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Videomicroscopy study of behavior of toluene in wet and dry heterogeneous porous media

Nguyen, Hung Manh, M.S.
Rice University, 1992
RICE UNIVERSITY

VIDEOMICROSCOPY STUDY OF BEHAVIOR OF TOLUENE IN WET AND DRY HETEROGENEOUS POROUS MEDIA

by

Hung M. Nguyen

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE MASTER OF SCIENCE

APPROVED, THESIS COMMITTEE

Clarence A. Miller, Chairman, Chemical Engineering, Committee Chairman

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J. David Hellums, A.J. Hartsook Professor, Chemical Engineering

Houston, Texas
August, 1991
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ABSTRACT

A novel bead-pack micromodel has been developed to observe directly with videomicroscopy movement and distribution of toluene in the subsurface, including effects of water infiltration, variations in the water table, and alcohol-water flushing.

If the medium was initially partially water-saturated, toluene spread downward along air-water interfaces, leaving behind very low residual saturation. It did not penetrate low-permeable strata that were water-saturated. If the medium was initially dry, toluene saturated only a small area where it was injected. Water infiltration displaced such toluene downward, ultimately trapping it as ganglia. Subsequent water drainage exposed some ganglia to air, allowing toluene to spread downward. Other ganglia in regions of low permeability remained trapped. Limited upward displacement of toluene occurred with the raising of the water table. However, the toluene was eventually trapped. Enhanced solubilization and mobilization of toluene were observed with a flushing mixture of isopropanol and water (50/50).
ACKNOWLEDGEMENTS

I would like to express my gratitude to the following people who helped make this thesis a reality:

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1. INTRODUCTION

More than 98 percent of available fresh water is ground water. In the United States, the pollution of aquifers can be disastrous because at least one half of the population depends on ground water as a source of drinking water. Presently, approximately one or two percent of the available groundwater resources have been contaminated, and the cost of cleaning up superfund sites is estimated at $100 billion over the next two decades (1).

1.1 The Subsurface

Ground water occurs in many types of geologic formations. An aquifer is a saturated permeable geologic unit that can transmit significant quantities of water under ordinary hydraulic gradients. Common aquifers consist of unconsolidated sands and gravels, permeable sedimentary rocks such as sandstones and limestones, and heavily fractured volcanic and crystalline rocks. Porosity is a quantitative property that describes the fraction of a medium that is available for fluid flow. It is related to the range in grain size, particle shapes, cementation, compaction, and fracturing, Table 1.1. Sphere-shaped grains will pack more tightly and have less porosity than particles of other shapes. If a sediment contains a mixture of grain sizes, the porosity will be
lowered. The smaller particles can fill the void spaces between the larger ones (2).

<table>
<thead>
<tr>
<th>Name</th>
<th>Size Range (mm)</th>
<th>Porosity(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.062-2</td>
<td>25-50</td>
</tr>
<tr>
<td>Silt</td>
<td>0.004-0.062</td>
<td>35-50</td>
</tr>
<tr>
<td>Clay</td>
<td>&lt;0.004</td>
<td>33-60</td>
</tr>
</tbody>
</table>

**Table 1.1 Size Range and Porosity of Sediments (3)**

Aquifers are classified as either unconfined or confined, Figure 1.1. A confined or artesian aquifer is completely filled with water under pressure and is overlain by a confining bed. An unconfined or water table aquifer is divided into an unsaturated zone and a saturated zone (4).

The unsaturated or vadose zone is divided into the moisture zone, the intermediate zone, and the capillary zone. The soil pores in the unsaturated zone are only partially filled with water and the fluid pressure is less than atmospheric. The occurrence of the capillary fringe in this region is due to the molecular attraction between the liquid phase and the aquifer material, and to the surface tension of the air-water interface. In general, the smaller the diameter of the pore space, the higher the capillary rise. In the saturated zone, soil pores are filled with water and the fluid pressure is greater than atmospheric. The water table is the level in the saturated area where the fluid pressure in the
pores is exactly atmospheric (1). 

![Figure 1.1. Groundwater contamination (4)](image)

1.2. Fluctuation in the Groundwater Levels

Groundwater levels are influenced by both nature and human activities, Figure 1.1. The hydrologic cycle is a process which describes the way which water moves continuously through aquifers, on the surface of the earth, and through the atmosphere. Water infiltrates the surface soil at a rate that decreases with time, Figure 1.2. Human activities such as well pumping for consumption or processes have a great deal of effect on the groundwater level. A summary of mechanisms that
lead to the fluctuation in groundwater levels is given in Table 1.2.

Fig. 1.2. Time-dependent rates of infiltration (3)

Ground water will flow in response to hydraulic potential gradients. Small pore dimensions and low fluid velocity in the aquifers assure that fluid flow is laminar. Darcy's Law is the equation of motion for laminar flow in porous media,

\[ Q = -KA \left( \frac{dh}{dl} \right) \]

\( Q \) is the total volumetric flow rate of fluid leaving; \( A \) is the area available for flow; \( K \) is the hydraulic conductivity; and \( dh/dl \) is known as the hydraulic gradient. Hydraulic conductivity is a measurement of how well an aquifer transmits water. It is directly proportional to the specific weight of
water and inversely proportional to the dynamic viscosity of water. It is influenced by the same factors that determine the medium's porosity. Hydraulic conductivity is variable for different types of rock material, Table 1.3. Since all aquifers are heterogeneous, hydraulic conductivity will vary from place to place.

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<th>Unconfined</th>
<th>Confined</th>
<th>Natural</th>
<th>Man-induced</th>
<th>Short-lived</th>
<th>Diurnal</th>
<th>Seasonal</th>
<th>Long-term</th>
<th>Climatic influence</th>
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<td>Agricultural irrigation and drainage</td>
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Table 1.2. Mechanisms that lead to variations in groundwater levels (5)
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<td>Clay</td>
<td>1E-9 - 1E-6</td>
</tr>
<tr>
<td>Silt</td>
<td>1E-6 - 1E-4</td>
</tr>
<tr>
<td>Fine Sands</td>
<td>1E-5 - 1E-3</td>
</tr>
<tr>
<td>Well-sorted Sands</td>
<td>1E-3 - 1E-1</td>
</tr>
<tr>
<td>Well-sorted Gravel</td>
<td>1E-2 - 1</td>
</tr>
</tbody>
</table>

Table 1.3 Hydraulic Conductivity of Sediments (3)

1.3. Groundwater Contamination

In 1979, Freeze & Cherry (2) published the first comprehensive text on the subject of groundwater contamination. Updated information on the migration of hazardous wastes in the subsurface can be found in Devinney et al.'s work (1). Lyman et al. (6) address the specific problem of petroleum contaminated soils near underground storage tanks. An overview of the problem of gasoline-contaminated soils is given in the following paragraphs.

Natural and synthetic substances can enter the groundwater because of human activities, or human interference with hydrological, physical, chemical and biological processes without any addition of substances, Figure 1.1. Pollutants may be gases, liquids or solids, and are classified as miscible or immiscible with water.

Aviation gasoline is immiscible with water. It is a mixture of many compounds (e.g., benzene, toluene, ethyl-
benzene, o-xylene). In the unsaturated zone, it exists primarily in three physical states: residual liquid contaminant, contaminant vapors, and contaminants dissolved in pore water, Figure 1.3. The rate and degree of partitioning of the residual liquid into the vapor phase and aqueous phase depend on site-specific (e.g., depth to groundwater, hydraulic conductivity, rainfall infiltration, soil temperature) and

---

**Fig. 1.3.** Representation of three different phases in which petroleum product can be found in unsaturated zone (6)
contaminant-specific factors (e.g., vapor pressure, water solubility, viscosity, liquid density, interfacial tension, soil sorption constant), as well as time.

