988) was to create a defined pool of either 1,1,1 TCA (trichloroethane) or TCE on the bottom of a glass flow cell. Schwille (1988) selected 1,1,1 TCA for its intermediate solubility (720 mg L⁻¹ at 25°C) in his first experiment, and TCE for its relatively high solubility (1100 mg L⁻¹ at 25°C) in his second experiment. The DNAPLs, 2 L in the first and 2.5 L in the second experiment, were added directly to the bottom through two vertical tubes connected to perforated horizontal tubes. The flow cell was then uniformly filled with a sand with a saturated hydraulic conductivity of 3.5 × 10⁻³ m s⁻¹. For both experiments, an even DNAPL distribution was visually observed. Water was subsequently injected and extracted through perforated tubes, positioned on either side of the flow cell, 16 cm above the bottom. No sampling ports were installed in the flow cell and only effluent samples were analyzed. For each experiment, the water injection rate was varied with time. Both experiments yielded nearly positive linear relationships between flow rate and DNAPL removal rate; however, Schwille (1988) stated that the results were not of adequate detail to allow the determination of a functional relationship governing DNAPL removal under the conditions of his experiments.

To study dissolution kinetics of TCA and TCE–TCA mixtures, Whelan et al. (1994) developed a procedure to create DNAPL pools in a glass tray, located at the bottom in a flow cell. A very useful section in their paper contains the descriptions of various failed techniques before a successful one was developed. The lower part of the tray contained a 1.6-cm-thick gravel layer, while the remainder was filled with aquifer sand. The formed pools had a distinct but not perfect flat upper surface. Dissolution experiments with TCE and TCE–TCA mixtures yielded concentrations much lower than the respective solubilities, even at sampling locations 6.2 cm above the glass tray. Dissolved concentrations at these locations were only 18% of the solubility of TCA. For binary mixtures, similar results were observed. Pool excavation showed that the fraction of sand penetrated by DNAPL at each layer increased with decreasing distance from the bottom, revealing that the researchers were not able to create a DNAPL pool with a perfectly flat surface.

Pearce et al. (1994), in a continuation of experiments discussed by Whelan et al. (1994), studied the factors that affect the dissolution dynamics of single-component DNAPL pools. Similar to what was found by Whelan et al. (1994), under conditions of steady and uniform horizontal flow, the dissolved DNAPL concentrations decreased with increasing vertical distance from the pool. The concentration gradient increased with increasing groundwater velocity. The vertical extent of the dissolved plume increased with increasing distance along the pool and decreasing groundwater velocity. In all cases, measured concentrations were a small fraction of the respective DNAPL solubility. A steady-state pool dissolution model, described by Hunt et al. (1988), for a pool with length L, was applied to compute transverse dispersivity values. The model is given by

\[ \nu \frac{\partial C}{\partial x} = D_z \frac{\partial^2 C}{\partial z^2} \]  \[1\]

where \( \nu \) is the average pore water velocity in the longitudinal direction \([L T^{-1}]\), \( C \) is the dissolved DNAPL concentration \([M L^{-3}]\), \( x \) and \( z \) are the longitudinal and vertical Cartesian coordinates \([L]\), respectively, and \( D_z \) is the transverse hydrodynamic dispersion coefficient \([L^2 T^{-1}]\). This coefficient can be written as \( D_z = \tau D_m + \alpha_z v \), where \( \tau \) is the tortuosity, \( D_m \) is the molecular diffusion coefficient, and \( \alpha_z \) is the transverse dispersivity. For the boundary conditions:

\[ C(0 \leq x \leq L, z = 0) = C_s \]
\[ C(x, z = \infty) = 0 \]
\[ C(x = 0, z) = 0 \]

where \( z = 0 \) indicated the top of the pool, \( C_s \) is the NAPL aqueous solubility, and the solution of Eq. [1] for \( 0 \leq x \leq L \) can be written as (Hunt et al., 1988)

\[ C(x,z) = C_s \text{erfc} \left( \frac{z}{2 \sqrt{D_z x/v}} \right) \]  \[2\]
An analysis of the results showed that the dispersion coefficients were only slightly larger than the diffusion coefficients and that a transverse dispersivity value of 0.0155 cm could be computed for all experiments.

Chrysikopoulos et al. (2000) designed a flow cell with a well-defined circular pool. This design was in response to the pool characteristics used by Whelan et al. (1994) and Pearce et al. (1994). Chrysikopoulos et al. (2000) commented, "The experimental protocols developed by Whelan et al. (1994) do not lead to a well-defined and flat pool–water interface. Formation of entrapped DNAPL ganglia in the upper half of the glass pan may occur during injection. Accurate determination of the pool–water interfacial area resulting from this setup is not a trivial task. Furthermore, the intrusion of a glass pipet in the aquifer may disturb the interstitial flow."

The new pool design consisted of a bottom plate with a 0.5-cm-deep and 7.6-cm-diameter circular depression, which was filled with 0.5-cm-diameter glass beads. The TCE was then added to the depression through a tube connected to a reservoir to form a pool. The void volume of the pool was estimated to be \( \sim \)12 cm\(^3\). Throughout the flushing experiments, the pool was kept filled with TCE. Hence, pool depletion was not considered. Another drawback of this design is that the TCE was not in the porous medium itself. The flow cell was packed with a kiln-dried Monterey sand under a water head of 5 cm. Liquid samples were taken during steady-state conditions from seven ports placed at different depths, primarily on the center axis of the flow cell. A total of three experiments were completed with different pore water velocities. The steady-state concentration distributions were analyzed using the analytical solution by Chrysikopoulos (1995) for a transport equation including retardation, dispersion, and kinetic dissolution. All transport parameters for this model were obtained independently, except for the average kinetic mass transfer coefficient. This coefficient could not be determined independently but was fitted using concentrations from a subset of the ports. The concentrations at the remaining ports, all located on the centerline of the aquifer, were then predicted using the analytical solution. The analytical solution was found to describe observed TCE plumes well. Important conclusions from the experiments were that observed aqueous TCE concentrations just 15 to 60 cm downgradient from the pool, and just a few centimeters above the upper boundary of the pool, were \(<4\%\) of the aqueous solubility. According to the researchers, this observation provides strong evidence in support of the notion that rate-limited dissolution of DNAPLs can be the cause of contaminant plumes that are dominated by concentrations several orders of magnitude less than the aqueous solubility. In addition, it was stated that the results also imply that observed concentrations exclusively at the parts per billion level do not preclude the existence of a DNAPL pool at a site.

The experiments reported by Dela Barre et al. (2002) were conducted in the same flow cell used by Chrysikopoulos et al. (2000); however, Dela Barre et al. (2002), introduced the DNAPL PCE (tetrachloroethene) in the porous medium atop impermeable (glass) and relatively impermeable (clay) surfaces at the bottom plate of the cell. The objectives of this study were to observe the controlled dissolution of DNAPL pools into an overlying aquifer, and to rigorously test an existing mathematical model (Chrysikopoulos, 1995) describing the dissolution of an ideally configured pool. In the first experiment, a pool containing 1 cm\(^3\) of PCE was placed on the bottom of the flow cell. In the second experiment, the pool was placed within a depression in the 1-cm clay layer that was placed on the bottom of the cell. The pools were irregular in shape, finite in mass, and resided within the porous medium, where interfacial forces were allowed to affect the pool surface. The porous medium was the same sand used by Chrysikopoulos et al. (2000). In the experiments, temporal sampling was conducted at a designated observation point. After steady-state conditions were reached, samples were obtained from up to 35 sampling locations. For the first experiment, variable flow rates were used, while for the second experiment, the flow rate was kept constant. As in the modeling approach by Chrysikopoulos et al. (2000), most of the parameters for the model were obtained independently, except for the value of the mass transfer coefficient. The researchers discovered that, despite the finite pool volumes, observed plumes achieved a quasi-steady-state distribution during extended time periods and that the effect of mass loss on pool geometry was minimal during the course of the experiments. It was also found that pool dissolution could be modeled reasonably well with a boundary layer theory assuming a simplistic circular pool and adjustment of a pool-average mass transfer coefficient. Modeling discrepancies were the largest closest to the pool due to the irregularities of the pool. An interesting observation was that the estimated mass transfer coefficient values were three to four times greater than those estimated in the dissolution study by Chrysikopoulos et al. (2000), involving an ideally configured pool, and two to three times greater than values predicted by a theoretically based mass transfer correlation for elliptical or circular pools. It was suggested that the most likely cause of these discrepancies was the pool dissolution model’s failure to address interfacial issues associated with the emplaced pool and overcompensation in the form of elevated mass transfer coefficients. The researchers stated that, partly based on findings from pore-scale research, pore-scale features of a DNAPL pool–water interface will impact dissolution and may change significantly as sufficient portions of the pool dissolve. They concluded that future research is needed focusing on the connection between pool dissolution and pore-scale mechanisms defining the pool–water interface.

The only LNAPL pool dissolution study was conducted by Voudrias and Yeh (1994). A rectangular pool, containing 1 L of dyed toluene, was constructed directly on top of the water table. One horizontal row of sampling ports was located 3 cm below the pool–water table interface. The experiment consisted of six stages with variable pore water velocity. The duration of each stage lasted from 48 to 500 h. The model of Hunt et al. (1988) was applied to the dissolved plumes under steady-state conditions. Transverse dispersivities ranged from 0.013
to 0.018 cm, which are comparable to the values computed by Pearce et al. (1994). The researchers also observed very steep vertical concentration gradients in groundwater flowing horizontally below the dissolving toluene pool. It was estimated that, under the current experimental conditions, the removal time would be between 8 and 12 yr.

An intermediate-scale flow cell experiment to study the flow of liquid and the transport of dissolved TCE (trichloroethylene) in a saturated, heterogeneous porous medium system was conducted by Oostrom et al. (1999a). In contrast to the other contributions discussed in this section, the pool was not directly emplaced but resulted from a spill from the top of the flow cell. The flow cell was packed with three layers and five lenses consisting of four different sands. All lenses and layers had horizontal interfaces, except the lowest interface, which was pointed down in the middle. Horizontal groundwater flow was imposed by manipulating the water levels in two end chambers. More than 0.5 L of dyed TCE was allowed to infiltrate at a constant rate into the porous medium from a narrow source located on the surface. Fluid samples were collected from 20 sampling ports to determine dissolved TCE concentrations. Visual observations and measured TCE saturations indicated that the spilled TCE accumulated on top of, but did not penetrate into, fine-grained sand lenses and layers but that some TCE infiltrated into medium-grained sand lenses. Most of the TCE finally pooled on top of a fine-grained sand layer located near the bottom of the flow cell. The simple Hunt et al. (1988) pool dissolution model was used to predict observed dissolved TCE concentrations. Results showed that the measured concentrations could only be predicted with unrealistically high transverse dispersivity values. The main reason for the discrepancy was that the observed TCE concentrations were the result of contributions of entrapped and pool dissolution.

The only dissolution study with a field DNAPL pool was conducted by Eberhardt and Grathwohl (2002). The study presented results in the largest intermediate-scale flow cell (7.43 m long by 2.75 m wide by 1.0 m high) reported here. The flow cell contained both a 2.5-m-long by 0.05-m-wide by 1.0-m-high coal tar pool and a 0.5-m-long by 1.0-m-high by 1.0-m-wide zone with entrapped NAPL. The entrapped NAPL dissolution is discussed below. The coal tar contained contaminants like BTEX (benzene, toluene, ethyl-benzene, xylene) and PAHs (polycyclic aromatic hydrocarbons). Three aquifer materials were used. A low-permeability sand was used at the bottom and below the entrapped zone. A medium-grained sand and a fine gravel were used to build up the main aquifer and a high-conductivity zone, respectively. The DNAPL pool was made by first excavating a 3-cm-deep depression in the fine sand layer at the bottom. The depression was then filled with aquifer sand, followed by emplacement of 40 kg (33.3 L) of coal tar. The coal tar pool had a 100% NAPL saturation. The total number of sampling ports for this large cell was only 46, which is remarkably low for a flow cell of this size. The flow velocity in the cell was 1.7 m d$^{-1}$ for the first 177 d. After that, it was increased to 5.1 m d$^{-1}$ for 42 d, then reduced to 3.4 m d$^{-1}$ for 21 d, and finally further reduced to 1.7 m d$^{-1}$ for the final 114 d. The total duration of the experiment was 354 d. The objectives of the pool dissolution study were to determine the validity of Raoult’s law for prediction of aqueous concentrations and to quantify the contribution of the transverse vertical dispersion on BTEX and PAH dissolution from a pool. Results showed that Raoult’s law was applicable for estimation of aqueous concentrations, assuming an activity coefficient of 1. Calculations based on a steady-state pool dissolution model (Hunt et al., 1988) showed that transverse vertical mixing, with a dispersivity value of 0.01 cm, dominated the pool dissolution process.

Dissolution of Entrapped Nonaqueous Phase Liquids

Anderson et al. (1992) and Reynolds et al. (1996) investigated dissolution of entrapped, circular source zones. The work of Imhoff et al. (1996) focused on dissolution fingering. Saba and Illangasekare (2000) used similarly shaped LNAPL zones to investigate rate-limited dissolution. The flow cell experiments reported by Brusseau et al. (2000, 2002) were designed to study the rate-limited dissolution of rectangular source zones with entrapped DNAPL. The only flow cell dissolution experiment with entrapped field NAPL was discussed by Eberhardt and Grathwohl (2002).

The emphasis of the research by Anderson et al. (1992) was on obtaining mass removal rates when groundwater is free to flow at least partially around a zone of a porous medium that contains entrapped solvent. The experiments were conducted in response to results from 1-D (one-dimensional) laboratory column studies, which indicated that when water is forced to flow through a zone with ample entrapped DNAPL, saturation concentrations can be achieved rapidly. The zone with entrapped DNAPL (PCE) had a cylindrical shape with a diameter of 15.2 cm and was placed in the middle of the flow cell. First, a sheet-metal cylinder was placed vertically into the center of the flow cell. The flow cell and cylinder were then filled with sand. The water table was set at 74 cm above the bottom. To produce the entrapped zone, dyed PCE was injected into the cylinder from the bottom until the PCE was even with the water table. Mobile PCE was subsequently siphoned off and water was again injected from the bottom to displace the remaining mobile PCE. Finally, the sheet metal was removed from the flow cell. This procedure yielded a zone with 13% entrapped PCE. A total of 81 sampling ports were installed in three horizontal rows and one vertical column at the effluent end of the tank. Experiments were completed at pore water velocities of 10, 30, 60, and 100 cm d$^{-1}$. Observed steady-state concentrations for all experiments were nearly similar. PCE concentrations in the center of the dissolved plume, emanating from the source zone, were at near saturation, even at water velocities of 100 cm d$^{-1}$. A main conclusion of the experiment was that reduction of mass removal due to reduced permeability in the solvent zone was found to be minimal.
The main objective of the experimental work by Reynolds et al. (1996) was to assess if mass transfer coefficients calibrated from 1-D dissolution data can be used to accurately model 3-D flow and dissolution. Circular sources containing entrapped toluene were used. It was observed that, contrary to the other work reported here, concentrations increased with distance. The reasons that were considered for this unexpected behavior were channeling within the sand, heterogeneous dissolution within the zone, and global flow deviation. Excavations of the cell did not provide support for the channeling suggestion. The second reason, isolated ganglia being dissolved and forming “mini-plumes” was thought to be the most likely. A modeling effort was able to duplicate the general trends exhibited by the experimental data, although adjustments were needed of the transverse dispersivity and relative permeability data.