Multiphase flow occurs when fluids other than water are moving in the subsurface. Many characteristic parameters are no longer constant when several fluids are present together and competing for the same pore space. Each fluid can be moving in a different direction and at a different rate. The number of processes increases because the effects of pumping/injection and evaporation affect each of the fluids present and, in addition, there can be transfer of mass between fluids.

The problem of multiphase flow in porous media has been studied for a number of years by petroleum and chemical engineers. A lot of what has been learned about interfacial and transport phenomena in oil reservoirs and in packed-bed reactors can be applied to the problem of contaminant transport.

Relative permeability theory (7) is currently used to model multiphase flow in porous media, where Darcy's Law is written for each phase. For example, given that flow for each fluid occurs in continuous channels, the following modification of Darcy's Law should apply to two-phase flow:

\[
\begin{align*}
Y_w &= \frac{kk_{rw}}{\mu_w} (\nabla p_w - \rho_w g) \\
Y_{nw} &= \frac{kk_{rnw}}{\mu_{nw}} (\nabla p_{nw} - \rho_{nw} g)
\end{align*}
\]
where \( k \) is the permeability of the medium, \( k_{rw} \) is the "relative permeability" of the wetting phase and \( k_{rmw} \) is the "relative permeability" of the non-wetting phase. Permeability of a medium is defined as

\[
k = K \left( \frac{\mu}{\rho g} \right)
\]

where \( K \) is the hydraulic conductivity, \( \mu \) is the viscosity, \( \rho \) is the density, and \( g \) is the gravitational acceleration. The relative permeabilities are dependent on the relative amounts of the phases present but not on flow rate, Figure 1.4. For given wettability conditions they should also be independent of fluid viscosities. There is some hysteresis, but it is often small and can usually be neglected. Note that zero values of relative permeability correspond to some amount of residual saturation of the phase. These results indicate that a discontinuous fluid phase can not flow. Three-phase flow is much more complex and is rather poorly understood. Hysteresis effects are also more important than in two-phase flow. An example of the relative permeabilities for three-phase flow is given in Figure 1.5.

There are primarily five technologies, Figure 1.6, used to remediate petroleum contaminated sites: soil venting, biorestoration, soil flushing, hydraulic barriers, and excavation. Soil venting refers to any technique that removes contaminant vapors from the unsaturated zone. Biorestoration
is a process where oxygen and nutrients are added to contaminated soil to promote the breakdown of contaminants by naturally occurring microorganisms. Soil flushing refers to a process where the zone of contamination is flooded with water or water-solvent or a water-surfactant mixture in order to dissolve the contaminants into the water or otherwise mobilize

![Graph showing relative permeabilities as a function of degree of saturation for a two-phase system](image1)

**Fig. 1.4.** Relative permeabilities as a function of the degree of saturation for a two-phase system (8)

![Graph showing relative permeabilities for three-phase flow](image2)

**Fig. 1.5.** Relative permeabilities for three-phase flow (8)
the residual contaminant to the producing wells. Physical barriers such as slurry walls and French drains have been used to allow for removal of accumulated free product from the unsaturated zone. Though excavation is commonly employed because it can be implemented quickly, the first four are preferred because they are performed with the contaminated soil remaining in place, which affords a greater degree of control over the release of contaminant vapors (6).

1.4. Previous Studies

The number of research projects in groundwater contamination has been on the increase within the last few years. One gasoline-contaminated site that has been studied extensively is the U. S. Coast Guard Traverse City in Michigan. In 1969, approximately 109,000 kg of aviation gasoline was accidentally spilled into the subsurface there, Figure 1.7. In 1985, Twenter et al. (9) found that the plume had extended up to the Grand Traverse Bay, where toluene and benzene were detected. Ostendorf et al. (10) estimated that approximately 72,400 kg remained as of December 1988. The oil phase, as free product and/or residual oil was detected 220 m from the source. In 1990, Chang et al. (11) investigated the in-situ recharge effect on ground water quality due to infiltrating water. They verified that the infiltration water carried contaminants from the residual oil in the unsaturated zone into the
Fig. 1.6. (a) Soil venting, (b) Bioremediation, (c) Soil flushing, (d) Hydraulic barrier (6)
groundwater beneath the capillary fringe zone.

Video microscopy and micromodels have been used extensively in petroleum engineering applications. In porous media study, video microscopy allows for the examination of processes that occur around a few individual particles and their adjacent pore spaces. Micromodels have not been used to study the behavior of petroleum products in porous media relative to
groundwater contamination until recently (8,12,13,14a-b). Schwille (12) used a single-layered bead pack to study infiltration of tetrachloroethylene, a solvent which is denser than water. He observed migration patterns such as one shown in Figure 1.8. Wilson et al. (14b) used etched glass micromodels to observe the infiltration of an organic liquid through the unsaturated zone to the water table.

**Fig. 1.8. Migration pattern (8)**

1.5. Research Objectives

The principal objective of this research effort is to develop a novel micromodel which can be used with video microscopy to identify those mechanisms associated with the trapping and mobilization of toluene in the unsaturated zone and near the water table in an unconfined aquifer such as the
one at Traverse City.

1.6. Thesis Outline

Modification of an existing microscope apparatus, development of the novel micromodel, selection of the fluid system, and experimental procedures are detailed in Chapter 2. The initial spreading and drainage of toluene is examined in Chapter 3. The effect of water infiltration and drainage on toluene is reported in Chapter 4. The effect of isopropanol-water flushing on toluene is discussed in Chapter 5. The effect of variations in water table on toluene is found in Chapter 6. Conclusions and recommendations are provided in Chapter 7.
2. EXPERIMENTAL METHODS

2.1. Videomicroscopy

Information on the technique of video microscopy can be found in a reference book by Inoué (15). A typical videomicroscopy system consists of a microscope, which is connected to a video camera, and video equipment for added special effects and data recording. The arrangement of the system in the Interfacial Phenomena Lab at Rice University is shown in Figure 2.1.

Because of the nature of the problem under investigation, a vertical-stage microscope apparatus was used. The existing vertical-stage Nikon microscope apparatus was modified in June 1990, mainly to accommodate the novel longer micromodel that will be discussed below. Moreover, the original homemade apparatus was composed of a number of individual components which were not properly aligned. The modified vertical-stage microscope, shown in Figure 2.2, includes a new specimen stage designed specifically for the new micromodel.

Objectives of 4X, and 10X magnification were used to study phenomena at different perspectives. The 4X objective provided views large enough to observe the overall mechanism and flow pattern. The 10X allowed investigation of pore level events.

A Nikon zoom ocular for videomicroscopy links the
microscope to a recently purchased Javelin JE3462RGB solid-state color video camera. A color video camera was used to allow for the identification of the different fluids present. The Javelin JE3462RGB camera is equipped with a MOS image sensor pickup device that allows it to produce clear pictures.
with no graphic distortion or residual image.

Figure 2.2. Modified vertical-view microscope

The modified microscope is equipped with two different light sources. The one located to the left of the specimen stage provides transmitted light and the other one provides reflected light. When they are both used at the same time, a 3-D image of the porous medium is obtained, Figure 2.3.

Video equipment shown in Figure 2.1 includes a BTX Cypher Time Code Generator, a Harris Time Base Corrector, a Harris HVS 690 Digital Frame Synchronizer, a FOR.A FM-60 Frame Memory, a IV-530 Contour Synthesizer, a IV-550 Video Scaler, a Videotek TSM-5A Waveform Monitor (WFM), a 3M Model 210 color
bar and sync generator (3M Model 210), video monitors, video recorders, video tape editing units, a Dunn Instrument Model 635 Compact Color Camera, and a Perceptive Systems PSICOM 327 Digital Image Processor (DIP). Information on these components can be found in Elsik's work (7).