Imhoff et al. (1996) used a relatively small 2-D flow cell to study the effects of porous medium structure, Darcy flux, initial entrapped NAPL saturation, median particle diameter, gravity, and NAPL composition on dissolution fingering through preferential flow paths. The model for dissolution fingering of a single component NAPL presented by Imhoff and Miller (1996) indicated that fingering depends only on the pore water velocity and the entrapped NAPL saturation; however, the remaining parameters were investigated for the following reasons: (i) porous medium structure was hypothesized to affect finger location; (ii) particle size would affect the size of ganglia and the length of the dissolution front, which might inhibit finger formation; (iii) gravity was assumed unimportant in the model; and (iv) NAPLs in the environment are frequently mixtures and it was important to show that dissolution fingering also occurs for mixed systems. The latter condition is not part of the theoretical model, because it assumes a thin dissolution front. It was further observed that Darcy flux and median particle diameter influenced the length of the dissolution front. In addition, results showed that fingers grew faster for smaller initial entrapped NAPL saturations and larger Darcy fluxes, were not affected by gravity, and occurred in an experiment with a TCE–toluene mixture. Variation of the finger growth rate with initial degree of NAPL saturation and Darcy flux are in agreement with the analysis of Imhoff and Miller (1996). In a 3-D experiment, fingers were found to grow >30 cm in length, while theoretical predictions indicated that they might grow to meters in length, depending on the flow rate, transverse mixing, and finger radius. Predictions using existing 1-D correlations not including fingering were shown to be significantly different from experimental observations of TCE dissolution. These results suggest that dissolution fingers can dramatically affect the distribution of NAPL saturations and aqueous phase solute concentrations; however, Imhoff et al. (1996) noted that when cleanup was defined as the disappearance of visible TCE ganglia, dissolution fingers led to a cleanup time that was only 10% longer than the predicted time based on the local equilibrium assumption. At the scale of these experiments, the effect on cleanup time is not large, but further study is recommended to assess the importance of dissolution fingering on cleanup time at the field scale.

The flow cell work by Saba and Illangasekare (2000) was motivated by the observation that mass transfer from entrapped NAPL in the subsurface takes place in 3-D groundwater flow fields but that most dissolution laboratory studies had been only 1-D. They argued that multidimensional studies were needed to capture more realistic conditions such as the heterogeneous distribution of entrapped NAPL ganglia and the potential for flow bypassing due to reduced water permeability. The main objective of this study was to evaluate the effects of flow dimensionality on NAPL dissolution in experiments using 2-D flow fields. Sources containing entrapped para-xylene were placed in an otherwise homogeneous sand pack. The packing procedure of the source zones is of interest. A 20-cm-long, 5.08-cm-high, and 5.08-cm-wide aluminum mold was filled with water-saturated sand. The mold end plates were coated with stainless steel screens and the internal walls were coated with greased gaskets to avoid wall effects. Para-xylene was injected into the mold until free phase LNAPL appeared in effluent. The saturation was found to be 0.85. To create a zone with entrapped NAPL, two pore volumes of deaired water were subsequently pumped into the mold at a low rate until the LNAPL was no longer displaced, as verified by visual observation of the effluent. The volume-averaged entrapped saturation was calculated to be 0.22. Uniform distribution throughout the sand was verified by dividing a test mold into six sections and obtaining the LNAPL saturation of each piece using ultraviolet spectroscopy. The results show that the saturations were reasonably constant for all sections. After the entrapped LNAPL was formed, the molds were stored in a freezer until they were emplaced in the flow cell. Following a tracer test to determine the dispersivity of the 0.60-mm sand, dissolution behavior under different groundwater velocities and entrapped NAPL source lengths (5.08, 10.15, and 15.24 cm) were investigated. The groundwater velocities ranged from 0.25 to 3.0 m d⁻¹ for each source length. A column of sampling ports was located a short distance downstream from the entrapped NAPL zone. In the dissolution experiments, the flowing aqueous phase appeared to infiltrate through the contaminated zones as multiple fingers rather than a uniform front. It was expected that concentrations would decrease with increasing velocity but the opposite was observed. This behavior was attributed to fingering of the aqueous phase through the contaminated zone, a concept introduced by Imhoff et al. (1996). A phenomenological model development yielded a relation that is expected to govern the mass
transfer inside a REV (representative elementary volume; Saba and Illangasekare, 2000):

\[
Sh = aRe^5Sc^3 \left( \frac{\theta_0 d_{50}}{\tau L^*} \right)^{\eta}
\]  

where Sh is the Sherwood number defined as \(Sh = k_{in} d_{in}^2 / D_m\), Re is the average Reynolds number along the contaminated zone given by \(Re = D / \nu\), and Sc is the Schmidt number given by \(Sc = \gamma / D_m\). The mass transfer coefficient \(k_{in} \left[ T^{-1} \right]\) is a lumped factor given by \(k_{in} = k_{in} d_{in}\) where \(k_{in}\) is the average mass transfer coefficient \([L T^{-1}]\) for the aqueous phase (subscript 1) and NAPL (subscript n) interface, and \(d_{in}\) is the specific interfacial area \([L^{-1}]\) between entrapped NAPL and groundwater. Furthermore, \(a, \beta, \alpha, \) and \(\eta\) are fitting parameters, \(d_{in}\) is the mean particle diameter \([L]\), \(D_m\) is the molecular diffusion coefficient \([L^2 T^{-1}]\), \(\nu\) is the aqueous phase velocity \([L T^{-1}]\), \(\tau\) is the tortuosity of the sand, \(\theta_0\) is the volumetric NAPL content, \(L^*\) \([L]\) is the path length the aqueous phase travels in the source zone, and \(\gamma\) is the kinematic viscosity \([L^2 T^{-1}]\) of water. The mass transfer coefficient is found in a commonly used form of the mass transfer relationship:

\[
J = k_{in}(C_s - C)
\]  

where \(J [M L^{-3} T^{-1}]\) is the mass flux from the NAPL to the aqueous phase, \(C_s [M L^{-3}]\) is the equilibrium aqueous phase concentration, and \(C [M L^{-3}]\) is the dissolved concentration in the bulk aqueous phase. In Eq. [3], the term \(\theta_0 d_{50} \nu / \tau L^*\) was proposed to represent the changing geometry in a contaminated zone block when NAPL is dissolved with time. The definition of \(L^*\) is not completely clear but Saba and Illangasekare (2000) stated that in numerical simulations, \(L^*\) is the length of the contaminated numerical soil block in the flow direction. This phenomenological model was implemented in the transport code MT3D (Zheng, 1990) and the dissolution experiments were simulated using a combination of MODFLOW (McDonald and Harbaugh, 1988) and MT3D. The values of all the parameters, except for the fitting parameters \(a, \beta,\) and \(\eta\), were obtained independently. The latter were obtained using the inverse model UCODE (Poeter and Hill, 1998). Saba and Illangasekare (2000) found that dissolution could be simulated using the relationship

\[
Sh = 11.34 Re^{0.2767} Sc^{0.33} \left( \frac{\theta_0 d_{50}}{\tau L^*} \right)^{1.037}
\]  

Mass transfer coefficient values for the simulations were computed by solving the equation \(Sh = k_{in} d_{in}^2 / D_m\) for \(k_{in}\). It was shown that this model produces lower dissolution rates than models developed from column experiments. The reason for this behavior is that, according to Saba and Illangasekare (2000), most of the relations developed for 1-D conditions do ignore the fact that the average value of the mass transfer coefficient decreases with an increase in the length of an entrapped NAPL zone. In the columns, water is forced through the entrapped NAPL zones, resulting in more dissolved NAPL. In 2-D flow fields, however, groundwater may bypass contaminated zones due to their lower permeability; however, entrapped zone bypassing was deemed unimportant by Anderson et al. (1992). The model (Eq. [5]) better predicted the dissolved concentration profiles in an independent experiment using a flow cell with three entrapped zones. The researchers argued that because of the inclusion of a length factor that takes into account the size of the contaminated zones, the proposed model is not constrained to the sizes of the LNAPL zones used in this study, and can be upscaled to different contaminated zone lengths; however, it should be noted that the effects of preferential dissolution have not been included in the model development. Saba and Illangasekare (2000) stated that this study can be seen as a first step in the evaluation of errors that might occur when laboratory data are used to make predictions in 3-D field systems. They also warned against using parameters obtained from 1-D simulations for multidimensional systems.

Brusseau et al. (2000) noted that aqueous phase concentration data often serve as the basis of decisions regarding remediation but that aqueous concentrations of NAPL constituents are often orders of magnitude lower than their equilibrium concentrations, even at sites where their presence has been confirmed. This severely constrains the use of concentration data for determining mass distributions. Knowledge of NAPL dissolution behavior under conditions prevalent at the field scale is critical for conducting risk assessments and implementing appropriate remediation strategies for NAPL-contaminated sites. In addition to pore-scale rate-limited mass transfer, factors that cause apparent rate-limited behavior are the result of limited contact between advecting water and NAPL. For instance, when bypass flow occurs due to reduced permeability, NAPL dissolution is affected. This situation might occur where entrapped NAPL resides in low permeability zones or when pooled NAPL severely reduces the aqueous permeability. Dilution in wells might also significantly reduce observed concentrations. The result of research shows that the magnitude of aqueous concentrations in the presence of NAPL can be significantly influenced by NAPL distribution, porous-media heterogeneity, and sampling method.

Dissolution experiments were conducted using an intermediate-scale flow cell packed with a medium-grained sand in which two zones of entrapped TCE saturation were emplaced (Brusseau et al., 2000). One (Zone 2) was created in the same medium-grained sand as used for the flow cell matrix, and the other was created in finer sand (Zone 1). Aqueous samples were obtained using depth-specific sampling, vertically integrated sampling, and the extraction well. A dual-energy \(\gamma\) radiation system was used to determine entrapped DNAPL saturations before and during the dissolution process. A tracer test (Br) was done to examine the potential influence of nonuniform flow and dilution-related factors on solute transport. The tracer solution contained a fluorescent dye for visual observations. Results show that nonuniform flow behavior was associated with the TCE zones. Specifically, the front was delayed slightly by Zone 2 and significantly by Zone 1. For Zone 2, dissolution occurred relatively uniformly
across the upgradient edge and continued progressively along the longitudinal axis of the zone. For Zone 1, mass removal was limited to the periphery. For this zone, the relative permeability was 80 times smaller. The NAPL dissolution and mass removal were strongly affected by heterogeneity. The results of this study indicate that nonuniform NAPL distribution, physical heterogeneity, and associated nonuniform flow considerably influenced the magnitude and location of NAPL dissolution. The magnitude of aqueous phase concentrations varied as a function of location and sampling method. The concentrations at the vertically integrated ports and the extraction well were less than the concentrations measured at the point-sampling ports, indicating dilution effects. This illustrates the importance of considering the type of sampling method used when analyzing and interpreting data. The smaller concentrations were caused by sampling-associated dilution rather than by rate-limited interphase mass transfer at the pore scale. The results reinforce the concept that the presence of a NAPL cannot be necessary ruled out even when aqueous concentrations are only a fraction of expected equilibrium concentrations (Brusseau et al., 2000).

Brusseau et al. (2002) described an experiment similar in design to the one discussed by Brusseau et al. (2000). In the second experiment, the lower zone (Zone 1) consisted of a 0.85 to 0.60-mm sand with entrapped TCE. The upper zone (Zone 2) contained entrapped DCA (dichloroethane). The solubility of DCA is about 8.6 g L\(^{-1}\) at room temperature vs. 1.1 g L\(^{-1}\) for TCE. A 3-D mathematical model was used to solve the governing equation for solute transport with dissolution of an immiscible liquid, described using the widely used first-order mass transfer equation. The Sherwood correlation used by Brusseau et al. (2002) is the one proposed by Powers et al. (1994):

\[
\text{Sh} = \alpha \text{Re}^\beta \delta^\gamma U_i^\delta \left( \frac{\theta_a}{\theta_{ao}} \right)^\beta_i \]

where \(d = d_{so}/d_M\) is a normalized grain size with \(d_M = 0.05\ cm\) (reference diameter), \(U_i = d_{so}/d_M\) is the uniformity index for the porous medium, \(d_{so}\) is the diameter of the media grains, 50% of which in weight are smaller than \(d_{so}\), \(\alpha\) and \(\beta\) are coefficients, and \(\theta_{ao}\) is the initial NAPL saturation, as determined with the dual-energy \(\gamma\) radiation system. Other parameters and variables in Eq. [6] were defined above. Column experiments were completed to independently determine initial dissolution rate coefficients. The columns were packed and flushed using similar methods as were used for the entrapped source zones in the flow cell. A 1-D mathematical transport model coupled to an optimization program was used to obtain initial dissolution rate coefficients. With the initial rate coefficients, the \(\alpha\) value in Eq. [6] could be computed. Brusseau et al. (2002) used the Sherwood equation differently than Saba and Illangasekare (2000). Equation [6] was not used to solve the inverse problem to obtain \(k_{in}\) values. Instead, Eq. [6] was used to convert the initial values obtained from the column experiments to discrete nodal values, accounting for spatial differences in the physical properties. Specifically, the initial mass transfer coefficient values for the flow cell experiment were computed as

\[
k_{in} = k_{in}' \left( \frac{d_{so}}{d_M} \right)^2 \frac{\text{Re}}{\text{Re}_c} \left( \frac{\delta}{\delta_i} \right) \left( \frac{U_i}{U_i'} \right)^{\beta_i} \]

where the primed variables are representative of the conditions used to obtain the measured initial values for the column experiments. The time dependency of \(k_{in}\) is given by

\[
k_{in}(t) = k_{in_0} \left[ \frac{\text{Re}(t)}{\text{Re}_c(t)} \right]^{\beta_i} \left( \frac{\theta_n(t)}{\theta_{no}} \right)^{\beta_n} \]

where the subscript 0 denotes initial local values. Brusseau et al. (2002) noted that this procedure has the advantage of producing predictions that are independent of the measured data. Hence, this is a more robust test of model performance than the calibration approach used by others (e.g., Saba and Illangasakere, 2000). Despite uncertainty in immiscible liquid distribution, sampling effects and permeability variability, the 3-D mathematical model produced good matches with the experimental data. The initial \(k_{in}\) values, obtained independently from the column experiments, appear to provide accurate predictions of the dissolution behavior in the flow cells. These values represent the contribution of local-scale processes; however, as was stated before, dissolution of immiscible liquids is also influenced by several larger scale factors. The research of Brusseau et al. (2002) suggests that the local-equilibrium approach can be used as an approximation to describe local-scale dissolution as long as the larger scale factors influencing dissolution are accounted for. Unfortunately, this information is often not available at field sites, and thus restricts the use of modeling approaches based on explicit descriptions of immiscible-liquid distribution. Brusseau et al. (2002) pointed out that the use of laboratory-scale dissolution rate coefficients or the local-equilibrium approach, in combination with simplified field-scale transport models that employ uniform NAPL distributions, will probably result in overpredicted concentration values and mass-removal rates. They suggested that upscaling procedures are needed to account for scale dependency for factors not accounted for explicitly in the modeling approach.

The only dissolution study of entrapped field DNAPL was conducted by Eberhardt and Grathwohl (2002). Details of this experiment were discussed above. The entrapped zone was constructed by mixing known amounts of DNAPL and wet porous media. A total of 11.4 kg (9.5 L) of coal tar was used to create the entrapped zone, resulting in a saturation of 4.96%. Regarding the entrapped DNAPL dissolution, the objectives of the study were to determine the validity of Raoult’s law for prediction of aqueous concentrations, and to test the local equilibrium assumption for entrapped coal tar dissolution. Results showed that Raoult’s law was applicable for estimation of aqueous concentrations, assuming an activity coefficient of 1. In addition, it could be demonstrated that the local equilibrium assumption could be used for an entrapped zone of this size. No significant
decrease of the fluxes of any of the compounds was observed during the total run time of the experiment, indicating that no additional mass transfer resistances arose. Some dissolution fingering was observed during the entrapped NAPL dissolution.

**Dissolution of Macroentrapped Nonaqueous Phase Liquids**

The work by Manivannan et al. (1996), Powers et al. (1998), and Nambi and Powers (2000) addressed processes governing the overall dissolution of the various NAPLs entrapped in a coarse sand lens in an otherwise fine-grained sand at a high saturation. Manivannan et al. (1996) used a coarse-grained rectangular lens with dimensions of 3 by 2 by 2 cm. The entrainment in the coarse sand lens was established through immiscible displacements using the entire pore volume of the cell. This procedure yielded an average saturation of ~0.10 to 0.20 in the fine-grained and 0.80 in the coarse-grained lens. After the formation of the two-phase system, the flow cell was flushed with clean water. A series of photographs was presented to document the dissolution process. First, it was observed that TCE was selectively removed around the periphery of the lens, indicating a bypassing of the lens due to a reduced aqueous phase permeability. Later, the dissolution also started to occur in the lens. Apparently, in addition to water bypassing around the DNAPL-contaminated coarse sand lens, sufficient water flowed through this region to cause an increase in relative permeability and effluent concentration with time. Two simple mathematical models were developed to explore possible physical phenomena contributing to the observed phenomena. The assumptions for the first model were that the DNAPL in finer sands dissolves first, followed by some flow of water through the coarse lens, leading to, finally, a greatly reduced DNAPL saturation in the lens. The second model assumes that water--DNAPL contact only occurs along the perimeter of the lens and that, as the DNAPL saturation in the contaminated lens is reduced, a larger fraction of the water will flow through the lens. Manivannan et al. (1996) showed that the first model produced the better results.

The experiments described by Powers et al. (1998) are a continuation of the work by Manivannan et al. (1996). For the 2-D studies, TCE, DCA, and o-toluidine were used in separate experiments. The nearly neutral density DNAPL o-toluidine, with a solubility of 16 500 ppm, was introduced to further isolate the dissolution processes from the multiphase flow phenomena caused by gravitational forces. The coarse sand lens was larger (5 by 2 by 3 cm) than in the study by Manivannan et al. (1996), and a different fine-grained sand was used. The emplacement process was changed to direct injection of a known volume of NAPL through a port installed in the back of the cell. This procedure created a high degree of NAPL saturation in the lens, while the surrounding fine-grained sand stayed clean. The 2-D experiments were designed to isolate processes controlling dissolution of lenses containing high saturations of NAPL. The experimental variables were aqueous phase velocity, type of NAPL, grain size of the coarse, and initial NAPL saturation. For a typical experiment with o-toluidine, photographic evidence showed that as time progressed, a reduction occurred in the overall NAPL saturation in the lens without an apparent spatial variability in saturation; however, random heterogeneities were apparent. More variability was observed using the denser DNAPLs TCE and DCA as a result of severe gravity drainage. For this reason, the experiments with TCE and DCA were not continued. Quantitatively, the effluent curves showed a gradual increase in concentration for the first 60 to 80 pore volumes, followed by a steep decline. The modeling combined MODFLOW (McDonald and Harbaugh, 1988) for flow and MT3D (Zheng, 1990) for transport, and was more extensive than for the Manivannan et al. (1996) study. The models were coupled by a mass balance subroutine to estimate the mass NAPL loss at each time step. The coarse sand was treated as a single REV with the NAPL saturation averaged throughout this volume. Relative permeability and dispersivities were not directly measured and the local equilibrium assumption was assumed for NAPL dissolution. As a result, Powers et al. (1998) stated that the modeling was only intended to show general trends, and not to match the data explicitly. In general, the model predictions were consistent with the overall trends in the experimental data, meaning that the simulations predict an increase in effluent concentrations, followed by a rapid decline. The model was most sensitive to estimates of the relative permeability in the coarse lens. As expected, the experimental data show more tailing than the model, which employed local equilibrium dissolution. For NAPL saturations larger than ~0.15, system hydrodynamics were indicated as the sole rate-limiting process. Below this value, rate-limited mass transfer reduced the observed concentrations.

Nambi and Powers (2000) completed several additional experiments using a similar design as described by Powers et al. (1998) to understand and identify the parameters controlling NAPL dissolution in heterogeneous systems. O-toluidine was again used to ensure uniform distribution. Several parameters that influence the hydrodynamics of the system, i.e., sand grain size, size and distribution of the different permeability zones, and the initial NAPL saturation, were varied. The experiments were motivated by speculations of Powers et al. (1998) that aqueous flow patterns within a heterogeneous system are largely responsible for variable effluent concentrations in the 2-D system of concern. Initial NAPL saturation and the intrinsic permeability ratio, two variables that affect the ratio of effective permeability between the NAPL-contaminated coarse sand and the surrounding fine sand, have the most significant impact on effluent concentrations. As NAPL saturations within the coarse lens were reduced below 0.3, thermodynamic equilibrium was not achieved, resulting in a rapid decline in measured concentrations at the effluent ports. During that stage, decreases in the NAPL interfacial area and increases in the aqueous phase velocity could both contribute to mass transfer.
rate limitations. Another critical parameter is the exterior surface area of the NAPL-contaminated zone. A wider zone and distribution throughout two distinct zones resulted in larger aqueous phase concentrations. Mass transfer correlations for these experiments were developed by Nambi and Powers (2003).

**ENHANCED REMEDIATION**

**Surfactant Flushing**

A number of surfactant-enhanced remediation experiments at the intermediate scale with both LNAPLs (Chevalier et al., 1998; Chu et al., 1996; Saba et al., 2001; Schwille, 1967) and DNAPLs (Conrad et al., 2002; Dong et al., 2004; Field et al., 1999, 2000; Oostrum et al., 1999b; Ramsburg and Pennell, 2001; Rathfelder et al., 2003; Schaerlaekens and Feyen, 2004; Taylor et al., 2001; Walker et al., 1998b) have been performed in recent years. The experiments reported by Rathfelder et al. (2003) were conducted to study the behavior of PCE releases after the porous medium was flushed with surfactant solutions. Since the objectives of Rathfelder et al. (2003) were related to flow behavior and not remediation, the study is discussed in our companion review. Specifics of the conducted experiments are provided in Table 2.

In general, surfactants are used to increase the total aqueous solubility of a NAPL or to decrease NAPL–water interfacial tension to promote mobilization (Lowe, 1997). Depending on the desired effect, appropriate surfactants need to be chosen. The chosen surfactants are delivered to entrapped and pooled regions through the aqueous solution. Surfactant molecules have both a hydrophilic and a hydrophobic site, and are classified as either anionic, cationic, or nonionic. Anionic and nonionic surfactants tend to be good solubilizers and are relatively nontoxic. Nonionic surfactants are less sensitive to the presence of salts than anionic surfactants. They are also often used as cosurfactants. Cationic surfactants tend to be toxic. At the critical micelle concentration, contaminants can partition into the interior (hydrophobic) part of the micelles, referred to as micellar solubilization (Abriola et al., 1995). Large contaminant concentration increases into aqueous solutions can thus be accomplished, which is the basis of using surfactant flushing as a promising remediation technique. The degree of solubility enhancement, characterized by the molar solubility ratio (i.e., the moles of contaminant solubilized per mole of surfactant), depends on the combination of NAPL and surfactant. These types of systems are typically referred to as Winsor Type I systems or single-phase microemulsions with the micelles residing in the water. At ultra-low interfacial tensions, a middle-phase microemulsion or Winsor Type III system can be formed. It exists as a separate phase with a density between that of water and the NAPL. Winsor Type II systems occur when the NAPL is rich in surfactant micelles containing water. The hydrophobic ends of the surfactant molecules are now pointed outward toward the NAPL. Winsor Type II systems must be avoided because of the partitioning of the surfactant into the NAPL phase. Prior testing in the laboratory is needed to obtain the optimum surfactant for a given NAPL.

The degree of interfacial tension reduction, and hence capillary force, required to mobilize NAPL can be characterized by the capillary number, the bond number, and the trapping number (Pennell et al., 1996). The capillary number, \( N_{Ca} \), represents the ratio of viscous (mobilizing) forces to capillary (resisting) forces and is defined as

\[
N_{Ca} = \frac{q_w \mu_w}{\sigma_{nw} \cos \theta}
\]  \[9\]

where \( q_w \) and \( \mu_w \) are the Darcy velocity and the dynamic viscosity of the aqueous phase, respectively, and \( \sigma_{nw} \) and \( \theta \) are the interfacial tension and contact angle, respectively, between the NAPL and the aqueous phase. The bond number, \( N_b \), represents the ratio of buoyancy (gravity) to capillary forces and is defined as

\[
N_b = \frac{\Delta \rho gkk_{rw}}{\sigma_{nw} \cos \theta}
\]  \[10\]

where \( \Delta \rho \) is the difference between the densities of the aqueous phase and NAPL, \( g \) is the gravitational field strength, \( k \) is the permeability, \( k_{rw} \) is the relative permeability to the aqueous phase, and the other variables have been defined above. For a vertically oriented pore, with NAPL displacement in the direction of the buoyancy force, the sum of the bond and capillary numbers, referred to as the total trapping number \( (N_{T}) \) controls the displacement (Pennell et al., 1996).

**Light Nonaqueous Phase Liquid Surfactant Flushing**

The first intermediate-scale experiment in which a surfactant mobilized a NAPL was the qualitative test reported by Schwille (1967). A relatively large amount of a heating oil had infiltrated directly above the capillary fringe of a highly permeable porous medium. After redistribution of the oil body, oil recovery was attempted by spraying the soil with an aqueous detergent solution. After the spraying, the oil reportedly moved quickly to a recovery ditch. Chu et al. (1996) investigated the removal of organic liquid (dodecane) contaminants with surfactant foams (Bioterge AS-40). It appeared that the foam bubbles enhanced the removal of dodecane primarily by (i) plugging clean areas through its stability in zones free of dodecane and its instability in contact with dodecane, and (ii) breaking dodecane into stable globules whose diameters are smaller than those of the pore necks through which they must travel to be removed. It should be pointed out that this experiment, although unique in nature and promising as a remediation strategy, was performed under idealized conditions in a 2-D flow cell of only 2.5-mm thickness. The results of the experiments were only discussed in qualitative terms.

Chevalier et al. (1998) tried to mobilize a gasoline spill in a variably saturated 2-D flow cell with the use of the surfactant solution dodecyl benzene sulfonate. The gasoline was positioned on top of the capillary fringe. The reduction in interfacial and surface tensions resulted in
the desaturation of the aqueous phase and the subsequent flow of gasoline into previously water-saturated pores. With time, the spill transformed from a semicircle to a long, thin lens. The researchers performed an analysis based on the capillary, the bond, and the total trapping number to see if pretreatment with a surfactant could be beneficial before activating LNAPL pumping. The analysis showed that treatment with a surfactant before oil pumping would remove more LNAPL than the usual sequence of pumping followed by a surfactant treatment. Surfactant pretreatment transforms entrapped LNAPL, which cannot be removed by pumping, into free and mobile LNAPL that can be removed.

In a 2-D entrapped LNAPL zone experiment, Saba et al. (2001) showed the complete removal of entrapped p-xylene from a rectangular lens with polyoxyethylene sorbitan monooleate (Tween 80). A total of three experiments were conducted with different surfactant flow velocities and NAPL source zone lengths of 5.1 and 20.3 cm, respectively. The preparation and emplacement of the entrapped NAPL zones were identical to those of Saba and Illangasekare (2000) for aqueous phase dissolution experiments. The researchers emphasized that the contaminant dissolution occurred from the boundaries of the source toward its center. This was in apparent contrast to the unidirectional dissolution front characteristic of 1-D experiments. The primary goal of this research was to obtain additional insight into the mechanisms of mass transfer under 2-D flow fields. A total of four Gilland–Sherwood relationships were proposed to describe the mass transfer. After a theoretical analysis, one of the four models was deemed to be inappropriate because of its limited application to high NAPL saturations. The values of the parameters in the relationships of the remaining three models were determined using a method similar to the one used in Saba and Illangasekare (2000). These three models produced the same level of confidence. Unfortunately, the models were not applied to an independent experiment.