Figure 2.3. 3-D image of a bilayer of glass beads of 321 microns in diameter using objective of 4x magnification

2.1. Micromodel Development

Micromodels have been frequently used in the study of multiphase flow in porous media. They allow visual observa-
tion of flow processes at the pore level. The various approaches to micromodel design and fabrication and the success of micromodels in illustrating mechanisms of multiphase flow, as well as their limitations, can be found in a review by Buckley (16). A brief summary is given here.

Over the years, research on transport and interfacial phenomena has resulted in a number of experimental models. They include capillary tube models, network models, bead packs, and rock models. A suitable model would possess physical properties such as the converging-diverging nature of the flow channels, porosity, hydraulic conductivity, pore size distribution, and the degree of connectivity similar to those found in ground water aquifers. Figure 2.4 shows the frequency of application of various types of micromodels.

At Rice, Elsik (7) developed a micromodel to study the effects of the capillary number in secondary and tertiary oil recovery processes. It consists of an optical rectangular capillary cell packed with a bilayer of monodisperse glass beads. He found that the opacity and scattering effects would be less for a bilayer system than it would be for other multilayer systems. The capillary has a path width of 200 μm and is packed with 109 μm glass beads in a hexagonal configuration, Figure 2.4. The pore throat diameters are 16 μm between beads and 24 μm along the wall. The two layers of beads result in a pore structure that is highly interconnected, allowing better physical representation of a three-
The micromodel developed for this work, Figure 2.6, was different from the one used by Elsik. It has dimensions 0.6x6x300 mm and is packed with a bilayer of sodium aluminum silicate based glass beads 321 ± 9.6 μm in diameter. The glass beads were purchased from Duke Scientific Corp. and the rectangular capillaries were obtained from Vitro Dynamics,
Inc. This particular combination of cell and beads was also chosen to promote the possibility of hexagonal close packing arrangement. To study the effect of particle-size heterogeneity, some flow cells were also made with a layer 5 cm in length of particles 85-120 microns in diameter. A 5 cm long stainless-steel hypodermic needle is inserted into the upper portion of the porous medium to allow for the injection of an

Fig. 2.6. Experimental micromodel
organic liquid such as toluene into the medium. The micromodel also has a side tube to show the level in the medium where the liquid is at atmospheric pressure.

The procedure used to construct the micromodels in this project is similar to that used in Elsik's work. One end of an unpacked capillary is covered with a 100 mesh stainless steel wire cloth (Gilson Co.). Stainless steel is used instead of woven polyester cloth to reduce the amount of water being held up in the porous medium during drainage. Epoxy is used to secure the wire cloth. Once the epoxy is cured, the covered end is inserted into a slit of a glass U-bend. On the other side of the slit, there is a smaller circular opening where a Hamilton hypodermic needle (5cm long, 0.36mm O.D.) is inserted into the capillary. Epoxy is again used to secure the capillary and needle to the glass U-bend. This is the top part of the flow cell.

The following procedure is used in packing the beads. A vacuum supply is connected to the top U-bend of the flow cell. The capillary is partially filled with glass beads and the vacuum source is then removed. The cell is held in the upright position and is tapped moderately on the bottom in the vertical direction. After a short time, areas of structured packing can be monitored by observing the way light reflects from macroscopic regions of the cell. While still in the vertical position, the vacuum is again applied to pick up some additional beads. The process is repeated until the capillary
is full. A tight seal between the second wire cloth and the packed beads may not be possible. The void space can be minimized by overpacking the capillary (leaving beads protruding from the end), and then very carefully placing the cloth over them. Epoxy is used to secure the wire cloth. This end of the capillary then gets inserted into the slit of the bottom end piece and is again secured with epoxy. A schematic drawing of the experimental micromodel is shown in Figure 2.7.

The porosity of the porous medium is determined by weighing the flow cell before and after it is packed with the glass beads. By knowing that the density of the glass beads is 2.42, the average porosity of the porous medium can be obtained.

The hydraulic conductivity of the porous medium is determined by flushing the flow cell from the top with water with different dyes. The porous medium is first saturated with a Trypan Blue/water solution (0.25g/L). While the medium is still saturated with the Trypan Blue/water solution, the top glass U-bend is quickly filled with a Direct Yellow/water solution (0.25g/L). The velocity of the Direct Yellow/water solution front is recorded and is used in Darcy's Law for a single-phase flow to estimate the hydraulic conductivity. Darcy's Law is used because the Reynolds number is less than 1. The physical characteristics of the micromodel and the sandy unconfined aquifer at Traverse City are compared in Table 2.1.
Fig. 2.7. Schematic drawing of the experimental micromodel

2.3. Fluid System

The fluid system investigated in this study includes
toluene, water, and air. Toluene was selected because it was studied by Chang et al. (11). It is less dense than water and is slightly soluble in water. The water used was purified using a SYBRON/Barnstead purification system.

<table>
<thead>
<tr>
<th></th>
<th>Traverse City (12)</th>
<th>Micromodel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Particle Size</td>
<td>0.177-0.5 mm</td>
<td>0.085-0.321 mm</td>
</tr>
<tr>
<td>2. Porosity</td>
<td>0.25-0.5</td>
<td>0.5-0.56</td>
</tr>
<tr>
<td>3. Hydraulic</td>
<td>0.042 cm/s</td>
<td>0.18-0.22 cm/s</td>
</tr>
<tr>
<td>Conductivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Packing Arrangement</td>
<td>Random</td>
<td>Random</td>
</tr>
</tbody>
</table>

Table 2.1. Physical Characteristics of the Micromodel

In order to distinguish between the phases, Trypan Blue and Sudan III Red were used. Trypan Blue (C_{34}H_{24}N_{6}O_{14}S_{4}Na_{4}) is a water-soluble dye, and Sudan III Red (C_{42}H_{16}N_{40}) is an oil-soluble dye. Water was dyed with Trypan Blue at 0.25g/L and toluene was dyed with Sudan III Red at 0.5 g/L. At these small concentrations, the physical characteristics of toluene and water changed very slightly, Table 2.2. Densities were measured with a Mettler/Paar digital densimeter. Viscosities were measured with a Brookfield cone and plate viscometer.
2.4. Experiments

Four types of experiments were conducted: (a) initial spreading and drainage of toluene, (b) water infiltration and drainage, (c) isopropanol-water flushing, and (d) variations in water table. After each experiment, the micromodel was first cleaned with acetone and water, then it was oven-dried at 120 °C for twenty-four hours before it was used again. All experiments were performed at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Water/TH</th>
<th>Toluene</th>
<th>Toluene/SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.9956</td>
<td>0.9962</td>
<td>0.8603</td>
<td>0.8612</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.89</td>
<td>0.89</td>
<td>0.54</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 2.2. Characteristics of Fluids

2.4.1. Initial Spreading and Drainage of Toluene

The purpose of this experiment was to observe the wetting behavior of the fluids and how the spreading behavior of toluene is influenced by the degree of water saturation and particle size. Figure 2.8 shows the profile of water saturation in a soil (17).