Dense Nonaqueous Phase Liquid Surfactant Flushing

Walker et al. (1998b) performed a surfactant-enhanced remediation experiment in an unsaturated coarse sand porous medium with a fine sand layer embedded. They attempted to clean up a PCE spill that had entered the porous medium with the water table near the bottom of the flow cell (Hofstee et al., 1998b). The location of the water table caused the coarse sand just below the fine sand layer to be unsaturated, while the bottom part of the fine sand layer was at or near saturation. The PCE spill entered and accumulated mostly in and below the fine sand layer. To hydraulically control the flow of the surfactant (Triton X-100) plume, the number of extraction ports and the extraction and influent pumping rates were varied. During the injection of the surfactant solution, Walker et al. (1998b) observed spontaneous spreading of the surfactant molecules. As a result of the decreased interfacial tension, the height of the saturated zone in the fine sand layer was reduced rapidly from approximately 20 to 4 cm. The researchers were able to show, through differential scanning calorimetry analysis, that the surfactant molecules prefer to reside at fluid–fluid interfaces rather than at fluid–solid interfaces. Walker et al. (1998b) also noted that drainage may be useful for air sparging or vapor extraction because more of the contaminated zone would be exposed to air. Upon entering the coarse sand below the fine sand layer, the surfactant plume formed definite fingers, which were attributed to a change in the porous medium properties at the fine–coarse sand interface and the increased density of the surfactant solution due to the solubilization of PCE. Walker et al. (1998b) demonstrated the importance of extraction well locations to promote removal of all PCE by the surfactant flushing process. They also reported the existence of milky Winsor Type I microemulsions.

Using a much more stratified porous medium and TCE as the DNAPL, Oostrom et al. (1999b) supported the basic findings of Walker et al. (1998b), i.e., unstable fingering and sinking of solutions containing solubilized TCE, formation of small TCE droplets, and milky, emulsion-like appearances. Oostrom et al. (1999b) used alternately pump-and-treat and surfactant (T-MAZ-80) flushing with a two-well system. Probably due to the added heterogeneity, only 60% of the TCE was removed. During excavation of the sand from the flow tank, free TCE was found in the bottom layer of fine sand, where it had been out of reach of the flushing solutions.

The effect of rate-limited micellar solubilization and subsurface layering on the recovery of PCE by 4% Tween 80 was clearly demonstrated by Taylor et al. (2001). They not only showed that the rate of PCE solubilization depended on the Darcy velocity, but that even under no-flow conditions, instantaneous equilibrium did not exist. Taylor et al. (2001) found that, similar to Walker et al. (1998b), the presence of fine layers resulted in an initial bimodal PCE distribution that consisted of high saturation zones or pools above fine layers and regions of entrapped PCE existing as entrapped droplets or ganglia. The entrapped NAPL was easily removed by Tween 80, but Taylor et al. (2001) encountered the most difficulty in removing the pooled PCE collected on top of the fine layers. They did not observe the entry of PCE into these fine layers. The PCE recovery was strongly affected by the low-permeability lenses as well as mass transfer limitations. The experiments showed clearly that the injected surfactant solutions, which were slightly denser than the ambient solution, flowed preferentially along the bottom of the flow cell. They argued that, for DNAPL pools above a confining layer, the use of denser surfactant solutions may be advantageous due to the tendency of such solutions to flow along the bottom of a contaminated aquifer. The experiments were simulated with the MISER code by Rathfelder et al. (2001). Model parameter values were derived from independent experiments. The model assumes an immobile PCE phase and rate-limited mass transfer for solubilization and surfactant sorption. An explicit formulation of the PCE–water interfacial area was incorporated to obtain an accurate
prediction of the solubilization process. Since PCE saturations were not directly measured, the initial saturation distribution needed for the MISER simulations was estimated from visual observation or obtained from a multiluid flow simulation of the PCE injection (Rathfelder et al., 2001). The uncertainties in the initial distribution caused discrepancies between model predictions and measured values.

When a porous medium has been exposed to a NAPL for a long time, the solid phase may become hydrophobic rather than hydrophilic. Such is the case with, for example, coal tars. Dong et al. (2004) were able to show, in very simple qualitative experiments, that coal tar could be mobilized at intermediate concentrations using polymeric surfactants. If the concentration of the surfactant was too high, dissolution of the coal tar would occur. If it was too low, no effect was measurable.

The flow cell work by Ramsburg and Pennell (2001) was done to test two surfactant formulations with either Tween 80 or Aerosol MA-80 in support of source zone remediation of PCE at a former dry cleaning facility. The saturated flow cell was packed with a lower permeability zone at the bottom and two narrow zones with low-permeability lenses in an otherwise medium-grained aquifer sand. The interfacial tension of Tween 80 solution with PCE was 4.90 dynes cm

2

. The Aerosol MA-80 interfacial tension with PCE was considerably lower at 0.160 dynes cm

2

, but the solubility was reported to be 76 360 mg L

1

. Both surfactant formulations were modified with salt to obtain densities >1.0 kg L

1

, which was desired to avoid density override effects and to achieve complete flushing of the swept volume (Ramsburg and Pennell, 2001). The results showed that the Tween 80 application resulted in PCE solubilization with a removal percentage of only 53%; however, although the Aerosol MA-80 was able to remove 78%, the application resulted in downward PCE mobilization. An analysis based on the trapping number showed that this result was not unexpected. As a result of this study, Aerosol MA-80, although a great solubilizer, was removed as potential surfactant to clean up the targeted field site.

Conrad et al. (2002) conducted controlled experiments using Aerosol MA and Tween 80 surfactants to increase the solubility of TCE in sand packs designed to be representative of a fluvial depositional environment. The TCE was injected from a point source in a fully water-saturated system. The final distribution of the TCE revealed a series of descending pools. The Aerosol MA surfactant caused extreme reductions (almost 50-fold) in the DNAPL–water interfacial tension, followed by mobilization into low-permeability regions, worsening the remediation problem. Application of the Tween 80 surfactant, with a smaller interfacial tension reduction, resulted in modest, manageable mobilization since the liquid TCE did not migrate into low-permeability regions. The favorable solubilization properties of TCE in a Tween 80 solution allowed a recovery of almost 90%. Conrad et al. (2002) noted that the propensity to mobilize during surfactant flushing is greatly enhanced when DNAPL is held in pools.

Schaerlaekenks and Feyen (2004) completed three experiments in which relatively small amounts of entrapped TCE were removed with a 2% Tween 80 solution using different flow rates. Only small amounts of TCE were injected to ensure that pooling would not occur at the bottom of the cell and that all TCE would be in the entrapped form. Similar to Saba et al. (2001), one of the goals of this work was to determine an applicable empirical mass transfer rate model for intermediate-scale experiments. The rate-limited solubilization process was simulated with the so-called NAPL code (Guarnaccia et al., 1997). The derived Gilland–Sherwood expression showed, not surprisingly, a strong correlation between the rate coefficient and the NAPL saturation and the Reynolds number. No attempts were made to apply the derived expression to other 2-D experiments. Schaerlaekenks and Feyen (2004) compared their 2-D expression with a relationship derived for earlier column experiments using the same porous materials and chemical. Consistent with Saba and Illangasekare (2000) and Saba et al. (2001), they found that the expression derived for the 2-D cell predicts lower mass transfer rates than the model that was obtained through column experiments. Schaerlaekenks and Feyen (2004) argued that the lower mass transfer rate in their 2-D systems could be attributed to bypassing of the DNAPL zone in a 2-D system due to a reduced permeability.

Single-well push–pull tests were conducted by Field et al. (1999, 2000). The experiments discussed in Field et al. (1999) were conducted to evaluate the ability of this test to characterize the enhanced solubilization of TCE by the surfactant DOWFAX (hexadecyl diphenyl oxide disulfonate). The experiments were performed in wedge-shaped cells to simulate the alternating radially divergent–convergent flow field in the vicinity of an injection–extraction well. Experiments with DOWFAX considerably increased the maximum concentration of the extracted solutions compared with flushings with water only; however, Field et al. (1999) also reported considerable sinking of the surfactant solution due to solubilization of TCE and subsequent accumulation of DOWFAX and dissolved TCE at greater depth. No mobilization or sinking of liquid TCE was observed. Based on their results, Field et al. (1999) stated that, despite the dissolved plume sinking, push–pull tests can provide useful information on surfactant-enhanced solubilization of NAPLs in the subsurface.

Surfactant effectiveness for enhancing NAPL solubility has been evaluated in the laboratory for a wide range of system-specific conditions, such as the type and concentration of surfactants and cosolvents, and the valence and concentrations of electrolytes present in the applied solutions and in the solid phase (Edwards et al., 1991; Rouse et al., 1993; Valsaraj and Thibodeaux, 1989). Consequently, it is to be expected that cation exchange between the liquid and solid phase will play a role in the effectiveness of surfactant-enhanced NAPL recovery in the subsurface. This was the topic of further research by Field et al. (2000) in a push–pull (single well) flow cell experiment. They assessed the potential for cation ex-
change to adversely affect the phase behavior of the surfactant Aerosol MA 80-1 (sodium dihexyl sulfosuccinate) and its solubilization of TCE in the subsurface. Based on batch experiments, they concluded that TCE solubility can either increase (at intermediate Ca\(^{2+}\) concentrations) or decrease (at high Ca\(^{2+}\) concentrations, either a Winsor Type II or III solution) in the surfactant solution they used. Their flow cell experiment showed that increasing concentrations of Ca\(^{2+}\) and Mg\(^{2+}\) resulted in the partitioning of sulfosuccinate into the entrapped TCE phase and smaller aqueous TCE concentrations than predicted from the solubilization isotherm. Field et al. (2000) also showed that quantities of exchangeable Ca\(^{2+}\) and Mg\(^{2+}\) could be substantially reduced by a 0.130 mol L\(^{-1}\) NaCl preflush, and restoring conservative sulfosuccinate transport, Winsor Type I phase behavior, and increased aqueous TCE concentrations. The simultaneous reduction of interfacial tensions, however, resulted in free TCE accumulation.

**Alcohol Flushing**

Alcohol flushing for environmental purposes, like surfactant flushing, is derived from an enhanced oil recovery technique mainly for crude oil recovery. Many alcohols are mutually miscible in both water and NAPL and possess a great ability to solubilize and mobilize NAPLs as pure phase by a combination of viscous and gravity forces, and via reduction of interfacial tensions (Grubb et al., 1997). When used in combination with surfactants (see combination schemes below), alcohols are sometimes referred to as cosolvents. Alcohols that are considered for remediation (e.g., ethanol, 1-propanol, and 2-propanol) are usually low-molecular-weight alcohols that are completely soluble in water. The fact that the specific gravities of LNAPls and many alcohols are <1 provides a tendency for both to accumulate near the water table. Intermediate-scale experiments for NAPL removal were reported by Grubb et al. (1997, 1998) and Palomino and Grubb (2004). When DNAPLs are being remediated with alcohols, concerns exist that the DNAPLs may mobilize and contaminate deeper regions previously not contaminated. Some of the earlier 1-D column experiments were conducted to promote DNAPL swelling, i.e., to have the alcohol partition into a DNAPL (e.g., Boyd, 1991; Brandes and Farley, 1993) to reduce its density. The experimental work of these researchers assessed the utility of alcohols for enhancing the mobilization of entrapped DNAPLs in 1-D columns through interfacial tension reduction and DNAPL swelling. Their investigations used isopropyl and tert-butyl alcohols in combination with the DNAPLs TCE and PCE. Downward migration during the upward flushing with alcohol–water mixtures was minimized because of the partitioning of alcohols into the DNAPLs. Most of the flow cell remediation experiments involving alcohol flushing of DNAPLs (Boyd et al., 2006; Grubb and Sitar, 1999; Lunn and Kueper, 1997, 1999a, 1999b; Roeder et al., 2001; Van Valkenburg and Annable, 2002) focused on mobilization reduction.

**Light Nonaqueous Phase Liquid Alcohol Flushing**

Grubb et al. (1997, 1998) used ethanol (density = 0.795 g cm\(^{-3}\)) flooding to remove the LNAPL toluene (density = 0.8605 g cm\(^{-3}\)) from a 2-D flow cell and observed the toluene to move downward along the water–alcohol interface. In Grubb et al. (1997), the flow cell was filled with a 0.85- to 0.60-mm Ottawa sand. Grubb et al. (1998) also used layered systems including two fine-grained sand layers. Small quantities (20 mL) of toluene were injected in the partly saturated cells and, after static equilibrium was achieved, the remediation scheme was initiated. Grubb et al. (1997, 1998) used a dual-flooding scheme consisting of a primary flood of pure ethanol followed by a secondary flood consisting of a 50:50 (v/v) ethanol–water mixture. They showed that the 50:50 blend is that it creates a viscous and dense fluid wedge below the toluene, enabling upward and downgradient mobilization (Grubb et al., 1998). The floods were introduced at the water table to minimize buoyancy flow of alcohol. During the first flood with pure ethanol, toluene mobilization was observed. The toluene moved downward, in a similar fashion that would have been expected for DNAPLs, to the ethanol–water interface. This location is expected based on the intermediate density of the toluene between ethanol and water. With time, toluene banking reduced the ability of the ethanol to remove additional toluene due to a reduced permeability. Trapped toluene was subsequently removed using a denser 50:50 (v/v) alcohol–water mixture. The removal rates of toluene in both the homogeneous and heterogeneous systems were estimated to be ~80%. Similar experiments were later repeated with the LNAPLs dodecane, octane, and toluene using larger LNAPL volumes (Palomino and Grubb, 2004) and yielded similar results. The high recovery rates (>80%) were considered by Palomino and Grubb (2004) to be impressive since no optimization was attempted. All experiments show a strongly stratified system according to the density of the fluids. This phenomenon allows for a gravimetric separation of the fluids since the interfaces were <1 cm thick. The researchers made the argument that it might be economically feasible to recover and recycle the concentrated ethanol–LNAPL mixture as a feedstock to the petroleum refining process.

**Dense Nonaqueous Phase Liquid Alcohol Flushing**

Ethanol and 1-propanol were compared for the removal of PCE pools by alcohol flooding using low upward hydraulic gradients in vertical column experiments by Lunn and Kueper (1997). They showed that, for alcohol concentration below the miscibility envelope, 1-propanol would partition predominantly into the PCE, while the ethanol would remain in the aqueous solution. Although increasing concentrations of both ethanol and 1-propanol would further reduce the interfacial surface tension, the density of the DNAPL was consequently only reduced by the 1-propanol through DNAPL swelling. Interestingly, the nonswelling alcohol ethanol reduced the density of the aqueous phase containing dissolved PCE. The two alcohols resulted into two dif-
ferent removal mechanisms. Ethanol floods included enhanced dissolution followed by miscible displacement, while 1-propanol removed PCE by swelling and interfacial tension reduction leading to immiscible displacement. The researchers, however, cautioned that downward PCE migration may still occur, both in free form with ethanol flooding (no density reduction) as well as during the initial stages with 1-propanol flooding. They recommended additional research with DNAPL-swelling alcohols and injection schemes where large alcohol slugs are delivered beneath the source zone.

Lunn and Kueper (1999a), using a similar experimental setup with pooled PCE, demonstrated the ability of 2-butanol to partition into the DNAPL and reduce its density to below that of water. The 2-butanol was introduced as a preflow, followed by a vertical miscible displacement with 1-propanol. For total alcohol additions of up to one pore volume, high recovery rates were achieved. Lunn and Kueper (1999a) presented formulae that evaluate downward mobilization potential. They commented that once the density of the DNAPL is reduced to that of water, the requirement for a vertical flood to negate downward mobilization might not be needed.

Hydrodynamic instabilities during alcohol flooding diminish the efficiency of DNAPL displacement. Unstable behavior has been identified (Lunn and Kueper, 1999b) as one of the primary causes for bypassing of DNAPL, alcohol dilution, and inefficient miscible displacement. To address the stability issue, improvements were made by Lunn and Kueper (1999b) by using a three-step alcohol flooding process, viz., an isobutanol preflow, a composite alcohol main flow, and a polymer solution postflow. The preflow (10% [v/v] isobutanol) accomplished a reduction in PCE density to approximately 1.0 kg L\(^{-1}\). The main flow (65% ethylene glycol and 35% 1-propanol [v/v]), which was neutrally buoyant, was used to displace the modified DNAPL with an inherently stable interface. Finally, the main flow was displaced by a postflow consisting of a xanthan gum polymer solution, also with a density of approximately 1.0 kg L\(^{-1}\), to reduce viscous fingering associated with water floods. Lunn and Kueper (1999b) reported a 99.8% mass recovery, using only 0.45 pore volumes of alcohol. The researchers recommended that future research focus on the delivery strategies for heterogeneous field situations.

During horizontal ethanol flooding experiments to remove TCE from homogeneous and layered systems, Grubb and Sitar (1999) observed rapid downward mobilization of TCE to occur at the leading edge of the ethanol front, indicating that interfacial tension reduction was more dominant than NAPL dissolution under the conditions of the experiment. Moreover, the mobilization of TCE appeared to be confined to the ethanol–water interface. They also observed downward dissolved TCE migration at relatively low flooding flow rates. The downward movement of the dissolved plumes was not unexpected, given that the maximum measured TCE concentrations were 360 000 mg L\(^{-1}\). The flow-rate-dependent sinking behavior of dissolved plumes had been observed earlier by, e.g., Oostrom et al. (1992). In addition to phase mobilization and dissolved plume sinking, the researchers also observed upward migration of ethanol through finer grained soils due to buoyancy. Grubb and Sitar (1999), who did not include preflooding in their experiments, warned that, in the field, upgradient and downward migration of TCE can occur in an uncontrolled fashion and that mobilization occurrences may be essentially undetectable, given the normal precision of field measurement techniques.

Roeder et al. (2001) obtained PCE density reduction by using tert-butyl alcohol. The main goal of the flow cell work was to investigate if phase density difference reversal could be applied for horizontal floods. Since the alcohol does not completely achieve phase density difference reversal, sucrose was added to the flushing solution to obtain concurrent density increases of the aqueous phase. The selected flooding solution of 40% tert-butyl alcohol, 15% sucrose, and 45% water (v/v) had a density of 1.024 kg L\(^{-1}\) and a viscosity of 11.4 g m\(^{-1}\) s\(^{-1}\). By manipulation of the aqueous density, the researchers attempted to avoid overriding of the alcohol flushing solution, which leads to lower remediation effectiveness. The bottom of the packing consisted of bentonite. A 56-cm zone of 0.30- to 0.50-mm sand was placed on the bentonite. A volume of 115 mL PCE was injected into the flow cell in sufficient amounts to create both entrapped and pooled DNAPL. Most of the injected PCE moved to the bottom of the flow cell and migrated horizontally on sand layers; however, ~25% of the PCE entered the bentonite. The horizontal displacement with the alcohol solution showed that density reversal did occur. In the swept zone, PCE removal was complete. In this particular case, the flushing solution caused underridding, which helped the mobilized NAPL rise to the top of the flow cell (Roeder et al., 2001).

Van Valkenburg and Annable (2002) observed the accumulation of pooled PCE into a lower confining layer during removal with alcohols. A nonswelling reagent alcohol (containing 90% ethanol) and the partitioning tert-butyl alcohol were used in the experiments at different concentrations. Results showed that, for the ethanol injections, interfacial tension reduction between the injected alcohol and the DNAPL caused more mass movement than DNAPL solubilization. The partitioning alcohol caused significant swelling of the PCE and delayed any downward mobilization due to density decreases. Expressions to calculate the entry pressure needed for a DNAPL to enter confining layers were presented by Van Valkenburg and Annable (2002) and later corrected by Roy and Smith (2004).

The experiments conducted by Boyd et al. (2006) investigated the influence of preflooding and gravity on PCE flushing with a mixture of ethylene glycol and 1-propanol. The flow cell experiments consisted of a PCE injection stage, a water flood to ensure full PCE entrapment, an optional alcohol preflow with a 10% isobutanol solution, followed by the actual alcohol flood. The flow cell was either horizontal or inclined at 15 or 30°. The results showed an increased recovery in the horizontal configuration when preflooding was used.
due to reduced interfacial tensions and swelling of the entrapped PCE; however, the preflood caused a decrease in PCE recovery when the flow cell was inclined. The decreased recovery was attributed to PCE mobilization and uncontrolled migration during the preflood and unstable finger formation during the main flood.

**Surfactant–Alcohol Flushing Combination Schemes**

Alcohol addition to surfactant solutions has been suggested to enhance solubilization kinetics, phase behavior, mobility control, and density control of the injection solution and microemulsion containing DNAPL. When large quantities of DNAPLs dissolve in the aqueous phase, as promoted by the use of surfactants, the ensuing microemulsion plumes may become unstable and migrate downward to previously uncontaminated areas. Kostarelos et al. (1998) avoided the downward migration problem of microemulsions by adding isopropanol to their surfactant solution. Taylor et al. (2004) used ethanol to modify the density of the surfactant flushing solution to allow better control of the surfactant delivery. Walker et al. (1998a) used combinations of surfactants and isopropanol to remove PCE from a saturated system using a very elaborate flushing scheme. Using rather elaborate schemes, Ramsburg and Pennell (2002) and Ramsburg et al. (2003, 2004) experimentally tested various forms of the DMD (density-modified displacement) method in which alcohol prefloods were used to convert DNAPL to LNAPL through alcohol partitioning before subsequent floods containing surfactants removed the converted NAPL.

The isopropanol employed by Kostarelos et al. (1998) was used in combination with the surfactant sodium dihexyl sulfocuccinate and the polymer xanthan gum in a flow cell experiment to remove a TCE spill. The mixture was used to address the problem of dense microemulsion downward migration in the absence of NAPL mobilization. The surfactant was selected because of its intermediate ability to dissolve TCE while not mobilizing it. The alcohol was selected because of its ability to partition into the microemulsion and hence reduce the density approximately to that of the ambient water. The polymer was selected because it increased the viscosity of the microemulsion solution. Both the addition of the alcohol and the polymer reduced the downward migration of the microemulsion. In other words, the plume remained stable under the conditions of the experiment. The method was not evaluated regarding its efficiency. Kostarelos et al. (1998) called their approach SEAR-NB (surfactant enhanced aquifer remediation at neutral buoyancy). Flow and transport calculations to design a SEAR-NB flood were presented by Shook et al. (1998). Kostarelos et al. (1998) claimed that using SEAR-NB, DNAPL can be removed even from aquifers “with no capillary barrier or an unknown or insufficient capillary barrier.”

Taylor et al. (2004) used ethanol in combination with Tween 80 to remove PCE from a heterogeneous system. In their experiments, the effects of rate-limited micellar solubilization, subsurface layering, and flushing solution density on solution delivery and PCE recovery were evaluated. In an experiment using the injection of a 4% Tween 80 and 5% ethanol flushing solution through a fully screened well, gravity override was observed resulting from a density difference of only 0.004 g cm\(^{-3}\), however, in a flush without the alcohol, the density of the injected solution was 1.002 g cm\(^{-3}\) and preferential flow along the bottom of the flow cell was observed. Taylor et al. (2004) noted that relatively small density contrasts can lead to nonuniform flow fields affecting contact between the flushing solution and DNAPL. In an attempt to minimize the preferential flow, the flushing solution was only delivered from a partly screened well. The resulting flush resulted in a greatly improved delivery of the remediation fluids and improved sweep efficiency. The simulator MISER (Rathfelder et al., 2001) was used to simulate the effects of the alcohol additions on fluid flow and PCE recovery. As was done for the surfactant flushing experiments described by Taylor et al. (2001), the initial saturation distribution needed for the MISER simulations was estimated from visual observation or obtained from a multifluid flow simulation of the PCE injection (Rathfelder et al., 2001). The comparisons between observed and predicted PCE concentrations were reasonable. Uncertainties in the initial distribution were assumed to have caused discrepancies between model prediction and measured values. The MISER model provided a good description of density-dependent flow in the flow cells.

Walker et al. (1998a) performed alcohol-enhanced surfactant remediation experiments in a saturated, coarse sand porous medium with an embedded fine sand layer. A PCE spill entered the porous medium from the surface and pooled on top of the fine sand layer (Hofstee et al., 1998a). Entrapped PCE was distributed above the fine layer and on either side of and below the fine sand layer. The researchers used different surfactants (Triton X-100, Tween 80) at different concentrations and isopropanol, either by itself or as a cosolvent, in combination with different flow regimes to enhance contact between the PCE and the surfactant–cosolvent solutions. In the end, 83.5% of the PCE had been removed from the flow cell as measured with a γ radiation system. Almost immediately from the start of the surfactant flushing, Walker et al. (1998a) noticed that traces of free PCE were moving in advance of the surfactant solution front. This was attributed to surfactant monomers moving ahead of the aqueous surfactant solution along the PCE–water interface and reducing the interfacial tension. It also allowed some of the free PCE in the form of streaks, consisting of small PCE droplets, to enter the fine layer. Although this contaminated a previously PCE-free region, it also increased the surface area available for contact with the surfactant solutions. The movement of these fine droplets would seem to be effected by the pore sizes. Pumping from multiple extraction ports (wells) had the effect of either converging or diverging the influent plume with respect to the fine layer and the pooled PCE, depending on the locations of the ports and the influent and extraction flow rates. The findings of Walker et al. (1998a) mimic results observed for the Borden (ON,
Canada) and Corpus Christi (TX) field trials (Fountain et al., 1991, 1995).

In a series of studies, Ramsburg and Pennell (2002), and Ramsburg et al. (2003, 2004) tested techniques using prefloods with partitioning alcohols and main floods with surfactants. Ramsburg and Pennell (2002) used a 6% $n$-butanol aqueous solution to achieve the conversion of TCE and chlorobenzene (CB) to a LNAPL, followed by a low-interfacial-tension surfactant solution containing 4% (4:1) Aerosol MA/Aerosol OT, 20% n-butanol, and 500 mg L$^{-1}$ CaCl$_2$. Liquid sampling showed that, after the prefloods, the NAPL samples were always less dense than the aqueous phase samples. Recoveries of 90% CB and 85% TCE were obtained after flushing with only 1.2 pore volumes of the surfactant solution. Ramsburg and Pennell (2002) stated that the minimal mobilization during the preflood and the near-complete intended mobilization during the main surfactant flood were consistent with trapping number calculations. They also noted that the results demonstrated the potential efficiency of their technique for DNAPL source remediation.

Ramsburg et al. (2003) conducted flow cell experiments to test efficiency enhancements for TCE by increasing alcohol delivery and extent of the partitioning during the preflood. Using a similar approach as Ramsburg and Pennell (2002), Ramsburg et al. (2003) used a preflood of a macroemulsion consisting of 4.7% Tween 80, 1.3% Span 80, and 15% 1-butanol in water to achieve the in situ density reduction of TCE before the recovery with a surfactant solution. The main-flood surfactant solution consisted of 10% Aerosol MA, 6% 1-butanol, and 50 mg L$^{-1}$ NaCl and 1 g L$^{-1}$ CaCl$_2$ and was used to displace and recover the NAPL. The flow cell was packed with low-permeability lenses surrounded by medium-grained sand. The DNAPL conversion was successful and the final recovery rate of TCE was 93%. The total volume of the preflood needed to obtain conversion was only 1.2 pore volumes, compared to the five pore volumes needed by Ramsburg and Pennell (2002). A large volume of the TCE (60%) was already recovered during the preflood. Ramsburg et al. (2003) concluded that the results held great promise for the remediation of DNAPL source zones, without the need for physical confinement. In a later study, Ramsburg et al. (2004) showed the potential of the DMD method to remove the even heavier PCE (compared with the previously used TCE) from a source zone. To convert this DNAPL, a surfactant-stabilized macroemulsion containing 15% (v/v) $n$-butanol in water was used to achieve the desired density reduction during preflooding. It was observed that the preflood of 1.2 pore volumes already removed 50% of the PCE. After the main flood, 91% of the PCE was recovered. The researchers compared these results with results obtained by Ramsburg et al. (2004) and Taylor et al. (2001). They concluded that the DMD method yielded higher recovery rates without causing downward mobilization.

**Dense Brine Strategies**

In a series of studies (Miller et al., 2000; Hill et al., 2001; Johnson et al., 2004), novel treatment technologies were introduced that include displacement or containment with dense brines. Attempts to remove free or pooled TCE from bench columns and flow cells with dense brine were made by Miller et al. (2000) using two approaches. In the first approach, the DNAPL was displaced upward due to buoyancy forces in a two-phase system. In the second approach, the DNAPL was displaced downward under gravitational forces in a three-phase system and collected on top of a dense brine layer that limited vertical transport (Miller et al., 2000). Results of the first approach showed that the TCE remaining after the brine displacement was distributed throughout the columns and flow cell in entrapped form while no evidence of free TCE existed. An experiment performed in a small 2-D flow cell with a porous medium thickness of ~2 mm showed that all free TCE seemed to have been removed by pushing it upward with the brine, thus achieving a 54.2% removal rate. In another experiment, the part near the top of the 2-D container had been drained and a surfactant solution was allowed to infiltrate before the brine was pushed upward. Because of the added mobilization due to interfacial tension reduction, this experiment yielded a 90% reduction in free TCE. The latter experiment seemed to be especially promising, because the researchers argued that the remaining residual TCE could easily be removed by soil vapor extraction in the vadose zone. A simple flow cell experiment was reported by Sanchez and Ely (1998) who made an attempt to remove TCE by KI. The description of the experimental design and results is rather minimal but the researchers stated that TCE removal was evident after the brine was introduced into the flow cell.