A spreading coefficient \( S_{1/s} \) is defined as

\[
S_{1/s} = \gamma_{SV} - \gamma_{LV} - \gamma_{Sl}
\]
where $\gamma$ is the interfacial tension, (s) is the solid, (l) is the liquid, and (v) is the vapor. The spreading coefficient for a wetting liquid is positive. If there is a finite contact angle $\theta$ such as shown in Figure 2.9, $S_{l/s}$ will be negative because the Young's equation dictates that (18)

$$S_{l/s} = \gamma_{lv} (\cos \theta - 1)$$

Fig. 2.8. Profiles of saturation and pressure in a soil (17)

Fig. 2.9. Contact Angle (19)

Clean glass has a high-energy surface so when either
water or toluene is in the porous medium alone, it should be the wetting phase. When both are present, water should be the wetting phase, toluene the intermediate wetting phase, and air the non-wetting phase. The spreading coefficient for toluene on water is 6.8, so toluene should spread on a water film (19).

During the experiment, the top and bottom of the flow cell was opened to atmospheric pressure. Depending on the specific situation to be studied, toluene either infiltrated the porous medium via the hypodermic needle or the top glass U-bend. Toluene was allowed to spread for a period of time until no significant changes in the fluid distribution in the porous medium were observed.

To create a partially water-saturated porous medium, water was injected from below via the bottom glass tube to a point just below the inserted end of the hypodermic needle. With the top of the side tube closed, water was then withdrawn from the flow cell. Additional draining was allowed to occur for approximately 24 hours.

2.4.2. Water Infiltration and Drainage

The purpose of this experiment was to observe mechanisms which involve the transport of residual toluene to the water table via water infiltration (e.g., rainfall). Figure 2.10 shows the changes in the moisture profile of the ground after
a rainfall (17).

Fig. 2.10. Changes in the moisture profile of the ground after a rainfall (17)

The transport of immiscible pollutants in the subsurface
depends on five physical and chemical processes: diffusion, advection, retardation, dispersion, and transformation. Diffusion is the process by which toluene moves from areas of higher concentration to areas of lower concentration. Under hydraulic gradient, advection causes the nonreactive solutes to travel at the same rate as the average linear velocity of the ground water. Solute which adsorb to the soil will not move as fast as the advection rate would dictate. Traverse City's soil has about 0.018% carbon so very little adsorption and retardation is expected (20). As the solutes are moving through the porous media, the process of hydrodynamic dispersion acts to dilute the solute. The pollutant can also evaporate or react with other substances.

Toluene does not have a strong affinity for glass beads and is slightly soluble in water (0.5g/L). In addition, there is no chemical interaction between toluene and water. When the top U-bend was filled with water, the capillary number of the infiltrating water into a saturated medium was about $5 \times 10^{-5}$. Capillary number is defined as

$$Ca = \frac{V \mu}{\gamma}$$

where $\gamma$ is the interfacial tension, $v$ is the superficial velocity, and $\mu$ is the viscosity.

The experiment involved setting up a toluene-contaminated porous medium. The porous medium was initially either dry or
partially water-saturated. About 10% pore volume of toluene was injected into the medium via the hypodermic needle and was allowed to spread downward for approximately one hour. Next, about 7.5 pore volumes of water was poured into the top glass U-bend; and the contaminated porous medium was flushed and drained for approximately 24 hours. Water infiltration and drainage of the contaminated medium were repeated until no significant changes in the fluid distribution were observed.

2.4.3. Isopropanol-water Flushing

Alcohol flooding has been considered for oil recovery (21–22) and more recently for removal of immiscible contaminants from aquifers (20). The basic idea is to have a miscible flood with no interfaces or at least to lower interfacial tension to where the capillary number is sufficiently large for displacement, Figure 2.11. A capillary number on the order of about 1E-3 is necessary to mobilize trapped oil ganglia. The objective here was not a systematic study of the process but to see how the effect of infiltration changed when the capillary number was high.

The procedures for this experiment were similar to those described in Section 2.4.2. A 2-propanol-water (50/50) solution was used to flush the contaminated medium. This particular combination was also used by McRae to flush the residual aviation gasoline from contaminated soil collected from the
Traverse City site.

![Diagram showing phases of miscible fluid displacement process](image)

Fig. 2.11. Schematic showing phases of miscible fluid displacement process (21)

2.4.4. Variations in Water Table

The purpose of this experiment was to examine the effects of the water table's variation on residual toluene. To simulate the variation of the water table due to events away from the location of interest, a Hamilton syringe is attached to the bottom glass tube and water is injected or withdrawn from the micromodel via a Harvard Pump 22. The pump 22 is a continuously variable dual syringe pump and allows for finer selection of flow rates.

It was noted that though the length of the micromodel was 30 cm, the water level in the porous medium could only be varied within an area of about 8 cm below the inserted end of the hypodermic needle. This was due to four reasons: (a) water retention, (b) capillary rise, (c) end effect caused by the wire cloth, and (d) capillary pressure hysteresis. The first three effects were minimized by the use of large glass beads and capillary, and metal wire cloth with large openings.
Capillary pressure hysteresis is a pressure difference between the imbibition and drainage processes, Figure 2.12. When water was raised in an initially dry medium, the difference between the level in the side tube and that in the porous medium was about 4 cm. If the water levels were then lowered, the difference between the two levels had to exceed about 15 cm before the water in the porous medium began to drain.

![Capillary pressure curve](image)

**Fig. 2.12.** Capillary pressure curve for a water-wet rock showing hysteresis between drainage and imbibition curve (16)

The experiment involved setting up a toluene-contaminated porous medium as per the procedure described in Section 2.4.2. The water level was then raised until the water level in the porous medium was about 1 cm above the contaminated area. Next, the water level was then lowered until the level in the side tube was approximately 1 cm above the bottom of the
rectangular capillary. The raising and lowering of the water level were repeated until no significant changes in the distribution of fluids was observed.
3. INITIAL SPREADING AND DRAINAGE OF TOLUENE

3.1. In an Initially Dry Homogeneous Medium

When toluene was poured into the top glass U-bend, it immediately entered the porous medium and advanced downward. The advancing toluene front was sharp and fairly horizontal, Figure 3.1. The entire porous medium was fully saturated with toluene within seconds.

When toluene was introduced into the porous medium via the hypodermic needle, it remained near the injection point, Figure 3.2. No significant spreading was observed, Figures 3.3 and 3.4. Over time, due to the process of evaporation, toluene began to break up into pendular rings, and eventually, only the sudan III red solid particles were left behind.

3.2. In an Initially Partially Water-saturated Homogeneous Medium

Via either the top glass U-bend or the hypodermic needle, toluene behaved differently when introduced into a partially water-saturated homogeneous medium, Figure 3.5. Figure 3.6 shows the same area as in Figure 3.5 but 5 minutes and 41 seconds after the toluene was injected into the medium. The advancing toluene front was not sharp or horizontal, and no spreading of toluene was observed in the area along the edge
of the cell where the glass surface was dry, Figure 3.7. It took several hours for the infiltrating toluene to travel the entire length of the porous medium.

The observed mechanism involved toluene displacing water from the larger pore spaces, and at the same time, draining in all directions along the air-water interfaces, Figures 3.8 and 3.9. As the displaced water moved downward, it created additional air/water interfaces. Over time, most of the injected toluene moved away from the injection point and the spreading was more extensive than in a dry medium, Figures 3.10 and 3.11 respectively.

3.3. In an Initially Dry Layered Medium

When infiltrating via the top glass U-bend, from the high-K to the low-K region, the advancing toluene front was sharp and fairly horizontal, Figure 3.1 (right cell). The infiltrating toluene front slowed down when it reached the low-K region, but had no problem penetrating it. However, going from the low-K to high-K region, the toluene front traveled along some preferred paths, Figure 3.12. It only took seconds for the toluene to travel the entire length of the porous medium. Over time, while the toluene in the porous medium evaporated as described in Section 3.1, the process was slower in the low-K region where there was a larger toluene saturation but a smaller air-toluene interfacial area, Figure
3.4. In an Initially Partially Water-saturated Layered Medium

Figure 3.14 shows a partially water-saturated layered medium the low-K layer saturated with water. When a small amount of toluene was introduced into the medium via the hypodermic needle, it spread downward as described in Section 3.2 and concentrated at the upper textural boundary between the high-K and low-K regions. Over time, very little of the toluene had worked its way into the low-K layer, Figure 3.15, owing to the absence of continuous air-water interfaces. If the water saturation in the low-K region was low and if the amount of infiltrating toluene was large as in Figure 3.16, toluene would eventually penetrate the entire thickness of the low-K region.

3.5. Discussion

The observations reported in this chapter indicate that the initial spreading and drainage of toluene in the unsaturated zone due to gravity is greatly enhanced by the presence of water, and that a major source of long-term release of toluene in a sandy aquifer will most likely be the contaminated silty or clayey strata within it.

The limited spreading of a small amount of toluene that
was injected into a dry medium is probably due to the fact that the glass surface was not absolutely clean and the fluids were dyed. Soils may have some surface contaminants as well. Impurities on the surface and surface roughness have been known to alter the spreading behavior of a liquid. For example, Figure 3.17 shows the advancing and receding contact angles of water on titania-coated glass as a function of the number of coating treatments. The advancing contact angle is the equilibrium contact angle measured when a plate is dipped into a liquid, and the receding contact angle is when the plate is withdrawn from the liquid (18).

The fingering of fluids passing from a low-K to a high-K region, Figure 3.12, has been previously observed in other studies (23). In a fine over coarse layered sand system, Glass et al. found: (a) the instability of the infiltration flow itself causes the formation of fingers in the bottom high-K layer, (b) the fingers, once formed, persist from one infiltration cycle to the next, and (c) the fingers can only be destroyed by artificially uniformizing the moisture content within the bottom layer by saturation and drainage.

While gravity is a major factor in the downward movement of toluene through the unsaturated zone, the presence of the air-water interface greatly enhances its effect. Wilson et al. (14.b) have observed this mechanism recently, and they conclude that this phenomenon will lead to lower residual saturation of the contaminant in the unsaturated than in the
saturated zone. In the present experiments, residual saturation was even lower when relatively small quantities of toluene were injected. Similar behavior has been observed in the gas injection process in oil recovery (24.a-b). Very high oil recoveries are possible when oil spreads over water, the reservoir is strongly water wet, and a continuous film of oil over water exists in the corners of pores invaded by the gas. Under the same experimental condition, low recovery was found for strongly non-spreading organic liquids such as isobutanol. In the present work, very little drainage along the air-water interfaces was observed when 1-butanol and n-dodecane were the organic liquids.

Some lateral spreading of toluene in a partially water-saturated medium is expected. Because of the narrow width of the capillary, both vertical and lateral spreading of toluene could not be observed at the same time. If the micromodel is placed in the horizontal position as shown in Figure 3.18, lateral spreading of the toluene can be observed. Visually, it was observed that over a few hours the toluene in Figure 3.18 spread approximately 4 cm away from the location where it was injected. The fact that the rate of lateral spreading was less than that during gravity drainage demonstrates that gravity makes a difference in the initial spreading of a contaminant in the unsaturated zone. By using an experimental trough, Schwille (12) had shown both the vertical and lateral spreading of tetrachloroethylene on fracture walls that were
partially water-saturated, Figure 3.19.

Sandy aquifers typically have silty or clayey lenses within them (25). If a sandy aquifer is partially water-saturated where the toluene is spilled, the migration pattern may not be as simple as shown in Figure 3.19. The downward movement of toluene may be retarded by the silty or clayey lenses, and there will be extensive lateral spreading at the textural interface. If these lenses are saturated with water, Farmer (26) has found that even a relatively thin, low permeability unit will inhibit downward percolation and force the contaminant to spread laterally. Unless the ponded toluene can generate a capillary pressure in excess of the displacement pressure of the lense, it will remain at the textural boundary (27). If the less-permeable lenses are partially water-saturated, toluene can penetrate them by spreading along the air-water interface. Upon drainage, toluene saturation in the less-permeable lenses will be relatively higher than the rest of the aquifer, and they will most likely become a major source for long-term release.

By knowing the distribution of the contaminants, the most effective method of removal may be selected. If the subsurface is initially dry, the use of a vacuum extraction system or excavation would be appropriate. Whereas, if the soil is initially partially water-saturated, the other three methods shown in Figure 1.6 may be preferable.

Slurry walls, grout curtains, sheet piling cutoff wall,
and leachate containment have been used as migration barriers. Each has its own advantages and disadvantages (1). If a sediment with a smaller hydraulic conductivity is to be used as a leachate liner, it is necessary for it to be water saturated. The water in the liner will minimize further downward movement of the contaminants and allow them to be removed.
Fig. 3.1. Advancing toluene front in a dry homogeneous medium (left)
Fig. 3.2. Toluene remains near the injection location in a dry medium
Fig. 3.3. Toluene front in a dry medium - initial

Fig. 3.4. Same location as in Figure 3.3 but 19 minutes and 43 seconds later
Fig. 3.5. A partially water-saturated homogeneous medium

Fig. 3.6. Same location as in Figure 3.5 but 5 minutes
41 seconds after toluene was introduced
Fig. 3.7. Advancing toluene front in a partially water-saturated homogeneous medium (left)
Fig. 3.8. Same location as Figure 3.5 during initial spreading of toluene

Fig. 3.9. Same location as in Figure 3.8 but 14 seconds later; note the thin film of toluene on the air-water interface
Fig. 3.10. Displacement of toluene away from the injection location

Fig. 3.11. Extensive spreading of toluene due to the presence of the air-water interface
Fig. 3.12. Advancing toluene front in a dry layered medium (right); the low-K region is located 4 cm from the inserted end of the hypodermic needle.
Fig. 3.13. High retention of toluene in the low-K region (right)
Fig. 3.14. A partially water-saturated layered medium

Fig. 3.15. Toluene concentration at the textural boundary between the high-K and low-K regions
Fig. 3.16. Advancing toluene front in a partially water-saturated layered medium (right)
Fig. 3.17. The advancing and receding contact angles of water on titania coated glass after treatment with trimethyldecylammonium chloride have been shown as a function of coating treatments with 1.1% polydimethyl titanate (16).

Fig. 3.18. Lateral spreading of toluene in a partially water-saturated medium:
(a) homogeneous (top), (b) layered (bottom)
Fig. 3.19. Lateral spreading of tetrachloroethylene in an experimental trough, initially partially water-saturated (12)
4. EFFECT OF WATER INFILTRATION AND DRAINAGE ON TOLUENE

4.1. Water Infiltration and Drainage

Water behaved basically the same as observed with toluene in a dry homogeneous or layered medium. It took a couple minutes for the 7.5 pore volumes of water in the U-bend to pass through the medium, Figure 4.1. After the infiltration was discontinued and water was allowed to drain, the medium became unsaturated, Figure 4.2. In subsequent water infiltrations, air was trapped as a discontinuous phase and water did not saturate the medium again, Figure 4.3. It took several hours for the 7.5 pore volume of water to pass through a partially water-saturated homogeneous medium.