The experimental work discussed by Hill et al. (2001) is a continuation of the experiments discussed by Miller et al. (2000). The motivation for this study came from their observation that little experimental data had been generated to develop a mature level of understanding of the problem, and few strategies had been developed specifically aiming at pool remediation in subsurface systems. Regarding the removal of pooled DNAPLs, Hill et al. (2001) made it clear that (i) the DNAPL must be mobilized as a free phase, (ii) the DNAPL migration must be controlled to allow recovery and prevent contaminant spreading, and (iii) the method must be relatively economical, requiring only a few pore volumes of an inexpensive flushing solution. Based on these three criteria and the findings of their earlier work (Miller et al., 2000), Hill et al. (2001) and Johnson et al. (2004) performed additional experiments. Hill et al. (2001) used brine barriers to avoid uncontrollable migration of TCE in 2- and 3-D experiments under both saturated and unsaturated conditions in highly heterogeneous systems. Hill et al. (2001) claimed that they were among the first to experiment with DNAPL pool formation and subsequent remediation in 3-D heterogeneous systems. Once the brine barriers were in place, surfactant solutions were added from the top and the extraction of the pooled TCE was started with a hypodermic needle. The recovery rates varied from 63 to 87%. It should be pointed out that all experiments by
Miller et al. (2000), Hill et al. (2001), and Johnson et al. (2004) were performed with the brine injected at the bottom of the flow cells. Under field conditions, this may not be so easily done as the brine, a dense aqueous phase liquid, will sink rapidly due to its much greater density than that of the ambient water (see e.g., Oostrom et al., 1992) if no relatively impermeable layer is available to control downward movement. Hill et al. (2001) also added cost, health concerns, and clay mobilization to the potential list of concerns related to this remediation technique. Despite all these concerns, the researchers felt that the results from their work were very encouraging. They recommended further research in minimizing DNAPL entrainment in the brine zone, fine-tuning surfactant solutions, implementation of the technique in numerical simulators, and exploring the technique for heterogeneous conditions. Vapor extraction was added as a final cleanup step by Johnson et al. (2004) and showed that, under laboratory conditions in small flow containers, the amount of TCE remaining in the porous medium could be reduced to ~1%. Johnson et al. (2004) noted similar research ideas as Hill et al. (2001) and they also recommended larger and more realistic experiments. The experiments by Hill et al. (2001) and Johnson et al. (2004) both show the effectiveness of the dense brine barrier strategy for DNAPL removal.

Hydraulic Nonaqueous Phase Liquid Recovery

Hydraulic removal of NAPL relies on the extraction of LNAPLs via wells or trenches, based on the manipulation of fluid gradients to drive free NAPL toward extraction locations. Extraction efforts are usually not capable of removing all of the NAPL from the aquifer. Oostrom et al. (2005c) provided a listing of several field studies where between 64 and 83% of LNAPL was not recovered. One reason for the limited recovery is entrainment in the cone of influence of the extraction wells. In some cases, the primary benefit that can be achieved with this technology is limiting future migration of NAPL due to reduced mobility.

Early LNAPL recovery flow cell experiments were reported by Schwille (1967). The visualization experiments showed that considerable volumes of LNAPL could be removed through simple pumping from a screened extraction well. Waddill and Parker (1997) used oil recovery experiments to validate the flow model ARMOS (Environmental Systems and Technologies, 1996) and to create a data set that could be used to enhance the code to account for three-phase hysteresis. Waddill and Parker (1997) argued that the controlled setting and laboratory instrumentation would reduce the uncertainty in parameter estimation, thus allowing the comparisons to focus on flow processes occurring during oil recovery. The flow cell was packed with a medium-grained sand and two wells were located on either end for pumping purposes. In the partially saturated flow cell, 15 L of the LNAPL Soltrol-130 was injected. After vertical equilibrium was obtained, one well was used to extract oil using oil skimming, while the other well was used to maintain a constant water table. More than half of the originally disposed LNAPL (8.1 L) could be extracted using oil skimming. In a second experiment, the recovered LNAPL was again injected and after equilibrium conditions were achieved, a constant gradient was imposed on the system to flush out free LNAPL. During the second experiment, 11.1 L of oil were removed; however, since the initial conditions for the experiments were not identical, the recovery volumes for the experiments should probably not be used to compare the two recovery methods. When the effects of hysteresis were incorporated into the ARMOS model, predicted and measured cumulative oil recovery were in reasonable agreement.

Sleep et al. (2000) conducted a 3-D experiment to create a data set to test a new formulation for LNAPL accumulation in observation wells and removal from recovery wells. The relatively large flow cell was filled with an 83-cm-thick lower layer consisting of fine-grained sand and an 86-cm-thick coarse-grained sand upper layer. The water table was located at 57 cm from the bottom. Five wells were installed. A total of 80 L of toluene was added and was allowed to redistribute for several weeks. Toluene was then removed from two wells by skimming oil at a depth between the air–oil and oil–water interfaces. The skimming allowed removal of ~15 L in 300 h. After the initial removal through oil skimming, two pumps were set up to remove water from one well and reinject it into another well. Only about 3 L of toluene were removed using this scheme for 240 h. It should be noted that it was not the intent of the researchers to maximize the removed volume but to create a data set for model testing. Predictions of the new model compared well with observed oil thicknesses in the observation wells. As for the ARMOS simulations conducted by Waddill and Parker (1997), the inclusion of pore geometry and fluid entrainment hysteresis was required to provide a good match with experimental data (Sleep et al., 2000).

Catalan and Dullien (1995) included a horizontal recovery well in their experiments investigating the effects of gravity drainage on previously entrapped LNAPL that was liberated following a lowering of the water table. The recovery well was placed at the bottom of the flow cell. Using a peristaltic pump, the free LNAPL that collected at the bottom of the cell after gravity drainage of previously entrapped LNAPL was removed. Approximately 60% of the previously entrapped LNAPL could be removed through pumping in a homogeneous packing; however, in a packing where the entrapped LNAPL was distributed in low- and medium-permeability lenses, the recovery rate was far less. The LNAPL in the lenses was either surrounded by water or it overlaid water-saturated zones (Catalan and Dullien, 1995).

In Situ Chemical Oxidation

In situ chemical oxidation (ISCO) is a technology that increases the mass flux from a source zone by destroying organic chemicals in situ and shows promise in breaking down chlorinated solvents present in aquifers and soils.
MnO$_4^-$ and MnO$_2$ precipitation, CO$_2$ production, and Co$_2$ absorption and removal. The researchers noted that MnO$_2$ precipitation and CO$_2$ production are competing reactions that can result in enhanced vapor transport and bypass flow in the porous media. They suggested that minimizing CO$_2$ production and removing excess CO$_2$ gas can be used to enhance the ability to remove contaminants from DNAPL pools.

Conrad et al. (2002) demonstrated the ISCO process in a packing designed to represent a fluvial depositional environment. The objective of this work was to visualize the remediation process. The TCE used in the experiment resulted in the DNAPL residing as a series of descending pools (Conrad et al., 2002). A relatively low concentration injection of MnO$_4^-$ was used to avoid excess CO$_2$ formation and to enhance the ability to visually observe the interaction between the MnO$_4^-$ solution and the TCE. Photographs of the experiments clearly showed the dark (brown–black) rinds of precipitated MnO$_2$ around the zones containing TCE. A second slug demonstrated that the rinds had effectively blocked off the TCE-containing zones from fluid movement. The majority of the MnO$_4^-$ solution in the second slug passed through the flow cell without reacting. It was also shown that during the course of several months, the rinds lost some of their structure, and the researchers commented that the rinds should probably not be relied on to provide isolation of the pools.

**Heat-Based In Situ Remediation**

The application of heat-based remediation techniques to remove contaminants involves the injection of hot gasses such as air or steam, hot water injection, or electromagnetic energy heating to heat the targeted NAPL-contaminated zone. The use of hot air in the field is limited by the low heat capacity of air (about 1 kJ kg$^{-1}C^{-1}$). Steam, with a heat capacity of approximately four times
that of air (≈4 J kg\(^{-1}\) °C\(^{-1}\)) and a heat of evaporation of 
>2000 J kg\(^{-1}\) has been used more extensively (Davis, 
1997). Steam, hot air, and hot water injection rely on the 
contact between the injected fluid and the NAPL for 
heat transfer and recovery. Hot air is useful to recover 
contaminants in the vapor phase, while steam injection 
combines vaporization and liquid contaminant removal 
in front of the steam zone. Hot water generally re-
covers NAPL only in the liquid phase through a reduc-
tion in NAPL viscosity and it might only be effective 
when the NAPL is not in entrapped form. Electromag-
etic energy heating has been applied in the low-
frequency (e.g., resistivity heating) and radio-frequency 
ranges. For the low-frequency-range heating technique, 
water in the pores spaces absorbs the applied energy and 
evaporation of water limits energy transport. In that case, 
the boiling point of water is the highest temperature 
than can be achieved, which might not be high enough for 
some semivolatile NAPLs (Davis, 1997). The tempera-
ture limitation is not applicable for the radio-frequency-
range techniques since the energy can be absorbed 
by the soil itself. The heating techniques have a greater 
potential to be effective in low-permeability media such 
as clays.

Of the various heat-based in situ remediation tech-
niques, only variations of the steam injection method 
have been investigated in flow cell experiments by 
Gudbjerg et al. (2004), Kaslusky and Udell (2005), She 
and Sleep (1999), and Schmidt et al. (2002). The steam 
injection technique results in the vaporization of NAPLs 
and, therefore, requires a soil vapor extraction compo-
nent. The method is especially advantageous in heterog-
enous porous media, as was shown in the flow cell 
experiments by She and Sleep (1999), who investigated 
the mechanisms in the removal of PCE from a saturated 
layered porous medium system by steam injection. It 
was observed that, although steam has a viscosity of 
about one-fiftieth of that of water, viscous fingering was 
minimal; however, considerable gravity override was 
observed, which can be a problem in the field (She 
and Sleep, 1999). Although TCE was completely removed 
from the flow cell, some of it left the cell through un-
favorable downward migration. She and Sleep (1999) 
suggested that steam should be injected below the con-
taminated zone to ensure that a condensation front of 
DNAPL does not occur on the lower edge of a steam 
zone. Schmidt et al. (2002) pointed out that such a 
scheme might be difficult to achieve in the field since 
the exact location and distribution of the NAPL contami-
nation is seldom known in sufficient detail.

Gudbjerg et al. (2004) used steam injection to remove 
TCE captured on a fine sand layer situated below the 
water table. In this case, boiling induced by heat con-
duction caused the free TCE to vaporize. Dissolved 
TCE was not removed by steam injection. The re-
searchers warned that if pooled TCE exhibits a pressure 
approaching the entry pressure of the underlying ma-
terial, a reduction in surface tension due to the increase 
in temperature may cause downward migration of the 
DNAPL. Simulations with the numerical simulator 
T2VOC (Falta et al., 1995) confirmed that heat-conduc-
tion-induced boiling was the dominant removal mecha-
nism. The original code needed to be modified to account 
for the distinct nonwetting fluid entry pressure for the 
porous media.

The concern that the application of steam injection 
may lead to downward migration of condensed DNAPL 
is a serious one and needs to be addressed (Schmidt 
et al., 2002). This downward migration may occur when 
evaporated DNAPL condenses and accumulates in the 
cooler soils at the edge of the heated region (Kaslusky 
et al., 2005). To overcome the concern of downward mi-
gration of the contaminant as a separate phase, Schmidt 
et al. (2002) successfully performed steam injection re-
medication experiments by using mixtures of steam and 
air. The performance of the mixtures was compared with 
injection of steam only. The NAPLs used in the partially 
saturated 2-D flow cell experiment, present at residual 
saturation values, were the LNAPL mesitylene (density 
= 0.865 kg L\(^{-1}\)) and the DNAPL DCB (1,2-dichloroben-
zone, density = 1.306 g cm\(^{-3}\)). By mixing steam and 
ambient air, a small amount of steam will condense and 
heat up the air to a temperature at which all of the water 
vapor in the air can be contained in the gas phase. 
Schmidt et al. (2002) showed how the temperature de-
creases with an increasing air/steam ratio, but pointed out 
that the mixture still has a higher energy content than, 
e.g., hot water or dry air. In their injection with steam 
only experiments, Schmidt et al. (2002) showed that all 
mesitylene and most of the DCB migrated downward to 
the saturated zone. But when using an air/steam mixture, 
the downward migration of the separate phase contam-
inant was prevented and all contaminant was recovered 
in the gas phase. They identified three mechanisms 
preventing downward migration: (i) removal of the 
contaminant with noncondensable air; (ii) more spatially 
distributed accumulation of the contaminant due to less 
steep temperature gradients; and (iii) lower velocity of 
the evaporation front compared with the velocity of the 
heat front. Regarding (i), the greater the mixing ratio of 
air to steam, the greater the number of pore volumes 
nEEDED to warm up the porous medium. Regarding (ii), 
because the air mixed in with the steam is being warmed 
up during the condensation of the steam, the temperature 
of the mixture decreases. This will cause a more gradual 
temperature gradient. In other words, a wider heat front 
exists than when only steam is used. Regarding (iii), 
Schmidt et al. (2002) noted that the ratio between the 
velocity of the evaporation front and the heat front has to 
be <1. The experiments were simulated with the T2VOC 
simulator (Falta et al., 1995). The code was able to provide 
a reasonable simulation of the experimental results using 
independently measured parameters. This result suggests 
that the model might be used to design and interpret steam 
injection applications.

Kaslusky and Udell (2005) also used coinjection of air 
and steam to prevent the downward migration of the 
DNAPL TCE. Their objective was to experimentally 
evaluate the optimum injection ratio that would elimi-
nate accumulation of DNAPL ahead of the temperature 
front, as calculated from applying a theoretical model 
(Kaslusky and Udell, 2002). Three horizontal experi-
ments were conducted in which it was attempted to remove TCE with steam only, air only, and a 0.33:1 air/steam coinjection. The pictures of the three experiments clearly show that the steam-only application caused the formation of a TCE bank with high saturations and subsequent downward migration. The injection with air, mimicking soil vapor extraction, resulted in DNAPL being preferentially removed in certain zones, making the remediation ineffective. The results of the coinjection were far more favorable. A rather fast complete cleanup, with removal through the vapor phase, was accomplished without the formation of a TCE bank. This result indicates that the theoretical model presented by Kasluský and Udell (2002) may be a valuable tool for choosing the appropriate injection ratio to limit the potential for downward DNAPL migration.