When water was poured into the top glass U-bend of an initially dry layered medium, it took about three minutes for the infiltrating water to cover the entire length of the porous medium. After the infiltration was discontinued and the water in the cell was allowed to drain, the medium became unsaturated with water. The low-K region had a larger water retention than the high-K regions, Figure 4.2. Water from subsequent infiltration traveled along some preferred paths and did not saturate the medium again, Figure 4.3. It took a little longer for the 7.5 pore volume of water to pass through a partially water-saturated layered medium than a partially water-saturated homogeneous medium.
4.2. In a Toluene-contaminated Homogeneous Medium

After a small amount of toluene was injected into an initially dry homogeneous medium via the hypodermic needle, Figure 4.4, the top glass U-bend was then filled with water to simulate ponded water on the surface of a toluene-contaminated soil. The displacement and trapping of toluene as ganglia by the advection effect was observed first, Figure 4.5. At high magnification, it was observed that the trapped toluene ganglia were indeed immobile, Figure 4.6, and that they dissolved into the infiltrating water over time, Figure 4.7.

When the source of water infiltration was removed, the drainage process began. As the contaminated water was draining out of the bottom of the flow cell, air was drawn into the medium from the top and the saturated region of toluene and water began to break up, Figure 4.8. The residual toluene was observed to be in two physical states: (a) toluene-covered water films, and (c) toluene ganglia entrapped by water. Thus, during drainage, some trapped toluene ganglia were released and spread downward along the newly created air-water interface, Figures 4.9 and 4.10.

During subsequent water infiltrations, while some of the toluene that was covering the water films did not come in contact with the infiltrating water, some was displaced and trapped as ganglia, Figure 4.11. Figures 4.12 and 4.13 show the dissolution of toluene trapped between the infiltrating
water and the air-water interfaces. Figure 4.14 shows dye particles remained at the air-water interfaces, an indication that evaporation of the toluene has occurred.

Another interesting observation was that the toluene ganglia entrapped by water remained immobilized during subsequent infiltrations and drainages. Figures 4.15 and 4.16 show two toluene ganglia that remained trapped after the medium was allowed to drain. During the next water infiltration, though the area in which these ganglia were located became more saturated with water, these two trapped ganglia did not move, Figure 4.17. The next drainage of the medium did not release the trapped toluene ganglia, Figure 4.18.

4.3. In a Toluene-contaminated Layered Medium

After a small amount of toluene was injected into the top high-K region of an initially dry layered medium, Figure 4.4, water was poured into the top glass U-bend. While some toluene was trapped by the infiltrating water in the top high-K region, the advection effect moved some toluene into the low-K layer, Figure 4.5. Once the toluene was trapped as ganglia, only its shrinkage by the solubility effect was observed.

Upon drainage of the medium, only a small amount of water was drained from the low-K region. Some of the toluene ganglia that were trapped in the top high-K region were
released and moved down to the top of the low-K region, Figure 4.8. As water drained from the medium, some of the toluene that was on top of the low-K region began to penetrate the low-K region along the newly created air-water interface.

During subsequent water infiltrations, not much of the infiltrating water entered the medium, and the saturation of fluids remained relatively the same. During subsequent water drainage, the toluene that was at the air-water interfaces in the top high-K region evaporated from the medium.

4.4. Discussion

Assuming that the contaminated area, where toluene was spilled, was initially dry, the mechanisms involves in the first water infiltration are simply those relevant to displacement of a non-wetting by a wetting fluid with trapping. A concise review of previous work in the petroleum engineering and fluid mechanics fields on the emplacement and mobilization of non-aqueous phase liquid can be found in a review by Hunt et. al (25).

The mobilization of the trapped toluene ganglia requires that the capillary number of the infiltrating water be sufficiently high. A capillary number on the order of about 1E-3 is necessary to mobilize trapped oil ganglia.

Because the capillary number of the infiltrating water was not large enough, the only way which trapped toluene can
be transported downward is by its dissolution into the infiltrating water. The literature on non-aqueous phase liquid (NAPL) dissolution into ground water has been recently reviewed and analyzed by Pfannkuck (25). The majority of this research addresses two phenomena that are rarely separated: mass transfer limitations and the changing composition of a multicomponent NAPL. The dissolution rates can be estimated from mass transfer coefficients correlated with fluid flow conditions.

It was noted in Section 4.2 that when the source of water infiltration was removed, some of the trapped toluene ganglia were able to drain downward along the newly created air-water interface. Lateral spreading is expected and it again can be illustrated with results from the work by Schwille (12), Figure 4.19.

The observations made concerning the effect of water infiltration suggest that the source of long-term residual gasoline release at Traverse City is most likely from those ganglia that are trapped by water, especially if they are located in the strata of lower hydraulic conductivity. The longer amount of time it took for the infiltrating water to pass through a toluene-contaminated layered medium that was initially partially water-saturated suggests that the infiltrating water would prefer to flow along some other less resistant pathways. Because water is the wetting phase, some of the infiltrating water should be able to go through the
low-K regions. However, unless the capillary number of the infiltrating water is large enough, the only way that the toluene trapped in the less permeable strata can work its way down to the water table is if some mass transfer takes place between the trapped ganglia and the infiltrating water or if the water which covered the trapped ganglia evaporates and exposes them to the continuous air pathway.

Almost all remediation of ground water at contaminated sites is by the pump-and-treat method, which involves soil flushing (28). Although the process takes a long period of time and costs a tremendous amount of money, its effectiveness is questionable. It was reported recently that the ground water contamination a site in New Jersey had come back to twice what it was before the cleanup (29). One possible explanation for this phenomena is that water evaporation could have exposed previously trapped ganglia which drain to the water table.

Cary et al. (30) have proposed that if the soil surface can be sealed and the air pressure raised above the air-entry pressure of the water-filled pore necks that encompass the organic liquid, then the air-water meniscus will rupture. This will allow a vapor escape route for the trapped organic liquid and also allow gravity drainage to water table. For lower vapor pressure organics, the injection of steam rather than compressed air has some advantages.
Fig. 4.1. Advancing water front in a dry medium: (a) homogeneous (left), (b) layered (right)
Fig. 4.2. A partially water-saturated medium: (a) homogeneous (left), (b) layered (right)
Fig. 4.3. A partially water-saturated medium during subsequent infiltrations: (a) homogeneous (left), (b) layered (right)
Fig. 4.4. A small amount of toluene is injected into a dry medium: (a) homogeneous (right), (b) layered (left)
Fig. 4.5. Displacement of toluene due to advection effect: (a) homogeneous (right), (b) layered (left)
Fig. 4.6. A trapped toluene ganglion

Fig. 4.7. The trapped ganglion in Figure 4.6 dissolves in the infiltrating water over 2 hours 27 minutes
Fig. 4.8. The medium drains after source of water infiltration was removed: (a) homogeneous (right), (b) layered (left)
Fig. 4.9. A trapped toluene ganglion

Fig. 4.10. Release of the trapped ganglion in Figure 4.9 due to drainage of medium
Fig. 4.11. During subsequent water infiltrations: (a) Trapped toluene ganglia, (b) toluene on air-water interfaces
Fig. 4.12. Toluene trapped between the infiltrating water and the air-water interface

Fig. 4.13. Toluene in Figure 4.12 dissolves in infiltrating water over 24 hours
Fig. 4.14. Dye Particles remained at the air-water interfaces, an indication that the evaporation of toluene has occurred.
Fig. 4.15. Toluene ganglia remain trapped after drainage

Fig. 4.16. Same as Figure 4.15 but higher magnification
Fig. 4.17. Trapped toluene ganglia in Figure 4.15 did not move during next water infiltration.