**Soil Vapor Extraction**

Soil vapor extraction (SVE) or soil venting is the most commonly used technique for remediation of unsaturated zones of the subsurface contaminated with volatile and semivolatile NAPLs. The technique is also often used in combination with other remediation methods that force movement of contaminated gas from the saturated to the unsaturated zone, such as air sparging (e.g., Heron et al., 2002), steam injection (Kasluský and Udell, 2005), and surfactant flushing combined with dense brine containment (Johnson et al., 2004). Although SVE applications have yielded considerable amounts of volatile organics in the field, high initial recovery rates are usually followed by long periods of low rates. Heron et al. (1998) listed slow diffusion of contaminants from low-permeability layers into areas with vapor exchange, vapor-phase retardation due to adsorption, limited volatility of the contaminant at in situ temperatures, and the presence of low-permeability soil layers as limiting factors for this technique. Despite the widespread use of SVE and the large number of potentially limiting factors (Heron et al., 1998), only a few intermediate-scale experiments (Ho and Udell, 1992; Oostrom et al., 2005b) have been conducted to directly investigate this technique.

Ho and Udell (1992) conducted a series of SVE experiments with single and binary hydrocarbons to visually observe the contaminant removal process and identify the physical mechanisms governing the transport of the contaminants. Seven experiments were conducted in which the flow cell was packed with up to two layers of dry sand of equal height. In two of the experiments, only the lower half of the cell was packed. The permeability ratio of the layered systems ranged from 14:1 to 160:1. A known quantity of either toluene or a toluene-o-xylene mixture was injected into the lower layer before the upper layer was emplaced. After packing was completed, air was forced through the system at a known rate using a vacuum pump. It was observed that, for all experiments, when air swept through the contaminated zone, the pool receded primarily from the upstream end, with less removal from the sides. In addition, the geometry of both single and binary pools changed in the same manner. Ho and Udell (1992) also showed that a permeability ratio of 100:1 was needed for diffusion-limited behavior to exist. For permeability ratios less than this, sufficient air will flow through the contaminated zone to create conditions similar to a homogeneous system.

Oostrom et al. (2005b) conducted a 2-D flow cell experiment to study the removal of the CCl₄ component of a DNAPL mixture from a layered porous medium by SVE with moist and dry air. A dual-energy γ radiation system was used at various times to unintrusively determine fluid saturations. The mixture mimics the DNAPL disposed at the Hanford Site in the state of Washington. The flow cell was packed with two sloped coarse sand and two sloped silt layers in an otherwise uniform matrix of medium-grained sand. The water table was located 2 cm from the bottom, creating variably saturated conditions. A 500-mL spill was introduced at the top of the flow cell from a small source area. It was observed that the DNAPL largely bypassed the silt layers but easily moved into the coarse sand layers. Residual DNAPL formed in the medium-grained sand matrix. The DNAPL also caused a distinct reduction of the capillary fringe. Most of the DNAPL ended up in a pool on top of the V-shaped fine sand at the bottom of the flow cell. Through four treatments with moist-air soil vapor extraction, most residual CCl₄ was removed from the medium-grained matrix and the coarse sand layers. The CCl₄ in these high-permeability zones is in direct contact with the moving air and its volatility, in combination with the air flow velocity, determined the initial removal rate. The moist SVE was not able to remove CCl₄ from the silt layers and from the inundated pool located on top of the fine-grained sand in the capillary fringe. These treatments demonstrate that the technique can be effectively used to remove volatile DNAPL components from permeable materials but that the method is not effective in removing DNAPL located in fine-grained materials and from inundated pools.

Through a water table reduction and subsequent soil vapor extraction with dry air, most of the CCl₄ in the silt layers and in the pool could be removed. With time, water removal through desiccation allowed increased direct contact between the flowing air and the DNAPL, allowing the removal of CCl₄ through volatilization. Although most of the CCl₄ located in the silt layers and the pool could be removed using SVE with dry air, the removal process, even in a relatively simple flow cell, was not efficient. In order for the moving air to access the CCl₄, relatively large amounts of water had to be removed, which was rather time consuming. In natural environments, increasing the accessibility of NAPL through water table lowering followed by desiccation might not be feasible. If the zone of interest cannot be isolated from its surroundings, water vapor movement in the gas phases and water flow due to induced capillary pressure differences will provide an almost infinite source of water. During the final stages of the desiccation, the underlying fine sand started to desaturate, allowing some of the DNAPL to infiltrate. The infiltration of DNAPL into a fine-grained porous...
medium is considered to be unfavorable and needs to be avoided in practical applications. Overall, almost 90% of the CCl₄ was removed from the flow cell.

**Air Sparging**

Air sparging involves the injection of clean air into the saturated zone of a porous medium in an attempt to volatilize contaminants and transport them to the vadose zone to be removed by soil vapor extraction. In the field, air sparging is usually combined with SVE by applying a vacuum to the subsurface. The soil vapor extraction system controls the air movement in the subsurface, preventing migration of the contaminated air into uncontaminated areas. In the field, air sparging at a site contaminated with DNAPL may potentially not be efficient because injected air has a tendency to flow around DNAPL areas, rather than through them (Heron et al., 2002). In addition, Ji et al. (1993) showed that injected air typically flows in large channels, bypassing large areas of the contaminated zones. Flow cell experiments using air sparging of LNAPL were reported by Rogers and Ong (2000) and Waduge et al. (2004). Heron et al. (2002) used air sparging to remediate the DNAPL PCE.

Rogers and Ong (2000) studied the effects of porous medium type, airflow rate, and air channel spacing on NAPL removal. Their flow cell was designed so that air could be injected through two channels with variable spacing. Small amounts of benzene (50 μL) were injected for each experiment. Rogers and Ong (2000) demonstrated that the removal efficiency of the LNAPL benzene (mass of benzene removed divided by the total mass of benzene initially present in the system) increased from 7.5 to 16.2% during the 168-h experiment when the particle size increased from 0.168 to 0.305 mm. The benzene removal efficiency was inversely related to the square of the distance between the LNAPL and constructed air channels. The presence of these air channels was shown to suppress lateral dissolved-phase benzene migration, but promoted vertical spreading. Rogers and Ong (2000) claimed that their work suggests that air sparging might be a useful remedial tool for the removal of volatile NAPLs in the subsurface and may be used to slow contaminant migration within the air channel boundaries.

Waduge et al. (2004) used air sparging in combination with soil vapor extraction. In their experimental setup, a coarse-grained layer was embedded in an otherwise fine-grained matrix. Depending on the level of soil heterogeneity, water table height, and the amount of entrapped vs. free (mobile) toluene LNAPL, Waduge et al. (2004) achieved different removal efficiencies of the zone source. The highest removal efficiency of 91% was reported when most of the source zone resided in the fine sand matrix and the water table was relatively low. Lower efficiencies were obtained when the toluene was entrapped in the coarse-grained sand. They concluded that it is very difficult to completely remove NAPL from heterogeneous porous media due to complex entrapment.

The flow cell experiment by Heron et al. (2002) was conducted to investigate the effect of pulsed air injection on the removal of PCE spilled into a medium-grained sand. The lower part of the flow cell was packed with a silt porous medium and acted as a fine-grained aquitard (Heron et al., 2002). A total of 100 mL of PCE was injected from the top in the partially saturated flow cell and allowed to redistribute for 48 h. After the redistribution period, the water table was lowered to the top of the silt layer and subsequently raised again to its original position to disperse the NAPL into a larger area. The sparge location was 12 cm above the sand–silt interface. A considerable amount of the PCE was located between this location and the interface. Sparging was applied at several air injection rates and pulse durations. Vacuum extraction was done simultaneously with the sparging at 1.5 times the sparging rate. The additional air was coming from passive inlets in the corners at the top of the box. After the sparging episodes were completed, the water table was lowered again, followed by destructive sampling of the porous medium. It was observed that, during air injection, the air moved up irregularly in several air channels and preferentially contacted areas. Although some benefits were observed from pulsed sparging, just slightly more than 50% of the PCE could be removed after extensive sparging. It was shown that sparging did not significantly affect the pooled DNAPL below the sparge point. Heron et al. (2002) noted that, in the field, air sparging filters are typically >10 cm long and air preferentially migrates out of the top of a screen. For that configuration, even when a sparge well is screened near pooled DNAPL at a textural interface, Heron et al. (2002) concluded that the majority of the air will probably be injected above the pooled zone and that air sparging for sites with DNAPL pools is an improper use of the technology.

**Humic Acid Enhanced Remediation**

In a pilot scale experiment, Van Stempvoort et al. (2002) showed how the enhanced solubility of petroleum-derived compounds in humic acid solutions improved the remediation technology. To establish a contaminant plume, they emplaced a diesel fuel source in a large flow container consisting of coarse sand and flushed the container with water alone for 51 d with a flow rate of 2 cm h⁻¹. The diesel fuel was emplaced in entrapped form below the water table. At 51 d, humic acid was added at a rate of approximately 1 g L⁻¹. Due to sorption to the sand, the effluent concentration of the humic acid had reduced to about 0.8 g L⁻¹. Of the BTEX compounds present, benzene and toluene were completely removed after 21 and 40 d of flushing, respectively. At Day 51, when the humic acid was added, quantities of ethyl-benzene and xylenes remained in the source, but they had been effectively removed after 95 d (~230 source pore volumes or ~0.9 total pore volume), although their solubility was little affected by the humic acid. The latter had, however, a profound effect on the solubilization and subsequent transport of the methylated naphthalene, with differences observed for
different components. The increased solubilities were attributed to the binding of these methylated naphthalenes to the aqueous huminic acid. Concomitant with the solubilization and transport, the researchers reported biodegradation by relatively diverse microbial populations, resulting in a “dynamic steady state” of contaminant concentrations. At this stage, the average rate of biodegradation of a contaminant within the aquifer was essentially equal to its dissolution rate at the source. After approximately 4 yr (~3500 source pore volumes or 14.0 total pore volumes, or about one source pore volume every 10 h), the methylated naphthalenes plume had virtually disappeared as concluded from the no-longer-detectable methylated naphthalenes concentrations. Van Stempvoort et al. (2002) also reported the existence of biofilms on the sand particles present in the source area, which raises concern for bioclotting. They also speculated that the biodegradation was largely controlled by mixing of the O₂-deficient plume with aerobic water along its perimeter. The researchers suggested that higher humic acid concentrations may be even more efficient in the removal of diesel fuel.

**Denitrification**

Hunter (2001) used a flow cell to demonstrate the usefulness of soybean-oil-coated sand particles to denitrify NO₃ and NO₂ present in groundwater. Nitrate in drinking water is a hazard to both humans and animals. In the past, shallow and deep trenches have been dug and backfilled with substrates containing sawdust, crop residue, oil, etc. They act as permeable barriers, with the substrates being the electron donors needed in the denitrification process. The barrier was most efficient during the first 10 wk of operation, but its efficiency steadily declined. Based on flow rates in the tank and the removal efficiency of NO₂, Hunter calculated a longevity of 2.5 to 12.5 yr for similar in situ conditions. It was pointed out that the advantage of using a vegetable oil over solid substrates was that oils can be injected through a well, avoiding the expensive part of digging and backfilling.

**Nonaqueous Phase Liquid Source Bioremediation**

The goal of bioremediation is to have bacteria break down specific, toxic compounds present in the soil or an aquifer. The two modes of operation that can be used are bioaugmentation and biostimulation. In the former case, the microorganisms that are introduced into the contaminated region are capable of transforming the target compound to a benign end product. In the latter case, microorganisms already present are expected to transform the target compound at a rate greater than under natural conditions by the addition of chemicals and nutrients to promote growth of the desired bacteria. In a laboratory flow cell, Adamson et al. (2003) were able to inoculate a nondechlorinating porous medium containing liquid PCE and reduce PCE to cis-dichloroethene and TCE by inoculating the near-source area of PCE with an active and stable dechlorinating culture. Eventually, however, vinyl chloride, a carcinogen, accumulated, while no further reduction seemed to take place. It is of interest to note that He et al. (2003) identified and isolated a bacterial group BAVI that was capable of further reducing the intermediate compounds to harmless ethyne; however, this reduction step has not yet been demonstrated in a flow cell containing liquid PCE.

**DISCUSSION AND RESEARCH RECOMMENDATIONS**

**Aqueous Dissolution**

The number of flow cell experiments dealing with NAPL dissolution by aqueous phase flow is rather limited. Several of the earlier contributions discussed pool emplacement in flow cell experiments (Pearce et al., 1994; Voudrias and Yeh, 1994; Whelan et al., 1994) and demonstrated steep concentration gradients near the pools but also the difficulties in making well-defined pool–water interfaces due to entrapped NAPL saturation formation. Chrysikopoulos et al. (2000) and Dela Barre et al. (2002) provided techniques to create pools with sharp NAPL–water interfaces. These techniques have led to dissolution data that better satisfied boundary conditions of analytical transport models. Since these pools are typically directly emplaced in the porous media, however, and homogeneous packings are used, these dissolution experiments do lack a connection to potential field conditions. For future experiments, less emphasis should be placed on the establishment of pools with a 100% NAPL saturation of perfect interfaces. Improved understanding of pool dissolution should be obtained by conducting flow cell experiments in heterogeneous porous media in which pools were established following spill events. Only one of the experiments (Oostrom et al., 1999a) investigated pool dissolution after a spill event. If the dissolution research is done to benefit a particular site, it is important to use the NAPL from that site because field NAPLs are usually more complex than the laboratory-grade single liquids used in most experiments. So far, Eberhardt and Grathwohl (2002) have conducted the only reported flow cell study of field NAPL dissolution.

Flow cell experiments can be effective tools to improve the understanding of dissolution upsampling of mass transfer processes. The analysis of entrapped NAPL dissolution performed by Saba and Illangasekare (2000) has shown that 1-D mass transfer Sherwood correlations could not be used to describe multidimensional dissolution. Instead, experiment-dependent correlations were needed to describe the dissolution process with sufficient accuracy. It is of great interest to see whether Sherwood-type mass transfer correlations can be used in flow cells with a higher degree of heterogeneity and a more complex NAPL distribution than used before. If meaningful relations can be developed for these systems, upsampling to field conditions might be a possibility. Detailed experiments, including NAPL saturation, dissolved concentration, and flow rate measurements, will also be quite helpful to investigate suggestions by Brusseau et al. (2002) that the local-equilibrium ap-
proach can be used as an approximation to describe local-scale dissolution as long as the larger scale factors influencing dissolution, such as the flow field and NAPL distribution, are accounted for. In the analysis of such experiments, it would be useful to determine what type of kinetic mass transfer Sherwood relations are needed when certain data are not considered.

Flow cell experiments with pooled and entrapped NAPL are also needed to further test the validity of equilibrium dissolution and Raoult’s law under various conditions. Some of the laboratory results (Eberhardt and Grathwohl, 2002) suggest that this law was valid under their experimental conditions; however, other researchers (e.g., Saba and Illangasekare, 2000; Brusseau et al., 2002) have shown that rate-limited mass transfer was prominent in their flow cell experiments. A series of detailed controlled dissolution experiments with single- and multicomponent NAPLs is needed to come to a better understanding of under which flow conditions and NAPL saturation distributions equilibrium dissolution is applicable.

The use of flow cell experiments to test the mass flux approach (Soga et al., 2004), either in conjunction with aqueous dissolution or enhanced remediation, appears to be highly appropriate. In this approach, mass flux measurements, combining measured dissolved concentrations and aqueous fluxes, are obtained. The approach can be a potential tool to assess and monitor baseline (pump-and-treat) and enhanced remediation efficiency, to predict future site-specific behavior, and to identify remediation targets (Soga et al., 2004). As an alternative to complete source removal, this approach relies on reducing the NAPL saturation below a certain level so that the mass flux emanating from the source meets an acceptable value. As Soga et al. (2004) have demonstrated, field-scale simulations of dissolution processes from complex NAPL source conditions indicate that an understanding of soil heterogeneity and NAPL morphology are needed to make meaningful predictions.

Flow cell experiments with known NAPL distributions and controlled heterogeneities, in which both dissolved concentrations and aqueous phase fluxes are obtained, are crucial for a thorough test of this approach. Flow cell experiments can provide the necessary data to test theoretical models forecasting remediation benefits or partial source removal. For instance, remediation benefit predictions using the mass removal theory by Sale and McWhorter (2001) are quite different from the predictions obtained by Wood et al. (2005). According to Wood et al. (2005), the differences between the predictions are related to assumptions about the flow field. Controlled flow cell experiments that provide information about flow fields and NAPL distribution are essential to test and verify these and other mass removal theories.

Enhanced Remediation

The reviewed flow cell experiments in this category investigated remediation through surfactant flushing, alcohol flushing, surfactant and alcohol flushing combinations, dense brine strategies, hydraulic NAPL removal, soil vapor extraction, air sparging, heat-based remediation, and bioremediation. As indicated by Johnson et al. (2004), future flow cell research related to NAPL remediation techniques should be focused toward developing mature field remediation techniques. They particularly recommended experimental work to investigate the effects of increased heterogeneity to obtain a closer resemblance to field conditions, to focus on outflow aqueous phase concentrations instead of removal percentages, to use increasingly larger scale experiments to increase the empirical knowledge base and give improved guidance for field-scale application, and to invest in the development of mathematical models that describe enhanced remediation.

With the exception of the work by Conrad et al. (2002) and Johnson et al. (2004), the experiments were conducted in either homogeneous or layered systems; however, it is obvious that real natural systems can be considerably more heterogeneous than the relatively simple systems investigated in this review. The removal of DNAPL in more heterogeneous systems might be less efficient than in the flow cell experiments. Recognizing that such experiments might be time consuming and difficult, we strongly agree with the statement of Johnson et al. (2004) that if we are to make realistic assessments of the performance of any technology, detailed experiments in controlled heterogeneous systems are necessary.

Another observation is that, for most flow cell experiments, the perceived success of a remediation is directly related to the NAPL fraction removed from the system. As indicated above, considerable recent effort has gone into mass flux approaches based on aqueous phase concentration as endpoints for NAPL sites. At field sites, remediation performance is usually assessed by comparing the resulting aqueous phase concentrations with established criteria. Based on recent developments in the mass flux approach (e.g., Soga et al., 2004), it is expected that, besides aqueous phase concentrations, obtaining mass fluxes will become increasingly important in experimental work. Future remediation experiments should be designed to include outflow and component concentration measurements to assess mass flux developments with time.

As indicated by Johnson et al. (2004), a mature level of understanding of a remediation technology is indicated when “a mathematical model for that system exists that describes observed behavior with adequate accuracy.” The data acquired in flow cell experiments can be of great importance for developing and validating numerical models. The experimental value is enhanced when the controlled setting and laboratory instrumentation leads to a reduction in the uncertainty in fluid and porous medium parameter estimation, allowing comparisons to focus on flow and transport processes (Waddill and Parker, 1997). In addition, numerical models may be useful to provide links between understanding the processes in controlled flow cell laboratory experiments and understanding technology performance at the field scale. In this light, it is remarkable that of the 51 reviewed enhanced remediation papers, numerical simulation was only attempted for experiments described in
seven contributions. The surfactant flushing experiments by Taylor et al. (2001) and the surfactant–alcohol flushing experiments by Taylor et al. (2004) were simulated with the MISER code (Rathfelder et al., 2001). Schaerlaekens and Feyen (2004) used the NAPL model (Guarnaccia et al., 1997) to develop a rate-limited surfactant solubilization model. Gudbjerg et al. (2004) and Schmidt et al. (2002) used the T2VOC code (Falga et al., 1995) to simulate steam injection. Hydraulic removal of NAPLs was numerically modeled by Waddill and Parker (1997) with the ARMS code (Environmental Systems and Technologies, 1996) and by Sleep et al. (2000). The reasons why the majority of the flow cell experiments was not subject to numerical analysis were probably associated with funding, scientific interest, code or modeler availability, and the complexity of the enhanced remediation technique. Unfortunately, even when numerical models become available in the future, it will be impossible for modelers to go back and use the data of several previous experiments because they do not provide the necessary basic information on fluid properties, hydraulic properties, and initial or boundary conditions. We hope that numerical simulation of flow cell experiments will become more important in the future; however, even when no numerical modeling is directly associated with the experimental work, future flow cell experiments should include pertinent parameter and initial and boundary condition information so that the produced data sets are complete and the experiments can be simulated by members of the scientific community.

It is obvious that experimentation at the intermediate flow cell scale has been instrumental in the development of some of the more promising techniques. For instance, after earlier flushing experiments with either single surfactants or alcohols demonstrated great DNAPL removal potential but serious problems with free phase mobilization and downward movement of dissolved components (e.g., Conrad et al., 2002; Taylor et al., 2001), subsequent flow cell experiments were conducted to study options to negate these effects. Improvements were demonstrated using DMD methods applying several flushings with multiple components (e.g., Ramsburg et al., 2004), dense barrier strategy methods, where downward movement is prevented using a brine barrier (e.g., Johnson et al., 2004), the SEAR-NB technique advocated by Kostarelos et al. (1998), and the multiflood alcohol flushing approach forwarded by Lunn and Kueper (1999b). These advanced methods involving surfactants and alcohols have shown that downward migration of DNAPL and sinking of dissolved DNAPL plumes or microemulsions can be avoided or controlled. All of these advanced methods will benefit from additional flow cell experimental research related to porous medium heterogeneity, mass flux measurements, and mathematical modeling. An ambitious but worthwhile exercise will be to compare the performance of these advanced remediation techniques (DMD, dense brine strategy, SEAR-NB, and multiflood alcohol flushing) in flow cells with similar packing and initial DNAPL distribution.

Besides the more general recommendations discussed above that are applicable to most remediation techniques, several remediation-type-specific observations and research recommendations can be made. The dense-brine remediation strategies described by Miller et al. (2000), Hill et al. (2001), and Johnson et al. (2004) involve the addition of dense brine to control the movement of DNAPL after mobilization. Research emphasis should be placed on brine recovery from the subsurface, including investigations of potential brine sinking in aquifer systems. The question of the fate of the injected brine is again complicated by subsurface heterogeneity. One aspect of the method is to extract DNAPL that has collected on top of the brine after a surfactant flush. The efficiency of the hydraulic DNAPL removal and the effect of the remaining entrapped DNAPL on aqueous concentrations need to be investigated.

Both the SEAR-NB technique (Kostarelos et al., 1998) and the viscosity and density manipulations for multifluid alcohol flushing (Lunn and Kueper, 1999b) use xanthan polymer additions to aid in the control of gravity and viscous forces. Besides using polymers for plume stabilization, the use of these components should be considered for enhanced access into lower permeability zones using mobility control features.

The potentially upward migration of LNAPL during surfactant or alcohol flushing is less controversial than downward DNAPL movement and usually results in easier removal of free NAPL. Straightforward techniques using single active components result in high removal efficiencies, although multiple flushing schemes (Grubb et al., 1997; 1998) may sometimes be useful. Flushing experiments using only surfactants, conducted by Schwill et al. (1967) and Chevalier et al. (1998), show that vadose zone surfactant flushing followed by LNAPL pumping of the free product might be more effective than starting out with oil pumping, followed by surfactant flushing, and finishing with another round of pumping. Additional research contrasting these two remediation schemes for the removal of gasoline or other petroleum products is recommended. Based on the successful and fast removal of the LNAPLs dodecane, octane, and toluene with ethanol, Palomino and Grubb (2004) have argued that the rising prices of petroleum were making the application of alcohol flooding for cleanup purposes economically feasible. Follow-up flow cell experimental research may be worthwhile, investigating the removal of gasoline or other petroleum products from the subsurface using alcohol or surfactant flushing.

Hydraulic recovery of NAPL using extraction wells is a widely used removal strategy. System design is often based on simplified equations for fluid movement (e.g., Charbeneau et al., 2000) based on nonhysteretic fluid distributions (e.g., Lenhard and Parker, 1990). The experiments by Waddill and Parker (1997) and Sleep et al. (2000) have demonstrated the need to include pore geometry and fluid entrainment hysteresis into numerical models for and accurate simulation of the observed phenomena. Several research topics related to hydraulic NAPL recovery are of interest. A more de-
tailed understanding of NAPL entrapment when free NAPL migrates toward extraction wells, NAPL entrapment in the cone of well depression, and observed decreases in NAPL recovery rates with time can be obtained through flow cell experimentation (Oostrom et al., 2005c).

The ISCO technique with MnO$_4^-_2$ has shown potential in terms of contaminant destruction but progress seems to have stalled because effective modifications to reduce both MnO$_2$ and CO$_2$ production appear to be difficult to develop. It should be noted that the technique has been tested in the laboratory with relatively high entrapped and pooled NAPL saturations. It might be that the ISCO method is more successful under conditions where the NAPL saturations are lower. Testing of methods in situations where the entrapped NAPL saturation is a few percentage points instead of the customary >10% saturation will shed light on that issue. The method might also be helped by the addition of other chemicals. Zhai et al. (2006) demonstrated some success with the addition of cosolvents to the MnO$_4^-_2$ solution to remove PCE in column studies. So far, all the ISCO flow cell experiments have been conducted with MnO$_4^-_2$. It will be useful to demonstrate the ability of other reagents such as H$_2$O$_2$, O$_3$, and Fenton's reagent to remediate DNAPL in multidimensional systems.

Heat-based remediation using coinjection of steam and air (e.g., Kaslusky and Udell, 2005) has been shown to remedy the downward movement of volatile DNAPL experienced when only steam is injected. The downward movement was observed in flow cell experiments by, e.g., She and Sleep (1999). The coinjection of air and steam and the subsequent demonstrations in flow cell experiments has elevated this technique to a promising DNAPL enhanced remediation method since the method is able to combine high removal percentages without unwanted downward migration of the contaminant. Several issues need additional flow cell investigation. The successful experimental coinjection work by Kaslusky and Udell (2005) was conducted in horizontal flow cells. Given documented negative aspects like gravity override (She and Sleep, 1999) and induced downward DNAPL mobilization, the method needs to be demonstrated for vertical experimental configurations. In addition, the applicability of the method needs to be tested in heterogeneous systems with multicomponent DNAPLs with various volatilities. Kaslusky and Udell (2005) noted that coinjection would ideally be applied as the first of three phases for steam injection extraction. The first phase includes heating the targeted soil area to vaporize highly volatile DNAPL, thus transporting the volatile components ahead of the thermal front to a recovery well. During the second phase, only steam will be injected to heat the soil to higher temperatures to vaporize lower volatility components. The third phase encompasses pressure cycling to remove lower volatility components from low-permeability zones. An experimental effort to show the utility of this three-phase approach to remove multicomponent DNAPL from heterogeneous porous media would be extremely valuable.

Soil vapor extraction is the most commonly used technique for remediation of unsaturated zones of the subsurface contaminated with volatile and semivolatile NAPLs, either as a stand-alone technique or in combination with methods such as steam stripping and air sparging to collect the contaminated vapors. Although SVE field applications have sometimes yielded considerable amounts of volatile organics, high initial recovery rates are usually followed by long periods of low rates. Heron et al. (1998) listed slow diffusion of contaminants from low-permeability layers into areas with vapor exchange, vapor-phase retardation due to adsorption, limited volatility of the contaminant at in situ temperatures, and the presence of low-permeability soil layers as limiting factors for this technique. Despite the widespread use of SVE and the large number of potentially limiting factors, it is remarkable that only a few intermediate-scale experiments (Ho and Udell, 1992; Oostrom et al., 2005b) have been conducted to investigate this technique.

The air sparging experiment by Heron et al. (2002) provided strong evidence that sparging would probably not significantly affect the pooled DNAPL at textural interfaces. They concluded that air sparging for sites with DNAPL pools is an improper use of the technology. The technique might still be useful for removal of dissolved contaminants or LNAPL but, based on the analysis by Heron et al. (2002), additional flow cell experiments to investigate removal of DNAPL through air sparging appear not to be necessary.

Methods like DNAPL source bioremediation and humic acid enhanced remediation have shown promise in preliminary flow cell experiments but additional research is needed for an improved assessment. For instance, in the only published flow cell experiment using bioremediation of liquid PCE (Adamson et al., 2003), accumulation of the carcinogen vinyl chloride was observed. It is obvious that this negative aspect needs to be addressed before this technique can be developed further.

ACKNOWLEDGMENTS

Pacific Northwest National Laboratory (PNNL) is operated by the Battelle Memorial Institute for the Department of Energy (DOE) under Contract DE-AC06-76RLO 1830. This research is partly funded by the Groundwater/Vadose Zone Integration Project funded through the DOE’s Richland Operations Office and the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE’s Office of Biological and Environmental Research and located at PNNL. Scientists interested in conducting intermediate-scale flow cell experiments in the Subsurface Flow and Transport Experimental Facility of the EMSL or using the STOMP (Subsurface Transport Over Multiple Phases) simulator are encouraged to contact M. Oostrom.

REFERENCES


Environmental Systems and Technologies. 1996. Areal multiphase organic simulator for free phase hydrocarbon migration and recovery: ARMSO version 5.2 user’s guide. ES&T, Blacksburg, VA.


Schwille, F. 1988. Dense chlorinated solvents in porous and fractured media. Model experiments. Lewis Publ., Chelsea, MI.