Fig. 4.18. Trapped toluene ganglia in Figure 4.15 did not move during next water drainage.
Fig. 4.19. Lateral spreading of tetraethylpyrophosphate in an experimental trough.
5. EFFECT OF ISOPROPANOL-WATER FLUSHING ON TOLUENE

5.1. In a Toluene-contaminated Homogeneous Medium

Figures 5.1 and 5.2 show the enhanced solubility and mobility of the trapped toluene ganglia after they came in contact with the flushing isopropanol(IPA)-water solution. If the medium was initially dry, the IPA-water solution would rapidly surround the toluene and displace it downward. Figures 5.3 and 5.4 show that the IPA-water solution initially prefers to travel through the area that is saturated with toluene and then spreads out into the dry area. Some toluene ganglia did get trapped behind the moving IPA-water front, but they were quickly solubilized by the flushing solution. It took about seven minutes for the IPA-water solution to flush the same amount of toluene out of the medium as in the experiments described in Section 4.2.

It took about 60 minutes for the IPA-water solution to clean a toluene-contaminated medium that was initially partially water-saturated, Figures 5.5 and 5.6. Though the toluene was either solubilized or displaced downward, air was trapped behind.

5.2. In a Toluene-contaminated Layered Medium

It took a little longer for the IPA-water mixture to
flush out toluene from an initially dry layered medium than from an initially dry homogeneous medium. Figures 5.7 and 5.8 show the advection effect at the top textural boundary and Figure 5.9 shows the advection effect at the bottom textural boundary, where toluene was getting pushed ahead by the infiltrating IPA-water front. Figure 5.10 shows the same location as in Figure 5.9 but after the IPA-water front had passed through it.

Relative to a contaminated layered medium that was initially dry, it took longer for the IPA-water mixture to displace toluene from a layered medium that was initially partially water-saturated, Figures 5.11 and 5.12. Figures 5.13 and 5.14 show the toluene front displacing water ahead of it as it moved downward.

5.3. Discussion

As was pointed out in Chapter 4, once the contaminant is trapped, water infiltration can only dissolve it, and this can takes years or even decades. With the use of an IPA-water mixture as a flushing fluid, toluene was displaced with minimal trapping. Although the interfacial tension values for the toluene/isopropanol-water are not available, based on information from similar systems, they probably decrease 1-2 orders of magnitude from values for toluene/water (7). Based on the experimental observations, the reduced interfacial
tension indeed made the capillary number of the isopropanol-water mixture high enough for displacement of toluene ganglia. Table 5.1 shows the increase in toluene solubility with the increase in weight percentage of isopropanol in a water-isopropanol solution.

<table>
<thead>
<tr>
<th>2-Propanol</th>
<th>Toluene</th>
<th>Water</th>
<th>2-Propanol</th>
<th>Toluene</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.3</td>
<td>4.0</td>
<td>55.7</td>
<td>47.9</td>
<td>33.6</td>
<td>18.5</td>
</tr>
<tr>
<td>49.7</td>
<td>9.0</td>
<td>46.3</td>
<td>37.0</td>
<td>55.6</td>
<td>7.4</td>
</tr>
<tr>
<td>51.1</td>
<td>15.4</td>
<td>33.5</td>
<td>34.7</td>
<td>63.5</td>
<td>4.8</td>
</tr>
<tr>
<td>49.4</td>
<td>24.7</td>
<td>25.9</td>
<td></td>
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</tr>
</tbody>
</table>

Table 5.1. Mutual solubility of 2-propanol/toluene/water (31)

Because it also took longer for the IPA-water mixture to displace the toluene from a layered medium that was initially partially water-saturated, the results in this chapter also suggest that toluene trapped by water in the strata of lower hydraulic conductivities would most likely be the source of long-term release. In an aquifer, the IPA-water mixture would like to bypass the contaminated low-K regions altogether if there are paths of lower resistance. Hence, the achievement of a high capillary number is not a guarantee that an immiscible contaminant will be completely displaced from a real heterogeneous aquifer.
Fig. 5.1. IPA-water flushing of a trapped toluene ganglion

Fig. 5.2. Same location as in Figure 5.1 but 1 second later
Fig. 5.3. Toluene in an initially dry homogeneous medium

Fig. 5.4. The infiltrating IPA-water mixture initially moves along the toluene-contaminated paths
Fig. 5.5. IPA-water flushing of a toluene-contaminated homogeneous medium, initially partially water-saturated

Fig. 5.6. Same location as in Figure 5.5 but 1 minute and 34 seconds later
Fig. 5.7. IPA-water flushing of a toluene-contaminated layered medium, initially dry

Fig. 5.8. Same location as in Figure 5.7 but 7 seconds later
Fig. 5.9. Infiltrating IPA-water front pushes toluene downward

Fig. 5.10. Same location as in Figure 5.9 but 9 minutes and 6 seconds later
Fig. 5.11. IPA-water flushing of a toluene-contaminated layered medium, initially partially water-saturated

Fig. 5.12. Same location as in Figure 5.11 but 12 minutes and 24 seconds later
Fig. 5.13. A partially water-saturated area in the high-K region below the advancing toluene front

Fig. 5.14. Advancing toluene front displaces the water shown in Figure 5.13
6. EFFECT OF VARIATIONS IN WATER TABLE ON TOluENE

6.1. Variations in Water Table

When the water level was raised at either 0.5 ft/day or 50 ft/day in an initially dry homogeneous porous medium, the water front was relatively flat and water saturated the entire medium, Figure 6.1. When the water level was lowered, water in the porous medium did not drain until the difference in water levels between the side tube and the porous medium was about 17 cm, and then it drained very slowly. When water level in the side tube was 1 cm above the bottom of the porous medium, the top of the saturated zone in the porous medium was about 2 cm below the inserted end of the hypodermic needle. When the water levels were again raised, water did not completely saturate the partially water-saturated area, but did form a fully saturated zone in the previously dry area above it, Figure 6.2.

In an initially dry layered medium, the low-K region filled very rapidly as soon as water reached its lower surface at any point. Some air was trapped at the lower textural boundary, Figure 6.5. Passing from the low-K to the upper high-K region, no water fingering was observed as it was with water infiltration reported in Chapter 4. When the water level in the side tube was lowered to the 1 cm level above the bottom of the porous medium, the top of the saturated zone
stopped at the top of the low-K region, an indication that the capillary pressure was not high enough to exceed the entry level value of the low-K region.

6.2. Initial Spreading and Draining of Toluene

With the water level in the side tube at 1 cm above the bottom of a partially water-saturated homogeneous medium as described above, 6.7% pore volume of toluene was injected into the medium. Toluene drained downward along the water-air interface, and pushed the top of the water-saturated zone down as much as 6.5 cm, Figure 6.3. If the flow cell was then left undisturbed for about 24 hours, a gradient of toluene concentration in the medium was observed, Figure 6.4. When additional toluene was injected into the medium, it also drained and pushed the top of the water-saturated zone downward, but not as much as with the first injection. The marks along the

\begin{center}
\begin{tabular}{c}
Water / Air \\
\hline
Water / Toluene / Air \\
\hline
Water / Toluene \\
\hline
Water
\end{tabular}
\end{center}

Fig. 6.4. Toluene concentration gradient in an initially partially water-saturated medium
side of the flow cell in Figure 6.3 show the location of the
top of the water-saturated zone after each injection. Under
the same conditions, similar behavior was observed with the
layered medium, Figure 6.5.

6.3. Effect of Variations in Water Table on Toluene

The effect of variations in the water table on toluene
that was injected into an initially dry medium was examined
first, Figure 6.6. With the water level raised at either 0.5
ft/day or 50 ft/day, when the top of the water-saturated zone
contacted the toluene, lateral spreading of toluene along the
air-water interface was observed, Figure 6.7. Because it is
the wetting phase, the upward-advancing water front then
penetrated the periphery of the toluene-saturated region until
the toluene became trapped as ganglia, Figure 6.8. If the
amount of toluene was bead-sized in volume, Figure 6.9, the
upward-advancing water front would lift it up slightly and
then trap it as a small ganglion, Figure 6.10. Figure 6.11
shows that when the water table was lowered, some of the
ganglia would drain downward along the newly-created air-water
interfaces. In some cases, mobile toluene coalesced with
large ganglia, causing them to be displaced downward without
being exposed to the air-water interface, Figures 6.12-13.

Figures 6.14-16 show the overall effect of the variations
in water table on toluene that was injected into an initially
water-saturated medium. When the water level was raised, toluene initially in the water/toluene/air region of Figure 6.14 was displaced upward but eventually trapped along with air below the water table. Toluene ganglia located in the water/toluene region of Figure 6.14, where there was no air, remained trapped. On closer inspection, the trapping and partial mobilization of toluene in the area above the water-saturated zone due to the variations in the water table were similar to those phenomena described previously in Chapter 4 involving infiltration and drainage, Figures 6.17-22.

6.4. Discussion

When the water level was raised in an initially dry layered medium, fingerling at the upper textural boundary did not occur, the expected result because the flow was not gravity-assisted (32). Some air was trapped at the lower textural boundary because of the width of the low-K layer.

The vertical equilibrium fluid distribution of water, toluene and air, Figure 6.4, was as expected per analysis presented by Farr et al. (33) and Parker and Lenhard (34). The downward displacement of the top of the water-saturated zone described in Section 6.2 simply resulted from the hydrostatic equilibrium between fluids in the porous medium and the side tube.

It has been known that a lighter-than-water non-aqueous
phase liquid (LNAPL) such as toluene does not distribute itself only as a distinct layer floating on top of a capillary fringe, and can be trapped below the water table (13, 25, 26, 35). Because the ganglia are immobile and toluene's solubility in water is low, the water will be contaminated for a long time.

Because mutual solubilities can affect the spreading behavior of an organic liquid on water (18), when the water table is lowered below the contaminated area, the contaminant's spreading behavior may be different from what it was initially. However, in this case, toluene drained along air-water interfaces in the micromodel whether or not the fluids were presaturated.
Fig. 6.1. Raising water level in a dry homogeneous medium
Fig. 6.2. When the water level was again raised, a saturated zone formed in the dry area above the region where water was previously drained.
Fig. 6.3. Initial spreading of toluene in an unsaturated homogeneous medium with the presence of a water table.
Fig. 6.5. Initial spreading of toluene in an unsaturated layered medium with the presence of a water table; Note some air trapped just below the low-K region
Fig. 6.6. Toluene injected into an initially dry homogeneous medium

Fig. 6.7. Lateral spreading of toluene along the air-water interface
Fig. 6.8. Trapping of toluene as ganglia by the raising of water table

Fig. 6.9. Toluene pendular rings above the upward-advancing water front
Fig. 6.10. Toluene in Figure 6.9 trapped as ganglia behind the upward-advancing water front

Fig. 6.11. Releasing of toluene along newly-created air-water interface by lowering of water table
Fig. 6.12. A contaminated area before the water level was lowered.

Fig. 6.13. Same location as in Figure 6.12 but during the lowering of water level.
Fig. 6.14. Vertical Distribution of toluene in the presence of a water table.
Fig. 6.15. Same flow cell as in Figure 6.14; Note upward displacement of toluene due to the raising of the water level.
Fig. 6.16. Same flow cell as in Figure 6.14; Similar fluid distribution even though the water level was raised and lowered three times.
Fig. 6.17. Toluene on air-water interface

Fig. 6.18. Same location as in Figure 6.17; note toluene that was on the air-water interface trapped as ganglia when the water level was raised
Fig. 6.19. Same location as in Figure 6.18; note toluene drained downward along newly-created air-water interface when the water level was lowered.
Fig. 6.20. Toluene ganglion entrapped by water

Fig. 6.18. The ganglion shown in Figure 6.20 was unaffected by the raising of the water level
Fig. 6.22. The ganglion shown in Figure 6.21 was unaffected by lowering of water level
7. CONCLUSIONS AND RECOMMENDATIONS

7.1. CONCLUSIONS

The combination of video microscopy and bead-pack micro-models is an excellent tool to study the basic mechanisms of fluid flow in aquifers with an immiscible contaminant. The results reported in this work lead to the following conclusions about the behavior of toluene in the unsaturated zone and near the water table:

(a) When some toluene was injected into a homogeneous partially water-saturated medium, it drained slowly along continuous air-water interfaces leaving almost no residual saturation. Thus, virtually all of a relatively small spill of an immiscible contaminant could eventually reach the water table.

(b) For other conditions toluene was observed to become trapped as ganglia in the unsaturated zone. For instance, trapping occurred when water infiltration followed injection of toluene into a dry medium. On subsequent drainage, many of the ganglia were exposed to air-water interfaces and drained as above. However, those ganglia in low-permeability strata or even in local regions of somewhat lower permeability remained trapped. Such ganglia are presumably the source of long-term contamination at sites such as Traverse City where a spill or leak of immiscible contaminant has occurred.
Infiltrating water flows past the ganglia, slowly leaching slightly soluble contaminants from them, as was observed during a recent field test at Traverse City (11).

(c) When toluene was present near the water table as a result of the drainage process described in (a), raising of the water table caused upward displacement of the toluene and eventual trapping of both toluene and air below the new water table. In an aquifer, toluene ganglia formed by this process could be a source of long-term contamination. When the water table was subsequently lowered, the air-water interfaces again formed continuous paths and toluene drainage was observed. Thus, fluctuation in the water table can produce mobilization and trapping which redistribute an immiscible contaminant even long after a spill or leak has occurred.

(d) Enhanced solubility and mobilization of toluene ganglia is possible with the use of an isopropanol-water mixture. Although a systematic study was not conducted, it is clear that the interfacial tension between the toluene-rich and water-rich phases falls to values small enough that ganglia of the former are mobilized. No such mobilization occurred in alcohol-free systems.

7.2. RECOMMENDATIONS

The micromodel used in this work is limited in some
respects and minor modification can be made to allow it to simulate more realistic situations. For example, the modified micromodel shown in Figure 7.1 is wider than that described in Chapter 2 and can be used to simulate an unconfined sandy aquifer with less-permeable strata of finite width. It consists of a rectangular capillary 1x15x300 mm in dimensions, packed mostly with glass beads 380-515 microns in diameter, but also with a few strata of beads 180-220 microns in diameter. Note that these less-permeable strata do not extend across the entire width of the capillary, in contrast to the micromodels employed previously. The modified micromodel has a smaller porosity (0.4) and a higher hydraulic conductivity (0.6 cm/s) than the one used in this study.

Of course, with the modified micromodel, some further experiments can be conducted with the fluid systems used in this study. For example, Figure 7.1 shows a complicated migration pattern of toluene caused by the presence of less-permeable strata; note that the toluene did not penetrate the water-saturated low-K strata as discussed in Chapter 3. Figure 7.2 shows the effect of water infiltration on the toluene-contaminated area shown in Figure 7.1; note that toluene did not enter the less-permeable strata but the infiltrating water displaced previous water there. Finally, Figure 7.3 shows the effect of water drainage; again note the high retention of water in the less-permeable strata and the draining of toluene along the newly-created air-water inter-
faces around the water-saturated strata.

Organic liquids which are denser than water such as tetrachloroethylene also present a great threat to aquifers. Though some phenomena similar to those reported in this study are expected, the density effect associated with these organic liquids should produce some differences in behavior near the water table.
Fig. 7.1. Initial spreading of toluene in a partially water-saturated heterogeneous medium
Fig. 7.2. Water infiltration into the same flow cell shown in Figure 7.1
Fig. 7.3. Water drainage of flow cell shown in Figure 7.2
REFERENCES


